fluorobenzene (Lancaster) was fractionally distilled before used. Adamantane (Aldrich) was used without further purification. Water was deionized and fractionally distilled from $KMnO_4$. All other reagents were commercial samples and used as received. The porphyrins, TPP,[14] *p*-FTPP,[14] *m*-FTPP,[14] *o*-FTPP,[14] *p*-CF_3TPP,[15] 2,6-F_2TPP,[16] *p*-CH_3OTPP,[16] and F_{20}TPP,[17] were made by literature methods. These complexes were then metalated by the method of Alder,[18] and the axial ligands, were exchanged by the method used by Ogoshi on the corresponding iron complexes.[19] These compounds after recrystallization, all gave satisfactory elemental analysis and electronic absorption spectra. Pentafluoroiodosylbenzene (PFIB),[20] and iodosylbenzene (PhIO),[21] prepared by literature methods, were titrated iodometrically and shown to be ≥99% pure. Both iodosylarenes were stored under argon at −25 °C.

Functionalization Reactions. The reactions were conducted and analyzed by similar procedures in all cases. In a typical reaction, 2×10^{-4} mol of iodosylarene (10 equiv based on metalloporphyrin catalyst) were added to a magnetically stirred degassed solution of 14.2 mg (2×10^{-5} mol) of $Mn^{III}TPPN_3$ in 5 mL of degassed benzene containing 8×10^{-4} mol of adamantane substrate, and, as a second liquid phase, 3.0 mL of saturated aqueous sodium halide (azide), under an Ar atmosphere contained in a 25- or 50-mL Schlenk flask. All reactions were carried out at 22 °C. After a reaction time of 3 h, the marginally soluble polymeric oxygen donor (PhIO or PFIB) had been consumed. Internal standard was added, and the contents of the reaction vessel analyzed immediately by GC and GC/MS.

Acknowledgment. We wish to thank the U.S. Army Research Office and ARCO Chemical Co. for support of this research and Susan D. Richardson for her assistance in acquiring mass spectral data on the metalloporphyrins.

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Notes

Determination of the Enantiomeric Purity of Chiral Allyl Alcohols and Allyl Ethers by ^{195}Pt NMR Spectroscopy

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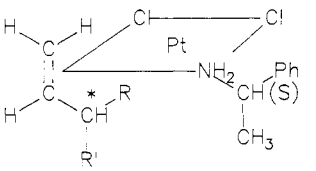
NMR methods have been widely used for determining the enantiomeric purity of organic compounds.[1] A possible approach is to convert an enantiomeric mixture to a diastereoisomeric pair with an appropriate chiral derivatizing agent and then to measure the resonances of the diastereotopic groups, most commonly by ^1H and ^{19}F NMR, and, occasionally, by ^{13}C and ^{31}P NMR.[1] No cases have been reported in which the enantiomeric purity was determined by detecting the ^{195}Pt NMR resonances of diastereoisomeric platinum(II) complexes.

In this paper we show how ^{195}Pt NMR measurements on the diastereoisomeric complexes *cis*-dichloro[(*S*)-α-methylbenzylamine][CH_2=CHCH(R)R′]Pt(II), **1**, (R = OH, OMe; R′ = alkyl or aryl) (Figure 1) can be used to determine the enantiomeric purity of chiral allyl alcohols and allyl ethers. The complexes were prepared by adding the unsaturated alcohol or ether to *cis*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II)[2] in $CHCl_3$ solution. On standing at room temperature for a few minutes, the unsaturated compound replaces the coordinated ethylene, and this reaction is driven to completion by removing ethylene.



R = OH, OMe; R' = alkyl or aryl

complex 1

Figure 1. Complexes *cis*-dichloro[(*S*)-α-methylbenzylamine]-[CH_2=CHCH(R)R′]platinum(II).

The complex *cis*-dichloro[(*S*)-α-methylbenzylamine]-[CH_2=CHCH(OH)Me]platinum(II), **1a**, forms four diastereoisomers, which arise from the chiral center in the alcohol and binding of the two prochiral faces of the double bond (Figure 2). The ^{195}Pt NMR spectrum (^{195}Pt $I = 1/2$, natural abundance 33.8%) of **1a** shows four well-resolved resonances due to these diastereoisomers at −2689, −2711, −2720, and −2740 ppm relative to Na_2PtCl_6 (Figure 3). In contrast, the analogous complex containing the *R* antipode of the same alcohol (optical purity >98%) shows only the resonances at −2689 and −2740 ppm (Figure 3), which must be assigned to the two epimers containing the *R* antipode. Thus the absorptions at −2711 and −2720 ppm are due to the two epimers containing the S antipode.

In addition, when complex **1a** is prepared by using an excess of the ethylene complex with respect to racemic α-methyl allyl alcohol (molar ratio 1.5:1), the sum of the areas of the two peaks produced by the *R* antipode at −2689 and −2740 ppm equals the sum of the areas of the

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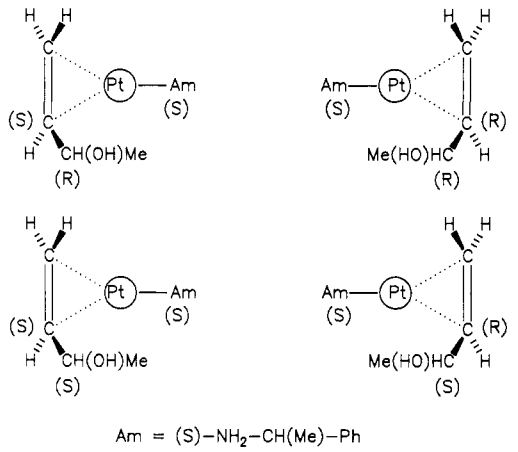

Figure 2. Diastereoisomeric complexes *cis*-dichloro[(*S*)-α-methylbenzylamine][CH_2=CHCH(OH)Me]platinum(II) formed by coordination of the *R* and *S* antipodes of CH_2=CHCH(OH)Me.

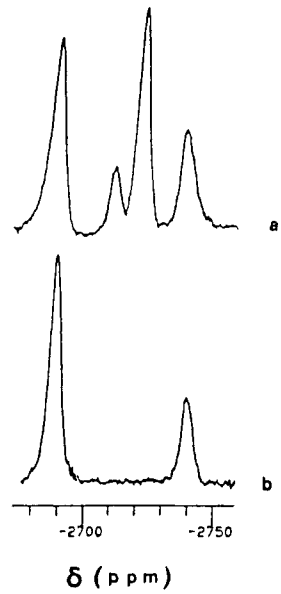

Figure 3. ^{195}Pt NMR spectra (64.3 MHz, acetone-d_6, in ppm referred to Na_2PtCl_6) of complex *cis*-dichloro[(*S*)-α-methylbenzylamine][α-methylallyl alcohol]platinum(II) **1a**. (a) Spectrum of the complex containing the racemate. (b) Spectrum of the complex containing the *R* antipode.

two peaks due to the *S* antipode at −2711 and −2720 ppm. In this case any enrichment due to preferential coordination of one antipode is avoided, so the ^{195}Pt NMR spectrum reflects the enantiomeric composition of the allyl alcohol used in the preparation of the complex.

As shown in Table I, the platinum spectra of other complexes containing allyl alcohols, **1b–d**, in which R′ is an alkyl or aryl group, show similar patterns: four resonances are detected in all cases with use of the racemic alcohol.

The investigation was extended to the diastereoisomeric complexes **1e,f** containing α-alkylallyl alkyl ethers. The complex *cis*-dichloro[(*S*)-α-methylbenzylamine][α-methylallyl methyl ether]platinum(II), **1e**, shows four ^{195}Pt resonances (Table I), whereas complex **1f**, containing α-methylallyl isopropyl ether, gives only three resonances at −2695, −2716, and −2732 ppm (Table I). As the sum of the areas of the peaks at −2695 and −2732 ppm equals the area of the signal at −2716 ppm, the absorptions at −2695 and −2732 ppm are assigned to the two epimers formed by the coordination of one antipode of the allyl ether, while the resonance at −2716 ppm is due to the other antipode.

Table I. ^{195}Pt NMR Chemical Shifts (δ in ppm from Na_2PtCl_6) of Diastereoisomeric Complexes *cis*-Dichloro[(*S*)-α-methylbenzylamine][CH_2=CHCH(R)R′]-platinum(II), 1[a]

R	R′	complex	δ
OH	Me	**1a**	−2689, −2711, −2720, −2740
OH	iPr	**1b**	−2700, −2719, −2741, −2757
OH	tBu	**1c**	−2660, −2680, −2696, −2707
OH	Ph	**1d**	−2667, −2678, −2690, −2698
OMe	Me	**1e**	−2698, −2721, −2743, −2763
OMe	iPr	**1f**	−2695, −2716, −2732

[a] Acetone-d_6, 25 °C. The ^{195}Pt resonance of the ethylene complex is at −2780 ppm.

We have suggested previously[3-5] that the small differences observed in the ^{195}Pt chemical shifts (Table I) are caused by different deshielding effects on the metal nucleus, arising from different conformations of the organic ligands in the four diastereoisomers.[6]

Our results clearly indicate that the ^{195}Pt NMR spectra of chiral platinum(II) complexes containing a primary amine cis to an allyl alcohol or an allyl ether can be used to detect the diastereoisomers containing the *R* or *S* antipode of the allyl compound. Thus the enantiomeric purity of allyl alcohols and allyl ethers can be easily evaluated.

The method is both practical and economical, because the complexes **1** are easily formed, only small amounts are needed (ca. 50–70 mg in a 5-mm tube), and the ^{195}Pt NMR measurement can be made more quickly than other separation methods. Further, the coordinated allyl ether can be displaced quantitatively from the complex by an excess of ethylene, so that both the ethylene complex and the chiral allyl ether can be recovered.

Experimental Section

Preparation of the Alcohols and Ethers. (*R,S*)-α-Methylallyl alcohol obtained from Aldrich was not purified further, but was directly resolved as described by Kenyon and Snellgrove.[7] α-Isopropylallyl alcohol,[8] α-*tert*-butylallyl alcohol,[8] and α-phenylallyl alcohol[9] were prepared from propenal and isopropylmagnesium bromide, *tert*-butylmagnesium bromide, and phenylmagnesium bromide, respectively. The methyl ethers were prepared from the corresponding alcohols by reaction first with sodium hydride and then with methyl iodide.[10] All compounds were purified by fractional distillation and characterized by ^{1}H NMR spectroscopy.

Preparation of Complexes 1a–f. Complex 1a. On treatment of *cis*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II)[2] (0.5 g, 1.2 mmol) in $CHCl_3$ solution (6 mL) with α-methylallyl alcohol (0.087 g, 1.2 mmol), the ethylene was immediately displaced. Removal of the solvent under vacuum afforded *cis*-dichloro[(*S*)-α-methylbenzylamine](α-methylallyl alcohol)Pt(II), complex **1a**, quantitatively as a pale yellow microcrystalline solid (0.55 g, 1.2 mmol). Crystallization of the crude product at room temperature from $CHCl_3$/pentane (6 mL, 1:2) yielded the complex **1a** as pale yellow crystals (0.33 g, 0.72 mmol), mp 148 °C. Anal.

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Calcd for $C_{12}H_{19}Cl_2NOPt$: C, 31.38; H, 4.17; N, 3.05. Found: C, 31.02; H, 4.30; N, 3.16.

By the same procedure, complex **1a** was also prepared from an excess of the ethylene complex with respect to the α-methylallyl alcohol (molar ratio 1.5:1) in $CHCl_3$ solution. In this case, the isolated solid was a mixture of **1a** and unreacted ethylene complex.

Complexes 1b-f. Complexes **1b-f** were obtained via the procedure described for complex **1a**. In all cases ethylene was substituted quantitatively by the unsaturated ether or alcohol. The complexes were crystallized from $CHCl_3$/pentane (1:2), yields after crystallization being about 60-70%. Elemental analyses and melting points of the crystallized complexes are as follows.

1b: mp 129 °C. Anal. Calcd for $C_{14}H_{23}Cl_2NOPt$: C, 34.50; H, 4.75; N, 2.87. Found: C, 34.22; H, 4.51; N, 3.07.

1c: mp 123 °C. Anal. Calcd for $C_{15}H_{25}Cl_2NOPt$: C, 35.93; H, 5.03; N, 2.79. Found: C, 35.22; H, 5.42; N, 2.53.

1d: mp 151 °C. Anal. Calcd for $C_{17}H_{21}Cl_2NOPt$: C, 39.17; H, 4.06; N, 2.69. Found: C, 40.24; H, 4.23; N, 2.51.

1e: mp 110 °C. Anal. Calcd for $C_{13}H_{21}Cl_2NOPt$: C, 32.99; H, 4.47; N, 2.96. Found: C, 32.87; H, 4.54; N, 2.42.

1f: mp 92 °C. Anal. Calcd for $C_{15}H_{25}Cl_2NOPt$: C, 35.93; H, 5.03; N, 2.79. Found: C, 34.57; H, 5.12; N, 2.31.

NMR Measurements. NMR spectra were recorded in acetone-d_6 on a Varian VXR-300 spectrometer operating at 64.3 MHz for ^{195}Pt. The ^{195}Pt resonance of *cis*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II) is at higher field (-2780 ppm) than the absorptions due to complexes **1a-f**. All ^{195}Pt NMR chemical shifts are referenced to Na_2PtCl_6 as external standard.

Thioaminyl Diradicals: An Electron Spin Resonance Spectroscopic Study[1]

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In a series of electron spin resonance (ESR) spectroscopic studies of a new class of nitrogen-centered free radicals, we have found that thioaminyls (RNSR′) are persistent nitrogen-centered free radicals. For instance, some thioaminyls have been isolated as radical crystals[2] or hydrazine-like dimers, which dissociate in solution into the corresponding radicals at room temperature.[3,4] These interesting persistent properties of thioaminyls can be interpreted as a result of significant stabilization of radicals by conjugative delocalization of the unpaired electron from nitrogen to sulfur.

The present work is concerned with an ESR study of aromatic thioaminyl diradicals,[5] which has been performed as part of a program directed toward the syntheses of organic ferromagnetic materials. In the present study we have found that thioaminyl diradicals in solution exists as diradical oligomers, which are in equilibrium with diamagnetic cyclic compounds that can be isolated as crystals. Herein we report generation of thioaminyl diradicals and their ESR spectra and isolation of the cyclic compounds and their characterization.

(1) ESR studies of nitrogen-centered free radicals 33. Part 32: Miura, Y.; Ohonishi, T. *J. Org. Chem.* **1988**, *53*, 3012-3016.
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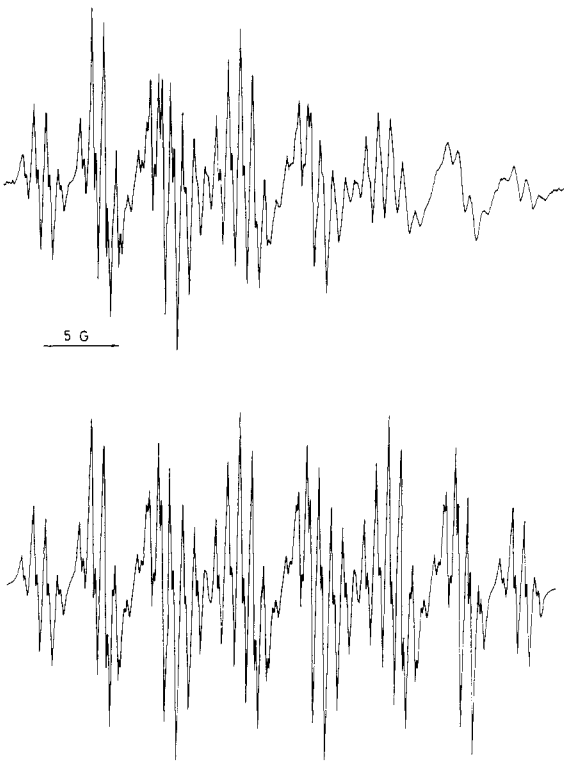
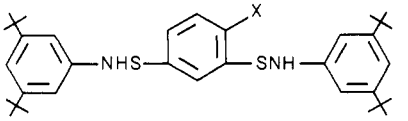


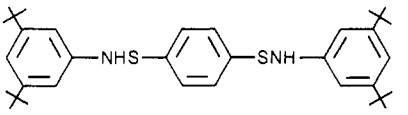
Figure 1. Experimental ESR spectrum of **3a** detected from a solution of **5a** in benzene at 17 °C (top) and computer-simulated ESR spectrum reconstructed by using the parameters listed in Table I (bottom).

Results and Discussion

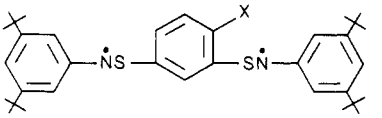
Thioaminyl diradicals **2** were generated by oxidation of precursors **1** with PbO_2. When PbO_2 was added to a stirred solution of **1** in benzene, the colorless solution immediately turned dark blue or dark greenish blue and the resulting colored solution gave an intense ESR signal. An ESR



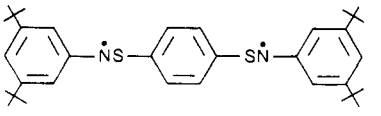
1a: X = H
b: X = Cl



1c



2a: X = H
b: X = Cl



2c

spectrum from a dilute solution of **2a** is illustrated in Figure 1. Although the radical solution was, after removal of the PbO_2, allowed to stand at room temperature for 1 day, the blue color still remained without fading. This observation indicates that the thioaminyl diradicals are

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