

Communications

1,3-Dipolar [3 + 2] Cycloaddition of *N*- α -Diphenyl Nitron to the Benzene Ligand in Reductively Activated $[\text{Mn}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)]^-$

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Summary: We have established that the η^4 -benzene ligand in $[\text{Mn}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)]^-$ undergoes a stepwise cycloaddition reaction with *N*- α -diphenyl nitron in a sequence in which the Lewis acid BF_3 is first used to induce nucleophilic addition of $[\text{Mn}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)]^-$ to *N*- α -diphenyl nitron. The BF_3 can be removed by protonation to give the neutral intermediate $[\text{Mn}(\text{CO})_3\{\eta^5\text{-C}_6\text{H}_6\text{CHPhN(Ph)OH}\}]$, which can be cyclized by addition of excess KH and PPNCl to drive ring closure and form $\text{PPN}[\text{Mn}(\text{CO})_3\{\eta^4\text{-C}_6\text{H}_6\{\text{CHPhN(Ph)O}\}}]$, containing an isoxazolidine ligand that is the [3 + 2] cycloaddition product of the nitron with benzene.

1,3-Dipolar [3 + 2] nitron–olefin cycloadditions are valuable reactions in organic synthesis, used to prepare five-membered heterocycles with simultaneous control of the stereochemistry of two contiguous carbon centers.^{1,2} The resulting heterocycles are valuable both in their own right and as synthetic intermediates, and con-

siderable attention has been paid to extending the scope of the reactions through the use of Lewis acids and metal complexes to catalyze or promote nitron–olefin cycloaddition reactions.³ Not surprisingly, [3 + 2] nitron–olefin cycloadditions have been limited to unconjugated alkenes and have not been reported for double bonds embedded in aromatic systems, but our previous observation that the uncoordinated double bond of the benzene ligand in $[\text{Mn}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)]^-$ (**1**[−]) reacts with diphenyl ketene ($\text{Ph}_2\text{C}=\text{C}=\text{O}$) to give a [2 + 2 + 2] cycloaddition product⁴ suggested that **1**[−] might participate in unprecedented nitron–arene cycloadditions.

Anticipation of the probable course of the reaction of **1**[−] with a nitron was facilitated by review of the course of the reaction of **1**[−] with diphenyl ketene.⁴ The [2 + 2 + 2] cycloaddition outcome had been somewhat surprising, since an antarafacial $\pi 2_s + \pi 2_a$ cycloaddition would have been symmetry allowed, but is consistent both with the expectation that the cyclobutane product of a $\pi 2_s +$

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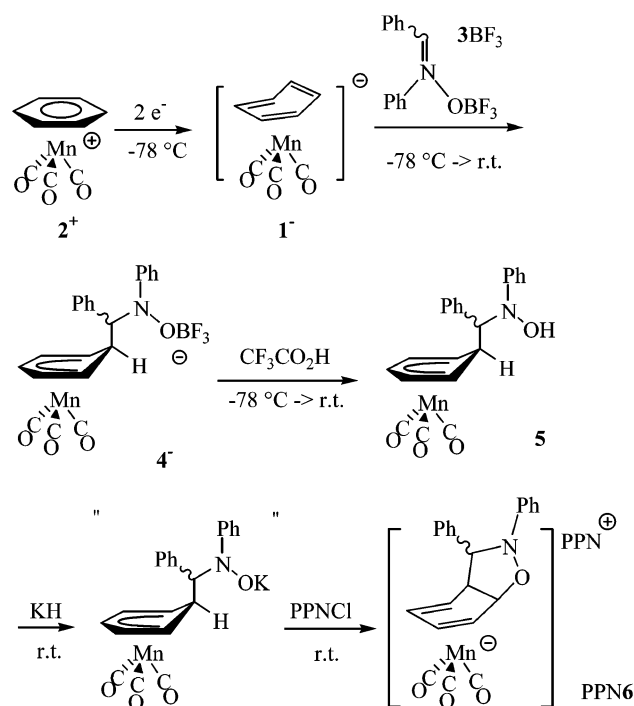
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Scheme 1



$\pi 2_a$ reaction would be more highly strained than the observed six-membered ring and with the stability anticipated for the 18-electron [Mn(CO)₃(η^5 -C₆H₆-*exo*-R⁻)] intermediate on the stepwise pathway proposed for the [2 + 2 + 2] cycloaddition. These observations led us to anticipate that [3 + 2] cycloaddition of a nitron to **1**⁻ could also be achieved by a stepwise path, and we now wish to report that this is the case.

No reaction was observed (IR) when *N*-α-diphenylnitrone ([CHPh=N(Ph)O], **3**) was added to the η^4 -arene complex **1**⁻, as prepared by two-electron reduction of [Mn(CO)₃(η^6 -C₆H₆)]PF₆ (**2**(PF₆)) at -78 °C,⁵ but reaction was observed when the nitron was activated by pretreatment with BF₃·Et₂O before addition to a solution containing **1**⁻. IR monitoring indicated formation of a product with carbonyl IR bands (ν_{CO} (THF) 2011.3 (s), 1934.5 (s), 1922.2 (s) cm⁻¹) in the range characteristic of neutral Mn(CO)₃ complexes. The course of the reaction was not dependent on when the BF₃·Et₂O was added to the mixture, and similar IR spectra were obtained when **1**⁻ and BF₃·Et₂O were mixed and **3** was then added and when **1**⁻ and **3** were mixed and BF₃·Et₂O was added to the reaction mixture. The manganese carbonyl product was obtained as spectroscopically pure material by removal of the solvent under reduced pressure, trituration into Et₂O, and addition of pentane to precipitate a salt of the compound. The organometallic portion of the product was formulated as [Mn(CO)₃{ η^5 -C₆H₆-*exo*-CHPhN(Ph)O·BF₃}]⁻ (**4**⁻; Scheme 1) on the basis of ¹H, ¹³C, and ¹⁹F NMR spectra (see the Supporting Information), but analytically clean samples of salts of this anion could not be obtained, despite repeated efforts, probably because of the presence of difficult to separate inorganic salts.

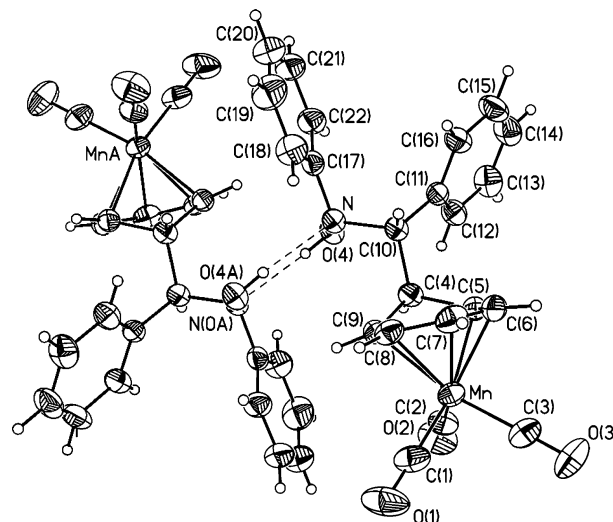


Figure 1. Molecular structure of **5** (probability ellipsoids are shown at the 50% level). Selected bond lengths (Å) and angles (deg): C4–C5 = 1.512(3), C4–C9 = 1.513(3), C4–C10 = 1.535(3), C5–C6 = 1.385(4), C6–C7 = 1.407(4), C7–C8 = 1.407(4), C8–C9 = 1.392(3), N–O4 = 1.453(2), N–C10 = 1.501(3), Mn–C7 = 2.120(3), Mn–C6 = 2.126(3), Mn–C8 = 2.132(3), Mn–C9 = 2.204(2), Mn–C5 = 2.220(2); O4–N–C10 = 106.9(2), C5–C4–C9 = 102.9(2), C5–C4–C10 = 113.2(2), C9–C4–C10 = 114.4(2), C6–C5–C4 = 119.3(2), C5–C6–C7 = 121.1(2), C8–C7–C6 = 117.3(2), C9–C8–C7 = 120.0(2), C8–C9–C4 = 119.8(2), N–C10–C4 = 109.1(2).

The connectivity of the organic ligand in **4**⁻ was confirmed by crystallographic characterization of a neutral derivative prepared by reaction of a fresh sample of **4**⁻ with 1 equiv of CF₃CO₂H. The acid was added to a sample of **4**⁻ that had been prepared in situ from **1**⁻ and **3**·BF₃ at -78 °C. The IR spectrum attributed to **4**⁻ did not change at this temperature, but when the mixture was warmed to ambient temperature, the spectrum changed to one with carbonyl bands (ν_{CO} (THF) 2013.6 (s), 1933.7 (s, br) cm⁻¹) typical of an uncharged Mn(CO)₃ complex. The product was extracted into pentane, and yellow crystals formed when the solution was concentrated and then held at 0 °C. A single-crystal diffraction study established that the product is [Mn(CO)₃{ η^5 -C₆H₆-*exo*-CHPhN(Ph)OH}] (**5**; Figure 1). The crystal structure shows that two hydrogen bonds (O–H···N) form a flat six-membered ring between two molecules. The chiral center C₁₀ differentiates the chemical shifts of H₅ and H₉ and of H₆ and H₈. The very similar IR and ¹H and ¹³C NMR spectra of **4**⁻ and **5** suggest that, as shown in Scheme 1, **4**⁻ has an η^5 -C₆H₆-*exo*-R⁻ structure like that established crystallographically for **5**. Complex **5** decomposes slowly at ambient temperatures but could be purified sufficiently for further reactions by extraction into pentane.

Deprotonation of the relatively acidic hydroxylamine group in **5** (this group resonates in ¹H NMR spectra at δ 7.84) offered a simple approach to enhancement of the reactivity of the *exo* substituent in **5**, and this was achieved by addition of excess KH to a solution of **5** in THF at ambient temperature. There is little immediate change in the IR spectrum, but a slow reaction does then occur, as indicated by the disappearance of IR bands attributable to **5** and the appearance of bands at lower frequencies characteristic of anionic complexes contain-

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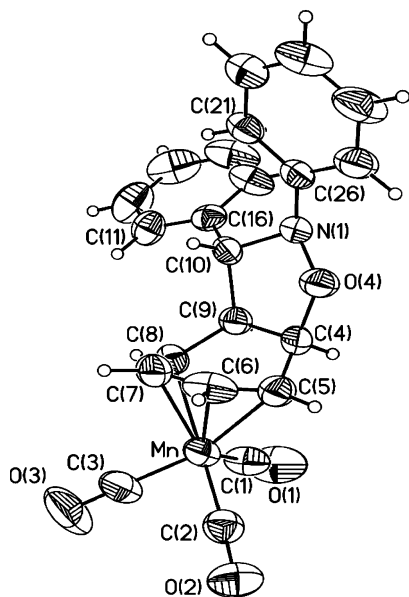


Figure 2. Molecular structure of $\mathbf{6}^-$ in PPN($\mathbf{6}$) (probability ellipsoids are shown at the 50% level). Selected bond lengths (Å) and angles (deg): N1–O4 = 1.462(4), N1–C10 = 1.488(4), C4–C5 = 1.481(6), C4–C9 = 1.527(5), C(4)–O(4) = 1.454(5), C5–C6 = 1.396(6), C6–C7 = 1.369(6), C7–C8 = 1.405(6), C8–C9 = 1.517(5), C9–C10 = 1.542(5), Mn–C7 = 2.071(4), Mn–C6 = 2.074(5), Mn–C5 = 2.125(4), Mn–C8 = 2.129(4); C4–O4–N1 = 107.5(3), O4–C4–C5 = 109.1(4), O4–C4–C9 = 105.7(3), C5–C4–C9 = 111.9(4), C6–C5–C4 = 119.3(4), C(7)–C(8)–C(9) = 118.6(4), C8–C9–C4 = 109.5(3), C8–C9–C10 = 114.4(3), C4–C9–C10 = 104.7(3).

ing the $\text{Mn}(\text{CO})_3$ group. The reaction is cleaner and faster (30 min) and the product has a better defined IR spectrum when PPNCl ($[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]\text{Cl}$) is added—this should displace the K^+ counterion and replace it with a noncoordinating PPN^+ counterion to increase the reactivity of the deprotonated hydroxylamine.⁶ The final THF solution has ν_{CO} IR bands at 1926.1 (s), 1826.2 (s, br), and 1811.9 (s, br) cm^{-1} , and after removal of the THF under vacuum an analytically pure (C, H) crystalline product was obtained from a diethyl ether solution at 0 °C over 3 days. The product was shown to be $\text{PPN}[\text{Mn}(\text{CO})_3\{\eta^4\text{-C}_6\text{H}_6\text{-exo-CHPhN(Ph)O}\}]$ (PPN($\mathbf{6}$); Figure 2) by a single-crystal diffraction study. ^1H and ^{13}C NMR spectra of the bulk material are quite distinct from those

of typical $\eta^5\text{-C}_6\text{H}_6\text{-exo-R}$ complexes and are consistent with formulation as the isoxazolidine-containing complex characterized by the single-crystal diffraction study.

Formation of the heterocycle in $\mathbf{6}^-$ is consistent with an exo ring closure in which there is nucleophilic addition of the oxide to an sp^2 carbon in the $\eta^5\text{-C}_6\text{H}_6\text{-exo-R}$ ligand (Scheme 1) with a concomitant reduction of the Mn oxidation state from +1 to –1. Exo-nucleophilic additions to cyclohexadienyl derivatives of Mn are rare,⁷ and earlier attempts to induce stepwise cyclization of complexes of $\text{Mn}(\text{CO})_3$ with unsaturated six- or seven-membered rings have been unsuccessful.⁸

We have not yet determined conditions under which the isoxazolidine ligand in $\mathbf{6}^-$ can be removed from the metal in a synthetically useful manner. Conditions that we have examined have included overnight treatment with O_2 at ambient temperatures, overnight treatment with CO at ambient temperatures, and addition of 1,3-cyclohexadiene to displace the diene ligand; unidentified cyclohexadienyl Mn complexes could be observed as major products (IR, ^1H NMR) under all these conditions, and no significant quantities of organic products could be isolated by preparative TLC. Despite this, our results do establish that the reductively activated $\eta^4\text{-benzene}$ in $\mathbf{1}^-$ can be induced to participate in an unprecedented 1,3-dipolar [3 + 2] cycloaddition reaction that ultimately results in addition of an $N\alpha$ -diphenyl nitron to the benzene ligand in $\mathbf{2}(\text{PF}_6)$. Intriguingly, the key ring-closing step in this reaction provides an analogue for the ring-closing step we have previously proposed to occur during the [2 + 2 + 2] cycloaddition of diphenyl ketene to $\mathbf{1}^-$.

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Supporting Information Available: Text giving experimental details for the synthesis and characterization of compounds and tables giving crystallographic data for $\mathbf{5}$ and PPN($\mathbf{6}$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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