Shvo’s Diruthenium Complex

\[(\eta^5-C_4Ph_4COHOCC_4Ph_4-\eta^5)\]
\[(\mu-H)(CO)_4Ru_2]\]

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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 complex 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(η4-Ph4C4CO), which is made from Ru3(CO)12 and tetraphenylnaphthalene.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 \( \beta \)-hydroxy ester derivatives with high enantiomeric purity in a one-pot procedure using Shvo complex as catalyst for racemization.\(^{10}\)

\[
\begin{align*}
\text{R1} & \quad \text{R2} \\
\text{OAc} & \quad + \\
1) & \quad \text{LDA/THF} \\
2) & \quad \text{sat. NH}_4\text{Cl (2 equiv)} \\
3) & \quad \text{Lipase (PS-C)} \\
4) & \quad \text{Cat. 1, 6 mol\%} \\
5) & \quad \text{p-ClC}_6\text{H}_4\text{OAc} \\
\text{TBME, 60 °C, 6 d}
\end{align*}
\]

(C) Oxidation of 5-unsaturated \( \beta \)-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.\(^{11}\)

(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
