A Better Solvent for Binuclear Lanthanide(III)-Silver(I) NMR Shift Reagent Studies

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A series of binuclear lanthanide(III)-silver(I) NMR shift reagents suitable for use with olefins, aromatics, halogenated compounds, and phosphines have recently been reported.[1-6] These previous studies have typically employed deuterated chloroform as the solvent. We report that considerably larger shifts are observed in the NMR spectra of substrates in the presence of these binuclear shift reagents when pentane is used as the solvent. The greatest improvements are observed for those classes of substrates that have the smallest equilibrium constants for association with Ag(I), chlorinated compounds and aromatics. This should expand the variety of weak Lewis bases that can be effectively studied with the binuclear Ln(III)-Ag(I) NMR shift reagents.

Results and Discussion

The shifts observed in the NMR spectrum of 1-chloropentane (0.1 M) and 1-bromopentane (0.1 M) in the presence of Dy(fod)$_3$/Ag(fod) (0.2 M) with $CDCl_3$ and pentane as the solvent are given in Table I. The ratio of the shifts in pentane to those in $CDCl_3$ for each substrate are also reported in Table I. The shifts observed in the NMR spectrum of 1-bromopentane are improved by 10-20% by employing pentane vs. $CDCl_3$ as the solvent. For 1-chloropentane a gain of approximately 100% is observed on switching the solvent to pentane. A similar 100% improvement was observed for 1-chlorobutane (0.1 M) with Dy(fod)$_3$/Ag(fod) (0.2 M) on changing the solvent from $CDCl_3$ to pentane. In a previous study it was shown that the equilibrium constant for association between Ag(I) and brominated compounds was larger than that of the analogous chlorinated derivatives.[2] The largest gains on changing solvents from $CDCl_3$ to pentane are obtained for those substrates that bond only weakly to silver.

The shifts observed in the NMR spectrum of toluene (0.1 M) were enhanced by approximately 50% on changing the solvent from $CDCl_3$ to pentane when either Eu(fod)$_3$/Ag(fod) (0.2 M) of Pr(fod)$_3$/Ag(fod) (0.2 M) was employed as the shift reagent. The data from these experiments are given in Table II. The improvements obtained for toluene with Eu(fod)$_3$/Ag(fod) in pentane were not enough, however, to provide for complete resolution of the aromatic resonances of toluene. The Eu(III) chelates must still be judged ineffective for most binuclear shift reagent applications.[2] For cyclohexene (0.1 M) with Yb(fod)$_3$/Ag(fod) (0.2 M), an enhancement of the shifts by approximately 15% was observed when pentane was substituted for $CDCl_3$ as the solvent. Olefins are known to bond more strongly to Ag(I) than aromatics.[7] The greatest improvements on changing the solvent from $CDCl_3$ to pentane are again obtained for those substrates that bond only weakly to Ag(I).

Table I. Shifts (ppm) in the Proton NMR Spectrum of 1-Chloropentane (0.1 M) and 1-Bromopentane (0.1 M) with Dy(fod)$_3$/Ag(fod) (0.2 M) in $CDCl_3$ or Pentane

	1-chloropentane				
solvent	H_1	H_2	H_3	H_4	H_5
$CDCl_3$	−7.87	−5.44	−3.87	−2.47	−1.76
pentane	−16.60	−11.17	−7.94	−5.40	−3.66
	2.11[a]	2.05	2.05	2.19	2.08
	1-bromopentane				
solvent	H_1	H_2	H_3	H_4	H_5
$CDCl_3$	−21.09	−14.65	−10.30	−6.87	−4.63
pentane	−25.42	−17.25	−11.87	−7.80	−5.00
	1.21[a]	1.18	1.15	1.14	1.08

[a] Ratio of the shift in pentane to the shift in $CDCl_3$.

Table II. Shifts (ppm) in the Proton NMR Spectrum of Toluene (0.1 M) with Eu(fod)$_3$/Ag(fod) (0.2 M) and Pr(fod)$_3$/Ag(fod) (0.2 M) in $CDCl_3$ or Pentane

	Eu(fod)$_3$/Ag(fod)			
solvent	*p*-H	*m*-H	*o*-H	Me
$CDCl_3$	1.10	1.05	0.75	0.42
cyclohexane	1.40	1.35	0.98	0.52
pentane	1.65	1.55	1.13	0.60
	1.50[a]	1.48	1.51	1.43
	Pr(fod)$_3$/Ag(fod)			
solvent	*p*-H	*m*-H	*o*-H	Me
$CDCl_3$	−1.87	−1.50	−1.08	*b*
pentane	−2.65	−2.20	−1.68	
	1.42[a]	1.47	1.56	

[a] Ratio of the shift in pentane to the shift in $CDCl_3$. [b] The methyl resonance was obscured by the pentane resonance.

Cyclohexane was also evaluated as a possible solvent for binuclear shift reagent studies. In all instances the binuclear reagents were not as soluble in cyclohexane. The shifts in the NMR spectrum of the substrate in cyclohexane, while larger than those recorded in $CDCl_3$, were not as large as those observed in pentane. The results for toluene with Eu(fod)$_3$/Ag(fod) in cyclohexane are given in Table II and are representative of the results observed for other substrates studied in all three solvents.

The chiral binuclear shift reagents Pr(facam)$_3$/Ag(hfth) and Yb(facam)$_3$/Ag(tta) were studied with *d,l*-camphene in pentane in the hopes of achieving larger shifts and improved enantiomeric resolution compared to the same combinations in $CDCl_3$.[6] In both instances, however, the shifts in the NMR spectrum of camphene were not sufficient to move the substrate resonances away from the large pentane resonance. Pentane is therefore impractical for most chiral binuclear shift reagent studies unless enantiomeric resolution is observed for the olefinic or aromatic resonances of the substrate.

The improvements when pentane is substituted for $CDCl_3$ as the solvent in binuclear shift reagent studies could be the result of a number of possible mechanisms. The most likely explanations are, first, that the equilibrium constant for association between the shift reagent and substrate may be higher in pentane. Second, the geometry of the shift reagent-substrate complex could exhibit a solvent dependency. In this instance the different shifts in the NMR spectra of the substrate would result from changes in the distance and angle terms in the pseudocontact shift equation.[8] Third, the lanthanide ion in the

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binuclear complex may have a magnetic susceptibility that is solvent dependent. This value is also taken into account in the pseudocontact shift equation.

In a study of the solvent effects on shift reagent experiments employing lanthanide tris chelates, the association constant between the shift reagent and substrate was found to be solvent dependent, while the geometry and magnetic susceptibility were independent of solvent.[9] The magnitude of the shifts in the NMR spectrum of a substrate in the presence of a lanthanide shift reagent are highly dependent on the equilibrium constant for association between the two.[10] The spectrum of a substrate in the presence of a lanthanide shift reagent is a time average of its spectrum in the complexed and uncomplexed form. Solvents that bond effectively to either the silver or lanthanide, acetone, acetonitrile, benzene, dimethyl sulfoxide, and carbon disulfide, significantly reduce the effectiveness of the binuclear reagents.[2]

A larger equilibrium constant for association in pentane compared to $CDCl_3$ may reflect a reduction in the competitive effects of the solvent for coordination sites on the shift reagent. This seems especially reasonable considering that the greater enhancements are observed for those substrates that bond only weakly to Ag(I). Chloroform is known to hydrogen bond to the π system of the β-diketone ligands in some metal chelate complexes.[11] It is also possible that the chloroform could bond to the silver by a Lewis acid–Lewis base interaction. Any such competition of the chloroform would be enhanced because of the large excess of solvent relative to substrate.

The induced shifts in the NMR spectrum of chloroform (0.1 M) in pentane were recorded with either $Dy(fod)_3$ or $Dy(fod)_3/Ag(fod)$ at a concentration of 0.2 M and were found to be 0.77 and 0.78 ppm, respectively. These values represent rather small induced shifts. They do indicate that the chloroform bonds to both shift reagents in some fashion; however, the ability of chloroform to compete with other substrates for coordination sites on the shift reagent would appear to be negligible. If the association constants are solvent dependent, it may result from changes in the solvent polarity alone. This conclusion was reached in a previous study of the solvent effects on lanthanide tris chelates.[9]

Without a more detailed study, a solvent dependence of the association constants, geometry, or magnetic susceptibility cannot be eliminated as a possible contributing factor to the observed solvent effects with binuclear Ln(III)–Ag(I) NMR shift reagents. For the study of aromatic and chlorinated compounds with the binuclear shift reagents, the use of pentane as the solvent is recommended.

Experimental Section

Proton NMR spectra were recorded on a Varian EM 360L spectrometer. Shift reagents were purchased from Aldrich Chemical Co. or prepared and purified according to literature procedures.[12] Binuclear shift reagent studies were carried out by using previously described procedures.[6] Pentane and cyclohexane were reagent grade, and all solvents, including $CDCl_3$, were stored over molecular sieves. The following nomenclature has been used to denote the various ligands: 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, H(fod); 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, H(hfth); 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, H(tta); and 3-(trifluoroacetyl)-*d*-camphor, H(facam).

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Registry No. $Dy(fod)_3$, 18323-98-3; $Eu(fod)_3$, 17631-68-4; $Pr(fod)_3$, 17978-77-7; $Ag(fod)_3$, 18716-26-2; 1-chloropentane, 543-59-9; 1-bromopentane, 110-53-2; toluene, 108-88-3; cyclohexene, 110-83-8; chloroform, 67-66-3; pentane, 109-66-0; cyclohexane, 110-82-7; *dl*-camphene, 565-00-4.

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Communications

Concerning Hydride Reduction of Diels–Alder Products of Danishefsky's Diene[1]

Summary: A nonacidic method for unveiling the latent α-enone moiety from a Diels–Alder adduct of Danishefsky's diene involves the use of lithium aluminum hydride to obtain an allylic alcohol, followed by manganese dioxide oxidation. A mechanism for the hydride-induced reaction is proposed.

Sir: Since its introduction in 1974,[5] Danishefsky's diene **2**, and variations thereof, have proved themselves to be agreeable[6–9] and versatile[10] for Diels–Alder reactions both

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