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Organometallic Chemistry. 12. Proton and Carbon-13 Nuclear Magnetic Resonance Study of Arenemercurinium Ions, the Intermediate Complexes of Aromatic Mercuration

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Arenemercurinium ion complexes were prepared and studied by proton and carbon-13 NMR spectroscopy. It is concluded that the complexes are involved in fast exchange.

Electrophilic substitution reactions of aromatic compounds proceed via a mechanism involving intermediates of the types 1–3.[2]

1	2	3
Mulliken outer π complex	π complex (benzonium ion)	σ complex (benzenium ion)
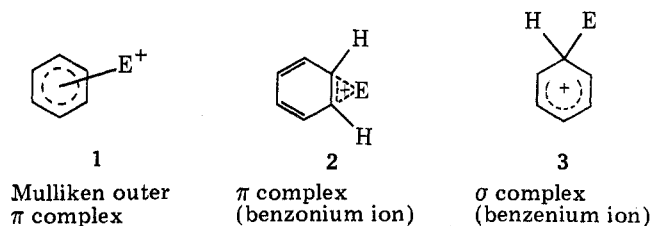
Protonated arenes (arenium ions 3) have been extensively studied,[3] but relatively little information is available regarding intermediates with other electrophiles. The heptamethyl 4 and heptaethylbenzenium ions are known from NMR studies,[4] and also from an x-ray crystallographic investigation of 4.[5] Recently, direct observation of long-lived σ-complexes in

4	5	6
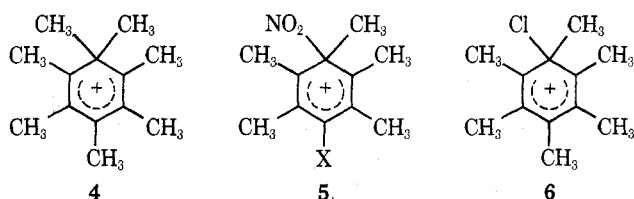
nitration[6,7] (5) and chlorination[7] (6) of hexasubstituted benzenes was also reported.

Although the existence of π-bonded aronium ions 2 is suggested by chemical evidence, they have never been observed as reaction intermediates. We have reported the preparation of bridged π complexes of olefin–mercurinium ions and have investigated them by NMR spectroscopy.[8] We considered, therefore, that a similar study of arenemercurinium ions might yield information on intermediate π-bonded complexes. Previously π-bonded complexes (of type 1) have been proposed for the mercurinium complexes of hexasubstituted benzenes from ^{1}H NMR studies,[9] while a σ complex was considered consistent with the complicated ^{1}H NMR spectrum obtained for the related pentamethylbenzenemercurinium ion.[9]

We now wish to report the results of our investigations by

^{1}H NMR and ^{13}C NMR spectroscopy of the intermediate complexes in aromatic mercurations.

Results and Discussion

Aromatics were mercurated using either mercuric trifluoroacetate or methylmercury acetate with excess fluorosulfuric acid in SO_2 solution.[9] ^{1}H NMR parameters of the intermediate arenemercurinium complexes so formed are summarized in Table I. In the ^{1}H NMR spectrum of monosubstituted benzenium ion complexes the ortho and meta protons show an AB-type quartet, the meta protons being further split by coupling with the para proton to give a doublet of doublets. Comparable spectra were obtained when *m*-methylanisole, 1,2,4-trimethoxybenzene, and pentamethylbenzene were mercurated. The observed spectra show some similarity to those obtained for monosubstituted ethylenearenium and benzenium ions (Table II).[10] Upon comparison, the ortho and meta protons of the mercurinium ion complexes are slightly shielded, the para proton more so, than the protons of the analogous arenium ions. However, the ^{1}H NMR spectra obtained from the mercurinium ion complexes of benzene, *m*-xylene, mesitylene, and 1,3,5-trimethoxybenzene are similar to those of the uncomplexed parent arenes except that the protons of the former show slight deshielding. No shifts characteristic of benzenium ions were observed.

Table III summarizes the ^{13}C NMR data for the arenemercurinium ion complexes investigated. For the arenemercurinium ions derived from monosubstituted benzenes, the ^{13}C NMR spectra show shifts characteristic of arenium ions. Upon complexation, ipso and ortho carbons become more deshielded, meta carbons are slightly deshielded, whereas shielding is observed for the para carbon. However, the shifts for the mercurinium complexes are not as large as for the corresponding ethylenearenium and arenium ions (Table II). On the other hand, unlike the corresponding arenium ions, the carbon-13 spectra of the mercurinium complexes of benzene, *m*-xylene, and mesitylene show symmetries related to their parent hydrocarbons, but not the arenium ions.
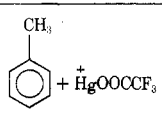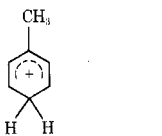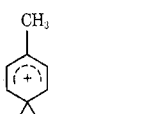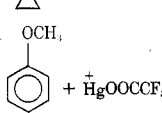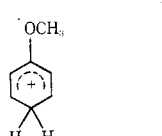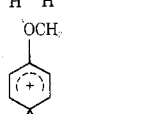
Based on the evidence of chemical shift data alone the possibility of the formation of σ complexes cannot be completely ruled out. The deshielding of the para proton and carbon in the monosubstituted complexes relative to the

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Table I. ^{3}H NMR Spectral Data of Arenemercurinium Ions in SO$_2$ Solution[a]

Arene	Ion registry no.	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	Other protons	Coupling constants, Hz	Temp, °C
Benzene	58747-09-4	8.33 (s)							−60
Toluene	58747-08-3	8.23 (d)	8.73 (dd)	7.47 (t)			CH$_3$, 3.00 (s)	$J_{2,3}$ = 7.5, $J_{3,4}$ = 5.5	−70
Anisole	58747-07-2	7.44 (d)	8.00 (dd)	7.03 (t)			OCH$_3$, 4.07 (s)	$J_{2,3}$ = 7.8, $J_{3,4}$ = 6.3	−40
Fluorobenzene	58747-10-7	7.97 (dd)	8.67 (m)	7.23 (um)				J_{H_2-F} = 22.0, $J_{2,3}$ = 8.5	−70
m-Xylene	58747-06-1	7.97 (um)		7.38 (dd)	8.47 (t)		CH$_3$, 2.77 (s)	$J_{4,5}$ = 6.4, $J_{2,4}$ = 1.4	−60
p-Methylanisole	58747-05-0	7.43 (s)		6.83 (d)	8.10 (dd)	7.32 (d)	CH$_3$, 2.71 (s), OCH$_3$, 4.07 (s)	$J_{4,5}$ = 6.0, $J_{5,6}$ = 8.0	−60
Mesitylene (1,3,5-trimethylbenzene)	58747-15-2	7.37 (s)					CH$_3$, 2.80 (s)		−60
1,3,5-Trimethoxybenzene	58747-13-0	6.03 (s)					OCH$_3$ 3.83 (s)		−40
1,2,4-Trimethoxybenzene	58747-14-1		7.43 (d)	7.33 (d)		7.80 (d)	OCH$_3$, 4.57 (s, 3 H), OCH$_3$, 4.60 (s, 6 H)	$J_{5,6}$ = 8.0	−40
1,2,3,4,5-Pentamethylbenzene	58747-12-9					6.63 (s)	CH$_3$, 2.67 (s, 9 H), CH$_3$, 2.43 (s, 6 H)		−60

[a] Chemical shifts in δ (ppm) refer to external Me$_4$Si capillary. The multiplicities are given in parentheses: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; u, unsolved.

Table II. Comparison of the Monosubstituted Arenemercurinium Ion Complexes with the Corresponding Ethylenearenium and Arenium Ions[a,b]

Compd	^{1}H NMR Data			^{13}C NMR Data			
	H$_o$	H$_m$	H$_p$	C$_i$	C$_o$	C$_m$	C$_p$
CH$_3$ + HgOOCF$_3$	8.23	8.73	7.47	169	135	148	90
CH$_3$ (H H)	8.48	9.43	5.05	201	139	181	49
CH$_3$	8.05	8.36		183	138	174	64
OCH$_3$ + HgOOCF$_3$	7.44	8.00	7.03	193	118	139	105
OCH$_3$ (H H)	7.5, 7.8	8.6, 9.0	4.5	193	129, 123	169, 176	42
OCH$_3$	7.47	8.12		170	123	174	49

[a] Data of ethylenearenium and arenium ions are obtained from ref 10. [b] o, ortho; m, meta; p, para, i, ipso refer to the substituent.

Table III. ^{13}C NMR Spectral Data of Arenemercurinium Ion Complexes[a,b]

Arene	C_1	C_2	C_3	C_4	C_5	Other carbon
Benzene	133.2					
	(128.6)					
Toluene	168.6	134.8	147.7	90.1		CH_3 24.2
	(137.8)	(129.3)	(128.5)	(125.6)		(21.2)
Anisole	192.6	118.4	139.0	105.2		OCH_3 57.0
	(158.9)	(113.2)	(128.7)	119.8		(54.7)
Fluorobenzene[c]	176.6	123.5	152.2	87.8		
	(163.8)	(114.6)	(130.3)	(124.3)		
m-Xylene	169.6	. 136.0		106.5	149.7	CH_3 23.0
	(137.5)	(130.1)		(126.4)	(128.3)	
Mesitylene	171.0	116.1				CH_3 22.97
	(137.4)	(127.1)				(21.0)

[a] All chemical shifts in δ ^{13}C (ppm) are referred to the external Me_4Si capillary. The chemical shifts of free arene are given in parenthesis for comparison. [b] The complexes generated with $Hg(CF_3COO)_2$ show trifluoromethyl carbon at δ 114.2 (q, $J_{C-F} = 283.8$ Hz) and carbonyl carbon at δ 161.6 (q, $J_{C-C-F} = 42.9$ Hz). [c] $J_{C_1-F} = 283.5$, $J_{C_2-F} = 21.8$, $J_{C_3-F} = 15$, and $J_{C_4-F} = 0$ Hz.

Table IV. J_{C-H} Coupling Constants (Hz) of Benzene, Fluorobenzene, and Mesitylene and Their Mercurinium Ion Complexes

		J_{C-H} (±5 Hz)	
		Parent arene	Mercurinium complex
Benzene		158	172
Mesitylene		154	165
Fluorobenzene	C_o	155[a]	176
	C_m	163	173
	C_p	161	163
Anisole	C_o	159	173[b]
	C_m	159	177
	C_p	162	177

[a] T. F. Page, Jr., *Mol. Phys.*, **13**, 523 (1967). [b] Chromium tricarbonyl complex from ref 13.

methylene protons and carbon in the corresponding arenium ions could be due to the effect of anistropy of the carbon-mercury bond. The "symmetric" spectra obtained for complexed benzene, m-xylene, etc., should then be explained by a fast inter- and/or intramolecular exchange of σ complexes.
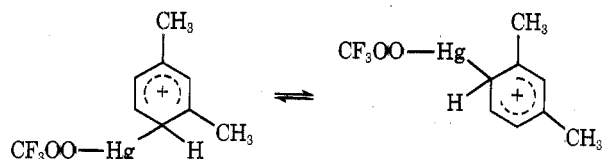
However, measurement of J_{C-H} coupling constants should differentiate between the two types of complex. If σ complexes are formed, the J_{C-H} coupling of the carbon at the site of mercuration should show a pronounced decrease in accordance with transformation from sp^2 to sp^3 hybridization. The J_{C-H} coupling constants for the complexes of benzene, fluorobenzene, and mesitylene together with those for the parent arenes and anisolechromium tricarbonyl are given in Table IV. No pronounced decrease of J_{C-H} coupling of the carbon at the site of mercuration upon complexation argues against the formation of σ complexes as the sole stable species observed. Recently a number of arene mercurous complexes were prepared, and the structure of these complexes, in analogy to those of similar argentous complexes, were shown by ^{13}C NMR to be molecularly bonded π complexes with fast bond shifts.[11]
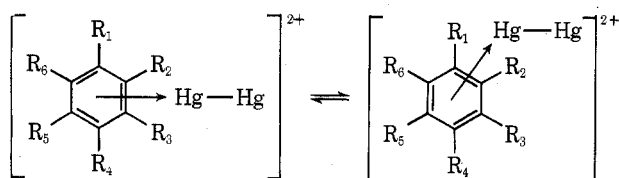
For these complexes both shielded and deshielded shifts (in comparison with the parent substrate) were observed for the ring carbons. Hg_2^{2+} shows a greater deshielding effect, attributed to its greater Lewis acidity compared to Ag^+. The shifts observed for the mercurinium ions of the present study are sufficiently different from those of either the Ag^+ or Hg_2^{2+} complexes, arguing against a similar structure. Furthermore, if the mercurinium complexes were π-bonded Mulliken-type outer complexes or similar to the arene cluster $Cr(CO)_3$ complexes,[12,13] a uniform downfield shift for all carbons relative to the free arene would be expected. This is contrary to what is observed, and thus the present data are inconsistent with the formation of π-bonded arenemercurinium ions. The best description for the arene mercurinium ion complexes is a rapid exchange of σ and π complexes.
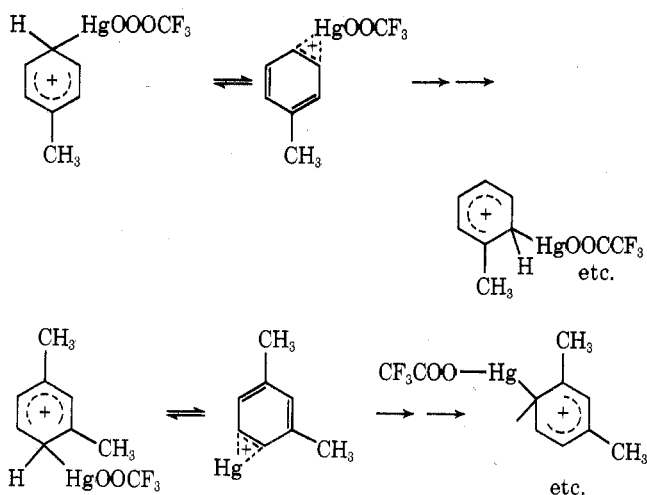
Such a rapid exchange is consistent with the reversibility and selectivity of aromatic mercuration reactions. At the same time data do not completely rule out an equilibrating σ-complexed system, in which the π-bridged complexes are only transition states.

Experimental Section

Mercuric trifluoroacetate and methylmercury acetate were purchased from Aldrich Chemical Co., and used without further purification. Fluorosulfuric acid was distilled before use.

Preparation of Complexes. An SO_2 solution at −78 °C of the parent arene was added, with vigorous stirring (vortex mixer), to a SO_2 solution containing excess $(CF_3COO)_2Hg$ or $CH_3COOHgCH_3$ and FSO_3H, also at −78 °C. This solution was then transferred to a precooled NMR probe for examination. Identical NMR spectra were obtained regardless of the other ligand or Hg. However, fluorobenzene was only mercurated by $(CF_3COO)_2Hg-FSO_3H$.

^{1}H NMR were recorded on a Varian A56/60 instrument fitted with

a variable temperature probe. ^{13}C NMR were recorded on a Varian XL-100 instrument fitted with a broad band decoupling and variable temperature probe.

Registry No.—Benzene, 71-43-2; toluene, 108-88-3; anisole, 100-66-3; fluorobenzene, 462-06-6; m-xylene, 108-38-3; p-methylanisole, 104-93-8; mesitylene, 108-67-8; 1,3,5-trimethoxybenzene, 621-23-8; 1,2,4-trimethoxybenzene, 135-77-3; 1,2,3,4,5-pentamethylbenzene, 700-12-9; mercuric trifluoroacetate, 13257-51-7; methylmercury acetate, 108-07-6; fluorosulfuric acid, 7789-21-1.

Supplementary Material Available. ^{1}H NMR spectra of anisole- and m-xylenemercurinium ions and ^{13}C NMR spectra of fluorobenzene- and anisolemercurinium ions (4 pages). For simplicity signals due to the counteranion were deleted. Ordering information is given on any current masthead page.

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Consecutive Decomposition Modes for *m*-Trifluoromethylphenylcopper in Ether[1]

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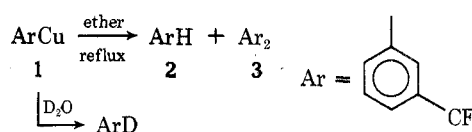
The decomposition of *m*-trifluoromethylphenylcopper in refluxing ether, both in the absence and presence of benzalacetophenone, has been monitored by withdrawing samples from time to time and quenching with D_2O. During the first phase of the decomposition, 3,3'-bis(trifluoromethyl)biphenyl (biaryl) is produced in both cases and, in the presence of the enone, conjugate addition occurs as well; this is the first reported case of a simple conjugate addition of an organocopper in the absence of lithium or magnesium salts. When approximately one-half of the organocopper has been consumed, the above behavior ceases and the remainder of the organocopper is converted to benzotrifluoride by removal of hydrogen from the solvent; such hydrogen removal was demonstrated by performing the decomposition in perdeuteriotetrahydrofuran and noting that the benzotrifluoride produced was monodeuterated to the extent of 46%. It is believed that the organocopper exists in these solvents as a cluster compound which splits out aryl groups pairwise, in competition with conjugate addition, until an intermediate such as Ar_4Cu_8 is reached; the latter then reacts with solvent by one of a number of possible mechanisms, which are discussed.

Results

While attempting to study one aspect of the mechanism of the Ullmann biaryl synthesis,[2] we made the intriguing observation that during the course of decomposition of *m*-trifluoromethylphenylcopper (1)[3] in ether solvents, the nature of the process changes markedly from the beginning to the end of the reaction. If this decomposition is carried out in refluxing ether and samples are withdrawn and quenched with water at various times, the quantities of benzotrifluoride (2, arene) in the quenched samples decrease and those of 3,3'-bis(trifluoromethyl)biphenyl (3, biaryl) increase until after about 6 h when the quantities of the two compounds cease changing.

However, it was soon found that those deceptively simple results mask quite surprising changes in the course of the reaction which start at about the time the quantities of products in the quenched samples become constant. This was ascertained by repeating the reaction, quenching the withdrawn samples with D_2O, and determining the yields in the quenched samples of biaryl (3) and arene (2) as well as the deuterium content of the latter (by combined gas chromatography–mass spectrometry); this procedure allows a distinction to be made between benzotrifluoride (ArH) which is present in the unquenched sample and that (ArD) which arises upon quenching

the reaction mixture, presumably by protonation of an organocopper compound.

$$\text{ArCu} \xrightarrow[\text{reflux}]{\text{ether}} \text{ArH} + \text{Ar}_2$$
$$\begin{array}{ccc} 1 & 2 & 3 \end{array}$$
$$\text{ArCu} \xrightarrow{D_2O} \text{ArD}$$

The first three columns of Table I indicate the raw data from such an experiment. The zero hour sample was withdrawn as soon as possible after the ether solution of arylcopper (1) and the gas chromatographic standard, durene, was removed from the glove box[4] in which it was prepared and before heat was applied. It is again seen that during the interval between 5 and 20 h, the quantities of biaryl and arene in the quenched samples become constant but that a substantial percent of the arene is monodeuterated and is thus derived from unreacted arylcopper; that is to say, even though reaction appears to cease some time between 5 and 20 h, a large amount of the arylcopper is still present. The fourth column indicates that, although there are some fluctuations in our material balance, owing mainly to the difficulty in sampling a mixture that becomes heterogeneous after a few hours (see below), the