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## Acceleration of ruthenium(II)- and rhodium(I)-catalyzed hydrogen-transfer reaction by rare earth metal triflates

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Abstract—The addition of  $Yb(OTf)_3$  as an additive considerably accelerates the  $RuCl_2(PPh_3)_3$ - and  $RhCl(PPh_3)_3$ -catalyzed hydrogen-transfer reduction of both aromatic and aliphatic ketones in which Ru:Yb ratios of 1:2–1:4 are critically important for achieving acceleration. © 2001 Elsevier Science Ltd. All rights reserved.

The hydrogen-transfer reaction remains a useful method for the reduction of ketones because of the advantages of simple and safe operation and low cost in bulk scale preparations over the use of hydride reagents and hydrogen gas (Scheme 1). The reactions have been proposed to proceed through a direct hydrogen-transfer between the donor and acceptor molecule by the promotion of main metal alkoxides including early transition metal alkoxides (Meerwein–Ponndorf–Verley (MPV) reduction) (Fig. 1(A))<sup>1,2</sup> and the metal hydride intermediate derived from late transition metal catalysts (Fig. 1(B)).<sup>3</sup> A different mechanism which involves a concerted transfer of both H<sup>+</sup> and H<sup>-</sup> (Fig. 1(C)) was also presented for the reaction catalyzed by the late transition metal catalysts such as ruthenium or iridium complexes.<sup>4</sup>



Scheme 1.





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Among the metal catalysts, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> is one of the conventional catalysts for hydrogen-transfer reactions.<sup>5</sup> The reaction, however, generally requires an elevated temperature and prolonged reaction time.

In this paper, we describe the highly efficient  $RuCl_2(PPh_3)_3$ - and  $RhCl(PPh_3)_3$ -catalyzed hydrogentransfer reductions of aromatic and aliphatic ketones with the aid of rare earth metal triflates.

Thus, propiophenone was smoothly reduced via the  $RuCl_2(PPh_3)_3$ -catalyzed hydrogen-transfer reaction in the presence of Yb(OTf)\_3 to near completion within 1 h, while the reduction proceeded much more sluggishly without the additive, resulting in a poor yield, as seen in Fig. 2. Some of the lanthanoide triflates, particularly Y(OTf)\_3 and Yb(OTf)\_3, were quite effective as additives for accelerating this type of reduction and the results are summarized in Table 1.<sup>6</sup>

There seems to be little relationship between the accelerating effect and the Lewis acidity of the rare earth metal triflates.<sup>7</sup> The reduction was highly depended on the molar ratio of  $RuCl_2(PPh_3)_3$  to  $Yb(OTf)_3$ . The ratios of 1:2 to 1:4 were the most promising, in contrast to the use of more than 5 equivalent molar  $Yb(OTf)_3$ , which inhibited the reaction nearly completely. The 1:1 ratio of  $RuCl_2(PPh_3)_3$  and  $Yb(OTf)_3$  gave a moderate result.

Other Lewis acids such as  $BF_3 \cdot OEt_2$ ,  $Ti(Oi-Pr)_4$ , EtAlCl<sub>2</sub>, ZnCl<sub>2</sub>, YbF<sub>3</sub> and YbCl<sub>3</sub> were ineffective for accelerating the reaction and SnCl<sub>2</sub> was inhibitory. The effects of Zn(OTf)<sub>2</sub> and Yb(OAc)<sub>3</sub> were moderate to give 68 and 78% yields, respectively, under typical conditions.<sup>8</sup>

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**Figure 2.** Time courses for the  $RuCl_2(PPh_3)_3$ -catalyzed reduction of propiophenone in refluxing isopropanol. (A) With  $Yb(OTf)_3$ ; (B) without  $Yb(OTf)_3$ .

Using the hydrogen-transfer reaction reinforced with a catalytic amount of  $Yb(OTf)_3$ , a series of ketones including aliphatic ketones such as 2-octanone and cyclohexanone<sup>9</sup> were readily reduced to secondary alcohols (Table 2).

On the other hand, the accelerating effect of the  $Yb(OTf)_3$  additive was also observed for the  $RhCl(PPh_3)_3$ -catalyzed hydrogen-transfer reduction,<sup>10</sup> which proceeded under milder conditions. Thus, the  $RhCl(PPh_3)_3$ -catalyzed hydrogen-transfer reduction of propiophenone smoothly proceeded at 35°C in the presence of added Yb(OTf)\_3 to afford 85–86% yields of the alcohol,<sup>11</sup> while 65–67% yields were obtained without the Yb(OTf)\_3 additive (Table 3). Much smaller amounts of catalyst (0.05–0.1 mol%) were sufficiently effective in catalyzing the reduction of ketones, when the reaction was performed above 35°C. Among the bases examined, *t*-BuOK was the best choice for this reaction.

The mechanism for the RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>-catalyzed hydrogen-transfer reduction of ketones has been estab**Table 1.** The hydrogen-transfer reduction of propiophenone catalyzed by  $RuCl_2(PPh_3)_3^a$ 



Entry	Additive (mol%)	Yield (%) <sup>b</sup>		
1	(None)	50		
2	$Yb(OTf)_{3}$ (0.2)	69		
3	Yb(OTf) <sub>3</sub> (0.4)	86		
4	Yb(OTf) <sub>3</sub> (0.6)	85		
5	Yb(OTf) <sub>3</sub> (0.8)	87		
6	Yb(OTf) <sub>3</sub> (1.0)	2		
7	$Sc(OTf)_{3}$ (0.4)	61		
8	$Y(OTf)_{3}$ (0.4)	88		
9	$La(OTf)_{3}$ (0.4)	72		
10	$Ce(OTf)_{3}$ (0.4)	83		
11	$Pr(OTf)_{3}$ (0.4)	64		
12	Nd(OTf) <sub>3</sub> (0.4)	66		
13	$Sm(OTf)_{3}$ (0.4)	19		
14	$Eu(OTf)_{3}$ (0.4)	38		
15	$Gd(OTf)_3$ (0.4)	64		
16	$Tb(OTf)_{3}$ (0.4)	64		
17	$Dy(OTf)_{3}$ (0.4)	48		
18	$Ho(OTf)_3$ (0.4)	80		
19	$Er(OTf)_{3}(0.4)$	44		
20	$Tm(OTf)_3$ (0.4)	67		
21	$Lu(OTf)_{3}$ (0.4)	58		

<sup>a</sup> Performed with  $\text{RuCl}_2(\text{PPh}_{3})_3$  (0.2 mol%) and NaOH (2.4 mol%) in the presence of rare earth triflates in refluxing isopropanol for 2 h. For a typical procedure, see Ref. 8.

<sup>b</sup> Isolated yields.

lished,<sup>13</sup> as depicted in Scheme 2. Based on the findings that the combination use of  $RuCl_2(PPh_3)_3$  and  $Yb(OTf)_3$  in a molar ratio of 1:2 (to 4) is most effective for the acceleration of reaction (Table 1, entries 3–5) and the use of AgOTf in place of  $Yb(OTf)_3$  is also effective (to give 72% yield of the alcohol), the additive  $Yb(OTf)_3$  might be expected to play a role in facilitating the displacement of the chlorine on Ru atom by

Table 2.	The	hydrogen-	-transfer	reduction	of	aromatic	and	aliphatic	ketones	with	RuCl <sub>2</sub> (	PPh <sub>3</sub> ) <sub>3</sub> <sup>a</sup>
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$R^{12} \sim R^2$		R'^	$R^2$

Entry	R <sup>1</sup>	<b>R</b> <sup>2</sup>	Time (h)	Yield (%) <sup>b</sup>		
				Yb(OTf) <sub>3</sub>	Without Yb(OTf) <sub>3</sub>	
1	Ph	Me	1	74	42	
2	Ph	Et	1	80	35	
3	Ph	<i>i</i> -Pr	1	33	14	
4	2-MeOC <sub>6</sub> H <sub>4</sub>	Me	0.5	85	57	
5	$4-\text{MeOC}_6\text{H}_4$	Me	2	56	30	
6	$4-ClC_6H_4$	Me	1	85	46	
7	$CH_3(CH_2)_5$	Me	0.5	75	22	
8	-(CH <sub>2</sub> ) <sub>5</sub> -		0.5	90	90	

<sup>a</sup> Performed with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.2 mol%) and NaOH (2.4 mol%) in the presence of Yb(OTf)<sub>3</sub> (0.4 mol%) in refluxing isopropanol. For a typical procedure, see Ref. 8.

<sup>b</sup> Isolated yields.

**Table 3.** The hydrogen-transfer reduction of propiophenone with  $RhCl(PPh_3)_3^a$ 



<sup>a</sup> Performed with RhCl(PPh<sub>3</sub>)<sub>3</sub> and *t*-BuOK in the presence of Yb(OTf)<sub>3</sub> in isopropanol for 2 h. For a typical procedure, see Ref. 12.

<sup>b</sup> Isolated yields.



## Scheme 2.

isopropanol to give Ru(*i*-PrO)<sub>2</sub>L<sub>3</sub> complexes, which would generate the active dihydride species, RuH<sub>2</sub>L<sub>3</sub>, by β-elimination. Thus, an equimolar mixture of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and Yb(OTf)<sub>3</sub> is effective enough to accelerate the reaction, though to a moderate extent (Table 1, entry 2). The mechanistic role of Yb(OTf)<sub>3</sub> in accelerating the hydrogen-transfer reaction is not clear at present.<sup>14</sup>

In conclusion, the RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>- and RhCl(PPh<sub>3</sub>)<sub>3</sub>-catalyzed hydrogen-transfer reactions reinforced with Yb(OTf)<sub>3</sub> provide a highly efficient procedure for the reduction of ketones, in which the molar ratio of Ru (Rh) and Yb is critical. This simple and promising method is of practical use and is readily applicable to the bulk-scale reduction of ketones.

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