Ru(II)- and Pt(II)-Catalyzed Cycloisomerization of ω-Aryl-1-alkynes. Generation of Carbocationic Species from Alkynes and Transition Metal Halides and Its Interception by an Aromatic Ring

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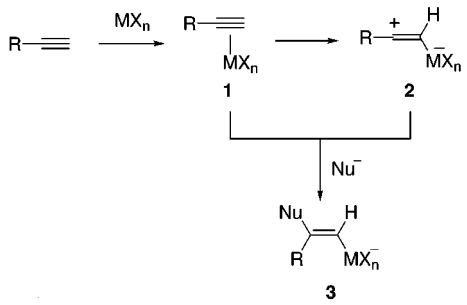
The treatment of aryl-1-alkynes, such as 4-aryl-1-butyne, 5-aryl-1-pentyne, and 6-aryl-1-hexyne, with catalytic amounts of transition metal chlorides, such as $PtCl_2$ and $[RuCl_2(CO)_3]_2$, at 80 °C in toluene results in cycloisomerization to give dihydronaphthalenes or dihydrobenzocycloheptenes, in which the cyclization mode is dependent on the length of the tethers. The reaction is limited to substrates containing terminal alkynes. A key step of the reaction is the intramolecular interception by an aromatic ring of the vinylmetal complex **2**, which contains a cation center at the β-position, generated from the electrophilic addition of transition metal halides toward an alkyne. The more electron-rich aryl systems are more reactive.

Nucleophilic attack on transition metal alkyne complexes represents a basic reaction in organometallic transformations. It is well-known that alkyne-coordinated π-complexes, such as **1**, undergo nucleophilic attack in an *anti*-manner to give the σ-vinyl transition metal complex **3** (Scheme 1).[1] Nucleophiles, such as H_2O, alcohols, carboxylic acids, amines, and carbanions, are typically used for this type of stoichiometric transformation. It is also generally believed that the catalytic addition of H_2O,[2] alcohols,[3] amines,[4] and carboxylic acids[5] to alkynes proceed via the intermediate complex **1**. However, complex **2**, which can be generated from **1** via the electrophilic addition of transition metal halides toward an alkyne, represents another possible intermediate prior to nucleophilic attack of alkynes. Complex **2** would be expected to be more reactive toward nucleophiles than **1** because of the presence of a cationic center. Isolation of the carbocationic complex **2** has not been reported, but the intermediacy of such a complex has been proposed by Dixneuf in the rearrangement reaction of 1-[4-(dimethylaminophenyl)]propargyl alcohol with a Ru(II) complex, in which the 4-(dimethylamino)phenyl group migrates to the positively charged β-carbon of the η^1-alkyne ruthenium complex.[6] Until recently, the chemical nature of this type of species has not been the subject of much attention.

Scheme 1



Recently, several studies of reactions of alkynes, as promoted by Lewis acids, with rather weak, carbon nucleophiles, such as allylsilanes, vinylsilanes, alkynylsilanes, and allylstannanes, have been reported. Jung reported that the addition of allylsilane to alkynes takes place in the presence of $AlCl_3$.[7] Yamamoto found that $EtAlCl_2$ and $HfCl_4$ also show catalytic activity with respect to the *trans*-addition of allylsilane to alkynes, and both the π-alkyne complex **1** and the vinyl complex **2** have been proposed as key intermediates in the $HfCl_4$-catalyzed reactions.[8,9] In the case of the $EtAlCl_2$-catalyzed intramolecular *trans*-addition of vinylsilanes with alkynes, **2** has been proposed as an important species.[10] The

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Baidossi, W.; Lahav, M.; Blum, J. *J. Org. Chem.* **1997**, *62*, 669 and references therein.

(3) Kataoka, Y.; Matumoto, O.; Tani, K. *Organometallics* **1996**, *15*, 5246. Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa, H.; Motomura, S. *J. Am. Chem. Soc.* **1994**, *116*, 3389. Wakabayashi, T.; Ishii, Y.; Ishikawa, K.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2123.

(4) Müller, T. E.; Grosche, M.; Herdtweck, E.; Pleier, A.-K.; Walter, E.; Yan, Y.-K. *Organometallics* **2000**, *19*, 170.

(5) Neveux, M.; Seiller, B.; Hagedorn, F.; Bruneau, C.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *451*, 133.

(6) Pilette, D.; Moreau, S.; Le Bozec, H.; Dixneuf, P. H.; Corrigan, J. F.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1994**, 409.

(7) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159. A mechanism involving a silyl-stabilized vinyl cation which produces from an alkyne and silyl cation is proposed. See also: Jung, I. N.; Yoo, B. R. *Synlett* **1999**, 519.

(8) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874. Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781.

(9) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781. Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5339. Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 13284.

(10) Asao, N.; Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3797.

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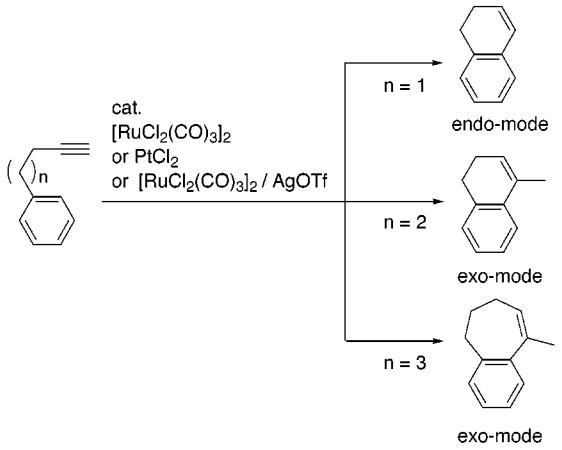
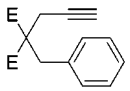
Scheme 2



addition of allylstannane to alkynes was achieved in the presence of $ZrCl_4$ as the catalyst.[11] Yamaguchi reported a series of the $GaCl_3$-mediated reactions of alkynes,[12−14] with intermediacy of either of the corresponding π-alkyne complex **1** or the vinyl gallium species **2** (M = Ga, X = Cl, n = 3).[13,14] Quite recently, the Lewis acid-catalyzed hydrosilylation of alkynes, in which **2** (M = Al, X = Cl, n = 3) is proposed as an intermediate, has been reported.[15]

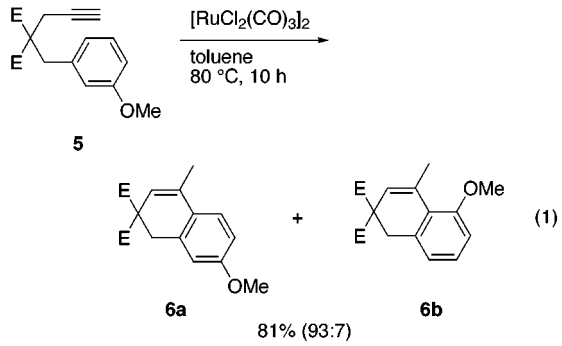
It was expected that an aromatic ring was capable of attacking the positively charged β-carbon in **2** because aromatic hydrocarbons are susceptible to electrophilic substitution.[16] We report herein the Ru(II)- and Pt(II)-catalyzed cycloisomerization[17−19] of ω-aryl-1-alkynes to dihydronaphthalenes or dihydrobenzocycloheptenes, the cyclization mode of which is dependent on the length of the tethers (Scheme 2). The key step of the reaction is the intramolecular interception of **2** by an aromatic ring.

Diethyl (benzyl)(propargyl)malonate (**4**) was initially treated with catalytic amounts of several transition metal complexes, such as $PtCl_2$, $[RuCl_2(CO)_3]_2$, $[IrCl(CO)_3]_n$, and $[Rh(OAc)]_2$, which were found to be effective as a catalyst for the skeletal reorganization of enynes.[17−19] In all cases,

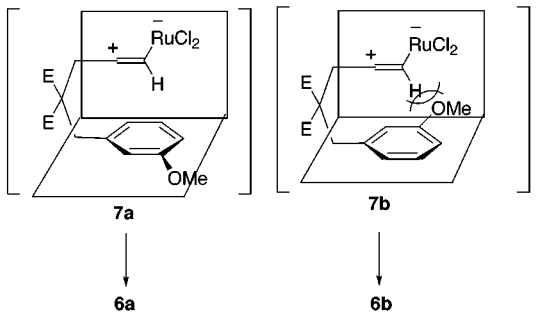


4

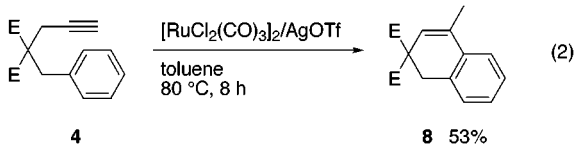
complex mixtures of products were obtained. A possible reason for this may be due to the insufficient electron density of the phenyl ring in **4**, relative to intercepting the vinyl cation in **2**. We then examined substrates, which contain an electron-rich aryl group, in place of **4**. The treatment of diethyl (*m*-methoxybenzyl)(propargyl)malonate (**5**) with 4 mol % of $[RuCl_2(CO)_3]_2$ in toluene at 80 °C for 10 h resulted in cyclization to the six-membered dihydronaphthalene derivatives **6a** and **6b**, in 81% isolated yield, in a ratio of 93:7 (eq 1). $PtCl_2$ also showed



a high catalytic activity (76% yield with 99:1 for 7 h). However, other metal complexes, such as $[RhCl(CO)_3]_2$, $[Rh(OOCCF_3)_2]_2$, $ReCl(CO)_5$, $[IrCl(CO)_3]_n$, $PdCl_2$, $MoCl_4$, $HfCl_4$, $Y(OTf)_3$, $La(OTf)_3$, $Yb(OTf)_3$, Lewis acids ($AlCl_3$, $TiCl_4$, $BF_3{\cdot}Et_2O$), and a Brönsted acid (CF_3SO_3H) did not catalyze the reaction of **5**. It should be noted that the formation of the C−C bond took place exclusively between the internal carbon on the alkyne and a position para to the methoxy group on the aromatic ring. The steric interaction between the H and the OMe group in the key intermediate **7** appears to explain the site selectivity. To produce **6b**, the reaction should proceed via **7b**, which has a considerable amount of steric congestion between the OMe group and H, compared with **7a**.



It was found that the use of AgOTf as an additive enhances the reactivity of the catalyst. The reaction of **5** in the presence of $[RuCl_2(CO)_3]_2$ (8 mol %)/AgOTf (16 mol %) was complete within 0.5 h, and a 78:22 mixture of **6a** and **6b** was obtained in a total yield of 86%. This result apparently shows that the addition of a Ag salt renders the catalyst more electrophilic and less selective. In fact, this catalytic system is applicable to the substrate **4**, which gave a complex mixture when the reaction was run in the absence of a Ag salt, as described above. The reaction of **4** in the presence of $[RuCl_2(CO)_3]_2$/AgOTf at 80 °C for 8 h gave **8** in 53% isolated yield (61% GC yield) (eq 2). Of the Ag salts examined, AgOTf was the most



(11) Asao, N.; Matukawa, Y.; Yamamoto, Y. *Chem. Commun.* **1996**, 1513. Matsukawa, Y.; Asao, N.; Kitahara, H.; Yamamoto, Y. *Tetrahedron* **1999**, *55*, 3779.

(12) Yamaguchi, M.; Sotokawa, T.; Hirama, M. *Chem. Commun.* **1997**, 743.

(13) Yamaguchi, M.; Kido, Y.; Hayashi, A.; Hirama, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1313. Kido, Y.; Yoshimura, S.; Yamaguchi, M.; Uchimaru, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1445.

(14) Kido, Y.; Yamaguchi, M. *J. Org. Chem.* **1998**, *63*, 8086.

(15) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494.

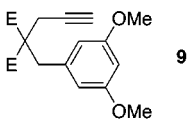
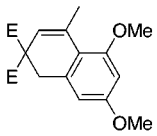
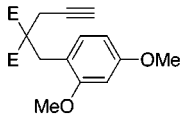
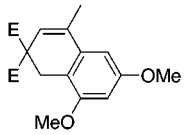
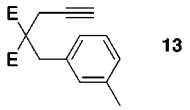
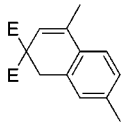
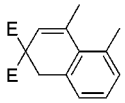
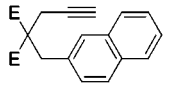
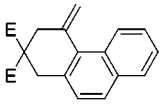
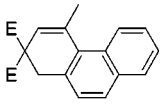
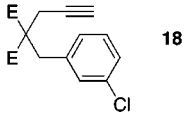
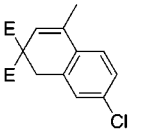
(16) A similar gallium complex (**2**) was proposed to be intercepted by intermolecular aromatics in the $GaCl_3$-promoted reaction of aromatics with alkynes. See ref 13.

(17) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049.

(18) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901.

(19) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104.

Table 1. Catalytic Cycloisomerization of 5-Aryl-1-pentynes[a]

substrate	products		
	$PtCl_2$	$[RuCl_2(CO)_3]_2$	$[RuCl_2(CO)_3]_2$/ AgOTf
 **9**		 **10**	
	82% 4 h	91% 4 h	83% 1 h
 **11**		 **12**	
	–	–	4%[b] 68 h
 **13**	 **14a**	 **14b**	
	47% (96:4) 72 h	13% (94:6) 28 h	66% (85:15) 1 h
 **15**	 **16**	 **17**	
	66% (58:42)[b, c] 25 h	18% (63:37)[c] 22 h	66% (52:48)[c] 2 h
 **18**		 **19**	
	–	–	14%[b] 26 h

[a] Reaction conditions: substrate (1 mmol), catalyst (0.08 mmol), toluene (5 mL) at 80 °C under N_2. [b] GC yield. [c] The ratio of exo and endo isomers.

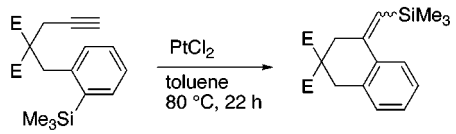
efficient for the reaction of **5**: $AgSbF_6$ (43% GC yield, 6 h), $AgPF_6$ (14%, 20 h), $AgBF_4$ (9%, 2 d), $AgOCOCF_3$ (1%, 20 h), $AgNO_3$ (2%, 24 h), Ag_2SO_4 (2%, 24 h). In contrast to $[RuCl_2(CO)_3]_2$, the addition of AgOTf was not effective in the $PtCl_2$-catalyzed reaction (9%, 26 h). Of the solvents examined, toluene and CF_3CH_2OH represent the solvents of choice; CH_3CN (4% for 20 h), dioxane (17% for 24 h), methylcyclohexane (16% for 24 h), CF_3CH_2OH (56% for 3 h). A lower reaction temperature (60 °C) in toluene decreased the yield to 44% (24 h).

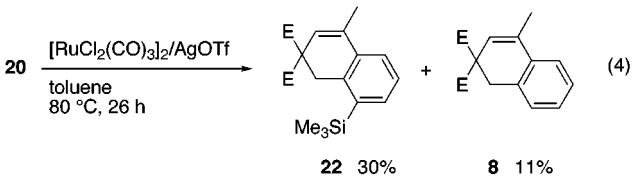
The results on the reaction of a variety of substrates are shown in Table 1. The reaction of diethyl (3,3-dimethoxybenzyl)(propargyl)malonate (**9**) gave a high yield of the corresponding product **10**, irrespective of the catalyst system. Not surprisingly, **11** is much less reactive, as anticipated. Even after 68 h, the substrate **11** was not completely consumed and the corresponding product **12** was obtained in 4% GC yield. It is apparent that the ease of cyclization is dependent on the electron-donating ability of the aromatic ring in the substrates. The reaction of **13** required a longer reaction time, and the product yields were somewhat low, compared with electron-rich systems such as **5** and **9**. However, the addition of AgOTf in the case of the $[RuCl_2(CO)_3]_2$-catalyzed reaction made the reaction extremely fast, as expected. Thus, the reaction of **13** was completed within 1 h, and isomeric mixtures of **14a** and **14b** were obtained, similar to that observed for the reaction of **5**. The reaction of naphthalene derivative **15** gave two products, **16** and **17** in a ratio of nearly 1:1. This result provides support for a reaction in which isomer **16** is a primary product which then isomerizes to **17** under the reaction conditions. It is important to note that the formation of the C−C bond exclusively took place at the α-position of the naphthalene ring, and this is consistent with the siteselectivly in the electrophilic substitution reactions. The substitution of an electron-withdrawing group, such as Cl, on the aromatic ring, as expected, resulted in a slower reaction. The reaction of **18** in the presence $[RuCl_2(CO)_3]_2$/AgOTf gave **19** in 14% GC yield, after 26 h.

It is well known that a trimethylsilyl group induces electrophilic substitution at the ipso position,[20] and as a result, we expected that the formation of a carbon−

(20) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, S. G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U. K., 1982; Vol. 2, Chapter 9.1.3.5, pp 47−51.

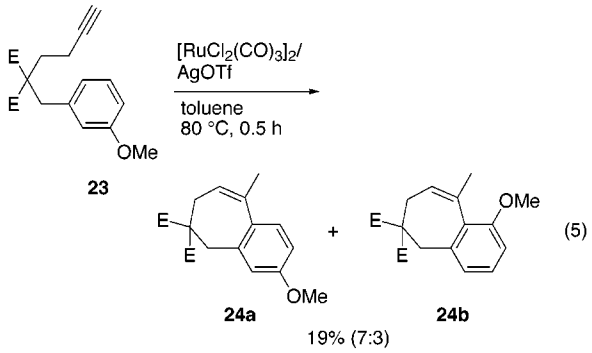
carbon bond would take place at this position, leading to a new transformation when **20** was used as the substrate. As expected, the $PtCl_2$-catalyzed reaction of **20** resulted in the formation of a C−C bond at the ipso position to give **21** in 35% GC yield (eqs 3 and 4). This reaction is a





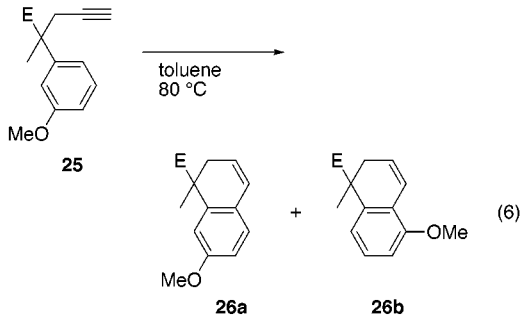
formal carbo-silylation to an alkyne.[10] In contrast, the usual cyclization product **22** was obtained in a moderate yield, along with desilylated product **8**, when a ruthenium catalyst system was employed.[21]

The reaction of a substrate which was one carbon longer, 6-aryl-1-hexyne **23**, resulted in the formation of a dihydrobenzocycloheptene framework (eq 5). The exo



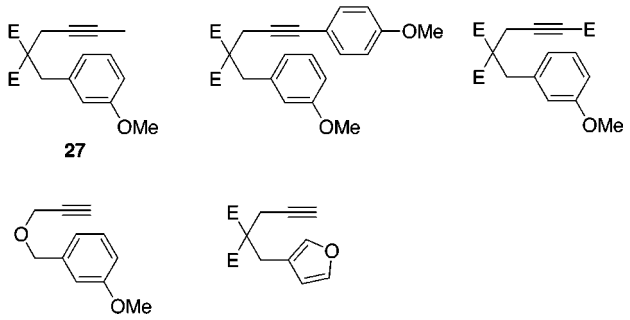
mode of cyclization was observed, similar to the reaction of 5-aryl-1-pentynes leading to dihydronaphthalenes, as shown above.

In contrast, a substrate which was one carbon shorter, cycloisomerized in the endo mode. The reaction of 4-aryl-1-butyne **25** resulted in a cyclization reaction to give dihydronaphthalene derivatives **26a** and **26b** but not the indene derivatives (eq 6).



$[RuCl_2(CO)_3]_2$	14 h	58% (76:24)
$PtCl_2$	12 h	33% (75:25)
$[RuCl_2(CO)_3]_2$/ AgOTf	11 h	complicated

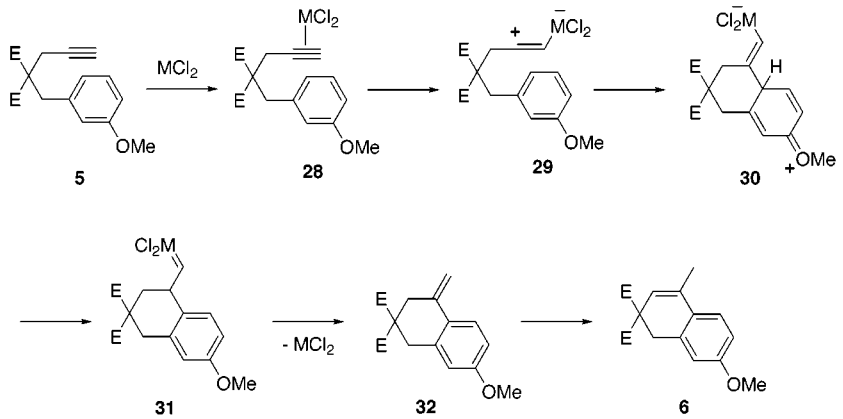
The substrates listed below were not applicable to the present reaction. The present cycloisomerization is limited to substrates having terminal alkynes. For example, the reaction of **27** gave a complicated mixture. The



presence of an oxygen atom in the tether resulted in cleavage of a propargyl carbon−oxygen bond to give benzyl alcohol. The furan ring failed to intercept the cation on **2**.

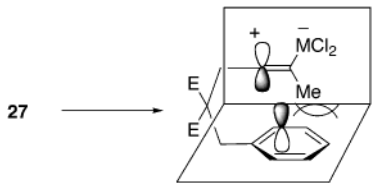
The proposed reaction mechanism is shown in Scheme 3. The initial reaction may involve the addition of the metal chloride to an alkyne, leading to a vinyl cation intermediate, containing an MCl_2 moiety, as in **29**. Complex **29** then undergoes electrophilic substitution to give **30**, which subsequently undergoes a 1,2-hydrogen shift with aromatization to give the carbenoid intermediate **31**.[22] The exo-methylene product **32** is formed as the initial product from complex **31**,[23] and then isomerizes to the more stable endo-isomer **6** under the reaction conditions employed here. The observation of the exo-isomer **16** in the reaction of **15** provides support for the

Scheme 3



fact that the exo-isomer is a primary product. Although we propose the intermediacy of the complex **29** as the key species in the reaction of **5**, the possibility that the π-complex **28** is directly converted to **30** cannot be excluded. The intramolecular aryl ring could directly attack at the alkyne carbon in **28** as a nucleophile in the *anti*-manner to give **30**. Although strong nucleophiles, such as H_2O, alcohols, and amines, are known to attack an alkyne-coordinated metal complex, there is, to our knowledge, no example of a nucleophilic attack of aromatics to π-alkyne complexes.

Compound **27** was not a suitable substrate for the present cycloisomerization, and gave a complex mixture. In the vinylmetal complex which contains a carbocation at the β-position (**34**), the arene ring is perpendicular to the olefin plane, suggesting steric repulsion between the arene ring and the Me group when the arene ring approaches the electron-deficient carbon in **34**.



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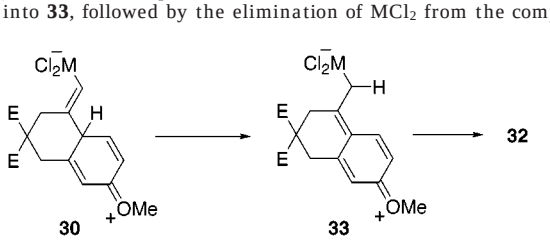
In summary, the present reaction demonstrates of the Ru(II)- or Pt(II)-catalyzed cycloisomerization of ω-aryl-1-alkynes to dihydronaphthalene and dihydrobenzocycloheptene derivatives.[24] The proposed key steps in the catalytic reaction are the generation of vinylmetal complex **2** (or **29**) which contains a cation at the β-position and the intramolecular interception of the complex **2** (or **29**) by the aromatic ring. Similar to Lewis acids which activate oxygenated compounds such as aldehydes, ketones, and epoxides by means of the coordination of the Lewis acid to the oxygen atom, Ru(II) or Pt(II) complexes activate an alkyne via the electrophilic addition to C−C triple bonds. Studies of the interception of the complex **2** by other functional groups are now underway, and we expect that these studies will permit the exploration of new organic transformations. The results obtained here suggest the intermediacy of vinylmetal complexes **2**, which contain a cation at the β-position, in the $RuCl_2$- and $PtCl_2$-catalyzed skeletal reorganization of enynes to 1-vinylcycloalkenes.[17−19]

(21) It is not clear whether **8** was formed via protodesilylation of **21** or **22**.

(22) An alternative path for the formation of **32** is the conversion of **30** into **33**, followed by the elimination of MCl_2 from the complex **33**.



(23) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1797.

(24) Recent papers on electrophile-induced cyclization to polycyclic aromatics, see: Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578. Magnus, P.; Mitchell, I. S. *Tetrahedron Lett.* **1998**, *39*, 4595.

Experimental Section

Typical Procedure. To a toluene (2 mL) solution of $[RuCl_2(CO)_3]_2$ (41 mg, 0.08 mmol) and AgOTf (41 mg, 0.16 mmol) was added a toluene (3 mL) solution of (2-propynyl)-(phenylmethyl)-2,2-propanedioic acid diethyl ester (**4**, 288 mg, 1 mmol) under N_2, and the resulting mixture was heated at 80 °C (oil bath) for 8 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$, extracted by Et_2O, and the extract was concentrated in vacuo. Purification by flash chromatography (hexane/EtOAc = 15/1) gave 152 mg of 1,2-dihydro-4-methyl-2,2-naphthalenedicarboxylic acid diethyl ester **8** (53%).

1,2-Dihydro-4-methyl-7-methoxy-2,2-naphthalenedicarboxylic Acid Diethyl Ester (6a): pale yellow solid; mp 56−58 °C; R_f 0.14 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.1 Hz, 6H), 2.10 (d, J = 1.3 Hz, 3H), 3.32 (s, 2H), 3.80 (s, 3H), 4.16 (m, 4H), 5.83 (s, 1H), 6.70−6.76 (c, 2H), 7.18 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 19.3, 34.8, 54.7, 55.0, 61.4, 111.3, 113.6, 118.8, 124.5, 126.5, 134.4, 134.5, 159.1, 170.4; IR (neat) 1742 s, 1614 s, 1576 s; MS, *m*/*z* (rel intensity %) 318 (M^+, 19), 173 (100). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.71; H, 6.92.

1,2-Dihydro-4-methyl-5-methoxy-2,2-naphthalenedicarboxylic Acid Diethyl Ester (6b). The ^{1}H NMR spectrum of **6b** was obtained from a 4:1 mixture of **6a** and **6b**: ^{1}H NMR ($CDCl_3$) δ 1.19 (t, J = 7.1 Hz, 6H), 2.28 (d, J = 1.3 Hz, 3H), 3.26 (s, 2H), 3.78 (s, 3H), 4.16 (m, 4H), 5.88 (s, 1H), 7.14 (d, J = 10.6 Hz, 1H).

1,2-Dihydro-4-methyl-2,2-naphthalenedicarboxylic Acid Diethyl Ester (8): colorless oil; bp 70−80 °C/2 mmHg; R_f 0.34 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.3 Hz, 6H), 2.14 (d, J = 1.3 Hz, 3H), 3.36 (s, 2H, 1-H), 4.11−4.23 (m, 4H), 5.97 (s, 1H), 7.18−7.25 (c, 4H); ^{13}C NMR δ 13.9, 19.3, 34.5, 54.7, 61.5, 121.3, 123.3, 126.8, 127.6, 127.8, 132.7, 133.4, 134.8, 170.4; IR (neat) 1740 s, 1646 m; MS, *m*/*z* (rel intensity %) 288 (M^+, 3), 143 (100). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.81; H, 7.07.

1,2-Dihydro-4,7-dimethoxy-2,2-naphthalenedicarboxylic Acid Diethyl Ester (10): white solid; mp 78−80 °C (hexane/EtOAc = 4/1); R_f 0.09 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.1 Hz, 6H), 2.23 (s, 3H), 3.23 (s, 2H), 3.75 (s, 3H), 3.80 (s, 3H), 4.09−4.21 (m, 4H), 5.75 (s, 1H), 6.32 (d, J = 2.6 Hz, 1H), 6.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 23.4, 36.5, 54.4, 55.2, 55.3, 61.5, 97.9, 105.4, 116.2, 119.8, 135.2, 136.9, 158.2, 159.8, 170.6; IR (KBr) 1726 s, 1638 w, 1606 s; MS, *m*/*z* (rel intensity %) 348 (M^+, 14), 202 (100). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H 6.94. Found: C, 65.63; H, 6.79.

1,2-Dihydro-6,8-dimethoxy-4-methyl-2,2-naphthalenedicarboxylic Acid Diethyl Ester (12): white solid; bp 84−85 °C (hexane/EtOAc = 4/1); R_f 0.19 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 6.9 Hz, 6H), 2.11 (s, 3H), 3.30 (s, 2H), 3.80 (s, 3H), 3.83 (s, 3H), 4.16 (m, 4H), 6.00 (s, 1H), 6.41 (s, 1H), 6.47 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 19.8, 26.6, 54.3, 55.2, 55.7, 61.4, 97.8, 101.2, 113.2, 122.0, 134.6, 134.9, 157.1, 159.0, 170.6; IR (neat) 1736 s, 1650 m, 1601 s; MS, *m*/*z* (rel intensity %) 348 (M^+, 11), 202 (100). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.44; H, 6.88.

1,2-Dihydro-4,7-dimethyl-2,2-naphthalenedicarboxylic Acid Diethyl Ester (14a): colorless oil; bp 100−105 °C/2 mmHg; R_f 0.21 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.3 Hz, 6H), 2.11 (d, J = 1.7 Hz, 3H), 2.31 (s, 3H), 3.31 (s, 2H), 4.08−4.25 (m, 4H), 5.90 (s, 1H), 7.01 (brs, 2H), 7.14 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.4, 21.2, 34.6, 54.8, 61.5, 120.3, 123.3, 127.4, 128.5, 130.8, 132.7, 134.8, 137.6, 170.6; IR (neat) 1738 s, 1618 w; MS, *m*/*z* (rel intensity %) 302 (M^+, 3), 157 (100). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.74; H, 7.46.

1,2-Dihydro-4,5-dimethyl-2,2-naphthalenedicarboxylic Acid Diethyl Ester (14b). The ^{1}H NMR spectrum of **14b** was obtained from a 6:1 mixture of **14a** and **14b**: ^{1}H NMR ($CDCl_3$) δ 2.26 (d, J = 1.7 Hz, 3H), 2.46 (s, 3H), 3.26 (s, 2H), 6.03 (s, 1H).

1,2,3,4-Tetrahydro-4-methylenephenanthrene-2,2-dicarboxylic Acid Diethyl Ester (16) Colorless liquid; bp 90−100 °C/2 mmHg; R_f 0.19 (hexane/EtOAc = 10/1); ^{1}H NMR

($CDCl_3$) δ 1.20 (t, J = 7.1 Hz, 6H), 3.16 (s, 2H, 3-H), 3.41 (s, 2H), 4.16 (q, J = 7.1 Hz, 4H), 5.51 (s, 1H), 5.52 (s, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.35−7.45 (m, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 8.43 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 35.7, 39.2, 55.4, 61.5, 117.6, 124.9, 125.1, 126.0, 126.4, 127.6, 128.3, 129.8, 131.8, 132.3, 133.1, 138.2, 170.8; IR (neat) 1740 s, 1636 m, 1600 m; MS, *m*/*z* (rel intensity %) 338 (M^+, 10), 191 (100); exact mass calcd for $C_{21}H_{22}O_4$ 338.1518, found 338.1525

1,2-Dihydro-4-methyl-2,2-phenanthrenedicarboxylic Acid Diethyl Ester (17): white solid; mp 102−104 °C (hexane/EtOAc = 4/1); R_f 0.15 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ 1.17 (t, J = 7.1 Hz, 6H), 2.51 (d, J = 1.3 Hz, 3H), 3.45 (s, 2H), 4.09−4.18 (m, 4H), 6.22 (s, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.39−7.46 (c, 2H), 7.70 (d, J = 8.3 Hz, 1H), 7.78−7.81 (m, 1H), 8.22 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 24.2, 36.8, 54.2, 61.6, 124.6, 124.7, 125.4, 125.8, 126.4, 128.4, 128.9, 130.0, 131.4, 132.8, 134.0, 135.8, 170.3; IR (KBr) 1736 s; MS, *m*/*z* (rel intensity, %) 338 (M^+, 11), 193 (100). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.33; H, 6.55.

1,2-Dihydro-7-chloro-4-methyl-2,2-naphthalenedicarboxylic Acid Diethyl Ester (19): white solid; mp 46−48 °C (hexane/EtOAc = 4/1); R_f 0.36 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.1 Hz, 6H), 2.11 (d, J = 1.3 Hz, 3H), 3.32 (s, 2H), 4.11−4.23 (m, 4H), 5.97 (s, 1H), 7.17 (c, 3H); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.3, 34.3, 54.6, 61.8, 121.8, 124.7, 126.9, 127.7, 132.0, 133.3, 134.1, 134.8, 170.1; IR (neat) 1737 s, 1597 m; MS, *m*/*z* (rel intensity %) 322 (M^+ for ^{35}Cl), 177 (100). Anal. Calcd for $C_{17}H_{19}O_4Cl$: C, 63.26; H, 5.93; Cl, 10.98. Found: C, 63.21; H, 5.88; Cl, 10.96.

(*Z*)-1,2,3,4-Tetrahydro-4-[(trimethylsilyl)methylene]-naphthalene-2,2-dicarboxylic Acid Diethyl Ester (21*Z*): pale yellow oil; bp 110−120 °C/3 mmHg; R_f 0.38 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 1.22 (t, J = 7.1 Hz, 6H), 3.06 (d, J = 1.3 Hz, 2H), 3.29 (s, 2H), 4.15 (q, J = 7.1 Hz, 4H), 5.58 (t, J = 1.3 Hz, 1H), 7.13−7.22 (c, 3H), 7.38 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.6, 14.2, 35.2, 43.0, 55.3, 61.5, 125.3, 127.3, 128.2, 128.3, 129.2, 134.8, 136.0, 149.0, 170.6; IR (neat) 1738 s, 1608 m; MS *m*/*z* (rel intensity, %) 360 (M^+, 2), 73 (100); exact mass calcd for $C_{20}H_{28}O_4Si$ 360.1757, found 360.1760.

(*E*)-1,2,3,4-Tetrahydro-4-[(trimethylsilyl)methylene]-naphthalene-2,2-dicarboxylic Acid Diethyl Ester (21*E*). The ^{1}H NMR spectrum of **21*E*** was obtained from a 86:14 mixture of **21*Z*** and **21*E***: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 3.15 (t, J = 0.7 Hz, 2H), 3.34 (s, 2H), 5.77 (s, 1H); MS *m*/*z* (rel intensity, %) 360 (M^+, 5), 75 (100).

1,2-Dihydro-4-methyl-8-(trimethylsilyl)-2,2-naphthalenedicarboxylic Acid Diethyl Ester (22): colorless oil; bp 80−90 °C/2 mmHg; R_f 0.54 (hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 9H), 1.23 (t, J = 7.1 Hz, 6H), 2.15 (d, J = 1.7 Hz, 3H), 3.45 (s, 2H), 4.18 (q, J = 7.1 Hz, 4H), 5.98 (s, 1H), 7.22 (t, J = 7.3 Hz, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.1, 14.0, 19.8, 34.8, 54.9, 61.6, 121.0, 124.6, 126.1, 133.8, 133.1, 135.3, 137.6, 138.1, 170.4; IR (neat) 1738 s; MS, *m*/*z* (rel intensity, %) 360 (M^+, 2), 73 (100); exact mass calcd for $C_{20}H_{28}O_4Si$ 360.1757, found 360.1758.

2,3-Dihydro-1*H*-8-methoxy-5-methyl-2,2-benzocycloheptenedicarboxylic Acid Diethyl Ester (24a): colorless liquid; bp 100−110 °C/2 mmHg; R_f 0.29 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 6H), 2.06 (s, 3H), 2.30 (d, J = 6.9 Hz, 2H), 3.07 (s, 2H), 3.81 (s, 3H), 4.19 (q, J = 7.1 Hz, 4H), 5.90 (t, J = 6.9 Hz, 1H), 6.82 (dd, J = 8.6, 2.6 Hz, 1H), 6.89 (d, J = 2.6 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.2, 31.0, 37.9, 55.1, 61.2, 67.4, 112.1, 115.9, 122.5, 127.0, 133.8, 137.8, 138.4, 158.0, 171.2; IR (neat) 1734 s, 1612 s; MS, *m*/*z* (rel intensity %) 332 (M^+, 17), 185 (100). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.68; H, 7.19.

2,3-Dihydro-1*H*-6-methoxy-5-methyl-2,2-benzocycloheptendicarboxylic Acid Diethyl Ester (24b): colorless liquid; bp 100−110 °C/2 mmHg; R_f 0.29 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.26 (c, 6H), 2.10 (c, 4H), 2.51 (br, 1H), 2.96 (br, 1H), 3.15 (br, 1H), 3.82 (s, 3H), 4.21 (br, 4H), 5.98 (t, J = 6.6 Hz, 1H), 6.83 (d, J = 7.9 Hz, 1H), 6.93 (d, J = 7.9 Hz, 1H), 7.16 (t, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 21.7, 30.7, 37.7, 55.4, 61.3, 66.8, 109.8, 122.9, 124.8, 127.7, 129.3, 137.4, 137.9, 156.7, 171.1; IR (neat) 1733 s, 1600 w; MS, *m*/*z* (rel intensity %) 332 (M^+, 10), 185 (100); exact mass calcd for $C_{19}H_{24}O_5$ 332.1614, found 332.1628.

1,2-Dihydro-7-methoxy-1-methyl-1-naphthalenecarboxylic Acid Ethyl Ester (26a): colorless oil; bp 70−75 °C/2 mmHg; R_f 0.06 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.3 Hz, 3H), 1.50 (s, 3H), 2.24 (ddd, J = 16.8, 4.3, 1.7 Hz, 1H), 2.96 (ddd, J = 16.8, 4.3, 1.7 Hz, 1H), 3.80 (s, 3H), 4.14 (q, J = 7.3 Hz, 2H), 5.84 (dt, J = 9.6, 4.3 Hz, 1H), 6.43 (d, J = 9.6 Hz, 1H), 6.72−6.78 (c, 2H), 7.01 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 23.9, 34.3, 46.4, 55.0, 60.8, 111.4, 112.3, 123.3, 126.0, 127.4, 139.2, 158.9, 176.1; IR (neat) 1728 s, 1612 s; MS, *m*/*z* (rel intensity %) 246 (M^+, 7), 173 (100). Anal. Calcd for $C_{15}H_{18}O_2$: C, 73.15; H 7.37. Found: C, 73.23; H, 7.17.

1,2-Dihydro-5-methoxy-1-methyl-1-naphthalenecarboxylic Acid Ethyl Ester (26b). The ^{1}H NMR spectrum of **26b** was obtained from a 1.2:1 mixture of **26a** and **26b**: ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H), 5.93−6.00 (dt, J = 9.9, 4.3 Hz, 1H), 5.96 (dt, J = 9.9 Hz, 4.3 Hz, 1H), 6.87 (d, J = 9.9 Hz, 1H), 7.16 (t, J = 8.1 Hz, 1H).

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Supporting Information Available: Full characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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