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One-Pot Synthesis of an Fe(II) Bis-Terpyridine Complex with Allosterically Regulated Electronic Properties

Charles W. Machan,[†] Mario Adelhardt,[‡] Amy A. Sarjeant,[†,§] Charlotte L. Stern,[†,§] Jörg Sutter,[‡] Karsten Meyer,[‡] and Chad A. Mirkin*,[†]

[†]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

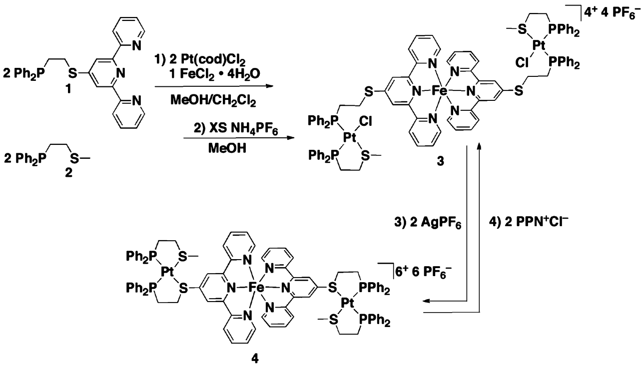
[‡]Department of Chemistry and Pharmacy, Inorganic Chemistry, University Erlangen-Nuremberg, Egerlandstrasse 1, D-91058 Erlangen, Germany

Ⓢ *Supporting Information*

ABSTRACT: Herein we report the one-pot synthesis of Fe(II) bis-terpyridine complexes with two peripheral square-planar Pt(II) bis-phosphinoalkylthioether moieties. These novel structures, which exhibit allosterically controllable electronic properties, are made by taking advantage of two orthogonal and high-yielding reactions. The prototypical complex can be structurally regulated through the reversible abstraction and introduction of chloride ions to the Pt(II) centers. This moves the Fe(II) center and two Pt(II) metal centers into and out of communication with each other, causing changes in the electronic structure of the complex and its corresponding optical and redox properties. The start and end points of the allosterically regulated system have been characterized by single-crystal X-ray diffraction and NMR, UV−vis, and ^{57}Fe Mößbauer spectroscopy.

The construction of supramolecular structures through metal-directed assembly represents a rapid and quantitative way of generating abiotic complexes capable of achieving selectivity and reactivity reminiscent of biological systems for many different types of chemical reactions.[1−8] Among these methods, the Weak-Link Approach (WLA)[2,5−7,9−13] stands out for its ability to generate structures from hemilabile ligands that can be reversibly converted between "closed" condensed intermediates and "open" flexible structures. With proper design, these two states can exhibit dramatically different stoichiometric or catalytic reactivities, thereby allowing one to create allosteric enzyme mimics,[2] including ones that mimic PCR target amplification and ELISA signal amplification,[14] exhibit adjustable host−guest chemistry,[15] and behave as switchable living-polymerization catalysts.[16] In general, the approach to these types of systems has been to design structures having steric limitations with respect to reactivity in the inactive state that are relieved when the structure is chemically toggled to the active state. An alternative approach is to learn how to use such allosteric control to regulate the electronic properties of an active metal center. This type of reversible switching of electronic environments could be particularly important in the areas of catalysis,[17,18] light harvesting,[19,20] single-molecule magnets,[21,22] and chemical detection.[23] Herein we report the one-pot synthesis of Fe(II) bis-terpyridine complexes with peripheral square-planar Pt(II) bis-phosphinoalkylthioether moieties (Scheme 1). These novel structures are made by taking advantage of two orthogonal, high-yielding reactions, and they exhibit allosterically controllable electronic properties, as evidenced by NMR, UV−vis, and ^{57}Fe Mößbauer spectroscopy.

Scheme 1. One-Pot Synthesis of Complex 3 and Subsequent Interconversion with Complex 4



We hypothesized that the use of terpyridine (which has a high binding affinity for many first-row transition metals) as a functional group would allow for the orthogonal complexation of metal centers (Fe^{2+} in this case) during the formation of WLA-type metal centers (Pt^{2+} in this case).[24−35] Ligand **1**, which features a terpyridine functionalized at the 4′ position with a hemilabile phosphinoalkylthioether (P,S) moiety, is indeed capable of this type of chemically orthogonal behavior. When 2 equiv of **1** were combined in a CH_2Cl_2/MeOH mixture with 2 equiv each of ligand **2** and [Pt(cod)Cl_2] (cod = 1,5-cyclooctadiene) and 1 equiv of $FeCl_2{\cdot}4H_2O$, a deep-purple solution formed (Scheme 1). In situ $^{31}P\{^1H\}$ NMR spectroscopic monitoring of the reaction mixture showed the formation of a single complex (**3**) containing two magnetically inequivalent P centers on the same Pt(II) center. Addition of excess NH_4PF_6 to this mixture resulted in the precipitation of a deep-purple powder. Single-crystal X-ray diffraction (XRD) analysis revealed the structure of **3**, in which the terpyridine moieties of two ligands **1** are bound in a distorted octahedral

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arrangement to a single Fe(II) center (Figure 1A).[36] The hemilabile P,S portion of each ligand **1** is bound only through P to a separate square-planar Pt(II) center, which also has one fully chelated ligand **2** bound in a cis arrangement with a single chloride ion occupying the remaining coordination site. All of the other characterization data were consistent with this structural assignment; the UV−vis spectrum and cyclic voltammogram (CV) of **3** were comparable to those of previously reported Fe(II) bis-terpyridine complexes (see below).[37−41]

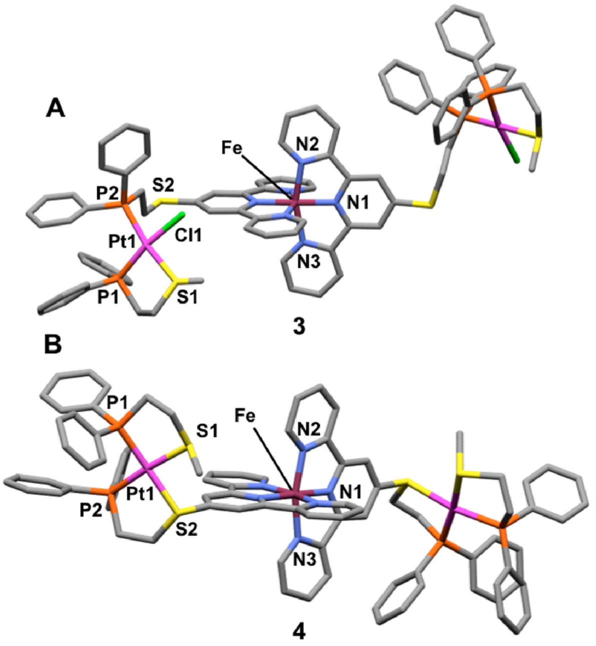


Figure 1. Solid-state X-ray crystal structures of (A) **3** and (B) **4** with outer-sphere anions and hydrogens omitted for clarity. C, gray; Cl, light green; P, orange; S, yellow; Pt, magenta; Fe, purple; N, blue.

This one-pot reaction takes advantage of a combination of two mutually compatible, well-established, and high-yielding reactions in order to form the heterometallic complex **3** quantitatively. First, it relies on the Halide-Induced Ligand Rearrangement (HILR) reaction,[42] which allows for the rapid assembly of two bis-heteroligated Pt(II) allosteric regulatory sites on the periphery of the bis-terpyridine complex. The HILR reaction is a self-sorting process facilitated by differences in the electron-donating ability of the thioether moieties that favors the formation of heteroligated complexes with mixed chelation modes.[11,43,44] Second, it takes advantage of the quantitative and rapid complexation of Fe(II) by 2 equiv of terpyridine, which has been heavily utilized by researchers since the discovery and first characterization of the terpyridine ligand.[35] Since we were interested in reversible WLA-type reactivity on the Pt(II) center as a way to regulate the properties of the Fe(II) center, we explored the chemistry of chloride abstraction from complex **3**. When **3** was dissolved in CH_2Cl_2 with 2 equiv of $AgPF_6$ and stirred vigorously for 1 h, a dark-purple precipitate formed and was isolated as analytically pure **4** (Scheme 1). XRD analysis of suitable single crystals of **4** revealed its solid-state structure (Figure 1B), which consists of Fe(II) bound in a distorted octahedral coordination environment to the terpyridine groups of two ligands **1**. Unlike **3**, the P,S portions of the two ligands **1** are fully chelated to distinct but structurally identical square-planar Pt(II) centers, each of which is also bound with one ligand **2** in a cis arrangement occupying the remaining coordination sites. All of the other characterization data were consistent with the proposed structure for **4**. Complex **4** could be quantitatively converted back into **3** in solution by the addition of 2 equiv of bis(triphenylphosphine)iminium chloride (PPN^+Cl^-) (Scheme 1), as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy [see the Supporting Information (SI)].

The UV−vis spectrum of **3** has a metal-to-ligand charge transfer (MLCT) band with λ_{max} = 569 nm assigned to the d−π* transition of the Fe(II) bis-terpyridine, and complex **4** exhibits a nearly identical transition with λ_{max} = 572 nm (see the SI).[27,37,45] However, the extinction coefficient of this band for **3** (19 869 ± 352 M^{-1} cm^{-1}) was substantially larger than that of the analogous band for **4** (15 686 ± 786 M^{-1} cm^{-1}). The small change in the position of λ_{max} indicates that the energy of this d−π* transition changes very little in the interconversion of **3** and **4**, but the relatively large change in extinction coefficient suggests that the transition dipole moment has shifted, diagnostic of a change in the electronic character of the bis-terpyridine Fe(II) portion of complexes **3** and **4**. In addition, both **3** and **4** were determined to be diamagnetic by variable-temperature SQUID studies, which is consistent with results for previously characterized model mononuclear Fe(II) bis-terpyridine complexes. The Fe−N bond distances observed crystallographically are also consistent with low-spin complexes (see the SI).[36,37,46]

More significant differences between complexes **3** and **4** were observed electrochemically. As expected, the CV of complex **3** showed a reversible $Fe^{II/III}$ oxidation wave at $E_{1/2}$ = 0.71 V, as predicted for the highest occupied molecular orbital (HOMO) of that complex (see the SI).[37,39,40] Importantly, in complex **4** the HOMO is no longer exclusively Fe-centered; instead, an as yet unassigned irreversible wave was observed at E_a = 0.24 V, making a direct comparison not as meaningful. However, comparison of the CVs for the irreversible waves assigned to separate terpy/terpy$^{\bullet-}$ transitions for **3** ($E_c^1 = -1.09$ V and $E_c^2 = -1.23$ V) and **4** ($E_c^1 = -0.73$ V and $E_c^2 = -0.89$ V) reveals a trend consistent with coordination of the Lewis acidic and therefore electron-withdrawing Pt(II) to the thioether attached to the terpyridine (see the SI).[27,47,48]

Indeed, ^{57}Fe Mößbauer spectroscopy of these complexes (Figure 2) provided a greater and more direct measure of the effect of the allosterically controlled position of the Pt(II) center with respect to the Fe(II) center. The observed isomer shifts (δ) for complexes **3** and **4** are compatible with low-spin (S = 0) iron(II) centers bound to (hard) nitrogen donor

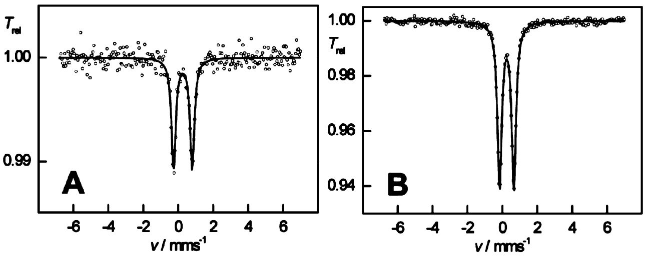


Figure 2. Zero-field ^{57}Fe Mößbauer spectra for (A) **3** and (B) **4** recorded at 77 K. **3**: δ = 0.27(1) mm s^{-1}; ΔE_Q = 1.06(1) mm s^{-1}; Γ_{fwhm} = 0.30(1) mm s^{-1}. **4**: δ = 0.25(1) mm s^{-1}; ΔE_Q = 0.82(1) mm s^{-1}; Γ_{fwhm} = 0.30(1) mm s^{-1}.

atoms.[49] As expected, **3** and **4** showed quadrupole splittings (ΔE_Q) consistent with an asymmetric octahedral coordination environment. The magnitude of this splitting decreased from 1.06(1) mm s^{-1} in **3** to 0.82(1) mm s^{-1} in **4**, which indicates a decrease in the asymmetry of the Fe(II) coordination environment and is in agreement with our characterization of **3** and **4**. Comparable trends in ΔE_Q have been observed previously with substituted pyridines at axial positions, suggesting that such changes can arise from significant differences in ligand character.[50] This means that the allosteric Pt(II) reactions have an effect on the electronic structure of the ligand, which in turn changes the electric-field gradient in the Fe(II) nucleus, resulting in a different ΔE_Q. This is direct confirmation that the electronic properties of the bis-terpyridine core can be regulated through allosteric reactions on the periphery. The influence of 4′-substituted terpyridine ligands on the electric-field gradient was studied independently. These studies showed that ΔE_Q increased with the inclusion of more strongly electron-donating moieties in a series of simple model complexes (see the SI).

These results can also be understood by computational studies of the orbital energy levels of a model complex. Density functional theory calculations (Parallel Quantum Solutions Computational Cluster) on model Fe(II) bis-terpyridine complex **5** functionalized with a methylthioether moiety at the 4′ positions (Figure 3) showed a significant contribution from the thioethers to both the HOMO and HOMO−1.[47] These degenerate MOs comprise a network of shared orbitals extending from the thioether lone pairs to the Fe(II) d_{xz} and d_{yz} orbitals, which are higher in energy than the exclusively metal-centered d_{xy} HOMO−2 (Figure 3). The ability of a ligand to be π-acidic at the trans positions in d^6 octahedral metal complexes is known to have an impact on the relative positioning of the d_{xz} and d_{yz} orbitals relative to the d_{xy} orbital.[51] On the basis of the shared orbital structure calculated for **5**, Pt−S bond formation in going from **3** to **4** would be expected to cause a relatively greater shift to lower energy for the HOMO and HOMO−1 (d_{xz} and d_{yz}) than for the HOMO−2 (d_{xy}). The calculations are consistent with not only a significant perturbation of the Fe center but also a pathway involving a specific set of orbitals (d_{xz} and d_{yz}).

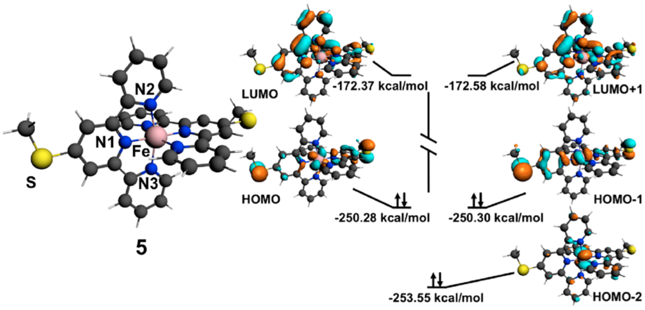
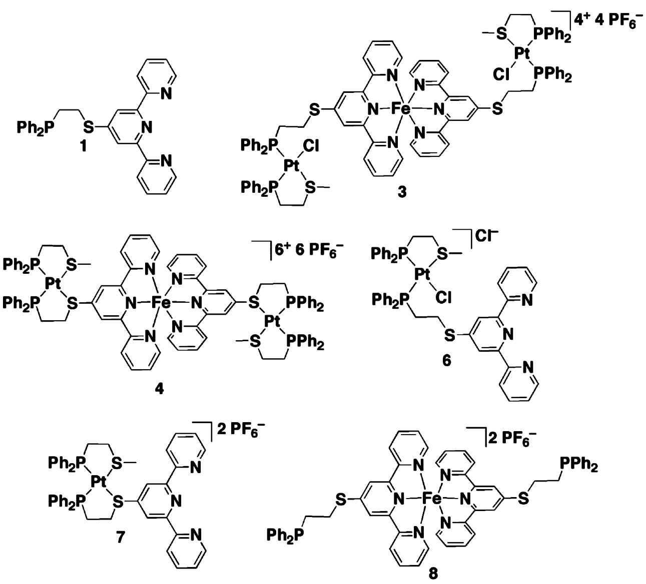


Figure 3. Kohn−Sham representations of the frontier MOs of complex **5** generated by the graphical user interface in ADF 2009.01.

To examine the individual reactions that dictate the assembly of **3** and **4**, we synthesized their constituent metal complexes independently from one another for individual study. Combining 1 equiv each of ligand **1**, ligand **2**, and Pt(cod)Cl_2 in CH_2Cl_2 resulted in the quantitative formation of complex **6** (Scheme 2), which served as a model for the Pt(II) portion of **3**. Complex **7** was cleanly generated from **6** under chloride-abstracting conditions and served as a model for the Pt(II) metal centers of **4** (Scheme 2). Independent synthesis of the Fe(II) bis-terpyridine portion of **3** was achieved by combining 2 equiv of ligand **1** with 1 equiv of $FeCl_2 \cdot 4H_2O$ in a CH_2Cl_2/MeOH mixture, which resulted in the quantitative formation of complex **8** (Scheme 2). CVs of **6** and **7** showed a shift toward more positive potentials in the irreversible waves assigned to the terpy/terpy$^{\bullet-}$/terpy$^{\bullet\bullet 2-}$ reductions (see the SI), similar to the shifts observed for complexes **3** and **4**. Single crystals of **6**, **7**, and **8** suitable for XRD analysis revealed molecular structures consistent with all other characterization data (see the SI).

Scheme 2. Structures of Complexes 1, 3, 4, 6, 7, and 8



We have shown that it is possible to assemble rapidly in a one-pot reaction a heterometallic complex, **3**, whose electronic structure can be reversibly switched by quantitative chemical reactions at allosteric Pt sites. The type of change observed between the bis-terpyridine cores of complexes **3** and **4** would normally require the independent synthesis of different ligands and subsequent complex assembly or changing the coordination number of the Fe(II) center. In this system, the Pt(II) centers on the periphery of the complex can be used as allosteric regulatory sites to perturb the electronic character of the Fe(II) bis-terpyridine portion of the molecule reversibly while maintaining the integrity of the Fe(II) coordination environment. The ability to shift the point of control from sterics to electronics in these complexes means that the accessibility of reactive states no longer requires the synthesis of large and complicated ligands to protect exclusively active metal sites. In fact, the realization of these reactions points toward the ability to generalize this platform for the construction of a wide variety of new allosterically regulated systems where in principle many different types of chemically orthogonal metals can be used. In doing so, we hope to develop complexes with unique catalytic,[18] optical,[19] and magnetic[22] properties that can be switched by chemical reactions at the WLA metal center.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
chadnano@northwestern.edu

Author Contributions

§A.A.S. and C.L.S. were responsible for the structural solutions of all single-crystal X-ray data.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Amouri, H.; Desmarets, C.; Moussa, J. *Chem. Rev.* **2012**, *112*, 2015.

(2) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 114.

(3) Safont-Sempere, M. M.; Fernandez, G.; Würthner, F. *Chem. Rev.* **2011**, *111*, 5784.

(4) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810.

(5) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618.

(6) Gianneschi, N. C.; Masar, M. S.; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825.

(7) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022.

(8) Takeuchi, M.; Ikeda, M.; Sugasaki, A.; Shinkai, S. *Acc. Chem. Res.* **2001**, *34*, 865.

(9) Machan, C. W.; Lifschitz, A. M.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 1469.

(10) Spokoyny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Sarjeant, A. A.; Stern, C. L.; Mirkin, C. A. *Nat. Chem.* **2011**, *3*, 590.

(11) Rosen, M. S.; Spokoyny, A. M.; Machan, C. W.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. *Inorg. Chem.* **2011**, *50*, 1411.

(12) Gianneschi, N. C.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 5326.

(13) Farrell, J. R.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 465.

(14) Yoon, H. J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 11590.

(15) Kuwabara, J.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 10074.

(16) Yoon, H. J.; Kuwabara, J.; Kim, J.-H.; Mirkin, C. A. *Science* **2010**, *330*, 66.

(17) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892.

(18) Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W. *Science* **1999**, *283*, 1524.

(19) Dobrawa, R.; Würthner, F. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4981.

(20) Kim, D.; Osuka, A. *Acc. Chem. Res.* **2004**, *37*, 735.

(21) Zeng, Y.-F.; Zhao, J.-P.; Hu, B.-W.; Hu, X.; Liu, F.-C.; Ribas, J.; Ribas-Ariño, J.; Bu, X.-H. *Chem.—Eur. J.* **2007**, *13*, 9924.

(22) Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2006**, *45*, 10197.

(23) Goze, C.; Ulrich, G.; Charbonnière, L.; Cesario, M.; Prangé, T.; Ziessel, R. *Chem.—Eur. J* **2003**, *9*, 3748.

(24) Constable, E. C.; Hermann, B. A.; Housecroft, C. E.; Neuburger, M.; Schaffner, S.; Scherer, L. J. *New J. Chem.* **2005**, *29*, 1475.

(25) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246.

(26) Constable, E. C.; Dunphy, E. L.; Housecroft, C. E.; Kylberg, W.; Neuburger, M.; Schaffner, S.; Schofield, E. R.; Smith, C. B. *Chem.—Eur. J.* **2006**, *12*, 4600.

(27) Chambers, J.; Eaves, B.; Parker, D.; Claxton, R.; Ray, P. S.; Slattery, S. J. *Inorg. Chim. Acta* **2006**, *359*, 2400.

(28) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373.

(29) Goodwin, H. A. *Top. Curr. Chem.* **2004**, *233*, 59.

(30) Choi, J. S.; Kang, C. W.; Jung, K.; Yang, J. W.; Kim, Y.-G.; Han, H. *J. Am. Chem. Soc.* **2004**, *126*, 8606.

(31) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Cush, R.; Russo, P. S.; Godínez, L. A.; Saunders, M. J.; Mohapatra, P. *Chem.—Eur. J.* **2002**, *8*, 2946.

(32) Davidson, G. J. E.; Loeb, S. J. *Dalton Trans.* **2003**, 4319.

(33) Rapenne, G.; Dietrich-Buchecker, C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 994.

(34) Constable, E. C.; Edwards, A. J.; Martinez-Manez, R.; Raithby, P. R.; Thompson, A. M. W. C. *J. Chem. Soc., Dalton Trans.* **1994**, 645.

(35) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1932**, 20.

(36) Baker, A.; Goodwin, H. *Aust. J. Chem.* **1985**, *38*, 207.

(37) Hathcock, D. J.; Stone, K.; Madden, J.; Slattery, S. J. *Inorg. Chim. Acta* **1998**, *282*, 131.

(38) Bochet, C. G.; Piguet, C.; Williams, A. F. *Helv. Chim. Acta* **1993**, *76*, 372.

(39) Braterman, P. S.; Song, J. I.; Peacock, R. D. *Inorg. Chem.* **1992**, *31*, 555.

(40) Arana, C.; Yan, S.; Keshavarz-K, M.; Potts, K. T.; Abrufia, H. D. *Inorg. Chem.* **1992**, *31*, 3680.

(41) Elsbernd, H.; Beattie, J. K. *J. Inorg. Nucl. Chem* **1972**, *34*, 771.

(42) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 14316.

(43) Ulmann, P. A.; Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A.; DiPasquale, A. G.; Rheingold, A. L. *Chem.—Eur. J.* **2007**, *13*, 4529.

(44) Ulmann, P. A.; Mirkin, C. A.; DiPasquale, A. G.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2009**, *28*, 1068.

(45) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759.

(46) Ayers, T.; Scott, S.; Goins, J.; Caylor, N.; Hathcock, D.; Slattery, S. J.; Jameson, D. L. *Inorg. Chim. Acta* **2000**, *307*, 7.

(47) Kirgan, R. A.; Rillema, D. P. *J. Phys. Chem. A* **2007**, *111*, 13157.

(48) Beer, P. D.; Gale, P. A.; Chen, G. C. *Coord. Chem. Rev.* **1999**, *185−186*, 3.

(49) Gütlich, P.; Bill, E.; Trautwein, A. X. *Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications*; Springer: Berlin, 2011.

(50) Cao, C.; Dahal, S.; Shang, M.; Beatty, A. M.; Hibbs, W.; Schulz, C. E.; Scheidt, W. R. *Inorg. Chem.* **2003**, *42*, 5202.

(51) Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299.