

Figure 1. 500-MHz ^1H NMR spectra (in benzene- d_6) of (a) products of reaction of $\text{Cp}_2(\text{Cl})\text{ZrH}$ and $\text{CH}_2=\text{CHPh}$ and (b) products of reaction of $\text{Cp}_2(\text{Cl})\text{ZrD}$ and $\text{CH}_2=\text{CHPh}$.

incorporation into $\text{Cp}_2(\text{Cl})\text{ZrCH}_2\text{CH}_2\text{Ph}$ is observed when it is treated with an equivalent of $\text{CHD}=\text{CDPh}$ (benzene- d_6 , 25 °C; ^1H NMR).

The fast process is remarkable, not only because it is specific for exchange between β -positions but also because it occurs rapidly after hydrozirconation is complete and without exchange with free styrene. Given these very restrictive requirements, we suggest the mechanism in Scheme I (shown for 1 only). The following points are particularly notable: (i) scrambling is catalyzed by a small amount of a zirconium alkyl hydride complex, $\text{Cp}_2(\text{H})\text{ZrR}$, produced from the Cp_2ZrH_2 present in the initial preparation of $\text{Cp}_2(\text{Cl})\text{ZrH}^6$ (exchange between metal and β -alkyl positions has previously been demonstrated in such a compound);¹⁰ (ii) the geometry of the olefin-dihydride intermediate must be that shown (otherwise this mechanism would interconvert 1 and 2 and thus provide facile α -exchange),¹¹ (iii) chain-propagating hydride-for-chloride exchange proceeds via bridged dimers (all such $\text{Cp}_2(\text{X})\text{ZrH}$ species are at least dimeric). In accord with the proposed mechanism, when solutions of 1- d_0 and 1- d_9 in benzene- d_6 , each containing ca. 0.5 equiv of acetone to convert any $[\text{Zr}-\text{H}]$ to $[\text{Zr}-\text{OCHMe}_2]$, are mixed, no H/D exchange is observed, even after 12 h.

Since stereospecific hydrozirconation can be effected in the neohexyl system,² scrambling must not take place there; we have verified that the reaction of $\text{Cp}_2(\text{Cl})\text{ZrD}$ with $\text{CH}_2=\text{CHCMe}_3$ gives no detectable isotopomers other than the expected $\text{Cp}_2(\text{Cl})\text{ZrCH}_2\text{CHDCMe}_3$. Which result is the anomaly: scrambling for styrene or the failure to

scramble for neohexene? Although a thorough study has not yet been carried out, no scrambling is found in the reactions of $\text{Cp}_2(\text{Cl})\text{ZrD}$ with $\text{CH}_2=\text{CHCH}_2\text{Ph}$ or $\text{PhCH}=\text{CHCH}_3$.¹² These preliminary results suggest that styrene is the special case; perhaps the olefin complex is stabilized by conjugation relative to alkyls 1 and 2,¹³ thus accelerating the β -elimination steps in Scheme I. It is striking that styrene is also special in that it gives significant amounts of the nonterminal hydrozirconation product, but this work suggests that these two manifestations of special behavior are not interconnected in any obvious manner.

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(12) NMR of the hydrozirconation products confirms Gibson's inference, again based only on derived alcohols,^{5a} that $\text{PhCH}_2\text{CH}=\text{CH}_2$ gives mostly the terminal and $\text{PhCH}=\text{CHCH}_3$ initially the benzylic which slowly rearranges to the terminal product. Full details, including the fate of a D label during the rearrangement, will be reported later.

(13) Stabilization of olefin-hydride relative to inserted alkyl by phenyl has been inferred for the sterically (but not electronically) similar systems $\text{Cp}_2\text{NbH}(\text{CH}_2=\text{CHR})$: Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* 1988, 110, 3134.

Synthesis and Spectroscopic Investigations of Optically Active Alkylaluminum Compounds of *l*-Ephedrine. The Crystal Structure of the $[\text{Me}_2\text{Al}(\text{O}-(R)\text{-CHC}_6\text{H}_5((S)\text{-CH}((S)\text{-NHCH}_3)\text{CH}_3))]_2$ Dimer: An Optically Active Five-Coordinate Aluminum Complex

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Summary: The reaction of *l*-ephedrine with a trialkylaluminum affords the compound $[\text{R}_2\text{Al}(\text{O}-(R)\text{-CHC}_6\text{H}_5((S)\text{-CH}((S)\text{-NHCH}_3)\text{CH}_3))]_2$ ($R = \text{Me}$, 1; $R = \text{Et}$, 2) in high yield. Compounds 1 and 2 contain a five-coordinate aluminum center with a central Al_2O_2 ring and an Al-N dative bond. The formation of the Al-N dative bond is stereospecific, resulting in 100% induction of optical activity at the nitrogen center. This is indicated from the optical rotations, $[\alpha]^{25}$, and confirmed by the crystal structure of 1. Compound 1 crystallizes in the tetragonal space group $P4_12_12$ with unit cell parameters $a = b = 8.614$ (1) Å, $c = 35.348$ (5) Å, $V = 2622.61$ (6) Å³, and D_{calc} = 1.12 g cm⁻³ for $Z = 4$. Least-squares refinement based on 891 observed reflections ($F_o \geq 2.5\sigma(F)$) converged at $R = 6.3\%$ ($R_w = 4.0\%$). The Al_2O_2 ring system is unsymmetrical with Al-O and Al-O' distances of 1.86 and 1.95 Å, respectively. The coordination around the Al atom can be further described as a distorted trigonal bipyramid with an exceptionally long Al-N bond of 2.19 Å. The molecules undergo a dynamic process which averages the nonequivalent Al-Me and Al-Et groups. This averaging process is thought to result from the dissociation of the Al-N bond without disruption of the Al_2O_2 ring and occurs with an activation energy of 24.4 kcal/mol for 1.

(10) Gell, K. J.; Schwartz, J. *J. Am. Chem. Soc.* 1978, 100, 3246.

(11) Since this result apparently requires that H-D exchange is facile but olefin rotation is very slow, one might speculate that the bonding is better described as metallacyclopropane-dihydrogen than as olefin-dihydride as shown in Scheme I. Alternatively, the interchange of H and D in the olefin-dihydride complex might occur by the "Tarzan swing" mechanism described for $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{WH}_2\text{D}]^+$; Parkin, G.; Bercaw, J. E. *Polyhedron* 1988, 7, 2053-2082.

Although several structures of organoaluminum complexes have been reported where the aluminum center is five-coordinate,¹⁻³ there have been no structurally characterized complexes in which the aluminum was bound to an optically active bidentate substituent. In this paper, we report the synthesis and characterization of two optically active organoaluminum complexes where the aluminum center is five-coordinate. These are the complexes $[R_2Al(O-(R)-CHC_6H_5((S)-CH((S)-NHCH_3)CH_3))_2]$, where R = methyl, 1, or ethyl, 2.

The synthesis of the title compounds involved the treatment of an Et_2O solution of *l*-ephedrine at 20 °C with 1 equiv of the corresponding R_3Al to give a precipitate of $[R_2Al(O-(R)-CHC_6H_5((S)-CH((S)-NHCH_3)CH_3))_2]$ in >95% for 1 and 84% for 2.⁴

The optical rotations, $[\alpha]^{25}$, for *l*-ephedrine, 1, and 2 are +3.7° (1.01 g/100 mL, toluene),⁵ -53.5° (1.0 g/100 mL, toluene), and -34.3° (0.96 g/100 mL, toluene), respectively. It is apparent from these values that the induction of optical activity at the nitrogen center significantly influences the $[\alpha]^{25}$. If the nitrogen center did not become optically active, then a general decrease in the $[\alpha]^{25}$ should be observed as the bulk of the alkyl substituent on the aluminum increases.⁶ Further, the optical rotation of 1 is temperature dependent shifting from -35.7° (25 °C) to -19.7° (38 °C) for a 0.43 g/100 mL solution consistent with a temperature-dependent equilibrium between five- and

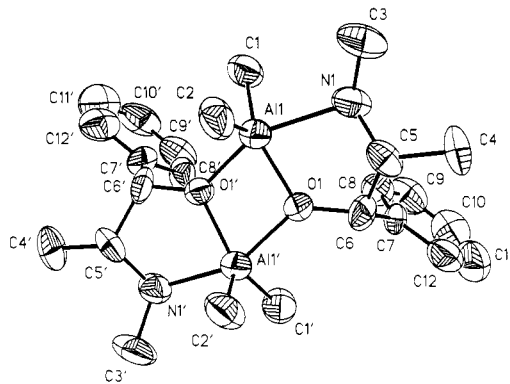


Figure 1. A ORTEP diagram of the $[Me_2Al(O-(R)-CHC_6H_5((S)-CH((S)-NHCH_3)CH_3))_2]$ dimer (1) with the atoms labeled. The primed atoms are symmetry-related; hydrogen atoms have been omitted for the sake of clarity. The important bond distances and angles are as follows: Al1-Al1' = 3.000 (4) Å; Al1-O1 = 1.864 (6) Å; Al1-O1' = 1.946 (7) Å; Al1-N1 = 2.193 (8) Å; Al1-C1 = 1.999 (8) Å; Al1-C2 = 1.989 (9) Å; Al1-O1-Al1' = 104.0 (3)°; O1-Al1-O1' = 74.8 (3)°; O1-Al1-N1 = 78.5 (3)°; O1-Al1-C1 = 127.7 (3)°; O1-Al1-C2 = 113.7 (3)°; O1'-Al1-N1 = 151.6 (3)°; O1'-Al1-C1 = 98.0(3)°; O1'-Al1-C2 = 100.0 (3)°; N1-Al1-C1 = 90.7 (3)°; N1-Al1-C2 = 99.3 (3)°; C1-Al1-C2 = 118.5(4)°.

Table I. Aluminum-Oxygen and Aluminum-Nitrogen Bond Distances (Å) in Selected Organoaluminum Derivatives

compound	Al-O	Al-N
$[Me_2Al(l\text{-mentholate})]_2^a$	1.84	
$[Me_2Al(l\text{-borneolate})]_2^a$	1.84	
$[Me_2Al(2\text{-allyl-6-methylphenoxide})]_2^b$	1.86	
$[(Me_2AlO-AlMe_3)_2]^{2-}; 2[As(CH_3)_4]^{2-}$	1.78, 1.80	
$[Me_2AlOC(Ph)N(Ph)CH(Me)O]_2^d$	2.05, 1.99, 1.86	
$[Me_2AlOC_2H_4OMe]_2^e$	2.27, 1.89, 1.83	
$[(i\text{-Bu})_2AlOCH_2\text{-}2\text{-C}_5\text{H}_4\text{N}]_2^f$	1.94, 1.85	2.13
$(Me_3Al)\cdot NCCCH_3^g$		2.02
$Cs[(Me_3Al)\cdot N_3]^h$		1.97
$K[Al_2(Me_3)_6SCN]^i$		1.94
$Cl_2AlN(C_2H_5)_2C_2H_4N(CH_3)_2^j$		1.77, 1.96
$[(Me_2Al)\cdot NMe_3]^k$		2.02
$(Me_3Al)\cdot \text{quinuclidine}^k$		2.06
$[Me-(S)-CH(C_6H_5)NHAIME_2]_2^l$		1.94, 1.95
$[Me_2Al(O-(R)-CHC_6H_5((S)-CH((S)-NHCH_3)CH_3))_2]$	1.95, 1.86	2.19

^a Reference 6. ^b Kumar, R.; Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics*, submitted for publication. ^c Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302. ^d Reference 2. ^e Reference 3. ^f Reference 1. ^g Atwood, J. L.; Seale, S. K.; Roberts, D. H. *J. Organomet. Chem.* **1973**, 51, 105. ^h Atwood, J. L.; Newberry, W. R. III *J. Organomet. Chem.* **1975**, 87, 1. ⁱ Zaworotko, M. J.; Atwood, J. L. *Inorg. Chem.* **1980**, 19, 268. ^j Atwood, J. L.; Milton, P. A. *J. Organomet. Chem.* **1973**, 52, 275. ^k Whitt, C. D.; Parker, L. M.; Atwood, J. L. *J. Organomet. Chem.* **1971**, 32, 291. ^l Robinson, G. H.; Sangokoya, S. A.; Rogers, R. D. *Polyhedron* **1988**, 7, 2727.

four-coordinate species; however, this also could result from other temperature-dependent effects.

The structure of 1 was confirmed by single-crystal X-ray diffraction studies⁷ and is shown in Figure 1. This structure shows several interesting features. First, the nitrogen center becomes chiral upon coordination to the aluminum atom and there is 100% induction of optical activity at the nitrogen center, which is determined from the space group $P4_12_1$, which requires that all of the ni-

(7) Crystal data at 293 K with $Cu K\alpha$ ($\lambda = 1.54178$ Å) radiation for 1: tetragonal, space group $P4_12_1$ (No. 92); $a = b = 8.614$ (1) Å, $c = 35.348$ (5) Å, $\alpha = \beta = \gamma = 90.000^\circ$, $V = 2622.61$ (6) Å³, D_{calc} = 1.12 g cm⁻³, and $Z = 4$; $R = 6.3\%$, $R_w = 4.0\%$. Intensity data were collected by using the $\theta/2\theta$ scans over the range 8–100° on a Nicolet P3/V diffractometer. A total of 1313 unique reflections were collected; 891 with $F_o \geq 2.5\sigma(F)$ were used in the final refinement.

(1) van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K.; Kojić-Prodić, B.; Spek, A. L. *Organometallics* **1985**, 4, 1701 and references therein.

(2) Kai, Y.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1972**, 45, 3392.

(3) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem.* **1983**, 95, 808.

(4) General experimental conditions: All solvents were purified and dried by standard techniques. Argon gas was purified by passing through a series of columns containing Deox catalyst, phosphorous pentoxide, and calcium sulfate. Aluminum alkyls (Aldrich: 2.0 M Me_3Al solution in toluene and 1.9 M Et_3Al solution in toluene) and *l*-ephedrine (Aldrich) were used as received. All glassware used in the synthetic work was oven dried, and standard Schlenk line techniques were employed. Optical rotations were recorded on a Perkin-Elmer 241 MC polarimeter at 25 °C. Routine ¹H and ¹³C NMR spectra were recorded on a General Electric QE 300 spectrometer at 25 °C. The chemical shifts were referenced to residual protic benzene-*d*₆ peaks ($\delta = 7.15$ ppm). Variable-temperature NMR studies were carried out on a GN 300 spectrometer on toluene-*d*₆ solutions. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. **Reaction of $AlMe_3$ with *l*-Ephedrine, 1.** *l*-Ephedrine (1.03 g, 6.23 mmol) was dissolved in Et_2O (60 mL), and $AlMe_3$ (3.12 mL, 6.23 mmol) was syringed as quickly as permitted by the evolution of methane gas (ca. 5 min). The resulting reaction was rapid and exothermic. A white precipitate formed as the solution was stirred for an additional period of 5 h. The solution was decanted leaving a white solid that was washed with 10–15 mL of very cold pentane and dried in vacuo. This solid was identified as $[Me_2Al(O-(R)-CHC_6H_5((S)-CH((S)-NHCH_3)CH_3))_2]$ and was recrystallized from hot toluene: Yield >95%; mp 215–216 °C. Anal. Calcd for $C_{12}H_{20}AlNO$: C, 65.14; H, 9.11; N, 6.33. Found: C, 64.67; H, 9.24; N, 6.21. ¹H NMR: δ 7.27–7.02 (m, 5 H), 4.90 (d, ³J = 5.8 Hz, 1 H), 2.81 (m, 1 H), 1.62 (d, ³J = 6.3 Hz, 3 H), 0.90 (m, 1 H), 0.24 (d, ³J = 6.6 Hz, 3 H), -0.51 (s, 3 H), -0.85 (s, 3 H). ¹³C NMR: δ 140.5, 128.3, 127.7, 127.5, 74.6 (O-CH), 57.7 (N-CH), 30.4 (N-CH₃), 14.4 (CH-CH₃), -7.7 (Al-C), -11.5 (Al-C). **Reaction of $AlEt_3$ with *l*-Ephedrine, 2.** The procedure for this reaction is the same as above using *l*-ephedrine (1.02 g, 6.17 mmol) and $AlEt_3$ (3.25 mL, 6.17 mmol). The volume of the solution was slowly reduced in vacuo leaving a white solid. The product was washed with 10–15 mL of very cold pentane and dried in vacuo and was identified as $[Et_2Al(O-(R)-CHC_6H_5((S)-CH((S)-NHCH_3)CH_3))_2]$; yield 84%; mp 122–124 °C. Anal. Calcd for $C_{14}H_{24}AlNO$: C, 67.44; H, 9.70; N, 5.62. Found: C, 65.06; H, 9.49; N, 5.57. ¹H NMR: δ 7.27–7.03 (m, 5 H), 4.95 (d, ³J = 5.6 Hz, 1 H), 2.93 (m, 1 H), 1.77 (d, ³J = 6.0 Hz, 3 H), 1.56 (vb, 3 H), 1.15 (m, 1 H), 1.05 (vb, 3 H), 0.25 (d overlapping m, ³J = 6.4 Hz, 5 H), -0.31 (vb, 2 H). ¹³C NMR: δ 140.4, 128.3, 127.7, 127.4, 127.5, 75.7 (O-CH), 58.0 (N-CH), 31.1 (N-CH₃), 14.5 (CH-CH₃), 11.6 (Al-C₂), 9.8 (Al-C₃), 3.5 (Al-C₁), 0.5 (Al-C₄).

(5) The optical rotation reported by Aldrich for *l*-ephedrine (catalogue no. 13,491-0), $[\alpha]^{25}$, -41°, is for a 1 N HCl solution with concentration of $c = 5$ g/100 mL.

(6) Sierra, M. L.; Kumar, R.; de Mel, V. S. J.; Oliver, J. P. *Organometallics*, submitted for publication.

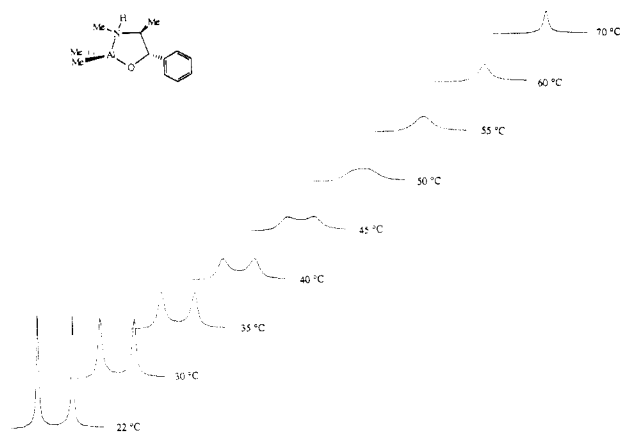


Figure 2. Variable-temperature ^1H NMR of **1** (0.205 M, toluene- d_6). Only the region associated with the methyl groups bound to aluminum is shown.

trogen atoms in the unit cell be equivalent. Second this is the first example of a monodentate secondary amine bound to a five-coordinate Al atom and has an unusually long Al-N distance of 2.19 Å. Third, the two methyl groups on aluminum, C1 and C2, are nonequivalent by symmetry. Each of these features influences the behavior of this compound. The first through the induction of the optical activity at the nitrogen already cited, while the second and third are of importance in the dynamic exchange processes associated with this molecule.

The geometry around the aluminum center can be described as distorted trigonal bipyramidal, where both aluminum methyl C atoms and the covalently bound O1 atom of the *l*-ephedrine substituent lie in the equatorial plane. The apical Al1-O1' distance is significantly longer (1.95 Å) than the equatorial Al1-O1 distance (1.86 Å). Table I compares the Al-O bond distances of several organoaluminum complexes which also contain an Al_2O_2 ring. The apical Al1-N1 dative bond length of 2.19 Å is significantly longer than those reported for other Al-N bonds (see Table I). This observation is in line with the results obtained by van Koten et al.¹ with the lengthening of the Al-N dative bond due to the geometry around the aluminum center and suggests that breaking the nitrogen-aluminum bond should be a relatively low-energy process. A further manifestation of this is seen in the relatively strained five-membered heterocyclic ring Al-O1-C6-C5-N1 which contains a relatively sharp O-Al-N angle of 78.5° and shows some distortion around the carbon atoms with significant deviation from tetrahedral geometry. A discussion of this will be presented in a full paper discussing this and related five-coordinate aluminum derivatives.

The variable-temperature ^1H NMR of **1** is shown in Figure 2. At 22 °C the methyl groups are nonequivalent which is consistent with the structure observed in the solid state. As the temperature is increased, the lines associated with these groups broaden and coalesce indicating that the magnetic environment is averaged on the NMR time scale. The energy of activation, ΔE_a , for this process was determined through the use of a deconvolution program⁸ and standard line-shape analysis. In complex **1**, the energy of activation is 24.4 kcal/mol, the rate of exchange is concentration independent, and the process is reversible. These results can best be interpreted in terms of a dissociate process in which the Al-N bond breaks permitting the two methyl groups to become equivalent on the NMR time scale. At the same time the Al_2O_2 ring remains intact

preserving the nature of the complex. When the bulk of the alkyl substituent bound directly to the aluminum is increased, from methyl to ethyl, the ΔE_a appears to decrease with exchange occurring near room temperature. This can be interpreted as a weaker Al-N dative interaction due to the steric interactions between the substituents on the aluminum in complex **2**.

In summary, the 100% induction of optical activity at the nitrogen center and the strength of the Al-N dative bond suggest that optically active neutral aluminum complexes, where the aluminum center is optically active, can be synthesized and isolated by simply changing the substituents on the aluminum. Work on the synthesis and structural identification of optically active aluminum complexes is continuing.

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Supplementary Material Available: Tables of positional and thermal parameters, complete listings of bond distances and angles, and least-squares planes and deviations (11 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Synthesis and Molecular Structure of Tetramethylbis(μ -pyridine-2-thiolato)dialuminum(III), $[\text{Me}_2\text{AlPyS}]_2$: An Example of a Unique Head-to-Head Bridged Pyridine-2-thiolato Ligand

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Summary: Reaction of pyridine-2-thiol (PySH) with trialkylaluminum, AlR_3 (R = Me, **1**; R = Et, **2**), affords the crystalline complexes tetramethylbis(μ -pyridine-2-thiolato)dialuminum(III) (**1**) and tetraethylbis(μ -pyridine-2-thiolato)dialuminum(III) (**2**) in quantitative yield. Compound **1** crystallizes in the monoclinic space group $C2/c$ with unit-cell parameters $a = 31.651$ (3) Å, $b = 8.364$ (1) Å, $c = 14.128$ (1) Å, $\beta = 103.84$ (1)°, $V = 3631.4$ (5) Å³, and $D_{\text{calcd}} = 1.22$ g cm⁻³ for $Z = 8$. Least-squares refinement based on 1452 observed reflections ($I \geq 2.5\sigma(I)$) converged at $R = 4.84\%$ ($R_w = 3.52\%$). The central core of the compound $[\text{Me}_2\text{AlPyS}]_2$ contains an unusual eight-membered $\text{S}_2\text{C}_2\text{N}_2\text{Al}_2$ ring with head-to-head bridging pyridine-2-thiolato ligands. In solution **1** undergoes an exchange process that averages the methyl groups at and above room temperature while at low temperature the methyl groups are fixed on the NMR time scale giving rise to a spectrum consistent with the solid-state structure. The ^1H NMR spectrum of the ethyl region of the compound **2**, observed at low temperature, is consistent with formation of diastereotopic methylene groups suggesting that in solution the aluminum atom has a five-coordinate structure. Again at room temperature and above the molecule undergoes exchange process causing the ethyl groups to become equivalent.

Pyridine-2-thiol can serve as a very versatile ligand eliminating hydrogen to form the anion PyS^- , which can coordinate through the sulfur, the nitrogen, or both with either formation of a four-membered chelate ring or for-

(8) General Electric GN 300 NMR spectrometer software, version V-8.