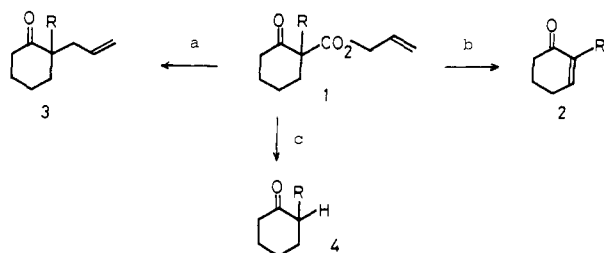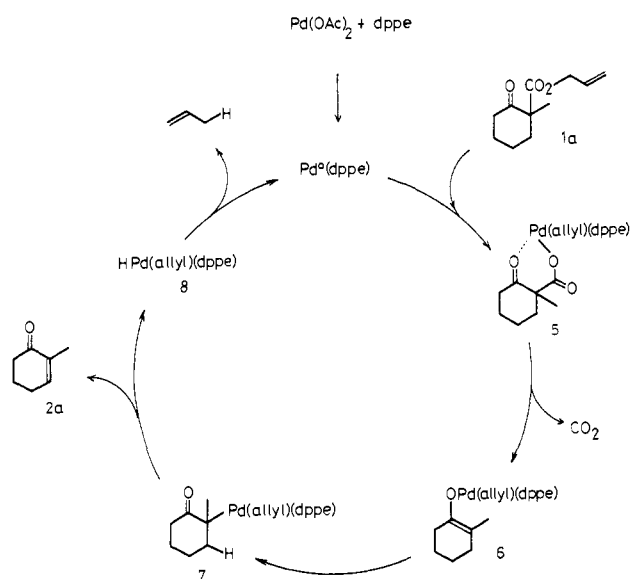Scheme I[a]

[a] Key: (a) Pd–PPh₃; (b) Pd–dppe in CH₃CN; (c) PdCl₂(PPh₃)₂, HCO₂NH₄ in dioxane.

Scheme II

products from allyl 2-pentylcyclopentanone-2-carboxylate and allyl 2-methylcyclododecanone-2-carboxylate (entries 8 and 9). The regioselective introduction of the olefin was fully confirmed by the reaction of 2,6-dialkylated cyclohexanone derivative (entries 11 and 12).

The main product of the reaction of **1** was **3** when the Pd–PPh₃ catalyst was used. Furthermore, **1a** was converted to 2-methylcyclohexanone (**4**, R = CH₃) in 87% yield by decarboxylation in boiling dioxane in the presence of ammonium formate by using PdCl₂(PPh₃)₂ as the catalyst.[3] Thus the above shown three useful Pd-catalyzed transformations are possible under different conditions, and they enhance the usefulness of the β-keto esters. Particularly the facile enone formation has high synthetic value, which is difficult to achieve by other means.[4]

The enone formation is explained by the following mechanism (Scheme II). The oxidative addition of the allyl ester **1a** to Pd(0) species, formed in situ from Pd(OAc)₂, affords allylpalladium β-keto carboxylate **5**,[5] which undergoes decarboxylation to produce the allylpalladium enolate complex **6**, which is in equilibrium with the carbon-bonded complex **7**. Then the enone **2a** is formed by the elimination of Pd–H from **7**. Finally the reductive elimination of the allylpalladium hydride complex **8** produces propene and regenerates the Pd(0) species. This reductive elimination step was confirmed by the fact that a 1:1 mixture of enone **12** and 1-phenylpropene was obtained from the cinnamyl ester of α,α-cyclopentanoacetoacetic acid (**11b**, entry 14).

The enone **2a** was also obtained by the palladium-catalyzed reaction of allyl enol carbonate **13** (Scheme III). The formation

Scheme III[a]
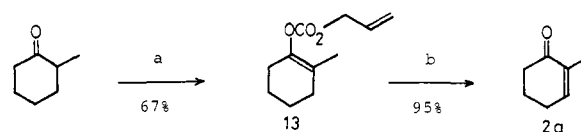
[a] Key: (a) *t*-AmONa in DME at 25 °C, and ClCO₂CH₂CH=CH₂ (excess); (b) Pd(OAc)₂–dppe (5 mol %) in CH₃CN reflux for 30 min.

of enone **2a** from **1a** and **13** strongly implies that both reactions proceed via the allylpalladium enolate **6** as the common intermediate.

Concerning the effect of the ligand on the course of the reaction, Yamamoto et al. reported that the thermal decomposition of *cis*-PdEt₂(PMe₂Ph)₂ gave butane by reductive coupling, and ethane and ethylene were obtained from *cis*-PdEt₂(dppe) by reductive elimination.[6] In this case, dppe induces the elimination to form olefin.

The conversion of ketones to α,β-unsaturated ketones by using Pd(II) salts directly[7,8] or via silyl enol ethers[9] and β-keto carboxylates[2] has been reported. But these reactions when carried out catalytically require the use of a cocatalyst to reoxidize the Pd(0).

Registry No. 1a, 7770-41-4; **1b**, 83135-28-8; **1c**, 83135-29-9; **1d**, 5453-93-0; **2a**, 1121-18-2; **2b**, 51577-39-0; **2c**, 83135-30-1; **3a**, 16178-87-3; **9a**, 83135-31-3; **9b**, 83135-32-4; **10**, 1208-44-2; **11a**, 83135-33-5; **11b**, 83135-34-6; **12**, 16112-10-0; Pd(OAc)₂, 3375-31-3; dppe, 1663-45-2; 2-(allyloxycarbonyl)-2-pentylcyclopentanone, 83135-35-7; 2-(allyloxycarbonyl)-2-methylcyclododecane, 83135-36-8; allyl 2-methyl-2-heptanylpropanoate, 83135-37-9; 2-cyclohexenone, 930-68-7; 2-allyl-2-cyclohexenone, 38019-50-0; 2,2-diallylcyclohexanone, 5277-36-1; 2-pentyl-2-cyclopentenone, 25564-22-1; 2-methyl-2-cyclododecenone, 83135-38-0; 2-methylene-3-monanone, 51756-19-5; 2-pentylidenecyclopentanone, 16424-35-4; 2-methylenecyclododecanone, 3045-76-9.

(6) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868–1880.

(7) Theissen, R. J. *J. Org. Chem.* **1971**, *36*, 752–757.

(8) Bierling, B.; Kirschke, K.; Oberender, H. *J. Pract. Chem.* **1972**, *314*, 170–180.

(9) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011–1013.

Chiroptical Properties of *trans*-Dichlorotetrakis(pyridine)cobalt(III) Ion. A Fixed Propeller Conformation

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Although extensive investigations have been carried out on the stereochemical studies of coordination compounds, few reports have been found on the chiral complexes having a restricted rotation.[1] This communication describes the possible existence of a chiral metal complex with a fixed propeller conformation.

trans-Dichlorotetrakis(pyridine)cobalt(III) ion has neither configurational chirality nor conformational chirality due to a chelate ring. However, because of the steric interaction between the 2,6-hydrogens of adjacent pyridine molecules, all four pyridine rings are expected to be obliquely inclined with respect to the CoN₄ plane. This produces the torsional isomerism about the metal–

(3) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613–616.

(4) For the oxidative decarboxylation of carboxylic acid to form olefin with Pb(OAc)₄, see: Scheldon, R. A.; Kochi, J. K., *Org. React.* **1972**, *19*, 279–421.

(5) Yamamoto, T.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600–5602.

(1) (a) Nakano, Y.; Seki, H. *Chem. Lett.* **1976**, 611. (b) Nakano, Y.; Sato, S. *Inorg. Chem.* **1980**, *19*, 3391. (c) Nakano, Y.; Sato, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1683.
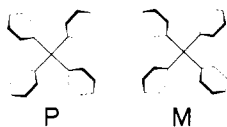
Figure 1. Pair of atropisomers that are possible for *trans*-[CoCl$_2$(py)$_4$]$^+$. P and M refer to the absolute configuration of the isomers.
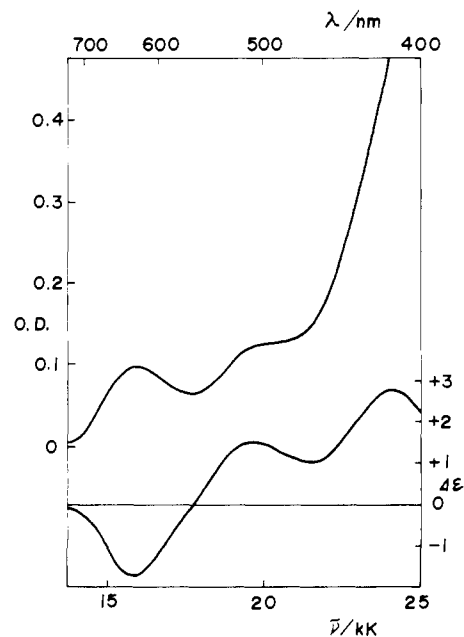
nitrogen bonds as shown in Figure 1.

Although the rotational barrier must be too small to fix the conformation, it may be possible to get one of the atropisomers through the formation of a diastereoisomer containing an optically active anion. Hydrogen dibenzoyltartrate ion (HDBT) has been chosen as the anion. Treatment of an aqueous solution of *trans*-[CoCl$_2$(py)$_4$]Cl·6H$_2$O with an excess of (−)$_{589}$-NH$_4$HDBT in water gave *trans*-[CoCl$_2$(py)$_4$]HDBT (I) as a green powder, which is scarcely soluble in water. Anal. C, H, N (Co calcd, 7.33; found, 7.29).

Figure 2 shows the absorption and circular dichroism (CD) spectra of I in a Nujol mull. They were measured by the opal glass method.[2] On the basis of the solid absorption spectrum, the thickness multiplied by the "concentration" of the Nujol mull was estimated with the assumption that the molar absorption coefficient of I is 45 cm^{-1} mol^{-1} dm^3 at 630 nm.[3] Then the quantitative CD spectrum of the Nujol mull was obtained as Figure 2 shows.

Bosnich and Harrowfield reported the induced CD spectra of (+)-α-bromocamphor-π-sulfonate ((+)-BCS) salts of [Co-(NH$_3$)$_6$]$^{3+}$, *trans*-[CoCl$_2$(en)$_2$]$^+$, and *trans-meso*-[CoCl$_2$(2,3,2-tet)]$^+$ (tet = 3,7-diazanonane-1,9-diamine).[4] They discussed three mechanisms as being responsible for the induced activity, i.e., the direct dissymmetric perturbation, the distortion of the metal–ligand bond, and the dissymmetric transformation of the cation, and suggested that a common mechanism was responsible for the induced activity of these three complexes.[5]

This might be also the case for I. However, an important difference between I and the (+)-BCS salts is in their CD intensities.[6] The intensity of I is comparable to those of the complexes having configurational activity and is higher than those of the complexes having conformational activity.[7] If the first or second mechanism is mainly responsible for the induced activity of I, it is difficult to understand why only I exhibits such a strong CD spectrum. Its high intensity could more readily be explained by assuming that I is composed of an atropisomer. Even though one of the four pyridine molecules in the complex cation is obliquely inclined with respect to the CoN$_4$ plane, the other three may be forced to be inclined similarly. Then the pyridine molecule is expected to give the optical activity of the same sign and magnitude as those of the other three molecules. One fourth of the $\Delta\epsilon$ value at 630 nm is roughly the same as the $\Delta\epsilon$ value of, e.g., *trans*-[CoCl$_2$(NH$_3$)$_2$(R-pn)]ClO$_4$ (pn = 1,2-propanediamine).[8] This assumption is also supported by the facts that *trans*-[CoCl$_2$(NH$_3$)$_4$]HDBT does not show any CD maxima, and *trans*-[CoCl$_2$(en)$_2$]HDBT exhibits a very weak spectrum under

(2) Taniguchi, Y.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 754.

(3) The molar absorption coefficient of I at the longest absorption maximum around 630 nm is 46.6 in dimethyl sulfoxide, 45.2 in dimethylformamide, and 41.9 in acetic acid.

(4) Bosnich, B.; Harrowfield, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4086.

(5) This implies that the third mechanism does not contribute to the induced activity, since *trans-meso*-[CoCl$_2$(2,3,2-tet)]$^+$ can possess neither conformational nor rotational chirality.

(6) Since ref 4 did not refer to the absorption spectra of the KBr disks, the CD intensities of (+)-BCS salts cannot be evaluated. However, from the reported sensitivity, their $\Delta\epsilon$ values are estimated to be less than one-tenth of that of I. The elipticity of the present Nujol mull was −0.110° at 630 nm.

(7) Although it is generally recognized that the conformational activity is weaker than the configurational activity, trans-disubstituted triethylenetetraamine complexes have a tendency to exhibit exceptionally strong CD spectra ((a) Buckingham, D. A.; Marzilli, P. A.; Sargeson, A. M. *Chem. Commun.* **1967**, 433. (b) Utsuno, S.; Sakai, Y.; Yoshikawa, Y.; Yamatera, H. *J. Am. Chem. Soc.* **1980**, *102*, 6903).

(8) (a) Hawkins, C. J.; Larsen, E.; Olsen, I. *Acta Chem. Scand.* **1965**, *19*, 1915. (b) Bosnich, B.; Harrowfield, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3425.

Figure 2. Absorption and circular dichroism spectra of *trans*-[CoCl$_2$-(py)$_4$](−)$_{589}$-HDBT in Nujol mull.

the same conditions as for the CD measurement of I. The $\Delta\epsilon$ values of the ethylenediamine complex are −0.020 at 600 nm and +0.012 at 460 nm, which are approximately 2 orders of magnitude less than the $\Delta\epsilon$ values of I.[9]

Thus, all the present available data suggest the presence of complex cations with a fixed propeller conformation in I. The conformation was instantaneously broken and no CD maxima were observed when I was dissolved in dimethyl sulfoxide, dimethylformamide, or acetic acid. On the other hand, an enantiomeric CD spectrum was observed when I was dissolved in methanol. The $\Delta\epsilon$ values of the solution were +3 × 10^{-3} at 630 nm, −1 × 10^{-3} at 510 nm, and −4 × 10^{-3} at 410 nm. Since these intensities are extremely low, it is impossible to ascribe the solution activity to any one definite origin.

The positions of the CD maxima in the solid state agree well with those of the solid absorption maxima within the region of the first absorption band. The negative band at 630 nm is assigned to the $^1A_1 \rightarrow {}^1E$ transition, and the positive band at 510 nm is assigned to the $^1A_1 \rightarrow {}^1A_2$ transition under D_4 symmetry. The ^1E excited state often splits to give two nondegenerate states, as in the case of *trans*-[CoCl$_2$(N)$_4$]-type complexes, when the complex ion has low symmetry.[8b] This is not the case for I, because the complex cation must belong to the D_4 group if the dihedral angle between the CoN$_4$ plane and a pyridine ring is equal to the other corresponding angles.

Since I was obtained as a powdery solid, the absolute configuration of I was not able to be determined by X-ray crystallography. However, the sign of the CD band should reflect the absolute configuration of the cation. Thus, (−)$_{630}^{CD}$ [CoCl$_2$(py)$_4$]$^+$ is assigned to the conformation P according to the hexadecadal regional rule.[10]

Acknowledgment. I express my thanks to Institute for Molecular Science (Japan), which permitted me to record the CD spectra of the present complexes.

Registry No. I, 83006-37-5; *trans*-[CoCl$_2$(py)$_4$]$^+$, 14077-25-9.

(9) The CD spectrum of *trans*-[CoCl$_2$(en)$_2$]HDBT in Nujol mull closely resembles that of *trans*-[CoCl$_2$(en)$_2$]Cl in L-2,3-butanediol, although both spectra are enantiometric with each other (Bosnich, B. *J. Am. Chem. Soc.* **1967**, *89*, 6143) and it is different from that of *trans*-[CoCl$_2$(en)$_2$](+)-BCS in a KBr disk (ref 4).

(10) (a) Mason, S. F. *Chem. Commun.* **1969**, 777. (b) Mason, S. F. *J. Chem. Soc.* **1971**, 667.