Anionic Manganese Tricarbonyl Complexes of C₇ and C₈ Cyclic Dienes and Polyenes: Synthesis and Reactions with Electrophiles

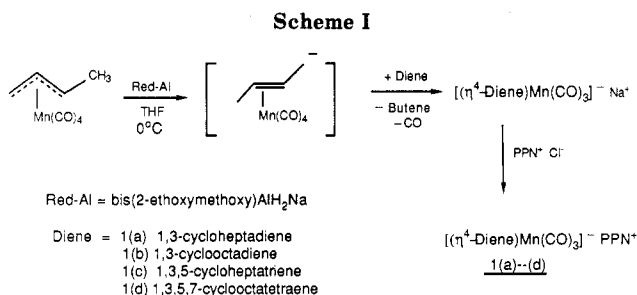Maurice Brookhart,* Seok K. Noh, Francis J. Timmers, and Yoon H. Hong

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Reduction of (methallyl)Mn(CO)$_4$ with bis(2-methoxyethoxy)AlH$_2^-$ in the presence of 1,3-cycloheptadiene, 1,3-cyclooctadiene, 1,3,5-cycloheptatriene, or 1,3,5,7-cyclooctatetraene yields (η^4-cycloheptadiene)Mn(CO)$_3^-$ (1a), (η^4-cyclooctadiene)Mn(CO)$_3^-$ (1b), (η^4-cycloheptatriene)Mn(CO)$_3^-$ (1c), and (η^4-cyclooctatetraene)-Mn(CO)$_3^-$ (1d), which were isolated as their PPN$^+$ salts. Protonation of 1a and 1b gives the agostic complexes (cycloheptenyl)Mn(CO)$_3$ (2a) and (cyclooctenyl)Mn(CO)$_3$ (2b) whose dynamic behavior and CO trapping reactions are reported. Protonation or methylation of 1c gives (cycloheptadienyl)Mn(CO)$_3$ or (6-*exo*-methylcycloheptadienyl)Mn(CO)$_3$, respectively. Protonation of 1d gives the monocyclic complex (η^5-cyclooctatrienyl)Mn(CO)$_3$ (8) which is in equilibrium at 25 °C via electrocyclic ring closure with (η^5-bicyclo[5.1.0]octadienyl)Mn(CO)$_3$ (10). Monocyclic 8 is fluxional and exhibits a degenerate 1,3-Mn shift, $\Delta G^\ddagger = 12.6$ kcal/mol. Addition of D$^+$ to 1d established exo D$^+$ (H$^+$) attack. Methylation of 1d gives (7-*exo*-methylcyclooctatrienyl)Mn(CO)$_3$ (9) for which an X-ray structural analysis is reported.

Introduction

While numerous preparative routes to (η^4-diene)iron tricarbonyl complexes are known and the chemistry of these systems has been extensively investigated,[1] isoelectronic anionic (diene)manganese tricarbonyl complexes have only recently been reported.[2] The (cyclohexadiene)Mn(CO)$_3^-$ and its derivatives can be generated by double hydride addition to benzene or substituted benzene manganese tricarbonyl cations (eq 1). The acyclic system (2-methylbutadiene)Mn(CO)$_3^-$ can be prepared by thermolysis of (1,1-dimethylallyl)Mn(CO)$_4$ and deprotonation of the resulting agostic species (eq 2). The unsub-

$$(1)$$

$$(2)$$

stituted parent system (butadiene)Mn(CO)$_3^-$ is not available via this route since thermolysis of (methallyl)-Mn(CO)$_4$ gives a very low yield of the unsubstituted agostic complex.[2d] Thus, while the routes shown in eq 1 and 2 are satisfactory for preparing cyclohexadiene and certain acyclic diene complexes, they are not applicable for making
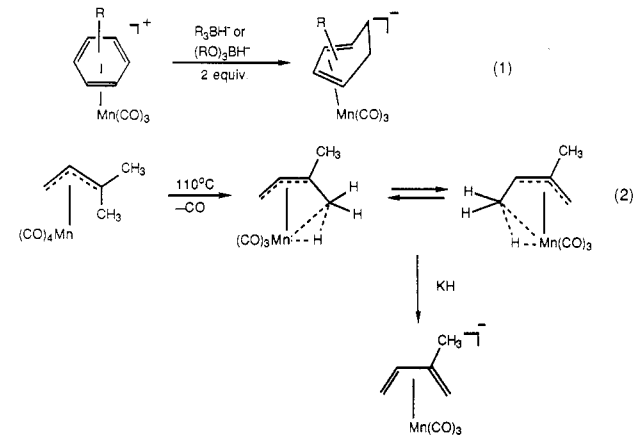
Scheme I

a wide variety of diene complexes.

We have discovered a general and moderately efficient route to (diene)Mn(CO)$_3^-$ complexes which involves hydride reduction of (η^3-allyl)Mn(CO)$_4$ complexes with bis-(2-methoxyethoxy)aluminum hydride in the presence of dienes. The reaction presumably occurs via formation of an (alkene)Mn(CO)$_4^-$ complex followed by exchange of the alkene and one CO for the diene ligand (see Scheme I, next section). We report here: (1) use of this method to prepare a series of cyclic (η^4-diene)Mn(CO)$_3^-$ complexes (η^4-diene = 1,3-cycloheptadiene, 1,3-cyclooctadiene, η^4-cycloheptatriene, and η^4-cyclooctatetraene), (2) formation of the agostic complexes (cycloheptenyl)Mn(CO)$_3$ and (cyclooctenyl)Mn(CO)$_3$ by protonation of the anionic diene complexes and a study of their dynamic behavior, (3) protonation, silylation, and methylation of (η^4-cycloheptatriene)Mn(CO)$_3^-$ and (η^4-cyclooctatetraene)Mn-(CO)$_3^-$, and (4) a study of the degenerate 1,3-manganese migration in (η^5-cyclooctatrienyl)Mn(CO)$_3$ together with its thermal isomerization via electrocyclic ring closure. Part of this work has been previously communicated.[2e]

Results and Discussion

General Synthetic Procedure and Characterization of [(η^4-Diene)Mn(CO)$_3$]$^-$ Salts. Synthesis of (diene)-manganese tricarbonyl anions is achieved by the reduction of methyallylmanganese tetracarbonyl with bis(2-methoxyethoxy)AlH$_2$Na (Red-Al) in the presence of dienes at 0 °C in THF. As shown in Scheme I the procedure is general and applicable to both cyclic dienes and polyolefins of various ring sizes with moderate to good yields. For best yields, it is important to use 1 equiv of Red-Al since excess Red-Al reacts with PPN$^+$Cl$^-$ to give a dark red compound which is very difficult to separate by the purification procedures used.

(1) (a) Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Peramon: Oxford, 1982; Vol. 4, pp 452–474. (b) Reihln, H.; Gruhl, A.; Hessling, G.; Pfrengle, O. *Liebigs Ann. Chem.* **1930**, *482*, 161. (c) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1985**, *107*, 1455. (d) Semmelhack, M. F.; Henderdon, J. *Organometallics* **1983**, *2*, 363. (e) Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, *1*, 1–46.

(2) (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (c) Brookhart, M.; Lukas, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161. (d) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365. (e) Brookhart, M.; Noh, S. K.; Timmers, F. *Organometallics* **1987**, *6*, 1829.

The reduction is conviently monitored by IR spectroscopy. The pattern and intensities of the CO bands of the sodium salts of these diene anions change little with diene (ν_{CO} of 2a–d = 1940 (s), 1840 (s), and 1785 (s) cm^{-1}). The complexity of the spectra has been attributed to ion pairing with the sodium cation.[2b] Metathesis with the noncoordinating counterion PPN$^+$ result in the simplification of this pattern (ν_{CO} of 1a–d = 1935 (s), 1838 (s), and 1815 (s) cm^{-1}). All of the diene and cyclic polyolefin anion PPN$^+$ salts, 1a–d, can be isolated as yellow crystalline solids in 30–70% yields (1a, 60%; 1b, 30%; 1c, 40%; 1d, 70%) by precipitations from methylene chloride with ether. All salts are sensitive to air and heat in the solid state but moderately stable in solution except 1b (see below).

The ^{1}H NMR spectrum of 1a indicates the presence of four olefinic protons typical of an η^4-diene moiety. Hydrogens H_1, H_4 appear as a doublet of doublet of doublets which arise from three inequivalent vicinal couplings. Hydrogens H_2, H_3 exhibit a multiplet from coupling to the adjacent vinyl protons and long-range coupling with aliphatic hydrogens typical of an η^4-diene unit. The ^{13}C chemical shifts and coupling constants support the assigned structure: 52.2 (d, J_{CH} = 156 Hz, $C_{1,4}$), 84.0 (d, J_{CH} = 159 Hz, $C_{2,3}$), 28.9 (t, J_{CH} = 123 Hz, $C_{1,7}$), 27.9 ppm (t, J_{CH} = 123 Hz, C_6).
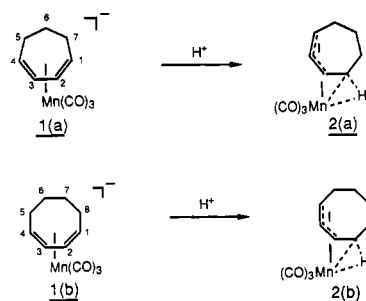
The [(1,3-cyclooctadiene)Mn(CO)₃]$^-$PPN$^+$ salt (1b) is prepared as a yellow solid in 30–40% yield. As a solid it is moderately stable at room temperature, but in solution this salt is unstable. Complete decomposition occurs after a few hours in CD₂Cl₂ at 25 °C. This intrinsic instability may be responsible for the relatively low yield since several recrystallizations are needed in the purification procedure. The ^{1}H NMR spectrum shows the presence of the typical η^4-diene fragment (2.45 (H_1, H_4), 4.75 ppm (H_2, H_3)) while the ^{13}C NMR spectrum of 1b shows four bands at 26.6, 29.7, 54.7, and 87.2 ppm identified as $C_{6,7}$, $C_{5,8}$, $C_{1,4}$, and $C_{2,3}$, respectively.

Complex 1c can be isolated as a yellow crystalline solid in moderate yield (35%) after several recrystallizations. The ^{1}H NMR spectrum of the (1,3,5-cycloheptatriene)-Mn(CO)₃ anion shows nearly the same pattern as that of the cycloheptatrieneiron tricarbonyl complex reported previously.[3] Assignments are given in the Experimental Section. The ^{13}C NMR spectrum of 1c shows seven well-resolved carbon signals at 32.0 ppm (t, J_{CH} = 126 Hz, C_7), 118.4 and 133.9 ppm for the uncoordinated vinyl carbons C_5, C_6, 49.2 and 52.2 ppm (C_1, C_4), and 83.6 and 91.6 ppm (C_2, C_3).
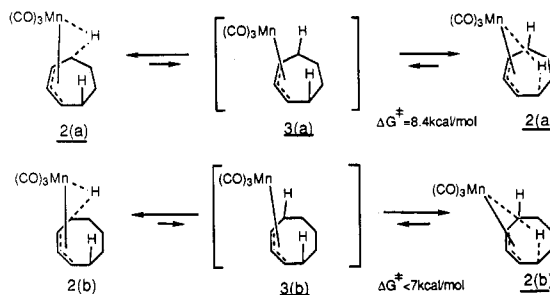
Complex 1d is obtained by using the Red-Al procedure in 70% yield. The IR spectrum of the dark red crystalline [C₈H₈Mn(CO)₃]$^-$PPN$^+$ showed ν_{CO} bands at 1950, 1865, and 1840 cm^{-1} (THF) which is about 20 cm^{-1} higher than ν_{CO} bands of other diene anions. This high shift is attributed to the presence of two electron-withdrawing vinyl groups on the ring and lack of electron-donating aliphatic groups. This effect is also observed in the iron tricarbonyl cyclooctatetraene complex.[4]

The ^{1}H NMR spectrum of 1d reveals a single sharp peak at 4.48 ppm which indicates rapid rotation of the cylooctatetraene ring at room temperature in analogy with the C₈H₈Fe(CO)₃ systems.[5] The rotation in (cyclooctatetraene)iron tricarbonyl, which is the result of 1,2-iron

(3) Brookhart, M.; Karel, K. J. *J. Organomet. Chem.* **1977**, *140*, 203.

(4) Bailey, R. T.; Lippincott, E. R.; Steele, D. *J. Am. Chem. Soc.* **1965**, *87*, 5346.

(5) (a) Kreiter, C. G.; Maasbo, A.; Anet, F. A. L.; Kaesz, H. D.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 3444. (b) Cotton, F. A.; Davison, A.; Faller, J. W. *Ibid.* **1966**, *88*, 4507. (c) Anet, F. A. L.; Kaesz, H. D.; Maasbol, A.; Winatein, S. *Ibid.* **1967**, *89*, 2489.

Scheme II

Scheme III

shifts, can be frozen out at low temperature (–150 °C), and four sets of protons can be observed.[5] The four sets of signals indicate that coordination of the cyclooctatetraene ring occurs via a 1,3-diene unit not via a 1,5-diene unit. The static ^{1}H NMR spectrum could not be observed for (cyclooctatetraene)manganese tricarbonyl anion in THF-d_8. No line broadening down to –110 °C is observed and lower temperatures result in precipitation of the salt. This observation indicates rapid ring rotation at –110 °C with a rate constant for 1,2-Mn shift greater than ca. 6 s^{-1} and $\Delta G^{\ddagger}$ < 8 kcal/mol (eq 3).
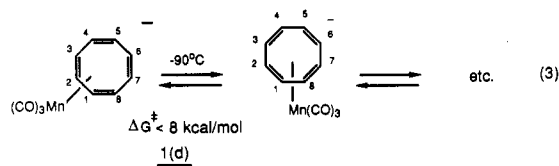
Protonation of [C₇H₁₀Mn(CO)₃]$^-$PPN$^+$ (1a) and [C₈H₁₂Mn(CO)₃]$^-$PPN$^+$ (1b): Dynamics of Agostic Species. The 7- and 8-membered-ring diene anions are both basic and nucleophilic in analogy with the 6-membered-ring diene anion complex. Protonation of the 7- and 8-membered-ring diene anions with H₂O or HBF₄ gives the agostic cycloheptenyl complex 2a and cyclooctenyl complex 2b (Scheme II).

Bridging complexes 2a and 2b show several characteristic features of agostic systems[6] including dynamic behavior, a low coupling constant between the bridging C and H, high-field chemical shifts for the bridging C and H, and acidic properties of the agostic hydrogen (see below).

Cycloheptenyl complex 2a exhibits two exchange processes observable by dynamic ^{1}H NMR spectroscopy which can be interpreted by invoking a 16-electron η^3-allyl intermediate, 3a, and a diene hydride intermediate, 4a. The more rapid exchange process occurs through the η^3-allyl intermediate which possesses a plane of symmetry through the metal, the central allyl carbon and bisects the C(6)–C(7) bond (see Scheme III). For example at 25 °C the

(6) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

Scheme IV

$\Delta G^{\ddagger} = 16.4\text{kcal/mol}$

$\Delta G^{\ddagger} > 19\text{kcal/mol}$

Scheme V
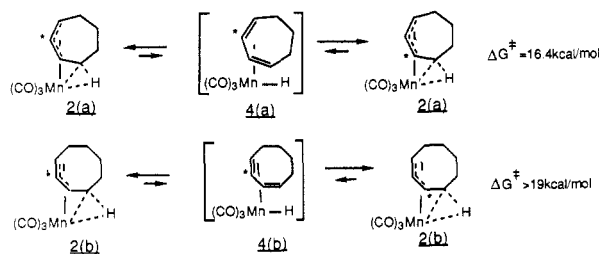
hydride signal at -5.66 ppm integrates for two protons and is assigned to the endo H_1 and H_5 hydrogens which alternately occupy the bridging position. Other resonances that average and that are consistent with this process include $H_2 = H_4$, $H_{1exo} = H_{5exo}$, $H_{6exo} = H_{7exo}$, and $H_{6endo} = H_{7endo}$.

At -100 °C the static spectrum is obtained causing the degeneracy of these pairs of protons to be lifted. The agostic hydrogen now appears at -12.4 ppm. Line-shape analysis[7] using the slow-exchange approximation gives an activation barrier for exchange of $\Delta G^{\ddagger} = 9.1$ kcal/mol. The intermediate **3a** is produced by dissociation of the C–H group from the metal.

The second, higher energy process has been studied by use of the spin inversion transfer (SIT) technique.[8] An activation barrier of $\Delta G^{\ddagger} = 16.4$ kcal/mol was determined for this exchange process. Cleavage of the agostic C–H leads to a diene hydride intermediate, **4a**. If the hydrogen migrates to the opposite (but equivalent) end of the diene, the net result is a 1,2-shift of the metal moiety on the endo side of the ring. Since the lower energy process is fast at this temperature, successive C–H bond cleavages allow the $Mn(CO)_3$ unit to traverse the entire ring in a series of 1,2-migrations. The net effect is to scramble all four endo hydrogens and, separately, the seven exo and olefinic hydrogens.

The bridging cyclooctenyl complex **2b** should also exhibit exchange processes similar to the cycloheptenyl complex. However, even at -110 °C the static spectrum of **2b** could not be obtained. Only slight line broadening is noted at low temperatures (-100 °C). From the line broadening noted one can obtain only an upper limit for $\Delta G^{\ddagger}$ of ca. 7 kcal/mol for the low-energy exchange process. For the second, higher-energy exchange process (Scheme IV), no line broadening at high temperatures (100 °C) is noted and thus a calculated lower limit for the exchange process is 19 kcal/mol. These $\Delta G^{\ddagger}$ values suggest that the two-electron, three-center interaction (Mn⋯H⋯C) in complex **2b** is weaker than those of the 6- and 7-membered ring agostic complexes. Furthermore, the energy difference between the diene hydride and the agostic species is greater than for the 6- and 7-membered rings.

On the basis of these observations, the cyclooctenyl bridging compound **2b** should trap two-electron donor ligands such as CO more efficiently due to the weaker interaction between manganese and the C–H bond compared with 6- and 7-membered ring compounds. We have previously reported[2] that under 1 atm of CO pressure an equilibrium is established between the cyclohexenyl bridging complex and the tetracarbonyl complex **5c** (Scheme V). At 1 atm of CO, complete conversion to complex **5c** is not obtained. Furthermore, purging with N_2 at 25 °C, **5c** rapidly decarbonylates to regenerate the
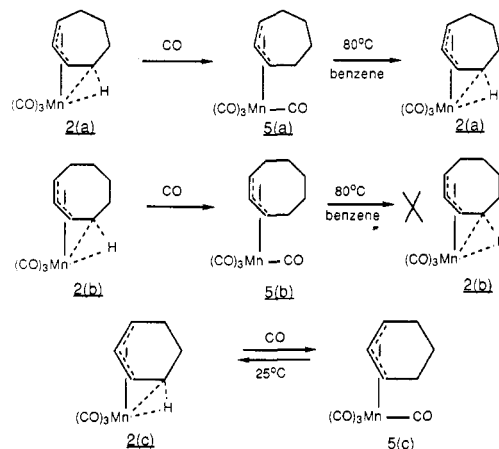
bridging complex **2c**. Treating cycloheptenyl complex **2a** with CO produces an immediate color change from orange to yellow, and the IR spectrum indicates complete conversion to tetracarbonyl complex **5a**. Heating **5a** at reflux in benzene (80 °C) for 1 h results in complete regeneration of the bridging complex **2a** via decarbonylation of **5a** (Scheme V). In the case of the cyclooctenyl bridging complex **2b**, exposure to 1 atm of CO produces the tetracarbonyl complex **5b** immediately. However, this tetracarbonyl complex does not decarbonylate to regenerate complex **2b** in refluxing benzene. Instead, general decomposition yielded an intractable material. These results support a weaker agostic interaction in complex **2b** relative to complex **2c**. The weaker interaction in **2b** is likely due to increased ring strain induced upon flattening a four-carbon unit (relative to the three-carbon allyl unit). This same effect is apparent from the much higher than normal barrier for generating the classical diene hydride intermediate (Scheme IV).

Reaction of $[C_7H_8Mn(CO)_3]^-PPN^+$ (1c) with Electrophiles. Protonation of **1c** with H_2O or HBF_4 gives quantitatively (η^5-cycloheptadienyl)manganese tricarbonyl (**6**) (eq 4). The product was characterized by its IR and

$$ (4) $$
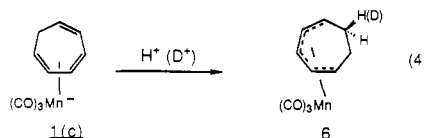
^{1}H NMR spectra which are identical with those previously reported.[9] To probe the stereochemistry of protonation, the cycloheptatriene anion **1c** was treated with D_2O. The product was determined to be 6-*6-exo-d* and establishes that protonation (deuteriation) occurs on the exo face of the ring. The exo and endo proton resonances were assigned by comparison of coupling patterns with the previously well-established assignments for the cycloheptadienyliron tricarbonyl complex.[10] The above result was confirmed by ^{2}H NMR of the product that showed only a single ^{2}H resonance with a chemical shift characterization of the exo position.

Methylation of the cycloheptatriene anion **1c** with CH_3OTf results in the carbon–carbon bond formation and production of (6-*exo*-methylcycloheptadienyl)manganese tricarbonyl (**7**). The ^{1}H NMR spectrum of **7** shows a methyl group as a sharp doublet ($J = 6.8$ Hz) at 0.45 ppm.

(7) Jackman, L. M.; Cotton, F. A. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1975.

(8) Dahquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406.

(9) King, R. B.; Ackermann, M. N. *Inorg. Chem.* **1974**, *13*, 637.

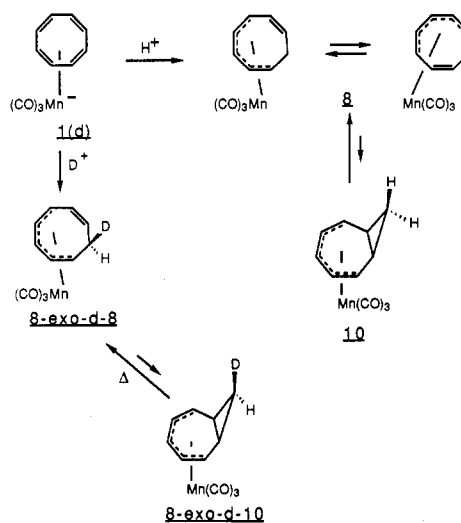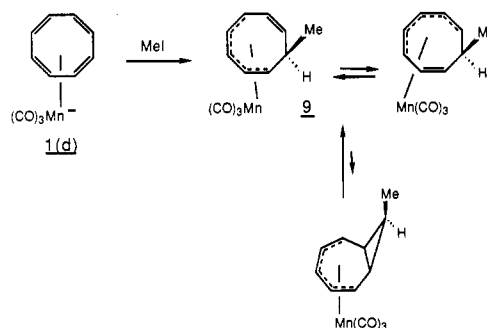(10) Haque, F.; Parson, P. L.; Tripathi, J. B. Pd. *J. Chem. Soc. C* **1971**, 743.

Scheme VI
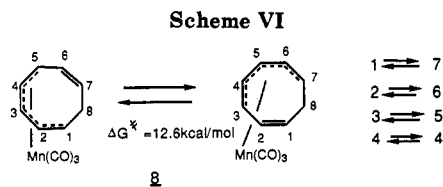
This same complex has been prepared by Haque et al.[10] from the reaction of the $[(\eta^6\text{-}C_7H_8)Mn(CO)_3]^+$ cation with methyllithium. Exo stereochemistry was established for the CH_3Li addition as well as for a variety of other nucleophiles (eq 5).
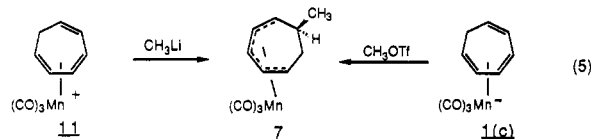
Silylation of the complex **1c** with $(CH_3)_3SiOTf$ results in formation of the (6-*exo*-(trimethylsilyl)cycloheptadienyl)manganese tricarbonyl complex. Decoupling experiments establish the exo stereochemistry.

Treating the $[(\eta^4\text{-}C_8H_8)Mn(CO)_3]^-PPN^+$ (**1d**) with acids results in formation of the cyclooctatrienylmanganese tricarbonyl complex **8**. The ^1H NMR spectrum at 25 °C shows one sharp triplet at 4.3 ppm and two very broad resonances (5.05 and 4.1 ppm) which suggests a fluxional process as shown in Scheme VI. This fluxional behavior was studied by variable-temperature NMR spectroscopy.[11] At -71 °C the static spectrum can be observed. Uncoordinated vinyl protons are seen at 5.11 ppm for H_7 and at 5.65 ppm for H_6. All five coordinated olefinic protons are well separated with well-resolved coupling at this temperature. Assignment of the endo and exo protons of C_8 can be determined from the value of the vicinal coupling constants and use of the monodeuterium-labeled compound at C_8 (vide infra). Upon warming, signal broadening and coalescence occur. The most striking feature during warming is the very sharp triplet pattern for H_4, which, since it is not exchanging with other protons, remains a sharp triplet at all temperatures (Scheme VI). A free energy of activation of 12.6 kcal/mol for this process is determined from line-shape analysis using the slow-exchange approximation.

The monocyclic complex **8** isomerizes at 45 °C to give the bicyclic complex **10** and an equilibrium is established between the two (8:10 = 6:1). King[9] reported synthesis of the monocyclic complex **8** but apparently did not observe this isomerization. The bicyclic complex **10** has been characterized by ^1H and ^{13}C NMR spectroscopy although it could not be separated from **8** due to interconversion at 25 °C. The ^1H resonances at 0.20 and 0.75 ppm were assigned to the cyclopropyl protons 8-endo-H and 8-exo-H, respectively, based on decoupling experiments which establish the following coupling constants: $J_{8x,8n} = 4.2$ Hz, $J_{8x,1} = J_{8x,7} = 4.3$ Hz, and $J_{8n,1} = J_{8n,7} = 8.3$ Hz. Reaction of the anionic cyclooctatetraene complex **1d** with D_2SO_4 gives a monodeuteriated complex 8-*8-exo-d* as a yellow crystalline solid as shown in Scheme VII. The stereochemistry of D^+ addition is established by heating 8-*8-d* to establish the 8 ⇌ 10 equilibrium and analyzing the ^1H NMR spectrum of the monodeuteriated **10** (Scheme VII). This spectrum shows the absence of the 0.75 ppm signal while the 0.2 ppm signal appears as a simple triplet ($J = $

(11) King[9] reported synthesis of **8** in low yield (10%) from the reaction between $[HMn(CO)_4]_3$ and cyclooctatetraene. Fluxional behavior of **8** was not reported.

Scheme VII

Scheme VIII

8.3 Hz), thus demonstrating exo incorporation of D^+.

Treatment of the cyclooctatetraene anion complex **1d** with CH_3I gives the 8-*exo*-methyl-substituted complex 9-*8-exo-CH₃* (Scheme VIII). The ^1H NMR spectrum at 25 °C shows three sharp resonances and four broad signals which indicates fluxional behavior. The sharp bands correspond to the nonexchanging protons H_4 and H_8 and the methyl protons. At -48 °C the static spectrum is obtained in which all eight ring protons are separated with well-resolved coupling. Uncoordinated vinyl protons appear at 4.89 ppm for H_7 and at 5.50 ppm for H_6 while the five complexed pentadienyl protons show a typical coupling pattern and appear between 2.4 and 4.8 ppm. At low temperatures, the ^{13}C NMR spectrum shows 12 carbon shifts due to inequivalency of all 12 carbons in the static molecule. Upon warming, exchanging pairs of protons broaden and finally merge. An activation barrier for this exchange carbons is determined from line-shape analysis using the slow-exchange approximation: $\Delta G^\ddagger = 16.1$ kcal/mol. This barrier is somewhat higher relative to the barrier for the unsubstituted complex **8** (12.6 kcal/mol). Upon heating **9** to temperatures as high as 75 °C, no bicyclic complex can be observed. It is likely that this observation implies a monocyclic/bicyclic equilibrium ratio of >~20, although a high kinetic barrier to the formation of the bicyclic complex cannot be ruled out. Higher temperatures or extensive heating at 75 °C results in decomposition.

Complex **9** is crystalline, and an X-ray structure was obtained. As shown by the ORTEP diagram (Figure 1) the methyl group occupies the 8-exo-position of the ring and establishes exo-methylation of the ring.

Silylation was carried out by treatment of **1d** with $(CH_3)_3SiOTf$ at -78 °C. The ^1H NMR spectrum of the
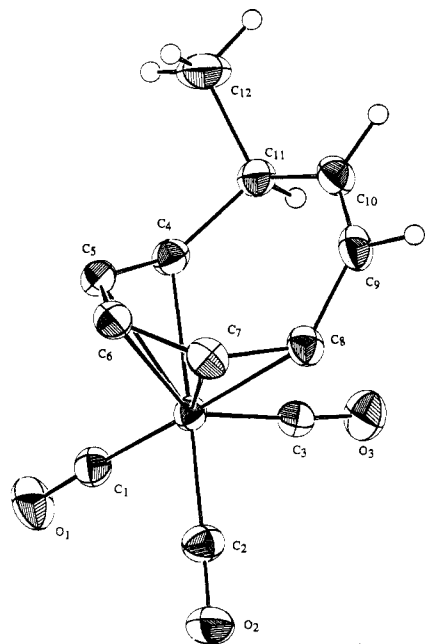
Figure 1. Molecular structure of (7-*exo*-methylcyclooctatrienyl)Mn(CO)$_3$ (9).

product shows three sharp bands due to H$_4$, H$_6$, and the (CH$_3$)$_3$Si group and four broad signals which indicate fluxional behavior. The sharp triplet at 1.94 ppm for H$_8$ exhibits $J_{8,7}$ = $J_{8,1}$ = 6 Hz. Thermal isomerization to the bicyclic complex does not occur. In analogy with protonation and methylation it is assumed that silylation also occurs by exo attack. The J = 6 Hz coupling of H$_8$ with H$_1$ and H$_7$ supports this supposition.

It is instructive to compare the reactivity of the manganese complexes with their corresponding iron analogues. The stereochemistry of proton addition to (cycloheptatriene)- and (cyclooctatetraene)iron tricarbonyl complexes is exo and occurs at the β-carbon of the uncomplexed double bond rather than at the iron center which would lead to endo protonation.[12] While the iron diene complexes are neutral, the manganese analouges are anionic and are expected to have more nucleophilic character at the metal center relative to the iron complexes. This factor could direct electrophilic attack to occur at the manganese atom (or the manganese–carbon bond) which would lead ultimately to endo substitution. However, the above results establish that protonation of the cycloheptatriene and cyclooctatetraene manganese complexes occurs exo and presumably at the β-carbon of the uncomplexed carbon–carbon double bond exactly analogous to the iron chemistry.

The anionic character of the manganese systems renders them much more nucleophilic than the analogous neutral iron systems. This is best illustrated by the fact that while C$_7$H$_9$Fe(CO)$_3$ and C$_8$H$_8$Fe(CO)$_3$ are unreactive to methylating reagents,[13] the manganese analogues 1c and 1d react rapidly to yield methyl-substituted dienyl complexes. As with protonation, methylation occurs exo and presumably at an uncoordinated double bond. There is little precedent for exo alkylation of polyolefin complexes. A previous report by Cooper involves the addition of benzyl bromide to (η^4-C$_6$H$_6$)Cr(CO)$_3$-2 and is apparently best rationalized by attack at an uncoordinated double bond.[14]

(12) (a) Davison, A.; McFarlane, W.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4821. (b) McFarlane, W.; Pratt, L.; Wilkinson, G. *Ibid.* **1963**, 2162.
(13) Graf, R. G.; Lillya, C. P. *J. Am. Chem. Soc.* **1972**, *94*, 8282.
(14) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644.

Table I. Crystallographic Data Collection Parameters for 9

Crystal Data	
mol formula	MnC$_{12}$H$_{11}$O$_3$
fw, g/mol	258.16
cryst system	orthorhombic
space group	*Pccn*
cell parameters	
a, Å	10.573 (6)
b, Å	26.637 (18)
c, Å	8.032 (6)
α, deg	90.0
β, deg	90.0
γ, deg	90.0
V, Å^3	2262.1
d(calcd), g/cm^3	1.516
Z	8

Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo K$_\alpha$ (0.710 73)
monochromator	Zr filter
linear abs coeff, cm^{-1}	12.101
scan type	$\omega/1.33\theta$
bkgd	25% of full scan width on both sides
θ limits	$2 < \theta < 28$
quadrant collected	+h,+k,+l
total no. of reflctns	3129
data with $I \geq 3\sigma(I)$	1849
no. of variables	145
R	5.0%
R_w	6.6%
goodness of fit	3.66
largest parameter shift	0.01

Table II. Final Positional Parameters and Their Standard Deviations for All Non-Hydrogen Atoms

atom	x	y	z
Mn	0.01867 (5)	0.09590 (2)	−0.04752 (7)
O1	0.2445 (3)	0.0311 (1)	−0.0383 (5)
O2	−0.0400 (3)	0.0507 (1)	0.2798 (4)
O3	0.1343 (3)	0.1898 (1)	0.0685 (4)
C1	0.1566 (4)	0.0562 (2)	−0.0450 (5)
C2	−0.0194 (4)	0.0681 (2)	0.1539 (5)
C3	0.0921 (4)	0.1522 (2)	0.0287 (5)
C4	0.0670 (4)	0.1277 (2)	−0.2922 (5)
C5	0.0032 (4)	0.0820 (2)	−0.3074 (5)
C6	−0.1109 (4)	0.0654 (2)	−0.2295 (5)
C7	−0.1762 (4)	0.0923 (2)	−0.1045 (6)
C8	−0.1552 (4)	0.1426 (2)	−0.0565 (6)
C9	−0.1618 (4)	0.1866 (2)	−0.1642 (6)
C10	−0.0907 (4)	0.2022 (2)	−0.2874 (6)
C11	0.0299 (4)	0.1800 (2)	−0.3464 (5)
C12	0.0332 (5)	0.1799 (3)	−0.5387 (6)

The formation and chemistry of the cyclooctatrienyl complex 8 has a clear analogy in the iron system (eq 6).[12,15]

$$(6)$$
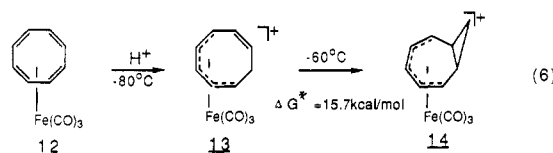
As noted, protonation of 12 occurs exo and at an uncom-

(15) Brookhart, M.; Davis, E. R.; Harris, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 7853.
(16) The isolated products from methylation and silylation of 1c are always contaminated with the unsubstituted complex 6. This result could be explained either from an electron transfer side reaction or from reaction of small amounts of water present.
(17) Programs used during solution and refinement were from the Enraf-Nonius structure determination package.
(18) $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and ρ = 0.01 is a correction factor.
(19) The function minimized was $\sum w(|F_o| - |F_c|)^2$.
(20) R(unweighted) = $\sum(|F_o| - |F_c|)/\sum|F_o|$ and R(weighted) = $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table III. Intramolecular Bond Distances (Å) for 9

Mn–C(1)	1.802 (2)	O(3)–C(3)	1.143 (2)
Mn–C(2)	1.824 (2)	C(4)–C(5)	1.398 (3)
Mn–C(3)	1.795 (2)	C(4)–C(11)	1.511 (3)
Mn–C(4)	2.201 (2)	C(5)–C(6)	1.429 (3)
Mn–C(5)	2.127 (2)	C(6)–C(7)	1.415 (3)
Mn–C(6)	2.160 (2)	C(7)–C(8)	1.410 (3)
Mn–C(7)	2.112 (2)	C(8)–C(9)	1.460 (3)
Mn–C(8)	2.221 (2)	C(9)–C(10)	1.311 (3)
O(1)–C(1)	1.146 (2)	C(10)–C(11)	1.483 (3)
O(2)–C(2)	1.134 (2)	C(11)–C(12)	1.545 (3)

Table IV. Intramolecular Bond Angles (deg)

C(1)–Mn–C(2)	86.1 (1)	C(4)–Mn–C(6)	71.8 (0)
C(1)–Mn–C(3)	97.8 (1)	C(4)–Mn–C(7)	92.9 (0)
C(1)–Mn–C(4)	92.7 (0)	C(4)–Mn–C(8)	87.0 (0)
C(1)–Mn–C(5)	88.3 (0)	C(5)–Mn–C(6)	38.0 (0)
C(1)–Mn–C(6)	107.5 (1)	C(5)–Mn–C(7)	72.9 (0)
C(1)–Mn–C(7)	140.0 (1)	C(5)–Mn–C(8)	90.1 (0)
C(1)–Mn–C(8)	177.8 (0)	C(6)–Mn–C(7)	38.6 (0)
C(2)–Mn–C(3)	97.6 (1)	C(6)–Mn–C(8)	70.4 (0)
C(2)–Mn–C(4)	178.6 (1)	C(7)–Mn–C(8)	37.9 (0)
C(2)–Mn–C(5)	141.6 (1)	C(5)–C(4)–C(11)	130.7 (2)
C(2)–Mn–C(6)	107.9 (1)	C(4)–C(5)–C(6)	129.6 (2)
C(2)–Mn–C(7)	87.6 (0)	C(5)–C(6)–C(7)	124.6 (2)
C(2)–Mn–C(8)	94.2 (0)	C(6)–C(7)–C(8)	126.7 (2)
C(3)–Mn–C(4)	83.2 (0)	C(7)–C(8)–C(9)	126.4 (2)
C(3)–Mn–C(5)	120.9 (1)	C(8)–C(9)–C(10)	132.4 (2)
C(3)–Mn–C(6)	144.9 (1)	C(9)–C(10)–C(11)	127.5 (2)
C(3)–Mn–C(7)	122.2 (1)	C(4)–C(11)–C(10)	119.9 (2)
C(3)–Mn–C(8)	84.3 (0)	C(4)–C(11)–C(12)	106.3 (2)
C(4)–Mn–C(5)	37.7 (0)	C(10)–C(11)–C(12)	109.9 (2)

plexed double bond to give **13**. Ring closure of **13** occurs at −60 °C ($\Delta G^{\ddagger}$ = 15.7 kcal/mol) to yield **14** quantitatively.[15] This contrasts with the manganese system in which the monocyclic isomer **8** is favored at equilibrium and ring closure occurs at 45 °C. Fluxional behavior of **13** was not detected at −60 °C. However, at this temperature only a process with $\Delta G^{\ddagger}$ < 10 kcal/mol would be detected, and thus no definitive comparison of **13** and **8** can be made.

Molecular Structure of (η^5-8-Methylcyclooctatrienyl)Mn(CO)₃ (9). The solid state structure of **9** is depicted in Figure 1 where the atomic numbering scheme is defined. The complex is crystallized from isopentane at −10 °C, and the crystal parameters and collection data are summarized in Table I. Final positional parameters for non-hydrogen atoms are listed in Table II, while bond distances and bond angles appear in Tables III and IV.

The molecular structure of **9** is quite similar to the structure of the (η^5-cyclohexadienyl)Mn(CO)₃ complex reported by Churchill.[21] The geometry around the d⁶ manganese(I) atom is approximately octahedral with the three facial carbonyl groups exhibiting ca. 90° CO–Mn–CO bond angles. All manganese–carbon distances and carbon–carbon distances in the dienyl fragment are similar to those observed previously for (cyclohexadienyl)manganese systems.[21,22] As expected the dienyl unit in the C₈ ring is more open than that in the 6-membered ring. For example, the C(5)–C(6)–C(7) angle in **9** is 124.6 (2)° whereas the analogous angle in (C₆H₇)Mn(CO)₃ is 118.6°. The C(9)–C(10) distance of 1.311 (3) Å is the expected value for an uncomplexed carbon–carbon double bond. The major reason for determining the structure of **9** was to establish the stereochemistry of the methylation reaction which is clearly exo as seen in Figure 1.

(21) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950.

(22) Walker, P. J. C.; Mawby, R. J. *J. Organomet. Chem.* **1973**, *55*, C39.

Summary

A general procedure for the preparation of [(η^4-diene)-Mn(CO)₃]⁻ complexes is reported and used to prepare stable PPN⁺ salts of (η^4-1,3-cycloheptadiene)Mn(CO)₃⁻ (**1a**), (η^4-1,3-cyclooctadiene)Mn(CO)₃⁻ (**1b**), (η^4-cycloheptatriene)Mn(CO)₃⁻ (**1c**), and (η^4-cyclooctatetraene)-Mn(CO)₃⁻ (**1d**).

These complexes are much more basic and nucleophilic than their neutral iron analogues. The cycloheptadiene and cyclooctadiene complexes undergo facile protonation to give agostic (cycloheptenyl)- and (cyclooctenyl)Mn(CO)₃ species **2a** and **2b** whose complex fluxional behavior and CO trapping reactions were studied. The cycloheptatriene and cyclooctatetraene complexes **1c** and **1d** undergo exo protonation to give (η^5-cycloheptadienyl)Mn(CO)₃ and (η^5-cyclooctatrienyl)Mn(CO)₃ complexes **6** and **8**, respectively. Monocyclic **8** equilibrates via electrocyclic ring closure with its bicyclic isomer, η^5-bicyclo[5.1.0]octadienyl)Mn(CO)₃. Both **1c** and **1d** undergo exo-methylation to yield (*exo*-6-methylcycloheptadienyl)Mn(CO)₃ and (*exo*-8-methylcyclooctatrienyl)Mn(CO)₃ which emphasizes the marked difference in reactivity toward electrophiles of these anionic complexes compared to the analogous iron complexes. Such reactivity differences and the ability to directly functionalize the complexed diene or polyolefin via reactions with electrophiles and to demetalate[2] such complexes make these manganese complexes potentially useful synthetic complements to the (diene)iron tricarbonyl systems.

Experimental Section

General Data. All reactions were carried out under a dry, oxygen-free atmosphere by using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through columns of BASF catalyst R3-11 and molecular sieves (4A). Tetrahydrofuran, diethyl ether, hexanes, benzene, and toluene were distilled from sodium/benzophenone ketyl prior to use. Methylene dichloride was distilled from phosphorus pentoxide prior to use. Isopentane and water were saturated with nitrogen gas by bubbling N₂ through the solvents for at least 20 min prior to use. White filtering aid (Celite) was stored in a 130 °C oven. Alumina used was Fisher activity III–IV, 80–200 mesh, and neutral.

Red-Al (bis(2-methoxyethoxy)aluminum hydride) was purchased as a 3.4 M solution in toluene (Aldrich) and used as purchased. 1,3-Cycloheptadiene, 1,3-cyclooctadiene, 1,3,5-cycloheptatriene, and 1,3,5,7-cyclooctatetraene were used as purchased. PPN⁺Cl⁻ was stored in a drying oven at 130 °C and weighed in air immediately prior to use. Gaseous carbon monoxide (Matheson) was used from the cylinder with no further purification. All other reagents were used as purchased unless otherwise noted.

¹H NMR spectra were recorded at 400 MHz on a Varian XL-400 FT NMR spectrometer, at 250 MHz on a Bruker WM-250 FT NMR spectrometer, and at 200 MHz on a IBM AC-200 FT NMR spectrometer. ¹³C NMR spectra were recorded at 100.59 MHz with the Varian XL-400, at 62.9 MHz with the Bruker WM-250, and at 50.3 MHz with the IBM AC-200 instruments. NMR samples were sealed under vaccuum (0.001 mmHg) in liquid N₂ to prevent decomposition. Tetrahydrofuran-d_8, toluene-d_8, benzene-d_6, and methylene-d_2 chloride were used after degassing by several freeze-pump-thaw cycles.

Infrared spectra were recorded on a Beckman spectrophotometer (IR 4250), and frequencies were assigned relative to a polystyrene standard. Solution spectra were obtained under anaerobic conditions using matched 0.10-mm calcium fluoride cells.

Elemental analyses were performed by Galbraith Laboratories, Inc.

Collection of Diffraction Data. Pale yellow crystals suitable for X-ray measurements were prepared in isopentane solution at −10 °C. Diffraction data were collected on an Enraf-Nonius

CAD-4 automatic diffractometer.[17] Twenty-five centered reflections found in the region $10.0° < \theta < 13.0°$ and refined by least-squares calculations revealed a primative orthorhombic system. The cell parameters are listed in Table I.

Data were collected on the crystal in the quadrant $(+h,+k,+l)$ under the conditions listed in Table I. Three reflections chosen as intensity standards were monitored every 3 h and showed no significant (<1.5%) decay. The crystal was checked every 300 reflections for recentering if necessary. Psi scans of nine reflections having $72° < \chi < 90°$ were used to calculate an empirical absorption correction. Only data with $I > 3\sigma(I)$[18] were used in structure solution and refinement. The data were reduced and corrected for Lorentz–polarization effects.

Solution and Refinement of the Structure. The heavy-atom method was used in solving the structure. The space group was assigned as $Pccn$ (No. 56) on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solutions of the Patterson map. The position of the manganese atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. Least-squares refinement[19] of the non-hydrogen atoms was done anisotropically by using 1849 reflections with $I > 3\sigma(I)$ and produced unweighted and weighted residuals of 6.3% and 8.6%,[20] respectively. Hydrogen positions were calculated by using a C–H distance of 0.95 Å and fixed. The final refinement resulted in residuals of $R = 5.0\%$ and $R_w = 6.6\%$.

$[(\eta^4\text{-}C_7H_{10})Mn(CO)_3]^-PPN^+$ (1a). $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ (2 g, 90 mmol) was dissolved in 100 mL THF. Excess 1,3-cycloheptadiene (2 equiv) was added to the solution at 0 °C followed by Red-Al (1 equiv). Within 5 min a color change is observed; an IR spectrum after 10 min shows only $[(\eta^4\text{-}C_7H_{10})Mn(CO)_3]^-Na^+$ (ν_{CO} = 1940 (s), 1840 (s), 1815 (s), and 1785 (s) cm^{-1}). To this anion solution was added $[((C_6H_5)_3P)_2N]^+Cl^-$ (5.1 g). After 10 min the solution was filtered through Celite and the red filtrate concentrated to a red oil in vacuo (0.01 mmHg). Trituration with diethyl ether (200 mL) followed by decantation three times gave a powder. The solid powder was recrystallized by dissolving in minimal CH$_2$Cl$_2$ (10 mL) followed by dropwise addition of diethyl ether (100 mL). The yellow crystals were collected on a glass frit and washed with 2 × 50 mL of diethyl ether. Recrystallization twice more from CH$_2$Cl$_2$/Et$_2$O using the same procedure resulted in 4.5 g (60% yield) of 1a. IR: (THF) ν_{CO} 1935, 1838, 1815 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.0–1.3 (m, H$_{6n,6x}$), 1.5–1.9 (m, H$_{5x,5n,7x,7n}$), 2.19 (ddd, H$_{1,4}$), 4.69 (m, H$_{2,3}$), 7.5–7.7 (m, PPN$^+$). ^{13}C NMR (CD$_2$Cl$_2$): δ 27.9 (t, J_{CH} = 123 Hz, C$_6$), 28.9 (t, J_{CH} = 122.6 Hz, C$_{5,7}$), 52.2 (d, J_{CH} = 156 Hz, C$_{1,4}$), 84.0 (d, J_{CH} = 159.4 Hz, C$_{2,3}$), 130–140 (PPN$^+$), 232.7 (s, 3CO's). This complex slowly decomposes (hours) at 25 °C and does not give satisfactory elemental analyses. After 1 day at 25 °C carbon deviations of 0.7–1.0% are found. Samples can be stored many days at –30 °C with little decomposition. ^{1}H NMR spectra of freshly prepared samples indicate high purity (>98%). This behavior is typical of salts 1b and 1c.

$[(\eta^4\text{-}C_8H_{12})Mn(CO)_3]^-PPN^+$ (1b). To a solution of $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ (2 g, 90 mmol) in THF (100 mL) at 0 °C was added 1,3-cyclooctadiene (2 equiv) followed by Red-Al (1 equiv). After reaction for 10 min at 0 °C, PPN$^+$Cl$^-$ (5.1 g) was added. After being stirred for 10 min, the solution was filtered through Celite and solvent evaporated to give a red oil. Addition of diethyl ether (200 mL) gave a sticky solid together with a dark red solution which was removed by decantation. Three recrystallizations of the sticky solid from CH$_2$Cl$_2$/Et$_2$O resulted in 2.8 g of yellow crystals (35% yield) of 1b. IR (THF): ν_{CO} 1935, 1838, 1815 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.0–1.4 (m, H$_{6x,6n,7x,7n}$), 1.8–2.1 (m, H$_{5x,5n,8x,8n}$), 2.45 (m, H$_{1,4}$), 4.75 (m, H$_{2,3}$), 7.5–7.7 (m, PPN$^+$). ^{13}C NMR (CD$_2$Cl$_2$): δ 26.6 (t, C$_{6,7}$), 29.7 (t, C$_{5,8}$), 54.7 (d, C$_{1,4}$), 87.2 (d, C$_{2,3}$), 130–140 (PPN$^+$). This complex is unstable at 25 °C and gave poor analyses (see above).

$[(\eta^4\text{-}C_7H_8)Mn(CO)_3]^-PPN^+$ (1c). To a solution of $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ (2 g, 90 mmol) in THF (100 mL) at 0 °C was added 1,3,5-cycloheptatriene (2 equiv) followed by Red-Al (1 equiv). After the solution was stirred for 10 min at 0 °C, PPN$^+$Cl$^-$ (5.1 g) was added. After 10 min of stirring the solution was filtered through celite and the red filtrate concentrated to a red oil in vacuo (0.001 mmHg). Addition of diethyl ether (200 mL) to this red oil gave a sticky red material together with a dark red solution.

The dark solution was removed by decantation. Three recrystallizations of the red solid from CH$_2$Cl$_2$/Et$_2$O gave a yellow solid, 2.5 g (30% of yield) of 1c. IR (THF): ν_{CO} 1935, 1840, 1820 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$) δ 2.2 (m, H$_{7x,7n}$, H$_4$) 2.53 (m, H$_1$), 4.5–4.9 (m, H$_{2,3,6}$), 5.9 (m, H$_5$), 7.5–7.7 (m, PPN$^+$). ^{13}C NMR (CD$_2$Cl$_2$): δ 32.0 (t, $^1J_{CH}$ = 126.5 Hz, C$_7$), 49.2 (d, $^1J_{CH}$ = 146.9 Hz, C$_1$), 83.6 (d, $^1J_{CH}$ = 160.6 Hz, C$_2$), 91.0 (d, $^1J_{CH}$ = 160.3 Hz, C$_3$), 118.4 (d, $^1J_{CH}$ = 152 Hz, C$_2$), 133.9 (d, C$_5$) 130–140 (PPN$^+$), 231.2 (s, 3 CO's). This complex is very unstable at 25 °C in the solid state and gave poor analyses (see above).

$[(\eta^4\text{-}C_8H_8)Mn(CO)_3]^-PPN^+$ (1d). $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ (2 g, 90 mmol) was dissolved in 100 mL of THF. 1,3,5,7-Cyclooctatetraene (2 equiv) was added to the solution at 0 °C followed by Red-Al (1 equiv). An IR spectrum after 10 min showed anion formation. To this anion solution was added PPN$^+$Cl$^-$ (5.1 g). After 10 min the solution was filtered through Celite and the red filtrate concentrated to a red oil in vacuo (0.001 mmHg). Addition of diethyl ether (200 mL) gave a dark red precipitate. After decantation, recrystallization three times gave dark red crystals, 4.5 g (60% yield) of 1d. IR (THF): ν_{CO} 1950, 1865, 1840 cm^{-1}. ^{1}H NMR (THF-d_8) δ 4.84 (s, H$_{1-8}$), 7.5–7.7 (m, PPN$^+$). ^{13}C NMR (THF-d_8): δ 94.1 (d, $^1J_{CH}$ = 149.5 Hz, C$_{1-8}$), 130–140 (PPN$^+$), 232.1 (3 CO's). Anal. Calcd for C$_{47}$H$_{38}$O$_3$NP$_2$Mn: C, 72.21; H, 4.90. Found: C, 72.09; H, 5.17. This salt is stable at 25 °C.

$(C_7H_{11})Mn(CO)_3$ (2a). $[(\eta^4\text{-}C_7H_{10})Mn(CO)_3]^-PPN^+$ (1 g) was dissolved in 10 mL of CH$_2$Cl$_2$ and cooled to –78 °C. HBF$_4$·Me$_2$O (1.2 equiv) was added dropwise to the anion solution which produced an immediate color change from yellow to orange. The solution was warmed to 20 °C, filtered through alumina and Celite, and concentrated in vacuo (0.001 mmHg) to a volume of 3–5 mL. Dropwise addition of isopentane (100 mL) caused a white solid (PPN$^+$BF$_4^-$) to precipitate from solution. The solution was filtered through Celite and concentrated in vacuo (0.001 mmHg) to give 0.2 g (70% yield) of 2a as an orange oil. IR (hexanes): ν_{CO} 2015, 1942, 1932 cm^{-1}. ^{1}H NMR (benzene-d_6): δ –5.66 (br m, H$_{1,5endo}$), 0.45 (m, H$_{6,7endo}$), 0.70 (m, H$_{6,7exo}$), 1.03 (m, H$_{1,5exo}$), 4.03 (q, J = 6 Hz, H$_{2,4}$), 4.5 (t, J = 6Hz, H$_3$). ^{13}C NMR (benzene-d_6): δ 18.9 (dt, J_{CH} = 108, 131 Hz, C$_{1,5}$), 23.7 (t, J_{CH} = 128 Hz, C$_{6,7}$), 69.6 (d, J_{CH} = 164 Hz, C$_{2,4}$), 96.2 (d, J_{CH} = 160 Hz, C$_3$), 222.2 (s, 3 CO's). Anal. Calcd for C$_{10}$H$_{11}$O$_3$Mn: C, 51.30; H, 4.74; Mn, 23.46. Found: C, 51.33; H, 4.83; Mn, 23.27.

$(C_8H_{13})Mn(CO)_3$ (2b). This complex was prepared in an analogous fashion to (cycloheptenyl)Mn(CO)$_3$ (2a) above with the following exceptions: 1.2 g of $[(\eta^4\text{-}C_8H_{12})Mn(CO)_3]^-PPN^+$ (1b) was used in place of 1a. Concentration of the isopentane extracts in vacuo gave 0.15 g (50% yield) of an orange oil of 2b. IR (hexanes): ν_{CO} 2015, 1940, 1930 cm^{-1}. ^{1}H NMR (toluene-d_8): δ –5.15 (m, H$_{1n,5n}$), 0.6–1.4 (m, H$_{1x,5x,6x,6n,7x,7n,8x,8n}$), 4.09 (dt, $^1J_{HH}$ = 8.0 Hz, H$_{2,4}$) 4.55 (dd, J_{HH} = 7.5 Hz, H$_3$). ^{13}C NMR (toluene-d_8): δ 21.7 (t, J_{CH} = 125 Hz, C$_7$), 22.9 (dd, J = 134, 113 Hz, C$_{1,5}$), 28.1 (t, $^1J_{CH}$ = 135 Hz, C$_{6,8}$), 69.0 (d, $^1J_{CH}$ = 156 Hz, C$_{6,8}$), 100.3 (d, $^1J_{CH}$ = 158 Hz, C$_3$), 223.6 (s, 3 CO's). This compound was thermally unstable and did not give satisfactory analyses.

$(\eta^5\text{-}C_7H_9)Mn(CO)_3$ (6). This complex was prepared in an analogous fashion to (cycloheptenyl)Mn(CO)$_3$ (2a) above with the following exceptions: 0.8 g of $[(\eta^4\text{-}C_7H_8)Mn(CO)_3]^-PPN^+$ (1c) was used in place of $[(\eta^4\text{-}C_7H_{10})Mn(CO)_3]^-PPN^+$ (1a). Concentration of the isopentane extracts in vacuo gave 0.2 g (80% yield) of 6 as a yellow oil. The product was characterized by its IR (ν_{CO}) and ^{1}H NMR spectra which are identical with those previously reported.[9]

$(C_7H_8D)Mn(CO)_3$ (6-d) via Deuteriation of $[(\eta^4\text{-}C_7H_8)$-$Mn(CO)_3]^-PPN^+$ (1c). Complex 1c was dissolved in 10 mL of CH$_2$Cl$_2$. The solution was cooled to 0 °C, and D$_2$O (1 equiv) was added via syringe which produced an immediate color change from orange to pale yellow. The solution was warmed to 20 °C and filtered through alumina and solvent evaporated in vacuo. Addition of isopentane (50 mL) caused a white solid (PPN$^+$OD$^-$) to precipitate out of solution. The solution was filtered through Celite and solvent evaporated in vacuo (0.001 mmHg) to give 6-6-exo-d.

$(\eta^5\text{-}C_8H_9)Mn(CO)_3$ (8). This complex was prepared in an analogous way to (cycloheptenyl)Mn(CO)$_3$ (2a) above with the following exceptions: 1.2 g of $[(\eta^4\text{-}C_8H_8)Mn(CO)_3]^-PPN^+$ (1d) was used in place of $[(\eta^4\text{-}C_7H_{10})Mn(CO)_3]^-PPN^+$ (1a). Concentration of the isopentane extracts in vacuo gave 0.3 g (85%) of 8 as a

yellow crystalline solid. This compound was characterized previously with only ^{1}H NMR at 25 °C.[9]

^{1}H NMR (toluene-d_8 at -79 °C): δ 1.89 (m, H_{8n}), 2.12 (m, H_{8x}), 2.84 (m, $H_{1,5}$), 4.18 (dd, J_{H2-H3} = 6.7, J_{H2-H1} = 10.4 Hz, H_2), 4.34 (dd, J_{H4-H5} = 10.3, J_{H4-H3} = 6.7 Hz, H_4), 4.56 (t, $J_{H3-H2,H4}$ = 6.7 Hz, H_3), 5.11 (dt, H_7), 5.65 (dd, J_{H6-H7} = 7.8, J_{H6-H5} = 10.5 Hz, H_6). ^{13}C NMR (toluene-d_8 at -79 °C): δ 25.5 (t, J_{CH} = 121.7 Hz, C_8), 59.4 (d, J_{CH} = 148.4 Hz, C_1), 62.4 (d, J_{CH} = 153.4 Hz, C_5), 91.9 (d, J_{CH} = 171.7 Hz, C_2), 94.0 (d, J_{CH} = 147.2 Hz, C_4), 99.5 (d, J_{CH} = 168.3 Hz, C_3), 122.6 (d, J_{CH} = 150.4 Hz, C_7), 129.1 (d, J_{CH} = 156 Hz, C_6), 219.8 (s, CO), 220.1 (s, CO), 227 (s, CO). Anal. Calcd for $C_{11}H_9O_3Mn$: C, 54.1; H, 3.7: Found: C, 54.07; H, 3.86.

($C_8H_8D)Mn(CO)_3$ (8-d) via Deuteriation of [($η^4$-C_8H_8)-$Mn(CO)_3$]$^-$PPN$^+$ (1d). A method similar to that used to prepare 6-d was used with following exceptions: [($η^4$-C_8H_8)Mn(CO)$_3$]$^-$PPPn$^+$ (1d) was used in place of 1d. D_2SO_4 was used for the deuteriating reagent instead of D_2O.

Bicyclo[5.1.0]octadienyl)manganese Tricarbonyl (10). Monocyclic complex 8 in 50 mL of benzene was heated to 50 °C for 10 h. The solvent was removed in vacuo (0.001 mmHg), and the product was examined by NMR to observe the formation of 10. 10 could not be isolated from the equilibrium mixture of 8. IR (hexane): $ν_{CO}$ 2020, 1960, 1940 cm^{-1}. ^{1}H NMR (toluene-d_8 at -79 °C): δ 0.2 (dt, J_{gem} = 4.2 Hz, $J_{8n-1,7}$ = 8.3 Hz, H_{8n}), 0.75 (dt, J_{gem} = 4.2 Hz, $J_{8x-1,7}$ = 4.3 Hz, H_{8x}), 1.2 (m, $H_{1,7}$), 3.8 (dd, $H_{3,5}$), 5.25 (dd, H_4). ^{13}C NMR (toluene-d_8, 25 °C): δ 32.3 (d, J_{CH} = 161 Hz, $C_{1,7}$), 39.2 (t, J_{CH} = 151 Hz, C_8), 86.9 (d, J_{CH} = 151 Hz, $C_{2,6}$), 91.5 (d, J_{CH} = 158 Hz. $C_{3,5}$), 95.7 (d, J_{CH} = 158 Hz, C_4).

Carbonylation and Decarbonylation of the Bridging Complexes 2a and 2b. Complex 2a or 2b was dissolved in a 100-mL benzene solution and CO was bubbled through this solution for 1 h. After 1 h the IR spectrum showed complete loss of the CO frequencies from 2a or 2b and new tetracarbonyl CO frequencies at 2040, 1970, 1960, and 1950 cm^{-1}. After the preparation of the tetracarbonyl compound was confirmed, the solution was heated in refluxing benzene for 2 h with Ar bubbling through the solution. The solution was cooled to 20 °C, and an IR was taken to observe the loss of tetracarbonyl CO frequencies. In the case of the tetracarbonylmanganese cycloheptenyl complex 2a was cleanly regenerated from heating. However, heating the tetracarbonylmanganese cyclooctenyl complex results in decomposition (IR).

Methylation of [($η^4$-Cycloheptatriene)Mn(CO)$_3$]$^-$PPN$^+$ (1c). [($η^4$-C_7H_8)Mn(CO)$_3$]$^-$PPN$^+$ (0.5 g) was dissolved in 10 mL of CH$_2$Cl$_2$ and cooled to -78 °C. MeOTf (1.1 equiv) was added dropwise to the anion solution which produced an immediate color change from orangish yellow to pale yellow. The solution was warmed to 20 °C and filtered through an alumina–Celite column and solvent evaporated in vacuo (0.001 mmHg). Addition of isopentane (100 mL) caused a white solid (PPN$^+$OTf$^-$) to precipitate out of solution. The solution was filtered through Celite and solvent evaporated to give 0.1 g (50%) of the product. The product was characterized by its IR ($ν_{CO}$) and ^{1}H NMR spectra which are identical with those previously reported.[16]

Methylation of [($η^4$-C_8H_8)Mn(CO)$_3$]$^-$PPN$^+$ (1d). [($η^4$-C_8H_8)Mn(CO)$_3$]$^-$PPN$^+$ (1g) was dissolved in 10 mL of THF. Excess (5 equiv) CH$_3$I was added at 25 °C and the solution stirred for 1 h. After 1 h a white solid (PPN$^+$I$^-$) precipitated out of solution with a color change from dark red to pale yellow. The solution was filtered through an alumina–Celite column and

concentrated in vacuo (0.001 mmHg) to a volume of 3–5 mL. Dropwise addition of isopentane (100 mL) caused more white solid (PPN$^+$I$^-$) to precipitate out of solution. The solution was filtered through Celite and solvent evaporated in vacuo (0.001 mmHg) to give 0.3 g (95% yield) of 9 as yellow crystals. IR (hexanes): $ν_{CO}$ 2020, 1960, 1940 cm^{-1}. ^{1}H NMR (toluene-d_8, -48 °C) δ 0.78 (d, J = 7.3 Hz, H's of CH$_3$), 2.44 (m, H_8), 2.9 (m, $H_{1,5}$), 4.11 (dd, J = 6.8, 10.9 Hz, H_2), 4.40 (dd, J = 6.8, 10.3 Hz H_4), 4.74 (t, J = 6.8 Hz, H_3), 4.98 (dt, H_7), 5.49 (ddd, H_6). ^{13}C NMR (toluene-d_8, -48 °C): δ 26.5 (q, J_{CH} = 138.7 Hz, C_9), 32.4 (d, J_{CH} = 119.2 Hz, C_8), 59.6 (d, J_{CH} = 154.7 Hz, C_1), 69.8 (d, J_{CH} = 142.1 Hz, C_5), 92.7 (d, J_{CH} = 154.1 Hz, C_2), 93.1 (d, J_{CH} = 155 Hz, C_4), 100.8 (d, J_{CH} = 167.2 Hz, C_3), 122.5 (d, J_{CH} = 155.4 Hz, C_7), 131.6 (d, J_{CH} = 155 Hz, C_6), 219.4 (s, CO), 219.8 (s, CO), 227.5 (s, CO). Anal. Calcd for $C_{12}H_{11}O_3Mn$: C, 55.83; H, 4.30. Found: C, 56.14; H, 4.31.

Silylation of [($η^4$-C_7H_8)Mn(CO)$_3$]$^-$PPN$^+$ (1c). To [($η^4$-C_7H_8)Mn(CO)$_3$]$^-$PPN$^+$ (0.5 g) in 10 mL of CH$_2$Cl$_2$ solution at -78 °C was added slowly TMSOTf (1.1 equiv) via syringe. An immediate color change was observed from yellow-orange to yellow. The solution was filtered through Celite–alumina and reduced to a volume of 3 mL. Isopentane (100 mL) was added which caused a white solid (PPN$^+$OTf$^-$) to crystallize out of solution. The solution was filtered through Celite and solvent evaporated to give as an oil 0.1g (50%).[16] IR (hexanes): $ν_{CO}$ 2020, 1960, 1940 cm^{-1}. ^{1}H NMR (benzene-d_6): δ -0.34 (s, H's of TMS), 0.88 (dd, J_{gem} = 14.5 Hz, J = 1, 7.1 Hz, H_7), 1.68 (m, J = 14.5, 7.5, 11 Hz, H_7), 2.16 (ddd, J = 11, 7.1, 5 Hz, H_8), 3.43 (dd, J = 7.5, 9.2 Hz, H_5), 3.72 (dd, J = 10.1, 5 Hz, H_1), 4.08 (dd, J = 6, 10.1 Hz, H_2), 4.59 (dd, J = 9.2, 6 Hz, H_4), 4.99 (dd, J = 6.6 Hz, H_3).

Silylation of [($η^4$-C_8H_8)Mn(CO)$_3$]$^-$PPN$^+$ (1d). This experiment was carried out in an analogous fashion to silylation of [($η^4$-C_7H_8)Mn(CO)$_3$]$^-$PPN$^+$ (1c) above with the following exceptions: 1 g of [($η^4$-C_8H_8)Mn(CO)$_3$]$^-$PPN$^+$ (1d) was used in place of 1c. Concentration of the isopentane extracts in vacuo gave 0.3 g of (8-exo-(trimethylsilyl)cyclooctatrienyl)Mn(CO)$_3$ as an oil. IR (hexanes): $ν_{CO}$ 2020, 1960, 1940 cm^{-1}. ^{1}H NMR (toluene-d_8, 25 °C): δ -0.28 (s, TMS), 1.94 (t, J = 6 Hz, H_8), 4.22 (br s, 2 H's), 4.54 (t, J = 8.9 Hz, H_4), 4.59 (br s, 1 H), 5.1 (br s, 1 H), 5.23 (br s, 2 H's). This oil is always contaminated with 10–15% of unsubstituted 8 which could not be separated.