Addition of Iminium Salts to the Reductively Activated Benzene in [Mn(η⁴-C₆H₆)(CO)₃]⁻

Sang-Hee Ko Park, Steven J. Geib,[†] and N. John Cooper*

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

Iminium salts [R$_2$C=NR$_2$]$^+$ are powerful electrophiles and valuable reagents in organic synthesis,[1] and their cationic nature suggested that they might offer a solution to a problem we faced in developing the chemistry of the benzene ligand in the Mn-(−I) complex [Mn(η⁴-C₆H₆)(CO)₃]⁻ (**1**⁻); this is activated with respect to protonation,[2] [2 + 2] dimerization,[3] and ketene addition,[4] but we have had surprisingly little success[5] in attempts to add simple carbon-centered electrophiles to give cyclohexadienyl complexes complementary to those prepared (partly because of interest in their potential applications in organic synthesis) by addition of nucleophiles to [Mn(η⁶-C₆H₆)(CO)₃]$^+$ (**2**$^+$).[6,7] Our discovery, however, that partial naphthalenide reduction of **2**$^+$ leads to addition of anionic **1**⁻ to cationic **2**$^+$ to give the cyclohexadienyl dimer [{Mn(CO)₃}₂{μ(η⁵-C₆H₆-η⁵-C₆H₆)}][8] suggested that cationic electrophiles might add to **1**⁻ and led us to examine the addition of iminium salts to the activated benzene (Scheme 1); this reaction provides the first examples of the addition of an iminium salt to an unsaturated ligand in a transition metal complex.

A solution of K**1** in THF prepared by potassium naphthalenide (KNap) reduction of a slurry of **2**PF₆ in THF at −78 °C[9] was added to a solution of [Ph₂C=NMe₂]BF₄[10] (**3**BF₄) in CH₃CN at −20 °C. The red-brown solution immediately turned red and then yellow as it warmed to room temperature. After solvent removal, a pentane soluble yellow adduct was isolated in 50% yield (70% ¹H NMR yield) following chromatography on basic alumina. Iminium salts have been reported to add to the metal centers of carbonylmetalates and other low-valent complexes to give η¹- or η²-aminomethyl complexes[11] or their derivatives[12] (or carbene complexes in the case of chloroiminium salts[13]),

Scheme 1
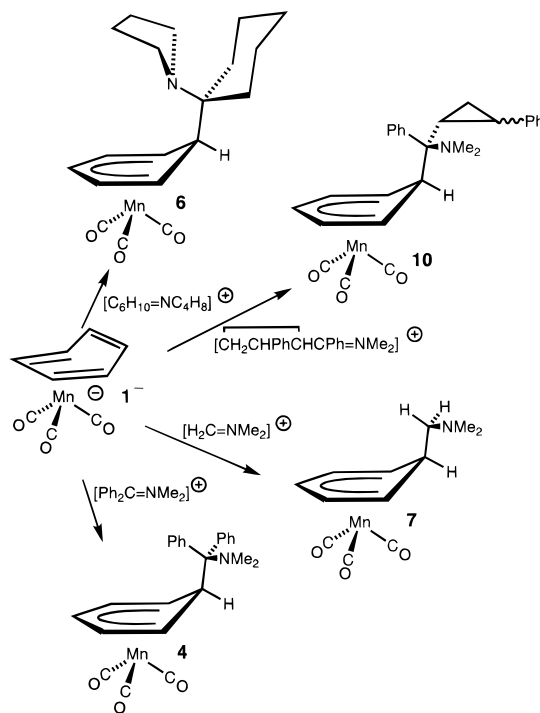
but a diffraction study[14] established that in this case the iminium salt had undergone an unprecedented addition to the benzene ligand to give the *exo*-aminoalkyl-substituted cyclohexadienyl complex [Mn(CO)₃(η⁵-C₆H₆CPh₂NMe₂)] (**4**) shown in Figure 1.

The reaction is sensitive to the precise reaction conditions, and it is particularly important that only 2.0 equiv of KNap be used. The reducing capacity of even modest excesses persists in the system (although the green color of naphthalenide anion is not observed) and decreases the addition yield. Use of 2.5 equiv of naphthalenide, for example, leads to **4** in ca. 35% yield.

Iminium salts can be readily prepared from most ketones, but it was not obvious that iminium addition to **1**⁻ would be a general reaction. We have, however, established that the dialkyliminium salt [(CH₂)₅C=N(CH₂)₄]BF₄ (**5**BF₄)[15] adds to the activated benzene in **1**⁻ on a 1 mmol scale to give the *exo*-aminoalkyl complex [Mn(CO)₃{η⁵-C₆H₆C(CH₂)₅N(CH₂)₄}] (**6**) in 54% isolated yield. Eschenmoser's salt, [H₂C=NMe₂]I, will add similarly to **1**⁻, although the yield of [Mn(CO)₃(η⁵-C₆H₆-CH₂NMe₂)] (**7**) is low (20%).

The exo stereochemistry of the reactions (confirmed for **6** and **7** by the observation of the characteristic 5−6 Hz coupling between the vicinal H and the endo H) establishes that iminium additions do not involve metal-mediated pathways (in contrast with the endo addition of D$^+$ to **1**⁻)[2] and raises an intriguing question as to whether they involve a two-electron process (**a** in Scheme 2) or an SET pathway (**b** in Scheme 2) in which intermediate organic and organometallic radicals couple; both pathways have been observed in other organometallic cation−anion annihilation reactions.[16]

The SET option is particularly attractive in the case of the diaryl addend **3**$^+$, since **3**$^+$ undergoes facile, reversible one-

[†] Address crystallographic correspondence to this author.

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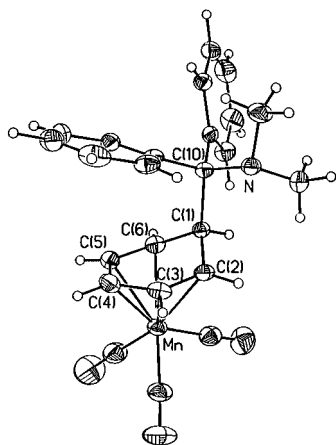
(14) Crystal data: monoclinic space group *P*2(1)/*c*, *Z* = 4, *a* = 14.253-(3) Å, *b* = 10.320(2) Å, *c* = 13.978(3) Å, *b* = 90.58(2)°, *V* = 2055.9(7) Å³. Refinement on *F*² converged at *R$_F$* = 3.98%, $_wR_{F^2}$ (all data) = 10.10%, with GOF(*F*²) = 1.034.

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Figure 1. Molecular structure of [Mn(CO)$_3$(η^5-C$_6$H$_6$CPh$_2$NMe$_2$)] (30% probability ellipsoids). Selected bond lengths (Å): Mn−C(2) = 2.250-(2), Mn−C(3) = 2.136(3), Mn−C(4) = 2.119(3), Mn−C(5) = 2.131-(3), Mn−C(6) = 2.216(2), C(1)−C(10) = 1.588(3), C(1)−C(2) = 1.507(3), C(2)−C(3) = 1.379(4), C(3)−C(4) = 1.403(4), C(4)−C(5) = 1.400(4), C(5)−C(6) = 1.392(4), C(6)−C(1) = 1.499(3). Dihedral angle between C(2),C(3),C(4),C(5),C(6) plane and C(1),C(2),C(6) plane = 35.7(2)°.

Scheme 2
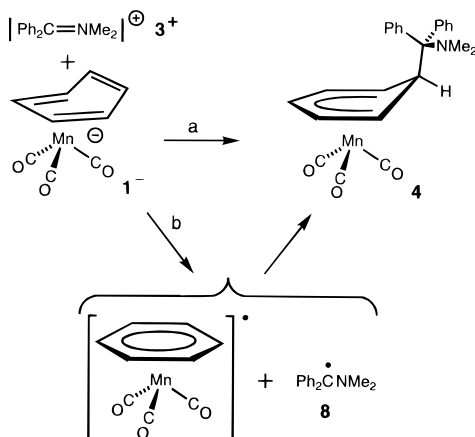
electron reduction to the Ph$_2$CNMe$_2$ radical (**8**).[17] We have determined that this couple is at −1.25 V (vs internal ferrocene/ferrocenium) in CH$_3$CN on a hanging mercury drop electrode, while the partially reversible two-electron reduction of **2**$^+$ to **1**$^-$ is at −1.26 V under these conditions, so that electron transfer from **1**$^-$ to **3**$^+$ is a thermodynamically accessible mechanistic step. The distinctive blue violet color of **8** is not observed during **2**$^+$ addition to **1**$^-$, establishing that **8** can only be a transient intermediate if it is present.

We have explored the possibility that **8** and "[Mn(η^6-C$_6$H$_6$)-(CO)$_3$]" radicals are transient intermediates in **3**$^+$ addition to **1**$^-$ by carrying out competition experiments designed to trap an intermediate organic or organometallic radical.[18] The choice of traps was restricted by the reactivity of many reagents with one of the starting materials; Bu$_3$SnH,[19] for example, reacts with **3**$^+$ as a hydride reductant. It does not, however, react with **1**$^-$, and we were able to mix Bu$_3$SnH with **1**$^-$ and add the mixture to **3**BF$_4$. Under these conditions Bu$_3$SnH did not interfere with

formation of **4**. Some other potential hydrogen atom sources cannot be premixed with **1**$^-$ because they are too acidic; thiophenol, for example, protonates **1**$^-$ to form [Mn(CO)$_3$(η^5-C$_6$H$_7$)], and in this case **1**$^-$ was added to a mixture of **3**BF$_4$ and PhSH: neither protonation of **1**$^-$ nor the ability of PhSH to act as a hydrogen atom source interfered with iminium addition to **1**$^-$.

The most sensitive competition experiments use intramolecular competition between a reaction sequence and a characteristic side reaction of the substrate derived radical, such as opening of a strained hydrocarbon ring,[18] and we examined such a sequence using the cyclopropyl-substituted iminium salt [CH$_2$CHPhCHCPh=NMe$_2$]BF$_4$[20−22] (**9**BF$_4$). This added to **1**$^-$ to give an *exo*-aminoalkyl product [Mn(CO)$_3$(η^5-C$_6$H$_6$CPhNMe$_2$-(CHCH$_2$CHPh)}] (**10**), obtained in 35% yield as an equal mixture of two diastereomers. The more polar of these was isolated, fully characterized, and shown by NMR to contain an intact cyclopropyl ring.

Our failure to obtain evidence for radical intermediates leads us to prefer a two-electron pathway for iminium additions to **1**$^-$ (although it is impossible to rule out an SET mechanism completely), and this is supported by the observation that **3**$^+$ and **5**$^+$ undergo similar additions to **1**$^-$ despite the fact that **5**$^+$ should be ca. 0.5 V harder to reduce than **3**$^+$.[17,23]

The absence of evidence for involvement of the "[Mn(η^6-C$_6$H$_6$)(CO)$_3$]" radical in the reaction of **1**$^-$ with **3**$^+$ emphasizes the contrast between the chemistry of **2**$^+$ and that of [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$H$_6$)]$^+$. Both are monocationic arene complexes of 3d metals, but the Mn cation undergoes two-electron reduction to **1**$^-$ (containing an electron-rich reactive benzene ligand[2−4,8]), while in the Fe system, the corresponding anion decomposes rapidly by loss of [C$_5$H$_5$]$^-$.[24] Conversely, a central feature of the Fe chemistry is reduction of the cation by one electron to the 19-electron complex [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$H$_6$)][25,26] (with chemistry dominated by its radical character), while the corresponding Mn complex is unstable with respect to disproportionation; the two systems offer access to complementary and fascinating benzene reaction manifolds.

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(21) Chosen because the Ph group on the unsaturated carbon makes **9**$^+$ as easy to reduce as possible given the need to introduce the cyclopropyl substituent, while the Ph group on the ring should accelerate ring opening of any intermediate one electron reduction product and compensate for the stabilizing effect of the Ph group on the C bound to N.

(22) The only identifiable reduction isolated after one-electron naphthalenide reduction of **9**BF$_4$ and a chromatographic workup is the ketone PhCH$_2$CH$_2$CH$_2$C(O)Ph: this is the hydrolysis product of the acid labile enamine PhCH$_2$CH$_2$CH=C(NMe$_2$)Ph, the anticipated product of cyclopropyl ring opening of the one-electron reduction product of **9**$^+$.

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