Tetrahedron Letters 54 (2013) 6196-6198

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Dicationic platinum porphyrin catalyzed cycloisomerization of enynes

Makoto Hasegawa^a, Takuya Kurahashi^{a,b,*}, Seijiro Matsubara^{a,*}

^a Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan ^b JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

ARTICLE INFO

ABSTRACT

Article history: Received 23 July 2013 Revised 26 August 2013 Accepted 30 August 2013 Available online 7 September 2013

Keywords: Platinum Porphyrin Cycloisomerization Transition-metal-catalyst

Transition-metal-catalyzed envne cycloisomerization is a useful synthetic methodology for the one-step, atom-economical construction of highly functionalized carbocyclic or heterocyclic compounds.^{1–12} This reaction has therefore been used for the synthesis of various kinds of pharmaceuticals, agrochemicals, and functionalized materials.^{13–17} The development of enyne cyclizations is therefore a research topic of great interest. Enyne cycloisomerization is generally triggered by the coordination of an alkyne moiety to an electron-deficient metal catalyst to afford key intermediates such as vinyl-metal and metal-alkylidene species. Over the decades, several metal catalysts for the cycloisomerization of enynes have been investigated intensively; for example, Pt,¹⁸ In,¹⁹ Ga,²⁰ Ru,²¹ Rh,²² Au,²³ and other metal catalysts have been reported.^{24,25} In terms of the Lewis acidities of the catalysts toward π -bonds, we presumed that higher-valent redox-stable complexes would be more effective for the cycloisomerization than lower-valent ones. Moreover, we supposed that cationic catalysts would be more effective for the reaction than non-cationic ones, because the positive charge and vacant coordination site on the catalyst allow coordination to the alkyne moiety. A number of platinum(II) complexes have been reported to be powerful catalysts for cycloisomerization.^{26–32} In the light of this knowledge, we assumed that dicationic high-valent platinum(IV) species would have a significant effect on the process. However, dicationic platinum(IV) species are relatively unstable under the reaction conditions because of their high

valences and charges. In order to solve this problem, we proposed structurally rigid tetradentate porphyrin ligands with a large π -conjugated planar aromatic structure; such ligands have a significant stabilizing effect on the metal center, so dicationic platinum(IV) species would become manageable metal catalysts, even under reaction conditions.³³ And thus, we supposed that a cationic high-valent platinum–porphyrin complex would be a promising catalyst for this reaction.³⁴ In this Letter, we report that a porphyrin ligand can stabilize dicationic platinum(IV) species, and that a dicationic platinum(IV) complex catalyzes the cycloisomerization of enynes to afford cyclic compounds. This is the first example of the use of a dicationic platinum(IV) porphyrin complex in the cycloisomerization of enynes.

Benzaldehyde and pyrrole were stirred in propionic acid at 160 °C for 30 min to afford tetraphenylporphyrin (TPP).³⁵ [Pt(TPP)] was synthesized by the reaction between PtCl₂ and TPP in benzonitrile at 210 °C for 12 h (Fig. 1).³⁶ [Pt(TPP)] was quantitatively oxidized to [Pt(TPP)]Cl₂ using H₂O₂ and HCl.^{37,38}

The oxidation number of platinum increased from II to IV as a result of this oxidation. $[Pt(TPP)](BF_4)_2$ was synthesized by treating $[Pt(TPP)]Cl_2$ with AgBF₄ in CH₂Cl₂ at ambient temperature for 12 h. After the reaction, the solution was filtered in order to remove the Ag salt, and the solvent was evaporated. $[Pt(TPP)](BF_4)_2$ was obtained in 65% yield. Because this platinum species had a high oxidation state and the counter-anion weakly coordinated with the metal center, we presumed that this platinum–porphyrin complex would behave as a strong Lewis acid, and that it would be effective for activation of unsaturated carbon–carbon triple bonds of enynes in cycloisomerizations.

Cycloisomerization of 1,6-enynes is successfully carried out in the presence of a dicationic platinum(IV) catalyst to afford five-membered ring systems. The use of a weakly coordinating axial ligand is the key to bringing out the catalytic activity of platinum porphyrin for the reaction. © 2013 Elsevier Ltd. All rights reserved.







^{*} Corresponding authors. Tel.: +81 75 383 2440; fax: +81 75 383 2438. *E-mail addresses:* kurahashi.takuya.2c@kyoto-u.ac.jp (T. Kurahashi), matsubara. seijiro.2e@kyoto-u.ac.jp (S. Matsubara).

^{0040-4039/\$ -} see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tetlet.2013.08.128



Figure 1. Preparation of platinum-porphyrin complex

We next briefly examined catalytic activity of the porphyrin catalyst with cycloisomerization of enynes. The cycloisomerization of 1a with [Pt(TPP)](BF₄)₂ in 1,2-dichloroethane (DCE) afforded the five-membered product 2a in 84% yield as the sole product (Table 1, entry 1). We then investigated the reaction conditions extensively, and found that the counter-anions and solvents had a profound effect on the reactivities of the catalysts. In the presence of [Pt(TPP)](SbF₆)₂, **2a** was obtained in 74% yield (entry 2). However, when [Pt(TPP)]Cl₂ was used as the catalyst, sufficient product was not obtained, probably because strong coordination of the chloride ion made the platinum center less cationic and less electrophilic. The effects of hexafluorophosphate, which is a weaker coordinating counter-anion than BF4 and SbF6, were also examined. The reaction with $[Pt(TPP)](PF_6)_2$ did not afford product **2a** (entry 4).³⁹ Furthermore, when [Pt(TPP)] was used as the catalyst, the desired product was not obtained (entry 5). The use of AgBF₄ in place of the cationic platinum complex afforded a trace amount of 2a (entry 6). Solvent effects were also investigated. The reaction in aromatic solvents, that is, benzene and toluene, afforded 2a in

Table 1

Optimization of reaction conditions^a

MeOOC MeOOC	Catalyst (2.5 Solvent, 80 ° a	mol%) C, 24 h MeOOC MeOOC	Ph 2a
Entry	Catalyst	Solvent	Yield ^b (%)
1	[Pt(TPP)](BF ₄) ₂	CICH ₂ CH ₂ CI	84
2	$[Pt(TPP)](SbF_6)_2$	CICH ₂ CH ₂ Cl	74
3	[Pt(TPP)]Cl ₂	CICH ₂ CH ₂ Cl	<1
4	$[Pt(TPP)](PF_6)_2$	CICH ₂ CH ₂ CI	<1
5	[Pt(TPP)]	CICH ₂ CH ₂ CI	<1
6	AgBF ₄	ClCH ₂ CH ₂ Cl	<5
7	$[Pt(TPP)](BF_4)_2$	Benzene	28
8	$[Pt(TPP)](BF_4)_2$	Toluene	43
9	$[Pt(TPP)](BF_4)_2$	1,4-Dioxane	<1
10	$[Pt(TPP)](BF_4)_2$	Acetonitrile	<1
11	[Cr(TPP)]BF ₄	ClCH ₂ CH ₂ Cl	19
12	[Mn(TPP)]BF ₄	CICH ₂ CH ₂ CI	<1
13	[Fe(TPP)]BF ₄	ClCH ₂ CH ₂ Cl	10

 a Reactions were carried out using the catalyst (2.5 mol %) and enyne 1a (0.2 mmol) in 1.0 mL of 1,2-dichloroethane (DCE) at 80 $^\circ C$ for 24 h.

^b NMR yields.

low yields (entries 7 and 8). Also, the desired product **2a** was not obtained in 1,4-dioxane and acetonitrile, which could coordinate to the platinum–porphyrin complex (entries 9 and 10). Other metal–porphyrin complexes, namely $[Cr(TPP)]BF_4$, $[Mn(TPP)]BF_4$, and $[Fe(TPP)]BF_4$, showed lower catalytic activities for the cycloisomerization than did the cationic platinum–porphyrin complexes (entries 11–13), because their metal centers were monocationic and had lower Lewis acidities than dicationic platinum(IV) species.

In order to demonstrate the scope of platinum–porphyrin-complex-catalyzed cycloisomerization of enynes, we carried out the reaction with various types of enynes and diynes under the optimized reaction conditions (Table 2.). The reaction using a substrate with a prenyl group afforded **2c** in low yield; this was attributed to the steric effect of the prenyl group (entry 2). The reaction with **1d**, bearing a terminal alkene moiety, was performed successfully to furnish **2d** in 72% yield (entry 3). The reaction with **1e** afforded the corresponding product **2e** in 89% yield (entry 4). In order to determine whether the stereochemistry of the alkene moiety of

Table	2	
Scope	of the	cycloisomerization



 a Reactions were carried out using [Pt(TPP)](BF_4)_2 (2.5 mol %) and enyne 1 (0.2 mmol) in 1.0 mL of 1,2-dichloroethane (DCE) at 80 °C for 24 h.

^b NMR yields.

^c Reactions were carried out for 12 h.



Scheme 1. Plausible reaction mechanism.

the substrate was preserved, **1f** and **1g** were reacted. Substrate **1f**, which had an *E*-form alkene moiety, afforded a product bearing an *E*-form alkene moiety, in 76% yield (entry 5). Similarly, using a substrate with a *Z*-form alkene moiety gave product **2g**, with a *Z*-form alkene moiety (entry 6). The information on the *E*- or *Z*-form of the alkene moiety of the substrate was preserved in the alkene moiety did not react at all (entries 7 and 9). The platinum–porphyrin complexes essentially activated the terminal alkyne group. This might be derived from the steric effect of the substrate was inactive in this reaction (entry 8). The cycloisomerization of 1,7-enynes and 1,6-enynes possessing oxygen or nitrogen tether moiety did not afford the products.

The reaction with substrates bearing substituents at the terminal olefinic carbon afforded the corresponding products stereoselectively. Taking into account the fact that stereoselectivity was preserved during the reaction, the reaction mechanism is assumed to be very similar to the previously reported one.^{26,27} A plausible mechanism for the platinum-porphyrin-catalyzed cycloisomerization of enynes is shown in Scheme 1. Coordination of the terminal alkyne of the substrate 1 to the platinum-porphyrin complex affords the vinyl-metal species **3**, which is stabilized by the alkene moiety and the porphyrin ligand. Considering the results of entries 7 and 9 in Table 2, internal alkyne moieties of substrates have difficulty in forming intermediate **3**, presumably because of the steric effect of the substituent at the terminal alkynyl carbon.⁴⁰ Then, a cyclobutane annulated five-membered intermediate 4 is formed. In the final step, the platinum-porphyrin complex is eliminated from 4 to give product 2. In this catalytic process, the porphyrin ligand may play an important role in stabilizing not only the dicationic platinum(IV) species but also the cationic intermediates such as **3** and **4** with its large π -conjugated planar aromatic structure.

In summary, we developed dicationic platinum(IV)–porphyrincatalyzed cycloisomerization of enynes. Dicationic high-valent platinum(IV) species were found to be effective in the catalytic process. The key to the success of this reaction is the use of a porphyrin ligand along with a weakly coordinating axial counter-anion ligand, which makes the platinum center cationic and sufficiently electrophilic to activate carbon–carbon triple bonds but also stable under the reaction conditions. Further efforts to expand the scope of the chemistry and studies of the detailed mechanism are currently underway in our laboratories.

Acknowledgments

This work was supported by JST, ACT-C and Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan. T.K. acknowledges the Asahi Glass Foundation, The Uehara Memorial Foundation, Tokuyama Science Foundation, and Kurata Memorial Hitachi Science and Technology Foundation.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.08. 128.

References and notes

- 1. Belmont, P.; Parker, E. Eur. J. Org. Chem. 2009, 6075.
- 2. Lee, S. I.; Chatani, N. Chem. Commun. 2009, 371.
- 3. Fürstner, A. Chem. Soc. Rev. 2009, 38, 3208.
- 4. Michelet, V.; Toullec, P. Y.; Genêt, J.-P. Angew. Chem., Int. Ed. 2008, 47, 4268.
- 5. Trost, B. M. Science 1991, 254, 1471.
- 6. Jiménez-Núñez, E.; Echavarren, A. M. Chem. Commun. 2007, 333.
- 7. Gorin, D. J.; Sherry, B. D.; Toste, F. D. Chem. Rev. 2008, 108, 3351.
- 8. Méndez, M.; Muñoz, M. P.; Echavarren, A. M. Chem. Rev. 2008, 108, 3326.
- 9. Nevado, C.; Echavarren, A. M. Synthesis 2005, 167.
- 10. Fairlamb, I. J. S. Angew. Chem., Int. Ed. 2004, 43, 1048.
- 11. Aubert, C.; Buisine, O.; Malacria, M. Chem. Rev. 2002, 102, 813.
- 12. Magnus, P.; Principe, L. M.; Slater, M. J. J. Org. Chem. 1987, 52, 1483.
- 13. Trost, B. M.; Braslau, R. Tetrahedron Lett. 1988, 29, 1231.
- 14. Trost, B. M.; Phan, L. T. Tetrahedron Lett. 1993, 34, 4735.
- 15. Zhang, Z.; Lu, X. Tetrahedron 1996, 7, 1923.
- 16. Yamada, H.; Aoyagi, S.; Kibayashi, C. Tetrahedron Lett. 1996, 37, 8787.
- 17. Lu, X.; Zhu, G.; Wang, Z.; Ma, S.; Ji, J.; Zhang, Z. Pure Appl. Chem. 1997, 69, 553.
- 18. Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. Organometallics 1996, 15, 901.
- 19. Miyanohana, Y.; Chatani, N. Org. Lett. 2006, 8, 2155.
- 20. Chatani, N.; Inoue, H.; Kotsuma, T.; Murai, S. J. Am. Chem. Soc. 2002, 124, 10294.
- 21. Schmidt, B. Angew. Chem., Int. Ed. 2003, 42, 4996.
- 22. Chakrapani, H.; Liu, C.; Widenhoefer, R. A. Org. Lett. 2003, 5, 157.
- Matsumoto, Y.; Selim, K. B.; Nakanishi, H.; Yamada, K.; Yamamoto, Y.; Tomioka, K. Tetrahedron Lett. 2010, 51, 404.
- 24. Sylvester, K. T.; Chirik, P. J. J. Am. Chem. Soc. 2009, 131, 8772.
- 25. Berk, S. C.; Grossman, R. B.; Buchwald, S. L. J. Am. Chem. Soc. 1994, 116, 8593.
- 26. Fürstner, A.; Stelzer, F.; Szillat, H. J. Am. Chem. Soc. 2001, 123, 11863.
- 27. Fürstner, A.; Davies, P. W.; Gress, T. J. Am. Chem. Soc. 2005, 127, 8244.
- 28. Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. Organometallics 2001, 20, 3704.
- 29. Zhang, L.; Sun, J.; Kozmin, S. A. Adv. Synth. Catal. 2006, 348, 2271.
- 30. Méndez, M.; Muñoz, M. P.; Echavarren, A. M. J. Am. Chem. Soc. 2000, 122, 11549.
- 31. Echavarren, A. M.; Nevado, C. Chem. Soc. Rev. 2004, 33, 431.
- 32. Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. Synlett 2006, 575.
- 33. Kataoka, Y.; Matsumoto, O.; Ohashi, M.; Yamagata, T. Chem. Lett. 1994, 1283.
- 34. Ozawa, T.; Kurahashi, T.; Matsubara, S. Org. Lett. 2012, 14, 3008.
- Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. J. Org. Chem 1967, 32, 476.
- Milgrom, L. R.; Zuurbier, R. J.; Gascoyne, J. M.; Thompsett, D.; Moore, B. C. Polyhedron 1992, 11, 1779.
- Milgrom, L. R.; Zuurbier, R. J.; Gascoyne, J. M.; Thompsett, D.; Moore, B. C. Polyhedron 1994, 13, 209.
- Mink, L. M.; Neitzel, M. L.; Bellomy, L. M.; Falvo, R. E.; Boggess, R. K.; Trainum, B. T.; Yeaman, P. Polyhedron 1997, 16, 2809.
- (a) Beck, W.; Sünkel, K. Chem. Rev. 1988, 88, 1405; (b) Krossing, I.; Raabe, I. Angew. Chem., Int. Ed. 2004, 43, 2066.
- 40. For example of the use of platinum(IV) complex for cycloisomerization of enyne, see: Oh, C. H.; Bang, S. Y.; Rhim, C. Y. Bull. Korean Chem. Soc. 2003, 24, 887.