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Self-Assembled Molecular Wires from Organoiron Metalloligands and Ruthenium Tetramesitylporphyrin

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A trinuclear assembly of two $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C(4-Py)}$ (Py = pyridyl) metalloligands apically coordinated to a ruthenium(II) tetramesitylporphyrin is demonstrated to behave as a molecular wire in the monooxidized state.

Since the pioneering work of Creutz and Taube,[1] Marcus and Hush,[2] and Robin and Day,[3] studies of intramolecular electron-transfer processes have sustained both a vibrant research base concerned with the most fundamental aspects of the electron-transfer reaction[4] and an increasing interest in molecular electronics.[5] In this latter context, various families of carbon-rich organometallic complexes were envisioned as potential wires, diodes, or related devices for information storage or processing at the molecular level.[5,6] It was recently shown that carbon-rich organometallic complexes can be interfaced with (semi)conducting supports, further stimulating the interest in these compounds for potential applications.[7] More specifically, in the field of organoiron derivatives, dinuclear architectures featuring $\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{FeC}\equiv\text{C}\}$ end groups in a mixed-valent (MV) state have been demonstrated to possess very large electronic couplings between remote metal centers over quite long distances.[8] However, synthetic access to such molecular-based bimetallic iron wires is often conditioned by the availability of a suitable organic bis(alkyne) precursor of the carbon-rich spacer and by the existence of suitable metalation, purification, and oxidation protocols. Thus, in order to open less synthetically demanding routes toward organoiron wirelike molecules $\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{FeC}\equiv\text{C}\}(\mu\text{-X})\{\text{C}\equiv\text{CFe}(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\}$, we have investigated the coordination reactions of several mononuclear compounds such as $(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{FeC}\equiv\text{C(4-Py)}$ (**1**) in which the redox-active organoiron fragment was appended to a coordinating unit toward inorganic complexes possessing two labile sites. In line with previous related works,[9−11] we anticipated that, from the conceptual combination of two such "metalloligands" and an appropriate central metallic connector, a molecular wire could result after monooxidation of the resulting assembly (**2**). In this respect, ruthenium(II) tetramesitylporphyrin (TMP) complexes appeared to us as promising connectors.[12,13] Accordingly, we now report a simple synthetic route to the trimetallic molecular wire

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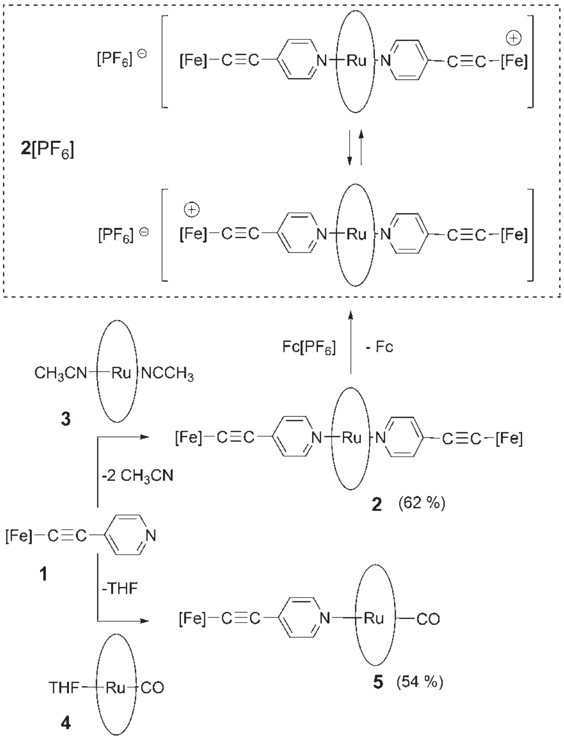
Scheme 1. Synthesis of Porphyrin Complexes **2** and **5** and of the Molecular Wire **2**[PF_6] ([Fe] = Fe(η^2-dppe)(η^5-C_5Me_5); Fc = Fe(η^5-C_5H_5)$_2$)[a]



[a] The Ru(TMP) core is shown schematically as a ring.

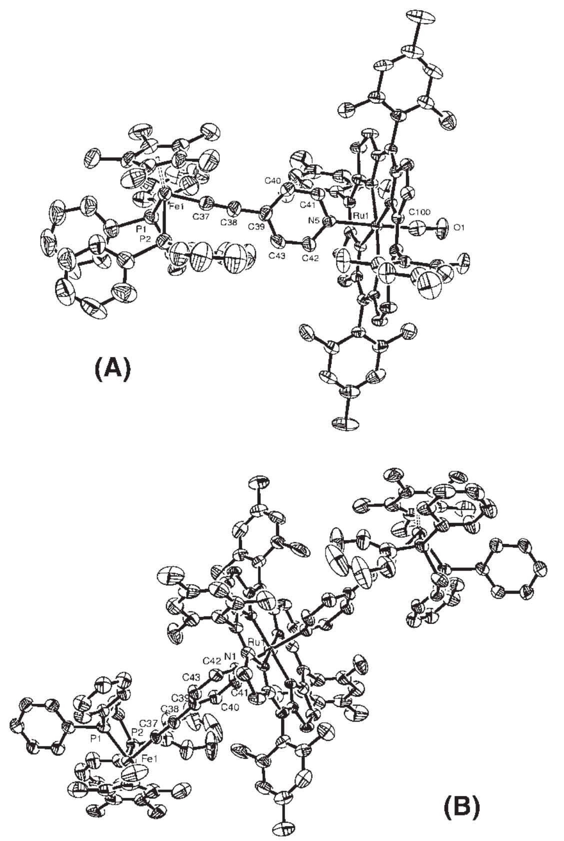


Figure 1. ORTEP representation of the porphyrin complex **5** (A) and **2** (B) with probability displacement ellipsoids at the 50% probability level.

2^+ by "self-assembly" of the known metalloligand **1** possessing a pendant 4-pyridyl group on this ruthenium connector and subsequent in situ oxidation (Scheme 1).

The reaction of metalloligand **1**[11] with the carbonyl/tetrahydrofuran (THF) precursor (THF)(CO)Ru(TMP) (**4**)[14] afforded a purple dinuclear adduct (**5**; Scheme 1), demonstrating that the steric effects of the mesityl groups at the meso positions of the porphyrin ring were not detrimental to the coordination chemistry of these fragments. The identity of **5** was confirmed by the usual spectroscopic methods and single-crystal X-ray diffraction (Figure 1A). The complexation of **1** to the Ru^{II} center of TMP is indicated by a slight shift of the $\nu_{C\equiv C}$ stretch to a lower wave numbers of ca. 40 cm^{-1},[11] and more clearly evidenced by the characteristic shifts to high field of the pyridyl protons in ^1H NMR because of their proximity to the porphyrin ring and associated ring currents.[15] Thus, doublets ($^3J_{HH}$ = 6.6 Hz) corresponding to the pyridyl protons appear at 4.32 and 1.38 ppm in chloroform-d_1. Notably, the characteristic $\nu_{C\equiv O}$ stretch of **5** at 1937 cm^{-1} is not significantly modified by substitution of the THF ligand for **1**.[16a,b]

The trinuclear assembly **2** was obtained in fair yield (62%) from the reaction of 2 equiv of **1** with the Ru^{II}(TMP) precursor **3** containing two labile acetonitrile ligands in apical positions (Scheme 1).[17] Complex **2** was also unambiguously characterized by mass spectrometry, IR and ^1H NMR spectroscopy, and single-crystal X-ray diffraction (Figure 1B). Characteristic spectroscopic features include the small shift of the $\nu_{C\equiv C}$ stretch in **2** relative to **1** by ca. 15 cm^{-1} to lower wave numbers and the observation of shielded pyridyl protons at 4.87 and 3.22 ppm ($^3J_{HH}$ = 6.6 Hz) in benzene-d_6.

Cyclic voltammetry (CH_2Cl_2/0.1 M [NBu_4][PF_6]) reveals two chemically reversible oxidation processes for the porphyrin monoadduct **5** (E = 0.02, 0.79 V vs SCE; Figure 2). A comparison with the redox potential of the free metalloligand **1** (E = −0.03 V) allows us to attribute the first redox event to oxidation of the Fe^{II} center. The small shift to more positive potentials relative to **1** is consistent with coordination of **1** to the Lewis acidic Ru^{II}(CO) center. The second oxidation in **5** corresponds to the monooxidation of the porphyrin ring.[16] In the case of the trimetallic complex **2**, three reversible oxidation waves are observed at −0.11, 0.02, and 0.27 V vs SCE. The first two are again attributed to the stepwise oxidations of the two Fe^{II} end groups, while the last one is attributed to oxidation of the Ru^{II} center of the porphyrin ring.[16c] This Ru-based oxidation now occurs at significantly lower

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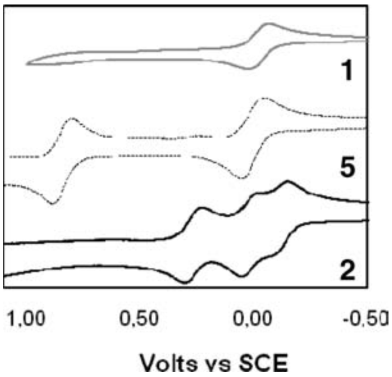

Figure 2. Cyclic voltammograms of compounds **1**, **2**, and **5** in dichloromethane (0.1 M $[NBu_4][PF_6]$) at 25 °C.

potential than that for the ring-based oxidation of **5** (0.27 vs 0.79 V). According to the potential difference of the first two iron-based redox processes ($\Delta E° \approx 0.13$ V), a thermodynamic comproportionation constant (K_c) of ca. 160 can be derived for the Fe^{III}/Fe^{II} MV complex $\mathbf{2}^+$.[5g] The MV form therefore has sufficient thermodynamic stability to be generated in solution by chemical or electrochemical oxidation. The same separation of these redox processes was also observed in CH_2Cl_2/0.1 M $[NBu_4][B(C_6F_5)_4]$ and given the low reorganization energy associated with oxidation of the (η^2-dppe)(η^5-C_5Me_5)Fe fragment,[8] suggests that the separation of the iron redox waves is more closely associated with electronic effects between the metal centers than ion pairing, solvation, or other factors.[18] The significant separation ($d_{Fe-Fe} \approx$ 19 Å based on the structural data available for **2**) also argues against significant Coulombic interactions between the redox sites. IR spectroelectrochemical experiments further establish the Fe-localized nature of the first redox process, with the $\nu_{C\equiv C}$ bands in **2** at 2035(m) and 2018(m) cm^{-1} evolving to two bands in $\mathbf{2}^+$ at 2016(w) and 1947(s) cm^{-1}. Further oxidation to $\mathbf{2}^{2+}$ was complicated by decomposition. The similarity of the IR profile of $\mathbf{2}^+$ with that of the 1,4-diethynylbenzene-bridged complex $[\{(\eta^5\text{-}C_5Me_5)(\eta^2\text{-dppe})FeC{\equiv}C\}(\mu\text{-}1,4\text{-}C_6H_4)\{C{\equiv}CFe(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)\}]^+$ ($\mathbf{6}^+$; $\nu_{C\equiv C}$ = 2016 and 1934 cm^{-1}) is remarkable.[8]

To further explore the nature of the MV complex $\mathbf{2}^+$, the near-IR (NIR) spectra were recorded after generation of $\mathbf{2}[PF_6]$ in the spectroscopic cell by the addition of ca. 1 equiv of ferricinium hexafluorophosphate ($Fc[PF_6]$) in dichloromethane and also by spectroelectrochemical methods. The NIR spectrum of $\mathbf{2}^+$ is apparently characterized by three relatively intense Gaussian-shaped bands at ca. 3750, 5900, and 7700 cm^{-1} (Supporting Information), but additional sub-bands might also be considered. None of these bands are associated with the spectrum of **2**. Furthermore, the addition of excess ($Fc[PF_6]$) or in situ electrochemical oxidation at higher potentials resulted in the collapse of this absorption envelope, the principal components of which are therefore likely correspond to intervalence charge-transfer (IVCT) process(es).[4a] The band envelope and underlying absorption bands are remarkably similar to the IVCT transitions observed for the MV complex $\mathbf{6}^+$ (4000, 6500, and 9000 cm^{-1}), further supporting the idea that these bands most likely arise from Fe−Fe charge-transfer processes.[8] The half-height bandwidth of the lowest-energy component in $\mathbf{2}^+$ arrived at by deconvolution is only in modestly good agreement with the Hush relationship for weakly coupled (class II) mixed-valence systems [$\Delta\nu_{1/2}$(obsd) = 2230 cm^{-1}; $\Delta\nu_{1/2}$(calcd) = 2940 cm^{-1}][2] but is in good agreement with that derived from the strongly coupled MV complex $\mathbf{6}^+$ [$\Delta\nu_{1/2}$(obsd) = 2110 cm^{-1}].[8] The close agreement of the spectroscopic parameters of $\mathbf{2}^+$ and $\mathbf{6}^+$ suggests a similarly strong coupling of the Fe centers across both bridges. The possibility of Ru → Fe processes lying within the band envelope cannot be rigorously excluded, but given the higher oxidation potential of the ruthenium/porphyrin moiety, such processes are likely to be obscured by the electronic transitions detected. Studies on binuclear complexes related to **5** are underway to address this point in more detail.

In conclusion, this work establishes that efficient molecular wires can be obtained in a very straightforward way by "plugging" redox-active metalloligands such as $\mathbf{1}^{0/+}$ into a ruthenium(II) porphyrin connector (or socket). Considering the previous attempts made with **1** using Pd^{II} or Pt^{II} connectors,[11] which resulted only in the isolation of localized, very weakly coupled, or noncoupled MV complexes,[11] this study also evidences that the choice of a more electron-rich central connector is crucial to obtaining an efficient wire. Work is now in progress to better understand the exact nature of the intramolecular electron-transfer events at the origin of the IVCT absorption detected for $\mathbf{2}[PF_6]$, to quantify the corresponding electronic couplings, and to examine further the scope of such self-assembled molecular wires in molecular electronics.

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Supporting Information Available: X-ray crystallographic data for complexes **2** and **5** in CIF format, experimental details for the synthesis and characterization of complexes **2** and **5**, the differential pulse voltammogram of **2**, and deconvolution of the NIR band envelope in $\mathbf{2}^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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