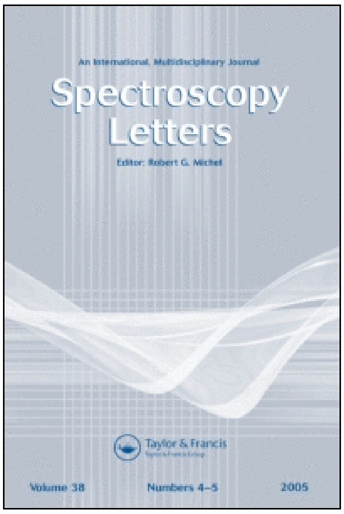

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BINUCLEAR NMR SHIFT REAGENTS. AN APPARENT ANOMALOUS EFFECT WITH VINCLOZOLIN.

Key Words: Lanthanide, Silver, NMR, Shift Reagents, Optical purity, Enantiomers, Chiral

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ABSTRACT

The 60 MHz ^{1}H NMR spectra of racemic vinclozolin, 1, have been studied at 28° in $CDCl_3$ solution with the chiral reagent tris[3-(heptafluoropropylhydroxymethylene)-d-camphorato]europium(III), 2, by incremental additions of (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)silver(I), 3. Although the solution of 1 with 2 displayed substantial downfield lanthanide-induced shifts, $\Delta\delta$, and enantiomeric shift differences, $\Delta\Delta\delta$, for selected nuclei, relative to the spectrum of unshifted 1, additions of 3 to the solution of 1 and 2 were unexpectedly found to dramatically reduce the magnitudes of both $\Delta\delta$ and $\Delta\Delta\delta$.

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INTRODUCTION

Binuclear shift reagents involving silver compounds with lanthanide shift reagents (LSR) have been shown to have considerable potential for inducing enhanced values of lanthanide-induced shift, $\Delta\delta$, and enantiomeric shift differences, $\Delta\Delta\delta$[1-7]. These enhancements for $\Delta\delta$ and $\Delta\Delta\delta$ have been reported for both ^{1}H and ^{13}C NMR with those compounds that typically give only small induced shifts with lanthanide shift reagents alone. Such compounds are typically weak Lewis bases such as arenes, alkenes and halides. LSRs by themselves are usually most effective with compounds possessing a basic site, such as an oxygen or nitrogen atom. Applications of these silver-lanthanide binuclear shift reagents have generally been limited to substrates with one or more of the functional groups (such as alkenes or aromatic rings) that bind poorly to lanthanides. There appear to be few reports using complex polyfunctional compounds containing more basic groups like carbonyls. Our studies with vinclozolin, 1, 3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-2,4- oxazolidinedione, with achiral and chiral LSRs[8,9] encouraged us to perform the present work employing the chiral tris[3-(heptafluoropropylhydroxymethylene)-d-camphorato]europium(III), 2, known as $Eu(hfc)_3$, in conjunction with (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) silver(I), 3, known as Ag(fod).

Since 1 with added 2 had been shown[8,9] to give substantial $\Delta\delta$ values, and to exhibit appreciable $\Delta\Delta\delta$ values for selected nuclei, we investigated additions of 3 to form the silver-lanthanide binuclear reagent. Our interest was the production of enhanced $\Delta\delta$ and $\Delta\Delta\delta$ values that might be expected to result if silver and lanthanide were specifically localized on the ethenyl group of 1.

EXPERIMENTAL

A sample of racemic vinclozolin (CH 283230) was provided by BASF Aktiengesellschaft through BASF Wyandotte Corp., Agricultural Chemicals Group, Parsippany NJ 07054. Stated purity was > 99.5%. $CDCl_3$ (99.8 atom % D) was dried and stored over 3A Molecular Sieves. The $CDCl_3$ and shift reagents 2 and 3 were obtained from Aldrich Chemical Co. and used as received except as noted. All spectra were run on a Varian EM-360A 60 MHz ^1H NMR spectrometer at a probe temperature of 28°C. Chemical shifts are reported in parts per million (δ) relative to TMS and are believed accurate to ± 0.05 ppm. Accurately weighed portions of 3 were added directly to the NMR sample tube containing a solution of 1 and 2, dissolved by shaking, and the spectra immediately run.

RESULTS AND DISCUSSION

In this present study, 3 was added to a solution containing 1 and 2. We had anticipated that if Ag(I) was preferentially complexed to the ethenyl group of 1 but lanthanide remained largely complexed to the carbonyl oxygens, ethenyl group protons would still be expected to have enhanced downfield shift. Ag(I) complexation to cyclohexene is known to produce downfield shifts of the olefinic protons[10] (but upfield shifts of the ^{13}C resonances of the double bond)[11]. Results with Ag(I)-LSR binuclear complexes are considered to involve exchange of ligands which is rapid on the NMR time scale[3,4]. Studies with Ag(I) alone suggest complexation and decomplexation with alkenes[12-14] or carbonyls[10] which is also fast on the NMR time scale.

When increments of 3 were added to a solution of 1 (0.387 molal in $CDCl_3$) containing 2 (2:1 ratio of 0.443), it was found that resonances were shifted upfield relative to their positions in the solution with 1 and 2 alone, prior to addition of 3. No other resonances were observed attributable to protons of 1, suggesting that fast exchange conditions still prevail for whatever species were present. Values of $\Delta\Delta\delta$ were simultaneously decreased. Attachment of an achiral (fod) ligand to the $Eu(hfc)_3$ coordination sphere could reduce the chirality of the complex, $[Eu(hfc)_3(fod)]^{-1}$ relative to 2, in which all three ligands are chiral, and this has been considered as a potential source of decreased $\Delta\Delta\delta$[4]. However, the apparent upfield shifts were unexpected. An explanation consistent with our results involves Ag(I) complexation on the carbonyl oxygens, competing for these sites with lanthanide. Ag(I) complexation at any other site (aromatic ring, halogens or alkene) would seem to be ruled out by the absence of enhanced downfield shifts for any of the protons of 1. [All protons in cyclohexene, toluene, acetophenone and 4-chloroacetophenone were shifted downfield by $AgBF_4$ in CH_2Cl_2[10]. However, if the main effect was to form a binuclear shift reagent complex of 1 [with Ag(I) at the carbonyl oxygens] at the expense of the complex of 1 and 2 (without silver) the net result would be an increase in the average distance from the protons to the paramagnetic lanthanide. This should decrease the lanthanide-induced downfield shifts and result in the observed apparent upfield shifts and decrease of $\Delta\Delta\delta$. An alternative effect that may contribute to the observed results might involve subtle steric effects involving Ag(I) complexation and leading to changes in geometry or conformation that are especially significant because of anisotropic effects. We favor the first explanation for its simplicity since the alternative explanation would require coincidental changes in all proton chemical shifts in the same direction. Results with 2 and 3 together are shown in FIGS. 1 and 2.

In an early study of equilibrium constants of silver-olefin complexes using gas chromatography, especially favorable interactions were reported for 1,5-dienes, such as 4-vinyl-1-cyclohexene[15]. Similarly, aqueous silver ion complexation of some olefinic alcohols and ketones such as 4-penten-1-ol was found to be consistent with a bidentate chelation of silver to account for relatively high equilibrium constants for complex formation[16]. This latter report noted equilibrium constants for silver ion complexation that were more than 290 times greater for 4-cyclooctenol relative to cyclooctanol, and more than 13 times greater for 4-cyclooctenone relative to cyclooctanone. The two analogs lacking the alkene moiety had comparable (small) equilibrium constants. Cyclooctene itself also had a very small equilibrium constant. The possibility of an analogous bidentate chelation

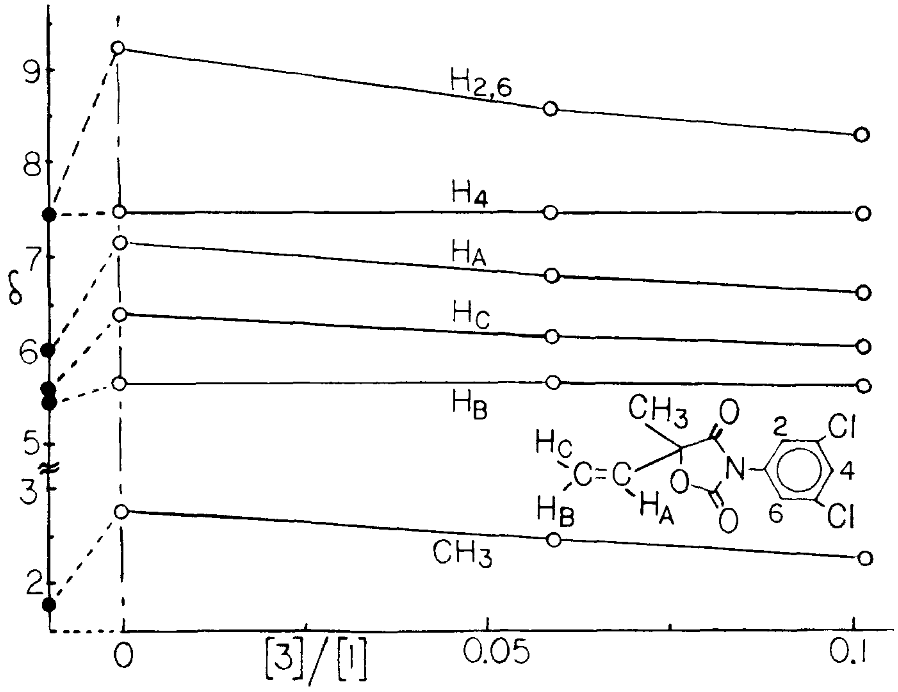

FIG. 1. Variation of chemical shift, δ, with molar ratio of 3:1 for additions of 3 to solution initially 0.387 molal in 1 with 2:1 molar ratio of 0.443. Filled circles (●) indicate δ values for 1 with no shift reagents added. See text.

in 1 could involve the ethenyl sidechain and the C-2 carbonyl of the ring. While this would support large ΔΔδ for H_c by proximity to the carbonyl and the shift reagent, decreased downfield proton chemical shifts for the ethenyl group of 1 with silver and 2 together would still demand increased distance from the europium as the most important overall effect. Rather modest deshielding of olefinic protons by silver ion[14,17,18] could still accom-

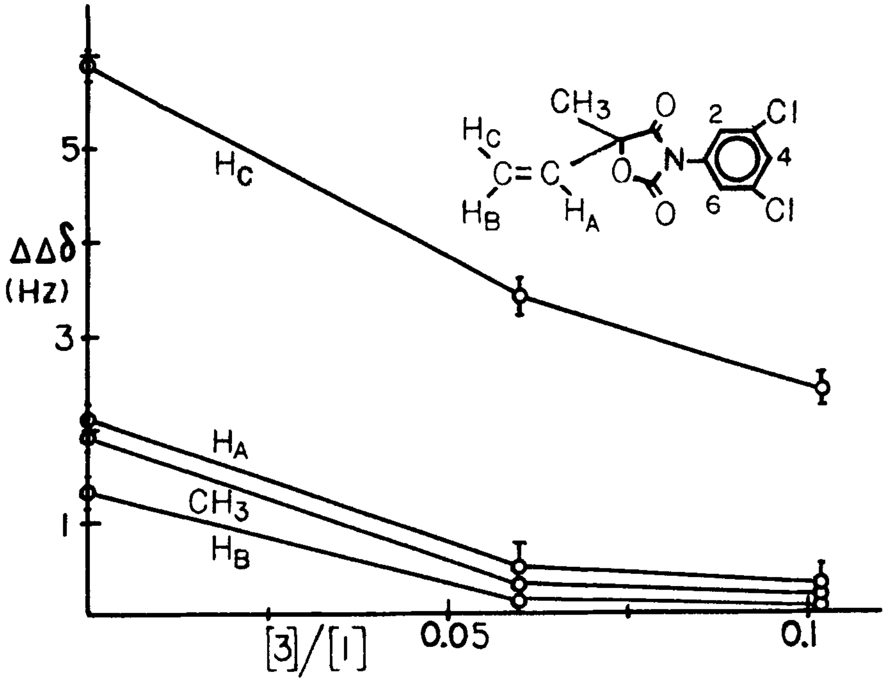

FIG. 2. Variation of enantiomeric shift differences, ΔΔδ (in Hz), with molar ratio of 3:1 for additions of 3 to solution of 1 and 2. See text and FIG. 1 caption.

modate our results. The work of Crist et al.[10] on simple aliphatic and aromatic ketones suggested that carbonyls act as n donors toward silver ion in contrast to simple alkenes and aromatic systems which acted as π donors. Prior studies with an amide, ε-caprolactam, supported coordination through the amide oxygen with $AgClO_4$[19]. The requirement that silver be coplanar with the relatively rigid five-membered ring of 1 in order to bond to a nonbonding pair of electrons on a carbonyl oxygen could have implications concerning the possible bidentate chelation of silver ion by 1.

In our runs with 1 and 2, Ag(fod) additions had to be terminated because of increasing precipitate formation. The selection of silver salt can have significant influence on Δδ magnitudes and on the mode of complexation with these binuclear reagents[20], and solubility effects must likewise be considered.

We have previously demonstrated the potential for direct optical purity determinations of 1 by use of 2. We have now reported the use of the binuclear shift reagent from 2 and 3 with a multifunctional compound possessing groups of relatively high basicity. This appears to be the first such study with a chiral molecule and a chiral LSR in which the carbonyl, a strong donor group for the LSR, is present. The observed decreases in Δδ and ΔΔδ for 1 when the binuclear reagent is used versus result with 2 by itself suggests that applications for this binuclear reagent with substrates possessing both strong and weak electron-donor groups must be further explored to permit improved selectivity in enhancing the Δδ and ΔΔδ values.

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