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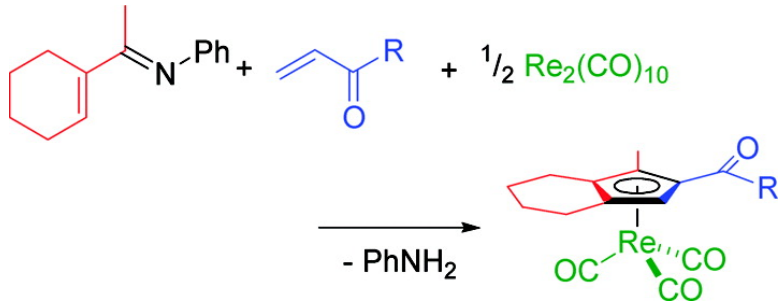

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Synthesis of Cp−Re Complexes via Olefinic C−H Activation and Successive Formation of Cyclopentadienes

Yoichiro Kuninobu,* Yuta Nishina, Takashi Matsuki, and Kazuhiko Takai*

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

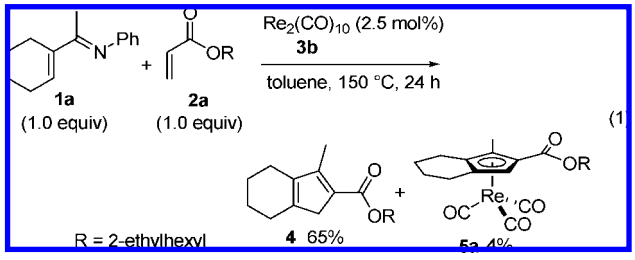
Received July 29, 2008; E-mail: kuninobu@cc.okayama-u.ac.jp; ktakai@cc.okayama-u.ac.jp

One of the most important categories of transition metal complexes is cyclopentadienyl (Cp) complexes.[1] Because the reactivity of Cp complexes can usually be controlled by changing the substituents of the Cp ring, many methods have been developed to introduce appropriate substituents at desired positions.[2] We disclose here a novel method for [3 + 2] construction of substituted cyclopentadienes from α,β-unsaturated ketimines and α,β-unsaturated carbonyl compounds initiated by olefinic C−H activation of the ketimines. The C−H activation, which is the key step in the reaction, is accomplished with a rhenium catalyst.

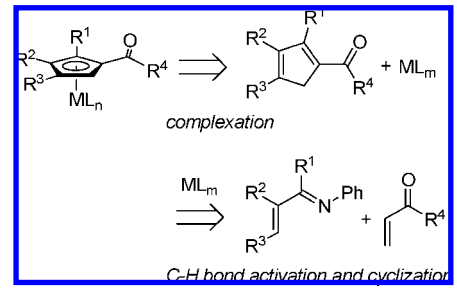
In addition, we found that cyclopentadienyl−rhenium (Cp−Re) complexes[3] can be prepared in a one step domino reaction involving the preparation of cyclopentadiene derivatives followed by the complexation with $Re_2(CO)_{10}$. Because substituted cyclopentadienyl complexes of group 7 metals have attracted much attention in the field of biochemistry and pharmaceuticals,[4] the method provides a new entry for the substituted Cp complexes.

The strategy for the synthesis of Cp−transition metal complexes is shown in Scheme 1. For the construction of substituted cyclopentadienes, the transition metal-catalyzed activation of an olefinic C−H bond and successive cyclization are key steps. The C−H bond activation at olefinic positions has been achieved with several transition metal complexes such as ruthenium and rhodium complexes;[5] however, the reactions are limited to the insertion of an unsaturated molecule into the generated M−H bond. For the successive cyclization, we thought that rhenium complexes may be suitable because the insertion of an α,β-unsaturated carbonyl compound occurs into a rhenium−carbon bond after the C−H activation.[6] The main problem is that it is not clear whether the olefinic C−H bond can be activated with the rhenium complexes.[7]

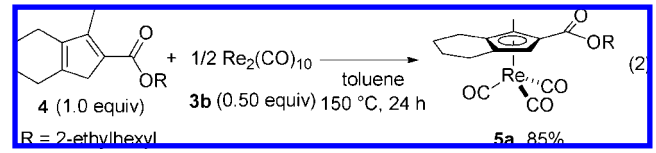
By the reaction between ketimine **1a** and 2-ethylhexyl acrylate (**2a**) in the presence of a rhenium catalyst, $[ReBr(CO)_3(thf)]_2$ (**3a**), both insertion of acrylate **2a** into an olefinic C−H bond of **1a**, and intramolecular cyclization proceeded, and cyclopentadiene derivative **4** was formed in 25% yield. By using $Re_2(CO)_{10}$ (**3b**) as a catalyst, the yield of **4** increased dramatically, and **4** was produced in 65% yield (eq 1). Interestingly, Cp−Re complex **5a** was also obtained in 4% yield as a side product.[8] This result indicates that the rhenium complex **5a** could be formed by a stoichiometric reaction between cyclopentadiene derivative **4** and the rhenium complex **3b**.



Scheme 1. Strategy for the Retrosynthesis of Cyclopentadienyl−Transition Metal Complexes



Thus, we examined the reaction between the isolated **4** and $Re_2(CO)_{10}$ (**3b**, 0.50 equiv), and found that Cp−Re complex **5a** was generated in 85% yield (eq 2). Although $[ReBr(CO)_3(thf)]_2$ (**3a**) also catalyzed the formation reaction of **4**, the Cp−Re complex **5a** was not formed with **3a**.

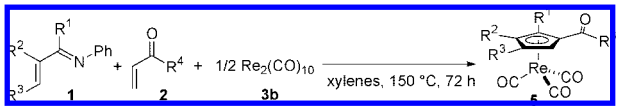


From the result in eq 2, we were encouraged to investigate the domino synthesis of a Cp−Re complex **5a** from substrates to give a ligand, and the rhenium complex **3b**. Treatment of ketimine **1a** having an olefin moiety and 2-ethylhexyl acrylate (**2a**) with $Re_2(CO)_{10}$ (**3b**) in xylenes at 150 °C for 72 h gave the Cp−Re complex **5a** in 94% yield as a colorless oil (Table 1, entry 1). *n*-Butyl-substituted Cp−Re complex **5b** was produced by the reaction between ketimine **1b** and **2a** (Table 1, entry 2). Acyclic α,β-unsaturated ketimine **1c** also provided the corresponding Cp−Re complex **5c** in 82% yield (Table 1, entry 3). Cp−Re complex **5d** was afforded from an α,β-unsaturated ketimine having an ether ring, **1d** (Table 1, entry 4). A vinyl ketone **2b** gave a mixture of Cp−Re complexes **5e** and **5e′** in 47% yield (Table 1, entry 5). Formation of **5e′** indicates that **2b** inserted into a rhenium−carbon bond in the opposite direction to acrylic ester **2a** and amide **2c**.[7c,9] Amide-substituted Cp−Re complex **5f** was also formed in 69% yield using acrylamide **2c** (Table 1, entry 6).

As a result of the above experiments, the proposed mechanism is as follows (Scheme 2): (1) coordination of a nitrogen atom of a ketimine to a rhenium center; (2) oxidative addition of a C−H bond of the ketimine to the rhenium center (C−H bond activation);[10] (3) insertion of an α,β-unsaturated carbonyl compound into a rhenium−carbon bond;[11] (4) intramolecular nucleophilic cyclization; (5) reductive elimination and the elimination of aniline to give a cyclopentadiene derivative; (6) the formation of a Cp−Re complex from the cyclopentadiene derivative and rhenium complex.

10.1021/ja805921f CCC: $40.75

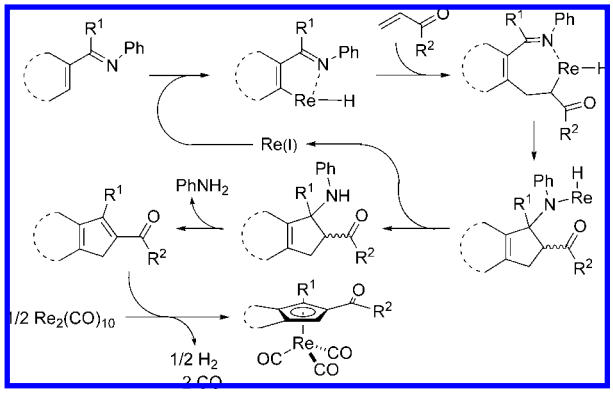
Table 1. Synthesis of Cyclopentadienyl−Rhenium Complexes **5** from Ketimines **1**, α,β-Unsaturated Carbonyl Compounds **2**, and a Rhenium Complex **3b**[a]



entry	Ketimine R¹	R²	R³		α,β-Unsaturated Carbonyl Compound R⁴	product	% yield[b]
1	Me	-(CH₂)₄-		**1a**	OCH_2CHEt^nBu (OR)[c] **2a**	**5a**	94 (98)
2	^{n}Bu	-(CH₂)₄-		**1b**	**2a**	**5b**	74 (79)
3	Me	Me	Me	**1c**	**2a**	**5c**	82 (99)
4[d]	Me	-O(CH₂)₃-		**1d**	**2a**	**5d**	36 (40)
5		**1a**			$^nC_5H_{11}$ **2b**	**5e**	47 (54)[e]
						5e'	
6[d]		**1a**			NMe_2 **2c**	**5f**	69 (75)

[a] **1** (1.0 equiv), **2** (1.0 equiv), **3b** (0.50 equiv). [b] Isolated yield. Yield determined by ^{1}HNMR is reported in parentheses. [c] R = CH_2CHEt^nBu. [d] Run at 180 °C. [e] **5e**/**5e′** = 1.0:1.8.

Scheme 2. Proposed Mechanism for the Formation of Cp−Re Complexes



In summary, we have succeeded in the activation of an olefinic C−H bond with rhenium complexes and utilized it in the domino synthesis of Cp−Re complexes from α,β-unsaturated ketimines, α,β-unsaturated carbonyl compounds, and $Re_2(CO)_{10}$. Although there have been many methods for the synthesis of Cp−transition metal complexes,[12] it is usually necessary to synthesize the Cp ligands in advance. In this reaction, the rhenium complex acts as both the catalyst for the formation of substituted Cp rings and a component of the desired complexes.[13] We hope this versatile and efficient method for the preparation of Cp complexes will find new applications.

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Supporting Information Available: General experimental procedure, characterization data for a cyclopentadiene derivative and cyclopentadienyl−rhenium complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The Cp−Re complex **5a** did not work as a catalyst for olefinic C−H bond activation. This result shows that cyclopentadiene derivative **4** was formed by rhenium catalyst **3b** in the first step.
(9) In the case of an arylimine, the regioselectivity of the insertion of an α,β-unsaturated ketone is the same as acrylic esters.[7c] We examined the existence of the interconversion between **5e** and **5e′**;[14] however, both **5e** and **5e′** remained unchanged under the reaction conditions with $Re_2(CO)_{10}$. It is still unclear why the insertion occurred in the opposite direction in the case of the α,β-unsaturated ketone.
(10) Rhenium-catalyzed C−H bond activation occurs only at the *ortho*-position of α,β-unsaturated ketimines. This is in sharp contrast to C−H bond activation with rhodium or ruthenium catalysts, where carbonyl oxygen atoms can also act as directing groups. This feature of the rhenium-catalyzed C−H activation enables α,β-unsaturated ketimines and carbonyl compounds to serve different roles.
(11) The insertion step did not occur with either α- or β-substituted acrylates (see ref 7c).
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