$PtCl_4$-catalyzed Cycloreorganization of 1,6- and 1,7-Enynes

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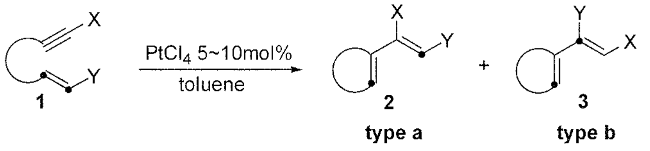
Received March 18, 2003

Key Words : Platinum, Enyne, Cycloreorganization

Transition metal catalyzed reaction of enynes has been the subject of extensive study, because enynes can form the metallacyclopentenes *via* simultaneous complexation with two unsaturated bonds.[1] The metallacyclopentenes can undergo β-elimination followed by reductive elimination to lead to the cycloisomerized products. When the rate of the β-elimination slows down, the reductive elimination of the metallacyclopentenes becomes competitive to lead to the bicyclic compounds or reorganized products. The latter is formally a metathesis of enynes. Since Katz reported skeletal reorganization of enynes catalyzed by a Fisher-type tungsten carbene complex,[2] Trost,[3] Mori,[4] and Murai[5] have reported similar enyne metatheses by various metal complexes containing Pd, Ru, Pt, Ir, *etc*.

Among these, $PtCl_2$ turned out to be the most efficient and convenient one, delivering the desired key building blocks in excellent yield. Recently, Fürstner[6] and Inoue[7] proposed cationic mechanisms of Pt-catalyzed metathesis of enynes. Although $PtCl_4$ was reported to show similar catalytic activity as $PtCl_2$ in a certain case, other Pt-based compounds such as $PtCl_2(COD)$, $PtCl_2(PhCN)_2$, PtO_2, $H_2Pt(OH)_6$, $Pt(acac)_2$, and $K_2[PtCl_6]$ have been reported to be totally inactive.[8] Still, more studies on the Pt-catalyzed reactions are necessary not only to interpret the reaction mechanism unambiguously but also to explore synthetic utility more. In our interest in developing new synthetic methodologies utilizing platinum compounds, we noticed that it is worthwhile to pursuit synthetic and mechanistic utility of $PtCl_4$.[9] We wish to report here scope and limitations of $PtCl_4$-catalyzed cycloreorganization of 1,*n*-enynes 1 as shown in Scheme 1.

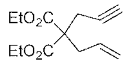
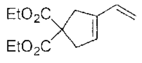
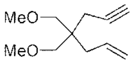
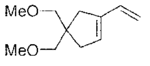
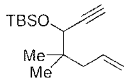
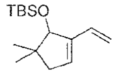
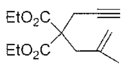
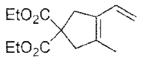
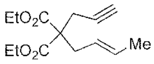
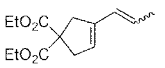
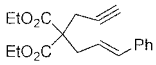
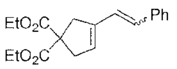
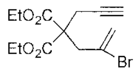
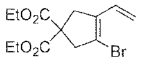
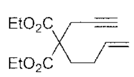
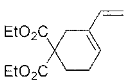
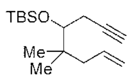
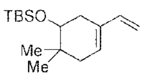
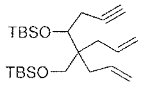
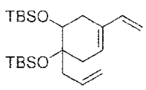
When the reaction of 1,6-enyne **1a** was carried out first by treatment of 5 mol % $PtCl_4$ in refluxing toluene, a skeletal reorganized product **2a** was isolated along with several byproducts. Formation of byproducts might result from either high reaction temperature or the acidic character of $PtCl_4$. Finally, this reaction occurred even at 0 °C in one hour to give the product **2a** in 96% yield. It showed that $PtCl_4$ has stronger catalytic activity than $PtCl_2$ based on the low reaction temperature and fast reaction time. Similar to $PtCl_2$-catalyzed reactions, toluene was a suitable solvent among various solvents like THF, 1,4-dioxane, acetonitrile, or DMF. The catalytic activity of $PtCl_4$ diminished dramatically by the presence of any coordinating ligand such as triphenylphosphine or even some solvents. The reaction did not proceed in acetonitrile or DMF. Addition of a catalytic amount of triethylamine led to stop the reaction completely.



Scheme 1

Under the optimal conditions, a variety of structural variations have been accommodated as summarized in Table 1. Enyne **1b** and **1c** at room temperature and 0 °C gave the product **2b** and **2c** in 92% and 59% yields, respectively (entry 2 and 3). The substitution of an alkyl or aryl group at

Table 1. $PtCl_4$-catalyzed Reaction of Enynes to 1-vinylcycloalkenes

entry		Temp (°C)	Time (h)	Product	% yield
1	 **1a**	0	1	 **2a**	96
2	 **1b**	rt	2	 **2b**	92
3	 **1c**	0	15	 **2c**	59
4	 **1d**	0	1	 **2d**	86
5	 **1e**	0	3	 **2e**	85
6	 **1f**	rt	3	 **2f**	90
7	 **1g**	50	1	 **2g**	66
8	 **1h**	reflux	4	 **2h**	68
9	 **1i**	reflux	4	 **2i**	88
10	 **1j**	100	1	 **2j**	70

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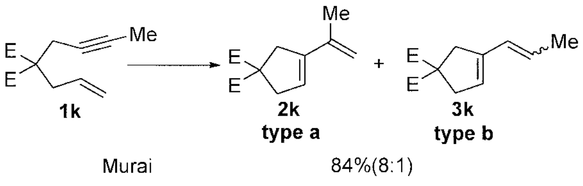
an olefinic part did not affect the reaction path (entry 4-7). Enyne **1d** at 0 °C for 1 hour gave the product **2d** as a sole product in 86% yield. Under these reaction conditions, enyne **1e** and **1f** bearing a terminal methyl and phenyl group also gave the products **2e** and **2f** in 85% and 90% yields, respectively, where the corresponding (*E*)-isomers were predominantly formed over the (*Z*)-isomers in about 2 : 1 ratio for **2e** and 20 : 1 for **2f**. The halide-substitution at an olefinic part retarded the reaction and decreased the product yields. For example, enyne **1g** gave the expected product **2g** in 66% yield. In all cases, the starting enynes were completely consumed and the isomeric purity of the products was high. The reaction of 1,7-enynes under the similar proceeded slowly but gave the corresponding 1-vinylcyclohexenes in good yields (entry 8-10). Enyne **1h** and **1i**, when refluxed for 4 h under the same conditions, gave the desired products **2h** and **2i** in 68% and 88% yields, respectively. The dienyne **1j** under the same conditions also proceeded to give the desired product **2j** in 70% yield.

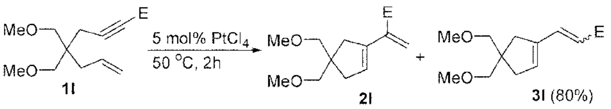
Contrast to enynes substituted at the olefinic carbons, enynes substituted at the acetylenic carbon gave a mixture of reorganized products under our conditions. Substitution at the triple bond led the reaction path to give **type b** product over **type a** product. The methyl-substituted enyne **1k** at 50 °C for 2 hours led to form a 1 : 9 mixture of **2k** and **3k** in combined 66% yield along with several unidentified products (eq 1). Oi and Inoue stated that cationic [Pt(dppp)(PhCN)$_2$]-(BF$_4$)$_2$-catalyzed reaction of the enyne **1k** having a methyl group on the acetylene terminal underwent **type b** rearrangement in 86% yield.[7] Chatani and Murai reported that PtCl$_2$-catalyzed reaction of the enyne **1k** predominantly underwent **type a** over **type b**.[5a] PtCl$_4$-catalyzed reaction of the enyne **1k** gave a 1 : 9 mixture of **2k** and **3k**, implying that the cationic character of the platinum catalyst might alter the reaction path to **type b** more. The cationic Pt catalyst can be coordinated toward the triple bond stronger than PtCl$_2$, so that C-C triple bond cleavage could occur to give the **type b** product.



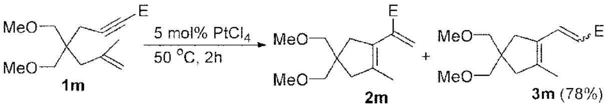
(1)

Murai	84%(8:1)
This study	66%(1:9)
Oi and Inoue	86%(3:7)

Then, we tested two enynes **1l** and **1m** bearing an electron-withdrawing group at the acetylenic position. Both **1l** and **1m** underwent cycloreorganization to give **type b** products **3l** and **3m** in 80% (*E/Z* = 5) and 78% (*E/Z* = 5) yields, respectively (eq 2-3). Since enynes conjugated with an electron-withdrawing group have low electron density and therefore can cleave the C-C triple bond more easily, more acidic PtCl$_4$-catalyzed reaction might be expected to give **type b** product. Mechanistic interpretation is still not clear. However, it is clear that this reaction requires an acidic Pt catalyst.



(2)



(3)

In summary, we have shown that various 1,6- and 1,7-enynes with a catalytic amount of PtCl$_4$ underwent cycloreorganization to 1-vinylcycloalkenes in high yield. Although the mechanism of these platinum-catalyzed cycloreorganization is not clear, the cationic character on the platinum catalyst might be important factor to control the reorganization pathways. The present PtCl$_4$-catalyzed reorganization provides a good synthetic methodology as a modified PtCl$_2$-catalyzed reaction. Further mechanistic study on PtCl$_4$-catalyzed reorganization of enynes is underway and will be reported in a near future.

Acknowledgment. We wish to acknowledge the financial support of KOSEF (R01-1999-000-00044-0), Korea, and Center of Molecular Design and Synthesis (CMDS).

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