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THE ENANTIOSELECTIVE ABILITY OF CHIRAL DIPHOSPHINE-RUTHENIUM COMPLEX IN ASYMMETRIC DEHYDROGENATION OF SECONDARY ALCOHOLS

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(-)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-buthane(diop) was found to be an efficient chiral ligand on using in Ru(II) catalyzed enantioselection of racemic alcohols with unsaturated additives. The dehydrogenation of PhEtCHOH by $Ru_2Cl_4((-)\text{-diop})_3$ with PhCH=CHCOPh at 165°C resulted in the formation of S-(-)-PhEtCHOH(11.0%e.e. at Conv.=56.8%).

The enantioselective dehydrogenation of racemic secondary alcohols(RR'CHOH) can be realized by means of Rh(I) or Ru(II) chiral phosphine complexes at the temperature over 120°C with or without unsaturated additives($R^1CH=CHR^2$),[1,2] and chiral Ru(II) complexes were found more active and selective than Rh(I) ones possessing the same chiral ligands.[2]

$$\left.\begin{array}{l}\text{R-RR'CHOH} \xrightarrow{\quad k_R \quad} \\ \text{S-RR'CHOH} \xrightarrow{\quad k_S \quad} \end{array}\right\rangle \xrightarrow[\text{R}^1\text{CH=CHR}^2]{\text{chiral Ru(II) complex}} \text{RR'C=O} + \text{R}^1\text{CH}_2\text{CH}_2\text{R}^2 \qquad (1)$$

However, the previously used $RuCl_2((+)\text{-nmdp})_3$(nmdp=neomenthyldiphenylphosphine) prepared in situ from $[\text{nmdp}]_0/[RuCl_2(PPh_3)_3]_0=6$ resulted in markedly low selection of racemic alcohols such as 1-phenylethanol, so that, more efficient chiral ligands are required for increasing the enantioselective ability of the Ru(II) complexes. In this regard, (+)- or (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)buthane(diop) has recently been found to be an effective chiral ligand when it was used in rhodium(I) catalyzed asymmetric hydrogenation of prochiral olefins.[3] In the present work, the efficiency of (-)-diop as a ligand of Ru(II) in Reaction(1) was examined in comparison with (-)-o-anisylmethylphenylphosphine(ampp), (+)-benzylmethylphenylphosphine(bmpp), and (+)-nmdp. When the dehydrogenation of 8.34×10^{-2}mol 1-phenylethanol by using 2mM $Ru_2Cl_4((-)\text{-diop})_3$ was carried out with 6.84×10^{-2}mol PhCH=CHCOMe at 165°C, the optical purity(O.P.) of the unreacted alcohol obtained by fractional distillation without any optically active contaminants increased as the conversion increased. The reaction follows a pseudo-first-order rate law (without racemization) up to Conv.≈65% with the constant k_R/k_S ratio which reflects the enantioselectivity (Table 1).

$$k_R=(\ln[R]_0/[R])/t=\ln(10^4/(100-\text{Conv.})(100-\text{O.P.}))/t \qquad (2a)$$

$$k_S=(\ln[S]_0/[S])/t=\ln(10^4/(100-\text{Conv.})(100+\text{O.P.}))/t \qquad \text{(t=reaction time)} \qquad (2b)$$

Among the isolated Ru(II) complexes made from $RuCl_2(PPh_3)_3$ and the chiral ligands using the phosphine exchange method[4], i.e., $Ru_2Cl_4((-)\text{-diop})_3$, $RuCl_2((-)\text{-ampp})_2(PPh_3)$, and $RuCl_2((+)\text{-bmpp})_3$ and the in situ prepared $RuCl_2((+)\text{-nmdp})_3$ complex, the

Table 1. Ru_2Cl_4((−)-diop)$_3$ Catalyzed PhMeCHOH Dehydrogenation with PhCH=CHCOMe(165°C)

Time (hr)	Conv. (%)	$-[\alpha]_D^{23}$ a) (deg.)	O.P. (%)	$10^6 k_R$ (s^{-1})	$10^6 k_S$ (s^{-1})	k_R/k_S	Products (mol%) b)		
							AP	PEE	Others
2	23.0	0.46	0.88	37.5	35.1	1.07	98.89	trace	——
3	32.7	0.65	1.24	37.8	35.5	1.06	83.56	15.51	0.93
4	41.0	0.92	1.75	37.9	35.4	1.07	87.01	12.33	0.66
6	54.9	1.28	2.44	38.0	35.7	1.06	88.00	11.38	0.62
8	65.3	1.49	2.84	37.8	35.8	1.06	88.37	11.17	0.46

a) $[\alpha]_D^{23}$ −52.5° (c 2.27, CH_2Cl_2).[5] b) AP=acetophenone; PEE=racemic- and meso-bis(1-phenylethyl) ether; Others=styrene and ethylbenzene.

Table 2. RR'CHOH Dehydrogenation(8.34×10^{-2}mol) by Chiral Ru(II) Complexes with or without $R^1CH=CHR^2$(6.84×10^{-2}mol) at 165°C a)

Complex	RR'CHOH b)	$R^1CH=CHR^2$	Time (hr)	Conv. (%)	$-[\alpha]_D$ c) (deg.)	O.P. (%)	k_R/k_S
Ru_2Cl_4((−)-diop)$_3$	I	PhCH=CHCOPh	27	57.5	3.26	6.21	1.16
	I	PhCH=CHCOMe	8	65.3	1.49	2.84	1.06
	I	$PhCH=CH_2$	70	40.0	0.83	1.59	1.06
	I	none	145	45.7	0.04	0.07	1.00_3
	II	PhCH=CHCOPh	24	56.8	4.41	11.0	1.30
	II	PhCH=CHCOMe	8	60.4	1.01	2.52	1.06
	II	MeCH=C(Me)CO_2H d)	8	68.4	2.55	4.85	1.09
$RuCl_2$((−)-ampp)$_2$-(PPh_3)	II	PhCH=CHCOPh	78	51.8	0.04	0.09	1.00_2
$RuCl_2$((+)-bmpp)$_3$	II	PhCH=CHCOPh	70	26.3	0.54	1.36	1.09
$RuCl_2$((+)-nmdp)$_3$	II	PhCH=CHCOPh	72	59.1	0.21	0.51	1.01

a) $[\text{complex}]_0$=4mM except the diop complex (2mM). b) I=PhMeCHOH; II=PhEtCHOH. c) $[\alpha]_D^{17-20}$(of II) +40.0° (c 5, C_6H_6).[6] d) O.P. of R-(−)-$MeCH_2CH(Me)CO_2H$ formed is 21.0%e.e.. All data (also those in Table 1) were obtained by the analyses with GC and polarimeter (UNION PM-101).

chlorine-bridged Ru_2Cl_4((−)-diop)$_3$ complex was actually effective for the enantioselection of the racemic alcohols, and the asymmetric fields formed by the coordination of $R^1CH=CHR^2$ into the chiral complex[7] substantially affected the selectivity.

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