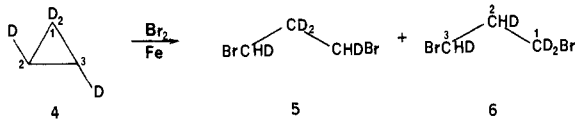
to establish the stereochemistry of the reaction.

In unsubstituted cyclopropane, stereochemistry must be ascertained by the use of isotopes. We have prepared *trans*-cyclopropane-*1,1,2,3-d*$_4$ (**4**), which in principle can distinguish each of the intermediates **1–3** for 1,3-bromination. Opening of the 2,3-bond produces **5**, and opening of the 1,2- or 1,3-bond produces



4 5 6

6, which exists in threo and erythro forms. The expected er-

erythro-6 threo-6

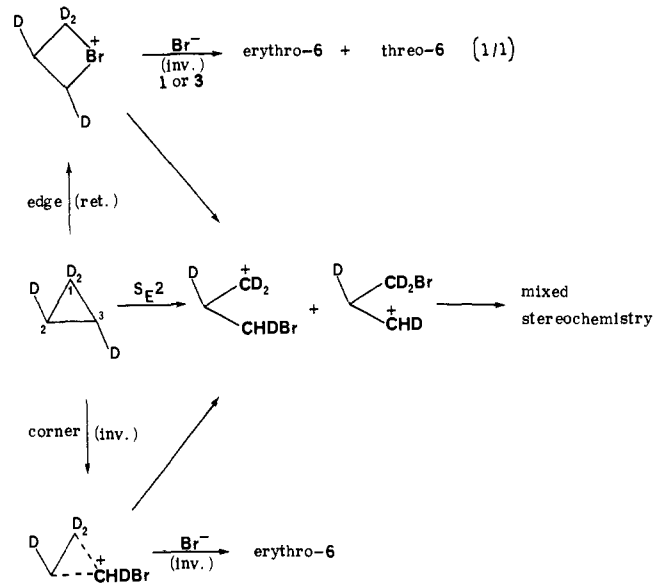
ythro/threo ratio for **6** is different for each mechanism. The stereoisomeric ratio for **6** may be determined from the ^{1}H resonance of the 2-proton. Although the two stereoisomers should give about the same chemical shift, they differ in their vicinal coupling constant with the 3-proton. The expected pair of doublets may be integrated to obtain the erythro/threo ratio. The proton resonances of **5** fall on those of the **3**-proton of 6, but these resonances are not of interest. In using **6** as our probe, we ignore the stereochemical consequences of 2,3-opening (to give **5**) and use the chemically equivalent 1,2- and 1,3-bonds.

Our synthesis of **4** began with *trans*-β-bromostyrene and led in four steps to cyclopropanecarboxylic-*2,2,trans-3-d*$_3$ acid.[7] Reduction with B_2D_6 to the D_5 alcohol, oxidation with PCC to the D_4 aldehyde, and stereospecific decarbonylation with Rh(PPh$_3$)$_3$Cl gave **4**. The trans stereochemistry was confirmed by the value of the vicinal coupling constant, 4.1 Hz, from the carbon-13 satellite. The aldehyde was 85% trans and 15% cis; this ratio should carry over to the cyclopropane product.

Bromination was begun at −78 °C in the absence of solvent and light, with a catalytic amount (0.1 equiv compared with cyclopropane) of iron filings, and was completed at room temperature for 24 h. The absence of radical contributions was confirmed by the lack of effect on the reaction mixture by addition of 0.1 equiv of isoamyl nitrite or *N*-bromosuccinimide. Under these conditions, the desired 1,3-dibromopropane was a major product. The resonance of interest at δ 2.35, from the 2-proton of **6**, was present as one doublet with $J = 7 \pm 0.5$ Hz, confirmed at 90, 270, and 500 MHz.[1] The maximum height of any second doublet was estimated to be <15%, corresponding to the extent of nonstereospecific label in **4**. The large, 7-Hz coupling is consistent with the anti arrangement in the major conformer of *erythro*-**6**. Thus we conclude that the trans cyclopropane gave only the erythro product, within the accuracy of the experiment (probably >85%).

Scheme I shows possible stereochemical outcomes for 1,3 opening (1,2 opening would give equivalent results). The most likely stereochemistry for edge bromination is retention for the electrophilic step and inversion for the nucleophilic step.[2] The electrophilic step leaves the stereochemistry intact. Nucleophilic attack then gives *erythro*-**6** and *threo*-**6** in equal amounts, since bromide can attack with equal likelihood at the 1- and 3-positions. Any retention/inversion or inversion/retention mechanism in fact will give a 1/1 erythro/threo ratio. An open carbocation from a one-step S_E2 mechanism or from any of various multistep reactons could have a stereospecific electrophilic step but a nonstereoselective nucleophilic step. Although there are several stereochemical variants, they all give mixed stereochemistries. Thus the observation of >85% *erythro*-**6** excludes edge bromination and open carbocation formation. The only exception would

Scheme I



be the unlikely case that edge attack occurs with inversion.

Corner bromination is the only reasonable mechanism consistent with the observed result. Attack at the corner position with inversion[8] followed by nucleophilic attack with inversion on ion **1** leads exclusively to *erythro*-**6**. If **1** were simply the S_E2 transition state leading to an open carbocation, a mixed stereochemistry should have been observed. The observed stereospecificity of the reaction requires an intermediate of the type **1**, which contains a formally pentavalent carbon. With **4** now in hand, we are studying additional electrophilic reactions of cyclopropane, in hopes of uncovering other unusual intermediates.

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(7) Berson, J. A.; Pederson, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122–143.

(8) Corner electrophilic attack also could occur with retention but is contrary to our observation. This pathway would lead to 1/1 erythro/threo, if nucleophilic attack occurs with inversion. In general, any inversion/inversion mechanism gives only *erythro*-**6**. Similarly, any retention/retention mechanism gives only *threo*-**6**. The corner-brominated intermediate shown in Scheme I is a structural variant of **2** and is not intended to imply any difference.

Paramagnetic Phosphine Shift Reagents: New Probes for the Study of Structures of Transition-Metal Complexes in Solution

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Conventional paramagnetic shift reagents utilize the Lewis base affinity of metal ions for binding of substrates.[1] We report here the first of a complementary group of shift reagents that bind to Lewis acids and that have great potential for the elucidation of structure of metal complexes in solution. Owing to the ubiquitous presence of phosphines in organometallics and current interest in structural identification of catalytic intermediates by NMR, we have initially focussed attention on shift reagents containing a phosphorus donor.

When the donor lies along a 3-fold axis of the complex the dipolar shift equations accurately allow the comparison of shifts calculated from distances and angles based on model compounds.[2,3]

(1) "NMR of Paramagnetic Molecules"; LaMar, G. N., Horrocks, DeW., Jr., Holm, R. H. Eds.; Academic Press: New York, 1973.
(2) White, D. L.; Faller, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 1548–1552; *Inorg. Chem.* **1982**, *21*, 3119–3122.

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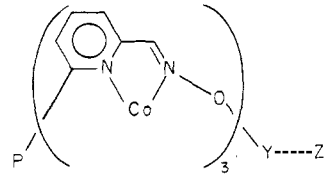
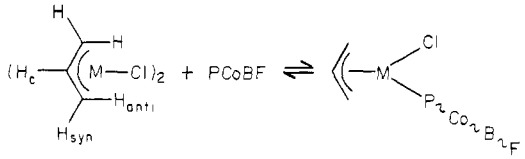
Furthermore, the high magnetic anisotropy of complexes of this type partially orients the molecules and provides additional structural information from dipolar[4] and quadrupolar couplings.[5] Some cobalt(II) complexes have high magnetic anisotropies, and shift reagents based on them are particularly well suited for a paramagnetic analogue of a conventional phosphine ligand. Reagents based on Holm's clathro chelates,[6,7] (**1a**), are appropriate points of departure.



Ia, Y = B; Z = F

In order to demonstrate the utility of this complex as a shift reagent we have examined its effect on the bridge-splitting reactions of allylmetal halide dimers (eq 1). In complexes where



(1)

the exchange rate is very fast, one would observe large shifts of the syn, anti, and central allyl protons proportional to the relative concentrations of the dimer and PCoBF (**1a**). The relative shifts of the H_{syn}, H_{anti}, and H_c protons presumably could be estimated from expected averaged values in the dipolar shift expression (2),

$$\Delta H/H = D(3\cos^2\theta - 1)/r^3 \qquad (2)$$

where r is the Co–H distance, and θ is the angle between the Co–H vector, and the Co–P vector, and D is a constant involving magnetic susceptibility terms.

The most structural information is available, however, under conditions of slow exchange of phosphine. For the palladium case, the rate for the phosphine exchange is sufficiently slow at −30 °C that the spectrum of the paramagnetic phosphine halide may be observed. The syn and anti protons trans to the phosphine are observed at δ 29.4 and 33.1, those cis to the phosphine at δ 48.1 and 43.6, and the central proton at δ 34.3, in accord with the qualitative expectation of the respective distances from the cobalt on the basis of eq 2.[3,8-11]

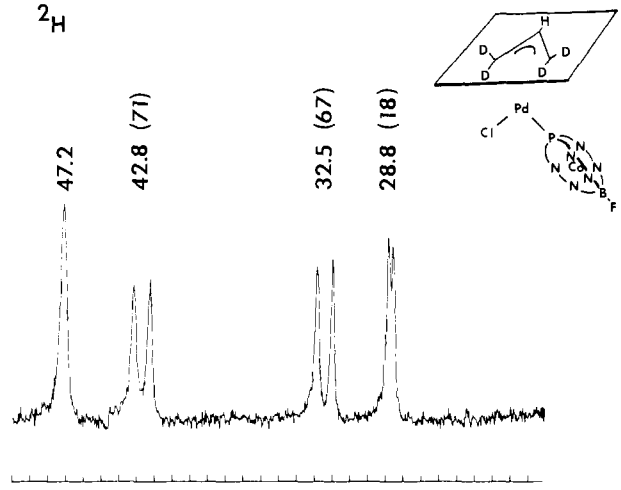


Figure 1. The 76.8-MHz ^{2}H NMR spectrum of terminally deuterated [(η^3-allyl)PdCl(PCoBF)]BF_4 in acetone at −25 °C.

The effects of partial orientation of the molecules as a result the anisotropic magnetic susceptibility can be observed in the ^{2}H spectra of the complex prepared from the terminally deuterated allyl (see Figure 1). The quadrupolar splittings should follow eq 3 and provide a relative measure of the angle between the C–D bond vectors and the Co–P vector, α.[12]

$$\Delta\nu_Q = \nu_Q^*(3\cos^2\alpha - 1) \qquad (3)$$

The splittings from the quadrupole interactions and the isotropic shifts should provide sufficient parameters to distinguish various models for the structure of the allyl. Since X-ray structural studies are available to provide approximate structural parameters for a number of allyl complexes,[13-16] as well as the PCoBF complex,[7] one should be able to readily assign the spectrum and estimate the relative shifts.

A model based on all of the hydrogens lying within the plane of the allyl moiety would seem reasonable on the basis of some earlier discussions of the bonding in allyls;[16] however, we find that substantial twisting of the termini is required to match both splitting and shift data.[17] The quadrupole splittings can be quite sensitive to angle parameters for eq 3 and should allow precise determinations of relative hydrogen positions.[18]

We anticipate, however, that there may be many straightforward applications for distinguishing isomeric structures, such as determining the geometry of $(H_2C{-}CH{-}C(CH_3)_2)$Pd(PCoBF)Cl. In this case, at 25 °C resonances are found at δ 35, 32, 26, 17 and 14 in a ratio of 1:1:1:3:3 corresponding to syn, anti, and central protons and the two methyl groups. Comparison to the shifts of the allylic protons of the unsubstituted allyl analogue clearly shows that the phosphine is trans to the dimethyl-substituted terminus of the allyl moiety,[19] as originally postulated for the triphenylphosphine analogue.[20]

(3) We are assuming that the isotropic shifts observed here are wholly determined by dipolar effects. We have shown this assumption to be valid in some related cobalt complexes.[2] We believe contact contributions are negligible in all of the cases discussed here and are carrying out further experiments to verify this.

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(8) The central proton resonance was assigned on the basis of the relative intensities in the terminally deuterated species.

(9) The observed shifts increase with decreasing temperature and are in the same relative order at −70 °C with shifts of δ 63.3, 57.1, 43.7, 42.5, and 37.2. The shifts of the diamagnetic zinc analogue are syn–cis, δ 4.67; anti–cis, δ 3.69; central, δ 6.28; anti–trans, δ 4.28; syn–trans, δ 5.12. This yields isotropic shifts of δ 58.6, 53.4, 37.4, 38.2, and 32.1, i.e., a ratio of 100:91:64:65:55. The −10 °C data yield a ratio of 100:92:65:66:56.

(10) The widths are 382, 270, 135, 124, and 90 Hz at −70 °C and decrease to 216, 162, 81, 81, and 72 Hz at −10 °C. Line widths of the terminal protons begin to increase above these temperatures owing to phosphine exchange and π–σ rearrangement. Line widths can be used as a further confirmation of assignment owing to their relationship to distance and angle parameters.[11]

(11) Sternlicht, H. *J. Chem. Phys.* **1965**, 42, 2250–2251. LaMar, G. N.; Metz, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 5611–5612. La Mar, G. N.; Faller, J. W. *J. Am. Chem. Soc.* **1973**, *95*, 3817–3818.

(12) The term ν_Q^* is determined by orientational order parameters, which are in turn affected by the magnetic susceptibility, both of which vary with temperature.[5] We are also assuming here that the field gradient of each C–D bond is effectively the same.

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(16) Smith, A. E. *Acta Crystallogr.* **1965**, *18*, 331–340.

(17) A model based on hydrogen atoms along the vectors of the methyl groups in $[((CH_3)_2C{-}CH{-}C(CH_3)_2)PdCl]_2$[14] provides reasonable agreement. Lengthening of the P–C bond trans to the phosphine should allow matching all of the parameters. Owing to the variability of the parameters, we will postpone the discussion of the fitting of the data to the full report of this work, which will include more appropriate X-ray data.

(18) The splitting is extremely sensitive when $\alpha \sim 55°$, but relatively insensitive when $\alpha \sim 0°$ or 90°.

(19) This compares to shifts of δ 36, 32, and 26 for the cis H_{syn} and H_{anti} terminal protons and the central proton in $(H_2C{-}CH{-}CH_2)$Pd(PCoBF)Cl at 25 °C. The shifts decrease with increasing temperature, as expected for the variation in magnetic susceptibility.

(20) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839–1851.

We propose that the use of these reagents should provide a valuable new approach to the determination of the structure of catalytic intermediates in solution. We are currently investigating derivatives **1b–g** (Y = B, Ga, Si; Z = C_6H_5, C_6D_5, which will provide internal standards so that (3 $\cos^2\alpha - 1$) for C-D and (3 $\cos^2\theta - 1)/r^3$ for Co–H, rather than relative values, can be determined.[21]

(21) We wish to acknowledge the support of the National Science Foundation for this research (CHE82-08042) and for its support of the NSF Northeast Regional NMR Facility (CHE79-16210).

Stereochemistry of the Enzymatic Ring Opening of 1-Aminocyclopropanecarboxylic Acid

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The amino acid 1-aminocyclopropanecarboxylic acid (ACPC), isolated from several plant tissues,[1] is an intermediate in the biosynthesis of the fruit-ripening hormone ethylene from methionine.[2] Pseudomonads can decompose ACPC to ammonia and 2-ketobutyrate via the PLP-linked enzyme ACPC deaminase.[3] From work in ^2H_2O it was shown that solvent protons are incorporated both at C-4 and, to some extent, at C-3 of the ketobutyrate, and this is consistent with a vinylglycyl-PLP imine intermediate[4] (Scheme I).

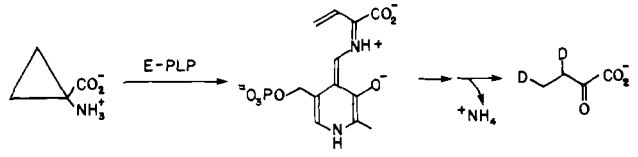
ACPC has two enantiotopic methylene groups, only one of which is expected to be processed by the deaminase to generate the methyl group of ketobutyrate. We have investigated this aspect of the reaction with specifically dideuterated ACPC specimens and herein report our results. The required substrates were prepared by two independent routes.

The Georgia synthesis began with 2,2-dichloro-1-phenylcyclopropanecarboxylic acid[5] (**3**), which was resolved with (+)- or (−)-α-methylbenzylamine to give the pure antipodes, $[\alpha]_D \pm 73°$ (CH_2Cl_2). For configurational assignment the enantiomerically pure methyl ester of (+)-**3** was reduced with 1.2 equiv of tri-*n*-butyltin hydride to give a mixture of monochloro esters from which the pure *Z* isomer **4**, mp 37–38 °C, $[\alpha]_D$ +190° (CH_2Cl_2), was isolated by chromatography[6] (Scheme II). $LiAlH_4$ reduction of **4**, followed by oxidation with pyridinium chlorochromate gave aldehyde **5**, $[\alpha]_D$ +211° (CH_2Cl_2), which, on treatment with Wilkinson's catalyst, afforded the known (1*S*,2*R*)-**6**, $[\alpha]_D$ +185° ($CHCl_3$).[8] The *R* configuration of (+)-**3** follows from the retention expected for the decarbonylation reaction.[9]

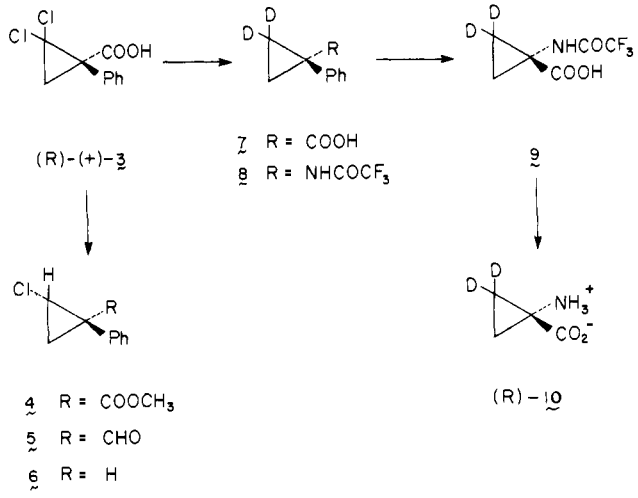
Reduction of (*R*)-**3** methyl ester with 2.5 equiv of tri-*n*-butyltin deuteride gave, after hydrolysis, the deuterated acid (*R*)-**7**, mp 84.5–85.5 °C, $[\alpha]_D$ +1.57° (CH_2Cl_2). Curtius rearrangement of **7** led to the amine, purified as the crystalline trifluoroacetamide **8**, mp 115–116 °C, $[\alpha]_D$ −1.28° (CH_2Cl_2). Oxidation of **8** with RuO_4 afforded acid (*R*)-**9**, mp 170 °C, $[\alpha]_D$ −0.90° (acetone), which was hydrolyzed to (*R*)-[2,2-$^2H_2$]ACPC (**10**). The *S* enantiomer of **9**, $[\alpha]_D$ +0.85°, was prepared from (−)-**3** in the same way and led to (*S*)-**10**.

In the Zürich synthesis acetate **11**, prepared from 3-methyl-3-butenoic acid by $LiAlD_4$ reduction followed by acetylation, was oxidized by SeO_2 and *tert*-butyl hydroperoxide to alcohol **12**, separated from concomitantly formed regioisomer by chromatography. Sharpless epoxidation[10] converted **12** to the *S* epoxide **13**. Reduction of an unlabeled specimen of **13** with $LiAlH_4$

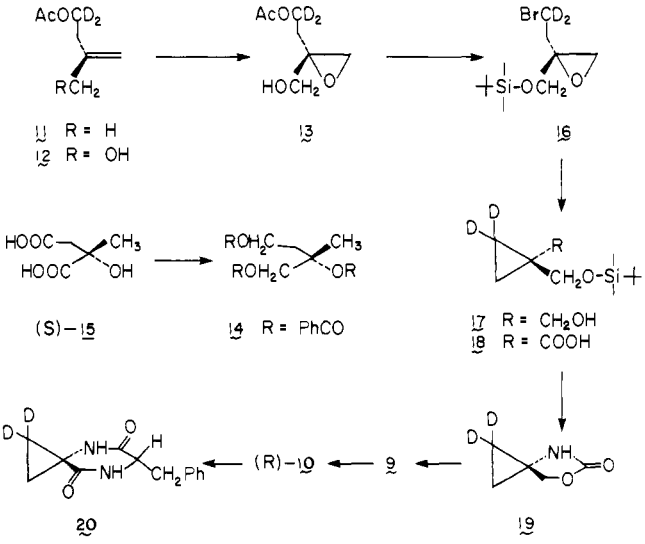
Scheme I



Scheme II



Scheme III



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