

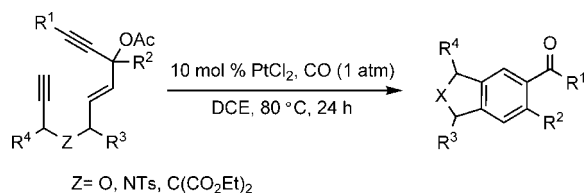
## Platinum-Catalyzed Cycloisomerization Reaction of 1,6-Enyne Coupling with Rearrangement of Propargylic Esters

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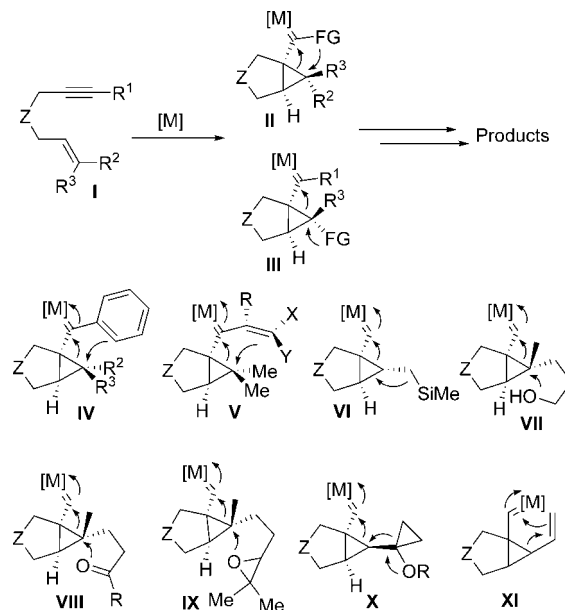
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A platinum-catalyzed cycloisomerization of 1,6-enyne coupling with the rearrangement chemistry of propargylic ester has been developed. Most probably, under platinum catalysis, propargylic ester undergoes the 1,3-acyloxy migration to afford metal allene intermediate, which is followed by the Diels–Alder-type reaction. 1,3-Acyloxy migration is the key step during the transformation.

In the last decades, platinum and gold complexes have emerged as powerful carbophilic  $\pi$ -acids for the activation of alkynes toward a variety of nucleophiles.<sup>1</sup> This strategy has been well applied in the cycloisomerization reactions of 1,*n*-enynes, which are attractive processes due to the high demands for atom economy in newly developed reactions.<sup>2–7</sup> Particularly intriguing of this transformation is the diversity and complexity generated by both the skeleton rearrangement and the influence of functional groups. In this content, aromatic groups,<sup>3</sup> alkenes,<sup>3,4</sup> silyl ethers,<sup>5</sup> alcohols,<sup>6</sup> aldehydes,<sup>7</sup> epoxides,<sup>7</sup> and ethers<sup>7</sup> are excellent partners in the cycloisomerization of 1,6-enynes. However, in most cases, these functional groups follow the same path in nucleophilic attack to promote the ring-opening of the intermediate cyclopropyl metal carbenes (Scheme 1). A limited exception was reported recently by Fürstner and co-workers.<sup>4</sup> It was found that the 1,6-enynes bearing another alkene group in the alkene position undergo formal intramolecular Diels–Alder

### SCHEME 1



reactions to afford desired products.<sup>4</sup> The mechanism was proposed via the rearrangement of the intermediate vinylcyclopropyl metal carbenes **XI**. Consequently, further studies on the reaction diversity of enynes governed by different functional groups are still attractive.

On the other hand, platinum- and gold-catalyzed transformations of readily available propargylic esters have received much attention in recent years.<sup>8</sup> The metal allene complexes are considered as common intermediates, which further react with various functional groups to give astonishingly diverse products (Scheme 2). What we are interested in is the effect of this functional group when introduced into the cycloisomerization of enynes. On the basis of previous efforts in this area,<sup>9</sup> we envision that 1,6-enyne **A** with the propargylic

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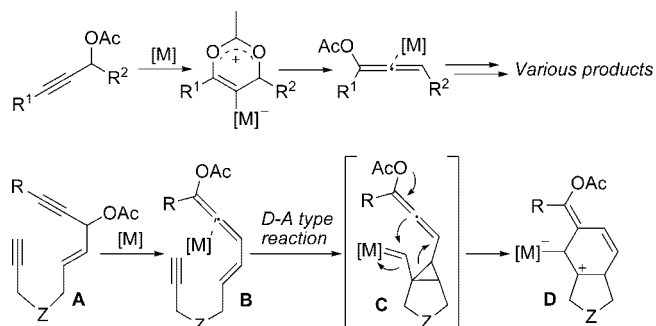
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SCHEME 2

TABLE 1. Optimization of Reaction Conditions<sup>a</sup>

entry	catalyst (mol %)	solution	<i>t</i> , °C	time, h	yield, %
1	PtCl <sub>2</sub> (10), CO (1 atm)	toluene	80	24	65
2	PtCl <sub>2</sub> (10), CO (1 atm)	CH <sub>3</sub> CN	80	24	NR <sup>b</sup>
3	PtCl <sub>2</sub> (10), CO (1 atm)	Dioxane	80	24	NR
4	PtCl <sub>2</sub> (10), CO (1 atm)	DCE	80	24	83
5	PtCl <sub>2</sub> (10), COD (40)	DCE	80	24	46
6	PtCl <sub>2</sub> (10)	DCE	80	36	41
7	Au(PPh <sub>3</sub> )BF <sub>4</sub> (5)	DCE	rt	3	6 <sup>c</sup>
8	Au(PPh <sub>3</sub> )SbF <sub>6</sub> (5)	DCE	rt	3	11 <sup>c</sup>
9	Au(PPh <sub>3</sub> )OTf (5)	DCE	rt	3	trace <sup>c</sup>
10	AuCl <sub>3</sub> (5)	DCE	rt	3	8 <sup>c</sup>
11	AuCl (5)	DCE	rt	3	trace <sup>c</sup>

<sup>a</sup> Reactions were conducted with 0.4 mmol of **1a** in 3 mL of solvent.

<sup>b</sup> No reaction. <sup>c</sup> Most of the material was decomposed.

ester in its alkene position might undergo Diels–Alder reaction after 1,3-migration of the acetate group, where the intermediate vinylcyclopropyl metal carbenes **C** might be involved (Scheme 2).<sup>4</sup> Herein, we report a platinum-catalyzed cycloisomerization of 1,6-enyne coupling with migration chemistry of propargylic esters.

Optimization studies of this transformation started with the use of enyne **1a** as the model substrate (Table 1). To our delight, the concept works nicely. Treatment of **1a** in the presence of 10 mol % of PtCl<sub>2</sub> under CO (1 atm)<sup>10</sup> afforded the desired aryl ketone **2a** in 65% yield after the reaction mixture was stirred in toluene (3 mL) at 80 °C for 24 h (entry 1). The nature of the solvent had a substantial effect on the efficiency of the reaction. No reaction was observed in either CH<sub>3</sub>CN or dioxane, whereas 1,2-dichloroethane (DCE) gave the best result (entries 1–4).

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TABLE 2. Scope Study of Platinum-Catalyzed Cyclization of Enynes<sup>a</sup>

entry	substrate	product	yield
1			83%
2			78%
3			81%
4			53%
5			67%
6			78%
7		—	NR <sup>b</sup>
8			78%
9			65%
10			58%

<sup>a</sup> All reactions were carried out with **1** (0.4 mmol) with 10 mol % of PtCl<sub>2</sub> under CO (1 atm) in DCE (3 mL) at 80 °C for 24 h. <sup>b</sup> No reaction.

Other platinum catalyst systems did not lead to an increase in yield (entries 5 and 6). Gold catalysts also catalyzed this cyclization, but in poor yields (entries 7–11). Thus, the use of PtCl<sub>2</sub> (10 mol %) and CO (1 atm) in DCE (3 mL) at 80 °C was found to be the most efficient and was subsequently used as the standard condition.

Under the optimized reaction conditions, various O-tethered enynes were investigated, as shown in Table 2. In most cases, the desired cyclized products were generated in good to high yields. The electronic properties of the substituent on the aryl group<sup>11</sup> attached to the alkyne affected the reaction. Electron-rich substituents gave results superior to those obtained from electron-



137.3, 136.6, 135.1, 133.6, 132.6, 129.9, 128.3, 127.6, 125.0, 124.2, 122.5, 53.6, 53.4, 21.5; IR (KBr,  $\text{cm}^{-1}$ ) 2923, 2853, 2255, 1739, 1660, 1597, 1448, 1348, 1281, 1167, 1092, 911, 730. Anal. Calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_3\text{S}$ : C, 70.00; H, 5.07; N, 3.71. Found: C, 69.93; H, 4.89; N, 3.77.

**Diethyl 5-Benzoyl-1*H*-2,2(3*H*)-dicarboxylate (2n).** **2n** was prepared according to the above method in 67% yield as an oil:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78–7.76 (d,  $J = 8.1$  Hz, 2 H), 7.66–7.55 (m, 3 H), 7.49–7.44 (m, 2 H), 7.31–7.28 (d,  $J = 7.8$  Hz, 1 H), 4.26–4.19 (q,  $J = 6.9$  Hz, 4 H), 3.66 (s, 2 H), 3.65 (s, 2 H), 1.29–1.24 (t,  $J = 6.9$  Hz, 6 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 171.2, 145.2, 140.4, 137.8, 136.6, 132.1, 129.8, 129.4, 128.1, 125.8, 123.9, 61.8, 60.3, 40.4, 40.1, 13.9; IR (neat,  $\text{cm}^{-1}$ )

2920, 2853, 1650, 1612, 1566, 1427, 1286, 1254, 1045, 904, 744. Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_5$ : C, 72.12; H, 6.05. Found: C, 72.03; H, 6.22.

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**Supporting Information Available:** Detailed experimental procedure and copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of all compounds as well as X-ray crystallography of **2d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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