

## New Class of Diiron Dithiolates Related to the Fe-Only Hydrogenase Active Site: Synthesis and Characterization of $[\text{Fe}_2(\text{SR})_2(\text{CNMe})_7]^{2+}$

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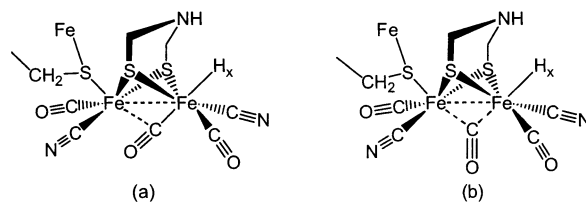
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Electron-rich polyisocyno derivatives  $\text{Fe}_2(\text{S}_2\text{C}_n\text{H}_{2n})(\text{CO})_{6-x}(\text{CNMe})_x$  ( $x \sim 4$ ) undergo oxidatively induced ( $\text{FeCp}_2^+$ ) reaction with additional CNMe to give  $[\text{Fe}_2(\text{SR})_2(\text{CNMe})_7](\text{PF}_6)_2$ , a new class of iron thiolates. Crystallographic characterization established that the  $34 e^-$  dinuclear core resembles the oxidized ( $\text{H}_2$ -binding) form of the active sites of the Fe-only hydrogenases, key features being the face-sharing bioctahedral geometry, the  $\mu$ -CX ligand, and an Fe–Fe separation of 2.61 Å. Oxidation of the phenylthiolate  $\text{Fe}_2(\text{SPh})_2(\text{CO})_2(\text{CNMe})_4$  led to mononuclear  $[\text{Fe}(\text{SPh})(\text{CNMe})_5](\text{PF}_6)$ , which is analogous to  $[\text{Fe}_2(\text{SR})_2(\text{CNMe})_{10}](\text{PF}_6)_2$  formed upon treatment of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CNMe})_7](\text{PF}_6)_2$  with excess CNMe.

Recent intensive efforts have been directed toward the synthesis of structural and functional models of the active sites of the Fe-only hydrogenases (Fe  $\text{H}_2$ -ase, see Figure 1).<sup>1–6</sup> These enzymes are highly active catalysts for the interconversion of protons and dihydrogen<sup>7</sup> and have the attraction that they are derived from base metals, vs platinum group metals usually necessary for hydrogen oxidation catalysis.<sup>8</sup> First generation models for the Fe  $\text{H}_2$ -ase active site (H-cluster) focused on iron(I) derivatives such as  $[\text{Fe}_2(\text{SR})_2(\text{CO})_4\text{L}_{2-n}(\text{CN})_n]^{4-}$  where  $\text{L} = \text{PMe}_3$ . These studies have led to new catalysts for proton reduction.<sup>9</sup> Our quest for diiron dithiolates capable of dihydrogen oxidation focuses on diferrous species, higher oxidation states being suited for  $\text{H}_2$  binding.<sup>10–12</sup>

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- (1) Evans, D. J. *J. Chem. Res., Synop.* **2001**, 297–303, 801–816 and references therein.
- (2) Li, H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 726–727.
- (3) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 12518–12527.
- (4) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 3268–3278.
- (5) Razavet, M.; Le Cloirec, A.; Davies, S. C.; Hughes, D. L.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **2001**, 3551–3552.
- (6) Zhao, X.; Hsiao, Y.-M.; Lai, C.-H.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **2002**, *41*, 699–708.
- (7) Frey, M. *ChemBioChem* **2002**, *3*, 153–160.
- (8) Koelle, U. *New J. Chem.* **1992**, *16*, 157–169.
- (9) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476–9477.
- (10) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chim. Acta* **1999**, *294*, 240–254.

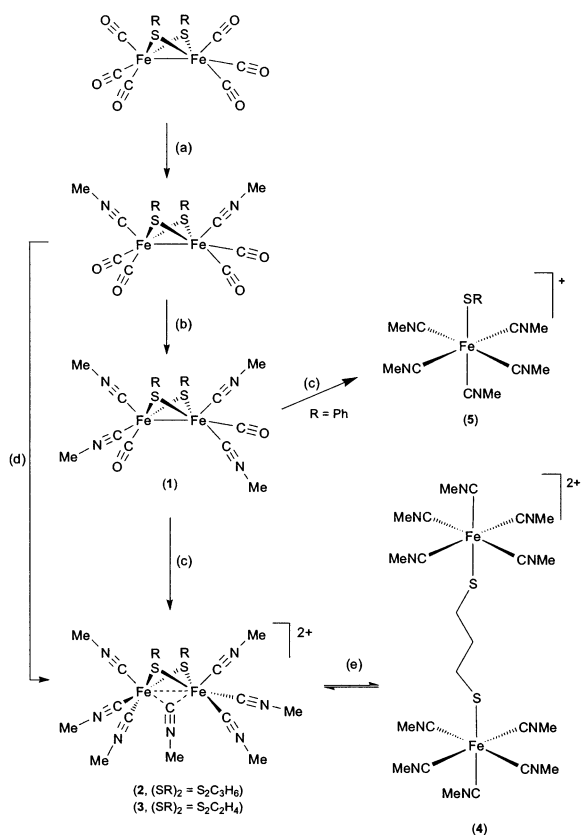


**Figure 1.** Reduced (a) and oxidized (b) active site structures proposed for the Fe-only hydrogenase in *Desulfuivibrio desulfuricans*.

The CO-inhibited and active forms of the binuclear active site feature a bridging or semi-bridging CO ligand,<sup>13–15</sup> which has proven difficult to replicate in synthetic models. Recently Pickett et al. described a transiently generated oxidized species with spectroscopic signatures indicative of the required  $\text{Fe}_2(\text{SR})_2\text{L}_6(\mu\text{-CO})$  donor set, but such species are unstable above  $-40^\circ\text{C}$ .<sup>16</sup> In this report, we describe a new class of diiron dithiolates based on isocyanides as surrogates for the mixed CO–CN<sup>-</sup> donor set; this new class of diiron species provides structural models for the  $\text{Fe}_2(\text{SR})_2\text{L}_6(\mu\text{-CX})$  active site of the Fe  $\text{H}_2$ -ases.

Recognizing that isocyanides are isoelectronic with CO but superior electron donors,<sup>17–20</sup> we reinvestigated the  $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_{6-x}(\text{CNMe})_x$  system for which we had previously reported the disubstituted derivative ( $x = 2$ ).<sup>3</sup> We found that treatment of  $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_6$  with excess CNMe in refluxing MeCN solution gave oxidatively sensitive polysubstituted derivatives such as  $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_2-$

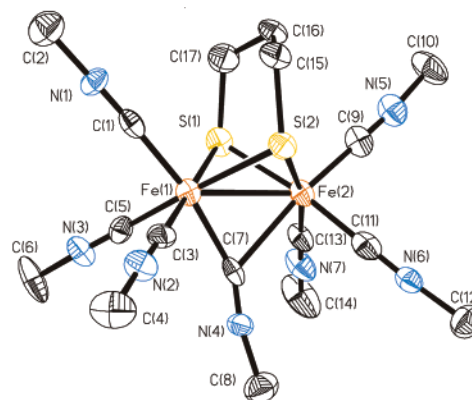
- (11) Kubas, G. J. *Metal Dihydrogen and  $\sigma$ -Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001.
- (12) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Mejia-Rodriguez, R.; Chiang, C.-Y.; Darensbourg, M. Y. *Inorg. Chem.* **2002**, *41*, 3917–3928.
- (13) Kaasjager, V. E.; Henderson, R. K.; Bouwman, E.; Lutz, M.; Spek, A. L.; Reedijk, J. *Angew. Chem. Int. Ed.* **1998**, *37*, 1668–1670.
- (14) Lemon, B. J.; Peters, J. W. *Biochemistry* **1999**, *38*, 12969–12973.
- (15) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853–1858.
- (16) Nicolet, Y.; de Lacey, A. L.; Vernède, X.; Fernandez, V. M.; Hatchikian, E. C.; Fontecilla-Camps, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 1596–1601.
- (17) Razavet, M.; Borg, S. J.; George, S. J.; Best, S. P.; Fairhurst, S. A.; Pickett, C. J. *Chem. Commun.* **2002**, 700–701.
- (18) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Wiley & Sons: New York, 1969.
- (19) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21–86.
- (20) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209–310.

**Scheme 1.** Synthesis and Chemical Oxidation of  $\text{Fe}_2(\text{SR})_2(\text{CO})_2(\text{CNMe})_4$ <sup>a</sup>

<sup>a</sup> Conditions: (a) excess CNMe, MeCN, 70 °C, 2 h; (b) excess CNMe, MeCN, 70 °C, 17 h; (c) excess CNMe, 1.6 equiv of  $\text{Cp}_2\text{FePF}_6$ , MeCN, 1 h; (d) excess CNMe, 1.6 equiv of  $\text{Cp}_2\text{FePF}_6$ , MeCN, 1 h; (e) 20 equiv of CNMe,  $\text{CD}_3\text{CN}$ , 30 h.

(CNMe)<sub>4</sub> (**1**, Scheme 1), the ethanedithiolate derivative of which was characterized crystallographically (see Suppl. Info.). Isocyanide adducts of iron thiolates have been reported sporadically<sup>21–26</sup> but have not been the subject of systematic investigation.

Treatment of **1**, generated in situ from  $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_6$  with 10 equiv of CNMe, with ca. 2 equiv of  $\text{Cp}_2\text{FePF}_6$  in MeCN afforded air-stable microcrystals of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CNMe})_7](\text{PF}_6)_2$  (**2**). The distinctive green color of **2** arises from a low-energy band at 620 nm ( $\epsilon = 1500 \text{ M}^{-1} \text{ cm}^{-1}$ ). From both structural and electronic perspectives, **2** is novel, consisting of a face-sharing bioctahedron (Figure 2).<sup>27</sup> Few diferrous thiolates exhibit Fe–Fe bonding;<sup>28–33</sup> important



**Figure 2.** Structure of the dication  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CNMe})_7](\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$  (**2**) with the thermal ellipsoids set at the 50% probability level. Selected distances (Å) and angles (deg): Fe(1)–Fe(2) 2.6342(12); Fe(1)–C(1) 1.864(6); Fe(1)–C(3) 1.759(7); Fe(1)–C(5) 1.762(6); Fe(1)–C(7) 1.952(5); Fe(2)–C(7) 2.300(5); Fe(2)–C(9) 1.824(6); Fe(2)–C(11) 1.872(6); Fe(2)–C(13) 1.864(5); Fe(1)–S(1) 2.2906(16); Fe(1)–S(2) 2.3011(15); Fe(2)–S(1) 2.2350(15); Fe(2)–S(2) 2.2709(15); Fe(1)–C(7)–N(4) 155.7(4); Fe(2)–C(7)–N(4) 128.2(4); C(7)–N(4)–C(8) 168.3(5).

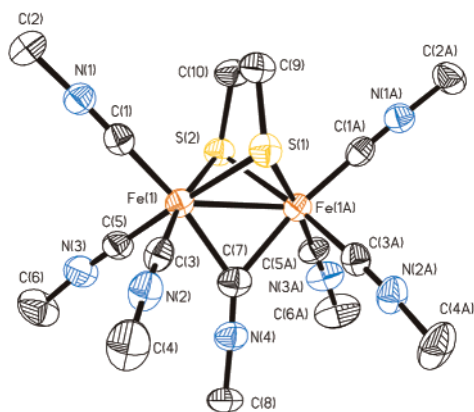
exceptions<sup>38</sup> include the Poilblanc dimers,<sup>9,12,34–37</sup>  $[\text{HFe}_2(\text{SR})_2(\text{CO})_4\text{L}_2]^+$ . Bridging isocyanides in low-valence complexes, e.g.,  $\text{Fe}_2(\text{CNBu}^t)_9$ ,<sup>39</sup> are typically strongly bent, whereas in **2** the  $\mu$ -CNMe ligand is relatively linear ( $\angle \text{C}–\text{N}–\text{C} = 168^\circ$ ). The linearity of the  $\mu$ -CNMe is consistent with little back-bonding in this diferrous species, which is expected to be rather electrophilic (see below). The 2.63 Å Fe–Fe distance is close to the Fe–Fe separations reported (2.6 Å) for the Fe-only hydrogenases,<sup>13–15</sup> vs 2.5 Å observed in earlier structural models based on  $[\text{Fe}]_2$ .<sup>3</sup>

Like the reduced Fe H<sub>2</sub>-ases, **2** also has a semibridging CX ligand, with Fe–( $\mu$ -CNMe) distances differing by 0.35 Å. Compound **2** is sufficiently unusual that we prepared and crystallographically characterized the related ethanedithiolate  $[\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)(\text{CNMe})_7](\text{PF}_6)_2$  (**3**), wherein the  $\mu$ -CNMe ligand is symmetrically positioned between the metals (Figure 3). The differing structures of **2** and **3** suggest that the two bonding modes observed for the  $\mu$ -CNMe are energetically similar.

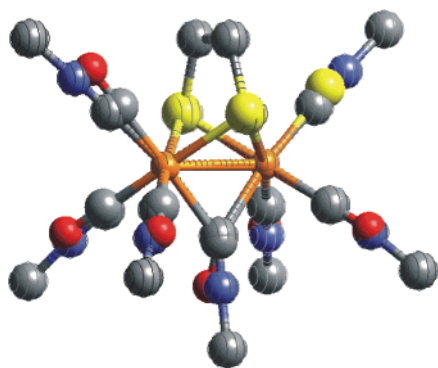
Both **2** and **3** bear a striking resemblance to the bimetallic core of the Fe H<sub>2</sub>-ases (Figure 4). The bridging CO ligand in the H-cluster, which has proven elusive from a modeling

- (21) Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6951–6957.  
 (22) Patin, H.; Le Rouzic, A.; Lhadi, E. K.; Darchen, A.; Mousser, A.; Grandjean, D. *J. Organomet. Chem.* **1989**, *375*, 101–114.  
 (23) Darchen, A.; Lhadi, E. K.; Patin, H.; Grandjean, D.; Mousser, A. *J. Organomet. Chem.* **1990**, *385*, C4–C8.  
 (24) Barriere, F.; Evans, D. J.; Hughes, D. L.; Ibrahim, S. K.; Talarmin, J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1999**, *21*, 957–964.  
 (25) Rauchfuss, T. B.; Contakes, S. M.; Hsu, S. C. N.; Reynolds, M. A.; Wilson, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 6933–6934.  
 (26) Cooper, L.; Davies, S. C.; Dilworth, J. R.; Hughes, D. L.; Konkol, M.; Richards, R. L.; Sanders, J. R.; Sobota, P. *Can. J. Chem.* **2001**, *79*, 490–494.  
 (27) Fe–Fe bonding in a face-sharing bitetrahedral molecule has also been observed: Henkel, G.; Chen, C. *Inorg. Chem.* **1993**, *32*, 1064–1065.  
 (28) Haines, R. J.; de Beer, J. A.; Greatrex, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1749–1757.

- (29) Schultz, A. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 518–525.  
 (30) Treichel, P. M.; Crane, R. A.; Matthews, R.; Bonnin, K. R.; Powell, D. *J. Organomet. Chem.* **1991**, *402*, 233–248.  
 (31) Arabi, M. S.; Mathieu, R.; Poilblanc, R. *Inorg. Chim. Acta* **1979**, *34*, L207–L208.  
 (32) Taylor, N. J.; Arabi, M. S.; Mathieu, R. *Inorg. Chem.* **1980**, *19*, 1740–1742.  
 (33) Bonnet, J. J.; Mathieu, R.; Poilblanc, R.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7487–7496.  
 (34) Fauvel, K.; Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1976**, *15*, 976–978.  
 (35) Arabi, M. S.; Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1979**, *177*, 199–209.  
 (36) Savariault, J.-M.; Bonnet, J.-J.; Mathieu, R.; Galy, J. C. R. *Hebd. Seances Acad. Sci., Ser. C* **1977**, *284*, 663–665.  
 (37) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Yarbrough, J. C.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 9710–9711.  
 (38) Karlin, K. D.; Lewis, D. L.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 6519–6521.  
 (39) Bassett, J. M.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton Trans.* **1981**, 219–227.



**Figure 3.** Structure of the dication in  $[\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)(\text{CNMe})_7](\text{PF}_6)_2 \cdot \text{MeCN}$  (**3**) with the thermal ellipsoids set at the 50% probability level. Selected distances ( $\text{\AA}$ ) and angles (deg): Fe(1)–Fe(1A) 2.6005(12); Fe(1)–C(1) 1.846(4); Fe(1)–C(3) 1.875(4); Fe(1)–C(5) 1.875(4); Fe(1)–C(7) 2.078(5); Fe(1)–S(1) 2.2507(12); Fe(1)–S(2) 2.2770(11); Fe(1)–C(7)–N(4) 141.26(10); C(7)–N(4)–C(8) 174.6(5).



**Figure 4.** Overlay of the crystallographic models of the dication in  $[\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)(\text{CNMe})_7](\text{PF}_6)_2 \cdot \text{MeCN}$  (**3**) with the H-cluster of the *Clostridium pasteurianum* (CpI) Fe-only hydrogenase,<sup>13</sup> where all diatomic ligands were modeled as CO in the H-cluster (orange, Fe; yellow, S; red, O; blue, N; gray, C). The atoms and bonds of the dication in **3** are shown with lines. The hydrogen atoms of **3** and the unidentified light atom bridging the sulfur atoms in the H-cluster have been omitted.

perspective, is closely matched by the bridging isocyanide ligand in **3**. The Fe–Fe distances in **2** and **3** are the best matches to those in the H-clusters to date.

Freshly prepared samples of **2** are generally contaminated with  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CNMe})_{10}]^{2+}$  (**4**), a brilliant yellow species characterized by distinctive  $^1\text{H}$  NMR and ESI-MS spectra. The 4:1 pattern for the Me  $^1\text{H}$  NMR resonances and the symmetric pattern for the propanedithiolate point to a pair of  $C_{4v}$  octahedra linked via a trimethylene chain (Scheme

1). Compound **4** forms when solutions of **2** are treated with an excess of CNMe in MeCN solution; the conversion is accelerated by light. Upon standing in solution, **4** partially reverts to **2** via expulsion of CNMe. Compound **3** also reacts with excess CNMe, but the NMR data indicate that the product is not a structural analogue of **4**. Further studies are underway.

In contrast to the synthesis of **2** and **3**, the oxidative decarbonylation of  $\text{Fe}_2(\text{SPh})_2(\text{CO})_{6-x}(\text{CNMe})_x$  gave exclusively the monomer  $[\text{Fe}(\text{SPh})(\text{CNMe})_5]^+$  (**5**, see Scheme 1). The  $C_{4v}$  local symmetry for this bright yellow  $\text{PF}_6^-$  salt was confirmed by X-ray crystallography (see Supporting Information). In contrast to **4**, however, **5** shows no tendency to condense into a  $(\mu\text{-SR})_2$  structure, even upon refluxing in MeCN solution. It is well-known that thiolates are excellent bridging ligands, but these experiments highlight the enhanced ability of dithiolates to stabilize the binuclear site.<sup>40,41</sup>

Preliminary experiments hint at possible extensions of **1** to include phosphine derivatives. For example,  $\text{Cp}_2\text{Fe}^+$  oxidation of  $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{PMe}_3)_2$  in the presence of CNMe gave a mixture of  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CNMe})_5(\text{PMe}_3)_2](\text{PF}_6)_2$  and  $[\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CNMe})_6(\text{PMe}_3)](\text{PF}_6)_2$ , identified by ESI-MS.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra are consistent with a mixture of stereochemically rigid isomers.

In summary, the following potentially fruitful research directions are indicated: (i) the oxidative decarbonylation of other  $\text{M}_x(\mu\text{-SR})_y(\text{CO})_z$  species should lead to new classes of di- and polynuclear cations, (ii) the substitutional and redox-based reactivity of  $[\text{Fe}_2(\text{SR})_2(\text{CNR})_7]^{2+}$  may afford models for the oxidized states of Fe H<sub>2</sub>-ase, and (iii) the photoreactivity of **2** and **3** bears investigation in view of the low-energy absorption band and the indications of photochemically induced ligand additions.

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**Supporting Information Available:** Crystallographic information files (CIF), experimental details, tables of crystallographic data, cyclic voltammograms, and IR and UV–vis spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(40) Adams, R. D.; Kwon, O. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 5322–5323.

(41) Sellmann, D.; Wille, M.; Knoch, F. *Inorg. Chem.* **1993**, *32*, 2534–2543.