

Organometallic Chemistry. VII. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study and the Bonding Nature of the Ethylenemercurinium Ion. Preparation and Study of the Norbornadiene- and 1,5-Cyclooctadienemethylmercurinium Ions¹

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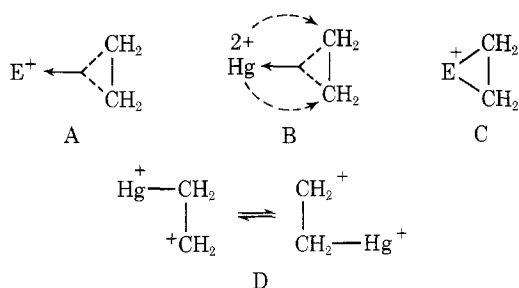
In continued study of the ethylenemercurinium ion its high-resolution carbon-13 NMR spectrum is reported. Based on the carbon chemical shift, and the carbon-proton coupling constant, the nature of bonding in the ethylenemercurinium ion is best characterized by the predominance of the forward donating σ component with a significant decrease in the electron density at the olefinic carbons. The first nonconjugated diolefin-mercurinium ion complexes, the norbornadiene- and 1,5-cyclooctadienemethylmercurinium ions, were also prepared by direct mercuriation of the diolefins with methylmercuric fluorosulfate, and studied by ^1H and ^{13}C NMR spectroscopy.

In recent publications from this laboratory the first direct observation of stable mercurinium ions of monoolefins was reported.² We would like now to report the extension of these studies, and a better understanding of the bonding nature in the ethylenemercurinium ion 1 based on its high-resolution ^{13}C NMR spectrum, as well the preparation of first mercurinium ions formed by the direct mercuriation of the nonconjugated diolefins, norbornadiene 2, and 1,5-cyclooctadiene 3.

Results and Discussion

Further Study of the Ethylenemercurinium Ion. The ethylenemercurinium ion 1 was prepared, as described, from the reaction of 2-methoxyethylmercuric chloride with excess $\text{HSO}_3\text{F-SbF}_5$ in SO_2 .³ The ^1H NMR spectrum consists of the reported singlet at δ 7.68 with satellites due to the proton-mercury coupling of $J_{^{199}\text{Hg-H}} = 190$ Hz.³ The proton-coupled high-resolution ^{13}C NMR spectrum consists of a triplet centered at $\delta_{^{13}\text{C}}$ 137.2 (from Me_4Si) with the proton-carbon coupling of $J_{\text{C-H}} = 170$ Hz.

If any electrophile E^+ approaches an olefin in electrophilic addition reactions, the initial bonding interaction was suggested to involve the formation of a molecularly bonded bridged π complex to form a two-electron, three-center bound species, as A.⁴ If d, or its hydride orbitals are available in the electrophile, according to the Chatt-Dewar-Duncanson bonding description,⁵ back donation becomes significant, as shown for the case of a mercurinium ion B. Subsequently, the π complex can either interact further to give a σ -bonded, three-membered ring (σ complex) C or open the three-center bond to give the corresponding β -substituted rapidly equilibrating carbenium ion D.





Recently, the ability of ^{13}C NMR spectroscopy to distinguish between σ - and π -complex intermediates in electrophilic addition reaction to alkenes has been demonstrated.^{6,7} The ^{13}C shift and $J_{\text{C-H}}$ coupling constants are dependent on a combination of factors.⁸ A net deshielding

at a nucleus is accompanied by a decrease of electron density, an increase in π character, or a decrease in the average electronic excitation energy.⁹ An increase of $J_{\text{C-H}}$ is observed when the electron density is decreased, the π character is increased, or especially a strained ring is formed. Based on both ^{13}C shifts ($\delta_{^{13}\text{C}}$ 69–74 for the parent, unsubstituted ions) and $J_{\text{C-H}}$ values (≈ 187 Hz), it has been proposed that the ethylenehalonium ions^{7,10,11} are best formulated as three-membered ring σ -bonded ions C. The substantial deshielding results from a decrease of π character by the formation of the bridged ion being more than compensated for by a decrease of electron density due to the polarization of positive charge on the electrophile. The increase of $J_{\text{C-H}}$ results from a preponderant increase of ring strain by the formation of a three-membered ring cyclic ion over the decrease of electron density and of π character. An approximately linear relation between ^{13}C shifts and $J_{\text{C-H}}$ coupling constants exists among cyclic halonium ions, ethylenearenium ions, and typical three-membered ring systems such as cyclopropane, ethylene oxide, ethylene sulfide, and *N*-methylaziridine.¹⁰ However, the ethylenemercurinium ion falls far away from this correlation.

Recent studies indicate that isolable halogen complexes of adamantylideneadamantane are π complexes due to steric hindrance.⁶ The significant deshielding observed (22–26 ppm) was proposed to result from a decrease of the electron density at the olefinic carbons predominating over a decrease of the π character. The same deshielding effect is now observed in the ethylenemercurinium ion, which is, therefore, also best formulated as the molecularly bonded π complex. The smaller deshielding (12.7 ppm) can be explained either by the weaker interaction or by the back donation of the π component in bonding as B, since back donation not only increases the total electron density but also reduces the π character of the olefinic carbons and results in an increase of shielding. Recent ^{13}C NMR studies on transition metal π complexes showed that the shielding for olefinic carbons is correlated with the relative magnitude of the π component in bonding. As the magnitude of the π component increases, a net increase in shielding is observed from Hg^+ (–12.7 ppm), Cu^+ (+28 ppm),¹³ Ag^+ (+14 ppm),^{6,12} Pt (+39–84 ppm),¹⁴ Rh (+61–85 ppm).¹⁵ The present ^{13}C study, consistent with theoretical calculation,¹⁶ indicates the predominance of the σ -bonding component in mercurinium ions due to the greater separation of the 6s and 5d orbitals in mercury.

The increase of the $J_{\text{C-H}}$ coupling constant (13.6 Hz) in ethylenemercurinium ion is consistent with the formation of B.^{12b,15} Comparison with the increase of coupling con-

Table I
Proton NMR Parameters of Methyl in Mercurinium Ions and Their Diolefinic Precursors^a

Compd	Solvent, temp, °C	-CH=	-CH ₂ -	-CH-	CH ₃ Hg-
 2 ^b	SO ₂	6.70 (t, <i>J</i> = 1.9 Hz)	1.96 (t, <i>J</i> = 1.6 Hz)	3.53 (sep)	
4	CH ₃ HgOSO ₂ F-SO ₂ , -70°	7.76 (t, <i>J</i> = 1.8 Hz)	2.17 (t, <i>J</i> = 1.4 Hz)	4.43 (sep)	1.37 (s)
 3 ^b	SO ₂	5.58 (s)	2.38 (uq)		
5	CH ₃ HgOSO ₂ F-SO ₂ , -70°	6.67 (um)	2.73 (um)		1.23 (s)

^a The proton NMR spectra were obtained on a Varian 56-60 instrument with a capillary of Me₄Si as reference. All chemical shifts are given relative to Me₄Si (parts per million). Multiplicity and coupling constants are given in parentheses: s, singlet; t, triplet; sep, septuplet; um, unresolved multiplet; and uq, unresolved quartet. ^b For previously reported proton NMR data, see ref 3.

stant from ethylene (*J*_{CH} = 157 Hz) to the highly strained cyclopropane ring (*J*_{CH} = 162 Hz) indicates that the even greater increase of coupling constant in ethylenemercurinium ion (*J*_{CH} = 170 Hz) can be due to the decrease in electron density upon complexation.¹⁷ Unlike other intermediate complexes of olefins with electrophiles, the observed ethylenemercurinium π complex, as the preferred stable species, seems to indicate that the participation of the π back donation (although a minor contribution) prevents rehybridization and formation of σ -bonded three-membered ring ion C.



The complete ¹H and ¹³C NMR spectra of the symmetrical ethylenemercurinium ion exclude the possibility of a static primary β -mercuryethyl cation D, even if Traylor suggested the possibility of vertical stabilization by σ - π conjugation¹⁸ (meaning electron delocalization with no subsequent molecular movement, i.e., bridging). The obtained ¹³C NMR data do not completely rule out the possibility of a rapidly equilibrating β -mercuryethyl cation system. However, the observed *J*_{199Hg-H} coupling of 190 Hz excludes any exchange process and argues against a rapidly equilibrating open chain ion, such as D.

The ethylenemercurinium ion is thus, based on its high-resolution ¹³C NMR spectroscopic study, a molecularly π -bonded species. As in most transition metal π complexes, both σ and π components are involved in bonding, but in the mercurinium ions the σ component is predominant. Furthermore, the electron density is reduced upon complexation and significant positive charge is developed on the carbon atoms.

Preparation and Study of Norbornadiene and 1,5-Cyclooctadienemethylmercurinium Ions. The methylmercurating agent used, methylmercuric fluorosulfate, was prepared by the reaction of a slight excess of dimethylmercury with fluorosulfuric acid in sulfur dioxide solution at -70°. The lack of excess acid results in a suitable and clear system for the investigation of mercurinium ions. Norbornadienemercurinium ion 4 and 1,5-cyclooctadienemercurinium ion 5 are formed when precooled 2 or 3 in pentane solution is slowly added with vigorous stirring to methylmercuric fluorosulfate in sulfur dioxide at -78°. The proton NMR data of 4 and 5 at -60° are summarized in Table I.

Both ions show similar NMR absorptions to those of their precursors, indicating that the dienes have not isomerized in the mercurinium complexes. The ¹H NMR spectra of the mercurinium ions are deshielded, especially the olefinic protons (where the deshielding is more than 1 ppm). Except for group 1B metals, most transition metal π complexes result in net shielding of olefinic protons.¹⁹ Whereas the silver ion complexes exhibit net deshielding,²⁰ the copper ion complexes are borderline cases.¹³ According to Dewar-Chart-Duncanson,⁵ the bonding in transition metal π complexes is composed of σ forward donation and

Table II
Carbon-13 NMR Parameters of Mercurinium Ions and Their Precursors^a

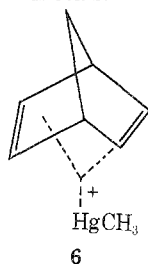
Compd	-CH=	CH ₂	CH methine
 2 ^b	144.26 (173.6)	74.86 (135.2)	50.23 (149.0)
4	152.69 (180.4)	76.71 (137.2)	53.46 (158.3)
 3 ^c	130.19	27.83	
5	139.68	29.84	

^a The spectra were recorded on a Varian HA-100 or XL-100 instrument by the Fourier transform method, at 25.2 MHz with a capillary of enriched CH₃I or Me₄Si as lock or reference at -60° in SO₂. ^b Previously reported spectra; see ref 23. ^c Previously reported spectra; see ref 14.

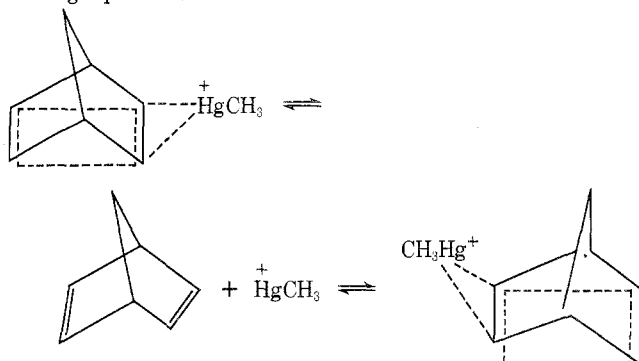
π back donation. The shielding effect of olefinic protons in ¹H NMR spectra has been proposed²² to result, at least in part, from the relative contributions of the σ and π components.^{20b,21} From these considerations, a greater π -bonding component results in the net shielding of the olefinic protons. The marked difference in silver ion complexes suggests that in these the σ component may predominate. Because of the greater separation of 5d and 6s orbitals of mercury, it is not surprising that the mercury π complexes consist almost entirely of the σ -bonding component. Based on molecular orbital calculations,¹⁶ the olefin transfers electron density to mercury and a significant positive charge is developed on the olefinic carbons. Therefore, the greatest deshielding is observed in mercurinium ions (2.1–2.4 ppm for monoolefinic protons).² However, both ions 4 and 5 show only half of the deshielding in comparison with that observed for the mercurinium ions of monoolefins. This indicates the participation of the second olefinic bond in the mercurinium ion formation of diolefins. As no proton-mercury coupling is observed in ions 3 and 4, it could indicate that fast exchange takes place in the system.

The carbon-13 NMR data of ions 4 and 5 are summarized in Table II. According to recent discussion of the carbon chemical shifts of transition metal π complexes,^{13,14a,21,24} the observed deshielding of olefinic carbons upon formation of mercurinium ions, consistent with the proton NMR spectra, is best rationalized on the basis of predominance of the σ -bonding component resulting in a significant decrease in the electron density at the olefinic carbons. Generally, norbornadiene complexes with transition metals in two distinct ways:^{19a} as a chelating ligand where the metal is situated in the endo position, and alternatively when the metal is situated in the exo position. When the metal is situated in the endo position, the π -electron density should concentrate between the ligand and the

metal. The electron density on the exo side decreases upon complexation, and the methylene carbons should be shielded, as observed in $C_7H_8Pt(CH_3)_2$,²⁵ $C_7H_8Fe(CO)_3$,²⁶ $C_7H_8Mo(CO)_3$,²⁷ and $C_7H_8Cr(CO)_3$.²⁷ The observed deshielding on the methylene carbons upon formation of mercurinium ions rules out the possible structure 6 to represent ion 7. Upon further consideration an exo-bonded structure is also consistent with the known norbornadiene π complexes of group 1B metals.²⁸



Based on the formation of nortricyclic product upon the mercuriation of 1²⁹ ion 3 is best rationalized by the following equilibrium.



The 1,5-cyclooctadiene-methylmercurinium ion is also considered to undergo similar equilibration. However, the small increase of J_{C-H} coupling constant (9 Hz) of the methine carbons upon formation of the mercurinium ion does not give definite proof for the homoallylic participation.

Experimental Section

Norbornadiene, 1,5-cyclooctadiene, and dimethylmercury were commercially available and used without further purification.

Methylmercuric fluorosulfate was prepared as previously described² except that a slight excess of dimethylmercury was used. Mercurinium ions were prepared by adding the corresponding diolefins in cold SO_2 to the stirred solution of methylmercuric fluorosulfate in SO_2 at -70° , as reported previously for alkenemercurinium ions.²

The 1H NMR spectra were obtained on a Varian A56/60A 1H NMR spectrometer.

The ^{13}C NMR spectra were obtained on a Varian XL-100 spectrometer. Fluorobenzene was used as external lock, and all chemical shifts are referred to the external Me_4Si (5% enriched) capillary.

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Registry No.—1, 38831-99-1; 2, 121-46-0; 3, 111-78-4; 4, 56666-11-6; 5, 56666-12-7; methylmercuric fluorosulfate, 43049-30-5.

Supplementary Material Available. The proton-coupled ^{13}C NMR spectrum of the ethylenemercurinium ion in SO_2 solution at -40° (Figure 1), the 1H NMR spectrum of the norbornadiene

methylenemercurinium ion in SO_2 solution at -70° (Figure 2), and the 1H NMR spectrum of 1,5-cyclooctadienemethylmercurinium ion in SO_2 solution at -70° (Figure 3) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JOC-75-3638.

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