Precise Control of the Formation of a Covalent and an Ionic Bond in Carbocation–Carbanion Combination Reactions[1]

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Received May 11, 1993•

The electronic effect on the selectivity of covalent or ionic bond formation was examined for the reaction of Kuhn's anion 1^- ($C_{67}H_{39}^-$; tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methide ion) and 1-aryl-2,3-dicyclopropylcyclopropenylium ions. The carbocation stability was progressively changed by varying the substituent on the phenyl ring, while the steric effect was kept essentially unchanged. The cations having the *p*-chlorophenyl ($\mathbf{2a}^+$), phenyl ($\mathbf{2b}^+$), *m*-methylphenyl ($\mathbf{2c}^+$), or *m*,*m*'-dimethylphenyl ($\mathbf{2d}^+$) group gave a covalent product, whereas a carbocation–carbanion salt was obtained from the cations having the *p*-methylphenyl ($\mathbf{2e}^+$) or *p*-methoxyphenyl ($\mathbf{2f}^+$) group. The reduction potentials E_{red} of the cations, as determined by cyclic voltammetry, showed that the formation of the covalent or ionic product is switched by a small difference in stability (≤0.4 kcal/mol) between $\mathbf{2d}^+$ and $\mathbf{2e}^+$. In chloroform, the salts $\mathbf{1}^-\mathbf{2e}^+$ and $\mathbf{1}^-\mathbf{2f}^+$ were transformed into covalent forms **1–2e** and **1–2f**, which can exist only in solution. When **1–(2a–d)** and $\mathbf{1}^-\mathbf{2e,f}^+$ were dissolved in DMSO, equilibrium between a covalent compound and ions was established. A plot of the free energy of heterolysis $\Delta G°_{het}$ for **1–(2a–f)** against the E_{red} of the corresponding cations $\mathbf{2a–f}^+$ showed that $\Delta G°_{het}$ decreases as the cation is more stabilized. The heterolysis in DMSO was shown to be enhanced by ca. 13 kcal/mol both by the steric congestion in the covalent molecules and the stabilization of the cyclopropenylium ions by solvation.

Introduction

Carbocation–carbanion coordination and its reverse reaction (heterolysis) are two of the most fundamental reactions in organic chemistry. However, there have been only a few examples[2–5] of direct observation of the equilibrium between a covalent compound and the corresponding carbocation and carbanion. The kinetic and thermodynamic behavior of such reactions should largely depend on the electronic stabilities of the ions as well as the steric and solvent effects.

Our previous studies on the reactions between stable carbocations and carbanions have revealed the apparent dependence of the product upon these effects. When substituted tropylium ions were allowed to react with tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methide ion $\mathbf{1}^-$ ($C_{67}H_{39}^-$, pK_a 5.9),[6] a series of cations classified as $\mathbf{3a}^+$ (pK_{R^+} 3.25–7.80) gave covalent products **1–3a** (ionically dissociative hydrocarbons),[3] whreas a more stable cation, $\mathbf{3b}^+$ (pK_{R^+} 8.7), gave an ionic product, $\mathbf{1}^-\mathbf{3b}^+$ (hydrocarbon salt).[3a,4] Covalent hydrocarbons **1–3a** partially heterolyzed into $\mathbf{1}^-$ and $\mathbf{3a}^+$ in DMSO; the free energy of heterolysis $\Delta G°_{het}$ was found to correlate linearly with the thermodynamic stability pK_{R^+} of the cation moiety.[3b,c] Application of Arnett's "master equations" [7] has revealed that the heterolysis of **1–3a** is facilitated by ca. 15 kcal/mol, owing to the steric congestion in the covalent molecules.[3b,c] The importance of the solvent effect was demonstrated by the single-electron transfer from $\mathbf{1}^-$ to $\mathbf{3b}^+$ to form a pair of radicals, $\mathbf{1}^•$ and $\mathbf{3}^•$, in less polar solvents, THF and chloroform.[4]

Although it is of great interest to examine the factors that differentiate the covalent and ionic bond formation, an increase in bulkiness often accompanies an increase in electronic stability, making it difficult to examine the electronic and steric effects independently. For instance, the first hydrocarbon salt was isolated from ions stabilized by bulky π-conjugating substituents.[3a] On the other hand, tricyclopropylcyclopropenylium ion $\mathbf{2g}^+$ ($pK_{R^+} \simeq 10$)[8] is one of the most stable hydrocarbon cations reported but is sterically less hindered than other π-delocalized cations. The hydrocarbon salt consisting of $\mathbf{2g}^+$ and $\mathbf{1}^-$ quantitatively gave a covalent compound (**1–2g**) in chloroform, whereas the salt $\mathbf{1}^-\mathbf{2g}^+$ was regenerated when the solvent was evaporated.[4b,5] This facile reversibility led us to examine the nature of the bond formation between substituted cyclopropenylium ions and $\mathbf{1}^-$. We chose a series of 1-aryl-2,3-dicyclopropylcyclopropenylium ions ($\mathbf{2a–f}^+$) as a candidate cation system. This system allows progressive change in the electronic stability by changing the substituent on the aryl group, while the steric factor is essentially unchanged. This paper describes the synthesis and electronic stabilities of new cations $\mathbf{2a}^+$ and $\mathbf{2c}^+–\mathbf{2f}^+$ and the properties of the products from $\mathbf{2a–f}^+$ and $\mathbf{1}^-$.

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• Abstract published in *Advance ACS Abstracts*, September 1, 1993.

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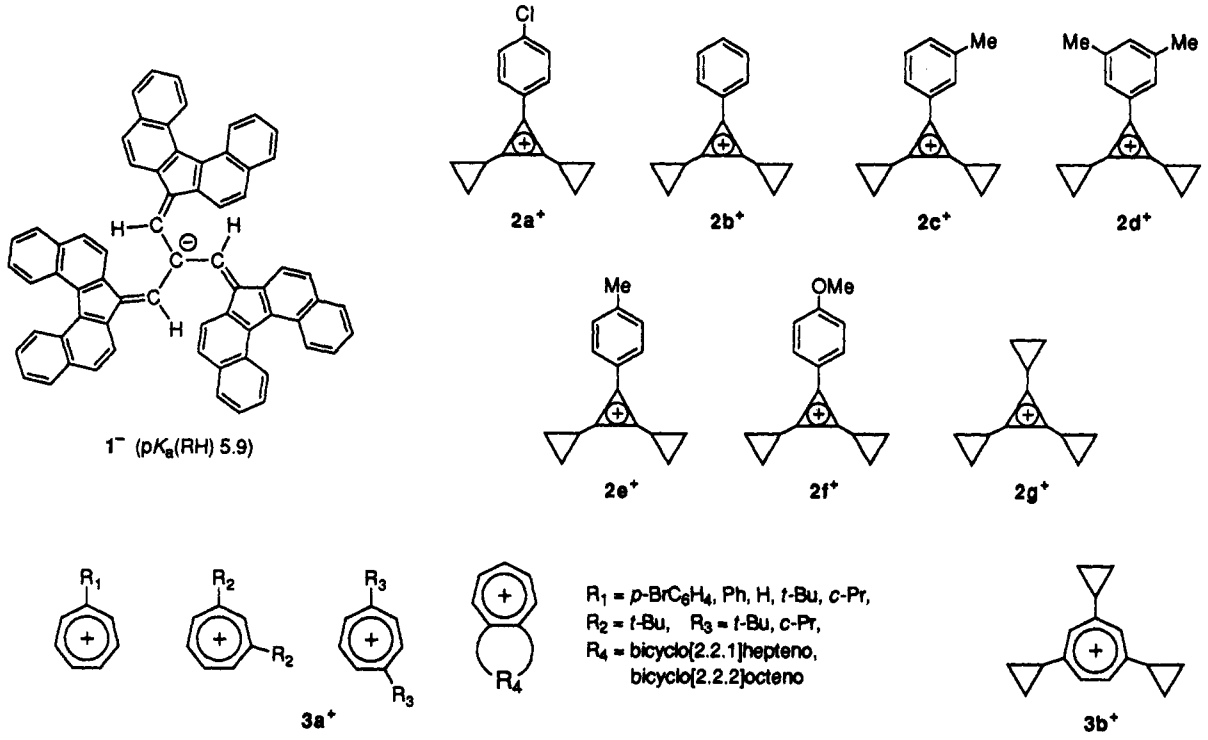
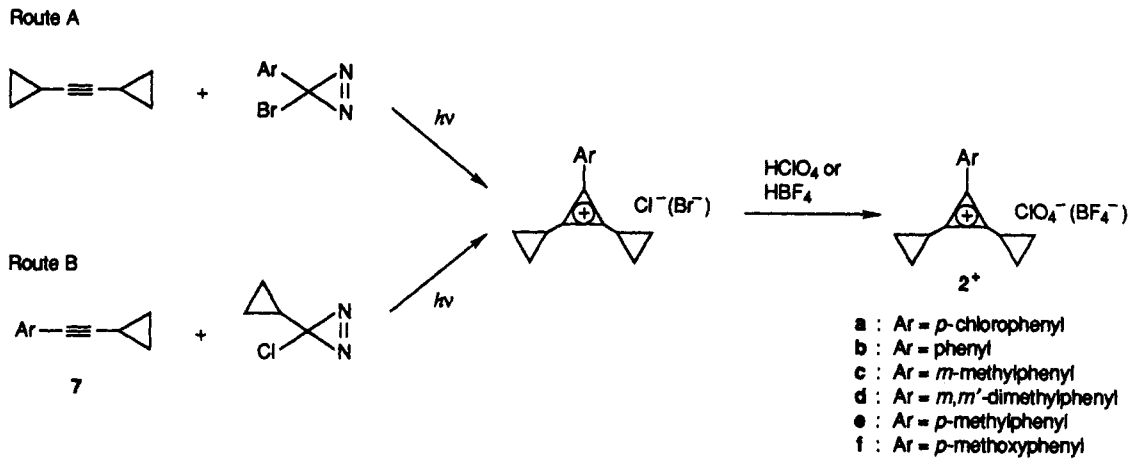
Chart I



Scheme I

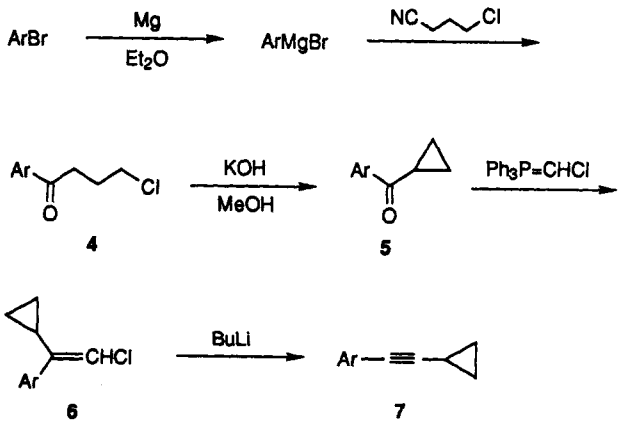


Results and Discussion

Synthesis of 1-Aryl-2,3-dicyclopropylcyclopropenylium Ions (2a–f⁺). In 1986, Moss and his co-workers[9] reported the synthesis of **2b⁺** by the addition of phenylfluorocarbene to dicyclopropylacetylene. Our new cations were prepared via either of two similar routes (Scheme I), i.e., the addition of an arylbromocarbene to dicyclopropylacetylene (for **2e⁺**; route A) or the addition of cyclopropylchlorocarbene to a 1-aryl-2-cyclopropylacetylene (for **2a,c,d,f⁺**; route B). New acetylenes 1-(*p*-chlorophenyl)-, 1-(*m*-methylphenyl)-, and 1-(*m,m'*-dimethylphenyl)-2-cyclopropylacetylene (**7a,c,d**) were synthesized by a route[10] involving aryl cyclopropyl ketones (Scheme II).

The carbene addition to the acetylenes was conducted in a Pyrex vessel under irradiation with a high-pressure mercury lamp using diazirines as carbene precursors.

Scheme II



Attempts to synthesize **2a⁺** and **2f⁺** by route A were not successful because of the very slow evolution of nitrogen from the corresponding arylbromodiazirines. The crude chlorides (or bromides) were converted to perchlorates by treating the aqueous solutions with 60% $HClO_4$. The

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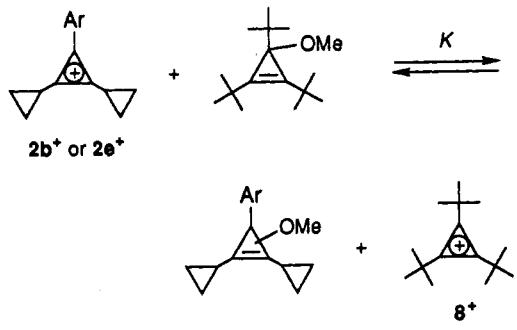
Table I. Selected ^{13}C NMR Data for 2a–g$^+$

compd	Ar	chemical shift (ppm)[a] ArC<	c-PrC<
2a$^+$ClO$_4^-$	*p*-chlorophenyl	154.9	168.3
2b$^+$BF$_4^-$	phenyl	155.6 (156.4)[b]	168.5 (169.4)[b]
2c$^+$ClO$_4^-$	*m*-methylphenyl	155.8	168.6
2d$^+$ClO$_4^-$	*m,m'*-dimethylphenyl	155.9	168.0
2e$^+$ClO$_4^-$	*p*-methylphenyl	155.2	167.4
2f$^+$ClO$_4^-$	*p*-methoxyphenyl	154.2	165.2
2g$^+$BF$_4^-$			169.7[c]

[a] In $CDCl_3$. [b] 2b$^+$F$^-$ in D_2O, ref 9. [c] In CD_3CN, ref 8a.

perchlorate salts were purified by column chromatography (2e$^+$ClO$_4^-$) or TLC (2a,c,d,f$^+$ClO$_4^-$) on SiO_2 using a highly polar solvent (CH_2Cl_2–MeCN 5:1, $R_f \simeq 0.2$) and recrystallized from CH_2Cl_2–AcOEt by slow evaporation of the CH_2Cl_2. Table I lists the ^{13}C NMR chemical shifts of the cyclopropenylium ring carbons of 2a–g$^+$. Other physical data are presented in the Experimental Section.

Relative Stabilities of 2b$^+$ and 2e$^+$. With regard to carbocation–carbanion combination reactions, the pK_{R^+} value is the most convenient index to assess the relative stabilities of cations. Moss and his co-workers[9] titrimetrically determined the pK_{R^+} value of 2b$^+$ to be 7.09 ± 0.05. However, this method did not appear to ensure sufficient precision for the estimation of small differences in the stabilities of 2a–f$^+$. Freedman et al.[11] have determined the relative stabilities of carbocations that are closely similar in free energy by observing alkoxide exchange equilibria. This technique was applied to the evaluation of the relative stabilities of 2b$^+$ and 2e$^+$ by using the tri-*tert*-butylcyclopropenylium ion (8$^+$)[12] as a reference cation. The methoxide exchange reaction between 8$^+$ and 2b$^+$ or 2e$^+$ (eq 1) was conducted by dissolving 3-methoxy-1,2,3-



(1)

tri-*tert*-butylcyclopropene and an equimolar amount of 2b$^+$BF$_4^-$ or 2e$^+$ClO$_4^-$ in CD_3CN at 25 °C in an NMR tube. After the mixture had reached equilibrium, the equilibrium constants of eq 1 were determined from ^1H NMR peak integrations to be 0.336 ± 0.061 and 0.234 ± 0.043 for 2b$^+$ and 2e$^+$, respectively.

Thus, the difference in free energy between these two cations is calculated to be 0.27 ± 0.21 kcal/mol, which corresponds to 0.20 ± 0.15 pK_{R^+} unit, affording a value of 7.29 ± 0.20 as the pK_{R^+} of 2e$^+$.

Reduction Potentials of 2a–f$^+$. The difficulty in obtaining sufficiently precise pK_{R^+} values prompted us to assess the cation stabilities by a different method. As reported by Okamoto et al.,[13] the reduction potentials E_{red} of substituted cyclopropenylium ions show a linear correlation with their pK_{R^+} values and hence can be used as a measure of the cation stability. The E_{red} values of 2a–f$^+$ were determined in MeCN by cyclic voltammetry using a Ag/AgNO$_3$ reference electrode. Each cation showed an irreversible reduction peak, the position of which was corrected with reference to ferrocene ($E_{1/2}$ = 0.083 V), added as an internal standard. The precision of the measurement is estimated to be ±0.01 V. The results, listed in Table II, indicate progressive increase in the cation stability within a narrow E_{red} range of 0.22 V, which corresponds to 5.1 kcal/mol. In analogy with aryltropylium ions,[14] the reduction potentials of 2a–f$^+$ showed a good linear correlation (r = 0.994) with the Hammett σ-constant[15] of the substituent (Figure 1).[16]

Table II. E_{red} and pK_{R^+} Values of 1-Aryl-2,3-dicyclopropylcyclopropenylium Ions 2a–f$^+$

compd	Ar	E_{red} (V)[a]	pK_{R^+}
2a$^+$ClO$_4^-$	*p*-chlorophenyl	-1.41_2	
2b$^+$BF$_4^-$	phenyl	-1.52_5	7.09 ± 0.05[b]
2c$^+$ClO$_4^-$	*m*-methylphenyl	-1.53_2	
2d$^+$ClO$_4^-$	*m,m'*-dimethylphenyl	-1.56_6	
2e$^+$ClO$_4^-$	*p*-methylphenyl	-1.58_3	7.29 ± 0.20[c]
2f$^+$ClO$_4^-$	*p*-methoxyphenyl	-1.63_2	

[a] CV peak potential vs Ag/AgNO$_3$ measured in MeCN with Bu$_4$N$^+$ClO$_4^-$ as the supporting electrolyte at 0.1 V/s; precision 0.01 V. [b] In 50% aqueous MeCN, ref 9. [c] Estimated from methoxide exchange experiments, see text.

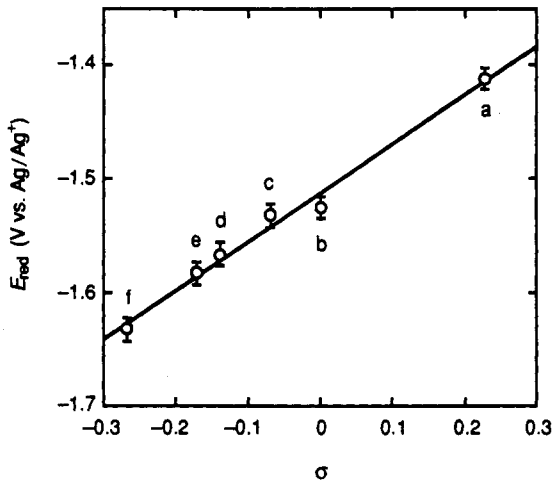


Figure 1. Plot of E_{red} of 2a–f$^+$ against the Hammett σ-constants.

Reactions of 2a–f$^+$ with 1$^-$. Despite similar thermodynamic stabilities of 2a–f$^+$, the reaction products from these cations and 1$^-$ were quite distinguishable. When a THF–MeCN solution of any one of 2a–d$^+$ (ClO$_4^-$ or BF$_4^-$ salts) was added to a deep green THF solution of 1$^-$K$^+$ under argon in the dark, the color turned brownish-orange, suggesting the formation of a covalent compound.[17] The inorganic salt (KClO$_4$ or KBF$_4$) was removed by evaporation of the solvent and subsequent extraction with benzene or chloroform. The IR spectrum (KBr disk, Table III) of the resulting orange powder showed an absorption by the cyclopropene ring at ca. 1820 cm^{-1}.

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(16) A plot E_{red} against σ^+-constants[15] showed poor linearity (r = 0.848).
(17) Unlike the deep green color of 1$^-$, its parent hydrocarbon 1-H and related derivatives 1-R (R = substituted cyclopropenyl and cycloheptatrienyl) are all orange to brownish-orange.[3-5] This color is considered characteristic of the π-conjugated system of the anionic moiety (see Figure 2) that is common to these compounds.

Table III. Properties of Covalent Compounds 1-(2a–d) and Salts 1⁻2e,f⁺

compd	crystalline form	yield (%)	mp[a] (°C)	Anal. obsd (calcd)	IR absorptions[b] (KBr disk, cm⁻¹)
1-2a	orange solid	~100	c	d	3047 (m), 3003 (m), 1822 (w, cyclopropene), 1512 (m), 1486 (m), 1343 (m), 1215 (w), 1090 (m), 1024 (m), 907 (w), 859 (w), 814 (s), 747 (s)
1-2b	orange solid	~100	c	d	3048 (m), 2923 (m), 2853 (m), 1818 (w, cyclopropene), 1512 (m), 1479 (w), 1444 (w), 1344 (m), 1218 (w), 1125 (w), 1029 (m), 858 (w), 814 (s), 745 (s), 677 (s)
1-2c	orange solid	~100	c	d	3047 (m), 2922 (m), 2851 (m), 1824 (w, cyclopropene), 1514 (m), 1479 (m), 1344 (m), 1218 (w), 1126 (w), 1029 (w), 859 (w), 815 (s), 745 (s), 677 (s)
1-2d	orange solid	~100	c	d	3048 (m), 1825 (w, cyclopropene), 1599 (m), 1513 (m), 1448 (m), 1375 (m), 1345 (m), 1217 (m), 1126 (w), 1022 (m), 858 (m), 815 (s), 746 (s)
1⁻2e⁺	dark green powder	62	164 dec	C: 93.97 (94.64) H: 5.17 (5.36)	1603** (w), 1503* (vs), 1445* (m), 1433** (m), 1388* (s), 1358** (w), 1298* (w), 1258* (m), 1238* (m), 1208* (m), 1168* (vs), 1158* (s), 1138* (vs), 918*,** (w), 878* (m), 853* (s), 815* (s), 798* (m), 748* (s)
1⁻2f⁺	dark green powder	61	~160 dec	C: 93.08 (93.23) H: 5.45 (5.28)	1598** (m), 1506* (vs), 1446* (m), 1417** (s), 1391* (s), 1298* (w), 1276** (w), 1256* (m), 1237* (m), 1208* (m), 1168* (vs), 1157* (s), 1137* (vs), 918*,** (w), 880* (m), 850* (s), 813* (s), 796* (m), 746* (s)

[a] Measured under air. [b] * and ** denote the absorptions of 1⁻ and 2⁺, respectively. [c] Thickened at ca. 120 °C and gradually changed to a brownish-red solid. [d] Not determined.

Table IV. ^1H and ^{13}C NMR Data for Covalent Compounds 1-(2a–f) in $CDCl_3$[a]

compd	nucls	chemical shift (ppm) cyclopropyl (1–4)	5	6	7	8 (J(Hz))	arom and olefinic	others
1-2a	^1H	1.90–1.82 (m, 1 H, H-1), 1.03–0.78 (m, 4 H, H-2(trans, cis)), 0.73–0.64 (m, 1 H, H-3), −0.13–−0.21 (m, 2 H, H-4(cis)), −0.33–−0.47 (m, 2 H, H-4(trans))			6.42[b]	6.46 (8.8)[c]	8.65–6.95 (41 H)	
	^{13}C	13.7 (C-3), 10.2, 9.1 (C-2), 8.3 (C-1), 4.2, 3.6 (C-4)	41.2	65.0	d	d	149.6–112.8	
1-2b	^1H	1.91–1.83 (m, 1 H, H-1), 1.02–0.68 (m, 5 H, H-2(trans, cis), 3), −0.17–−0.23 (m, 2 H, H-4(cis)), −0.36–−0.42 (m, 2 H, H-4(trans))			6.43[b]	6.47 (8.3)[c]	8.65–6.94 (42 H)	
	^{13}C	13.7 (C-3), 10.1, 9.0 (C-2), 8.2 (C-1), 4.1, 3.6 (C-4)	41.2	65.1	d	d	149.8–113.9	
1-2c	^1H	1.95–1.85 (m, 1 H, H-1), 1.06–0.70 (m, 5 H, H-2(trans, cis), 3), −0.14–−0.23 (m, 2 H, H-4(cis)), −0.34–−0.42 (m, 2 H, H-4(trans))			6.44[b]	6.48 (8.8)[c]	8.66–6.95 (41 H)	2.16 (CH_3)
	^{13}C	13.8 (C-3), 10.0, 9.0 (C-2), 8.3 (C-1), 4.2, 3.7 (C-4)	41.1	65.2	d	d	149.7–113.8	21.3 (CH_3)
1-2d	^1H	1.97–1.87 (m, 1 H, H-1), 1.05–0.73 (m, 5 H, H-2(trans, cis), 3), −0.14–−0.22 (m, 2 H, H-4(cis)), −0.33–−0.41 (m, 2 H, H-4(trans))			6.45[b]	6.49 (8.3)[c]	8.67–6.83 (40 H)	2.15 (CH_3)
	^{13}C	13.9 (C-3), 10.0, 9.0 (C-2), 8.3 (C-1), 4.3, 3.7 (C-4)	40.9	65.3	d	d	149.8–113.9	21.2 (CH_3)
1-2e	^1H	1.93–1.80 (m, 1 H, H-1), 1.05–0.67 (m, 5 H, H-2(trans, cis), 3), −0.15–−0.28 (m, 2 H, H-4(cis)), −0.34–−0.44 (m, 2 H, H-4(trans))			6.42[b]	6.47 (8.4)[c]	8.63–6.95 (41 H)	2.41 (CH_3)
	^{13}C	13.7 (C-3), 10.0, 8.8 (C-2), 8.2 (C-1), 4.1, 3.5 (C-4)	41.0	65.1	d	d	149.9–113.8	21.5 (CH_3)
1-2f	^1H	1.90–1.80 (m, 1 H, H-1), 1.02–0.64 (m, 5 H, H-2(trans, cis), 3), −0.19–−0.26 (m, 2 H, H-4(cis)), −0.38–−0.44 (m, 2 H, H-4(trans))			6.42[b]	6.47 (8.3)[c]	8.64–6.80 (41 H)	3.83 (OCH_3)
	^{13}C	13.6 (C-3), 9.8, 8.8 (C-2), 8.1 (C-1), 4.1, 3.5 (C-4)	40.9	65.2	d	d	159.2–114.1	55.3 (OCH_3)

[a] ^1H NMR at 270 MHz; ^{13}C NMR at 67.5 MHz. The numbering system for compounds 1-(2a–f) is shown in Figure 2. [b] Broad singlet. [c] Doulet. [d] Overlapped by other aromatic carbon signals.

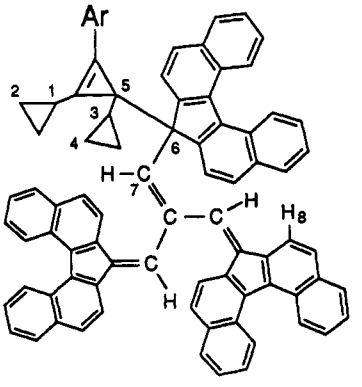

Figure 2. Structure of the covalent compounds 1-(2a–f).

The ^1H and ^{13}C NMR data (Table IV) indicated that the products have the covalent structures shown in Figure 2. No other isomers or unknown products were detected. A broad singlet proton signal at ca. 6.4 ppm (H-7) and a quaternary carbon signal at ca. 65 ppm (C-6) indicate the covalent bond formation between C-5 and C-6. Interestingly, the covalent bond did not form at the cyclopropenylium ring carbon bearing the aryl group.[18] This result may be explained by the steric hindrance by the phenyl ring and the higher positive charge located on the cyclopropenylium ring carbons bearing the cyclopropyl group. The major distribution of the positive charge on these carbons was demonstrated by the downfield shift of their ^{13}C NMR signals (Table I). Fortunately, this selective formation locates the aryl group at a position where the steric effect of the *meta* or *para* substituents is unimportant. Among the aromatic proton signals, a fine doublet at around 6.5 ppm is notable. Presumably this is assigned to the highly shielded H-8 proton (see Figure 2). Although the stable conformations of the covalent compounds are not clear, they seem to be more congested than the parent hydrocarbon 1-H. A highly shielded signal has been also observed for the covalent compounds obtained from 1⁻ and substituted tropylium ions.[3b,c] The covalent com-

(18) A similar selectivity has been reported for the reaction of 1-ethyl-2,3-diphenylcyclopropenylium ion with methyl and benzyl anions; see: Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1976**, 4685.

pounds 1-(2a-d) were stable under air but gradually decomposed during attempted purification by TLC (SiO_2) or recrystallization.

In contrast to the immediate formation of covalent compounds from **2a-d**$^+$, the deep green color of carbanion 1$^-$ persisted when a solution of **2e**$^+ClO_4^-$ or **2f**$^+ClO_4^-$ was added to a solution of 1$^-K^+$. Evaporation of the solvent yielded a dark green residue, from which organic components were extracted with chloroform. Removal of the chloroform followed by reprecipitation (THF-MeCN) afforded the salts 1$^-$**2e**$^+$ and 1$^-$**2f**$^+$ as dark green powders, whose IR spectra (KBr disk) consisted of the absorptions of 1$^-$ and **2e**$^+$ or **2f**$^+$ superimposed. The elemental analyses and IR spectra of these products are summarized in Table III. Their NMR spectra in chloroform will be described later.

The salts consisting of pentakis(methoxycarbonyl)-cyclopentadienide ion and tropylium ion[19] or substituted cyclopropenylium ions[19,20] have been characterized as charge-transfer complexes by the long-wavelength absorption found in their electronic spectra. The visible-near-IR region electronic spectra of the salts 1$^-$**2e**$^+$ and 1$^-$**2f**$^+$, however, showed only the absorption of 1$^-$ (λ_{max} 697 nm) in DMSO solution (see below) or in the solid state; no charge-transfer band was observed up to 2500 nm. Hence, 1$^-$**2e**$^+$ and 1$^-$**2f**$^+$ are classified as charge-separated salts rather than charge-transfer complexes.

It turns out from the reduction potentials of **2a-f**$^+$ that the product of the reaction with 1$^-$ changes abruptly from a covalent compound to a salt as the stability of the cation moiety is gradually increased. The borderline between the two types of reactions lies between **2d**$^+$ and **2e**$^+$. The slight difference (0.017 V) in the E_{red} values of these cations suggests that only a slight difference (0.4 kcal/mol or less) in electronic stability can switch the type of bond completely.

Behavior of the Salts 1$^-$2e$^+$ and 1$^-$2f$^+$ in Chloroform. We have reported[4b,5] that the hydrocarbon salt 1$^-$**2g**$^+$ underwent coordination when dissolved in chloroform to produce the corresponding covalent compound **1-2g**. This compound was not isolated in the solid state but was converted into the salt 1$^-$**2g**$^+$ at the moment of crystallization when the solvent was evaporated. This clean reversibility suggested the possibility that the salts of the closely related structures 1$^-$**2e**$^+$ and 1$^-$**2f**$^+$ also exist as covalent forms in nonpolar solvents. As expected, the deep green color of solid 1$^-$**2e**$^+$ and 1$^-$**2f**$^+$ completely changed to brown when dissolved in chloroform or benzene, indicating the formation of covalent compounds. The ^1H and ^{13}C NMR spectra (Table IV) of the brown $CDCl_3$ solution indicated the presence of **1-2e** or **1-2f** alone, in which a new covalent bond had been formed between C-5 and C-6 (see Figure 2). The solutions regenerated dark green solids on evaporation of the solvent. Thus, in analogy with **1-2g**, the covalent compounds **1-2e** and **1-2f** can exist only in solution.

Behavior of the Covalent Compounds 1-(2a-d) and the Salts 1$^-$2e,f$^+$ in DMSO. Despite the complete difference in the solid-state properties between 1-(2a-d) and 1$^-$**2e,f**$^+$, they all exist as covalent compounds in chloroform solution. The behavior of these compounds was further examined in a polar solvent, DMSO.

(19) LeGoff, E.; LaCount, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1354.
(20) Maas, G.; Weber, H. M.; Exner, R.; Salbeck, J. *J. Phys. Org. Chem.* **1990**, *3*, 459.

Table V. Thermodynamic Data for Heterolysis of 1-(2a-f) in DMSO at 25 °C

starting compd	initl concn ($\times 10^{-5}$ M)	α	K_{het}[a] ($\times 10^{-4}$ M)	$\gamma^{\pm 2}$	$K°_{het}$[b] ($\times 10^{-4}$ M)	$\Delta G°_{het}$ (kcal/mol)
1-2a	7.23	0.535	0.445	0.969	0.431	5.96
	8.55	0.553	0.585	0.965	0.565	5.80
1-2b	7.29	0.652	0.891	0.965	0.860	5.55
	8.56	0.652	1.05	0.962	1.01	5.45
1-2c	7.39	0.863	4.02	0.960	3.85	4.66
	7.58	0.866	4.24	0.959	4.07	4.63
1-2d	6.18	0.868	3.53	0.963	3.40	4.73
	6.58	0.821	2.48	0.963	2.39	4.94
	7.14	0.831	2.92	0.961	2.80	4.85
	7.20	0.832	2.97	0.961	2.85	4.84
1-2e$^+$	7.88	0.874	4.78	0.958	4.58	4.56
1-2f$^+$	6.98	0.855	3.49	0.961	3.35	4.74
	8.02	0.881	5.23	0.958	5.01	4.50

[a] K_{het} = initl concn $\times \alpha^2/(1-\alpha)$. [b] $K°_{het} = K_{het} \times \gamma^{\pm 2}$.

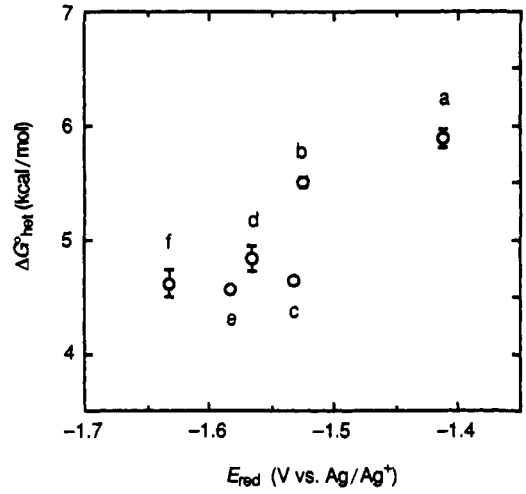

Figure 3. Plot of $\Delta G°_{het}$ for 1-(2a-f) determined in DMSO at 25 °C against E_{red} of **2a-f**$^+$.

The orange solids of **1-(2a-d)** gave deep green solutions when dissolved in DMSO. The electronic spectra of these solutions showed the partial dissociation of the covalent molecules into 1$^-$ (λ_{max} 697 nm, log ϵ 5.18) and **2a-d**$^+$. Similarly, the salts 1$^-$**2e**$^+$ and 1$^-$**2f**$^+$ underwent partial coordination into the covalent form in DMSO, as indicated by the presence of only 85-88% of the theoretical amount of 1$^-$ at the concentration of $\sim 10^{-4}$ M. These findings indicate that **1-(2a-d)** and 1$^-$**2e,f**$^+$ exist as equilibrium mixtures of the covalent compound and the ions in DMSO (eq 2).

$$\text{1-(2a-f)} \overset{K°_{het}}{\rightleftarrows} \text{1}^- + \text{2a-f}^+ \qquad (2)$$

The thermodynamic equilibrium constants of heterolysis $K°_{het}$ were calculated from the degree of dissociation α using the Debye-Hückel limiting law (Table V).[21] A plot of the free energy of heterolysis $\Delta G°_{het}$ for **1-(2a-f)** against the E_{red} values of **2a-f**$^+$ (Figure 3) showed a general tendency that $\Delta G°_{het}$ becomes less exergonic as the cation is more stabilized. The absence of a marked difference in $\Delta G°_{het}$ between **1-(2a-d)** and **1-2e,f** suggests that a certain solid-state property is concerned with the abrupt switching of the crystalline form upon changing the substituent. Presumably, the balance between the energy of heterolysis of the C-C σ-bond and the lattice energy in the salt form

(21) The derivation of $\Delta G°_{het}$ is described in ref 3c.

Table VI. Enthalpy and Entropy of Heterolysis for 1-2a,b,d in DMSO

compd	run	temp (°C)	initl concn[a] (× 10^{-5} M)	α	K_{het}[b] (× 10^{-4} M)	$\gamma^{\pm 2}$	$K°_{het}$[c] (× 10^{-4} M)	$\Delta H°_{het}$ (kcal/mol)	$\Delta S°_{het}$ (eu)
1-2a	1	50	6.85	0.598	0.609	0.968	0.590	−0.27	−20.2
		25	7.23	0.595	0.632	0.967	0.611		
	2	50	6.87	0.624	0.711	0.967	0.688	−0.36	−20.2
		40	7.00	0.624	0.725	0.967	0.701		
		25	7.25	0.623	0.746	0.966	0.721		
1-2b	1	50	6.90	0.699	1.12	0.965	1.08	−1.16	−21.7
		25	7.27	0.715	1.31	0.964	1.26		
	2	50	6.88	0.747	1.52	0.964	1.46	−0.46	−19.0
		40	7.01	0.747	1.55	0.964	1.49		
		25	7.26	0.748	1.61	0.963	1.55		
1-2d	1	50	6.34	0.768	1.61	0.965	1.56	−0.46	−18.8
		25	6.69	0.769	1.71	0.964	1.65		
	2	50	5.90	0.780	1.63	0.966	1.58	−0.29	−18.3
		40	6.01	0.780	1.66	0.965	1.60		
		25	6.22	0.778	1.70	0.965	1.64		

[a] Changes in the concentration due to heat expansion have been calibrated, ref 3c. [b] K_{het} = initl concn × $\alpha^2/(1-\alpha)$. [c] $K°_{het} = K_{het} \times \gamma^{\pm 2}$.

determines the product. There might be a possibility that extraneous mechanical energy causes interconversion between the two forms. Indeed, the orange-colored solid of **1-2b** partially heterolyzed to give a green color when pulverized in a vibrating ball mill, exhibiting piezochromism.

Table VI summarizes the enthalpy and entropy of heterolysis of some covalent compounds calculated from the temperature dependence of $K°_{het}$. Arnett has reported[7] an empirical relationship (master equations) for predicting the heat of heterolysis of a C–C σ-bond into a resonance-stabilized carbocation and carbanion. From the equation for tertiary cations,

$$\Delta H_{het}\ (\text{kcal/mol}) = 8.895 - 0.648(\text{p}K_{R^+}) + 1.294(\text{p}K_a)$$

the ΔH_{het} for **1-2b** is estimated to be 11.9 kcal/mol. The observed $\Delta H°_{het}$ is ca. 13 kcal/mol smaller than expected, indicating that heterolysis is markedly facilitated in the present system. This significant lowering of $\Delta H°_{het}$ can be ascribed to the steric congestion in the covalent molecules and the stabilization of the cyclopropenylium ions by solvation. The large negative $\Delta S°_{het}$ values also suggest the strong solvation to cyclopropenylium ions due to the high donating ability of DMSO. We have reported[3b,c] similar steric and solvation effects on the thermodynamic parameters for the heterolysis into 1^- and substituted tropylium ions.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Hitachi 215 or a Perkin-Elmer 1600 spectrophotometer. Electronic spectra were taken on a Hitachi 200-10 or a Shimadzu UV-365 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL GSX270 (270 MHz) spectrometer. ^{13}C NMR spectra were recorded on a JEOL GSX270 (67.8 MHz) or a JEOL FX90 (22.5 MHz) spectrometer. The assignments of ^{13}C NMR signals are based on DEPT or off-resonance decoupling spectra. Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto, Japan. A Sartorius 4503MP6 microbalance was used for precise weighing.

4-Chlorophenyl cyclopropyl ketone (**5a**) was purchased from Aldrich. Dimethyl sulfoxide (DMSO) was kept for at least a week over molecular sieves (4A) and distilled under vacuum over calcium hydride. Tetrahyrofuran and diethyl ether were freshly distilled over benzophenone ketyl under a nitrogen atmosphere. Acetonitrile was refluxed and distilled over phosphorus pentoxide.

1-Aryl-4-chloro-1-butanones 4c, 4d, and 4f. A typical procedure is as follows. To (*m*-methylphenyl)magnesium bromide in ether (120 mL), which had been prepared from *m*-bromotoluene (24.8 g, 0.145 mol) and magnesium (3.5 g, 0.14 mol), was added 4-chlorobutyronitrile (15.0 g, 0.145 mol) in ether (100 mL) under reflux. After the mixture had been refluxed further for 2 h, 10% HCl (130 mL) was added and the reaction mixture was extracted with ether (3 × 100 mL). The organic layer was washed with 10% NaCl (3 × 100 mL), dried ($MgSO_4$), and evaporated to give a yellow liquid, which was chromatographed over SiO_2 (hexane–CH_2Cl_2 3:1) to afford 12.1 g of essentially pure 4-chloro-1-(*m*-methylphenyl)-1-butanone (**4c**) as a faintly yellow liquid.

4c: pale yellow liquid; yield 42%; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.76–7.72 (m, 2 H), 7.34–7.28 (m, 2 H), 3.63 (t, 2 H, J = 6.3 Hz, H_γ), 3.11 (t, 2 H, J = 7.1 Hz, H_α), 2.38 (s, 3 H, CH_3), 2.23–2.13 (m, 2 H, H_β); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 198.7 (C=O), 138.1, 136.5 (C), 133.6, 128.2, 128.2, 124.9 (CH), 44.4, 35.1, 26.6 (CH_2), 21.0 (CH_3); IR (liquid film) 1685, 1604, 1586, 1436, 1370, 1320, 1249, 770, 689 cm^{-1}.

4d: pale yellow liquid; yield 39%; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.55 (s, 2 H), 7.16 (s, 1 H), 3.63 (t, 2 H, J = 6.3 Hz, H_γ), 3.10 (t, 2 H, J = 6.8 Hz, H_α), 2.34 (s, 6 H, CH_3), 2.22–2.12 (m, 2 H, H_β); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 198.8 (C=O), 137.9, 136.6 (C), 134.5, 125.5 (CH), 44.4, 35.1, 26.6 (CH_2), 20.9 (CH_3); IR (liquid film) 1685, 1606, 1446, 1382, 1323, 1303, 1180, 1159 cm^{-1}.

4f:[10] pale red liquid; yield 32%; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.95 (d, 2 H, J = 8.1 Hz), 6.93 (d, 2 H, J = 8.1 Hz), 3.86 (s, 3 H, CH_3), 3.66 (t, 2 H, J = 6.1 Hz, H_γ), 3.11 (t, 2 H, J = 6.6 Hz, H_α), 2.23–2.18 (m, 2 H, H_β); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 197.5 (C=O), 163.4, 129.7 (C), 130.1, 113.6 (CH), 44.6, 34.7, 26.8 (CH_2), 55.4 (CH_3); IR (liquid film) 1677, 1601, 1576, 1511, 1317, 1260, 1234, 1173, 1031 cm^{-1}.

Aryl Cyclopropyl Ketones 5c, 5d, and 5f. A typical procedure is as follows. 4-Chloro-1-(*m*-methylphenyl)-1-butanone (**4c**) (12.1 g, 0.0616 mol) was added to a solution of KOH (12.9 g, 0.229 mol) in methanol (100 mL) at room temperature. After the mixture had been stirred for 12 h, water (100 mL) was added and the mixture was extracted with ether (3 × 100 mL). The ether layer was dried ($MgSO_4$) and evaporated to give 9.0 g of essentially pure cyclopropyl *m*-methylphenyl ketone (**5c**) as a faintly yellow liquid, which was used for the next reaction without further purification.

5c: pale yellow liquid; yield 91%; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.81–7.79 (m, 2 H), 7.34–7.29 (m, 2 H), 2.64 (tt, 1 H, J = 7.3, 4.2 Hz, CH), 2.39 (s, 3 H, CH_3), 1.24–1.19 (m, 2 H, CH_2), 1.03–0.97 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 200.5 (C=O), 138.0, 137.8 (C), 133.2, 128.3, 128.2, 125.0, 16.9 (CH), 11.3 (CH_2), 21.1 (CH_3); IR (liquid film) 1668, 1604, 1585, 1439, 1386, 1253, 1161, 1046, 895, 734 cm^{-1}.

5d: pale yellow liquid; yield 99%; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.62 (s, 2 H), 7.17 (s, 1 H), 2.65 (tt, 1 H, J = 7.9, 4.6 Hz, CH), 2.36 (s, 6 H, CH_3), 1.24–1.18 (m, 2 H, CH_2), 1.03–0.96 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 200.8 (C=O), 138.0, 137.9 (C), 134.2, 125.7, 17.0 (CH), 11.4 (CH_2), 21.1 (CH_3); IR (liquid film) 1669, 1604, 1443, 1388, 1293, 1204, 1174, 1160, 1065, 901 cm^{-1}.

5f:[10] pale yellow liquid; yield 95%; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.00 (d, 2 H, J = 8.8 Hz), 6.94 (d, 2 H, J = 8.8 Hz), 3.86 (s, 3 H, CH_3), 2.62 (tt, 1 H, J = 7.8, 4.4 Hz, CH), 1.23–1.17 (m, 2 H, CH_2), 1.02–0.95 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ

198.9 (C=O), 163.2, 130.9 (C), 130.1, 113.5, 16.5 (CH), 11.0 (CH_2), 55.3 (CH_3); IR (liquid film) 1663, 1601, 1422, 1385, 1233, 1261, 1170, 1030, 992, 838 cm^{-1}.

(*E*)- and (*Z*)-β-Chloro-α-cyclopropylstyrenes 6a, 6c, 6d, and 6f. A typical procedure is as follows. To a mixture of (chloromethyl)triphenylphosphonium chloride (24.4 g, 70.2 mmol; purchased from Aldrich or synthesized according to the literature[22]), piperidine (5.99 g, 70.3 mmol), and ether (50 mL) was added 1.6 M BuLi in hexane (47 mL, 75 mmol) over 20 min at room temperature with mechanical stirring. The resulting yellowish brown suspension was stirred further for 4 h. Cyclopropyl *m*-methylphenyl ketone (**5c**, 8.82 g, 55 mmol) in ether (25 mL) was added over 30 min, and the resulting suspension was stirred overnight at room temperature. The reaction mixture was filtered, and the filtrate was washed with 10% HCl (3 × 150 mL) and dried ($MgSO_4$). Evaporation of the solvent gave a pale yellow liquid, which was chromatographed over SiO_2 (hexane) to afford 6.1 g of a mixture of (*E*)- and (*Z*)-β-chloro-α-cyclopropyl-*m*-methylstyrene (**6c**) as a colorless liquid.

The *E*/*Z* ratios were determined from the integrations of the cyclopropyl methine protons (**6a** and **6c**) or the methoxy protons (**6f**). The assignment of the NMR signals to each isomer is based on the assumption that the cyclopropyl methine proton is more deshielded in the *E*-isomer than in the *Z*-isomer.[23] In the case of **6d**, the two isomers could be separated by column chromatography.

6a: pale yellow liquid; yield 70%; *E*/*Z* = 29/71; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.35–7.08 (m, 8 H), 6.11 (s, =CHCl (*E*)), 6.09 (s, =CHCl (*Z*)), 2.07–2.00 (m, cyclopropyl CH (*E*)), 1.67–1.57 (m, cyclopropyl CH (*Z*)), 0.88–0.33 (m, 8 H, CH_2 (*E* and *Z*)); ^{13}C NMR ($CDCl_3$, 67.5 MHz, signals of the *E*-isomer are marked with an asterisk) δ 143.2*, 142.8 (>C=), 117.1*, 113.5 (=CHCl), 136.3*, 135.8, 133.6*, 133.5 (C), 129.9, 129.6*, 128.3, 128.2*, 17.2, 12.4* (CH), 5.7*, 5.3 (CH_2); IR (liquid film) 1490, 1093, 1017, 877, 825, 800 cm^{-1}.

6c: colorless liquid; yield 57%; *E*/*Z* = 37/63; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.26–6.92 (m, 8 H), 6.07 (s, =CHCl (*E*)), 6.05 (s, =CHCl (*Z*)), 2.34 (s, CH_3 (*Z*)), 2.30 (s, CH_3 (*E*)), 2.06–2.03 (m, cyclopropyl CH (*E*)), 1.67–1.58 (m, cyclopropyl CH (*Z*)), 0.83–0.35 (m, 8 H, CH_2 (*E* and *Z*)); ^{13}C NMR ($CDCl_3$, 67.5 MHz, signals of the *E*-isomer are marked with an asterisk) δ 144.4*, 144.1 (>C=), 116.2*, 112.6 (=CHCl), 137.6, 137.5, 137.5, 137.3 (C, *E* and *Z*), 129.1*, 129.0, 128.3, 128.3*, 127.9, 127.8*, 125.6*, 125.5, 17.3, 12.4* (CH), 5.5*, 5.2 (CH_2), 21.4, 21.3* (CH_3); IR (liquid film) 1604, 1485, 1028, 921, 818, 777, 760, 706 cm^{-1}.

6d (*Z*-isomer): colorless crystals; yield 58%; mp 51–52 °C; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.92 (s, 1 H), 6.87 (s, 2 H), 6.02 (s, 1 H, =CHCl), 2.30 (s, 6 H, CH_3), 1.65–1.55 (m, 1 H, cyclopropyl CH), 0.70–0.63 (m, 2 H, CH_2), 0.49–0.43 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 144.3 (>C=), 112.4 (=CHCl), 137.4, 137.2 (C), 129.2, 126.1, 17.3 (CH), 5.2 (CH_2), 21.3 (CH_3); IR (KBr disk) 1605, 1052, 923, 860, 821, 789, 714 cm^{-1}.

6d (*E*-isomer): colorless liquid; yield 35%; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.88 (s, 1 H), 6.75 (s, 2 H), 6.03 (s, 1 H, =CHCl), 2.26 (s, 6 H, CH_3), 2.10–2.00 (m, 1 H, cyclopropyl CH), 0.82–0.74 (m, 2 H, CH_2), 0.42–0.36 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 144.5 (>C=), 115.9 (=CHCl), 137.6, 137.3 (C), 129.1, 126.3, 12.4 (CH), 5.6 (CH_2), 21.1 (CH_3); IR (liquid film) 1601, 1032, 845, 739, 701 cm^{-1}.

6f:[10] pale yellow liquid; yield 85%; *E*/*Z* = 38/62; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.32–6.80 (m, 8 H), 6.05 (s, 1 H, =CHCl (*E* and *Z*)), 3.81 (s, CH_3 (*Z*)), 3.78 (s, CH_3 (*E*)), 2.12–2.03 (m, cyclopropyl CH (*E*)), 1.68–1.58 (m, cyclopropyl CH (*Z*)), 0.84–0.35 (m, 8 H, CH_2 (*E* and *Z*)); ^{13}C NMR ($CDCl_3$, 67.5 MHz, signals of the *E*-isomer are marked with an asterisk) δ 143.9*, 143.3 (>C=), 115.7*, 112.4 (=CHCl), 159.1*, 158.9, 130.0*, 129.7 (C), 129.7, 129.6*, 113.4, 113.3*, 17.3, 12.5* (CH), 5.5*, 5.2 (CH_2), 55.2*, 55.1 (CH_3); IR (liquid film) 1608, 1511, 1288, 1248, 1178, 1037, 835 cm^{-1}.

1-Aryl-2-cyclopropylacetylenes 7a, 7c, 7d, and 7f. A typical procedure is as follows. To a THF solution (50 mL) of β-chloro-α-cyclopropyl-*m*-methylstyrene (**6c**, *E*/*Z* = 37/63, 5.92 g, 30.7 mmol) was added 1.6 M BuLi in hexane (25 mL, 40 mmol) over 15 min under argon with ice-bath cooling, and the mixture was stirred for 3 h at room temperature. Water (15 mL) was added, and the organic layer was washed with 10% NaCl (3 × 50 mL) and dried ($MgSO_4$). Removal of the solvent gave a yellow liquid, which on chromatography over SiO_2 (hexane) afforded 2.1 g of essentially pure 1-cyclopropyl-2-(*m*-methylphenyl)acetylene (**7c**) as a colorless liquid.

New acetylenes (**7a**, **7c**, and **7d**) were further purified by distillation in a Kugelrohr apparatus for the purpose of elemental analyses.

7a: colorless liquid; yield 36%; bp (ot) 150–153 °C/5 mmHg; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.28 (d, 2 H, *J* = 8.8 Hz), 7.21 (d, 2 H, *J* = 8.8 Hz), 1.42 (tt, 1 H, *J* = 8.1, 5.4 Hz, CH), 0.90–0.77 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 133.3, 122.4, 94.4, 74.7 (C), 132.8, 128.4, 0.1 (CH), 8.6 (CH_2); IR (liquid film) 2234, 1490, 1091, 1014, 954, 827 cm^{-1}. Anal. Calcd for $C_{11}H_9Cl$: C, 74.79; H, 5.14; Cl, 20.07. Found: C, 74.94; H, 5.10; Cl, 19.80.

7c: colorless liquid; yield 44%; bp (ot) 145–148 °C/5 mmHg; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.18–7.00 (m, 4 H), 2.26 (s, 3 H, CH_3), 1.40 (tt, 1 H, *J* = 8.1, 5.4 Hz, CH), 0.83–0.75 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 137.6, 123.7, 92.9, 75.9 (C), 132.1, 128.6, 128.2, 128.0, 0.1 (CH), 8.5 (CH_2), 21.1 (CH_3); IR (liquid film) 2225, 1603, 1486, 884, 784, 692 cm^{-1}. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.77.

7d: colorless liquid; yield 38%; bp (ot) 113–120 °C/0.2 mmHg; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.99 (s, 1 H), 6.84 (s, 2 H), 2.22 (s, 6 H, CH_3), 1.40 (tt, 1 H, *J* = 7.8, 5.4 Hz, CH), 0.82–0.74 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 137.5, 123.5, 92.5, 76.0 (C), 129.2, 129.2, 0.1 (CH), 8.5 (CH_2), 20.9 (CH_3); IR (liquid film) 2230, 1599, 887, 849, 690 cm^{-1}. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.90; H, 8.41.

7f: colorless liquid; yield 61% (lit.[10] 82%); ^1H NMR ($CDCl_3$, 270 MHz) δ 7.30 (d, 2 H, *J* = 8.8 Hz), 6.78 (d, 2 H, *J* = 8.8 Hz), 3.76 (s, 3 H, CH_3), 1.42 (tt, 1 H, *J* = 8.1, 5.1 Hz, CH), 0.88–0.73 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 159.0, 116.0, 91.7, 75.4 (C), 132.9, 113.7, 0.1 (CH), 8.4 (CH_2), 55.1 (CH_3); IR (liquid film) 2233, 1607, 1511, 1288, 1247, 1172, 1032, 832 cm^{-1}.

1-Aryl-2,3-dicyclopropylcyclopropenylium Ions 2a–f⁺. Route A. 1,2-Dicyclopropyl-3-phenylcyclopropenylium tetrafluoroborate (**2b⁺**BF_4^-) was synthesized according to the literature:[9] colorless prisms; mp 127.5–128.5 °C (lit.[9] mp 123–125 °C); ^1H NMR ($CDCl_3$, 270 MHz) δ 7.90 (d, 2 H, *J* = 7.1 Hz), 7.82 (t, 1 H, *J* = 7.6 Hz), 7.69 (t, 2 H, *J* = 7.6 Hz), 2.81 (tt, 2 H, *J* = 7.8, 4.3 Hz, CH), 1.99–1.91 (m, 4 H, CH_2), 1.81–1.74 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 168.5 (c-PrC<), 155.6 (ArC<), 118.8 (C), 137.2, 134.4, 130.3, 9.2 (CH), 16.5 (CH_2); UV (MeCN, λ_{max} (log ε)) 203 (4.40), 225 (3.96), 269 (4.38) nm; IR (KBr disk) 1590, 1495, 1420, 1045 br, 905, 890, 770, 680 cm^{-1}.

2e⁺ClO_4^- was prepared by the addtion of (*p*-methylphenyl)-bromocarbene to dicyclopropylacetylene in a manner similar to that reported[9] for the preparation of **2b⁺**. Anhydrous LiBr (13.0 g, 0.150 mol) and *p*-methylbenzamidine hydrochloride[24] (5.02 g, 0.0294 mol) were dissolved intio DMSO (125 mL)–pentane (60 mL). To this mixture was added rapidly a cold 1.2 M NaOBr solution[24] (220 mL, 0.26 mol) with vigorous stirring (5 min) and the temperature of the reaction mixture maintained below 30 °C by ice-bath cooling. After additional stirring for 1 h at 0 °C, water (120 mL) was added. The organic layer was separated, and the aqueous layer was extracted with pentane (4 × 30 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure at 0 °C to give 3-bromo-3-(*p*-methylphenyl)diazirine as a yellow oil (2.12 g, 34%): ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 38.2 (lit.[24] 38.3); IR (liquid film) 1560 cm^{-1} (lit.[24] 1560 cm^{-1}). The addition of (*p*-methylphenyl)bromocarbene to dicyclopropylacetylene was conducted as follows. In a Pyrex flask, 3-bromo-3-(*p*-methylphenyl)diazirine (1.91 g, 9.04 mmol) was dissolved in dicyclopropylacetylene[25] (0.637 g, 6.00 mmol) and irradiated with a high-pressure mercury lamp at 5 °C. After

(22) Köbrich, G.; Trapp, H.; Flory, K.; Drischel, W. *Chem. Ber.* **1966**, *99*, 689.

(23) The cyclopropyl methine proton of (*Z*)-α-chloro-β-cyclopropyl-*p*-methylstyrene is more deshielded by ca. 0.5 ppm than that of the corresponding *E*-isomer.[10]

(24) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

(25) Köbrich, G.; Merkel, D.; Thiem, K.-W. *Chem. Ber.* **1972**, *105*, 1683.

1 h, the resulting pale brown precipitate was collected and the remaining solution was subjected to further irradiation. This cycle was repeated three times (total irradiation time 6 h). The precipitate from each cycle was dissolved in water (1 mL) and treated with 60% $HClO_4$ (1 mL). This mixture was extracted with CH_2Cl_2 (4 × 2 mL), and the organic layer was dried ($MgSO_4$) and evaporated to give crude **2e**$^+ClO_4^-$. The combined crude products from the three cycles (0.24 g in total) were chromatographed over SiO_2 (CH_2Cl_2–MeCN 5:1). The main fraction was dissolved in CH_2Cl_2–AcOEt (4:1) and recrystallized by slow evaporation of the CH_2Cl_2 to give 0.13 g (4% based on the diazirine) of analytically pure **2e**$^+ClO_4^-$ as pale yellow crystals: mp 184.5–185.5 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.77 (d, 2 H, J = 8.0 Hz), 7.49 (d, 2 H, J = 8.0 Hz), 2.80 (tt, 2 H, J = 7.8, 4.3 Hz, CH), 2.52 (s, 3 H, CH_3), 1.99–1.91 (m, 4 H, CH_2), 1.79–1.73 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 167.4 (c-PrC<), 155.2 (ArC<), 149.6, 116.1 (C), 134.6, 131.1, 9.3 (CH), 16.3 (CH_2), 22.3 (CH_3); UV (MeCN, λ_{max} (log ε)) 209 (4.36), 232 sh (3.82), 278 (4.41) nm; IR (KBr disk) 1605, 1430, 1090 br, 920, 900, 830 cm^{-1}. Anal. Calcd for $C_{16}H_{17}O_4Cl$: C, 62.24; H, 5.55; Cl, 11.48. Found: C, 62.07; H, 5.44; Cl, 11.75.

Route B. The perchlorate salts of **2a,c,d,f**$^+$ were synthesized by the addition of cyclopropylchlorocarbene to 1-aryl-2-cyclopropylacetylenes. The detailed method has been reported for the synthesis of tricyclopropylcyclopropenylium tetrafluoroborate (**2g**$^+BF_4^-$).[8] A typical procedure is as follows. A solution of NaCl (43 g) in 230 mL of aqueous sodium hypochlorite (~6%) was added dropwise into an ice-cooled DMSO solution (100 mL) containing 2.08 g (17.8 mmol) of cyclopropanecarboxamidine hydrochloride and 6.70 g of LiCl over 8 min under 5 mmHg. The generated 3-chloro-3-cyclopropyldiazirine vapor was condensed into a U-shaped trap (Pyrex) containing 0.669 g (4.28 mmol) of 1-cyclopropyl-2-(*m*-methylphenyl)acetylene (**7c**) cooled by liquid nitrogen. The mixture in the trap was irradiated for 5 h at 5 °C, and the resulting chloride was converted to perchlorate in a manner similar to that described under Route A. The crude perchlorate salt was chromatographed on a TLC plate (SiO_2, CH_2Cl_2–MeCN 5:1). The main fraction was dissolved in CH_2Cl_2–AcOEt (5:2) and recrystallized by slow evaporation of the CH_2Cl_2 to give 49 mg of analytically pure **2c**$^+ClO_4^-$.

2a$^+ClO_4^-$: colorless rods; yield 5% (based on the evolved N_2); mp 171–172 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.91 (d, 2 H, J = 8.3 Hz), 7.63 (d, 2 H, J = 8.3 Hz), 2.78 (tt, 2 H, J = 7.6, 4.2 Hz, CH), 1.97–1.91 (m, 4 H, CH_2), 1.73–1.70 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 168.3 (c-PrC<), 154.9 (ArC<), 144.0, 117.5 (C), 135.8, 130.8, 9.5 (CH), 16.9 (CH_2); UV (MeCN, λ_{max} (log ε)) 211 (4.41), 230 sh (3.90), 278 (4.45) nm; IR (KBr disk) 1592, 1472, 1429, 1091 br, 918, 623 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_4Cl_2$: C, 54.73; H, 4.29; Cl, 21.54. Found: C, 54.58; H, 4.33; Cl, 21.49.

2c$^+ClO_4^-$: colorless needles; yield 10% (based on the evolved N_2); mp 154–155 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.70–7.53 (m, 4 H), 2.82 (tt, 2 H, J = 7.8, 4.2 Hz, CH), 2.49 (s, 3 H, CH_3), 2.00–1.92 (m, 4 H, CH_2), 1.80–1.74 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 168.6 (c-PrC<), 155.8 (ArC<), 140.7, 118.9 (C), 138.2, 134.7, 131.7, 130.2, 9.6 (CH), 16.6 (CH_2), 21.2 (CH_3); UV (MeCN, λ_{max} (log ε)) 206 (4.50), 273 (4.41) nm; IR (KBr disk) 1441, 1089 br, 911, 693, 621 cm^{-1}. Anal. Calcd for $C_{16}H_{17}O_4Cl$: C, 62.24; H, 5.55; Cl, 11.48. Found: C, 62.08; H, 5.58; Cl, 11.46.

2d$^+ClO_4^-$: colorless plates; yield 9% (based on the evolved N_2); mp 160.5–161 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.51 (s, 2 H), 7.44 (s, 1 H), 2.82 (tt, 2 H, J = 7.8, 4.4 Hz, CH), 2.44 (s, 6 H, CH_3), 1.99–1.92 (m, 4 H, CH_2), 1.76–1.70 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 168.0 (c-PrC<), 155.9 (ArC<), 140.3, 118.5 (C), 139.1, 131.8, 9.2 (CH), 16.4 (CH_2), 20.8 (CH_3); UV (MeCN, λ_{max} (log ε)) 208 (4.55), 277 (4.45) nm; IR (KBr disk) 1599, 1435, 1094 br, 915, 870, 692, 623 cm^{-1}. Anal. Calcd for $C_{17}H_{19}O_4Cl$: C, 63.26; H, 5.93; Cl, 10.98. Found: C, 62.98; H, 5.96; Cl, 11.03.

2f$^+ClO_4^-$: colorless plates; yield 7% (based on the evolved N_2); mp 108–109 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.89 (d, 2 H, J = 8.8 Hz), 7.16 (d, 2 H, J = 8.8 Hz), 3.95 (s, 3 H, CH_3), 2.76 (tt, 2 H, J = 7.8, 4.4 Hz, CH), 1.92–1.85 (m, 4 H, CH_2), 1.70–1.64 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 165.2 (c-PrC<), 154.2 (ArC<), 167.0, 110.9 (C), 137.4, 116.1, 8.9 (CH), 15.8 (CH_2), 56.2 (CH_3); UV (MeCN, λ_{max} (log ε)) 221 (4.29), 245 sh (3.52), 307 (4.55) nm; IR (KBr disk) 1597, 1423, 1268, 1092 br, 914, 623 cm^{-1}. Anal. Calcd for $C_{16}H_{17}O_5Cl$: C, 59.17; H, 5.28; Cl, 10.92. Found: C, 58.93; H, 5.36; Cl, 10.80.

3-Methoxy-1,2,3-tri-*tert*-butylcyclopropene. To a suspension of tri-*tert*-butylcyclopropenylium perchlorate[12] (**8**$^+ClO_4^-$, 189 mg, 0.616 mmol) in methanol (2 mL) was added sodium methoxide (33 mg, 0.61 mmol) in methanol (8 mL), and the mixture was stirred at room temperature for 10 min. Water (15 mL) was added, and the product was extracted with ether (3 × 10 mL). The ether layer was dried ($MgSO_4$), and the solvent was evaporated to give practically pure 3-methoxy-1,2,3-tri-*tert*-butylcyclopropene (purity ≥ 95% by ^{1}H NMR) as a colorless oil (102 mg, 69%): ^{1}H NMR (CD_3CN, 270 MHz) δ 2.83 (s, 3 H), 1.23 (s, 18 H), 0.95 (s, 9 H).

Determination of the Relative Stability of 2b$^+$ **and 2e**$^+$ **by Methoxide Exchange Reaction.** A solution of **2b**$^+BF_4^-$ (8.280 mg, 0.0294 mmol) and 3-methoxy-1,2,3-tri-*tert*-butylcyclopropene (6.999 mg, 0.0294 mmol) in CD_3CN (0.7 mL) was placed in an NMR tube, degassed (<10^{-4} mmHg) by four freeze–pump–thaw cycles, and sealed under vacuum. The solution was allowed to equilibrate at room temperature for 24 h and then subjected to ^{1}H NMR analysis (270 MHz). The ratio of **2b**$^+$ relative to **8**$^+$ was determined to be 1.53:1 by integrating the aromatic proton signals of **2b**$^+$ (7.70–8.00 ppm) and the *tert*-butyl signal of **8**$^+$ (1.51 ppm).

The stability of **2e**$^+$ relative to **8**$^+$ was determined in the same way by integrating the cyclopropyl methine proton signals of **2e**$^+$ (2.63–2.73 ppm) and the *tert*-butyl signal of **8**$^+$.

Cyclic Voltammetry of 2a–f$^+$**.** The reduction potentials of **2a–f**$^+$ were determined by means of cyclic voltammetry with a Hokuto-Denko Model HA-104 potentiostat equipped with a Hokuto-Denko Model HB-107A function generator. A three-electrode cell was used, consisting of a BAS 11-2012 glassy carbon working electrode, a Pt wire counterelectrode, and a Ag/$AgNO_3$ (0.01 M in MeCN) reference electrode. The measurements were carried out at a scan rate of 0.1 V/s for MeCN solutions containing 1 mM of the sample and 0.1 M of $Bu_4N^+ClO_4^-$ as a supporting electrolyte. Cations **2a–f**$^+$ showed irreversible reduction peaks, the positions of which were corrected with reference to ferrocene ($E_{1/2}$ = 0.083 V), added as an internal standard. The widths of the reduction peaks of **2a–f**$^+$ were small and nearly constant ($E_p - E_{p/2}$ = 65–77 mV). These values are essentially the same as observed for added ferrocene and close to the one derived from theory (56.5 mV[26]) for reversible systems. The difference between oxidation and reduction peak potentials for ferrocene was 60–66 mV, which is also very close to the theoretical value (59 mV[26]) for reversible systems.

Generation of Kuhn's Anion (1$^-$**).** As has been reported by Kuhn and Rewicki[6] and by us,[4b] 1$^-$ was quantitatively generated when the hydrocarbon 1-H was dissolved in DMSO. The anion 1$^-$ was also generated from 1-H and *t*-BuOK in THF. The UV–vis absorptions of 1$^-$ have been reported previously.[4b] Precautions were taken to protect the anion solution from visible light, since the radical 1$^\bullet$ was found to be readily formed by photoinduced electron transfer occurring even by room light.

Synthesis of Covalent Compounds 1–(2a–d). General procedure. To a stirred THF solution (2 mL) of 1-H (0.03 mmol) was added a 5% excess amount of *t*-BuOK in THF (0.07 M) under argon at room temperature. After 5 min, a THF–MeCN solution (1:1 (v/v), 0.2 mL) of the equimolar amount of **2a–d**$^+ClO_4^-$ (or BF_4^-) was added. Dilution of the mixture with benzene or chloroform (3 mL) followed by evaporation of the solvent afforded an orange solid, from which the organic product was extracted with benzene or chloroform (3 × 0.5 mL). The combined solutions were filtered through a membrane filter (0.5 μm) to remove inorganic substances. The covalent compounds **1–(2a–d)** (see Figure 2) were obtained as orange solids in almost quantitative yields. Their NMR spectra showed no isomers but a small amount (≤1.5 wt %) of THF. The IR and NMR data are summarized in Tables III and IV. They decomposed gradually in solution during attempted purification by recrystallization or TLC.

Synthesis of Salts 1$^-$**2e**$^+$ **and 1**$^-$**2f**$^+$**.** A solution of **2e**$^+ClO_4^-$ or **2f**$^+ClO_4^-$ (0.03 M) in THF–MeCN (1:1 (v/v), 1.5 mL) was added dropwise to a solution containing an equimolar amount of 1$^-$K$^+$ prepared from 1-H and a 5% excess of *t*-BuOK in THF (0.06 M)

(26) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; pp 219, 229.

under argon. The deep green mixture was stirred for 5 min in the dark, and then the solvent was evaporated under vacuum. The residue (dark green solid) was dissolved in $CHCl_3$ (1 mL) and filtered through a membrane filter (0.5 μm) to remove inorganic substances. The reddish-brown filtrate was evaporated to afford a dark green solid again, which was dissolved in THF (0.3 mL) and reprecipitated by adding MeCN (1 mL) with stirring. The dark green precipitate was filtered, washed with MeCN (3 × 0.5 mL) under argon, and dried under vacuum. The resulting salts were stored under vacuum in the dark at −10 °C. Their NMR spectra in chloroform were measured as follows. The sample (15–30 mg) was placed in an NMR sample tube under argon, and the tube was quickly evacuated (<10^{-4} mmHg) in the dark. Chloroform-*d* (0.7 mL, containing TMS), which had been degassed in the presence of P_2O_5, was distilled into the NMR tube cooled with liquid nitrogen. After the tube had been sealed off, the solution was subjected to ^1H and ^{13}C NMR analyses. The resulting data are summarized in Table IV.

Electronic Spectra. The UV–vis spectra of the DMSO solutions of **1**–(**2a**–**d**), **1**-**2e**$^+$, and **1**-**2f**$^+$ were measured in vacuo or under argon. The detailed procedure has been described previously.[3c,4b] For the measurement of solid-state electronic spectra, a mixture of KBr (200 mg) and **1**-**2f**$^+$ (0.5 mg) was finely ground with a vibrating ball mill and pressed under a pressure of 500 atm in vacuo into a transparent disk (13-mm diameter). The spectrum was recorded using a disk consisting of KBr alone as a reference.

Acknowledgment. This work was supported by a grant from the Inamori Foundation and Grant-in-aid for Scientific Research on Priority Areas (No. 01648002 and No. 03214102) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **1**–(**2a**–**f**) (13 pages). This material is contained in 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.