of other noninteracting carbanions is in progress.

Acknowledgment. We thank the National Science Foundation and the Committee on Research of the University of California for financial support.

Registry No. **1**, 95189-24-5; **2**, 95189-83-6; CH_2Ph_2, 101-81-5; $CHPh_3$, 519-73-3.

Supplementary Material Available: Tables of data collection and refinement summaries, fractional coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates and stereoviews of the unit cells of **1** and **2** (14 pages). Ordering information is given on any current masthead page.

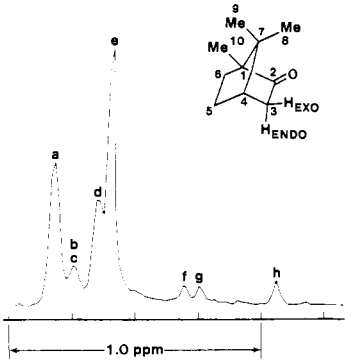

Figure 1. ^2H- and ^1H-decoupled 100.6-MHz ^{13}C NMR of the C-3 and C-4 region of a mixture of **1**–**4**. C-4 peaks: a, **1**; b and c, **2** and **3**; d, **4**. C-3 peaks: e, **1**; f, **3**; g, **2**; h, **4**.

NMR Method To Detect Stereospecific Deuterium Labeling at Diastereotopic Methylene Hydrogens: Selective $^1H,^{13}C$ Heteronuclear Shift Correlation

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Labeling studies employing NMR detection of hydrogen isotopes are becoming increasingly common because of the insight they offer into biological and chemical mechanisms.[1] The most widely used isotope, deuterium, is routinely observed by changes induced in ^1H NMR spectra,[2] by direct ^2H NMR,[2g,3] or by differences in the ^{13}C NMR spectra of carbons that are directly attached to deuterium (e.g., α-isotope shifts)[3b,4] or two bonds away (β-isotope shifts).[5] Despite the utility of these methods, determining which of two diastereotopic hydrogens on a methylene group is deuterium labeled is often difficult.[6] Modern NMR pulse

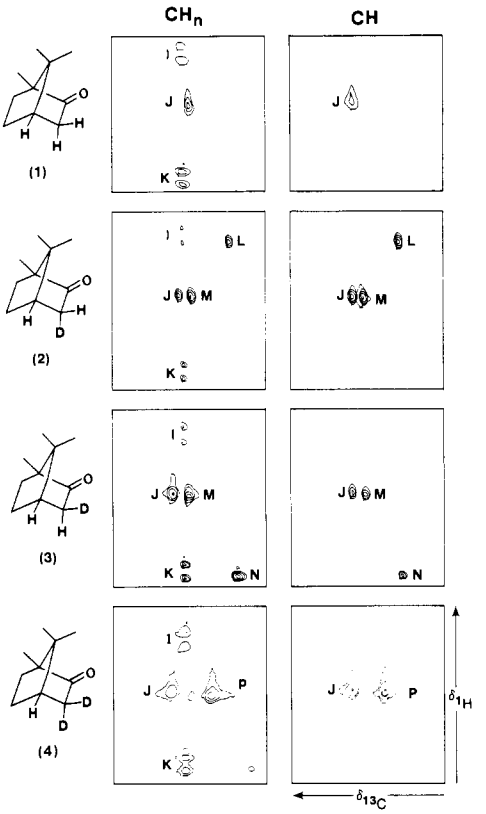

Figure 2. Normal (CH_n) and selective (CH) ^2H-decoupled heteronuclear ($^1H,^{13}C$) chemical shift correlation plots[20] of the region containing the C-3 methylene and C-4 methine of camphor. In each plot the chemical shift increases from 1.76 to 2.43 ppm for ^1H on the vertical axis and from 42.76 to 43.93 ppm for ^{13}C (right to left) on the horizontal axis.

methods[7] have been applied to deuterated systems[4b,8] but have not yet been tested for such stereochemical analysis. In this paper

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we describe the use of two-dimensional selective $^1H,^{13}C$ heteronuclear shift correlation NMR spectroscopy[9] with ^2H decoupling for observation of stereospecifically deuterium-labeled methylene groups.

Camphor (**1**) was chosen as a test case because the exchangeable C-3 methylene hydrogens are well resolved in the ^1H NMR spectrum (endo 3H 1.84 ppm, exo 3H 2.36 ppm) but the C-3 and C-4 carbon resonances appear within 0.1 ppm of each other in ^{13}C NMR spectra. Examination of **1** by spin-echo Fourier transform (SEFT)[7,10] and 2D INADEQUATE[7a,11] confirmed an earlier ^{13}C NMR assignment.[12,13d] However, the normal heteronuclear proton–carbon shift correlation[7b,14] (supplementary material) and homonuclear proton–proton decoupling experiments showed that a recent ^1H NMR assignment[15] must be corrected to the original description.[13a] Endo-, exo-, and bis-deuterated camphors **2**, **3**, and **4**, respectively, were prepared by literature procedures[16,17] and were mixed in varying proportions with unlabeled material (**1**). The proton and deuterium decoupled ^{13}C NMR spectra of the C-4 and C-3 region at 43.5 ppm proved quite complex because of the presence of β-isotope shifts at C-4 as well as α-isotope shifts at C-3 with different magnitudes for exo and endo deuterium (Figure 1). In addition, the relative chemical shift positions of C-3 and C-4 resonances vary noticeably with slight temperature and concentration changes although the magnitudes of all isotope shifts remain constant within experimental error.

Normal heteronuclear $^1H,^{13}C$ shift correlation experiments[14] with deuterium decoupling on mixtures of **2**, **3**, or **4** with unlabeled camphor (**1**) produced the plots shown in the left-hand column of Figure 2. The selective heteronuclear correlation pulse sequence[9d] with deuterium decoupling and with the variable pulse angle θ set to 90° gave the simpler CH plots in the right-hand column which display only carbons bearing a single proton. In each case I and K are signals due to the C-3 methylene group of **1** bearing exo and endo hydrogens, respectively. Resonance J results from the C-4 methine group of **1**. Comparison of the complete and the "CH only" correlation plots of pure **1** to the corresponding ones of mixtures of **1** with **2** or **3** shows the appearance of two additional signals: M and either L or N. Signal M arises from the C-4 methine being shifted upfield on the horizontal ^{13}C chemical shift axis due to the presence of single deuteriums at C-3 (i.e., β-isotope shifts[5]). The L and N peaks are C-3 carbons bearing a single proton in the exo and endo positions, respectively. Separations between I and L and between K and N represent the large upfield α-isotope shift exerted by deuterium on carbon.[18] In the dideuterated camphor **4**, P is due to the C-4 signal, which is shifted by two β deuteriums. Clearly, comparison of the CH plots of unlabeled and partially deuterated compounds can rapidly identify which diastereotopic methylene hydrogen is isotopically substituted, even if other carbon resonances appear within 0.1 ppm.

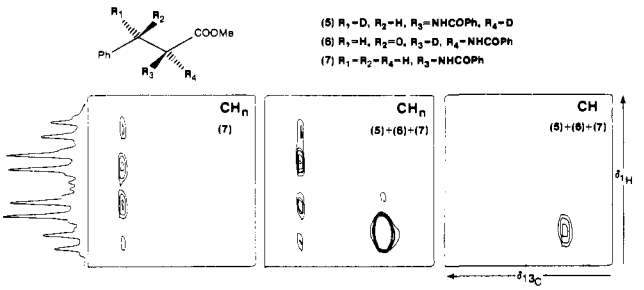

Figure 3. Normal (CH_n) and selective (CH) ^2H-decoupled heteronuclear ($^1H,^{13}C$) chemical shift correlation plots[20] of the methylene region of **7** and of its mixture with **5** and **6**. The corresponding ^1H NMR of **7** is shown on the vertical axis (3.12–3.36 ppm).

In order to test this method in a more common situation where the diastereotopic hydrogen chemical shifts are very similar, we prepared a racemic mixture of (2*S*,3*S*)- and (2*R*,3*R*)-*N*-benzoyl[2,3-$^2H_2$]phenylalanine methyl esters **5** and **6** by literature procedures.[17,19] Although the methylene carbon at 38.0 ppm is well separated from other resonances, the C-3 hydrogens of unlabeled material **7** appear close together at 3.20 and 3.29 ppm in the ^1H NMR spectrum. The new CH signal in the complete and selective correlation plots (Figure 3) clearly shows that the downfield methylene hydrogen is deuterium labeled. Interestingly, a small upfield shift in the position of the deuterated species can be seen on the vertical proton chemical shift axis,[18] as well as the large α-isotope shift on the horizontal ^{13}C axis.

This technique employs the high chemical shift dispersion available in ^{13}C NMR to separate the signals of interest and avoids obscuring the methylene proton AB system through resonance broadening common in ^2H NMR. The large deuterium-induced α-isotope shift on the methylene carbon and the ability to selectively observe the appearance of monodeuterated methylenes as new CH groups further isolate the key resonances. Because of the ease of performing such experiments (if ^2H decoupling and ^{19}F lock are available) and the high visibility of labeled groups, the method should be widely applicable in mechanistic and biochemical studies.[21]

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Acknowledgment. We are grateful to Dr. Richard N. Moore, Glen Bigam, and Dr. Thomas T. Nakashima for valuable discussions. These investigations were supported by the Natural Sciences and Engineering Research Council of Canada, Alberta Heritage Foundation for Medical Research, and the National Institutes of Health (GM29826).

Registry No. 5, 95250-95-6; **6**, 95250-96-7; **7**, 3005-61-6; camphor, 76-22-2.

Supplementary Material Available: Listing of ^1H and ^{13}C NMR data of **1**, INADEQUATE and full $^1H,^{13}C$ correlation spectra of **1**, and summary of Eu(fod)$_3$ experiments (5 pages). Ordering information is given on any current masthead page.

Cadmium-113 Chemical Shift Tensor in Cadmium Diethyl Phosphate: A Step toward Understanding Divalent Cation-Phospholipid Interactions

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Solids NMR methods have made major contributions to the characterization of biological membranes. The partial averaging of ^{13}C and ^{31}P chemical shift tensors, in particular, have been useful in studies of the motional and structural properties of phospholipids.[1-5] Such studies could be extended to the ionic portions of divalent ion-anionic lipid complexes important in membrane function,[6] if a suitable probe nucleus and sufficient model compound studies existed for the cations involved. We present here an illustration that ^{113}Cd can be used as such a probe and present model compound data for this nucleus.

Model compound studies are normally conducted on a single crystal, which can be rotated in an applied magnetic field to uniquely determine tensor elements in a molecular frame. In the case of ^{113}Cd some crystalline complexes have been studied,[7-11] but these do not include the phosphate complexes that would be most suitable as models for membrane work.[4,5]

We present here a partial determination of the ^{113}Cd chemical shift tensor of Cd in a diethyl phosphate complex in an effor to provide suitable model compound data. Our inability to obtain crystals of sufficient size for single-crystal studies has prevented a complete determination. However, the needlelike form of the crystals and the coincidence of one tensor element with the long axis of the crystals has allowed unique orientation of one element in the molecular frame and accurate determination of the magnitude of all three tensor elements.[12] To illustrate the feasibility of extension to membrane preparations, data on a dispersion of the Cd complex with the anionic lipid dimyristoylphosphatidic acid (DMPA) are also presented.

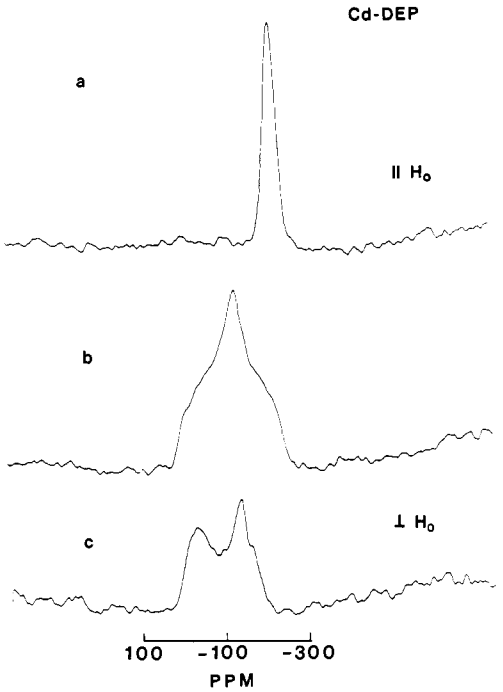

Figure 1. ^{113}Cd spectra of Cd-diethyl phosphate crystals (a) aligned parallel to the field, (b) as a powder, and (c) aligned perpendicular to the field.

Table I. Orientational Data for the Most Shielded Element of the Cadmium Diethyl Phosphate Shift Tensor

bond	bond dist, Å	angle from tensor element, deg
Cd-O12	2.228	56.6
Cd-O22	2.228	123.6
Cd-O21′	2.451	71.9
Cd-O11′	2.448	108.2
Cd-O21	2.290	34.1
Cd-O11	2.289	145.9

$Cd((EtO)_2PO_2)_2$ was prepared as described elsewhere.[13] The needlelike crystals of approximate dimensions 0.5 mm by 0.5 mm by 5.0 mm were packed into a 5-mm NMR tube with long axes parallel to the tube. Dimyristoylphosphatidic acid was synthesized from dimyristoylphosphatidylcholine (Sigma, St. Louis, MO) as described previously.[14,15] The Cd-DMPA complex formed by the addition of equimolar $CdCl_2$ to an aqueous dispersion of phosphatidic acid[14] was collected and transferred to a 10-mm-diameter NMR tube for study.

NMR spectra were obtained on a Bruker CXP-200 spectrometer operating at 44 MHz for ^{113}Cd. In all cases, spectra were obtained using cross-polarization from protons for sensitivity enhancement. A 4-μs proton pulse was followed by a 5-ms contact time and acquisition with a ^1H decoupling field present. In most cases, the spectra are the result of overnight accumulation with a 2-4-s recycle time.

Shift tensor elements were extracted from powder spectra using computer simulation of line shapes. The simulation is based on that described by Seelig[1] and assumes a constant Lorentzian line width, independent of orientation. Tensor elements are referenced to 1 M $Cd(ClO_4)_2$ with negative values indicating upfield shifts.

Figure 1 presents powder and oriented ^{113}Cd spectra of Cd-diethyl phosphate. The powder spectrum (b) is totally asymmetric

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