fied by elemental analyses and a pattern of infrared ν(CO) frequencies similar to those found in the previously reported[4] polycyanovinylmanganese pentacarbonyl derivatives. A similar reaction of 1-bromopentacyanobutadiene with $NaW(CO)_3C_5H_5$ gives a complex mixture from which the corresponding pentacyanobutadienyl derivative $(NC)_2C{=}C(CN)C(CN){=}C(CN)W(CO)_3C_5H_5$ (IV, M = W) can be isolated in low yield by chromatography. This pentacyanobutadienyl derivative was identified by elemental analyses, the expected pattern of infrared ν(CO) frequencies for an $RW(CO)_3C_5H_5$ derivative, and the expected single C_5H_5 ^1H NMR resonance. A similar attempt to prepare the molybdenum analogue IV (M= Mo) gave a complex mixture from which a pure product could not be separated.

The infrared ν(C=C) frequencies of the pentacyanobutadienyl transition metal derivatives III and IV (M = W) appear at 1524 ± 1 and 1503 ± 3 cm^{-1} which are about 25 cm^{-1} lower than the ν(C=C) frequencies found in the corresponding 1-halopentacyanobutadienes I (X = Cl and Br). This decrease in the ν(C=C) frequencies of a cyanoolefin upon forming a σ bond to a metal carbonyl unit is a consequence of partial donation of electrons from the filled metal d orbitals into the antibonding orbitals of the carbon–carbon double bond. The magnitude of this effect (~25 cm^{-1}) in the pentacyanobutadienyl transition metal derivatives III and IV (M = W) is less than that of the corresponding effect (90–100 cm^{-1}) in the previously reported[4] polycyanovinyl transition metal derivatives since only one of the two carbon–carbon double bonds of the pentacyanobutadienyl system is adjacent to the transition metal system. The infrared spectra of pentacyanobutadienyl transition metal derivatives III and IV (M = W) exhibit two ν(CN) frequencies at 2245 ± 1 and 2233 ± 3 cm^{-1} in contrast to the 1-halopentacyanobutadienes I (X = Cl and Br) which exhibit only a single ν(CN) frequency at 2248 ± 1 cm^{-1}. The lower of the ν(CN) frequencies in the metal complexes III and IV (M = W) can arise largely from the cyano group bonded to the same carbon as the transition metal. Again this lowering of the ν(CN) frequency by ~10 cm^{-1} can arise from partial donation of the transition metal d electrons into the antibonding orbitals of the carbon–nitrogen triple bond.

A characteristic property of cyano olefins[15] and hexacyanobutadiene[12] is the formation of charge transfer complexes with aromatic hydrocarbons. The 1-halopentacyanobutadienes (I, X = Cl and Br) form red solid charge-transfer complexes with hexamethylbenzene in contrast to the reported[12] black solid charge transfer complex formed from hexacyanobutadiene and hexamethylbenzene. 1-Ethoxypentacyanobutadiene forms a yellow solid charge-transfer complex with hexamethylbenzene. Qualitative inspection of the colors of these hexamethylbenzene charge transfer complexes suggests the following observations: (1) Replacement of a cyano group with a halogen weakens the charge transfer complexes because part of the planar delocalized system is lost. (2) Replacement of a cyano group with an ethoxy group weakens the charge transfer complexes more than a halogen atom because of the nonplanarity of the ethoxy groups.

Acknowledgment. We are indebted to the Office of Naval Research for partial support of this work.

Registry No.—I (X = Cl), 62139-51-9; I (X = Br), 62139-52-0; II, 62139-53-1; III, 62227-95-6; IV, 62227-96-7; tetraethylammonium pentacyanobutadien-1-olate, 62139-55-3; oxalyl chloride, 79-37-8; oxalyl bromide, 15219-34-8; disodium *trans*-hexacyanobutenediide, 28804-86-6; $NaMn(CO)_5$, 13859-41-1; $NaW(CO)_3C_5H_5$, 12107-36-7.

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Quaternary Ammonium Halides as Powerful Lanthanide Shift Donors

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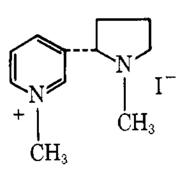
Received December 14, 1976

Lanthanide shift reagents (LSR) have been of considerable use in a wide variety of structural problems, ranging from the determination of relative configurations to the assessment of enantiomeric purity.[1] The simplicity of this nuclear magnetic resonance technique belies the complexity of the mechanisms[2] responsible for observed shifts. This complexity has stimulated investigations into the interactions of the shift reagent and the substrate, especially for substances having two or more sites[3] capable of complexation.

We now report our observation that proton resonances of quaternary ammonium halides are more strongly shifted by $Eu(fod)_3$ than the corresponding resonances of related tertiary amine functionalities.[12] This is a striking finding in that amines have been considered to be the strongest donors among all the previously examined functional groups.[3]

N-Methylnicotinium iodide (1), of interest as a chemical[4] and biological[5] analogue of nicotine, was examined in $CDCl_3$ solution with $Eu(fod)_3$ (Figure 1). Two sites of complexation can be a priori suggested for **1**: at the pyrrolidine nitrogen's lone pair electrons and at the quaternary ammonium iodide functionality. The induced shift gradients clearly indicate that significantly larger shifts are observed for the pyridine ring protons than for the pyrrolidine ring protons. The relative order of lanthanide induced shift (LIS) observed ($C_6H > {}^+NCH_3 > C_5H > C_2H \gg N'CH_3$) implies that the Eu is located near the quaternary center.



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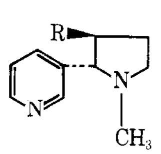


2, R = H
3, R = CH_3

We propose that the quaternary ammonium iodide acts as a LIS donor by $Eu(fod)_3$ complexation with the counterion of the quaternized nitrogen, I^-; the resulting $Eu(fod)_3$–I^- complex is in turn associated with the positively charged

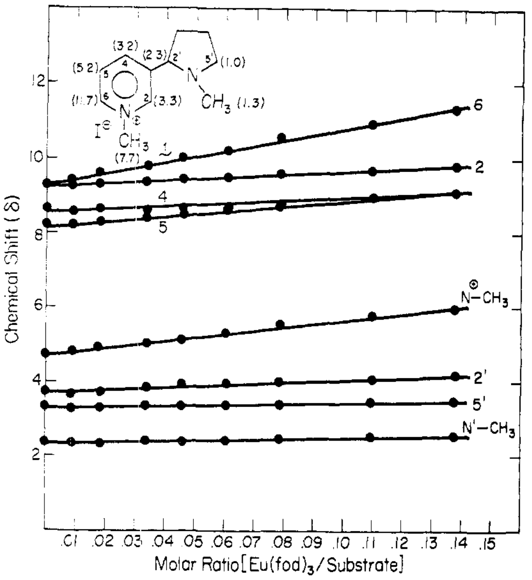


Figure 1. Lanthanide shift study of *N*-methylnicotinium iodide (1) with Eu(fod)$_3$. The relative LIS are shown in parentheses adjacent to the corresponding proton position.

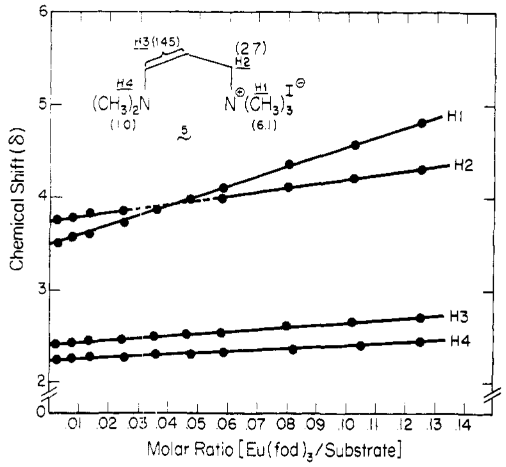


Figure 2. Lanthanide shift study of dimethylaminotrimethylpropylammonium iodide (5) with Eu(fod)$_3$.

moiety.[6] Chloroform, being a nonpolar solvent, probably enhances the LIS by forcing the Eu(fod)$_3$-I$^-$ complex close to the positive charge distribution.[8]

Eu(fod)$_3$ is a Lewis acid, and competitive LIS studies have shown relationships between donor power and functional group basicity (directly proportional)[1] and steric hindrance to complexation (inversely proportional).[9] Indeed, recent LIS studies of nicotine (2)[10a] and *trans*-3′-methylnicotine (3)[10b] have shown significantly greater shifts for the pyridyl ring protons than the pyrrolidine ring protons for these compounds, and steric inhibition to complexation at the more basic pyrrolidine nitrogen was cited as causal. Similarly, one might expect that the pyrrolidine nitrogen of 1 would be sterically blocked.

An alternative explanation of our LIS results would involve pyrrolidine nitrogen complexation and an unusual LIS angle dependency. In order (1) to establish that complexation occurs with the iodide counterion, and (2) to more accurately compare the donor power of quaternary ammonium halides with uncharged tertiary amines, two additional experiments were performed.

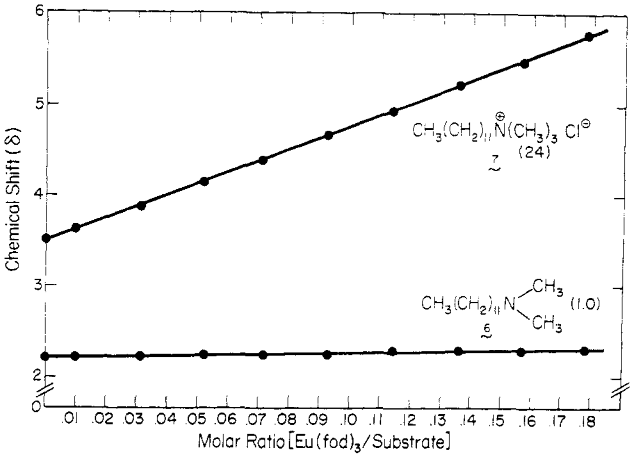
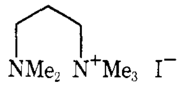


Figure 3. Competitive lanthanide shift study of dimethyldodecylamine (6) and trimethyldodecylammonium iodide (7) with Eu(fod)$_3$. The resonances of the N-CH$_3$ groups are plotted as a function of LSR/substrate.

Firstly, quaternary salt **5**, the monomethiodide of *N,N,N′,N′*-tetramethyl-1,3-propanediamine (4), was examined in the presence of Eu(fod)$_3$. As shown in Figure 2, significantly greater LIS were observed for protons closer to the quaternary nitrogen than to protons closer to the tertiary amine. To completely eliminate ambiguities due to LIS involving difunctional molecules, a second type of competitive complexing was examined. A 1:1 mixture of *N,N*-dimethyldodecylamine (**6**) and *N,N,N*-trimethyldodecylammonium chloride (**7**) in CDCl$_3$ was treated with Eu(fod)$_3$. As shown in Figure 3, the *N*-methyl groups in the quaternary salt **7** underwent a LIS almost 25 times greater than the LIS of the *N*-methyl groups in the tertiary amine **6**. These two experiments clearly establish that the quaternary ammonium halide moiety is a more powerful LIS donor than the corresponding tertiary amines.[12]



5

$CH_3(CH_2)_{11}\overset{+}{N}(CH_3)_3\ Cl^-$

7

A closer examination of the relative LIS of the nicotinoids **1–3** reveals an interesting result. For **2** and **3**, the shifts of the pyridyl ring protons are somewhat symmetrical; i.e., the LIS of C$_2$H and C$_6$H are very similar.[10] It is likely that the LSR complexes with the pyridine lone pair electrons of **2** and **3** along the C$_4$-N axis; however, for **1**, C$_6$H has the largest shift gradient and the order of LIS suggests complexation on (or close to) the C$_6$-C$_3$ axis para to the pyrrolidine ring. The atomic bulk of the iodide counterion in **1** and consequently the bulk of the Eu(fod)$_3$-I$^-$ must meet severe steric repulsions due to the *N*-methylpyrrolidine ring in any attempt for symmetrical complexation with the substituted pyridine ring. In addition, charge is delocalized throughout the heterocyclic ring, and, in part, onto the pyrrolidine ring. We have shown[4] that through-space interactions between the pyrrolidine nitrogen and the pyridine ring occur in **1**, and this interaction, coupled with the delocalization phenomenon and the steric hindrance considerations, serves in favor of nonsymmetrical complexation.

The use of organic counterions, e.g., CH$_3$CO$_2$$^-$ or C$_6$H$_5$CO$_2$$^-$, will allow one to monitor the LIS of both the cation and the anion in these quaternary nitrogen salts. This information, coupled with the McConnell-Robertson relationship,[1] may allow the evaluation of ion-ion phenomena in nonpolar solution. However, the relative contributions of contact and pseudocontact shifts at these relative concentrations and experimental conditions must be first determined.[11,12]

Experimental Section

All NMR spectra were recorded on either a Varian Associates A-60A or XL-100 spectrometer and are referenced to internal tetramethylsilane. *N*-Methylnicotinium iodide was prepared by iodomethylation of nicotine in acetic acid as previously described.[4] Dimethyldodecylamine and trimethyldodecylammonium chloride were obtained from Lachat Chemicals, Inc., MeQuon, Wis., and dried under vacuum and stored over P_2O_5 until used. Eu(fod)$_3$ was freshly sublimed immediately before use. All transfers of LSR were made under dry nitrogen.

3-Dimethylaminotrimethylpropylammonium Iodide (5). To a solution of 10.0 g (77 mmol) of *N,N,N′,N′*-tetramethyl-1,3-propanediamine in 150 mL of benzene was added all at once 5.5 g (38 mmol) of iodomethane (caution: cancer suspect agent). A precipitate immediately formed. After 25 h, the precipitate was filtered, washed with additional benzene, and dried under high vacuum giving 10.1 g (98% based on iodomethane) of **5**, mp 173.5–174 °C.

Anal. Calcd for $C_8H_{21}N_2I$: C, 35.30; H, 7.78; N, 10.30; I, 46.63. Found: C, 35.13; H, 7.68; N, 10.36; I, 46.42.

Representative Procedure of LIS Study. A solution of known concentration of quaternary salt was prepared in an oven-dried NMR tube. To this solution were added known volumes of a Eu(fod)$_3$ solution prepared to known molarity. NMR spectra were recorded after each addition. The relative concentration of Eu(fod)$_3$:substrate was kept below 0.2:1. Replicate experiments were performed.

Acknowledgment. Discussions with Drs. T. Phil Pitner, A. Kassman, and J. F. Whidby are acknowledged with pleasure.

Registry No.—**1**, 21446-46-8; **4**, 62126-65-2; **5**, 110-95-2; **6**, 112-18-5; **7**, 112-00-5; iodomethane, 74-88-4.

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(8) The shifts observed in these studies may be viewed as a counterion modification effect. Schiementz [*Tetrahedron*, **29**, 741 (1974), and earlier papers in this series] has shown that the anion $B(C_6H_5)_4^-$ can act as an effective shift reagent for quaternary ammonium cations in, e.g., R_4N^+ $B(C_6H_5)_4^-$ salts.

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(11) Following the completion of this portion of our work, K. B. Lipkowitz reported (Ph.D. Thesis, Montana State University, 1975, pp 171–178, Xerox University Microfilms No. 76-13,307) a LIS study of a sulfonium iodide. Two modes of lanthanide complexation are suggested, either with the remaining lone pair on sulfur or the halide counterion.

(12) **Note Added in Proof.** A competitive shift study between *N*-methyldodecylamine and **7** led to results nearly identical with those shown in Figure 3, i.e., significantly greater LIS were observed for the *N*-methyl and *N*-methylene protons of the quaternary salt than for the corresponding protons of the free base. A similar competitive study between dodecylamine and **7** resulted in nonlinear LIS, indicating the probable need for association constant determinations in these systems.

Thermolysis of *N*-Acyl Substituted 2-Allylthioimidazolines. Evidence for a [3,3] Sigmatropic Rearrangement

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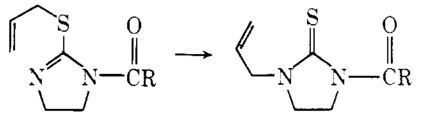
Thermal allylic rearrangements have been a subject of continuing synthetic[1] and mechanistic[2] interest. In relation to a current project dealing with the mechanism of biotin catalysis,[3] *N*-acetyl-2-allylthioimidazoline (**1a**) and *N*-carbomethoxy-2-allylthioimidazoline (**1b**) were prepared as potential model substrates. In light of the molecular framework of **1a** and **1b** it also became of interest to investigate the thermal properties of each of these compounds.

Pyrolysis of **1a** (145 °C, 72 h) gave the rearranged imidazolidinethione (**2a**) as the only product in 75% yield. Conversion of **1a** → **2a** could be monitored by the characteristic downfield NMR shift of the acetyl methyl protons from δ 2.20 to δ 2.80.[4]

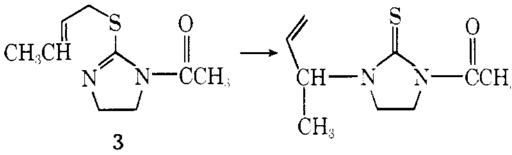


1a, R = CH_3
b, R = OCH_3

2a, R = CH_3
b, R = OCH_3

Mechanistically, the thermal allylic rearrangement of **1a** can be formulated in terms of a number of different dissociative-recombination and concerted reaction pathways. Additional insight into the mechanism operative in this system comes from the thermolysis of compound **3**. *N*-Acetyl-2-crotylthioimidazoline (**3**) was readily prepared by the treatment of *N*-acetylimidazolidinethione[5] with a commercial mixture of 1-bromo-2-butene (80%) and 3-bromo-1-butene (20%) and triethylamine. Despite the possibility of forming a number of different positional isomers, a 91% yield of **3** (a mixture of *E* and *Z* isomers) was obtained.

Thermolysis of **3** under comparable reaction conditions (145 °C, 30 h) gave a 90% yield of *N*-acetyl-*N′*-(3′-butenyl)imidazolidinethione (**4**) as the only isolated product. Support for the indicated substitution pattern in the butenyl side chain comes from three complementary NMR observations. First, the lone methine proton resonance was identified as part of the complex multiplet at δ 5.10–6.04 by two successive proton decoupling experiments. Double irradiation of the protons at δ 1.23–1.30 in compound **4** simplified the multiplet at δ 5.10–6.04. Correspondingly, when the multiplet at δ 5.10–6.04 was doubly irradiated, the doublet at δ 1.23–1.30 collapsed into a singlet. Second, a comparison of the NMR spectrum of **2a** with that of **4** showed that the resonance associated with the allylic methylene protons (δ 4.22–4.40) in the former compound was absent in the spectrum of compound **4**. Third, an upfield shift of the high-field methyl proton resonance from δ 1.60–1.82 in **3** to δ 1.23–1.30 in **4** was noted. The resonance at ca. δ 1.60 is a diagnostic peak for vinylic methyl protons,[6] and the absence of this resonance in the spectrum of **4** is a further evidence of structure. The thermal rearrangement can



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4