

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 [(η^5 -C₄Ph₄COHOCC₄Ph₄- η^5) (μ -H)(CO)₄Ru₂]

Compiled by R. Prabhakaran

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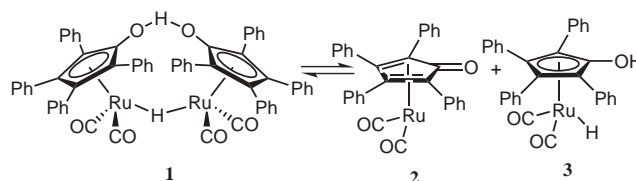
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Introduction

After robust diruthenium complex **1** was reported by Shvo,¹ 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.² Recently, a modified procedure for the synthesis of Shvo com-

plex was reported by Bäckvall and co-workers.³ Shvo complex serves as an effective catalyst in many organic transformations, including the reduction of aldehydes and ketones to alcohols,⁴ bimolecular disproportionation reaction of aldehydes to esters,⁵ isomerization of allylic alcohols⁶ and oxidation of alcohols.⁷ In addition, Shvo complex as a racemization catalyst in dynamic kinetic resolution (DKR) is well precedented.⁸

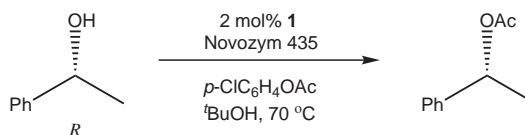


Preparation

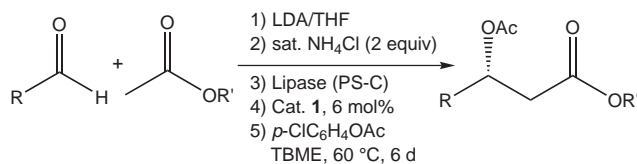
Shvo complex can be synthesized from Ru(CO)₃(η^4 -Ph₄C₄CO), which is made from Ru₃(CO)₁₂ and tetraphenylcyclopentadienone.³

Abstracts

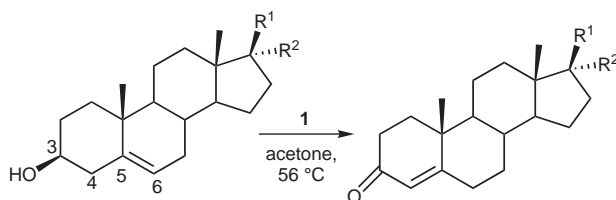
(A) Shvo complex catalyzed the in situ racemization of secondary alcohols, which then underwent enzyme-catalyzed DKR, in the preparation of enantiomerically pure acetates.³ The same catalyst has also been used for the racemization of amines and then applied to the synthesis of enantiomerically pure amines.⁹



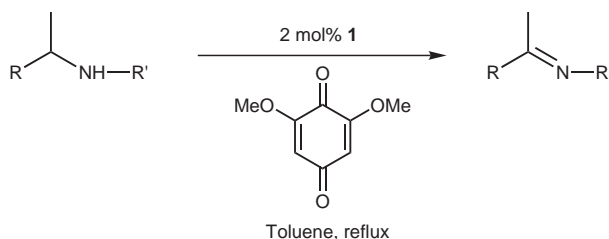
(B) The combination of enzyme-catalyzed DKR and an aldol reaction provided an access to β -hydroxy ester derivatives with high enantiomeric purity in a one-pot procedure using Shvo complex as catalyst for racemization.¹⁰



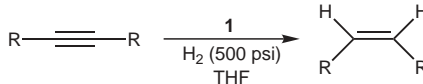
(C) Oxidation of 5-unsaturated 3β -hydroxy steroids to the corresponding 4-en-3-one derivatives can be achieved by acetone at reflux in the presence of a Shvo catalyst. The reaction proceeds via a ruthenium-catalyzed dehydrogenation and subsequent hydrogen transfer to acetone with concomitant double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



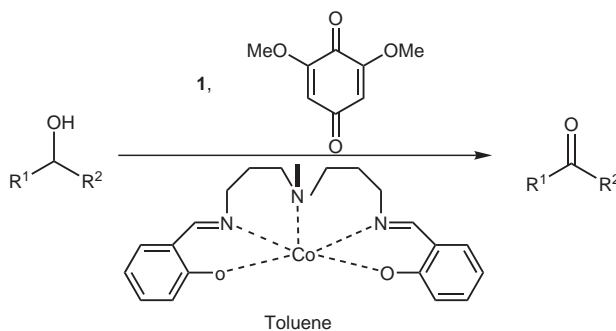
(D) Shvo complex is able to catalyze the transfer dehydrogenation of amines to imines under mild conditions using 2,6-dimethoxybenzoquinone as oxidant.¹²



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



(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.^{2a}



References

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