Cyclization

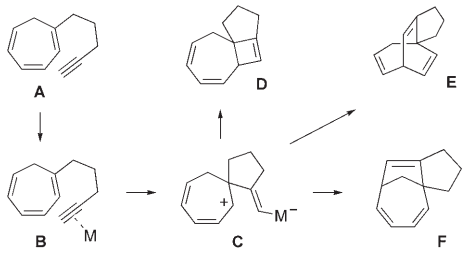
DOI: 10.1002/anie.200705482

$PtCl_2$-Catalyzed [6+2] Cycloaddition of Alkynes Tethered to Cycloheptatriene**

Alphonse Tenaglia and Sylvain Gaillard*

Transition-metal-catalyzed cycloisomerization reactions of enynes have attracted considerable attention because of their high synthetic potential for the construction of useful carbo- and heterocyclic structural features.[1] Important advances in this timely area of research have been achieved using late-transition metals (for example, Ru, Pt, and Au) as π-acid catalysts.[2] In this context, novel modes of connection between alkenes and alkynes still remain an attractive field of investigation, although the chemoselectivity of the reactions often depends on the structural patterns of the substrates. The cycloisomerization of polyene-ynes takes advantage of additional unsaturated bond(s) to trap transient reactive intermediates, thus allowing the elaboration of complex polycycles. For example, the gold-catalyzed cycloisomerization of dienynes affords Diels–Alder adducts,[3] whereas cyclohexadienyl alkynes generate tetracycles.[4,5] In the particular case of aryl-tethered alkynes, the cycloisomerization with various electrophilic metal catalysts afforded Friedel–Crafts-type compounds, but these reactions generally required electron-rich arenes.[6] As part of our recent studies on the cobalt-catalyzed intermolecular [6+2] cycloaddition of cycloheptatriene (CHT) with alkynes,[7] we were intrigued by the behavior of CHT tethered to alkynes in cycloisomerization reactions involving π-acid catalysts. In these reactions, nucleophilic attack of CHT on an electrophilic metal-coordinated alkyne **B** is expected to generate a pentadienyl cation **C** which may evolve through ring closure to produce [2+2], [4+2], and/or [6+2] adducts (Scheme 1).

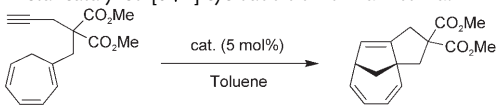
Herein, we report the platinum-catalyzed cycloisomerization of 1-(pent-4-ynyl)-1,3,5-cycloheptatrienes, in which connections are made between the carbon termini of the triene and the acetylenic carbon atoms, to afford tricyclotrienes **F**, similar to a formal intramolecular [6+2] cycloaddition.



Scheme 1. [*n*+2] Cycloadditions through metal-catalyzed cycloisomerization of 1-(pent-4-ynyl)-1,3,5-cycloheptatriene.

Exposure of triene-yne **1a** to catalytic amounts of $PtCl_2$ (5 mol%) in toluene at room temperature resulted in a complete and clean conversion into a single adduct **2a**[8] in 94% yield (Table 1, entry 10). The cycloisomerization proceeded with excellent chemoselectivity, whereas heating at 80°C in toluene in the absence of catalyst resulted in the recovery of unchanged **1a** (Table 1, entry 1). To the best of our knowledge, intramolecular [6+2] cycloaddition reactions between alkynes and CHT have been only been achieved by using tricarbonyl(η⁶-7-*exo*-alkynyl-1,3,5-cycloheptatriene)-chromium(0) complexes at high temperatures (140–170°C).[9] In comparison, the present cycloisomerization is performed catalytically and under mild conditions (room temperature), and affords higher yields without preliminary coordination of the triene to the metal. A catalyst loading as little as 1 mol% can be used, but the reaction time increases

Table 1: Metal-catalyzed [6+2] cycloaddition of **1a** into **2a**.[a]



1a **2a**

Entry	Catalyst	*T* [°C]	*t* [h]	Yield [%][b]
1	none	80	24	–
2	$InCl_3$	110	24	–
3	$RhCl_3 \cdot n H_2O$	80	24	6[c]
4	$[RhCl(PPh_3)_3]$	80	24	8[c]
5	$RuCl_3 \cdot n H_2O$	80	24	7[c]
6	$[\{RuCl_2(CO)_3\}_2]$	65	8	77
7	$AuCl_3$	25	5	90
8	Pt/C	80	24	7[c]
9	PtI_2	25	5	39
10	$PtCl_2$	25	5	94

[a] Conditions: **1** (0.36 mmol), catalyst (5 mol%), toluene ($c = 0.1$ M). [b] Yields of isolated products after column chromatography. [c] Determined by ^1H NMR spectroscopic analysis.

[*] Dr. A. Tenaglia, Dr. S. Gaillard
Laboratoire de Synthèse Asymétrique
UMR 6180 CNRS
Université d'Aix-Marseille P. Cézanne
Faculté des Sciences et Techniques de St Jérôme, Case A62
Avenue Escadrille Normandie Niemen
13397 Marseille Cedex 20 (France)
Fax: (+33) 4-9128-2742
E-mail: alphonse.tenaglia@univ-cezanne.fr

[**] We would like to thank the CNRS for financial support, Dr. I. De Riggi (ECM, Marseille) for help with the NMR studies, and Dr. M. Giorgi (Spectropole, Université P. Cezanne, Marseille) for the X-ray analyses. S.G. gratefully acknowledges the MNERT for a doctoral fellowship.

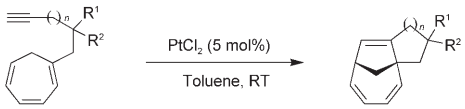
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

significantly (16 h instead of 5 h) and with a slight decrease in yield (86% instead of 94%). Interestingly, under these conditions, the reaction can be scaled-up, thus allowing for the efficient preparation of **2a** on a gram scale.

The cycloisomerization of **1a** to afford **2a** was examined with other metal salts and complexes (Table 1). $[\{RuCl_2(CO)_3\}_2]$[5a,10,11] (Table 1, entry 6) and $AuCl_3$[10,11a,12] (Table 1, entry 7) proved satisfactory, whereas rhodium complexes were poor catalysts (Table 1, entries 3 and 4). The higher efficiency of $PtCl_2$, compared to PtI_2, is in agreement with its higher electrophilicity (Table 1, entries 9 and 10).[13] The reaction can be conducted in a wide range of solvents—THF (85%), acetone (91%), and toluene (94%) were the most effective—but performing the reaction in MeOH, MeCN, or DMF left **1a** unchanged.

The reaction scope with respect to the type of tether and its length was also investigated (Table 2). The formal

Table 2: $PtCl_2$-catalyzed [6+2] cycloaddition of alkynes tethered to cycloheptatriene.



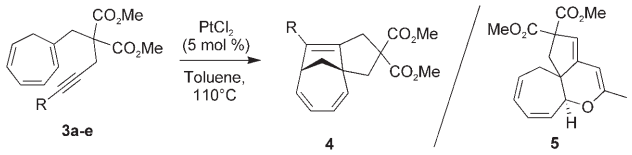
1b-l **2b-l**

Entry	Trienyne	*n*	R	Adduct	Yield [%][a]
1	**1b**	1	$R^1=R^2=SO_2Ph$	**2b**	66
2[b]	**1c**	1	$R^1=R^2=CN$	**2c**	79
3	**1d**	1	$R^1=R^2=CH_2OAc$	**2d**	92
4	**1e**	1	$R^1=R^2=CH_2OTs$	**2e**	85
5	**1f**	1	R^1, $R^2=CH_2OCMe_2OCH_2$	**2f**	82
6	**1g**	1	R^1, $R^2=CH_2OC(O)OCH_2$	**2g**	72
7	**1h**	1	$R^1=H$, $R^2=CO_2Me$	**2h**	99 (4:1)[c,d]
8	**1i**	1	$R^1=H$, $R^2=CH_2OAc$	**2i**	83 (4:1)[c]
9	**1j**	1	$R^1=H$, $R^2=CH_2OBn$	**2j**	86 (2.8:1)[c]
10	**1k**	1	$R^1=H$, $R^2=CH_2Br$	**2k**	75 (3.3:1)[c]
11[e]	**1l**	2	$R^1=R^2=CO_2Me$	**2l**	53

[a] Yields of isolated compounds after column chromatography. [b] 65 °C, 12 h. [c] Diastereomeric ratio (d.r.) determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [d] For the major diastereomer, the sustituent R^2 is *anti* to the methano bridge; see the Supporting Information. [e] 100 °C, 18 h in a CO atmosphere. RT = room temperature. Ts = toluene-4-sulfonyl, Bn = benzyl.

[6+2] cycloaddition under the initial conditions (5 mol% $PtCl_2$, $c=0.1$ M, toluene, RT) proceeded efficiently with triene-ynes **1b–l** carrying acetal, ether, ester, sulfonate, cyclic carbonate, or halide substituents. Even **1c** with nitrile groups, which are known for their ability to coordinate with metal salts, afforded **2c**,[14] but the reaction required higher temperature (65 °C; Table 2, entry 2). In all cases, no other adduct could be detected by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. Monosusbtitued substrates **1h–k** were converted into the corresponding [6+2] cycloadducts **2h–k** as a mixture of diastereomers (d.r. 2.8:1–4:1; Table 2, entries 7–10). Lengthening the tether by one carbon unit, such as in **1l**, did not result in the [6+2] cycloaddition occurring under the usual conditions. Carrying out the reactions at higher temperatures (80–100 °C), or in the presence of silver salts (AgOTf, $AgPF_6$, or $AgSbF_6$) to generate cationic Pt^{2+} species, afforded the expected adduct **2l** together with significant decomposition of the starting materials.[10,12,15] Gratifyingly, the reaction of **1l** at 100 °C in a CO atmosphere[16] resulted in complete conversion and the isolation of **2l** in 53% yield (Table 2, entry 11).

Substrates **3a–e** with an internal alkyne moiety proved to be reluctant to cycloisomerize even if the reactions were conducted at 110 °C (Scheme 2). Alkyl- (**3a**,**b**) or phenyl-



3a-e **4** **5**

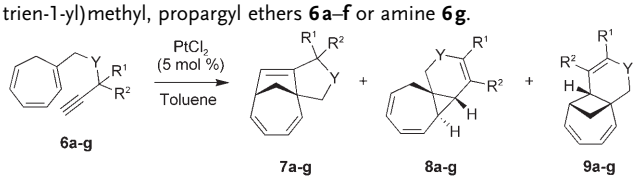
3a / 3b / 3c R = Me / allyl / Ph — **4d** (64%)
3d R = CO_2Me
3e R = COMe — **4e** (22%) (NMR) — **5** (39%)

Scheme 2. Platinum-catalyzed cycloisomerization of trienynes **3a–e**.

substituted (**3c**) substrates were recovered unchanged while electron-deficient alkynes (**3d**,**e**) afforded the [6+2] cycloadducts **4d**,**e**, albeit in fair to low yields. Skeletal reorganization[11b] or metathesis[17] products, such as those observed in cycloisomerizations of 1,6-enyoates (or enynones), were not detected. The heterocyclic adduct **5** (39%), which was formed from **3e** as a single diastereomer, suggested the interception of the putative cationic intermediate **C** (Scheme 1) by the pendant acetyl group.

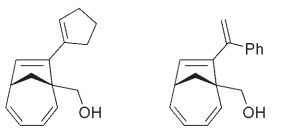
The cycloisomerization of trienynes **6a–g** bearing a heteroatom in the tether was also examined (Table 3). Besides the desired [6+2] cycloadducts **7**, dihydropyranes or tetrahydropyridines **8** were formed with concomitant 1,2-hydrogen or 1,2-alkyl migration.[18] Additionally, new adducts

Table 3: Platinum-catalyzed cycloisomerization of (cyclohepta-1,3,5-trien-1-yl)methyl, propargyl ethers **6a–f** or amine **6g**.



6a-g **7a-g** **8a-g** **9a-g**

6a Y = O, $R^1=R^2=H$
6b Y = O, $R^1=R^2=Me$
6c Y = O, $R^1=R^2=(CH_2)_4$
6d Y = O, $R^1=R^2=(CH_2)_5$
6e Y = O, $R^1=Me$, $R^2=Ph$
6f Y = O, $R^1=R^2=Ph$
6g Y = NTs, $R^1=R^2=H$



10 **11**

Entry	Substrate	Conditions	Yields [%] (**7**/**8**/**9**)[a]
1	**6a**	80 °C, 10 h	48/34/–
2	**6b**	80 °C, 12 h	41/46 (**8b**/**9b** = 1:1.7)[b]
3	**6c**	25 °C, 7 days	41/41/–
4	**6c**	80 °C, 10 h	–/40/–[c]
5	**6d**	80 °C, 14 h	34/–/19
6	**6e**	80 °C, 12 h	78 (d.r. 2.81:1)/–/–[d]
7	**6f**	80 °C, 30 h	68/–/–
8	**6g**	90 °C, 10 h	45/10/31

[a] Yields of isolated products. [b] Not separated. [c] Adduct **10** (51%) was also formed. [d] Adduct **11** (20%) was also formed.

such as **9** (which feature a cyclobutane ring), **10**, or **11** were observed depending on the structural patterns of the precursors **6** and/or the reaction conditions. For example, the reaction of **6c** at room temperature required seven days for completion and afforded **7c** (41%) and **8c** (41%; Table 3, entry 3). When the reaction was carried out at 80°C for 10 h, the "ring-opening" adduct **10** (51%) was formed at the expense of **7c**, while **8c** (40%) was observed without a significant change in yield (Table 3, entry 4).

Control experiments showed that exposure of **7c** to the same reaction conditions did not give the bicyclic structure **10**, but allowed the recovery of **7c** with partial degradation.[19] A small variation in the ring size of the tertiary propargylic ethers (**6c**,**d**) dramatically changed the selectivity of the reaction. For example, under quite similar conditions, while **6c** afforded **8c** (40%) and **10** (51%), **6d** was converted into **7d** (34%) and **9d** (19%; Table 3, entries 4 and 5). Since formation of products **8** and **9** involved a 1,2-hydrogen (or alkyl) shift, the question of a shared common intermediate or the possibility of **8**→**9** interconversion arose. Indeed, subjecting **8g** to $PtCl_2$ (5 mol%) in toluene (85°C, 16 h) led to **9g** in nearly quantitative yield.[20] The [6+2] cycloaddition is favored with triene-ynes **6e** and **6f** that bear at least one phenyl substituent at the propargylic position (Table 3, entries 6 and 7). In these cases, it is worth noting that **8** and **9** were not formed.

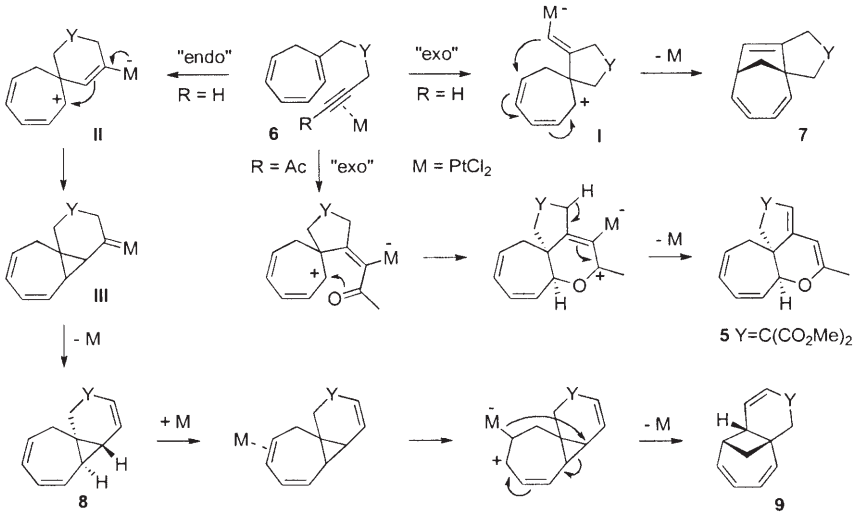
A mechanistic scheme accounting for the structural diversity of adducts arising from the cycloisomerization reactions of **6** is proposed in Scheme 3.[21] The pentadienyl cation **I**[22] derived from the established *exo*-cyclization mode would undergo a kind of "concerted" electron redistribution to release [6+2] adducts **7**. If the alkyne carries an acyl substituent, the carbonyl group would intercept the initially formed cation to give the dihydropyran **5**. The *endo*-cyclization mode would drive the reaction to product **8** through zwitterion **II** and platinacarbene **III** intermediates. The **III**→**8** transformation is assumed to occur through a 1,2-hydrogen or alkyl shift before elimination of the metal species. The latter case is evident from the ring-expansion adducts **8c** and **9d** observed from the geminal-substituted precursors **6c** and **6d**, respectively (Table 3, entries 3 and 5). The formation of **9** from **8** (see above) might involve the coordination of Pt^{2+} species to the remote double bond of **8** followed by an electronic redistribution involving cleavage of the cyclopropane ring.

The opening of the tetrahydrofuran ring of **7c** (or **7e**) triggered by adventitious HCl (generated from the $PtCl_2$ catalyst) to give a stabilized tertiary allylic cation[23] may explain the formation of adduct **10** (or **11**).

In summary, we have developed a platinum-catalyzed room-temperature intramolecular [6+2] cycloaddition of alkynes tethered to cycloheptatriene to afford cyclopentane-fused bicyclo[4.2.1]nona-2,4,7-trienes. Complex heterocyclic compounds were obtained when this reaction was applied to substrates containing a heteroatom (O, N) in the tether. At higher temperature, a formal [6+1] cycloaddition was observed at the expense of the intramolecular vinylcyclopropanation pathway.

Received: November 30, 2007
Published online: February 18, 2008

Keywords: cycloaddition · enynes · platinum · polycycles · strained molecules



Scheme 3. Proposed mechanisms for the cycloisomerization of **6**. M = $PtCl_2$.

[1] a) B. M. Trost, M. J. Krische, *Synlett* **1998**, 1–16; b) C. Aubert, O. Buisine, M. Malacria, *Chem. Rev.* **2002**, *102*, 813–834; c) G. C. Lloyd-Jones, *Org. Biomol. Chem.* **2003**, *1*, 215–236; d) S. T. Diver, A. J. Giessert, *Chem. Rev.* **2004**, *104*, 1317–1382; e) A. M. Echavarren, C. Nevado, *Chem. Soc. Rev.* **2004**, *33*, 431–436; f) C. Bruneau, *Angew. Chem.* **2005**, *117*, 2380–2386; *Angew. Chem. Int. Ed.* **2005**, *44*, 2328–2334; g) S. Ma, S. Yu, Z. Gu, *Angew. Chem.* **2006**, *118*, 206–209; *Angew. Chem. Int. Ed.* **2006**, *45*, 200–203; h) C. Nieto-Oberhuber, S. Lopez, E. Jiménez-Núñez, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 5916–5923.

[2] A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449.

[3] A. Fürstner, C. C. Stimson, *Angew. Chem.* **2007**, *119*, 9001–9005; *Angew. Chem. Int. Ed.* **2007**, *46*, 8845–8849.

[4] S. M. Kim, J. H. Park, S. Y. Choi, Y. K. Chung *Angew. Chem.* **2007**, *119, 6284–6287; Angew. Chem. Int. Ed.* **2007**, 46, 6172–6175; *Angew. Chem. Int. Ed.* **2007**, *46*, 6172–6175.

[5] For examples in which vicinal biscyclopropanes were formed by the cycloisomerization of dienynes, see a) Ru: N. Chatani, K. Kataoka, S. Murai, N. Furukawa, Y. Seki, *J. Am. Chem. Soc.* **1998**, *120*, 9104–9105; b) B. P. Peppers, S. T. Diver, *J. Am. Chem. Soc.* **2004**, *126*, 9524–9525; Pt: c) E. Mainetti, V. Mouries, L. Fensterbank, M. Malacria, J. Marco-Contelles, *Angew. Chem.* **2002**, *114*, 2236–2239; *Angew. Chem. Int. Ed.* **2002**, *41*, 2132–2135; d) J. Marco-Contelles, N. Arroyo, S. Anjum, E. Mainetti, N. Marion, K. Cariou, G. Lemière, V. Mouries, L. Fensterbank, M. Malacria, *Eur. J. Org. Chem.* **2006**, 4618–4633; Au: e) C. Nieto-Oberhuber, M. Paz Muñoz, E. Bunuel, C. Nevado, D. J. Cardenas,

A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 2456 – 2460; *Angew. Chem. Int. Ed.* **2004**, *43*, 2402 – 2406; f) C. Nieto-Oberhuber, S. Lopez, M. Paz Muñoz, E. Jimenez-Nunez, E. Bunuel, D. J. Cardenas, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1694 – 1702.

[6] a) N. Chatani, H. Inoue, T. Ikeda, S. Murai, *J. Org. Chem.* **2000**, *65*, 4913 – 4918; b) H. Inoue, N. Chatani, S. Murai, *J. Org. Chem.* **2002**, *67*, 1414 – 1417; c) A. Fürstner, V. Mamane, *J. Org. Chem.* **2002**, *67*, 6264 – 6267; d) S. J. Pastine, S. W. Youn, D. Sames, *Org. Lett.* **2003**, *5*, 1055 – 1058; e) S. J. Pastine, D. Sames, *Org. Lett.* **2003**, *5*, 4053 – 4055; f) B. Martin-Matute, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757 – 5766; g) S. J. Pastine, S. W. Youn, D. Sames, *Tetrahedron* **2003**, *59*, 8859 – 8868; h) V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556 – 4575; i) Y. Zhang, R. P. Hsung, X. Zhang, J. Huang, B. W. Slafer, A. Davis, *Org. Lett.* **2005**, *7*, 1047 – 1050; j) C. Nevado, A. M. Echavarren, *Synthesis* **2005**, 167 – 182; k) C. Ferrer, A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 1123 – 1127; *Angew. Chem. Int. Ed.* **2006**, *45*, 1105 – 1109.

[7] M. Achard, A. Tenaglia, G. Buono, *Org. Lett.* **2005**, *7*, 2353 – 2356.

[8] The structure of **2a** was established by ^{1}H and ^{13}C NMR spectroscopy and by comparison with the NMR data of similar compounds; see Ref. [7] and [9].

[9] J. H. Rigby, M. Kirova, N. Niyaz, F. Mohammadi, *Synlett* **1997**, 805 – 806.

[10] M. Méndez, M. P. Muñoz, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2001**, *123*, 10511 – 10520.

[11] For similar catalytic activity profiles of $[RuCl_2(CO)_3]_2$ and $PtCl_2$, see a) N. Chatani, T. Morimoto, T. Muto, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 6049 – 6050; b) N. Chatani, N. Furukawa, H. Sakurai, S. Murai, *Organometallics* **1996**, *15*, 901 – 903.

[12] For similar catalytic activity profiles of $AuCl_3$ and $PtCl_2$, see M. P. Muñoz, J. Adrio, J. A. Carretero, A. M. Echavarren, *Organometallics* **2005**, *24*, 1293 – 1300.

[13] K. Fagnou, M. Lautens, *Angew. Chem.* **2002**, *114*, 26 – 49; *Angew. Chem. Int. Ed.* **2002**, *41*, 26 – 47.

[14] A single-crystal X-ray analysis of cycloadduct **2c** secured the tricyclic structure of the adduct. CCDC 655906 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] S. Oi, I. Tsukamoto, S. Miyano, Y. Inoue, *Organometallics* **2001**, *20*, 3704 – 3709.

[16] The strong π-acid character of this ligand, which increases the electrophilicity of the metal center while being sufficiently labile, has been exploited in some platinum-catalyzed cycloisomerizations: a) A. Fürstner, P. W. Davies, T. Gress, *J. Am. Chem. Soc.* **2005**, *127*, 8244 – 8245; b) A. Fürstner, P. W. Davies, *J. Am. Chem. Soc.* **2005**, *127*, 15024 – 15025; c) A. Fürstner, C. Aïssa, *J. Am. Chem. Soc.* **2006**, *128*, 6306 – 6307.

[17] a) A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785 – 6786; b) A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863 – 11869.

[18] For recent examples of 1,2-shifts in carbenoids, see a) J. Sun, M. P. Conley, L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2006**, *128*, 9705 – 9710; b) H. Kusama, Y. Miyashita, J. Takaya, N. Iwasawa, *Org. Lett.* **2006**, *8*, 289 – 292; c) F. Xiao, J. Wang, *J. Org. Chem.* **2006**, *71*, 5789 – 5791, and references therein; d) H. Funami, H. Kusama, N. Iwasawa, *Angew. Chem.* **2007**, *119*, 927 – 929; *Angew. Chem. Int. Ed.* **2007**, *46*, 909 – 911; e) J. H. Lee, F. D. Toste, *Angew. Chem.* **2007**, *119*, 930 – 932; *Angew. Chem. Int. Ed.* **2007**, *46*, 912 – 914; f) C. R. Smith, E. M. Bunnelle, A. J. Rhodes, R. Sarpong, *Org. Lett.* **2007**, *9*, 1169 – 1171; g) A. S. Dudnik, V. Gevorgyan, *Angew. Chem.* **2007**, *119*, 5287 – 5289; *Angew. Chem. Int. Ed.* **2007**, *46*, 5195 – 5197.

[19] Attempts to convert tricyclic ether **7e** into bicyclic alcohol **11** resulted in the same observations.

[20] Subjecting a mixture of **8b** and **9b** (1:1.7; Table 3, entry 2) to the same conditions resulted in total consumption of **8b** but the reaction suffered from substantial degradation of the starting materials.

[21] We warmly thank one reviewer for helpful comments.

[22] Alternatively, α-cyclopropylplatinacarbene intermediates could be involved. Attempts to trap these highly reactive species from **1a** through oxidation with Ph_2SO or cyclopropanation of norbornene were unsuccessful and afforded exclusively **2a** in excellent yields; a) C. A. Witham, P. Mauleon, N. D. Shapiro, B. D. Sherry, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 5838 – 5839; b) S. López, E. Herrero-Gomez, P. Pérez-Galan, C. Nieto-Oberhuber, A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 6175 – 6178; *Angew. Chem. Int. Ed.* **2006**, *45*, 6029 – 6032.

[23] To test this assumption, we attempted to trap the stabilized cation with nucleophilic species. Indeed, treatment of **7f** with boron trifluoride and triethylsilane afforded **12** (51%), by reductive ring cleavage, and oxatriquinane **13** (24%), by isomerization through participation of the phenyl substituent. See the Supporting Information..