Cationic Platinum-Complex-Catalyzed Skeletal Reorganization of Enynes

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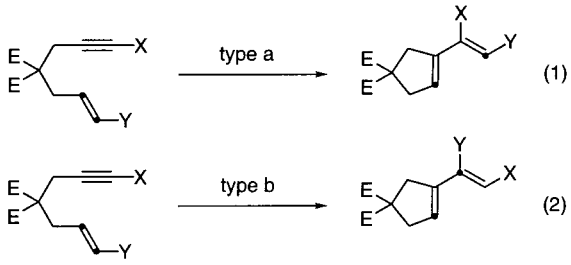
The skeletal reorganization of 1,6-enynes into 1-vinylcyclopentenes was catalyzed by a cationic platinum complex under extremely mild conditions. The unusual rearrangement of the carbon skeleton, involving the cleavage of both the double and triple carbon−carbon bonds, was observed in certain cases and confirmed by ^{13}C- and ^{2}H-labeling experiments. Reaction mechanisms describing the rearrangement of carbocations are proposed.

Introduction

The transition-metal-catalyzed cyclization of enynes and diynes appears to be a highly promising approach for ring construction under very mild conditions.[1] The reaction does not require additional reactants and produces few byproducts, making this procedure desirable in terms of synthesis efficiency and the minimization of atomic waste. Among such catalytic cyclizations, the conversion of 1,6-enynes to 1-vinylcyclopentenes is a very useful and interesting reaction. This reaction is called enyne metathesis or skeletal reorganization and involves carbon−carbon bond cleavage and the reconstruction of new carbon−carbon bonds. Katz[2] and Mori[3] reported skeletal reorganization catalyzed by a Fisher-type tungsten carbene complex and Grubb's ruthenium carbene complex, respectively. The reaction mechanism of these metal-carbene-catalyzed cyclizations involves the formation of a metallacyclobutene by the [2 + 2] cycloaddition of the carbene moiety of the catalyst with alkyne followed by a ring-closing metathesis reaction with olefin. Trost developed the Pd-catalyzed cyclization of 1,6-enynes to give 1-vinylcyclopentenes.[4] The reaction mechanism proposed involves a tetravalent palladacycle generated by the oxidative cyclization of the enyne. Subsequent reductive elimination of the palladium from the palladacycle generates a bicyclic cyclobutene that undergoes electrocyclic ring opening to give the product. Chatani and Murai reported the $[RuCl_2(CO)_3]_2$- and $PtCl_2$-catalyzed efficient skeletal reorganization of 1,6-enynes to 1-vinylcyclopentenes.[5,6] In these reactions, a cyclopropyl carbene complex was suggested to be an intermediate. It was later clarified that the authors had succeeded in capturing the carbenoid by olefin intramolecularly.[7] The $PtCl_2$-catalyzed reaction was subsequently applied to the formal syntheses of streptorubin B and metacycloprodigiosin.[8] In these skeletal reorganizations, the carbon−carbon double bond is cleaved normally and the two carbons are placed at the 2-position of the cyclopentene ring thus formed and at the terminus of the vinyl group (type A, eq 1). In this type



A rearrangement, a substituent on the acetylene terminal (X) is introduced inside the vinyl group and a substituent on the olefin terminal (Y) is oriented toward the terminus of the vinyl group. An unusual rearrangement was reported as a rare case,[4a,5,6] in which both the double and triple carbon−carbon bonds are cleaved and the four carbons are arranged alternately (type B, eq 2). The positions of the substituents X and Y of the product are the opposite of those of type A products. The type B pathway is very interesting from a mechanistic point of view; however, the exact reaction mechanism has yet to be clarified. During the course of developing a new catalytic reaction using a cationic transition-metal complex, we found that a certain cationic platinum complex exhibited high activity for the skeletal reorganization of 1,6-enynes, preferentially affording type B products. The bond relationships of the rearrangement were confirmed by ^{13}C- and ^{2}H-labeling experiments.

(1) Review: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34. (b) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1.
(2) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.
(3) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020.
(4) (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (b) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850. (c) Trost, B. M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085.
(5) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049.
(6) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901.
(7) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104.
(8) (a) Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305. (b) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785.

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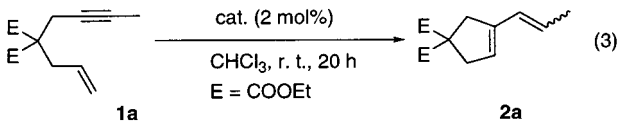
Table 1. Skeletal Reorganization of 1a Catalyzed by Platinum or Palladium Complexes[a]

entry	catalyst	yield (%)[b]	*E*/*Z*[c]
1	$[Pt(dppe)(PhCN)_2](BF_4)_2$	75	55/45
2	$[Pt(dppp)(PhCN)_2](BF_4)_2$	74	28/72
3	$[Pt(dppb)(PhCN)_2](BF_4)_2$	72	29/71
4	$[Pt(PPh_3)_2(PhCN)_2](BF_4)_2$	3	58/42
5	$Pt(dppp)Cl_2$	0	
6	$Pt(PPh_3)_2Cl_2$	0	
7	$[Pd(dppp)(PhCN)_2](BF_4)_2$	0	
8	$[Pd(PPh_3)_2(PhCN)_2](BF_4)_2$	0	

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (0.01 mmol), 1 mL of $CHCl_3$, room temperature, 20 h, N_2 atmosphere. [b] Isolated yield. [c] Determined by ^1H NMR.

Results

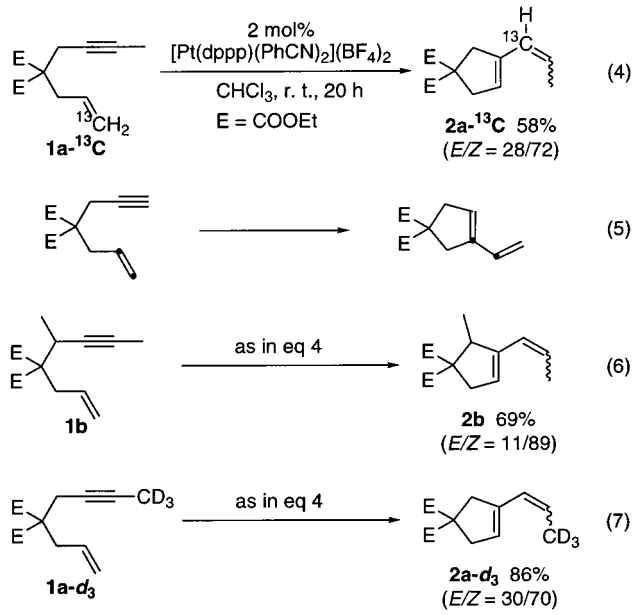
Initially, the reaction of 1,6-enyne **1a** having a methyl group on the acetylene terminus was examined. The reaction was conducted in $CHCl_3$ at room temperature for 20 h in the presence of 2 mol % of cationic platinum complexes. This procedure afforded the cyclyzed product **2a** having a methyl group on the terminal of the vinyl group, which was assumed to be the type B product (eq 3). No type A product was observed by either GC-MS



(3)

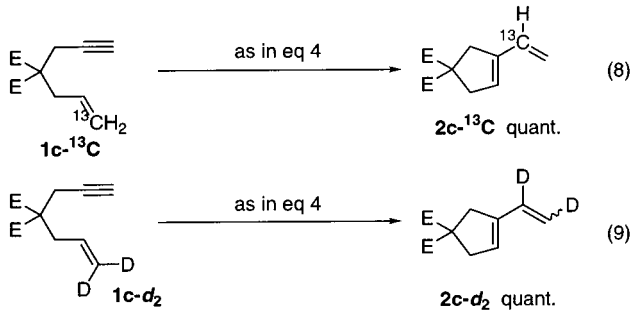
or NMR analysis. The effect of the various catalysts in this reaction is shown in Table 1. A series of cationic platinum complexes coordinated with bidentate diphosphine ligands such as dppe, dppp, and dppb exhibited good catalytic activities, affording the product in approximately 75% yield (entries 1−3). Although almost the same amounts of *E* and *Z* isomers were obtained for dppe (entry 1), the *Z* isomer was obtained preferentially in the cases of dppp and dppb (entries 2 and 3). The complex coordinated with the monodentate ligand of PPh_3 exhibited only minor catalytic activity (entry 4). Neither neutral dichloroplatinum complexes such as $PtCl_2(dppp)$ and $PtCl_2(PPh_3)_2$ nor cationic palladium complexes such as $[Pd(dppp)(PhCN)_2](BF_4)_2$ and $[Pd(PPh_3)_2(PhCN)_2](BF_4)_2$ exhibited catalytic activity under the same reaction conditions (entries 5−8). $CHCl_3$ and CH_2Cl_2 were suitable solvents for this cyclization, and no reaction occurred in other solvents such as THF, acetone, acetonitrile, and nitromethane.

To obtain information regarding the bond relationship of the rearrangement, ^{13}C- and ^2H-labeling experiments were carried out. The treatment of **1a-^{13}C** (^{13}C-labeled at the olefin terminal) with the platinum complex $[Pt(dppp)(PhCN)_2](BF_4)_2$ exclusively afforded **2a-^{13}C**, in which the ^{13}C atom is enclosed inside the propenyl group, as shown in eq 4. Although another reorganization pattern where the triple bond is cleaved and the double bond is inserted into the cleaved acetylenic carbons (eq 5) is conceivable, it is inhibited by reaction using the 1,6-enyne **1b,** which has a methyl group at the propargyl position and which forms the product **2b** having the methyl group on the same side of the propenyl group (eq 6). If the reaction proceeds according to eq 5, the methyl group should be at the opposite side



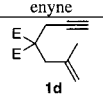
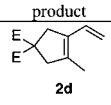
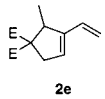
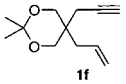
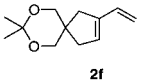
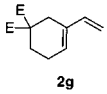
of the propenyl group. These results clearly indicate that type B cyclization takes place in the reaction of **1a**. Hydrogen atoms on the methyl group of **1a** do not migrate during the cyclization, judging from the control experiment using CD_3-substituted enyne **1a-*d*$_3$**, as shown in eq 7. Unfortunately, enynes having a phenyl and an ethoxycarbonyl group at the alkyne terminus did not react under our reaction conditions.

The reaction of an unsubstituted enyne **1c** proceeded smoothly, affording the cyclized product **2c** in quantitative yield. The ^{13}C-labeling experiment for **1c-^{13}C** revealed that type B cyclization also takes place in the case of this unsubstituted enyne (eq 8). The reaction of



enyne **1c-*d*$_2$** labeled with deuterium at the olefin terminal demonstrated that the two deuterium atoms were equally distributed both inside and at the terminal of the vinyl group of the product **1c-*d*$_2$** (eq 9), which is in agreement with the results reported previously by Trost et al.[4a] and Murai et al.[6] This indicates that the 1,2-hydrogen shift is involved in the reaction pathway. Table 2 shows the results of other enynes without the substituent on either the olefin or acetylene terminals. The reaction of enyne **1d** substituted with a methyl group at the internal olefinic carbon did not proceed cleanly, affording the product **2d** in only 22% yield and unidentifiable nonvolatile byproducts (entry 1). The enyne **1e** substituted with the methyl group at the propargyl position gave the expected product **2e**, as in the case of **1b** (eq 6) in 87% yield (entry 2). The geminal ester groups can be replaced with an acetonide of two

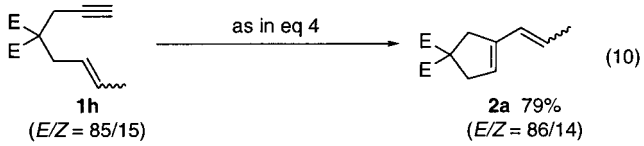
Table 2. Skeletal Reorganization of Enynes Catalyzed by [Pt(dppp)(PhCN)$_2$](BF$_4$)$_2$[a]

entry	enyne	product	yield (%)[b]
1	 **1d**	 **2d**	22
2	 **1e**	 **2e**	87
3	 **1f**	 **2f**	100
4	 **1g**	 **2g**	27

[a] Reaction conditions: enyne **1** (0.5 mmol), catalyst (0.01 mmol), 1 mL of $CHCl_3$, room temperature, 20 h, N_2 atmosphere. [b] Isolated yield.

hydroxymethyl groups (**1f**) to give the product **2f** in quantitative yield (entry 3). The 1,7-enyne **1g** gave the six-membered-ring product **2g** in a modest yield of 27% (entry 4).

We next examined the reaction of an enyne **1h** having a methyl group on the olefin terminal. Surprisingly, the reaction of this enyne gave the cyclized product **2a** having the methyl group on the terminal of the vinyl group, which was the same product as that from the reaction of enyne **1a** having a methyl group on the acetylene terminal (eq 10). In this case, the *E* isomer



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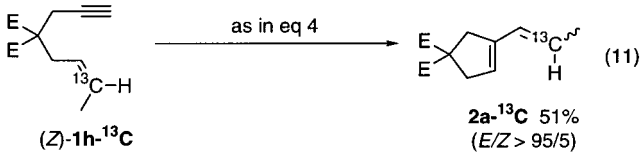

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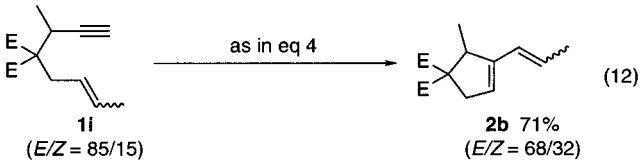
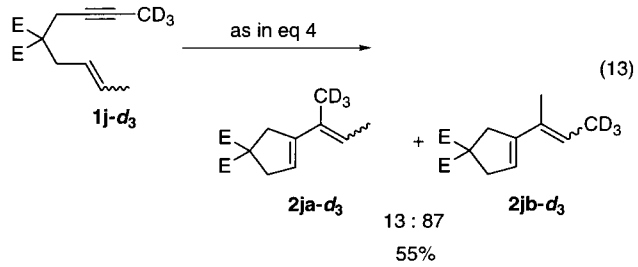


(12)

was formed preferentially. We performed the ^{13}C-labeling experiment again for this enyne **1h**. The reaction of **1h-^{13}C** labeled with ^{13}C at the outside of the olefin exclusively gave the product **2a-^{13}C**, having the ^{13}C atom outside the double bond of the propenyl group. This result clearly indicates that type A rearrangement occurs in this case (eq 11). The reaction of an enyne **1i** bearing a methyl group at the propargyl position also gave a type A product **2b** in 71% yield with an *E*/*Z* ratio of 68/32 (eq 12).

As stated above, the enyne having a methyl group on the acetylene terminal underwent type B rearrangement, whereas the enyne having a methyl group on the olefin terminal underwent type A rearrangement. In light of this, we examined an enyne **1j** having methyl groups on both the acetylene and olefin terminals. The reaction gave the *E*/*Z* mixture of the cyclized product **2j** having the methyl groups on both carbons of the vinyl group. As the products of type A and type B rearrangement are the same in this case, the CD_3-substituted enyne **1j-*d*$_3$** was used to discriminate these two methyl groups. The result was that the type B product **2jb-*d*$_3$** was formed preferentially, having the CD_3 group at the terminal of the vinyl group (eq 13).

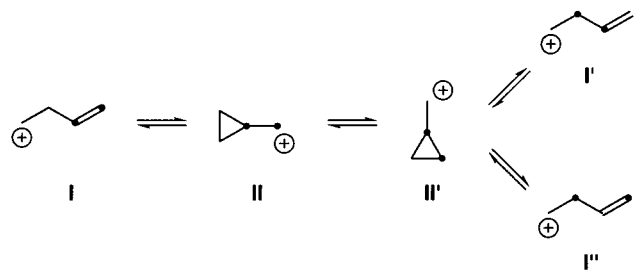


(13)

Discussion

Fürstner et al. pointed out that carbocationic intermediates, homoallyl−cyclopropylmethyl−cyclobutyl cations, may be involved in their $PtCl_2$-catalyzed cyclization of 1,6-enynes.[8] In the present skeletal reorganization, we considered that the carbocationic species would also be generated as intermediates by virtue of the electron-deficient character of the cationic platinum complex and that the generation of the carbocationic intermediates is most likely to explain such an unusual rearrangement. Both the type A and type B rearrangements can be explained by the rearrangement of homoallyl and cyclopropyl methyl cations, as shown in Scheme 1. The

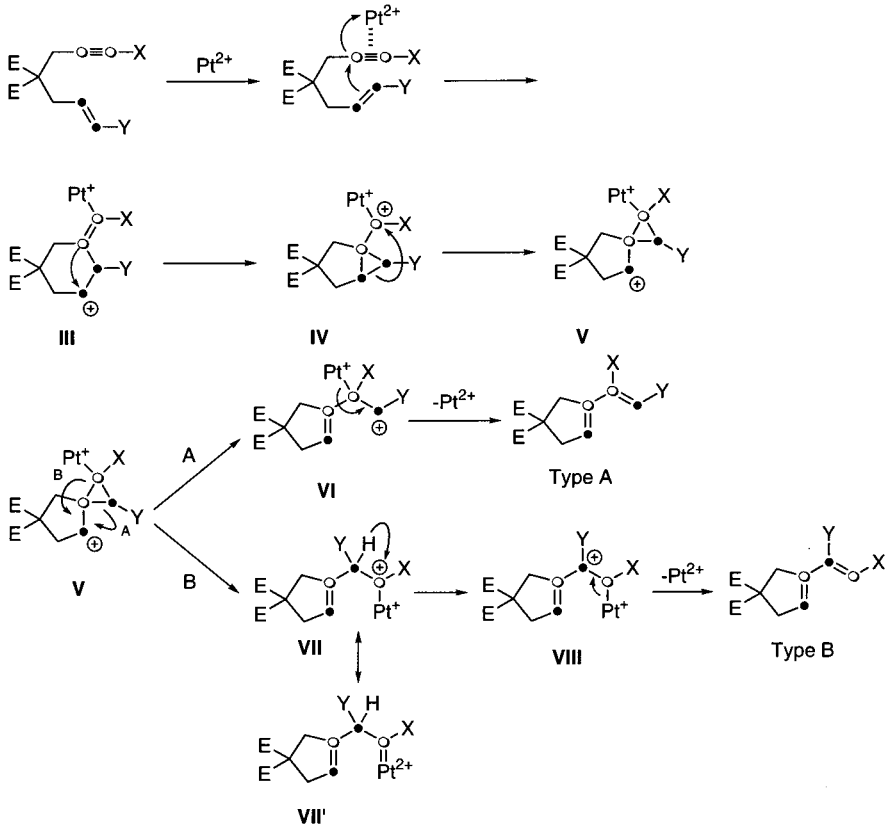
Scheme 1



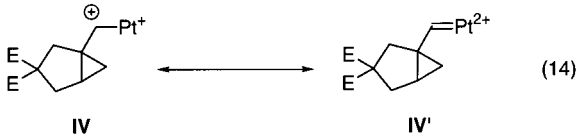
homoallyl cation **I** generates the stable cyclopropyl methyl cation **II**.[9] The recombination of the carbons generates the cyclopropyl methyl cation **II′**,[9] which then regenerates the homoallyl cations **I′** and **I″** having different carbon arrangements. Scheme 2 shows possible pathways of the skeletal reorganization of 1.6-enynes. For clarity, acetylenic carbons are indicated by white circles and olefinic carbons are indicated by black circles. The cationic platinum complex coordinates to the triple bond, and the intramolecular attack of the olefin generates the six-membered homoallyl cation **III**. This homoallyl cation undergoes the same rearrangement as that shown in Scheme 1. **III** gives the bicyclic cyclopropyl carbinyl cation **IV** and subsequently rearranges into the cyclopropyl carbinyl cation **V**. The cationic intermediate **IV**, where Pt^{2+} bonds to the cationic carbon,

(9) For comprehensive discussions, see: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 312−326 and references therein.

Scheme 2



can be considered to be the carbene complex **IV′**, as shown in eq 14. **IV′** is the same intermediate as that



proposed by Murai et al. in their $PtCl_2$-catalyzed skeletal reorganization of 1,6-enynes.[6,7] However, in our catalytic system, electron-deficient Pt^{2+} centers would give the intermediate **IV** a carbocationic character. Hence, there are two possible pathways for these products. The cleavage of the bond between the white and black carbons of **V** (Scheme 2) gives the five-membered homoallyl cation **VI** having a carbon order of black, white, white, black. Subsequent elimination of platinum would give the type A product. The cleavage of the bond between the two white carbons gives the five-membered homoallyl cation **VII**, having a carbon order of black, white, black, white. After the 1,2-migration of hydrogen, elimination of platinum from **VIII** gives the type B product. Similar reaction pathways from **V** to type A and type B products were proposed by Trost et al. in their palladium-catalyzed skeletal reorganization of 1,6-enynes.[4a] As stated above, the formation of **2c-*d*$_2$** from deuterized enyne **1c-*d*$_2$**, in which deuterium isotopes are distributed equally inside and at the terminal of the vinyl group, supports the 1,2-migration of hydrogen, which is also known to be involved in the elimination of metals from complexes such as **VII** or its carbene form **VII′**.[10] The preferential formation of *Z* isomers in the type B pathway would be rationalized according to the discussion by Rosenblum et al., in which (*Z*)-1-deuteriopropene was formed from a carbenoid complex, $[Cp(CO)_2Fe{=}CDCH_2CH_3]^+$.[10a]

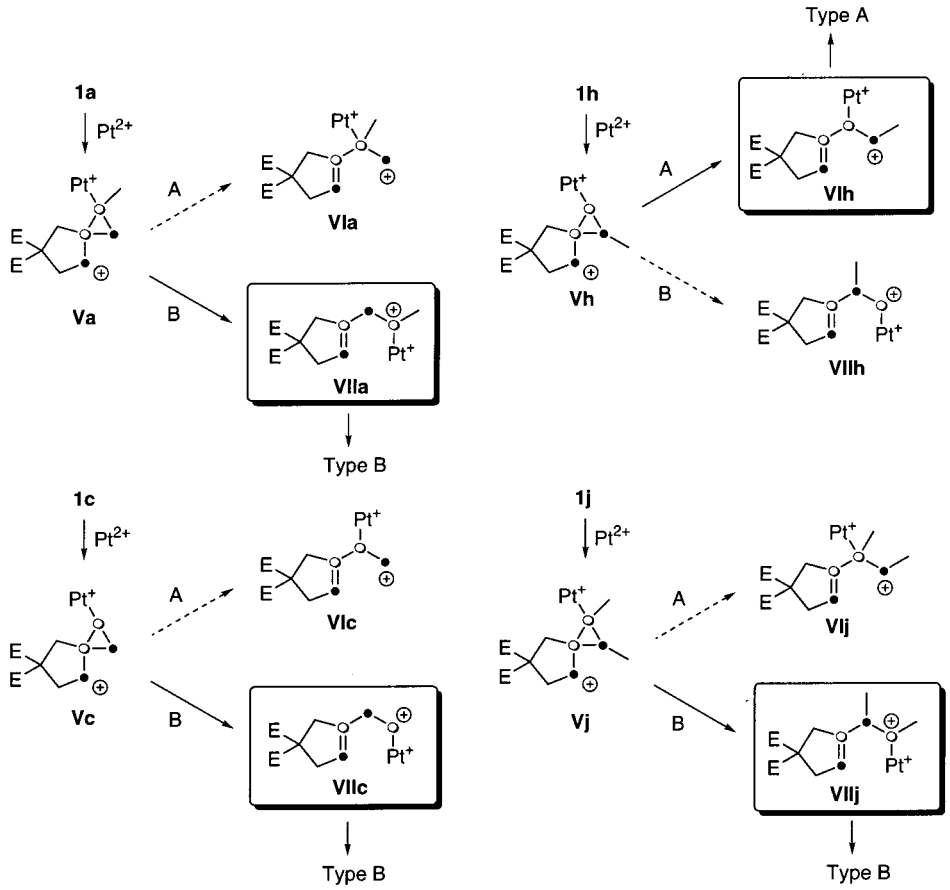
The selection of either the type A or type B pathway is expected to be dependent on the stability of the homoallyl cations **VI** and **VII**. Scheme 3 summarizes the key step (**V** to **VI** or **VII**) for four typical enynes: **1a**, **1c**, **1h**, and **1j**. The cyclopropyl carbinyl cation **Va** generated from **1a** forms a more substituted and thus stable cation **VIIa**, rather than the less substituted cation **VIa**, giving the type B product. For the same reason, **Vc** and **Vj** generated from **1c** and **1j**, respectively, would form **VIIc** and **VIIj** preferentially. However, in the case of **1h**, the intermediate **Vh** should generate the secondary carbocation **VIh**, giving the type A product. Although the difference between the stability of **VIh** and **VIIh** does not appear to be large, the easier one-step formation of the product (by elimination of Pt^{2+}) from **VIh** would make the type A pathway preferential.

Conclusion

The cationic platinum complex coordinated with diphosphine catalyzes the skeletal reorganization of 1,6-enynes, affording 1-alkenylcyclopentenes under mild conditions. The reaction favors the formation of unusual type B products, in which four carbons of acetylene and olefin are arranged alternately. Reaction pathways

(10) (a) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (c) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. (d) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (e) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

Scheme 3



involving the rearrangement of homoallyl and cyclopropylcarbinyl cations were proposed.

Experimental Section

General Information. All reactions were carried out in Schlenk tubes using anhydrous solvents under N_2. $CHCl_3$ was dried over CaH_2 and distilled before use. It is important to remove a trace of ethanol from $CHCl_3$, which is added as stabilizer. Otherwise the reaction stops. NMR spectra were recorded using $CDCl_3$ as the solvent. Elemental analyses were carried out in the Microanalytical Laboratory of the Institute for Chemical Reaction Science, Tohoku University. Spherical silica gel (100−210 μm, Kanto Chemical) was used for column chromatography. Cationic platinum complexes were prepared as reported before.[11] Enynes **1** were prepared from diethyl allylmalonate or crotylmalonate and corresponding propargyl bromides.[5,6,12] A typical procedure is as follows. To a suspension of NaH (1.19 g, 49.6 mmol) in DMF (40 mL) was added slowly diethyl allylmalonate (8.96 g, 44.8 mmol) at 0 °C and stirred for 0.5 h. To the reaction mixture was added propargyl bromide (5.79 g, 48.7 mmol), and the mixture was stirred at room temperature for 4 h. The reaction was quenched by adding saturated aqueous NH_4Cl (200 mL) and extracted with Et_2O (50 mL × 3). The organic layer was washed with water (100 mL × 3) and dried over $MgSO_4$. After the solvent was removed in vacuo, the residue was distilled (0.03 mmHg, 85 °C) to give the enyne **1c**. ^{1}H NMR (500 MHz): δ 5.62 (1H, ddt, J = 17.0, 10.1, 9.9 Hz), 5.19 (1H, d, J = 17.0 Hz), 5.13 (1H, d, J = 10.1 Hz), 4.21 (4H, q, J = 7.1 Hz), 2.80 (2H, d, J = 9.9 Hz), 2.80 (2H, s), 2.02 (1H, s), 1.26 (6H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz): δ 169.7, 131.7, 119.8, 78.9, 71.4, 61.6, 56.6, 36.3, 22.5, 14.0. IR (neat): 3286, 2982, 1737, 1642, 1441, 1367, 1289, 1216, 1146, 1096, 1070, 926, 857 cm^{-1}.

Preparation of Enyne 1a-*d*$_3$. To a solution of **1c** (4.77 g, 20.0 mmol) in THF (40 mL) was added 1.52 M *n*-BuLi in hexanes (14.1 mL, 21.4 mmol) over a period of 1 h at −78 °C. After the addition, HMPA (8 mL) and then CD_3I (3.84 g, 26.5 mmol) were added to the reaction mixture at −78 °C and the mixture was warmed gradually to room temperature. The reaction was quenched by adding saturated aqueous NH_4Cl (200 mL), and the mixture was extracted with Et_2O (50 mL × 3). The organic layer was washed with water (100 mL × 3) and dried over $MgSO_4$. After the solvent was removed in vacuo, the residue was distilled (0.03 mmHg, 95 °C) to give the enyne **1a-*d*$_3$** (3.88 g, 76%). ^{1}H NMR (500 MHz): δ 5.64 (1H, ddt, J = 16.9, 10.1, 7.5 Hz), 5.16 (1H, d, J = 16.9 Hz), 5.11 (1H, d, J = 10.1 Hz)), 4.20 (4H, q, J = 7.1 Hz), 2.78 (2H, d, J = 7.5 Hz), 2.73 (2H, s), 1.25 (6H, t, J = 7.1 Hz).

1j-*d*$_3$ was prepared from **1h** and CD_3I by the same procedure as for **1a-*d*$_3$**. ^{1}H NMR (500 MHz, mixture of *E*, *Z*): δ 5.55−5.60 (1H, m), 5.23−5.26 (1H, m), 4.19 (4H, q, J = 7.1 Hz), 2.81 (0.30H, d, J = 7.9 Hz), 2.71 (2H, s), 2.70−2.72 (1.70H, m), 1.66 (0.45H, d, J = 7.9 Hz), 1.64 (2.55H, d, J = 7.9 Hz), 1.24 (6H, t, J = 7.1 Hz).

Preparation of 1a-^{13}C. A mixture of PPh_3 (1.53 g, 5.84 mmol) and $^{13}CH_3I$ (1.00 g, 7.00 mmol) in THF (20 mL) was stirred at 50 °C for 1 h. Precipitated white solid was collected and dried in vacuo to give $^{13}CH_3PPh_3I$ (2.12 g, 90%). To a mixture of $^{13}CH_3PPh_3I$ (208 mg, 0.514 mmol) and 3,3-bis(ethoxycarbonyl)propanal, prepared by hydrolysis of (2,2-diethoxyethyl)propanedionic acid diethyl ester[13] (96.1 mg,

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0.475 mmol), in THF (20 mL) was added 1.0 M NaHMDS in THF (1.2 mL, 1.2 mmol) at −78 °C, and the mixture was warmed gradually to room temperature. After the mixture was stirred for 12 h, 1-bromo-2-butyne (190 mg, 1.43 mmol) was added and the mixture was stirred a further 3 h. The reaction was quenched by adding saturated aqueous NH_4Cl (100 mL), and the mixture was extracted with Et_2O (30 mL × 3). The organic layer was washed with water (50 mL × 3) and dried over $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by silica gel chromatography (8:1 hexanes/AcOEt) to give the enyne **1a-^{13}C** (59.3 mg, 49%). ^{1}H NMR (500 MHz): δ 5.64 (1H, ddt, J = 16.9, 10.1, 7.5 Hz), 5.16 (1H, dd, J = 16.9 Hz, J_{CH} = 154.5 Hz), 5.11 (1H, dd, J = 10.1 Hz, J_{CH} = 157.9 Hz), 4.20 (4H, q, J = 7.1 Hz), 2.78 (2H, d, J = 7.5 Hz), 2.73 (2H, q, J = 2.6 Hz), 1.76 (3H, t, J = 2.6 Hz), 1.25 (6H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz): δ 170.1, 132.1, 119.5 (strong), 78.7, 73.4, 61.4, 57.0, 36.4, 22.9, 14.1, 3.5. IR (neat): 3286, 2982, 1737, 1642, 1441, 1367, 1289, 1216, 1146, 1096, 1070, 926, 857 cm^{-1}.

1c-^{13}C was prepared from 3,3-bis(ethoxycarbonyl)propanal, $^{13}CH_3PPh_3I$, and propargyl bromide in the same procedure of **1a-^{13}C**. ^{1}H NMR (500 MHz): δ 5.62 (1H, ddt, J = 17.0, 10.1, 9.9 Hz), 5.19 (1H, dd, J = 17.0 Hz, J_{CH} = 154.7 Hz), 5.13 (1H, dd, J = 10.1 Hz, J_{CH} = 158.2 Hz), 4.21 (4H, q, J = 7.1 Hz), 2.80 (2H, d, J = 9.9 Hz), 2.80 (2H, s), 2.02 (1H, s), 1.26 (6H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz): δ 169.7, 131.7, 119.8 (strong), 78.9, 71.4, 61.6, 56.6, 36.3, 22.5, 14.0.

1c-*d*$_2$ was prepared from 3,3-bis(ethoxycarbonyl)propanal, CD_3PPh_3I, and propargyl bromide in the same procedure of **1a-^{13}C**. ^{1}H NMR (500 MHz): δ 5.62 (1H, m), 4.21 (4H, q, J = 7.1 Hz), 2.80 (2H, d, J = 9.9 Hz), 2.80 (2H, s), 2.02 (1H, s), 1.26 (6H, t, J = 7.1 Hz).

Preparation of (*Z*)-1h-^{13}C. A 1.52 M solution of *n*-BuLi in hexanes (0.66 mL, 1.00 mmol) was added to a suspension of $^{13}CH_3PPh_3I$ (405 mg, 1.00 mmol) in THF (15 mL) at −78 °C. After the mixture was stirred for 0.5 h, methyl iodide (710 mg, 5.04 mmol) was added and the mixture was warmed to room temperature. After this mixture was stirred for 12 h, precipitated white solid was collected to give $CH_3{}^{13}CH_2PPh_3I$. To a mixture of $CH_3{}^{13}CH_2PPh_3I$ (324 mg, 0.775 mmol) and 3,3-bis(ethoxycarbonyl)propanal (156 mg, 0.772 mmol) in THF (20 mL) was added 1.0 M NaHMDS in THF (1.6 mL, 1.6 mmol) at −78 °C and the mixture was warmed gradually to room temperature. After the mixture was stirred for 12 h, propargyl bromide (134 mg, 1.13 mmol) was added and the mixture was stirred for a further 3 h. The reaction was quenched by adding saturated aqueous NH_4Cl (100 mL), and the mixture was extracted with Et_2O (30 mL × 3). The organic layer was washed with water (50 mL × 3) and dried over $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by silica gel chromatography (8:1 hexanes/AcOEt) to give the enyne **(*Z*)-1h-^{13}C** (60.1 mg, 31%). ^{1}H NMR (400 MHz): δ 5.65 (1H, dm, J_{CH} = 153.7 Hz), 5.18−5.21 (1H, m), 4.17−4.25 (4H, m), 2.84 (2H, m), 2.78 (2H, d, J = 2.7 Hz), 2.00 (1H, t, J = 2.7 Hz), 1.66 (3H, m), 1.25 (6H, t, J = 7.1 Hz). ^{13}C NMR (100 MHz): δ 169.9, 128.9 (strong), 119.8, 79.2, 71.1, 61.6, 56.8, 29.3, 22.4, 14.0. IR (neat): 3284, 2982, 1736, 1439, 1367, 1281, 1208, 1096, 1051, 969, 858 cm^{-1}.

Catalytic Cyclization. A typical procedure is as follows. Enyne **1** (0.5 mmol) was added to a solution of $[Pt(dppp)(PhCN)_2](BF_4)_2$ (10.9 mg, 0.01 mmol) in $CHCl_3$ (1.0 mL), and the mixture was stirred at room temperature for 20 h. Ether (10 mL) was added to the mixture, and the precipitate was filtered off. After the solvent was removed in vacuo, the residue was purified by silica gel chromatography (10:1 hexanes/AcOEt) to give the product **2**. The products (*E*)-**2a**, **2c**, **2d**,[5] and **2g**[6] were identified by comparing the spectral data with reported ones. Characterization data for the other products follow.

(*Z*)-2a. ^{1}H NMR (500 MHz): δ 5.93 (1H, d, J = 11.6 Hz), 5.52 (1H, dq, J = 11.6, 7.2 Hz), 5.50 (1H, br s), 4.21 (4H, q, J = 7.1 Hz), 3.25 (2H, br s), 3.05 (2H, br s), 1.83 (3H, d, J = 7.2 Hz), 1.26 (6H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz): δ 172.1, 138.6, 126.7, 126.4, 125.1, 61.5, 59.5, 43.0, 40.1, 14.9, 14.0. IR (neat): 2981, 1733, 1446, 1366, 1253, 1184, 1070, 862, 822 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.17; H, 7.86.

(*Z*)-2b. ^{1}H NMR (500 MHz): δ 5.81 (1H, d, J = 12.8 Hz), 5.63 (1H, dq, J = 12.8, 6.9 Hz), 5.44 (1H, brs.), 4.20 (4H, m), 3.61 (1H, q, J = 7.3 Hz), 3.34 (1H, d, J = 17.7 Hz), 2.78 (1H, d, J = 17.7 Hz), 1.81 (3H, d, J = 6.9 Hz), 1.25 (6H, m), 0.98 (3H, d, J = 7.3 Hz). ^{13}C NMR (125 MHz): δ 172.2, 170.3, 143.7, 127.7, 124.1(2), 63.9, 61.4, 61.2, 46.7, 38.5, 15.1, 14.7, 14.1, 14.0. IR (neat) 2932, 1734, 1458, 1251, 1153 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.74; H, 8.52.

(*E*)-2b. ^{1}H NMR (500 MHz): δ 6.06 (1H, d, J = 15.9 Hz), 5.73 (1H, dq, J = 15.9, 6.6 Hz), 5.33 (1H, br s), 4.18 (4H, m), 3.64 (1H, q, J = 7.4 Hz), 3.34 (1H, d, J = 17.7 Hz), 2.74 (1H, d, J = 17.7 Hz), 1.78 (3H, d, J = 6.6 Hz), 1.24 (6H, m), 0.99 (3H, d, J = 7.4 Hz). ^{13}C NMR (125 MHz): δ 172.1, 170.0, 146.1, 126.7, 126.2, 121.8, 64.7, 61.3, 61.2, 43.2, 37.6, 18.4, 14.2, 14.1-(2). IR (neat): 2932, 1734, 1458, 1251, 1153 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.72; H, 8.44.

2e. ^{1}H NMR (500 MHz): δ 6.36 (1H, dd, J = 17.7, 10.9 Hz), 5.49 (1H, br s), 5.23 (1H, d, J = 17.7 Hz), 5.12 (1H, d, J = 10.9 Hz), 4.25−4.11 (4H, m), 3.70 (1H, q, J = 7.1 Hz), 3.35 (1H, d, J = 18.1 Hz), 2.78 (1H, dd, J = 18.1, 3.1 Hz), 1.27 (3H, t, J = 7.2 Hz), 1.23 (3H, t, J = 7.2 Hz), 1.01 (3H, d, J = 7.1 Hz). ^{13}C NMR (125 MHz): δ 170.0, 146.4, 131.5, 125.1, 114.8, 64.8, 61.4, 61.3, 42.7, 37.9, 14.2, 14.1, 14.0. IR (neat): 2979, 1732, 1640, 1592, 1463, 1366, 1249, 1152, 1061, 962, 905, 860, 827 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.39; H, 7.79.

2f. ^{1}H NMR (500 MHz) δ 6.51 (1H, dd, J = 17.3, 10.7 Hz), 5.61 (1H, br s), 5.08 (1H, d, J = 17.3 Hz), 5.06 (1H, d, J = 10.7 Hz), 3.70 (4H, s), 2.38 (2H, s), 2.35 (2H, s), 1.46 (3H, s), 1.45 (3H, s). ^{13}C NMR (125 MHz): δ 140.8, 133.4, 128.4, 114.3, 97.7, 69.4, 40.7, 40.3, 38.4, 24.0, 23.8. IR (neat): 2963, 1718, 1412, 1261, 1022, 800, 665 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.01; H, 9.55.

2j (Major Isomer). ^{1}H NMR (500 MHz): δ 5.44 (1H, br s), 5.40 (1H, q, J = 7.2 Hz), 4.21 (4H, q, J = 7.1 Hz), 3.19 (2H, brs.), 3.07 (2H, br s), 1.79 (3H, s), 1.72 (3H, d, J = 7.2 Hz), 1.26 (6H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz): δ 172.2, 140.4, 131.4, 124.3, 123.1, 61.5, 59.2, 42.8, 40.2, 23.5, 15.1, 14.0. IR (neat): 2979, 1733, 1447, 1366, 1251, 1183, 1072 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.38; H, 7.98.

2j (Minor Isomer). ^{1}H NMR (500 MHz): δ 5.53 (1H, q, J = 7.0 Hz), 5.48 (1H, br s), 4.19 (4H, q, J = 7.2 Hz), 3.14 (2H, br s), 3.09 (2H, br s), 1.78 (3H, s), 1.72 (3H, d, J = 7.0 Hz), 1.25 (6H, t, J = 7.2 Hz). ^{13}C NMR (125 MHz): δ 172.3, 142.5, 131.5, 122.9, 120.6, 61.5, 58.7, 40.8, 40.4, 14.0, 13.8, 13.6. IR (neat): 2981, 1733, 1446, 1366, 1252, 1183, 1096, 1073, 1015, 863, 782 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.47; H, 8.11.

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