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Reductive Dimerization of the Cyclohexadienyl Complex $[Mn(CO)_3(\eta^5\text{-}C_6H_7)]$ through a Radical Pathway

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*Summary: Slow naphthalenide reduction of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ (**1**) generates the transient anionic radical $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]^{\bullet-}$ (**4**$^{\bullet-}$), which adds as a nucleophile to **1** to form, after further reduction, $[Mn(CO)_3\{\eta^4\text{-}C_6H_7\text{−}CO\text{−}Mn(\eta^5\text{-}C_6H_7)(CO)_2\}]^{2-}$, while fast reduction of **1** at low temperature gives $[\{Mn(CO)_3\}_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-}C_6H_7\text{−}C_6H_7)]^{2-}$, a dimer of **4**$^{\bullet-}$. Both reactions suggest that formation of transient **4**$^{\bullet-}$ allows access to new reaction manifolds in which the cyclohexadienyl ligand of the classic complex **1** has been activated to further reactions.*

The complex $[Mn(CO)_3(\eta^5\text{-}C_6H_7)]$ (**1**) was the first reported cyclohexadienyl complex of a transition metal, prepared by hydride addition to $[Mn(CO)_3(\eta^6\text{-}C_6H_6)]^+$ (**2**$^+$) in 1964.[1] Complex **1** and its derivatives have been extensively studied,[2] but relatively few reactions have resulted in additional modification of the benzene-derived ring, except for the nucleophilic addition reactions that occur when the η^5-cyclohexdienyl ring in **1** is activated by replacement of one CO ligand with NO^+.[2b,d] We now wish to report activation of the cyclohexadienyl ring through one-electron reduction of the metal center to give an odd-electron complex that undergoes several surprising new reactions that do involve the cyclohexadienyl ligand.

Reduction of **1** was achieved by slow dropwise addition of 1 equiv of 0.2 M KNap/THF into a mixture of **1** (prepared by reduction of **2**PF_6 and subsequent protonation[3]) and 18-crown-6 in THF at −78 °C. The IR spectrum of the resulting solution contained four bands at 1920 (m), 1876 (m), 1828 (s), and 1807 (s) cm^{-1}, consistent with the presence of two monoanionic metal centers. This mixture was converted into a yellow crystalline compound by removal of solvent, extraction into DME, and crystallization at −30 °C from a concentrated DME solution. The complex is unstable at room temperature in the solid state and in solution but is believed to be $[K(18\text{-crown-6})]_2[Mn(CO)_3\{\eta^4\text{-}C_6H_7\text{−}CO\text{−}Mn(\eta^5\text{-}C_6H_7)(CO)_2\}]$ ($[K(18\text{-C-6})]_2$**3**) (24% yield, based on **2**PF_6) by IR comparison with samples of $[K(\text{cryptate-}2,2,2)]_2$**3**[4] prepared in low yield in a similar manner and characterized crystallographically (Figure 1), using crystals grown from $MeCN/Et_2O$ in 3 days at −30 °C.

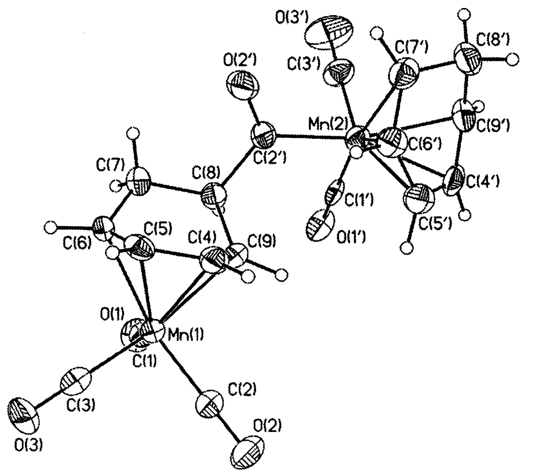

Figure 1. Molecular structure of **3**$^{2-}$ in $[K(\text{cryptate-}2,2,2)]_2$**3** (probability ellipsoids are shown at the 50% level).

We propose that the initial intermediate from this slow-addition reduction is the radical anion $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]^{\bullet-}$ (**4**$^{\bullet-}$) and that this adds as a nucleophile to one carbonyl carbon of a second molecule of **1** to form $[Mn(CO)_3\{\eta^4\text{-}C_6H_7\text{−}CO\text{−}Mn(\eta^5\text{-}C_6H_7)(CO)_2\}]^{\bullet-}$ (**5**$^{\bullet-}$), a species that will accept an electron to give the product **3**$^{2-}$ (Scheme 1, path A). This proposed reaction pathway is reminiscent of that for the previously reported acylation of the carbonyl of **1** with organolithium reagents.[5]

Changes observed in IR spectra when only $^1/_2$ equiv of KNap was added to a solution of **1** under these slow-addition reaction conditions support our proposed mechanism. The spectrum indicates the presence of both starting material **1** and **3**$^{2-}$, and a reasonable interpretation is that only half of the starting material has been reduced to **3**$^{2-}$ at the middle point because **5**$^{\bullet-}$ competes effectively with **1** for reducing reagent. Addition of a radical trapping reagent, Bu_3SnH, at the halfway point causes no change in the IR spectrum, consistent with the interpretation above.

To block reaction by path A in Scheme 1, we attempted a procedure in which all of **1** is reduced rapidly at −78 °C by fast (<1 s) addition of 1 equiv of 0.2 M KNap/THF into a solution of **1** at −78 °C. After 1 equiv

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[1] Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479.

[2] For reviews, see (a) Pearson, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, Chapter 29. (b) Mcdaniel, K. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 6, Chapter 4. (c) McDaniel, K. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, Chapter 6. (d) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, Chapter 9. (e) Roell, B. C.; McDaniel, K. F.; Vaughan, W. S.; Macy, T. S. *Organometallics* **1993**, *12*, 224.

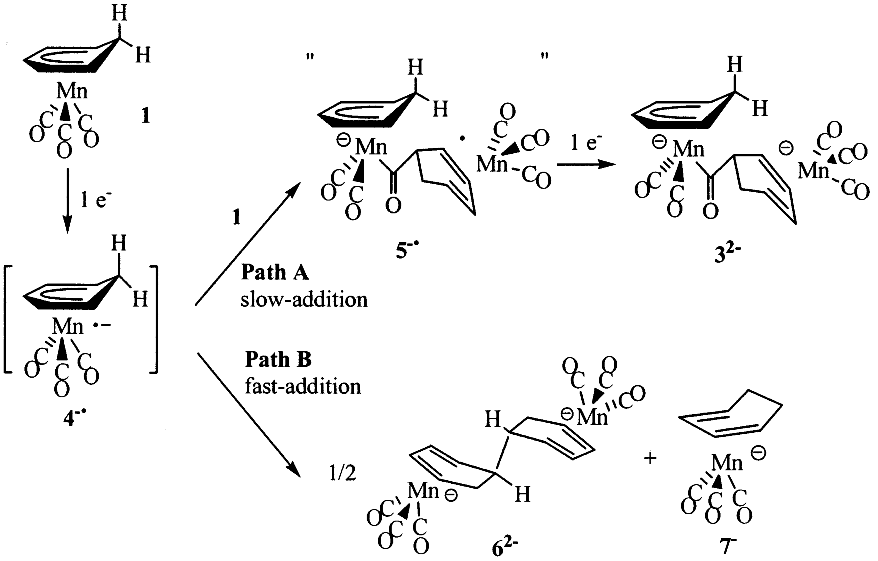
[3] Made as reported in: Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657.

[4] cryptate-2,2,2 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane.

[5] (a) Sheridan, J. B.; Padda, R. S.; Chaffee, K.; Wang, C.; Huang, Y.; Lalancette, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1539 and references therein. (b) Yu, R.; Chen, J.; Wang, X.; Wu, Q.; Liu, Q. *J. Organomet. Chem.* **1996**, *516*, 81−89.

10.1021/om0305667 CCC: $25.00

Scheme 1



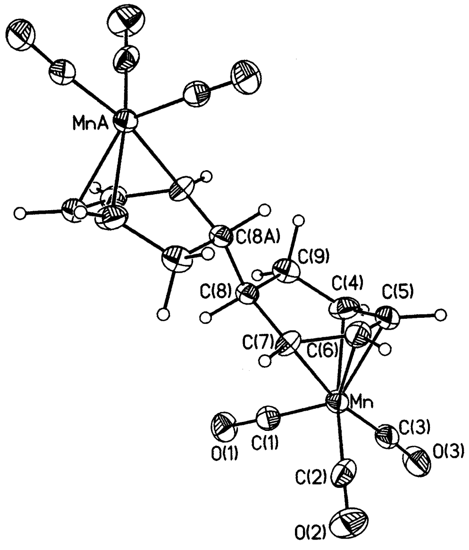


Figure 2. Molecular structure of 6^{2-} in [K(cryptate-2,2,2)]$_2$**6** (probability ellipsoids are shown at the 50% level).

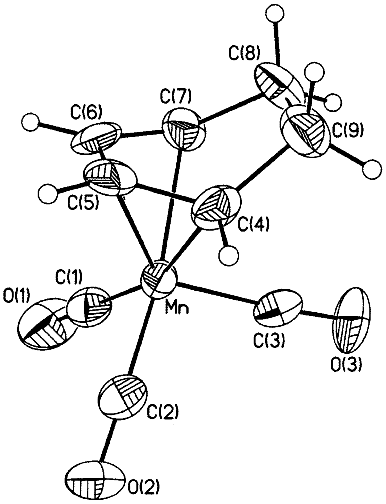


Figure 3. Molecular structure of 7^- in PPN**7** (Probability ellipsoids are shown at the 50% level).

of cryptate-2,2,2 had been added, trace amounts of unstable crystalline [K(cryptate-2,2,2)]$_2$[{Mn(CO)$_3$}$_2$(μ_2-η^4:η^4-C_6H_7−C_6H_7)] ([K(cryptate-2,2,2)]$_2$**6**) could be isolated after 5 days at 0 °C, as established by a single-crystal X-ray diffraction study of [K(cryptate-2,2,2)]$_2$**6** (Figure 2). It is reasonable to infer that the first step in the reaction is reduction of all Mn centers to $\mathbf{4}^{\bullet-}$ followed by a simple radical coupling (Scheme 1, path B).

The intermediacy of the radical anion $\mathbf{4}^{\bullet-}$ is consistent with crystallization of PPN[Mn(η^4-C_6H_8)(CO)$_3$] (PPN**7**)[6] at 0 °C as a minor product from the fast reduction of **1**. The nature of this compound was established by a single-crystal X-ray diffraction study, which identified the molecular structure shown in Figure 3. Spectral data for 7^- are consistent with the data reported in an article by Brookhart;[7] formation of 7^- by H$^\bullet$ abstraction from the solvent by $\mathbf{4}^{\bullet-}$ is a reasonable source of 7^- and supports the existence of $\mathbf{4}^{\bullet-}$ in the reaction manifold that follows reduction of **1**.

The optimal conditions described above can be used to prepare solutions of either 3^{2-} or 6^{2-} that contain few impurities (IR), but isolated yields of [K(18-crown-6)]$_2$**3** and [K(cryptate-2,2,2)]$_2$**6** are low and unreliable. We believe that this reflects the sensitivity of these materials, and we have been able to confirm that the reduction reactions give clean products under the conditions described above through reoxidation of the solutions with 0.5 equiv of Ph_3PbCl to regenerate **1**. Quantitative solution IR established that **1** was formed from 3^{2-} and from 6^{2-} in 78% yield and in a somewhat variable 40−70% yield, respectively.

Reduction of **1** to 6^{2-} has intriguing implications for an earlier mechanistic study, in which we reported that two-electron reduction of **2**PF_6 leads to a [2 + 2] cyclodimerization through [{Mn(CO)$_3$}$_2$(μ_2-η^5:η^5-C_6H_6−C_6H_6)] (**8**), in which the first of the new C−C bonds has been formed by an anion/cation addition.[8,9] We had been unable in earlier work to establish how **8** is further

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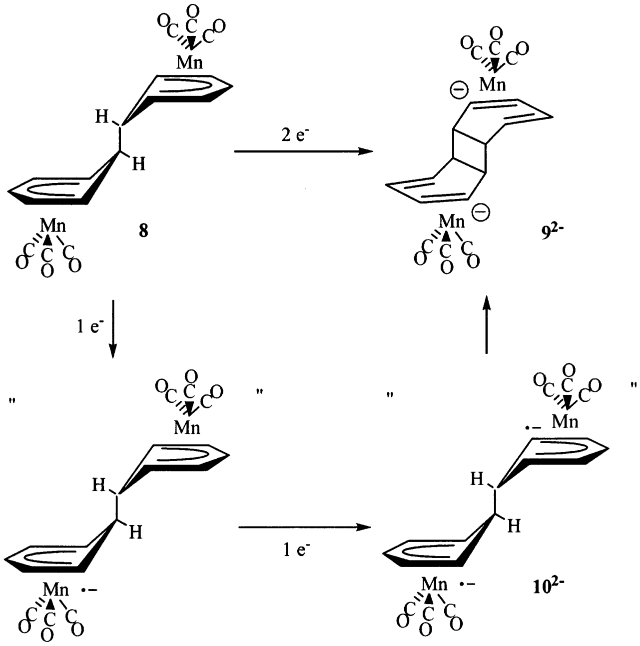
[6] PPNCl = bis(triphenylphosphoranylidene)ammonium chloride.

[7] Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.

[8] Thompson, R. L.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 8691.

[9] Lee, S.; Lovelace, S. R.; Arford, D. J.; Geib, S. J.; Weber, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 4190.

Scheme 2



reduced to give the [2 + 2] product $[\{Mn(CO)_3\}_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-}C_6H_6{-}C_6H_6)]^{2-}$ (**9**$^{2-}$), but reduction of **1** to **6**$^{2-}$ suggests that **8** could be reduced as shown in Scheme 2 to give the dianionic intermediate **10**$^{2-}$ in which formation of a second C−C bond is directly analogous to the reaction in which **6**$^{2-}$ is formed.

It has become increasingly clear in recent years that reactive 19-electron species can be valuable intermediates in the modification of unsaturated hydrocarbyl ligands in a number of organometallic systems, with the most notable example being the 19-electron sandwich complex $[Fe(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6R_6)]$ extensively explored by Astruc and co-workers.[10] More recent examples include related research in ruthenium[11] and iridium,[12] together with closely related chemistry in which $[Mn(CO)_3(\eta^6\text{-}styrene)]^+$ is reduced to a 19-electron species that can form a range of dinuclear products.[13] The present result establishes that **1** can similarly be reduced through a one-electron reduction manifold involving intermediate **4**$^{\bullet-}$ and that this species allows access to unusual new classes of reactions involving the hydrocarbyl ligand of the best known example of a transition-metal cyclohexadienyl complex. Intriguingly, both the Astruc chemistry and our results are now being paralleled by developments in the chemistry of benzenoid radical anions that only have alkali-metal counterions to stabilize them.[14]

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Supporting Information Available: Text giving the experimental details for the synthesis and characterization of compounds **3**$^{2-}$, **6**$^{2-}$, and **7**$^{-}$ and tables giving crystallographic data for [Kcryptate-2,2,2]$_2$**3**, [Kcryptate-2,2,2]$_2$**6**, and PPN**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] (a) Jamon, J.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758. (b) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377. (c) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36.

[11] Gusev, O. V.; Ievlev, M. A.; Peterleitner, M. G.; Peregudova, S. M.; Denisovich, L. I.; Petrovskii, P. V.; Ustynyuk, N. A. *J. Organomet. Chem.* **1997**, *534*, 57.

[12] Gusev, O. V.; Peterleitner, M. G.; Ievlev, M. A.; Kal'sin, A. M.; Perovskii, P. V.; Denisovich, L. I.; Ustynyuk, N. A. *J. Organomet. Chem.* **197**, *531*, 95.

[13] (a) Son, S. U.; Lee, S. S.; Chung, Y. K. *J. Am. Chem. Soc.* **1997**, *119*, 7711. (b) Hsu, S. C. N.; Yeh, W.-Y.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **1998**, *120*, 13250.

[14] Hitchcock, R. B.; Lappert, M. F.; Protchenko, A. V. *J. Am. Chem. Soc.* **2001**, *123*, 189.