CHEMISTRY LETTERS, pp. 407 - 410, 1985.

ENANTIOSELECTIVE SYNTHESIS OF A NOVEL TYPE OF OPTICALLY ACTIVE OCTAHEDRAL COMPLEXES, *trans*-$[Co(AB)_2(X)(Y)]$. THE ESSENTIAL ROLE OF AXIAL LIGATION FOR Co-C σ-BOND FORMATION IN THE REACTION OF A Co(I) COMPLEX WITH OLEFINS

Yoshiaki OHGO* and Seiji TAKEUCHI
Niigata College of Pharmacy, 5829 Kamishin'ei-cho, Niigata 950-21

$\underline{C}(+)_{578}$- and $\underline{A}(-)_{578}$-$(XCH_2CH_2)(PPD)_2$(pyridine)Co [X = CN or $COOCH_3$; PPD = (*E*,*E*)-1-phenyl-1,2-propanedione dioxime mono anion] have been synthesized by the enantioselective alkylation of $[Co^I(PPD)_2]^-$ with $H_2C{=}CHX$ in the presence of chiral amines, demonstrating the essential role of axial ligation for Co-C σ-bond formation.

Studies of the syntheses and the reactions of optically active alkyl transition metal complexes will provide precise information about the elementary processes of various catalytic reactions. We have already reported the preparation and reactions of C-chiral alkyl cobaloxime complexes.[1-3] The question how Co-C σ-bond formation occurs in the reaction of Co(I) complexes with olefins, and the possibility of finding a novel type of chiral complexes stimulated our interest in the synthesis of Co-chiral octahedral complexes.

To our knowledge, optically active octahedral complexes in which achiral bidentate chelate ligands are coordinated to metal in *trans*, square-planar geometry (Fig. 1) are unknown so far.

Previous X-ray structural studies[4] on the 1-phenylethylamine(1-PEA)-coordinated cobaloxime complexes have revealed that 1-PEA is fixed in a conformation in which the hydrogen atom at the α-carbon falls into the concavity surrounded by Co and, N, O, H, O', and N' of the in-plane ligands. If we use an unsymmetrically substituted glyoxime such as (*E*,*E*)-1-phenyl-1,2-propanedione dioxime mono anion [(*E*,*E*)-PPD], (*R*)-1-PEA should preferentially coordinate to one of the two prochiral faces of the planar *trans*-Co[(*E*,*E*)-PPD]$_2$, in order to avoid a repulsive interaction between the phenyl groups of the in-plane ligands and 1-PEA (Fig. 2).

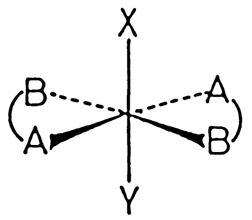


Fig. 1.

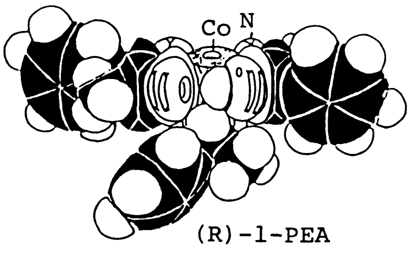
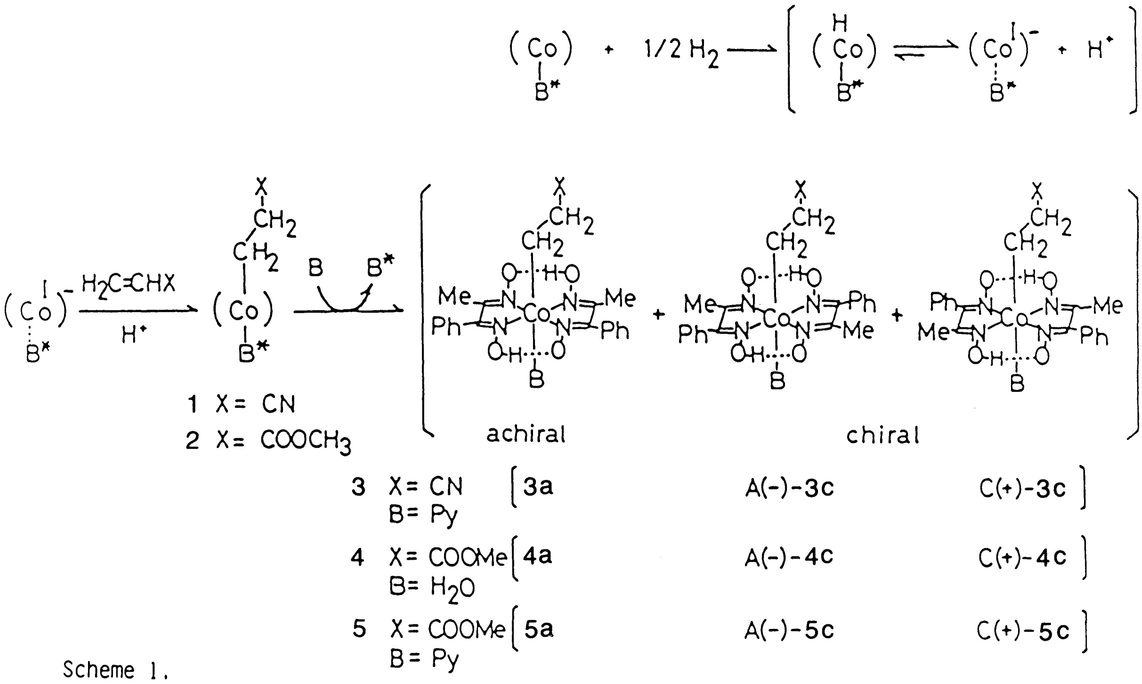


Fig. 2.

We show here that the enantioselective reaction does occur to yield a novel type of optically active octahedral complexes in the reaction of a Co(I) complex with certain olefins, thus demonstrating an essential role of axial base coordination for the Co-C σ-bond formation.

The Co[(E,E)-PPD]$_2$, prepared from CoCl$_2$ and (E,E)-PPD, were allowed to react with acrylonitrile or methyl acrylate in the presence of chiral amines under a hydrogen atmosphere in benzene. The chiral amine of the products was replaced by an achiral ligand, pyridine (py) or water, to give an isomeric mixture (3, 4, or 5) of an achiral complex (3a, 4a, or 5a) and a chiral complex (3c, 4c, or 5c) having chirality only at the cobalt atom, as shown in Scheme 1. Microanalyses, IR and ^{1}H NMR spectra of 3 and 5 agreed with those expected from 2-substituted ethylCo[(E,E)-PPD]$_2$(py).5) Chiral and achiral complexes, which can be separated by recrystallization and silica-gel column chromatography, differ from one another in their ^{1}H NMR chemical shifts of CH$_3$ (PPD) [3c(δ2.10), 3a(δ2.12); 5c(δ2.07), 5a(δ 2.09)].5) From the intensity ratio of each pair of signals (δ2.10/δ2.12 or δ2.07/δ 2.09), the ratio of chiral and achiral complexes can be estimated in every reaction, for which the observed rotation was corrected to give the rotation of the chiral complex (Table 1). The resolutions of chiral amine-coordinated complexes (1 and 2) were unsuccessful. However, the solubilities of the optically active crystals and racemic crystals of 3c and 4c were different fortunately, and thus, optically pure enantiomers could be obtained by recrystallization.



Scheme 1.

The compound (+)-3c was shown by an X-ray structure determination to have the configuration drawn at the right side of Scheme 1.6) CD spectra of (+)$_{578}$-3c and (+)$_{578}$-5c are very similar to each other7) and both enantioselective reactions give the same stereochemical result. Thus, (+)-3c and (+)-5c should have the same absolute configuration. We have tentatively used here the C, A-notation.8) The chirality symbols A and C are assigned for the complexes shown at the middle and the right (in the square brackets) of Scheme 1, respectively.

Table 1. Enantioselective Alkylation of Bis[(E,E)-1-phenyl-1,2-propanedionedioximato]cobalt(I) with CH_2=CHX in Benzene

Entry	X	Chiral amine	Products		
			$[\alpha]^{23}_{578}$/°	%e.e.[f]	Major enantiomer
1	CN	(R)-1-PEA[a]	+39	11	C(+)-3c[d]
2	CN	(S)-1-PEA	-36	10	A(-)-3c
3	CN	(R)-1-NpEA[b]	+6.8	2	C(+)-3c
4	CN	(1R,2S)-ADPE[c]	+136	37	C(+)-3c
5	CN	(R)-2-Amino-2-phenylethanol	-220	60	A(-)-3c
6	COOMe	(R)-1-PEA	+40	10	C(+)-5c[e]
7	COOMe	(S)-1-PEA	-39	9	A(-)-5c
8	COOMe	(R)-1-NpEA	+4	1	C(+)-5c
9	COOMe	(R)-2-Amino-2-phenylethanol	-250	59	A(-)-5c

a) PEA: Phenylethylamine. b) NpEA: (1-Naphthyl)ethylamine. c) ADPE: 2-amino-1,2-diphenylethanol. d) Maximum optical rotation of C(+)-3c: $[\alpha]^{23}_{578}$ +368.7° (c 0.1036, chloroform). e) Maximum optical rotation of C(+)-5c: $[\alpha]^{23}_{578}$ +421.1° (c 0.0482, chloroform). f) Based on maximum optical rotation [see d) and e)].

Enantioselectivities varied greatly with the structures of the chiral amines (Table 1). When R(+)- and S(-)-1-PEA were used, enantiomers C and A were predominant (10% e.e.), respectively, and the reactions with R(-)-2-amino-2-phenylethanol, which has steric features similar to (S)-1-PEA gave enantiomers with configuration A in relatively high enantioselectivity (60% e.e.) even at ambient temperatures. As was expected, enantioselective reactions occurred that yielded a novel type of optically active, octahedral complexes with the chirality predicted by inspection of the CPK model (Fig. 2).

Syntheses of alkylcobaloxime complexes from olefins have been extensively studied.[9)] However, there is not much information available about the precise mechanism for the elementary processes involved in Co-C σ-bond formation.[9,10)] The present results reveal that Co-C σ-bond formation must proceed through an associative mechanism involving both the chiral base and the olefins in the transition state and this also implies that electronic migration from Co(I) to the X-substituted carbon (to form Co-C σ-bond) essentially requires an axial ligation.

The authors are grateful to Prof. Yoichi Shimura, Osaka University, and Prof. Hiroshi Kobayashi, Tokyo Institute of Technology, for helpful discussions and

encouragement.

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5) **C**(+)-**3c**: about four recrystallizations of **3**(from Entry 1) from benzene/hexane gave a maximum and constant rotation (see Table 1). IR(KBr) 2237(w, C≡N), 1545(s, C=N) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ1.80-1.87 (m, 2H, CH_2Co), δ2.10 (s, 6H, CH_3 of PPD), δ2.13-2.20 (m, 2H, CH_2CN), δ7.26-7.50 (m, Ph and β-H of py), δ7.82 (t, 1H, J 7.7 Hz, γ-H of py), δ8.70 (m, 2H, α-H of py). **3a**: $[\alpha]^{23}_{589}$ = $[\alpha]^{23}_{578}$ = 0. IR(KBr) 2237(w, C≡N),1545(s, C=N) cm^{-1} ; the ^{1}H NMR spectrum is almost identical with that of **3c**, except that the signal due to CH_3 of PPD appears at a lower field (δ2.12), compared with that of **3c** (δ 2.10). Repeated recrystallizations and column chromatographic purifications of **4** (from Entry 6) gave optically pure (+)-**4c**: $[\alpha]^{23}_{578}$ +795° (c 0.02, 1%MeOH/$CHCl_3$). The aqua complex (+)-**4c** was treated with pyridine to give (+)-**5c** (for optical rotation, see Table 1). IR(KBr) 1729(s, $COOCH_3$), 1545(s, C=N) cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ1.98-2.06 (m, CH_2Co), δ2.07 (s, 6H, CH_3 of PPD), δ2.10-2.19(m, 2H, CH_2COOCH_3), δ3.62 (s,3H, $COOCH_3$), δ7.25-7.50 (m, Ph and β-H of py), δ7.79(t, 1H, J 7.7 Hz, γ-H of py), δ8.72 (m, 2H, α-H of py). **5a**: $[\alpha]^{23}_{589}$ = $[\alpha]^{23}_{578}$ = 0. The ^{1}H NMR spectrum is almost identical with that of **5c**, except that the signal due to CH_3 of PPD appears at a lower field (δ 2.09), compared with that of **5c** (δ2.07).

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7) CD spectra (CH_2Cl_2) (+)-**3c**: $[\theta]_{484}$ +1.67x10^4, $[\theta]_{383}$ -3.7x10^4, $[\theta]_{256}$ +11.97x10^4. (+)-**5c**: $[\theta]_{490}$ +1.47x10^4, $[\theta]_{381}$ -2.9x10^4, $[\theta]_{255}$ +9.92x10^4.

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(Received December 17, 1984)