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Homotrimetallic Oxazolo-Ferrocene Complexes Displaying Tunable Cooperative Interactions between Metal Centers and Redox-Switchable Character

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A synthetic procedure based on the aza-Wittig reaction of α-azidoacetyl ferrocene or 1,1′-bis(α-azidoacetyl)ferrocene with mono-, di-, and triacyl chlorides and triphenylphosphine has been developed to prepare the new homotrimetallic ferrocene complexes **6**, **9**, and **10** containing at least two oxazole rings in the conjugation chain. Complexes **9** and **10** exhibited three and two reversible redox processes, respectively, indicating significant electrostatic interaction between the iron centers in these complexes. Protonation properties of complexes **9**−**13** have been assesed by use of ^{1}H NMR and cyclic voltammetry measurements.

Introduction

The reason for the widespread interest in the study of molecular systems containing more than one metallocene is that, with certain π-conjugated bridges, the metal centers are no longer independent of each other. These organometallic assemblies are key design targets for the study of electron-transfer processes,[1] the fabrication of nanostructured materials,[2] the formation of liquid crystalline organometallic polymers,[3] the construction of molecular devices,[4] and the creation of dendrimers containing organometallic fragments.[5]

It is quite obvious that homobimetallic complexes in which two ferrocene units are coupled intimately through suitable bridging units are more likely to display these sort of properties and serve as important benchmarks for the optimization of synthetic methods and for the investigation of intramolecular (intrachain) communication among the covalently linked ferrocene units. The shortest bridge is just one bond, and the biferrocene itself and some methylated derivatives have been intensively studied[6] as well as biferrocenes bridged by π-unsaturated units[7] or heteroaromatic rings[8] (thiophene and furan). It should be mentioned that bridges between ferrocenes that consist of main-group elements such as Si, Sn, or S transmit electronic effects at least as efficiently as a π-unsaturated carbon−carbon bridge over short distances.[9]

Although biferrocenes linked by alkene bridges present high electron transmision efficiency, their thermal and photochemical instability possess several drawbacks. On the other hand, the efficiency of the more stable aromatic systems appears limited by excessive charge confinement. The very stable oxazole ring possesses a sextet of π-electrons. However, the ease with which the

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[1] (a) Benniston, A. C.; Goulle, V.; Harriman, A.; Lehn, J. M.; Marczinke, B. *J. Phys. Chem.* **1994**, *98*, 7798. (b) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704. (c) Harriman, A.; Odobel, F.; Sauvage, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 9461. (d) Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 595. (e) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100. (f) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921.

[2] Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Riceunto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211.

[3] (a) Dembek, A. A.; Burch, R. R.; Feiring, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2087. (b) Altmann, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569. (c) Altmann, M.; Enkelmann, V.; Lieser, G.; Bunz, U. H. F. *Adv. Mater.* **1995**, *7*, 716. (d) Oriol, L.; Serrano, J. L. *Adv. Mater.* **1995**, *7*, 248.

[4] (a) Lehn, J. M. In *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (b) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (c) Ward, M. D. *Chem. Ind.* **1996**, 568.

[5] (a) Serroni, S.; Denti, G.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1493. (b) Newkome, G. R.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Cargill-Thompson, A. M. W. *J. Chem. Soc., Chem. Commun.* **1993**, 925. (c) Liao, Y. H.; Moss, J. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1774. (d) Achar, S.; Puddephatt, R. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 847. (e) Tzalis, D.; Tor, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1043. (f) Faust, R.; Diederich, F.; Gramlich, V.; Seiler, P. *Chem. Eur. J.* **1995**, *1*, 111. (g) Amoroso, A. J.; Cargill-Thompson, A. M. W.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828. (h) Harriman, A.; Hissler, M.; Ziessel, R.; De Cian, A.; Ficher, J. *J. Chem. Soc., Dalton Trans.* **1995**, 4067. (i) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203. (j) Muller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *127*, 607.

[6] (a) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331. (b) Webb, R. J.; Hagen, P. M.; Wittebort, R. J.; Sorai, M. *Inorg. Chem.* **1992**, *31*, 1791. (c) Rittinger, S.; Buchholz, D.; Delville-Desbois, M. H.; Linares, J.; Varret, F.; Boese, R.; Zsolnai, L.; Huttner, G.; Astruc, D. *Organometallics* **1992**, *11*, 1454. (d) Hudeczeck, P.; Köhler, F. H. *Organometallics* **1992**, *11*, 1773. (e) Dong, T. Y.; Lee, T. Y.; Lee, S. H.; Lee, G. H.; Peng, S. M. *Organometallics* **1994**, *13*, 2337. (f) Dong, T. Y.; Huang, C. H.; Chang, C. K.; Hsieh, H. C.; Peng, S. M.; Lee, G. H. *Organometallics* **1995**, *14*, 1776. (g) Dong, T. Y.; Chang, C. K.; Lee, S. H.; Lai, L. L.; Chiang, M. Y. N.; Lin, K. J. *Organometallics* **1997**, *16*, 5816. (h) Hilbig, H.; Hudeczek, P.; Köhler, F. H.; Xie, X.; Bergerat, P.; Kahn, O. *Inorg. Chem.* **1998**, *37*, 4246.

[7] (a) Ribon, A. C.; Launay, J. P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735. (b) Meo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (c) Heilg, O. M.; Herker, M. A.; Hiller, W.; Köhler, F. H.; Schell, A. *J. Organomet. Chem.* **1999**, *574*, 94. (d) Barlow, S.; Murphy, V. J.; Evans, J. S. O.; O'Hare, D. *Organometallics* **1995**, *14*, 3461.

[8] (a) Justin Thomas, K. R.; Lin, J. T.; Wen, Y. S. *J. Organomet. Chem.* **1999**, *575*, 301. (b) Justin Thomas, K. R.; Lin, J. T.; Lin, K. J.; *Organometallics* **1999**, *18*, 5285. (c) Justin Thomas, K. R.; Lin, J. T.; Wen, Y. S. *Organometallics* **2000**, *19*, 1008.

[9] (a) Pannell, K. H.; Dementiev, V. V.; Li, H.; Cervantes-Lee, F.; Nguyen, M. T.; Díaz, A. F. *Organometallics* **1994**, *13*, 3644. (b) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (c) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797. (d) Zechel, D. L.; Foucher, D. A.; Pudelski, J. K.; Yap, G. P. A.; Rheingold, A. L.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1995**, 1893.

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oxazole ring undergoes Diels−Alder reactions with dienophiles and autoxidation with singlet oxygen indicates that the delocalization is quite incomplete; hence, it has but little aromatic character. Due to this, polyferrocene systems with oxazole conjugation may be considered a good tradeoff between the efficiency of ethylenic systems and the stability of the aromatic ones. Additionally, the nitrogen atom in the oxazole conjugated spacer, able to act as a ligand toward metal ions, could be of interest for the construction of heterobimetallic systems, which can behave as redox-switched receptors with the capability of selectively sensing ionic-guest species via electrochemical and/or optical methodologies.[10]

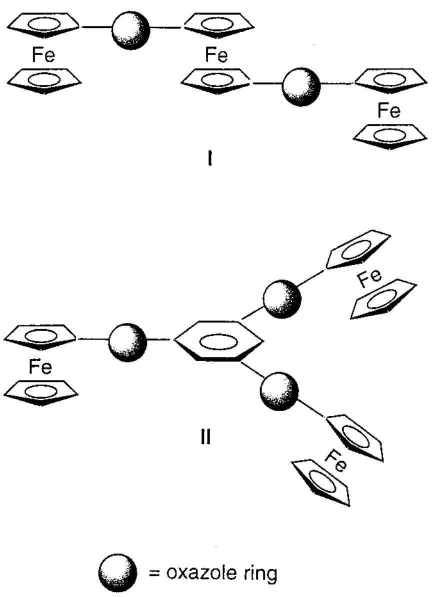
In a continuation of our studies on the synthesis of ferrocenyl-substituted azaheterocycles,[11] we wish to present here the synthesis and redox behavior of tris(ferrocene) complexes type I and II bearing two or three oxazole rings, respectively, using the iminophosphorane methodology.[12] The persistent advantage of this approach is flexibility with respect to the tethering groups between the metal centers. In this context, electronic structure and/or length of the spacer have been systematically varied to gain insight into the redox behavior of the unreported oxazolo-ferrocene complexes prepared. The trinuclear congeners reported herein are potential building blocks for organometallic molecules (Chart 1).

Results and Discussion

The synthesis of the ferrocenyloxazole derivatives is based on the aza-Wittig reaction of acyl chlorides with iminophosphoranes derived from the appropriate α-azido carbonyl compound. Although this methodology has been successfully applied to the synthesis of oxazole derivatives,[13] no reaction of dicarbonyl and tricarbonyl chlorides with iminophosphoranes derived from α-azidocarbonyl compounds has been reported to the best of our knowledge. In this context, it has been found that aza-Wittig reactions of several kinds of dicarbonyl chlorides with *N*-aryliminophosphoranes are very substrate-dependent.[14]

The required aza-substituted ferrocene precursors have been prepared as follows. The α-azidocarbonylferrocene **2** has been prepared in 78% overall yield from acetylferrocene trimethylsilylenol ether by bromination followed by halogen-azido substitution.[11e]

Chart 1



The bis(azide) **5** has been prepared from 1,1′-diacetylferrocene **3** by the two-step sequence: (a) metalation of **3** with LDA at −78 °C followed by sequential treatment with chlorotrimethylsilane and NBS provides 1,1′-bis(α-bromoacetyl)ferrocene **4** in 79% yield, and (b) reaction of **4** with sodium azide or polymeric quaternary ammonium azide[15] leads to **5** in 80% yield (Scheme 1).

At first, formation of homotrimetallic complexes was attempted by using the triazaphosphadiene pathway,[16] in view of the excellent results obtained from the reaction of azides with tertiary phosphines and acyl chlorides to give five-membered rings.[17] In this way, the reaction is carried out with the acyl chloride present before addition of the phosphine. Thus, addition of triphenylphosphine to a mixture of α-azidoacetylferrocene **2** and the acyl chloride derived from the 1,3,5-benzenetricarboxylic acid, in the presence of polymer-supported BEMP, afforded the homotrimetallic complex **6**, in 45% yield, after chromatographic purification (Scheme 2).

With the aim of preparing related homotrimetallic complexes we turned our attention to the aza-Wittig reaction between the azides **2** and **5** and acyl chlorides derived from the ferrocene system, which would give rise to tris(ferrocene) complexes in which the three ferrocene units are linked by two oxazole rings.

To this end, the ferrocene acyl components of choice were chlorocarbonyl ferrocene[18] **7** and 1,1′-bis(chlorocarbonyl)ferrocene[19] **8**, respectively. The tris(ferrocene)-complex **9** was prepared in 40% yield from the reaction of α-azidoacetylferrocene **2** with triphenylphosphine and 1,1′-bis(chlorocarbonyl)ferrocene **8** in the presence of polymer-supported BEMP, whereas the formation of the isomer **10** was accomplished in 35% yield by the same

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[10] (a) Constable, E. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 407. (b) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79. (c) Medina, J. C.; Goodnow, T. T.; Rojas, M. T.; Atwood, J. L.; Lynn, B. C.; Kaifer, A. E.; Gokel, G. W. *J. Am. Chem. Soc.* **1992**, *114*, 10583. (d) Delavaux-Nicot, B.; Guari, Y.; Douziech, B.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 585. (e) Beer, P. D.; Graydon, A. R.; Sutton, L. R. *Polyhedron* **1996**, *15*, 2457. (f) Beer, P. D.; Szenes, F.; Balzani, V.; Sala, C. M.; Drew, M. G. B.; Dent, S. W.; Maestri, M. *J. Am. Chem. Soc.* **1997**, *119*, 11864. (g) Chesney, A.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K.; Goldenberg, L. M. *J. Chem. Soc., Chem. Commun.* **1998**, 667.

[11] (a) Molina, P.; Pastor, A.; Vilaplana, M. J.; Ramirez de Arellano, M. C. *Tetrahedron Lett.* **1996**, *37*, 7829. (b) Molina, P.; Pastor, A.; Vilaplana, M. J.; Velasco, M. D.; Ramirez de Arellano, M. C. *Organometallics* **1997**, *16*, 5836. (c) Molina, P.; Tárraga, A.; Curiel, D.; Ramírez de Arellano, M. C. *Tetrahedron* **1999**, *55*, 1417. (d) Molina, P.; Tárraga, A.; López, J. L.; Martínez, J. C. *J. Organomet. Chem.* **1999**, *584*, 147. (e) Tárraga, A.; Molina, P.; Curiel, D.; López, J. L.; Velasco, M. D. *Tetrahedron* **1999**, *55*, 14701. (f) Tárraga, A.; Molina, P.; López, J. L. *Tetrahedron Lett.* **2000**, *41*, 2479.

[12] For a review see: Molina, P.; Vilaplana, M. J. *Synthesis* **1994**, 1197.

[13] (a) Zbiral, E.; Bauer, E.; Stroh, J. *Monatsh. Chem.* **1971**, *102*, 168. (b) Molina P.; Fresneda, P. M.; Almendros, P. *Synthesis* **1993**, 54. (c) Molina, P.; Fresneda, P. M.; Almendros, P. *Heterocycles* **1993**, *36*, 2255.

[14] (a) Aubert, T.; Farnier, M.; Guilard, R. *Synthesis* **1990**, 149. (b) Aubert, T.; Farnier, M.; Guilard, R. *Tetrahedron* **1991**, *47*, 53.

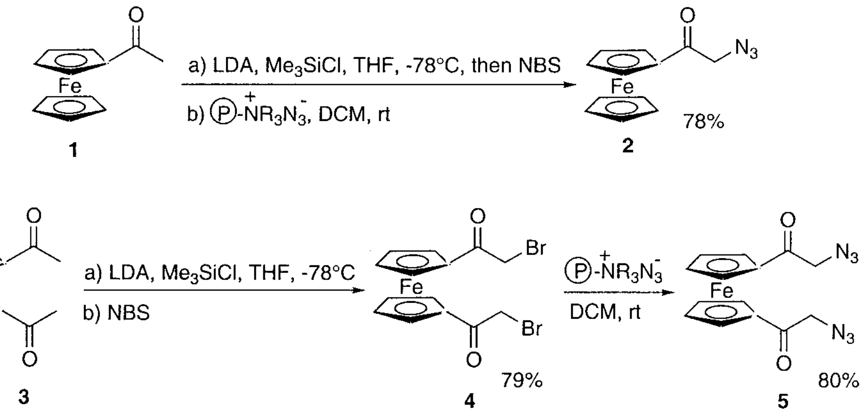
[15] Hassner, A.; Stern, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 478.

[16] Shalev, D. E.; Chiacchiera, S. M.; Radkowsky, A. E.; Kosower, E. M. *J. Org. Chem.* **1996**, *61*, 1689.

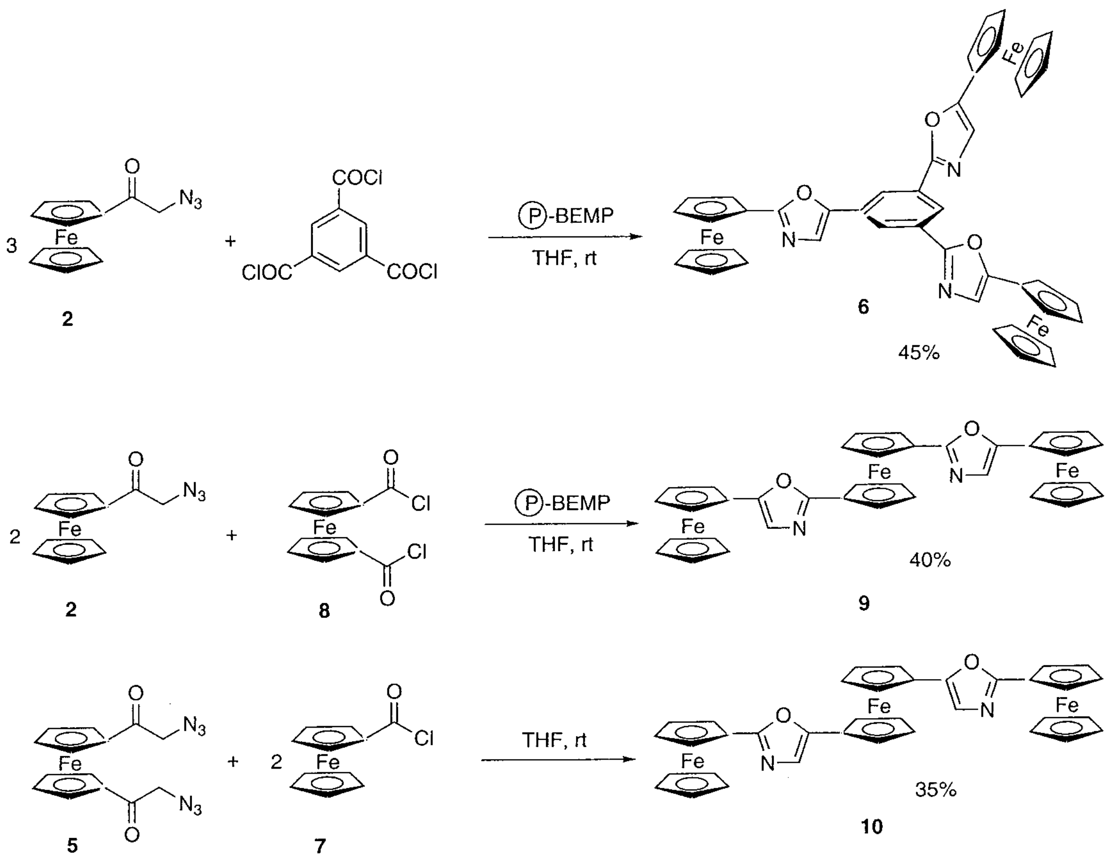
[17] Fresneda, P. M.; Molina, P.; Sanz, M. *Synlett* **2000**, 1190.

[18] Mabrouk, S. T.; Hart, W. P.; Rausch, M. D. *J. Organomet. Chem.* **1996**, *527*, 43.

Scheme 1



Scheme 2



method starting from 1,1′-bis(α-azidoacetyl)ferrocene **5** and chlorocarbonylferrocene **7** without the need of using base (Scheme 2).

Cyclic voltammetry (CV) was used to investigate the possibility of electronic communication between the metal centers in the homotrimetallic complexes **6**, **9**, and **10**, respectively. Significant metal–metal interaction would be indicated by two or three distinct oxidation waves in CV. The resulting data are collected in Table 1 and illustrated in Figure 1. First, the electrochemical behavior of simple ferrocenyl oxazoles deserves some comments (Chart 2). First, 5-ferrocenyl oxazoles **11** are more easily oxidized than the isomeric 2-ferrocenyl oxazoles **12**, $E_{1/2}$ = 0.517 vs 0.582 V, which is in agreement with the results of MO calculations of varying degrees of sophistication of the oxazole ring which mostly place a higher electron density at position C(5) than C(2).[20] Second, the 2,5-bis(ferrocenyl)oxazole **13** (Figure 1B) undergoes two succesive reversible one-electron oxidations with $\Delta E_{1/2}$ = 140 mV, indicating a moderate interaction through the heterocyclic oxazole ring between the two iron sites. In the field of tris(ferrocene) molecules, it is worth noting that the nature of the chain length and the element type between the three ferrocene units proved to be crucial. Molecules in which the three ferrocene units are appended to triaza crown ethers or aromatic rings exhibit a single-step oxidation process.[21] In contrast, tris(ferrocenes) having

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(19) Hammond, P. J.; Bell, A. P.; Hall, C. D. *J. Chem. Soc., Perkin Trans. 1* **1983**, 707.

(20) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389.

(21) (a) Beer, P. D.; Crowe, D. B.; Ogden, M. I.; Drew, M. G. B.; Main, B. *J. Chem. Soc., Dalton Trans.* **1993**, 2107. (b) Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646.

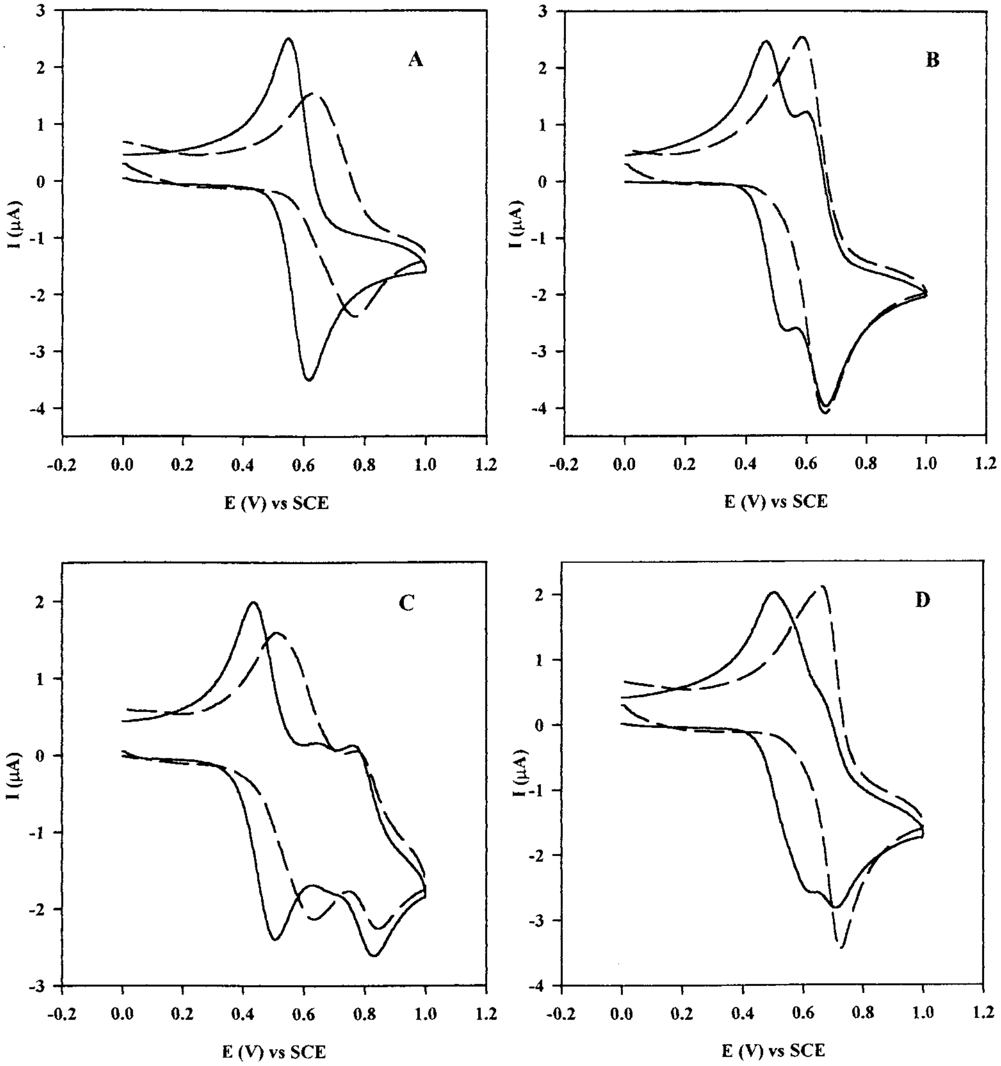
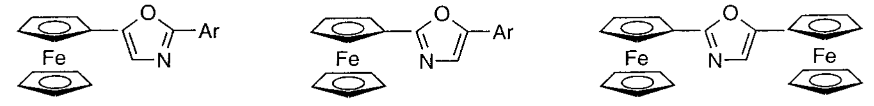


Figure 1. Cyclic voltammograms of complexes **12** (A); **13** (B); **9** (C); **10** (D) (solid lines) and their protonated species **12·H$^+$** (A); **13·H$^+$** (B); **9·H$^+$·H$^+$** (C); **10·H$^+$·H$^+$** (D) (dashed lines). Scan rate 200 mV s^{-1}.

Chart 2



11 **12** **13**

Ferrocene-C(5)oxazole Ferrocene-C(2)oxazole

ferrocenyl units either appended to cyclopropene or linked to open-chain frames displayed one-electron oxidation steps.[22] When the tris(ferrocene) complex **6** was subjected to CV measurement, only one characteristic superimposed single-step oxidation process[23] was observed. For molecules with multiple noninteracting sites a peak-to-peak separation matching that of a one-electron step is consistent with theory.[24] This fact implies that the central aromatic spacer does not allow the relevant peripheral ferrocenyl subunits to communicate electronically with each other, and they are oxidized independently. Analogous phenylene- and biphenylene-linked diferrocene species also showed no voltammetry splitting.[25]

The cyclic voltammogram of the tris(ferrocene)complex **9** (Figure 1C) in CH_3CN/CH_2Cl_2 (3:2) solution showed three reversible oxidation waves, suggesting that each of the three ferrocene units exhibits a unique

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(22) (a) Fry, A. J.; Jain, P. S.; Krieger, R. L. *J. Organomet. Chem.* **1981**, *214*, 381. (b) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; Le Vanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506. (c) Atzkern, H.; Hiermeier, J.; Kohler, F. H.; Steck, A. *J. Organomet. Chem.* **1991**, *408*, 281.

(23) (a) Ammar, F.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *47*, 215. (b) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.

(24) Flanagan, J. B.; Margell, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(25) (a) Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998. (b) Bunel, E.; Campos, R.; Ruz, J.; Valle, L.; Chadwick, I.; Santa Ana, M.; Gonzalez, G.; Manriquez, J. M. *Organometallics* **1988**, *7*, 474. (c) Bunel, E. E.; Valle, L.; Jones, N. L.; Carrol, P. J.; Gonzalez, M.; Muñoz, N.; Manriquez, J. M. *Organometallics* **1988**, *7*, 789. (d) Hollandsworth, C. B.; Hollis, W. G., Jr.; Slebodnick, C.; Deck, P. A. *Organometallics* **1999**, *18*, 3610.

Table 1. Cyclic Voltammetry for Various Ferrocene Complexes and Their Protonated Species

compound	$E_{1/2}$ (V)[a]	$\Delta E_{1/2}$ (V)	Δ (mV)[b]
ferrocene	0.407		70
6	0.520		
9	0.468	0.328	73
	0.796		73
9·$\mathbf{H^+}$·$\mathbf{H^+}$	0.575	0.234	120
	0.809		69
10	0.565		128
	0.705[c]		
10·$\mathbf{H^+}$·$\mathbf{H^+}$	0.691		64
11	0.517		64
11·$\mathbf{H^+}$·$\mathbf{H^+}$	0.524		65
12	0.582		67
12·$\mathbf{H^+}$	0.696		137
13	0.501	0.140	71
	0.641		67
13·$\mathbf{H^+}$	0.624		82

[a] All half-wave potentials are referred to SCE electrode, scan rate 0.2 V s^{-1}. [b] Peak-to-peak separation between the resolved reduction and oxidation wave maxima. [c] E_{pa} are referred.

redox couple. However the central wave, in particular the oxidation peak, is already virtually unresolvable. The separation between the first and the third oxidation events is 328 mV. These data indicate significant electrostatic interaction between the iron centers; in the absence of any interaction we would expect two waves in 2:1 ratio corresponding to the two ferrocene environments present. We believe that one peripheral ferrocene will be the first center to be oxidized, as it is linked to the oxazole ring at position 5. Subsequent oxidation presumably corresponds to generation of a dication in which the charge is borne by the peripheral ferrocenes, and the third oxidation involves the formation of a trication. Probably the high positive value of the last oxidation process could be due to the fact that the central ferrocene subunit is linked to two oxazole rings at the more electron-withdrawing position 2, as well as to the Coulombic effect of the neighboring ferrocenium species formed by initial oxidations.

In the cyclic voltammogram of the tris(ferrocene) complex **10** (Figure 1D) two oxidations events in 2:1 ratio[26] with a separation of 80 mV were located and a conjugate peak for the reduction of the trication is barely perceptible. In fact, the redox waves were considerably broadened, as noticed from the larger ΔE_p value, and probably indicate three closely spaced redox waves. It looks reasonable to suggest that the peripheral ferrocene subunits will be the first centers to be oxidized. The second potential presumably corresponds to generation of the trication by oxidation of the central ferrocene, which is linked to two electron-deficient oxazole rings.

One of the most interesting attributes of the bis(ferrocene) complex **13** and the tris(ferrocene) complexes **9** and **10** is the presence of two or three ferrocene redox-active moieties in proximity of the proton-binding oxazole site. Binding and electron-transfer events can influence each other owing to the short distance between their respective sites. Binding events could affect the thermodynamic electron-transfer process between the iron centers. Conversely, the magnitude of the electron-transfer rate in bis- or tris(ferrocenium) systems may change the proton-binding affinity. Thus, CV of **13**, **9**, and **10** in the presence of variable concentrations of protons affords a simple and effective way for estimating the communication between the redox and binding sites.

Stepwise addition of $HBF_4 \cdot Et_2O$ to a solution of complex **13** in CH_3CN/CH_2Cl_2 (3:2) resulted in a clear evolution of the first wave from $E_p = 0.505$ to 0.635 V, whereas there was no affect on the second (Figure 1B). Remarkably, the current intensity of the cathodic peak of the second wave increases, while that of the first one decreases with a linear dependence on the equivalents of the added acid. In particular, the second wave reaches the maximum current intensity value at 1.0 equiv of added acid, and at this point the first wave disappears (addition of more acid does not change further the electrochemical response). The area of this wave is almost equal to the sum of the area of the two waves observed before the addition of acid. The occurrence of this wave at the same potential for the free complex suggests that after oxidation of the ferrocene unit linked at position 5 the adduct is deprotonated and subsequent oxidation takes place on the free complex.

The ease with which the very weak basic oxazole ring ($pK_a = 0.8 \pm 0.2$) is protonated in compound **13** can be rationalized by invoking the known propensity of the ferrocenyl group to act as a neighboring group.[27] Under the acidic conditions, the oxazole ring is protonated easily with the neighboring group participation from the ferrocenyl moiety at position 2 to give the corresponding ferrocenyl-stabilized carbenium ion. The redox potential of the 2-ferrocenyl oxazole **12** is shifted toward the more positive value of 114 mV by protonation under the same conditions, indicating a strong electrostatic interaction between the highly electron-deficient oxazolium cation and the adjacent ferrocene center, making the oxidation of the latter much more difficult than in the neutral complex.[28] This shift was accompanied by a drastic flattening of the cathodic and anodic peaks (Figure 1A).

Addition of substoichiometric quantities of $HBF_4 \cdot Et_2O$ to a solution of the tris(ferrocene)complex **9** in CH_3CN/CH_2Cl_2 (3:2) induced the disappearance of the first and second waves accompanied by concomitant appearance of a new redox couple identical to that observed for **13**·$\mathbf{H^+}$, whereas there was no affect on the third (Figure 1C). The peak current of the new redox couple increases with the concentration of H^+ ion, until 2 equiv was added; at this point, the original first and second redox couples disappear and the new redox couple reached full development. The resulting two redox couples in 2:1 ratio with a separation of 250 mV are due to the reversible oxidation of the two peripheral and central ferrocenyl moieties, respectively, in the **9**·$\mathbf{H^+}$·$\mathbf{H^+}$ complex.

Electrochemical behavior of complex **10** upon protonation was quite similar to that observed for **13** (Figure 1D). Stepwise addition of acid leads to an anodic shift of the peripheral ferrocene subunits. Apparently the oxidation process of the dication [$Fe^+-Fe-Fe^+$] to the trication [$Fe^+-Fe^+-Fe^+$] lies in the same region, so the CV showed essentially one oxidation wave.

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[26] Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *12*, 1709.

[27] (a) Gokel, G. W.; Marquarding, D.; Ugi, I. K. *J. Org. Chem.* **1972**, *37*, 3052. (b) Woltersdorf, M.; Kranich, R.; Schunalz, H.-G. *Tetrahedron* **1997**, *53*, 7219.

[28] Plenio, H.; Yang, J.; Diodone, R.; Heinze, J. *Inorg. Chem.* **1994**, *33*, 4098.

Scheme 3. Schematic Representation of the Electrochemically Induced Deprotonation/Reprotonation of $9 \cdot H^+H^+$

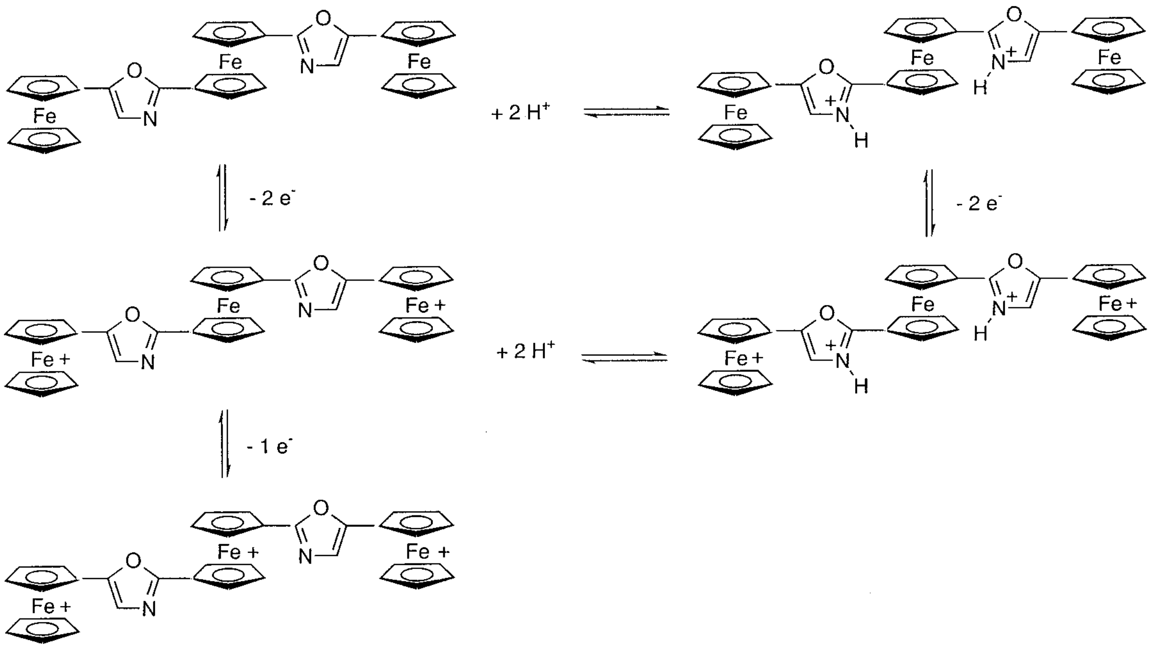

Table 2. Chemical Shifts of the Ferrocene Protons in Complexes 9–13 and Their Protonated Species

	ferrocene-C(2)oxazole			ferrocene-C(5)oxazole		
compound	α	*β*	Cp	α	*β*	Cp
9	4.97	4.40		4.58	4.31	4.10
$\mathbf{9 \cdot H^+ \cdot H^+}$	5.10	4.52		4.71	4.30	4.20
$\Delta\delta$	0.13	0.12		0.13	0.01	0.1
10	4.93	4.41	4.18	4.57	4.34	
$\mathbf{10 \cdot H^+ \cdot H^+}$	5.14	4.78	4.33	4.96	4.61	
$\Delta\delta$	0.21	0.37	0.15	0.39	0.27	
11				4.66	4.36	4.14
$\mathbf{11 \cdot H^+}$				4.80	4.57	4.25
$\Delta\delta$				0.14	0.21	0.09
12	4.96	4.43	4.17			
$\mathbf{12 \cdot H^+}$	5.30	4.89	4.37			
$\Delta\delta$	0.34	0.46	0.20			
13	4.95	4.41	4.19	4.65	4.34	4.16
$\mathbf{13 \cdot H^+}$	5.24	4.85	4.37	5.24	4.85	4.37
$\Delta\delta$	0.29	0.44	0.18	0.59	0.51	0.21

A ^{1}H NMR investigation was undertaken in order to complement the electrochemistry study and in order to gain a better understanding of the factors that determine the extent of this redox-switched bonding in complexes **9**–**13**. Compounds were dissolved in $CDCl_3$ and treated with $HBF_4 \cdot Et_2O$, and the signals of the ferrocenyl protons were shifted until the protonation was complete. Further acid addition of up 2 equiv for **11**–**13** and 4 equiv for **9**–**10** had almost no effect on the position of the NMR signals.

The chemical shift data of the ferrocenyl protons are listed in Table 2. Assignments of the chemical shifts in complex **13** and consequently in complexes **9** and **10** were made by comparison with those observed in the 5-ferrocenyloxazole **11** (ferrocene-C(5)-oxazole) and the 2-ferrocenyloxazole **12** (ferrocene-C(2)-oxazole). The Hα protons of the protonated species $\mathbf{9 \cdot H^+ \cdot H^+}$ and $\mathbf{10 \cdot H^+ \cdot H^+}$ were assigned to the larger of the four positive chemical shifts.[29]

The ^{1}H NMR analysis of the protonated species revealed significant chemical shift changes relative to the free complexes. Subsequent addition of 1 equiv of C_5D_5N to the protonated species "regenerated" the ^{1}H NMR spectra, which were essentially identical to those recorded initially for free complexes. For **12**, the resonances at 4.17, 4.43, and 4.96 ppm move to 4.37, 4.89, and 5.30 ppm in $\mathbf{12 \cdot H^+}$, which are quite close to those found in ferrocenylallylium cations.[30]

The bis(ferrocenyl)complex **13**, which clearly displayed two sets of well-separated signals for the two ferrocene subunits, upon protonation showed only one set of signals downfield shifted. The resulting spectrum of $\mathbf{13 \cdot H^+}$ was found to be almost identical to that of $\mathbf{12 \cdot H^+}$.

In tris(ferrocene)complexes **9** and **10**, the two peripheral ferrocenes are magnetically equivalent, so that two sets of signals in 2:1 ratio were observed for the peripheral and central ferrocenes, respectively. Upon protonation, all signals were significantly downfield shifted, this change being higher in $\mathbf{10 \cdot H^+ \cdot H^+}$ than in $\mathbf{9 \cdot H^+ \cdot H^+}$.

In Scheme 3 we address the electrochemically induced deprotonation/reprotonation of the representative complex **9**.

In the neutral form the tris(ferrocene)complex **9** will be protonated, as evidenced by ^{1}H NMR titration. The adduct $\mathbf{9 \cdot H^+ \cdot H^+}$ shows two reversible redox couples. The first process is shifted (130 mV) toward more positive potential values, while the second one occurs practically at the same potential as that observed for the free complex. The positive shift of the potential corresponding to the first oxidation process, which is almost the same as those observed for $\mathbf{12 \cdot H^+}$ and $\mathbf{13 \cdot H^+}$, can be explained on the basis of the unfavorable interaction between the two electron-deficient oxazolium cations with the two peripheral ferrocene centers in close proximity, taking place in the $\mathbf{9 \cdot H^+ \cdot H^+}$ adduct. The occurrence of the second oxidation process at the same

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(29) Pickett, T. E.; Richards, C. J. *Tetrahedron Lett.* **1999**, 5251.

potential for the free complex **9** suggests that, after oxidation of the two ferrocenes' termini, the adduct is disrupted and the succesive oxidation takes place on the free complex.

The reasons that the adduct $[Fe^+-Fe-Fe^+]\cdot H^+\cdot H^+$ is deprotonated could be due either to the proximal mutual electrostatic charge repulsion between the ferrocenium cations and the oxazolium rings or to the fact that the oxidation of the ferrocenyl to the ferrocenium group prevents neighboring group participation,[31] which probably decreases the basicity of the oxazole ring, making it not basic enough to be protonated.

Conclusions

The present investigation has explored a new methodology that permits the synthesis of a new sort of ferrocene derivative containing three ferrocene subunits linked by oxazole rings, which is based on the reaction of α-azidoacetylferrocene derivatives with several acyl chlorides. In some of the described compounds, the ferrocenyl subunits interact with each other and, moreover, the extent of interaction is tunable, since it is dependent on the position at which they are linked to the oxazole ring. In addition, a reversible switching can be induced by chemical input (protonation) and where the outputs are spectroscopical (^{1}H NMR) and electrochemical (CV). In principle, both outputs can be used to process information at the molecular level. We believe that the present strategy could well be applicable to varied structural motifs.

Additional experimental refinement, binding properties with metals, and application of our strategy especially in the construction of polyferrocene assemblies bearing "mixed" five-membered rings are in progress in our laboratory.

Experimental Section

General Procedures. All reactions were carried out under N_2 and using solvents that were dried by routine procedures. Compounds **11**, **12**, and **13** were prepared according to the literature procedures.[11e] Column chromatography was performed with the use of silica gel (60 A C.C. 70−200 μm, sds) as the stationary phase. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 (200 MHz) or a Varian Unity 300 (300 MHz). The EI mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument. The cyclic voltammetric measurements were performed on a QUICELTRON potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Cyclic voltammetry was performed with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a SCE reference electrode. The experiments were carried out with a 5×10^{-4} M solution of sample in dry CH_2Cl_2/CH_3CN (2:3) containing 0.1 M $(n\text{-}C_4H_9)_4ClO_4$ as supporting electrolyte. All the potential values reported are relative to an SCE electrode at room temperature. Ferrocene was used as an external reference both for potential calibration and for reversibility criteria. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min, and the working electrode was cleaned after each run.

1,1′-Bis(α−bromoacetyl)ferrocene (4). To a solution of diisopropylamine (3.1 mL, 22.2 mmol) in dry THF (30 mL), at −78 °C and under nitrogen atmosphere, was dropped *n*-butyllithium 1.6 M in hexane (13.9 mL, 22.2 mmol), and the mixture was stirred for 1 h. Then, a solution of 1,1′-diacetylferrocene (2 g, 7.4 mmol) in dry THF (60 mL) was dropped. The mixture was stirred for 2 h, and chlorotrimethylsilane (2.5 mL, 20 mmol) was injected all at once. After 3 h NBS (3.5 g, 20 mmol) was added in a single addition, and the mixture was stirred at −78 °C overnight. The crude was evaportated at reduced pressure, and the residue was chromatographed on a silica gel column, using CH_2Cl_2/EtOAc, 20:1, as eluent. The final product (2.1 g, 79%) was isolated as a dark orange solid after evaporation to dryness; mp 83−86 °C. IR (Nujol) cm^{-1}: 1683, 1452, 1376, 1287, 1221, 1165, 1072. ^{1}H NMR ($CDCl_3$): δ 4.12 (s, 4H), 4.64 (t, 4H, $J = 1.8$ Hz), 4.89 (t, 4H, $J = 1.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 31.51, 71.74, 74.52, 195.04. EIMS *m/z* (rel intensity): 430 ($M^+ + 2$, 25), 428 (M^+, 39), 426 ($M^+ - 2$, 37), 268 (47), 240 (36), 212 (42), 135 (65), 92 (40), 81 (29), 78 (100), 63 (39), 56 (50). Anal. Calcd for $C_{14}H_{12}Br_2FeO_2$: C, 39.30; H, 2.83. Found: C, 39.45; H, 2.58.

1,1′-Bis(α-azidoacetyl)ferrocene (5). To a solution of 1,1′-bis(α-bromoacetyl)ferrocene (1 g, 2.3 mmol) in acetone (15 mL) was added sodium azide (1.5 g, 23 mmol) in one portion. The mixture was stirred at room temperature for 3 h and then filtered through a silica gel pad. The solution was evaporated at reduced pressure, giving the product as a dark orange solid (0.8 g, 80%); mp 123−126 °C. IR (Nujol) cm^{-1}: 2103, 1682, 1462, 1382, 1290, 1253, 1080, 1041. ^{1}H NMR ($CDCl_3$): δ 4.18 (s, 4H), 4.62 (s, 4H), 4.83 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 55.37, 70.73, 74.10, 197.08. EIMS *m/z* (rel intensity): 352 (M^+, 18), 296 (16), 278 (18), 269 (26), 212 (26), 177 (27), 149 (48), 121 (93), 56 (100). Anal. Calcd for $C_{14}H_{12}FeN_6O_2$: C, 47.75; H, 3.43; N, 23.87. Found: C, 47.65; H, 3.20; N, 24.03.

1,3,5-Tris(5-ferrocenyloxazol-2-yl)benzene (6). To a mixture of α-azidoacetylferrocene (0.4 g, 1.48 mmol), 1,3,5-benzenetricarbonyl chloride (0.13 g, 0.49 mmol), and the polymer-supported BEMP (0.65 g) in dry Et_2O (20 mL) was slowly dropped a solution of triphenylphosphine (0.44 g, 1.7 mmol) in the same solvent (10 mL) at room temperature and under nitrogen atmosphere. The mixture was stirred for 24 h, and the resin was then removed by filtration. The solution was evaporated to dryness under reduced pressure, and the residue was chromatographed on a silica gel column, using EtOAc/*n*-hexane, 1:3, as eluent. After evaporating to dryness the residue was triturated in Et_2O to give **6**, in 45% yield, as an solid, analytically pure sample; mp > 300 °C. IR (Nujol) cm^{-1}: 1601, 1446, 1412, 1129, 1106, 1024, 1000, 957, 910, 720. ^{1}H NMR ($CDCl_3$): δ 4.19 (s, 15H), 4.41 (t, 6H, $J = 1.8$ Hz), 4.76 (t, 6H, $J = 1.8$ Hz), 7.18 (s, 3H), 8.82 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 66.14, 69.35, 69.76, 72.10, 122.22, 124.26, 129.14, 152.60, 158.94. EIMS *m/z* (rel intensity): 831 (M^+, 100), 416 (40), 186 (9), 121 (11). Anal. Calcd for $C_{45}H_{33}Fe_3N_3O_3$: C, 65.02; H, 4.00; N, 5.05. Found: C, 65.22; H, 3.87; N, 5.20.

1,1′-Bis(5-ferrocenyloxazol-2-yl)ferrocene (9). It was prepared in 40% yield as described above for **6**, using 1,1′-ferrocenedicarbonyl dichloride (0.19 g, 0.61 mmol); mp 77−79 °C. IR (Nujol) cm^{-1}: 1617, 1536, 1457, 1254, 1128, 1108. ^{1}H NMR ($CDCl_3$): δ 4.13 (s, 10H), 4.31 (t, $J = 1.8$ Hz, 4H), 4.40 (t, $J = 1.8$ Hz, 4H),4.58 (t, $J = 1.8$ Hz, 4H), 4.97 (t, $J = 1.8$ Hz, 4H), 6.82 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 65.61, 68.17, 68.71, 69.36, 70.03, 71.23, 71.58, 121.47, 150.32, 160.33. EIMS *m/z* (rel intensity): 688 (M^+, 100), 557 (24), 344 (21), 121 (6). Anal. Calcd for $C_{36}H_{28}Fe_3N_2O_2$: C, 62.83; H, 4.10; N, 4.07. Found: C, 62.55; H, 4.23; N, 3.89.

1,1′-Bis(2-ferrocenyloxazol-5-yl)ferrocene (10). To a solution of 1,1′-bis(α-azidoacetyl)ferrocene (**5**) (0.29 g, 0.81

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[30] Lukasser, J.; Angleitner, H.; Schottenberger, H.; Kopacka, H.; Schwiger, M.; Bildstein, B.; Ongania, K. H.; Wurst, K. *Organometallics* **1995**, *14*, 5566.

[31] Alonso, F.; Davies, S. G.; Elend, A. S.; Haggit, J. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 257.

mmol) and chlorocarbonylferrocene (0.4 g, 1.62 mmol) in dry THF (20 mL) was slowly dropped a solution of triphenylphosphine (0.49 g, 1.87 mmol) in the same solvent (10 mL) at room temperature under nitrogen. The mixture was stirred for 24 h and then evaporated to dryness under reduced pressure. The crude product was chromatographed on a silica gel columm, using EtOAc/*n*-hexane, 2:1, as eluent. After evaporating to dryness, the product was triturated with Et_2O to give **10** in 35% yield; mp 150−152 °C. IR (Nujol) cm^{-1}: 1615, 1588, 1440, 1128, 1109. ^1H NMR ($CDCl_3$): δ 4.18 (s, 10H), 4.34 (s, 4H), 4.41 (s, 4H), 4.57 (s, 4H), 4.93 (s, 4H), 6.93 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 67.12, 67.42, 69.55, 70.05, 70.50, 71.23, 74.49, 122.12, 149.06, 162.54. EIMS *m*/*z* (rel intensity): 688 (M^+, 100), 623 (29), 557 (40), 344 (27), 121 (7). Anal. Calcd for $C_{36}H_{28}Fe_3N_2O_2$: C, 62.83; H, 4.10; N, 4.07. Found: C, 62.90; H, 3.89; N, 4.13.

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