The correlation of the small differences between R_{MH} and r_{eff} with oxygen and proton hyperfine coupling constants does not seem meaningful. On the other hand, it is of interest to comment on the calculated proton hyperfine coupling constants themselves. They show no clear trend in the series of the $M(H_2O)_6^{2+}$ complexes. The good agreement with the experiment for $Mn(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{2+}$ may therefore be fortuitous. It should, in this connection, be borne in mind that the absolute values of the calculated spin densities at the sites of the protons are very small, two orders of magnitude smaller than their counterpart at the sites of the oxygen atoms.

The next point to discuss concerns the effects of neglecting certain integrals in eq 3. It can be seen in Tables II and III that the pseudo-one-center approximation is reasonable for the case of oxygen, but that the errors in the calculated r_{eff} for the hydrogen atoms are not quite negligible. The use of the real one-center approximation, i.e., the neglect of the effect of the electron-spin distribution on one atom on the spin-differential field gradient on another center, should on the other hand definitely be avoided, because it gives a very substantial underestimation of r_{eff}. It is in this connection interesting to note a correlation between the type of field gradient integral treatment and the conclusions about the validity of the point dipole approximation reached by different authors. Thus, Waysbort and Navon,[9,10] who postulated small deviations from the point dipole approximation for protons in simple inorganic ligands, seem to have included all the integrals. On the other hand, Doddrell, Gottlieb, and co-workers[7,8] make approximations similar to our one-center or pseudo-one-center and suggest much larger deviations from the Solomon–Bloembergen equation in the case of acetylacetonate complexes.

In conclusion, the calculations performed in this work show that the point dipole approximation inherent in the Solomon–Bloembergen equation is well motivated for the water protons in the series $M(H_2O)_6^{2+}$. For the oxygen atoms the deviations vary strongly with metal ion. It is considerable for copper(II) and nickel(II), whereas for manganese(II) it is practically negligible. In biological applications where manganese(II) is often used, the symmetry of the complexes will be different than for the hexaaquo complexes. All ligands will not be the same and tetrahedral coordination may also occur. However, we believe that for the case of water protons coordinated to Mn^{2+} which is bound to an enzyme, the above conclusion will still hold. This must of course be tested by further calculations on other complexes. These calculations are currently in progress at this laboratory.

The above discussion does however not imply that the application of the Solomon–Bloembergen expression for T_{1I}^{-1} (given in eq 4) to the study of water binding to metal enzymes in general is straightforward. The explicit form of the spectral density term $J(\omega_i,\tau_j)$ in eq 4 which is usually applied[3-5] is valid only under the condition that the electron spin relaxation times are longer than the relevant correlation time (the Redfield limit). For the case of $S > {}^1/_2$ ions bound to macromolecules as well as in some other situations, this condition may not be fulfilled. Various attempts to generalize the form of the spectra density term to cover the non-Redfield limit have been presented,[11,35-40] but none of the suggested treatments is completely general.

Acknowledgment. This work has been supported by the Swedish Natural Science Research Council. We are indebted to professor Håkan Wennerström for valuable discussions.

Registry No. $Mn(H_2O)_6^{2+}$, 15365-82-9; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Co(H_2O)_6^{2+}$, 15276-47-8; $Cu(H_2O)_6^{2+}$, 14946-74-8.

---

(35) Koenig, S. H.; Brown, R. D.; Studebaker, J. *Cold Spring Harbor Symp. Quant. Biol.* **1972**, *26*, 551.

(36) Hwang, L. P.; Anderson, C. F.; Friedman, H. L. *J. Chem. Phys.* **1975**, *62*, 2098.

(37) Anderson, C. F.; Hwang, L. P.; Friedman, H. L. *J. Chem. Phys.* **1976**, *64*, 2806.

(38) Friedman, H. L.; Holz, M. ; Herz, H. G. *J. Chem. Phys.* **1979**, *70*, 3369.

(39) Pegg, D. T.; Doddrell, D. M. *Aust. J. Chem.* **1976**, *29*, 1869.

(40) Pegg, D. T.; Doddrell, D. M. *Aust. J. Chem.* **1976**, *29*, 1885.

Nuclear Magnetic Resonance Studies of Terpenes with Chiral and Achiral Lanthanide(III)–Silver(I) Binuclear Shift Reagents

Thomas J. Wenzel and Robert E. Sievers*

Contribution from the Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado 80309.

Received May 11, 1981

Abstract: Certain binuclear metal β-diketonate complexes consisting of a lanthanide(III) tetrakis chelate anion with a silver(I) counterion are effective NMR shift reagents for olefinic and aromatic substrates. The silver in the ion pair forms a bond with the olefinic or aromatic, and shifts are observed in the NMR spectrum of the substrate because of the proximity of the paramagnetic lanthanide. Significant alterations are produced in the complex NMR spectra of terpenes such as α- and β-pinene, camphene, and Δ-3-carene in the presence of these shift reagents. In contrast with the excellent shifts in the spectra of olefins and aromatic compounds observed with fluorinated β-diketonate complexes of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione or (trifluoroacetyl)-*d*-camphor, shifts with 2,2,6,6-tetramethyl-3,5-heptanedione chelates are much smaller. In addition, through proper choice of a chiral lanthanide chelate and silver β-diketonate, it is possible to distinguish certain dextro and levo resonances of enantiomers.

We have recently reported the development of new silver-containing NMR shift reagents that are effective for aromatics, olefins, halogenated compounds, and phosphines.[1,2] The shift reagents are binuclear complexes formed in solution from a lanthanide(III) β-diketonate and silver(I) β-diketonate. We believe that an ion pair involving a tetrakis lanthanide chelate anion is formed. The silver cation is capable of bonding to a soft Lewis

---

(1) Wenzel, T. J.; Bettes, T. C.; Sadlowski, J. E.; Sievers, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 5903.

(2) Wenzel, T. J.; Sievers, R. E. *Anal. Chem.***1981**, *53*, 393.

0002-7863/82/1504-0382$01.25/0

base such as an olefin while the paramagnetic lanthanide is capable of inducing shifts in the NMR spectrum of the olefin. In this paper we report the application of these shift reagents to a number of terpenes. Terpenes typically have rigid structures containing more than one ring and one or more double bonds. The NMR spectra of the olefins are quite complex, and the rigid-ring conformations result in the nonequivalence of the ring protons. Through the use of binuclear shift reagents it is possible to spread out the NMR spectra so that spin-decoupling experiments can be performed and unique resonances can be assigned to almost all of the ring protons.

In addition, through proper choice of a chiral lanthanide chelate and silver β-diketonate it is possible to distinguish certain dextro and levo resonances of enantiomeric pairs. The ability of a compound of known chirality to interact differently with a set of optical isomers has been known for some time and was first applied to lanthanide NMR shift reagents by Whitesides and Lewis.[3] Since that time other effective chiral lanthanide shift reagents have been developed.[4-8] Since the early reports a wide variety of chiral compounds have been studied with these shift reagents, and a review article has appeared.[9] Only one report describing the differentiation of enantiomers of a chiral olefin compound has been published; for this Eu((trifluoroacetyl)-*d*-camphorate)$_3$ with silver trifluoroacetate was used.[10] In this paper we report the use of both achiral and chiral silver β-diketonates that, when added to chiral lanthanide chelates to form binuclear complexes, are effective for resolving certain resonances of dextro and levo enantiomers. The silver β-diketonates used in the formation of these shift reagents are more soluble in chloroform than silver trifluoroacetate, and the higher concentrations of shift reagent that can be used lead to larger shifts.

Experimental

Apparatus. Proton NMR spectra were recorded with a Varian EM-390 spectrometer at 90 MHz. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, CO.

Reagents. All chemicals were used as received without further purification. Silver nitrate was obtained from Fisher Scientific Co., Fair Lawn, NJ. Chloroform-*d* was obtained from Stohler Isotope Chemicals, Waltham, MA. Tetramethylsilane was obtained from Alfa Division of Ventron Corp., Danvers, MA. The 3-(trifluoroacetyl)-*d*-camphor (also called 3-((trifluoromethyl)hydroxymethylene)-*d*-camphor) was obtained from Eastman Kodak Co., Rochester, NY. The Pr(hfbc)$_3$ was obtained from Aldrich Chem. Co., Milwaukee, WI.

Synthesis Procedures. The Ln(fod)$_3$ chelates were synthesized and purified according to the procedure of Springer et al.[11] or obtained from Aldrich Chem. Co., Milwaukee, WI. The Ln(facam)$_3$ chelates, where Ln = the trivalent lanthanide ions Eu(III), Pr(III), or Yb(III), were synthesized and purified according to the procedure of Schurig[12] or obtained from Aldrich Chemical Co. The synthesis of Ag(fod) and Ag(tfa) has been previously described.[1,2] These are now available commercially from Aldrich Chemical Co.

(A) Preparation of (3-(Trifluoroacetyl)-3-camphorato)silver(I) (Ag(facam)). This compound was prepared by a procedure identical to that used for the synthesis of Ag(fod) and Ag(tfa);[1,2] yield, 88%. Anal. Calcd: C, 40.59; H, 3.97; F, 16.05. Found: C, 40.02; H, 4.30; F, 14.89.

(B) Preparation of (2,2,6,6-Tetramethyl-3,5-heptanedionato)silver (I) (Ag(thd)). To a solution of 1 g of AgNO$_3$ in 100 mL of distilled water was added a suspension of 1.2 g of Na(thd) in 100 mL of methanol. The solution immediately turned brown and a light brown precipitate separated. After the solution was stirred for 5 min, the solid was collected by suction filtration and dried in vacuo over P$_4$O$_{10}$ for 24 h. The product was stored in a light-proof container.

(C) Preparation of Silver(I) Tetrakis(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europate(III) (Ag[Eu(fod)$_4$]). To 100 mL of chloroform was added 3.5 g of K[Eu(fod)$_4$], which was prepared by a previously reported procedure,[13] and 0.5 g of AgBF$_4$, and the solution was covered to keep out as much light as possible. The solution was stirred for 10 min, and the KBF$_4$ that precipitated out was removed by filtration. The chloroform was then removed by rotary evaporation to leave a dark yellow solid, Ag[Eu(fod)$_4$], that melts over the range of 85–90 °C. *Anal.* Calcd for Ag[Eu(C$_{40}$H$_{40}$F$_{28}$O$_8$]: C, 33.35; H, 2.80; F, 36.93. Found: C, 33.56; H, 3.02; F, 36.72.

(D) Preparation of Silver(I) Tetrakis((trifluoroacetyl)-*d*-camphorato)praseodymate(III) (Ag[Pr(facam)$_4$]). To 20 mL of chloroform was added 0.88 g of Pr(facam)$_3$ and 0.36 g of Ag(facam). The solution was covered with aluminum foil to keep out as much light as possible, and it was shaken until all the material had dissolved. The chloroform was then removed by vacuum rotary evaporation to leave a pale green solid, Ag[Pr(facam)$_4$], which was stored in a light-proof container. The material decomposed over the range of 160–170 °C. *Anal.* Calcd for Ag[Pr(C$_{48}$H$_{56}$F$_{12}$O$_8$)]: C, 46.58; H, 4.56; F, 18.42. Found: C, 46.43; H, 4.83; F, 17.93.

The compounds Ag[Pr(fod)$_4$], Ag[Yb(fod)$_4$], Ag[Yb(facam)$_4$]·2H$_2$O, Ag[Pr(fod)$_3$(tfa)], and Ag[Pr(facam)$_3$(tfa)]·2H$_2$O were synthesized by an identical procedure. In some cases a small amount of insoluble material was removed by filtration prior to removal of the solvent. Ag[Yb(fod)$_4$] is a yellow solid that melts over the range 93–100 °C. Anal. Calcd for Ag[Yb(C$_{40}$H$_{40}$F$_{28}$O$_8$)]: C, 32.87; H, 2.76; F, 36.39. Found: C, 32.72; H, 2.99; F, 36.13. Ag[Pr(fod)$_4$] is a pale green solid that melts over the range 85–88 °C. Anal. Calcd for Ag[Pr(C$_{40}$H$_{40}$F$_{28}$O$_8$)]: C, 33.61; H, 2.82; F, 37.21. Found: C, 33.21; H, 2.93; F, 36.26. Ag[Yb(facam)$_4$]·2H$_2$O is a tan solid that gradually decomposes above 150 °C. Anal. Calcd for Ag[Yb(C$_{48}$H$_{56}$F$_{12}$O$_8$)]·2H$_2$O: C, 44.14; H, 4.63; F, 17.46. Found: C, 44.14; H, 4.76; F, 17.33. Ag[Pr(fod)$_3$(tfa)] is a pale green solid that melts at 100 °C. Anal. Calcd for Ag[Pr(C$_{35}$H$_{34}$F$_{24}$O$_8$)]: C, 32.65; H, 2.66; F, 35.42. Found: C, 32.45; H, 2.91; F, 35.56. Ag[Pr(facam)$_3$(tfa)]·2H$_2$O is a pale green solid that decomposes over the range 137–143 °C. Anal. Calcd for Ag[Pr(C$_{41}$H$_{46}$F$_{12}$O$_8$)]·2H$_2$O: C, 41.75; H, 4.27; F, 19.33. Found: C, 41.19; H, 4.11; F, 18.13.

NMR Studies. The required amounts of the lanthanide chelate, the silver compound, and the substrate were added to a solution of 1% Me$_4$Si in chloroform-*d* and shaken for 2 min. The mixture was then centrifuged and the supernatant decanted into an NMR tube for analysis. During these procedures and up until recording the spectrum, the solutions were kept covered with aluminum foil to exclude light. In the figure captions the concentrations shown are those calculated based on what was added but represent only upper limits since some insoluble material was removed in most cases.

Results and Discussion

The lanthanide(III)–silver(I) binuclear complexes that we have developed require the existence of two equilibria in order to function as NMR shift reagents for terpenes. The silver ion must be bonded to the lanthanide β-diketonate, and the terpene must be bonded to the silver. Evidence indicates that addition of a silver(I) β-diketonate to a lanthanide(III) tris β-diketonate in solution leads to the formation of a lanthanide(III) tetrakis chelate anion to which the silver is ion paired. The nature of the interaction of the silver with the tetrakis complex remains unknown, but a number of potential mechanisms ranging from coordination of the chelate ligands to the silver to a purely electrostatic interaction can be envisioned. The terpene then bonds to the silver in this ion pair.

$$\mathrm{Ln}(\beta\text{-dik})_3 + \mathrm{Ag}(\beta\text{-dik}) \rightleftharpoons \mathrm{Ag}[\mathrm{Ln}(\beta\text{-dik})_4] \qquad (1)$$

$$\mathrm{Ag}[\mathrm{Ln}(\beta\text{-dik})_4] + \text{terpene} \rightleftharpoons (\text{terpene})\mathrm{Ag}[\mathrm{Ln}(\beta\text{-dik})_4] \qquad (2)$$

The formation of similar types of ion pairs is well-known for the lanthanides,[13-16] although it has never been demonstrated with silver(I) as the cation in the pair. We therefore synthesized the Ag[Ln(β-diketonate)$_4$] complexes, and these were studied by mass spectral and elemental analysis. The mass spectrum of the Ag[Eu(fod)$_4$] complex is of special interest. Both silver (^{107}Ag, 51.82%; ^{109}Ag, 48.18%) and europium (^{151}Eu; 47.82%; ^{153}Eu,

---

[3] Whitesides, G. M.; Lewis, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 6979.

[4] Goering, H. L.; Eikenberry, J. N.; Koermer, G. S. *J. Am. Chem. Soc.* **1971**, *93*, 5913.

[5] Fraser, R. R.; Petit, M. A.; Saunders, J. K. *J. Chem. Soc., Chem. Commun.* **1971**, 1450.

[6] McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038.

[7] Sievers, R. E. U. S. Patent 3 700 410, Oct 24, 1972.

[8] Goering, H. L.; Eikenberry, J. N.; Koermer, G. S. U. S. Patent 3 915 641, Oct 28, 1975.

[9] Sullivan, G. R. *Top. Stereochem.* **1978**, *10*, 287 and references therein.

[10] Meyers, A. I.; Ford, M. E. *J. Org. Chem.* **1976**, *41*, 1735.

[11] Springer, C. S., Jr.; Meek, D. W.; Sievers, R. E. *Inorg. Chem.* **1967**, *6*, 1105.

[12] Schurig, V. *Tetrahedron Lett.* **1972**, 3297.

[13] Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.

[14] Bauer, H.; Blanc, J.; Ross, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 5125.

[15] Bennett, M. J.; Cotton, F. A.; Legzdins, P.; Lippard, S. J. *Inorg. Chem.* **1968**, *7*, 1770.

[16] Burns, J. H.; Danford, M. D. *Inorg. Chem.* **1969**, *8*, 1780.

52.18%) exist naturally as two isotopes of approximately 50% abundance that are separated by two mass units. Any fragment containing one silver and one europium should appear as a three-peak cluster of relative areas 1:2:1 with each peak in the cluster separated by two mass units. In the high mass region of the mass spectrum of $Ag[Eu(fod)_4]$ there are a number of these clusters evident, and the mass standard tris(perfluoroheptyl)-*s*-triazine was used to assign one of these to the $Ag[Eu(fod)_3]^+$ fragment. Similar fragments were also observed for the other silver–lanthanide ion pairs.

The ion pairs, when added to a solution of an aromatic or olefin, produce an NMR spectrum identical with that observed when the lanthanide(III) tris β-diketonate chelate and silver(I) β-diketonate added individually are mixed. An ion pair such as $K[Eu(fod)_4]$ can be dissolved in chloroform, and addition of $AgBF_4$, a chloroform-soluble salt, produces a precipitate, presumably KBF_4. After removal of the precipitate, when a substrate such as toluene was added, the NMR spectrum was shifted almost identically with that observed when $Eu(fod)_3$ and Ag(fod) are added individually in equimolar quantities.

The ligands of the ion pair play an important part in the ability of the ion pair to alter the NMR spectra of olefins or aromatics.[2] The lanthanide chelates of fod work effectively with either Ag(fod) or Ag(tfa). The lanthanide complexes of 2,2,6,6-tetramethyl-3,5-heptanedione, H(thd), have been widely used as NMR shift reagents and were tested for their ability to form the binuclear complexes with silver β-diketonates and shift the NMR spectra of olefins and aromatics. The shifts in the NMR spectrum of toluene were recorded when either $Pr(thd)_3$ or $Yb(thd)_3$ with various silver β-diketonates was added. When 0.2 M $Pr(thd)_3$ or $Yb(thd)_3$ in $CDCl_3$ was used with 0.2 M Ag(fod), Ag(tfa), or Ag(thd) and 0.1 M toluene, no appreciable shifts were observed in the NMR spectrum of the toluene. A similar result was observed for 1-hexene when $Yb(thd)_3$ with either Ag(fod) or Ag(tfa) was added. The poor shifts with the $Ln(thd)_3$ silver complexes may result from an inability to form the tetrakis chelate ion pair, the species believed to be the active shift reagent complex. Alternatively, even if formed, the silver in the nonfluorinated thd tetrakis complex may not form as stable a complex with toluene or olefins as the fluorine-containing ion pairs.

Lanthanide(III) tetrakis β-diketonate chelate ion pairs with the ligands tfa or hfa are known, yet the NMR spectra of toluene or 1-hexene were not altered in the presence of the silver-containing ion pairs. In previous studies, it has been shown that the lanthanide(III) tris chelates of tfa, hfa, or acac are not effective shift reagents for nitrogen or oxygen containing compounds.[17-20] A possible explanation for this is that the substrate in these shift reagent–substrate complexes is not held in only a few preferred geometric configurations relative to the lanthanide chelate.[19,20] This complete randomization leads to an NMR spectrum that does not exhibit any appreciable shifts due to the presence of the lanthanide. It is interesting to note that silver–lanthanide ion pairs with three or more tfa or hfa ligands do not function effectively as shift reagents.

Shifts in the NMR spectrum of toluene have also been recorded after the addition of Ag(thd) with $Pr(fod)_3$ or $Yb(fod)_3$. In both cases, the shifts observed with Ag(thd) were much smaller than those observed with the same concentration of Ag(fod) or Ag(tfa). The solubility of Ag(thd) in the presence of the lanthanide chelate and the toluene is comparable to that of Ag(fod), so the smaller shifts may result from weaker complex formation or subtle changes in the magnetic environment of the toluene in the resulting complex.

The shifts (ΔH_i) observed in the NMR spectrum of a substrate are highly dependent on a number of factors that are described by the McConnell–Robertson equation.[21,22]

$$\Delta H_i/H = K[(3\cos^2\theta_i - 1)/r_i^3]$$

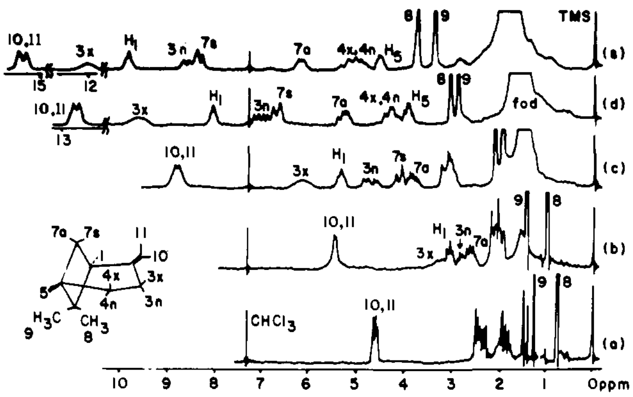

Figure 1. Proton NMR spectrum of 0.1 M β-pinene in $CDCl_3$ with (a) no shift reagent, (b) 0.01 M $Yb(fod)_3$ + 0.01 M Ag(fod), (c) 0.05 M $Yb(fod)_3$ + 0.05 M Ag(fod), (d) 0.1 M $Yb(fod)_3$ + 0.1 M Ag(fod), and (e) 0.2 M $Yb(fod)_3$ + 0.2 M Ag(fod). In all figures the concentrations shown are those that would have resulted, on the basis of amounts added to the $CDCl_3$, if all constituents were completely soluble; see Experimental Section.

The constant *K* contains the magnetic **g** tensors for the shift reagent–substrate complex, and these are usually eliminated by calculating the ratio of the shifts so that the constant need not be considered. This leaves the two primary parameters, r_i, the distance from the lanthanide to the *i*th nucleus, and θ_i, the angle between the principal magnetic axis of the complex and a line drawn from the nucleus of interest to the lanthanide ion. Both of these parameters are important in determining the magnitude and direction of the shift of a nucleus; however, as the value of r_i is made increasingly larger, the θ_i values are very nearly the same while the r_i value may vary significantly, and the dependency of the shift on the angular term decreases.[23,24] In a lanthanide–silver–terpene complex, the terpene is considerably farther away from the lanthanide when compared to a substrate that can bond directly to the lanthanide. For this reason, the distance term was emphasized in assigning the resonances to their respective protons for the terpenes we have studied.

The terpenes that we have studied with conventional binuclear achiral shift reagents are β-pinene, α-pinene, Δ-3-carene, and camphene. In all cases, the shifts observed when binuclear complexes with europium as the lanthanide metal were used were too small to be of much interpretive value. For this reason, we have employed binuclear shift reagents involving ytterbium(III), as an ion that generally induces downfield shifts larger than those observed for europium.

The NMR spectrum of β-pinene (without shift reagent) is shown in Figure 1a. The spectrum is quite complex, and only the origins of the resonances of the two methyl groups, 8 and 9, can be identified. Following the addition of increasing amounts of $Yb(fod)_3$ and Ag(fod), the series of spectra in Figure 1b–e were obtained. Downfield shifts are observed for all of the resonances, and unique resonances can be identified for almost all the different protons. The olefinic protons, H_{10} and H_{11}, which exhibit the same chemical shift in the original spectrum, are partially resolved into two resonances in the presence of the binuclear complex. Distinguishing the origin of each peak is not yet possible however.

In the set of shifted spectra, a rather large coupling is observed between the 3-exo and 3-endo protons. Spin decoupling of one leads to a collapse of the doublet arising from the other. A similar result is observed for the 7-anti and 7-syn protons. In previous studies of pinane and norbornane compounds, large geminal coupling constants have been observed, and the magnitude depends upon the H–C–H angle.[25-27] Presumably, the 4-endo and 4-exo

---

(17) Sanders, J. K. M.; Williams, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 641.
(18) Green, R. D.; Sinha, S. P. *Spectrosc. Lett.* **1971**, *4*, 411.
(19) Evans, D. F.; Wyatt, M. *J. Chem. Soc., Chem. Commun.* **1973**, 339.
(20) Horrocks, W. D. *J. Am. Chem. Soc.* **1971**, *93*, 6800.
(21) McConnell, H. M.; Robertson, R. E. *J. Chem. Phys.* **1958**, *29*, 1361.
(22) Reuben, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1975**, *9*, 1.
(23) Briggs, J.; Hart, F. A.; Moss, G. P. *J. Chem. Soc. Chem. Commun.* **1970**, 1506.
(24) Fraser, R. R.; Wigfield, Y. Y. *J. Chem. Soc. Chem. Commun.* **1970**, 1471.

protons would exhibit such a coupling if these protons were completely resolved. The two bridgehead protons, H_1 and H_5, remain as relatively narrow resonances in the shifted spectra due to the absence of any geminal coupling. Proton 1 is assigned to the resonance that exhibits the larger shift because of its closer proximity to the olefin bond. Its also interesting that decoupling of H_1 leads to a noticeable change in the resonance for H_5. The H_5 resonance changes from a quartet to a triplet. The two protons are in a W-shaped configuration and long-range coupling of this nature has been previously observed.[28,29]

The assignment of the three geminally coupled pairs to specific resonances is based on both spin-decoupling data and the relative magnitude of the shifts. Also, before assignment of the resonances, the nature of the silver bonding to β-pinene must be assumed. The two sides of the olefin bond in β-pinene are nonequivalent. On one side, a methyl group points toward the silver bonding site, while the other side has a proton pointing toward the double bond. A silver complex with β-pinene has been isolated; however, no structural data were given.[30] Silver bonding to olefins is known to be highly dependent on steric factors,[31,32] and for this reason we have assumed that steric interactions will be minimized if the silver ion is bonded to the double bond on the side away from the methyl group. Based on this assumption, for the two pairs of geminally coupled protons that are fully resolved, 3-exo,endo and 7-anti, syn, we would expect H_{3x} and H_{7s} to exhibit the larger shifts. In addition, since H_{3x} is only one carbon away from the unsaturated bond, it should be shifted the farthest of all these resonances. The spin-decoupling data lend further support to this assignment. The protons at the 3- and 4-positions should show some significant mutual coupling. This is observed, as decoupling of H_{3x} leads to a noticeable change in the shape of the complex resonance assigned to the 4-exo and 4-endo protons, while the resonances assigned to H_1, H_5, H_{7s}, and H_a remain unchanged. Decoupling of the resonance assigned to H_{4x} and H_{4n} changes the overall shape of the H_{3x} and H_{3n} resonances from broad signals into large doublets. These doublets result from the geminal coupling of H_{3x} and H_{3n}.

Decoupling of H_1 leads to the collapse of the resonance assigned to H_{7a} to a doublet of doublets. The same effect is observed for H_{7a} when H_5 is decoupled. As expected, the resonances assigned to H_1 and H_5 change their appearance as H_{7a} is decoupled. This shows that the resonance assigned to H_{7a} must be at the 7-position between H_1 and H_5. The significant difference in the shape and coupling of the resonances for the 7-anti and 7-syn protons is entirely reasonable, since coupling constants in rigid compounds of this type are very dependent on the dihedral angle between two specific protons, a phenomenon defined by the Karplus equation.[33]

The only protons left to be assigned are the methyl groups. In earlier studies, it was established that the methyl group 8 in pinane and its derivatives always appears upfield of group 9 in the NMR spectrum due to the magnetic anisotropy of the cyclobutane ring.[34] On addition of the shift reagent, group 8 exhibits substantially larger shifts, and by the spectrum in Figure 1d, it appears downfield of group 9. This is much the same effect that was observed for H_{7a} and H_{7s}. The larger shift for group 8 is probably due to the fact that it is directed toward the olefin group while group 9 points away. This causes group 8 to be significantly closer to the silver and the lanthanide, resulting in larger shifts.

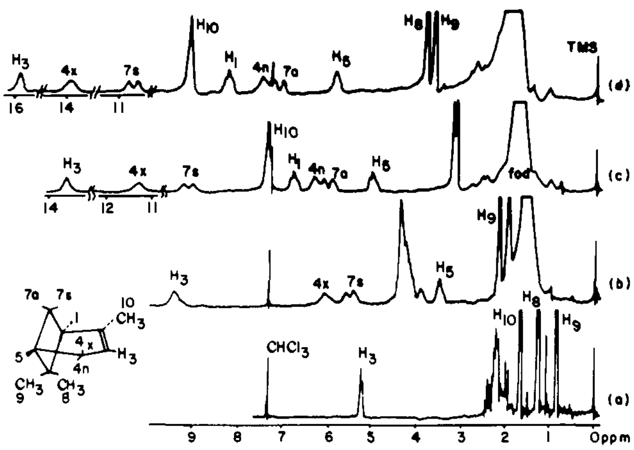

Figure 2. Proton NMR spectrum of 0.1 M *d,l*-α-pinene in $CDCl_3$ with (a) no shift reagent, (b) 0.05 M $Yb(fod)_3$ + 0.05 M Ag(fod), (c) 0.1 M $Yb(fod)_3$ + 0.1 M Ag(fod), and (d) 0.15 M $Yb(fod)_3$ + 0.15 M Ag(fod). The peak labeled fod arises from the *tert*-butyl protons of the shift reagent.

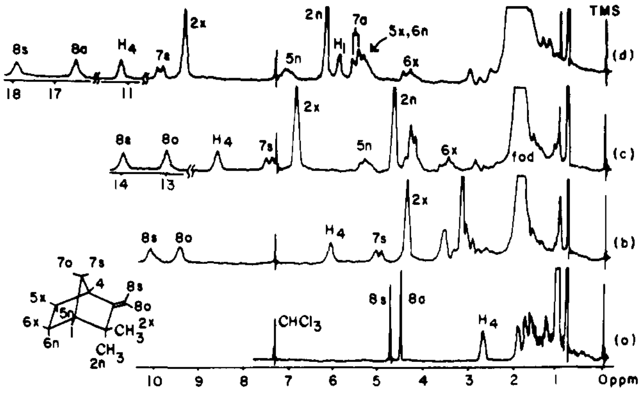

Figure 3. Proton NMR spectrum of 0.1 M *d,l*-camphene in $CDCl_3$ with (a) no shift reagent, (b) 0.05 M $Yb(fod)_3$ + 0.05 M Ag(fod), (c) 0.1 M $Yb(fod)_3$ + 0.1 M Ag(fod), and (d) 0.2 M $Yb(fod)_3$ + 0.2 M Ag(fod).

Earlier studies of hydroxypinanes[35,36] and aminopinanes[37] with lanthanide shift reagents have been reported. The splitting patterns that we have observed for the various protons of β-pinene on addition of the binuclear complex agree very well with those observed for protons at the same position in these pinane derivatives. In addition, our assignments agree with the assignments made in the earlier studies.

The unshifted NMR spectrum of α-pinene is shown in Figure 2a. In this spectrum, the olefin proton, 3, and the three methyl groups, 8, 9, and 10, can be identified. The other six ring protons form a complex multiplet. The results obtained by adding increasing amounts of $Yb(fod)_3$ with Ag(fod) are shown in Figure 2b–d. For this compound, unique resonances are now observable for all the different protons. The results are quite similar in many respects to those already observed for β-pinene. Again, the geminal coupling between the 7-anti and 7-syn and 4-exo and 4-endo protons is observed, although the 7-anti and 7-syn resonances are broadened. The two bridgehead protons, H_1 and H_5, remain as relatively narrow peaks. As observed in β-pinene, long-range coupling is present between H_1 and H_5.

For α-pinene we have again assumed that the silver binds to the side of the olefin bond away from methyl group 8. With this assumption, the resonances were assigned to their respective protons on the basis of both spin-decoupling data and the relative magnitude of the shifts. The coupling for each resonance also agrees with those reported in a previous study of the NMR spectrum of α-pinene.[38]

---

(25) Gutowsky, H. S.; Karplus, M.; Grant, D. M. *J. Chem. Phys.* **1959**, *31*, 1278.

(26) Banwell, C. N.; Sheppard, N. *Mol. Phys.* **1960**, *3*, 351.

(27) Laszlo, P.; Schleyer, von R. P. *J. Am. Chem. Soc.* **1964**, *86*, 1171.

(28) King, R. W.; Butler, P. E. "Abstracts of Papers", 142nd National Meeting of the American Chemical Society, Atlantic City, NJ, Sept 1962; American Chemical Society: Washington, DC, 1962. Abstract p84 Q.

(29) Gagnaire, D.; Payo-Subiza, E. *Bull. Soc. Chim. Fr.* **1963**, 2623.

(30) Comyns, A. E.; Lucas, H. J. *J. Am. Chem. Soc.* **1957**, *79*, 4339.

(31) Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.*, 1962, *84*, 4697.

(32) Gil-Av, E.; Herling, J. *J. Phys. Chem.* **1962**, *66*, 1208.

(33) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.

(34) Nakagawa, N.; Saito, S. *Tetrahedron Lett.* **1967**, 1003.

(35) Paasivirta, J.; Hakli, H.; Widen, K. G. *Org. Magn. Reson.* **1974**, *6*, 380.

(36) Hinckley, C. C.; Brumley, W. C. *J. Magn. Reson.* **1976**, *24*, 239.

(37) Sen, E. C.; Jones, R. A. *Tetrahedron* **1972**, *28*, 2871.

(38) Bates, R. B.; Thalacker, V. P. *J. Org. Chem.* **1968**, *33*, 1730.

It is interesting that for α-pinene, H_{7s} exhibits a larger shift than H_{4x} as well as the olefin proton H_3. At the concentrations used to obtain the spectrum in Figure 2d, the olefin proton has shifted 11 ppm while H_{7s} has shifted at least 11.5 ppm. This probably results because H_{7s} is pointed directly out toward the olefin bond and must be quite close to the silver when it is bonded to α-pinene. The broadened nature of the resonance for H_{7a} is most likely due to its proximity to the silver and the lanthanide, since no coupling other than the geminal coupling to H_{7a} was observed in the series of spin decoupling experiments.

The unshifted spectrum of camphene is shown in Figure 3a. The rigid carbon skeleton of the type found in camphene has been one of the most widely studied of the polycyclic compounds.[39-47] A number of studies have been performed on polycyclic compounds with suitable donor groups such as carbonyls or hydroxyls that can bond directly to lanthanide shift reagents.[48-55] Figure 3b–d show the spectra obtained after addition of $Yb(fod)_3$ with Ag(fod) to camphene. Because the olefinic group does not bond directly to lanthanides, no appreciable shift is observed by adding $Yb(fod)_3$ until Ag(fod) is also added to form $Ag[Yb(fod)_4]$ in situ. The shifted spectra are considerably more informative, and many of the protons appear as unique resonances.

Rather large coupling constants are observed between geminal protons. In the spectra, the geminally coupled protons are either large doublets such as the H_{7s} and H_{7a} resonances or broadened resonances because of other coupling, as observed for the protons at the 5- and 6-positions. The bridgehead protons H_1 and H_4 appear as relatively narrow resonances and are assigned on the basis that H_4 is much closer to the site of silver bonding and should shift farther. The position of silver bonding is dependent on steric factors. For minimization of the steric interactions, it seems likely that preferential bonding of the silver on the same side of the olefin bond as the 2-exo-methyl group occurs.

The assignment of the various protons is based on spin-decoupling experiments and relative distances of the protons from the olefin bond. Decoupling of H_{7s} leads to the collapse of the doublet observed for H_{7a} to a singlet. The relatively large shifts observed for H_{7s} result since it is oriented toward the site of silver complexation. Protons H_{5x} and H_{6n} are assigned to the unresolved multiplet since decoupling of this resonance caused the collapse of two other protons, H_{5n} and H_{6x} into rather sharp signals. The magnitude of the coupling was indicative of geminal pairs, so the unresolved multiplet arises from protons at the 5- and 6-positions. Decoupling of the H_{5x} and H_{6n} resonance also results in a noticeable sharpening of the resonance for H_4. Spin decoupling of the resonance assigned to H_{6x} causes H_1 to collapse to a sharp singlet, indicating that the two carbons are bound to adjacent carbons. The distinction of the 5-exo,endo and 6-exo,endo protons is based on their relative distances from the olefin bond. Of these four protons, H_{5n} is the closest while H_{6x} is the farthest away. For this reason, H_{6x} is assigned to the resonance that shifts the least of the three, and H_{5n} is assigned to the one that is shifted the farthest. Also, H_{5n} showed no observable coupling to either H_1 or H_4, so it seems reasonable that the unresolved H_{5x} and H_{6n} protons occupy an exo and endo position on adjacent carbons, and H_{5x} is the proton in the unresolved multiplet that is coupled to the bridgehead proton H_4.

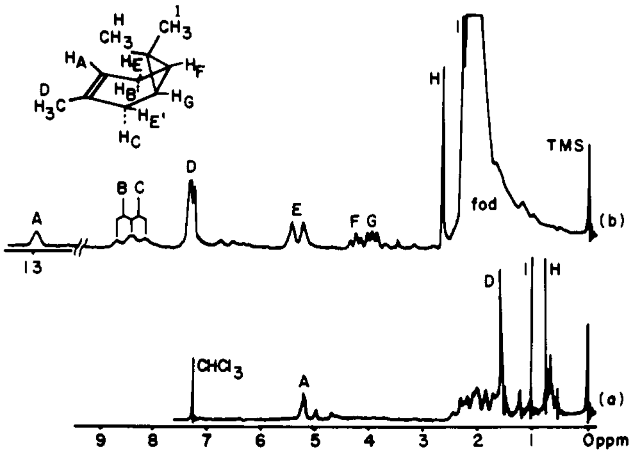

Figure 4. Proton NMR spectrum of 0.1 M Δ-3-carene in $CDCl_3$ with (a) no shift reagent and (b) 0.2 M $Yb(fod)_3$ + 0.2 M Ag(fod).

The methyl groups 2x and 2n, which overlap in the unshifted spectrum, are readily resolved in the presence of the shift reagent. Group 2x is assigned to the resonance that is shifted farther because it is closer to the preferred site of silver bonding. The olefin protons H_{8s} and H_{8a} are resolved in the unshifted spectrum and H_{8s} was assigned to the downfield resonance in a previous NMR study of camphene.[56] As the shift reagent is added, the syn proton exhibits the larger shift of the two.

Δ-3-Carene has previously been shown to exist in the boat conformation.[57] In the unshifted spectrum shown in Figure 4a, the three methyl groups, D, H, and I, and the olefin proton can be identified. From the shifted spectra obtained after the addition of $Yb(fod)_3$ with Ag(fod), considerably more information can be obtained. Decoupling of the broad resonance for protons B and C leads to the collapse of resonance E and E′ into a small doublet. This doublet actually appears to result from a partial resolution of the E and E′ protons, rather that through coupling. In spin-decoupling experiments no observable coupling was noted between the E or E′ and F or G protons. In addition, decoupling of the B and C resonance caused both F and G to collapse from triplets to doublets. This indicates that the resonance for E and E′ corresponds to two protons, one of which is geminally coupled to B, and the other to C. The larger shifts for B and F vs. C and G, respectively, arise from the fact that silver–olefin bonding is very dependent on steric interactions. For Δ-3-carene, the silver–olefin bond is probably unsymmetrical because of the presence of methyl group D, and the silver is expected to align itself closer to the carbon bound to proton A. An unsymmetrical bond should enhance the shifts for B and F, since these protons will be closer to the silver. Apparently, this is not enough of a difference, though, to cause the equatorial E and E′ protons to become completely resolved.

The distinction of the B and C vs. the E protons is also based on the nature of the silver bond to Δ-3-carene. In the boat conformation, the methyl group H extends over one side of the olefin bond and should severely limit the ability of silver to bond at this site. The silver is expected to preferentially complex on the opposite side of the olefin bond adjacent to the B and C protons. This results in substantially larger shifts for B and C vs. E.

The methyl groups H and I have been assigned in an earlier study.[57] In the presence of the shift reagent, H exhibits much larger shifts and eventually lies downfield of I. This is reasonable

---

(39) Musher, J. I. *Mol. Phys.* **1963**, *6*, 93.

(40) Flautt, T. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 3212.

(41) Subramanian, P. M.; Emerson, M. T.; LeBel, N. A. *J. Org. Chem.* **1965**, *30*, 2624.

(42) Tori, K.; Aono, K.; Hata, Yy.; Muneyuki, R.; Tsuji, T.; Tanida, H. *Tetrahedron Lett.* **1966**, 9.

(43) Anet, F. A. L.; Lee, H. H.; Sudmeier, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 4431.

(44) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724.

(45) Ayras, P.; Paasivirta, J. *Suom. Kemistil. B* **1969**, *42*, 61.

(46) Gloux, J.; Guglielmi, M. *Tetrahedron Lett.* **1969**, 2935.

(47) Marchand, A. P.; Marchand, N. W. *Tetrahedron Lett.* **1971**, 1365.

(48) Hinckley, C. C. *J. Org. Chem.* **1970**, *35*, 2834.

(49) Demarco, P. V.; Elzey, T. K.; Lewis, R. B.; Wenkert, E. *J. Am. Chem. Soc.* **1970**, *92*, 5734.

(50) Paasivirta, J. *Suom. Kemistil. B* **1971**, *44*, 132.

(51) Tori, K.; Yoshimura, Y.; Muneyuki, R. *Tetrahedron Lett.* **1971**, 333.

(52) Liu, K. T. *Tetrahedron Lett.* **1972**, 5039.

(53) Korvola, J. *Suom. Kemistil. B* **1973**, *46*, 265.

(54) Abraham, R. J.; Coppell, S. M.; Ramage, R. *Org. Magn. Reson.* **1974**, *6*, 658.

(55) Liu, K. T. *J. Chin. Chem. Soc. (Taipei)* **1976**, *23*, 1.

(56) Grover, S. H.; Stothers, J. B. *J. Am. Chem. Soc.* **1969**, *91*, 4331.

(57) Acharya, S. P. *Tetrahedron Lett.* **1966**, 4117.

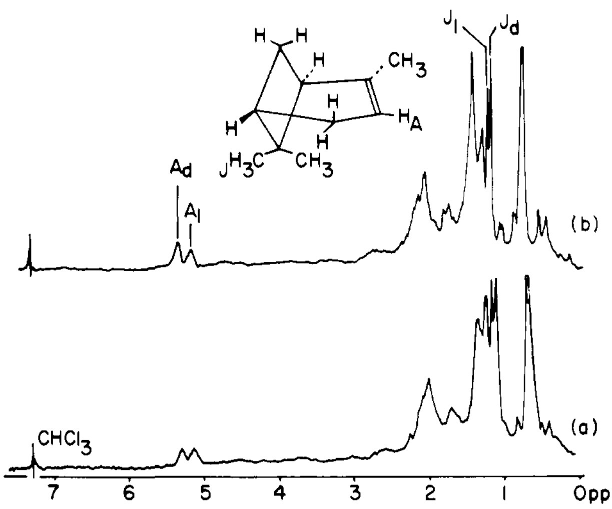

Figure 5. Proton NMR spectrum of 0.1 M *d,l*-α-pinene in $CDCl_3$ with (a) 0.1 M $Pr(hfbc)_3$ + 0.1 M Ag(facam), mixture 50% of each α-pinene enantiomer, and b) 0.1 M $Pr(hfbc)_3$ + 0.1 M Ag(facam), mixture 60% in dextro and 40% in levo enantiomers.

since, in the boat conformation, H lies much closer than I to the site of silver bonding and should be affected more by the paramagnetic lanthanide.

Chiral Studies. The general approach for differentiating optical isomers of olefins is to use a chiral lanthanide tris β-diketonate with either Ag(fod), Ag(tfa), or Ag(facam). Only the last of these silver β-diketonates is itself chiral; however, the Ag[Ln(β-diketonate)$_4$] ion pairs formed in situ between a chiral lanthanide chelate and an achiral silver β-diketonate are optically active and frequently allow one to distinguish between dextro and levo enantiomers of olefins. While it should be possible in principle to use an achiral lanthanide chelate with Ag(facam), in practice none of the enantiomeric pairs tested with this mixture were differentiated. In previous studies with chiral shift reagents it has proven impossible to predict a priori which of the enantiomers would exhibit the larger shift.[9] The same inability to predict relative shifts of enantiomeric olefins has been encountered with chiral binuclear complexes. Perhaps as knowledge of the behavior of closely related enantiomeric pairs increases, prediction of absolute configurations based on NMR data will become possible, but present understanding of structures of the complexes is too primitive to permit this now.

As expected, the compound α-pinene in the presence of an achiral shift reagent, shown in Figure 2, exhibits only one resonance for the olefin proton. By contrast the result obtained by using chiral $Pr(hfbc)_3$ with Ag(facam) in a mixture that is 50% in each enantiomer is shown in Figure 5a. Two resonances are now observed for the olefin proton. The result obtained by using the same ratio of binuclear complex to α-pinene in a mixture that has been enriched in the *d* enantiomer is shown in Figure 5b. The enhancement of only one of the two resonances of the olefin proton is apparent, and this resonance is assigned to the dextro form. With this shift reagent, which we assume to be Ag[Pr(facam)(hfbc)$_3$] formed in situ, the only other resonance that exhibits a dextro and levo component is that of the methyl group 9, and in the enriched mixture, the *d* resonance can be identified as the one that has shifted the farthest. It should be noted that the proton resonance of methyl group 9 of the dextro isomer is shifted farther upfield than the levo methyl, while the reverse is true for proton 3. In previous studies performed with chiral lanthanide shift reagents, there has been much debate as to whether the different shifts of the enantiomers are due to different stabilities of the resulting lanthanide–substrate complexes or due to different magnetic environments created by the different geometries of the dextro and levo complexes with the chiral lanthanide chelate.[6,9] If the bond stabilities were different one enantiomer should consistently exhibit the larger shifts. Since this is not the case when $Pr(hfbc)_3$ and Ag(facam) are added to *d,l*-α-pinene, the distinction of the *d* and *l* enantiomers observed in the NMR spectrum must be due to magnetic differences in the diastereomers formed in situ.

A comparison of chiral binuclear complexes formed by adding $Pr(facam)_3$ with various silver β-diketonates with *d,l*-α-pinene was performed. In all cases we have studied employing $Pr(facam)_3$, the relative order of the shifts was Ag(tfa) > Ag(fod) > Ag(facam). An inspection of the three spectra for α-pinene showed that while the relative shifts were different, the ability to distinguish and resolve the dextro and levo component of the olefin proton of α-pinene was almost identical for all the binuclear complexes, with perhaps the $Pr(facam)_3$/Ag(facam) combination giving the most complete resolution.

Another similar example involving α-pinene is the result obtained upon addition of $Pr(hfbc)_3$ with Ag(tfa). Only the resonances for the dextro and levo 7-syn protons exhibited separate peaks. Identification was achieved by studying a solution enriched in the dextro compound. Neither the olefin proton nor methyl group 9 exhibited unique resonances for each enantiomer, as observed when $Pr(hfbc)_3$ with Ag(facam) was used. In principle, all of the dextro protons should be in more or less different magnetic environments than the levo nuclei, and it is not obvious why discernible differentiation of more of the resonances does not result. Since no systematic basis for choice of the best chiral shift reagent has yet evolved, it may often be necessary to study a particular enantiomeric pair with a variety of binuclear complexes in order to obtain the best resolution of the dextro and levo peaks.

One other curious observation meriting discussion is the apparent downfield shift of the olefin proton for the *d* enantiomer of α-pinene (Figure 5) in the presence of Ag[Pr(facam)(hfbc)$_3$] relative to the analogous peak in the absence of the binuclear shift reagent (Figure 2). Praseodymium shift reagents generally induced upfield shifts, and, in every other case we have studied by using binuclear complexes with praseodymium, upfield shifts have been observed. The apparent downfield shift for the resonance of this olefin proton is actually due to two competing phenomena—an upfield shift due to the presence of the Pr and a downfield shift that results from the silver complexation to the olefin. Such complexation shifts are found to be quite small for all protons except those bound to the carbons involved in the double bond. At the concentrations used in this study, the downfield silver complexation shift was larger than the upfield shift induced by the Pr, with the result that the resonance appears downfield of its original unshifted position.

Another chiral compound that we have studied extensively is *d,l*-camphene. As expected, the spectrum obtained by using an achiral shift reagent (Figure 3) shows no differences in the dextro and levo components of camphene. The results for the two olefin protons of *d,l*-camphene when chiral $Pr(hfbc)_3$ and Ag(tfa) were added are shown in Figure 6a–d. Both olefinic protons exhibit two resonances, arising from the complexation of the *d* and *l* enantiomers with the optically active chiral binuclear chelate to form two diastereomers. From the figure it is apparent that there is a slight preponderance of one of the enantiomers. In the spectrum in Figure 6d, separate *l* and *d* resonances appear for H_4, but unfortunately they overlap with another peak in the spectrum. Figure 6e shows the resolution of the *d* and *l* protons in methyl resonance 2x in the presence of $Pr(hfbc)_3$ and Ag(tfa). In contrast to the olefin protons, the predominant enantiomer in this methyl group in the mixture exhibits the larger shift. This is similar to the results observed for α-pinene and proves once again that the distinction of the *d* and *l* enantiomers must be due principally to magnetic environment differences of the nuclei rather than to significantly differing stability constants of the shift reagent–camphene diastereomeric complexes.

The effects on the NMR spectrum of *d,l*-camphene when $Pr(facam)_3$ and Ag(tfa) were added were also studied. The resolution of the *d* and *l* olefin protons was not as complete as with $Pr(hfbc)_3$/Ag(tfa), and some interferences with the peaks from nuclei in the shift reagent occur. Both of the methyl groups, 2x and 2n, are resolved into their *d* and *l* components, and the minor component exhibits the larger shift in both of these. This

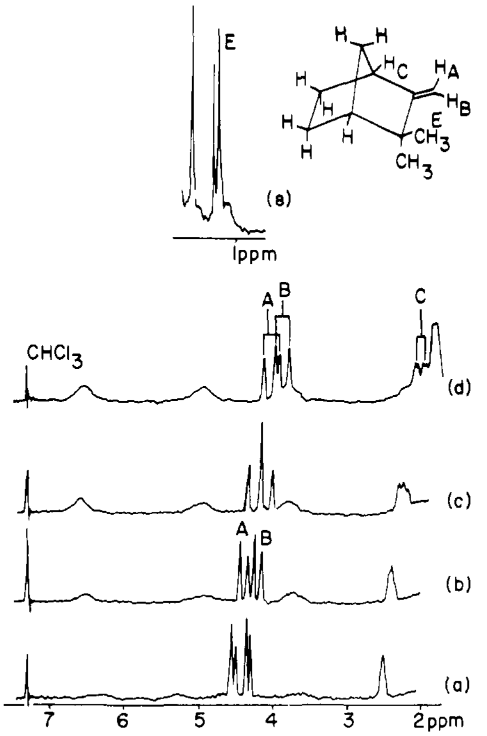

Figure 6. Partial proton NMR spectrum of 0.1 M *d,l*-camphene in $CDCl_3$ with (a) 0.01 M $Pr(hfbc)_3$ + 0.01 M Ag(tfa), (b) 0.02 M $Pr(hfbc)_3$ + 0.02 M Ag(tfa), (c) 0.03 M $Pr(hfbc)_3$ + 0.03 M Ag(tfa), (d) 0.05 M $Pr(hfbc)_3$ + 0.05 M Ag(tfa), and (e) 0.05 M $Pr(hfbc)_3$ + 0.05 M Ag(tfa).

is in contrast to the results for $Pr(hfbc)_3$ with Ag(tfa), where the methyl group of the major component shifted farther. What might appear to be a rather minor change of a CF_3 group to a $CF_2CF_2CF_3$ group on the ligands of the lanthanide chelate apparently changes the geometry and hence the magnetic environment of the resulting shift reagent–camphene complex to a rather significant extent.

In certain instances, downfield shifts in the NMR spectrum of a substrate may result in better spectral clarification than upfield shifts. To induce downfield shifts, europium chelates are typically used; however, the shifts observed by using binuclear complexes involving europium are quite small, and for none of the olefins so far studied were we able to resolve *d* and *l* proton resonances with europium binuclear complexes. Fortunately, ytterbium chelates also induce downfield shifts that are typically larger in magnitude than those of europium, without severe line broadening. In the spectra of camphene with increasing amounts of $Yb(facam)_3$ and Ag(tfa), four different protons (the olefin proton, the two methyl groups 2x and 2n, and the bridgehead proton H_1) exhibit separate resonances for the dextro and levo enantiomers. In all cases, the resonances attributable to the minor component shifted farther.

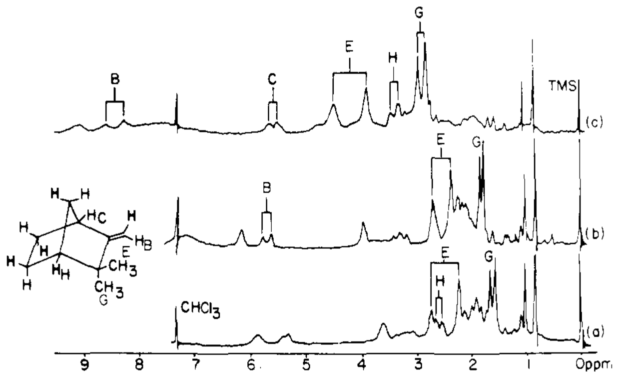

Figure 7. Proton NMR spectrum of 0.1 M *d,l*-camphene in $CDCl_3$ with (a) 0.05 M $Yb(facam)_3$ + 0.05 M Ag(fod), (b) 0.05 M $Yb(facam)_3$ + 0.05 M Ag(tfa), and (c) 0.05 M $Yb(facam)_3$ + 0.05 M Ag(facam).

In Figure 7a–c, a comparison of spectra of *d,l*-camphene to which $Yb(facam)_3$ together with each of three different silver β-diketonates was added is illustrated. The shifts obtained by using Ag(fod) or Ag(tfa) are quite similar in magnitude, although some interesting differences are noted in the degree of enantiomeric resolution for certain protons. One particular example is methyl group 2n. With Ag(tfa), larger shifts are observed than with Ag(fod); however, the differences in the *d* and *l* shifts are greater when Ag(fod) was employed. Neither of these compare, however, to the results obtained with $Yb(facam)_3$ and Ag(facam), which are shown in Figure 7c. With this combination, both the shifts and the degree of enantiomeric resolution are significantly enhanced. In this spectrum five different protons, the olefin proton 8, both bridgehead protons, H_1 and H_4, and both methyl groups, 2x and 2n, exhibit separate resonances for the dextro and levo enantiomers. This is probably the result of forming a binuclear complex, $Ag[Yb(facam)_4]$, in which all four of the β-diketonate ligands are optically active, rather than only three of the four, as in the other cases. Accordingly, stereospecificity of interaction to maximize differences in magnetic environments in the two diastereomers is greater than in the other cases.

Acknowledgment. The encouragement of William Harris of the National Science Foundation is gratefully acknowledged. The support of the National Science Foundation through Grant CHE 79-13022 is greatly appreciated.

Registry No. Ag(facam), 70697-35-7; Ag(thd), 79827-25-1; $Ag[Eu(fod)_4]$, 79816-44-7; $K[Eu(fod)_4]$, 79816-45-8; $Ag[Pr(facam)_4]$, 79816-46-9; $Ag[Pr(fod)_4]$, 79816-47-0; $Ag[Yb(fod)_4]$, 79816-48-1; $Ag[Yb(facam)_4]$, 79816-49-2; $Ag[Pr(fod)_3(tfa)]$, 79816-50-5; $Pr(facam)_3$, 38053-99-5; $Pr(fod)_3$, 17978-77-7; $Yb(fod)_3$, 18323-96-1; $Yb(facam)_3$, 38054-03-4; Ag(fod), 76121-99-8; Ag(tfa), 69070-40-2; β-pinene, 127-91-3; *d*-α-pinene, 7785-70-8; *l*-α-pinene, 7785-26-4; *d*-camphene, 5794-03-6; *l*-camphene, 5794-04-7; Δ-3-carene, 13466-78-9; $Pr(hfbc)_3$, 38832-94-9.