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Coordination Chemistry Reviews 249 (2005) 911–918
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Review

Shvo's diruthenium complex: a robust catalyst

R. Karvembu, R. Prabhakaran, K. Natarajan*

Department of Chemistry, Bharathiar University, Coimbatore 641046, India

Received 26 March 2004; accepted 29 September 2004
Available online 26 November 2004

Contents

Abstract

Shvo's diruthenium complex is an active catalyst in a considerable number of homogeneous reactions. Its catalytic activity is mainly due to the fact that it dissociates into two monomeric ruthenium species in solution under thermal conditions. We review the applications under three major headings i.e., oxidation, reduction and dynamic kinetic resolution.

Keywords: Diruthenium complex; Oxidation; Reduction; Racemization; Dynamic kinetic resolution

1. Introduction

Ruthenium complexes play a central role in many organic transformations as versatile catalyst due to its reversible and accessible oxidation states [1–3]. Recently, several groups including ours have been engaged in devel-

* Corresponding author. Tel.: +91 422 2422222; fax: +91 422 2422387.
E-mail address: k_natraj6@yahoo.com (K. Natarajan).

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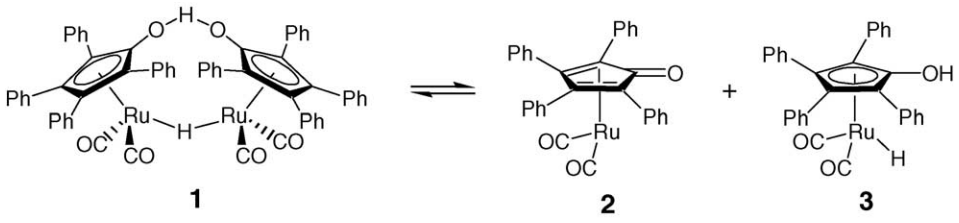
doi:10.1016/j.ccr.2004.09.025



Scheme 1.

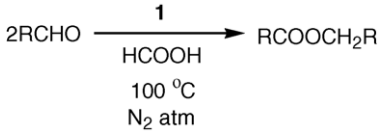
oping efficient ruthenium catalysts for different types of organic reactions [4–19]. Besides, researchers have been looking for a multipurpose catalyst, i.e., a single complex that catalyzes various industrially important reactions. It has been found that $[RuCl_2(PPh_3)_3]$, prepared by Stephenson and Wilkinson [20], is an excellent catalyst in a large number of reactions such as oxidation [2], reduction [21], oxidative cleavage of vic-diols [22], isomerization of allylic alcohols [23], reductive cyclization of nitroarenes with trialkylamines [24], racemization of alcohols [25], etc.

Shvo et al. have synthesized a robust diruthenium complex **1**, which finds enormous utility in organic synthesis as a versatile catalyst [26]. It is now called the Shvo complex. It is much superior to $[RuCl_2(PPh_3)_3]$ in terms of yields of products and compatibility under given reaction conditions [25]. Most notably, the Shvo complex does not require a base for isomerization of allylic alcohols [27] and Oppenauer-type oxidation of 3β-hydroxy steroids [28] in contrast to $[RuCl_2(PPh_3)_3]$. The main reason for its efficient catalytic activity is that it dissociates into **2** and **3** in the reaction mixture under thermal conditions (Scheme 1). These 16-electron species **2** and 18-electron complex **3** play a vital role in catalytic cycle [29,30]. Recently, a modified procedure for the synthesis of the Shvo complex has been reported by Bäckvall and co-workers [25]. In this review, we portray the recent developments on the Shvo complex catalyzed organic reactions.

2. Oxidation reactions

2.1. Disproportionation of aldehydes to esters

The Shvo complex catalyze the homogeneous bimolecular disproportionation reaction of aldehydes to give esters in the presence of small amounts of formic acid [31] (Scheme 2).



Scheme 2.

Increasing the electron density on the metal and the ligand was found to accelerate the reaction. Kinetic studies reveal that the rate = k[catalyst]$^{1/2}$[aldehyde].

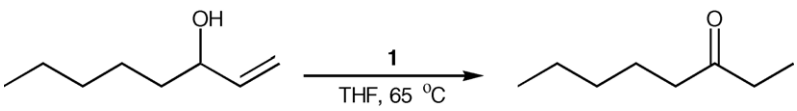
2.2. Isomerization of allylic alcohols to saturated ketones

The Shvo catalyst is found to effect the isomerization of allylic alcohols to ketones without any base [27] (Scheme 3). In the case of $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(p\text{-cymene})_2]$ as catalysts, K_2CO_3 is essential to increase the rate of reaction. It was believed that the bimetallic complex (Shvo catalyst) is in equilibrium with two monometallic species (Scheme 1) and one of these has negatively charged oxygen. This alkoxide can act as a base, thus promoting the formation of ruthenium alkoxide.

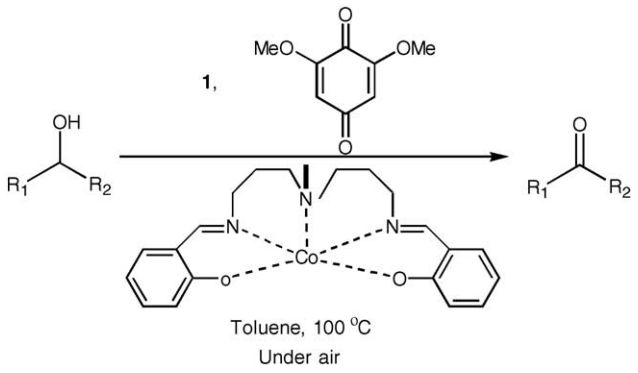
2.3. Aerobic oxidation of alcohols

Combination of the Shvo catalyst, 2,6-dimethoxy quinone and Co-macrocycle affords an efficient catalytic system for the aerobic oxidation of various secondary alcohols [29, 32] (Scheme 4).

The principle for this aerobic oxidation is reminiscent of biological oxidation of alcohols via the respiratory chain and involves selective electron/proton transfer. The Shvo complex dehydrogenates the alcohol and the hydrogens abstracted are transferred to an electron rich quinone. The hydroquinone thus formed is reoxidised by the air with the aid of Co–salen complex (Scheme 5). This triple catalytic system works at an oxygen concentration that is low



Scheme 3.



Scheme 4.

enough to allow the reaction to be performed cheaply and safely.

2.4. Oppenauer-type oxidation of 3β-hydroxy steroids

The Shvo complex catalyze the oxidation of 5-unsaturated 3β-hydroxy steroids to the corresponding 4-en-3-one derivatives in acetone at reflux [28] (Scheme 6). The reaction proceeds via a ruthenium catalyzed dehydrogenation and subsequent hydrogen transfer to acetone with concomitant double bond migration.

2.5. Oxidation of alcohols with chloroform

The Shvo complex has been found to be a quite effective catalyst for oxidation of secondary alcohols and primary diols to give ketones [33] and lactones in chloroform with sodium carbonate. In this reaction, sodium carbonate acts as hydrogen chloride acceptor (Scheme 7).

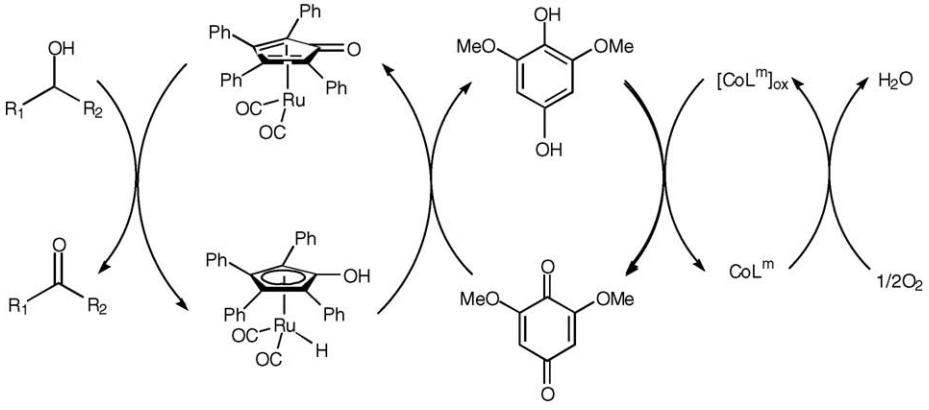
2.6. Dehydrogenation of aromatic amines to imines

Dehydrogenation of aromatic amines to imines catalyzed by **1** in presence of 2,6-dimethoxybenzoquinone or 2,6-dimethoxybenzoquinone/MnO_2 as oxidant has been reported by Bäckvall and co-workers [34] (Scheme 8). Detailed mechanistic studies of hydrogen transfer reactions have also been reported [35–37].

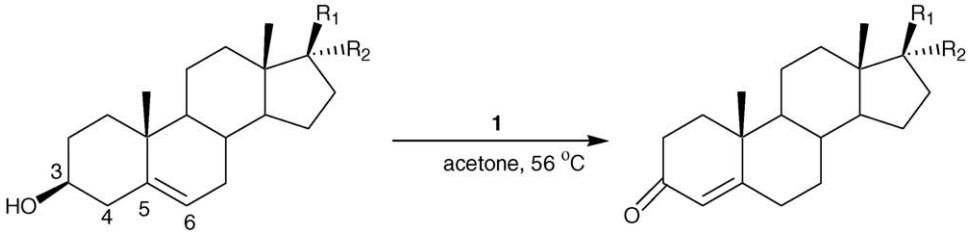
3. Reduction reactions

3.1. Hydrogenation of alkynes

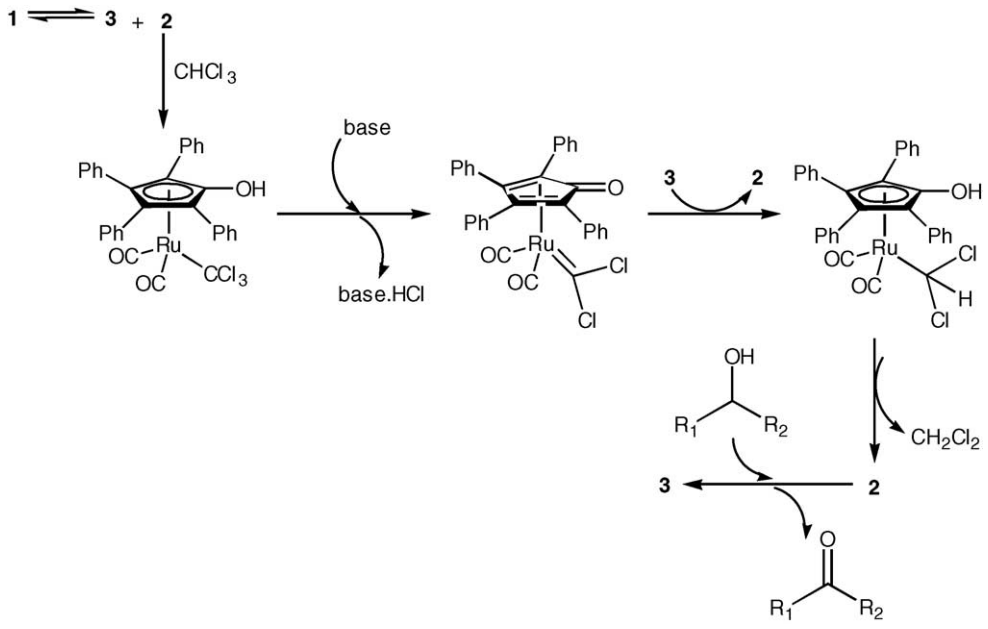
The Shvo complex serves as a catalyst precursor for the hydrogenation of alkynes [38] (Scheme 9). A catalytic cycle has been proposed on the basis of experimental observations (Scheme 10). The sequence $2 \rightarrow 4 \rightarrow 5$ represents an irreversible side reaction path that quenches the hydrogenation cycle. Substantial hydrogenation of alkynes still takes place due to the competitive transformation of **2** to **3** by oxidative addition of H_2.



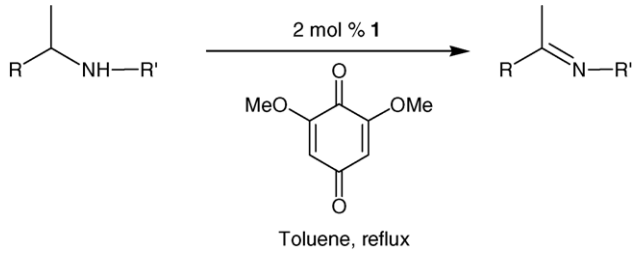
Scheme 5.



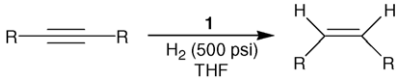
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

3.2. Reduction of ketones with formic acid

Catalytic activities of the Shvo complex were examined in the metal-catalyzed reduction of aldehydes and ketones to alcohols using formic acid as hydrogen source [39]. Use of excess formic acid results in the acceleration of reaction rate and the corresponding formate esters were isolated as sole products. Though alkenes are not reactive, double bonds conjugated to a carbonyl group are selectively reduced under the reaction conditions.

Recently, several catalytic systems have been developed for transfer hydrogenation of ketones [40–44]. The yields and TON are comparable with the Shvo complex. However, these catalysts are effective only in the presence of base or additives whereas the Shvo complex does not require any additives [28]. This makes the Shvo complex a valuable catalyst.

4. Racemization reaction coupled with dynamic kinetic resolution (DKR)

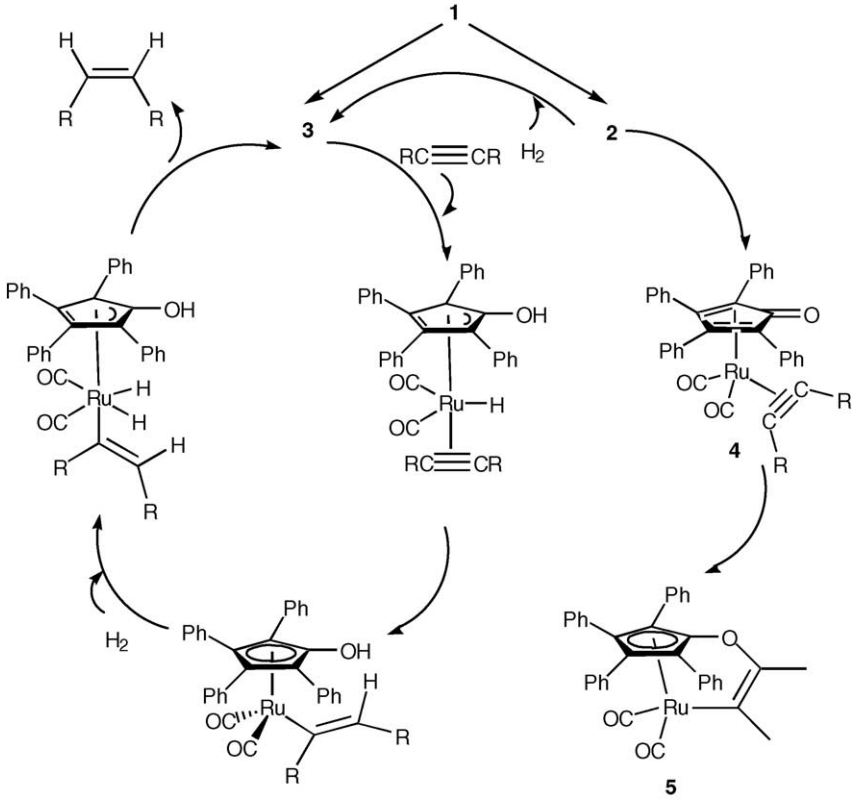
The use of metal-based racemization catalysts with enzymes as the resolution catalysts for the DKR of alcohols, amines and esters is one of the hot research topics in the area of asymmetric synthesis [45–49]. An excellent observation in this field is that the Shvo complex acts as efficient catalyst for the racemization of secondary alcohols and amines. Besides, the Shvo complex is compatible under DKR conditions, whereas complexes like $[RuCl_2(PPh_3)_3]$ gave poor results when combined with enzyme and acyl donor [50].

Park and co-workers have recently found that aminocyclopentadienyl ruthenium chloride catalyzes the racemization of alcohols at room temperature and is also compatible under DKR conditions [51]. The yields and % ee of chiral products have been found to be higher than those obtained with the Shvo complex as catalyst. But all other racemization catalysts [45–49] reported so far are less effective when compared to the Shvo complex.

4.1. DKR of secondary alcohols

The Shvo complex is able to catalyze the complete recemization of (+)-(*R*)-1-phenylethanol without any base (Scheme 11). The ruthenium-catalyzed racemization was then combined with an enzyme-catalyzed transesterification using Novozym 435 [25].

Among the various acyl donors screened, 4-chlorophenylacetate was found to be effective in the ruthenium- and enzyme-catalyzed DKR of racemic 1-phenylethanol using enzyme Novozym 435 and the Shvo catalyst (Scheme 12). Studies of the reaction in different sol-



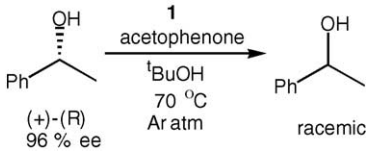
Scheme 10.

vents showed that non-polar solvents gave the better results. With this process, a variety of racemic secondary alcohols were transformed to the corresponding enantiomerically pure acetates. In most cases, the reaction proceeds with >99% ee and in good yields.

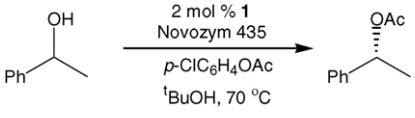
4.2. Conversion of ketones or enol acetates to chiral acetates

Park and co-workers developed a highly efficient one-pot process for asymmetric transformations of ketones or enolacetates to chiral acetates. A lipase and the Shvo complex catalyze the asymmetric transformations proceeding through at least four different reactions concerted in one reaction vessel. 2,6-Dimethylheptan-4-ol was chosen as a suitable hydrogen donor and 4-chlorophenylacetate was used as an acyl donor for the conversion of ketones [52] (Scheme 13).

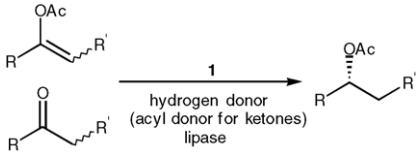
The practical applications of the processes were hindered by separation problems caused by 2,6-dimethylheptan-4-one and unreacted 4-chlorophenylacetate in the product mixtures.



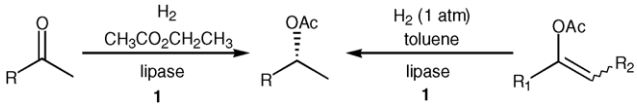
Scheme 11.



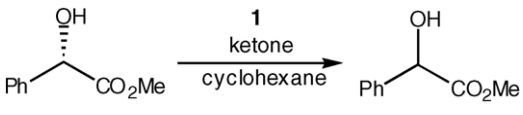
Scheme 12.



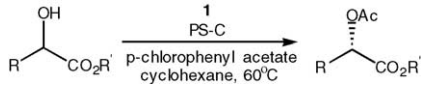
Scheme 13.



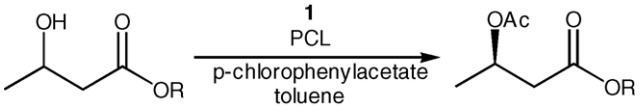
Scheme 14.



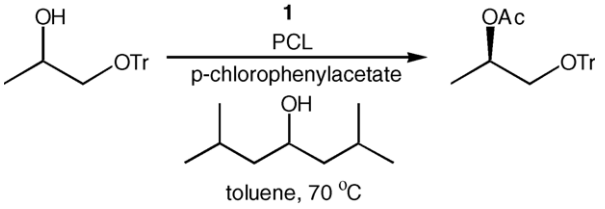
Scheme 15.



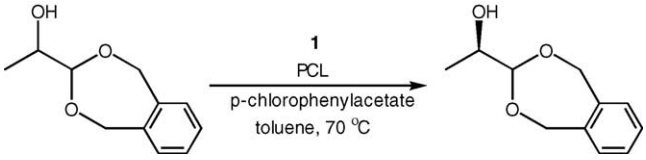
Scheme 16.



Scheme 17.



Scheme 18.

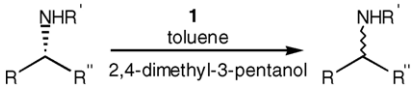


Scheme 19.

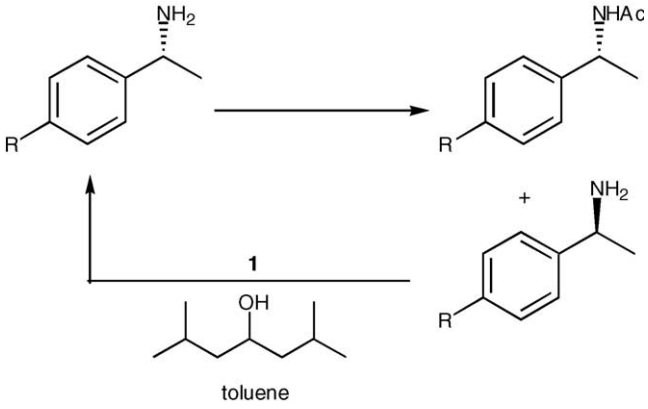
Hence, the same group solved the separation problems by using molecular hydrogen or formic acid as a hydrogen donor and ethylacetate as an acyl donor [53]. Ketones were transformed to chiral acetates using a lipase and the Shvo complex under 1 atm of hydrogen gas in ethylacetate. Molecular hydrogen was also effective for the transformation of enol acetates to chiral acetates without any acyl donors with the same catalytic system (Scheme 14).

4.3. DKR of α-hydroxy acid esters

The Shvo complex has been selected as a suitable catalyst for the racemization of (*S*)-methylmandelate after surveying various ruthenium catalysts [54]. The use of cyclohexane as the solvent and employing 20 mol% of methyl-2-oxo-2-phenylacetate as ketone led to substantial racemization (Scheme 15).



Scheme 21.



Scheme 22.

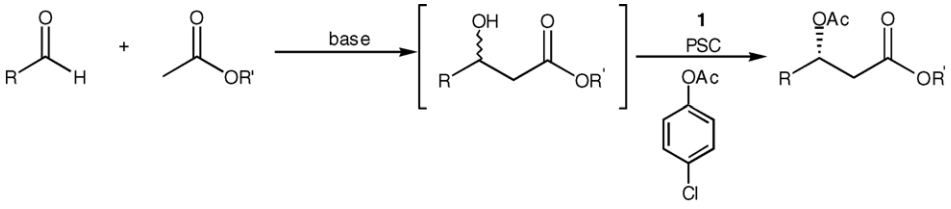
In some cases, the effect of ketone was insignificant and therefore, it was omitted. The racemization was then combined with enzymatic transformation (Scheme 16).

4.4. DKR of hydroxy acids, diols and hydroxy aldehydes protected with a bulky group

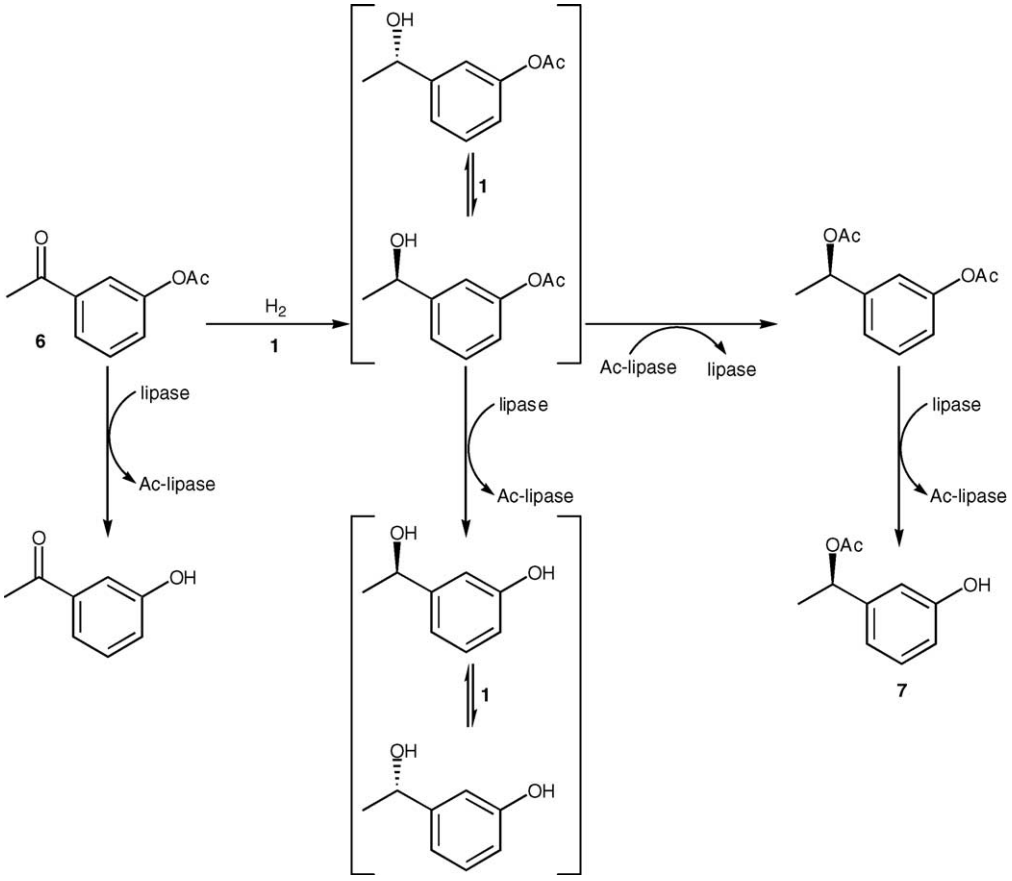
The DKRs of the protected β-hydroxybutyrates in which the carboxy functionality can be protected with four different bulky groups including benzyl, (*p*-methoxyphenyl)methyl, biphenylmethyl and *tert*-butyl have been carried out (Scheme 17) [55]. The enantiomeric excess was the highest in the case of *tert*-butyl protecting group. Hence, *tert*-butyl group is the best protecting group as steric auxillary for the efficient DKR of β-hydroxybutyrate.

Monoprotected 1,2-diols, in which the primary alcohols were protected with the trityl group, were subjected to DKR [55] (Scheme 18). The alcohol additive (2,6-dimethyl-4-heptanol) acts as a reductant to reduce the formation of ketone. The yield and ee were good in all the cases.

The DKR of protected hydroxy aldehyde in which 1,2-benzenedimethanol was employed as protecting group, was



Scheme 20.



Scheme 23.

performed using **1** and PCL [55]. The reaction carried out for 3 days provided 95% yield and 98% ee (Scheme 19).

4.5. Enantioselective synthesis of β-hydroxy acid derivatives

The DKR and aldol reaction have been combined to get enantiomerically enriched (99% ee) β-hydroxy ester derivatives in a one-pot procedure [56] (Scheme 20).

4.6. Racemization of amines

The amines were racemized using the Shvo complex as catalyst and 2,4-dimethyl-3-pentanol as hydrogen donor (Scheme 21) [57]. The amine racemization has also been combined with an enzymatic kinetic resolution as depicted in Scheme 22.

4.7. Asymmetric transformations of acyloxyphenol ketones

A lipase/Shvo complex catalyzed multipathway process proposed for the asymmetric conversion of 3'-acetoxyacetophenone (**6**) to (*R*)-1-(3-hydroxyphenyl) ethylacetate (**7**) is described in Scheme 23. The scope of the catalyst is extended to various similar substrates. The chiral products obtained are useful as intermediates for the synthesis of chiral drugs such as rivastigmine and its analogues for the treatment of Alzheimer's disease [58].

5. Conclusions

For the past few years, an investigation on the role of organometallic compounds in organic synthesis is gaining momentum due to its direct application in various industries. In this connection, the Shvo complex is found to be very effective for oxidation, reduction and racemization reactions. The Shvo complex and Novozym 435 catalyzed dynamic kinetic resolution will be of considerable use in preparing enantiomerically enriched secondary alcohols. Besides, this compound does not require base in transfer hydrogenation reactions and isomerization of allylic alcohols. The rapidity with which publications in this system appear is an indication that this diruthenium organometallic compound will definitely contribute to large number of catalysis investigations in the future.

References

[1] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97.
[2] S.-I. Murahashi, H. Takaya, Acc. Chem. Res. 33 (2000) 225.
[3] A. Dijksman, A. Marino-Gonzalez, A.M.I. Payeras, I.W.C.E. Arends, R.A. Sheldon, J. Am. Chem. Soc. 123 (2001) 6826.
[4] R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 219.
[5] R. Karvembu, K. Natarajan, Polyhedron 21 (2002) 1721.
[6] R. Karvembu, S. Hemalatha, R. Prabhakaran, K. Natarajan, Inorg. Chem. Commun. 6 (2003) 486.
[7] R. Karvembu, C. Jayabalakrishnan, K. Natarajan, Transit. Met. Chem. 27 (2002) 574.
[8] R. Karvembu, C. Jayabalakrishnan, N. Dharmaraj, S.V. Renukadevi, K. Natarajan, Transit. Met. Chem. 27 (2002) 631.
[9] E. Choi, C. Lee, Y. Na, S. Chang, Org. Lett. 4 (2002) 2369.
[10] K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. 36 (1997) 285.
[11] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, R. Noyori, Angew. Chem. Int. Ed. 37 (1998) 1703.
[12] S. Dutta, P.K. Bhattacharya, J. Mol. Cat. A: Chem. 188 (2002) 45.
[13] K. Joju Davis, D. Sinou, J. Mol. Cat. A: Chem. 177 (2002) 173.
[14] R.A. Sheldon, I.W.C.E. Arends, A. Dijksman, Catal. Today 57 (2000) 157.
[15] A. Dijksman, J.M. Elzinga, Y.X. Li, I.W.C.E. Arends, R.A. Sheldon, Tetrahedron: Asymmetry 13 (2002) 879.
[16] N.E. Leadbeater, J. Org. Chem. 66 (2001) 2168.
[17] W.H. Fung, W.-Y. Yu, C.-M. Che, J. Org. Chem. 63 (1998) 2873.
[18] D. Chatterjee, A. Mitra, S. Mukherjee, J. Mol. Cat. A: Chem. 165 (2001) 295.
[19] M.-J. Kim, Y.I. Chung, Y.K. Choi, H.K. Lee, D. Kim, J. Park, J. Am. Chem. Soc. 125 (2003) 11494.
[20] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.
[21] T. Ohkuma, H. Ooka, M. Yamakawa, T. Ikariya, R. Noyori, J. Org. Chem. 61 (1996) 4872.
[22] E. Takezawa, S. Sakaguchi, Y. Ishii, Org. Lett. 1 (1999) 713.
[23] R. Uma, M.K. Davies, C. Crévisy, R. Grée, Eur. J. Org. Chem. (2001) 3141.
[24] C.S. Cho, T.K. Kim, B.T. Kim, T.J. Kim, S.C. Shim, J. Organomet. Chem. 650 (2002) 65.
[25] B. Persson, A.L.E. Larsson, M.L. Ray, J.-E. Bäckvall, J. Am. Chem. Soc. 121 (1999) 1645.
[26] Y. Shvo, D. Czarkie, Y. Rahamim, J. Am. Chem. Soc. 108 (1986) 7400.
[27] J.-E. Bäckvall, U. Andreasson, Tetrahedron Lett. 34 (1993) 5459.
[28] M.L.S. Almeida, P. Kočovsky, J.-E. Bäckvall, J. Org. Chem. 61 (1996) 6587.
[29] G. Csjernvik, A.H. Éu, L. Fadini, B. Pugin, J.-E. Bäckvall, J. Org. Chem. 67 (2002) 1657.
[30] C.P. Casey, S.W. Singer, D.R. Powell, R.K. Hayashi, M. Kavana, J. Am. Chem. Soc. 123 (2001) 1090.
[31] N. Menashe, Y. Shvo, Organometallics 10 (1991) 3885.
[32] G.-Z. Wang, U. Andreasson, J.-E. Bäckvall, Chem. Commun. (1994) 1037.
[33] H.M. Jung, J.H. Choi, S.O. Lee, Y.H. Kim, J.H. Park, J. Park, Organometallics 21 (2002) 5674.
[34] A.H. Éll, J.S.M. Samec, C. Brasse, J.-E. Bäckvall, Chem. Commun. (2002) 1144.
[35] Y.R. Santosh Laxmi, J.-E. Bäckvall, Chem. Commun. (2000) 611.
[36] A.H. Éll, J.B. Johnson, J.-E. Bäckvall, Chem. Commun. (2003) 1652.
[37] J.B. Johnson, J.-E. Bäckvall, J. Org. Chem. 68 (2003) 7681.
[38] Y. Shvo, I. Goldberg, D. Czerkie, D. Reshef, Z. Sterin, Organometallics 16 (1997) 133.
[39] N. Menashe, E. Salant, Y. Shvo, J. Organomet. Chem. 514 (1996) 97.
[40] D.G.I. Petra, P.C.J. Kamer, P. van Leeuwen, K. Goubitz, A.M. Van Loon, J.G. de Vries, H.E. Schoemaker, Eur. J. Inorg. Chem. (1999) 2335.
[41] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc. Dalton Trans. (2001) 2989.
[42] K. Mashima, T. Abe, K. Tani, Chem. Lett. (1998) 1199.
[43] M. Ito, M. Hirakawa, K. Murata, T. Ikariya, Organometallics 20 (2001) 379.
[44] T. Ohkuma, M. Koizumi, M. Yoshida, R. Noyori, Org. Lett. 2 (2000) 1749.
[45] M.-J. Kim, Y. Ahn, J. Park, Curr. Opin. Biotechnol. 13 (2002) 578.
[46] F.F. Huerta, A.B.E. Minidis, J.-E. Bäckvall, Chem. Soc. Rev. 30 (2001) 321.
[47] O. Pàmies, J.-E. Bäckvall, Chem. Rev. 103 (2003) 3247.
[48] H. Pellissier, Tetrahedron 59 (2003) 8285.
[49] M.-J. Kim, Y.I. Chung, Y.K. Choi, H.K. Lee, D. Kim, J. Park, J. Am. Chem. Soc. 125 (2003) 11494.
[50] A.L. Larrson, B.A. Persson, J.-E. Bäckvall, Angew. Chem. Int. Ed. 36 (1997) 1211.
[51] J.H. Choi, Y.H. Kim, S.H. Nam, S.T. Shin, M.-J. Kim, J. Park, Angew. Chem. Int. Ed. 41 (2002) 2373.
[52] H.M. Jung, J.H. Koh, M.-J. Kim, J. Park, Org. Lett. 2 (2000) 409.
[53] H.M. Jung, J.H. Koh, M.-J. Kim, J. Park, Org. Lett. 2 (2000) 2487.
[54] F.F. Huerta, Y.R. Santosh Laxmi, J.-E. Bäckvall, Org. Lett. 2 (2000) 1037.
[55] M.-J. Kim, Y.K. Choi, M.Y. Choi, M.J. Kim, J. Park, J. Org. Chem. 66 (2001) 4736.
[56] F.F. Huerta, J.-E. Bäckvall, Org. Lett. 3 (2001) 1209.
[57] O. Pàmies, A.H. Éll, S.M. Samec, N. Hermanns, J.-E. Bäckvall, Tetrahedron Lett. 43 (2002) 4699.
[58] M.-J. Kim, M.Y. Choi, M.Y. Han, Y.K. Choi, J.K. Lee, J. Park, J. Org. Chem. 67 (2002) 9481.