

Its nmr ( $\text{CDCl}_3$ ) spectra of the regioselective O-demethylated isoapocodeine demonstrated 11-methoxy singlet at 3.61 and the quartet of 1-peri hydrogen at 8.20. The hydroxy proton broad singlet appeared at 5.90 which caused  $\text{D}_2\text{O}$  exchange to disappear. Four aromatic protons (2, 3, 8 and 9 H) appeared as a multiplet centered at 6.96 and the N-methyl singlet at 2.55. This assignment is corroborated in the work of Baarschers, *et al.*,<sup>12</sup> and with an authentic sample of the natural origin of isoapocodeine. The observed regioselectivity of the ether cleavage in the aporphine systems represent, to the best of our knowledge, the first demonstration of this action, although a number of enzyme systems have been noted.<sup>13</sup>

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## Stereospecific Coordination of *trans*-1,2-Diaminocyclohexane in the Reaction with Dichloro Platinum (II) Complexes of Optically Active 2,2'-Diamino-1,1'-binaphthyl

Moo-Jin Jun

Department of Chemistry, Yonsei University, Seoul 120, Korea.

Chul Fan Liu

Department of Chemistry, University of Illinois, Chicago, Illinois 60680, U.S.A. (Received December 19, 1984)

Stereospecific coordination has been observed when the racemic mixture of bidentates coordinated to the dichloro platinum (II) complexes of optically active diamino skewed biaryls.<sup>1-3</sup> While the stereospecific coordination of racemic mixtures has long been known,<sup>4-6</sup> such behavior by a diamino skewed biaryl is known only recently.<sup>1-3,6</sup> In the present work the stereoselective behavior of another skewed biaryl, 2,2'-diamino-1,1'-binaphthyl (dabn), is studied. The racemic mixture of *trans*-1,2-diaminocyclohexane is chosen for this purpose.

### Experimental

2,2'-Diamino-1,1'-binaphthyl (dabn) was prepared and resolved by known method.<sup>7,8</sup> *Trans*-1,2-diaminocyclohexane was resolved by the method of Asperger and Liu.<sup>9</sup>

$[\text{Pt}(\text{R-dabn})\text{Cl}_2] \cdot \text{H}_2\text{O}$ . 0.40 g of R-dabn was dissolved in 50 ml of warm aqueous ethanol, which was then added dropwise to a solution of 0.58 g of  $\text{K}_2\text{PtCl}_4$  in 50 ml of water. The mixture was heated and stirred at a temperature of 60–70°C for

one hour. The mixture was cooled and the golden product was collected in a sintered glass filter. The product was washed with water and ethanol, and air dried. Anal. Calcd. for Pt Found : C, 43.30 ; H, 3.27 ; N, 2.59 ; Cl, 12.76.

$[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})\text{Cl}_2] \cdot \text{H}_2\text{O}$ . 0.23 g of unresolved chxn and 1.11 g of  $[\text{Pt}(\text{R-dabn})\text{Cl}_2] \cdot \text{H}_2\text{O}$  were dissolved in 350 ml of water. The mixture was stirred and heated at a temperature of 50–60°C for 9 hrs. The solution was cooled and filtered to remove any unreacted reactants. It was then concentrated on a rotary evaporator until crystallization. The mixture was stored in a refrigerator overnight. The product was collected, washed with ice-cold water and ethanol, and air dried. The product was recrystallized once from 0.02 M HCl. Yield : 0.36 g (27%). Anal. Calcd. for  $\text{Pt C}_{26}\text{H}_{30}\text{N}_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  : C, 46.71 ; H, 4.82 ; N, 8.38 ; Cl, 10.60 Found : C, 46.67 ; H, 4.84 ; N, 8.43 ; Cl, 10.54.

$[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})\text{Cl}_2] \cdot \text{H}_2\text{O}$ . This was made by a similar method described above using  $[\text{Pt}(\text{S-dabn})\text{Cl}_2] \cdot \text{H}_2\text{O}$  in place of  $[\text{Pt}(\text{R-dabn})\text{Cl}_2] \cdot \text{H}_2\text{O}$ . Yield : 0.28 g (26%). Anal. Calcd. for  $\text{Pt C}_{26}\text{H}_{30}\text{N}_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  : C, 46.71 ; H, 4.82 ; N, 8.38 ; Cl, 10.60

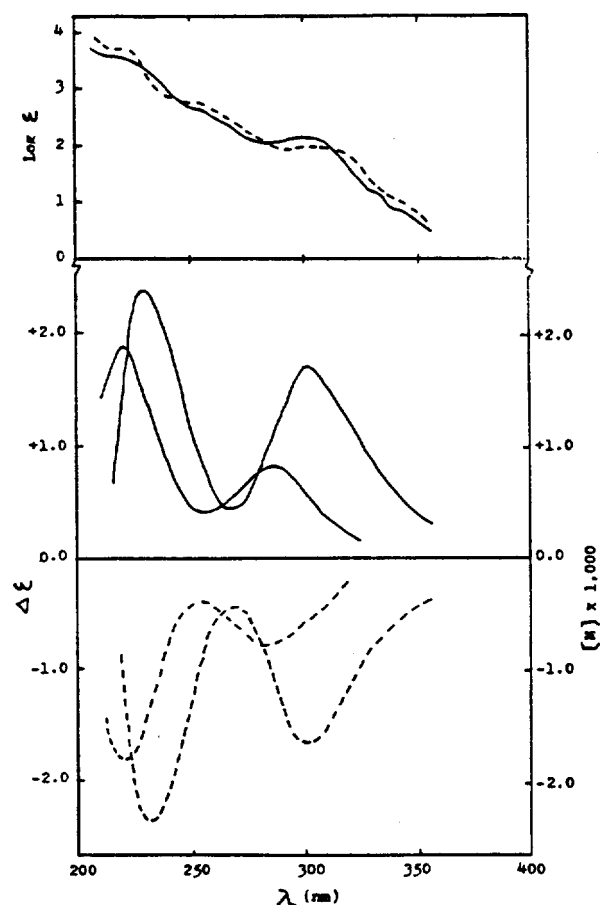
Found : C, 46.70 ; H, 4.78 ; N, 8.44 ; Cl, 10.59.

Standard  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  and  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]\text{Cl}_2$  Complexes. The  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  standard complex was prepared from  $[\text{Pt}(\text{R-dabn})\text{Cl}_2] \cdot \text{H}_2\text{O}$  and  $\text{R,R-chxn}$  according to the method described above. *Anal.* Calcd. for  $\text{Pt C}_{26}\text{H}_{30}\text{N}_4\text{Cl}_2$  : C, 48.03 ; H, 4.65 ; N, 8.62 ; Cl, 10.90. Found : C, 47.98 ; H, 4.70 ; N, 8.66 ; Cl, 10.84. The  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]\text{Cl}_2$  standard complex was also obtained from  $[\text{Pt}(\text{S-dabn})\text{Cl}_2] \pm \text{H}_2\text{O}$  and  $\text{S,S-chxn}$ . *Anal.* Found : C, 47.95 ; H, 4.69 ; N, 8.59 ; Cl, 10.91.

**Instruments Used.** The UV-visible spectra was obtained using Cary 14 UV-Visible spectrophotometer. Circular dichroism spectra were measured using Jasco Model 20 ORD/CD Spectrophotometer. Elemental analyses were done by Micro-Tech Laboratories, Skokie, Illinois.

## Results and Discussion

Figure 1 shows the absorption, ORD, and CD spectra of the standard complex,  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$ , which was prepared from  $[\text{Pt}(\text{R-dabn})\text{Cl}_2]$  and  $\text{R,R-chxn}$ . The coordinated  $\text{R,R-chxn}$  has been found to take the  $\lambda$  chelate ring conformation from X-ray crystallographic study.  $\text{R-dabn}$ , when coordinated to metal ion, has no choice but to take a  $\lambda$  chelate ring conformation. Thus, the two chelate rings in the  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  complex will have  $\lambda\lambda$  conformation.

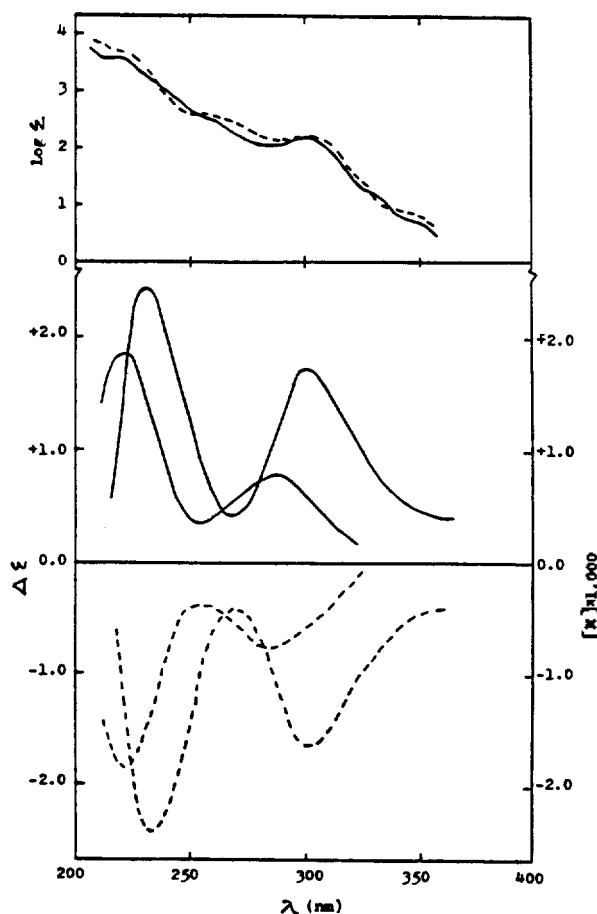


**Figure 1.** The electronic absorption, ORD, and CD spectra of  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  (—) and  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]\text{Cl}_2$  (---) standard complexes prepared using, respectively, optically active  $\text{R,R-chxn}$  and  $\text{S,S-chxn}$ .

mation.

The ORD and CD curves of the  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  (Figure 2) obtained from racemic  $\text{chxn}$  and  $[\text{Pt}(\text{R-dabn})\text{Cl}_2]$  are very similar to those of the corresponding standard complex (Figure 1). The pattern and signs of cotton effect suggest that  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  prepared from racemic  $\text{chxn}$  has  $\lambda\lambda$  conformation. Although study using the molecular models shows that in the  $\lambda\lambda$  conformation the hydrogens on opposing nitrogens are staggered in the case of  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$ , it is quite remarkable that only the  $\text{R}$  enantiomer out of the racemic  $\text{chxn}$  has coordinated during the reaction with  $[\text{Pt}(\text{R-dabn})\text{Cl}_2]$ . In the  $\lambda\lambda$  conformation the nonbonded interaction between hydrogens on opposing nitrogens should be minimized.<sup>3,10</sup>

From the consideration of the nonbonded interaction and the most stable chelate ring conformation, it is not surprising to find out experimentally that only the  $\text{S}$ -enantiomer of racemic  $\text{chxn}$  has coordinated in the reaction of racemic  $\text{chxn}$  with  $[\text{Pt}(\text{S-dabn})\text{Cl}_2]$ . The similarity between the ORD and CD curves of  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]\text{Cl}_2$  obtained from racemic  $\text{chxn}$  (Figure 2) and those of the standard  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]\text{Cl}_2$  prepared from resolved  $\text{S,S-chxn}$  indicates that the two chelate rings in  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]^{2+}$  moiety take the same  $\delta$  conformation, which is the favored and most stable conformation for both  $\text{S-dabn}$  and  $\text{S,S-chxn}$ . In the  $\delta\delta$  conformation the hydrogens on opposing nitrogens are staggered and the



**Figure 2.** The electronic absorption, ORD, and CD spectra of  $[\text{Pt}(\text{R-dabn})(\text{R,R-chxn})]\text{Cl}_2$  (—) and  $[\text{Pt}(\text{S-dabn})(\text{S,S-chxn})]\text{Cl}_2$  (---) prepared from racemic  $\text{chxn}$ .

nonbonded interaction between those hydrogens becomes least among any other conformations such as  $\delta\lambda$  or  $\lambda\lambda$  conformations.

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## Convenient Method for the Preparation of Active Carbonates, Active Carbamates, and Ureas Using Di-2-Pyridyl Carbonate

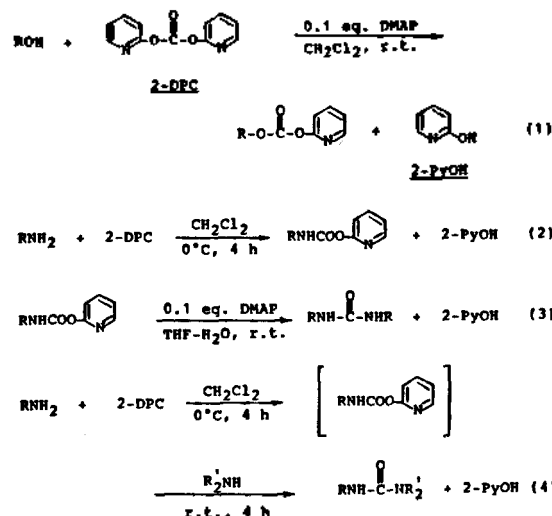
Suggak Kim† and Young Kwan Ko

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea  
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As part of our research program directed toward the synthetic utility of active esters and carbonates containing 2-pyridyl<sup>1-4</sup> or 1-benzotriazolyl group,<sup>5,6</sup> we have recently reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling reagent for the direct esterification of carboxylic acids.<sup>4</sup> We now wish to report a convenient method for the preparation of active carbonate, active carbamates, and ureas using di-2-pyridyl carbonate.

Since a variety of active carbonates having *t*-butyl and benzyl group are well-known amino protective reagents for peptide synthesis,<sup>7</sup> reaction of an alcohol with di-2-pyridyl carbonate was studied and we found that several synthetically useful active carbonates could be conveniently prepared from di-2-pyridyl carbonate and an alcohol in the presence of 4-dimethylaminopyridine (DMAP)<sup>8</sup> (eq. 1). Reaction of benzyl alcohol with an equimolar amount of 2-DPC in the presence of 0.1 equiv of DMAP in methylene chloride at room temperature in 2 h gave benzyl 2-pyridyl carbonate in 70% yield, whereas the reaction did not occur in the presence of triethylamine. *t*-Butyl 2-pyridyl carbonate<sup>2</sup> was obtained in 80% yield by treatment of *t*-butyl alcohol with an equimolar amount of 2-DPC in the presence of 0.1 equiv of DMAP in methylene chloride at room temperature for 12 h. Similarly, methyl 2-pyridyl carbonate was obtained in 78% yield within 1 h under the similar conditions.

When 2-DPC was reacted with several amines in methylene chloride at 0°C for 4 h, the corresponding 2-pyridyl carbamates were obtained in high yields along with a small amount of the corresponding ureas (eq. 2). For example, reaction of 2-DPC with an equimolar amount of benzylamine at 0°C in 4 h gave *N*-benzyl, 2-pyridyl carbamate in 83% yield along with 4%



of dibenzylurea after silica gel column chromatographic separation. Furthermore, it is noteworthy that the reaction did not afford the corresponding isocyanates and 2-pyridyl carbamates obtained here did not decompose thermally into the corresponding isocyanates and 2-hydroxypyridine. Some typical isolated yields of 2-pyridyl carbamates were:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCOO-2-Py}$ , 81%;  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NHCOO-2-Py}$ , 82%; cyclo- $\text{C}_6\text{H}_{11}\text{NHCOO-2-Py}$ , 84%.

Reaction of 2-pyridyl carbamates with 0.1 equiv of DMAP in aqueous tetrahydrofuran did not give the original amines but the symmetrical ureas (eq. 3). The reaction proceeded cleanly at room temperature and required 12-24 h for completion of the reaction. Some typical isolated yields of the symmetrical ureas were:  $\text{C}_6\text{H}_5\text{CH}_2\text{NHCONHCH}_2\text{C}_6\text{H}_5$ , 99%;  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCONHCH}_2\text{CH}_2\text{CH}_3$ , 92%;  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)$