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Synthesis and Redox Properties of Crowded Triarylphosphines Possessing Ferrocenyl Groups

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Crowded triarylphosphines possessing ferrocenyl groups [(4-ferrocenyl-2,6-diisopropylphenyl)$_n$(2,4,6-triisopropylphenyl)$_{3-n}$P (**5a**, $n = 1$; **5b**, $n = 2$; **5c**, $n = 3$)] were synthesized by the reaction of the corresponding arylcopper(I) reagents with the diarylchlorophosphines. Structures of the triarylphosphines were studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, and the characteristic patterns of the proton signals of the 2,6-isopropyl groups and upfielded ^{31}P chemical shifts suggest structural similarities of the triarylphosphine moiety to the previously reported tris(2,4,6-triisopropylphenyl)phosphine (**2**). X-ray crystallography of **5c** also revealed that the structure around the phosphorus is similar to that of **1**, where the average bond angle and length around the phosphorus atom are 110.8° and 1.854 Å, respectively. According to the electrochemical measurements, phosphines **5a**, **5b**, and **5c** are reversibly oxidized in two, three, and four steps, respectively, which suggests significant electronic interaction among the triarylphosphine and the ferrocene redox centers as well as weak interaction among the ferrocene redox centers. The EPR spectra obtained at cryogenic temperature after oxidation of phosphines **5a**, **5b**, and **5c** are superpositions of those for the cation radicals of the crowded triarylphosphine and ferricinium. The solution spectra obtained at 293 K, which consist of two lines typical of the cation radical of the crowded triarylphosphines, become weaker as the number of the ferrocenyl groups increases and the cation radical of **5c** does not show EPR signals. These findings suggest not only instability of the tetra(cation radical) of **5c** but also the course of oxidation where the ferrocenyl groups in the periphery of the molecules are oxidized at first.

Introduction

Construction of multistep reversible redox systems has attracted considerable interest from the fundamental to practical viewpoints. Since the key structures applicable as stable redox centers are still limited, development of novel redox centers is actively explored. Although nitrogen compounds such as triarylamines[1] have long been accepted as the redox centers of functional molecules, their heavier main group counterparts have not attracted such attention because most of them are generally unstable in oxidized/reduced as well as neutral forms. Recently we and others reported construction of multistep redox systems carrying phosphorus redox centers such as sterically protected diphosphenes[2] and phosphaethenes.[3] Crowded triarylphosphines such as trimesitylphosphine (**1**)[4] are known to be reversibly oxidized to the stable cation radicals at low potential and are expected to work as the redox centers in multistep redox systems (Scheme 1). Structures of the crowded triarylphosphines and the related compounds have been extensively studied because the structural change around the phosphorus atom and the dynamic behavior of the substituents are worth much attention.[5] The structure around the phosphorus atom is closely related to the redox properties, and the low oxidation potential and stability of the cation radicals can be explained

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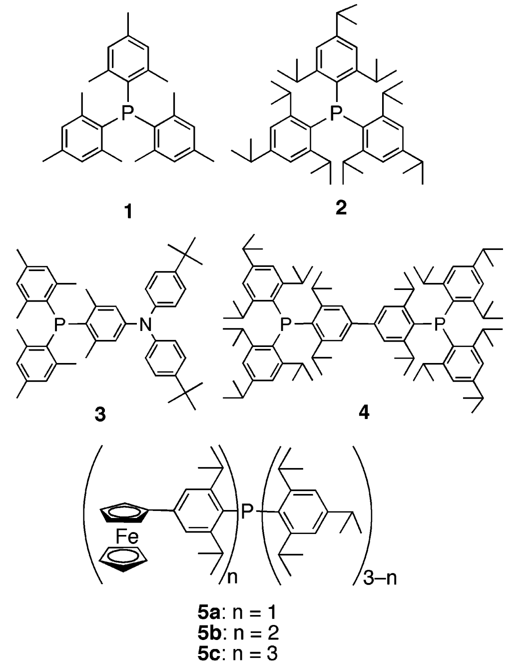
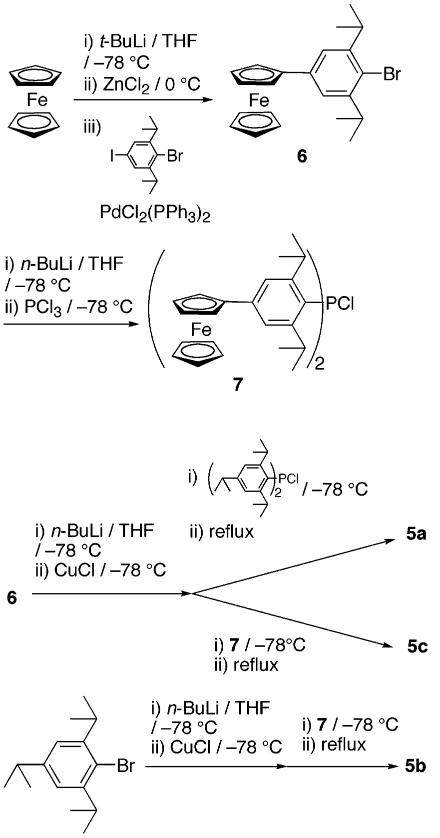
(1) Recent examples: (a) Selby, T. D.; Blackstock, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 12155−12156. (b) Selby, T. D.; Blackstock, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 7152−7153. (c) Okada, K.; Imakura, T.; Oda, M.; Murai, H.; Baumgarten, M. *J. Am. Chem. Soc.* **1996**, *118*, 3047−3048. (d) Wienk, M. M.; Janssen, R. A. J. *Chem. Commun.* **1996**, 267−268. (e) Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, *62*, 448−449. (f) Yano, M.; Sato, K.; Shiomi, D.; Ichimura, A.; Abe, K.; Takui, T.; Itoh, K. *Tetrahedron Lett.* **1996**, *51*, 9207−9210. (g) Sato, K.; Yano, M.; Furuichi, M.; Shiomi, D.; Takui, T.; Abe, K.; Itoh, K.; Higuchi, A.; Katsuma, K.; Shirota, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6607−6613. (h) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1−25. (i) Louie, J.; Hartwig, J. F.; Fry, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 11695−11696. (j) Lambert, C.; Nöll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434−8442. (k) Low, P. J.; Paterson, M. A. J.: Puschmann, H.; Goeta, A. E.; Howard, J. A. K.; Lambert, C.; Cherryman, J. C.; Tackley, D. R.; Leeming, S.; Brown, B. *Chem.—Eur. J.* **2004**, *10*, 83−91.

10.1021/ic051038l CCC: $33.50

Scheme 1



Scheme 2. Synthesis of Crowded Triarylphosphines Carrying Ferrocenyl Groups



by thermodynamic stabilization by the structural change and kinetic stabilization by the bulky substituents.[6] Although **1** has been regarded as one of the most typical crowded triarylphosphines, more crowded triarylphosphines, which have larger bond angles and lengths around the phosphorus atom, have been synthesized recently. Tris(9-anthryl)phosphine[7] has a unique structure and optical properties arising from the anthryl groups that can be modulated by simple derivatization.[8] We synthesized tris(2,4,6-triisopropylphenyl)-phosphine (**2**), which is oxidized at lower potential to a more stable cation radical than **1**, and demonstrated the structure−properties relationship among several crowded triarylphosphines.[9] On the other hand, we have employed triarylphosphine moieties similar to **1** as the redox center, but model compounds, such as aminophosphinobenzene **3**, proved to be irreversible redox systems at room temperature probably due to insufficient stability of the phosphorus redox center.[10] Therefore, we employed more crowded triarylphosphine moieties similar to **2** as the phosphorus redox sites, and biphenyl **4**, which was synthesized as the first attempt, was shown to be a considerably stable two-step redox system.[11]

Herein, we report the synthesis and structure of triarylphosphines **5a**, **5b**, and **5c** carrying ferrocenyl groups. To investigate intramolecular interaction of the phosphorus redox center with the donors, ferrocenes have been chosen as the second redox sites. Ferrocenes are also reversibly oxidized to stable radicals (ferriciniums) at low potential, and the synthesis and various intramolecular interactions of the large number of the compounds carrying ferrocenyl and other redox sites have been extensively studied.[12] The ferrocenes connected to phosphines[13] and amines[14] have also attracted considerable attention, although the group 15 elements act as linkers rather than redox sites in many cases.

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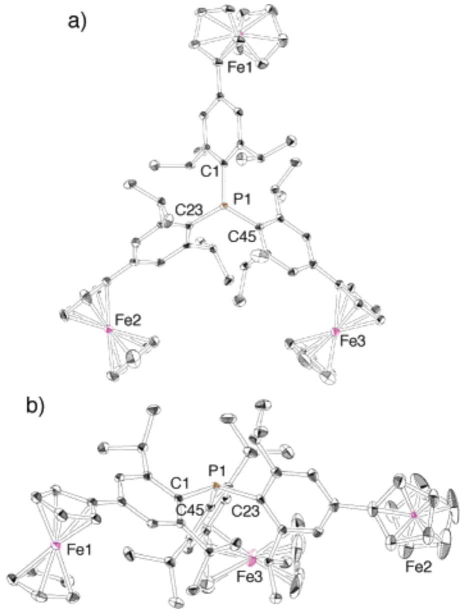

Figure 1. ORTEP drawings of **5c** with 50% thermal ellipsoids. Solvents and hydrogen atoms are omitted for clarity. (a) Top view; (b) side view. Selected bond lengths (Å) and angles (deg): P1−C1, 1.852(2); P1−C23, 1.853(2); P1−C45, 1.857(2); C1−P1−C23, 110.90(10); C1−P1−C45, 113.36(9); C23−P1−C45, 108.23(9).

(Ferrocenylaryl)phosphines **5a**, **5b**, and **5c** are not only regarded to be model compounds for practical molecules such as multistep redox systems or functional polyradicals, but they are also expected to reveal properties of the newly developed crowded triarylphosphine structure.

Results and Discussion

Synthesis and Structure. The crowded triarylphosphine moieties analogous to **2** have been synthesized by reaction of an arylcopper(I) reagent with phosphorus chlorides.[9,11] (4-Ferrocenylaryl)phosphines **5a**, **5b**, and **5c** were similarly synthesized by using the arylcopper(I) reagent or diarylchlorophosphine carrying 4-ferrocenyl-2,6-diisopropylphenyl groups (Scheme 2). The ferrocenes carrying (diphenylphosphino)phenyl groups have been synthesized by a palladium-catalyzed Suzuki coupling of the boronic acid of ferrocene with (bromophenyl)diphenylphosphine oxides, followed by reduction with trichlorosilane.[15] We admit the analogous way is worth pursuing, but construction of the crowded triarylphosphine moiety in the final step seems better for the synthesis of a series of the (ferrocenylaryl)phosphines **5**. 4-Ferrocenylbromobenzene **6** was synthesized by palladium-catalyzed cross coupling of ferrocenylzinc chloride[16] with 2-bromo-1,3-diisopropyl-5-iodobenzene.[11] Lithiation of **6** followed by reaction with phosphorus trichloride gave diarylchlorophosphine **7**. Bromobenzene **6** was converted to the corresponding arylcopper(I) reagent and allowed to react with chlorobis(2,4,6-triisopropylphenyl)phosphine[11,17] and **7** to afford (4-ferrocenyl-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (**5a**) and tris(4-ferrocenyl-2,6-diisopropylphenyl)phosphine (**5c**), respectively. On the other hand, reaction of the arylcopper(I) reagent prepared from 2,4,6-triisopropylbromobenzene with **7** afforded bis(4-ferrocenyl-2,6-diisopropylphenyl)(2,4,6-triisopropylphenyl)phosphine (**5b**). Phosphines **5a**, **5b**, and **5c** were isolated as air-stable solids and displayed an orange color typical of ferrocenyl compounds. ^{31}P NMR (162 MHz, CDCl$_3$) signals are observed in a high-field area (δ −51.6 (**5a**), −50.9 (**5b**), −51.0 (**5c**)) typical of crowded triarylphosphines such as **3** (δ −52.4).[9] The ^{1}H and ^{13}C NMR spectra of **5c** at 294 K are rather simple despite the crowded structure. The 4-ferrocenyl-2,6-diisopropylphenyl group gives only one aromatic, one methine, and two methyl signals as if the aromatic substituent

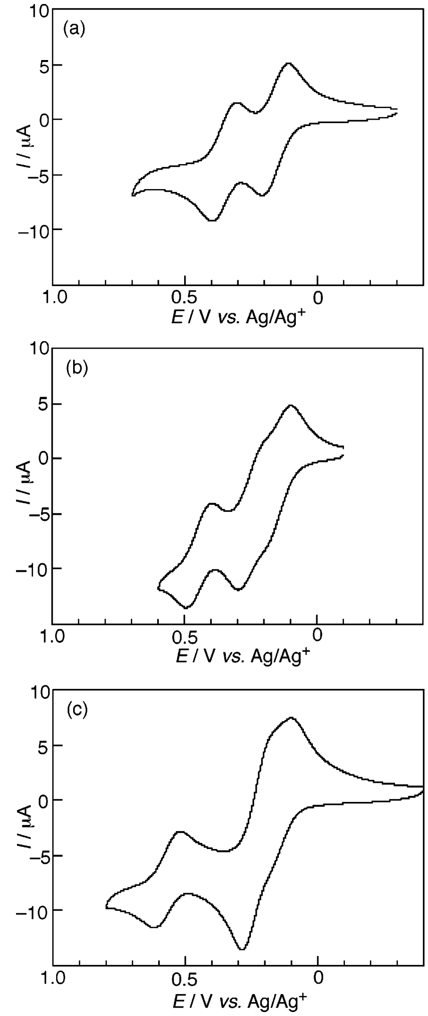

Figure 2. Cyclic voltammograms of (a) **5a**, (b) **5b**, and (c) **5c** at 293 K. Conditions: glassy carbon, Pt wire, and Ag/0.01 M AgNO$_3$/0.1 M n-BuNClO$_4$/CH$_3$CN as working, counter, and reference electrodes, respectively [$E_{1/2}$(ferrocene/ferricinium) = 0.18 V]. Scan rate = 30 mV s^{-1}. A substrate (ca. 10^{-4} M) was dissolved in dichloromethane with 0.1 M n-Bu$_4$NClO$_4$ as a supporting electrolyte.

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Table 1. Oxidation Potentials of (Ferrocenylaryl)phosphines and Related Compounds Obtained by Cyclic Voltammetry[a]

compd	$^1E_{1/2}$/V	$^2E_{1/2}$/V	$^3E_{1/2}$/V	$^4E_{1/2}$/V	$\Delta E(^2E_{1/2}-^1E_{1/2})$/V	$\Delta E(^3E_{1/2}-^2E_{1/2})$/V	$\Delta E(^4E_{1/2}-^3E_{1/2})$/V
5a	0.16	0.35			0.19		
5b	0.16	0.23	0.44		0.07	0.21	
5c	0.16	0.23	0.23	0.57	0.07	0	0.34
2	0.16						
6	0.20						

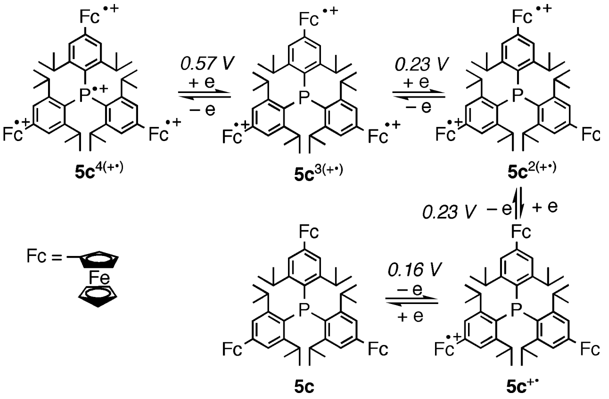
[a] Versus Ag/Ag$^+$ in dichloromethane with 0.10 M *n*-Bu$_4$NClO$_4$ [$E_{1/2}$(ferrocene/ferricinium) = 0.18 V], scan rate = 30 mV s^{-1}, and T = 293 K.

except for the ferrocenyl groups is *C*2 symmetrical relative to the P−C bond. The 4-ferrocenyl-2,6-diisopropylphenyl and 2,4,6-triisopropylphenyl groups of phosphines **5a** and **5b**, where one of the three aryl groups is different, are also observed as *C*2 symmetrical similar to **5c**, but the two 2,4,6-triisopropylphenyl and 4-ferrocenyl-2,6-diisopropylphenyl groups of **5a** and **5b** are observed as if they are two different *C*2 symmetrical aryl groups. These phenomena suggest averaging due to rapid inversion of the phosphorus atom and slow enantiomerization of the helicity of the propeller composed of the three aromatic rings. Similar averaging in the NMR spectra is also observed for **2**.[9] UV−vis spectra of **5a**, **5b**, and **5c** have absorption characteristic of both the ferrocenes (λ_{max} 442 (**5a**), 443 (**5b**), 450sh nm (**5c**)) and the crowded triarylphosphines (λ_{max} 344 (**5a**), 351 (**5b**), 357 nm (**5c**)). Ferrocenylarene **6** also displays the corresponding absorption responsible for an orange color at a similar wavelength (λ_{max} 448 nm). On the other hand, introduction of the ferrocenyl substituents leads to a red shift of the absorption corresponding to triarylphosphine as compared with **2** (λ_{max} 327 nm).[9] The molecular structure of **5c** was further investigated by X-ray crystallography (Figure 1). The bond lengths and angles around the phosphorus reflect the crowded structure, and the average C−P bond length and angle (1.854 Å, 110.8°) are similar to those of **2** (1.845 Å, 111.5°).[9]

Redox Properties. Redox properties of **5a**, **5b**, and **5c** were studied by cyclic voltammetry (Figure 2), and the oxidation potentials are summarized in Table 1. Phosphine **5a** shows two-step reversible redox waves ($^1E_{1/2} = 0.16$, $^2E_{1/2} = 0.35$ V vs Ag/Ag$^+$) with the difference of the oxidation potentials ($\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$) as 0.19 V. Since **2** ($E_{1/2}$ = 0.16 V)[9] and **6** ($E_{1/2}$ = 0.20 V) are oxidized at similar potentials, the considerably large ΔE suggests substantial electronic interaction between the phosphorus and the iron redox centers. Although the assignment of the first and the second oxidation waves is not clear, the cyclic voltammograms of **5b** and **5c** and EPR study indirectly indicate that the first oxidation takes place on the ferrocenyl group (see below).

The cyclic voltammogram of phosphine **5b** consists of three reversible redox waves ($^1E_{1/2} = 0.16$, $^2E_{1/2} = 0.23$, $^3E_{1/2} = 0.44$ V). Since the second wave is severely overlapped with the first one, oxidation potentials are further confirmed by Osteryoung square wave voltammetry. As compared with the ΔE of **5a**, a smaller difference between the first and second oxidation potentials (ΔE = 0.07 V) and a larger difference between the second and the third ones (ΔE = 0.21 V) suggest the redox process of **5b**, where the first and the second oxidations take place on the ferrocenyl group and the third one occurs on the phosphorus atom so as to minimize electrostatic repulsion between the positive charges.

Scheme 3. Oxidation of **5c**



Phosphine **5c** shows an unresolved large redox wave followed by a reversible one, which can be interpreted to be a three-step reversible redox process with the second oxidation as a two-electron process ($^1E_{1/2}$ = 0.16 V, $^{2,3}E_{1/2}$ = 0.23 V, $^4E_{1/2}$ = 0.57 V) from comparison with the Osteryoung square wave voltammogram. The first and second oxidation waves of phosphine **5c** can be attributed to the oxidation of the ferrocenyl groups, and the last oxidation wave can be attributed to the oxidation of the phosphine unit similarly to **5b** (Scheme 3). The difference between the first and second oxidation potentials (ΔE = 0.07 V), which reflects electrostatic repulsion among the ferriciniums across the triarylphosphine framework, is similar to that of **5b**. On the other hand, the difference between the second and third oxidation potentials becomes reasonably larger (ΔE = 0.34 V) than that for **5b**, since it reflects repulsion between the positive charges on the three ferrocenyl groups and the phosphorus.

EPR Study of Cation Radicals. To observe the oxidation products of (ferrocenylaryl)phosphines **5a**, **5b**, and **5c** directly, the chemical oxidation was studied by EPR spectroscopy. Since X-band EPR spectra of ferricinium cations are generally observed only at cryogenic temperature due to rapid relaxation,[18] the samples were cooled to cryogenic temperature just after contact with the oxidant.

Oxidation of ferrocenylarylphosphines **5a**, **5b**, and **5c** with silver(I) perchlorate in dichloromethane gave purple solutions, and the EPR spectra of the frozen solutions at 5 K and those of the fluid solution at 293 K are shown in Figure 3. The EPR spectra at 5 K are interpreted to be a superposition of the signals of the phosphorus cation radical on those of ferricinium, which suggests small dipole−dipole interac-

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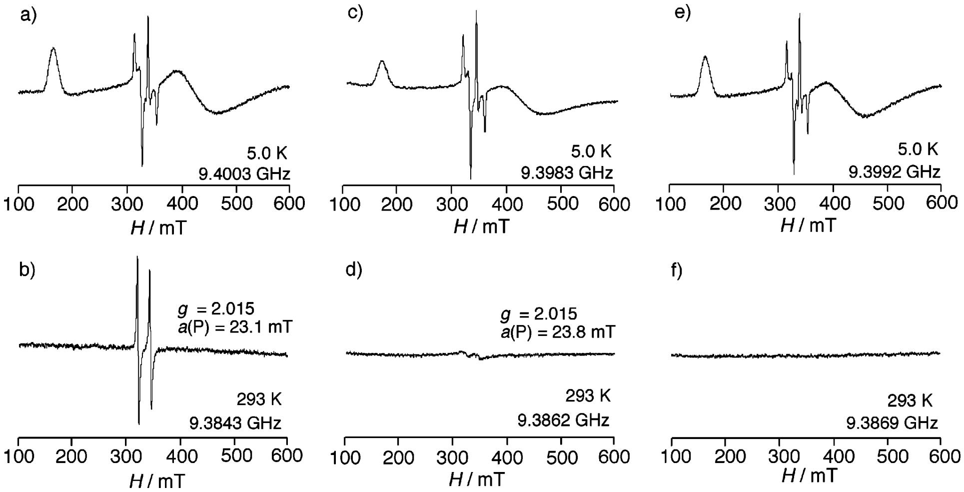

Figure 3. EPR spectra obtained after oxidation of **5** with $AgClO_4$ in dichloromethane: **5a** at (a) 5 and (b) 293 K; **5b** at (c) 5 and (d) 293 K; **5c** at (e) 5 and (f) 293 K.

Table 2. EPR Parameters of Cation Radicals of **5a**, **5b**, and **5c**, and Related Compounds[a]

	solution		frozen solution					
			phosphorus cation radical				ferricinium	
compd	g	$a(^{31}P)$/mT	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}(^{31}P)$/mT	$a_{\perp}(^{31}P)$/mT	$g_{\parallel}$	$g_{\perp}$
5a	2.015	23.1	2.003	2.009	40.7	10.2	4.10	1.59
5b	2.015	23.8	2.003	2.0015	40.0	10.4	4.10	1.59
5c			2.005	2.021	38.6	10.5	4.09	1.59
2	2.007	23.7	2.002	2.009	41.7	13.0		
6							4.05	1.50
ferricinium[b]							4.36	1.30

[a] Measured in dichloromethane. [b] Reference 18.

tion between the radical centers. The anisotropic hyperfine coupling constants with ^{31}P nucleus, which are summarized in Table 2, are similar to those of **2** reflecting the structural similarities. The anisotropic *g* values of the ferricinium moieties are close to those corresponding to **6** rather than ferricinium.[18] The signals of the ferricinium around $g = 4.1$ and 1.6 broaden as temperature is raised and disappear at 60 K; on the other hand, signal intensities of the phosphorus cation radical follow a Curie law from 5 to 130 K. The EPR spectrum of the cation radical of **5a** in solution is regarded as a doublet due to the hyperfine coupling with ^{31}P nucleus ($a(^{31}P) = 23.1$ mT at $g = 2.015$), which is similar to that of $\mathbf{2}^{\bullet+}$. However, as the number of ferrocenyl substituents increases, the EPR signals become weaker, and the cation radical of **5c** does not show any signals at 293 K. As shown by the cyclic voltammograms, the phosphorus cation radical centers of tri(cation radical) $\mathbf{5b}^{3(\bullet+)}$ and tetra(cation radical) $\mathbf{5c}^{4(\bullet+)}$ are thermodynamically destabilized by electrostatic repulsion with positive charges on the ferrocenyl groups and become more reactive than that of $\mathbf{2}^{\bullet+}$. Thus, the phosphorus cation radical centers are lost due to decomposition or back electron transfer at high temperature in solution.

Conclusion

Crowded triarylphosphines possessing one, two, or three 4-ferrocenyl-2,6-diisopropylphenyl substituents were synthesized by the reaction of the corresponding arylcopper(I) reagent with the phosphorus chlorides. These (ferrocenylaryl)phosphines are good model compounds to study intramolecular interaction between the crowded triarylphosphine moiety and the donors. The triarylphosphine moieties similar to **2** as well as ferrocenyl groups serve as reversible redox sites, and the whole molecules become multistep reversible redox systems. Considerable electronic interaction between the phosphorus and the ferrocenyl redox sites and weak interaction among the ferrocenyl redox sites contribute construction of the multistep redox systems. Although the EPR study supports formation of both the phosphorus-centered cation radicals and the ferricinium cations, exchange and dipole−dipole interactions are too small to be detected. The crowded triarylphosphine moieties employed in this work turned out to contribute formation of considerably stable redox systems; however, the phosphorus redox sites are not stable enough for tri- and tetra(cation radicals). Further investigation is in progress on intramolecular interaction between the crowded triarylphosphine moieties and various functional sites such as acceptors and radicals as well as development of more stable phosphorus redox centers.

Experimental Section

General. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AV400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are expressed as δ downfield from external tetramethylsilane. The chemical shifts were calibrated to the residual proton of the deuterated solvents (δ 7.25 for chloroform-*d*, δ 7.20 for benzene-d_6, δ 5.32 for dichloromethane-d_2) or the carbon of the deuterated solvent (δ 77.0 for chloroform-*d*, δ 128.5 for benzene-d_6). ^{31}P NMR chemical shifts are expressed as δ downfield from external 85% H_3PO_4. Mass spectra were measured on a Hitachi M-2500S with electron impact (EI) ionization at 70 eV or a JEOL HX-110 with fast atom bombardment (FAB) ionization using *m*-nitrobenzyl alcohol matrix. Fourier transform ion cyclotron resonance (FT-ICR) mass spectra were measured on a Bruker APEX III with electron spray ionization (ESI). Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. UV−vis and IR spectra were measured on a Hitachi U-3210 and Horiba FT-300 spectrometers, respectively. Microanalyses were performed at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Merck silica gel 60 and Sumitomo basic alumina (KCG-30) were used for column chromatography. All reactions were carried out under argon. Tetrahydrofuran was distilled from sodium diphenylketyl under argon just prior to use.

Synthesis. 4-Ferrocenyl-2,6-diisopropylbromobenzene (6). To a solution of ferrocene (380 mg, 2.04 mmol) in tetrahydrofuran (15 mL) was added *tert*-butyllithium (2.71 mL, 1.51 M in pentane) at −78 °C. The reaction mixture was stirred for 15 min and warmed to 0 °C in 30 min. Anhydrous zinc chloride (794 mg, 5.83 mmol) dried over a flame in vacuo was added through a solid-dropping tube at 0 °C, and the mixture was stirred for 30 min at 0 °C. A suspension of 2,6-diisopropyl-4-iodobromobenzene (500 mg, 1.36 mmol) and bis(triphenylphosphine)palladium(II) dichloride (143 mg, 204 mmol) in tetrahydrofuran (13 mL) was added into the orange suspension of ferrocenylzinc chloride at 0 °C, and the mixture was stirred for 12 h and then allowed to warm to room temperature. The reaction mixture was concentrated in vacuo and purified by column chromatography (SiO$_2$, hexane) and gel permeation chromatography (JAIGEL 1H + 2H/chloroform) to afford **6** (171 mg, 0.40 mmol, 29%). **6**: Orange solid, mp 100−102 °C; ^{1}H NMR (400 MHz, CDCl$_3$, 293 K) δ 7.24 (s, 2H, arom), 4.62 (t, 2H, *J* = 1.62 Hz, C$_5$H$_4$), 4.32 (t, 2H, *J* = 1.59 Hz, C$_5$H$_4$), 4.06 (s, 5H, C$_5$H$_5$), 3.52 (2H, sept, *J* = 6.82 Hz, *o*-C*H*(CH$_3$)$_2$), 1.30 (d, 12H, *J* = 6.85 Hz, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, CDCl$_3$, 293 K) δ 147.33 (s, *o*-arom), 138.28 (s, *p*-arom), 123.89 (s, *ipso*-arom), 122.39 (s, *m*-arom), 85.84 (s, C$_5$H$_4$), 69.59 (s, C$_5$H$_5$), 68.82 (s, C$_5$H$_4$), 66.87 (s, C$_5$H$_4$), 33.41 (s, *o*-*C*H(CH$_3$)$_2$), 23.13 (s, *o*-CH(*C*H$_3$)$_2$); IR (KBr) 2966, 2927, 2902, 2866, 1595, 1460, 1417, 1383, 1360, 1327, 1124, 1105, 1068, 1018, 881, 818, and 501 cm^{-1}; UV−vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ϵ) 448 (2.58), 283 nm (4.12); LRMS (EI, 70 eV) *m*/*z* (rel intensity) 426 (M$^+$ + 2; 95), 424 (M$^+$; 100), 380 (M$^+$ − CH(CH$_3$)$_2$; 28), 330 (M$^+$ − Br − CH$_3$; 13), 314 (M$^+$ − Br − 2 × CH$_3$; 9); HRMS (EI, 70 eV) *m*/*z* found 424.0484. Calcd for C$_{22}$H$_{25}$BrFe: M, 424.0489. Found: C, 62.63; H, 6.05%. Calcd for C$_{22}$H$_{25}$BrFe: C, 62.15; H, 5.93%.

(4-Ferrocenyl-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (5a). To a solution of **6** (210 mg, 0.49 mmol) in tetrahydrofuran (8 mL) was added butyllithium (0.47 mL, 1.57 M in hexane) at −78 °C. The mixture was stirred for 30 min, and CuCl (49.0 mg, 0.49 mmol) was added through a solid-dropping tube at −78 °C. The mixture was stirred for 30 min at −78 °C, warmed to room temperature, stirred for 1 h, and then cooled to −78 °C. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (234 mg, 0.49 mmol) in tetrahydrofuran (6 mL) was added into the dark-green suspension of the arylcopper(I) reagent at −78 °C, and the mixture was stirred for 2 h at −78 °C, then refluxed for 12 h, and cooled to room temperature. The reaction mixture was concentrated in vacuo and purified by column chromatography (Al$_2$O$_3$, hexane) to afford **5a** (130 mg, 0.16 mmol, 34%). **5a**: Orange solid, mp 180−183 °C; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.35 (d, 2H, *J* = 3.13 Hz, arom), 7.05 (d, 4H, *J* = 3.17 Hz, Tip-*m*), 4.63 (d, 2H, *J* = 1.51 Hz, C$_5$H$_4$), 4.19 (t, 2H, *J* = 1.77 Hz, C$_5$H$_4$), 4.00 (s, 5H, C$_5$H$_5$), 3.96−3.80 (m, 6H, *o*-C*H*(CH$_3$)$_2$), 2.79 (sept, 2H, *J* = 6.54 Hz, *p*-C*H*(CH$_3$)$_2$), 1.45 (d, 6H, *J* = 6.32 Hz, *o*-CH(C*H*$_3$)$_2$), 1.44 (d, 12H, *J* = 6.54 Hz, *o*-CH(C*H*$_3$)$_2$), 1.23 (d, 12H, *J* = 6.90 Hz, *p*-CH(C*H*$_3$)$_2$), 1.02 (d, 6H, *J* = 6.54 Hz, *o*-CH(C*H*$_3$)$_2$), 0.95 (d, 12H, *J* = 6.01 Hz, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 153.64 (d, J_{PC} = 18.15 Hz, Ar-*o*), 153.54 (d, J_{PC} = 18.16 Hz, Tip-*o*), 149.93 (s, Tip-*p*), 140.38 (s, Ar-*p*), 133.23 (d, J_{PC} = 23.95 Hz, Ar-*ipso*), 132.60 (d, J_{PC} = 23.71 Hz, Tip-*ipso*), 122.54−122.50 (d x 2, Tip-*m*), 122.28 (d, J_{PC} = 4.39 Hz, Ar-*m*), 85.58 (s, C$_5$H$_4$), 70.03 (s, C$_5$H$_5$), 69.31 (s, C$_5$H$_4$), 66.95 (s, C$_5$H$_4$), 66.81 (s, C$_5$H$_4$), 34.45 (s, *p*-*C*H(CH$_3$)$_2$), 32.50 (d, J_{PC} = 17.96 Hz, *o*-*C*H(CH$_3$)$_2$), 32.44 (d, J_{PC} = 17.41 Hz, *o*-*C*H(CH$_3$)$_2$), 25.04 (s, *o*-CH(*C*H$_3$)$_2$), 25.00 (s, *o*-CH(*C*H$_3$)$_2$), 24.91 (s, *o*-CH(*C*H$_3$)$_2$), 24.10 (s, *p*-CH(*C*H$_3$)$_2$), 24.00 (s, *p*-CH(*C*H$_3$)$_2$), 23.61 (s, *o*-CH(*C*H$_3$)$_2$), 23.44 (s, *o*-CH(*C*H$_3$)$_2$), 23.28 (s, *o*-CH(*C*H$_3$)$_2$); ^{31}P NMR (162 MHz, C$_6$D$_6$) δ −51.6 (s); IR (KBr) 2966, 2929, 2868, 1633, 1601, 1547, 1462, 1419, 1383, 1360, 1308, 1238, 1161, 1128, 1103, 1063, 1028, 1003, 933, 879, 816, 787, 648, 525, and 505 cm^{-1}; UV−vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ϵ) 442 (2.93), 344 nm (4.36); FABMS *m*/*z* (rel intensity) 783 (M$^+$ + 1; 92), 662 (M$^+$ − Fe − Cp + 1; 2), 579 (M$^+$ − Tip; 5), 437 (M$^+$ − FcAr; 41), 395 (M$^+$ − FcAr − *i*-Pr + 1; 4), 380 (M$^+$ − FcAr − *i*-Pr − CH$_3$ + 1; 50), 346 (FcAr + 1; 100); FT-ICR-MS (ESI, positive) *m*/*z* found 782.4643. Calcd for C$_{52}$H$_{71}$PFe$^+$: M$^+$, 782.4637. Found: C, 78.88; H, 9.01%. Calcd for C$_{52}$H$_{71}$PFe·0.5C$_2$H$_5$OH: C, 78.98; H, 9.25%.

Chlorobis(4-ferrocenyl-2,6-diisopropylphenyl)phosphine (7). To a solution of **6** (157 mg, 0.37 mmol) in tetrahydrofuran (8 mL) was added butyllithium (0.24 mL, 1.56 M in hexane) at −78 °C. The mixture was stirred for 30 min, and phosphorus trichloride (0.02 mL, 0.18 mmol) was added at −78 °C. The mixture was stirred for 6 h at −78 °C, warmed to room temperature, concentrated in vacuo, and purified by column chromatography (SiO$_2$, hexane, AcOEt:hexane = 1:12) to afford **7** (120 mg, 0.16 mmol, 85%). **7**: Orange oil; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.45 (d, 4H, *J* = 3.08 Hz, arom), 4.58 (t, 4H, *J* = 1.34 Hz, C$_5$H$_4$), 4.19 (t, 4H, *J* = 1.86 Hz, C$_5$H$_4$), 4.16 (m, 4H, *o*-C*H*(CH$_3$)$_2$), 3.99 (s, 10H, C$_5$H$_5$), 1.26 (d, 12H, *J* = 6.69 Hz, *o*-CH(C*H*$_3$)$_2$), 1.23 (d, 12H, *J* = 6.67 Hz, *o*-CH(C*H*$_3$)$_2$); ^{31}P NMR (162 MHz, C$_6$D$_6$) δ 88.4 (s); FT-ICR-MS (ESI, positive) *m*/*z* found 756.2038. Calcd for C$_{44}$H$_{50}$PClFe$_2$$^+$: M$^+$, 756.2032.

Bis(4-ferrocenyl-2,6-diisopropylphenyl)(2,4,6-triisopropylphenyl)phosphine (5b). To a solution of 2,4,6-triisopropylbromobenzene (158 mg, 0.56 mmol) in tetrahydrofuran (7 mL) was added butyllithium (0.35 mL, 1.58 M in hexane) at −78 °C. The reaction mixture was stirred for 20 min, and CuCl (55.2 mg, 0.56 mmol) was added through a solid-dropping tube at −78 °C. The mixture was stirred for 45 min, warmed to room temperature, stirred for 1 h, and then cooled to −78 °C. A solution of **7** (106 mg, 0.14 mmol) in tetrahydrofuran (8 mL) was added to the dark-green suspension of the arylcopper(I) reagent at −78 °C, and the mixture was stirred for 2 h at −78 °C, refluxed for 12 h, cooled to room temperature, concentrated in vacuo, and purified by column chromatography (Al$_2$O$_3$, hexane, AcOEt:hexane = 1:11) to afford **5b** (80 mg, 0.086 mmol, 62%). **5b**: Orange solid, mp 175−178 °C (dec); ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.46 (d, 4H, *J* = 3.18 Hz, arom), 7.16 (d, 2H, *J* = 3.24 Hz, Tip-*m*), 4.64 (d, 4H, *J* = 1.77 Hz, C$_5$H$_4$), 4.19 (t, 4H, *J* = 1.79 Hz, C$_5$H$_4$), 4.01 (s, 10H, C$_5$H$_5$), 3.98−3.78 (m, 6H, *o*-C*H*(CH$_3$)$_2$), 2.80 (sept, 1H, *J* = 6.87 Hz, *p*-C*H*(CH$_3$)$_2$), 1.47 (d, 12H, *J* = 6.76 Hz, *o*-CH(C*H*$_3$)$_2$), 1.45 (d, 6H, *J* = 6.68 Hz, *o*-CH(C*H*$_3$)$_2$), 1.24 (d, 6H, *J* = 6.91 Hz, *p*-CH(C*H*$_3$)$_2$), 1.06 (d, 6H, *J* = 5.80 Hz, *o*-CH(C*H*$_3$)$_2$), 1.04 (d, 6H, *J* = 6.02 Hz, *o*-CH(C*H*$_3$)$_2$), 0.97 (d, 6H, *J* = 6.63 Hz, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 153.59 (d, J_{PC} = 18.17 Hz, *o*-arom), 153.56 (d, J_{PC} = 18.46 Hz, *o*-arom), 153.48 (d, J_{PC} = 18.28 Hz, *o*-arom), 140.51 (s, Tip-*p*), 132.96 (d, J_{PC} = 23.58 Hz, Ar-*ipso*), 132.34 (d, J_{PC} = 23.40 Hz, Tip-*ipso*), 122.57 (d, $J_{PC} = 4.31$ Hz, Tip-*m*), 122.32 (d, $J_{PC} = 3.82$ Hz, Ar-*m*), 85.52 (s, C_5H_4), 70.05 (s, C_5H_5), 69.36 (s, C_5H_4), 66.99 (s, C_5H_4), 66.82 (s, C_5H_4), 34.46 (s, *p*-*C*H(CH_3)$_2$), 32.53 (d, $J_{PC} =$ 18.06 Hz, Tip-*o*-*C*H(CH_3)$_2$), 32.48 (d, $J_{PC} = 17.26$ Hz, Ar-*o*-*C*H-(CH_3)$_2$), 25.07 (s, *o*-CH(*C*H_3)$_2$), 25.00 (s, *o*-CH(*C*H_3)$_2$), 24.94 (s, *o*-CH(*C*H_3)$_2$), 24.11 (s, *p*-CH(*C*H_3)$_2$), 24.00 (s, *p*-CH(*C*H_3)$_2$), 23.65 (s, *o*-CH(*C*H_3)$_2$), 23.51 (s, *o*-CH(*C*H_3)$_2$), 23.31 (s, *o*-CH(*C*H_3)$_2$); ^{31}P NMR (162 MHz, C_6D_6) δ −50.9 (s); IR (KBr) 2966, 2929, 2906, 2887, 2864, 2825, 2806, 2763, 1600, 1462, 1383, 1104, 1028, 816, and 507 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 443 (3.34), 351 nm (4.47); FABMS *m*/*z* (rel intensity) 924 (M^+; 100), 804 ($M^+ -$ Fe − Cp; 6), 721 ($M^+ -$ Tip; 2), 579 ($M^+ -$ FcAr; 13), 330 (M^+ − FcAr − Tip − CH_3; 22); FT-ICR-MS (ESI, positive) *m*/*z* found 924.4153. Calcd for $C_{59}H_{73}PFe_2^+$: M^+, 924.4143. Found: C, 76.29; H, 8.14%. Calcd for $C_{59}H_{73}PFe_2$: C, 76.62; H, 7.96%.

Tris(4-ferrocenyl-2,6-diisopropylphenyl)phosphine (5c). To a solution of **6** (89.6 mg, 0.21 mmol) in tetrahydrofuran (6 mL) was added butyllithium (0.16 mL, 1.58 M in hexane) at −78 °C. The reaction mixture was stirred for 30 min, CuCl (23 mg, 0.23 mmol) was added through a solid-dropping tube at −78 °C, and the mixture was stirred for 1 h at −78 °C. A solution of **7** (79.8 mg, 0.10 mmol) in tetrahydrofuran (5 mL) was added into a dark-green suspension of the arylcopper(I) reagent at −78 °C, and the mixture was stirred for 30 min at −78 °C, refluxed for 12 h, and cooled to room temperature. The reaction mixture was concentrated in vacuo and purified by column chromatography (Al_2O_3, hexane, AcOEt:hexane = 1:12) to afford **5c** (25 mg, 0.023 mmol, 23%). **5c**: Orange solid, mp 191−191 °C (dec); ^{1}H NMR (400 MHz, C_6D_6) δ 7.49 (d, 6H, $J = 3.19$ Hz, arom), 4.66 (d, 6H, $J = 1.56$ Hz, C_5H_4), 4.20 (t, 6H, $J = 1.66$ Hz, C_5H_4), 4.02 (s, 15H, C_5H_5), 3.92 (m, 6H, *o*-C*H*(CH_3)$_2$), 1.49 (d, 18H, $J = 6.69$ Hz, *o*-CH(C*H*$_3$)$_2$), 1.09 (d, 18H, $J = 6.63$ Hz, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, C_6D_6) δ 153.54 (d, $J_{PC} =$ 18.34 Hz, *o*-arom), 140.65 (s, *p*-arom), 132.72 (d, $J_{PC} = 23.02$ Hz, *ipso*-arom), 122.38 (d, $J_{PC} = 4.39$ Hz, *m*-arom), 85.50 (s, C_5H_4), 70.07 (s, C_5H_5), 69.39 (s, C_5H_4), 67.03 (s, C_5H_4), 66.84 (s, C_5H_4), 32.53 (d, $J = 17.58$ Hz, *o*-*C*H(CH_3)$_2$), 25.04 (s, *o*-CH(*C*H_3)$_2$), 23.55 (s, *o*-CH(*C*H_3)$_2$); ^{31}P NMR (162 MHz, C_6D_6) δ −51.0 (s); IR (KBr) 2966, 2941, 2929, 2906, 2889, 2866, 1601, 1543, 1460, 1417, 1385, 1103, 1065, 1026, 1003, 881, 816, 791, and 507 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 450sh (3.34), 357 nm (4.39); FABMS *m*/*z* (rel intensity) 1066 (M^+; 100), 946 ($M^+ -$ Fe − Cp; 7), 721 (M^+ − FcAr; 20), 330 (M^+ − FcAr − *i*-Pr; 67); FT-ICR-MS (ESI, positive) *m*/*z* found 1066.3659. Calcd for $C_{66}H_{75}PFe_3^+$: M^+, 1066.3649. Found: C, 72.92; H, 7.03%. Calcd for $C_{66}H_{75}$-$PFe_3 \cdot 2C_2H_5OH$: C, 72.54; H, 7.57%.

X-ray Crystallography. Single-crystal data were collected using a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). A total of 51 5.00° oscillation images were collected, each being exposed for 25.0 min. The structure was solved by direct methods (SIR92),[19] expanded using Fourier techniques (DIRDIF94),[20] and refined by full matrix least squares on *F*. The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included but not refined. The structure solution, refinement, and graphical representation were carried out using the teXsan package.[21] Crystal data of **5c**$\cdot 0.5C_6H_{14}$: $C_{69}H_{82}Fe_3P$, $M = 1109.92$, orange platelet grown from hexane, crystal dimensions 0.45 × 0.45 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.3594(6)$, $b = 20.6361(7)$, $c =$ 10.6119(5) Å, $\alpha = 102.842(1)$, $\beta = 109.590(2)$, $\gamma = 90.417(3)°$, $V = 2876.9(2)$ Å^3, $D_c = 1.281$ g cm^{-3}, $\mu = 0.814$ mm^{-1}, $T =$ 90(1) K, $Z = 2$, $F(000) = 1178.00$. Of 25 230 reflections measured ($2\theta_{max} = 51.0°$), 10 086 were observed [$I > 0.0\sigma(I)$] ($R_{int} = 0.043$). Variable parameters 659. Goodness of fit $S = 1.28$ for observed reflections, and $R_1 = 0.038$ for $I > 2.0\sigma(I)$, $R = 0.048$, $R_w = 0.056$ for all reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.89 and −0.71 e Å^{-3}, respectively. CCDC 261625.

Cyclic Voltammetry. Cyclic voltammetry was performed on a BAS CV-50W controller with glassy carbon, Pt wire, and Ag/0.01 M $AgNO_3$/0.1 M *n*-$BuNClO_4/CH_3CN$ as working, counter, and reference electrodes, respectively [$E_{1/2}$(ferrocene/ferricinium) = 0.18 V]. A substrate ca. 10^{-4} M was dissolved in dichloromethane with 0.1 M *n*-Bu_4NClO_4 as a supporting electrolyte, and the solution was degassed by bubbling with nitrogen gas.

EPR Measurement. X-band EPR spectra were measured on a Bruker ESP300E spectrometer. Samples were dissolved in dichloromethane, which was distilled over calcium hydride, degassed by freeze-and-thaw cycles, and transferred to a sample by bulb-to-bulb distillation. Oxidation was carried out in a H-shaped sealed tube. An Oxford ESR900 continuous flow liquid helium cryostat was used for the variable-temperature measurement at cryogenic temperature.

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Supporting Information Available: Osteryoung square wave voltammograms of **5b** and **5c**, EPR spectrum of the cation radical of **6**, and crystallographic information files (CIF) of **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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