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$PtCl_2$-Catalyzed Tandem Triple Migration Reaction toward (*Z*)-1,5-Dien-2-yl Esters

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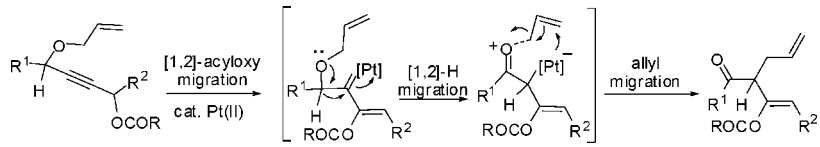
ABSTRACT



A novel method for the selective synthesis of (*Z*)-1,5-dien-2-yl esters has been developed though Pt(II)-catalyzed tandem 1,2-acyl and 1,2-hydride migration, along with an allyl migration reaction of propargylic carboxylates with electronically unbiased internal alkynes. The unusual selectivity of 1,2-acyloxy migration was realized.

In recent years, transition-metal-catalyzed isomerization of propargylic carboxylates has led to the development of a number of atom-economy cycloisomerization and tandem reactions.[1] Particularly interesting is reactivity of these easily accessible compounds in the context of platinum chloride, which has been recognized to induce highly selective skeletal rearrangements and cycloisomerizations and, hence, has become a widely used catalyst.[2] Remarkably, propargylic carboxylates are versatile substrates in platinum catalysts and have been transformed into various synthetically valuable products via 1,3-acyloxy[3] and 1,2-acyloxy[4] migration (Scheme 1, complex **A**). In this context, it is relevant that the Sarpong group has reported the stereoselective Pt(II)-catalyzed propargylic esters into cycloisomerization products which takes

[†] Lanzhou University.

(1) For recent reviews, see: (a) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271. (b) Marco-Contelles, J.; Soriano, E. *Chem. Eur. J.* **2007**, *13*, 1350. (c) Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2750. (d) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (e) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (f) Correa, A.; Marion, N.; Fensterbank, L.; Malacria, M.; Nolan, S. P.; Cavallo, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 718.

(2) For reviews, see: (a) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813. (b) Méndez, M.; Mamane, V.; Fürstner, A. *Chemtracts—Org. Chem.* **2003**, *16*, 397. (c) Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215. For selected examples of skeletal rearrangements, see: (d) Mamane, V.; Gress, T.; Krause, H.; Fürstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654. (e) Fürstner, A.; Hannen, P. *Chem. Commun.* **2004**, 2546. (f) Mamane, V.; Hannen, P.; Fürstner, A. *Chem. Eur. J.* **2004**, *10*, 4556. (g) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244. (h) Fehr, C.; Galindo, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2901. (i) Fürstner, A.; Hannen, P. *Chem. Eur. J.* **2006**, *12*, 3006. (j) Fürstner, A.; Aissa, C. *J. Am. Chem. Soc.* **2006**, *128*, 6306.

(3) For selected examples of 1,3-acyloxy migration not cited in the reviews listed in ref 1, see: (a) Correa, A.; Marion, N.; Fensterbank, L.; Malacria, M.; Nolan, S. P.; Cavallo, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 718. (b) Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868. (c) Barluenga, J.; Riesgo, L.; Vicente, R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2007**, *129*, 7772. (d) Lemière, G.; Gandon, V.; Cariou, K.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2007**, *9*, 2207. (e) Marion, N.; Carlqvist, P.; Gealageas, R.; De Frémont, P.; Maseras, F.; Nolan, S. P. *Chem. Eur. J.* **2007**, *13*, 6437. (f) Cariou, K.; Mainetti, E.; Fensterbank, L.; Malacria, M. *Tetrahedron* **2004**, *60*, 9745. (g) Brabander, J. K. D.; Liu, B.; Qian, M. *Org. Lett.* **2008**, *10*, 2533, and references therein.

(4) For selected examples of 1,2-acyloxy migration, see: (a) Prasad, B. A. B.; Yoshimoto, F. K.; Sarpong, R. *J. Am. Chem. Soc.* **2005**, *127*, 12468. (b) Pujanauski, B. G.; Prasad, B. A. B.; Sarpong, R. *J. Am. Chem. Soc.* **2006**, *128*, 6786. (c) Motamed, M.; Bunnelle, E. M.; Singaram, S. W.; Sarpong, R. *Org. Lett.* **2007**, *9*, 2167. (d) Smith, C. R.; Bunnelle, E. M.; Rhodes, A. J.; Sarpong, R. *Org. Lett.* **2007**, *6*, 1169. (e) Hardin, A. R.; Sarpong, R. *Org. Lett.* **2007**, *9*, 4547. (f) Soriano, E.; Marco-Contelles, J. *J. Org. Chem.* **2007**, *72*, 1443. (g) Mainetti, E.; Mouriès, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132, and references therein.

(5) For a study with Pt(II) as catalyst, see ref 4e. Propargylic esters bearing terminal alkynes typically undergo *5-exo-dig* cyclization using Ru, Pt, or Au catalysts. Internal alkynes bearing alkyl or aryl substituents usually undergo *6-endo-dig* cyclization. (a) Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019. (b) Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8503.

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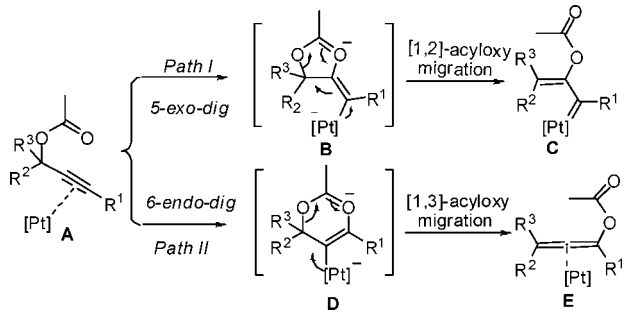
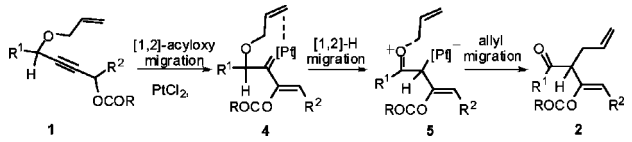
Scheme 1. Proposed Pathways for Pt-Catalyzed Isomerization of Propargyl Carboxylates



place via path *I*.[4b,f,5] From the previous works, it seems that propargylic carboxylates normally undergo 1,2-acyloxy migration with propargylic esters with terminal or electron-deficient C−C triple bonds, while those with electronically unbiased internal C−C triple bonds prefer 1,3-acyloxy migration (via path *II*).[6] Examples of the propargylic carboxylates undergoing 1,2-acyloxy migration in propargylic esters with internal C−C triple bonds are limited.[4e,6]

In the context of our ongoing efforts to develop tandem reactions,[7] we found that Pt carbenoids might be perfect intermediates in a domino process.[8] We envision that propargylic esters **1** with electronically unbiased internal alkynes could realize 1,2-acyloxy migration selectively under Pt(II) catalysis to form alkenyl Pt carbenoid **4**,[6a] which might induce the migration of neighboring groups when assisted with the allylic oxygen group (Scheme 2). Then the oxygen

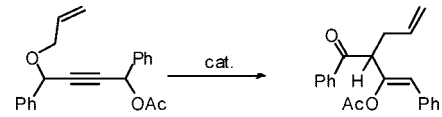
Scheme 2. Design a Pt-Catalyzed Formation of (*Z*)-1,5-Dien-2-yl Esters



heteroatom promotes a 1,2-hydride migration to the Pt carbenoid moiety in **4**[6,9] to afford allylic oxygen cation intermediates **5**, which promotes an allyl migration[10] to afford (*Z*)-1,5-dien-2-yl esters **2**. Herein, we report a novel Pt(II)-catalyzed tandem 1,2-acyloxy, 1,2-hydride, and allyl migration reaction of propargylic carboxylates **1**, which contain electronically unbiased internal alkynes, to (*Z*)-1,5-dien-2-yl esters **2**. In this reaction, 1,2-acyloxy migration and 1,2-hydride migration were key steps, and a new carbon−carbon formation was also achieved.

Initially, we started by using 0.3 mmol of 4-(allyloxy)-1,4-diphenylbut-2-ynyl acetate **1a** and 5 mol % of $PtCl_2$ in toluene at room temperature, and no reaction was observed. When the temperature was increased to 80 °C, the desired product (*Z*)-3-benzoyl-1-phenylhexa-1,5-dien-2-yl acetate **2a**[11] was formed in 48% yield. However, the reaction was fairly slow and required 24 h to go to completion (Table 1,

Table 1. Transition-Metal Catalysts for the Transformation of **1a** to **2a**



1a **2a**

entry	catalyst	solvent	*T* (°C)	time (h)	yield[a] (%)
1[b]	$PtCl_2$ (5 mol %)	toluene	rt	24	0
2	$PtCl_2$ (5 mol %)	toluene	80	24	48
3	$PtCl_2$/COD (5 mol %)	toluene	80	12	55
4	$PtCl_2$/CO (5 mol %/1 atm)	toluene	80	6	69
5	$PtCl_2$/CO (10 mol %/1 atm)	toluene	80	4.5	78
6	AuCl (10 mol %)	toluene	80	24	0
7	$AuCl_3$ (10 mol %)	toluene	80	24	0
8	$NaAuCl_4{\cdot}2H_2O$ (10 mol %)	toluene	80	24	0
9	$Au(PPh_3)Cl/AgSbF_6$ (5 mol %/10 mol %)	toluene	80	24	0
10[c]	CuI (10 mol %)	toluene	80	24	0
11	$PtCl_2$/CO (10 mol %/1 atm)	DCE	80	10	0
12	$PtCl_2$/CO (10 mol %/1 atm)	CH_3CN	80	10	0

[a] Isolated yield. [b] 93% of **1a** was recovered. [c] 85% of **1a** was recovered.

entries 1 and 2). In an attempt to accelerate this transformation, the mixture was stirred under an atmosphere of CO (1

(6) (a) Li, G.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 3740. (b) Shi, X.; Gorin, D. J.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 5802. (c) Amijs, C. H. M.; Lopez-Carrillo, V.; Echavarren, A. M. *Org. Lett.* **2007**, *9*, 4021. (d) Blaszykowski, C.; Harrak, Y.; Goncalves, M.-H.; Cloarec, J.-M.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2004**, *6*, 3771.

(7) (a) Shu, X.-Z.; Liu, X.-Y.; Xiao, H.-Q.; Ji, K.-G.; Guo, L.-N.; Qi, C.-Z; Liang, Y.-M. *Adv. Synth. Catal.* **2007**, *349*, 2493. (b) Shu, X.-Z.; Liu, X.-Y.; Xiao, H.-Q.; Ji, K.-G.; Guo, L.-N.; Qi, C.-Z; Liang, Y.-M. *Adv. Synth. Catal.* **2008**, *350*, 243. (c) Shu, X.-Z.; Liu, X.-Y.; Ji, K.-G.; Xiao, H.-Q.; Liang, Y.-M. *Chem.—Eur. J.* **2008**, *14*, 5282. (d) Ji, K.-G; Shen, Y.-W.; Shu, X.-Z.; Xiao, H.-Q.; Bian, Y.-J.; Liang, Y.-M. *Adv. Synth. Catal.* **2008**, *350*, 1275.

(8) For selected examples of platinum carbenes as reactive intermediates, see: (a) Méndez, M.; Echavarren, A. M. *Eur. J. Org. Chem.* **2002**, 15. (b) Mechanistic investigation: Martin-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757.

(9) For 1,2-hydride migration in Au− and Pt−carbenoid intermediates, see: (a) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863. (b) Sromek, A. W.; Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10500. (c) Fehr, C.; Farris, I.; Sommer, H. *Org. Lett.* **2006**, *8*, 1839. (d) Lee, J. H.; Toste, F. D. *Angew. Chem.* **2007**, *119*, 930; *Angew. Chem., Int. Ed.* **2007**, *46*, 912. (e) Funami, H.; Kusama, H.; Iwasawa, N. *Angew. Chem.* **2007**, *119*, 927; *Angew. Chem., Int. Ed.* **2007**, *46*, 909. (f) Shi, F.-Q.; Li, X.; Xia, Y.; Zhang, L.; Yu, Zh.-X. *J. Am. Chem. Soc.* **2007**, *129*, 15503. (g) Zhang, G.; Catalano, V. J.; Zhang, L. *J. Am. Chem. Soc.* **2007**, *129*, 11358.

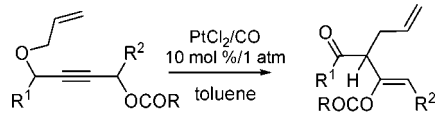
(10) For selected examples of Pt-catalyzed allyl migration, see: (a) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863. (b) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024. (c) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785. (d) Nakamura, I.; Sato, T.; Terada, M.; Yamamoto, Y. *Org. Lett.* **2008**, *10*, 2649. (e) Cariou, K.; Ronan, B.; Mignani, S.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1881. (f) Crone, B.; Kirsch, S. F. *Chem. Eur. J.* **2008**, *14*, 3514.

(11) The stereochemistry of (*Z*)-1,5-dien-2-yl esters were clearly established with NOESY experiments. For details, see the Supporting Information.

atm), and 6 h was necessary to effect the rearrangement of **1a**, providing the desired product **2a** in 69% yield (Table 1, entry 4). To our delight, on increasing the amount of catalyst to 10 mol %, a 78% yield of **2a** was obtained after 4.5 h (Table 1, entry 5). With other catalysts and solvents, no desired product **2a** was obtained (Table 1, entries 6 and 12). Thus, the use of $PtCl_2$ (10 mol %) in toluene at 80 °C under an atmosphere of CO (1 atm) was found to be the most efficient and used as the standard conditions.

To study the scope of this formation of (*Z*)-1,5-dien-2-yl esters, various representative propargylic carboxylates **1a**−**j** were then submitted to the above conditions, as depicted in Table 2. Thus, a tandem 1,2-acyloxy, 1,2-hydride and allyl

Table 2. Pt(II)-Catalyzed Synthesis of (*Z*)-1,5-Dien-2-yl esters **2** from Propargylic Carboxylates **1**[a]



1 **2**

	1		**2**	yield[b] (%)
	R, R^1, R^2			
1	Me, Ph, Ph	**1a**	**2a**	78
2	Me, Ph, *p*-Me-C_6H_4	**1b**	**2b**	79
3	Me, Ph, *p*-Cl−C_6H_4	**1c**	**2c**	72
4	Me, Ph, furyl	**1d**	**2d**	68
5	Me, Ph, 2-styrene-	**1e**	**2e**	55
6	Me, *p*-Cl−C_6H_4, *p*-Cl−C_6H_4	**1f**	**2f**	53
7	Me, *p*-Me-C_6H_4, Ph	**1g**	**2g**[12]	55
8	Ph, Ph, Ph	**1h**	**2h**	75
9	*m*−Br-C_6H_4, Ph, Ph	**1i**	**2i**	85
10	3,5-dinitrophenyl, Ph, Ph	**1j**	**2j**	78

[a] Conditions: 0.3 mmol of **1a** with 10 mol % of catalyst in toluene (3.0 mL) under an atmosphere of CO (1 atm) at 80 °C. [b] Isolated yield.

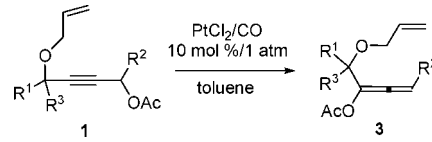
migration reaction of propargylic carboxylates **1a-j** proceeded smoothly to provide corresponding products **2a**−**j** in moderate to good yields. The reaction works well with aromatic R^2 groups.

Electron-rich aryl groups showed better results than those with an electron-withdrawing group in this tandemreaction (entries 2 vs 3). Substrate **1d** with a heteroaromatic R^2 group can also afford the desired product **2d** in 68% yield. The derivatives **1g** gave the expected 1,5-dien-2-yl esters **2g**, but as a mixture of stereoisomers (*Z*/*E* = 2/1).[12] The role of the nucleophilic acyloxy group was examined with a series of esters **1h**−**j**, and the desired products **2h**−**j** were smoothly obtained in 75−85% yield.

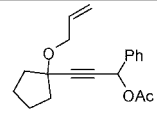
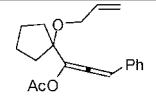
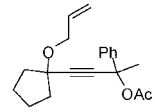
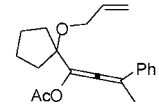
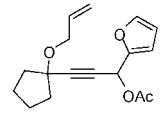
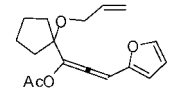
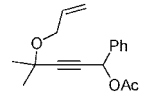
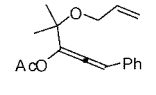
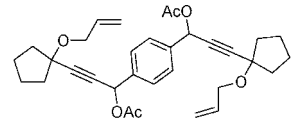
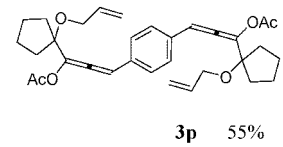
Furthermore, to expand the scope of this reaction, we also investigated a range of propargylic carboxylates **1**, which contain aliphatic R^1 and R^3 groups (Table 3). To our surprise, only 1,2-dienyl acetates **3** were obtained in moderate to excellent yields.

(12) From the ^{1}H NMR spectrum, the ratio of the isomers is *Z*/*E* = 2/1.

Table 3. $PtCl_2$-Catalyzed Double 1,2-Acyloxy Migration for the Synthesis of 1,2-Dienyl Acetates **3** from Propargylic Carboxylates **1**[a]



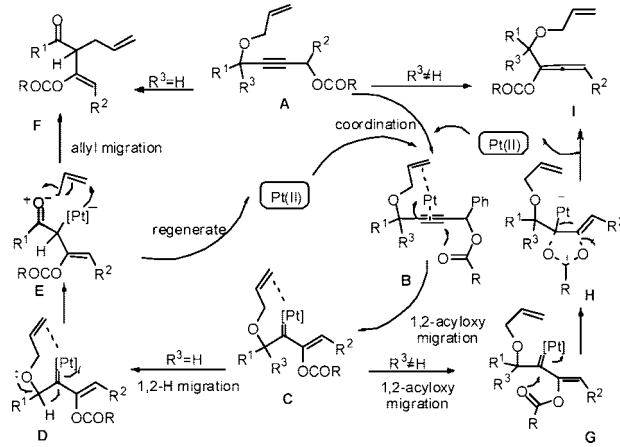
1 **3**

entry	**1**		**3**		yield[b]
1		**1l**		**3l**	83%
2		**1m**		**3m**	93%
3		**1n**		**3n**	87%
5		**1o**		**3o**	65%
6		**1p**		**3p**	55%

[a] Conditions: 0.3 mmol of **1a** with 10 mol % of catalyst in toluene (3.0 mL) under an atmosphere of CO (1 atm) at 80 °C. [b] Isolated yield.

On the basis of the above observations, we propose the following plausible mechanisms for this cascade transformation (Scheme 3). (i) Coordination of the alkynyl and alkenyl moiety of **A** to the Pt catalyst gives the complex **B**. (ii) According to path *I*, 1,2-acyloxy migration produces Pt carbenoid intermediate **C** (via 5-*exo*-*dig* cyclization/ring

Scheme 3. Proposed Mechanism



opening). (iii) When R^1 are aromatic groups and R^3 is H, then the oxygen heteroatom promotes 1,2-hydride migration to the Pt carbenoid moiety and produces allylic oxygen cation **E** through **D** process. (iv) Allylic oxygen cation **E** causes an allyl migration and affords 1,5-dien-2-yl esters **F**, during which the Pt anion may capture the allyl cation and regenerate the catalyst. (v) When R^1 and R^3 are aliphatic groups, R^1 or R^3 do not undergo 1,2-alkyl migration, while the nucleophilic acyloxy group in **G** undergoes 1,2-acyloxy migration and gives 1,2-dienyl acetates **I**,[13] which may be undergoing a *5-exo-dig cyclization/ring-opening process.*[14]

In summary, a novel method for the selective synthesis of (*Z*)-1,5-dien-2-yl esters has been developed through a Pt(II)-catalyzed tandem triple-migration reaction of propargylic carboxylates with electronically unbiased internal alkynes. The unusual selectivity of 1,2-acyloxy migration was realized. A more detailed investigation on the mechanism, as well as the scope of this cascade, is ongoing in our laboratory.

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Supporting Information Available: Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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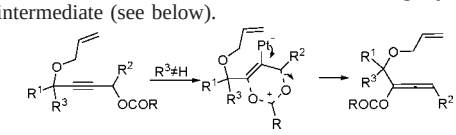
(13) When R^1 and R^3 are aliphatic groups, the reaction may involve double 1,2-acyloxy migrations and account for the 1,3-acyloxy migration. Alternatively, the reaction may undergo 1,3-acyloxy migration process, and 1,2-dienyl acetates could be formed from 6-*endo-dig* cyclization/ring opening intermediate (see below).



(14) A recent calculation suggests that double 1,2-acyloxy migrations can also account for the 1,3-acyloxy migration and all these transformations are reversible. For reference, see ref 3a.