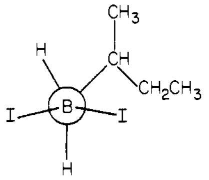
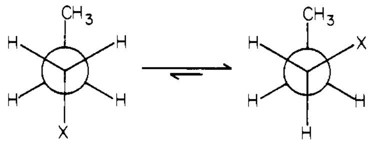


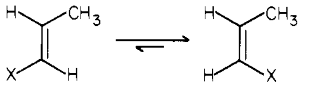
This suggests the operation of stabilizing attractive nonbonded interactions such as those used to account for the greater thermodynamic stability of the "gauche" conformation over the "anti" in 1-halopropanes[13] (eq 2).



(2)

X = F, Cl, Br

A similar interaction has been proposed[14] to account for the greater stability of the "cis" form of the 1-halopropenes[15] over the "trans" (eq 3).



(3)

X = F, Cl, Br

Irrespective of mechanistic considerations, the results of the above study provide, for the first time, a synthetically useful manipulative control on the migrational selectivity of the boron atom. We hope to utilize this for organic synthesis in the future.

Acknowledgment. We are grateful for the financial support of Exxon Research and Engineering Corp. and the National Science Foundation (CHE-8301145).

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(14) (a) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 3087. (b) English, A. D.; Palke, W. E. *Ibid.* **1973**, *95*, 8536. (c) Bingham, R. C. Ibid. **1976**, *98*, 535.

(15) (a) Harwell, K. E.; Hatch, L. F. *J. Am. Chem. Soc.* **1955**, *77*, 1682. (b) Crump, J. W. *J. Org. Chem.* **1963**, *28*, 953.

Stepwise Assembly of Heterometallic M_4S_4 Clusters. The Structure of $(MeCp)_2V_2Fe_2(NO)_2S_4$: A 58e Cubane

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A focus of our research is the development of cluster assembly reactions employing organometallic chalcogenide precursors.[2,3] To a certain extent, this effort parallels related work leading to inorganic sulfide aggregates from MoS_4^{2-}.[4] Recently we reported the preparation of a series of iron carbonyl-containing clusters from $(MeCp)_2V_2S_4$ (**1**, MeCp = η^5-$CH_3C_5H_4$) of core stoichiometries FeV_2S_4, FeV_2S_3, and $PtFeV_2S_4$.[3] Extension of this work to include metal nitrosyls has led to the following achievements: (i) the synthesis of the first electron-deficient organo M_4S_4 clusters, (ii) the characterization of the first closed deltahedral cluster featuring an $M(NO)_2$ vertex, and (iii) the directed synthesis of an $M_2M'M''S_4$ cubane cluster.

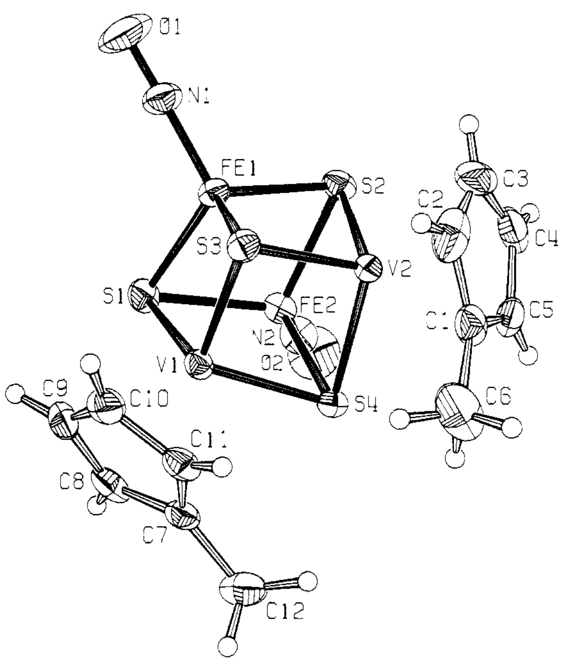

Figure 1. ORTEP plot of the $(MeCp)_2V_2(NO)_2S_4$ molecule with thermal ellipsoids drawn at the 35% level.

Treatment of $(MeCp)_2V_2S_4$[5] with an excess of $Hg[Fe(NO)(CO)_3]_2$ in boiling toluene afforded a 65% yield of $(MeCp)_2V_2Fe_2(NO)_2S_4$ (**2**) as analytically pure black crystals from methanol.[6] Subsequent to chromatography on silica gel, this species was characterized by IR, mass spectrometry, and single-crystal X-ray diffraction.

The results of the X-ray structure analysis[7] established that **2** consists of a distorted $V_2Fe_2S_4$ cubane core (Figure 1). Three types of intermetallic contacts are observed including an Fe–Fe bond of 2.59 Å that is similar to that seen in other S-bridged iron dimers. The four Fe–V bond distances of 2.75 Å are similar if a little shorter than those observed in related compounds.[3] In comparison with the few standards available,[5,8] the V···V distance of 2.95 Å indicates an interaction that is weak but significant; the corresponding distances in the $V_2(\mu$-η^2-$S_2)_2$ subunits of the diamagnetic linear chain compound VS_4 are 2.83 and 3.22 Å.[9] We tentatively conclude that the electron deficiency in **2** is largely associated with the vanadium centers giving rise to longer V–M bonding.

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(1) Alfred P. Sloan Fellow 1983–1985, Camille and Henry Dreyfus Teacher–Scholar 1983–1988.

(2) Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290. Bogan, L. E., Jr.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429. Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 1854.

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(4) Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455. Muller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

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(6) Anal. Calcd for $C_{12}H_{14}N_2O_2S_4V_2Fe_2$: C, 25.72; H, 2.52; N, 5.00; Fe, 19.94; V, 18.19. Found: C, 25.88; H, 2.47; N, 4.91; Fe, 19.79; V, 18.18. IR(CCl_4) 1765 and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) 27.98 (d), 7.75 (s); EI mass spectrum (70 eV), *m/e* (relative intensity) 560 (258 M^+), 530 (20, M^+ – NO), 500 (100, M^+ – 2NO); field-desorption mass spectrum 560 (M^+).

(7) $(C_5H_4CH_3)_2V_2Fe_2(NO)_2S_4$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.616$ (2) Å, $b = 20.219$ (5) Å, $c = 9.746$ (2) Å, $\beta = 99.16$ (2)° $V = 1870.8$ (7) Å^3, $Z = 4$, $\mu = 28.98$ cm^{-1} (Mo Kα, $\lambda = 0.71069$). A total of 3767 reflections ($3° < 2\theta < 55°$) were collected on a Syntex $P2_1/n$ diffractometer of which 3321 were used. Of these reflections, 2407 with $F_o > 3\sigma(F_o)$ were used in subsequent solution and refinement. $R = 2.3\%$ and $R_w = 2.8\%$.

(8) For a recent partial listing of V–V bond lengths see: Elschenbroich, C.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905.

(9) Allmann, R.; Baumann, I.; Kutoglu, A.; Rösch, H.; Hellner, E. *Naturwissenschaften* **1964**, *51*, 263. Klemm, W.; Schnering, H. G. *Ibid.* **1965**, *52*, 12.

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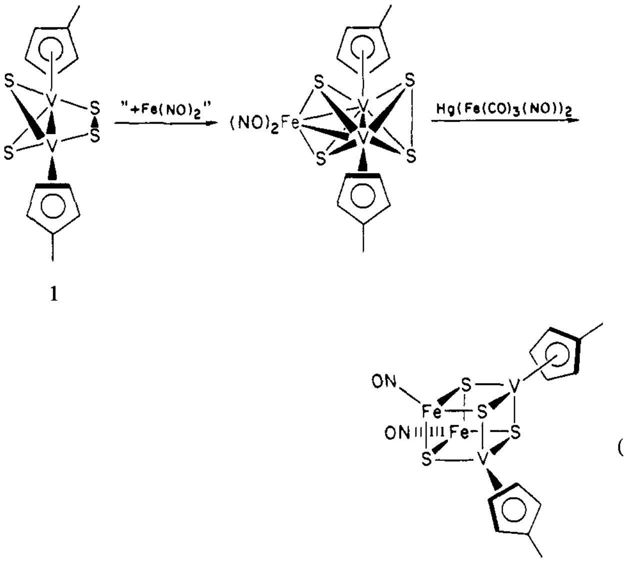
As a 58e molecule, **2** is a unique example of an electron-deficient organo M_4S_4 cluster. Its magnetic moment is 1.91 μ_B (27 °C), which is less than the 2.7 μ_B value expected for two unpaired electrons. Its magnetism and structure support the proposal that **2** is reasonably described as containing two interacting $17e^-$ V vertices contained within an electron-precise $Fe_2(NO)_2S_4$ matrix.

Reaction of **1** with 2 equiv of Co(NO)(CO)$_3$ in refluxing CH_2Cl_2 (80 mL/mmol **1**, 3 h) in the presence of 4 equiv of Me_3NO as a decarbonylation reagent gave $(MeCp)_2V_2Co_2(NO)_2S_4$ (**3**) in ~95% yield.[10] This compound was found to be very stable both oxidatively and thermally and was easily isolated in crystalline form. Like **2**, compound **3** has two strong ν_{NO} bands in its IR spectrum, and its 70-eV electron-impact mass spectrum features a strong molecular ion in addition to a $(MeCp)_2V_2Co_2S_4$ parent ion. For these reasons we assume that **3** is structurally similar to **2**. By conventional valence shell electron count, **3** is a 60e cluster; however, it differs from the majority of such clusters in that it is paramagnetic.[11] Therefore **3** cannot be a normal electron-precise cluster but is proposed to contain two weakly interacting $17e^-$ V vertices, which could explain its magnetic moment of 2.73 μ_B (27 °C). Further discussion on this point is deferred until we complete the characterization of **3** by X-ray diffraction.[10]

Insight into the mechanism of assembly of $V_2M_2S_4$ clusters from the V_2S_4 precursor is provided by the isolation of a V_2MS_4 intermediate. The compound $(MeCp)_2V_2Fe(NO)_2S_4$ can be obtained in low yields only at the very early stages in the synthesis of **2** from **1** (eq 1). It was isolated chromatographically, crystallized from methanol, and thoroughly characterized.[12] Purified $(MeCp)V_2Fe(NO)_2S_4$ reacts with $Hg[Fe(NO)(CO)_3]_2$ in refluxing THF to give **2** in high yield. Unlike all of the other new compounds described in this work, this V_2Fe species is diamagnetic. Structurally, it consists of a planar $V_2Fe(NO)_2$ array perpendicular to the FeS_4 plane. In contrast, its derivative **2** consists of interpenetrating M_4 and S_4 tetrahedra. $(MeCp)_2V_2Fe(NO)_2S_4$ also assumes special interest as it is the first example of a closed deltahedral[13] cluster featuring an $M(NO)_2$ vertex. Polynitrosyl clusters are rare, reflecting in large measure the elusiveness of the $M(NO)_2$ unit cluster chemistry.

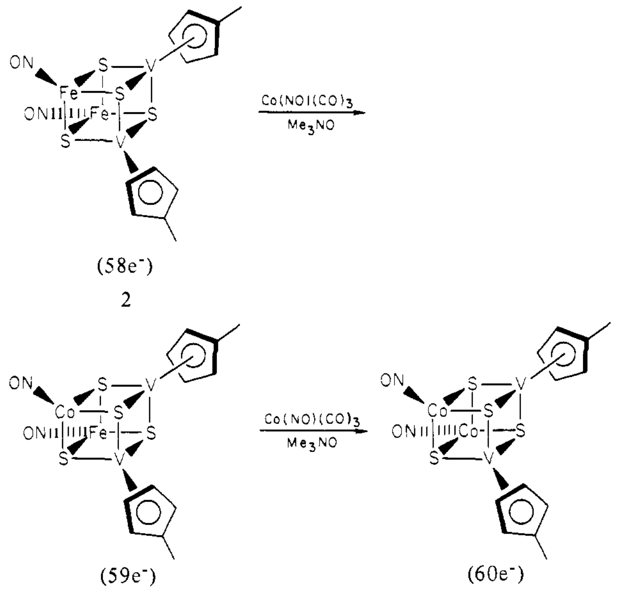


1

2

(1)

The hybrid of **2** and **3**, $(MeCp)_2V_2CoFe(NO)_2S_4$ (**4**) can be prepared in nearly quantitative yield by treatment of THF solutions (30 mL/0.2 mmol of **2**, 67 °C, 1 h) of **2** with 4 equiv of Co(NO)(CO)$_3$. The compound was isolated as analytically pure black crystals from CH_2Cl_2–CH_3OH and was characterized by IR and mass spectrometry. A convenient and consistent feature of the transmetalation reaction is that **4** is intermediate in chromatographic polarity (TLC and HPLC on SiO_2) between **2** and **3** although the latter is not observed under the stated reaction conditions. Furthermore **2**, **3**, and **4** are distinguishable by their IR spectra in the ν_{NO} region. Under more forcing conditions, **2** reacts with Co(NO)(CO)$_3$ giving **3**, again in quantitative yield (eq 2). Attempted synthesis of **4** from the reaction of Co(NO)(CO)$_3$ and $(MeCp)_2V_2Fe(NO)_2S_4$ is not successful because the V_2CoFeS_4 cube undergoes transmetalation faster than it is formed from the V_2FeS_4 precursor.



(58e⁻)

2

(59e⁻)

4

(60e⁻)

3

(2)

We are currently examining the kinetics of the transmetalation reaction, this study together with the structure of $(MeCp)_2V_2Co_2(NO)_2S_4$ will be reported upon completion.[15]

Acknowledgment. This research was supported by the National Science Foundation.

Registry No. 1, 87174-39-8; **2**, 87174-40-1; **3**, 87174-41-2; **4**, 87174-42-3; $(MeCp)_2V_2Fe(NO)_2S_4$, 87174-43-4; $Hg[Fe(NO)(CO)_3]_2$, 63270-61-1; Co(NO)(CO)$_3$, 14096-82-3.

Supplementary Material Available: Tables of selected bond distances and angles, positional parameters, thermal parameters, and final and observed structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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(10) Anal. Calcd. for $C_{12}H_{14}N_2O_2S_4V_2Co_2$: C, 25.45; H, 2.49; N, 4.95; Co, 20.82; V, 17.99. Found: C, 25.71; H, 2.40; N, 5.14; Co, 21.55; V, 17.50. IR(CCl_4) 1785 and 1762 cm^{-1}; EI mass spectrum (70 eV), *m/e* (relative intensity) 566 (30, M^+), 536 (25, $M^+ - NO$), 506, (100, $M^+ - 2NO$); field-desorption mass spectrum 566 (M^+). This species crystallizes in the monoclinic spacegroup $P2_1/n$. Precession photographs indicate that $a = 9.67$ Å, b 20.10 Å, $c = 9.78$ Å, and $\beta = 98.8°$, these values are quite similar to those found for **2**.[7]

(11) For recent discussions on the electronic structure of M_4E_4 clusters, see: Chu, C. T.-W.; Lo, F. Y.-K.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3409; Bottomley, F.; Grein, F. *Inorg. Chem.* **1982**, *21*, 4170.

(12) Anal. Calcd for $C_{12}H_{14}N_2O_2S_4V_2Fe$: C, 28.58; H, 2.80; N, 5.55. Found: C, 28.21; H, 3.13; N, 5.28. IR (CCl_4) 1758 and 1722 cm^{-1}; ^1H NMR ($CDCl_3$) 5.0 (4 H, m), 1.95 (3 H, s); field-desorption mass spectrum 504 (M^+). The compound has been characterized by single-crystal X-ray diffraction.

(13) Wade, K. *Adv. Inorg. Radiochem.* **1976**, *18*, 1.

(14) Anal. Calcd for $C_{12}H_{14}N_2O_2S_4FeCoV_2$: C, 25.59; H, 2.51; N, 4.97. Found: C, 25.65; H, 2.71; N, 4.58. IR (CCl_4): 1785 and 1745 cm^{-1}; EI mass spectrum (70 eV), *m/e* (relative intensity) 563 (54, M^+), 533 (54, $M^+ - NO$), 503 (100, $M^+ - 2NO$); field-desorption mass spectrum 563 (M^+); $\mu_{eff} = 1.71$ μ_B (27 °C). Magnetic measurements were made using a SQUID magnetometer.

(15) The recently reported reaction of $(C_5Me_5)_2M_2S_4$ (M = Cr, Mo) and $Co_2(CO)_8$ gives diamagnetic products that on the basis of analytical and spectroscopic data are proposed to be cubanes of the formula $(C_5Me_5)_2M_2Co_2(CO)_2S_4$: Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1982**, *240*, C41.

J. Am. Chem. Soc. **1983**, *105*, 6510-6511

"Electron-Imbalanced" Metallocenophanes. Synthesis and Molecular Structure of [1,3-Bis(η^5-cyclopentadienyl)propane](3,5-dichloropyridine)manganese(II)

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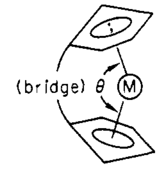
Notably absent from the (non-ferrocene) organometallic chemistry literature are reports of oxidation state II "electron-imbalanced"[1] metallocenophanes having bridges short enough to create distortions in the ground state; this situation persists despite the attention that has been drawn[2,3] to the importance of "bending" the cyclopentadienyl (Cp) rings along metallocene reaction coordinates. Structures of type **1** are expected to have $\theta < 180°$ for first-row transition metals and for bridges formed by $(CH_2)_x$, $x = 1, 2, 3$; however—excepting ferrocenophane[4] chemistry—no such structure has been reported. Under certain circumstances, stabilization of structure **1** by additional ligands bound to one or more of the three potential acceptor hydrid orbitals[2] centered on M may be anticipated. Indeed the only known ligand-stabilized short-bridge oxidation state II metallocenophane is [1,2-bis(η^5-cyclopentadienyl)ethane]dicarbonyltitanium(II), for which detailed structural information is unavailable.[5,6] In view of the expected[2,3] chemical activation inherent in structures of type **1**, we have initiated efforts aimed at the synthesis of such species. Our initial studies have involved manganocene ($MnCp_2$) chemistry, as this metallocene is known to be extremely reactive toward cyclopentadienyl exchange[7] and toward ligand addition;[8] in addition $MnCp_2$ and ring-substituted manganocenes are known to be near spin cross-over points.[9] We report here the synthesis and molecular structure of the high-spin[10] complex [1,3-bis(η^5-cyclopentadienyl)propane](3,5-dichloropyridine)manganese(II) (**2**).



1

The most generally applicable synthetic approach to non-iron metallocenophanes involves the reaction of bridged dicyclopentadienyl dianions with anhydrous metal salts (the "direct" method).[11] To date, published yields of metallocenophanes prepared by the direct method are low.[11,12] We have found that **2** can be prepared by an approach analogous to the direct method in which no solvent is used.[13] Typically 0.86 g (4.7 mmol) of solid $Li_2[C_5H_4(CH_2)_3C_5H_4]$[14] is ground intimately with 1.0 g (4.7 mmol) $MnBr_2$ (anhydrous). The solid mixture is heated in vacuo to 200-220 °C for 40 min during which time a red/orange oil distills up the flask to coat the walls. The oil is extracted into 50 mL of benzene and filtered, followed by addition of a 2-fold excess of 3,5-dichloropyridine. After 1 h of stirring, benzene is removed to yield an orange-red solid. This solid sublimes at 55-65 °C (0.15 torr) to yield a rhombohedral ruby-red crystalline solid.[15]

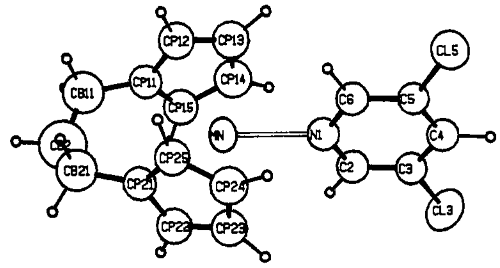


Figure 1. View of **2** perpendicular to the pseudotwofold axis. The plane of the pyridine ring makes an acute angle of 40° to the page. Selected distances and angles: Mn-Cp(carbon) (range) 2.402 (8)-2.483 (7), Mn-Cp(centroid 1) 2.15 (2), Mn-Cp(centroid 2) 2.13 (2), C-C in Cp's (range) 1.33 (1)-1.42 (1), Mn-N1 2.310 (6), CB11-CB21 2.52 (1), CP11-CP21 3.29 (1), N1-CP13,14,23,24 (range) 3.18 (1)-3.25 (1) Å; Cp(centroid 1)-Mn-Cp(centroid 2) 140 (2)°, CP11-CB11-CB2 119.9 (8)°, CB11-CB2-CB21, 116 (1)°, CB2-CB21-CP21 118.7 (8)°. Interplanar angles: Cp ring 1/Cp ring 2, 37.2°; pyridine/Cp ring 1, 21.9°; pyridine/Cp ring 2, 15.3°; CB11-CB2-CB21/CP11-CB11-CP21-CB21, 57.9°.

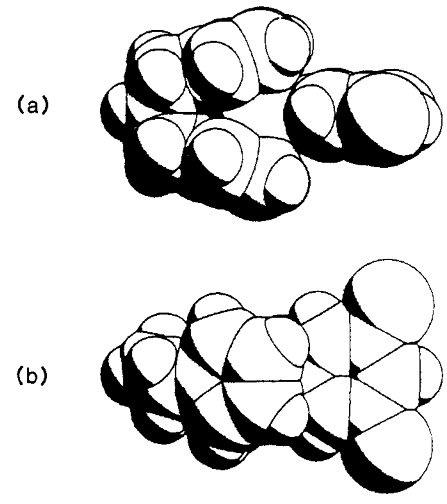


Figure 2. Space-filling drawings of **2** showing (a) side and (b) top views of the molecule: both views are perpendicular to the pseudotwofold axis. Atom sizes were defined by van der Waals radii as follows: Mn 1.98, Cl 1.80, C 1.77, N 1.58, and H 1.17 Å.

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(1) "Electron imbalance": number of electrons in antibonding e_1'' plus the number of vacancies in the bonding a_1' and e_2' levels (for high-spin manganocenes the imbalance is 5), see: Haaland, A. *Acct. Chem. Res.* **1979**, *12*, 415-422.

(2) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742.

(3) Brintzinger, H. H.; Lohr, L. L.; Wong, K. L. T. *J. Am. Chem. Soc.* **1975**, *97*, 5146-5155.

(4) Recent leading ferrocenophane references: (a) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Rettig, S. J.; Willis, A. J. *Organometallics* **1983**, *2*, 128-135. (b) Fujita, E.; Gordon, B.; Hillman, M.; Nagy, A. *J. Organomet. Chem.* **1981**, *218*, 105-114. (c) Deeming, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 4, pp 487-491.

(5) Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159-167.

(6) Beyond ref 5, only two additional non-iron M(II) metallocenophanes (each with a "long" bridge) have been reported: (a) Nickelocene with a $-CH_2CH_2(C{=}O)CH_2CH_2-$ bridge: Eilbracht, P. *Chem. Ber.* **1976**, *109*, 3136-3141. (b) Tungstenocene with a $-CH_2CH{=}CHCH_2-$ bridge: Chong, K. S.; Green, M. L. H. *Organometallics* **1982**, *1*, 1586-1590.

(7) Switzer, M. E.; Rettig, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 687-688.

(8) (a) Switzer, M. E. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1973. (b) Wilkinson, G. W.; Cotton, F. A.; Birmingham, J. M. *J. Inorg. Nucl. Chem.* **1956**, *2*, 95-113.

(9) (a) Switzer, M. E.; Wang, R.; Rettig, M. F.; Maki, A. H. *J. Am. Chem. Soc.* **1974**, *96*, 7669-7674. (b) Ammeter, J. H.; Bucher, R.; Oswald, N. *Ibid.* **1974**, *96*, 7833-7835. (c) Evans, S.; Green, M. L. H.; Jewitt, B.; King, G. H.; Orchard, A. F. *J. Chem. Soc., Faraday Trans.* **1974**, *2*, 356-376.

(10) Magnetic moment (297 K): 5.98 ± 0.08 μ_B [measured by the superconducting quantum interference detection (SQUID) technique]. Data from 15 to 297 K indicate normal paramagnetic behavior.

(11) Luttringhaus, A.; Kullik, W. *Angew. Chem.* **1958**, *70*, 438; *Makromol. Chem.* **1961**, 44-46, 669.

(12) (a) For monobridged ferrocenes, 0.025%-50% yields, depending upon bridge length: Shul'pin, G. B.; Rybinskaya, M. I. *Rus. Chem. Rev.* (*Engl. Transl.*) **1974**, 43, 716-732. (b) For monobridged [Ti(η^5-$C_5H_4(CH_2)_x$-η^5-$C_5H_4)Cl_2$], 4-30% depending upon bridge length: Smith, J.; Von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175-185 and references therein.

(13) We have experienced problems with yields and reproducibility in synthesis of manganocenes in ethereal solvents. Synthesis of metallocenes without solvents has been reported by: Reid, A. F.; Wailes, P. C. Australian Patent 290355, 1970; *Chem. Abstr.* **1972**, P132939.

(14) $Li_2[C_5H_4(CH_2)_3C_5H_4]$ was prepared from modification of the procedures reported by: Dormond, A.; Ou-Khan; et Tirouflet, J. *J. Organomet. Chem.* **1976**, *110*, 321-326 (we replaced NaH with *n*-butyllithium).

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