

Notes

Improved Synthesis of $[\text{Mn}(\text{CO})_5\text{OClO}_3]$, a Versatile Reagent for the Preparation of Cationic (Polyene)manganese(I) Complexes. Crystal Structure of $[(\eta^4\text{-}1,5\text{-Cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$

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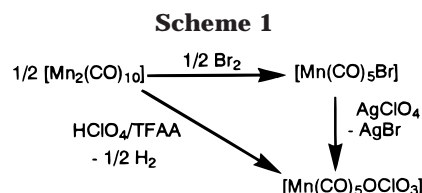
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Summary: The title complex is synthesized in one step from $[\text{Mn}_2(\text{CO})_{10}]$ and is used to prepare cationic $[(\eta^4\text{-diene})\text{Mn}(\text{CO})_4]^+$ and $[(\eta^6\text{-triene})\text{Mn}(\text{CO})_3]^+$ complexes, including $[(\eta^4\text{-}1,5\text{-cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$ for which an X-ray crystal structure is reported. The kinetics of $[(\eta^4\text{-norbornadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$ conversion to $cis\text{-}[(\text{CH}_3\text{CN})_2\text{Mn}(\text{CO})_4]^+$ are also studied.



Introduction

Manganese(I) carbonyl fragments can be potentially used to coordinate various polyenes, thereby activating them toward nucleophilic attack. The resulting complexes include $[(\eta^6\text{-triene})\text{Mn}(\text{CO})_3]^+$,^{1,2} $[(\eta^4\text{-diene})\text{Mn}(\text{CO})_4]^+$,³ and $[(\eta^2\text{-olefin})\text{Mn}(\text{CO})_5]^+$.⁴ Of these, the η^6 -arene complexes are by far the best known, having found application in organic synthesis.^{5,6} The arene complexes are usually obtained through oxidation of manganese carbonyl to $[\text{Mn}(\text{CO})_5\text{Br}]$ using bromine (Scheme 1), followed by halide abstraction using $\text{Ag}(\text{I})$

or AlCl_3 .^{2,7} When silver perchlorate is used, an air-stable perchlorato complex, $[\text{Mn}(\text{CO})_5\text{OClO}_3]$, can be isolated.⁸ The latter functions as a stabilized 16-electron cation. It has been shown to react with a wide variety of donor ligands to produce $[\text{Mn}(\text{CO})_5\text{L}]\text{ClO}_4$,⁸ as well as with arenes to form $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]\text{ClO}_4$.⁹ A stable trifluoromethanesulfonato ("triflate") complex of pentacarbonylmanganese(I) can also be prepared using silver triflate.¹⁰

Recently, we have shown that manganese carbonyl is oxidized by strong acid in trifluoroacetic anhydride (TFAA) solvent, allowing direct preparation of the arene complexes without the need for bromine or silver.² We now show that, in the absence of donor ligands and when the acid used is HClO_4 , $[\text{Mn}(\text{CO})_5\text{OClO}_3]$ is produced in high yield. This species has proved useful in the synthesis of the little-known $[(\eta^4\text{-diene})\text{Mn}(\text{CO})_4]^+$ complexes as well as the arene complexes.

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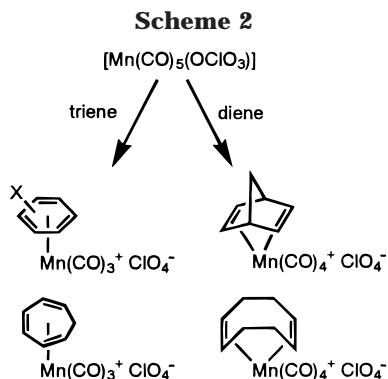
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Results and Discussion

The perchlorato complex [Mn(CO)₅OCIO₃] was prepared from [Mn₂(CO)₁₀] in very high yield in a single step using HClO₄ and TFAA solvent (0 °C, 1.5 h, 94%). When scaled up to 3 g, the yield was still good (75%). The product is precipitated as analytically pure crystals and is readily identified by infrared spectroscopy (IR). The analogous triflate complex, [Mn(CO)₅(OS(O)₂CF₃)], has been prepared using HOS(O)₂CF₃ in TFAA. The triflate yield was consistently lower (42%) than that of the perchlorate owing to difficulties in precipitation and purification of the product. The perchlorate complex has been used in the synthesis of cationic diene and triene complexes, as indicated in Scheme 2. The reaction conditions used are quite mild: boiling CH₂Cl₂, 2–20 h.

Cationic complexes of the nonconjugated dienes, bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) and 1,5-cyclooctadiene (1,5-COD), were synthesized from [Mn(CO)₅OCIO₃] in good yield, the products spontaneously precipitating from refluxing CH₂Cl₂. However, attempts to prepare the tetracarbonyl cations of conjugated (or readily aromatized) dienes failed in all cases. Attempts to coordinate 1,3- or 1,4-cyclohexadiene generated sizable yields of [(η⁶-C₆H₆)Mn(CO)₃]⁺, which was readily identified by IR¹¹ and ¹H NMR (comparison to authentic sample). Aromatization of cyclohexadiene requires the loss of H₂. However, gas chromatographic/mass spectrometric analysis of the soluble residue from these reactions revealed no evidence of cyclohexene. Hence, it does not appear that cyclohexadiene functions as a hydrogen scavenger. Cyclopentadiene reacted with [Mn(CO)₅OCIO₃] to produce a moderate amount of the cyclopentadienyl product, [(η⁵-C₅H₅)Mn(CO)₃]⁺, which was also identified by IR and ¹H NMR. On the other hand, other conjugated dienes (including 1,3-cyclooctadiene, isoprene, and 2,3-dimethyl-1,3-butadiene) were found to be essentially unreactive, affording the recovery of [Mn(CO)₅OCIO₃] (35–60%).

The [(η⁴-diene)Mn(CO)₄]⁺ products are subject to nucleophilic displacement of the diene. Over the course of about an hour in CH₃CN, they convert to a product having carbonyl IR bands at 2133 (vw), 2056 (s), and 2004 (m). The release of NBD from the metal complex was observed by ¹H NMR in CD₃CN on the same time scale. Therefore, it was concluded that the initial product is the previously unreported complex *cis*-[(CH₃CN)₂Mn(CO)₄]⁺. After several hours this product converted to *fac*-[(CH₃CN)₃Mn(CO)₃]⁺ (IR 2063 (s), 1975 (s, br)).^{11,12} An IR kinetic study of the initial CH₃CN solvolysis of the NBD complex to the bis-acetonitrile

Table 1. Kinetics Data for the Solvolysis of [(η⁴-Norbornadiene)Mn(CO)₄]ClO₄, 0.509 mM, 25.0 ± 0.2 °C

[CH ₃ CN], M ^a	t _{1/2} , s	10 ⁴ k _{obs} , s ⁻¹	10 ⁵ k _{obs} [CH ₃ CN] ⁻¹ , M ⁻¹ s ⁻¹
5.0	5960	1.16	2.32
10.0	3850	1.80	1.80
15.0	2990	2.32	1.55
19.1 ^b	2180	3.18	1.66

^a Diluted in CH₃NO₂. ^b Pure CH₃CN.

product at 25.0 ± 0.2 °C was carried out under pseudo-first-order conditions. The results are shown in Table 1. The highly linear ln(abs) vs time plots confirmed that the reaction was first-order with respect to the NBD complex, and the linearity of k_{obs} vs [CH₃CN] indicated that the reaction was also first-order with respect to the nucleophile. The average second-order rate constant was 1.83 × 10⁻⁵ M⁻¹ s⁻¹. Previous studies involving CH₃CN displacement of the arene in [(η⁶-arene)Mn(CO)₃]⁺^{11,13} and phosphite and phosphine displacement of the diene in [(η⁴-diene)M(CO)₄] (M = Cr, Mo, W)¹⁴ have revealed similar dependencies. These results have generally been interpreted via a mechanism involving rate-limiting nucleophilic displacement of the first alkene unit of the polyene, in the present case producing [(η²-diene)Mn(CO)₄(NCCH₃)]⁺. This is followed by rapid ligand loss and further solvent attack.

Only a single report of [(η⁴-diene)Mn(CO)₄]⁺ species can be found in the literature.³ It involves the synthesis of the 1,5-COD complexes of [M(CO)₄]⁺ (M = Mn, Re) from [M(CO)₅Cl] and AlCl₃ in the presence of the diene. These species were shown to react with hydride to produce η¹,η²-cyclooctenyl complexes. No structural analysis was reported. Therefore, we undertook an X-ray crystal structure determination for the COD complex.¹⁵ Experimental details are provided in Table 2, positional and isotropic thermal parameters for the non-hydrogen atoms are in Table 3, and important bond lengths and angles are in Table 4. A thermal ellipsoid drawing is shown in Figure 1. Although several d⁶ octahedral 1,5-COD complexes are known,¹⁶ no unsubstituted [(η⁴-1,5-COD)M(CO)₄] structure has yet been reported. The new manganese structure bears similarities to the previously solved [(η⁴-1,5-COD)M(CO)₃-(P(OMe)₃)] complexes (M = Cr, *mer* isomer;¹⁷ W, *fac* isomer¹⁸) and to [(η⁴-diCOT)Mo(CO)₄]¹⁹ (diCOT = a bridged dimer of cyclooctatetraene). The present structure possesses rigorous C_{2v} symmetry and exhibits

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(15) An X-ray structure was solved for the NBD complex also. However, increases in standard reflection intensity and cell volume and a decrease in the extinction coefficient during data collection suggested that irradiation of the crystal produced an increase in disorder. Although the solution was of rather poor internal consistency, the gross structure was akin to that of the 1,5-COD complex.

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Table 2. Crystal Data and Structure Refinement for $[(\eta^4\text{-1,5-Cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$

A. Crystal Data	
empirical formula	$\text{C}_{12}\text{H}_{12}\text{ClMnO}_8$
fw	374.61
cryst size, mm	$0.56 \times 0.58 \times 0.64$
cryst syst	orthorhombic
lattice params, Å	$a = 11.063(2)$ $b = 11.9283(13)$ $c = 10.883(2)$
volume, Å ³	1436.1(4)
space group	<i>Pbcn</i>
Z	4
density (calcd), mg m ⁻³	1.733
abs coeff, mm ⁻¹	1.143
B. Intensity Measurements	
temp, K	298(2)
scan type	ω
F_{000}	760
θ range for data collection, deg	2.51–26.00
index ranges	$-1 \leq h \leq 13, -1 \leq k \leq 14,$ $-1 \leq l \leq 13$
reflins collected	1899
independent reflins	1415 ($R_{\text{int}} = 0.0585$)
abs corr	empirical
max. and min. transmission	0.405, 0.359
C. Structure Solution and Refinement	
refinement method	full-matrix least-squares on F^2
no. of data, restraints, params	1415, 0, 102
goodness of fit of F^2	0.895
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0462, wR2 = 0.1208$
R indices (all data)	$R1 = 0.0724, wR2 = 0.1325$
extinction coeff	0.022(2)
largest peak and hole in diff map, e Å ⁻³	0.799, -0.311

nearly perfect octahedral ligand arrangement around the metal. The carbonyls are staggered with respect to the ring. The manganese atom lies 1.685 Å above the center of the plane produced by the four vinyl carbons. The carbonyls that are situated *trans* to another carbonyl are slightly longer than those that are oriented *trans* to an olefinic bond.

Wink has shown that conjugated and nonconjugated dienes have differing donor/acceptor properties.¹⁶ The more accessible LUMO of the former makes them more effective π -back-bonding ligands. Wink has further shown that this difference is reflected in the structural properties of d^6 $[(\eta^4\text{-diene})\text{ML}_4]^+$ complexes. Thus, while complexes of conjugated dienes show serious distortions from octahedral ligand arrangement, nonconjugated dienes show very little distortion. Although no manganese structures were available for inclusion in Wink's study, $[(\eta^4\text{-1,5-COD})\text{Mn}(\text{CO})_4]^+$ fits the established pattern very well. It seems likely that the minimal ability of the electron-deficient $[\text{Mn}(\text{CO})_4]^+$ fragment to donate electron density to the low-lying LUMO of the conjugated dienes underlies the observed instability of these complexes found in the present study.

Several $[(\eta^6\text{-triene})\text{Mn}(\text{CO})_3]\text{ClO}_4$ species were synthesized from $[\text{Mn}(\text{CO})_5\text{OClO}_3]$. The yields are shown in Table 5. Satisfactory results were anticipated for these reactions since the AgClO_4 abstraction of halide from $[\text{Mn}(\text{CO})_5\text{X}]$ is known to allow coordination of aromatic ligands.^{2,9} The reactions were typically clean, as judged by IR, requiring several hours at reflux in CH_2Cl_2 . Yellow, crystalline products either precipitated during the course of the reaction or were precipitated upon the addition of ether.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $[(\eta^4\text{-1,5-Cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$

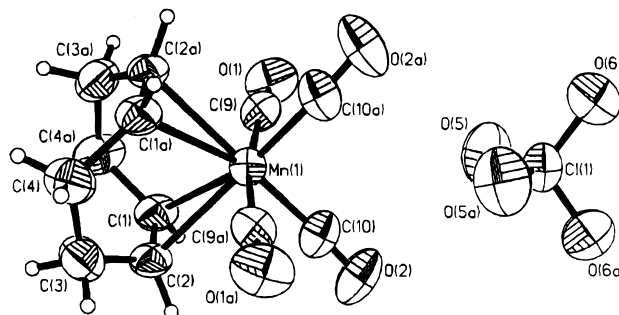
	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq}), \text{Å}^2$
Mn(1)	0	3093(1)	2500	38(1)
C(1)	252(3)	1671(3)	1064(3)	51(1)
C(2)	1265(3)	1689(3)	1779(3)	48(1)
C(3)	1547(4)	844(4)	2766(4)	64(1)
C(4)	712(4)	779(4)	3824(4)	72(1)
C(9)	-1340(4)	3229(3)	1466(3)	49(1)
C(10)	748(4)	4121(4)	1489(3)	55(1)
O(1)	-2138(2)	3372(3)	847(3)	74(1)
O(2)	1252(3)	4708(3)	860(3)	80(1)
O(5)	-562(4)	6614(3)	1589(3)	94(1)
O(6)	-886(3)	7995(3)	3082(3)	84(1)
Cl(1)	0	7303(1)	2500	56(1)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^4\text{-1,5-Cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$

Mn(1)–C(10)	1.844(4)	Mn(1)–C(9)	1.868(4)
Mn(1)–C(2)	2.319(4)	Mn(1)–C(1)	2.323(4)
C(1)–C(2)	1.364(5)	C(2)–C(3)	1.505(6)
C(3)–C(4)	1.479(5)	C(9)–O(1)	1.124(4)
C(10)–O(2)	1.126(4)	Cl(1)–O(6)	1.430(4)
Cl(1)–O(5)	1.430(3)		
C(10)–Mn(1)–C(9)	86.5(2)	C(10)–Mn(1)–C(2)	90.4(2)
C(9)–Mn(1)–C(2)	109.7(2)	C(10)–Mn(1)–C(1)	91.7(2)
C(9)–Mn(1)–C(1)	75.7(2)	C(2)–Mn(1)–C(1)	34.18(13)
C(2)–C(1)–Mn(1)	72.8(2)	C(1)–C(2)–C(3)	124.5(4)
C(1)–C(2)–Mn(1)	73.1(2)	C(3)–C(2)–Mn(1)	111.5(2)
C(4)–C(3)–C(2)	117.5(3)	O(1)–C(9)–Mn(1)	176.3(4)
O(2)–C(10)–Mn(1)	176.3(4)	O(6)–Cl(1)–O(5)	109.9(2)

^a Only independent bond lengths and angles listed; see Experimental Section.

**Figure 1.** Thermal ellipsoid drawing of $[(\eta^4\text{-1,5-cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$ at the 50% probability level.**Table 5. Synthesis Results for $[(\eta^6\text{-Triene})\text{Mn}(\text{CO})_3]\text{ClO}_4$ Complexes**

arene	preparation time, h	yield, %	IR ($\nu_{\text{CO}}, \text{CH}_3\text{NO}_2$)
1,3,5-trimethoxybenzene	4.5	85	2069, 2004
1,2,4,5-tetramethylbenzene	3.0	60	2069, 2010
dibenzopyrrole (carbazole)	4.0	83	2067, 2007
cycloheptatriene	2.0	66	2078, 2022

We have also attempted to form the complexes $[(\eta^2\text{-olefin})\text{Mn}(\text{CO})_5]\text{ClO}_4$ (olefin = cyclopentene, 1-pentene, norbornylene, *cis*-stilbene, phenylacetylene, and 3-hexyne). Upon stirring the perchlorate complex and the olefin together in various ratios in CH_2Cl_2 at room temperature or reflux, new carbonyl IR bands are observed. These bands (2162 (vw), 2117 (vw), 2078 (s), 2042 (w)) suggest the formation of electron-deficient pentacarbonyl species. The spectra appear to be in agreement with those of previously reported ethylene and propylene

complexes.⁴ However, $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$ was invariably recovered from these reactions. If, in fact, the olefin complexes are being formed, it would seem that the perchlorate ligand is competing with the olefins for coordination to the strongly electrophilic $[\text{Mn}(\text{CO})_5]^+$ fragment.

In summary, we have demonstrated a one-step, high-yield synthesis of the useful Mn(I) carbonyl complex $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$. This species has demonstrated behavior consistent with facile release of the 16-electron $[\text{Mn}(\text{CO})_5]^+$, which coordinates sufficiently electron-rich polyene ligands with the loss of the appropriate number of carbonyl ligands.

Experimental Section

General Methods. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR using a liquid cell with CaF_2 windows, and ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were collected using a General Electric QE-300 spectrometer. Microanalyses were carried out by Atlantic Microlaboratories, Norcross, GA.

Materials. All solvents were dried and purified according to standard methods. Dienes were purchased from Aldrich and distilled from CaH_2 prior to use. Trifluoroacetic anhydride (TFAA) was purchased from Aldrich and used as received.

Preparation of $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$. TFAA (15 mL) was cooled to 0 °C, and $[\text{Mn}_2(\text{CO})_{10}]$ (1.50 g, 3.85 mmol) was added. The suspension developed a brown color. Aqueous HClO_4 (3 mL, 60% solution) was then added dropwise. During 1.5 h stirring at 0 °C, the mixture became a clear, orange solution. The TFAA was removed under vacuum, and the resulting yellow slurry was dried over MgSO_4 . Boiling CH_2Cl_2 (10 mL) was then added, and the suspension was hot-filtered. The yellow, crystalline product was precipitated by the addition of diethyl ether and dried under vacuum (2.12 g, 7.20 mmol, 94%). IR (ν_{CO} , CH_2Cl_2): 2157 (vw), 2074 (s), 2023 (w) cm^{-1} . The reaction has been carried out on a larger scale: 3.00 g of $[\text{Mn}_2(\text{CO})_{10}]$, 20 mL of TFAA, 4 mL of HClO_4 solution. It is especially important when using a larger scale that the HClO_4 be added slowly to avoid a large exotherm. The triflate complex is prepared in a similar fashion, except that removal of water with MgSO_4 is unnecessary and recrystallization is carried out from a small volume of diethyl ether.

Preparation of $[(\eta^4\text{-Norborene})\text{Mn}(\text{CO})_4]\text{ClO}_4$. $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$ (2.50 g, 8.49 mmol) and NBD (ca. 2 mL) were dissolved in 100 mL of CH_2Cl_2 and refluxed under N_2 for 5 h. A bright yellow, crystalline precipitate slowly formed. The mixture was cooled and the precipitate collected, washed with diethyl ether, and dried under vacuum (2.86 g, 7.99 mmol, 94%). Anal. Found: C, 36.93; H, 2.21. Calcd for $\text{C}_{11}\text{H}_8\text{ClMnO}_8$: C, 36.85; H, 2.25. ^1H NMR (CD_3NO_2): δ 1.80 (bs, 2 H, CH_2), 4.13 (bs, 2 H, $\text{CH}^{\text{bridgehead}}$), 5.79 (bs, 4 H, CH^{vinyl}). ^{13}C NMR (CD_3NO_2): δ 49.0, 67.8, 85.9, 208.6 (MCO), 215.7 (MCO). IR (ν_{CO} , CH_3NO_2): 2118 (m), 2067 (sh), 2046 (s) cm^{-1} .

Preparation of $[(\eta^4\text{-1,5-Cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$. This complex was prepared by a method similar to that of the norbornadiene complex (20 h reflux, 55% yield). ^1H NMR (CD_3NO_2): δ 2.47 (d, $J = 9.2$ Hz, 4 H, CH_2^{exo}), 3.00 (bd, $J = 11.4$, 4 H, $\text{CH}_2^{\text{endo}}$), 5.20 (bs, 4 H, CH^{vinyl}). ^{13}C NMR (CD_3NO_2): δ 30.0, 104.6, 209.4 (MCO), 216.3 (MCO). IR (ν_{CO} , CH_3NO_2): 2113 (m), 2060 (sh), 2038 (s) cm^{-1} .

Preparation of $[(\eta^6\text{-Benzene})\text{Mn}(\text{CO})_3]\text{ClO}_4$ from Cyclohexadienes. $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$ (0.135 g, 0.458 mmol) and 1,4-cyclohexadiene (0.131 g, 1.63 mmol) were refluxed in 50 mL of CH_2Cl_2 under N_2 in the dark for 20 h. A pale yellow precipitate slowly formed. The mixture was cooled and the precipitate collected, washed with diethyl ether, and dried under vacuum (0.114 g, 0.361 mmol, 79%). Similar results

were obtained using 1,3-cyclohexadiene (66% yield). ^1H NMR (CD_3COCD_3): δ 6.94 (s, 6 H). IR (ν_{CO} , CH_3NO_2): 2082 (s), 2027 (s, br) cm^{-1} .

Preparation of $[(\eta^5\text{-Cyclopentadienyl})\text{Mn}(\text{CO})_3]$ from Cyclopentadiene. $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$ (0.119 g, 0.404 mmol) and cyclopentadiene (0.0515 g, 0.779 mmol) were refluxed in 50 mL of CH_2Cl_2 under N_2 in the dark for 16.5 h. A black, insoluble precipitate was removed via filtration. The filtrate was evaporated and chromatographed on alumina with diethyl ether. After solvent evaporation, the orange oil was dried under vacuum (0.0206 g, 0.101 mmol, 25%). ^1H NMR (CDCl_3): δ 4.76 (s, 5 H). IR (ν_{CO} , CH_2Cl_2): 2022 (s), 1932 (s, br) cm^{-1} .

Preparation of $[(\eta^6\text{-Dibenzopyrrole})\text{Mn}(\text{CO})_3]\text{ClO}_4$. $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$ (0.150 g, 0.509 mmol) and dibenzopyrrole (carbazole, 0.259 g, 1.55 mmol) were refluxed in 20 mL of CH_2Cl_2 under N_2 for 4 h. The mixture was concentrated under vacuum and precipitated by the addition of diethyl ether. The pale yellow product was washed with diethyl ether and dried under vacuum (0.172 g, 0.425 mmol, 83%). Found: C, 44.25; H, 2.24; N, 3.45. Calcd for $\text{C}_{15}\text{H}_8\text{ClMnNO}_7$: C, 44.53; H, 1.99; N, 3.46. ^1H NMR (CD_3COCD_3): δ 6.43 (t, $J = 6.4$, 1 H), 6.97 (t, $J = 6.6$, 1 H), 7.44 (d, $J = 7.0$, 1 H), 7.55 (t, $J = 7.3$, 1 H), 7.85 (m, 2 H), 8.24 (d, $J = 6.6$, 1 H), 8.51 (d, $J = 7.9$ 1 H). ^{13}C NMR (CD_3COCD_3): δ 84.6, 88.4, 95.6, 99.8, 111.6, 119.6, 120.8, 121.6, 123.8, 140.7, 145.1. Similar results were obtained using other arenes.

Attempted Preparation of Conjugated $[(\eta^4\text{-Diene})\text{Mn}(\text{CO})_4]\text{ClO}_4$ and $[(\eta^2\text{-Olefin})\text{Mn}(\text{CO})_5]\text{ClO}_4$ Complexes. $[\text{Mn}(\text{CO})_5\text{OCIO}_3]$ and conjugated diene or olefin (2.0–3.0 equiv) were refluxed in CH_2Cl_2 . Reaction progress was monitored by IR. Cationic products were precipitated using diethyl ether.

Solvolysis Kinetics of $[(\eta^4\text{-Norborene})\text{Mn}(\text{CO})_4]\text{ClO}_4$. Solvolysis reactions were carried out under pseudo-first-order conditions by dissolving the NBD complex (5.09 mM) into a solution of CH_3CN in CH_3NO_2 , which was pre-equilibrated to and maintained at 25.0 ± 0.2 °C in a Fisher Isotemp model 910 thermostatic bath. Samples were periodically withdrawn and immediately examined by IR spectroscopy. The loss of the diene ligand was measured by the decrease in the absorbance of the IR band at 2118 cm^{-1} .

X-ray Diffraction Study of $[(\eta^4\text{-1,5-Cyclooctadiene})\text{Mn}(\text{CO})_4]\text{ClO}_4$. Suitable crystals were grown by diffusion of diethyl ether into a nitromethane solution of the compound at 25 °C. One of the mostly transparent yellow block-shaped crystals was cut and glued to a glass fiber. X-ray data collection was carried out at 25 °C using a Siemens P4 single-crystal diffractometer (Mo $K\alpha$ radiation, 0.710 73 D) controlled by XSCANS version 2.1 software.²⁰ Omega scans were used for data collection, at variable speeds from 10 to 60 deg min^{-1} . Three standard reflections were measured after every 97 reflections; they showed an 8.4% decrease in intensity over the course of the data collection, and corrections were made for their variation. Data reduction included profile fitting and an empirical absorption correction based on 406 ψ -scan reflections. In the initial refinement, a small correction was made for the presence of extinction.

The structure was determined by direct methods and refined initially by use of programs in the SHELXTL 5.1 package,²¹ which were also used for all figures. Both the cation and the anion lie on a 2-fold axis along 0, y , $1/4$, so only half of each is independent. All six independent hydrogen atoms appeared in a difference map, and each was introduced in an ideal position, riding on the atom to which it is bonded. Each was refined with isotropic temperature factors 20% greater than that of the ridden atom. All other atoms were refined with

(20) XSCANS, X-ray Single-Crystal Analysis System; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1993.

(21) Sheldrick, G. M. *SHELXTL/PC*, Integrated System for Data Collection, Processing, Structure Solution and Refinement; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

anisotropic thermal parameters. Final refinement on F^2 was carried out using SHELXL 93.²²

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(22) Sheldrick, G. M. *SHELXL 93*, Program for the Refinement of Crystal Structures; University of Göttingen, Germany, 1993.

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Supporting Information Available: Crystallographic data: tables of bond lengths and angles, anisotropic displacement parameters, hydrogen fractional coordinates, and selected torsion angles (4 pages). Ordering information is given on any current masthead page.

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