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Synthesis and properties of diiron complexes with heteroaromatic linkers: An approach for modulation of organometallic molecular wire

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Dedicated to Professor Claude Lapinte for his invaluable contribution to organometallic chemistry.

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ABSTRACT

Metal complexes with two redox active organometallic Cp*(dppe)Fe—C≡C— units bridged with N-methylpyrrole (**3**), furan (**4**) and dipyrrolylethene (**6**) have been synthesized and characterized by ^{1}H and ^{31}P NMR, IR and ESI-MS spectroscopy as well as X-ray diffraction study (for **3**). Cyclic voltammograms of **3** and **4** show two reversible redox waves ascribed to iron centered redox processes, and the comproportionation constants (K_C) of their mixed valence species were determined to be 5.8×10^6 and 1.0×10^6, respectively. UV–Vis–NIR spectra of **3**$^+$ and **4**$^+$ contain intense absorption bands in the NIR region ascribed to intervalence charge transfer processes. The complexes with electronic coupling (V_{ab}) values of 2950 (**3**) and 2665 cm^{-1} (**4**) were classified as class III compounds according to the Robin–Day classification. These data suggest that the electronic interaction between the two iron centers is stronger than those of the *p*-phenylene and thienylene derivatives. Complex **6**, a pyrrole analogue of the photochromic dithienylethene complexes, turns out not to show photochromic behavior, indicating that the heteroaromatic component influenced significantly on photochromic behavior.

1. Introduction

Construction of molecule-based electronic circuits, which are usually composed of the π-conjugated carbon system, has been one of the important scientific challenges over the last several decades [1] since the report on molecular rectifier by Aviram and Ratner [2]. In this context, controlling and fine-tuning of the performance of molecular devices have been key issues for the development of molecular circuit. One of effective ways to functionalize the molecular devices is incorporation of heteroatom into the π-carbon backbone and, in fact, a variety of molecular devices containing heteroaromatic rings have been reported so far [3].

Molecules bearing redox active organometallic termini bridged by π-conjugated carbon linkers are expected to act as molecular wires, and their performance can be determined on the basis of the extent of stabilization of a hole or an electron generated upon 1e$^-$ oxidation or reduction, respectively, by delocalization over the bridging ligand [4–6]. Strong metal–carbon interaction resulting from π-backbonding from the metal filled d-orbitals to the empty ligand π*-orbitals allows long-distance metal–metal interactions and thus electron/hole transportation over the distance of nano-meter scale [4,6]. Particularly, organometallic molecular wires with Cp*Fe(dppe) termini, which was first developed by Lapinte [4a,5] and later by us [6], have attracted attention due to their rich electrochemical properties. A variety of diiron complexes with π-conjugated and non-conjugated linkers has been explored and their wire-like performance has been investigated [4a,6]. On the other hand, a limited number of examples of the molecular wires with heteroaromatic bridges have been studied so far [7]. Lapinte and coworkers have reported that a 2,5-diethynylthiophene-linked molecular wire **1** showed wire-like performance better than that of a 1,4-diethynylbenzene derivative **2** [8]. Furthermore, molecular wires bridged by diethynylpyridine shows distinct electronic interactions between the diiron fragments depending on the substitution patterns the pyridine ring [9]. We also reported that the benzodifuran- and benzodithiophene-linked molecular wires show good wire-like performance [10]. Organometallic molecular wires with heteroaromatic linkers, however, have not been always studied extensively.

Recently, we successfully developed photoswitchable molecular wires containing the photochromic dithienylethene linker [11]. The extent of the interaction between the metal centers and the efficiency of the photoswitching behavior can be tuned by varying the terminal metal fragments [11]. The influence of the heteroaromatic rings on organometallic molecular switches, however, remains to be uncovered. Herein, we disclose syntheses and properties of diiron molecular wires consisting of N-methylpyrrole-, furan- and dipyrrolylethene(DPE)-linkers with the Cp*Fe(dppe) end groups.

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2. Experimental

2.1. General methods

All manipulations were carried out under a N_2 atmosphere by using standard Schlenk tube techniques. THF and ether (Na–K alloy), CH_2Cl_2 (P_2O_5), and MeOH ($Mg(OMe)_2$) were treated with appropriate drying agents, distilled, and stored under nitrogen. ^1H and ^{31}P NMR spectra were recorded on Bruker AC-200 (^1H, 200 MHz; ^{31}P, 80 MHz) and JEOL JMN-EX-300 spectrometers (^1H, 300 MHz; ^{31}P 121.5 MHz). Solvents for NMR measurements were dried over molecular sieves, degassed, and stored under nitrogen.

UV–Vis and IR spectra (KBr pellets and in CH_2Cl_2) were obtained on a JASCO V570 and FTIR 5300 spectrometer, respectively. UV and visible-light irradiations were performed with an Ushio high-pressure mercury lamp (UM-452; $\lambda < 360$ nm with a U-360 cut-off filter). Electrochemical measurements (CV and DPV) were made with a BAS 100B/W analyzer (observed in CH_2Cl_2; [complex] = ca. 2×10^{-3} M; $[NBu_4PF_6] = 0.1$ M; working electrode: Pt, counter electrode: Pt, reference electrode: $Ag/AgNO_3$; scan rates were 100 mV/s (CV) and 20 mV/s (DPV)). After the measurement, ferrocene (Fc) was added to the mixture and the potentials were calibrated with respect to the Fc/Fc^+ redox couple. Simulations of the electrochemical and spectroscopic data were performed with Origin 7.5. Elemental analyses were performed at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. The di-ethynylated furan [15], pyrrole [16], and DPE [13] and the metal precursors [Cp*Fe(dppe)Cl] [17] were prepared by following the published procedures. Other chemicals were purchased and used as received. HOMO and LUMO energies were computed using Spartan10′ software [18]. The results of X-ray diffraction study of **3** have been deposited at the Cambridge Crystallographic Data Center (CCDC 989003).

2.2. Preparation of **3**

A mixture of 2,5-bis(trimethylsilylethynyl)-N-methylpyrrole (180 mg, 0.66 mmol) and 0.4 M KOH/MeOH solution (20 mL) was stirred for 1 h under ambient condition. After evaporation of the volatiles the residues were extracted with hexane and washed with H_2O. The separated organic phase was dried over Na_2SO_4. The filtrate was evaporated to give crude 2,5-diethynyl-N-methylpyrrole as an orange solid (81.0 mg, 0.627 mmol), which was subject to the next step without further purification. (2,5-diethynyl-N-methylpyrrole. ^1H NMR ($CDCl_3$): δ 3.35 (s, $C{\equiv}C{-}H$, 2H), 3.70 (s, N-CH_3, 3H), 6.38 (s, pyrrole, 2H)). A mixture of Cp*Fe(dppe)Cl (781 mg, 1.25 mmol), KPF_6 (253 mg, 1.38 mmol), and 2,5-diethynyl-N-methylpyrrole (81.0 mg, 0.627 mmol) was dissolved in MeOH/THF (10:3 mL) and stirred at r.t. for 18 h. The volatiles were removed under reduced pressure and the residue was washed with ether (5 mL × 3 times) to give the iron vinylidene intermediate. To a mixture of the iron vinylidene complex and THF (10 mL) was added *tert*-BuOK (100 mg, 0.893 mmol), and the mixture was stirred for 30 min at r.t. The volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2 and subjected to a short almina pad. The solvent was removed under reduced pressure and the residue was washed with pentane (5 mL × 3 times) and diethyl ether (5 mL × 3 times). Crystallization form CH_2Cl_2 and pentane afford **3** (409 mg, 0.313 mmol, 50%) as brown crystals. IR (KBr): 2049 cm^{-1} ($C{\equiv}C$). ^1H NMR (C_6D_6): δ 1.56 (s, Cp*, 30H), 1.88–2.72 (m, CH_2 in dppe, 8H), 3.36 (s, N–CH_3, 3H), 6.15 (s, pyrrole, 2H), 7.03–8.05 (m, Ph in dppe, 40H). ^{31}P NMR (C_6D_6): δ 101.5 (s, dppe). ESI-MS (*m/z*): Calc. for $C_{81}H_{83}Fe_2NP_4$ (**3**) 1305: Found 1305 $[M]^+$. UV–Vis (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 356 ($2.68 \times 10^4$). *Anal.* Calc. for $C_{81}H_{83}Fe_2NP_4$ (**3**): C, 74.49; H, 6.41; N, 1.07. Found: C, 74.17; H, 6.32; N, 1.06%.

2.3. Preparation of **4**

A mixture of Cp*Fe(dppe)Cl (625 mg, 1.00 mmol), KPF_6 (200 mg, 1.10 mmol), KF (65 mg, 1.10 mmol), and 2,5-bis(trimethylsilylethynyl)furan (130.0 mg, 0.500 mmol) was dissolved in MeOH/THF (10:1 mL) and stirred for 17 h at r.t. The volatiles were removed under reduced pressure. To a mixture of the residue and THF (10 mL) was added *tert*-BuOK (84 mg, 0.750 mmol), and the mixture was stirred for 1 h at r.t. The volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2 and passed through a Celite plug. The volatiles were removed under reduced pressure and the residue was crystallized from toluene and pentane, and then CH_2Cl_2 and pentane to give **4** (594 mg, 0.459 mmol, 92%) as brown powders. IR (KBr): 2040 cm^{-1} ($C{\equiv}C$). ^1H NMR (C_6D_6): δ 1.54 (s, Cp*, 30H), 1.82–2.67 (m, CH_2 in dppe, 8H), 6.04 (s, furan, 2H), 6.89–8.12 (m, Ph in dppe, 40H). ^{31}P NMR (C_6D_6): δ 100.7 (s, dppe). ESI-MS (*m/z*): Calc. for $C_{80}H_{80}Fe_2OP_4$ (**4**) 1293: Found 1293 $[M]^+$. UV–Vis (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 373 ($3.72 \times 10^4$). *Anal.* Calc. for $C_{80.2}H_{80.4}Cl_{0.4}Fe_2OP_4$ (**4** $\cdot(CH_2Cl_2)_{0.2}$): C, 73.53; H, 6.19. Found: C, 73.29; H, 6.48%.

2.4. Preparation of mono- and dicationic complexes

To a mixture of a neutral diiron complex (~0.03 mmol) and THF (10 mL) was added $[FeCp_2](PF_6)$ (1 equiv. for monocation and 2 equiv. for dication) at −78 °C, stirred for 15 min at the same temperature and then for 30 min at r.t. The volatiles were removed under reduced pressure and the residue was washed with diethyl ether (5 mL × 3 times) and recrystallized from CH_2Cl_2/pentane for monocation and from acetone/diethyl ether for dication.

$\mathbf{3}^+$: IR (CH_2Cl_2): 1978 cm^{-1} ($C{\equiv}C$). ESI-MS (*m/z*): Calc. for $C_{81}H_{83}Fe_2NP_4$ ($\mathbf{3}^+$) 1305: Found 1305 $[M{-}PF_6]^+$. UV–Vis–NIR (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 418 ($1.27 \times 10^4$), 448 ($1.55 \times 10^4$), 508 ($2.89 \times 10^4$), 712 ($2.60 \times 10^3$), 1690 ($3.09 \times 10^4$).

$\mathbf{3}^{2+}$: IR (CH_2Cl_2): 1937 cm^{-1} ($C{\equiv}C$). ^1H NMR (acetone-d_6): δ 1.41 (s, Cp*, 30H), 4.15 (s, N-CH_3, 3H), 6.89 (s, pyrrole, 2H), 7.27–7.79 (m, Ph in dppe, 40H). ^{31}P NMR (acetone-d_6): δ 86.8 (s, dppe), −142.8 (septet, $J_{P-F} = 706$ Hz). UV–Vis–NIR (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 263 ($5.78 \times 10^4$), 400 ($8.80 \times 10^3$), 863 ($7.87 \times 10^4$).

$\mathbf{4}^+$: IR (CH_2Cl_2): 1989 cm^{-1} ($C{\equiv}C$). ESI-MS (*m/z*): Calc. for $C_{80}H_{80}Fe_2OP_4$ ($\mathbf{4}^+$) 1293. Found 1293 $[M{-}PF_6]^+$. UV–Vis–NIR (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 259 ($6.64 \times 10^4$), 409 ($1.09 \times 10^4$), 543 ($1.80 \times 10^4$), 716 (sh, 2.70×10^3), 1858 (2.54×10^4).

$\mathbf{4}^{2+}$: IR (CH_2Cl_2): 1922 cm^{-1} (vw, $C{\equiv}C$). ^1H NMR (acetone-d_6): δ 1.41 (s, Cp*, 30H), 6.89 (s, furan, 2H), 7.27–7.79 (m, Ph in dppe, 40H). ^{31}P NMR (acetone-d_6): δ 82.3 (s, dppe), −142.8 (septet, $J_{P-F} = 706$ Hz). UV–Vis–NIR (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 270 ($5.24 \times 10^4$), 408 ($1.00 \times 10^4$), 767 ($5.64 \times 10^4$).

2.5. Preparation of **6**

The title complex was synthesized in a manner similar to that of the pyrrole complex **3** from Cp*Fe(dppe)Cl (781 mg, 1.25 mmol), KPF_6 (253 mg, 1.38 mmol), and diethynylated DPE (56.0 mg, 0.136 mmol). Yellow solid, 84%. IR (KBr): 2046 cm^{-1} ($C{\equiv}C$). ^1H NMR (C_6D_6): δ 1.52 (s, Cp*, 30H), 1.86 (s, pyrrole-CH_3, 6H), 1.86–2.55 (m, CH_2 in dppe, 8H), 2.80 (s, N–CH_3, 6H), 6.45 (s, pyrrole, 2H), 6.90–7.95 (m, Ph in dppe, 40H). ^{31}P NMR (C_6D_6): δ 100.9 (s, dppe). HR-ESI-MS (*m/z*): Calc. for $C_{93}H_{92}F_6N_2P_4Fe_2$ (**6**) 1586.4813. Found 1586.3986 $[M]^+$. UV–Vis–NIR (CH_2Cl_2): λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$) 310 ($1.40 \times 10^4$), 430 ($2.80 \times 10^3$).