Anal. Calcd for $C_{13}H_{20}O_3$: mol wt, 224.1412. Found: mol wt, 224.1392 (MS).

Registry No.—**1**, 6066-49-5; **8**, 3553-34-2; **9**, 6697-07-0; **10**, 62006-38-6; **11**, 62006-39-7.

References and Notes

(1) G. Ciamician and P. Silber, *Ber.*, **30**, 492, 501, 1419, 1424, 1427 (1897).
(2) C. W. Wilson III, *J. Food Sci.*, **35**, 766 (1970).
(3) H. J. Gold and C. W. Wilson III, *J Org. Chem.*, **28**, 985 (1963).
(4) H. J. Gold and C. W. Wilson III, *J. Food Sci.*, **28**, 484 (1963).
(5) E. Guenther in "The Essential Oils", Vol. 4, Van Nostrand, New York, N.Y., 1950, p 599.
(6) Y. R. Naves, *Helv. Chim. Acta*, **26**, 1281 (1943).
(7) H. J. Gold and C. W. Wilson III, *Proc. Fla. State Hort. Soc.*, **74**, 291 (1961).
(8) The sedative effects on mice of celery oil phthalide components are described elsewhere.
(9) This assignment is corroborated by spectra of various conjugated cyclohexadiene carboxylic esters: W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *J. Org. Chem.*, **27**, 1851 (1962).
(10) A possible 5,6-dihydrophthalide system would require greater signal complexity in the downfield region, due to coupling of each vinyl proton with two adjacent aliphatic protons. Also, the large cis-vinyl coupling (J = 10 Hz) would not be present.
(11) D. H. R. Barton and J. X. DeVries, *J. Chem. Soc.*, 1916 (1963).
(12) K. Takeda, H. Minato, and M. Ishikawa, *J. Chem. Soc.*, 4578 (1964).
(13) B. B. Brodie, *J. Pharm. Pharmacol.*, **8**, 1 (1956).

Some 1-Pentacyanobutadienyl Derivatives[1]

R. B. King* and J. W. Howard, Jr.[2]

Department of Chemistry, University of Georgia,
Athens, Georgia 30602

Received February 15, 1977

In 1972 reactions of polycyanovinyl halides with metal carbonyl anions were first reported[3] to give good yields of stable polycyanovinyl transition metal derivatives.[4] Subsequent work[5,6] showed that further reactions of these polycyanovinyl transition metal derivatives gave a variety of unusual and interesting cyanocarbon transition metal complexes including compounds containing terminal[7,8] and bridging[3,4] dicyanovinylidene ligands, dicyanoketeneimmonium derivatives,[9] novel types of chelates,[9] and new polycyano olefin complexes.[10]

This extensive new area of transition metal chemistry created by the discovery of polycyanovinyl transition metal derivatives made of interest the preparation and reactions of similar transition metal polycyanobutadienyl derivatives. This suggested an investigation of reactions of halopolycyanobutadienes with metal carbonyl anions. However, since halopolycyanobutadienes were completely unknown at that time, it was first necessary to develop methods for their preparation. This paper describes the methods for the preparation of 1-halopentacyanobutadienes that we first developed in 1972 as well as their reactions with certain metal carbonyl anions to give pentacyanobutadienyl transition metal derivatives.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 621 spectrometer with grating optics. Mass spectra were determined using a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Relative intensities are given in parentheses with the indicated relative intensities for the ions containing chlorine and bromine being the sums of the ions containing the two major isotopes (i.e., ^{35}Cl and ^{37}Cl for chlorine and ^{79}Br and ^{81}Br for bromine). Melting points are taken in capillaries and are uncorrected.

Tetracyanoethylene was purchased from Kay-Fries Chemicals Inc., New York, N.Y., and converted to tetraethylammonium pentacyanobutadien-1-olate via tetracyanoethane[11] and disodium hexacyanobutenediide[12] by the published procedure.[13] Metal carbonyl derivatives were obtained by procedures similar to those used in previous work.[4]

Preparation of 1-Chloropentacyanobutadiene. A solution of 10.0 g (30.8 mmol) of tetraethylammonium pentacyanobutadien-1-olate in 150 mL of redistilled 1,2-dimethoxyethane was added to a solution of 7.7 g (5.2 mL, 60.8 mmol) of redistilled oxalyl chloride in 50 mL of redistilled 1,2-dimethoxyethane. After stirring for 34 h at room temperature, the reaction mixture was filtered to remove a tan precipitate. Solvent was then removed at ~25 °C (40 mm). The residue was extracted with dichloromethane. Excess diethyl ether was added to the filtered dichloromethane extract to precipitate 3.22 g of unreacted tetraethylammonium pentacyanobutadien-1-olate (32% recovery), identified by its infrared spectrum. After removal of this precipitate by filtration followed by evaporation of the filtrate at ~25 °C (40 mm), sublimation of the residue at 110–125 °C (0.2 mm) gave 1.91 g (29% conversion, 42% yield) of white, crystalline 1-chloropentacyanobutadiene: mp 195 °C dec; infrared spectrum (KBr) 2245 (w), 1540 (m), 1524 (m), 1399 (vw), 1378 (vw), 1357 (m), 1315 (sh), 1277 (w), 1234 (m), 1226 (m), 1208 (w, sh), 1028 (w), 1000 (m), 978 (w), 924 (vw), 900 (m), 806 (vw), 778 (m), 771 (w, sh), 654 (vw), 623 cm^{-1} (vw); ultraviolet spectrum (CH_3CN) 329 nm (ϵ 4700), 315 (6400), 264 (9200), 253 (11 400); mass spectrum $C_9N_5Cl^+$ (100), $C_8N_4Cl^+$ (6), $C_9N_5^+$ (13), $C_8N_4^+$ (9), $C_7N_3^+$ (15), $C_5N_3^+$ (7), $C_6N_2^+$ (16), C_3NCl^+ (15), $C_4N_2^+$ (33), C_4N^+ (10), C_3N^+ (7), C_2N^+ (9).

In repeat experiments the yields of 1-chloropentacyanobutadiene were erratic.

Anal. Calcd for C_9ClN_5: C, 50.5; H, 0.0; N, 32.8. Found: C, 49.4, 51.2; H, 0.3, 0.8; N, 33.1; 32.6.

Preparation of 1-Bromopentacyanobutadiene. A. From $[(C_2H_5)_4N][C_4(CN)_5O]$ and Oxalyl Bromide. A solution of 10.0 g (308 mmol) of tetraethylammonium pentacyanobutadien-1-olate in 100 mL of redistilled 1,2-dimethoxyethane was added to a solution of 7.2 g (3.0 mL, 33.3 mmol) of oxalyl bromide in 150 mL of 1,2-dimethoxyethane. After stirring for 22 h at room temperature solvent was removed at 40 °C (40 mm). The residue was extracted with two 250-mL portions of benzene. Evaporation of the filtered benzene extracts at ~40 °C (40 mm) gave a pale brown residue. Fractional sublimation of this residue first gave 0.33 g of an unidentified substance at 110–125 °C (0.2 mm) which was not investigated further since its infrared spectrum showed the absence of cyano groups. After removal of this substance, further vacuum sublimation at 130–135 °C (0.2 mm) gave 0.56 g (7% conversion, 12% yield) of 1-bromopentacyanobutadiene, identified by its infrared spectrum (see below). The residue remaining from the benzene extraction was crystallized from a mixture of dichloromethane and diethyl ether to give 4.1 g (41% recovery) of unreacted tetraethylammonium pentacyanobutadien-1-olate.

B. From $Na_2C_4(CN)_6$ and Bromine. A mixture of 10.1 g (~40 mmol) of disodium *trans*-hexacyanobutenediide [dried at 110 °C (0.1 mm) for 20 h], 4.0 mL (11.7 g, 73.1 mmol as Br_2) of bromine, and 80 mL of hexane was stirred for 25 h at room temperature. The reaction mixture was then evaporated to dryness at 40 °C (40 mm). Excess bromine was removed by pumping at 25 °C (0.1 mm) for 12 h. The dark brown residue was extracted with two 150-mL portions of benzene followed by one portion of 1,2-dichloroethane. Evaporation of the combined extracts at ~40 °C (40 mm) followed by vacuum sublimation at 135 °C (0.2 mm) gave 0.9 g (9% yield) of 1-bromopentacyanobutadiene: mp 228 °C dec; infrared spectrum (KBr) 2251 (w), 1549 (m), 1531 (m), 1401 (w), 1375 (m), 1348 (vw), 1276 (w), 1265 (m), 1220 (m), 1211 (vw), 1199 (vw), 1030 (vw), 1021 (w), 1002 (vw), 925 (vw), 911 (w), 872 (vw), 809 (vw), 784 (m), 777 cm^{-1} (w); ultraviolet spectrum (CH_3CN) 333 nm (ϵ 3700), 313 (4400), 265 (9600), 253 (9700); mass spectrum $C_9N_5Br^+$ (100), $C_9N_5^+$ (95), $C_8N_4^+$ (5), $C_7N_3^+$ (40), $C_5N_3^+$ (19), $C_6N_2^+$ (20), $C_4N_2^+$ (42), C_4N^+ (13), C_3N^+ (7), C_2N^+ 12).

Anal. Calcd for C_9BrN_5: C, 41.8; H, 0.0; N, 27.1; Br, 31.0. Found: C, 41.9; H, 0.3; N, 27.1; Br, 30.6.

Preparation of 1-Ethoxypentacyanobutadiene. A mixture of 0.30 g (1.4 mmol) of 1-chloropentacyanobutadiene, 10 mL of absolute ethanol, and 50 mL of tetrahydrofuran was boiled under reflux for 24 h. Removal of solvent at ~40 °C (40 mm) followed by crystallization from a mixture of dichloromethane and hexane gave a total of 0.30 g (96% yield) of 1-ethoxypentacyanobutadiene. Sublimation of the crude product at 110 °C (0.15 mm) gave the analytical sample as white crystals: mp 130–132 °C; infrared ν(CN) 2245 (w), ν(C=C) 1570 (m) and 1535 cm^{-1} (m); ^1H NMR spectrum CH_2 at τ 5.28 (quartet, J = 7 Hz), CH_3 at τ 8.44 (triplet, J = 7 Hz); ultraviolet spectrum (CH_3CN) 347 nm (ϵ 7500), 337 (6600), 270 (10 200).

Anal. Calcd for $C_{11}H_5N_5O$: C, 59.2; H, 2.2; N, 31.4. Found: C, 59.7; H, 2.4; N, 30.4.

Reaction of 1-Bromopentacyanobutadiene with $NaMn(CO)_5$. A solution of $NaMn(CO)_5$ was prepared by stirring a solution of 1.0 g (2.55 mmol) of $Mn_2(CO)_{10}$ in 50 mL of redistilled tetrahydrofuran with an amalgam of 0.2 g (8.7 mg-atoms) of sodium metal in 5 mL of mercury for 1.5 h. This solution was treated at −78 °C with a solution of 0.9 g (3.5 mmol) of 1-bromopentacyanobutadiene in 100 mL of redistilled tetrahydrofuran. After the resulting green mixture was stirred for 1 h at room temperature, solvent was removed at 25 °C (40 mm). The residue was extracted with dichloromethane. Addition of hexane to the filtered dichloromethane extracts followed by slow solvent removal at ~25 °C (40 mm) and addition of hexane gave 0.27 g (21% yield) of yellow $(NC)_2C{=}C(CN)C(CN){=}C(CN)Mn(CO)_5$. The analytical sample was obtained by chromatography of the filtrate on Florisil in dichloromethane solution followed by recrystallization from mixtures of dichloromethane and hexane to give a yellow solid: mp 140 °C dec; infrared spectrum ν(CO) frequencies at 2142 (s), 2090 (m), and 2048 cm^{-1} (vs) in CH_2Cl_2; ν(CN) frequencies at 2246 (w) and 2236 cm^{-1} (w) in KBr; and ν(C=C) frequencies at 1525 (s) and 1505 cm^{-1} (m) in KBr.

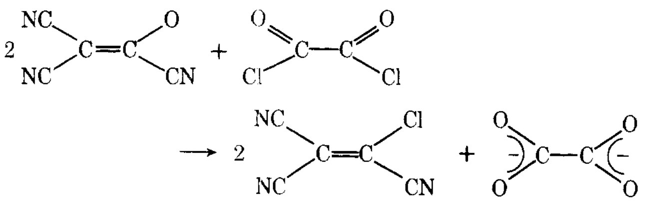
Anal. Calcd for $C_{14}MnN_5O_5$: C, 45.0; H, 0.0; N, 18.8; O, 21.4. Found: C, 45.0; H, 0.0; N, 18.4; O, 22.0.

Reaction of 1-Bromopentacyanobutadiene with $NaW(CO)_3C_5H_5$. A solution of $NaW(CO)_3C_5H_5$ was prepared by boiling under reflux a mixture of 1.41 g (4 mmol) of $W(CO)_6$ and 5 mmol of sodium cyclopentadienide (from NaH and cyclopentadiene) in 1,2-dimethoxyethane solution. This solution was treated at −78 °C with 1.03 g (4 mmol) of 1-bromopentacyanobutadiene. After stirring for 2 h at room temperature, the solvent was removed at ~40 °C (40 mm). A concentrated solution of the purple residue in dichloromethane was chromatographed on a Florisil column. Red-violet ($[C_5H_5W(CO)_3]_2$), orange ($C_5H_5W(CO)_3Br$), and magenta (unidentified) bands were first successively eluted from the chromatogram with mixtures of dichloromethane and hexane. Further elution of the next yellow-brown band with pure dichloromethane followed by evaporation of the eluate and two successive crystallizations from mixtures of dichloromethane and hexane gave 0.05 g (2.5% yield) of yellow $(NC)_2C{=}C(CN)C(CN){=}C(CN)W(CO)_3C_5H_5$: mp 185–190 °C dec; infrared spectrum ν(CH) frequency at 3121 cm^{-1} (w) in KBr; ν(CN) frequencies at 2245 (w) and 2230 cm^{-1} (w) in KBr; ν(CO) frequencies at 2050 (s) and 1955 cm^{-1} (vs) in CH_2Cl_2; ν(C=C) frequencies at 1523 (m) and 1500 cm^{-1} (m) in KBr; ^1H NMR spectrum in $(CD_3)_2CO$, τ (C_5H_5) 3.85.

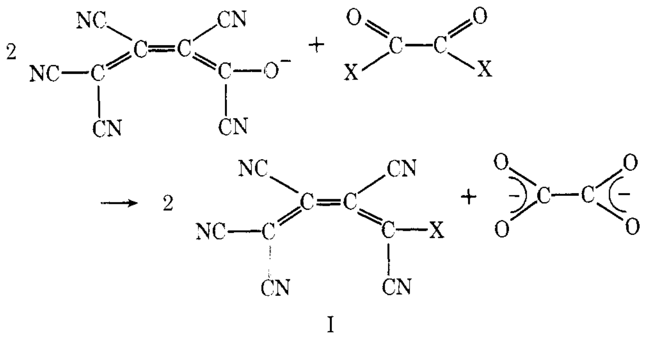
Anal. Calcd for $C_{17}H_5N_5O_3W$: C, 39.9; H, 1.0; N, 13.7; O, 9.4. Found: C, 40.3; H, 1.4; N, 12.9; O, 10.1.

Results and Discussion

The reaction of tetramethylammonium tricyanoethenolate with oxalyl chloride in 1,2-dimethoxyethane has been reported[14] to provide a convenient synthesis of tricyanovinyl chloride according to the following scheme:



Our syntheses of 1-halopentacyanobutadienes use the completely analogous reactions of tetraethylammonium pentacyanobutadien-1-olate with oxalyl halides in 1,2-dimethoxyethane according to the following schemes (X = Cl or Br):



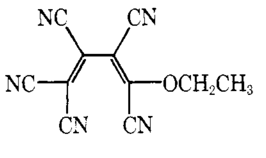
I

The yields of the 1-halopentacyanobutadienes from these reactions were somewhat erratic for reasons that are not completely clear. Alternative reagents for conversion of the tetraethylammonium pentacyanobutadiene-1-olate to 1-chloropentacyanobutadiene (I, X = Cl) are $POCl_3$ in 1,2-dimethoxyethane and thionyl chloride in dichloromethane, but neither of these reagents appears to offer any advantages over oxalyl chloride.

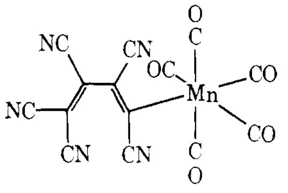
During the course of some work on hexacyanobutadiene, an alternative synthesis of 1-bromopentacyanobutadiene (I, X = Br) was discovered. The reaction of disodium hexacyanobutenediide with bromine vapor is reported[12] to result in oxidation to give hexacyanobutadiene. However, in this work the reaction of disodium hexacyanobutenediide with excess bromine in hexane solution was found to proceed differently resulting in replacement of one cyano group with bromine to give 1-bromopentacyanobutadiene. Speculation on the mechanism of this interesting reaction appears premature.

The spectroscopic properties of the 1-halopentacyanobutadienes (I, X = Cl and Br) are in accord with the proposed structures. The infrared spectra exhibit the expected ν(CN) frequencies at 2248 ± 3 cm^{-1} as well as symmetric and antisymmetric ν(C=C) frequencies at 1545 ± 5 and 1528 ± 4 cm^{-1}, respectively. The mass spectra exhibit the expected molecular ions. These molecular ions $C_9N_5X^+$ fragment most readily by halogen loss to give $C_9N_5^+$ followed by successive CN losses to give $C_8N_4^+$, $C_7N_3^+$, and $C_6N_2^+$. The last ion may be derived from 1,4-dicyanobutadiyne, $NCC{\equiv}CC{\equiv}CCN$. Another important ion is $C_4N_2^+$ possibly derived from dicyanoacetylene. In the chloro derivative I (X = Cl) cyano loss from the molecular ion to give $C_8N_4Cl^+$ apparently can compete with the more usual chlorine loss to give $C_9N_5^+$, whereas the analogous $C_8N_4Br^+$ was not found in the corresponding bromo derivative I (X = Br) apparently because of the lower strength of carbon–bromine bonds relative to carbon–chlorine bonds.

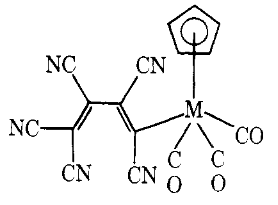
The halogen atoms in the 1-halopentacyanobutadienes were found to be relatively reactive toward nucleophiles similar to the halogen atoms in polycyanovinyl halides. Thus treatment of 1-chloropentacyanobutadiene (I, X = Cl) with ethanol readily leads to replacement of the chlorine with an ethoxy group to form 1-ethoxypentacyanobutadiene (II). The compound II was also isolated when diethyl ether was used to crystallize the crude product from tetraethylammonium pentacyanobutadien-1-olate and oxalyl chloride.



II



III



IV

The halogen atoms in the 1-halopentacyanobutadienes (I) were also found to be reactive toward metal carbonyl anions to give pentacyanobutadienyl transition metal carbonyl derivatives. Thus the reaction of 1-bromopentacyanobutadiene with $NaMn(CO)_5$ gives the manganese pentacarbonyl derivative $(NC)_2C{=}C(CN)C(CN){=}C(CN)Mn(CO)_5$ (III) identified 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 ($\sim$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 $\sim$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.

References and Notes

(1) Portions of this work were presented at the 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 1972, Abstracts, Paper 255.

(2) Postdoctoral research associate, 1971–1972.

(3) R. B. King and M. S. Saran, *J. Am. Chem. Soc.*, **94**, 1784 (1972).
(4) R. B. King and M. S. Saran, *J. Am. Chem. Soc.*, **95**, 1811 (1973).
(5) R. B. King, *Ann. N.Y. Acad. Sci.*, **239**, 171 (1974).
(6) R. B. King in "Organotransition Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, pp 37–47.
(7) R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 1053 (1972).
(8) R. B. King and M. S. Saran, *J. Am. Chem. Soc.*, **95**, 1817 (1973).
(9) R. B. King and M. S. Saran, *Inorg. Chem.*, **14**, 1018 (1975).
(10) M. S. Saran and R. B. King, paper presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975, Abstracts, No. INOR-25; R. B. King, M. S. Saran, D. P. McDonald, and S. P. Diefenbach, manuscript in preparation.
(11) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).
(12) O. W. Webster, *J. Am. Chem. Soc.*, **86**, 2898 (1964).
(13) O. W. Webster, *J. Am. Chem. Soc.*, **88**, 4055 (1966).
(14) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).
(15) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

Quaternary Ammonium Halides as Powerful Lanthanide Shift Donors

Jeffrey I. Seeman* and Ronald L. Bassfield

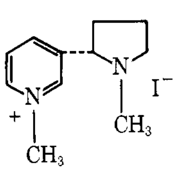
Philip Morris Research Center, P.O. Box 26583,
Richmond, Virginia 23261

Received December 14, 1976

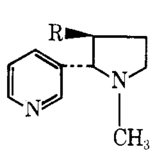
Lanthanide shift reagents (LSR) have been of considerable use in a wide variety of structural problems, ranging from the determination of relative configurations to the assessment of enantiomeric purity.[1] The simplicity of this nuclear magnetic resonance technique belies the complexity of the mechanisms[2] 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.



1



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