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New Polypyridine Ligands Functionalized with Redox-Active Fe(II) Organometallic Fragments

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We report in this Communication the isolation and characterization, including structure determinations, of 2,2′,6′,2′′-terpyridine (**2**) and 2,2′-bipyridine (**3**) ligands bearing two redox-active "(η^2-dppe)(η^5-C_5Me_5)Fe$C\equiv C$–" moieties grafted to the 5 and 5′′ positions of terpy or to the 5 and 5′ positions of bipy. These "metalloligands" have been complexed with Ru(II) and Mo(0), providing new heterotrinuclear complexes displaying intense absorptions around 700 and 600 nm, respectively, for the Fe_2Ru/terpy and Fe_2Mo/bipy species. In both cases, the Fe(II)/Fe(III) oxidation potentials of the free ligands became more positive by more than 50 mV upon complexation.

Judicious spatial or topological arrangements of redox-active end groups can lead to molecular architectures presenting unique properties for information storage or information processing at the molecular level.[1] In the field of carbon-rich organometallics,[2] it has been shown in several cases that the "(η^2-dppe)(η^5-C_5Me_5)Fe$C\equiv C-$" fragment can impart interesting electronic properties to various molecular assemblies.[3] Attaching such redox-active organoiron fragments to multidentate ligating units opens up novel topological possibilities, as we recently demonstrated with compounds having an *N*-aryl-(2-pyridyl)aldimine chelating site.[4] In principle, fluorescence switching might be envisaged by changing the redox state of the organoiron end group[5] or the nature of the central ion.[6] Furthermore, when the ligand has more than one redox-active substituent appended, one should also be able to tune the electronic communication between the two redox-active end groups by simply changing the complexed metal center. While some examples of alkynyl electron-rich metalloligands bearing one redox-active site connected to a diimine unit are known,[7] to the best of our knowledge, no multidentate ligands carrying several electron-rich redox-active organometallic end groups have been reported so far.

Chelating polypyridine ligands are well-known to bind strongly to various transition-metal ions and, thus, isolation of derivatives based on these chelating units was particularly attractive.[8] Our first attempts at isolating a 2,2′-bipyridine ligand functionalized with redox-active organoiron end groups using the classical synthetic approach (i.e., the vinylidene route) failed.[9] Here, we report the preparation and characterization of terpyridine- (terpy) and bipyridine- (bipy)

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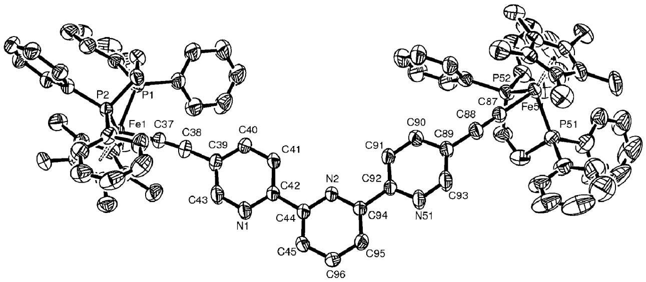
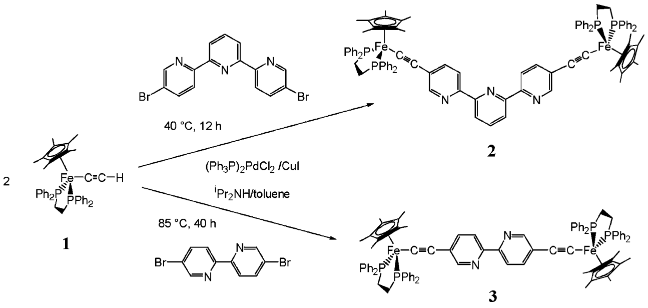


Figure 1. ORTEP representation of the 2,2′,6′,2″-terpyridine compound **2** with probability displacement ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): Fe1−(Cp*)$_{\text{centroid}}$ 1.741, Fe1−P1 2.1925(12), Fe1−P2 2.1812(11), Fe1−C37 1.888(4), C37−C38 1.210(5), C38−C39 1.441(5); P1−Fe1−P2 86.30(4), Fe1−C37−C38 174.1(4), C37−C38−C39 174.6(5), N1−C42−C44−N2 172.8, N51−C92−C94−N2 178.7.

Scheme 1. Synthesis of the Metalloligands **2** and **3**



bridged Fe(II) derivatives using the versatile C−C coupling chemistry of the terminal acetylideiron(II) complex **1** (Scheme 1). Additionally, we briefly report the complexation of the free bipy and terpy subunits with Mo(0) and Ru(II), respectively.

When 2 equiv of complex **1**[10] were reacted with the known 5,5″-dibromo-2,2′,6′,2″-terpyridine[11] under typical "metalla-Sonogashira" coupling conditions, the desired bifunctionalized terpyridine **2** was isolated in good yields following procedures previously reported.[12] Single crystals were grown by slow evaporation of a diethyl ether solution of the complex, and the solid-state structure of **2** was determined (Figure 1). The compound crystallizes in the triclinic $P\bar{1}$ group as a diethyl ether solvate and exhibits familiar geometrical features for an electron-rich iron(II) acetylide complex.[13] The terpy ligand adopts a planar conformation, with the two Fe atoms lying ca. 17.3 Å apart.

Isolation of the related bipy derivative **3** in a similar way from the corresponding 5,5′-dibromo-2,2′-bipyridine[14] proved much more difficult and required harsher conditions. Eventually, **3** was isolated by fractional crystallization from the crude reaction mixture, albeit in very poor yields (ca. 15%). Single crystals of this compound were grown upon slow evaporation of diethyl ether/benzene solutions of **3** (Figure 2). The compound crystallizes in the triclinic $P\bar{1}$ space group with two molecules in the asymmetric unit solvated by benzene. In both molecules, the bond distances and angles are typical for such Fe(II) complexes.[13] Again, the bipy ligand adopts a planar conformation, with the two Fe atoms lying ca. 16 Å apart.

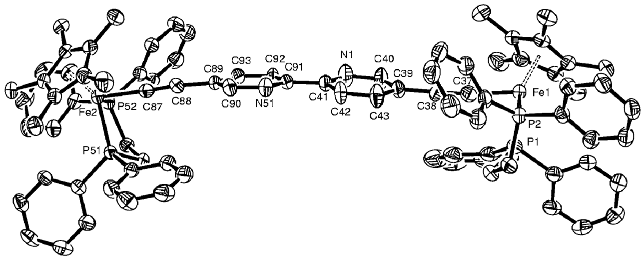
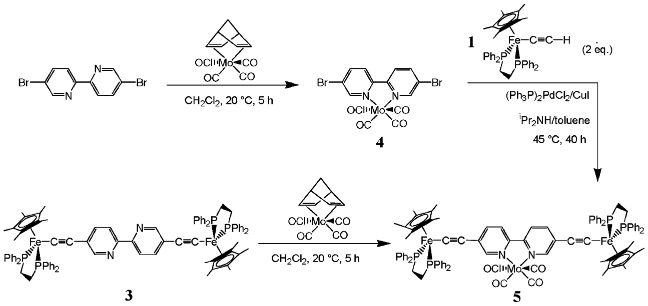


Figure 2. ORTEP representation of one molecule in the asymmetric unit for the 2,2′-bipyridine compound **3** with probability displacement ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): Fe1−(Cp*)$_{\text{centroid}}$ 1.736, Fe1−P1 2.1679(12), Fe1−P2 2.1786(13), Fe1−C37 1.887(4), C37−C38 1.186(6), C38−C39 1.467(6); P1−Fe1−P2 86.02(5), Fe1−C37−C38 174.4(4), C37−C38−C39 177.9(5), N1−C41−C91−N51 175.9.

Scheme 2. Synthesis of Complex **5**



Puzzled by the rather harsh conditions needed to achieve the coupling of **1** with 5,5′-dibromo-2,2′-bipyridine, we tried this reaction with **4**, a bipy unit precomplexed with molybdenum tetracarbonyl (Scheme 2). Interestingly, this approach provided access to **5** in 85% yield under much milder conditions. Note that complex **5** can also be prepared quantitatively in a single step from the metalloligand **3** and [(norbornadiene)Mo(CO)$_4$]. Single crystals of complex **5** were obtained in 25% yield from toluene/*n*-pentane mixtures. This compound crystallizes in the *P*21/*a* space group with one molecule each of *n*-pentane and toluene in the asymmetric unit. The complexation of the Mo center reinforces the planarity of the bipy fragment, but otherwise negligible structural modifications were observed (Figure 3).

Complexation of the Mo center to the bipy unit was clearly established by diagnostic $\nu_{\text{C}\equiv\text{O}}$ stretches, by the shift to more positive potentials of the Fe-centered oxidations for **5** relative to **3** ($\Delta E° = 0.07$ V) induced by the Lewis acidic nature of the Mo coordinated to the bipy unit in **5**[12b] and by the detection of a new pseudoreversible redox event near 0.74

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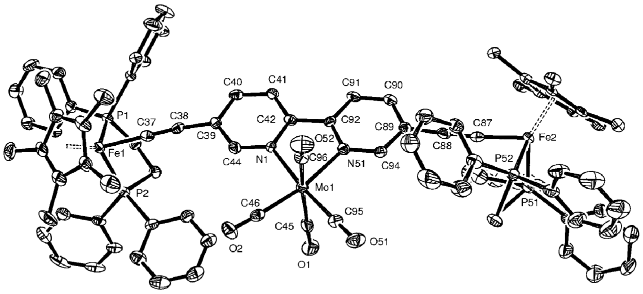


Figure 3. ORTEP representation of complex **5** with probability displacement ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): Fe1−(Cp*)$_{\text{centroid}}$ 1.731, Fe1−P1 2.1866(12), Fe1−P2 2.1796(12), Fe1−C37 1.892(4), C37−C38 1.204(5), C38−C39 1.439(5), Mo−C45 2.053(5), C45−O1 1.136(5), Mo−C46 1.973(4), C46−O2 1.151(4), Mo−N1 2.235(3); P1−Fe1−P2 85.99(4), Fe1−C37−C38 177.5(4), C37−C38−C39 173.3(4), N1−C41−C91−N51 0.7, N1−Mo−N51 72.92(11), C95−Mo−C46 90.87(16), C46−Mo−C45 87.97(16).

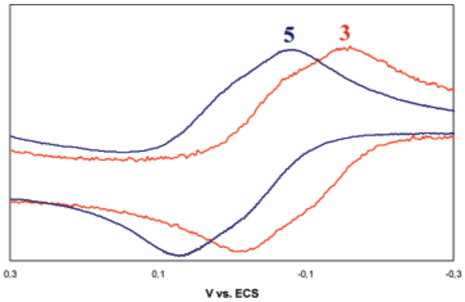


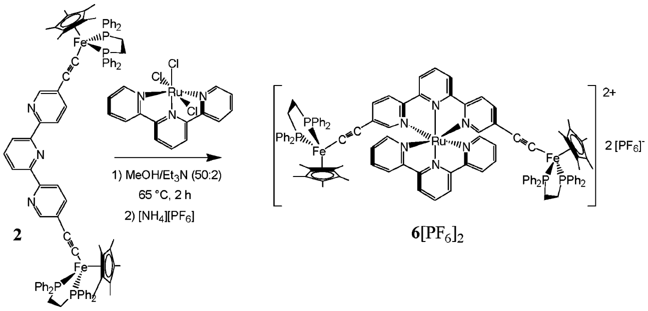
Figure 4. Fe(II)/Fe(III) oxidations in cyclic voltammograms of compounds **3** and **5** (CH_2Cl_2, [n-Bu_4N][PF_6] (0.1 M), at Pt electrode at 0.1 V/s).

V vs SCE, which possibly corresponds to a Mo-centered oxidation.[15]

Note that, in the cyclic voltammograms of both **3** and **5**, the two Fe-centered oxidations were barely separated (Figure 4), suggesting weak electronic coupling between the two redox centers. Complexation of the Mo center induced no significant changes in the electronic communication between the two organoiron end groups, as indicated by a negligible change in the peak separation (see the Supporting Information). The conversion of **3** to **5** produced a new absorption at 442 nm corresponding to a $d_{Mo} \rightarrow (\pi^*)_{bipy}$ metal-to-ligand charge-transfer (MLCT) band[16] and a bathochromic shift from 487 to 606 nm of the $d_{Fe} \rightarrow (\pi^*)_{C\equiv CAr}$ MLCT band, which is largely responsible for the orange to blue color change observed in the conversion (see the Supporting Information).

Finally, when **2** was reacted with 2,2′,6′,2″-terpyridineruthenium trichloride[17] in refluxing methanol (Scheme 3), the new heteroleptic bis(terpyridine)ruthenium(II) complex **6**[PF_6]$_2$ was isolated in modest yields (32%) after metathesis of the chloride for hexafluorophosphate. This compound was unambiguously characterized by ^{1}H NMR, Fourier transform IR, and liquid secondary ion mass spectrometry. Also, its supposed structure is supported by a very poor diffraction data set obtained on a small monocrystal. Again, both the cyclic voltammetry and UV−vis data were consistent with coordination of the {(terpy)Ru^{II}} moiety to the terpyridine ligand **2**. An anodic potential shift ($\Delta E° = 0.18$ V) of the Fe-centered oxidation in **6**[PF_6]$_2$ relative to **2** was induced by the dicationic Ru(II) center (see the Supporting Information). In contrast to what was previously observed with the bipy derivatives, the two Fe-centered oxidations were not resolved in any of these compounds. A new quasi-reversible redox event was detected near the solvent edge, at −1.24 V vs SCE, which likely corresponds to the first terpy-centered reversible reduction of a heteroleptic bis(terpyridine) complex like **6**[PF_6]$_2$.[18] Also, upon going from **2** to **6**[PF_6]$_2$, the appearance of a new absorption at 481 nm corresponding to the $d_{Ru} \rightarrow (\pi^*)_{terpy}$ MLCT band was detected[17] along with a significant shift of the $d_{Fe} \rightarrow (\pi^*)_{C\equiv CAr}$ MLCT band from 464 nm in the metalloligand **2** to near 700 nm. This transition is basically responsible for the dark-blue color of the resulting trinuclear complex (see the Supporting Information).

Scheme 3. Synthesis of Complex **6**[PF_6]$_2$



In conclusion, we have synthesized in single steps two new dimetalated polypyridine ligands bearing redox-active organoiron sites from the terminal acetylide complex **1** and brominated polypyridine ligands. Complexation of the free central coordination sites by Mo(0) or Ru(II) was feasible under mild conditions. In both cases, the $d_{Fe} \rightarrow (\pi^*)_{C\equiv CAr}$ MLCT absorption band shifted from 487 to 606 nm in the 2,2′-bipyridine case or to 700 nm in the 2,2′,6′,2″-terpyridine case. In the bipy/Mo and terpy/Ru complexes **5** and **6**$^{2+}$, the potential of the Fe(II)/Fe(III) couple increased by 70 and 180 mV, respectively, with respect to the uncomplexed ligand. Work is currently in progress to improve the synthetic access to these remarkable metalloligands and also to study details of the spectroscopic properties of the mixed complexes **5** and **6**$^{2+}$.

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Supporting Information Available: Synthetic and crystallographic (CIF) details, electronic spectra, and voltammetry for **2**, **3**, **5**, and **6**[PF_6]$_2$. This material is available free of charge via the Internet at http:/pubs.acs.org.

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(18) A third reversible redox event likely corresponding to the second reduction of the complex was detected near −1.65 V vs SCE in anhydrous acetonitrile.[17]