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Ferrocenyl-Capped *p*-Phenylenediamine as a Redox-Switching System

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Terminal redox-active ferrocenyl groups were introduced into the redox-active *p*-phenylenediamine bridging spacer, which can be oxidized to the *p*-quinonediimine, to provide a redox-switching system with electronic communication between the ferrocenyl groups through the redox-active π-conjugated bridging spacer. The communication was controlled by redox interconversion between the *p*-phenylenediamine and *p*-quinonediimine spacers. Furthermore, two palladium complexes were demonstrated to be introduced to the oxidized quinonediimine moiety, affording the multimetallic complex, in which the complexed quinonediimine serves as an electron sink.

Introduction

Bimetallic complexes composed of terminal redox-active transition metals and π-conjugated bridging spacers have received much attention as functional materials, in which interest has been focused on the electronic communication through the π-conjugated spacers.[1] Control of the communication between the terminal redox-active transition metals through the π-conjugated spacer is required to apply to a wide variety of molecular devices.[2] Redox switching for electronic communication by changing the redox states of the π-conjugated spacer in the conjugated bimetallic complex has been investigated.[2a–2c,2f,2g,2l,2o] The phenylenediamine, the redox-active π-conjugated unit of polyanilines, exists in three redox forms: the neutral phenylenediamine, the partially oxidized phenylenediamine radical cation, and the oxidized quinonediimine. In the bimetallic [M–L–M] complex with a phenylenediamine bridging spacer, the delocalization of the oxidized [M^+–L–M] species by hole transfer ([M^+–L–M] = [M–L^+–M] = [M–L–M^+]) would be possible through the phenylenediamine bridging spacer, which is considered to be able to accommodate a hole with ease on the basis of the redox-active properties of the phenylenediamine. In contrast, further oxidation of the bridging spacer is not possible in the case of the oxidized quinonediimine bridging spacer. Also, the oxidation process of the phenylenediamine is irreversibile, which involves loss of two H^+. Once oxidized, the ligand cannot be rereduced easily without two H^+ being added. Thus, the oxidized quinonediimine becomes kinetically stabilized. From this point of view, redox switching for the electronic communication between terminal redox-active transition metals is envisioned to be achieved by the redox state of the redox-active phenylenediamine bridging spacer. In contrast, two nitrogen atoms of the *p*-quinonediimines have been revealed to be capable of participating in the complexation to afford the conjugated complexes.[3,4] In a previous paper, controlled complexation with the oxidized quinonediimine unit was demonstrated to afford the conjugated polymeric complex, the conjugated trimetallic macrocycle, or the conjugated bimetallic complex, depending on the coordination modes.[4] The complexation of the quinonediimine derivatives with transition metals is expected to afford the redox-active conjugated multimetallic complexes, in which the redox properties of the quinonediimine moiety would be modulated. In this context, we embarked upon the introduction of terminal redox-active transition metals into the redox-active *p*-phenylenediamine bridging spacer to provide a new class of redox-switching system for electronic communication through the π-conjugated bridging spacer, and the redox-active conjugated multimetallic complex based on the introduction of the palladium(II) complexes into the oxidized quinonediimine moiety.

Results and Discussion

p-Phenylenediamine **1** bearing terminal ferrocene moieties was synthesized by $Pd_2(dba)_3$/(±)-BINAP catalyzed amination of 4-bromophenylferrocene with *p*-phenylenediamine in 26% yield. The X-ray crystal structure of **1** reveals a twist conformation of the *p*-phenylenediamine spacer as shown in Figure 1. Selected bond lengths and angles are listed in Table 1. π-Conjugation of **1** would require the orientation of each phenylene ring within a limited range of locations parallel to the Cp ring. Steric interactions, however, rotate each phenylene ring away from this

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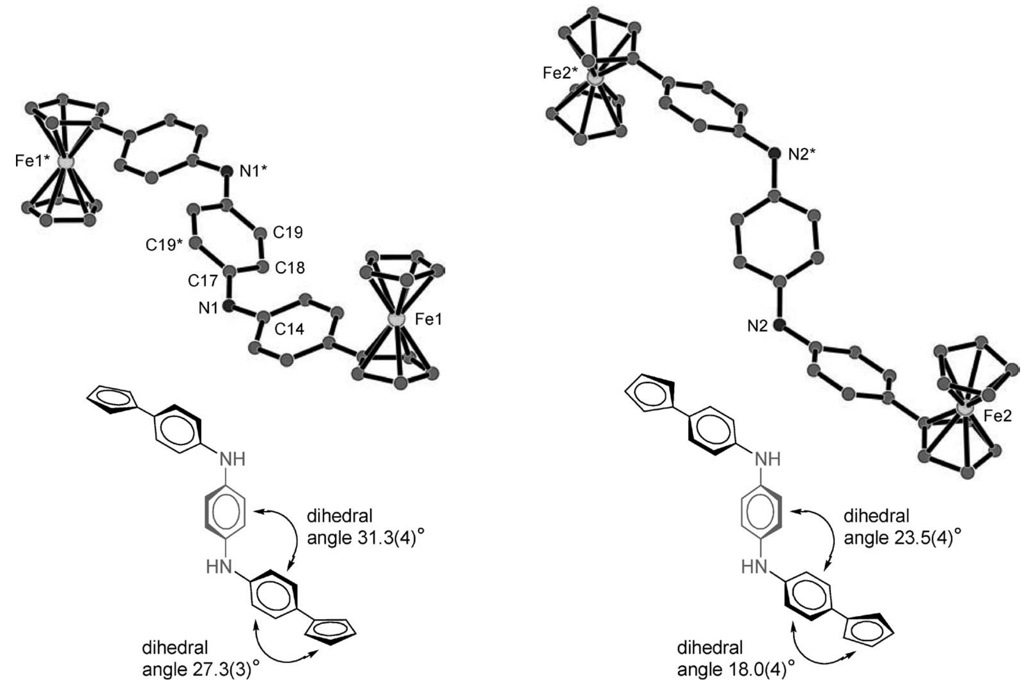
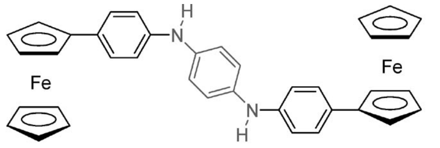


Figure 1. Molecular structure of **1** (hydrogen atoms are omitted for clarity). Two independent molecules exist in an asymmetric unit.

orientation, resulting in a twisted conformation to set an observed dihedral angle of 27.3(3)° between the phenylene and Cp planes and 31.3(4)° between the phenylene and central phenylene planes. Furthermore, two independent molecules exist in an asymmetric unit to adopt the opposite twist conformation. Another molecule showed a dihedral angle of 18.0(4)° between the phenylene and Cp planes, and 23.5(4)° between the phenylene and central phenylene planes.



1

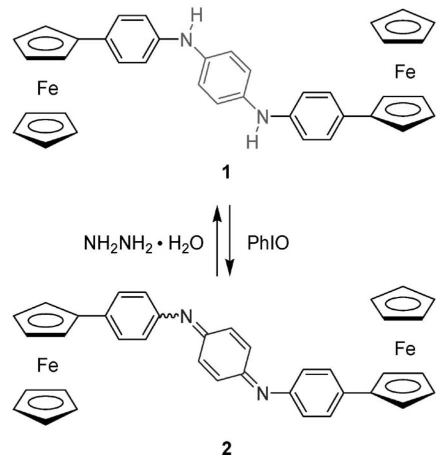
p-Phenylenediamine **1** was readily oxidized with PhIO to give *p*-quinonediimine **2** (Scheme 1). In the ^{1}H NMR spectrum of **2**, two sets of peaks attributable to the *syn*- and *anti*-quinonediimine isomers (1:1 ratio) were observed at 298 K in CD_2Cl_2. In contrast, **2** was quantitatively reduced to **1** with $NH_2NH_2{\cdot}H_2O$.

The redox properties of **1** and **2** were investigated by cyclic voltammetry. *p*-Phenylenediamine derivative **1** in dichloromethane exhibited four one-electron redox waves ($E_{1/2}$ = –0.13, –0.03, 0.16, 0.49 V vs. Fc/Fc$^+$) as shown Figure 2a. The waves at –0.13 and –0.03 V are assigned to the successive one-electron oxidation processes of the ferrocene moieties, and the waves at 0.16 and 0.49 V are assignable to the successive one-electron oxidation of the phenylenediamine moiety. The electronic communication was observed through the *p*-phenylenediamine bridging spacer. The extent of the ferrocenyl–ferrocenyl interaction is estimated from the wave splitting, $\Delta E_{1/2}$ = 0.10 V. The corresponding equilibrium constant (K_c) for the comproportionation reaction ([Fc–Fc] + [Fc$^+$–Fc$^+$] = 2 [Fc$^+$–Fc]) is 49, indicating that the partially oxidized **1**$^+$ could be classified as a Class II mixed-valence species according to the Robin–Day classification.[5] According to the cyclic voltammogram of **1**, phenylenediamine-based oxidation occurs after the two Fc/

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **4***anti*.

	1[a,b]		**4***anti*[a,b]	
Bond lengths				
N1–C14	1.41(1)	1.38(2)	1.43(1)	1.44(1)
N1–C17	1.40(1)	1.40(2)	1.29(1)	1.33(2)
C17–C18	1.399(10)	1.39(1)	1.44(2)	1.44(2)
C17–C19	–	1.38(2)	1.47(1)	1.42(1)
C17–C19*	1.38(1)	–	–	–
C18–C19	1.38(1)	–	–	–
C18–C19*	–	1.36(2)	1.36(2)	1.35(2)
Pd1–N1	–	–	2.045(8)	2.059(8)
Pd1–N2	–	–	1.925(9)	1.939(9)
Pd1–N3	–	–	2.027(9)	1.99(1)
Pd1–N4	–	–	2.008(9)	2.03(1)
Bond angles				
C14–N1–C17	125.9(6)	125.6(8)	120.6(8)	122.6(9)
N1–Pd1–N2	–	–	177.2(4)	179.0(4)
N1–Pd1–N3	–	–	98.3(4)	99.3(4)
N1–Pd1–N4	–	–	101.2(3)	98.3(4)
N2–Pd1–N3	–	–	79.7(4)	80.8(5)
N2–Pd1–N4	–	–	80.9(4)	81.5(5)
N3–Pd1–N4	–	–	160.6(4)	162.4(5)
Pd1–N1–C14	–	–	116.2(6)	115.1(7)
Pd1–N1–C17	–	–	123.1(7)	122.0(7)

[a] The molecule sits on an inversion center. [b] Two independent molecules exist in the asymmetric unit.



Scheme 1. Redox interconversion between **1** and **2**.

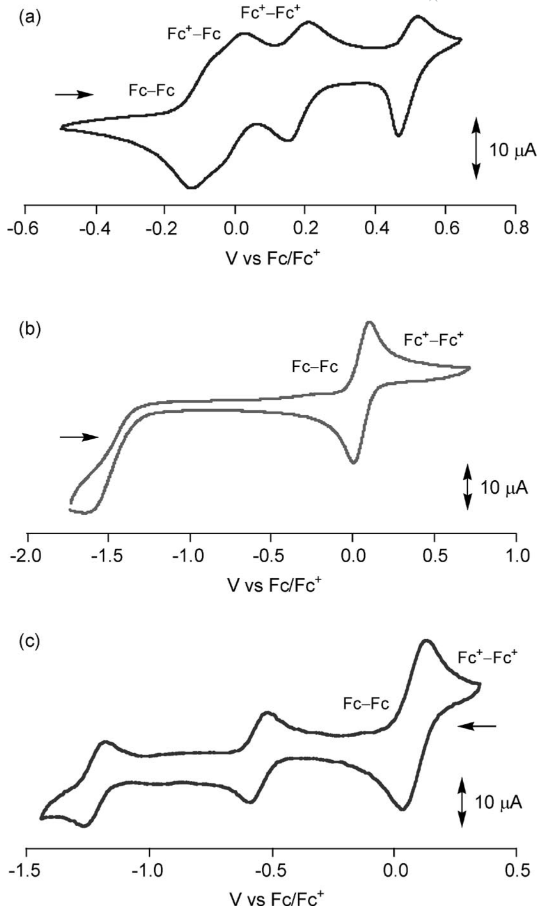
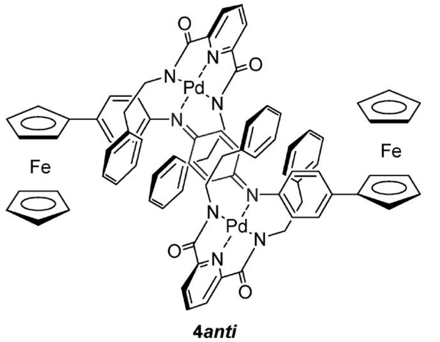


Figure 2. Cyclic voltammograms of (a) **1**, (b) **2**, and (c) **4** in dichloromethane (5.0×10^{-4} M) containing 0.1 M Bu_4NBF_4 at a glassy carbon working electrode with scan rate 100 mV s^{-1} under an atmosphere of Ar.



4*anti*

Fc^+ oxidations. However, the chemical oxidation of compound **1** results in phenylenediamine-based oxidation, but not metal-based oxidation. It is likely to be related to the irreversibility of the phenylenediamine-based oxidation process accompanied with loss of two H^+. Once oxidized, rereduction of the ligand cannot occur easily without two H^+ being added, which are not available from an organic solvent. Thus, the kinetically stabilized quinonediimine might be formed. The result of **1** is in sharp contrast to the redox behavior of **2** in dichloromethane, in which the redox couples of the quinonediimine and ferrocene moieties were observed as an irreversible reduction wave at –1.66 V and a simultaneous oxidation wave of two ferrocenyl moieties at 0.005 V, respectively (Figure 2b). In the case of oxidized form **2**, the electronic communication between the terminal ferrocene moieties was suppressed. These findings indicate that the redox switching for the electronic communication is achieved by the redox-active *p*-phenylenediamine bridging spacer. This phenomenon is likely to depend on the mechanism of intervalence charge transfer. Oxidized species $\mathbf{1}^+$ ([Fc^+–L–Fc]) generated by oxidation of **1** would be delocalized by hole transfer ([Fc^+–L–Fc] = [Fc–L^+–Fc] = [Fc–L–Fc^+]) through the *p*-phenylenediamine bridging spacer, which could accommodate a hole with ease. This delocalization depends on the redox properties of the *p*-phenylenediamine moiety. The *p*-phenylenediamine is well known to be readily oxidized to the partially oxidized phenylenediamine radical cation and then to the quinonediimine. In contrast, further oxidation of the bridging spacer is not possible in the case of the *p*-quinonediimine bridging spacer, and the delocalization by hole transfer is restricted.

Complexation of **2** with the palladium(II) complex [(L^1)-Pd(MeCN)] (**3**) bearing one interchangeable coordination site, which was prepared by treatment of $Pd(OAc)_2$ with the N-heterocyclic tridentate podand ligand *N*,*N′*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide (L^1H_2),[4a,6] led to the formation of the conjugated palladium homobimetallic complex [(L^1)Pd(**2**)Pd(L^1)] (**4**). The X-ray crystal structure of 1:2 complex **4** indicates that it is present as **4***anti* with an *anti* configuration in a crystal state with the two [(L^1)Pd] units bridged by the quinonediimine spacer as shown in Figure 3. Selected bond lengths and angles are listed in Table 1. The twist conformation is verified by a dihedral angle of 15.8(5)° between the phenylene and Cp planes and an angle of 21.9(4)° between the phenylene and quinonediimine planes. Two independent molecules exist in an asymmetric unit. Another molecule showed a dihedral angle of 5.2(5)° between the phenylene and Cp planes, and 43.1(4)° between the phenylene and central phenylene planes. Two independent molecules showed different orientations of the terminal ferrocenyl groups probably due to packing interactions.

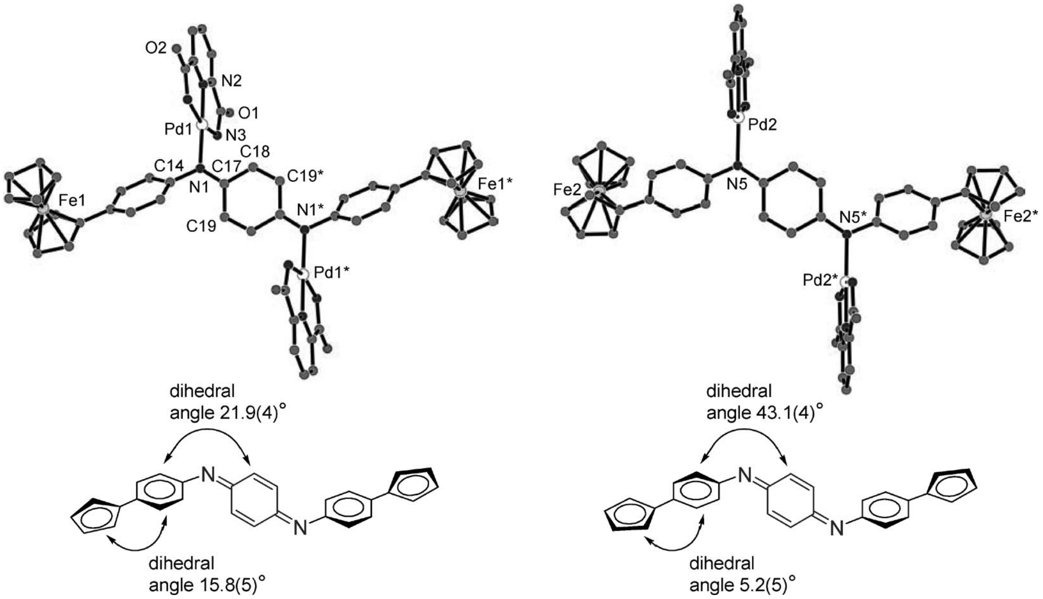


Figure 3. Molecular structure of **4***anti* (the phenylethyl moieties and hydrogen atoms are omitted for clarity). Two independent molecules exist in an asymmetric unit.

The cyclic voltammogram of conjugated complex **4** in dichloromethane exhibited three separate redox waves at $E_{1/2}$ = –1.25, –0.57, 0.07 V vs. Fc/Fc$^+$ as shown in Figure 2c. The waves at –1.25 and –0.57 V are assignable to the successive one-electron reduction of the quinonediimine moiety. The redox wave of the ferrocene moieties was observed as one wave at 0.07 V, indicating no electronic communication between the terminal ferrocene moieties. The ESR spectrum of $\mathbf{4}^{\cdot-}$ in dichloromethane showed signals centered at g = 2.006 with hyperfine coupling (A_N = 6.2 G; A_H = 1.2 G; A_{Pd} = 3.2 G). The unpaired electron appears to be located mostly on the quinonediimine moiety, although some delocalization onto the metals is suggested by the weak satellite lines due to ^{105}Pd coupling.

Conclusions

Terminal redox-active ferrocenyl groups were introduced into a redox-active *p*-phenylenediamine bridging spacer, which could be oxidized to a *p*-quinonediimine. The redox-switching for electronic communication between the ferrocenyl groups was achieved, and it depends on the irreversibility of the phenylenediamine-based oxidation process concomitant with the loss of two H$^+$ and the kinetically stabilized quinonediimine. The present switching system utilizing the redox properties of the π-conjugated bridging ligands is considered to provide a useful approach to molecular switching materials. Furthermore, the two palladium complexes were introduced to the oxidized quinonediimine moiety to afford a multimetallic complex, in which the incorporated metals play an important role as metallic dopants and the complexed quinonediimine serves as an electron sink. Generally, the radical anion generated by reduction of the quinonediimine moiety appears to be unstable, although this depends on the availability of a proton source.[7] In the complexed quinonediimine, the added electrons are considered to be delocalized over the Pd^{II}–quinonediimine d–π* system. The redox-active conjugated complexes composed of the redox-active conjugated spacers are envisioned to provide not only functional electronic materials, but also redox catalysts.

Experimental Section

General: *p*-Phenylenediamine was obtained from Wako Pure Chemical Co., Ltd and purified by recrystallization from absolute ethanol. $Pd_2(dba)_3$, (±)-BINAP, and *t*BuONa were purchased from Aldrich. PhIO was obtained from Tokyo Chemical Industry Co., Ltd. 4-Bromophenylferrocene was prepared according to the literature.[8] Toluene and dichloromethane used as solvents were purified and dried by standard methods.[9] *N*,*N'*-Bis(2-phenylethyl)-2,6-pyridinedicarboxamide (L^1H_2) and the palladium(II) complex [(L^1)-Pd(MeCN)] (**3**) were prepared according to the method reported in a previous paper.[4a,6] Melting points were determined with a Yanagimoto Micromelting Point Apparatus and are uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 Plus spectrometer. ^{1}H NMR spectra were recorded with Varian MERCURY 300 (300 MHz) and JEOL JNM-ECP400 (400 MHz) spectrometers with tetramethylsilane as an internal standard. Mass spectra were run with a JEOL JMS-700 mass spectrometer.

Synthesis of 1 Bearing the Terminal Ferrocenyl Groups: 4-Bromophenylferrocene (102.3 mg, 0.30 mmol), *p*-phenylenediamine (16.2 mg, 0.15 mmol), $Pd_2(dba)_3$ (27.4 mg, 0.03 mmol), (±)-BINAP (37.2 mg, 0.06 mmol), and *t*BuONa (40.3 mg, 0.42 mmol) were mixed in toluene (8.0 mL). The reaction mixture was heated at refluxed under an atmosphere of Ar for 24 h. The reaction mixture was then cooled to room temperature, diluted with dichloromethane, and washed with water. The aqueous layer was then extracted with dichloromethane, and the combined organic layer was dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was chromatographed on alumina column (30% of ethyl acetate/hexane). *p*-Phenylenediamine **1** was isolated in 26% as an orange platelet crystal by recrystallization from dichloromethane/hexane. M.p. 175–176 °C (decomp.). IR (KBr): ṽ = 3384, 3081, 3039, 1610, 1529, 1508, 1452 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.37 (d, *J* = 8.7 Hz, 4 H), 7.08 (s, 4 H), 6.94 (d, *J* = 8.7 Hz, 4 H), 5.69 (br. s, 2 H), 4.58 (t, *J* = 1.8 Hz, 4 H), 4.26 (t, *J* = 1.8 Hz, 4 H), 4.04 (s, 10 H) ppm. MS (FAB): *m*/*z* = 628 [M$^+$]. $C_{38}H_{32}Fe_2N_2{\cdot}0.5H_2O$ (637.37): calcd. C 71.61, H 5.22, N 4.39; found C 71.88, H 5.07, N 4.47.

Synthesis of 2 Bearing the Terminal Ferrocenyl Groups: A mixture of phenylenediamine **1** (12.6 mg, 0.02 mmol) and PhIO (4.4 mg, 0.02 mmol) in dichloromethane (5.0 mL) was stirred under an atmosphere of Ar at room temperature for 1 h. The resulting mixture was filtered, and the filtrate was evaporated in vacuo. Quinonediimine **2** was isolated quantitatively as a violet solid by washing the residue with acetonitrile. M.p. 138–140 °C (decomp.). IR (KBr): ṽ = 3079, 3055, 2923, 2853, 1594, 1575, 1559, 1508, 1474, 1441 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, *syn*:*anti* = 1:1.2): δ = 7.53 (d, *J* = 8.7 Hz, 4 H, *anti*), 7.50 (d, *J* = 8.7 Hz, 4 H, *syn*), 7.12–7.11 (m, 2 H, *syn*), 7.05–6.98 (m, 4 H, *anti*), 6.90–6.89 (m, 2 H, *syn*), 6.88 (d, *J* = 8.7 Hz, 4 H, *anti*), 6.86 (d, *J* = 8.7 Hz, 4 H, *syn*), 4.70 (t, *J* = 1.9 Hz, 4 H, *anti*), 4.67 (t, *J* = 1.9 Hz, 4 H, *syn*), 4.37 (t, *J* = 1.9 Hz, 4 H, *anti*), 4.35 (t, *J* = 1.9 Hz, 4 H, *syn*), 4.06 (s, 10 H, *anti*), 4.06 (s, 10 H, *syn*) ppm. HRMS (FAB) calcd. for $C_{38}H_{30}N_2Fe_2$ [M]$^+$ 626.1108; found 626.1117.

Preparation of the Conjugated Palladium Homobimetallic Complex [(L^1)Pd(2)Pd(L^1)] (4): A mixture of quinonediimine **2** (6.26 mg, 0.01 mmol) and [(L^1)Pd(MeCN)] (**3**; 10.4 mg, 0.02 mmol) was stirred in dichloromethane (2.0 mL) under an atmosphere of Ar at room temperature for 2 h. After evaporation of the solvent, the homobimetallic complex **4** was isolated quantitatively as a dark-blue solid. M.p. 187–189 °C (decomp.). IR (KBr): ṽ = 3082, 3057, 3023, 2923, 2853, 1592, 1577, 1559, 1507, 1462 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, *syn*:*anti* = 1:1.6): δ = 9.19 (s, 2 H, *syn*), 8.98 (dd, *J* = 10.3, 2.2 Hz, 2 H, *anti*), 8.09 (t, *J* = 8.1 Hz, 2 H, *anti*), 8.07 (t, *J* = 8.1 Hz, 2 H, *syn*), 7.74 (d, *J* = 8.0 Hz, 4 H, *anti*), 7.73 (d, *J* = 8.0 Hz, 4 H, *syn*), 7.71 (d, *J* = 8.8 Hz, 4 H, *anti*), 7.67 (d, *J* = 8.8 Hz, 4 H, *syn*), 7.62 (dd, *J* = 10.3, 2.2 Hz, 2 H, *anti*), 7.58 (d, *J* = 8.8 Hz, 4 H, *anti*), 7.56 (d, *J* = 8.8 Hz, 4 H, *syn*), 7.33 (s, 2 H, *syn*), 7.08 (t, *J* = 7.0 Hz, 16 H, *syn* and *anti*), 7.01 (t, *J* = 7.0 Hz, 8 H, *syn* and *anti*), 6.92 (d, *J* = 7.0 Hz, 8 H, *syn*), 6.87 (d, *J* = 7.0 Hz, 8 H, *anti*), 4.80 (t, *J* = 1.8 Hz, 4 H, *syn*), 4.76 (t, *J* = 1.8 Hz, 4 H, *anti*), 4.56 (t, *J* = 1.8 Hz, 4 H, *syn*), 4.53 (t, *J* = 1.8 Hz, 4 H, *anti*), 4.04 (s, 5 H, *syn*), 4.00 (s, 5 H, *anti*), 3.31–3.16 (m, 8 H, *syn* and *anti*), 2.93–2.86 (m, 8 H, *syn* and *anti*), 2.66–2.53 (m, 8 H, *syn* and *anti*), 2.44–2.34 (m, 8 H, *syn* and *anti*) ppm. HRMS (FAB) calcd. for $C_{84}H_{72}N_8O_4Fe_2Pd_2$ [M]$^+$ 1582.2488; found 1582.2506. $C_{84}H_{72}Fe_2N_8O_4Pd_2{\cdot}0.5CH_2Cl_2$ (1624.52): calcd. C 62.47, H 4.53, N 6.90; found C 62.82, H 4.55, N 6.72.

Electrochemical Experiments: Cyclic voltammetry was performed with a BAS CV-50W voltammetry analyzer in deaerated dichloromethane containing 0.1 M Bu_4NBF_4 as a supporting electrolyte under an atmosphere of Ar at 298 K with a three-electrode system consisting of a platinum working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/AgCl (0.01 M) reference electrode (BAS) at 100 mV s^{-1} scan rate. Redox potentials are given vs. Fc/Fc$^+$.

ESR Spectrum Measurement: All glassware was flame dried prior to measurement and cooled under an atmosphere of Ar. Solvents were purified by the standard methods and deaerated with Ar or freeze–pump–thaw degassed prior to use. ESR spectrum was taken under an atmosphere of Ar at 286 K by using a Bruker ESP 300 spectrometer. For spectroscopic purposes, $\mathbf{4}^{\cdot-}$ was generated by treatment of **4** with 1 equiv. of cobaltocene in dichloromethane under an atmosphere of Ar at room temperature. The *g* value was calibrated by using an Mn^{2+} marker.

X-ray Structural Analysis: All measurements for **1** and **4***anti* were made with a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K_α radiation. The structure of **1** was solved by direct methods and expanded by using Fourier techniques. Non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. The structure of **4***anti* was solved by heavy-atom Patterson methods and expanded by using Fourier techniques. Non-hydrogen atoms excluding the C30–34, C39–43, C80–81, C84, and C87–93 carbon atoms were refined anisotropically. Dichloromethane solvent molecule was treated isotropically. Some carbon atoms of the main complex were tried for modeling the disorder. However, a good result was not obtained probably due to the data quality. In this context, the C30–34, C39–43, C80–81, C84, and C87–93 carbon atoms were refined isotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are summarized in Table 2. CCDC-633394 (for **1**) and -633395 (for **4***anti*) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data for **1** and **4***anti*.

	1	**4***anti*
Empirical formula	$C_{38}H_{32}N_2Fe_2$	$C_{84}H_{72}N_8O_4Fe_2Pd_2{\cdot}0.5CH_2Cl_2$
Formula weight	628.36	1624.52
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)
a [Å]	8.0682(3)	22.921(1)
b [Å]	13.2113(7)	25.069(1)
c [Å]	14.1620(5)	29.802(1)
α [°]	70.863(3)	
β [°]	89.589(1)	100.015(1)
γ [°]	89.607(3)	
V [Å^3]	1426.1(1)	16863(1)
Z	2	8
$D_{\text{calcd.}}$ [g cm^{-3}]	1.463	1.280
μ(Mo-K_α) [cm^{-1}]	10.48	8.39
T [°C]	4	4
λ(Mo-K_α) [Å]	0.71069	0.71069
R_1[a]	0.081	0.108
wR_2[b]	0.226	0.294

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Supporting Information (see footnote on the first page of this article): ESR spectrum of $\mathbf{4}^{\cdot-}$.

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[1] For reviews, see: a) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759; b) A. Harriman, J.-P. Sauvage, *Chem. Soc. Rev.* **1996**, *25*, 41; c) F. Paul, C. Lap-

inte, *Coord. Chem. Rev.* **1998**, *178/180*, 431; d) R. Ziessel, M. Hissler, A. El-ghayoury, A. Harriman, *Coord. Chem. Rev.* **1998**, *178/180*, 1251; e) J. A. McCleverty, M. D. Ward, *Acc. Chem. Res.* **1998**, *31*, 842; f) P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863; g) A. Ceccon, S. Santi, L. Orian, A. Bisello, *Coord. Chem. Rev.* **2004**, *248*, 683; h) K. Venkatesan, O. Blacque, H. Berke, *Dalton Trans.* **2007**, 1091; i) Y. Yamanoi, H. Nishihara, *Chem. Commun.* **2007**, 3983.

[2] a) P. R. Auburn, A. B. P. Lever, *Inorg. Chem.* **1990**, *29*, 2551; b) L. F. Joulié, E. Schatz, M. D. Ward, F. Weber, L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.* **1994**, 799; c) M. D. Ward, *Chem. Soc. Rev.* **1995**, *24*, 121; d) G. A. Neyhart, J. T. Hupp, J. C. Curtis, C. J. Timpson, T. J. Meyer, *J. Am. Chem. Soc.* **1996**, *118*, 3724; e) G. A. Neyhart, C. J. Timpson, W. D. Bates, T. J. Meyer, *J. Am. Chem. Soc.* **1996**, *118*, 3730; f) M. D. Ward, *Chem. Ind.* **1997**, 640; g) T. E. Keyes, R. J. Forster, P. M. Jayaweera, C. G. Coates, J. J. McGarvey, J. G. Vos, *Inorg. Chem.* **1998**, *37*, 5925; h) S. Fanni, C. Di Pietro, S. Serroni, S. Campagna, J. G. Vos, *Inorg. Chem. Commun.* **2000**, *3*, 42; i) S. Fraysse, C. Coudret, J.-P. Launay, *Eur. J. Inorg. Chem.* **2000**, 1581; j) R. C. Rocha, H. E. Toma, *Inorg. Chem. Commun.* **2001**, *4*, 230; k) A. Tárraga, P. Molina, D. Curiel, M. D. Velasco, *Organometallics* **2001**, *20*, 2145; l) R. H. Laye, S. M. Couchman, M. D. Ward, *Inorg. Chem.* **2001**, *40*, 4089; m) C. Di Pietro, S. Serroni, S. Campagna, M. T. Gandolfi, R. Ballardini, S. Fanni, W. R. Browne, J. G. Vos, *Inorg. Chem.* **2002**, *41*, 2871; n) A. Tárraga, P. Molina, D. Curiel, M. D. Velasco, *Tetrahedron Lett.* **2002**, *43*, 8453; o) A. P. Meacham, K. L. Druce, Z. R. Bell, M. D. Ward, J. B. Keister, A. B. P. Lever, *Inorg. Chem.* **2003**, *42*, 7887; p) H. Tannai, K. Tsuge, Y. Sasaki, *Inorg. Chem.* **2005**, *44*, 5206; q) C. N. Carlson, B. L. Scott, R. L. Martin, J. D. Thompson, D. E. Morris, K. D. John, *Inorg. Chem.* **2007**, *46*, 5013.

[3] a) E. F. G. Herington, *J. Chem. Soc.* **1959**, 3633; b) K. Rieder, U. Hauser, H. Siegenthaler, E. Schmidt, A. Ludi, *Inorg. Chem.* **1975**, *14*, 1902; c) H.-Y. Cheng, G.-H. Lee, S.-M. Peng, *Inorg. Chim. Acta* **1992**, *191*, 25; d) D. Conner, K. N. Jayaprakash, T. B. Gunnoe, P. D. Boyle, *Organometallics* **2002**, *21*, 5265.

[4] a) T. Moriuchi, S. Bandoh, M. Miyaishi, T. Hirao, *Eur. J. Inorg. Chem.* **2001**, 651; b) T. Moriuchi, M. Miyaishi, T. Hirao, *Angew. Chem. Int. Ed.* **2001**, *40*, 3042; c) T. Moriuchi, M. Kamikawa, S. Bandoh, T. Hirao, *Chem. Commun.* **2002**, 1476; d) T. Hirao, *Coord. Chem. Rev.* **2002**, *226*, 81; e) T. Hirao (Ed.), *Redox Systems Under Nano-Space Control*, Springer, Berlin, **2006**; f) T. Moriuchi, J. Shiori, T. Hirao, *Tetrahedron Lett.* **2007**, *48*, 5970.

[5] a) M. Robin, P. Day, *Adv. Inorg. Radiochem.* **1967**, *10*, 247; b) C. Creutz, *Prog. Inorg. Chem.* **1981**, *30*, 1. A Class II system presents a weak interaction between the two homometals (preserving some properties of the monomer), which is expected because of the distance between the two metals given by the spacer.

[6] T. Moriuchi, S. Bandoh, Y. Miyaji, T. Hirao, *J. Organomet. Chem.* **2000**, *599*, 135.

[7] G. E. Wnek, *Synth. Met.* **1986**, *15*, 213.

[8] M. Iyoda, T. Kondo, T. Okabe, H. Matsuyama, S. Sasaki, Y. Kuwatani, *Chem. Lett.* **1997**, *26*, 35.

[9] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Butterworth Heinemann, Amsterdam, The Netherlands, **2003**.

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