

PtCl₂-Catalyzed Conversion of 1,6- and 1,7-Enynes to 1-Vinylcycloalkenes. Anomalous Bond Connection in Skeletal Reorganization of Enynes

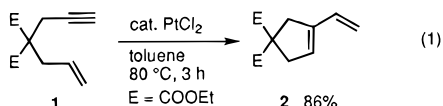
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Summary: The treatment of 1,6- and 1,7-enynes with a catalytic amount of PtCl₂ in toluene at 80 °C results in skeletal reorganization (cyclorearrangement) of the enynes to give 1-vinylcycloalkenes in high yields. A deuterium labeling experiment indicates that two mechanistic paths are operating for the cyclorearrangement. The nature and position of substituents affect the reaction course. Anomalous carbon–carbon bond formation is attained selectively in the reaction of 1,6-enynes having an ester group at the terminal acetylenic carbon.

Recently we have reported [RuCl₂(CO)₃]₂-catalyzed skeletal reorganization (i.e., cyclorearrangement) of enynes to 1-vinylcycloalkenes (such as that in eq 1; vide



infra) with high chemical yields and high selectivity (>98% isomeric purity in all cases).¹ The reaction involves simultaneous C–C bond cleavage and C–C bond formation. Attention to similar transformations of enynes has been paid recently by several groups. Trost reported that tetrakis(methoxycarbonyl)palladacyclopentadiene, a Pd(II) complex, catalyzed the skeletal reorganization of 1,6-enynes to 1-vinylcyclopentenes.² Katz³ and Mori⁴ reported that the treatment of enynes with a catalytic amount of a tungsten or chromium carbene complex gave 1-vinylcycloalkenes. Recently, Mori found that the ruthenium carbene complex (Ru=CHCH=CPh₂)(PCy₃)₂Cl₂⁵ is also active for the conversion of 1,6-, 1,7-, and 1,8-enynes to 1-vinylcycloalkenes.⁶ Although these transformations are formally similar to each other, they would proceed via different mechanisms. Trost proposed that the initial step of their reaction is formation of a palladacyclopentene complex, a Pd(IV) complex,⁷ via oxidative cyclization of enynes. In the case of carbene-complex-catalyzed reactions, it is believed that formation of metalacy-

clobutenes by the [2 + 2] cycloaddition of the carbene moiety of the catalyst with an alkyne in enynes would initiate the catalytic reaction. On the other hand, our reaction¹ is likely to involve intermediacy of a slipped, polarized η^1 -alkyne complex bearing a positive charge at the β position via an (η^2 -alkyne)ruthenium complex, although the mechanism of the reaction requires further investigation.⁸ The intermediacy of such a carbocationic complex was recently proposed by Dixneuf in the rearrangement reaction of 1-[4-(dimethylamino)phenyl]propargyl alcohol with Ru(II) complex, in which the 4-(dimethylamino)phenyl group migrates to the positively charged β carbon of the (η^1 -alkyne)ruthenium complex.⁹ An (η^1 -alkyne)aluminum complex was also postulated as a trigger species in MeAlCl₂-mediated rearrangement of 1-(trimethylsilyl)propargyl alcohol trimethylsilyl ethers to 2-trimethylsilyl enones.¹⁰ η^1 -Alkyne complexes are proposed as intermediates along one reaction pathway for the rearrangement of η^2 -alkyne complexes to vinylidene complexes.¹¹ An (η^1 -alkyne)palladium complex bearing a positive charge at the β position is proposed as a key species in the insertion of an alkyne into the Pd–C bond of palladacycles.^{12,13} We provide feasibility that some catalytic reactions reported so far which are generally believed to proceed via η^2 -alkyne complexes might involve slipped η^1 -alkyne complexes as an actual key species. If such a process was operating in the Ru(II)-catalyzed skeletal reorganization of enynes,¹ it would be expected that the Ru(II) complex may not be the only catalyst for the skeletal reorganization of enynes because it is well-known that a variety of transition metals may coordinate with an alkyne through its π system.¹⁴ Indeed, we found that complexes such as [RhCl(CO)₂]₂, [IrCl-

(8) The η^1 -alkyne complex bearing a positive charge at the β position may exist in equilibrium with the carbene which can undergo intramolecular cyclopropanation to give a cyclopropylalkylidene complex, which seems to be a reactive intermediate in the present reaction. A study of the reaction mechanism is underway. See also Trost, B. M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085.

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

(10) Enda, J.; Kuwajima, I. *J. Chem. Soc., Chem. Commun.* **1984**, 1589.

(11) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(12) Ryabov, A. D.; van Eldik, R.; Le Borgne, G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386.

(13) The theoretical study of the alkyne insertion into the Pd–CH₃ bond of PdCl(CH₃)(NH₃)(CH=CH) indicated that at least in the CH=CH case the η^1 -alkyne complex seems not to be involved; however, the geometry of the transition state corresponds to η^1 coordination of the alkyne. de Vaal, P.; Dedieu, A. *J. Organomet. Chem.* **1994**, *478*, 121.

(14) 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.

[®] Abstract published in *Advance ACS Abstracts*, January 1, 1996.

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

(2) (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (b) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647. (c) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850.

(3) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.

(4) Watanuki, S.; Ochifuji, N.; Mori, M. *Organometallics* **1994**, *13*, 4129.

(5) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974.

(6) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020.

(7) For a recent paper on Pd(IV), see: Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; Traill, P. R.; White, A. H. *Organometallics* **1995**, *14*, 199 and references cited therein.

(CO)₃Ir, PtCl₂, ReCl(CO)₅, and AuCl₃ can also cause the skeletal reorganization of enynes. Among these, PtCl₂ is the most effective and active catalyst for a variety of enynes. We here wish to report PtCl₂-catalyzed skeletal reorganization of 1,6- and 1,7-enynes to 1-vinylcycloalkenes. A characteristic feature of the PtCl₂-catalyzed reaction is the wide applicability of enynes, some of which is not applicable in Ru(II)-catalyzed reaction.¹ In addition, anomalous carbon–carbon bond formation was observed in a deuterium-labeling experiment and also in the reaction of 1,6-enynes having a substituent at the terminal acetylenic carbon.

The treatment of 1,6-enyne **1** with 4 mol % of PtCl₂ in toluene at 80 °C under nitrogen for 3 h resulted in skeletal reorganization to give 3-ethenyl-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (**2**) in 86% isolated yield (>99% isomeric purity) (eq 1).¹⁵ No byproducts can be observed by ¹H NMR or capillary GC analysis of the crude reaction mixtures.¹⁶ A variety of platinum complexes were examined for their ability to catalyze reaction 1. Although PtCl₄ worked comparably (79% yield, 2 h) to PtCl₂, PtCl₂(PPh₃)₂, PtCl₂(COD), PtI₂, and Pt(SPh)₂ had no catalytic activity. Both the presence of a halide ion on platinum and the absence of any other ligands on platinum seem to be essential for the reaction to proceed.¹⁷ Solvents such as THF (36% yield), anisole (15%), dioxane (28%), DMF (4%), and cyclohexane (13%) were not suitable for reaction 1.

The selected results are summarized in Table 1.¹⁸ In all cases, the starting enynes were completely consumed and the isomeric purity of the products was quite high (>98%). No byproducts could be detected by GC and ¹H NMR in all cases.¹⁶ 1,6-Enynes **3** (propargyl alcohol type), **5** (allyl alcohol type), **7** (disubstituted olefin), and **9** (trisubstituted olefin) underwent selective skeletal reorganization in the presence of PtCl₂, as similar to the case of [RuCl₂(CO)₃]₂.¹ Whereas Ru(II)-catalyzed reaction of **11** (cyclic olefin) gave three isomeric products including the expected product **12** and two unidentified compounds, the PtCl₂-catalyzed reaction of **11** gave exclusively **12** in high yield (entry 5). The reaction proceeded equally well with an enyne having a chloro atom on the olefinic carbon (entry 6).¹⁹

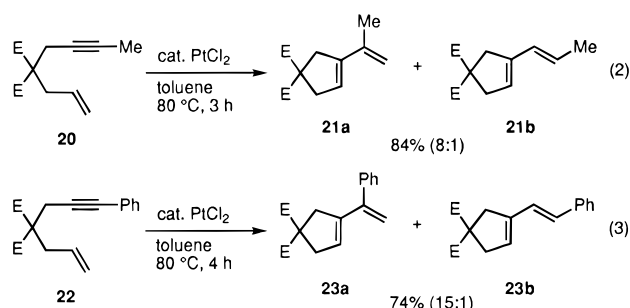
It should be noted that enynes having Cl, Br, Me, and Ph at the terminal acetylenic carbon are applicable to the present reaction, being different from the Ru(II)

Table 1. PtCl₂-Catalyzed Reaction of Enynes to 1-Vinylcyclopentenes^a

entry	enyne	product	yield ^b time
1			93% 1 h
2			76% 1 h
3			66% 20 h
4			97% 1 h
5			97% 1 h
6			70% ^c 5 h
7			76% 1 h
8			69% 1 h

^a Reaction conditions: enyne (1 mmol), PtCl₂ (0.04 mmol), toluene (5 mL), at 80 °C under N₂. ^b Isolated yield based on the enyne. ^c A small amount of **15** was obtained. See ref 19.

catalytic process. The reaction of enynes having halogen atom, **16** and **18**, gave the corresponding 1-(1-halovinyl)cyclopentenes **17** and **19**, respectively (entries 7 and 8 in Table 1). The reaction of **20** with 8 mol % of PtCl₂ at 80 °C was complete in 3 h to afford two isomers **21a,b** with a ratio of 8:1 (eq 2). Formation of **21b** is



interesting with respect to reaction mechanism, because it involves an unusual change in bond relationship.

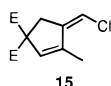
(15) In an attempt to isolate or to detect the intermediates along with the skeletal reorganization, **1** was treated with a stoichiometric amount of PtCl₂ at 25, 40, and 80 °C, and the reactions were monitored by ¹H NMR. In all cases, the only peaks we can see were those from **1** and/or **2**, and no other peaks can be detected.

(16) Small amounts of insoluble polymeric materials have been formed in some cases, causing incomplete material balances.

(17) Ineffectiveness of PtI₂ may be due to its poor solubility.

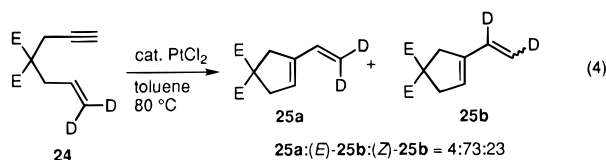
(18) All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra. See the Supporting Information.

(19) A small amount (1–2%) of **15** was also formed as a byproduct. On the other hand, **14** was obtained in 52% yield along with **15** in 23% yield when the reaction of **13** was run using 4 mol % of [RuCl₂(CO)₃]₂ as the catalyst in toluene at 80 °C for 38 h. Formation of **15** might proceed via chloro–metalation of catalysts to **13**. Chloro–metalation of PtCl₂(CO)₂ and RuCl₂(CO)₂(PMe₂Ph)₂ to dimethyl acetylenedicarboxylate is a precedent. Canziani, F.; Garlaschelli, L.; Malatesta, M. C. *J. Organomet. Chem.* **1978**, *146*, 179. Holland, P. R.; Howard, B.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 231.



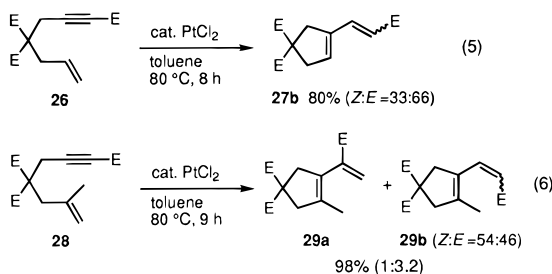
While the olefinic terminal carbon in **20** migrates onto the alkyne carbon bearing methyl group to give **21a**, in a formal sense, insertion of the olefinic terminal carbon in **20** into the C–C triple bond would give **21b**. Reorganization leading to type **a** product (such as **21a**, etc.) has usually been encountered in skeletal reorganization of enynes reported so far,^{1–4,6} and the bond connection occurs as one expected for metathesis; formation of cyclobutene is via a [2 + 2] cycloaddition followed by cycloreversion. Thus, formation of **21a** is the case. The catalytic reaction is applicable to the substrate having a phenyl group, **22**, and a 15:1 mixture of **23a,b** was obtained (eq 3).

The anomalous C–C bond formation was also observed in an ²H labeling experiment using **24**, which gave **25a,b** with 4:96 ratio (eq 4).²⁰ This result clearly



indicates that two mechanistic paths are operating for the present reaction. Substitution either at the terminal olefinic carbon (**7**, **9**, and **11**) or at the terminal acetylenic carbon (**16**, **18**, **20**, and **22**) favors the path leading to type **a** product. In contrast, unsubstituted enyne **1** (or **24**) favors an anomalous path leading to type **b** product.

Our efforts have been made to search the system producing selectively type **b** product. After many attempts, we finally found that ester-substituted enyne **26** underwent skeletal reorganization to give exclusively **27b** in 80% yield (eq 5). Substitution of methyl group

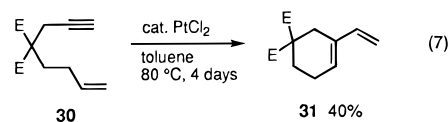


at the olefinic part still favored the formation of type **b** product (eq 6). It seemed that an electron-withdrawing group on the terminal acetylenic carbon atom promotes

(20) Trost also made an observation similar to that in eq 4 by an ²H-labeling study. See ref 2a. However, Trost has not observed a type **b** product except for the labeling reaction.

the formation of type **b** product although the selectivity was affected by the nature of the substituents at the olefinic functionality.

The reaction of 1,7-enyne **30** proceeded slowly (4 days), but the corresponding 1-vinylcyclohexene **31** was isolated in 40% yield (eq 7).



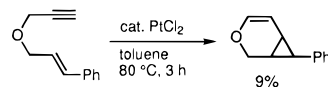
In summary, PtCl₂ is shown to be an efficient catalyst for transformation of enynes to 1-vinylcycloalkenes.²¹ In the reaction of enynes having a terminal acetylenic moiety, substitution of the alkene has little effect on the efficiency of the present reaction; in all cases, the yields are in the range of 66–97%. A deuterium labeling experiment indicates that two mechanistic paths are operating for the present reaction. The nature and position of substituents affect the reaction course.

Acknowledgment. This work was supported in part by grants from the Ministry of Education, Science, Sports, and Culture of Japan. Thanks are given to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining MS, HRMS, 600-MHz NMR, and elemental analyses.

Supporting Information Available: Text giving special data and elemental analyses for the products (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(21) The reaction of cinnamyl propargyl ether under standard reaction conditions resulted in complete consumption of the starting material, and a clean reaction was observed by GC; however, the only product isolated was 7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene in 9% yield. Most of the enyne would polymerize.



Quite recently, Blum reported that the conversion of allyl propargyl ethers to 3-oxabicyclo[4.1.0]hept-4-enes effectively proceeded when PhC≡CCH₂OCH₂CH=CHR (R = H, Ph, 1-C₁₀H₇) was reacted in the presence of PtCl₄: Blum, J.; Beer-Kraft, H.; Badrieh, Y. *J. Org. Chem.* **1995**, *60*, 5567.