

# Synthesis of Dimanganese Complexes from the Reduction of Cationic Tricarbonylmanganese Styrene Derivatives

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**Abstract:** Styrene derivatives of the manganese tricarbonyl cation have been synthesized through the reaction of  $\text{Mn}(\text{CO})_5\text{BF}_4$  with excess styrene derivatives in refluxing  $\text{CH}_2\text{Cl}_2$ , and their chemical reduction has been studied. Treatment of [(styrene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> (**1(H)**) with 1.0 equiv of  $\text{Cp}_2\text{Co}$  in  $\text{CH}_2\text{Cl}_2$  or THF led to isolation of bimetallic **2(H)**. Treatment of [(1,1-diphenylethylene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> (**1(Ph)**) with 1.0 equiv of  $\text{Cp}_2\text{Co}$  in  $\text{CH}_2\text{Cl}_2$  yielded three different bimetallic compounds, **2(Ph)**, **3(Ph)**, and **4(Ph)**. The molecular structures of **2(H)**, **2(Ph)**, **3(Ph)**, and **4(Ph)**, determined by X-ray crystallography, were quite different from those of known bimetallics. Compounds **2(H)** and **2(Ph)** have the  $\eta^5:\eta^3$  bonding pattern, where a  $\text{Mn}(\text{CO})_4$  moiety is coordinated to the styrene in an  $\eta^3$ -fashion. Compound **3(Ph)** has the  $\eta^5:\eta^5$  bonding pattern with two  $\text{Mn}(\text{CO})_3$  moieties  $\pi$ -coordinated to a ligand derived from a coupling of 1,1-diphenylethylenes through the *ipso* carbon atom. Compound **4(Ph)** has a metal–metal bond with no bridging carbonyls; one of the manganese atoms is coordinated by 1,1-diphenylethylene and two carbonyls and the other by the  $\text{Mn}(\text{CO})_5$ . There are multiple reduction pathways available to (arene) $\text{Mn}(\text{CO})_3$ <sup>+</sup> cations having a vinyl substituent on the arene ring.

## Introduction

The reductive activation of organometallic complexes has found numerous applications.<sup>1</sup> Recently, it has been shown that reduction of [(arene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> complexes can lead to arene ring-slippage,<sup>2</sup> CO substitution,<sup>3</sup> and bimetallic species resulting from carbon–carbon and metal–metal bond formation.<sup>4,5</sup> Thus, the electrochemical or chemical reduction of [(arene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> can lead to radical coupling through the arene ring to give cyclohexadienyl (Ch) complexes,<sup>4</sup> [(Ch) $\text{Mn}(\text{CO})_3$ ]<sub>2</sub>. It can also lead to CO dissociation and subsequent dimerization to the Mn–Mn bonded species, [(arene) $\text{Mn}(\text{CO})_2$ ]<sub>2</sub>.<sup>6</sup> Which product is obtained depends on the experimental conditions and the specific arene. Other possible products include the ring-slipped  $\eta^4$ -anion, [( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>) $\text{Mn}(\text{CO})_3$ ]<sup>−</sup>,<sup>2</sup> formed by two-electron reduction of [(benzene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> and the cyclodimerized analogue {[ $\text{Mn}(\text{CO})_3$ ]<sub>2</sub>{ $\mu$ -( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>- $\eta^4$ -C<sub>6</sub>H<sub>6</sub>)}}]<sup>2−</sup>.<sup>7</sup> Reduction of [(arene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> in the presence of phosphorus–donor nucleophiles induces rapid electron-transfer-catalyzed CO substitution.<sup>3</sup>

Recently, we have been interested in the chemical reduction of arene manganese carbonyl cations containing a vinyl sub-

stituent on the arene ring. Because of the importance of the chemistry of styrene, styrene derivatives of chromium carbonyls and cyclopentadienyl iron derivatives have been synthesized and studied,<sup>8,9</sup> but styrene derivatives of manganese tricarbonyl complex have not been described. We have now found, however, that [(styrene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup>, **1(H)**, can be synthesized by the silver method<sup>10</sup> under mild reaction conditions. It was anticipated that reduction of **1(H)** would yield a bimetallic complex in analogy to that described above. Indeed, chemical reduction of **1(H)** was found to yield a dimanganese compound, but one that differs fundamentally from known bimetallics. A concurrent study of the electrochemical reduction of **1(H)** was attempted. It was not pursued because the immediate polymerization of styrene liberated from **1(H)** became a problem. In this paper, we report and discuss the novel products formed by the chemical reduction of cationic manganese tricarbonyl complexes of styrene derivatives.

## Results and Discussion

**Synthesis of 1(R) (R = H, Ph).** Unlike many [(arene) $\text{Mn}(\text{CO})_3$ ]<sup>+</sup> complexes, attempts to synthesize [(styrene) $\text{Mn}(\text{CO})_3$ ]-[BF<sub>4</sub>], **1(H)**, by the usual Fischer–Hafner method<sup>11</sup> were unsuccessful. Excess styrene was used as the solvent, and polymeric materials were obtained in which some of the arene rings were coordinated by  $\text{Mn}(\text{CO})_3$ <sup>+</sup>. When styrene was treated with  $\text{Mn}(\text{CO})_5\text{ClO}_4$  in refluxing  $\text{CH}_2\text{Cl}_2$ , a polymeric material was again obtained due to the polymerization of **1(H)**. The IR spectrum contained bands characteristic of the coordinated Mn–

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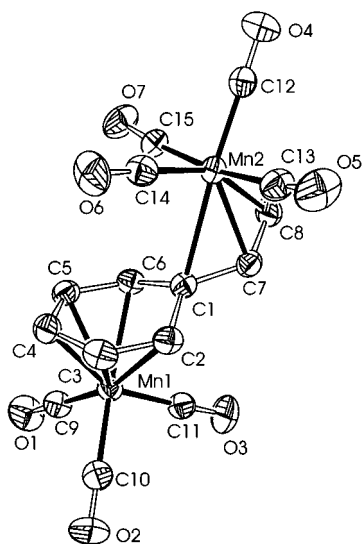
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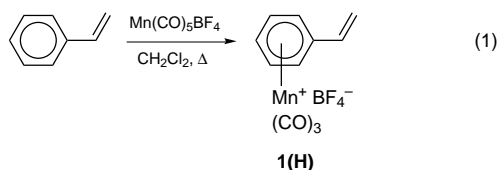
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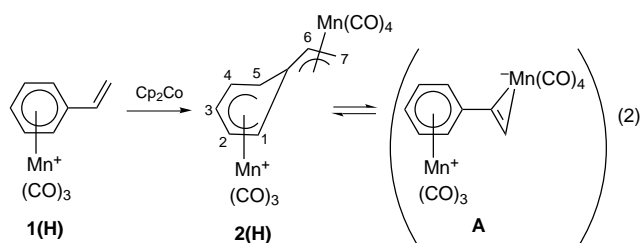
**Figure 1.** ORTEP drawing of **2(H)**. Thermal ellipsoids are shown at the 40% level.

(CO)<sub>3</sub><sup>+</sup> moieties and no absorptions in the vinyl region. However, treatment of styrene with Mn(CO)<sub>5</sub>BF<sub>4</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub> afforded **1(H)** as the BF<sub>4</sub><sup>-</sup> salt in 68% isolated yield (eq 1). In contrast with [(styrene)Cr(CO)<sub>3</sub>], **1(H)** is easily polymerized in polar organic solvent such as acetone and nitromethane. Thus, to get a pure compound, the crude product



has to be recrystallized rapidly. The same method also gave **1(Ph)** in 85% yield. In contrast with **1(H)**, compound [(1,1-diphenylethylene)Mn(CO)<sub>3</sub>][BF<sub>4</sub>], **1(Ph)**, was quite stable in polar organic solvent.

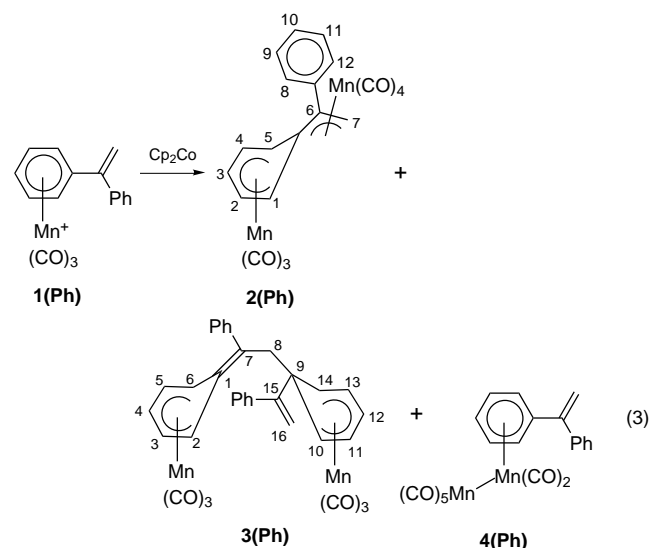
**Reduction of 1(R).** The reduction of **1(H)** has been studied with several reducing agents. When **1(H)** was treated with NaNap (or LiNap) in THF, the manganese salt slowly dissolved as the reaction proceeded. The reaction was quite complex, and we failed to isolate any major products. However, treatment of **1(H)** with 1.0 equiv of Cp<sub>2</sub>Co in CH<sub>2</sub>Cl<sub>2</sub> or THF produced the bimetallic complex **2(H)** in 31% yield, which contains a Mn(CO)<sub>4</sub> moiety coordinated to the styrene in an η<sup>3</sup>-fashion (eq 2). The use of 2.0 equiv of Cp<sub>2</sub>Co did not change the yield.



Compound **2(H)** is stable under N<sub>2</sub> in the solid state and suffers no detectable decomposition over 1 h in CH<sub>2</sub>Cl<sub>2</sub>. The bimetallic nature and the η<sup>5</sup>:η<sup>3</sup> bonding pattern of **2(H)** were confirmed by an X-ray structure determination (Figure 1). This is the first example of two manganese carbonyl moieties π-coordinated to a monoarene frame. The Mn(2)–C(1) bond distance (2.421–(3) Å) is quite long compared to the bond distances in other

allyl manganese complexes,<sup>12</sup> which typically have an Mn–C distance of 2.18 Å, and reflects the weak bonding interaction. The Mn(2)–C(1) bond distance is comparable to the distance between Mn(1) and C(1) (2.651(3) Å). The η<sup>3</sup>-allyl fragment is bonded to the metal in an asymmetric fashion (C(7)–Mn(2) and C(8)–Mn(2) are 2.139(4) and 2.170(4) Å, respectively). The bond distance (1.401(5) Å) of C(7)–C(8) is close to that (1.390(12) Å) of the coordinated ethylenic double bond in CpMn(CO)<sub>2</sub>(CH<sub>2</sub>=CHCOCH<sub>3</sub>).<sup>13</sup> Furthermore, the bond distances between C(7)–Mn(2) and C(8)–Mn(2) are quite similar to those (2.149(8) and 2.175(7) Å, respectively) of manganese to ethylenic carbon atoms in CpMn(CO)<sub>2</sub>(CH<sub>2</sub>=CHCOCH<sub>3</sub>).<sup>13</sup> The fold angle (30.6°) between planes C(2)–C(3)–C(4)–C(5)–C(6) and C(2)–C(1)–C(6) is small compared with those in other cyclohexadienylmanganese complexes: 43° in [(η<sup>5</sup>-C<sub>6</sub>H<sub>7</sub>)Mn(CO)<sub>3</sub>],<sup>14</sup> 41° in [{η<sup>5</sup>-(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>C)<sub>2</sub>CH-C<sub>6</sub>H<sub>6</sub>}Mn(CO)<sub>3</sub>],<sup>15</sup> 39.6° in [{(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)W(CO)<sub>3</sub>CH<sub>3</sub>}-η<sup>5</sup>-C<sub>6</sub>H<sub>5</sub>]Mn(CO)<sub>3</sub>,<sup>16</sup> and 38.0° in [(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)-η<sup>5</sup>-C<sub>6</sub>H<sub>5</sub>]Mn(CO)<sub>3</sub>.<sup>17</sup> Thus, we expect that there should be a small contribution of the zwitterionic bonding mode **A** in the structure. Compound **2(H)** was inert to both PhMgBr and MeI. However, when **2(H)** was treated with Br<sub>2</sub>, we could observe through IR spectroscopy the formation of **1-(H)**.

When **1(Ph)** was reduced by Cp<sub>2</sub>Co, **2(Ph)** and **3(Ph)** were the major products and **4(Ph)** was a minor product (eq 3). The



product distribution varied from one experiment to the next, suggestive of radical intermediates, the production and fate of which depend on adventitious impurities. Interestingly, when Cp<sub>2</sub>Co in THF was added dropwise to the solution of **1(Ph)** in THF, **4(Ph)** was obtained as a major product. Compounds **2(Ph)**, **3(Ph)**, and **4(Ph)** are stable in solid state, but quite sensitive in solution. The X-ray structure of **2(Ph)** (Figure 2) is very close to that of **2(H)**. The Mn(2)–C(1) bond distance (2.560(3) Å) is even longer than that in **2(H)**. Interestingly, the Mn(2)–C(8) bond is the shortest. The fold angle between

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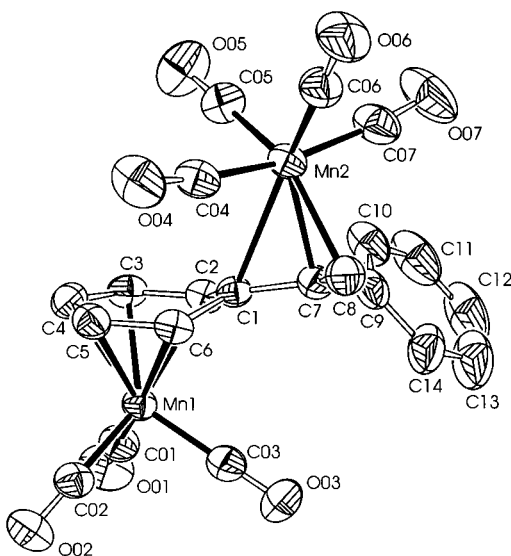
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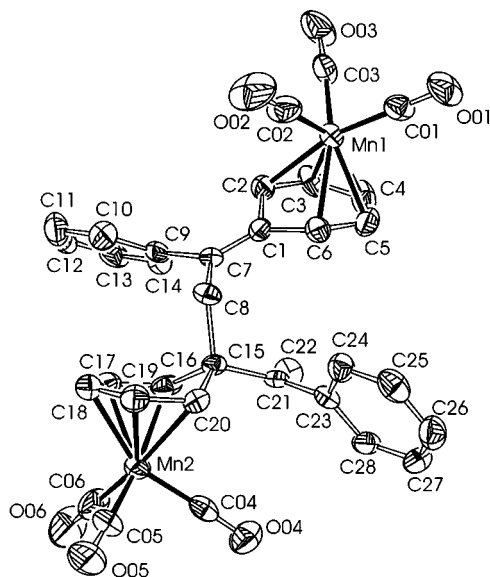
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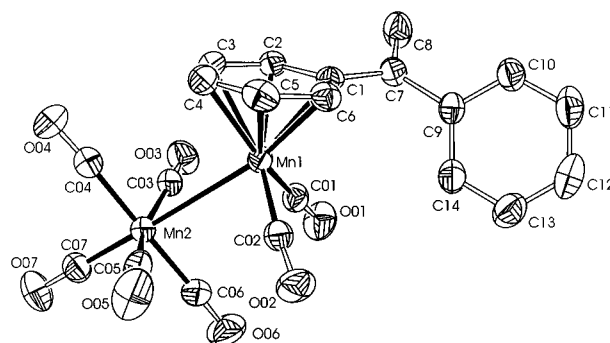
**Figure 2.** ORTEP drawing of **2(Ph)**. Thermal ellipsoids are shown at the 40% level.



**Figure 3.** ORTEP drawing of **3(Ph)**. Thermal ellipsoids are shown at the 40% level.

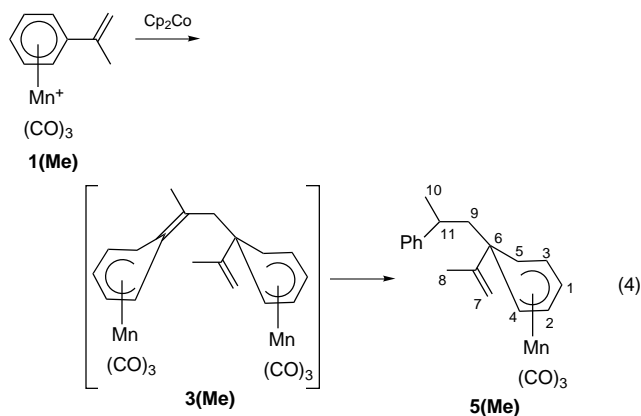
planes C(2)–C(3)–C(4)–C(5)–C(6) and C(2)–C(1)–C(6) is 27.4°. Thus, we expect that there should be a contribution of the zwitterionic bonding mode **A** as in **2(H)**. Compound **3-Ph** has the  $\eta^5:\eta^5$  bonding pattern with two Mn(CO)<sub>3</sub> moieties  $\pi$ -coordinated to a ligand derived from coupling of 1,1-diphenylethylenes through the *ipso* carbon atom. The X-ray structure of the thermally stable complex **3(Ph)** is shown in Figure 3. The C(1)–C(7) bond distance (1.344(11) Å) is consistent with a C–C double bond.<sup>18</sup> The fold angle between planes C(2)–C(3)–C(4)–C(5)–C(6) and C(2)–C(1)–C(6) is 30.1°, a value quite similar to that (30.6°) found with **2(H)**. The angle (43.1°) between planes C(16)–C(17)–C(18)–C(19)–C(20) and C(16)–C(15)–C(20) is similar to 43° observed in  $[(\eta^5\text{-C}_6\text{H}_7)\text{Mn}(\text{CO})_3]$ .<sup>14</sup> Given the structure of **3(Ph)**, we envisioned that the Mn(CO)<sub>3</sub> group coordinated to the plane of C(2)–C(3)–C(4)–C(5)–C(6) would be relatively easily liberated. When  $[(\alpha\text{-methylstyrene})\text{Mn}(\text{CO})_3][\text{BF}_4]$  was treated with Cp<sub>2</sub>Co, compound **5(Me)**, presumably derived from **3(Me)**, was

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**Figure 4.** ORTEP drawing of **4(Ph)**. Thermal ellipsoids are shown at the 40% level.

obtained as one of the major products (eq 4). Complex **4(Ph)**,



the X-ray structure of which is given in Figure 4, is dark brown due to the presence of a metal–metal bond. The substitution of one CO by Mn(CO)<sub>5</sub> does not affect in a significant way the bonding between Mn and the arene ring and between Mn and the two remaining carbonyl groups. The Mn–Mn bond distance (2.9144(6) Å) is quite long, but close to the Mn–Mn distance in Mn<sub>2</sub>(CO)<sub>10</sub>.<sup>19</sup>

Although radical intermediates were not detected experimentally, the structure of products **2–4** may be suggestive of such species. However, Cooper *et al.*<sup>20</sup> reported that the radical  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]$  was thermodynamically unstable with respect to disproportionation to  $[(\eta^4\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^-$  and  $[(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^+$ . They suggested the anion/cation addition route to explain the formation of dimer  $\{[\text{Mn}(\text{CO})_3]_2[\mu\text{-}(\eta^5\text{-C}_6\text{H}_6)\eta^5\text{-C}_6\text{H}_6]\}$  by the reduction of  $[(\text{benzene})\text{Mn}(\text{CO})_3]^+$ . Whether we follow a radical–radical coupling or an anion/cation addition mechanism, it is still difficult to explain explicitly the formation of several of the reduction products, and we sought further information from additional reactions. When **1(H)** was treated with Cp<sub>2</sub>Co in the presence of excess MeI, **2(H)** was obtained as a major product. Thus, there was no coupling between an intermediate radical (or an anion) and electrophilic MeI. When **1(H)** was treated with nucleophiles such as RMgX (R = Me, Ph), NaP(O)(OMe)<sub>2</sub>, NaBH<sub>3</sub>CN, LiCH<sub>2</sub>CO<sub>2</sub>tBu, LiCMe<sub>2</sub>CN, and NaCN, the nucleophilic addition products were obtained.<sup>21</sup> We never observed formation of bimetallics or addition to the *ipso*-carbon. Interestingly, treatment of **1(H)** with Me<sub>3</sub>NO led to isolation of **2(H)**. However, **2(Ph)** was not obtained by the reaction of **1(Ph)** with Me<sub>3</sub>NO. Right now we do not have any plausible mechanisms to explain the formation of the novel

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**Table 1.** Crystal Data and Structure Refinements for **2(H)**, **2(Ph)**, **3(Ph)**, and **4(Ph)**

	<b>2(H)</b>	<b>2(Ph)</b>	<b>3(Ph)</b>	<b>4(Ph)</b>
chem formula	C <sub>15</sub> H <sub>8</sub> Mn <sub>2</sub> O <sub>7</sub>	C <sub>21</sub> H <sub>12</sub> Mn <sub>2</sub> O <sub>7</sub>	C <sub>34</sub> H <sub>24</sub> Mn <sub>2</sub> O <sub>6</sub>	C <sub>21</sub> H <sub>12</sub> Mn <sub>2</sub> O <sub>7</sub>
fw	410.09	486.19	638.41	486.19
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> , Å	6.815(3)	7.165(3)	9.910(3)	12.9462(8)
<i>b</i> , Å	18.982(3)	10.102(3)	12.716(3)	10.4840(9)
<i>c</i> , Å	12.133(2)	14.952(2)	22.839(7)	14.6236(14)
$\alpha$ , deg	90	96.71(2)	90	90
$\beta$ , deg	98.50(2)	102.64(2)	90.16(2)	89.916(7)
$\gamma$ , deg	90	103.00(2)	90	90
<i>V</i> , Å <sup>3</sup>	1552.4(7)	1013.2(5)	2877.9(13)	1984.8(3)
<i>Z</i>	4	2	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.755	1.594	1.473	1.627
$\theta$ range for data collected	2.01–24.97	1.42–24.97	1.78–24.98	1.39–24.97
data	2214	2575	2350	3185
parameters	223	277	379	271
<i>R</i>	0.0369	0.0402	0.0660	0.0442
<i>wR</i> <sup>2</sup>	0.0878	0.0948	0.1462	0.0739

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **2(H)**, **2(Ph)**, **3(Ph)**, and **4(Ph)**

<b>2(H)</b>							
C1–C7	1.401(5)	C7–C8	1.401(5)	Mn2–C1	2.421(3)	Mn2–C7	2.139(3)
Mn2–C8	2.170(4)	C1–C2	1.465(5)	Mn1–C2	2.244(3)	Mn1–C3	2.140(3)
C1–C7–C8	126.7(3)	C1–Mn2–C12	165.96(14)	C2–C1–C6			108.5(3)
C3–C4–C5	117.7(4)	C8–Mn2–C04	92.0(2)	Mn2–C06–O06			179.0(4)
C3–C4–C5	117.3(3)	C8–Mn2–C14	152.7(2)	Mn2–C12–O4			179.1(3)
<b>2(Ph)</b>							
C1–C7	1.406(5)	C7–C8	1.419(6)	Mn2–C1	2.560(3)	Mn2–C7	2.178(4)
Mn2–C8	2.118(4)	Mn1–C2	2.234(4)	Mn1–C4	2.136(4)	Mn1–C01	1.803(4)
C1–C7–C8	121.2(4)	C1–Mn2–C06	157.8(2)	C2–C1–C6			108.6(3)
C3–C4–C5	117.7(4)	C8–Mn2–C04	92.0(2)	Mn2–C06–O06			179.0(4)
<b>3(Ph)</b>							
C1–C7	1.344(11)	C7–C8	1.503(11)	C7–C9	1.489(12)	C21–C22	1.320(11)
Mn1–C2	2.232(8)	Mn1–C3	2.131(9)	Mn1–C4	2.103(10)	Mn1–C01	1.789(10)
C8–C15–C21	110.2(7)	C15–C21–C22	121.2(7)	C1–C7–C8			123.8(8)
C01–Mn1–C03	88.8(4)	Mn1–C01–O01	179.1(9)	C3–C4–C5			117.4(10)
<b>4(Ph)</b>							
Mn1–Mn2	2.9144(6)	C1–C7	1.492(3)	C7–C8	1.327(4)	C7–C9	1.488(4)
Mn1–C01	1.792(3)	Mn1–C1	2.176(2)	Mn1–C4	2.190(3)	Mn2–C07	1.795(3)
Mn2–C04	1.845(3)	C1–C6	1.409(4)	C6–C5	1.410(4)	C01–O01	1.149(3)
C07–Mn2–Mn1	172.55(10)	Mn1–C02–O02	175.1(3)	Mn2–C07–O07			178.5(3)
C7–C9–C10	119.0(3)	C1–C7–C8	119.2(3)	Mn2–Mn1–C02			83.27(9)

bimetallic compounds. To firmly establish the reduction mechanism, further investigation is needed.

In conclusion, we have demonstrated that there are multiple reduction pathways available to (arene)Mn(CO)<sub>3</sub><sup>+</sup> cations having a vinyl substituent on the arene ring. This phenomenon appears to be general for the [(arene)Mn(CO)<sub>3</sub>]<sup>+</sup> complexes containing an unsaturated substituent on the arene.<sup>22</sup> We are currently attempting to extend this work to other arene transition metal complexes.

## Experimental Section

**General Information.** All solvents were purified by standard methods, and all synthetic procedures were done under nitrogen atmosphere. Reagent grade chemicals were used without further purification.

Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University or the Chemical Analytic Center, KIST. <sup>1</sup>H NMR spectra were obtained with a Varian XL-200 or a Bruker AMX-500 instrument. Infrared spectra were

recorded on a Shimadzu IR-470 spectrometer. Mass spectra were recorded on a VG ZAB-E double-focusing mass spectrometer.

**Synthesis of [(styrene)Mn(CO)<sub>3</sub>][BF<sub>4</sub>], **1(H)**.** A mixture of Mn(CO)<sub>5</sub>Br (1.0 g, 3.6 mmol) and AgBF<sub>4</sub> (0.71 g, 3.6 mmol) in 40 mL of CH<sub>2</sub>Cl<sub>2</sub> was refluxed for 1 h without exposure to light. To the reaction mixture was added styrene (0.63 mL, 5.4 mmol). The resulting solution was heated at reflux for 6 h. After evaporation of the solvent, the residue was recrystallized by Et<sub>2</sub>O/CH<sub>3</sub>NO<sub>2</sub>. The yield was 68% (0.80 g). IR (CH<sub>3</sub>NO<sub>2</sub>)  $\nu_{\text{CO}}$  2075, 2020 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.02 (m, 5 H, Ph), 6.84 (dd, *J* = 10.6, 14.1 Hz, 1 H), 6.48 (d, *J* = 17.6 Hz, 1 H), 5.96 (d, *J* = 11.0 Hz, 1 H) ppm. Anal. Calcd for C<sub>11</sub>H<sub>8</sub>BF<sub>4</sub>MnO<sub>3</sub>: C, 40.05; H, 2.44. Found: C, 40.19; H, 2.49.

**Synthesis of [(1,1-diphenylethylene)Mn(CO)<sub>3</sub>][BF<sub>4</sub>], **1(Ph)**.** The same procedure was followed as in the synthesis of **1(H)**. Yield: 85%. IR (CH<sub>3</sub>NO<sub>2</sub>)  $\nu_{\text{CO}}$  2070, 2020 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.49 (m, 5 H, Ph), 6.95 (m, 5 H, coordinated Ph), 6.38 (s, 1 H, H<sup>8 $\beta$</sup> ), 6.02 (s, 1 H, H<sup>8 $\alpha$</sup> ) ppm. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>BF<sub>4</sub>MnO<sub>3</sub>: C, 50.29; H, 2.98. Found: C, 50.36; H, 3.09.

**Reduction of **1(H)**.** Cobaltocene (0.14 g, 0.6 mmol) was dissolved in 10 mL of THF, and the solution was stirred for 10 min at room temperature. To the THF solution was added **1(H)** (0.20 g, 0.6 mmol). After the solution was stirred for 30 min, any solid precipitates were filtered off and the filtrate was concentrated and column chromatographed on a silica gel column by eluting with hexane/diethyl ether (v/v, 5:1). The collected eluant was evaporated and redissolved in 10

(22) Chemical reduction of (*trans*- $\beta$ -methylstyrene)Mn(CO)<sub>3</sub><sup>+</sup>, (PhC $\equiv$ CH)-Mn(CO)<sub>3</sub><sup>+</sup>, ( $\alpha$ -methylstyrene)Mn(CO)<sub>3</sub><sup>+</sup>, and (vinylthiophene)Mn(CO)<sub>3</sub><sup>+</sup> followed similar reaction courses. These results will be published in due course.

mL of pentane. The pentane solution was kept in a freezer. After 1 day, **2(H)** was precipitated and filtered. The yield was 31% (78 mg). Single crystals of **2(H)** suitable for X-ray study were grown with use of diethyl ether and hexane. IR (hexane)  $\nu_{\text{CO}}$  2016, 1962, 1945  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.00 (tt,  $J = 1.2, 5.5$  Hz,  $\text{H}^3$ ), 5.37 (t,  $J = 6.0$  Hz,  $\text{H}^4$ ), 5.31 (ddd,  $J = 1.3, 5.5, 7.5$  Hz,  $\text{H}^2$ ), 4.12 (ddd,  $J = 1.3, 2.4, 7.5$  Hz,  $\text{H}^1$ ), 4.05 (dd,  $J = 7.1, 11.7$  Hz,  $\text{H}^6$ ), 3.38 (d,  $J = 7.3$  Hz,  $\text{H}^5$ ), 2.54 (dd,  $J = 3.3, 7.1$  Hz,  $\text{H}^{7\text{-exo}}$ ), 1.88 (dd,  $J = 3.3, 11.7$  Hz,  $\text{H}^{7\text{-endo}}$ ) ppm. Anal. Calcd for  $\text{C}_{15}\text{H}_8\text{MnO}_7$ : C, 43.94; H, 1.96. Found: C, 43.83; H, 1.85.

**Reduction of 1(Ph).** Cobaltocene (0.14 g, 0.74 mmol) was dissolved in 20 mL of THF. The solution was stirred for 10 min. To the THF solution was added **1(Ph)** (0.30 g, 0.74 mmol). After the solution was stirred for 30 min, any precipitates were filtered off and the filtrate was evaporated. The residue was chromatographed on a silica gel column by using hexane/diethyl ether (v/v, 50:1). The first yellow band eluted was **3(Ph)**, the second dark red band was **4(Ph)**, and the last red band was **2(Ph)**. Compounds **2(Ph)** and **4(Ph)** are unstable in air. Thus, to get pure **2(Ph)** and **4(Ph)**, they must be recrystallized in pentane under  $\text{N}_2$ . The product distribution varied from one experiment to the next. When cobaltocene (0.14 g) in 10 mL of THF was added dropwise to the solution of **1(Ph)** (0.30 g) in 10 mL of THF, **4(Ph)** was obtained as a major compound. Analytical data for **2(Ph)**: IR (pentane)  $\nu_{\text{CO}}$  2020, 1967, 1959, 1939  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 7.5$  Hz, 2 H,  $\text{H}^{8,12}$ ), 7.38 (t,  $J = 7.5$  Hz, 2 H,  $\text{H}^{9,11}$ ), 7.27 (t,  $J = 7.4$  Hz, 1 H,  $\text{H}^{10}$ ), 5.89 (t,  $J = 5.5$  Hz, 1 H,  $\text{H}^3$ ), 5.57 (t,  $J = 6.1$  Hz, 1 H,  $\text{H}^2$ ), 5.50 (t,  $J = 6.9$  Hz, 1 H,  $\text{H}^4$ ), 4.69 (d,  $J = 8.1$  Hz, 1 H,  $\text{H}^5$ ), 3.82 (d,  $J = 7.0$  Hz, 1 H,  $\text{H}^1$ ), 2.88 (d,  $J = 3.7$  Hz, 1 H,  $\text{H}^{7\text{-exo}}$ ), 2.38 (d,  $J = 3.7$  Hz, 1 H,  $\text{H}^{7\text{-endo}}$ ) ppm. Anal. Calcd for  $\text{C}_{21}\text{H}_{12}\text{Mn}_2\text{O}_7$ : C, 51.88; H, 2.49. Found: C, 51.60; H, 2.28.

Analytical data for **3(Ph)**: IR (pentane)  $\nu_{\text{CO}}$  2014, 1950, 1938  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.4 – 6.9 (m, 10 H, Ph), 5.63 (t,  $J = 5.5$  Hz,  $\text{H}^4$ ), 5.57 (t,  $J = 4.6$  Hz,  $\text{H}^{12}$ ), 5.27 (s,  $\text{H}^{16}$ ), 5.10 (s,  $\text{H}^{16}$ ), 4.90 (m,  $\text{H}^{3,5}$ ), 4.64 (t,  $J = 5.6$  Hz,  $\text{H}^{11}$  or  $^{13}$ ), 4.16 (t, 5.6 Hz,  $\text{H}^{11}$  or  $^{13}$ ), 3.97 (m,  $\text{H}^{2,6}$ ), 3.10 (d, 6.6 Hz,  $\text{H}^{10}$  or  $^{14}$ ), 2.60 (d, 6.6 Hz,  $\text{H}^{10}$  or  $^{14}$ ), 2.38 (d, 13.9 Hz,  $\text{H}^8$ ), 2.15 (d, 13.9 Hz,  $\text{H}^8$ ) ppm. Anal. Calcd for  $\text{C}_{34}\text{H}_{24}\text{Mn}_2\text{O}_6$ : C, 63.96; H, 3.79. Found: C, 63.62; H, 3.58.

Analytical data for **4(Ph)**: IR (pentane)  $\nu_{\text{CO}}$  2058 (w), 1997 (w), 1972 (s), 1962 (s), 1948 (w)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.37 (m, 5 H, Ph), 5.84 (br s, 1 H), 5.65 (br s, 1 H), 5.46 (m, 5 H, protons on the coordinated phenyl ring) ppm. Anal. Calcd for  $\text{C}_{22}\text{H}_{12}\text{Mn}_2\text{O}_8$ : C, 51.88; H, 2.46. Found: C, 51.96; H, 2.32.

**Reduction of 1(Me).** Cobaltocene (0.14 g, 0.74 mmol) was dissolved in 20 mL of THF. The solution was stirred for 10 min. To the THF solution was added **1(Me)** (0.25 g, 0.74 mmol). After the

solution was stirred for 30 min, any precipitates were filtered off and the filtrate was evaporated. The residue was chromatographed on a silica gel column by eluting with hexane/diethyl ether (v/v, 50:1). The first yellow band eluted was **5(Me)**. The second and the third dark red bands could not be characterized due to the low stability of the corresponding compounds. The product distribution varied from one experiment to the next. Analytical data for **5(Me)**: IR (pentane)  $\nu_{\text{CO}}$  2010, 1947, 1935  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.23 (t,  $J = 7.5$  Hz, 2 H, Ph), 7.13 (t,  $J = 7.3$  Hz, 1 H, Ph), 7.03 (d,  $J = 7.4$  Hz, 2 H, Ph), 5.66 (t,  $J = 5.1$  Hz, 1 H), 5.24 (s, 1 H), 5.00 (s, 1 H), 4.78 (t,  $J = 6.4$  Hz, 1 H), 4.30 (t,  $J = 6.5$  Hz, 1 H), 3.16 (d,  $J = 7.4$  Hz, 1 H), 2.65 (d,  $J = 7.3$  Hz, 1 H), 2.41 (m, 1 H), 1.77 (s, 3 H,  $\text{CH}_3$ ), 1.27 (dd,  $J = 8.8, 14.0$  Hz, 1 H), 1.15 (dd,  $J = 4.8, 14.0$  Hz, 1 H), 1.01 (d,  $J = 7.0$  Hz, 3 H,  $\text{CH}_3$ ) ppm; HRMS ( $m/z$ )  $\text{M}^+$  calcd 376.0871, obsd 376.0873.

**X-ray Structure Determinations of 2(H), 2(Ph), 3(Ph), and 4(Ph).** Crystals of **2(H)** were grown by slow evaporation of its solution in hexane. Crystals of **2(Ph)** were grown similarly in pentane under nitrogen atmosphere. Crystals of **3(Ph)** were grown in diethyl ether/hexane. Crystals of **4(Ph)** were grown by slow evaporation of a hexane solution in a freezer.

Diffraction experiments were performed by using an Enraf-Nonius CAD4 automated diffractometer with an  $\omega$ - $2\theta$  scan method. Unit cells were determined by centering 25 reflections in the appropriate  $2\theta$  range. Other relevant experimental details are listed in Table 1. The selected bond distances and angles are shown in Table 2. The structure was solved by direct method with SHELXS-86 and refined by full-matrix least squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically by using the riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

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**Supporting Information Available:** Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom positional and displacement parameters for **2(H)**, **2(Ph)**, **3(Ph)**, and **4(Ph)** (24 pages). See any current masthead page for ordering and Internet access instructions.

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