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Graphical Abstract

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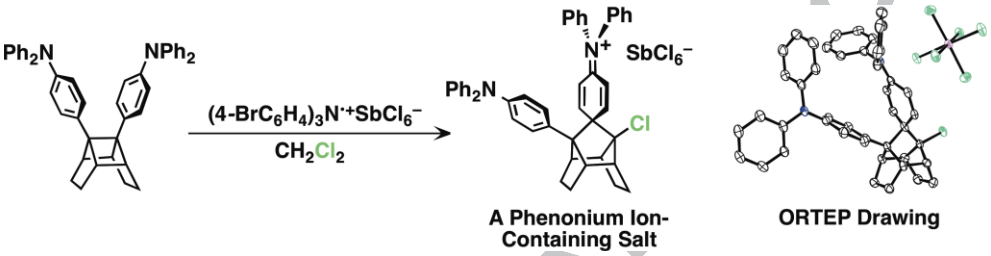

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Unexpected Formation of a Phenonium Ion-Containing Salt by Single Electron-Transfer Oxidation of a Cage Compound Possessing Triphenylamine Moieties

Yutaro Kuramoto[a], Yasunori Matsui[a,b], Eisuke Ohta[a,b], Hiroyasu Sato[c], and Hiroshi Ikeda[a,b]*

[a]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*
[b]*The Research Institute for Molecular Electronic Devices (RIMED), Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*
[c]*Rigaku, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan*

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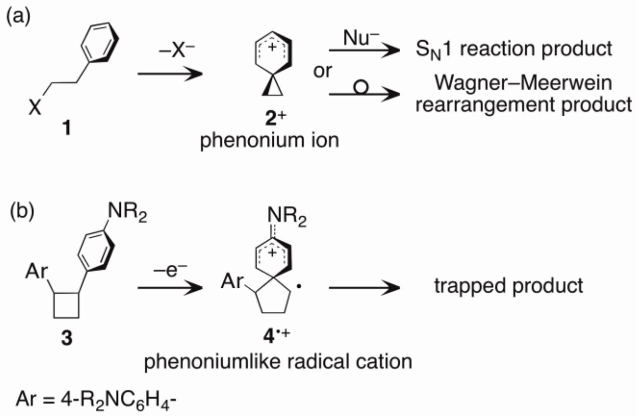
ABSTRACT

The phenonium ion-containing salt **6**-$Cl^+SbCl_6^-$ was unexpectedly generated in the tris(4-bromophenyl)aminium hexachloroantimonate-promoted, single electron-transfer oxidation reaction of 9,10-bis(4-diphenylaminophenyl)tetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane (**5**). X-Ray crystallographic analysis and quantum chemical calculations reveal that the cation in **6**-$Cl^+SbCl_6^-$ contains a unique bridging phenonium ion structure that is stabilized by the presence of a cross-conjugated *N*,*N*-diphenyldivinyliminium ion (3-diphenylamino-1,3-cyclohexadienyl cation). It is noteworthy that **6**-$Cl^+SbCl_6^-$ is a trapped product of a phenoniumlike radical cation **6**$^{\bullet+}$, the radical cation mutant of **2**$^+$.

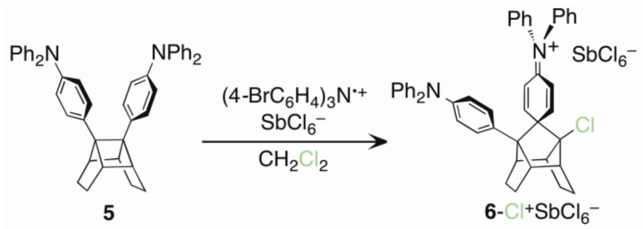
1. Introduction

Phenonium ions (*e.g.*, **2**$^+$, Scheme 1a)[1a] play roles as transient intermediates in processes involving the intermediacy of carbocation, in which neighboring aryl group participation takes place.[1b] These intermediates have been studied utilizing both theoetical[2] and experimental methods.[3] Generally, phenonium ions, in which the positive charge is delocalized over the 1,3-cyclohexadienyl moiety, are formed in S_N1 or Wagner–Meerwein rearrangement reactions of 2-haloethylbenzenes (*e.g.*, **1**). From the time when Olah and co-workers reported the ^1H NMR analysis of the structure and reactivity of a phenonium ion derivative,[3a] those of related species have received intense interest.[4]



Scheme 1. Neighboring group participation by aryl groups yielding (a) the parent phenonium ion **2**$^+$ in S_N1 or Wagner–Meerwein rearrangement reactions of **1** and (b) the corresponding radical cation **4**$^{\bullet+}$ in SET-oxidation reaction of **3**.

Previously, we described the unique reactivity of 1,4-diarylbicyclo[2.2.0]hexane derivatives under photoinduced electron-transfer (PET) conditions.[5] As a part of the continuing investigation in this area, we have studied the reactivity profile of the structurally-related cage compound, 9,10-bis(4-diphenylaminophenyl)tetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane (**5**, Scheme 2). In the effort, we observed that the unexpected stable phenonium ion-containing salt **6**-$Cl^+SbCl_6^-$ is formed in single electron-transfer (SET)-oxidation reaction of **5** with tris(4-bromophenyl)aminium hexachloroantimonate, $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$. Below, we report the results of this investigation, including findings arising from X-ray crystallographic analysis and theoretical studies, and propose a mechanism for formation of **6**-$Cl^+SbCl_6^-$, which correponds to a trapped product of a phenoniumlike radical cation **4**$^{\bullet+}$ (Scheme 1b), a radical cation mutant of the parent phenonium ion **2**$^+$.



Scheme 2. SET-oxidation reaction of **5** with $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$.

2. Results and Discussion

Preparation of 5. The cage compound **5** was synthesized using a two-step route starting with bis(4-bromophenyl)ethyne[6] (**7**, Scheme 3). The sequence involves successive photocyclization reactions[7] (a 400-W high-pressure Hg lamp) of **7** with 1,5-cyclooctadiene that produce a cage compound **8** in 41% yield. Formation of **5** was then accomplished in 42% yield employing a

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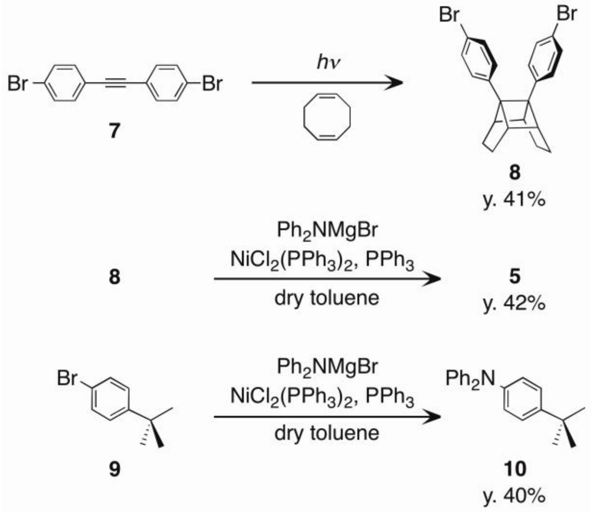
[*] Corresponding author. Tel./fax: +81 72 254 9289.
E-mail address: ikeda@chem.osakafu-u.ac.jp (H. Ikeda).

Buchwald–Hartwig reaction[8] of **8**. The simple model triphenylamine analog **10**[9] was also prepared from 1-bromo-4-*tert*-butylbenzene (**9**) by using a similar method.



Scheme 3. Preparations of **5** and **10**.

Cyclic Voltammetry (CV). To evaluate the behavior of **5** under SET-oxidation conditions, it and the simple model **10** were subjected to CV analysis (CH$_2$Cl$_2$, 0.1 M *n*-Bu$_4$N$^+$BF$_4^-$, Fig. 1). While the cyclic voltammogram of **10** contains a pseudo reversible wave at E_{AP} = +1.12 V vs SCE, that of **5** contains an irreversible anodic peak at E_{AP} = +0.78 V. These results indicate that **5** undergoes a chemical reaction following SET-oxidation.[10] The difference between the E_{AP} of **10** and **5** is consistent with the difference between their HOMO energies calculated by using density functional theory (DFT) (**10**: –5.16 eV, **5**: –4.81 eV, B3LYP/6-31++G**).[11–14] The difference is likely the consequence of through-space and -bond electronic interactions of the two triphenylamine moieties in **5**.

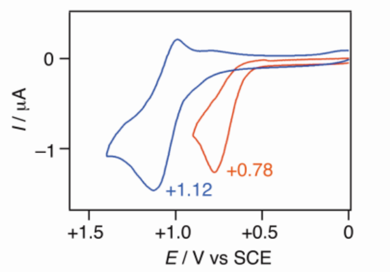


Fig. 1. Cyclic voltammograms of **10** (blue) and **5** (red) in CH$_2$Cl$_2$ containing 0.1 M *n*-Bu$_4$N$^+$BF$_4^-$. Scan rate: 0.1 Vs^{-1}, reference electrode: SCE, working and counter electrodes: Pt

Absorption Spectra of Transients Formed by Laser Flash Photolysis (LFP) under PET Conditions. To gain further insight into the SET-promoted reaction of **5**, a transient absorption spectroscopy of **10** and **5** (10 mM in CH$_2$Cl$_2$) was carried out using LFP (λ_{EX} = 355 nm) under PET conditions with *N*-methylquinolinium tetrafluoroborate[15] (NMQ$^+$BF$_4^-$, 1 mM) as a light-absorbing, electron-accepting sensitizer and biphenyl (0.4 M) as a co-sensitizer (Fig. 2). PET of **10** on LFP leads to formation of an intense, long-lived transient with absorption bands at λ_{AB} = 580 and 675 nm (Fig. 2a)[16,17] assignable to **10**$^{\bullet+}$. This assignment is in line with electronic transitions calculated by using the time dependent (TD)-DFT method (Fig. 3a, blue, λ_{ET} = *ca*. 536–662 nm).

In contrast, PET of **5** on LFP leads to formation of a long-lived transient with an absorption band in the UV region (Fig. 2b, λ_{AB} < 400 nm) and no species having absorption bands at the longer wavelength even 500 ns after the light pulse. Interestingly, this observation is not consistent with the intense electronic transitions at λ_{ET} = 769 nm that are predicted for **5**$^{\bullet+}$ using theoretical methods (Fig. 3a). Thus, it appears that **5**$^{\bullet+}$ undergoes rapid chemical reaction(s), as was suggested by the CV results, even though no identifiable products were found in the PET reaction mixture. As a matter of fact, **5**$^{\bullet+}$, generated by SET-oxidation of **5** using (4-BrC$_6$H$_4$)$_3$N$^{\bullet+}$SbCl$_6^-$ in CH$_2$Cl$_2$, undergoes rearrangement reaction to form **6**-Cl$^+$SbCl$_6^-$, as described below. The isolated **6**-Cl$^+$SbCl$_6^-$ exhibits absorption bands in the UV region (Fig. 3b, green curve), and the electronic transitions of **6**-Cl$^+$ are predicted at the similar wavelength region by utilizing TD-DFT method (Fig. 3b, green bars). Incidentally, the absorption wavelength of **6**-Cl$^+$SbCl$_6^-$ resembles that of the transient generated upon LFP for **5** under PET conditions, suggesting that a cationic species, for example **6**-Cl$^+$, is probably generated under the PET conditions.

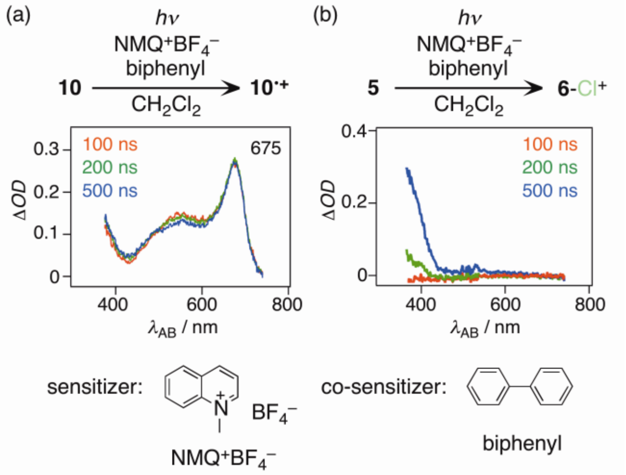


Fig. 2. Transient absorption spectra upon PET reactions of **10** (a) and **5** (b) in CH$_2$Cl$_2$ triggered by LFP (355 nm). [**10** or **5**] = 10 mM, [NMQ$^+$BF$_4^-$] = 1 mM, [biphenyl] = 0.4 M.

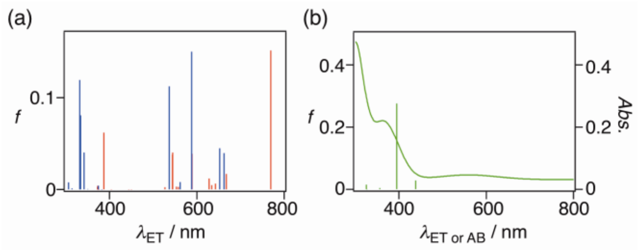


Fig. 3. Electronic transitions of **10**$^{\bullet+}$ (a, blue bars), **5**$^{\bullet+}$ (red bars), and **6**-Cl$^+$ (b, green bars) calculated at the TD-UB3LYP/6-31G* level of theory[12] and UV-Vis spectrum of **6**-Cl$^+$SbCl$_6^-$ in CH$_2$Cl$_2$ (b, green curve).

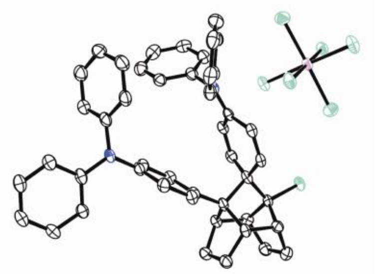
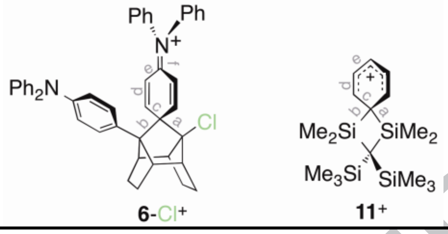


Fig. 4. ORTEP drawing of the X-ray crystallographic data of **6**-Cl$^+$SbCl$_6^-$.

SET-Oxidation of 5 Using $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^-$. To gain further insight into the nature of the reaction, SET-oxidation of **5** was explored. Reaction of **5** with $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^-$ (1 eq) in CH_2Cl_2 leads to formation of the isolatable salt **6**-$Cl^+SbCl_6^-$ in 95% yield (Scheme 2). The unique bridging structure of the cation portion of this salt was initially assigned by using ^{1}H NMR and IR, and finally made unambiguously by employing X-ray crystallographic analysis (Fig. 4).[18]

The unique cross-conjugated *N*,*N*-diphenyldivinyliminium structure of **6**-Cl^+ is associated with a significant degree of bond alternation observed upon an analysis of the bond length (L) data displayed in Table 1. Note that the L_f value of 1.34 Å for this cation is midway between that of an amine C–N single bond length (*e.g.* 1.42 Å calculated for **5**) and an iminium ion C=N double bond [*e.g.* 1.29 Å for $(CH_3)_2C{=}N^+(CH_3)_2$]. Thus, **6**-Cl^+ is a diphenylamino-stabilized phenonium ion. These findings contrast with previous descriptions of a silylated phenonium ion (**11**$^+$, Table 1) reported by Lickiss and co-workers.[19] In the case of **11**$^+$, small bond alternation and long C–Si bonds (2.10 and 2.02 Å for L_a and L_b) are observed, suggesting the presence of a high degree of aromaticity caused by the β-silicon effect[20] rather than a phenoniumlike structure.

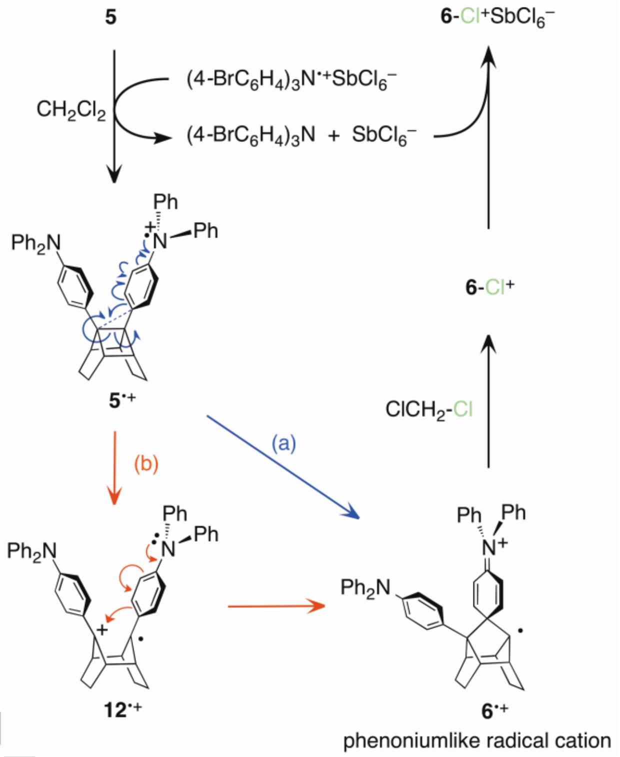
Table 1. Selected Bond Lengths (L) in **6**-Cl^+ and **11**$^+$ Obtained by using X-Ray Crystallographic Analysis



phenonium ion	L_a / Å	L_b / Å	L_c / Å	L_d / Å	L_e / Å	L_f / Å
6-Cl^+	1.54	1.60	1.49	1.34	1.42	1.34
11$^{+\,a}$	2.10	2.02	1.41	1.37	1.36	–

^{a} Ref. 19.

Plausible Mechanisms. A reasonable mechanism for reaction of **5** with $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^-$ to produce **6**-$Cl^+SbCl_6^-$ is given in Scheme 4. In the route, initial SET-oxidation of **5** yields the corresponding aminium radical cation **5**$^{\bullet+}$, which undergoes a 1,2-shift to generate the stabilized phenonium-containing radical cation **6**$^{\bullet+}$ (corresponding to **4**$^{\bullet+}$ in Scheme 1) via either a concerted (path a) or stepwise process (path b), the latter of which proceeds through the ring-open radical cation **12**$^{\bullet+}$. Finally, chlorine atom abstraction by **6**$^{\bullet+}$ from CH_2Cl_2 gives **6**-$Cl^+SbCl_6^-$. Note that SET-oxidation of **5** in CH_3CN rather than dichloromethane results in formation of a complex product mixture. A stoichiometric consideration on the reaction of **5** with one equivalent of $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^-$ in CH_2Cl_2 giving **6**-$Cl^+SbCl_6^-$ in 95% yield suggests that the chlorine atom in **6**-Cl^+ comes from CH_2Cl_2 rather than $SbCl_6^-$.



Scheme 4. Plausible mechanisms (a) and (b) for the generation of **6**-$Cl^+SbCl_6^-$ in the SET-oxidation reaction of **5** using $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^-$ in CH_2Cl_2.

3. Conclusion

In conclusion, the phenonium ion containing salt **6**-$Cl^+SbCl_6^-$ was unexpectedly generated in the SET-oxidation reaction of the diaryltetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane derivative **5** with $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{\bullet+}\text{SbCl}_6^-$. Interestingly, this finding represents only the second example of the isolation of a salt containing a phenoniumlike structure. The analysis of molecular geometry and electronic structure of **6**-Cl^+ indicates the cation can be regarded as a phenonium ion, which has a cross-conjugated divinyliminium structure stabilized by strong electron-donating diphenylamino moiety. Insight obtained from this effort should enable the development of new chemical reactions of radical cations in which neighboring group participation is involved.

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Supplementary Data

Supplementary Data associated with this article can be found, in the online version, at doi:XXXXX

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