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Communications

Electrophilic Addition of the Carbene Ligand in $[\mathrm{Fe(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\{{=}\mathrm{CMe(OMe)}\}]^+$ to the Reductively Activated Benzene Ligand in $[\mathrm{Mn(CO)_3}(\eta^4\text{-}\mathrm{C_6H_6})]^-$

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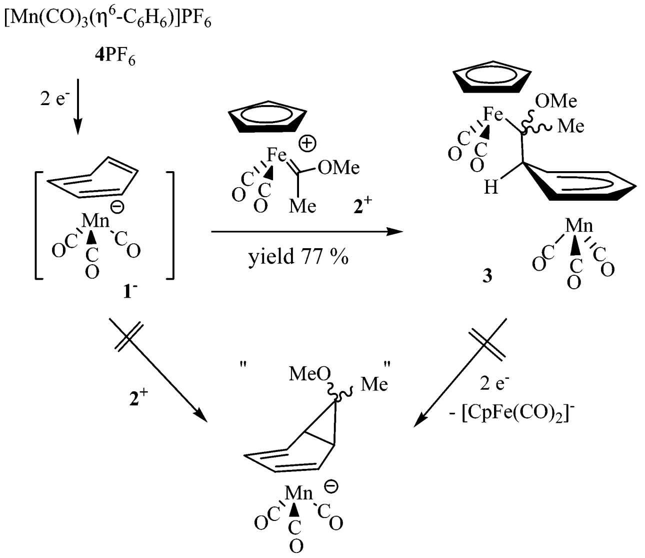
*Summary: The iron carbene cation $[\mathrm{Fe(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\{{=}\mathrm{CMe(OMe)}\}]^+$ reacts with reductively activated $[\mathrm{Mn(CO)_3}(\eta^4\text{-}\mathrm{C_6H_6})]^-$ to form the carbene/benzene adduct $[\mathrm{Mn(CO)_3}\{\eta^5\text{-}\mathrm{C_6H_6}{-}\mathrm{CMe(OMe)Fe(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}]$ (**3**). Reduction of **3** is proposed to give species in which there are ferrocyclic benzene-derived ligands.*

It is well-established that transition-metal carbene complexes are versatile reagents for organic synthesis[1] and that electrophilic iron carbene complexes in particular will cyclopropanate alkenes selectively under mild conditions.[2] These reactions are, however, restricted to unconjugated alkenes, and recent work from our laboratories suggested that it might be possible to extend cyclopropanations by electrophilic carbene complexes to arene substrates through the use of complexes in which the arene has been activated toward electrophiles by η^4 coordination to a reduced metal center. We have, for example, reported that the uncoordinated double bond of the benzene ligand in $[\mathrm{Mn(CO)_3}(\eta^4\text{-}\mathrm{C_6H_6})]^-$ ($\mathbf{1}^-$) reacts with diphenylketene to form a six-membered ring through an unexpected [2 + 2 + 2] cycloaddition[3] and with *N*,α-diphenyl nitrone to form a five-membered ring through a stepwise 1,3-dipolar [3 + 2] cycloaddition.[4] Our intent was to deliver the carbene fragment from $[\mathrm{Fe(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\{{=}\mathrm{CMe(OMe)}\}]^+$ ($\mathbf{2}^+$) to $\mathbf{1}^-$ to make a three-membered ring (Scheme 1), but we have determined that there is instead addition of the entire iron carbene cation to $\mathbf{1}^-$. The Fe−C bond is retained in the bimetallic product $[\mathrm{Mn(CO)_3}\{\eta^5\text{-}\mathrm{C_6H_6}{-}\mathrm{CMe(OMe)}{-}\mathrm{Fe(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}]$ (**3**), and further reduction of **3** is proposed to give a dianionic bimetallic product in which the benzene-derived ligand is part of a ferracycle.

Scheme 1



Brookhart's literature procedure[5] was used to synthesize the desired carbene starting material $\mathbf{2}\mathrm{CF_3SO_3}$. At −78 °C, a solution of $\mathbf{1}^-$ made from $[\mathrm{Mn(CO)_3}(\eta^6\text{-}\mathrm{C_6H_6})]\mathrm{PF_6}$ ($\mathbf{4}\mathrm{PF_6}$) and 2.2 equiv of potassium naphthalenide (KNap) was mixed with a solution of 1.1 equiv of $\mathbf{2}\mathrm{CF_3SO_3}$ in THF in a double Schlenk tube. The product was extracted into pentane. After pentane and naphthalene were removed under vacuum, the solid was redissolved in pentane, and **3** (77% yield) was recrystallized from concentrated pentane at −30 °C (Scheme 2).

The product **3** was identified as analytically pure $[\mathrm{Mn(CO)_3}\{\eta^5\text{-}\mathrm{C_6H_6}{-}\mathrm{CMe(OMe)}{-}\mathrm{Fe(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}]$ by inspection of NMR[6] spectra and by a single-crystal X-ray diffraction study, which shows (Figure 1) a chiral bridge carbon between the η^5-cyclohexadienyl ligand and the iron metal center. In the solid state, the methoxy and methyl groups on the chiral bridge carbon are held over the η^5-cyclohexadienyl ligand, probably because of the

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[1] For recent reviews see: (a) Zaragoza Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: New York, 1999. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (c) Taber, D. F. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 3, p 1045.

[2] (a) Kerber, R. C. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G., Abel, E. W., Eds., Pergamon: New York, 1995; Vol. 7, p 101. (b) Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G., Abel, E. W., Eds.; Pergamon: New York, 1995, Vol. 7, p 939. (c) Ruck-Braun, K.; Mikulas, M.; Amrhein, P. *Synthesis* **1999**, 727.

[3] Lee, S.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 9572.

[4] Shao, L.; Geib, S. J.; Badger, P. D.; Cooper, N. J. *Organometallics* **2003**, *22*, 2811.

[5] Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[6] ^{1}H NMR ($\mathrm{C_6D_6}$): δ 4.97 (t, 1H), 4.49 (t, 1H), 4.41 (t, 1H), 4.14 (s, 5H), 3.25 (t, 3H), 2.92 (s, 3H), 0.99 (s, 3H). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 223.6 (CO of Mn), 218.9 (CO of Fe), 217.8 (CO of Fe), 101.0 (C), 96.7 (d, 2CH), 86.7 (5CH), 78.5 (CH), 62.5 (CH), 60.2 (CH), 51.6 (CH), 51.4 ($\mathrm{OCH_3}$), 30.0 ($\mathrm{CH_3}$).

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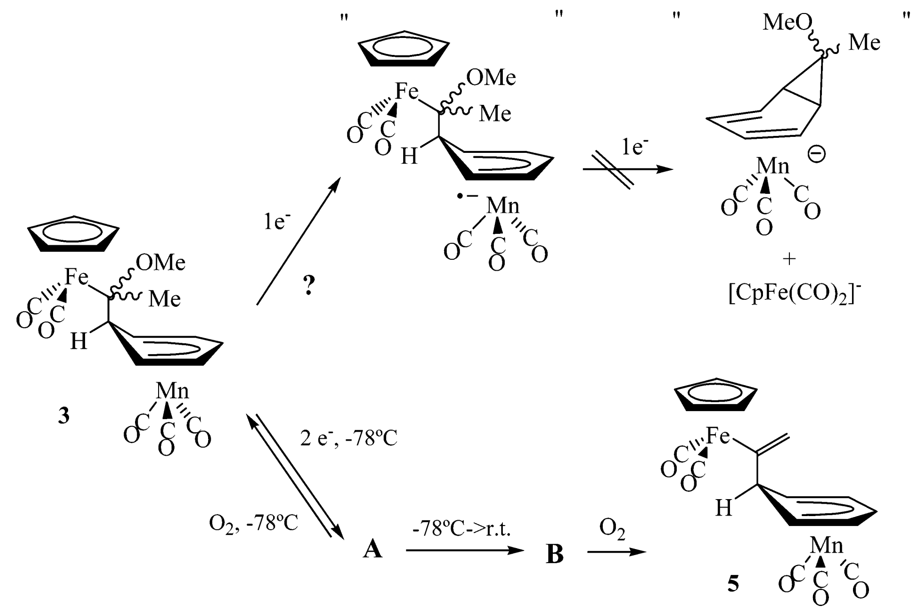
Scheme 2



steric bulk of the $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ fragment. The chirality of **3** influences its NMR spectra, as seen from the varying chemical shifts of diastereotopic H_3 (δ 4.49) and H_5 (δ 4.41). Similarly, the carbonyls of the iron center have two peaks in the ^{13}C NMR spectra. The chemical shifts of C_2 (δ 62.5) and C_6 (δ 60.2) are also distinct.

In an attempt to activate adduct **3** for further reaction and, hence, to force formation of the target cyclopropane, we reduced **3** with KNap. On the basis of studies of one-electron reduction of $[Mn(CO)_3(\eta^5\text{-}C_6H_7)]$,[7] we believed that two-electron reduction would give an intermediate anion from which $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ could leave. The remainder of the reduced **3** could then undergo an intramolecular C−C bond formation reaction (Scheme 2).

In practice, reduction of **3** followed a surprising and unprecedented alternative pathway. IR monitoring of carbonyl bands did indicate that **3** could be reduced by naphthalenide (although somewhat more than 2 equiv of KNap was needed for complete reduction), and reduction of a THF solution of **3** with 2.8 equiv of 0.2 M KNap/THF at −78 °C gave a solution with an anionic metal center, unknown **A** (Scheme 2), with IR absorption peaks (ν_{CO} only, THF) at 1920.5 (m) and 1828.1 (s, br) cm^{-1}, in a typical range for an anionic manganese carbonyl. After the reduced solution was warmed to ambient temperature for more than 1 h, IR spectra showed that **A** slowly changed into the closely related species **B** (IR peaks, ν_{CO} only, THF, at 1927.1 (s), 1839.1 (s, br), and 1817.7 (m) cm^{-1}). Attempts to isolate the anionic species **A** and **B** or derivatize them with electrophiles have been unsuccessful to date.

Evidence for the nature of **A** and **B** was ultimately provided by oxidation reactions with O_2 that gave reasonable yields of neutral products **3** (the starting material for the reduction) and $[Mn(CO)_3\{\eta^5\text{-}C_6H_6\text{−}C(\text{=}CH_2)\text{−}Fe(CO)_2(\eta^5\text{-}C_5H_5)\}]$ (**5**), respectively (Scheme 2).

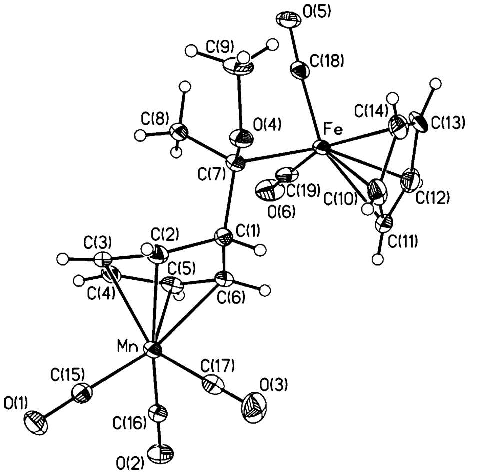


Figure 1. Molecular structure of **3** (probability ellipsoids are shown at the 50% level). Selected bond lengths (Å) and angles (deg): Fe−C(7) = 2.132(5), C(1)−C(6) = 1.516(7), C(1)−C(2) = 1.517(7), C(1)−C(7) = 1.563(6), C(2)−C(3) = 1.395(7), C(3)−C(4) = 1.391(7), C(4)−C(5) = 1.424(7), C(5)−C(6) = 1.393(7); C(6)−C(1)−C(2) = 102.7(4), C(6)−C(1)−C(7) = 119.2(4).

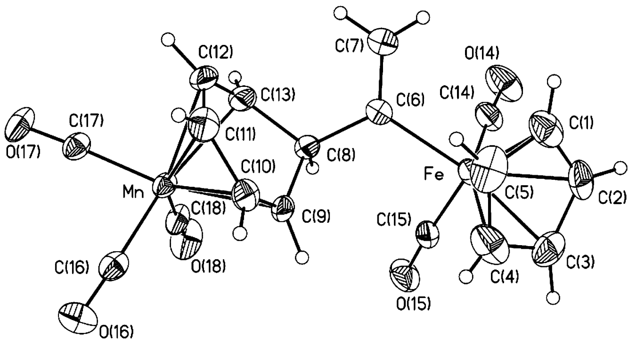
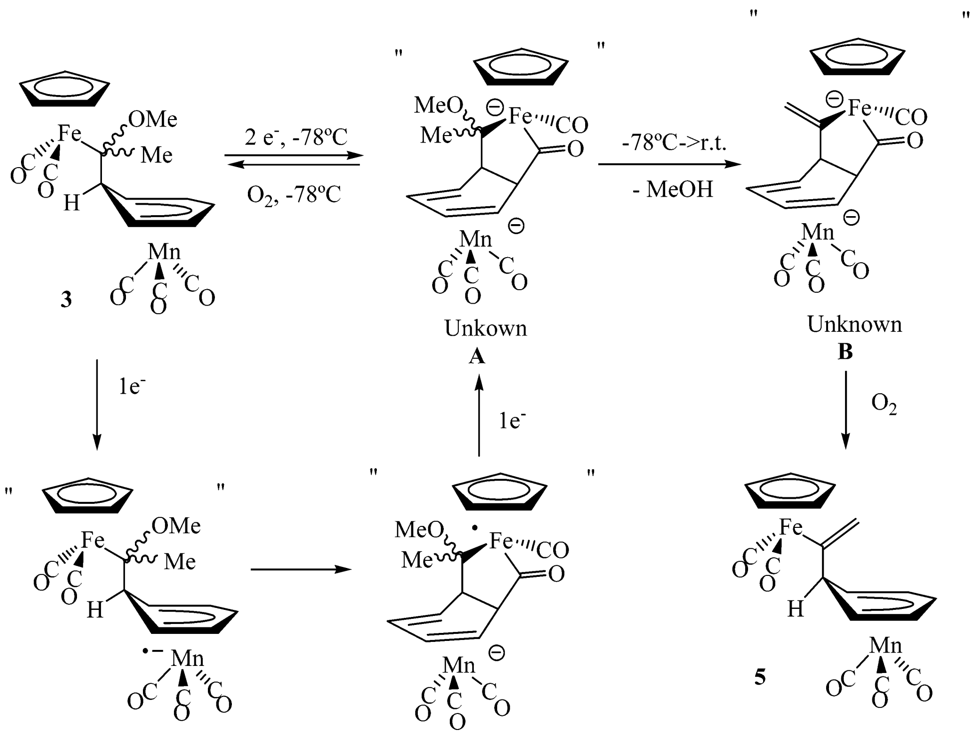


Figure 2. Molecular structure of **5** (showing one of the two independent molecules in the cell unit; probability ellipsoids are shown at the 50% level). Selected bond lengths (Å) and angles (deg): C(6)−C(7) = 1.323(5), C(6)−C(8) = 1.531(4), Fe−C(6) = 2.028(3), C(8)−C(9) = 1.510(4), C(8)−C(13) = 1.518(4), C(9)−C(10) = 1.391(4), C(10)−C(11) = 1.417(5), C(11)−C(12) = 1.408(5), C(12)−C(13) = 1.382(5); C(7)−C(6)−C(8) = 120.6(3), C(7)−C(6)−Fe = 120.6(3), C(8)−C(6)−Fe = 118.8(2), C(9)−C(8)−C(13) = 102.0(3).

Scheme 3



At −78 °C, **3** was obtained in a yield of 69% by purging the reduced solution of **A** with excess O_2 immediately after the reduction. At ambient temperature, after the IR spectrum of **A** had already changed into that of **B**, purging the solution with excess O_2 gave only **5** in 25% yield. This neutral product **5** was characterized by IR, NMR,[8] and single-crystal X-ray diffraction (Figure 2).

Since **3** can be reduced/oxidized reversibly at −78 °C, **A** must be closely related to the starting material **3**. One possible structure for **A** is shown in Scheme 3—we propose that the first one-electron reduction of **3** gives the expected 19-electron Mn complex as a transient intermediate, and this radical anion could then undergo intramolecular nucleophilic reaction with the carbonyl of the Fe metal center and further reduction to form **A** (Scheme 3). Dianionic **A** is not stable at ambient temperature and could decompose to **B** by loss of MeOH. Oxidations of **A** and **B** would reasonably give the starting material **3** and complex **5** as stable products, respectively.

We conclude that the potential [2 + 2] reaction manifold that could lead in a concerted or stepwise fashion to the cyclopropane illustrated in Scheme 1 is less accessible than a simple trans addition of the electrophilic carbene ligand in $\mathbf{2}^+$ to the nucleophilic benzene in $\mathbf{1}^-$ to give **3**. This unusual complex of Mn(I), with an organometallic substituent on the cyclohexadienyl ligand, undergoes a reductive reaction that we propose involves formation of an iron-centered metallacycle that can be reopened by oxidation; access to metallacycle **A** and its room-temperature derivative **B** from the carbene complex $\mathbf{2}^+$ demonstrates that $\mathbf{2}^+$ does offer an approach to the derivatization of the benzene ligand in $\mathbf{1}^-$.

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Supporting Information Available: Text giving the experimental details for synthesis and characterization of compounds **3** and **5** and tables giving crystallographic data for **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Shao, L.; Geib, S. J.; Badger, P. D.; Cooper, N. J. *Organometallics* **2003**, *22*, 3977.

(8) ^1H NMR (C_6D_6): δ 5.38 (s, 1H), 4.95 (s, 1H), 4.89 (t, 1H), 4.22 (t, 2H), 4.00 (s, 5H), 3.12 (t, 2H), 2.97 (t, 1H). ^{13}C NMR (acetone-d_6): δ 223.8 (CO), 217.1 (CO), 160.5 (C), 122.9 (CH_2), 95.9 (CH), 86.1 (CH), 80.2 (CH), 61.1 (CH), 50.2 (CH).