`ASYMMETRIC INDUCTION IN OXYGENATION OF STYRENE CATALYZED BY COBALT SCHIFF BASE COMPLEX

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Summary: The oxygenation of styrene catalyzed by optically active cobalt Schiff base complexes in 2-propanol gives an enantiomer excess of 1-phenylethanol. The asymmetric induction may be accomplished in two steps: addition of CoH species to styrene and decomposition of 1-phenylethyl hydroperoxide.

Cobalt Schiff base complexes [Co(SB)] are quite interesting because of their characteristic activities in oxygenation reactions. For example, in aprotic solvents, they exhibit dioxygenase-like activity in addition to the reversible formation of dioxygen complexes.<sup>1,2</sup> In protic solvents, on the other hand, they are oxidized irreversibly to cobalt(III) species<sup>3</sup> and turn to promote monooxygenations of organic molecules, 4 including ketonization of alkenes by catalytic oxygenation in ethanol.<sup>5,6</sup> On the mechanism for this interesting monooxygenation of the alkene substrate, Hamilton et al.<sup>5</sup> have discussed the addition of Co(SB)(00H) to the substrate, whereas we have proposed the addition of Co(SB)(H) to the substrate followed by the insertion of dioxygen into the resulting organocobalt complex intermediate (Scheme 1). $^{6}$ We have also found that the oxygenation of styrene catalyzed by nonplanar four coordinate Co(SB) including  $Co(L^{1})$  and  $Co(L^{2})$  gives 1-phenylethanol as the main product, resulting probably from hydrogen transfer from the alcoholic solvent to 1-phenylethyloxyl radical stabilized by a paramagnetic interaction with the cobalt catalysts.<sup>6</sup> If the proposed mechanism (Scheme 1) is the case, the application of a suitable asymmetric cobalt Schiff base complex as the catalyst should give an enantiomer excess of 1-phenylethanol. Little has been known about the asymmetric hydroxylation of a prochiral alkene using a dioxygen-metal complex catalyst system.

Thus, in the present work, the oxygenation of styrene catalyzed by optically active cobalt Schiff base complexes  $[Co(SB^*)]$ ,  $Co(L^1) - Co(L^6)$ ,<sup>8</sup> has been investigated, and the asymmetric induction in the 1-phenylethanol product has actually been observed (Table 1).



PhCH=CH<sub>2</sub> + 0<sub>2</sub>  $\xrightarrow{\text{Co}(SB^*)}$  HO  $\xrightarrow{\text{Me}}$  H + H  $\xrightarrow{\text{Me}}$  OH ROH Ph Ph (R-) (S-)

Table 1. Asymmetric induction for 1-phenylethanol formed by the oxygenation of styrene with optically active cobalt Schiff base complexes<sup>a)</sup>

Rur	n Co(SB*)	ROH	Reaction	Reaction	PhCH*(Me)OH	
			temp./°C	time/h	Yield/% <sup>b</sup>	e.e./%
1	$(R)-Co(L^1)$	EtOH	40	4	26	0 <sup>d</sup>
2	$(R) - Co(L^2)$	EtOH	40	7 days	29	3.1 (R-) <sup>d</sup>
3	$(R)-Co(L^2)$	EtOH	60	5	28	6.7 (R-) <sup>d</sup>
4	$(s)-co(L^2)$	EtOH	60	5	30	6.0 (s-) <sup>d</sup>
5	$(R) - Co(L^2)$	i-PrOH <sup>C</sup>	60	1.5	26	14.3 $(R-)^{d}(15^{e})$
6	$(S) - Co(L^2)$	i-Pr)H <sup>C</sup>	60	0.5	28	14.2 (s-) <sup>d</sup>
7	$(S) - Co(L^2)$	i-PrOH <sup>C</sup>	40	5 days	27	10.9 (s-) <sup>d</sup>
8	$(R) - Co(L^3)$	i-PrOH <sup>C</sup>	60	2	23	5.2 (R-) <sup>e</sup>
9	$(1R, 2R) - Co(L^4)$	i-PrOH <sup>C</sup>	60	1	19	2.1 (S-) <sup>d</sup>
10	$(R)-Co(L^5)$	i-PrOH <sup>C</sup>	60	5	30	38.0 (R-) <sup>f</sup>
11	$(R)-Co(L^6)$	i-PrOH <sup>C</sup>	60	5	18	7.0 (R-) <sup>f</sup>

<sup>a</sup> Reaction conditions: styrene (4.4 mmol), Co(L\*) (0.44 mmol), ROH (60 ml) under 1 atm of oxygen; conversion of styrene, 99%. <sup>b</sup> Isolated yield. <sup>c</sup> A mixture of i-PrOH (25 ml) and CH<sub>2</sub>ClCH<sub>2</sub>Cl (25 ml) was used to dissolve the complex. <sup>d</sup> Determined by optical rotation (cyclopentane solution; c, 7.0 at 25 °C):[ $\alpha$ ]<sup>25°</sup><sub>D</sub> = +43.1° (c, 7.19 in cyclopentane) for (R)-PhCH\*(OH)Me<sup>9</sup> is reffered as the standard. <sup>e</sup> Determined by <sup>1</sup>H NMR using Eu(hfc)<sub>3</sub> as the shift reagent. <sup>f</sup> Determined by HPLC using a CHIRALCEL (Daiseru Chem. Co.).

 $(R)-Co(L^2)$  and  $(S)-Co(L^2)$  give (R)- and (S)-l-phenylethanol, respectively, with the same e.e. value (Table 1; Run 5, 6), indicating the generality and the reproducibility of the present asymmetric induction. The asymmetric induction depends on the the structure of the cobalt complex. It is noted that the methyl group in  $Co(L^2)$  plays an important role for the asymmetric induction (Run 1, 2 and Run 5, 8: MeO < Me). However, the methyl group in  $Co(L^{b})$  seems to be unfavourable (Run 10, 11). The asymmetric induction is in any event affected sensitively by the bulkiness of the ligand in Co(SB\*), although the conflicting effect of the methyl group is not yet fully The observations that the higher e.e. value is obtained in understood. 2-propanol than in ethanol as well as at the higher temperature are implicated in the reaction rate: the faster reaction results in the higher enantiomer excess of 1-phenylethanol. In order to know the asymmetric induction process the decomposition of  $(\pm)-1$ -phenylethyl hydroperoxide, one of the potential intermediates, with Co(SB\*) was investigated. It is found that an enantiomer excess of 1-phenylethanol is obtained (Table 2).

Co(SB*)	HP/Co(SB*)	Solvent	Reaction temp./%C	PhCH*( yield/% <sup>b</sup>	OH)Me e.e./%
$(R) - Co(L^2)$	10	i-PrOH <sup>C</sup>	60	15	6.1 (R-) <sup>d</sup>
$(R) - Co(L^2)$	10	i-PrOH <sup>C</sup>	25	15	18.0 (R-) <sup>e</sup>
$(R) - Co(L^5)$	10	i-PrOH <sup>C</sup>	25	31	27.0 (R-) <sup>e</sup>
(R)-Co(L <sup>6</sup> )	10	$i-PrOH^{C}$	25	15	10.0 (R-) <sup>e</sup>

Table 2. Asymmetric decomposition of PhCH(OOH)Me (HP)<sup>a</sup>

<sup>d</sup> Determined by optical rotation. <sup>e</sup> Determined by HPLC.

The formation of an excess of (R)-l-phenylethanol (Table 2) is rationalized by assuming prolongation of the life time of (R)-l-phenylethoxyl radical, which can abstract hydrogen from 2-propanol, resulting from asymmetric interaction with (R)-Co(L), while the other enantiomer, (S)-l-phenylethoxyl radical, would be decomposed rapidly to acetophenone.

However, the observed e.e. value of the product in Table 2 is smaller than that in Table 1. Therefore, it may be reasonably considered that the asymmetric induction in the oxygenation of styrene is achieved by two steps: the addition of HCo(SB\*) to styrene to form a diastereomer excess of PhMeCHCo(SB\*) (Scheme 1, step a), which undergoes partly racemization during the subsequent dioxygen insertion reaction, and the asymmetric decomposition of 1-phenylethyl hydroperoxide caused by the interaction with the optically

active Co(SB\*) catalyst (Scheme 1, step b), being in agreement with the proposed mechanism.<sup>6</sup>



Scheme 1

Since the incorporation of dioxygen into optically active organocobaloximes is known to proceed as a radical process giving optically inactive alkylperoxo cobalt(III) complexes, <sup>10</sup> the present results suggest that the stereochemistry for the radical dioxygen incorporation process would depend on the structure of the ligand. Further investigations on the detailed mechanism for the present asymmetric induction is in progress.

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