Communication

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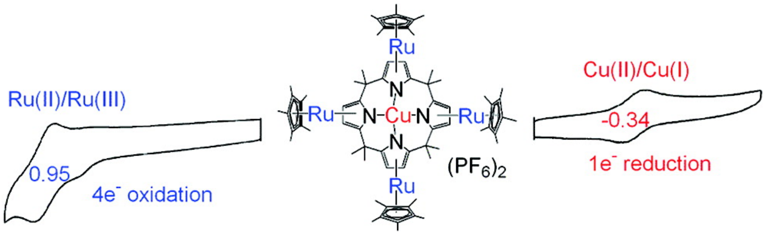

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Design and Synthesis of Polymetallic Complexes Based on *meso*-Calix[4]pyrrole: Platforms for Multielectron Chemistry

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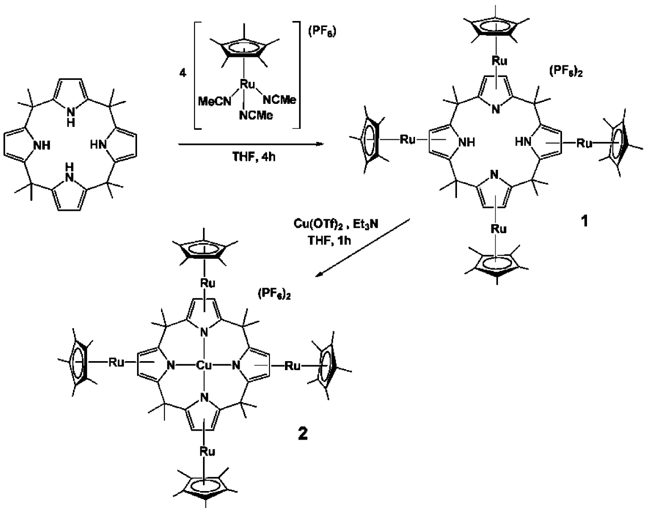
Important chemical transformations such as oxygen reduction,[1] nitrogen fixation,[2] and redox reactions involving hydrogen[3] are efficiently mediated by metalloenzymes that contain bi- or multimetallic reactive sites. The elegance and complexity of these active sites has provided an ongoing incentive to prepare systems that allow the stabilization of several "redox" metal centers in close proximity to each other, both to model natural chemical systems and to probe the fundamental properties of synthetic complexes that contain a large number of metal centers constrained within a single ligand system. In this Communication, we report the use of calix[4]pyrrole as a scaffold for the concurrent complexation of five metal centers, namely, four Ru(II) cations and one Cu(II) ion.

Although calix[4]pyrroles (also called *meso*-octaalkylporphyrinogens) were discovered by Baeyer in 1886,[4] they were not widely studied until recently, when they were rediscovered, first as versatile ligands (in their respective tetraanionic forms)[5] and then as effective anion receptors.[6] In particular, the coordination chemistry of the calix[4]pyrroles was extensively studied by Floriani and co-workers[5] who showed that they are able to coordinate metal ions in a σ and/or π manner depending on the nature of the metal. In spite of the rich π coordination displayed by these easy-to-prepare (and now commercially available) macrocycles, to the best of our knowledge, they have not been explored as ligands for the stabilization of multimetallocene-type species. While π surface metalation has been studied in a number of other systems and exploited for the synthesis of anion receptors, including calixarenes,[7] cyclotetraveritol,[8] and cryptophanes,[9] extending this chemistry to include calix[4]pyrroles would offer an advantage in that further central metal complexation should be possible.

The synthesis of the tetrakisruthenocene calixpyrrole derivative (**1**) and its copper(II) complex (**2**) is shown in Scheme 1. These species are of interest because they are built up using a core ligand that contains 32 non-hydrogen atoms but allows for the stabilization of complexes containing four or five redox active metal centers in close proximity. As such, complexes **1** and **2** provide an interesting complement to the multi-metallocene dendrimers and other large systems that have been proposed as "electron reservoirs" by Astruc almost three decades ago.[10]

The tetranuclear ruthenium complex **1** was readily prepared in 91% yield by treating *meso*-octamethylcalix[4]pyrrole with [RuCp*-$(CH_3CN)_3$]PF_6 in THF under reflux for 4 h (Scheme 1). The ^1H NMR spectrum of the isolated product revealed that two of the pyrrolic NH protons are deprotonated during the reaction, presumably as a result of the high acidity of these atoms in the metalated calixpyrrole. This "partial" deprotonation is specifically inferred from the presence of two different sets of signals for the pyrrole moieties and Cp* ligands in the ^1H NMR and ^{13}C NMR spectra.

Scheme 1



The reaction of **1** with $Cu(OTf)_2$ in the presence of triethylamine resulted in clean isolation of the pentametallic complex **2** (Scheme 1). A single-crystal X-ray structure (Figure 1) reveals the presence of four RuCp* fragments η^5-bonded to the four pyrroles. The sequence is up and down, so that two Ru(II) centers are bound to the upper face of the macrocycle and two at the bottom face. The Cu(II) ion is complexed by the four central nitrogen atoms. While these donor atoms adopt a near-planar geometry, tetrahedral distortion of the metal center is observed.

The electrochemistry of **1**, **2**, and the parent calixpyrrole was studied by cyclic voltammetry in PhCN. Earlier studies of *meso*-octamethylcalix[4]pyrrole showed two irreversible oxidations in CH_2Cl_2,[11] but in PhCN, the first oxidation is reversible and located at $E_{1/2} = 0.82$ V followed by a second process at $E_p = 1.32$ V, both centered at the pyrrole rings (see Supporting Information, Figure S1). Interestingly, quantitative ESR studies of the radical species generated in these processes revealed that the oxidations are monoelectronic. This unexpected behavior, which is thought to reflect the presence of weak electronic coupling between the pyrroles, is currently under further investigation.

A cyclic voltammogram of **2** in PhCN is shown in Figure 2. There is a reversible one-electron reduction at $E_{1/2} = -0.34$ V assigned to a Cu(II)/Cu(I) reaction. The reversible nature of this reduction is noteworthy. Reversible reductions are crucial in several biological systems (i.e., blue copper proteins, cytochrome *c*

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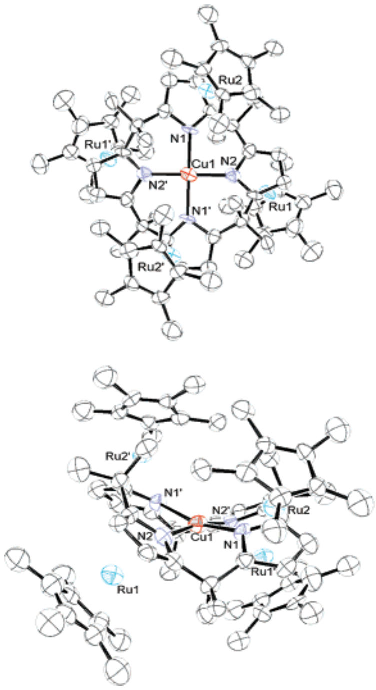

Figure 1. Top and side views of complex **2** showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. The hydrogen atoms and the PF_6^- ions are not shown.

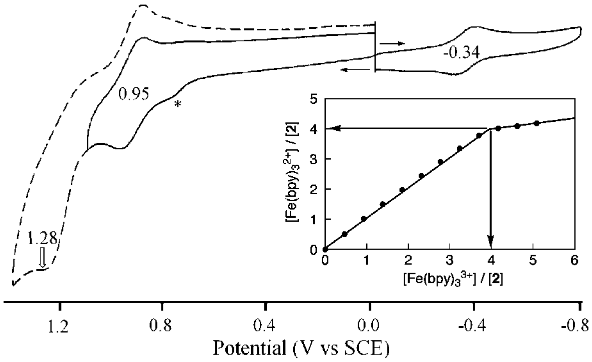

Figure 2. Cyclic voltammogram of **2** in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V s^{-1}. Oxidation of decomposition product indicated by $*$. Inset: Plot of $[Fe(bpy)_3^{2+}]/[\mathbf{2}]$ vs $[Fe(bpy)_3^{3+}]/[\mathbf{2}]$ from the UV−vis spectral titration of **2** with $Fe(bpy)_3^{3+}$ in CH_3CN.

oxidase); however, they have proven difficult to reproduce with synthetic analogues, a fact attributed, in part, to the different coordination geometries preferred by Cu(I) (tetrahedral) and Cu(II) (square planar). The flexibility of the calixpyrrole framework and the intermediary "planar-tetrahedral" environment of the Cu(II) ion in complex **2** are, apparently, key factors in stabilizing the Cu(II)/Cu(I) couple.[12]

Compound **2** also undergoes a reversible oxidation at $E_{1/2} = 0.95$ V. The oxidation peak current is 4 times that of the reduction, consistent with the four linked ruthenocene fragments undergoing concurrent oxidation. Additional support for a four-electron transfer comes from a spectrally monitored titration of **2** by $Fe(bpy)_3^{3+}$ in CH_3CN (cf. Figure 2). ESR spectra of the resulting four-electron oxidized products of **1** and **2** reveal formation of a species containing 4 molar equiv of Ru(III) (see Supporting Information, Figures S2 and S3). This species was characterized by both large g values ($g_{/\!/} = 2.339$ and $g_{\perp} = 2.067$)[13] and a high degree of hyperfine interaction involving the pyrrolic nitrogen atoms ($A_{/\!/}(N) = 170$ G).

Further analysis of the cyclic voltammogram of **2** revealed a small decomposition peak at $E_p = 0.80$ V, ascribed to a ruthenium-free species, and a larger irreversible oxidation at $E_p = 1.28$ V.

The tetrametallic complex **1** undergoes a similar reversible four-electron oxidation at $E_{1/2} = 0.95$ V, with the ESR spectrum of the resulting species resembling that produced from **2** (cf. Supporting Information, Figures S1 and S3). In this case, however, a second oxidation is not seen within the investigated solvent window, nor are any signals ascribable to Cu(II) reduction seen in this copper-free complex.

In conclusion, we present a facile and versatile strategy for the synthesis of polynuclear complexes based on the calixpyrrole skeleton. While additional analyses are needed, preliminary studies reveal that complexes **1** and **2** display reversible four-electron oxidations, a finding that makes them of interest as possible easy-to-synthesize electron reservoirs. In the case of **2**, a reversible Cu(II)/Cu(I) couple is seen that could prove useful in terms of enzyme modeling. Efforts to extend this generalized metalation approach to other nonconjugated oligopyrrolic macrocycles are also underway.

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Supporting Information Available: Synthetic and experimental details and X-ray structural data. Electrochemical (Figure S1) and ESR (Figures S2 and S3) data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Collman, J. P.; Boulatov, R.; Sunderland, C. J.; Fu, L. *Chem. Rev.* **2004**, *104*, 561−588.
(2) (a) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200*, 379−409. (b) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385−401.
(3) Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268−275.
(4) Baeyer, A. *Chem. Ber.* **1886**, *19*, 2184−2185.
(5) Floriani, C.; Floriani-Moro, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 3, pp 385−420.
(6) (a) Gale, P. A.; Sessler, J. L.; Král, V.; Lynch, V. M. *J. Am. Chem. Soc.* **1996**, *118*, 5140−5141. (b) Gale, P. A.; Anzenbacher, P., Jr.; Sessler, J. L. *Coord. Chem. Rev.* **2001**, *222*, 57−102.
(7) Staffilani, M.; Hancok, K.; Steed, J. W.; Holman, K. T.; Atwood, J. L.; Juneja, R. V.; Burkhalter, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 6324−6335.
(8) Holman, K. T.; Halihan, M. M.; Steed, J. W.; Jurisson, S. S.; Atwood, J. L.; Burkhalter, R. S.; Mitchell, A. R.; Steed, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 9567−9576.
(9) Robert, M. F.; Travis, K. H. *J. Am. Chem. Soc.* **2005**, *127*, 16364−16365.
(10) (a) Astruc, D.; Hamon, J.-R.; Althoff, G.; Roman, E. *J. Am. Chem. Soc.* **1979**, *101*, 5445−5447. (b) Astruc, D. *Acc. Chem. Res.* **2000**, *33*, 287−298.
(11) Tabba, H. D.; Cavaleiro, J. A. S.; Jeyakumar, D.; Graça, P.; Neves, P. M. S.; Smith, K. M. *J. Org. Chem.* **1989**, *54*, 1943−1948.
(12) We are aware of only one other tetrapyrrolic system displaying a reversible Cu(II)/Cu(I) process, namely, the mono-N-alkylated tetraphenylporphyrins. Reduction potentials between −0.25 and −0.42 V vs Ag/AgCl were seen in CH_3CN depending on the cation. Kuila, D.; Kopelove, A. B.; Lavallee, D. K. *Inorg. Chem.* **1985**, *24*, 1443−1446.
(13) Large g values have been observed for other Ru(III) cyclopentadienyl species: Shaw, A. P.; Ryland, B. L.; Norton, J. R.; Buccella, D.; Moscatelli, A. *Inorg. Chem.* **2007**, *46*, 5805−5812.

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