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Oxidation of an allene compound bearing 1,8-dichloroacridene moieties and photolysis of the halogenated allene compound for the generation of triplet carbenes†

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New allene compounds, 5c and 5d, bearing 1,8-dichloroacridene moieties were synthesized, and the oxidation of 5c and 5d was performed to generate thermally stable triplet carbenes. Since the oxidation resulted in the formation of decomposition products, the photolysis of brominated allene compound 18 was performed. UV–vis measurement at low temperatures indicated the generation of intermediates with decreasing starting material 18, although the efficiency of photolysis was quite low. ESR and electron spin transient nutation (ESTN) spectra suggested that the multiplicity of intermediates is triplet, probably the target triplet carbene 6d is generated. In terms of $|D|$ values of the intermediates, ESR showed that unpaired electrons are more effectively delocalized in 6d by the introduction of nitrogen atoms in the skeleton (biradical character in Scheme 1). The observed triplet species 6d was not stable enough to isolate. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: triplet carbene; allene; oxidation

INTRODUCTION

Although singlet carbenes are thermodynamically stabilized by adjacent heteroatoms,[1] triplet carbenes are much more difficult to stabilize, and the synthesis of isolable triplet carbenes is a worthwhile challenge.[2–6] Based on kinetic stabilization by the introduction of inert bulky substituents to protect the carbenic center, Tomioka et al. have reported two long-living carbenes **1**[4] and **2**[5] in solution. Diarylcarbene **1** was found to survive for nearly one day in benzene at room temperature. Dianthrylcarbene **2**, which is further stabilized by strong resonance effects, survived nearly two weeks under the same conditions. However, the isolation of triplet carbenes in the solid state still remains to be achieved, although the Tomioka group has succeeded in the solid state structural characterization of several diarylcarbenes that are partially generated by the irradiation of diazo precursor crystals.[6] Thus, the search for other precursors with more effective steric protecting groups around the carbenic center is important for improving carbene stabilization.

Recently, we proposed a new strategy for the generation of triplet carbenes (Scheme 1) to avoid the use of diazo compounds, for which the introduction of rigid steric protecting groups at the peri positions was seemingly difficult. Our method was based on the two-electron oxidation of allenic precursors bearing two thioxanthene or acridene moieties.[7–9]

Thus, we attempted the oxidation of allenic compound **3** bearing two dimethoxythioxanthene moieties[10] that was previously reported by our group (Scheme 2). However, the oxidation of **3** did not furnish a stable triplet carbenic species but instead provided ketal **4**, likely via a singlet ground-state carbene.[7] According to theoretical calculations, this decomposition resulted from the vinyl cation character of the generated dicationic species. This closed-shell singlet ground state was calculated to be more stable than the corresponding triplet state by $\Delta E_{CS-T} = -6.7$ kcal/mol at the B3PW91/6-31G(d) level of theory.

We also examined the generation of a triplet carbene by the oxidation of allenic precursor **5a** bearing nitrogen atoms in place of the ring sulfur atoms.[8] Two-electron oxidation of **5a** afforded dimer **7** as the product, which could be assumed to have arisen via **6a**. Successful trapping of the reactive intermediate by tetramethylpiperidine *N*-oxide (TEMPO) suggested the intermediacy of triplet carbene **6a**. In addition, we found that the oxidation of allene **5b** yields tetracation **9** as an unexpected product having a partial singlet biradical character through demethylation and dimerization (Scheme 2).[9]

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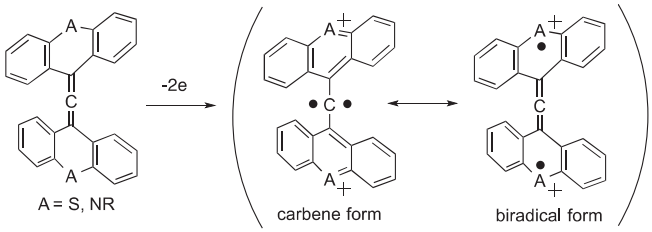
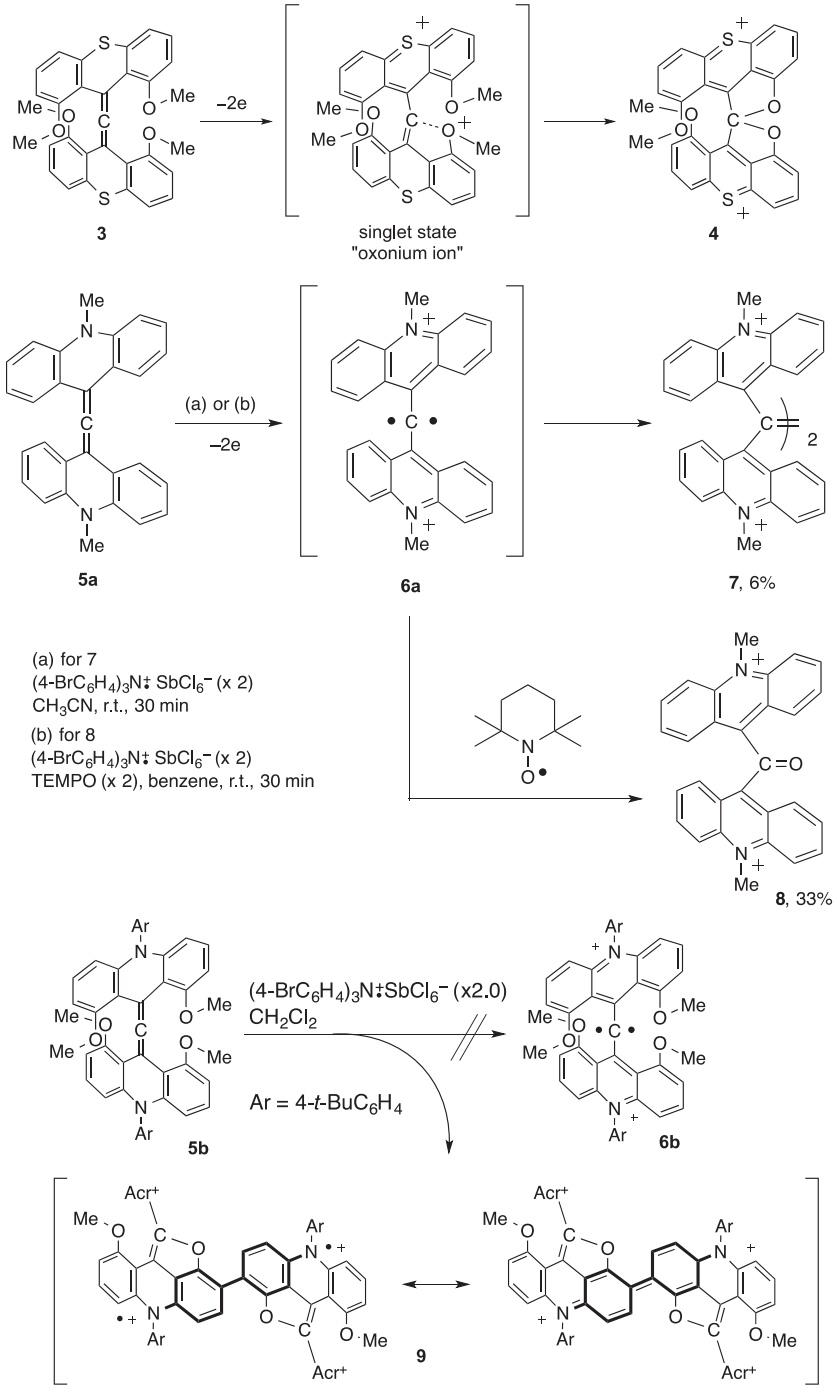


Scheme 1. Oxidation of allenic precursors

Therefore, we need to introduce other substituents at the 1,8-positions. Although triplet carbenes easily react with alkyl groups to provide decomposed compounds through C—H insertion,[11] halogens are recognized to be normally reactive with singlet carbenes but are not reactive with their triplet counterparts. Tomioka et al. have studied system **1** bearing halogen atoms as steric protection groups (Fig. 1).[4,12] Kinetic stabilization using halogens resulted in dramatic lifetime improvement in comparison with diphenylcarbene (lifetime ca. 2 μs).

Herein, we report the synthesis of the allenic precursor **5c** and its oxidation, with attempts at the photolytic generation of the triplet carbene **6d** from **5d** via **18** (Scheme 3).



Scheme 2. Our previous attempts at generation of stable triplet carbenes

RESULTS AND DISCUSSION

Synthesis of allene compounds 5c and 5d bearing 1,8-dichloroacridene moieties

First, the synthesis of acridone bearing chlorine atoms **14** was performed. The *tert*-butoxycarbonyl (*t*-Boc) group of **11** is needed to allow selective dilithiation. The alkylation of **13** afforded the acridones **14a** and **14b** in 15% (5 steps) and 24% (5 steps), respectively.[13] Although the reaction of the acridone **14** with $Ph_3P=CH_2$ to afford the corresponding olefin **15** failed due to steric crowding around carbonyl groups, the reaction of **14** with MeMgBr followed by the treatment with *p*-TsOH succeeded to provide the desired olefins **15a** and **15b**. The reaction of **14** with **15** and Tf_2O followed by treatment with DBU afforded the desired allenes **5c** and **5d** in 47% and 51%, respectively (Scheme 4).

The allenic character is shown in the ^{13}C NMR spectrum (213.5 ppm for **5d**, and there is no data for **5c** because of insolubility in DMSO-d_6, $CDCl_3$). Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2/hexane, and their structures are shown in Fig. 2. X-ray analysis revealed a bent allene framework with C—C—C = 164.9(3)° for **5c** and 165.6(2)° for **5d** (*Cf.* 168.0(2)° for **5b**[9]). The larger deviation may be due to the steric crowding of substituents in **5c** and **5d** (see Fig. 3).

Oxidation reactions of 5c and 5d

In the CV measurements of **5c** and **5d**, two reversible peaks were observed. The first and second oxidation peaks ($E_{1/2}$ = 0.98 and 1.22 V for **5c**, 1.03 and 1.31 V for **5d**) might be assigned to the desired reaction to generate dicationic species. Based on differential pulse voltammetry (DPV) of **5d** measured with one equivalent of decamethylferrocene (Fc*) as a reference material, it was confirmed that each peak corresponded to a one-electron oxidation process (Fig. 4).

Conditions—solvent: CH_2Cl_2, supporting electrolyte: $TBAPF_6$, room temperature.

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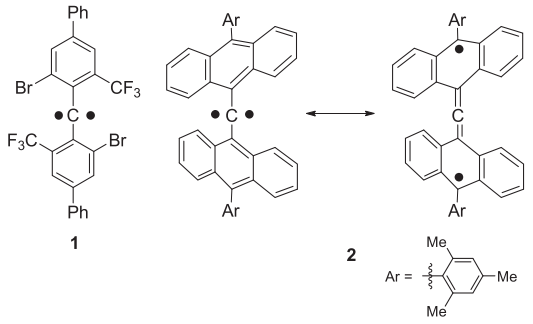
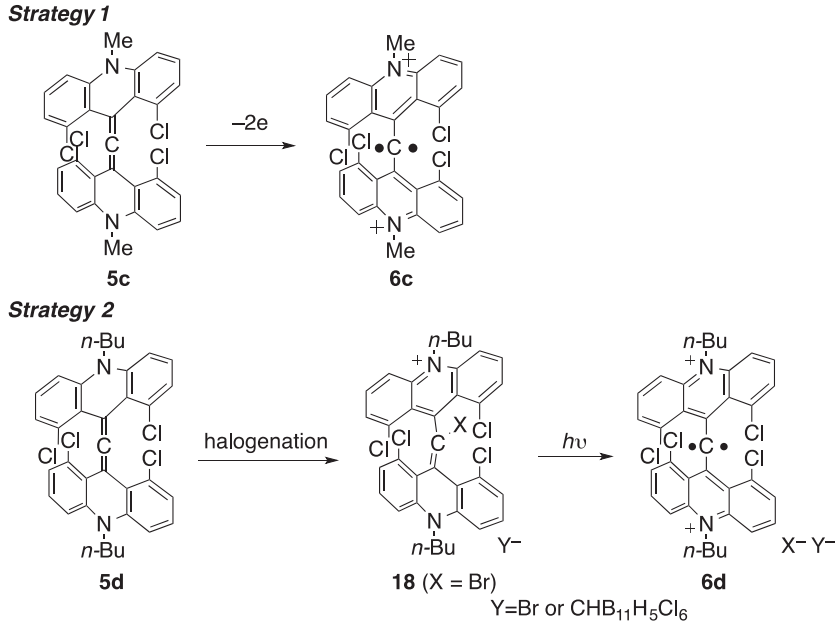


Figure 1. Examples of reported triplet carbenes



Scheme 3. Two synthetic strategies for synthesizing triplet carbenes bearing chlorine atoms

As expected, the oxidation potentials of **5c** and **5d** clearly indicate that the introduction of the electron-withdrawing group (Cl) leads to more difficult oxidation ($E_{1/2}$ = 0.44 and 0.76 V for **5b**).

Although the oxidized species seemed to be stable on the basis of the reversibility in CV, the chemical oxidation of **5c** with $(2,4\text{-}Br_2C_6H_3)_3N^{\bullet+}SbCl_6^-$ or SbF_5 afforded the cation **17**, which has a hydrogen atom at the central carbon (Scheme 5 and Fig. 5).

There are two plausible reaction mechanisms. The first is a single electron oxidation followed by hydrogen abstraction, as shown in Scheme 5. Due to the electron-withdrawing property of chlorine atoms, it is difficult to double-oxidize the allenic precursor **5c**. The isolation of radical cation **16** has failed thus far. The second possible mechanism is a protonation of the allenic precursor **5c**. Since the strong oxidants, such as SbF_5, are easily hydrolyzed to generate a small amount of acid, the protonation of allene compound **5c** could take place. The reaction of allene **5c** with TFA at room temperature also generated cation species **17**. To prevent protonation, the oxidation of **5c** with SbF_5 under excess base, such as 1,2,2,6,6-pentamethylpiperidine, was attempted as shown in Scheme 5. However, the desired reaction did not occur because the excess base itself trapped the oxidants.

Photolysis of the halogenated allene compounds

A different method, the photolysis of the halogenated allene compound **18**, was also performed to overcome the difficult oxidation of allenic precursors bearing chlorine atoms (Scheme 6). In this case, since the removed halide ion becomes a counter anion, there is no byproduct. Thus, a clean reaction was expected, similar to that of the photolysis of the diazo compounds reported by Tomioka.[2] Although it is difficult to photolyze the vinyl bromide **18** comprising electron deficient cationic skeletons, we hoped that ESR parameters ($|D|$ and $|E|$) of the partially generated triplet species by the photolysis of **18** at a low temperature would allow us to understand the structural features.

The halogenation of the allene precursor **5d** was performed as shown in Scheme 6. *N*-butyl groups on nitrogen were introduced to improve solubility. The reaction of **5d** with $n\text{-}Bu_4NBr_3$ (x1) provided **18** with a yield of 57%. Furthermore, the bromide counter ions were exchanged to the carborane ions $CHB_{11}H_5Cl_6^-$, and single crystals suitable for X-ray analysis were obtained (Fig. 6).

The chemical cleavage of a C—Br bond is only reported in the case of neutral vinyl bromides, and the cleaving of a C—Br bond is difficult when the substituents on vinyl bromide are electron-withdrawing groups.[14] We also tried to cleave the C—Br bond photochemically. After photolysis of **18**, we detected a small amount of a generated triplet species by UV–vis, ESR spectroscopy. Irradiation (350 nm) of **18** ($CHB_{11}H_5Cl_6$) in the degassed 2-MeTHF matrix at 80 K resulted in the appearance of new absorption bands (580 nm), which correspond to the calculated bands of the triplet dication species (1116 (f = 0.0463), 565 (f = 0.0827) and 564 (f = 0.0797) nm at B3PW91/6-311 + G(2d, p) level). Simultaneously, the peaks of the starting material **18** (491 and 800 nm) disappeared. A low conversion efficiency interferes with the analysis of decomposition products (see Fig. 7).

ESR and electron spin transient nutation (ESTN)[15] measurements helped us determine the multiplicity of the intermediate observed by UV–vis spectroscopy. After irradiation (355 nm) in the degassed 2-MeTHF matrix at 80 K, an ESR spectrum measured at 20 K showed peaks (g = 2.0063), indicating the existence of unpaired electrons. Upon raising the temperature, these peaks disappeared at ca. 100 K in the degassed 2-MeTHF. The center peak disappeared first. Thus, there were two components in the matrix (Fig. 8).

The spectra at 80 and 100 K were scaled up for clarity.

Next, ESTN measurements were performed at 20 K to decide the multiplicity of the observed intermediates (Fig. 9). Equation 1 gives the nutation frequency (ω_n).

$$\omega_n = \sqrt{S(S+1) - m(m-1)}\,\omega_1 \qquad (1)$$

The nutation frequency for doublet species (ω_1) depends on the measuring instrument, and in this case, ω_1 = 15 MHz. Thus, the nutation frequency for triplet species (ω_2) is 21 MHz. As the observed nutation frequency is ca. 20.2 MHz, the spin-multiplicity of both intermediates is triplet.

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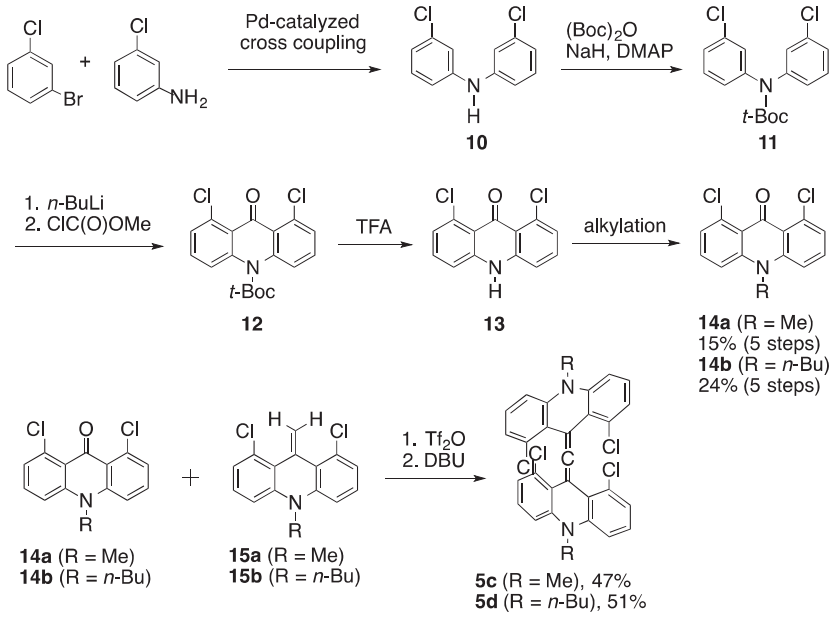

Scheme 4. Synthesis of **5c** and **5d**

The spin Hamiltonian can be written as Eqn 2.

$$H = \mu_B S \cdot g \cdot B_0 + S \cdot D \cdot S \quad (2)$$

Spectral simulations of electron spin echo detected ESR spectra by Eqn 2 (see Fig. 10) indicate that two components have similar but slightly different structures (component 1: $|D| = 0.0058\ cm^{-1}$, $|E| = 0.0006\ cm^{-1}$; component 2: $|D| = 0.0075\ cm^{-1}$, $|E| = 0.0025\ cm^{-1}$). The zero-field splitting parameters, $|D|$ and $|E|$ (interaction energies in cm^{-1}), measure the magnetic dipole interaction of the unpaired electrons in the absence of an external field. $|D|$ is a measure of the average distance r between the unpaired electrons. The relation between $|D|$ and r can be written as Eqn 3.

$$D = -\frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)\frac{(g\mu_0)^2}{r^3} \quad (3)$$

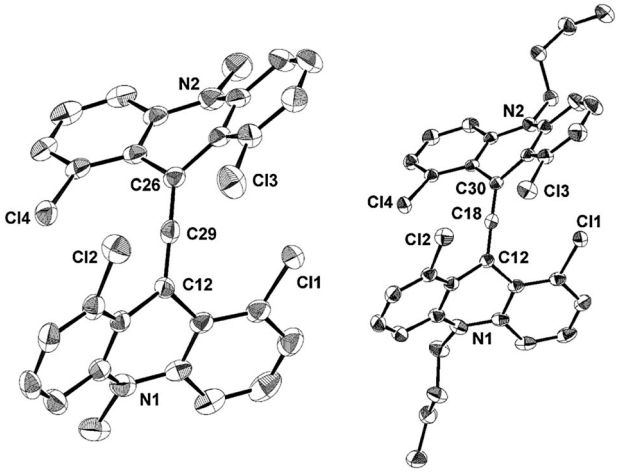

Figure 2. ORTEP drawings of allene compounds **5c** (left) and **5d** (right) with thermal ellipsoids shown at the 50% probability level. Solvents and all hydrogen atoms are omitted for clarity

The delocalization of the two electrons is inversely proportional to $|D|$. On the other hand, $|E|$ is a measure of the difference in the magnitude of the magnetic dipole moment among triplet species, so increasing the symmetrical property of two electrons leads to a smaller $|E|$.

Compared with $|D|$ ($0.113\ cm^{-1}$) and $|E|$ ($0.0011\ cm^{-1}$) values of the reported triplet di(9-anthryl)carbene,[4b] the $|D|$ and $|E|$ values of the observed components 1 and 2 are much smaller. Thus, ESR measurement and simulation after photolysis of **18** led to the estimation that intermediates (components 1 and 2) would have an almost linear bond geometry at the carbene center.

The average distance between the unpaired electrons calculated by the point-dipole approximation 3 was estimated as 7.7 and 7.1 Å for components 1 and 2, respectively. These values are close to the distance between nitrogen atoms, 8.2 Å, determined from the optimized structure of the desired triplet dicationic species **6d**, indicating that the unpaired electrons mainly exist on the nitrogen atoms in **6d**. Therefore, **6d** can be depicted as a bis-radical dication connected by allenic moieties (Scheme 1).

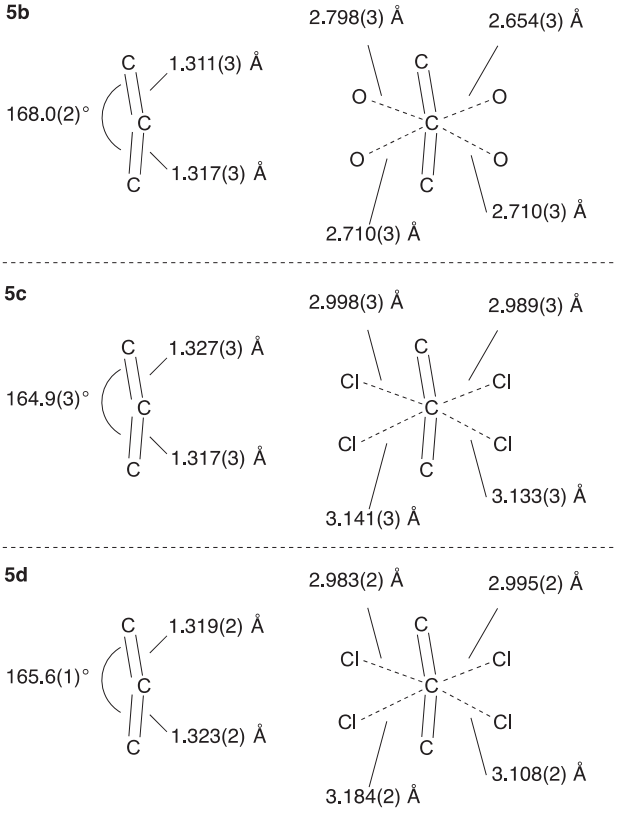

Figure 3. Comparison of structures around the allenic moiety in **5b**, **5c** and **5d**

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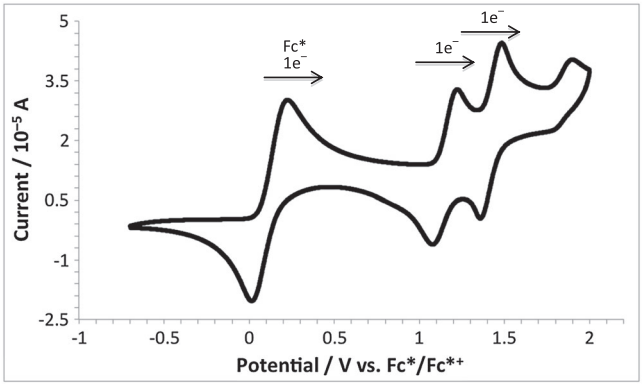


Figure 4. CV of **5d**

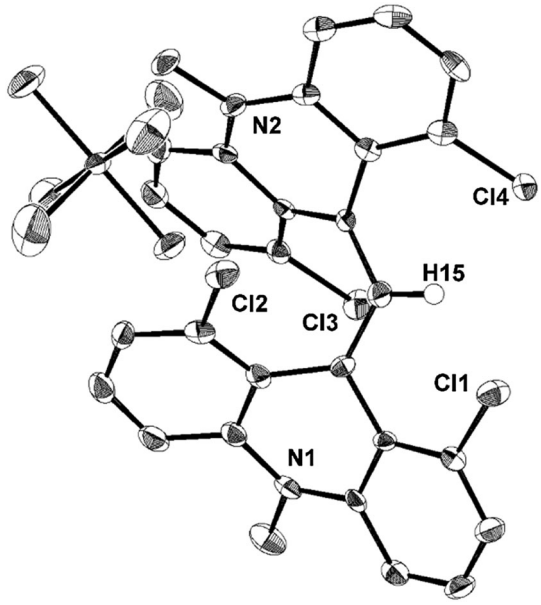


Figure 5. ORTEP drawing of **17** generated by the reaction of **5c** with SbF_5, with the thermal ellipsoids shown at the 50% probability level. Hydrogen atoms excepting H15 are omitted for clarity

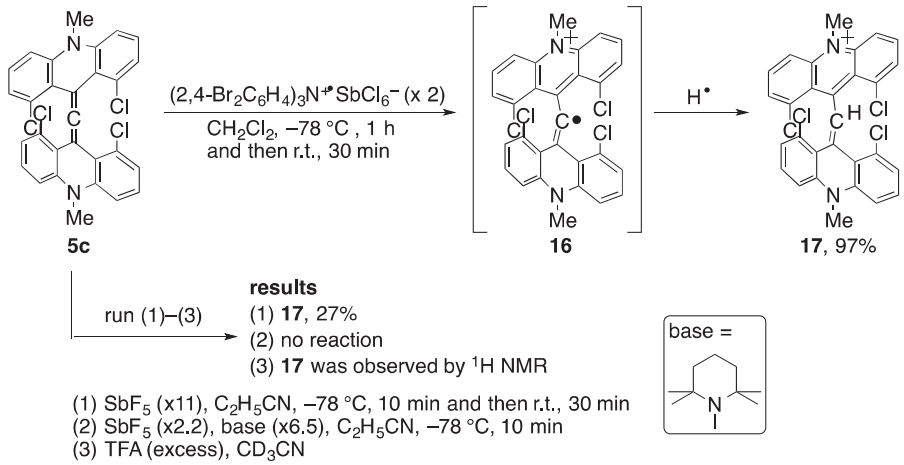
CONCLUSION

The oxidation of allenic precursors **5c** bearing chlorine atoms at the 1,8-positions on acridene moieties with aminium radical cations afforded the cationic decomposed compound **17** via one-electron oxidation. To achieve two-electron oxidation, reactions with stronger oxidants, such as SbF_5, were performed. However, hydrogen abstraction or protonation by an acid impurity took place. Introduction of chlorine atoms resulted in failure, which was likely due to difficult oxidation because of the electron-withdrawing nature of Cl.

The photolysis of brominated allene compound **18** was also performed. Although we could not characterize the decomposed products because of the low conversion efficiency of the photolysis, UV–vis measurement at low temperatures indicated the generation of the intermediates with decreasing starting material **18**. ESR and ESTN spectra suggested that the multiplicity of intermediates is triplet.

The triplet species is likely **6d**. ESR showed that unpaired electrons are more effectively delocalized by the introduction of nitrogen atoms in the skeleton (biradical character in Scheme 1) in terms of $|D|$ values of the triplet species.

Since **6d** has not been isolated due to its instability, steric protecting groups that are inert toward triplet carbenes and that enable a facile oxidation are crucial. Synthesis and oxidation of allene compounds bearing such substituents at the 1,8-positions are currently in progress.



Scheme 5. Oxidation of **5c**

EXPERIMENTAL SECTION

General procedures

The ^{1}H NMR (400 MHz) chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual $CHCl_3$ (δ = 7.26 ppm), residual protonated DMSO–d_6 (δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by $CDCl_3$ (δ = 77.0 ppm), DMSO–d_6 (δ = 39.52 ppm). CH_2Cl_2 was purified by distillation from CaH_2 under N_2 atmosphere. Ether, hexane and THF were purified by passing through a Glass Contour solvent dispensing system under an N_2 atmosphere.

Synthesis of 10

The solution of 1-bromo-3-chlorobenzene (11.7 mL, 100 mmol), 3-chloroaniline (10.6 mL, 100 mmol), $Pd_2(dba)_3$·$CHCl_3$ (540 mg, 0.522 mmol, 0.52 mol%), *o*-(dicyclohexylphosphino)biphenyl (240 mg, 0.685 mmol, 0.69 mol%) and sodium *tert*-butoxide (14.4 g, 150 mmol) in dioxane (250 mL) was heated to reflux for 36 h. After cooling to room temperature, the reaction mixture was filtered through Celite to remove any insoluble residues. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography (Silica gel, CH_2Cl_2: *n*-hexane = 1:2) to afford **10** (20.7 g, 86.9 mmol, 87%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (t, 2H, J = 8 Hz), 7.05 (s, 2H), 6.94 (d, 2H, J = 8 Hz), 6.93 (d, 2H, J = 8 Hz), 5.73 (s, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.07 (CH), 116.13 (CH), 117.86 (CH), 121.59 (CH), 130.52 (C), 143.61 (C)

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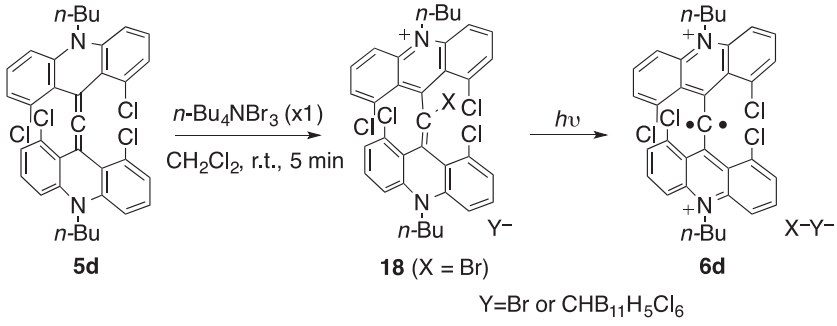


Scheme 6. New strategy for the generation of the desired triplet carbenes **6d**

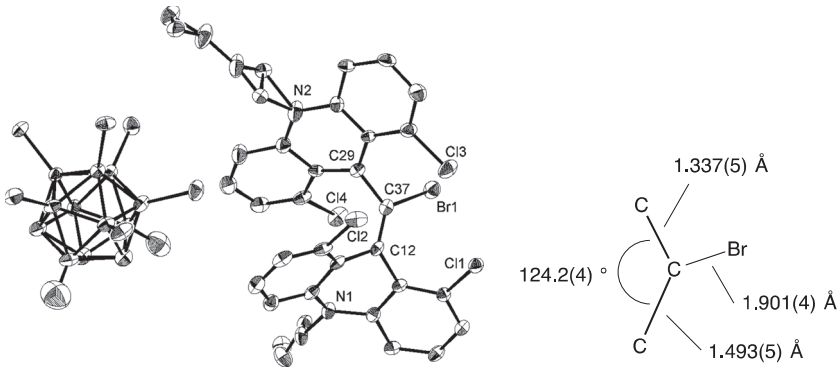
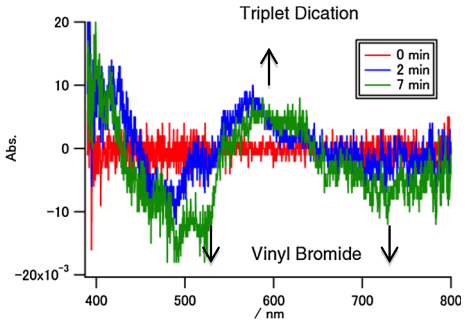


Figure 6. ORTEP drawing of **18** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms are omitted for clarity



	λ / nm	*f*
vinyl bromide[1)]	800	
	491	
	379	
singlet dication [2)]	759	0.2069
	428	0.0903
	401	0.0642
	398	0.0573
triplet dication [2)]	1116	0.0463
	565	0.0827
	564	0.0797

(1) experimental data in 2M-THF
(2) calculated at B3PW91/6-311 + G(2d, p) level

Figure 7. Time change of UV–vis spectrum of **18** under irradiation (350 nm) in the degassed 2-MeTHF matrix at 80 K (left) and the TD-DFT calculation at the B3PW91/6-311 + G(2d, p) level of theory (right)

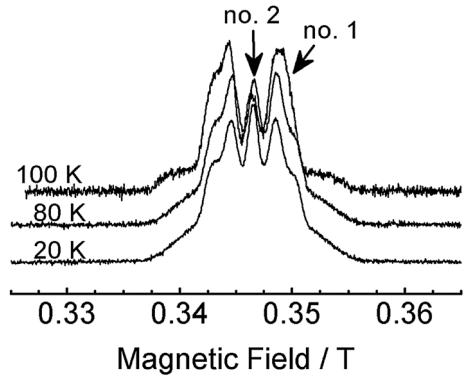


Figure 8. Temperature changes of electron spin echo detected ESR spectra from 20 to 100 K after irradiation (355 nm) of **18** in the degassed 2-MeTHF matrix at 80 K

Anal. calcd for $C_{12}H_9NCl_2$: C 60.53, H 3.81, N 5.88%. Found: C 60.06, H 3.67, N 5.58%.

HRMS (ESI) *m/z* calcd for $[C_{12}H_{10}NCl_2]^+$ 238.019 ($^{35}Cl—^{35}Cl$) 240.0161 ($^{35}Cl—^{37}Cl$) 242.0131 ($^{37}Cl—^{37}Cl$). Found 238.0186 ($^{35}Cl—^{35}Cl$) 240.0156 ($^{35}Cl—^{37}Cl$) 242.0126 ($^{37}Cl—^{37}Cl$)

Synthesis of 11

The stirred suspension of **10** (10.0 g, 42.0 mmol), NaH (50% in oil, 2.05 g, 42.7 mmol), DMAP (125 mg, 1.02 mmol) and $(Boc)_2O$ (11.5 mL, 50.1 mmol) in THF (130 mL) was heated to reflux for 10.5 h. The reaction mixture was cooled to room temperature and treated with water. The resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with $NaHCO_3$, brine and dried (K_2CO_3). Removal of the solvent followed by column chromatography (SiO_2, hexane: CH_2Cl_2 = 2:1) afforded **11** (13.4 g, 40.0 mmol, 95%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (t, 2H, *J* = 8 Hz), 7.21 (s, 2H), δ7.18 (d, 2H, *J* = 8 Hz), δ7.08 (d, 2H, *J* = 8 Hz), 1.45 (s, 9H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.35 (CH3), 82.19 (C), 125.37 (CH), 126.36 (CH), 127.34 (CH), 130.00 (CH), 134.49 (C), 143.84 (C), 153.14 (C)

Anal. calcd. for $C_{17}H_{17}Cl_2NO_2$: C 60.37, H 5.07, N 4.14%. Found: C 60.71, H 5.02, N 4.13%.

Synthesis of 12

To a stirred solution of **11** (3.38 g, 10.0 mmol) in THF (24 mL) under argon, *n*-BuLi (1.57 M in *n*-hexane, 12.8 mL, 20.0 mL) was added at −78 °C. The mixture was stirred for 5 h at −78 °C, followed by the addition of dry ether (240 mL) and methyl chloroformate (0.95 mL, 12.3 mmol) at −78 °C. After stirring for 1 h at −78 °C, the solution was treated with $NaHCO_3$ aq. The mixture was then extracted with ether. The combined organic layer was washed with brine and dried (K_2CO_3). The solvent was concentrated using a rotary evaporator, and the resulting residue was washed with hexane to afforded **12** (1.18 g, 3.24 mmol, 32%) as a white solid.

Mp. 119-120 °C (decomp)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, 2H, *J* = 8 Hz), 7.43 (t, 2H, *J* = 8 Hz), 7.37 (d, 2H, *J* = 8 Hz), 1.52 (s, 9H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.35 (CH3), 82.19 (C), 125.37 (CH), 126.36 (CH), 127.34 (CH), 130.00 (CH), 134.49 (C), 143.84 (C), 153.14 (C)

Anal. calcd for $C_{18}H_{15}Cl_2NO_3$: C 59.36, H 4.15, N 3.85%. Found: C 58.97, H 3.75, N 3.53%.

Synthesis of 13

The solution of **12** (1.06 g, 2.91 mmol) in TFA (3.0 mL, 40 mmol) was stirred for 9 h. The reaction mixture was treated with H_2O, 10% NaOH aq. The resulting solid was washed with $NaHCO_3$ aq. **13** (690 mg, 2.61 mmol, 90%) was obtained as a yellow solid.

^{1}H NMR (DMSO-d_6, 400 MHz,) δ 6.63 (t, 2H, *J* = 8 Hz), 6.44 (d, 2H, *J* = 8 Hz), 6.25 (d, 2H, *J* = 8 Hz)

^{13}C NMR (DMSO-d_6, 100 MHz) δ 116.59 (C), 117.92 (CH), 124.00 (CH), 132.68 (C), 133.05 (CH), 142.66 (C), 175.21 (C)

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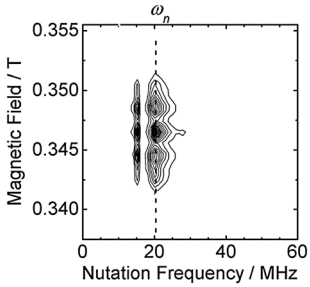
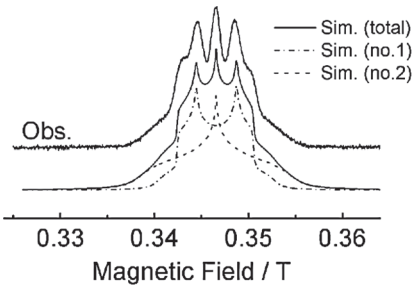


Figure 9. ESTN spectrum measured at 20 K after irradiation (355 nm) of **18** in the degassed 2-MeTHF matrix at 80 K



Component	1	2
$\lvert D \rvert$ / cm^{-1}	0.0058	0.0075
$\lvert E \rvert$ / cm^{-1}	0.0006	0.0025

Figure 10. Spectral simulation of ESR spectrum

HRMS (ESI) *m/z* calcd for $[C_{13}H_7ONCl + Na]^+$ 285.9803 (^{35}Cl—^{35}Cl), 287.9773 (^{35}Cl—^{37}Cl), 289.9744 (^{37}Cl—^{37}Cl). Found 285.9797 (^{35}Cl—^{35}Cl), 287.9767 (^{35}Cl—^{37}Cl) 289.9748 (^{37}Cl—^{37}Cl)

Synthesis of 14a

To a stirred suspension of **13** (55.7 mg, 0.211 mmol), NaH (50% in oil, 55.1 mg, 1.15 mmol) in THF (3 mL), iodomethane (0.025 mL, 0.41 mmol) was added at 0 °C. The mixture was stirred for 24 h at room temperature and treated with H_2O. The solvent was removed using a rotary evaporator. The mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried (K_2CO_3). Removal of the solvent followed by recrystallization (CH_2Cl_2/hexane) afforded **14a** (36.7 mg, 0.132 mmol, 63%) as a yellow solid.

Mp. 282–283 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (t, 2H, *J* = 8 Hz), 7.32 (d, 2H, *J* = 8 Hz), 7.28 (d, 2H, *J* = 8 Hz), 3.82 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.06 (CH3), 113.29 (CH), 121.16 (C), 124.53 (CH), 130.32 (C), 132.30 (CH), 134.39 (C), 144.13 (C)

Anal. calcd. for $C_{14}H_9Cl_2NO_1$: C 60.46, H 3.26, N 5.04%. Found: C 60.26, H 3.33, N 4.96%

Synthesis of 5c

15a: To a solution of **14a** (110 mg, 0.396 mmol) in the dry THF (4.0 mL) under argon, MeMgBr (1.06 M in THF, 0.79 mL, 5.8 mmol) was dropwise added at room temperature. After the reaction mixture was heated to reflux for 1 day, the reaction mixture was treated with saturated NH_4Cl aq. The reaction mixture was then extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried (K_2CO_3). The solvent was removed using a rotary evaporator; *p*-toluenesulfonic acid (72.3 mg, 0.380 mmol) and CH_2Cl_2 (2.0 mL) were then added to the residue. After stirring for 1 h at room temperature, the reaction mixture was purified by column chromatography (silica, CH_2Cl_2) to afford the desired olefin **15a** (32 mg, 0.11 mmol, 57%) as a yellow solid.

5c: To a solution of the ketone **14a** (182 mg, 0.653 mmol) and freshly prepared olefin **15a** (183 mg, 0.662 mmol) in the dry CH_2Cl_2 (12 mL) under argon, Tf_2O (0.135 mL, 0.802 mmol) was added at room temperature and heated to reflux for 2 h. DBU (0.8 mL, 5.3 mmol) was added to the mixture. The reaction mixture was stirred for 3 h at room temperature. After removing the solvents, the resulting residue was washed with MeCN and purified by recrystallization (CH_2Cl_2/hexane) to afford the desired allene **5c** (167 mg, 0.312 mmol, 47%) as a pale yellow solid.

Mp. 295–296 °C (decomp.)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, 4H, *J* = 8 Hz), 7.00 (dd, 4H, *J* = 8 Hz, *J* = 1 Hz), 6.78 (dd, 4H, *J* = 8 Hz, *J* = 1 Hz), 3.39 (s, 6H)

^{13}C NMR measurement cannot be measured because of bad solubility for organic solvents.

Anal. calcd. for $C_{29}H_{16}Cl_4N_2$: C 64.95, H 3.38, N 5.22%. Found: C 65.26, H 3.47, N 5.47%

UV–vis (CH_2Cl_2) 381 nm

Synthesis of 14b

The solution of **13** (924 mg, 3.50 mmol), *n*-BuI (0.6 mL, 5.3 mmol), 50% NaOH (10 mL), ethyl methyl ketone (10 mL) and BTEAC (84 mg, 0.37 mmol, 11 mol%) was stirred for 14 h at 75 °C. After cooling to room temperature, the reaction mixture was poured into hot water and the precipitate was filtered and washed with $NaHCO_3$ aq., CH_2Cl_2. The solvent was concentrated using a rotary evaporator to afford the desired acridone **14b** (1.11 g, 3.47 mmol, 99%) as a yellow solid.

Mp.151–152 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, 3H, *J* = 7 Hz), 1.55 (m, 2H), 1.94 (q, 2H, *J* = 8 Hz), 4.21 (dd, 2H, *J* = 8 Hz), 7.27 (d, 2H, *J* = 8 Hz), 7.32 (d, 2H, *J* = 8 Hz), 7.50 (t, 2H, *J* = 8 Hz)

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.09 (CH3), 20.15 (CH2), 28.89 (CH2), 48.46 (CH2), 113.33 (CH), 120.88 (C), 124.83 (CH), 132.40 (CH), 134.68 (C), 143.30 (C), 176.89 (C)

Anal. calcd. for $C_{17}H_{15}Cl_2NO$: C 63.76, H 4.72, N 4.37%. Found: C 63.56, H 4.37, N 4.28%

Synthesis of 5d

15b: To a solution of **14b** (83.4 mg, 0.260 mmol) in the dry THF (2.0 mL) under argon, MeMgBr (1.06 M in THF, 0.40 mL, 0.42 mmol) was dropwise added at room temperature. After the reaction mixture was heated to reflux for 2 h, the reaction mixture was treated with saturated NH_4Cl aq. The reaction mixture was then extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried (K_2CO_3). The solvent was removed using a rotary evaporator; *p*-toluenesulfonic acid (55 mg, 0.29 mmol) and CH_2Cl_2 (2.0 mL) were then added to the residue. After stirring for 1 h at room temperature, the reaction mixture was purified by column chromatography (silica, CH_2Cl_2) to afford the desired olefin **15b** (38 mg, 0.12 mmol, 46%) as a yellow solid.

5d: To a solution of the ketone **14b** (1.45 g, 4.54 mmol) and freshly prepared olefin **15b** (1.44 g, 4.54 mmol) in the dry CH_2Cl_2 (50 mL) under argon, Tf_2O (0.95 mL, 5.5 mmol) was added at room temperature and heated to reflux for 2 h. DBU (7.0 mL, 45 mmol) was added to the mixture. The reaction mixture was stirred overnight at room temperature. After removing the solvents, the resulting residue was washed with MeCN and *n*-hexane afford the desired allene compound **5d** (1.45 g, 2.33 mmol, 51%) as a pale yellow solid.

Mp. 278–279 °C (decomp.)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.07 (t, 4H, *J* = 8 Hz), 6.96 (d, 4H, *J* = 8 Hz), 6.92 (d, 4H, *J* = 8 Hz), 3.88 (t, 4H, *J* = 8 Hz), 1.70 (quint, 4H, *J* = 8 Hz), 1.24 (sext, 4H, *J* = 8 Hz), 0.84 (t, 6H, *J* = 8 Hz)

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^{13}C NMR ($CDCl_3$, 100 MHz) δ 213.5 (C=C=C), 142.6 (C), 132.6 (C), 127.8 (CH), 122.8 (CH), 120.2 (C), 111.5 (CH), 101.7 (C), 47.4 (CH_2), 28.2 (CH_2), 19.8 (CH_2), 13.8 (CH_3)

Anal. calcd. for $C_{35}H_{30}Cl_4N_2$: C 67.75, H 4.87, N 4.37%. Found: C 67.98, H 4.44, N 5.01%

UV–vis (CH_2Cl_2) 385 nm

Reaction of 5c with $(2,4\text{-}BrC_6H_3)_3N^{\bullet+}SbCl_6^-$

A solution of **5c** (40.8 mg, 0.0761 mmol) and $(2,4\text{-}BrC_6H_3)_3N^{\bullet+}SbCl_6^-$ (128 mg, 0.156 mmol) in dry CH_2Cl_2 (3.0 mL) was stirred for 1 h at −78 °C and then for 2 h at room temperature. The solvent was removed in vacuo, and then the residue was washed with ether. **17**·$SbCl_6$ (64.1 mg, 0.0735 mmol, 97%) was obtained as brown solid.

^{1}H NMR (400 MHz, CD_3CN) δ 4.17 (s, 6H), 6.92 (dd, 2H, *J* = 8 H, *J* = 1 Hz), 7.32 (t, 2H, *J* = 8 Hz), 7.69 (dd, 2H, *J* = 8 Hz, *J* = 1 Hz), 7.72 (dd, 2H, *J* = 8 Hz, *J* = 1 Hz), 7.81 (t, 2H, *J* = 8 Hz), 7.87 (dd, 2H, *J* = 8 Hz, *J* = 1 Hz), 9.18 (s, 1H)

UV–vis (CH_2Cl_2) of **17**·$SbCl_6$ 854, 501, 432, 383 nm

Reaction of 5c with SbF_5

To a solution of SbF_5 (202 mg, 0.93 mmol) in dry C_2H_5CN (1.0 mL), **5c** (46 mg, 0.086 mmol) was added and stirred for 10 min at −78 °C, and then for 30 min at room temperature. After removing the solvent, recrystallization from CH_3CN at room temperature afforded **17**·SbF_6 (18 mg, 0.023 mmol, 27%) as black crystal.

UV–vis (CH_2Cl_2) of **17**·SbF_6 854, 501, 432, 383 nm

Reaction of 5c with SbF_5 in the presence of 1,2,2,6,6-pentamethylpiperidine

To a solution of **5c** (50 mg, 0.093 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.1 mL, 0.6 mmol) in dry CH_2Cl_2 (1.0 mL), SbF_5 (43 mg, 0.20 mmol) in dry C_2H_5CN (0.5 mL) was added and stirred for 10 min at −78 °C, and then for 3 h at room temperature. The solvent was removed in vacuo, and ^{1}H NMR indicated that the reaction did not proceed.

Reaction of 5c with TFA

To a solution of **5c** (5 mg, 9 μmol) in CD_3CN (0.60 mL) under air, TFA (3 drops) was added at room temperature. The ^{1}H NMR of the solution indicated the product is monocationic species **17**.

Synthesis of vinyl bromide 18

To the mixture of **5d** (57 mg, 0.11 mmol) and *n*-Bu_4NBr_3 (52 mg, 0.11 mmol), CH_2Cl_2 (2.0 mL) was added at 0 °C and stirred for 5 min. After removing the solvent, recrystallization from CH_3CN/ether afforded **18**·Br (49 mg, 0.062 mmol, 57%) as a black solid.

To the mixture of **18**·Br (329 mg, 0.423 mmol) and $Cs[CHB_{11}H_5Cl_6]$ (228 mg, 0.472 mmol), CH_3CN (6.0 mL) was added at room temperature and stirred for 3 h. After removing the solvent, the residue was washed with CH_2Cl_2 and the filtrate was evaporated followed by recrystallization from CH_3CN/ether to afford **18**·$CHB_{11}H_5Cl_6$ (24 mg, 0.023 mmol) as a dark red solid.

Anal. calcd. for $C_{36}H_{36}B_{11}BrCl_{10}N_2$: C 41.18, H 3.46, N 2.67%. Found. C 40.94, H 3.57, N 2.62%

UV–vis (2-MeTHF) 800, 491, 379 nm

UV–vis (CH_2Cl_2) 811, 498, 379 nm

X-ray crystal structural analysis

Crystals suitable for X-ray structure determination were mounted on a CCD diffractometer, and irradiated with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173 K for data collection. The structures were solved by a direct method using the SIR2004 program,[16] the SIR-97 program[17]

Table 1. Crystallographic data for **5c**, **5d** and **17**·SbF_6

Compound	**5c**	**5d**	**17**·SbF_6
Formula	C29H18Cl4N2	C35H30Cl4N2	C29H19Cl4F6N2Sb
Molecular weight	536.25	620.41	773.01
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*P*21/n	*P*21/c	*P*-1
Color	Pale yellow	Pale yellow	Pale red
Habit	Plate	Plate	Plate
Crystal dimens, mm	0.25 × 0.19 × 0.16	0.57 × 0.48 × 0.15	0.22 × 0.06 × 0.01
a, Å	9.5812(9)	10.6487(10)	7.976(3)
b, Å	17.0124(15)	13.6146(12)	11.789(4)
c, Å	14.5975(13)	20.6223(18)	15.238(5)
α, deg	90	90	107.076(7)
β, deg	93.096(2)	103.329(2)	92.811(7)
γ, deg	90	90	96.658(8)
V, Å^3	2375.9(4)	2909.2(5)	1355.2(8)
Z	4	4	2
D_{calc}, g cm^{-3}	1.499	1.416	1.894
Abs coeff, mm^{-1}	0.521	0.436	1.480
F(000)	1096	1288	760
Radiation; *λ*, Å	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Temp, K	173(2)	173(2)	173(2)
Data collected	+*h*, +*k*, ±*l*	±*h*, ±*k*, ±*l*	+*h*, +*k*, ±*l*
Data/restrains/param	5431/0/318	6660/0/372	7851/0/590
R_1 [$I > 2\sigma(I)$]	0.0589	0.0365	0.0512
wR_2 (all data)	0.1326	0.0895	0.0800
GOF	1.019	1.054	1.050
Solv. for crystallization	CH_2Cl_2/*n*-hexane	CH_2Cl_2/*n*-hexane	CH_3CN

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Table 2. Crystallographic data for **18**·$CHB_{11}H_5Cl_6$

Compound	**18**·$CHB_{11}H_5Cl_6$
Formula	C36H38B11BrCl10.22 N2
Molecular weight	1059.70
Crystal system	Orthorhobic
Space group	*P*bca
Color	Pale red
Habit	plate
Crystal dimens, mm	$0.22 \times 0.06 \times 0.01$
a, Å	13.811(9)
b, Å	32.59(2)
c, Å	19.634(13)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	8838(10)
Z	8
D_{calc}, g cm^{-3}	1.593
Abs coeff, mm^{-1}	1.582
F(000)	4254
Radiation; λ, Å	Mo Kα, 0.71073
Temp, K	173(2)
Data collected	$+h$, $+k$, $\pm l$
Data/restrains/param	7851/0/590
R_1 [$I > 2\sigma(I)$]	0.0433
wR_2 (all data)	0.1152
GOF	1.026
Solv. for crystallization	CH_3CN/ether

or the SHELX-97 program.[18] Refinement on F^2 was carried out using full-matrix least-squares with the SHELX-97 program.[18] All non-hydrogen atoms were refined using anisotropic thermal parameters. Selected crystallographic parameters are summarized in Tables 1 and 2.

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