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Isolation, Structure, and Reactivity of a Novel Chloro–Arenium Cation for Electrophilic (Transfer) Chlorinations

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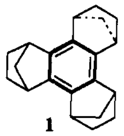
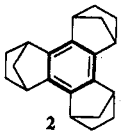
Cationic σ-complexes of aromatic hydrocarbons with various electrophiles (E^+) are especially relevant to the behavior of reactive intermediates in electrophilic aromatic substitutions.[1] Although spectroscopic evidence exists for such aromatic complexes with heteroatom E^+ (*e.g.*, NO_2^+, Br^+, etc.) in solution,[2,3] no crystalline salt has been isolated heretofore to unambiguously establish their molecular structure and to ascertain their chemical reactivity. Accordingly, we now report (a) the first isolation of a cationic chlorine–aromatic complex, (b) its structural characterization, and (c) its ability to transfer positive chlorine (*i.e.*, $E^+ = Cl^+$) and to effect electron transfer with various aromatic donors.

Especially efficacious for the formation of the arenium σ-complexes are the aromatic donors **1** and **2** as *anti* and *syn* isomers, respectively.[4] For example, a solution of **1** and the



1



2

chlorinating agent $SbCl_5$[5] in dichloromethane at −78 °C deposited a brightly colored solid, which upon recrystallization from a hexane/dichloromethane mixture at −20 °C afforded well-formed ruby-red crystals ($\mathbf{A_a}$) in excellent yields.[6] The treatment of the isomeric (*syn*) aromatic donor **2** with $SbCl_5$ under the same conditions yielded brightly colored crystals ($\mathbf{A_s}$) which were visually indistinguishable from $\mathbf{A_a}$.[7]

Single crystal analysis by X-ray crystallography at −50 °C established the chemical composition of $\mathbf{A_a}$ to consist of the salt $\mathbf{1}\text{-}Cl^+SbCl_6^-$.[8] The molecular structure of the cationic moiety is illustrated by the ORTEP diagram in Figure 1, which shows the unique chlorine atom in $\mathbf{1}\text{-}Cl^+$ to be directly bonded to a single aromatic carbon atom from the less hindered face of **1** so as to minimize the steric congestion arising from the transannular ethano (C_8–C_9) bridge.[9] The attachment of chlorine to the aromatic C_1 generates a cyclohexadienyl ring system which is distorted [*e.g.*, C_1–C_6 (1.52 Å) is significantly longer than C_1–C_2 (1.46 Å), and C_5–C_6 (1.35 Å) approximates a normal double bond] in a manner reminiscent of that rising from a Mills–Nixon effect.[10] Such a chromophoric unit, coupled with the relatively long carbon–chlorine bond distance of 1.86 Å,[11] is associated with the unusual colors of $\mathbf{1}\text{-}Cl^+$. Thus the UV–vis spectrum of $\mathbf{1}\text{-}Cl^+SbCl_6^-$ in dichloromethane solution shows a well-resolved absorption band with $\lambda_{max} = 510$ nm and $\epsilon_{max} = 4700\ M^{-1}\ cm^{-1}$, which is responsible for the intense red color. Moreover, the same spectrum is obtained from the diffuse reflectance of the ruby-red crystals of $\mathbf{A_a}$. It is important to emphasize that the electronic transition at $\lambda_{max} = 510$ nm in $\mathbf{1}\text{-}Cl^+$ occurs at significantly lower energy than that ($\lambda \sim 350$–400 nm) previously reported for related aromatic σ-complexes derived from either protonation or alkylation (*i.e.*, $E^+ = H^+, CH_3^+$).[12]

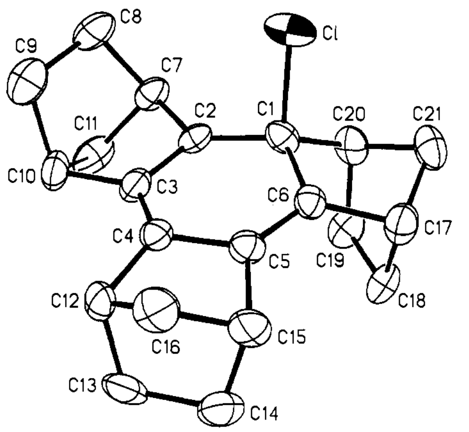
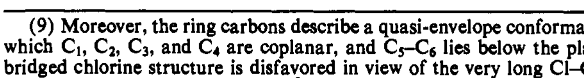


Figure 1. ORTEP diagram of the chloro–arenium cation ($\mathbf{1}\text{-}Cl^+$) with the hydrogens omitted for clarity.

We attribute the unique features of $\mathbf{1}\text{-}Cl^+$ to a structure that may be viewed as a positive chlorine atom stabilized (solvated) by an aromatic ligand acting as a σ-donor in a manner qualitatively described earlier for Wheland intermediates[1] and related arenium ions.[3] Such a structural formulation of $\mathbf{1}\text{-}Cl^+$ as a chloro–arenium ion is clearly reflected in the ease with which it effects Cl^+ transfer to various donors as follows.

Olefinic Donor. When an ice-cold solution of diadamantylidene **3** was mixed with an equimolar amount of $\mathbf{1}\text{-}Cl^+SbCl_6^-$ in dichloromethane, the red color was immediately bleached at −10 °C. Colorless crystals of $\mathbf{3}\text{-}Cl^+SbCl_6^-$ were collected at −78 °C, and they were unambiguously identified by spectral (IR) comparison with an authentic sample.[13] Quantitative isolation of $\mathbf{3}\text{-}Cl^+SbCl_6^-$ together with GC-MS analysis of the filtrate for the neutral aromatic donor (**1**) established the unequivocal 1:1 stoichiometry for Cl^+ transfer in eq 1.



(1)

Aromatic Donors. Treatment of $\mathbf{1}\text{-}Cl^+SbCl_6^-$ with mesitylene in dichloromethane solution led to the discharge of the red color

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(1) Taylor, R. *Electrophilic Aromatic Substitution;* Wiley: New York, 1990.

(2) Koptyug, V. A. Arenium Ions—Structure and Reactivity. In *Contemporary Problems in Carbonium Ion Chemistry III;* Rees, C., Ed.; Springer: New York, 1984.

(3) (a) Olah, G. A.; Lin, H. C.; Mo, Y. K. *J. Am. Chem. Soc.* **1972,** *94,* 3667. (b) Loktev, V. F.; Korchagina, D. V.; Shubin, V. G. *Izv. Nauk SSSR Otd. Khim. Nauk* **1974,** *10,* 2374.

(4) For the synthesis of the *anti/syn* isomers of 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro[1,4:5,8:9,12]trimethanotriphenylene, see: Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980,** *102,* 6863.

(5) Kovacic, P.; Sparks, A. K. *J. Am. Chem. Soc.* **1960,** *82,* 5740. Also see: Kovacic, P. In *Friedel Crafts and Related Reactions, Vol. IV;* Olah, G. A., Ed.; Interscience: New York, 1965.

(6) Typically, a dichloromethane solution of **1** (0.50 g) at −78 °C was treated with 2 equiv (1.08 g) of antimony pentachloride under an argon atmosphere to afford ruby-red crystals of $\mathbf{A_a}$ (1.1 g, 93%). The same procedure was used to prepare $\mathbf{A_s}$ from **2**.

(7) Ruby-red crystals of $\mathbf{A_a}$ and $\mathbf{A_s}$ persisted in air for rather prolonged periods. However, in dichloromethane solutions, $\mathbf{A_s}$ was significantly less stable than $\mathbf{A_a}$.

(8) Crystal data for $\mathbf{A_a}$: $C_{21}H_{24}Cl^+SbCl_6^-\cdot CH_2Cl_2$, MW = 731.28, monoclinic, $P2_1/n$, $a = 8.523(3)$, $b = 12.441(3)$, and $c = 26.535(6)$ Å, $V = 2797$ Å^3, $Z = 4$, Mo Kα radiation, crystal dimensions 0.08 × 0.45 × 0.65 mm. The crystal structure was solved by heavy-atom methods (Patterson and Fourier synthesis) and refined by full matrix least-squares analysis, the 3092 unique reflections with $I > 3\sigma(I)$ converging at $R = 0.045$.

(9) Moreover, the ring carbons describe a quasi-envelope conformation in which C_1, C_2, C_3, and C_4 are coplanar, and C_5–C_6 lies below the plane. A bridged chlorine structure is disfavored in view of the very long Cl–C_2 and Cl–C_6 distances of 2.56 and 2.73 Å, respectively.

(10) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930,** 2510. Also see: Vaughan, J.; Welch, G. J.; Wright, G. J. *Tetrahedron* **1965,** *21,* 1665.

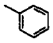
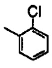
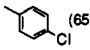
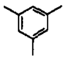
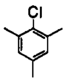
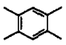
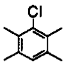
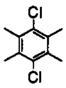
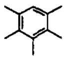
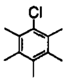
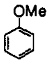
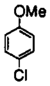
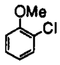
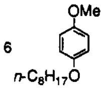
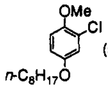
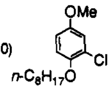
(11) See: Allen, F. H; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987,** S1-S19.

(12) (a) Compare Koptyug, V. A. in ref 2, p 96 ff. (b) Reid, C. *J. Am. Chem. Soc.* **1954,** *76,* 3264. (c) Doering, W. von E.; Saunders, M.; Boyton, H. G.; Earhart, H. W.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958,** *4,* 178.

(13) Nugent, W. A. *J. Org. Chem.* **1980,** *45,* 4533.

0002-7863/94/1516-8414$04.50/0

Table 1. Electrophilic (Transfer) Chlorination of Aromatic Donors with **1**-Cl$^+$SbCl$_6^-$ ^{a}

	donor	products^b (%)				time (h)^c	yield (%)^d
1			(35)		(65)	24	10
		"	(35)	-	(65)	6.0^e	75
2				-		1.0	98
3			(95)		(5)	0.2	93
4				-		0.2	100
5			(90)		(10)	0.2	98
6			(50)		(50)	0.2	93

^{a} In dichloromethane solution of 0.015 M **1**-Cl$^+$SbCl$_6^-$ and 3 equiv of aromatic donor at 25 °C, unless otherwise specified. ^{b} Products were characterized by GC-MS comparison of authentic samples and quantified by GC using internal standard method. Isomer distribution in parentheses. ^{c} The reaction mixture was stirred until red color bleached. ^{d} Excess aromatic donor and **1** quantitatively recovered. ^{e} Large excess (30 equiv) of toluene used.

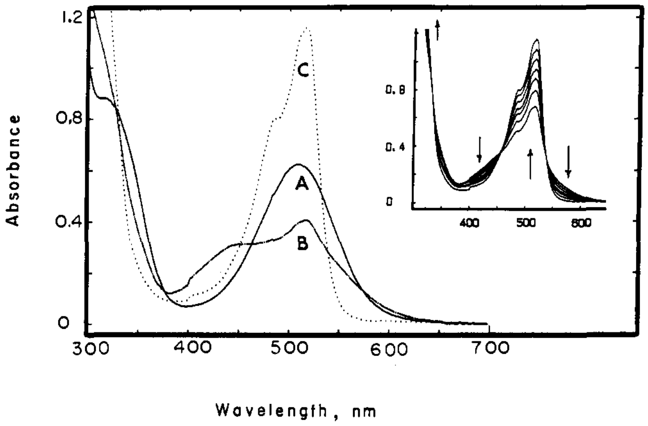
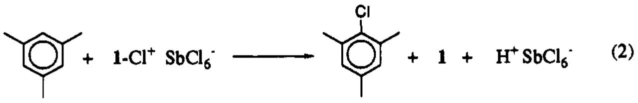


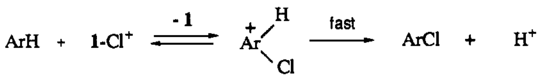
Figure 2. Spectral transformation of 1.3 × 10^{-4} M **1**-Cl$^+$ (spectrum A) to **4**-Cl$^+$ (spectrum B) by treatment with an equimolar amount of aromatic donor **4** in dichloromethane at –78 °C and the subsequent conversion to the aromatic radical cation **4**$^{\bullet+}$ (spectrum C) upon slight warming to –40 °C. Inset: spectral change accompanying the transformation of **4**-Cl$^+$ to **4**$^{\bullet+}$ with clear isosbestic points.

within 1 h at room temperature. Workup of the colorless reaction mixture yielded chloromesitylene and **1** in quantitative yields according to the stoichiometry in eq 2.



(2)

Rapid bleaching and highly efficient chlorine transfer were observed when the relatively electron-rich aromatic donors in Table 1 were used (see columns 3 and 4). Contrastingly, a red solution of **1**-Cl$^+$SbCl$_6^-$ and the weaker aromatic donor toluene persisted overnight, and subsequent workup indicated a low conversion to a 35:65 mixture of *o*- and *p*-chlorotoluene. Such a strong dependence of aromatic chlorination with **1**-Cl$^+$ on the strength of the aromatic donor (ArH), together with the isomeric product distributions, is consistent with Cl$^+$ transfer of the type generally considered for electrophilic chlorination, as given in eq 3.[14]

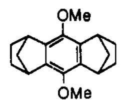


$$\mathrm{ArH} + \mathbf{1}\text{-Cl}^+ \overset{-\mathbf{1}}{\rightleftharpoons} \overset{+}{\mathrm{Ar}}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{Cl}} \xrightarrow{\text{fast}} \mathrm{ArCl} + \mathrm{H}^+ \qquad (3)$$

Spectral evidence of such a Cl$^+$ transfer was obtained with a series of very electron-rich aromatic donors with ArH = **4**-**6** in eq 3.[15] For example,

$$\mathbf{4} + \mathbf{1}\text{-Cl}^+ \xrightarrow[-78\ ^\circ\mathrm{C}]{-\mathbf{1}} [\mathbf{4}\text{-Cl}^+] \xrightarrow[>-40\ ^\circ\mathrm{C}]{} \mathbf{4}^{+\cdot} + (\mathrm{Cl}) \qquad (4)$$

the hexasubstituted aromatic donor **4** reacted rapidly with **1**-Cl$^+$SbCl$_6^-$ at –78 °C to afford a yellow solution, the absorption spectrum [see spectrum B in Figure 2 with $\lambda_{\max}$ = 520, 450 sh nm] of which was tentatively assigned to the chloro–arenium adduct **4**-Cl$^+$. Upon slight warming, the spectrum B was rapidly transformed into the spectrum C of the aromatic cation radical **4**$^{\bullet+}$ according to eq 4.[16] The quantitative nature of the transformation (**4**-Cl$^+$ → **4**$^{\bullet+}$) was established by the presence of clear isosbestic points as in Figure 2 (inset). Similar spectral changes were noted for aromatic donors **5** ($\lambda_{\max}$ = 420, 486 sh nm) and **6** ($\lambda_{\max}$ = 500, 445 sh nm); but the lability of the chloro–arenium intermediates decreased in the order **6**-Cl$^+$ ≫ **4**-Cl$^+$ ≫ **5**-Cl$^+$ to produce cation radicals **4**$^{\bullet+}$ ($\lambda_{\max}$ = 518, 486 sh nm), **5**$^{\bullet+}$ ($\lambda_{\max}$ = 480, 450 sh nm) and **6**$^{\bullet+}$ ($\lambda_{\max}$ = 446, 466 sh nm), respectively.[17] In the latter case, it is noteworthy that GC-MS analysis of the final (spectral) solution indicated excellent yields (>90%) of the isomeric chloro(dialkoxy)benzenes (compare Table 1, last entry).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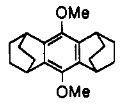
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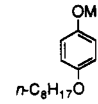
6

We hope that the synthesis of aromatic donors related to **1** and **2** will provide the opportunity to isolate other labile arenium cations.[18]

Acknowledgment. We thank J. D. Korp for the crystallographic assistance and the National Science Foundation, the R. A. Welch Foundation, and the Texas Advanced Research Project for financial assistance.

Supplementary Material Available: Tables of crystal structure data for **A**$_a$ (**1**-Cl$^+$SbCl$_6^-$) including atomic coordinates, anisotropic thermal parameters, bond lengths and angles (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) (a) Note that *o*/*p* chlorinations of toluene and anisole in Table 1 yield the same isomeric mixtures obtained *via* conventional (electrophilic) procedures (de la Mare, P. B. D *Electrophilic Halogenation*; Cambridge University Press: New York, 1976). (b) Chlorination of various aromatic donors with **2**-Cl$^+$SbCl$_6^-$ under similar conditions yielded the same chloroarenes. Interestingly, anisole did not produce any chlorinated products.

(15) The stoichiometry for Cl$^+$ transfer from **1**-Cl$^+$ requires a 2-electron change and is evaluated iodometrically as: **1**-Cl$^+$ + 2I$^-$ → **1** + Cl$^-$ + I$_2$.

(16) Note that the ruby-red crystals were ESR silent, both in solution (CH$_2$Cl$_2$, CH$_3$CN) and in the solid state.

(17) Rathore, R.; Bosch, E.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1157.

(18) The unique molecular morphology of aromatic donors **1** and **2** forces the chloronium moiety to occupy a "protected lacuna" as defined by Busch, D.H. and Alcock, N. W. (*Chem. Rev.* **1994**, *94*, 585) and thus allows the otherwise very reactive chloro–arenium salts to be isolated.