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

J. Tracy Weed, Michael F. Rettig,* and Richard M. Wing*

Department of Chemistry, University of California
Riverside, California 92521

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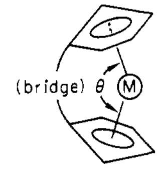
Notably absent from the (non-ferrocene) organometallic chemistry literature are reports of oxidation state II "electron-imbalanced"[1] metallocenophanes having bridges short enough to create distortions in the ground state; this situation persists despite the attention that has been drawn[2,3] to the 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**).



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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]

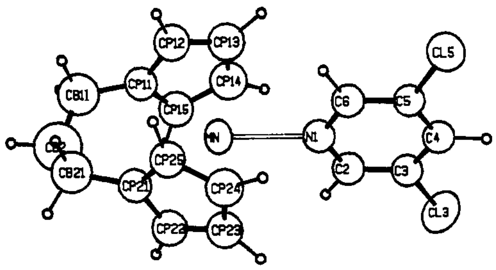

Figure 1. View of **2** perpendicular to the pseudotwofold axis. The plane of the pyridine ring makes an acute angle of 40° to the page. Selected distances and angles: Mn–Cp(carbon) (range) 2.402 (8)–2.483 (7), Mn–Cp(centroid 1) 2.15 (2), Mn–Cp(centroid 2) 2.13 (2), C–C in Cp's (range) 1.33 (1)–1.42 (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°.

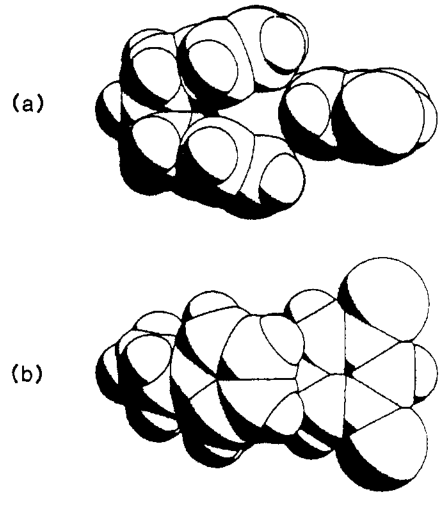

Figure 2. Space-filling drawings of **2** showing (a) side and (b) top views of the molecule: both views are perpendicular to the pseudotwofold axis. Atom sizes were defined by van der Waals radii as follows: Mn 1.98, Cl 1.80, C 1.77, N 1.58, and H 1.17 Å.

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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): $5.98 \pm 0.08\ \mu_B$ [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 $[Ti(\eta^5\text{-}C_5H_4(CH_2)_x\text{-}\eta^5\text{-}C_5H_4)Cl_2]$, 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 290 355, 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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The sublimed, extremely air-sensitive crystals of **2** were found to be suitable for structure determination by X-ray crystallography.[16]

The molecular structure of **2** (Figures 1 and 2) confirms isolation of the monomeric [3]-manganocenophane as its 3,5-dichloropyridine adduct. Important distances and angles are given in the caption to Figure 1. The Mn-C distances in high-spin **2** are comparable to those in high-spin manganocene [2.380 (6) Å] and in 1,1′-dimethylmanganocene [2.433 (8) Å].[1] The two Mn–Cp interactions are the same, as indicated by the Mn–centroid distances. The bridge lies nearly on the pseudotwofold axis (the CP11–CB11–CP21–CB21 plane makes an angle of 6.5° with the Cp(centroid 1)–Mn–Cp(centroid 2) plane, and the nitrogen is placed neatly between pairs of Cp carbons, with nonbonded N- - -C distances near the sum of the van der Waals radii.

Structurally related to **2** are dichloro[1,3-(η^5-cyclopentadienyl)propane]M(IV), M = titanium (**3**), zirconium (**4**), hafnium (**5**).[17] In each of these molecules the $(CH_2)_3$ bridge is rotated ca. 36° away from the pseudotwofold axis, in contrast to **2**. In **3–5** the bridge location 36° away from the pseudotwofold axis accommodates the chlorine ligands—again between pairs of nonbonded carbons. We believe that, at the distances and angles involving the three-carbon link in **2–5**, the location of the link at ca. 0° or 36° to the twofold axis is primarily controlled by the ligand–cyclopentadienyl carbon nonbonded repulsions. On the basis of our examination of Dreiding models, it appears that placement of a $(CH_2)_3$ bridge 72° from the pseudotwofold axis is not likely, because this bridge is too small to span the required distance.

The range of the CCC angles in the bridge in **2** is similar to the 113.9(5)°–117.8(6)° range reported[17] for **3–5**. Even with the large bridge CCC angles in **2**, carbons CB11 and CB21 are displaced 0.11 (1) and 0.10 (1) Å, respectively, from the best Cp planes, to the side opposite manganese.[18] We suggest that unusually high negative charge density on CP11 and CP21 (other CP carbons as well) contributes to additional geminal carbon interactions to open CP11–CB11–CB2 and CP21–CB21–CB2 and that the preferred relief of this strain are bends at CP11–CB11 and CP21–CB21 rather than an increase of θ with increases of four N- - -C nonbonded repulsions.

The bonding in **2** may be described by the bent metallocene model.[2] In the equatorial plane half-filled frontier acceptor orbitals of $1a_1$, b_2, and $2a_1$ symmetry are available to interact with the nitrogen lone pair. The bond to nitrogen is best described as $(2a_1)^2(2a_1{}^*)^1$. The "half-bond" character of this molecular orbital is reflected in the unusually long Mn–N1 interaction [2.310 (6) Å].

In preliminary work, we have found that manganocene binds *two* molecules of 3,5-dichloropyridine under isolation conditions identical with those described for **2**. We are currently investigating $(-CH_2-)_3$ bridge geometric restraints as a possible significant contributor to the dramatic difference in Lewis acidity of **2** compared to $MnCp_2$. We are also working toward isolation of base-free "short-bridge" "electron-imbalanced" metallocenophanes.

Acknowledgment. This work was supported by the University of California Committee on Research, by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a Grant-in-Aid to J.T.W. from the Society of Sigma Xi. The SQUID Susceptometer system was purchased through a grant to the University of Southern California (NSF CHE 8211349). We thank Professor Christopher Reed and Dr. Peter Boyd for assistance with the SQUID device.

Registry No. 2, 87174-48-9; $Li_2[C_5H_4(CH_2)_3C_5H_4]$, 87174-47-8; $MnBr_2$, 13446-03-2; bis(η^5-2,4-cyclopentadien-1-yl)bis(*N*-3,5-dichloropyridine)manganese, 87174-49-0.

Supplementary Material Available: Tables of positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[15] The yield of red/orange oil based on $MnBr_2$ was 29% and is believed to be a mixture of monomer and oligomers. The yield of **2** based on the red/orange oil was 11% or an overall yield based on $MnBr_2$ of 3%.

[16] The structure was solved on the basis of a model including disorder in the location of CB2 (29% of CB2's are found "reflected" through the CP11–CB11–CP21–CB21 plane). Reported results involving CB2 are based on the major (71%) CB2 site. A full account of the crystallography is given: Weed, J. T. Ph.D. Thesis, University of California, Riverside, CA, 1983.

[17] (a) Ti(IV): Epstein, E. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 211–218. (b) Zr(IV): Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *J. Organomet. Chem.* **1974**, *80*, 79–90. (c) Hf(IV): Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880–2885.

[18] Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91–101 (definition of β, which is 4.0° in **2**).

Trimethylenemethane Cation Radical: Photosensitized (Electron-Transfer) Generation and Reactivity[1]

Yasutake Takahashi, Tsutomu Miyashi,* and Toshio Mukai

Photochemical Research Laboratory, Faculty of Science
Tohoku University, Sendai 980, Japan

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Because of the unique structural and mechanistic features of a trimethylenemethane species,[2] both the photochemical[3a,b] and thermal[2] reactions of methylenecyclopropanes have been extensively explored. The ordinary photolysis of methylenecyclopropanes, however, seems not to generate any trimethylenemethane species since the photolysis of methylenecyclopropanes differs markedly from their thermolysis.[3] We report here the photosensitized (electron-transfer) generation of a novel trimethylenemethane species, a cation radical, and its reactivity, which provides both the degenerate methylenecyclopropane rearrangement and the very efficient molecular oxygen trapping.

While 2,2-diphenyl-1-methylenecyclopropane **1a**[3c,d] efficiently quenches luminescence of anthraquinone,[4] no chemical change was observed upon irradiation of **1a** with anthraquinone as an electron-acceptor sensitizer in acetonitrile at 15 °C with >350-nm light under Ar. Irradiation of the dideuterio analogue d_2-**1a** under the same conditions, however, provided the degeneracy in d_2-**1a** that is similar to that observed in the thermolysis of d_2-**1a**.[3d] Thus, d_2-**1a** gradually diminished during irradiation with an increase in the ratio of d_2-**1a′**/d_2-**1a** and a ca. 1:1 mixture of d_2-**1a** and d_2-**1a′** was isolated in a quantitative yield after a 2-h irradiation.[5] The chloranil sensitization also involved the degenerate rearrangement, but neither phenanthraquinone nor benzophenone sensitized. These evidences together with the calculated free-energy change (ΔG)[6] required for the possibility of an electron

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[1] Organic Photochemistry. 64. No. 63, see: Kumagai, T.; Kawamura, Y.; Mukai, T. *Tetrahedron Lett.* **1983**.

[2] Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 311 and references cited therein.

[3] (a) Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 7606. (b) Gros, W. A.; Luo, T.; Gilbert, J. C. *Ibid.* **1976**, *98*, 2019. (c) Gilbert, J. C.; Kurzawa, F. *J. Org. Chem.* **1979**, *44*, 2123. (d) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2168.

[4] Quenching experiments were carried out in aerated acetonitrile at 20 °C. The Stern–Volmer slopes ($k_q\tau$) for **1a**, **1b**, **1c**, and **1d** are 1.58×10^3, 9.08×10^2, 1.55×10^4, and 2.60×10^4 M^{-1}, respectively. The quenching rate constants (k_q) for **1a**, **1b**, **1c**, and **1d** are calculated to be 5.6×10^8, 3.2×10^8, 5.5×10^9, and 9.3×10^9 $M^{-1}\ s^{-1}$, respectively, on the basis of the triplet lifetime of anthraquinone, 2.8×10^{-6} s in the above conditions, which was estimated by using a diffusion-controlled quencher, 1,2,4,5-tetramethoxybenzene ($E_{1/2}{}^{ox} = +0.75$ V vs. SCE, $\Delta G = -25.1$ kcal/mol, $k_q\tau = 4.25 \times 10^4$ M^{-1}), by the reported method.[6a]

[5] The structures of d_2-**1a** and d_2-**1a′** were determined by comparisons of ^1H NMR chemical shifts with those reported.[3d]

[6] (a) Calculated by using half-wave reduction potentials ($E_{1/2}{}^{red}$)[6b] and triplet energies (E_T)[6c] of the sensitizers and oxidation potentials[8] of **1**: Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) $E_{1/2}{}^{red}$(chloranil) = +0.01 V vs. SCE, $E_{1/2}{}^{red}$(anthraquinone) = −0.94 V vs. SCE, and $E_{1/2}{}^{red}$(phenanthraquinone) = −0.66 V vs. SCE: Peover, M. E. *J. Chem. Soc.* **1962**, 4540. $E_{1/2}{}^{red}$(benzophenone) = −1.72 V vs. SCE: Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1973. (c) E_T(chloranil) = 62 kcal/mol: Kasha, M. *Chem. Rev.* **1947**, *41*, 401. E_T(anthraquinone) = 62.7 kcal/mol and E_T(benzophenone) = 69.2 kcal/mol: Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973. E_T(phenanthraquinone) = 50 kcal/mol: Farid, S.; Scholz, K.-H. *J. Chem. Soc., Chem. Commun.* **1969**, 572.

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