

# Novel Ruthenium- and Platinum-Catalyzed Sequential Reactions: Synthesis of Tri- and Tetrasubstituted Furans and Pyrroles from Propargylic Alcohols and Ketones\*\*

Yoshiaki Nishibayashi, Masato Yoshikawa,  
Youichi Inada, Marilyn Daisy Milton,  
Masanobu Hidai,\* and Sakae Uemura\*

Studies on multiple catalysts within the same medium to obtain desired products from simple starting materials are one of the current and important topics in synthetic chemistry.<sup>[1]</sup> The action of multiple catalysts lessens the reaction time and the yield loss by avoiding the isolation and purification of intermediates in multiple step sequences. Some interesting results in which multiple and different transition metal catalysts work in the same medium were reported,<sup>[2]</sup> but in most cases the reaction conditions, such as reaction temperature and reaction atmosphere, need to be changed on the way, or the successive addition of catalysts is necessary according to the reaction steps.<sup>[3]</sup>

Quite recently, we reported the ruthenium-catalyzed efficient propargylic substitution reactions of propargylic alcohols with various heteroatom- and carbon-centered nucleophiles to give the corresponding functionalized propargylic products in high yields with complete regioselectivities.<sup>[4]</sup> Noteworthy, the reactions are catalyzed only by thiolate-bridged diruthenium complexes<sup>[5]</sup> such as  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SR})_2\text{RuCp}^*\text{Cl}]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{R} = \text{Me}$  (**1a**), *i*Pr (**1b**), *n*Pr (**1c**)). The result prompted us to investigate the transition metal-catalyzed sequential reaction of functionalized propargylic products, which have a terminal alkyne, because organic compounds with a terminal alkyne are known to be converted into more valuable compounds by various transition metal catalysts.<sup>[6,7]</sup> We have now found a novel sequential reaction system by using heterobimetallic

[\*] Prof. Dr. S. Uemura, Dr. Y. Nishibayashi, M. Yoshikawa, Y. Inada, Dr. M. D. Milton  
Department of Energy and Hydrocarbon Chemistry  
Graduate School of Engineering  
Kyoto University  
Yoshida, Sakyo-ku, Kyoto 606-8501 (Japan)  
Fax: (+81) 75-753-3573  
E-mail: uemura@scl.kyoto-u.ac.jp  
Prof. Dr. M. Hidai  
Department of Materials Science and Technology  
Faculty of Industrial Science and Technology  
Tokyo University of Science  
Noda, Chiba 278-8510 (Japan)  
Fax: (+81) 471-23-9362  
E-mail: hidai@rs.noda.sut.ac.jp

[\*\*] This work was supported by a Grant-in-Aid for Scientific Research (No. 13305062) from the Ministry of Education, Science, Sports, and Culture of Japan.



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

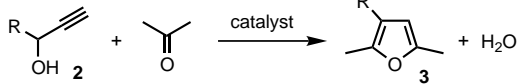
catalysts to give the corresponding tri- and tetra-substituted furans and pyrroles in moderate to high yields with complete regioselectivity from the reaction of propargylic alcohols with ketones in the presence of a catalytic amount of both **1a** and PtCl<sub>2</sub>. In this reaction system, two different catalysts simultaneously promote their catalytic cycles in the same medium. Preliminary results are described herein.

Treatment of 1-phenyl-2-propyn-1-ol (**2a**) in acetone in the presence of **1a** (10 mol %), NH<sub>4</sub>BF<sub>4</sub> (20 mol %), and PtCl<sub>2</sub> (20 mol %) at reflux temperature for 36 h afforded 2,5-dimethyl-3-phenylfuran (**3a**) in 75 % yield as measured by GLC (64 % yield of the isolated product; Table 1, entry 1). A prolonged reaction time improved the yield of **3a** (Table 1, entries 2 and 3). The reaction proceeded even in the presence of smaller quantities of **1a** (5 mol %) and PtCl<sub>2</sub> (10 mol %; Table 1, entry 4). Noteworthy, the bimetallic system of **1a** and PtCl<sub>2</sub> is essential to promote the catalytic formation of **3a** effectively. Other transition-metal complexes, such as Pd(OAc)<sub>2</sub>, [PdCl<sub>2</sub>(MeCN)<sub>2</sub>] and PdCl<sub>2</sub> were ineffectual, while AuCl<sub>3</sub><sup>[8]</sup> worked effectively but an intermediate diketone was also formed (see below; Table 1, entry 5). The use of various propargylic alcohols resulted in the formation of the corresponding 3-aryl and 3-alkenyl substituted 2,5-dimethylfuran (**3b–3h**) in moderate to high yields with a complete regioselectivity (Table 1, entries 6–12). Unfortunately, the reaction of 1-cyclohexyl-2-propyn-1-ol did not proceed at all (Table 1, entry 13).

Reactions of propargylic alcohols with other ketones were similarly carried out. Typical results are shown in Table 2. Formation of the corresponding 3-aryl-2,4,5-trimethylfurans (**3j–3l**) was observed in the reactions of propargylic alcohols (**2a**, **2b**, **2d**) with 2-butanone (Table 2; entries 1–3). The reaction of **2a** with 3-pentanone under the same reaction conditions gave 2-ethyl-3,5-dimethyl-4-phenylfuran (**3m**) in 85 % yield (Table 2, entry 4). Noteworthy, the formation of other regioisomers of furans was not observed in all cases. The reactions of various propargylic alcohols with cyclohexanone gave the expected 3-aryl-2-methyl-4,5,6,7-tetrahydrobenzofurans (**3n–3p**) in high yields (Table 2, entries 5–7). From **2a** and cycloheptanone, 2-methyl-3-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan (**3q**) was obtained in 66 % yield, but no reaction occurred with cyclopentanone (Table 2, entries 8 and 9, respectively).



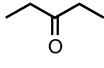
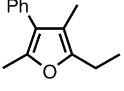

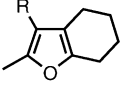
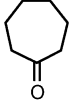
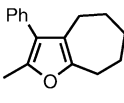

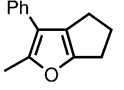
To obtain some information of the reaction mechanism, the relationship between the product yields and the reaction time was investigated in the reaction between **2a** and acetone in the presence of **1a** and PtCl<sub>2</sub> (Figure 1). This time profile

**Table 1:** Reaction of propargylic alcohol (**2**) with acetone in the presence of [Cp\*<sub>2</sub>RuCl(μ-SMe)<sub>2</sub>RuCp\*Cl] (**1a**) and PtCl<sub>2</sub>.<sup>[a]</sup>

				
Entry	R	Cat (mol %)	t [h]	Yield of <b>3</b> [%] <sup>[b]</sup>
1	Ph ( <b>2a</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	36	<b>3a</b> , 64 (75) <sup>[c]</sup>
2	Ph ( <b>2a</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	72	<b>3a</b> , 69
3	Ph ( <b>2a</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (10)	100	<b>3a</b> , (83) <sup>[c]</sup>
4	Ph ( <b>2a</b> )	<b>1a</b> (5) and PtCl <sub>2</sub> (10)	110	<b>3a</b> , (74) <sup>[c]</sup>
5	Ph ( <b>2a</b> )	<b>1a</b> (10) and AuCl <sub>3</sub> (20)	36	<b>3a</b> , (36) <sup>[c,d]</sup>
6	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ( <b>2b</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	72	<b>3b</b> , 65
7	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>2c</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	36	<b>3c</b> , 52
8	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	72	<b>3d</b> , 57
9	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ( <b>2e</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	72	<b>3e</b> , 74
10	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ( <b>2f</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	36	<b>3f</b> , 54
11	2-naphthyl ( <b>2g</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	72	<b>3g</b> , 64
12	Ph <sub>2</sub> C=CH- ( <b>2h</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	36	<b>3h</b> , 29
13	cyclohexyl ( <b>2i</b> )	<b>1a</b> (10) and PtCl <sub>2</sub> (20)	36	<b>3i</b> , 0

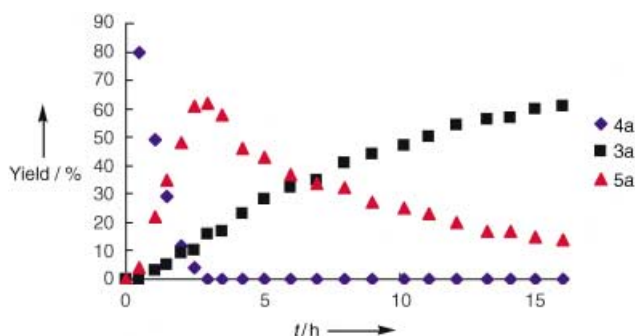
[a] All the reactions of **2** (0.60 mmol) with acetone (30 mL) were carried out in the presence of catalysts and NH<sub>4</sub>BF<sub>4</sub> (20 mol %) at reflux temperature. [b] Yield of isolated compound. [c] Yield obtained by GLC. [d] 3-Phenyl-2,5-hexanedione was also formed with 27 % yield obtained by GLC.

**Table 2:** Reaction of propargylic alcohol (**2**) with ketone in the presence of [Cp\*<sub>2</sub>RuCl(μ-SMe)<sub>2</sub>RuCp\*Cl] (**1a**) and PtCl<sub>2</sub>.<sup>[a]</sup>

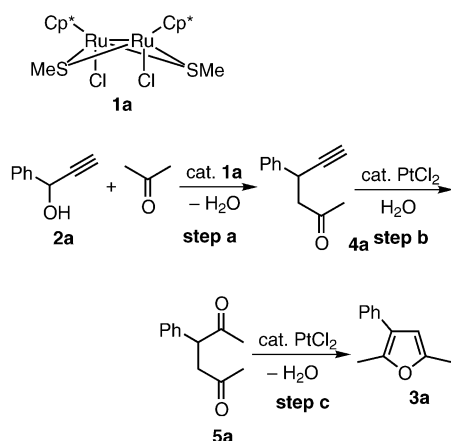
Entry	<b>2</b>	Ketone	Furan ( <b>3</b> )	Yield of <b>3</b> , % <sup>[b]</sup>
1	R = Ph ( <b>2a</b> )			R = Ph, 72 ( <b>3j</b> )
2	R = <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ( <b>2b</b> )			R = <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> , 78 ( <b>3k</b> )
3	R = <i>p</i> -FC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )			R = <i>p</i> -FC <sub>6</sub> H <sub>4</sub> , 65 ( <b>3l</b> )
4 <sup>[c]</sup>	R = Ph ( <b>2a</b> )			85 ( <b>3m</b> )
5	R = Ph ( <b>2a</b> )			R = Ph, 75 ( <b>3n</b> )
6	R = <i>p</i> -FC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )			R = <i>p</i> -FC <sub>6</sub> H <sub>4</sub> , 75 ( <b>3o</b> )
7	R = <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ( <b>2e</b> )			R = <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> , 69 ( <b>3p</b> )
8	R = Ph ( <b>2a</b> )			66 ( <b>3q</b> )
9	R = Ph ( <b>2a</b> )			0 ( <b>3r</b> )

[a] All the reactions of **2** (0.60 mmol) with ketone (30 mL) were carried out in the presence of **1a** (0.06 mmol), PtCl<sub>2</sub> (0.12 mmol) and NH<sub>4</sub>BF<sub>4</sub> (0.12 mmol) at reflux temperature for 36 h. [b] Isolated yield. [c] For 72 h.

indicates the following: At first, **2a** is transformed rapidly into γ-ketoalkyne (**4a**) by the catalysis of **1a** (Scheme 1, step a).<sup>[4b]</sup> Then, hydration of the alkyne moiety in **4a** by the produced H<sub>2</sub>O slowly gives the 1,4-diketone, **5a**, by the catalysis of PtCl<sub>2</sub> (Scheme 1, step b).<sup>[9]</sup> Intramolecular cyclization of the produced diketone then follows, which results in the formation of the furan, **3a**, also by the catalysis of PtCl<sub>2</sub> (Scheme 1, step c).<sup>[9b]</sup> This result clearly indicates that two different

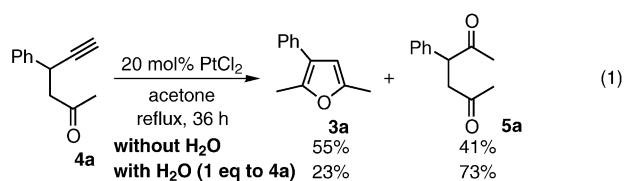


**Figure 1.** Time profile of the reaction of propargylic alcohol (**2a**) with acetone in the presence of  $[\text{Cp}^*\text{RuCl}(\mu\text{-SMe})_2\text{RuCp}^*\text{Cl}]$  (**1a**; 10 mol%) and  $\text{PtCl}_2$  (20 mol%).



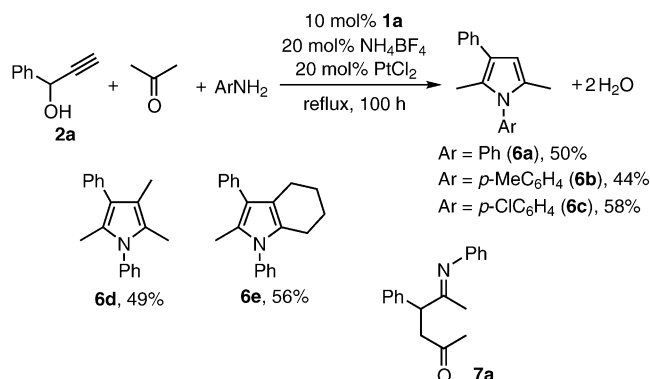
**Scheme 1.** Reaction of 1-phenyl-2-propyn-1-ol with acetone in the presence of  $[\text{Cp}^*\text{RuCl}(\mu\text{-SMe})_2\text{RuCp}^*\text{Cl}]$  and  $\text{PtCl}_2$ .

catalysts, such as **1a** and  $\text{PtCl}_2$ , can promote their catalytic cycles in the same medium. Separately, the transformation of **4a** into **3a** and **5a** was confirmed in the presence of  $\text{PtCl}_2$  [Eq. (1)]. However, even upon adding stoichiometric



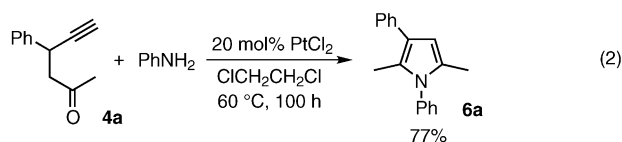
amounts of water to **4a**, its conversion into **3a** via **5a** was slower than that in the present reaction system, thus showing that the coexistence of **1a** and  $\text{PtCl}_2$  promotes this conversion more smoothly.

When the above new catalytic reactions were carried out in the presence of aniline derivatives (5 equiv relative to **2a**), the corresponding tri- and tetra-substituted pyrroles (**6**) were produced in moderate isolated yields with complete regioselectivity (Scheme 2).<sup>[10]</sup> No formation of the corresponding furans and other regioisomers of **6** was observed in all cases. Nucleophilic attack of anilines on the carbon-carbon triple bond in **4a** catalyzed by  $\text{PtCl}_2$  may give the corresponding



**Scheme 2.** Reactions of 1-phenyl-2-propyn-1-ol with ketones and anilines in the presence of  $[\text{Cp}^*\text{RuCl}(\mu\text{-SMe})_2\text{RuCp}^*\text{Cl}]$  and  $\text{PtCl}_2$ .

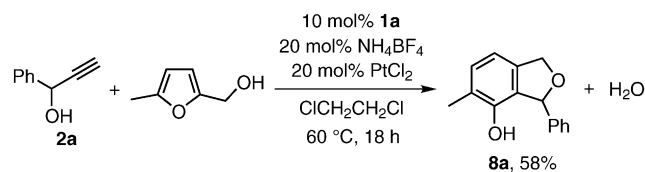
imines (**7a**).<sup>[11]</sup> Cyclization of **7a** catalyzed by  $\text{PtCl}_2$  may produce the substituted pyrrole (**6a**). It was confirmed that the reaction of **4a** with aniline in the presence of  $\text{PtCl}_2$  afforded **6a** in 77% isolated yield [Eq. (2)]. This result



indicates that sequential three-component coupling reaction by the catalysis of **1a** and  $\text{PtCl}_2$  occurs in the same medium.

The bimetallic system of **1a** and  $\text{PtCl}_2$  can be applied to other sequential catalytic reactions. A typical example is shown in Scheme 3. The reaction of propargylic alcohol (**2a**) with 5-methyl-2-furyl-methanol in the presence of a catalytic amount of both **1a** and  $\text{PtCl}_2$  in 1,2-dichloroethane at 60 °C for 18 h afforded the corresponding phenol derivative **8a** in 58% yield.<sup>[12]</sup> Propargylation of the furyl-methanol with **2a** was promoted by **1a** to give the corresponding furylmethyl propargylic ether,<sup>[4a]</sup> which was subsequently transformed into the corresponding phenol derivative by the so far known catalysis of  $\text{PtCl}_2$ .<sup>[13]</sup>

In summary, we have found novel ruthenium- and platinum-catalyzed sequential reactions to afford the corresponding tri- and tetra-substituted furans or pyrroles<sup>[14]</sup> from propargylic alcohols with ketones, or with ketones and anilines, respectively, in moderate to good yields with high regioselectivities. Two different kinds of catalysts **1a** and  $\text{PtCl}_2$  sequentially promote each catalytic cycle in the same medium. Some phenol derivatives can also be prepared from propargylic alcohols and furyl-methanol by this bimetallic



**Scheme 3.** Reaction of 1-phenyl-2-propyn-1-ol with 5-methyl-2-furyl-methanol in the presence of  $[\text{Cp}^*\text{RuCl}(\mu\text{-SMe})_2\text{RuCp}^*\text{Cl}]$  and  $\text{PtCl}_2$ .

system. Further investigations involving the elucidation of the detailed reaction mechanism and broadening the scope of this sequential catalytic systems are currently in progress.

## Experimental Section

A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with acetone catalyzed by  $[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{-RuCp}^*\text{Cl}]$  (**1a**) and  $\text{PtCl}_2$  is described below. Complex **1a** (38 mg, 0.06 mmol),  $\text{NH}_4\text{BF}_4$  (12 mg, 0.12 mmol), and  $\text{PtCl}_2$  (31 mg, 0.12 mmol) were placed in a 50 mL flask under  $\text{N}_2$ . Anhydrous acetone (30 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol), the reaction flask was kept at reflux temperature for 36 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC ( $\text{SiO}_2$ ) with EtOAc-hexane (1/9) to give 2,5-dimethyl-3-phenylfuran<sup>[15]</sup> (**3a**) as a colorless oil (66.5 mg, 0.38 mmol, 64% yield);  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.28 (s, 3H), 2.40 (s, 3H), 6.10 (s, 1H), 7.21–7.37 ppm (m, 5H);  $^{13}\text{C}$  NMR (67.5 Hz,  $\text{CDCl}_3$ ):  $\delta$  = 12.9, 13.4, 106.9, 121.4, 126.0, 127.3, 128.5, 134.5, 145.8, 149.7 ppm.

Received: February 13, 2003 [Z51170]

**Keywords:** domino reactions · heterocycles · homogeneous catalysis · platinum · ruthenium

- [1] For recent reviews, see a) L. F. Tietze, *Chem. Rev.* **1996**, 96, 115; b) E. K. Beuken, B. L. Feringa, *Tetrahedron* **1998**, 54, 12985; c) G. Poli, G. Giambastiani, A. Heumann, *Tetrahedron* **2000**, 56, 5959.
- [2] For recent examples: examples where two catalysts activated different functional groups in the same medium, a) M. Sawamura, M. Sudoh, Y. Ito, *J. Am. Chem. Soc.* **1996**, 118, 3309; b) S. Kamijo, Y. Yamamoto, *Angew. Chem.* **2002**, 114, 3364; *Angew. Chem. Int. Ed.* **2002**, 41, 3230, and references therein. Examples where two different catalytic cycles proceeded in the same medium, c) R. W. Barnhart, G. C. Bazan, T. Mourey, *J. Am. Chem. Soc.* **1998**, 120, 1082; d) N. Jeong, S. D. Seo, J. Y. Shin, *J. Am. Chem. Soc.* **2000**, 122, 10220; e) Z. J. A. Komon, G. M. Diamond, M. K. Leclerc, V. Murphy, M. Okazaki, G. C. Bazan, *J. Am. Chem. Soc.* **2002**, 124, 15280.
- [3] For recent examples, see a) P. A. Evans, J. E. Robinson, *J. Am. Chem. Soc.* **2001**, 123, 4609; b) B. M. Choudary, N. S. Chowdary, S. Madhi, M. L. Kantam, *Angew. Chem.* **2001**, 113, 4755; *Angew. Chem. Int. Ed.* **2001**, 40, 4620; c) J. L. Christopher, W. Bielawski, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, 123, 11312; d) T. Shimada, K. Mukaide, A. Shinohara, J. W. Han, T. Hayashi, *J. Am. Chem. Soc.* **2002**, 124, 1584; e) J. Tian, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Angew. Chem.* **2002**, 114, 3788; *Angew. Chem. Int. Ed.* **2002**, 41, 3636; f) S. U. Son, K. H. Park, Y. K. Chung, *J. Am. Chem. Soc.* **2002**, 124, 6838; g) B. M. Trost, M. R. Machacek, *Angew. Chem.* **2002**, 114, 4887; *Angew. Chem. Int. Ed.* **2002**, 41, 4693; h) A. E. Sutton, B. A. Seigal, D. F. Finnegan, M. L. Snapper, *J. Am. Chem. Soc.* **2002**, 124, 13390.
- [4] a) Y. Nishibayashi, I. Wakiji, M. Hidai, *J. Am. Chem. Soc.* **2000**, 122, 11019; b) Y. Nishibayashi, I. Wakiji, Y. Ishii, S. Uemura, M. Hidai, *J. Am. Chem. Soc.* **2001**, 123, 3393; c) Y. Inada, Y. Nishibayashi, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2002**, 124, 15172; d) Y. Nishibayashi, G. Onodera, Y. Inada, M. Hidai, S. Uemura, *Organometallics* **2003**, 22, 873.
- [5] The thiolate-bridged diruthenium complexes (**1**) were found to provide unique bimetallic reaction sites for activation and transformation of various terminal alkynes, see: Y. Nishibayashi, M. Yamanashi, I. Wakiji, M. Hidai, *Angew. Chem.* **2000**, 112, 3031; *Angew. Chem. Int. Ed.* **2000**, 39, 2909, and references therein.
- [6] a) K. Ohe, T. Yokoi, K. Miki, F. Nishino, S. Uemura, *J. Am. Chem. Soc.* **2002**, 124, 526; b) K. Miki, F. Nishino, K. Ohe, S. Uemura, *J. Am. Chem. Soc.* **2002**, 124, 5260; c) Y. Nishibayashi, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2002**, 124, 7900; d) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.* **2002**, 124, 11846; e) Y. Nishibayashi, Y. Inada, M. Yoshikawa, M. Hidai, S. Uemura, *Angew. Chem.* **2003**, 115, 1533; *Angew. Chem. Int. Ed.* **2003**, 42, 1495.
- [7] For recent examples, see a) J. L. Pail, S. Dérien, C. Bruneau, B. Demerseman, L. Toupet, P. H. Dixneuf, *Angew. Chem.* **2001**, 113, 2996; *Angew. Chem. Int. Ed.* **2001**, 40, 2912; b) M. Méndez, M. P. Muñoz, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2001**, 123, 10511; c) A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, 123, 11863; d) Y. Sheng, D. G. Musaev, K. S. Reddy, F. E. McDonald, K. Morokuma, *J. Am. Chem. Soc.* **2002**, 124, 4149; e) B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.* **2002**, 124, 4178; f) K.-L. Yeh, B. Liu, C.-Y. Lo, H.-L. Huang, R.-S. Liu, *J. Am. Chem. Soc.* **2002**, 124, 6510; g) H. Kusama, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2002**, 124, 11592.
- [8] A. Stephen, K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem.* **2000**, 112, 2382; *Angew. Chem. Int. Ed.* **2000**, 39, 2285.
- [9] a) W. Hiscox, P. W. Jennings, *Organometallics* **1990**, 9, 1997; b) W. Baidossi, M. Lahav, J. Blum, *J. Org. Chem.* **1997**, 62, 669; c) E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, *Angew. Chem.* **2002**, 114, 4745; *Angew. Chem. Int. Ed.* **2002**, 41, 4563.
- [10] A novel one-pot pyrrole synthesis has been reported, see R. U. Braun, K. Zeitler, T. J. J. Muller, *Org. Lett.* **2001**, 3, 3297.
- [11] Nucleophilic addition of amines on a  $\text{C}\equiv\text{C}$  triple bond mediated by a platinum complex has been reported, see a) T. E. Müller, A.-K. Pleier, *J. Chem. Soc. Dalton Trans.* **1999**, 583; b) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, 98, 675, and references therein.
- [12] The molecular structure of **8a** was unambiguously determined by X-ray analysis. CCDC 203160 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [13] a) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, 122, 11553; b) B. Martín-Matute, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2001**, 113, 4890; *Angew. Chem. Int. Ed.* **2001**, 40, 4754.
- [14] For recent examples of the preparation of substituted furans and pyrroles, see a) C.-F. Lee, L.-M. Yang, T.-Y. Hwu, A.-S. Feng, J.-C. Tseng, T.-Y. Luh, *J. Am. Chem. Soc.* **2000**, 122, 4992; b) A. V. Kel'in, A. W. Sromek, V. Gevorgyan, *J. Am. Chem. Soc.* **2001**, 123, 2074; c) J. A. Marshall, E. A. V. Devender, *J. Org. Chem.* **2001**, 66, 8037; d) A. V. Kel'in, V. Gevorgyan, *J. Org. Chem.* **2002**, 67, 95; e) J. T. Kim, A. V. Kel'in, V. Gevorgyan, *Angew. Chem.* **2003**, 115, 102; *Angew. Chem. Int. Ed.* **2003**, 42, 98.
- [15] T. S. Balaban, M. Hiegemann, *Tetrahedron* **1992**, 48, 9827.