

# Stereoselective Reactions of 2,3-Diaminobutane with Platinum(II). Complexes of Optically Active 6,6'-Dimethyl-2,2'-diaminobiphenyl

Moo-Jin Jun<sup>†</sup> and Sung Rack Chol

Department of Chemistry, Yonsei University Seoul 120, Korea (Received November 5, 1984)

Stereospecific coordination of racemic 2,3-diaminobutane has been observed in the reaction with platinum(II) complexes of optically active 6,6'-dimethyl-2,2'-diaminobiphenyl. The reaction between [Pt(R-dmdabp)Cl<sub>2</sub>] (R-dmdabp is R-6,6'-dimethyl-2,2'-diaminobiphenyl) and unresolved bn (bn is 2,3-diaminobutane) has yielded [Pt(R-dmdabp)-(R-bn)]Cl<sub>2</sub> only, while the reaction of [Pt(S-dmdabp)Cl<sub>2</sub>] with unresolved bn has yielded [Pt(S-dmdabp)-(S-bn)]Cl<sub>2</sub> only. On the other hand, the standard [Pt(R-dmdabp)-(R-bn)]Cl<sub>2</sub> complex has been independently prepared from the reaction of [Pt(R-dmdabp)Cl<sub>2</sub>] with R-bn, and the standard [Pt(S-dmdabp)-(S-bn)]Cl<sub>2</sub> from the reaction of [Pt(S-dmdabp)Cl<sub>2</sub>] with S-bn. The stereospecific behavior of the racemic 2,3-diaminobutane is thus confirmed from the comparison of these Pt(II) complexes prepared using racemic bn with the standard Pt(II) complexes prepared using R-bn or S-bn.

## Introduction

Ever since Theilacker's discovery that chelate rings can be puckered in the bis(diamine)platinum(II) complexes,<sup>1</sup> it has long been realized that the nonplanar nature of the chelates could be a source of dissymmetry. The two phenyl rings of R-6,6'-dimethyl-2,2'-diaminobiphenyl(R-dmdabp) has been found to be puckered by more than 70 degrees in angle<sup>2</sup> and thus provide a good source of dissymmetry owing to such non-planarity of the chelate rings when coordinated to a metal ion. Cobalt(III) complexes of dmdabp have been reported,<sup>3,4</sup> and the diamine and dichloro platinum(II) complexes of dmdabp have recently been prepared,<sup>5,6</sup> in which the dmdabp ligand has shown complete stereospecificity. Such complete stereospecificity has prompted us to study the stereoselective reactions between racemic mixture of 2,3-diaminobutane and platinum(II) complexes of optically active dmdabp ligands. It will be shown here that optically inactive racemic mixture of 2,3-diaminobutane coordinates stereoselectively to the platinum(II) complex of R-dmdabp.

## Experimental

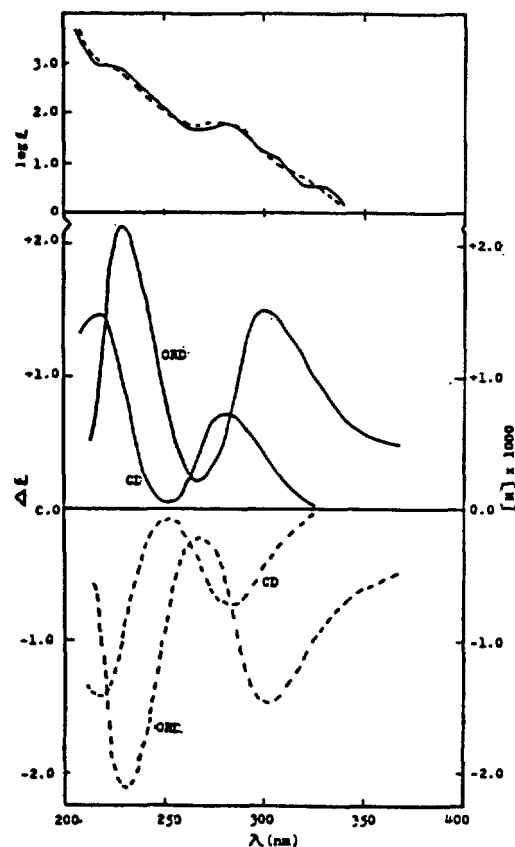
**Preparation and Resolution of 6,6'-Dimethyl-2,2'-diaminobiphenyl.** This was described elsewhere.<sup>5,6</sup>

**Resolution of 2,3-Diaminobutane.** (±)-2,3-Diaminobutane was resolved according to the method known in the literature using (±)- or (-)- tartaric acid.<sup>7,8</sup>

[Pt(R-dmdabp)-(R-bn)]Cl<sub>2</sub>. 0.96 g of [Pt(R-dmdabp)Cl<sub>2</sub>]<sup>6</sup> and 0.018 g of 2,3-diaminobutane(bn) were suspended in 300 ml of water, which was stirred and heated a temperature of 45–45 °C for 10 hrs. The solution was cooled and filtered, and was concentrated on a rotary evaporator. When crystallization just occurred, the mixture was placed in an ice bath. The crystals were collected on a sintered glass funnel, washed successively with ice-cold water, ethanol, ether, and air dried. The product was recrystallized from 0.03 M HCl. Yield: 0.40g (35 %), *Anal.* Calcd. for Pt C<sub>18</sub>H<sub>29</sub>N<sub>4</sub>Cl<sub>2</sub>: C, 38.10; H, 5.15; N, 9.87; Cl, 12.50. Found: C, 37.98, H, 5.20; N, 9.81; Cl, 12.38

[Pt(S-dmdabp)-(S-bn)]Cl<sub>2</sub>·H<sub>2</sub>O. This was prepared by the same method as that described above using [Pt(S-dmdabp)Cl<sub>2</sub>]<sup>6</sup> in place of [Pt(R-dmdabp)Cl<sub>2</sub>]. Yield: 0.33g (31 %). *Anal.* Calcd. for Pt C<sub>18</sub>H<sub>29</sub>N<sub>4</sub>Cl<sub>2</sub>·H<sub>2</sub>O: C, 36.92; H, 5.33; N, 9.57; Cl, 12.11. Found: C, 37.00; H, 5.30; N, 9.61; Cl, 12.04.

**Standard Complexes of [Pt(R-dmdabp)-(R-bn)]Cl<sub>2</sub> and [Pt(S-dmdabp)-(S-bn)]Cl<sub>2</sub>.** These standard complexes were prepared employing the same method described above using op-



**Figure 1.** Electronic absorption, ORD, and CD spectra of the standard complexes of [Pt(R-dmdabp)-(R-bn)]Cl<sub>2</sub> (—) and [Pt(S-dmdabp)-(S-bn)]Cl<sub>2</sub> (---), prepared using, respectively, R-bn and S-bn.

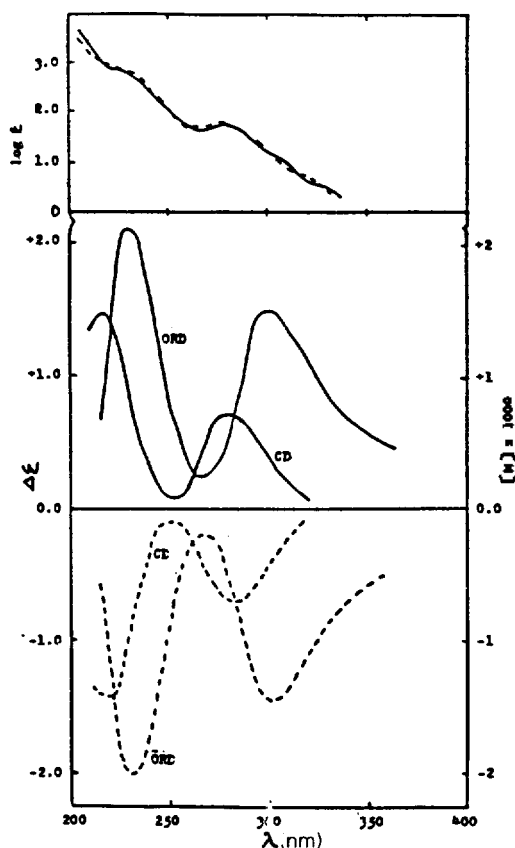
tically active 2,3-diaminobutane. The standard complex of  $[\text{Pt}(\text{R-dmdabp})(\text{R-bn})]\text{Cl}_2$  was prepared from  $[\text{Pt}(\text{R-dmdabp})\text{Cl}_2]$  and R-bn. Yield: 0.28g (31%). Anal. Calcd. for  $\text{Pt C}_{18}\text{H}_{29}\text{N}_4\text{Cl}_2$ : C, 38.10; H, 5.15; N, 9.87; Cl, 12.50. Found: C, 38.01; H, 5.19; N, 9.94; Cl, 12.44. The standard  $[\text{Pt}(\text{S-dmdabp})(\text{S-bn})]\text{Cl}_2$  was obtained from  $[\text{Pt}(\text{S-dmdabp})\text{Cl}_2]$  and S-bn. Yield: 0.22g (30%). Anal. Calcd. for  $\text{PtC}_{18}\text{H}_{29}\text{N}_4\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$ : C, 37.50; H, 5.16; N, 9.72; Cl, 12.30. Found: C, 37.42; H, 5.19; N, 9.73; Cl, 12.31.

**Instruments Used.** The electronic absorption spectra were obtained using a Cary 14 UV-Vis. Spectrophotometer. Circular dichroism spectra were measured using a Jasco Model 20 ORD/CD Spectrophotometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

## Results and Discussion

The complex of  $[\text{Pt}(\text{R-dmdabp})(\text{R-bn})]\text{Cl}_2$  was obtained from  $[\text{Pt}(\text{R-dmdabp})\text{Cl}_2]$  in two ways; one is the standard complex prepared from  $[\text{Pt}(\text{R-dmdabp})\text{Cl}_2]$  and resolved R-bn, and the other is the complex prepared from the reaction between  $[\text{Pt}(\text{R-dmdabp})\text{Cl}_2]$  and racemic mixture of bn. Likewise, the complex of  $[\text{Pt}(\text{S-dmdabp})(\text{S-bn})]\text{Cl}_2$  was prepared from  $[\text{Pt}(\text{S-dmdabp})\text{Cl}_2]$  in two ways; one is the standard complex obtained using resolved S-bn and the other the complex made from the bn racemic mixture.

Figure 1 shows the absorption, ORD, and CD spectra of the  $[\text{Pt}(\text{R-dmdabp})(\text{R-bn})]\text{Cl}_2$  standard complex along with those



**Figure 2.** Electronic absorption, ORD, and CD spectra of  $[\text{Pt}(\text{R-dmdabp})(\text{R-bn})]\text{Cl}_2$  (—) and  $[\text{Pt}(\text{S-dmdabp})(\text{S-bn})]\text{Cl}_2$  (---) prepared using racemic 2,3-diaminobutane.

of the  $[\text{Pt}(\text{S-dmdabp})(\text{S-bn})]\text{Cl}_2$  standard complex. The absorption, ORD, and CD spectra of the other complexes prepared from racemic mixture of bn are shown in Figure 2.

Comparison of the ORD and CD spectra of the  $[\text{Pt}(\text{R-dmdabp})(\text{R-bn})]\text{Cl}_2$  standard complex (Figure 1) with those of the  $[\text{Pt}(\text{R-dmdabp})(\text{R-bn})]\text{Cl}_2$  complex (Figure 2) prepared from unresolved bn indicates the fact that only the R enantiomer of bn has been coordinated to the Pt(II) ion during the reaction between the unresolved bn and the  $[\text{Pt}(\text{R-dmdabp})\text{Cl}_2]$  complex. Such stereoselective behavior can be understood from a careful examination of molecular models of R-bn and S-bn along with the model of the  $[\text{Pt}(\text{R-dmdabp})\text{Cl}_2]$  complex. In the bis(diamine) complex containing R-bn and R-dmdabp the hydrogens on opposing nitrogens are staggered. When the model containing S-bn is made with the same R-dmdabp, the hydrogens are almost totally eclipsed, if both methyl groups on the asymmetric carbons are to be in equatorial position. Certainly the biggest contribution to the complete stereospecificity observed in this work is this nonbonded interaction between the hydrogens bonded to opposing nitrogens. Such nonbonded interaction has been attributed to the stereoselective behavior of other platinum(II) complexes.<sup>9,10</sup>

Comparison of the ORD and CD spectra of  $[\text{Pt}(\text{S-dmdabp})(\text{S-bn})]\text{Cl}_2$  obtained using the racemic mixture of bn (Figure 2) with those of the  $[\text{Pt}(\text{S-dmdabp})(\text{S-bn})]\text{Cl}_2$  standard complex, on the other hand, shows that Only the enantiomer of bn has been coordinated during the reaction between  $[\text{Pt}(\text{S-dmdabp})\text{Cl}_2]$  and unresolved bn. Study using the molecular models shows that the hydrogens on opposing nitrogens are staggered in the diamine complex containing S-dmdabp and S-bn, while those same hydrogens are almost totally eclipsed in the case of the bis(diamine) complex containing S-dmdabp and R-bn. Certainly, judging from the patterns and positions of peaks of ORD and CD spectra of the complexes prepared in this work, a fine example of an extreme case of stereospecificity shown by racemic ligands is demonstrated in the present study.

## References

- (1) W. Z. Theilacker, *Z. Anorg. Chem.*, **234**, 161 (1937).
- (2) L. H. Pignolet, R. P. Taylor and W. D. Horrocks, *J. Amer. Chem. Soc.*, **91**, 5457 (1969).
- (3) W. T. Jordan, C. Y. Lin and B. E. Douglas, *J. Coord. Chem.*, **3**, 103 (1973).
- (4) T. Tanimura, H. Ito, J. Fujita, K. Saito, H. Hirai and K. Yamasaki, *ibid.*, **3**, 161 (1973).
- (5) M. J. Jun and S. R. Choi, Submitted for publication to *J. Korean Chem. Soc.* (1984).
- (6) M. J. Jun, C. R. Radlowski and C. F. Liu, Submitted for publication to *Inorg. Chem.* (1984).
- (7) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 950 (1952).
- (8) B. Bosnich and W. R. Kneen, *Inorg. Chem.*, **9**, 2191 (1970).
- (9) M. J. Jun, C. Radlowski and C. F. Liu, Accepted for publication (in print) by Polyhedron (1984).
- (10) M. J. Jun, C. Radlowski and C. F. Liu, *Inorganica Chim. Acta*, **86**, 101 (1984).