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Catalytic redox isomerization of allylic alcohols with rhodium and iridium complexes with ferrocene phosphine-thioether ligands

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ABSTRACT

Complexes [M(P,SR)(diene)X] where (P,SR) = CpFe[1,2-C_5H_3(PPh$_2$)(CH$_2$SR)] (M = Ir, R = tBu or Bn diene = cod, X = Cl; M = Rh, diene = cod or nbd; X = BF$_4$ or Cl) were used as precatalysts for the redox isomerization of various allylic alcohols (7a–e) to the corresponding saturated ketones (8a–e) and or hydrogenation to the saturated alcohol (9a–e). In optimization studies using 1-phenyl-2-propen-1-ol (7a) in THF and in iPrOH/MeONa, the only observed product was the saturated alcohol 1-phenyl-1-propanol (9a) when working under a 30 bar H$_2$ pressure, but activation for only 1 min under H$_2$ pressure and then continuation under 1 bar of H$_2$ or Ar led to increasing amounts of the allylic isomerization product propiophenone (8a). Continued reaction under H$_2$ converted (8a) into (9a). The Rh precatalysts were more active than the Ir analogues. For the rhodium precatalysts (3) and (4), the redox isomerization reaction could be carried out after precatalyst activation in iPrOH/MeONa under Ar at 82 °C (without H$_2$) with complete conversion in 1 h (1% catalyst loading). However, longer reaction times resulted in slow transfer hydrogenation of (8a) leading to (9a) with low enantiomeric excess. Extension of the H$_2$-free activation of the Rh precatalysts in iPrOH to other allylic alcohol substrates (7b–d) yielded the corresponding ketones with good to excellent yields and excellent chemoselectivities under appropriate conditions.

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1. Introduction

The isomerization of primary and secondary allylic alcohols into the corresponding aldehydes and ketones is of a great interest, especially because it is an atom economical reaction and provides valuable synthetic intermediates [1–7]. Great effort has been devoted to the development of this reaction leading to significant achievements. Efficient asymmetric catalytic systems have been developed [8–22] as well as catalytic systems in green solvents [23–37] such as water or supported versions [38–40]. An additional interest of this reaction is the possibility to couple it with other transformations by taking advantage of the high reactivity of the enolate- intermediates with various electrophiles

[41]. Thus, tandem reactions were used for the preparation of α-halogenoketones [42–44], β-hydroxy and β-amino ketones [45–48], cyclopentenones [49], etc [18,21]. Allylic isomerization has also been coupled with hydrogenation or transfer hydrogenation to yield saturated alcohols [17,20,31,54]. Although various metals such as iron, copper, nickel or palladium [46,55] have been used, most of the catalysts used so far are based on ruthenium [56–65], rhodium and iridium [66–70], mainly with phosphorus and nitrogen-donor ligands [1–6].

In this article, we wish to present our results on the first use of chiral P,S ligands [71–75] in the redox allylic isomerization reaction. Our group has contributed to the development of chiral ligands based on P and S donor atoms with the synthesis of the 1,2-substituted ferrocenes (P,SR) shown in Fig. 1 [76]. These ligands can be efficiently obtained in enantiomerically pure form or as a racemic mixture [76]. The use of these ligands in complexes of different metals has led to a number of catalytic applications in asymmetric allylic substitution [77,78], asymmetric methoxycarbonylation of alkenes [79] and hydrogenation of alkynes, alkenes,
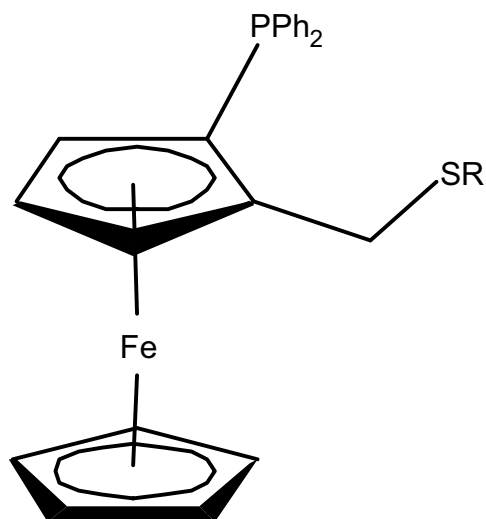
Fig. 1. Structure of P,SR ligands used in this study.

imines and ketones [80–84]. Here we report the application of the rhodium and iridium complexes [M(P,SR)(diene)X] (M = Ir, Rh; diene = cyclooctadiene, norbornadiene; X = BF$_4$, Cl, see Fig. 2) [80,81,86] in the isomerization of allylic alcohols.

2. Experimental

2.1. General considerations

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were carefully dried by conventional methods and distilled under argon before use. The iridium and rhodium complexes [M(P,SR)(diene)X] (M = Ir, Rh; R = tBu, Bz; diene = NBD, COD; X = BF$_4^-$, Cl) were prepared according to a published procedure from (R/S)-2-diphenylphosphanyl-(R-thiomethyl)ferrocene ligands (R = tBu, Bz) and [Ir(COD)Cl]$_2$ [80,81], [Rh(COD)Cl]$_2$, [Rh(NBD)Cl]$_2$ or [Rh(COD)$_2$]BF$_4$ [86]. Optical purities and the yields for the hydrogenation experiments were determined by NMR spectroscopy and GC: Supelco BETADEX^{TM} 225 (reactions of **6a**, isotherm at 105 °C), Supelco SPB-20 (reactions of **6e**, 30 °C for 7 min then heating 15 °C/min up to new isotherm at 120 °C), NMR yield determination (reactions of **6b–d**).

2.2. General procedure for the 1-phenyl-2-propene-1-ol allylic isomerization in THF

A solution containing 6.4×10^{-3} mmol of precatalyst and 0.13 mmol of substrate (20 equiv.) in 2 mL of THF was transferred into a 5 mL glass vial which was then placed under argon into a stainless steel autoclave equipped with a magnetic stirring bar. The reaction vessel was pressurized with H$_2$ to 30 bar and stirred for the

desired time at room temperature. Then pressure was released and the reaction vessel was stirred for the desired time at controlled temperature under a dihydrogen atmosphere at 1 bar. Alternatively, after venting the H$_2$ pressure used for the catalyst activation, the residual H$_2$ was purged with argon by continuous flushing before continuing the reaction. The pure products were obtained by chromatography of the reaction mixture on silica gel using dichloromethane as eluent and then analyzed by NMR spectrosopy and chiral GC for the determination of the yields and enantiomeric excesses.

2.3. General procedure for the 1-phenyl-2-propene-1-ol allylic isomerization in iPrOH

2.3.1. Precatalyst activation by H$_2$

A solution containing 6.4×10^{-3} mmol of precatalyst, 3.2×10^{-2} mmol of CH$_3$ONa (5 equiv.) and 0.64 mmol of substrate (100 equiv.) in 2 mL of isopropanol was transferred into a 5 mL glass vial which was then placed under argon into a stainless steel autoclave equipped with a magnetic stirring bar. The reaction vessel was pressurized with H$_2$ to 30 bar and stirred for the desired time at controlled temperature. The reaction was stopped by venting the H$_2$ atmosphere. The pure products were obtained by chromatography of the reaction mixture on silica gel using dichloromethane as eluent and analyzed by NMR spectroscopy and chiral GC for the determination of the yields and enantiomeric excesses.

2.3.2. Precatalyst activation by iPrOH

A solution containing 6.4×10^{-3} mmol of precatalyst, $3.2 \cdot 10^{-2}$ mmol of CH$_3$ONa (5 equiv.) and 0.64 mmol of substrate (100 equiv.) in 2 mL of isopropanol was prepared in a Schlenk tube under an argon atmosphere and stirred for the desired time at the reflux temperature. The pure products were obtained by chromatography of the reaction mixture on silica gel using dichloromethane as eluent and analyzed by NMR spectroscopy and chiral GC for the determination of the yields and enantiomeric excesses.

3. Results and discussion

3.1. Catalytic studies carried out in THF

The substrate chosen for our initial studies was racemic 1-phenyl-2-propene-1-ol (**7a**). We first attempted the thermal activation of the (**1**)–(**6**) precatalysts to carry out the redox isomerization of allylic alcohol (**7a**), but no rearrangement was observed in refluxing THF overnight. This lack of reactivity may be related to the need to activate the precatalyst by diene ligand removal, as discussed previously [80,83,85]. We therefore decided to use a hydrogen source to reduce the diene ligand in order to open the metal coordination sphere [14,15,19]. When the reaction was
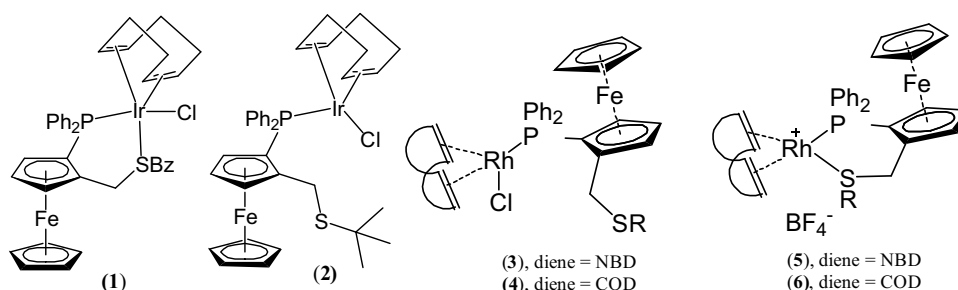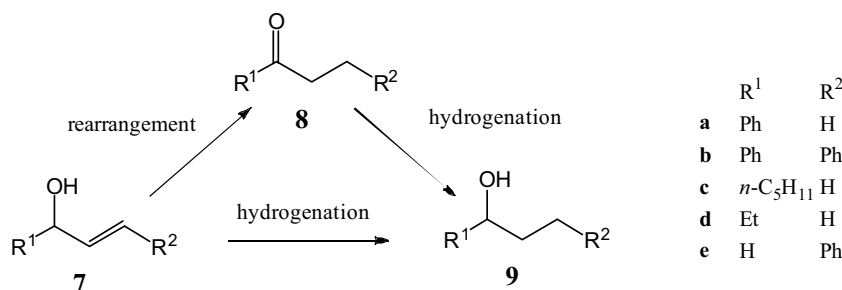

(**3**), diene = NBD
(**4**), diene = COD

(**5**), diene = NBD
(**6**), diene = COD

Fig. 2. Structure of the iridium and rhodium complexes used in this study.

Table 1
Hydrogenation of 1-phenyl-2-propene-1-ol (**7a**) in THF[a].

Entry	Catalyst	Conversion, %	Yield of (**8a**), %	Yield of (**9a**), %
1	(*R*)-(**2**)	55	0	55
2	(*R*)-(**3**)	100	0	100
3	(*R*)-(**5**)	100	0	100
4	(*R*)-(**4**)	75	0	75
5	(*R*)-(**2**)	100	0	100

[a] Reaction conditions: catalyst (6.4×10^{-3} mmol), 1-phenyl-2-propene-1-ol (**7a**) (0.13 mmol), T = 25 °C and P_{H2} = 30 bar, reaction time 1 h, solvent = THF (2 mL). The conversions were determined by GC.

Table 3
Results of the reaction of 1-phenyl-2-propene-1-ol (**7a**) in *i*PrOH[a].

Entry	Catalyst	Conversion, %	Yield of (**8a**), %	Yield of (**9a**), %
1	(*R*)-(**3**)	95	0	95
2	(*R*)-(**4**)	100	0	100
3	(*R*)-(**6**)	100	0	100

[a] Reaction conditions: catalyst (6.4×10^{-3} mmol), NaOMe (3.2×10^{-2} mmol), 1-phenyl-2-propene-1-ol (7a) (0.64 mmol), T = 25 °C and P_{H2} = 30 bar, reaction time 2 h, solvent = Pr^{i}OH (2 mL). The conversions were determined by GC.

carried out under pressure (30 bar of H$_2$) and at room temperature, allylic alcohol was converted to 1-phenyl-1-propanol (**9a**) (see Table 1). Interestingly, the rhodium catalysts were more efficient than the iridium one in this process and, as already documented in the literature for other hydrogenation reactions [87], the complexes bearing the nbd ligand are more active than the corresponding complexes bearing the cod ligand. Although this phenomenon may be interpreted as an effect of the diene nature on the catalytic activity, implying that the diene remains coordinated to the metal in the active species, it is also consistent with the well known faster removal of nbd by hydrogenation relative to cod and thus to a shorter induction time for the nbd system in catalysis [87]. Alcohol (**9a**) can result from the direct hydrogenation of the C=C bond of (**7a**) or from the hydrogenation of the C=O double bond of the product of redox isomerization, propiophenone (**8a**) (see Scheme 1) [88]. No ketone (**8a**) has been observed during these experiments, even after incomplete conversions showing that if any (**8a**) produced, it must be quickly hydrogenated to (**9a**) under these experimental conditions. In addition, 1-phenyl-1-propanol (**9a**) was found to be racemic indicating that either the ketone hydrogenation has very low enantioselectivity or that (**9a**) results from the direct C=C double bond hydrogenation of racemic (**7a**) without any chiral resolution, leaving the asymmetric carbon already present in (**7a**) untouched.

In order to avoid full substrate hydrogenation and to observe any possible isomerization to the ketone intermediate, the autoclave was pressurized with H$_2$ at 30 bar for only 1 min at room temperature, then the pressure was released and the reaction vessel was stirred for the desired time at reflux under a dihydrogen atmosphere of 1 bar. Under these conditions, the alcohol (**9a**) was still the main reaction product but the redox isomerization product (**8a**) was also observed (see Table 2, entries 1–3). By replacing dihydrogen by argon after the 1 min activation time, it was possible to obtain more ketone (Table 2, runs 4–9). The comparison of the results obtained after 2 h and 16 h suggests a fast C=C bond hydrogenation during the minute under dihydrogen and a slower allylic alcohol isomerization at longer reaction times under argon. Ketone (**8a**) could even be obtained with good selectivity (93%, Table 2, entry 9).

3.2. Catalytic studies carried out in isopropanol with dihydrogen activation

The reaction was also carried out in *i*PrOH instead of THF, in the presence of NaOMe (5 equiv relative to the catalyst) under 30 bar of hydrogen, using only the more active rhodium precatalysts. Excellent conversions were obtained like in THF (*cf.* Tables 3 and 1) but again only racemic 1-phenyl-1-propanol (**9a**) was obtained and no ketone isomerization product was observed.

Scheme 1. Possible pathways leading from (**7**) to (**8**) and (**9**).

	R^1	R^2
a	Ph	H
b	Ph	Ph
c	*n*-C$_5$H$_{11}$	H
d	Et	H
e	H	Ph

Table 2
Results of the isomerization/hydrogenation reaction of 1-phenyl-2-propene-1-ol (**7a**) in THF under various reaction conditions[a].

Entry	Catalyst	Conversion, %	Time, h	Yield of (**8a**), %	Yield of (**9a**), %	(**8a**)/(**9a**)
1	(*R*)-(**2**)	35[b]	2	2	33	6/94
2	(*R*)-(**4**)	92[b]	2	5.5	86.5	6/94
3	(*R*)-(**3**)	79[b]	2	4	75	5/95
4	(*S*)-(**1**)	9[c]	2	2.5	6.5	27/73
5	(*R*)-(**3**)	15[c]	2	2.5	12.5	17/83
6	(*R*)-(**6**)	30[c]	2	8	22	27/73
7	(*S*)-(**1**)	56[c]	16	44	12	78/22
8	(*R*)-(**3**)	52[c]	16	43	9	83/17
9	(*R*)-(**6**)	100[c]	16	93	7	93/7

[a] Reaction conditions: catalyst (6.4×10^{-3} mmol), 1-phenyl-2-propene-1-ol (**7a**) (0.13 mmol), solvent = THF (2 mL). The conversions were determined by GC.

[b] P_{H2} = 30 bar, 25 °C, 1 min, then P_{H2} = 1 bar, 70 °C.

[c] P_{H2} = 30 bar, 25 °C, 1 min, then Ar, 70 °C.

Table 4
Results of the reaction of allylic alcohols (**7**)[a] in *i*PrOH in the absence of H$_2$.

Entry	Catalyst	Substrate	t, h	Conversion, %	Yield of (**8**), %	Yield of (**9**), %	*ee*, %[b]
1	(*R*)-(**3**)	(**7a**)	1	100	100	0	–
2	(*R*)-(**4**)	(**7a**)	1	56	100	0	–
3	(*R*)-(**3**)	(**7a**)	6	100	66	34	17
4	(*R*)-(**4**)	(**7a**)	6	100	81	19	14
5	(*R/S*)-(**3**)	(**7b**)	16	88	88	0	–
6	(*R/S*)-(**4**)	(**7b**)	16	84	84	0	–
7	(*R/S*)-(**3**)	(**7c**)	16	100	100	0	–
8	(*R/S*)-(**4**)	(**7c**)	16	54	54	0	–
9[c]	(*R/S*)-(**3**)	(**7d**)	20.5	56	56	0	–
10[c]	(*R/S*)-(**3**)	(**7d**)	45	99	99	0	–
11	(*R/S*)-(**3**)	(**7e**)	16	4	4	0	–
12	(*R/S*)-(**3**)	(**7e**)	16	2	2	0	–

[a] Reaction condition: catalyst (6.4×10^{-3} mmol), NaOMe (3.2×10^{-2} mmol), allylic alcohol (0.64 mmol), T = 82 °C. The conversion and ee were determined by GC.
[b] The *ee* is reported with respect to the *R*- configuration.
[c] Reaction run at RT.

3.3. Catalytic studies carried out in isopropanol without dihydrogen activation

Finally, again in order to avoid the hydrogenation reaction and increase the selectivity in favor of the ketone, we checked whether the precatalyst could be activated by isopropanol itself under transfer hydrogenation reaction conditions, in the absence of dihydrogen. It is in fact known from the literature that [MCl(COD)L] compounds (M = Rh, Ir) react with β-H containing alkoxides at room temperature to yield COD-containing hydride products by ketone elimination and these species were shown to be active in transfer hydrogenation catalysis [89–93]. The reaction was carried out in *i*PrOH in the presence of a base (NaOMe) under an argon atmosphere at reflux. After 1 h (Table 4, entries 1–2), (**7a**) was selectively converted to the allylic isomerization product (**8a**) in good to excellent yields, proving the efficient activation of the precatalyst under these conditions. When the reaction time was increased to 6 h, however, significant amounts of alcohol (**9a**) resulting from the transfer hydrogenation of (**8a**) could also be observed (Table 4, entries 3–4). The transfer hydrogenation was slow and only slightly enantioselective (*ee* up to 17%). With this information in hands, we decided to check whether this dihydrogen-free procedure could be used for catalytic redox isomerization of other allylic alcohols with good selectivity in favor of the carbonyl compounds (see Table 4). Indeed, the expected ketones (**8**) were obtained in good to excellent yields and very high chemoselectivities for all investigated substrates (see Table 4), although the reaction was very slow for (**7e**) with both racemic rhodium complexes **3** and **4**. Only for substrate (**7a**) was a subsequent slow and poorly enantioselective transfer hydrogenation observed over 6 h (entries 3–4), whereas for substrates (**7b-d**) no evidence of transfer hydrogenation was observed over as many as 45 h.

The nature of the active catalyst remains for the moment unknown. As stated above, hydride-diene species should be formed upon interaction of methoxide or isopropoxide at room temperature, but how these species evolve upon reflux is a question that has not been addressed in detail in previous investigations. We are now carrying out studies in this direction and will report the corresponding results in due course.

4. Conclusions

In conclusion, the rhodium and iridium complexes of ferrocene phosphine-thioether ligands described in this paper are efficient catalysts for the hydrogenation of the allylic alcohol (**7a**) to racemic (**9a**), probably by direct hydrogenation of the C=C double bond. However, competitive alcohol isomerization to the saturated ketone (**8a**) occurs upon replacing dihydrogen with argon after a short activation step (1 min under 30 bar of dihydrogen). Perhaps the most interesting new discovery of our study is that the rhodium precatalysts can be activated in basic isopropanol without using any hydrogen, yielding the allylic isomerization products in good to excellent yields and very high chemoselectivities, comparing well with some other catalytic systems [1–6]. This procedure does not require pressure reactor and then could be more practical on laboratory scale. The catalytic reactions were carried out with rather good catalytic activities (only 1 mol% at temperature ranging from RT to 82 °C) [1–70]. Indeed, we have so far only tested a limited number of substrates. To compare more accurately the performance of the catalytic systems described in this article with other catalytic systems, an extension of this catalytic transformation to a broader substrate scope will be necessary. Further work is in progress in our laboratories.

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