4190 *J. Am. Chem. Soc.* **1996,** *118,* 4190−4191

# Reductively Induced Dimerization of the Ligated Benzene in $[Mn(\eta^6-C_6H_6)(CO)_3]^+$: Formation of the Initial C−C Bond by Anion/Cation Addition

Sijoon Lee, Sherri R. Lovelace, Debra J. Arford,
Steven J. Geib, Stephen G. Weber, and N. John Cooper*

*Department of Chemistry, University of Pittsburgh*
*Pittsburgh, Pennsylvania 15260*

*Received July 6, 1995*

We recently discovered that reductive dimerization of $[Mn(\eta^6-C_6H_6)(CO)_3]^+$ ($\mathbf{1}^+$) gives $[\{Mn(CO)_3\}_2\{\mu(\eta^4-C_6H_6-\eta^4-C_6H_6)\}]^{2-}$ ($\mathbf{2}^{2-}$), in which the Mn centers are connected by a bridging tetrahydrobiphenylene ligand.[1] This unprecedented transition metal promoted dimerization is an interesting addition to the known reactions of benzene, and our interest in potential applications has led to a mechanistic study which has now established (Scheme 1) that the reaction proceeds through the dimer $[\{Mn(CO)_3\}_2\{\mu(\eta^5-C_6H_6-\eta^5-C_6H_6)\}]$ (**3**), which is itself formed by addition of $[Mn(\eta^4-C_6H_6)(CO)_3]^-$ ($\mathbf{4}^-$) to $\mathbf{1}^+$ to give the key C−C bond. An ionic coupling step is in surprising contrast with the radical coupling mechanism established for reductive dimerization of $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_6)]^+$ to $[\{Fe(\eta^5-C_5H_5)\}_2\{\mu(\eta^5-C_6H_6-\eta^5-C_6H_6)\}]$[2,3] and raises the intriguing possibility of using the reaction to cross couple arenes since there is a clear distinction between the arenes in $\mathbf{4}^-$ and $\mathbf{1}^+$ prior to coupling.

Although dinuclear $\mathbf{2}^{2-}$ is formally a [2 + 2] dimer of the $\eta^4$-benzene complex $[Mn(\eta^4-C_6H_6)(CO)_3]^-$ ($\mathbf{4}^-$),[4] it is not formed by direct dimerization of $\mathbf{4}^-$ since the dimer cannot be isolated from reactions in which $\mathbf{4}^-$ has been preformed. These conditions involve rapid addition of 2 equiv of potassium naphthalenide ($KC_{10}H_8$; KNap) to a stirred slurry of $\mathbf{1}PF_6$ in THF at −78 °C and were established to favor formation of $\mathbf{4}^-$ by comparison of the 62% yield of $[Mn(\eta^5-C_6H_7)(CO)_3]$ (**5**) formed by $CF_3CO_2H$ protonation[4] with the lower yields of **5** obtained after reduction under other conditions.

*Slow* reduction of $\mathbf{1}^+$ by dropwise addition (2 h) of 2 equiv of KNap to a slurry of $\mathbf{1}PF_6$ in THF at −78 °C gives negligible $\mathbf{4}^-$ (since protonation gives negligible **5**), but gives $\mathbf{2}^{2-}$ in much better yield (49% as $[PPN]_2\mathbf{2}$; $PPN^+ = [Ph_3PNPPh_3]^+$) than we reported previously.[1] This suggests that slow reduction optimizes formation of the bis-cyclohexadienyl dimer **3**, which we have shown[1] is a competent intermediate for formation of $\mathbf{2}^{2-}$. Consistent with this we have determined that slow *one*-electron reduction of $\mathbf{1}^+$ gives an optimal 83% one-pot yield of **3** (with the molecular structure[5] in Figure 1[6]),[7,8] which can be further reduced to $[PPN]_2\mathbf{2}$ in 43% isolated yield. The pivotal role of **3** in interconversions of $\mathbf{1}^+$ and $\mathbf{2}^{2-}$ is further emphasized by reoxidation of $\mathbf{2}^{2-}$ to **3** in 69% yield by $O_2$.

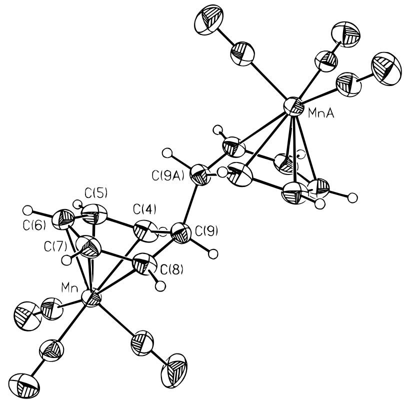
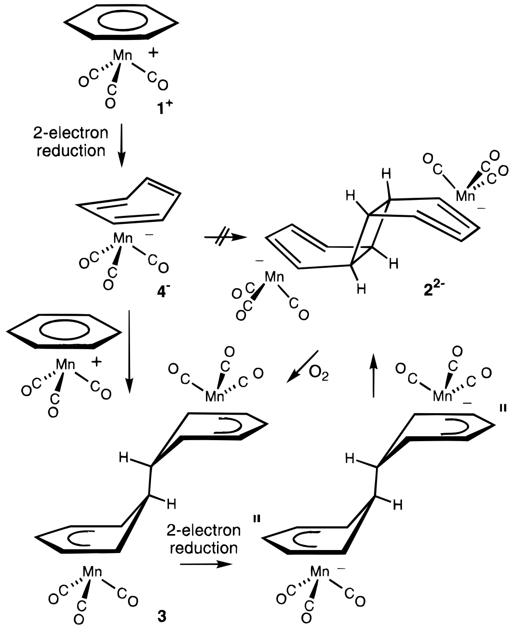


**Figure 1.** Molecular structure of $[\{Mn(CO)_3\}_2\{\mu(\eta^5-C_6H_6-\eta^5-C_6H_6)\}]$ (50% probability ellipsoids). Selected bond lengths (Å): Mn−C(4) = 2.223(2), Mn−C(5) = 2.142(2), Mn−C(6) = 2.131(2), Mn−C(7) = 2.135(2), Mn−C(8) = 2.224(2), C(4)−C(5) = 1.387(3), C(4)−C(9) = 1.509(3), C(5)−C(6) = 1.416(3), C(6)−C(7) = 1.417(3), C(7)−C(8) = 1.395(3), C(8)−C(9) = 1.511(3), C(9)−C(9a) = 1.547(4). Dihedral angle between C(4), C(5), C(6), C(7), C(8) plane and C(4), C(9), C(8) plane = 41.8(1)°.

**Scheme 1**



Formation of **3** is central to formation of $\mathbf{2}^{2-}$ because it gives the first of the two new C−C bonds and locks in the exo stereochemistry, and we initially assumed that the sequence was similar to the established reduction of $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_6)]^+$ to $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_6)]$ followed by dimerization to $[\{Fe(\eta^5-C_5H_5)\}_2\{\mu(\eta^5-C_6H_6-\eta^5-C_6H_6)\}]$.[2,3] We were unable, however, to obtain IR or EPR evidence for the intermediacy of the corresponding $[Mn(C_6H_6)(CO)_3]$ radical (**6**), and this led to an electrochemical examination of the reduction of $\mathbf{1}^+$.

Cation $\mathbf{1}^+$ gives reproducible cyclic voltammograms in $CH_3CN$ on hanging mercury drop electrodes. At −15 °C a reduction is observed at −1.04 V (Figure 2) which approaches chemical reversibility ($i_a/i_c$ ca. 0.85 at scan rates >2 V/s). The reduction

---

[1] Thompson, R. L.; Geib, S. J.; Cooper, J. *J. Am. Chem. Soc.* **1991**, *113*, 8961.

[2] (a) Nesmayanov, A. N.; Denisovich, L. I.; Gubin, S. P.; Vol'kenau, N. A.; Sirotkina, E. I.; Bolesova, I. N. *J. Organomet. Chem.* **1969**, *20*, 169. (b) Nesmayanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S.; Petrakova, V. A. *J. Organomet. Chem.* **1973**, *61*, 329. (c) Nesmayanov, A. N.; Vol'kenau, N. A.; Petrakova, V. A. *J. Organomet. Chem.* **1977**, *136*, 363.

[3] (a) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758. (b) Rasjasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Oswald, N.; Michaud, P.; Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400. (c) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

[4] Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657.

[5] Crystal data: monoclinic space group $C2/c$, $Z = 4$, $a = 21.008(4)$ Å, $b = 7.113(1)$ Å, $c = 11.468(2)$ Å, $\beta = 94.60(1)°$, $V = 1708.2(6)$ Å$^3$, $d_{calcd} = 1.688$ Mg m$^{-3}$, $\mu = 1.510$ mm$^{-1}$, $\lambda = 0.710\ 73$ Å, $T = 233$ K. Of the 2799 reflections measured in the $3.5 < 2\theta < 55.0°$ range, 2494 unique reflections were used in the structure solution by direct methods. Refinement on $F$ converged at $R = 2.54\%$, $_wR_F = 3.32\%$, with GOF = 0.80. Details will be published elsewhere.

[6] Only one other structurally characterized dimer with a $\mu(\eta^5-C_6H_6-\eta^5-C_6H_6)$ ligand[7] and one complex with an analogous mesitylene-derived ligand have been reported.[8]

[7] Andrianov, V. G.; Struchkov, Yu. T.; Petrakova, V. A.; Vol'kenau, N. A. *Koord. Khim.* **1986**, *12*, 978.

[8] Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. J. *Organometallics* **1989**, *8*, 286.

S0002-7863(95)02217-7 CCC: $12.00

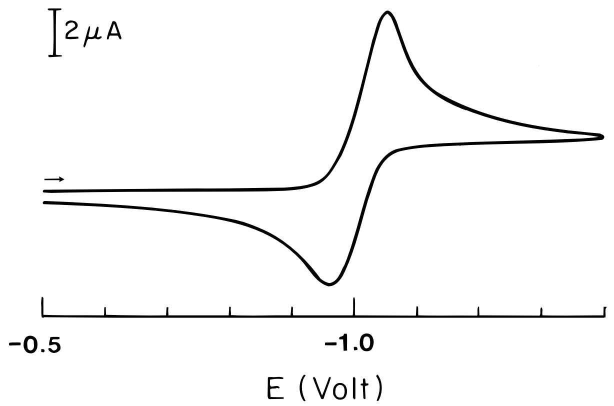


**Figure 2.** Cyclic voltammogram of $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ on a hanging mercury drop electrode in $CH_3CN$ (0.1 mol $L^{-1}$ $[NEt_4][ClO_4]$) at −15 °C and 0.5 V $s^{-1}$. Potentials are reported relative to Ag/AgCl.

current $i_c$ can be used to calculate[9] that this is a two-electron reduction (as confirmed by chronocoulometry:[9] $n = 1.8$) on the assumption that $\mathbf{1}^+$ has a diffusion constant similar to that of ferrocenium under the same conditions. As in related examples in the literature of two-electron reduction of $\eta^6$-arene complexes,[10] two-electron reduction implies that $\mathbf{1}^+$ is reduced directly to $\mathbf{4}^-$ and that the radical **6** is thermodynamically unstable with respect to disproportionation to $\mathbf{1}^+$ and $\mathbf{4}^-$.

With a switching potential of −2.5 V, a second, smaller ($i_{c2}/i_{c1}$ of ca. 0.25) reduction becomes visible with an onset at ca. −2.1 V. At room temperature this is more pronounced ($i_{c2}/i_{c1}$ ca. 0.35), and $i_a/i_{c1}$ for the first reduction decreases to ca. 0.4. This behavior suggests that the second reduction involves a species formed from $\mathbf{4}^-$ in a secondary reaction such as addition of $\mathbf{4}^-$ to $\mathbf{1}^+$ to give **3**, a reaction with precedent in the many reports of the addition of nucleophiles to $\mathbf{1}^+$.[11] Consistent with this interpretation, $n$ for the first reduction drops to 1.6 (chronocoulometry) at 29.5 °C as the $\mathbf{1}^+$ near the electrode surface is depleted. The second reduction is at the same potential as an irreversible reduction ($n = 2$ from $i_c$), which is the sole feature in CVs of **3**, and is assigned to a two-electron reduction of **3**, which initiates formation of $\mathbf{2}^{2-}$ (Scheme 1).

We have confirmed that **3** can be formed by addition of $\mathbf{4}^-$ to $\mathbf{1}^+$ using a reaction vessel with two bulbs connected by a short port. Both sides were loaded with $\mathbf{1}\mathbf{PF}_6$ (0.2 g) suspended in THF (5 mL), and one bulb was maintained at −78 °C while 2 equiv of KNap in THF (5.25 mL of a 0.2 mol $L^{-1}$ solution) were added by syringe. Mixing the reduced solution with the $\mathbf{1}\mathbf{PF}_6$ suspension gave **3** in 42% isolated yield.

The CV data establish that $[Mn(C_6H_6)(CO)_3]$ (**6**) is thermodynamically unstable with respect to $\mathbf{1}^+$ and $\mathbf{4}^-$, but they do not rule out a kinetic role for the monomeric radical **6** in the addition of $\mathbf{4}^-$ to $\mathbf{1}^+$. To probe this we carried out crossover experiments using $d_6$-$\mathbf{1}^+$ and $d_6$-$\mathbf{4}^-$.

Addition of $d_6$-$\mathbf{4}^-$ to $d_0$-$\mathbf{1}^+$ gave a 17:81:2 mixture of $d_0$-, $d_6$-, and $d_{12}$-**3** which was predominantly the heterodimer $d_6$-**3**.[12] The high $d_0$ to $d_{12}$ ratio is ascribed to loss of some reactive $\mathbf{4}^-$ during the reaction, as confirmed by a $d_0$-$\mathbf{4}^-$ to $d_6$-$\mathbf{1}^+$ addition which yielded a 9:72:19 mixture.[13] Formation of $d_0$ and $d_{12}$ homodimers in these cross additions is indicative of some scrambling, but the predominance of the heterodimer rules out electron transfer to form **6** radicals which are free to exchange before they couple. *If* **6** is on the main reaction pathway, it can only be as radical pairs, which only sometimes live long enough to escape the solvent cage. More probably, some approaches of $\mathbf{4}^-$ anions to $\mathbf{1}^+$ cations result in additions, while others result in two-electron transfers within anion/cation pairs (e.g., to convert a $d_6$-$\mathbf{4}^-$, $d_0$-$\mathbf{1}^+$ pair to a $d_6$-$\mathbf{1}^+$, $d_0$-$\mathbf{4}^-$ pair) which can separate and exchange before coupling.[14] Electron pair exchange is consistent with the fact that $\mathbf{1}^+$ undergoes a two-electron reduction to $\mathbf{4}^-$, and the simultaneous operation of nucleophilic addition and electron transfer pathways is consistent with Kochi's reports that there is a fine balance between addition and electron transfer manifolds in ion-pair annihilation reactions of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$ with $[Fe(dienyl)(CO)_3]^+$ complexes.[15]

We conclude that the $\eta^4$-benzene complex $\mathbf{4}^-$ *is* a key intermediate in the formation of its [2 + 2] dimer $\mathbf{2}^{2-}$, but that its role is to add to the cationic precursor $\mathbf{1}^+$ and provide an anion/cation addition route to the intermediate dimer **3**. The contrast between this and the radical route to related dimers of Fe(II)[2,3] reflects the contrast between the tendency of $[Mn(C_6H_6)(CO)_3]$ to disproportionate and the stability to disproportionation of $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)]$.

**Acknowledgment.** We thank the National Science Foundation for financial support (CHE 9113808), Mr. Greg Meisner and Dr. Kasi Somayajula for assistance with the mass spectrometry, and Mr. Robert Cody for recording negative ion CI mass spectra at JEOL in Danvers, MA.

JA952217C

---

(9) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(10) For leading references, see: (a) Rieke; R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420. (b) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheidi, V. *Organometallics* **1983**, *2*, 347. (c) Plitzko, K.-D.; Wehrle, G.; Gollas, B.; Rapko, B.; Dannheim, J.; Boekelheidi, V. *J. Am. Chem. Soc.* **1990**, *112*, 6556. (d) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(11) (a) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, Chapter 29. (b) Semmelhack, M. F. In *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, Chapter 2.4.

(12) Isotopic compositions were determined by negative ion chemical ionization mass spectrometry. Unlabeled **3** gives a strong molecular ion (ca. 30%) with appropriate $^{13}C$ satellites, together with an $[M - 2]^-$ peak of variable intensity. This arises from $H_2$ elimination (presumably across the bridgehead) since there are similar $[M - 3]^-$ and $[M - 4]^-$ peaks (from HD and $D_2$ elimination) below the molecular ions of $d_6$-**3** and $d_{12}$-**3**. The intensities of the $M^-$ and the H*H* elimination peaks were summed to calculate isotopic distributions.

(13) In control experiments we established that no $d_6$ dimer was formed when a 1:1 solution of $d_0$- and $d_{12}$-**3** in THF was kept at 5 °C for 1 week and that there is no equilibrium isotope effect for formation of **3**: reduction of a 1:1 mixture of $d_0$-$\mathbf{1}^+$ and $d_6$-$\mathbf{1}^+$ gave a 25:53:22 mixture of $d_0$-, $d_6$-, and $d_{12}$-**3**.

(14) Dual pathways might reflect the need for a particular orientation of the ions if a collision is to result in C−C bond formation.

(15) (a) Lehmann, R. E.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 458. (b) Lehmann, R. E.; Kochi, J. K. *Organometallics* **1991**, *10*, 190. (c) Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 4491.