P2, Al1, 2Al2, Al3, and P3, Al1, Al2, 2Al3. P1 is the only phosphorus that is coordinated with two, instead of one, octahedral aluminum. Thus, the ^{31}P peak at -33.6 ppm must be assigned to P1.

Figure 3 also shows that the cross-peaks of the phosphorus lines at -23.3 and -27.5 ppm with the tetrahedral aluminum have different ^{27}Al chemical shifts, 38.3 and 40.3 ppm, respectively. From ^{27}Al DOR experiments,[8] it can be derived that the line at 38.3 ppm corresponds to the ^{27}Al with the largest quadrupolar interaction. This is further substantiated by the larger line width in the F1 dimension. Bearing in mind that the P2 cross-peak with tetrahedral aluminum arises from the dipolar coupling to two Al2 and one Al3, and the P3 cross-peak from coupling to one Al2 and two Al3, we now have two possibilities. If the Grobet assignment for Al2 and Al3 is correct, then P2 resonates at -23.3 ppm and P3 at -27.5 ppm. This must be reversed when the Engelhardt assignment is correct. We conclude that this new type of 2D experiment is a useful tool for the correlation of NMR spectra.

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Chiral N-Substituted Porphyrins Related to Heme Inactivation Products. First Crystallographic Determination of Absolute Stereochemistry and Correlation with Circular Dichroism

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There are various naturally occurring and artificial porphyrins with enantiotopic faces (prochiral) due to specific arrangements of the peripheral substituents, and they can be converted into chiral porphyrins.[1-4] From a biological viewpoint, chiral N-substituted porphyrins with asymmetric nitrogen atoms are the most attractive.[5] Ortiz de Montellano et al. have demonstrated that iron protoporphyrin IX is denatured into the N-substituted derivatives during the metabolic processes mediated by hemoproteins.[6] Since protoporphyrin IX has enantiotopic faces, the *N*-substituted derivatives are chiral. In fact, some optically active N-substituted protoporphyrins IX have been isolated from metabolic systems.[7] However, to date, there are no chiral N-substituted porphyrins whose absolute structures have been defined by X-ray crystallography. The present communication describes the first crystallographic determination of the absolute configuration of a chiral *N*-(2-hydroxyalkyl)etioporphyrin I derivative (**5b**), related to the products of the inactivation of cytochrome P-450 with olefins,[8] and provides a clear correlation with circular dichroism.

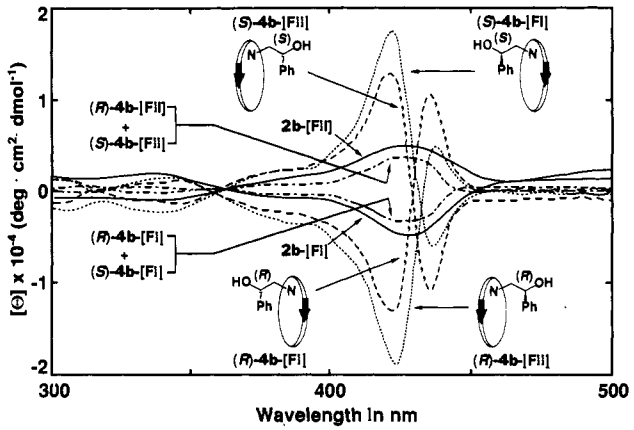
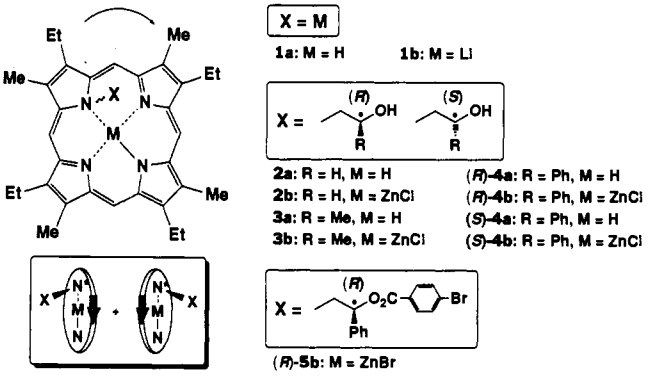


Figure 1. Circular dichroism spectra ($CHCl_3$, 4.3 × 10^{-5} M) of the chlorozinc complexes of the isomers of chiral *N*-(2-hydroxyethyl)etioporphyrin I (**2b**) and *N*-[2-hydroxy-2-phenylethyl]etioporphyrin I (**4b**). The arrows in the schematic illustrations of the isomers indicate the Me → Et sequence in each pyrrole unit.



For the synthesis of a series of *N*-(2-hydroxyalkyl)etioporphyrins I,[9] a novel, efficient route was used, which involves nucleophilic ring opening of epoxides with lithiated etioporphyrin I (**1b**).[10] For example, the reaction of **1b** with ethylene oxide followed by metalation afforded the chlorozinc complex of *N*-(2-hydroxyethyl)etioporphyrin I (**2b**)[11] in 96% yield. When monosubstituted epoxides such as propylene oxide and styrene oxide were reacted with **1b**, they were cleaved exclusively at the O-CH_2 bonds with retention of configuration, to give **3b** and **4b**, respectively, in 78 and 76% yields.[11] In all these cases, no N, N′-disubstituted porphyrins were formed.

Due to the enantiotopic structure of etioporphyrin I (**1a**), **2** should be racemic, while **3** and **4** should be mixtures of diastereoisomers. The isomers of **2a**-**4a** in the free-base forms[11] were resolved by chiral HPLC.[1] For example, racemic **2a** showed two elution peaks with comparable peak areas (fraction I, **2a**-[FI]; fraction II, **2a**-[FII]). On the other hand, for diastereoisomeric *N*-[(*R*)-2-hydroxy-2-phenylethyl]etioporphyrin I ((*R*)-**4a**) derived

† Responsible for the X-ray crystallography in this work.

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(11) All these compounds were unambiguously identified by ^1H NMR or FAB-HRMS, and characterized by UV-visible spectroscopy.

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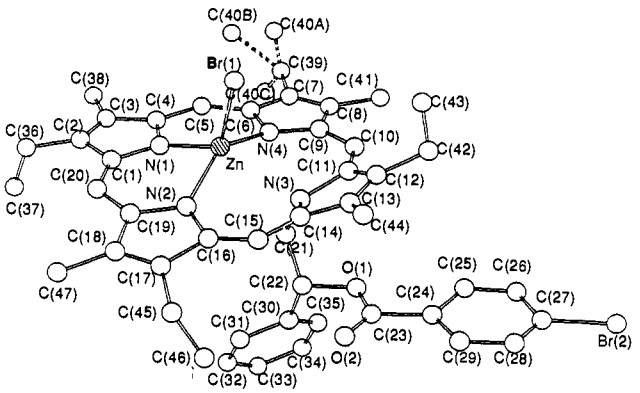

Figure 2. Molecular structure of the bromozinc complex of (*S*)-*N*-[(*R*)-2-(4′-bromobenzoyloxy)-2-phenylethyl]etioporphyrin I ((*R*)-**5b**-[FI]). Selected distances (Å) and angles (degrees): Zn–N(1) 2.04(2), Zn–N(2) 2.08(2), Zn–N(3) 2.13(2), Zn–N(4) 2.13(2), Zn–Br(1) 2.39(2), N(3)–C(21) 1.47(3); Br(1)–Zn–N(1) 120.8(6), Br(1)–Zn–N(3) 98.1(6).

from (*R*)-styrene oxide, two elution peaks with different peak areas (ratio of 2:1 for (*R*)-**4a**-[FI]/(*R*)-**4a**-[FII]) were observed. A similar observation was made for (*S*)-**4a** derived from (*S*)-styrene oxide (peak area ratio of 1:2 for (*S*)-**4a**-[FI]/(*S*)-**4a**-[FII]), indicating the possible discrimination of the two enantiotopic faces of **1b** in the N-alkylation with chiral epoxides.

The circular dichroism (CD) profiles of the stereoisomers of the zinc complexes (**2b**) and (**4b**) are shown in Figure 1. The enantiomers **2b**-[FI] and **2b**-[FII] showed negative and positive CD bands, respectively, in the Soret region (426 nm, Figure 1), which were perfect mirror images of each other with $|[\theta]|$ of ca. 5000 deg·cm^2·dmol^{-1}. In contrast, the diastereoisomers of **4b** showed split Cotton effects with enhanced intensities (Figure 1), where the mirror-image spectral patterns for (*R*)-**4b**-[FI] and (*S*)-**4b**-[FII] ((*R*)-**4b**-[FII] and (*S*)-**4b**-[FI]) indicate that these are the enantiomeric pair. The splitting and enhancement of the CD are obviously due to the induced CD associated with the presence of a chiral, chromophoric N-substituent in proximity to the porphyrin chromophore. When (*R*)-**4b**-[FI] ((*R*)-**4b**-[FII]) was mixed with an equimolar amount of (*S*)-**4b**-[FI] ((*S*)-**4b**-[FII]) to cancel the contribution of the induced CD, the resulting spectrum was virtually identical to that of **2b**-[FI] (**2b**-[FII]) (Figure 1).

The X-ray diffraction analysis was successful on a single crystal of the bromozinc complex ((*R*)-**5b**-[FI]),[12] derived from the diastereoisomer (*R*)-**4b**-[FI] by esterification of the hydroxy group in the N-substituent with 4-bromobenzoyl chloride followed by axial ligand exchange with NaBr. The molecular structure (Figure 2) shows that the N-alkylated pyrrole ring is tilted by 29° from the reference plane of the three nonalkylated nitrogen atoms. When the molecule is viewed from the same side of the alkylated nitrogen atom, the methyl → ethyl sequence at the β-positions of every pyrrole unit is clockwise. Based on this molecular structure, the configurations of (*R*)-**4b**-[FI] and the other three diastereoisomers can be assigned as schematically shown in Figure 1. Thus, the isomers of free-base **4a** eluting first (**4a**-[FI]) and second (**4a**-[FII]) respectively take *S*- and *R*-configurations at the alkylated nitrogen atoms. When these stereochemical structures are correlated with the CD spectra of the mixtures (*R*)-**4b**-[FI] + (*S*)-**4b**-[FI] and (*R*)-**4b**-[FII] + (*S*)-**4b**-[FII] in Figure 1, it can be concluded that the chiral free-base *N*-alkyletioporphyrin I with an *S*-configuration at the alkylated nitrogen atom shows a negative CD band in the Soret region, while the antipode with *R*-configuration shows a positive CD band.

(12) Crystal data and structure determination: orthorhombic; $P2_12_12$; a = 28.933(6), b = 13.171(3), c = 13.942(3) Å; D_{calcd} = 1.158 g·cm^{-3}; Z = 4. Intensity data were collected on a Rigaku AFC-5R (rotating anode) diffractometer and refined by full-matrix least-squares techniques. Out of 8560 reflections observed, as few as 2488 satisfied $I > 3\sigma(I)$; thus only the heavier atoms were refined anisotropically. One of the ethyl groups was disordered. The final R, R_w, and GOF were 0.086, 0.116, and 3.89, respectively.

Further studies are in progress to establish the general rule for deducing the structure–circular dichroism relationship of a series of chiral porphyrins with asymmetric nitrogen atoms.

Supplementary Material Available: Listings of detailed synthetic procedures and spectral data for **2a**–**4a** and **2b**–**4b**, crystal data and experimental conditions, positional and thermal parameters for (*R*)-**5b**-[F1], and bond distances and angles (11 pages); observed and calculated structure factors for (*R*)-**5b**-[F1] (18 pages). Ordering information is given on any current masthead page.

A Versatile Route to the β-Substituted π-Allyl Complexes via Addition to a Cationic η^3-Propargyl Complex of Platinum

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π-Allyl complexes constitute an important class of compounds in organometallic chemistry, and they are useful for organic synthesis.[1] Metal-activated allylic functionalization further increases the versatility of such complexes.[2] A recent study on the η^3-propargyl complex by Casey et al. showing that the central carbon of a (propargyl)rhenium complex is prone to nucleophilic addition, yielding the β-substituted metallacyclobutene,[3] prompts us to report our independent discovery of a cationic η^3-propargyl complex of Pt(II). The unique propargyl feature remarkably enhances its reactivity toward a wide spectrum of organic substrates, opening a convenient path to the β-substituted π-allyl derivatives. Thus our work contributes to remedy the paucity of methodology in the synthesis of β-substituted π-allyl complexes.

In a typical procedure, *trans*-Pt(η^1-CH═C═CH$_2$)(Br)(PPh$_3$)$_2$ (**1**) (460 mg) was reacted with an equimolar amount of $AgBF_4$ (118 mg, 1.1 equiv) in 7 mL of degassed CH_2Cl_2 at −30 °C, which instantaneously resulted in the formation of a novel cationic η^3-propargyl derivative [Pt(η^3-CH$_2$CCH)(PPh$_3$)$_2$](BF$_4$) (**2**).[4] After AgBr was removed by filtration, the addition of degassed hexane to the solution caused the crystallization of whitish-yellow product. The isolated yield of **2** was 80% (370 mg). In the solid state, **2** is stable under dry nitrogen but rapidly deteriorates in air. It also suffers slow thermal decomposition in solutions at 20 °C. In various NMR spectra,[5] all ^{1}H, ^{13}C, and ^{31}P resonances of **2** show coupling only to a single ^{195}Pt nucleus and to two ^{31}P nuclei, suggesting that **2** is a mononuclear species with the Pt-(η^3-C$_3$H$_3$)(PPh$_3$)$_2$ composition. In the ^{1}H-coupled ^{13}C NMR

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