experimental Ψ rotation curve. The refinement procedure was taken by a full-matrix least squares. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, Vol. IV. Computing programs were from the NRCVAX package.[10] The crystal data are listed in Table II. The selected bond distances and the bond angles are collected in Table III. The ORTEP drawings are shown in Figures 1–4. Structure factors and complete data are supplied as supplementary material.

Kinetic Study. All kinetic runs were monitored on a HP8425A UV–vis spectrophotometer. The temperature was controlled with a Julabo F10-UV water circulator at an accuracy of ±0.01 °C. Reactions of complex **2a** with PPh_3 were followed by monitoring the absorbance change at 512 nm, and the reactions of **2a** with MeCN were monitored at 436 nm. The pseudo-first-order conditions were maintained by holding the concentrations of the entering ligands in large excess. A linearity of the plot of ln $(D_t - D_\infty)$ versus time lasting for at least 4 half-lives was considered to be the requirement for first-order results. The first-ordr condition was also double-checked by the variation of the initial concentration of **2a**. Data analysis was done by using a nonlinear least-squares program.

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Supplementary Material Available: Tables of complete crystal data, bond lengths and angles, atomic coordinates, and thermal parameters for complexes **2b**, **3b**, **4a**, and **4b** (26 pages); listings of structure factors (83 pages). Ordering information is given on any current masthead page.

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Preparation, Characterization, and Reactivity of (η^5-Pentamethylbenzyl)manganese Tricarbonyl

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Initially observed as a minor product in the reaction of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3PF_6$ (**1**) with $KBH(OCH(CH_3)_2)_3$ (THF, 25 °C), the title compound, $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_3$ (**2**) has been synthesized and isolated in good yield by the reaction of KH with **1** (THF/hexane, 25 °C). Deprotonation of **1** using $LiN(i\text{-}Pr)_2$, $KOC(CH_3)_3$, or $LiC(CH_3)_3$ (THF/hexane, 25 °C) also produces **2** in good yield. The structure of **2**, established by X-ray crystallography, reveals the presence of the $\eta^5\text{-}C_6(CH_3)_5({=}CH_2)$ ligand. The cell dimensions for the orthorhombic crystal, space group *Pbca*, $a = 12.840$ (6) Å, $b = 14.635$ (2) Å, $c = 15.227$ (5) Å, were obtained by a least-squares fit to 25 orientation reflections, and the *R* values were $R_1 = 0.027$ and $R_2 = 0.023$ for 1866 independent reflections of which the 963 reflections greater than 2σ above background were used in the least-squares refinement. The methylene of **2** is reprotonated by NH_4PF_6 to re-form **1**. Complex **2** reacts with PhC(O)Cl at the exocyclic methylene to form the cationic complex $(\eta^6\text{-}C_6(CH_3)_5(CH_2C(O)Ph))Mn(CO)_3^+$, isolated as the PF_6^- salt **5**, after metathesis with NH_4PF_6. Reactions of CH_nX_{4-n} (X = Cl, $n = 0, 1$; X = Br, $n = 1$) with **2** give the complexes $(\eta^6\text{-}C_6(CH_3)_5(CH_2CH_nX_{3-n}))Mn(CO)_2X$ (**6**, X = Cl, $n = 0$; **7**, X = Cl, $n = 1$; **8**, X = Br, $n = 1$). A photoinitiated radical chain mechanism, proposed to explain these observations, is supported by the observation of retarded reaction rates upon addition of 9,10-dihydroanthracene. Complex **2** reacts with I_2 to form $(\eta^6\text{-}C_6(CH_3)_5(CH_2I))Mn(CO)_3^+$ isolated as the PF_6^- salt **9**, after subsequent metathesis. Methyl iodide reacts with **2** to form two products, $(\eta^6\text{-}C_6(CH_3)_5(CH_2CH_3))Mn(CO)_2I$ (**10**) and **1**. Formation of the latter is proposed to occur by an electron-transfer mechanism. Two equivalents of Bu_3SnH reacts with **2** to form $(endo\text{-}\eta^5\text{-}(C_6(CH_3)_6H))Mn(CO)_3$ (**endo-4**). Complex **2** does not undergo hydrogenation to produce **endo-4** using 2% Pd/C catalyst.

Introduction

The reactivity of (arene)manganese tricarbonyl cations, $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3^+$ (**1**), has been the topic of extensive investigation.[1] All reported derivatives of **1** have been formed either by nucleophilic attack at the aromatic ring or at a carbonyl carbon or by substitution of a carbonyl by neutral or negative ligands. A wide variety of nucleophiles are reported to attack the aromatic ring of **1**, leading to the formation of (η^5-cyclohexadienyl)manganese tricarbonyl compounds.[2] Attack by nucleophilic anions, Y, at a carbonyl carbon has led to the formation of $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2C(O)Y$ (Y = R^-, Ar^-, OR^-, OAr^-, NR_2^-).[3] Recent studies have resulted in successful high-yield conversion of **1** to complexes of the type $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2L$ (L = halide, H, and alkyl).[4]

In the course of studying the reactions of various hydride sources with $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3PF_6$ (**1**),[1] we have observed the formation of the title compound, $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_3$ (**2**). This compound, formed by deprotonation of a ring methyl, represents the second

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example of an η^5-pentamethylbenzyl ligand. The compound, $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2)Fe(\eta\text{-}C_5H_5)$ (3), has been reported to possess an η^5-pentamethylbenzyl ligand with reactivity at the exocyclic methylene, which is characteristic of a highly activated double bond.[5] It should also be noted that $[(\eta^6\text{-}(C_6(CH_3)_5(CH_2^-))Cr(CO)_3]K^+$ has been reported to have a very nucleophilic methylene, which is attributed to localized negative charge.[6] We report here the synthesis, characterization, structure determination, and preliminary observations of the reactivity of 2.

Experimental Section

The ^{1}H NMR spectra were recorded on a 90-MHz JEOL FX90Q spectrometer operating at 298 K. The ^{13}C NMR spectra were recorded at 360 MHz on a Bruker WM-360 spectrometer operating at 223 K. Infrared spectra were recorded on a Mattson Cygnus 25 FTIR spectrometer. The mass spectrometry was performed in the University of Iowa High Resolution Mass Spectrometry Facility using a VG ZAB-HF high-resolution instrument. The data were collected in either 70 eV electron impact (EI) or fast atom bombardment (FAB) modes. The FAB ion source used was the standard VG Analytical, Inc., system equipped with a saddle field atom gun. Xenon was used for the bombarding fast atom beam; typical operating conditions were beam energies of 8 keV and neutral beam currents equivalent to 1.5 mA supplied by an ION TECH (Model B 50) current and voltage regulator meter. The crystal structure was determined from data collected with an Enraf-Nonius CAD-4 diffractometer at the Iowa X-Ray Crystallography Facility. All reactions were performed under argon atmosphere. The solvents were purified by standard literature techniques described in Perrin and Perrin[7] and were deoxygenated prior to use. All (η^6-arene)manganese tricarbonyl cations were prepared by the methods described by Wilkinson and Winkhaus.[1a,b,8] Potassium hydride, purchased from Aldrich in mineral oil, was washed with hexane before use. $Mn(CO)_5Br$ was synthesized by standard literature techniques[9] from $Mn_2(CO)_{10}$ acquired from Strem Chemicals. Iodomethane, 1-iodoheptane, ammonium hexafluorophosphate, 9,10-dihydroanthracene (9,10-DHA), and Pd/C catalyst were purchased from Aldrich. A 1 M solution of tributyltin hydride in tetrahydrofuran (THF) was prepared prior to use. Trimethylamine *N*-oxide was dried by azeotropic removal of the water in toluene. All NMR solvents were stored in the inert atmosphere box for sample preparation. The elemental analyses were performed by Desert Analytics.

Synthesis of $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_3$ (2). To a 100-mL Schlenk flask was added a several fold excess of KH in mineral oil. The KH was washed two times with 20-mL portions of dry, deoxygenated hexane, which was carefully removed from the flask via cannula after the KH had settled to the bottom. The residual hexane was removed from the KH under vacuum. After the flask was refilled with argon, 0.446 g (1.00 mmol) of 1 was added under positive argon flow. After the solids were thoroughly mixed by stirring under vacuum, the flask was filled with argon and 55 mL of dry, deoxygenated hexane was added via cannula. After the mixture was stirred until the solids were dispersed, 5–10 mL of dry, deoxygenated THF was added. During an 8-h reaction period with continuous stirring, the solution changed from pale yellow to yellow-green. After the solids were allowed to settle, the solution, containing the products, was transferred to another 100-mL Schlenk flask via cannula. Following solvent removal under vacuum, the septum was replaced with a cold finger. The flask, under full vacuum, was immersed in a mineral oil bath, which was slowly raised to 65 °C. When the temperature had reached 45 °C, uncoordinated hexamethylbenzene and the byproduct $(exo\text{-}C_6Me_6H)Mn(CO)_3$ (**exo-4**) had already sublimed to the cold finger. After removal of these materials from the cold finger, the sublimation was continued for another 10 h. This produced yellow crystalline 2 in 51.8% isolated yield. The ^{1}H NMR and FTIR data are found in Table I. The other analytical data were as follows: ^{13}C NMR (d_6-acetone, −55 °C, undecoupled) δ 223.7 (CO), 146.4 (unbound ring C), 104.4 (ring C), 84.7 (CH_2, $J_{C\text{-}H}$ = 158 Hz), 78.2 (ring C), 22.9–14.5 (CH_3); MS (EI) *m/e* (% abundance, assignment) 300 (11.03, $M^{\bullet+}$), 272 (3.49, $[M - CO]^+$), 244 (2.27, $[M - 2CO]^+$), 216 (22.55, $[M - 3CO]^+$), 161 (87.97, $[M - 3CO - Mn]^+$), 147 (100, $[M - 3CO - Mn - CH_2]^+$). Anal. Calcd for $C_{15}H_{17}MnO_3$: C, 61.11; H, 6.17. Found: C, 61.20; H, 6.36.

Table I. ^{1}H NMR and IR Data

compd	^{1}H NMR δ, ppm	IR μ_{CO}, cm^{-1}
2	3.85 (s, 2 H), 1.80 (s, 3 H), 1.59 (s, 6 H), 1.33 (s, 6 H)[a]	2006, 1933, 1917[b]
5	6.43 (br, 5 H), 3.51 (s, 2 H), 1.83 (s, 3 H), 1.14 (s, 6 H), 1.29 (s, 6 H)[c]	2053, 1991, 1718[b]
6	3.83 (s, 2 H), 1.92 (s, 3 H), 1.57 (br, 12 H)[a]	1979, 1932[b]
7	3.56 (t, 2 H), 1.96 (s, 3 H), 1.51 (br, 12 H)[a]	1976, 1929[b]
8	6.21 (t, 1 H), 3.49 (d, 2 H), 1.82 (s, 3 H), 1.65 (br, 12 H)[a]	1975, 1930[b]
9	4.78 (s, 2 H), 3.51 (s, 3 H), 2.62 (s, 12 H)[c]	2059, 1999[b]
10	2.29 (br, 15 H), 1.24 (q, 2 H), 0.05 (t, 3 H)[a]	1965, 1921[b]
11	7.44 (br, 4 H), 6.68 (br, 6 H), 2.62 (s, 2 H)[c]	2077, 2012, 1932[b]
14	8.23 (br, 2 H), 7.67 (br, 3 H), 7.24 (br, 2 H), 5.90 (br, 3 H), 5.13 (q, 1 H), 1.28 (d, 3 H)[c]	2075, 2011, 1936, 1722[a]
17	5.20 (br, 5 H), 3.73 (s, 2 H), 2.43 (s, 6 H), 2.15 (s, 6 H), 1.22 (s, 3 H)[c]	2101, 1976, 1936, 1722[a]

[a] C_6D_6. [b] In THF. [c] In $CD_3C(O)CD_3$.

X-ray Data Collection for 2. A yellow-orange tabular crystal, 0.12 × 0.27 × 0.44 mm, [010] × [101] × [−1,0,1], was mounted on a diffractometer with the ϕ axis approximately parallel to [−1,0,1]. Graphite monochromated Mo Kα radiation, average wavelength = 0.71073 Å, was used to collect data at 295 K using an ω scan range, 0.7 + 0.35 tan θ, background at 25% below and above range; the horizontal aperture was varied from 2.5 to 3.0 mm depending on the angle; the scan speed ranged from 1–4 deg/min for a hemisphere with θ varying from 1 to 20°; the scan speed was 0.7–2.5 deg/min for a hemisphere with θ varying from 15 to 22.5°. Lorentz, polarization, and empirical adsorption corrections were made (μ = 9.7 cm^{-1}, maximum and minimum corrections, 0.94–1.0 on *F*). Three standards used to monitor crystal decay indicated a maximum decline in *F* of 11%, so intensity corrections for decay were made. A total of 5624 reflections were measured for the hemisphere ($-h,\pm k,\pm l$) in reciprocal space for θ varying from 1 to 20°; averaging gave 1565 independent reflections, with an internal agreement of 2.8% on *F*. For a partly overlapping region in reciprocal space, θ varying from 15 to 22.5°, 5202 reflections were measured, yielding 1446 net averaged reflections, internal agreement of 4.4% on *F*. Merging the two sets gave 1866 independent reflections of which the 963 reflections greater then 2σ above background were used in the least-squares refinement. The cell dimensions for the orthorhombic crystal, space group *Pbca*, *a* = 12.840 (6) Å, *b* = 14.635 (2) Å, *c* = 15.227 (5) Å, were obtained by a least-squares fit to 25 orientation reflections.

The structure was solved by direct methods and refined by full-matrix least squares. All hydrogen atoms were located from difference electron density maps after the non-hydrogen atoms had been fit by anisotropic thermal parameters. Hydrogen atoms were not refined but placed in idealized positions. Anisotropic refinement on all non-hydrogen atoms (173 variables, including scale and extinction) gave *R* values of R_1 = 0.027 and R_2 = 0.023; the standard deviation of an observation of unit weight = 1.06; the maximum parameter shift/estimated error was less than 0.01;

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Table II. Crystal Data Summary

empirical formula	$MnC_{15}H_{17}O_3$
color of cryst	yellow-orange
cryst dimens, nm	0.12 × 0.27 × 0.44
space group	*Pbca*
cell dimens	
temp, K	295
a, Å	12.840 (6)
b, Å	14.635 (2)
c, Å	15.227 (5)
Z	8
wavelength, Å	0.71073
mol wt	300.22
ω scan range	0.7 + 0.35 tan θ
background	25%, above and below range
horizontal aperture, mm	2.5–3.0
scan speed, deg/min (θ from 1 to 20°)	1–4
scan speed, deg/min (θ from 15 to 22.5°)	0.7–2.5
linear abs coeff, cm^{-1}	9.7
max and min corrections on *F*	0.94–1.0
cryst decay, %	11
reflns collected (1–20°)	5624
independent reflns	1565
reflns collected (15–22.5°)	5202
independent reflns	1446
independent reflns (2 sets merged)	1866
reflns > 2σ	963
R_1	0.027
R_2	0.023
std dev, observn of unit wt	1.06
max param shift/est error	0.01

Table III. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, $Å^2$
Mn	0.35547 (5)	0.21922 (4)	0.58803 (4)	3.29 (1)
O1	0.1838 (2)	0.2601 (2)	0.7090 (2)	6.27 (8)
O2	0.5012 (2)	0.3390 (2)	0.6818 (2)	6.39 (9)
O3	0.3244 (3)	0.3709 (2)	0.4654 (2)	6.42 (9)
C1	0.3826 (3)	0.0861 (2)	0.6546 (3)	4.2 (1)
C2	0.4623 (3)	0.1070 (2)	0.5965 (3)	4.1 (1)
C3	0.4391 (3)	0.1267 (2)	0.5083 (3)	4.1 (1)
C4	0.3344 (3)	0.1246 (2)	0.4819 (3)	4.2 (1)
C5	0.2565 (4)	0.1017 (3)	0.5412 (3)	4.1 (1)
C6	0.2821 (3)	0.0532 (3)	0.6206 (3)	4.5 (1)
C7	0.4036 (5)	0.0743 (3)	0.7523 (4)	7.8 (2)
C8	0.5763 (4)	0.1102 (3)	0.6277 (4)	7.4 (2)
C9	0.5264 (4)	0.1420 (3)	0.4410 (4)	7.6 (1)
C10	0.3055 (4)	0.1485 (3)	0.3866 (3)	7.4 (2)
C11	0.1409 (4)	0.1068 (3)	0.5158 (4)	7.1 (1)
C12	0.2170 (4)	−0.0010 (3)	0.6646 (4)	7.8 (2)
C13	0.2512 (3)	0.2466 (3)	0.6618 (3)	3.96 (9)
C14	0.4444 (3)	0.2907 (3)	0.6447 (3)	4.2 (1)
C15	0.3348 (3)	0.3110 (2)	0.5135 (3)	4.4 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table IV. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, $Å^2$
H7A	0.463	0.108	0.768	10.1*
H7B	0.345	0.096	0.785	10.1*
H7C	0.414	0.011	0.765	10.1*
H8A	0.578	0.121	0.689	9.6*
H8B	0.609	0.053	0.615	9.6*
H8C	0.612	0.158	0.598	9.6*
H9A	0.550	0.084	0.420	9.9*
H9B	0.500	0.177	0.393	9.9*
H9C	0.582	0.174	0.468	9.9*
H10A	0.341	0.202	0.369	9.5*
H10B	0.233	0.158	0.383	9.5*
H10C	0.325	0.099	0.349	9.5*
H11A	0.133	0.148	0.469	9.2*
H11B	0.118	0.048	0.498	9.2*
H11C	0.102	0.127	0.565	9.2*
H12A	0.242	−0.052	0.697	8.2*
H12B	0.144	0.010	0.665	8.2*

[a] Starred atoms were refined isotropically.

the maximum peak height on the electron density difference map was 0.18 $e^-/Å^3$. Weights used in refinement are $1/s^2(F)$, where $s^2(F)$ is the larger of two estimates of error, the propagated error due to counting error, or the estimated error based on agreement of equivalent reflections. All crystallographic calculations were made by using the SDP set of programs of Enraf-Nonius Corporation. The crystal data are summarized in Table II, and the positional parameters are given in Tables III and IV.

Reaction of 2 with NH_4PF_6. To compound 2 (0.153 g, 0.512 mmol) under argon in a 50-mL Schlenk flask was added 25 mL of dry, deoxygenated THF via cannula. The resulting solution was transferred to a second flask containing NH_4PF_6 (0.152 g, 1.00 mmol) in 5 mL of THF. After the solution was stirred for 30 min, the product, identified by FTIR and ^1H NMR as the reprotonated cation 1, was formed in quantitative yield.

Synthesis of (η^6-$C_6(CH_3)_5(CH_2C(O)Ph)$)$Mn(CO)_3PF_6$ (5). To compound 2 (0.153 g, 0.512 mmol) under argon in a 50-mL Schlenk flask was added 25 mL of dry, deoxygenated THF via cannula. After syringe addition of benzoyl chloride (0.232 mL, 0.281 g, 2.00 mmol), the resulting solution was stirred for 5 h. The reaction appeared to be quantitative by FTIR spectroscopy. Following metathesis with excess NH_4PF_6 in acetone, the solvent was removed by rotary evaporation. After washing with diethyl ether, the solids were redissolved in minimal acetone and recrystallized with ether. The isolated yield was 0.454 g (82.6%) of golden yellow crystals. The FTIR and ^1H NMR data are found in Table I. The other analytical data were as follows: MS (FAB, thioglycerol matrix) *m/e* (% abundance, assignment) 405 (18.17, M^+), 321 (29.34, $[M - 3CO]^+$), 301 (100.00, $[M - PhCO + H]^+$), 245 (19.53, $[M - PhCO - 2CO + H]^+$), 217 (74.04, $[M - PhCO - 3CO + H]^+$), 161 ($[M - PhCO - 3CO - Mn]^+$). Anal. Calcd for $C_{22}H_{22}F_6MnO_4P$: C, 48.02; H, 4.03. Found: C, 48.14; H, 4.15.

Synthesis of (η^6-$C_6(CH_3)_5(CH_2CCl_3)$)$Mn(CO)_2Cl$ (6). To compound 2 (0.153 g, 0.512 mmol) under argon in a 50-mL Schlenk flask was added 25 mL of dry, deoxygenated THF via cannula. Upon addition of a large excess of CCl_4 with stirring in the laboratory light, the contents of the flask immediately turned red-purple. An FTIR spectrum recorded at this time indicated that the reaction had gone to completion. However, the product was not stable in the light, and after 30 min, the red color was gone. The reaction was repeated in the solvent d^6-benzene in a 5-mm NMR tube to obtain the ^1H NMR spectrum. The FTIR and ^1H NMR data are found in Table I. The instability of 6 prevented further spectroscopic characterization and precluded isolation in pure form.

Synthesis of (η^6-$C_6(CH_3)_5(CH_2CDCl_2)$)$Mn(CO)_2Cl$ (7). Combination of compound 2 (0.136 g, 0.456 mmol) with a large excess of $CDCl_3$, using the procedure described for the synthesis of 6, resulted in immediate formation of red-purple coloration. After 5 min, the IR spectrum indicated complete reaction. The product was more stable in light and air than 6. After addition of silica gel, the solvent was removed from the flask via rotary evaporation. After placing the resulting red powder onto a dry packed silica gel column and covering the red layer with a layer of pure silica gel, the column was eluted with pure hexane to remove any organic byproducts. Following elution of the column with 20/80 acetone/hexane, the solvent was removed from the solution via rotary evaporation. The isolated yield was 0.100 g (56.0%) of red-purple crystals. The FTIR and ^1H NMR data are found in Table I. The other analytical data were as follows: MS (EI) *m/e* (% abundance, assignment) 245 (100.0, $[M - Mn - 2CO - Cl]^+$), 247 (55.25, $[M - Mn - 2CO - Cl]^+$). Anal. Calcd for $C_{15}H_{17}DCl_3MnO_2$: C, 45.89; H, 4.87. Found: C, 45.21; H, 4.67.

Synthesis of (η^6-$C_6(CH_3)_5(CH_2CHBr_2)$)$Mn(CO)_2Br$ (8). Combination of compound 2 (0.149 g, 0.495 mmol) with a large excess of $CHBr_3$, using the procedure followed in the synthesis of 6, led to the formation of red-purple coloration at a rate that was noticeably slower than observed with the chlorocarbon reactions. After the mixture was stirred for 20 min, the complex was purified in the same manner as 7. The isolated yield was 0.201

g (77.4%) of red-purple crystals. The FTIR and ^{1}H NMR data are found in Table I. The other analytical data were as follows: MS (FAB, sulfolane matrix) *m/e* (% abundance, assignment) 643 (34.63, [M + sulfolane + H^+), 644 (22.75, $[M + sulfolane + H]^+$), 645 (97.34, $[M + sulfolane + H]^+$), 646 (32.99, $[M + sulfolane + H]^+$), 647 (100.00, $[M + sulfolane + H]^+$) 648 (19.88, $[M + sulfolane + H]^+$), 649 (31.15, $[M + sulfolane + H]^+$). Anal. Calcd for $C_{15}H_{18}Br_3MnO_3$: C, 34.32; H, 3.46. Found: C, 33.87; H, 3.28.

Synthesis of (η^6-$C_6(CH_3)_5(CH_2I)$)$Mn(CO)_3PF_6$ (9). To compound **2** (0.140 g, 0.468 mmol) under argon in a 50-mL Schlenk flask was added 25 mL of dry, deoxygenated THF via cannula. To a second flask was added 0.119 g (0.468 mmol) of I_2, which was dissolved in 10 mL of THF. After addition of the first solution to the second solution via cannula, the mixture was stirred for 4 h. The solution FTIR spectrum suggested a cationic complex was formed. Following metathesis of the product with a 2-fold excess of NH_4PF_6 in acetone, the solvent was removed by rotary evaporation. The solid, after being washed with diethyl ether followed with hexane to remove major impurities, was dissolved in acetone and recrystallized by the addition of diethyl ether. The isolated yield was 0.211 g (78.9%) of yellow solid. The FTIR and ^{1}H NMR data are found in Table I. The other analytical data were as follows: MS (FAB, sulfolane) *m/e* (% abundance, assignment) 427 (100.00, M^+), 343 (61.27, $[M - 3CO]^+$), 301 (21.08, $[M - I + H]^+$), 272 (2.74, $[M - CO - I]^+$), 245 (5.02, $[M - 2CO - I + H]^+$), 217 (26.01, $[M - 3CO - I + H]^+$), 161 (70.01, $[M - 3CO - I - Mn]^+$). Anal. Calcd for $C_{15}H_{17}F_6IMnO_3P$: C, 31.49; H, 2.99. Found: C, 31.60; H, 3.20.

Synthesis of (η^6-$C_6(CH_3)_5(CH_2CH_3)$)$Mn(CO)_2I$ (10). Complex **2** (0.160 g, 0.534 mmol) was added to a 50-mL Schlenk flask. After purging the reaction vessel with argon and addition of 25 mL of dry, deoxygenated THF, deoxygenated CH_3I (0.1 mL) was added via syringe. The mixture turned red over a period of 8 h in laboratory light. Following addition of silica (5 mL), the solvent was removed on a rotary evaporator. The resulting red powder was completely dried under vacuum, placed onto a dry packed silica gel column, and covered with pure silica. The column was first eluted with hexane to remove any organic byproducts. Elution with 10/90 acetone/hexane permitted isolation of a red band, while a yellow band, which moved very slowly, was subsequently removed with pure acetone. The acetone was removed from the red solution by rotary evaporation. A yield of 0.125 g (56.5%) of purple crystals was removed by filtration from the remaining hexane. The FTIR and ^{1}H NMR are found in Table I. The second material was cationic and was purified in the same manner as **5**. It was identified as **1** by FTIR and ^{1}H NMR. Anal. Calcd for $C_{15}H_{20}IMnO_2$: C, 43.50; H, 4.87. Found: C, 43.54; H, 5.01.

Reaction of 2 with Bu_3SnH. Complex **2** (0.123 g, 0.410 mmol) was added to a 50-mL Schlenk flask. After the flask was purged with argon, it was filled with 25 mL of dry, deoxygenated THF. To the stirring mixture was added 0.41 mL (0.410 mmol) of 1 M Bu_3SnH in THF. After 30 min, the FTIR spectrum of the reaction mixture showed an approximately 50/50 mixture of starting material and **endo-4**. The ^{1}H NMR of the isolated complex confirmed this assignment. Addition of 2 equiv of Bu_3SnH, using the same procedure as described for the addition of 1 equiv, produded **endo-4** quantitatively as observed by FTIR spectroscopy.

Attempted Catalytic Hydrogenation of 2. To a pressure reaction apparatus, containing 0.100 g of 2% Pd/C commercial catalyst and 0.128 g (0.425 mmol) of **2** was added approximately 25 mL of dry, deoxygenated THF through the syringe port via cannula. After the mixture was stirred under 40 psi H_2 for 6 h, no reaction was observed by FTIR spectroscopy. The activity of the catalyst was verified by quantitative hydrogenation of cyclohexene to cyclohexane under identical conditions in 6 h.

Results and Discussion

Synthesis and Characterization of 2. This complex was originally identified as a minor product in the reaction of KH and **1** in pure THF which gave **exo-4** as the major product. It was subsequently discovered that the synthesis in hexane with addition of some THF, apparently to solubilize the KH, markedly increased the formation of **2** and gave much less **exo-4**. The FTIR spectrum from the reaction mixture displayed features that were not consistent with spectra previously reported for derivatives of (arene)manganese tricarbonyl. The most obvious feature of the spectrum was the presence of the bands associated with the terminal and bridging carbonyls of $[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2]_2$ (**20**).[10] The reaction system also contained large amounts of precipitate, also identified as **20**. The second unusual feature of the spectrum was the three bands observed in the terminal carbonyl region that were similar but not the same as the bands observed for a mixture of the endo- and exo isomers of **4**. The shapes of the peaks suggested the presence of two sets of overlapping bands. It was presumed that one of the species was either the endo- or exo isomer of **4**. A ^{1}H NMR spectrum (d_6-benzene) of the solids isolated from the reaction mixture by sublimation indicated that there were three products present. The first two products were identified as hexamethylbenzene and **exo-4**. The third species had peaks associated with inequivalent arene methyls and a peak in the methylene region. This suggested that a reaction had taken place at the hexamethylbenzene ring. The ^{1}H NMR data, considered in conjunction with the three bands in the FTIR spectrum, suggested that the $Mn(CO)_3$ fragment was uneffected. The parent peak at *m/e* 300 in the mass spectrum of the isolated material suggested that **2** had been formed by deprotonation of a ring methyl of **1**. The resulting ligand, η^5-pentamethylbenzyl, has **3** as the only precedent in the literature.[5] In the ^{13}C NMR spectrum of **2** the peak at 223.7 ppm is assigned to the CO carbons and at 146.4 ppm to the unbound ring carbon, and the exocyclic methylene carbon is a triplet at 84.7 ppm, with a ^{13}C–^1H coupling constant of 158 Hz. The ^{13}C chemical shifts and the coupling constant agree very well with the NMR data collected by Astruc[5a] for **3**.[11]

Not all strong bases are observed to deprotonate **1** to form **3**. For example, it has been observed that OH^- reacts with **1** in mixed water/acetone solvent to form **20** quantitatively upon mixing.[12] In methanol, OH^- reacts with **1** to form $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2(C(O)Me)$.[2c] These observations lead to the suggestion that sterically bulky bases should be more likely to form the desired product. Use of the sterically hindered base $Li(N(i\text{-}Pr)_2)$ with **1** in hexane resulted in the formation of **2** in 80% spectroscopic yield. Solvent removal produced an oil from which **2** could not be isolated by sublimation. The bases, $LiC(CH_3)_3$ and $KOC(CH_3)_3$, were observed to react with **1** to form 20% spectroscopic yields of **2** in THF. The reaction of **1** with KEt_3BH and $K(i\text{-}PrO)_3BH$ gave **2** in 5–10% spectroscopic yield, **20** in 5–10% yield, and a mixture of **endo-4** and **exo-4** in 75–85% yield. The relative ratios of endo/exo were ~25/75 for $K(i\text{-}PrO)_3BH$ and ~75/25 for KEt_3BH. This observation supports the proposal that most hydride sources can act as strong bases in addition to acting as nucleophiles. With KH, as observed in this study, the behavior can be controlled by selection of solvent. However, it was observed that both $NaBH_4$ and $n\text{-}Bu_4NBH_4$ did not form any **20** or **2** in THF. Instead, they formed **endo-4** and/or **exo-4**.

As was previously discussed, numerous hydride sources have been reported to react with **1** to form both the endo and exo isomers of **4**. It was observed in these studies that the reaction of KH with **1** to form **4** gave exclusively the

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[10] Schlom, P. J.; Baenziger, N. C.; Eyman, D. P. Manuscript in preparation.

[11] ^{1}H NMR (δ, ppm, C_6D_6): C_5H_5, 3.48 (s, 5); CH_2, 3.60 (s, 2); CH_3, 2.07 (s, 9), 1.76 (s, 6), ^{13}C NMR (δ, ppm, C_6D_6): C_5H_5, 75.64; CH_3, 16.31, 16.9; cyclohexadienyl, 145.0, 90.1, 83.5, and 57.05 ($J_{C\text{-}H}$ = 156.5 Hz).

[12] Schauer, S. J.; Eyman, D. P. Manuscript in preparation.

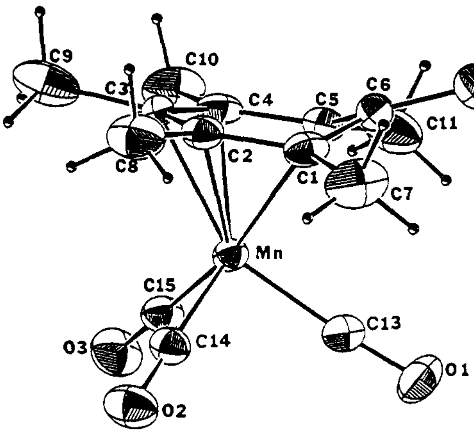

Figure 1. ORTEP diagram for **2**.

exo isomer. The complex **endo-4** has been postulated to form by direct exo attack of hydride on the arene ring of **1**, whereas evidence has been presented to support the proposal that the exo isomer is formed in the decomposition of (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$(C(O)H) (**21**).[13] This may be explained by considering migration of the hydride to the endo side of the ring either directly or from manganese after ring slippage and carbonyl migratory deinsertion of **21**. The observed product distribution suggests that the reaction of **1** with KH is limited to nucleophilic attack at a bound carbonyl to give **21** or to deprotonation of an arene ring methyl. The lack of **endo-4** suggests that either KH cannot attack the ring from the exo side or that it is consumed by a subsequent reaction after formation.

The source of **20** in the reaction mixture has yet to be determined. Early in these studies, it was postulated that the dimer was the result of reaction between **2** and **endo-4** because no **endo-4** was found in the reaction mixture. It was thought that possibly the exocyclic methylene of **2** removes the exo hydrogen of **endo-4** to produce, after rearrangement, two identical 19-electron radicals that could both lose CO and couple, forming **20**. This idea was dismissed after the observation that a mixture of pure **2** and pure **endo-4** does not react in THF to form **20**. It was observed that the addition of **endo-4** to **2** in deoxygenated THF stopped the formation of **20**, which was always observed as a slow reaction when pure **2** was dissolved in dry, deoxygenated THF.

Crystallographic Study of 2. The crystallographic study was undertaken to establish the molecular structure of **2** and to compare it with the published structure of **3**. The results of the X-ray crystallographic study are illustrated in the ORTEP plot in Figure 1. Selected distances and angles are listed in Table V. As Figure 1 indicates, the molecule has a "piano stool" structure with an η^5-coordinated pentamethylbenzyl ligand. The "legs" of this structure are oriented in an eclipsed configuration relative to the ring carbons.

The short C–C distance (1.332 (6) Å) between the unbound ring carbon and the exocyclic methylene carbon is consistent with a C–C double bond. Because **3** was reported to have a rotation of the C12(H12A,B) grouping about the bond to C6 and a location of C12 below the C5/C6/C1 plane, special consideration was given in the last refinement steps to determine if similar features were evident in this molecule. All hydrogens atoms were located in difference electron density maps. For the methyl groups, C7, C8, C9, C10, C11, the hydrogen positions were "regularized" and held in fixed positions during subsequent refinement. With the H12A,B atoms fixed in the positions as found from electron density maps, the refinement converged at $R = 0.029$ and $R_w = 0.039$. From the electron density difference map, H12A and H12B appeared such that C6–C12–H12A = 116.9°, C12–H12A = 1.14 Å; C6–C12–H12B = 109.8°, C12–H12B = 1.09 Å; and H12A–C12–H12B = 132.2°. The H12A and H12B atoms were idealized in the C6/C12/H12A/H12B plane with C–H bond distances of 0.95 Å and angles of 121, 121, and 118°. Refinement with all H atoms fixed gave R's of 0.026 and 0.034. Adjusting the PWT factor in the weights to zero gave the R's reported for the final refinement of 0.026 and 0.023. From this final model, the angles between plane normals are C1/C2/C3/C4/C5 vs C5/C6/C1 = 32 (2)°, C1/C2/C3/C4/C5 vs C5/C6/C1/C12 = 27 (1)°, and C6/C12/H12A/H12B vs C5/C6/C1 = 38°. The displacement of C12 from the plane of C5/C6/C1 is −0.021 (2) Å. From this value and the C6–C12 bond distance, the angle between the C5/C6/C1 plane and the C6–C12 vector was determined to be 9.1 (9)°. The extent of rotation of the CH_2 about the C6–C12 double bond is uncertain since no error terms are available from the hydrogen atom positions.

Table V. Selected Bond Lengths and Angles for (η^5-$C_6(CH_3)_5({=}CH_2)$)Mn(CO)$_3$

	Bond Lengths (Å)		
Mn–C1	2.223 (4)	Mn–C13	1.793 (5)
Mn–C2	2.144 (4)	Mn–C14	1.773 (5)
Mn–C3	2.112 (5)	Mn–C15	1.779 (5)
Mn–C4	2.145 (5)	C13–O1	1.143 (5)
Mn–C5	2.254 (5)	C14–O2	1.161 (5)
		C15–O3	1.151 (5)
C1–C2	1.386 (6)	C1–C7	1.523 (7)
C2–C3	1.407 (7)	C2–C8	1.539 (6)
C3–C4	1.403 (7)	C3–C9	1.535 (7)
C4–C5	1.389 (7)	C4–C10	1.538 (7)
C5–C6	1.439 (6)	C5–C11	1.536 (7)
C1–C6	1.471 (7)	C6–C12	1.332 (6)
	Bond Angles (deg)		
C13–Mn–C14	92.6 (3)	C2–C3–C4	118.5 (5)
C13–Mn–C15	96.9 (2)	C2–C3–C9	120.8 (5)
C14–Mn–C15	87.7 (2)	C4–C3–C9	120.8 (5)
C3–C4–C5	120.6 (5)	C3–C2–C1	119.8 (5)
C3–C4–C10	119.7 (5)	C3–C2–C8	119.4 (5)
C5–C4–C10	119.7 (5)	C1–C2–C8	120.8 (5)
C4–C5–C6	120.1 (5)	C2–C1–C6	119.7 (4)
C4–C5–C11	121.4 (6)	C2–C1–C7	121.1 (6)
C6–C5–C11	117.1 (5)	C6–C1–C7	117.5 (5)
C5–C6–C1	109.5 (5)	C5–C6–C12	124.9 (6)
		C1–C6–C12	124.6 (5)

Reactions of 2. Examination of the reactivity of **2** has led to the observation of some expected reactions plus some unexpected reactions. The first reactions investigated was the protonation of **2** using NH_4PF_6 in THF. The reaction, which was observed by FTIR spectroscopy, proceeded quantitatively in seconds to form **1** (Scheme I). This reaction shows that the coordinated η^5-pentamethylbenzyl ligand is the strong conjugate base of a relatively weak acid. It is anticipated that any Bronstead acid will react with **2** in a similar manner to form **1**.

The nucleophilic character of the exocyclic methylene of **2** was explored by observing its reaction with benzoyl chloride. This reaction, although apparently slower than that reported for **3**,[5b] was nearly quantitative as determined by FTIR spectroscopy. The FTIR spectrum of the product **5** (Scheme I) had carbonyl stretching bands at 2053 and 1991 cm^{-1}, characteristic of terminal carbonyls of cationic manganese tricarbonyl complexes, and a band at 1718 cm^{-1}, characteristic of ketones. The product was relatively air stable, which allowed it to be purified by chromatography

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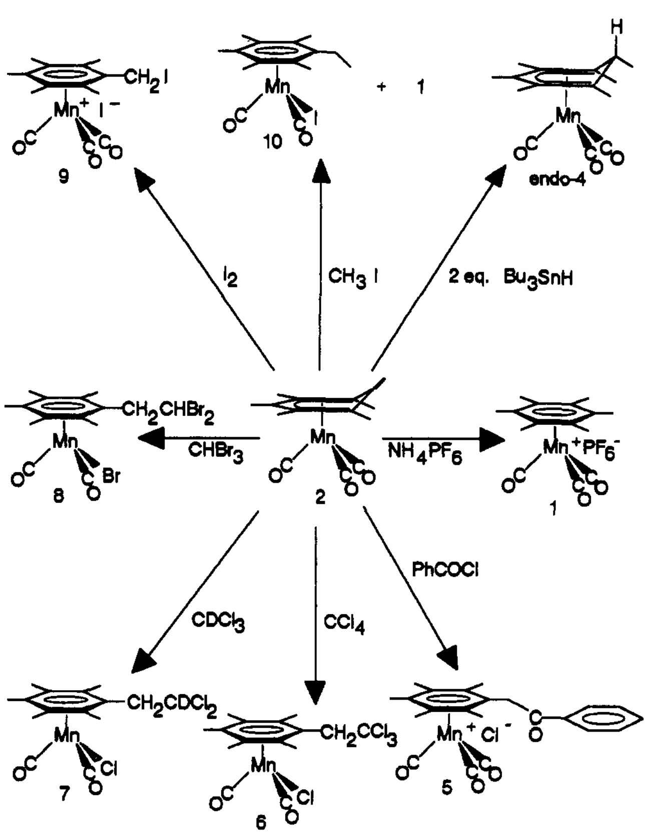
[13] Wilmoth, M. A.; Bernhardt, R. J.; Eyman, D. P.; Huffman, J. C. *Organometallics* 1986, *5*, 2559.

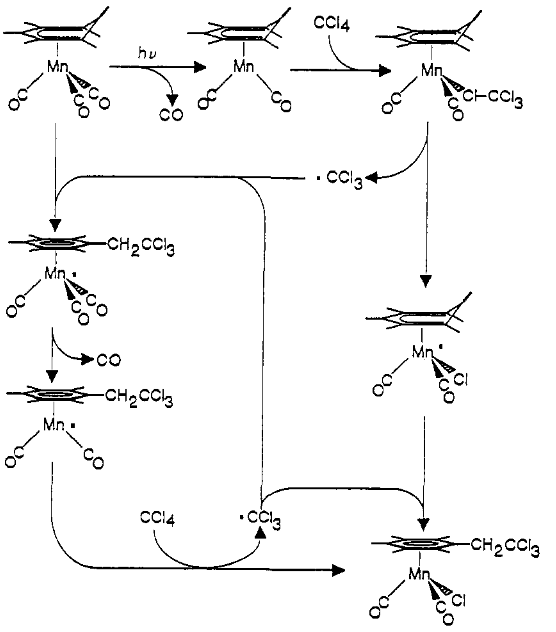
Scheme I



and recrystallization after metathesis in acetone with NH_4PF_6. The product was characterized by ^1H NMR spectroscopy and FAB mass spectrometry using a thioglycerol matrix. The molecular ion was observed as well as a fragmentation pattern characteristic of (arene)manganese tricarbonyl complexes.

During an approximate density determination for a crystal of **2** using a crystal flotation technique, it was observed that solid **2** reacts with pure CCl_4 to form a red product. When CCl_4 was added to **2** in THF in the laboratory light, **2** was observed to completely react to give a red solution. The FTIR spectrum of the solution had new peaks at 1979 and 1932 cm^{-1}, which are characteristic of (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$Cl (**22**).[4] The red faded completely within 30 min in the laboratory light. It became evident that the formation of **6** was induced by light, but **6** itself was unstable in light. This was consistent with the observation that **22** was light sensitive in THF solution and slowly decomposed even in the solid form in light. The product complex **6** could not be successfully isolated as the pure solid from the reaction mixture. The reaction was repeated in a 5-mm NMR tube in which **2** was dissolved in d_6-benzene, while in the inert atmosphere box. The septum-sealed tube was removed from the box, and CCl_4 was added via syringe. The tube was shaken in the light and then was wrapped in tissue paper to prevent photodecomposition of the product, until the ^1H NMR spectrum could be recorded. The recorded ^1H NMR spectrum indicated the presence of five methyl groups in 1:2:2 ratio and one methylene group. This observation combined with the FTIR spectrum is consistent with the structure shown in Scheme I. Similar 1,n reactions (n = 3, 4) of CCl_4 have been reported with other organometallic species.[14]

Scheme II



To obtain additional information about the structure of **6**, the reaction of **2** with $CDCl_3$ was studied. This reaction, somewhat slower than the CCl_4 reaction, produced the red product **7** (Scheme I), which was sufficiently stable to allow isolation on a short silica gel column. The FTIR spectrum of **7** was nearly identical with that of **6**, but the ^1H NMR spectrum of **7** was different in that the methylene resonance was split into a triplet by the deuterium in the $CDCl_2$ group. The EI mass spectrum of **7** did not show the molecular ion, but the ions associated with the anticipated free arene were observed. The isotope pattern of the peaks associated with the arene showed that it contained two Cl's.[15] Complex **7** eventually decomposed in light after several days.

The reaction of $CHBr_3$ with **2** in THF gave results that further support the interpretation of the reaction of **2** with CCl_4. This reaction, which proceeded even slower than the reaction of **2** with $CDCl_3$, produced a red solution that appeared relatively stable in laboratory light. Liquid chromatographic isolation and storage of the product **8** were performed assuming that the solid was light sensitive. The FTIR spectrum gave two carbonyl bands similar to those of (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$Br.[4] The ^1H NMR spectrum displayed a doublet and a triplet consistent with the presence of the CH_2CHBr_2 group. The FAB mass spectrum in sulfolane led to the structure proposed in Scheme I. The isotope pattern of the highest molecular weight ions was consistent with computer-simulated patterns for a species containing three Br's. It should also be noted that this cluster of peaks contained molecular ion plus H and sulfolane (the FAB matrix). The fragmentation was consistent with (η^6-$C_6(CH_3)_2(CH_2CHBr_2)$)Mn(CO)$_2$Br, in which individual fragments had characteristic isotope patterns indicating the number of bromine atoms present.

A proposed radical chain mechanism for reactions of halocarbons with **2** is presented in Scheme II. The initiation step of the reaction, photodissociation of CO from **2**, generates a reactive 16e$^-$ species. This species reacts with the halocarbon, CH_nX_{4-n} (n = 0, 1), to form a coordinated halocarbon complex similar to those reported or

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[14] (a) Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1989**, *28*, 3837. (b) Green, M. L. H.; Pratt, L.; Wilkinson, G. J. *J. Chem. Soc.* **1959**, 3753. (c) Dahl, T.; Moberg, C. *Acta. Chim. Scand.* **1973**, *27*, 728.

[15] The observed isotopic cluster matched a computer-simulated cluster for the molecular formula of the arene $C_6(CH_3)_5CH_2CDCl_2$.

proposed in many other cases.[16] The C–X bond of the coordinated halocarbon, weakened by coordination, homolytically cleaves to form CH_nX_{3-n} ($n = 0, 1$) radical and $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_2X$ radical. An alternative explanation for the formation of the halocarbon radical would involve oxidative addition of CH_nX_{4-n} followed by homolysis of the metal–carbon bond to produce the radical. For steric reasons, we favor the halocarbon complex mechanism. In the next step, the CH_nX_{3-n} radical reacts with a second molecule of **2** at the exocyclic methylene to produce a species that after rearrangement to give hexahapticity produces a $19e^-$ metal-centered radical. The $19e^-$ species spontaneously loses a CO to form a $17e^-$ complex, which abstracts a halogen from a second equivalent of CH_nX_{4-n} to produce the final product and regenerate CH_nX_{3-n} radical. This step could possibly involve another halocarbon complex. This completes one full cycle of the propagation process. The termination step can occur either by CH_nX_{3-n} radical coupling or by reaction of CH_nX_{3-n} with the $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_2X$ radical. The second of these termination steps produces the final product.

This mechanism is consistent with several observations made during studies of the reaction of **2** with the halocarbons, CCl_4, $CHCl_3$, and $CHBr_3$. When the reactants were combined in the dark, and the reaction mixture was not exposed to laboratory light, no reaction was observed. When the reaction mixture was briefly exposed to light and then subsequently kept in the dark, the reaction proceeded to completion but at a reduced rate relative to that observed when the system was continually exposed to light.

Addition of the known radical mechanism inhibitor, 9,10-DHA, to the $CHCl_3$ reaction mixture resulted in retardation of the reaction so that the half-life increased by more than a factor of 100. Similar retardation of the reaction rate was observed for CCl_4 and $CHBr_3$. This retardation is probably due to disruption of the propagation cycle by reaction of 9,10-DHA with the halocarbon radical. This proposal is consistent with the observation of CH_2Cl_2 in the ^1H NMR spectrum of the $CHCl_3$ reaction mixture. In addition, the reaction did not proceed in the dark after brief exposure to light when 9,10-DHA was present in the reaction mixture. These observations suggest that in the presence of 9,10-DHA the light reaction proceeds as a photodriven process represented by the five steps across the top and down the right-hand side of Scheme II. The halocarbon radical involved in the final step is probably formed by the removal of halogen from a reactant halocarbon by hydroanthracene, which is produced by loss of hydrogen from 9,10-DHA, to the initially formed halocarbon radical.

The reaction of I_2 with **2**, followed by subsequent metathesis with NH_4PF_6, produced only one product, **9**, probably by nucleophilic attack of the exocyclic methylene on I_2. The absence of iodine in the metal coordination sphere suggests that the radical chain mechanism is not operative. The reaction of I_2 with **2** gave rapid formation of **9** but produced no detectable dimeric product which could have arisen by reaction of **2** with **9**.

The nucleophilic character of **2**, displayed in the reaction with benzoyl chloride, suggests that other simple nucleophilic displacement processes should be possible. The very slow reaction of **2** with CH_3I, rather than generating a product arising from nucleophilic displacement of halide, gave two products, **1** and **10**. The formation of **10**, which can be explained by the mechanism outlined in Scheme II, would involve an intermediate methyl iodide complex. The second product of this reaction, **1**, which is also observed in very small quantities in the reactions of **2** with CCl_4, $CHCl_3$, and $CHBr_3$, is isolated in greater than 40% yield after metathesis with NH_4PF_6. These observations may relate to the anticipated slower homolytic cleavage of the iodine–carbon bond in the methyl iodide complex to form a methyl radical. The fastest reaction of **2** in the presence of methyl iodide is apparently the formation of **1** by the same mechanism, which leads to its formation in the reactions of **2** with the other halocarbons. Although we have no evidence to support a proposed mechanism for the formation of **1**, it may occur by an electron transfer from **2** to the halocarbon. The resulting metal-centered radical cation, $(\eta^5\text{-}C_6(CH_3)_5({=}CH_2))Mn(CO)_3^{\bullet+}$, after rearrangement to the exocyclic methylene-centered radical, $(\eta^6\text{-}C_6(CH_3)_5(CH_2))Mn(CO)_3^{\bullet+}$, could extract a hydrogen atom from solvent THF to produce **1**. Astruc observed similar results in the reactions of **3** with various alkyl halides.[5b]

The reaction of **2**, at the exocyclic methylene, with a hydrogen atom source may furnish a reaction pathway for the slow decomposition of **2** in THF with the formation of **20**. The addition of 9,10-DHA to **2** in THF did not give products consistent with transfer of a hydrogen atom to **2** but did terminate the slow conversion of **2** to **20**.[17] This observation suggests that **2** does not exist in solution in radical form but that the conversion of **20** involves a radical pathway. When Bu_3SnH was used as a hydrogen atom source, 1 equiv reacted with only $^1/_2$ equiv of **2** to produce $^1/_2$ equiv of **endo-4**, as identified by IR and ^1H NMR spectroscopies. Addition of 2 equiv of Bu_3SnH to **2** gave quantitative formation of **endo-4**.

It was observed that Me_3NO would not transfer an oxygen atom to the exocylic double bond of **2** to form an epoxide or to one of the carbonyl carbons to form an intermediate CO_2 complex. The latter observation was somewhat surprising because Me_3NO usually reacts with metal carbonyls that have carbonyl stretching frequencies above 2000 cm^{-1}.[18] Since the highest CO stretching frequency of **2** is at 2008 cm^{-1}, it was anticipated that the

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reaction might proceed to form a Me_3N complex after the release of CO_2.

Astruc found that **3** could be hydrogenated by using Pd/C with 1 atm of hydrogen in less than 1 h under ambient conditions to form a previously reported cyclohexadienyl complex.[5b] The hydrogenation of the exocyclic double bond of **2** using 2% Pd/C catalyst of established activity did not proceed even at 40 psi hydrogen over a 12-h period. This is a perplexing observation because **2** should be no more sterically hindered to hydrogenation than **3** and the anticipated product, **endo-4**, is a stable species.

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Supplementary Material Available: Table of general displacement parameter expressions and a least-squares plane drawing (2 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Reactivity of $Ru(H_2)(H)_2(PPh_3)_3$: Dimerization To Form $(PPh_3)_2(H)Ru(\mu\text{-H})_3Ru(PPh_3)_3$ and Decarbonylation of Ethanol under Mild Conditions

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Loss of H_2 from $RuH_4(PPh_3)_3$ (**1**) leads to formation of $RuH_2(PPh_3)_3$; this intermediate has been shown to dimerize with loss of a phosphine to form $(PPh_3)_2(H)Ru(\mu\text{-H})_3Ru(PPh_3)_3$ (**3**). Formation of $RuH_2(PPh_3)_3$ in the presence of ethanol leads to decarbonylation of the alcohol and formation of $RuH_2(PPh_3)_3(CO)$ (**7**), under the mild conditions of nonbasic solutions at 25 °C. Reaction of **1** with methanol, 1-propanol, or benzyl alcohol at 60 °C also results in decarbonylation and formation of **7**. The mechanisms of formation of these complexes are discussed.

Introduction

Recognition of the fact that a dihydrogen molecule can act as an intact metal-bound ligand[1] has resulted in many studies regarding the basic premises of oxidative addition of H_2. The kinetics and thermodynamics of rotation, dissociation, and oxidative addition of the H_2 molecule have been studied,[2] as well as deprotonation[3] and isotopic substitution.[1,4] However, one of the more valuable qualities of an H_2 ligand is its lability; dissociation of H_2 provides an extremely reactive unsaturated metal complex, in some cases retaining hydride ligands, which can act as reducing equivalents in subsequent reactions.[5]

We report here our observations regarding the facile and reversible dissociation of H_2 from $RuH_4(PPh_3)_3$[6] (postulated to be $Ru(H_2)(H)_2(PPh_3)_3$[7,8]), a process that leads to formation of the reactive 16-electron intermediate $RuH_2(PPh_3)_3$. We have found that dimerization and loss of a phosphine from this intermediate yields $(PPh_3)_2(H)Ru(\mu\text{-H})_3Ru(PPh_3)_3$, while reaction with ethanol at 25 °C results in decarbonylation and formation of $RuH_2(CO)(PPh_3)_3$.[9]

Experimental Section

General Procedures. All manipulations were carried out under a prepurified atmosphere of the indicated gas, using standard Schlenk and drybox techniques. Solvents were dried and deoxygenated by using conventional procedures. $RuCl_2$-

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