JOC*Article*

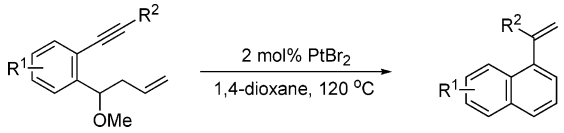
$PtBr_2$-Catalyzed Consecutive Enyne Metathesis−Aromatization of 1-(1-Methoxy-but-3-enyl)-2-(1-alkynyl)benzenes: Dual Role of the Pt Catalyst

Gan B. Bajracharya, Itaru Nakamura, and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

yoshi@yamamoto1.chem.tohoku.ac.jp

Received September 30, 2004



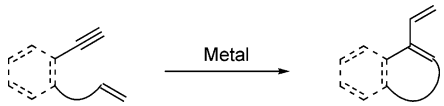
1,7-Enynes **1**, connected through an aromatic ring and bearing a leaving methoxy group at the 4-position, underwent the $PtBr_2$-catalyzed enyne metathesis followed by aromatization in one pot to afford vinyl naphthalenes **3** in good to acceptable yields. The cyclobutene intermediate **11a** and another intermediate **2a** were isolated, indicating that $PtBr_2$ acts as a dual role catalyst: (1) as a transition metal catalyst, it induces the enyne metathesis to produce **11a** starting from **1a**, and (2) as a Lewis acid catalyst, it facilitates elimination of MeOH from **2a** to give the aromatized product **3a**.

Introduction

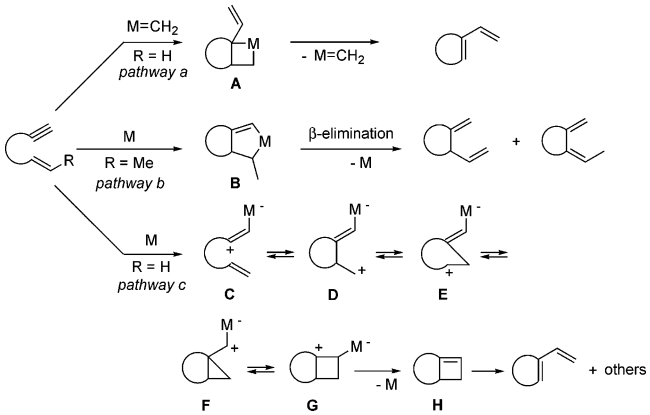
In the past decade, the metal-mediated cycloisomerization of 1,*n*-enynes has emerged as an extremely attractive and unique tool for the one-pot synthesis of various types of cyclic compounds (Scheme 1).[1] A wide range of transition metal complexes have been used for this transformation.[2−8]

On the basis of the mechanisms involved in the enyne metathesis, the cycloisomerization can be classified into three categories. First is the metal carbene-mediated enyne metathesis and second is the cycloisomerization through metallacyclic intermediates (Scheme 2). The metal carbene reacts first with the yne unit and the resulting carbene complex further reacts with the ene unit to give the intermediate **A**, which subsequently produces the 1,3-dienes together with the metal carbene catalyst (pathway a). The oxidative metallacycloaddition to enynes forms the metallacycle **B**, which undergoes subsequent β-hydride elimination to give a mixture of the 1,3- and 1,4-dienes (pathway b). The third category involves the π-complexation of an electrophilic transition metal onto the alkyne moieties that leads to the forma-

SCHEME 1. Cycloisomerization of 1,*n*-Enynes



SCHEME 2. Mechanisms in Enyne Metathesis



(1) For reviews on enyne metathesis, see: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34−42. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281. (c) For textbook, see: Tsuji, J. *Palladium Reagents and Catalysts*: *Innovations in Organic Synthesis*; John Wiley & Sons: Chichester, UK, 1995; pp 476−488. (d) Ojima, I.; Tzamarioudaki, M.; Li, Z. Y.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635−662. (e) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1−16. (f) Mori, M. *Top. Organomet. Chem.* **1998**, *1*, 133−154. (g) Trost, B. M. *Chem. Eur. J.* **1998**, *4*, 2405−2412. (h) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657−1668. (i) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067−2096. (j) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813−834. (k) Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Adv. Synth. Catal.* **2002**, *344*, 585−595. (l) Poulsen, C. S.; Madsen, R. *Synthesis* **2003**, 1−18. (m) Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215−236. (n) Schmidt, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 4996−4999. (o) Fairlamb, I. J. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1048−1052. (p) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317−1382. (q) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127−2198.

10.1021/jo048273q CCC: $30.25
Published on Web 01/05/2005

tion of the polarized η^1-alkyne complex **C** bearing a positive charge at the β-position (pathway c). Delocalization of a positive charge produces the isomers **D**, **E**, **F**, and **G**. Finally, the intermediate **H** is afforded through bond rearrangement processes, which produces the 1,3-diene along with other products.

Trost,[2f,i] Murai,[3a,5a,b] and Fürstner[3b,d−f] proposed the formation of the cyclopropylmetal carbene intermediate (**F** in Scheme 2) in the Pd(II)-, Rh(II)-, Ru(II)-, and Pt-(II)-catalyzed skeletal rearrangements of enynes that produces conjugated dienes.[9] Murai et al. used a wisely designed starting material and succeeded in trapping the carbene intermediate in the Pt-catalyzed cyclization of enynes.[5b] Recently, Echavarren and co-workers reported that 1,6-enynes react with alcohols or water in the presence of $PtCl_2$ to give new carbo- or heterocycles with alkoxy or hydroxy functional groups via formation of the cyclopropyl platinum−carbene intermediate.[10]

Generally, the cycloisomerization of 1,6-enynes affords the products with a newly generated five-membered ring. Obviously, one may expect the formation of a six-membered ring by cyclization of 1,7-enynes. However, formation of a six-membered ring from 1,7-enynes in the metathesis reaction is not easy due to the poorer ability of 1,7-enynes to function as a bidentate ligand.[1j] Trost partially solved this problem by introducing a free carboxylic acid substituent at the alkene terminus that coordinated with the metal in the catalytic cycle.[2g] Murai et al. reported a few examples of cyclorearrangement of 1,7-enynes catalyzed by metal halides (e.g., $PtCl_2$ and $GaCl_3$ etc.) leading to the formation of six-membered rings.[3a,h] However, compare to the 1,6-enynes, 1,7-enynes are rarely used in the enyne cycloisomerization reaction. Furthermore, reports on formation of an aromatic ring in the enyne cyclization are very rare.[11,12] Recently, Pérez-Castells et al. apparently reported the formation of a naphthalene derivative as the side product by means of the intramolecular Pauson-Khand reaction of aromatic enynes promoted by molecular sieves in the presence of

(2) For Pd-catalyzed cycloisomerization of enynes, see: (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636−1638. (b) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636−644. (c) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647−3650. (d) Trost, B. M.; Pfrengle, W.; Urabe, H.; Dumas, J. *J. Am. Chem. Soc.* **1992**, *114*, 1923−1924. (e) Trost, B. M.; Chang, V. K. *Synthesis* **1993**, 824−832. (f) Trost, B. M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085−1087. (g) Trost, B. M.; Gelling, O. J. *Tetrahedron Lett.* **1993**, *34*, 8233−8236. (h) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5, 9421−9438. (i) Trost, B. M.; Hashmi, A. S. K. *J. Am. Chem. Soc.* **1994**, *116*, 2183-2184. (j) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255−4267. (k) Trost, B. M.; Romero, D. L.; Rise, F. *J. Am. Chem. Soc.* **1994**, *116*, 4268−4278. (l) Goeke, A.; Sawamura, M.; Kuwano, R.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 662−663. (m) Yamada, H.; Aoyagi, S.; Kibayashi, C. *Tetrahedron Lett.* **1996**, *37*, 8787−8790. (n) Trost, B. M.; Li, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6625−6633. (o) Oh, C. H.; Rhim, C. Y.; Hwang, S. K. *Chem. Lett.* **1997**, 777−778. (p) Yamada, H.; Aoyagi, S.; Kibayshi, C. *Tetrahedron Lett.* **1997**, *38*, 3027−3030. (q) Widenhoefer, R. A.; Stengone, C. N. *J. Org. Chem.* **1999**, *64*, 8681−8692. (r) Trost, B. M.; Krische, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 6131−6141. (s) Trost, B. M.; Haffner, C. D.; Jebaratnam, D. J.; Krische, M. J.; Thomas, A. P. *J. Am. Chem. Soc.* **1999**, *121*, 6183−6192. (t) Harada, K.; Tonoi, Y.; Kato, H.; Fukuyama, Y. *Tetrahedron Lett.* **2002**, *43*, 3829−3832. (u) Fairlamb, I. J. S.; Pike, A. C.; Ribrioux, S. P. C. P. *Tetrahedron Lett.* **2002**, *43*, 5327−5331.

(3) For Pt-mediated cyclization of enynes, see: (a) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901−903. (b) Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305−8314. (c) Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801−3810. (d) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785−6786. (e) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863−11869. (f) Mamane, V.; Gress, T.; Krause, H.; Fürstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654−8655. (g) Bernard, M.; Cariou, K.; Mainetti, E.; Mouriés. V.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2004**, *126*, 8656−8657. (h) For $GaCl_3$-mediated cyclization of enynes, see: Chatani, N.; Inoue, H.; Kotsuma, T.; Murai, S. *J. Am. Chem. Soc.* **2002**, *124*, 10294−10295.

(4) For Rh-mediated cyclization of enynes, see: (a) Wender, P. A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164−4165. (b) Gilbertson, S. R.; Hoge, G. S.; Genov, D. G. *J. Org. Chem.* **1998**, *63*, 10077−10080. (c) Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490−6491. (d) Cao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 4104−4106. (e) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198−8199. (f) Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457−3460. (g) Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 4526−4529. (h) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 6370−6371. (i) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 11472−11473. (j) Tong, X.; Li, D.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7601−7607. (k) Mikami, K.; Kataoka, S.; Yusa, Y.; Aikawa, K. *Org. Lett.* **2004**, *6*, 3699−3701.

(5) For Ru-mediated cyclization of enynes, see: (a) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049−6050. (b) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104−9105. (c) Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158−9159. (d) Trosy, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 9728−9729. (e) Paih, J. L.; Rodríguez, D. C.; Dérien, S.; Dixneuf, P. H. *Synlett* **2000**, 95−97. (f) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714−715. (g) Sémeril, D.; Cléran, M.; Bruneau. C.; Dixneuf, P. H. *Adv. Synth. Catal.* **2001**, *343*, 184−187. (h) Ackermann, L.; Bruneau, C.; Dixneuf, P. H. *Synlett* **2001**, 397−399. (i) Sémeril, D.; Cléran, M.; Perez, A. J.; Bruneau. C.; Dixneuf, P. H. *J. Mol. Catal. A*: *Chem.* **2002**, *190*, 9−25. (j) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, *124*, 5025−5036. (k) Mori, M.; Saito, N.; Tanaka, D.; Takimoto, M.; Sato, Y. *J. Am. Chem. Soc.* **2003**, *125*, 5606−5607. (l) For Ir-mediated cyclization of enynes, see: Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai, S. *J. Org. Chem.* **2001**, *66*, 4433−4436.

(6) For Ti-catalyzed cyclization of enynes, see: (a) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 4912−4913. (b) Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261−4264. (c) Suzuki, K.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1996**, *118*, 8729−8730. (d) Urabe, H.; Suzuki, K.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 10014−10027. (e) Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976−1977.

(7) For Zr-mediated cyclization of enynes, see: (a) Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *Synlett* **1994**, 110−112. (b) Miura, K.; Funatsu, M.; Saito, H.; Ito, H.; Hosomi, A. *Tetrahedron Lett.* **1996**, *37*, 9059−9062. (c) Negishi, E.-i.; Ma, S.; Sugihara, T.; Noda, Y. *J. Org. Chem.* **1997**, *62*, 1922−1923.

(8) For Ni/Cr-, Ni-, and Ni/Zn-mediated cyclization of enynes, see: (a) Ni/Cr: Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268−5270. (b) Ni: Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286−1288. (c) Ni/Zn: Savchenko, A. V.; Montgomery, J. *J. Org. Chem.* **1996**, *61*, 1562−1563.

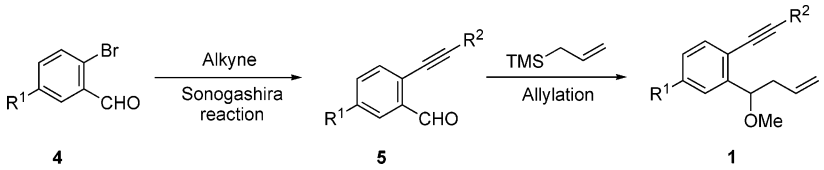
(9) For recent formulations of the reaction mechanism, see: (a) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704−3709. (b) Mainetti, E.; Mouriés, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132−2135.

(10) (a) Méndez, M.; Muñoz, M. P.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11549−11550 and references therein. (b) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511−10520. (c) Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 2627−2635. (d) Nevado, C.; Charruault, L.; Michelet, V.; Nieto-Oberhuber, C.; Muñoz, M. P.; Méndez, M.; Rager, M.-N.; Genêt, J.-P.; Echavarren, A. M. *Eur. J. Org. Chem.* **2003**, 706−713. See also: (e) Fernández-Rivas, C.; Méndez, M.; Nieto-Oberhuber, C.; Echavarren, A. M. *J. Org. Chem.* **2002**, *67*, 5197−5201. (f) Echavarren, A. M.; Méndez, M.; Muñoz, M. P.; Nevado, C.; Martín-Matute, B.; Nieto-Oberhuber, C.; Cárdenas, D. J. *Pure Appl. Chem.* **2004**, *76*, 453−463.

(11) For recent advances in the transition metal-catalyzed formation of aromatic rings, see: (a) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901−2915 and references therein. (b) W: Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518−519. (c) Shen, H.-C.; Pal, S.; Lian, J.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 15762−15763. See also: (d) Imamura, K.-i.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 4081−4084.

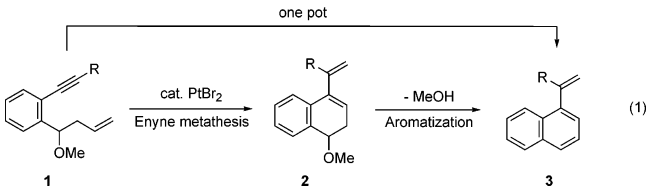
(12) For the transition metal-catalyzed cyclization of heterocycles through a Friedal-Crafts-type reaction and/or formation of cyclopropylmetal−carbenes, see: (a) Dankwardt, J. W. *Tetrahedron Lett.* **2001**, *42*, 5809−5812. (b) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264−6267. (c) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757−5766.

SCHEME 3. Preparation of Starting Materials



a stoichiometric amount of $Co_2(CO)_8$.[13] The same group subsequently utilized the aromatic enynes in the Grubbs catalyst-mediated ring-closing metathesis producing 1,3-dienes, which underwent a subsequent Diels–Alder process to construct natural product frameworks.[14] To the best of our knowledge, a naphthalene core has not been prepared by the transition metal-mediated enyne metathesis–aromatization employing 1,7-enynes including an aromatic ring in the tether part.

We report that a six-membered ring can readily be obtained in good to acceptable yields in the enyne metathesis of 1,7-enynes **1** by using $PtBr_2$ catalyst (eq 1). Here, $PtBr_2$ exhibits a dual role: (1) as a transition



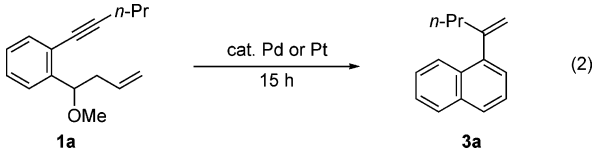
metal, $PtBr_2$ catalyzes the enyne metathesis to produce the six-membered 1,3-dienes **2**, and (2) as a Lewis acidic catalyst, $PtBr_2$ assists elimination of MeOH from **2** to afford the vinylnaphthalene derivatives **3**.

Results and Discussion

The starting materials **1** were prepared by the allylation of *o*-alkynylbenzaldehydes **5** (Scheme 3). The precursors **5** were prepared from the corresponding 2-bromobenzaldehyde derivatives **4** with a Sonogashira cross-coupling.[15] The direct allylation of the *o*-alkynylbenzaldehydes **5** was carried out by reaction with allyltrimethylsilane in the presence of scandium triflate at ambient temperature to produce the corresponding aromatic enynes **1**.[16] Alternatively, the acetalization[17] of **5**, followed by allylation also produced the desired 1,7-enyne.

First, we used **1a** as a model substrate for optimization of the reaction conditions (eq 2). The results are summarized in Table 1. We found that in the presence of 10 mol % of $PdBr_2$ in MeCN at 100 °C, the enyne **1a** underwent cyclization–aromatization to afford 1-(1-methylenebutyl)naphthalene **3a** in 38% isolated yield (entry

TABLE 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	additive (40 mol %)	temp, °C	yield, %[b]
1	$PdBr_2$	MeCN		100	42 (38)
2	$PdCl_2$	MeCN		100	34
3	$PtCl_2$	MeCN		100	44
4	$PtCl_2(PhCN)_2$	MeCN		100	41
5	$PtCl_2(CH_3CN)_2$	MeCN		100	47
6	$PtBr_2$	MeCN		100	49
7	$PtBr_2$	MeCN		120	53
8	$PtBr_2$	1,4-dioxane		120	56
9	$PtBr_2$	hexane		120	46
10	$PtBr_2$	toluene		120	43
11	$PtBr_2$			120	7
12	$PtBr_2$	1,4-dioxane	*p*-benzoquinone	120	51
13	$PtBr_2$	1,4-dioxane	*β*-pinene	120	49
14[c]	$PtBr_2$	1,4-dioxane		120	79
15[d]	$PtBr_2$	1,4-dioxane		120	81 (75)

[a] The reaction of **1a** (0.3 mmol) was carried out in the presence of 10 mol % of catalyst under Ar for 15 h unless otherwise noted. [b] Yield calculated from ^1H NMR integration with CH_2Br_2 as an internal standard; the isolated yield is in parentheses. [c] 2 mol % of catalyst was used. [d] 1 mol % of catalyst was used.

1). Similarly, $PdCl_2$, $PtCl_2$, $PtCl_2(PhCN)_2$, and $PtCl_2(CH_3CN)_2$ afforded the product **3a** in comparable yields (entries 2–5). The yield of the product was slightly improved by using $PtBr_2$ as a catalyst (entry 6). The use of other catalysts such as $Pd(PPh_3)_4$, $Pd_2(dba)_3{\cdot}CHCl_3$, $Pt(PPh_3)_4$, $NiBr_2(PPh_3)_2$, $RhCl(PPh_3)_3$, etc. did not afford **3a** at all. We also evaluated some Lewis acids, for example, $Cu(OTf)_2$, AgOTf, $AuBr_3$, $GaCl_3$, etc., in 1,4-dioxane, but the reaction did not proceed. The yield of the product was improved by increasing the temperature up to 120 °C (entry 7). Among the solvents examined, 1,4-dioxane provided the best results (compare entry 8 with entries 9 and 10). Under neat conditions, the product yield was drastically reduced (entry 11). The use of additional additives that were thought to enhance the reaction rate by π-coordination, such as *p*-benzoquinone and *β*-pinene,[18] did not improve the product yield (entries 12 and 13). *When the loading of $PtBr_2$ was reduced* to 2 mol % in 1,4-dioxane (0.15 M), a high yield of the product was obtained (entry 14). A better yield was obtained by further lowering the loading of catalyst to 1 mol % (entry 15).

Next, we examined the scope of this reaction. The results are summarized in Table 2. It is noteworthy to mention that only 1 mol % of $PtBr_2$ is sufficient to promote this reaction; however, longer reaction times

(13) Blanco-Urgoiti, J.; Casarrubios, L.; Dominguez, G.; Pérez-Castells, J. *Tetrahedron Lett.* **2001**, *42*, 3315–3317 and references therein.

(14) . (a) Rosillo, M.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Tetrahedron Lett.* **2001**, *42*, 7029–7031. (b) Rosillo, M.; Domínguez, G.; Casarrubios, L.; Amador, U.; Pérez-Castells, J. *J. Org. Chem.* **2004**, *69*, 2084–2093.

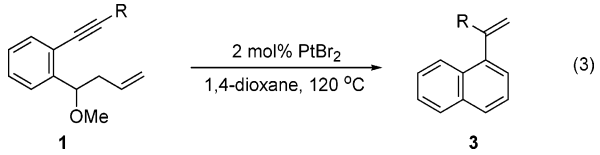
(15) For a review, see: Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of Transition Metal Catalyst in Organic Synthesis*; Springer-Verlag: Berlin, Germany, 1999; Chapter 10.

(16) Yadav, J. S.; Subba Reddy, B. V.; Srihari, P. *Synlett* **2001**, 673–675.

(17) Luche, J.-L.; Gemal, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 976–977.

(18) Recently, we found that the use of *p*-benzoquinone or *β*-pinene as an additional additive enhanced the reaction rate in the Pt-catalyzed intramolecular carboalkoxylation of alkynes, see: Nakamura, I.; Bajracharya, G. B.; Wu, H.; Oishi, K.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 15423–15430.

TABLE 2. Synthesis of Vinylnaphthalenes[a]

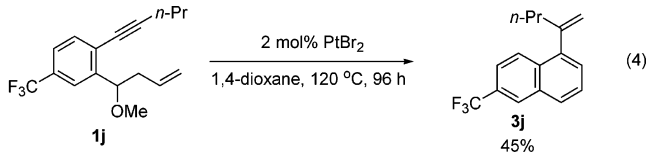


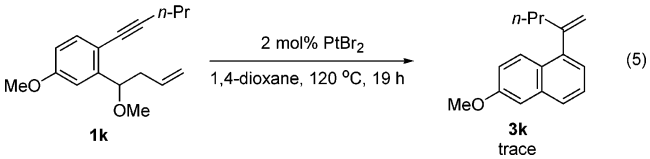
entry	1	R	time, h	yield of 3,[b] %
1	**1b**	*n*-Bu	79	52[c]
2[d]	**1b**	*n*-Bu	117	35[c]
3	**1c**	*n*-Hex	21	60
4[d]	**1c**	*n*-Hex	45	60
5	**1d**	cyclopropyl	93	50[c]
6	**1e**	cyclohexyl	168	52[c]
7	**1f**	Ph	45	76
8	**1g**	*p*-CF_3-C_6H_4	83	69
9	**1h**	*p*-Me-C_6H_4	92	51[c]
10[e]	**1i**	*p*-MeO−C_6H_4	88	43

[a] The reaction of **1** (0.5 mmol) was carried out in the presence of 2 mol % of $PtBr_2$ in 1,4-dioxane at 120 °C under Ar unless otherwise noted. [b] Isolated yield. [c] Significant amounts of starting material were recovered. [d] 1 mol % of $PtBr_2$ was used. [e] 5 mol % of $PtBr_2$ was used.

were required when we employed substrates **1b** and **1c** (compare entries 1 and 2 and entries 3 and 4). Hence, use of 2 mol % of $PtBr_2$ in 1,4-dioxane was chosen as the standard conditions for further studies. In the presence of 2 mol % of $PtBr_2$ in 1,4-dioxane at 120 °C, the cyclization−aromatization of **1b** and **1c** afforded the corresponding vinylnaphthalenes **3b** and **3c**, respectively, in moderate yields (entries 1 and 3). Longer reaction times were observed with cyclopropyl and cyclohexyl substituents on the alkynyl terminus (entries 5 and 6). The reaction of **1f** proceeded smoothly producing **3f** in 76% yield (entry 7). Trifluoromethyl, methyl, and methoxy substituents at the para position of the aromatic ring, as in **1g**, **1h**, and **1i**, were tolerated under the reaction conditions and produced the corresponding products in good to acceptable yields (entries 8−10).

The reaction of **1j** bearing an electron-withdrawing substituent on the para position of the aromatic ring proceeded in a similar manner to afford **3j** in 45% yield (eq 4). The reaction of **1k** bearing an electron-donating group on the aromatic ring produced only a trace amount of the product **3k** (eq 5).[19]





A plausible reaction mechanism is outlined in Scheme 4. First, in a manner similar to that of the ordinary transition metal complexes, the electron-rich alkynyl π-bond of **1** coordinates to the electron-deficient $PtBr_2$ as shown in **6**, and subsequently the intermediate **7** is generated. Cyclization of **7** would occur in *exo*-fashion to produce **8**. A subsequent rearrangement leads to formation of the platinum−carbene complex **9** as shown in route a. Alternatively, a rearrangement takes place to form the more stable tertiary carbocationic species **10** as depicted in route b. The skeletal rearrangement of both **9** and **10** leads to the formation of the cyclobutene intermediate **11**. Formation of the cyclobutene intermediate **11** may be explained also via formation of the platinacyclopentene intermediate **12** by oxidative coupling followed by the reductive elimination of PtLn. Although this pathway is not completely ruled out, we prefer the mechanism proceeding via the zwitterionic vinylmetal complex **7** because Pt(0) [or Pd(0)] completely halted the enyne metathesis reaction. Under reflux reaction conditions, rearrangement of the cyclobutene intermediate **11** takes place to generate the 1,3-diene **2**. At this stage, $PtBr_2$ acts as a Lewis acid and induces the elimination of MeOH from **2**, leading to the aromatized final product **3**.

The intermediates **11** and **2** were isolated successfully in support of the proposed mechanism. The substrate **1a**, upon treatment with 4 mol % of $PtBr_2$ with MeCN as a solvent at lower temperature (60 °C), afforded the cyclobutene derivative **11a** in a moderate yield under nonoptimized reaction conditions (Scheme 5).[20] The reaction of **11a** in the presence of a catalytic amount of $PtBr_2$ at elevated temperature (120 °C) in CH_3CN afforded the final product **3a**. In the absence of the catalyst, when **11a** was heated at 120 °C in MeCN, the thermodynamically stable 1,3-diene **2a** was produced. Treatment of **2a** with $PtBr_2$ (2 mol %) in CH_3CN at 120 °C gave the final product **3a**.

Conclusion

The 1,7-enynes, connected through an aromatic ring and bearing a methoxy group at the 4-position, underwent Pt-catalyzed enyne metathesis followed by aromatization to afford vinylnaphthalene derivatives in one pot. Although formation of a six-membered ring through enyne metathesis is not easy, this procedure allows a quick access to a new six-membered ring. The presence of a methoxy substituent in the tether further extends the scope of this reaction to generate an aromatic ring. The dual role of $PtBr_2$ as a transition metal catalyst and a Lewis acid was exemplified in this reaction. The cyclobutene intermediate in the reaction was isolated and fully characterized, which supported that pathway c (Scheme 2) was involved in the metathesis. Further research and improvement of the reaction conditions are under investigation in our laboratory.

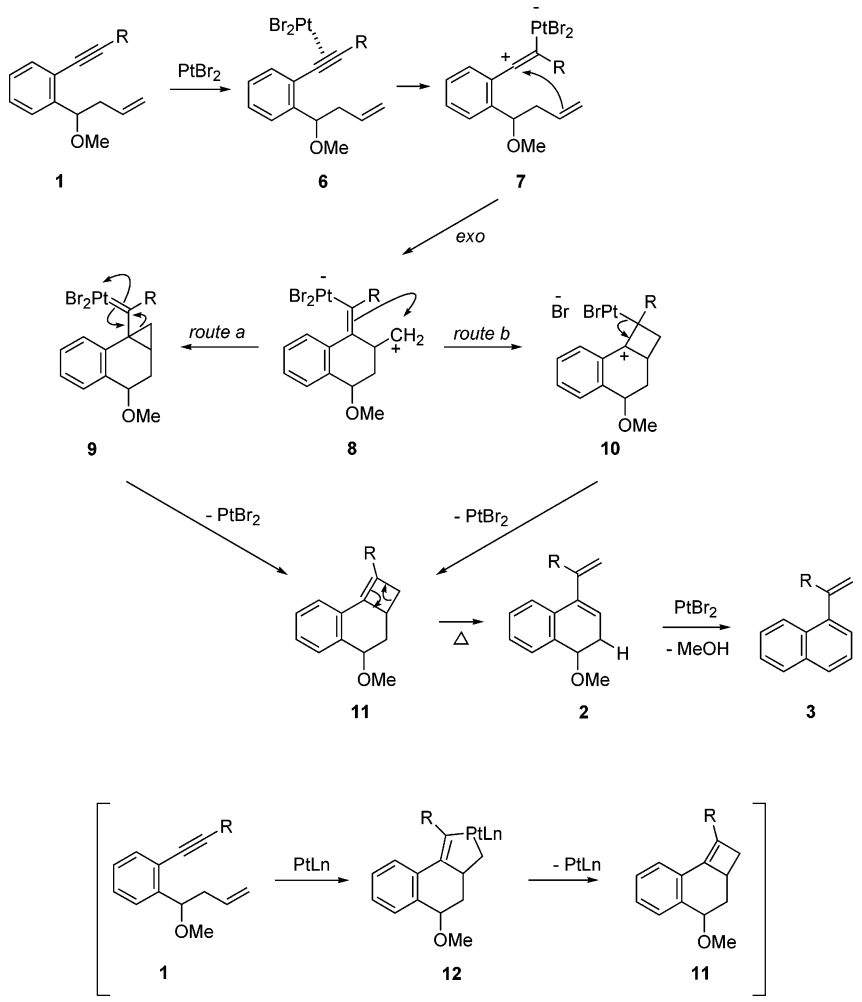
Experimental Section

Materials. Starting materials **1** were prepared from the coupling of corresponding 2-bromobenzaldehyde derivatives with alkynes by using a Sonogashira reaction[15] followed by scandium triflate-catalyzed allylation with allyltimethylsilane.[16] 2-Bromobenzaldehyde, alkynes, and allyltrimethylsi-

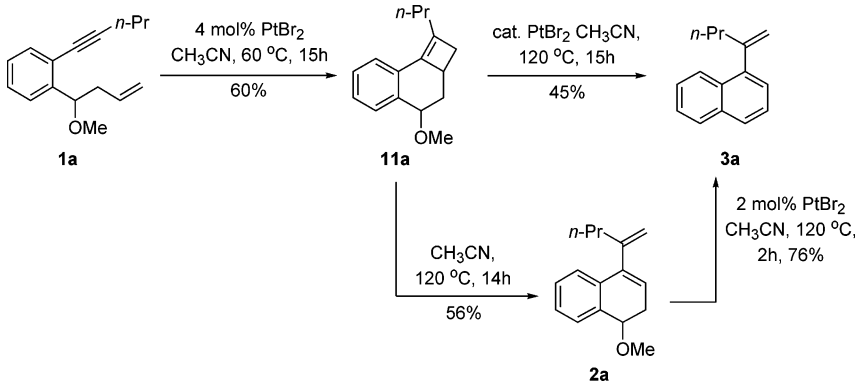
(19) The starting material **1k** was decomposed under the reaction conditions.

(20) Structure of **11a** was fully characterized by NMR experiments [see the Supporting Information].

SCHEME 4. A Plausible Reaction Mechanism



SCHEME 5



lane were purchased and used as received. 2-Bromo-5-(trifluoromethyl)benzaldehyde[21] and 2-bromo-5-methoxybenzaldehyde[22] were prepared according to the reported procedures. Cyclopropylacetylene was prepared according to the literature.[23] All the catalysts used were commercially available.

Representative Procedure for the Preparation of 1-(1-Methylenebutyl)naphthalene (3a). To a mixture of $PtBr_2$ (1.1 mg, 0.003 mmol, 1 mol %) and 1-(1-methoxy-but-3-enyl)-2-(pent-1-ynyl)benzene (**1a**) (68.5 mg, 0.3 mmol) was added 1,4-dioxane (2.0 mL, 0.15 M) under an argon atmosphere in a Wheaton microreactor. The mixture was stirred for 20 min at room temperature then heated at 120 °C for 15 h. The product was filtered through a short column of SiO_2 with hexane/ethyl acetate (4/1) as an eluent, and the resulting filtrate was

(21) (a) Šindelář, K.; Dlabač, A.; Metyšová, J.; Kakáč, B.; Holubek, J.; Svátek, E.; Sedivý, Z.; Protiva, M. *Collect. Czech. Chem. Commun.* **1975**, *40*, 1940−1959. (b) Perchonock, C. D.; Uzinskas, I.; McCarthy, M. E.; Erhard, K. F.; Gleason, J. G.; Wasserman, M. A.; Muccitelli, R. M.; DeVan, J. F.; Tucker, S. S.; Vickery, L. M.; Kirchner. T.; Weichman, B. M.; Mong, S.; Scott, M. O.; Chi-Rosso, G.; Wu, H.-L.; Croole, S. T.; Newton, J. F. *J. Med. Chem.* **1986**, *29*, 1442−1452.

(22) Gies, A.-E.; Pfeffer, M. *J. Org. Chem.* **1999**, *64*, 3650−3654.

(23) Corley, E. G.; Thompson, A. S.; Huntington, M. In *Organic Synthesis*; Hart, D. J., Ed.; 1999; Vol. 77, pp 131−235.

concentrated. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate; 100/1) to afford 1-(1-methylenebutyl)naphthalene (**3a**) in 75% yield (44.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 1.48−1.39 (m, 2H), 2.49 (t, J = 7.4 Hz, 2H), 5.07 (d, J = 2.0 Hz, 1H), 5.39−5.38 (m, 1H), 7.27 (dd, J = 1.2, 6.8 Hz, 1H), 7.48−7.40 (m, 3H), 7.76−7.74 (m, 1H), 7.86−7.82 (m, 1H), 8.06−8.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.3, 40.8, 115.1, 124.9, 125.1, 125.5, 125.6, 125.8, 127.0, 128.1, 131.2, 133.6, 141.4, 148.8. IR (neat) 3059−2870, 1636, 1590, 1506, 1463, 903, 801, 778 cm^{-1}. Anal. Calcd for $C_{15}H_{16}$ (196.29): C, 91.78; H, 8.22. Found: C, 92.05; H, 8.13. HRMS (EI) calcd for $C_{15}H_{16}$ (M^+) 196.1252, found 196.1248.

Supporting Information Available: Characterization data and spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO048273Q