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Syntheses, Properties, and Redox Behaviors of Di(1-azulenyl)ferrocenylmethyl Cations and 1,3-Bis[(1-azulenyl)ferrocenylmethylium]azulene Dication

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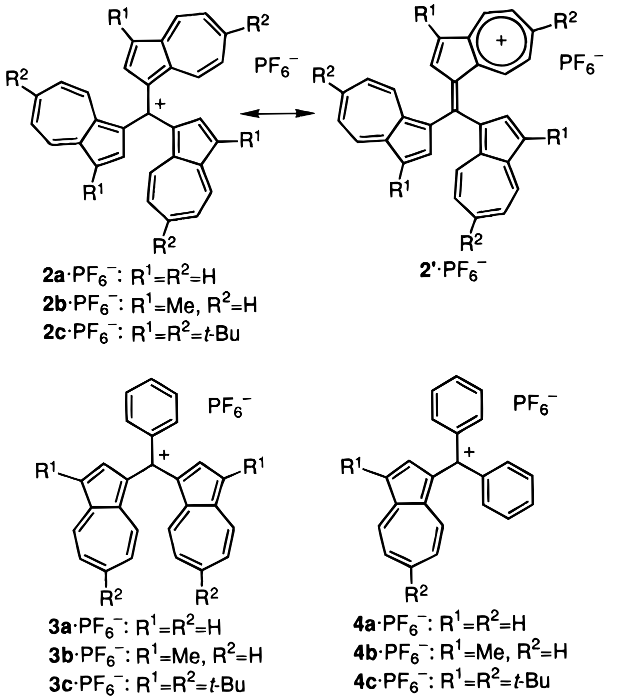
The titled stable mono- and dications, di(1-azulenyl)ferrocenylmethyl cation (**5a**) and its 3,3′-dimethyl (**5b**) and 3,3′,6,6′-tetra-*tert*-butyl (**5c**) derivatives, as well as the corresponding dication, 1,3-bis[(1-azulenyl)ferrocenylmethylium]azulene dication (**6**), were prepared by hydride abstraction of the corresponding hydrocarbons, di(1-azulenyl)ferrocenylmethanes (**7a**−**c**) and 1,3-bis[(1-azulenyl)ferrocenylmethyl]azulene (**8**), and their properties were fully characterized. These cations showed extreme stabilities with high pK_R^+ values. The values of **5a**−**c** were determined in 50% aqueous acetonitrile to be 12.2 ± 0.3, 12.2 ± 0.4, and 12.5 ± 0.4, respectively. The two cation units in the dication **6** were neutralized via two steps at the pH values of 8.8 ± 0.5 and 11.6 ± 0.5, which correspond to the pK_R^+ values of the dication and the half-neutralized monocation, respectively. The redox properties of the ferrocene rings in the mono- and dications (**5a**−**c** and **6**) were barely changed by the connection with extremely stable di(1-azulenyl)methylium units. The cyclic voltammetries of **5a**−**c** indicated that these cations undergo a reversible one-electron oxidation (+0.42 to +0.47 V vs Ag/Ag^+), as well as a reversible one-electron reduction (−0.76 to −0.87 V) in acetonitrile. Similarly, the dication **6** showed a reversible one-step, two-electron oxidation (+0.51 V), which was ascribed to the oxidation of two ferrocene rings.

Introduction

We have recently reported the synthesis of a series of azulene analogues of triphenylmethyl cation (**1**), i.e., tri(1-azulenyl)methyl (**2a**), di(1-azulenyl)phenylmethyl (**3a**), and (1-azulenyl)diphenylmethyl (**4a**) hexafluorophosphates and their derivatives (e.g., 3-methyl (**2b**, **3b**, and **4b**) and 3,6-di-*tert*-butyl (**2c**, **3c**, and **4c**) derivatives), by hydride abstraction of the corresponding hydrocarbons (Chart 1).[1] The pK_R^+ value measurements of these cations exhibited that the methyl cations which were stabilized by two (**3a**−**c**) or three (**2a**−**c**) azulene rings showed extraordinary stability with high pK_R^+ values (e.g., **2a**, 11.3, **3a**, 10.5; and **4a**, 3.0).[1a−c] The high stabilities of these cations are ascribed to the contribution of the resonance forms of the azulene ring such as **2′** and also to steric effects on the three rings attached to the methyl cation. Recently much attention has been focused on multistage redox systems because of their special properties such as conductivity and organic ferromagnetism.[2] It is of interest to construct stable cationic multistage redox systems by connecting some redox systems with the extremely stable carbocation and examine how the redox properties would be changed. In view of the redox properties of the ferrocene ring[3] and extreme stabilities of the di(1-azulenyl)methylium units, whose stabilities are almost comparable with those of the tri(1-azulenyl)methyl cations, we have now prepared the extremely stable ferrocenylmethyl cations stabilized by two 1-azulenyl units, i.e., di(1-azulenyl)ferrocenylmethyl hexafluorophosphate ($5a{\cdot}PF_6^-$) and its 3,3′-dimethyl ($5b{\cdot}PF_6^-$) and 3,3′,6,6′-tetra-*tert*-butyl ($5c{\cdot}PF_6^-$) derivatives, as well as the analogous dication, i.e., 1,3-bis[(1-azulenyl)ferrocenylmethylium]azulene dihexafluorophos-

Chart 1



$2a{\cdot}PF_6^-$: $R^1=R^2=H$
$2b{\cdot}PF_6^-$: $R^1=Me$, $R^2=H$
$2c{\cdot}PF_6^-$: $R^1=R^2=t\text{-}Bu$

$2'{\cdot}PF_6^-$

$3a{\cdot}PF_6^-$: $R^1=R^2=H$
$3b{\cdot}PF_6^-$: $R^1=Me$, $R^2=H$
$3c{\cdot}PF_6^-$: $R^1=R^2=t\text{-}Bu$

$4a{\cdot}PF_6^-$: $R^1=R^2=H$
$4b{\cdot}PF_6^-$: $R^1=Me$, $R^2=H$
$4c{\cdot}PF_6^-$: $R^1=R^2=t\text{-}Bu$

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(1) (a) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1991**, *32*, 773−776. (b) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 751−754. (c) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409−1436. (d) Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 3723−3726. (e) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2639−2648. (f) Ito, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2011−2016. (g) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Chem. Lett.* **1995**, 475−476. (h) Ito, S.; Fujita, M.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3611−3620.

(2) Deuchert, K.; Hünig, S. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 875−958.

(3) (a) Sabbatini, M. M.; Cesarotti, E. *Inorg. Chim. Acta* **1977**, *24*, L9−L10. (b) Grimes, H.; Logan, S. R. *Inorg. Chim. Acta* **1980**, *45*, L223−L224.

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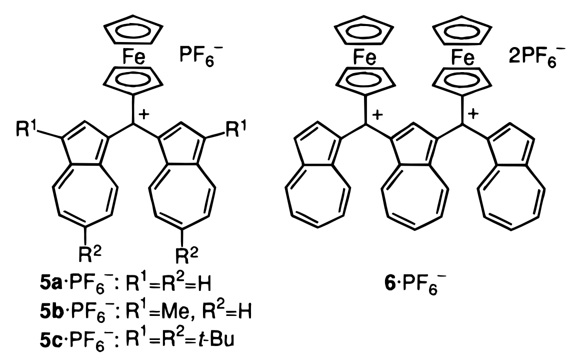
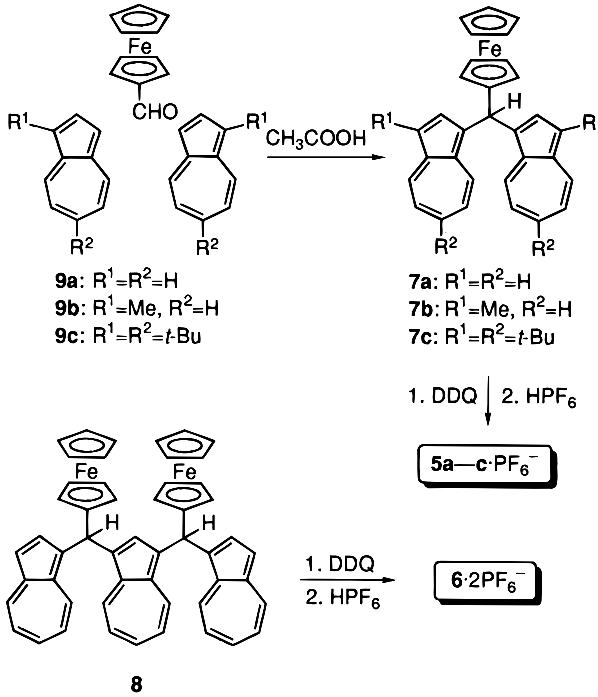
Chart 2



Scheme 1



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phate ($6{\cdot}2PF_6^-$) (Chart 2), and examined their redox behaviors by cyclic voltammetry (CV).

Results and Discussion

Synthesis. The synthesis of $5a{-}c{\cdot}PF_6^-$ and $6{\cdot}2PF_6^-$ was accomplished by hydride abstraction from the corresponding methane derivatives (**7a**−**c** and **8**). The reaction of 2 molar equiv of azulene (**9a**) and its 1-methyl (**9b**) and 1,6-di-*tert*-butyl (**9c**)[1b,c] derivatives with ferrocenecarboxaldehyde in acetic acid at room temperature for 7 days afforded **7a**−**c** in 19, 86, and 57% yields, respectively, together with 1,3-bis[(1-azulenyl)ferrocenylmethyl]azulene (**8**) in 10% yield, in the case of **9a** (Scheme 1). The trimeric product **8**, which was characterized by 600 MHz ^{1}H NMR spectra, was an inseparable diastereomeric mixture (*dl* and *meso* forms) with a ratio of 1:1.1. Hydride abstraction of **7a**−**c** with DDQ in dichloromethane at room temperature followed by the addition of a 60% aqueous HPF_6 solution yielded $5a{-}c{\cdot}PF_6^-$ in 94, 100, and 94% yields, respectively. Similarly, the oxidation of **8** with 2 molar equiv of DDQ, followed by the addition of an HPF_6 solution, afforded the corresponding dihexafluorophosphate ($6{\cdot}2PF_6^-$) in 77% yield. The dication **6** was extremely stable and storable in crystalline state, but it gradually decomposed to unidentified materials in solution even at room temperature.

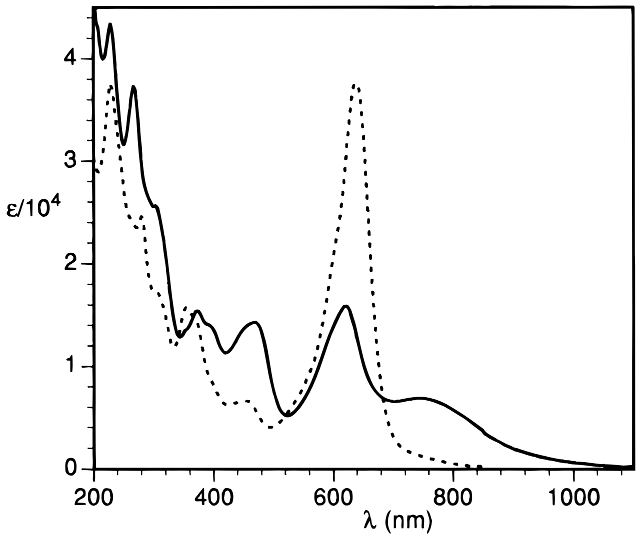

Figure 1. UV−vis spectra of $5a{\cdot}PF_6^-$ (solid line) and $3a{\cdot}PF_6^-$ (broken line) in acetonitrile.

Spectroscopic Properties. High-resolution mass spectra of monocation **5a**−**c** and dication **6** ionized by FAB showed correct $M^+ - PF_6$ ion peaks, which indicated the cationic and dicationic structures of these compounds. The characteristic bands of hexafluorophosphate were observed at around 838−840 (strong) and 558 (medium) cm^{-1} in their IR spectra, which also supported the cationic structure of these compounds. The UV−vis spectrum of $5a{\cdot}PF_6^-$ in acetonitrile and that of $3a{\cdot}PF_6^-$ were shown in Figure 1. In the electronic spectra the strong absorptions in the visible region ($5a{\cdot}PF_6^-$, 621 (log ϵ 4.20); $5b{\cdot}PF_6^-$, 655 (4.23); and $5c{\cdot}PF_6^-$, 657 nm (4.31)) exhibit a hypsochromic shift by 18, 21, and 24 nm, respectively, as compared with the corresponding phenyl analogues ($3a{-}c{\cdot}PF_6^-$).[4] The longest wavelength absorptions of these compounds ($5a{\cdot}PF_6^-$, 746 (log ϵ 3.84); $5b{\cdot}PF_6^-$, 711 (4.09 sh); and $5c{\cdot}PF_6^-$, 693 nm (4.28 sh)) indicate a charge transfer from the ferrocene ring to the di(1-azulenyl)methylium unit. The ^{1}H NMR chemical shifts of the methine protons of **7a**−**c** (**7a**, 6.44; **7b**, 6.38; and **7c**, 6.33 ppm, respectively) showed a slight upfield shift, compared to those of di(1-azulenyl)phenylmethane (**10a**) and its 3,3′-dimethyl (**10b**) and 3,3′,6,6′-tetra-*tert*-butyl (**10c**) derivatives (**10a**, 6.74; **10b**, 6.67; and **10c**, 6.63 ppm, respectively),[1c] precursors for **3a**−**c**. These signals disappeared on the ^{1}H NMR spectra of the cations **5a**−**c**. Thus, the ^{1}H NMR spectra were also indicative of a cationic structure of these compound. The chemical shift (^{13}C NMR) of central cationic carbons in $5a{-}c{\cdot}PF_6^-$ ($5a{\cdot}PF_6^-$, 172.84; $5b{\cdot}PF_6^-$, 168.73; and $5c{\cdot}PF_6^-$, 168.43 ppm, respectively) are almost comparable with those in the phenyl analogues $3a{-}c{\cdot}PF_6^-$ ($3a{\cdot}PF_6^-$, 165.54; $3b{\cdot}PF_6^-$, 161.58; and $3c{\cdot}PF_6^-$, 161.11 ppm, respectively).[1c]

Thermodynamic Stability. As a measure of the thermodynamic stability, the $pK_R{}^+$ values of cations **5a**−**c** were determined spectrophotometrically at 25 °C in a buffer solution prepared in 50% aqueous MeCN.[1c,5] The

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[4] A similar hypsochromic shift was observed between $2a{-}c{\cdot}PF_6^-$ and $3a{-}c{\cdot}PF_6^-$. The longest wavelength absorption maxima of $2a{-}c{\cdot}PF_6^-$ are 614 (log ϵ 4.70), 652 (4.57), and 650 nm (4.62), respectively, which are hypsochromic shifts by 25, 24, and 31 nm, respectively, as compared with $3a{-}c{\cdot}PF_6^-$.[1c]

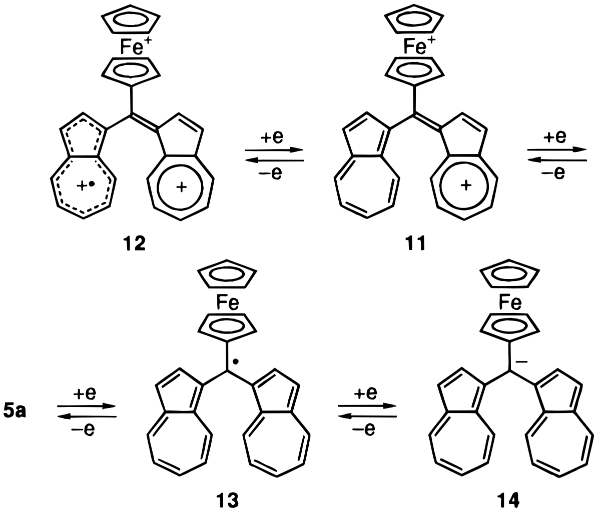
[5] (a) Kerber, R. C.; Hsu, H. M. *J. Am. Chem. Soc.* **1973**, *95*, 3239−3245. (b) Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470−2479.

Table 1. pK_R^+ Values[a] and Redox Potentials[b] of 5a–c, 6, and 3a–c[1a,c]

	pK_R^{+c}	E_1^{red}	E_2^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}
5a	12.2 ± 0.3 (51%)	−0.76	(−1.58)	+0.47	(+1.08)	
5b	12.2 ± 0.4 (36%)	−0.79	(−1.65)	+0.43	(+0.95)	
5c	12.5 ± 0.4 (38%)	−0.87	(−1.74)	+0.42	(+0.95)	
6	8.8 ± 0.5, 11.6 ± 0.5 (27%)	(−0.54)	(−0.65)	+0.51	(+1.03)	(+1.13)
3a	10.5	−0.66	(−1.52)	(+1.04)		
3b	10.8	−0.70	(−1.57)	(+0.90)		
3c	12.4	−0.78	(−1.64)	+0.88	(+1.38)	

[a] The pK_R^+ values were determined by spectrophotometrically at 25 °C in a buffered solution prepared in 50% aqueous acetonitrile. [b] The redox potentials were measured by cyclic voltammetry (V vs Ag/Ag$^+$, 0.1 M Et_4NClO_4 in MeCN, Pt electrode, and scan rate 100 mV s^{-1}). In the case of irreversible waves, which are shown in parentheses, E^{ox} and E^{red} were calculated as E_{pa} (anodic peak potential) −0.03 and E_{pc} (cathodic peak potential) +0.03 V, respectively. [c] Regenerated absorptions (%) of cations in the visible region by acidification of the alkaline solution with HCl are shown in parentheses.

Scheme 2



values of **5a**–**c** are summarized in Table 1 along with those of **3a**–**c**. As expected by the stabilizing effect of ferrocene unit,[6] the pK_R^+ values of **5a**–**c** are slightly increased, compared to those of the phenyl analogues. The pK_R^+ value of **5a** (12.2) is extremely high for a methyl cation.[7] The bulky *tert*-butyl substituents on the azulene rings at 3,3′,6,6′-positions slightly stabilized the cation (**5a**) by their steric and also by their inductive electronic effects induced by the contribution of C–C hyperconjugation with the π-systems.[1b,c] The pK_R^+ values of the *tert*-butyl derivative (**5c**) are higher by 0.3 p*K* unit than those of **5a** and **5b**. In the case of dication **6** the two cation units were neutralized in two steps at pH 8.8 and 11.6, which correspond to the pK_R^+ of the dication and the half-neutralized monocation, respectively. Thus, dication **6** itself is even more destabilized than monocation **5a** by 3.4 p*K* units, whereas the half-neutralized monocation of **6** is almost as stable as the monocation **5a**. The lower pK_R^+ values for **6** reflect destabilization due to the reduction of an azulene ring contributing to the stabilization and the electrostatic repulsion of the two positive charges. The neutralization of these cations (**5a**–**c** and **6**) is not completely reversible due to the instability of the neutralized products under the conditions of the pK_R^+ measurement. After the measurement, acidification of the alkaline solutions of **5a**–**c** and **6** with HCl regenerated the characteristic absorption of the cations in the visible region in 27–51% only. Rather large errors (±0.3 to ±0.5) for the pK_R^+ values of these cations are due to a low reversibility of the neutralization, which causes some fluctuation in the absorbance of the UV–vis spectra.

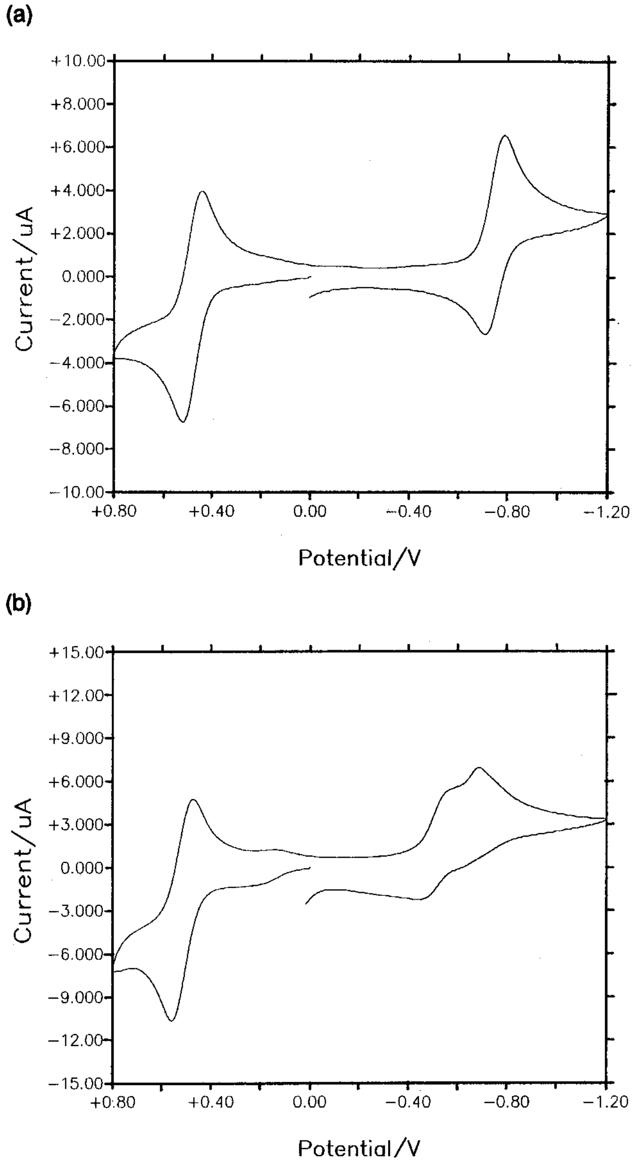


Figure 2. Cyclic voltamograms of (a) **5a**·PF_6^- and (b) **6**·$2PF_6^-$ (1 mM) in MeCN containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate, 100 mV s^{-1}.

Redox Properties. Although **5a**–**c** are carbocations, these compounds readily oxidized to form a ferrocenium ion such as **11** (Scheme 2). The redox potentials (V vs Ag/Ag$^+$) of **5a**–**c**·PF_6^- are also summarized in Table 1 together with those of the phenyl analogues (**3a**–**c**·PF_6^-). While the oxidation was irreversible for the monocation **3a** under the conditions of CV measurement at a scan rate of 100 mV s^{-1} (+1.04 V), cation **5a** exhibited a reversible oxidation wave at +0.47 V vs Ag/Ag$^+$ as shown in Figure 2a, with the oxidation potential lower than that of **3a** by about 0.6 V. Similarly, the oxidation of **5b** and **5c** also showed a reversible wave at +0.43 and +0.42 V,

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[6] (a) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304–2316. (b) Hill, E. A.; Wiesner, R. *J. Am. Chem. Soc.* **1969**, *91*, 509–510.

[7] The pK_R^+ value of a phenyl analog of **5a**, diphenylferrocenylmethyl cation, is only 0.75,[6b] which is higher by 7.2 p*K* units than that of triphenylmethyl cation.

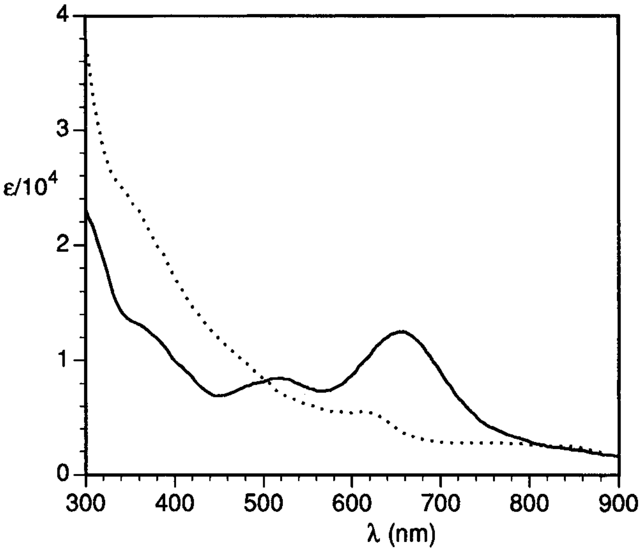

Figure 3. UV−vis spectra of the electrolitic oxidation (solid line) and reduction (broken line) products of **5a** in acetonitrile at room temperature.

respectively. This clearly indicates the generation of a dication species (**11**) resulting from the oxidation of a ferrocene ring. The oxidation potentials of the ring in **5a**−**c** are barely positive by only 0.3−0.4 V compared with that of parent ferrocene (0.10 V).

The UV−vis spectrum measured upon electrolytic oxidation of **5a** in acetonitrile at room temperature was shown in Figure 3. The spectrum showed an absorption in the visible region at 656 nm (log ϵ 4.10). The electrolytic oxidation of **5a** exhibited a disappearance of the longest wavelength absorption of **5a**, which arose from a charge transfer from the ferrocene ring to the di-(1-azulenyl)methylium unit. Thus, it also supported the generation of a dication species (**11**) resulting from the oxidation of a ferrocene ring.

The second oxidation waves of these compounds **5a**−**c**·PF_6^- were irreversible and were observed at around +0.95 to +1.08 V upon CV (Figure 2a). These values were almost equal to the E_1^{ox} values of **3a**−**c** (+0.88 to +1.04 V), which are ascribed to the oxidation of an azulene ring to produce a dication radical species.[1c] Therefore, the second irreversible waves for **5a**−**c** at around +0.95 to +1.08 V are ascribed to the oxidation of an azulene ring to produce a trication radical species such as **12**.

The oxidation behaviors of dication **6** are entirely similar to those of the monocations (**5a**−**c**). The first oxidation wave of **6** at +0.51 V was also reversible under the conditions of CV measurement at a scan rate of 100 mV s^{-1} (Figure 2b). The barely separated second and third oxidation waves (+1.03 and +1.13 V) of **6** are irreversible. The first oxidation wave of **6** was in the potential range comparable to those of related monocations **5a**−**c**. Therefore, it apparently corresponds to the oxidation of two ferrocene rings by a one-step, two-electron oxidation process to form a tetracation species. The next waves of **6** were ascribed to the oxidation of azulene rings, by comparison with those of monocations (**5a**−**c**).

In contrast to the high stabilities, monocations **5a**−**c**, as well as dication **6**, readily underwent one-electron reduction to form radical species such as **13**. The reduction of **5a**−**c**·PF_6^- in acetonitrile showed a reversible wave at around −0.76 to −0.87 V and an irreversible wave at around −1.58 to −1.74 V upon CV, which is due to the formation of an anion species such as **14**. Reduction potentials that are about 0.1 V more negative for **5a**−**c** than for **3a**−**c** indicate the stabilization of the di-(1-azulenyl)methylium units by the ferrocene ring. The reduction potential of the *tert*-butyl derivative (**5c**), the most negative among these compounds, corresponds to its high electrochemical stability. These results clearly indicate that the free radical species generated from the cations **5a**−**c** are also stable under the conditions of CV measurement, similar to those generated from **3a**−**c**.

When the UV−vis spectrum was measured under the electrolytic reduction of **5a** in acetonitrile at room temperature, the strong absorption of **5a** in the visible region disappeared as shown in Figure 3. Although it obviously exhibited the reduction of the cation **5a**, the free radical species (**13**) generated by the one-electron reduction of the cation **5a** appears to be rather unstable upon the conditions of UV−vis measurement. There is no apparent absorption at the UV−vis spectrum owing to the moiety of azulene rings.

The reduction of dication **6** exhibited a voltammogram that was characterized by barely separated irreversible two-step reduction waves at −0.54 and −0.65 V. The first reduction potential is more positive than that of **5a** by 0.22 V, which reflects the destabilization due to the reduction of an azulene ring contributing to the stabilization and the electrostatic repulsion of the two positive charges.

The redox properties of the ferrocene rings in the mono- and dications (**5a**−**c** and **6**) were barely changed by the connection with extremely stable di(1-azulenyl)methylium units. These new systems (**5a**−**c** and **6**) exhibit the electron-donating property of ferrocene in addition to the electron-accepting property of the extremely stable carbocation. These extremely stable carbocations may be exploited in the construction of new redox systems by using conductivity and organic ferromagnetism.[8]

Experimental Section

General Procedures. Melting points were determined on a micro melting point apparatus and are uncorrected. Mass spectra were obtained usually at 70 eV. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded at 90 MHz (22.5 MHz), at 500 MHz (125 MHz), and/or at 600 MHz (150 MHz). Voltammetry measurements were carried out with an electrochemical workstation equipped with Pt working and auxiliary electrodes

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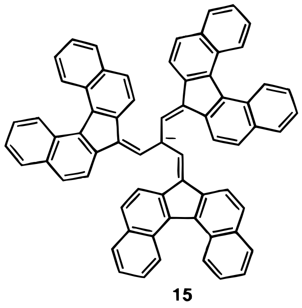
[8] **5c** formed charge-transfer complex with Kuhn's anion **15**.[9] **5c·15**: black powder; mp 180−182 °C; IR (KBr disk) ν_{max} 1507, 1165, 1154, 1138 cm^{-1}. Powder conductivity of the salt **5c·15** was 3.8 × 10^4 [Ω·cm].



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[9] (a) Kuhn, R.; Rewicki, D. *Angew. Chem.* **1967**, *79*, 648−649. (b) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Kinoshita, T.; Aonuma, S.; Nagai, M.; Miyabo, A. *J. Org. Chem.* **1990**, *55*, 996−1002.

and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte, at a scan rate of 100 mV s^{-1}. In the case of irreversible waves, E^{ox} and E^{red} were calculated as E_{pa} (anodic peak potential) −0.03 and E_{pc} (cathodic peak potential) +0.03 V, respectively. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

General Procedure for the Reaction of Azulenes (9a−c) with Ferrocenecarboxaldehyde. A solution of azulene (**9a**−**c**) and ferrocenecarboxaldehyde in glacial acetic acid was stirred at room temperature for 7 days under an Ar atmosphere. The solvent was removed in vacuo. The residue was diluted with CH_2Cl_2. The organic layer was washed with 5% aqueous $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and/or gel permeation chromatography (GPC) with $CHCl_3$. The product was further purified by recrystallization.

Di(1-azulenyl)ferrocenylmethane (7a). The general procedure was followed using azulene (**9a**) (1.28 g, 10.0 mmol) and ferrocenecarboxaldehyde (1.07 mg, 5.00 mmol) in glacial acetic acid (60 mL). Column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ afforded methane **7a** (296 mg, 19%), 1,3-bis[(1-azulenyl)ferrocenylmethyl]azulene (**8**) (177 mg, 10%), and recovered **9a** (376 mg, 29%). **7a:** green needles; mp 156.0−157.0 °C; MS (70 eV) m/z (rel inten) 452 (M^+, 100); ES (CH_2Cl_2) λ_{max}, nm 239 (log ϵ 4.59), 275 (4.85), 350 (3.94), 366 (3.90), 604 (2.79), 654 (2.70), 724 (2.24); ^1H NMR (500 MHz, $CDCl_3$) δ 8.482 (d, $J = 9.8$ Hz, 2H), 8.219 (d, $J = 9.5$ Hz, 2H), 7.793 (d, $J = 4.0$ Hz, 2H), 7.484 (dd, $J = 9.8, 9.8$ Hz, 2H), 7.284 (d, $J = 4.0$ Hz, 2H), 7.044 (dd, $J = 9.8, 9.8$ Hz, 2H), 7.035 (dd, $J = 9.8, 9.5$ Hz, 2H), 6.439 (s, 1H), 4.125 (dd, $J = 1.8, 1.8$ Hz, 2H), 4.097 (dd, $J = 1.8, 1.8$ Hz, 2H), 3.882 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.931, 137.604, 137.232, 136.559, 134.396, 134.187, 133.188, 122.400, 121.591, 116.729, 95.208, 68.780, 68.625, 67.225, 36.716. Anal. Calcd for $C_{31}H_{24}Fe$: C, 82.31; H, 5.35. Found: C, 82.02; H, 5.58. **8:** green crystals; mp 147.0−149.0 °C; MS (70 eV) m/z (rel inten) 776 (M^+, 79), 327 (25), 326 (100), 203 (27), 202 (43), 128 (36); ES (CH_2Cl_2) λ_{max}, nm 239 (log ϵ 4.76), 277 (4.99), 349 (4.10), 365 (4.09), 608 (2.93); ^1H NMR (600 MHz, C_6D_6) δ 8.388 (d, $J = 9.4$ Hz, 2H), 8.366 (d, $J = 9.6$ Hz, 2H), 8.345 (d and d, $J = 9.6$ Hz and $J = 9.4$ Hz, 4H), 8.213 (s and s, 2H), 8.023 (d, $J = 3.9$ Hz, 2H), 7.21 (d, $J = 9.0$ Hz, 2H), 7.900 (d, $J = 3.9$ Hz, 2H), 7.871 (d, $J = 9.0$ Hz, 2H), 7.274 (d, $J = 3.9$ Hz, 2H), 7.189 (d, $J = 3.9$ Hz, 2H), 7.109 (dd, $J = 9.8, 9.8$ Hz, 2H), 7.095 (dd, $J = 9.8, 9.8$ Hz, 2H), 7.031 (dd, $J = 9.8, 9.8$ Hz, 1H), 6.978 (dd, $J = 9.8, 9.8$ Hz, 1H), 6.674 (dd, $J = 9.8, 9.0$ Hz, 2H), 6.654 (dd, $J = 9.8, 9.6$ Hz, 2H), 6.643 (dd, $J = 9.8, 9.0$ Hz, 2H), 6.635 (dd, $J = 9.8, 9.6$ Hz, 2H), 6.613 (dd, $J = 9.8, 9.4$ Hz, 2H), 6.557 (dd, $J = 9.8, 9.4$ Hz, 2H), 6.435 (s, 1H), 6.405 (s, 1H), 4.195 (ddd, $J = 2.4, 1.2, 1.2$ Hz, 2H), 4.141 (ddd, $J = 2.4, 1.2, 1.2$ Hz, 2H), 4.104 (ddd, $J = 2.4, 1.2, 1.2$ Hz, 2H), 4.071 (ddd, $J = 2.4, 2.4, 1.2$ Hz, 2H), 4.043 (ddd, $J = 2.4, 2.4, 1.2$ Hz, 2H), 4.037 (ddd, $J = 2.4, 1.2, 1.2$ Hz, 2H), 3.991 (ddd, $J = 2.4, 2.4, 1.2$ Hz, 2H), 3.950 (ddd, $J = 2.4, 2.4, 1.2$ Hz, 2H), 3.808 (s, 5H), 3.802 (s, 5H); HRMS calcd for $C_{52}H_{40}Fe_2$ 776.1828, found 776.1841. Anal. Calcd for $C_{52}H_{40}Fe_2$: C, 80.43; H, 5.19. Found: C, 80.35; H, 5.40.

Bis(3-methyl-1-azulenyl)ferrocenylmethane (7b). The general procedure was followed using 1-methylazulene (**9b**) (713 mg, 5.01 mmol) and ferrocenecarboxaldehyde (537 mg, 2.51 mmol) in glacial acetic acid (30 mL). Column chromatography on silica gel with CH_2Cl_2 afforded methane **7b** (1.03 g, 86%): green prisms; mp 187.0−188.0 °C; MS (70 eV) m/z (rel inten) 480 (M^+, 100), 340 (30), 141 (22); ES (CH_2Cl_2) λ_{max}, nm 242 (log ϵ 4.56), 278 (4.86), 357 (3.95), 633 (2.80), 689 (2.71); ^1H NMR (90 MHz, $CDCl_3$) δ 8.38 (d, $J = 9.5$ Hz, 2H), 8.07 (d, $J = 9.2$ Hz, 2H), 7.59 (s, 2H), 7.41 (dd, $J = 9.8, 9.8$ Hz, 2H), 6.91 (dd and dd, $J = 9.8, 9.5$ Hz and $J = 9.8, 9.2$ Hz, 4H), 6.38 (s, 1H), 4.10 (s, 4H), 3.88 (s, 5H), 2.58 (s, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 138.50, 137.03, 134.17, 133.28, 132.74, 132.43, 124.56, 120.60, 95.48, 68.83, 68.65, 67.12, 36.11, 12.82; HRMS calcd for $C_{33}H_{28}Fe$ 480.1541, found 480.1541. Anal. Calcd for $C_{33}H_{28}Fe$: C, 82.50; H, 5.87. Found: C, 82.07; H, 6.03.

Bis(3,6-di-*tert*-butyl-1-azulenyl)ferrocenylmethane (7c). The general procedure was followed using 1,6-di-*tert*-butylazulene (**9c**) (729 mg, 3.03 mmol) and ferrocenecarboxaldehyde (328 mg, 1.53 mmol) in glacial acetic acid (30 mL). Column chromatography on silica gel with CH_2Cl_2 afforded methane **7c** (589 mg, 57%): green plates; mp 149.0−150.5 °C; MS (70 eV) m/z (rel inten) 676 (M^+, 100); ES (CH_2Cl_2) λ_{max}, nm 243 (log ϵ 4.52), 285 (4.92), 358 (4.00), 375 (3.94), 615 (2.81); ^1H NMR (90 MHz, $CDCl_3$) δ 8.49 (d, $J = 11.0$ Hz, 2H), 8.35 (d, $J = 11.2$ Hz, 2H), 7.75 (s, 2H), 7.10 (d and d, $J = 11.2$ Hz and $J = 11.2$ Hz, 4H), 6.33 (s, 1H), 4.10−3.99 (m, 4H), 3.92 (s, 5H), 1.54 (s, 18H), 1.50 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 159.89, 137.36, 135.56, 134.06, 133.97, 131.72, 131.20, 118.76, 117.87, 95.74, 68.85, 68.63, 66.77, 38.08, 35.70, 33.23, 32.32, 31.80; HRMS calcd for $C_{47}H_{56}Fe$ 676.3731, found 676.3734. Anal. Calcd for $C_{47}H_{56}Fe$: C, 83.41; H, 8.34. Found: C, 83.83; H, 8.41.

General Procedure for the Preparation of Monocations 5a−c·PF_6^- and Dication 6·2PF_6^-. DDQ was added at room temperature to a solution of di(1-azulenyl)ferrocenylmethanes (**7a**−**c**) or 1,3-bis[(1-azulenyl)ferrocenylmethyl]azulene (**8**) in CH_2Cl_2. The solution was stirred at the same temperature for 5−15 min until the reaction was complete. A 60% aqueous HPF_6 solution was added to the reaction mixture. After the solution was stirred at room temperature for an additional 5 min, water was added to the mixture. The resulting suspension was filtered with suction. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (3−5 mL), and then Et_2O or hexane (50−100 mL) was added to the solution. The precipitated crystals were collected by filtration, washed with Et_2O, and dried in vacuo to give hexafluorophosphates **5a**−**c**·PF_6^- and **6**·2PF_6^-. The product was further purified by recrystallization from CH_2Cl_2/ether or CH_2Cl_2/hexane.

Di(1-azulenyl)ferrocenylmethyl Hexafluorophosphate (5a·PF_6^-). The general procedure was followed using DDQ (138 mg, 0.606 mmol), di(1-azulenyl)ferrocenylmethane (**7a**) (227 mg, 0.502 mmol), and 60% HPF_6 (5 mL) in CH_2Cl_2 (50 mL). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **5a**·PF_6^- (283 mg, 94%): brown powder; mp 136.0−141.0 °C; MS (FAB) m/z 451 (M^+-PF_6); IR (KBr disk) ν_{max} 1466, 1396, 1378, 1282, 840, 558 cm^{-1}; ES (MeCN) λ_{max}, nm 229 (log ϵ 4.64), 268 (4.57), 374 (4.19), 467 (4.16), 621 (4.20), 746 (3.84); ^1H NMR (500 MHz, $CDCl_3$) δ 8.678 (d, $J = 9.2$ Hz, 2H), 8.608 (d, $J = 4.4$ Hz, 2H), 7.850 (dd, $J = 9.6, 9.5$ Hz, 2H), 7.817 (dd, $J = 9.5, 9.2$ Hz, 2H), 7.746 (d, $J = 4.4$ Hz, 2H), 7.391 (d, $J = 9.8$ Hz, 2H), 7.259 (dd, $J = 9.8, 9.6$ Hz, 2H), 5.496 (dd, $J = 1.8, 1.8$ Hz, 2H), 5.109 (dd, $J = 1.8, 1.8$ Hz, 2H), 4.490 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.839, 151.346, 145.866, 143.339, 143.021, 141.403, 138.504, 132.724, 132.624, 131.861, 124.917, 85.865, 79.304, 77.513, 73.424; HRMS calcd for $C_{31}H_{23}Fe^+$ 451.1149, found 451.1150. Anal. Calcd for $C_{31}H_{23}FePF_6$: C, 62.44; H, 3.89. Found: C, 62.86; H, 4.29.

Bis(3-methyl-1-azulenyl)ferrocenylmethyl Hexafluorophosphate (5b·PF_6^-). The general procedure was followed using DDQ (296 mg, 1.31 mmol), bis(3-methyl-1-azulenyl)ferrocenylmethane (**7b**) (487 mg, 1.01 mmol), and 60% HPF_6 (10 mL) in CH_2Cl_2 (100 mL). Recrystallization from CH_2Cl_2/ether gave hexafluorophosphate **5b**·PF_6^- (633 mg, 100%): deep green powder; mp 209.0−211.5 °C dec; MS (FAB) m/z 479 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 1474, 1453, 1430, 1408, 1372, 1346, 838, 558 cm^{-1}; ES (MeCN) λ_{max}, nm 232 (4.55), 269 (4.44), 386 (4.22), 497 (3.96), 655 (4.23); ^1H NMR (90 MHz, $CDCl_3$) δ 8.54 (m, 2H), 8.47 (s, 2H), 7.93−7.64 (m, 4H), 7.41−7.14 (m, 4H), 5.37 (s, 2H), 5.05 (s, 2H), 4.45 (s, 5H), 2.75 (s, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 168.73, 148.97, 146.87, 142.91, 142.54, 138.09, 137.81, 133.33, 131.56, 131.23, 85.46, 78.30, 76.99, 72.84, 13.14; HRMS calcd for $C_{33}H_{27}Fe^+$ 479.1462, found 479.1462. Anal. Calcd for $C_{33}H_{27}FePF_6$: C, 63.48; H, 4.36. Found: C, 64.04; H, 4.83.

Bis(3,6-di-*tert*-butyl-1-azulenyl)ferrocenylmethyl Hexafluorophosphate (5c·PF_6^-). The general procedure was followed using DDQ (168 mg, 0.740 mmol), bis(3,6-di-*tert*-butyl-1-azulenyl)ferrocenylmethane (**7c**) (339 mg, 0.501 mmol), and 60% HPF_6 (5 mL) in CH_2Cl_2 (50 mL). Recrystallization from CH_2Cl_2/hexane gave hexafluorophosphate **5c**·PF_6^- (388 mg, 94%): deep green powder; mp 177.5−183.5 °C dec; MS (FAB) *m/z* 675 ($M^+ - PF_6$); IR (KBr disk) ν_{max} 2968, 1468, 1438, 1370, 1338, 1244, 1210, 838, 558 cm^{-1}; ES (MeCN) λ_{max}, nm 234 (log ϵ 4.62), 273 (4.57), 301 (4.51), 382 (4.27), 486 (4.03), 657 (4.31); ^1H NMR (90 MHz, $CDCl_3$) δ 8.96 (d, J = 10.8 Hz, 2H), 8.33 (s, 2H), 8.00 (d, J = 10.8 Hz, 2H), 7.39 (s, 4H), 5.33 (s, 2H), 4.99 (s, 2H), 4.71 (s, 5H), 1.69 (s, 18H), 1.39 (s, 18H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 168.43, 167.88, 146.78, 146.63, 145.41, 140.28, 138.88, 137.57, 130.95, 129.55, 85.04, 77.17, 77.05, 72.38, 39.09, 33.45, 31.50, 31.40; HRMS calcd for $C_{47}H_{55}Fe^+$ 675.3653, found 675.3652. Anal. Calcd for $C_{47}H_{55}FePF_6$: C, 68.78; H, 6.75. Found: C, 69.01; H, 6.41.

1,3-Bis[(1-azulenyl)ferrocenylmethylium]azulene Dihexafluorophosphate (6·2PF_6^-). The general procedure was followed using DDQ (138 mg, 0.610 mmol), 1,3-bis[(1-azulenyl)ferrocenylmethyl]azulene (**8**) (197 mg, 0.254 mmol), and 60% HPF_6 (5 mL) in CH_2Cl_2 (50 mL). Recrystallization from CH_2Cl_2/ether gave dihexafluorophosphate **6**·2PF_6^- (208 mg, 77%): deep green powder; mp > 300 °C; MS (FAB) *m/z* 919 ($M^+ - PF_6$), 775 ($M^+ - 2PF_6 + H$); IR (KBr disk) ν_{max} 1456, 1430, 1383, 1277, 839, 558 cm^{-1}; ES (MeCN) λ_{max}, nm 229 (log ϵ 4.82), 261 (4.69), 407 (4.37), 475 (4.34), 650 (4.47), 775 (4.13); ^1H NMR (600 MHz, MeCN-d_3) δ 8.947 (br d, J = 4.4 Hz, 2H), 8.870 (d, J = 9.5 Hz, 2H), 8.643 (br s, 1H), 8.202 (dd, J = 9.5, 9.5 Hz, 2H), 8.176 (d, J = 9.8 Hz, 2H), 8.143 (dd, J = 9.5, 9.5 Hz, 2H), 8.091 (t, J = 9.6 Hz, 1H), 7.934 (d, J = 4.4 Hz, 2H), 7.808 (d, J = 9.9 Hz, 2H), 7.740 (dd, J = 9.8, 9.5 Hz, 2H), 7.712 (dd, J = 9.9, 9.6 Hz, 2H), 5.775 (br s, 4H), 5.342 (br s, 4H), 4.547 (s, 10H); ^{13}C NMR (150 MHz, MeCN-d_3) δ 153.817, 147.847, 147.086 (br), 145.065, 144.887 (br), 144.350, 142.090, 140.676, 140.427 (br), 135.248 (br), 134.040, 133.802 (br), 132.814 (br), 127.238, 87.071 (br), 81.034 (br), 77.978 (br), 74.300. Anal. Calcd for $C_{52}H_{38}Fe_2P_2F_{12}$: C, 58.67; H, 3.60. Found: C, 60.48; H, 3.88.

The pK_R^+ Value. The sample solutions of the hexafluorophosphates **5a**−**c**·PF_6^- and **6**·2PF_6^- were prepared by dissolving the hexafluorophosphate in a glycine (0.1 M) solution (50 mL) and diluting the solution to 100 mL by adding MeCN. The sample solution with lower acidity was made by further alkalification with 20% aqueous NaOH. The pH of each sample was determined on a pH meter calibrated with standard buffers before use. The observed absorbances at the specific absorption maxima of the cation **5a**−**c** and **6** were plotted against the pH, giving classical titration curves whose midpoints were taken as the pK_R^+ values.

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Supporting Information Available: Spectral data and detailed synthetic procedures of compounds **5a**−**c**·PF_6^-, **7a**−**c**, **6**·2PF_6^-, and **8**. ^1H and ^{13}C NMR spectra for all mentioned compounds (41 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.

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