

# SYNLETT Spotlight 98

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## Shvo's Diruthenium Complex [( $\eta^5$ -C<sub>4</sub>Ph<sub>4</sub>COHOCC<sub>4</sub>Ph<sub>4</sub>- $\eta^5$ ) ( $\mu$ -H)(CO)<sub>4</sub>Ru<sub>2</sub>]

Compiled by R. Prabhakaran

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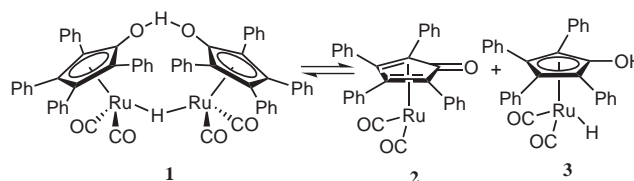
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### Introduction

After robust diruthenium complex **1** was reported by Shvo,<sup>1</sup> it found enormous utility in organic synthesis as a versatile catalyst, and it is now called Shvo complex. The main reason for its efficient catalytic activity is that it dissociates into **2** and **3** in the reaction mixture under thermal conditions. The 16-electron species **2** and 18-electron complex **3** play vital roles in the catalytic cycle.<sup>2</sup> Recently, a modified procedure for the synthesis of Shvo com-

plex was reported by Bäckvall and co-workers.<sup>3</sup> Shvo complex serves as an effective catalyst in many organic transformations, including the reduction of aldehydes and ketones to alcohols,<sup>4</sup> bimolecular disproportionation reaction of aldehydes to esters,<sup>5</sup> isomerization of allylic alcohols<sup>6</sup> and oxidation of alcohols.<sup>7</sup> In addition, Shvo complex as a racemization catalyst in dynamic kinetic resolution (DKR) is well precedented.<sup>8</sup>

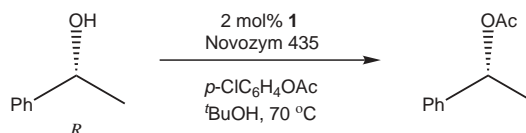


### Preparation

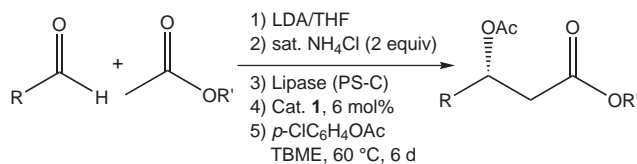
Shvo complex can be synthesized from Ru(CO)<sub>3</sub>( $\eta^4$ -Ph<sub>4</sub>C<sub>4</sub>CO), which is made from Ru<sub>3</sub>(CO)<sub>12</sub> and tetraphenylcyclopentadienone.<sup>3</sup>

### Abstracts

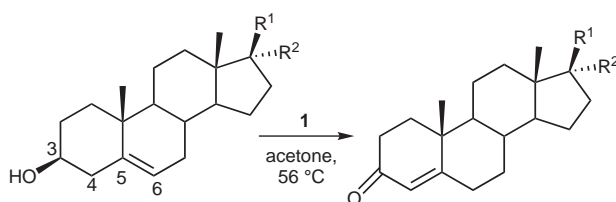
(A) Shvo complex catalyzed the in situ racemization of secondary alcohols, which then underwent enzyme-catalyzed DKR, in the preparation of enantiomerically pure acetates.<sup>3</sup> The same catalyst has also been used for the racemization of amines and then applied to the synthesis of enantiomerically pure amines.<sup>9</sup>



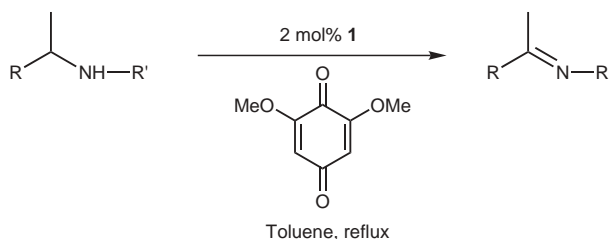
(B) The combination of enzyme-catalyzed DKR and an aldol reaction provided an access to  $\beta$ -hydroxy ester derivatives with high enantiomeric purity in a one-pot procedure using Shvo complex as catalyst for racemization.<sup>10</sup>



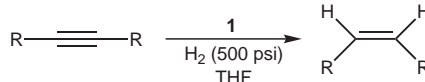
(C) Oxidation of 5-unsaturated  $3\beta$ -hydroxy steroids to the corresponding 4-en-3-one derivatives can be achieved by acetone at reflux in the presence of a Shvo catalyst. The reaction proceeds via a ruthenium-catalyzed dehydrogenation and subsequent hydrogen transfer to acetone with concomitant double bond migration.<sup>11</sup>



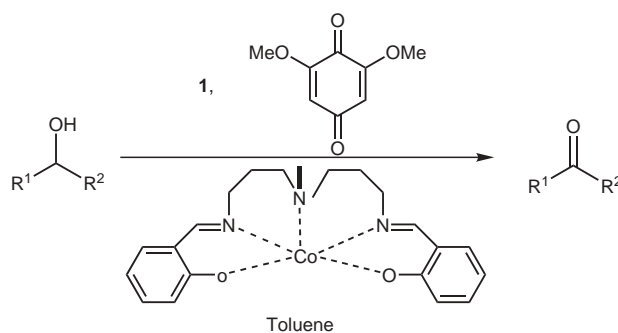
(D) Shvo complex is able to catalyze the transfer dehydrogenation of amines to imines under mild conditions using 2,6-dimethoxybenzoquinone as oxidant.<sup>12</sup>



(E) Complex **1** serves as a catalyst precursor for the hydrogenation of alkynes.<sup>13</sup>



(F) Efficient aerobic oxidation of alcohols was developed via biomimetic catalytic system. Complex **1** dehydrogenates the alcohol and the hydrogens abstracted are transferred to an electron-rich quinone. The hydroquinone thus formed is reoxidized by air with the aid of Co-Salen complex.<sup>2a</sup>



## References

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