Communications to the Editor

New Binuclear Lanthanide NMR Shift Reagents Effective for Aromatic Compounds

Sir:

Since Hinckley's first report on lanthanide shift reagents,[1] the field has experienced tremendous growth, and a number of reviews have appeared in this area.[2-5] Lanthanide shift reagents possess a remarkable ability to alter the NMR spectra of oxygen- and nitrogen-containing compounds; however, there has been only limited success in developing NMR shift reagents for weak nucleophiles such as olefins and aromatics. The only report of a shift reagent for olefins appeared in 1975 by Evans et al.[6] In their system, silver heptafluorobutyrate apparently acted as a bridge between an olefin and a lanthanide shift reagent. We report the use of two silver β-diketonates, formed from the anions of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (fod) and 1,1,1-trifluoro-2,4-pentanedione (tfa), as new bridging compounds. These binuclear silver β-diketonate–lanthanide complexes induce considerably larger shifts in the spectra of aromatic compounds than those observed with silver heptafluorobutyrate. The enhanced solubility of the silver β-diketonate–lanthanide complexes may lead to these larger shifts, although in some instances it appears that the larger shifts are due to the formation of a more stable binuclear complex or to differences in the average magnetic environments produced by the various silver β-diketonate–lanthanide shift-reagent pairs.

In the preparation of Ag(fod), a solution of 9.6 g of H(fod) in 5 mL of methanol was neutralized with 8.1 mL of 4 M aqueous NaOH, and this solution was added to a stirred solution of 5.5 g of silver nitrate in 75 mL of water. The white precipitate was collected by suction filtration and dried in vacuo over P_4O_{10}. Anal. Calcd for $AgC_{10}H_{10}O_2F_7$: Ag, 26.76; C, 29.80; H, 2.50; F, 33.00. Found: Ag, 23.89 ± 1; C, 28.39; H, 2.38; F, 31.44. Ag(tfa) was prepared in a similar manner. Anal. Calcd for $AgC_5H_4O_2F_3$: Ag, 41.34; C, 23.01; H, 1.54; F, 21.84. Found: Ag, 40.67 ± 1; C, 22.47; H, 1.52; F, 20.80. All NMR spectra were recorded on a Varian EM390 spectrometer at 90 MHz.

Partenheimer and Johnson[7] and Gibson et al.[8] have synthesized olefin or phosphine silver β-diketonate complexes and reported a reversible interaction between the substrate and silver, as well as acceptable solubility in nonpolar solvents. We have found that these compounds can also bond to lanthanide shift reagents. The substrate is then held in a preferred configuration relative to the lanthanide, and selective shifts are observed in the NMR spectrum. As an example, the proton spectrum of triphenylphosphine exhibits substantial shifts in the presence of these new shift reagents. In a previous study of triphenylphosphine, no proton shifts were observed with Eu(thd)$_3$.[9]

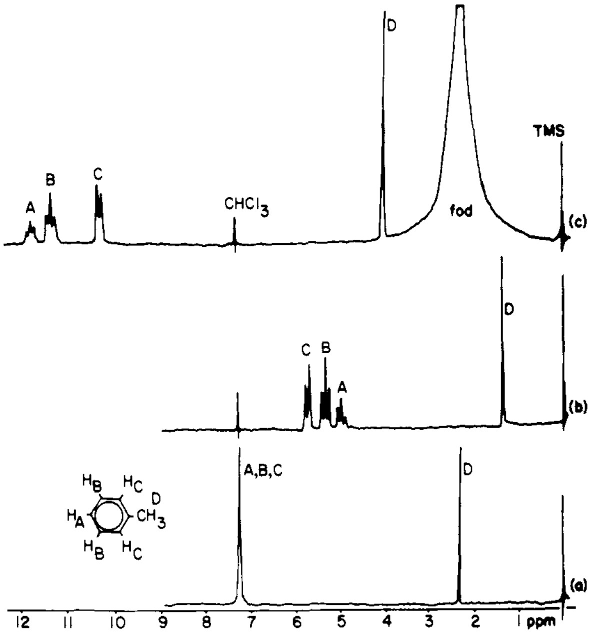

Figure 1. Proton NMR spectrum of 0.1 M toluene in $CDCl_3$ with (a) no shift reagent, (b) 0.2 M Pr(fod)$_3$, 0.2 M Ag(tfa), and (c) 0.2 M Yb(fod)$_3$, 0.2 M Ag(fod).

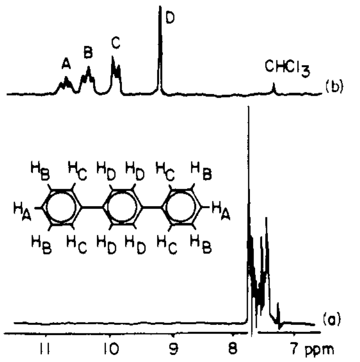

Figure 2. Proton NMR spectrum of 0.1 M *p*-diphenylbenzene in $CDCl_3$ with (a) no shift reagent and (b) 0.4 M Yb(fod)$_3$, 0.4 M Ag(fod).

The spectrum of toluene is shown in Figure 1a. The spectrum obtained after addition of Pr(fod)$_3$ (Aldrich Chemical Co., Milwaukee, WI) and Ag(tfa) is shown in Figure 1b. Praseodymium chelates generally induce upfield shifts, and the resonances attributed to each set of equivalent protons are completely resolved. Silver–aromatic or silver–olefin bond strengths and stabilities are known to be very dependent on steric factors.[10-12] Silver appears to occupy a preferred complexation site farthest removed from steric encumbrances imposed by the methyl group; accordingly, proton A is shifted the farthest and is split by both B protons into a triplet with relative area one. The B protons exhibit an intermediate shift, and since each B proton is adjacent to an A and C proton, the B protons should appear as a doublet of doublets. Since the coupling constants are essentially the same, the resonance appears as a triplet with relative area two. The A protons shift the least, are adjacent to only one proton, and result in a doublet with relative area two. The Yb(fod)$_3$/Ag(fod) toluene spectrum is shown in Figure 1c. The shifts are downfield and larger in magnitude than the Pr(fod)$_3$-induced shifts. Irradiation of the doublet resulted in the collapse of the B triplet to a doublet. The doublet C collapses to a singlet upon irradiation of the B triplet. These results confirm the assignments proposed above.

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The spectra of more complex aromatic compounds such as *p*-diphenylbenzene can also be clarified by using these new binuclear complexes. This compound has four sets of equivalent protons; however, the NMR spectrum consists of two complex multiplets. The spectrum obtained after addition of $Yb(fod)_3$ and Ag(fod) is shown in Figure 2b. The silver appears to be bonded at the sterically least encumbered position, with the result that proton A shifts the farthest. Protons A, B, and C exhibit a pattern identical with that observed for the aromatic protons of toluene. Protons D on the center ring are not coupled with the other protons, and the resonance appears as a singlet.

These shift reagents are also capable of inducing substantial shifts in the NMR spectra of olefins and phosphines. A detailed study of other aromatic, olefin, and phosphine-containing compounds will be reported in a future publication.[13]

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(13) Wenzel, T. J., Sievers, R. E., to be published.

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Structure and Dynamic Behavior of Transition-Metal Ions in Aqueous Solution: An EXAFS Study of Electron-Exchange Reactions[1]

Sir:

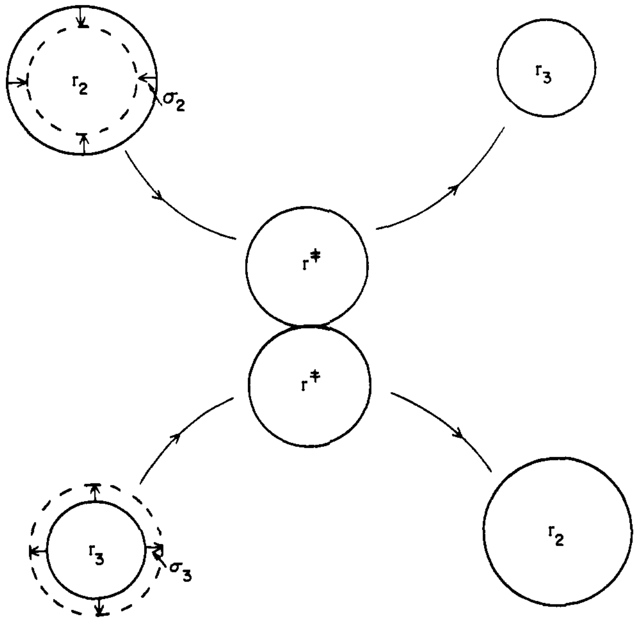

Figure 1. Simplified pictorial representation of $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ electron exchange; the σ values are the root-mean-square displacement amplitudes; arrows indicate the direction of the breathing motion (after Marcus, ref 14).

Table I. Metal-Oxygen Interatomic Distances in $M(H_2O)_6^{n+}$ (n = 2, 3)

concn, M	solution			crystal
	M^{n+}	r(EXAFS)[b]	r(X-ray)[c]	r(X-ray)
1	Cr^{3+}	1.966	1.98	
1	Cr^{2+}[a]	1.984		
1	Mn^{2+}	2.177	2.20	
1	Fe^{2+}	2.095	2.12	2.13[d]
1	Fe^{3+}	1.990	2.00	1.99[e]
1	Cu^{2+}[a]	1.940	1.94 (eq) 2.43 (ax)	

[a] In this complex, only the first shell neighbors are considered.[32] [b] These values were measured with solutions acidified with 0.5-1.5 M $HClO_4$. In the cases of Cr^{3+} and Fe^{3+}, the solutions were acidified to 3 M or even 6 M $HClO_4$ to avoid dimer formation. Estimated errors are within ±0.010 Å; k^2 and k^3 weighting gives results within this accuracy. [c] From ref 28-30. [d] Average from ref 20-22. [e] Reference 23.

The extended X-ray absorption fine structure (EXAFS) phenomenon has become a powerful tool for structure determination in the immediate vicinity of an atom of identified Z.[2-13] In this paper, we demonstrate the power of EXAFS for the study of kinetics and reaction mechanisms in solution. Of particular concern here are the metal-ligand bond distances and the associated Debye-Waller factors of $M(H_2O)_6^{n+}$ complexes in aqueous solution. Let us consider $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ (Figure 1); with the bond lengths and Debye-Waller factor information obtained directly from ions in solution, we can estimate the parameters relevant to the kinetics of the electron-exchange reaction (eq 1). Most theories[14-18] which describe such reactions are based

$$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+} \quad (1)$$

on the Franck-Condon principle: there must be formed a transition state in which the coordination shells of the two reactants have adjusted to identical configurations. According to theory,[19] the difference between the Fe-O radii of $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, $r_2 - r_3$, is the most critical parameter. Until now, X-ray crystal structure data[20] have been employed for estimates of this

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