(Arene)tricarbonylmanganese(I) Complexes: A Preparative Study. Crystal Structure of $[(\eta^6\text{-}C_6H_5CH_2COCH_2Ph)Mn(CO)_3]BF_4$

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Received April 28, 1994®

The scope of $[(\eta^6\text{-arene})Mn(CO)_3]^+$ synthesis is investigated. Methods of preparation involve abstraction of bromide from $[Mn(CO)_5Br]$ by $AlCl_3$ or Ag(I) or, alternatively, oxidation of $[Mn_2(CO)_{10}]$ by strong acid. Arenes which bear the following substituents can be coordinated: alkyl, aryl, alkoxy, chloro, hydroxy, fused heterocycle aromatic rings, and nonconjugated carbonyl. The degree of electron donation to the ring is the principal factor in determining the likelihood of coordination. Highly electron-deficient aromatics such as nitro, cyano, and those conjugated to carbonyls will not metalate. The use of aluminum chloride leads to rearrangements of some alkylbenzenes and substitution reactions of some aryl halides. In the case of *o*-dichlorobenzene, this substitution yields the unusual complex $[(\eta^6\text{-}2\text{-}ClC_6H_4Mn(CO)_5)Mn(CO)_3]^+$. Other new complexes reported include those of dibenzothiophene, 1,3-diphenylacetone, deoxybenzoin, and phenol. A crystal structure of $[(\eta^6\text{-}C_6H_5CH_2COCH_2Ph)Mn(CO)_3]BF_4$ is reported: space group $P2_1/c$, $a = 12.5429(12)$ Å, $b = 12.465(2)$ Å, $c = 12.109(2)$ Å, $\beta = 106.128(10)°$, $V = 1818.8(5)$ Å^3, $Z = 4$, $D_{calc} = 1.592$ mg m^{-3}, $R = 0.0570$, and $\omega R2 = 0.1609$ on 2331 reflections with $F^2 > 2.0\sigma(F^2)$.

Introduction

π-Arene complexes of transition metals were first prepared through the work of Hein prior to 1920.[1] However, the true nature of Hein's "polyphenylchromium"[2] compounds remained a mystery until 1956 when Zeiss[3] was able to propose π-coordinated structures based in part on the work of Fischer and Hafner.[4] The latter investigators demonstrated that cationic π-aromatic compounds could be prepared under reducing conditions in the presence of a strong Lewis acid, reaction 1. The Fischer–Hafner reaction has since been

$$CrCl_3 + Al + AlCl_3 + C_6H_6 \rightarrow [(\eta^6\text{-}C_6H_6)_2Cr]^+ + \ldots \quad (1)$$

found to be of general utility for the preparation of cationic π-arene complexes. Using this method, $[(\eta^6\text{-arene})FeCp]^+$ can be easily synthesized from ferrocene.[5] Reduction is not necessary when metal halides of the desired oxidation state are available; for instance $FeCl_2$ may be used to prepare $[(\eta^6\text{-arene})_2Fe]^{2+}$,[5] and $[Mn(CO)_5Br]$ to make $[(\eta^6\text{-arene})Mn(CO)_3]^+$. Aluminum chloride serves as a halide ion abstractor as demonstrated in reaction 2, which occurs upon heating in

$$[Mn(CO)_5Br] + AlCl_3 \rightarrow [Mn(CO)_5]^+ + AlCl_3Br^- \quad (2)$$

hydrocarbon solvent. Coordination of an aromatic molecule to $[Mn(CO)_5]^+$ is presumably associative in nature. Papers by Wilkinson[6] and, later, Pauson,[7] Sweigart,[8] and others[9-11] have described Fischer–Hafner synthesis of several hydrocarbon and halocarbon (arene)manganese carbonyl cations (see Table 1).

The $[Mn(CO)_5]^+$ fragment can also be generated via halide abstraction, using silver(I) ion, reaction 3.[21] In

$$[Mn(CO)_5Br] + Ag^+ \rightarrow [Mn(CO)_5]^+ + AgBr \quad (3)$$

1981, Pauson[22] suggested that this route might be suitable for the preparation of the (arene)manganese cations. Pearson[12] later demonstrated this method, preparing $[(\eta^6\text{-}o\text{-}C_6H_4(OMe)_2)Mn(CO)_3]^+$. Pauson's further claim[22] that the solvent complex, $[Mn(CO)_3(OCMe_2)_3]^+$, could react with arenes to produce $[(\eta^6\text{-arene})Mn(CO)_3]^+$ has remained unsubstantiated. This route seems dubious since the tris-solvent complex is known to have greater thermodynamic stability than

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® Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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0276-7333/94/2313-3972$04.50/0

Table 1. Previously Reported $[(\eta^6\text{-arene})Mn(CO)_3]^+$ Complexes[a]

arene	yield (%)	ν_{CO} (cm^{-1})	ref
	Fischer−Hafner		
C_6H_6	N.R.	2080, 2026[b]	6, 8
C_6H_5Me	N.R.	2079, 2021[b]	6, 8
1,2-$C_6H_4Me_2$	N.R.	2076, 2019[b]	6, 8
1,3,5-$C_6H_3Me_3$	N.R.	2072, 2015[b]	6, 8
C_6H_5OMe	64	2077, 2019[c]	7, 8
C_6H_5Cl	64	2085, 2033[c]	7
4-ClC_6H_4Me	70	2083, 2030[c]	7
C_6H_5Br	N.R.	2085, 2033[c]	7
tetralin[e]	10	2060, 1995[d]	9
9,10-dihydroanthracene[f]	N.R.	2070, 2010, 1995[d]	9
dodecahydrotriphenylene	52	2050, 1988[g]	10
2,4-$Me_2C_6H_3OMe$	N.R.	N.R.	11
	Silver(I)		
1,2-$C_6H_4(OMe)_2$	66	N.R.	12
$C_6H_5CMe_3$	10	2070, 2020[h]	13
$(C_6H_5)_2O$	N.R.	N.R.	14
C_6H_5OMe	N.R.	N.R.	14
2,6-$(MeO)_2C_6H_3Et$	78	2069, 2003[g]	15
2,6-$(MeO)_2C_6H_3{}^iPr$	61	2069, 2002[g]	15
$C_6H_5Si(OCH_2CH_2)_3N$ and *p*-substituted analogs	26−90	2070, 2010[h,i]	16
indole and N-substituted indoles	60−90	2069, 2008[g,i]	17
benzofuran	60	2080, 2019[g,i]	17
aromatic steroids	51−91	2070, 2004[g,g]	18
	TFA Anhydride		
C_6H_6	75	N.R.	19
C_6H_5Me	50	N.R.	19
1,3,5-$C_6H_3Me_3$	67	N.R.	19
C_6H_5OEt	27	N.R.	19
3-Cl-2-MeC_6H_3OMe	77	2081, 2014[k]	20

[a] All IR bands of strong intensity; N.R. = not reported. [b] In acetone. [c] In CH_3CN. [d] KBr disk. [e] Produced from naphthalene or tetralin. [f] Produced from anthracene. [g] In CH_2Cl_2. [h] Film on NaCl. [i] Unsubstituted analog. [j] Dimethylpodocarpic acid complex. [k] In $CHCl_3$.

the arene complex.[8] Several additional (arene)manganese(I) complexes have been produced via the silver(I) method during the last decade.[13−18] For the most part, those arenes which have been successfully coordinated bear electron-donating alkoxy and alkyl substituents. A notable exception to this trend is the recent coordination of a series of phenylsilatranes (4-$RC_6H_4Si(OCH_2CH_2)_3N$; R = H, Me, Cl, OMe, *t*-Bu) to $[Mn(CO)_3]^+$ by Chung and co-workers.[16] The silver method has very recently been employed in the preparation of indoles[17] and aromatic steroids.[18]

Yet a third route to $[(\eta^6\text{-arene})Mn(CO)_3]^+$ first appeared in 1984 in the Soviet literature.[19] This method also apparently makes use of $[Mn(CO)_5]^+$, which is generated according to reaction 4. Strongly acidic conditions are used, and the reaction may be carried out starting with $[Mn_2(CO)_{10}]$, $[Mn(CO)_5Br]$, or $[Mn_2(CO)_8(\mu\text{-}Cl)_2]$. The simple homoleptic carbonyl is preferable, since a separate oxidative addition step (and the associated yield loss) is thus avoided. Despite the harsh reaction conditions, the Soviet workers isolated several complexes in good yield (Table 1). Recently, Pearson has also used this trifluoroacetic (TFA) anhydride reaction to produce the 3-chloro-2-methylanisole complex.[20]

$$[Mn_2(CO)_{10}] + 2H^+ + (CF_3CO)_2O\ (\text{solvent}) \rightarrow 2[Mn(CO)_5]^+ + H_2 \quad (4)$$

Table 2. Synthesis Results for $[(\eta^3\text{-arene})Mn(CO)_3]^+$

arene	yield (%)			ν_{CO}[a] (cm^{-1})
	Fischer−Hafner	silver(I)	TFA anhydride	
C_6H_6	85	32	87	2086, 2026
1,3,5-$C_6H_3Me_3$	57	19	64	2072, 2012
1,2,4,5-$C_6H_2Me_4$	63[b]	66	78	2069, 2008
$C_6H_5CH_2CHMe_2$	41	80	75	2082, 2023
$(C_6H_5CH_2)_2$	42[b]	67	76	2081, 2023
$(C_6H_5)_2$	39	29	56	2081, 2023
naphthalene	[c]	0	[d]	2078, 2018
C_6H_5Cl	64[e]	6	80	2087, 2036
C_6H_5Br	[f]	9	77[g]	2089, 2033
1,2-$C_6H_4Cl_2$	[h]	0	0	2089, 2046[i]
4-MeC_6H_4OMe	56[e,j]	52	60	2076, 2013
$(C_6H_5)_2O$	88	55	72	2081, 2021
C_6H_5OH	0	69	74[g]	2077, 2017
dibenzothiophene	35	16	89	2077, 2021
$(C_6H_5CH_2)_2CO$	49	33	59	2082, 2023, 1724 (w)
$C_6H_5CH_2COPh$	2	59	77	2082, 2024, 1691 (w)

[a] In CH_2Cl_2; all band intensities strong except as noted. [b] Mixture of isomers due to rearrangement. [c] Tetralin complex isolated in 10% yield; see ref 9. [d] Trace (by IR). [e] Reference 7. [f] Benzene complex isolated in 66% yield. [g] Product contaminated with $[Mn(CO)_6]^+$. [h] $[(2\text{-}ClC_6H_4Mn(CO)_5)Mn(CO)_3]^+$ isolated in 29% yield. [i] In *o*-$C_6H_4Cl_2$. [j] Anisole product.

Table 3. Aromatic Substrates Which Did Not Coordinate to $[Mn(CO)_3]^+$

	acetophenone ethylene glycol ketal (**4**)	
benzyl alcohol	benzaldehyde	benzoic acid
coumarine (**5**)	4-cyanotoluene	*N,N*-dimethylaniline
1-indanone	4-methoxyacetophenone	4-nitroanisole
phenoxytrimethylsilane	phenyl acetate	phenylacetylene
safrole	tropolone	

Finally it should be noted that an indirect method is also available for the synthesis of certain arene complexes. Cationic chloroarene complexes are known to undergo nucleophilic substitution reactions.[5] Thus the reaction of $[(\eta^6\text{-}C_6H_5Cl)Mn(CO)_3]^+$ with alcohols in the presence of base affords aromatic ether complexes.[7,16c,20,23] Similarly its reaction with amines produces aniline complexes. The latter fact is especially significant as no direct route has yet provided the coordinated aniline products. Nevertheless, being an indirect route, the substitution reaction lies outside the scope of the current study.

The cationic arene complexes of manganese are of synthetic interest. The reaction of carbon-based nucleophiles with these species occurs in high yield with

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Table 4. ^{1}H-NMR Data for New $[(\eta^6\text{-arene})Mn(CO)_3]^+$ Complexes

arene	^{1}H-NMR[a,b]
1,2,4,5-$C_6H_2Me_4$	6.79 (s, 2 H, H_{aryl}), 2.50 (s, 12 H, Me)
$C_6H_5CH_2CHMe_2$	6.84 (mult, 3 H, $H_{m,p}$), 6.66 (d, $J = 5.4$, 2 H, H_o), 2.69 (d, $J = 6.6$, 2 H, CH_2), 2.00 (m, 1 H, CH), 0.98 (d, $J = 6.2$, 6 H, Me)
$(C_6H_5CH_2)_2$	7.28 (mult, 5H, H_f), 6.90 (t, $J = 6.4$, 2 H, H_m), 6.69 (mult, 3 H, $H_{o,p}$), 3.14 (mult, 4 H, CH_2CH_2)
$(C_6H_5)_2$	8.03 (mult, 2 H, H_{mf}), 7.65 (mult, 3 H, $H_{pf,of}$), 7.29 (d, $J = 6.7$, 2 H, H_o), 7.16 (t, $J = 6.5$, 2 H, H_m), 6.82 (t, $J = 6.3$, 1 H, H_p)
$(2\text{-}ClC_6H_4Mn(CO)_5)$[c]	7.20 (d, $J = 6.6$, 1 H, H_3), 6.99 (d, $J = 6.8$, 1 H, H_6), 6.86 (t, $J = 6.2$, 1 H, H_5), 6.46 (t, $J = 6.3$, 1 H, H_4)
4-$CH_3C_6H_4OMe$	6.98 (d, $J = 5.6$, 2 H, H_{aryl}), 6.43 (d, $J = 5.6$, 2 H, H_{aryl}), 4.10 (s, 3 H, OMe), 2.45 (s, 3 H, Me)
$(C_6H_5)_2O$	7.64 (t, $J = 7.8$, 2 H, H_{mf}), 7.49 (t, $J = 7.5$, 1 H, H_{pf}), 7.42 (d, $J = 8.3$, 2 H, H_{of}), 7.19 (t, $J = 6.7$, 2 H, H_m), 6.45 (d, $J = 7.0$, 2 H, H_o), 6.38 (t, $J = 6.3$, 1 H, H_p)
C_6H_5OH	6.94 (t, $J = 6.3$, 2 H, H_m), 6.01 (mult, 3 H, $H_{o,p}$)
dibenzothiophene[d]	8.72 (d, $J = 7.8$, 1 H, H_8), 8.31 (d, $J = 8.0$, 1 H, H_5), 8.16 (d, $J = 6.9$, 1 H, H_1), 8.04 (d, $J = 7.1$, 1 H, H_4), 7.92 (t, $J = 7.5$, 1 H, H_6), 7.83 (t, $J = 7.6$, 1 H, H_7), 7.07 (t, $J = 6.5$, 1 H, H_3), 6.88 (t, $J = 6.5$, 1 H, H_2)
$(C_6H_5CH_2)_2CO$	7.28 (m, 5 H, H_f), 6.86 (t, $J = 6.0$, 2 H, H_m), 6.79 (t, $J = 6.0$, 1 H, H_p), 6.69 (d, $J = 6.0$, 2 H, H_o), 4.30 (s, 2 H, CH_2), 4.04 (s, 2 H, CH_2)
$C_6H_5CH_2COPh$	8.12 (d, $J = 7.2$, 2 H, H_{of}), 7.69 (t, $J = 7.0$, 1 H, H_{pf}), 7.58 (t, $J = 6.7$, 2 H, H_{mf}), 6.88 (m, 5 H, $H_{o,m,p}$), 4.82 (s, 2 H, CH_2)

[a] All spectra in CD_3COCD_3; J values given in Hz. [b] Subscript f refers to noncoordinated ring. [c] Relative positions of Cl and $Mn(CO)_5$ to H_{3-6} unknown. [d] For numbering scheme, see text.

Table 5. ^{13}C-NMR Data for New $[(\eta^6\text{-arene})Mn(CO)_3]^+$ Complexes

arene	^{13}C-NMR[a,b]
1,2,4,5-$C_6H_2Me_4$	(218), 115.7, 103.8, 18.0
$C_6H_5CH_2CHMe_2$	(216), 123.7, 103.8, 101.1, 99.0, 43.5, 31.5, 22.1
$(C_6H_5CH_2)_2$	(216), 140.4, 129.7, 129.6, 127.6, 123.8, 103.3, 101.4, 99.6, 37.2, 36.8
$(C_6H_5)_2$	(216), 133.0, 132.3, 130.6, 128.9, 120.9, 103.9, 99.3, 98.3
$(2\text{-}ClC_6H_4Mn(CO)_5)$	(217, 208), 143.3, 131.2, 116.3, 101.5, 101.3, 98.9
4-$CH_3C_6H_4OMe$	(218), 148.6, 108.3, 105.4, 84.3, 58.9, 19.1
$(C_6H_5)_2O$	152.7, 149.0, 132.0, 128.5, 121.5, 105.9, 92.6, 86.2
C_6H_5OH	(218), 154.2, 107.0, 86.7, 86.1
dibenzothiophene	143.2, 140.1, 136.4, 132.9, 131.5, 128.2, 125.6, 125.1, 124.2, 123.7, 122.9, 122.3
$(C_6H_5CH_2)_2CO$	(216), 203.2, 134.9, 130.8, 129.4, 127.9, 116.0, 103.3, 102.2, 100.6, 49.9, 46.0
$C_6H_5CH_2COPh$	(216), 195.5, 136.8, 134.8, 129.7, 129.2, 116.1, 103.7, 102.0, 100.9, 43.2

[a] All spectra in CD_3COCD_3. [b] Mn−CO peaks, where observed, indicated in parentheses.

Table 6. Analysis Results (%) for New $[(\eta^6\text{-arene})Mn(CO)_3]^+X^-$ Complexes

arene	X^-	decomp pt[a] (°C)	theory		found	
1,2,4,5-$C_6H_2Me_4$	BF_4^-	217	C	43.37	C	43.40
			H	3.93	H	3.91
$C_6H_5CH_2CHMe_2$	PF_6^-	131	C	37.34	C	36.15
			H	3.38	H	3.16
$(C_6H_5CH_2)_2$	BF_4^-	161	C	50.03	C	49.46
			H	3.47	H	3.43
$(C_6H_5)_2$	BF_4^-	166	C	47.41	C	46.11
			H	2.66	H	2.80
$(2\text{-}ClC_6H_4Mn(CO)_5)$	PF_6^-	117	C	28.48	C	28.05
			H	0.68	H	0.69
			Mn	18.61	Mn	18.60
4-$CH_3C_6H_4OMe$	BF_4^-	126	C	37.97	C	37.73
			H	2.90	H	2.78
$(C_6H_5)_2O$	PF_6^-	200	C	39.67	C	39.59
			H	2.22	H	2.26
C_6H_5OH	BF_4^-	223	C	33.79	C	33.81
			H	1.89	H	1.85
dibenzothiophene	BF_4^-	155	C	43.93	C	41.50
			H	1.97	H	1.90
$(C_6H_5CH_2)_2CO$	BF_4^-	132	C	49.57	C	49.02
			H	3.24	H	3.56
$C_6H_5CH_2COPh$	BF_4^-	134	C	48.38	C	47.75
			H	2.87	H	2.95

[a] All complexes decomposed before melting with darkening of color and/or evolution of gas.

the formation of new carbon−carbon bonds.[11,13,16,17,24] With a choice of three direct synthetic routes to the metalated arene, it appeared desirable to explore the strengths and limitations of each. Therefore in the current study, a variety of aromatic compounds have been subjected to each set of reaction conditions. The scope of arene coordination to $[Mn(CO)_3]^+$ is discussed below.

Results

A list of the tested arenes which were found to coordinate to $[Mn(CO)_3]^+$ is presented in Table 2. It may be noted that most of the arenes which could be coordinated yielded a measurable amount of product via each of the three methods. This is reasonable given the common intermediate ($[Mn(CO)_5]^+$) for all three routes. Table 3 lists those aromatics tested which gave no clear indication of the desired product under any circumstances. Tables 4−6 contain characterization data for all new $[(\eta^6\text{-arene})Mn(CO)_3]^+$ species. All of the $[(\eta^6\text{-arene})Mn(CO)_3]^+$ salts are pale yellow powders. They are soluble in polar organic solvents. They are air- and moisture-stable in the solid state and in solution decompose only slowly under air.

As expected, coordination of alkyl-substituted aromatics was uniformly successful. The tested arenes were benzene, mesitylene, durene, isobutylbenzene, and bibenzyl. Yields were variable but were usually best using the TFA anhydride method. The surprisingly low yield value for mesitylene by silver could not be improved. The preparation of the durene complex was accompanied by rearrangements of the methyl groups when Fischer−Hafner conditions were employed. Proton NMR of the durene Fischer−Hafner product revealed that about 52% consisted of the unrearranged 1,2,4,5-tetramethylbenzene complex. The other two tetramethylbenzene isomers gave complexes comprising about 30 and 18% of the total product. No rearrangements were found for mesitylene or isobutylbenzene. The bibenzyl Fischer−Hafner product also appeared to be a mixture but could not be further characterized.

Biphenyl could be metalated in fair yield. However, attempted coordination of naphthalene was unsuccessful, although TFA anhydride gave a trace yield of a product exhibiting the expected IR bands. This product was too unstable to characterize further.

Haloarene coordination resulted in low yields using the silver(I) synthesis. Chlorobenzene was easily attached to $[Mn(CO)_3]^+$ via the other methods, however. Fischer−Hafner reaction of bromobenzene produced the benzene complex (in 66% yield), despite evidence of

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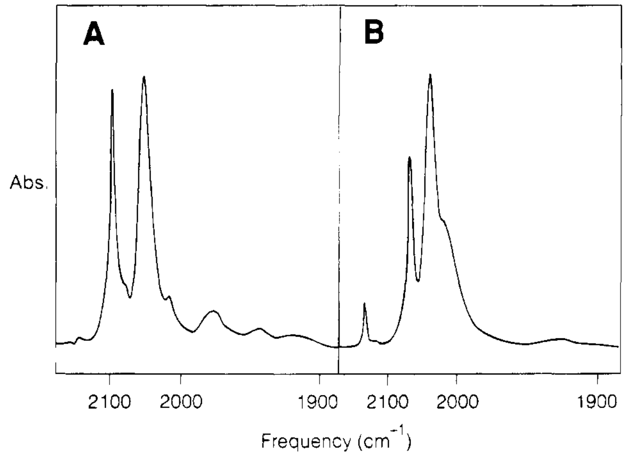


Figure 1. Infrared spectra of (A) the Fischer–Hafner reaction *in situ* $[(\eta^6\text{-}2\text{-}C_6H_4Cl_2)Mn(CO)_3]AlCl_3Br$ in *o*-$C_6H_4Cl_2$ solvent and (B) the isolated product $[(\eta^6\text{-}2\text{-}ClC_6H_4Mn(CO)_5)Mn(CO)_3]PF_6$ in acetone solvent.

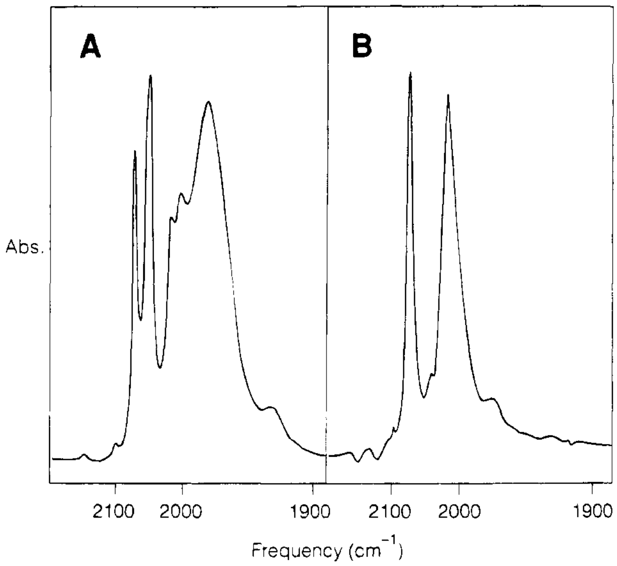
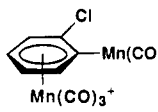
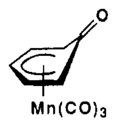


Figure 2. Infrared spectra of (A) the silver(I) reaction *in situ* mixture of $[(\eta^6\text{-}C_6H_5OH)Mn(CO)_3]BF_4$ and $[(\eta^5\text{-}C_6H_5O)Mn(CO)_3]$, **2**, in CH_2Cl_2 and (B) the same mixture after addition of a drop of $HBF_4{\cdot}OEt_2$, which protonates **2**.

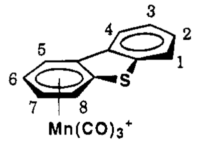
Chart 1



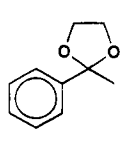
1



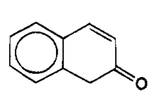
2



3



4



5

initial C_6H_5Br coordination. Since the halobenzene may be used as the reaction solvent and since the product $[(\eta^6\text{-}C_6H_5X)Mn(CO)_3]AlCl_3Br$ is soluble in it, infrared spectra were recorded before aqueous workup. These spectra clearly indicated the haloarene complexes: X = Cl, 2087, 2036 cm^{-1}; X = Br, 2083, 2031 cm^{-1}. The appearance of the lower frequency band (E symmetry in C_{3v}) above 2030 cm^{-1} was indicative of the electron-poor haloarene complex. While the chlorobenzene complex showed no change in the IR (2087, 2036 cm^{-1}) after aqueous workup, the product of the bromobenzene synthesis showed bands at 2085 and 2025 cm^{-1}. This indicated that the benzene complex had been formed. The identities of the isolated products were further confirmed by ^{1}H-NMR. Only the TFA anhydride method give an acceptable yield of $[(\eta^6\text{-}C_6H_5Br)Mn(CO)_3]^+$. However this product was slightly contaminated with $[Mn(CO)_6]^+$.

o-Dichlorobenzene yielded no product by silver or TFA anhydride. Nevertheless an unusual transformation occurred in the Fischer–Hafner reaction. Following IR identification of the desired dihalogenated arene complex in *o*-dichlorobenzene solvent (2089, 2046 cm^{-1}; Figure 1A), workup afforded a product with a more complicated IR pattern (Figure 1B). The infrared spectrum in Figure 1B suggests the presence of both $[Mn(CO)_3]$ (2076, 2028 cm^{-1}) and $[Mn(CO)_5]$ (2137, 2047, 2014 cm^{-1}) fragments. No change in the spectrum was evident after the product was carefully recrystallized, supporting the conclusion that it represented a single substance. Data from ^{1}H- and ^{13}C-NMR indicated an η^6-*o*-disubstituted-arene. Elemental analysis (C, H, Mn) supported the formula $C_{14}H_4O_8ClPF_6Mn_2$. Structure **1** (Chart 1) is proposed for this bimetallic complex. Unfortunately, this unusual compound has thus far proved resistant to growth of crystals suitable for X-ray diffraction. Compound **1** reacts with nucleophiles such as hydride and trimethylphosphine, giving cyclohexadienyl products which continue to exhibit both sets of metal carbonyl bands.

Aromatics bearing an oxygen atom on the ring were generally found to metalate. Phenyl ether and *p*-methylanisole provided yields similar to those for alkylbenzenes. Phenol however did not coordinate using the Fischer–Hafner method. The phenol complex was successfully prepared by both silver and TFA anhydride methods. However the latter was complicated by byproduct formation of $[Mn(CO)_6]^+$. When preparation was attempted using silver(I) in nonacidified CH_2Cl_2, a nearly equal mixture of the phenol complex (2073, 2018 cm^{-1}) and its conjugate base, **2** (2048, 1981 cm^{-1}), was noted by infrared spectroscopy, as shown in Figure 2A. Acidification of the mixture led to complete reprotonation at the ketone oxygen, Figure 2B. Several η^5-oxocyclohexadienyl complexes, similar to **2**, for various metals are known.[25]

The novel dibenzothiophene (DBT) complex (**3**) was synthesized in high yield by TFA anhydride and in low yields by the other methods. It is a bright yellow solid and shows NMR behavior indicating the coordination of a single fused benzene ring to manganese. A variety of transition metal complexes bearing S-bound DBT are

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(25) (a) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995. (b) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Torroni, S.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Organomet. Chem.* **1980**, *188*, C31. (c) Dahlenburg, L.; Hock, N. *J. Organomet. Chem.* **1985**, *284*, 129. (d) Heppert, J. A.; Boyle, T. J.; Takusagawa, F. *Organometallics* **1989**, *8*, 461. (e) Piorko, A.; Zhang, C. H.; Reid, R. S.; Lee, C. C.; Sutherland, R. G. *J. Organomet. Chem.* **1990**, *395*, 293. (f) Koelle, U.; Wang, M. H.; Raabe, G. *Organometallics* **1991**, *10*, 2573.

known.[26] However only two other η^6-complexes have been reported.[27] The η^5-mode is unknown for DBT, although thiophene itself has been coordinated in η^5-fashion to $[Mn(CO)_3]^+$ using the silver(I) method.[28] Comparison of the proton NMR data for **3** and the previously reported $[(\eta^6\text{-DBT})RuCp]^+$ and $[(\eta^6\text{-DBT})Rh(\eta^4\text{-norbornadiene})]^+$ yielded an interesting observation. Proton chemical shifts for the uncomplexed ring in each DBT complex were readily identified, being shifted very little from that of free DBT. In the ruthenium and rhodium cations, the protons in the coordinated ring showed an upfield shift relative to their noncoordinated counterparts of about 0.8 ppm. By contrast **3** exhibited a downfield shift of roughly 0.7 ppm. The DBT ligand was unique among the arenes in this study in displaying this downfield shift upon coordination. This deshielding effect can perhaps be attributed to a combination of the very strong electron-withdrawing ability of the $[Mn(CO)_3]^+$ moiety and resonance deshielding. The coordinated ring protons of $[(\eta^6\text{-indole})Mn(CO)_3]^+$ and $[(\eta^6\text{-benzofuran})Mn(CO)_3]^+$ both show a mixture of upfield and downfield shifts, while protons on the heterocycle ring are shifted sharply downfield.[17]

New complexes were also formed using the β-ketoaromatics 1,3-diphenylacetone and deoxybenzoin. Both of these species gave NMR spectra which indicated a single arene ring coordinated to the metal. In the case of the deoxybenzoin product, protons on the ring which is out of conjugation with the carbonyl underwent the upfield shift indicative of coordination. The protons on the conjugated ring were essentially unshifted. A single crystal X-ray structure was obtained for the 1,3-diphenylacetone complex and is discussed below.

Two substrates, phenoxytrimethylsilane and phenyl acetate, did not provide the expected products due to a hydrolysis reaction, which must be attributed to the presence of adventitious water in the case of the silver method. The product obtained in both of these cases was $[(C_6H_5OH)Mn(CO)_3]^+$, along with its conjugate base, **2**. These complexes were readily identified by infrared spectroscopy and by their distinctive acid/base behavior. Several of the arenes tested reacted to such an extent with TFA anhydride/HBF_4 as to render them useless. The latter group included the following: tropolone, benzyl alcohol, and phenyl acetylene. Neither could these arenes be affixed to $[Mn(CO)_3]^+$ via the Fischer–Hafner or silver routes.

Discussion

Scope of the Metalation Reaction. Comparison of Tables 2 and 3 provides, for the first time, a moderately comprehensive summary of the scope of metalation. Three factors are of potential significance in determining the relative coordinating abilities of various aromatic molecules. These are the acid-sensitivity, the electronic character, and the presence of lone pair-bearing heteroatoms on the arene. Although the three are interrelated, the electronic character of the arene substrate is apparently the most important. The $[Mn(CO)_3]^+$ fragment is recognized as being highly electron-deficient.[29] Therefore electron donation to the ring via resonance or induction is expected to activate the arene, stabilizing the desired product. Consequently, electron-donating substituents, such as alkyl and ether groups, are readily tolerated. Aromatic rings bearing one or more electronegative atoms are subject to electron donation via induction. Therefore it was reasonable that phenol and dibenzothiophene should join indole and benzofuran[17] as usable substrates. $[(\eta^6\text{-}C_6H_5OH)Mn(CO)_3]^+$ had been tentatively identified by Pauson,[7,22] who asserted that it was highly acidic. It has also been prepared very recently by Chung.[30] In the current study, its high acidity has been confirmed. The DBT complex was prepared in high yield by TFA anhydride. In contrast to the behavior of other heterocycles, such as indole and benzofuran, DBT coordination using the silver(I) method occurred in low yield. A possible explanation is that the soft heteroatom sulfur coordinates more effectively with the silver ion than does nitrogen or oxygen.

Electron-deficient arenes were expected to coordinate only very weakly, if at all, to $[Mn(CO)_3]^+$. Nevertheless, aryl substituents, *e.g.* in biphenyl, are not sufficiently electron-withdrawing to prevent coordination, although the yields were low to moderate for all methods. Naphthalene was chosen as a representative fused-ring aromatic hydrocarbon. Resonance electron withdrawal occurs to a large extent for naphthalene. Although the $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]^+$ complex was reported in 1961 through Fischer–Hafner synthesis, no spectroscopic data were given.[6] More recently Stobart and Zaworotko demonstrated that, in the presence of $AlCl_3$, naphthalene and anthracene are reduced, providing the η^6-complexes of tetralin and 9,10-dihydroanthracene.[9] These authors further claimed that they could synthesize the naphthalene complex via another (unspecified) route but found it to be highly sensitive to arene displacement reactions. This is consistent with the known lability of naphthalene in the isoelectronic $[(\eta^6\text{-}C_{10}H_8)Cr(CO)_3]$.[31] In the present study, the (naphthalene)manganese(I) complex was identified in trace amounts by infrared only.

The activated substrate *N,N*-dimethylaniline failed to coordinate. However the likely protonation of this compound under the acidic reaction conditions would produce the highly electron-deficient anilinium ion. Electron deficiency also prevented metalation of arenes bearing cyano, nitro, and α-carbonyl groups. Due to the pervasiveness of the carbonyl group in organic synthesis, a variety of carbonyl aromatics were examined. Repositioning of the carbonyl carbon from α to β with respect to the phenyl was found to allow coordination. In the case of deoxybenzoin, metalation was completely regioselective favoring the nonconjugated ring. This provided strong evidence that it is conjugation of the carbonyl that precludes arene coordination. The failure

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of such conjugated rings to coordinate to $[Mn(CO)_3]^+$ is almost certainly due to the electron deficiency of the ring, rather than competitive σ-coordination (*vide infra*). Resonance electron withdrawal can be disrupted by the formation of a ketal, such as the ethylene glycol ketal of acetophenone (**4**). The electron density at the ring in **4** is still low due to induction, however. Only the mildly acidic silver method was employed in an attempt to coordinate this acid-sensitive ketal. No coordinated product was found. Mass spectrometry showed the ketal to be intact after the failed coordination attempt. Coumarin (**5**) also failed to form a π-complex. The carbonyl in coumarin lies at a remote position from the fused benzene but is in conjugation with it, facilitating electron withdrawal. Finally, despite its lesser degree of inductive deactivation, *p*-methoxyacetophenone also failed to coordinate.

The chemistry of halogenated aromatics with $[Mn(CO)_3]^+$ has proved to be interesting. Aryl halides are electron-donating via resonance but are electron-withdrawing through induction. Overall they are deactivating toward Friedel–Crafts chemistry and may be expected to coordinate only with difficulty. Their Fischer–Hafner chemistry was previously investigated by Pauson.[7,22] He found that chlorobenzene could be coordinated in 64% yield, but bromobenzene underwent significant debromination to give a mixture of $[(\eta^6\text{-}C_6H_5Br)Mn(CO)_3]^+$ and $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+$. In the current study, it was shown that substitution of the bromine occurs during the hydrolysis step of the Fischer–Hafner synthesis. The mechanism involved is rather obscure. Conditions during the hydrolysis step are highly acidic given the excess of aluminum chloride. However, electrophilic attack on the complex by H^+ (liberating "Br^+") would be very surprising since the complex is highly electron deficient. A free radical mechanism cannot be ruled out. A similar electrophilic substitution appears to occur during the hydrolysis of the *o*-dichlorobenzene cation, resulting in the formation of **1**. For both chlorobenzene and bromobenzene, yields were reproducibly under 10% via silver(I). This may be due to the high affinity of silver for complexation with halogens, resulting in a deactivated $Ph{-}X{-}Ag^+$ complex.

A second factor which affected coordination to $[Mn(CO)_3]^+$ was the acid sensitivity of the aromatic substrates. All three methods which produce $[(\eta^6\text{-arene})Mn(CO)_3]^+$ operate under acidic conditions. Only the silver(I) synthesis employs stoichiometric amounts of a mild and highly halide-specific Lewis acid which is unlikely to react with most arenes. The other methods require an excess of strong Lewis or Bronsted acid, which will destabilize some arenes. Moreover, lone pair-bearing functionalities can form complexes with strong Lewis acids (such as aluminum chloride), leading to a lessening of electron density in the π-system. One serious difficulty caused by the use of strong acid was the decomposition of substrates such as tropolone, benzyl alcohol, and phenyl acetylene. However none of these substrates coordinated via the milder silver(I) method. Acid-promoted reactions were also evident with aromatic ketones. These substrates were observed to produce brightly colored solutions within several minutes in the TFA anhydride/HBF_4 mixture, even in the absence of $[Mn_2(CO)_{10}]$. Nevertheless, metalation was usually able to compete with these side reactions in the case of nonconjugated ketones. An acid reaction product was evident in the case of *p*-methoxyacetophenone. Upon reaction via the TFA anhydride method, deacylation occurred, resulting in a 17% yield of $[(\eta^6\text{-anisole})Mn(CO)_3]BF_4$.

Another acid-induced problem was that of alkyl rearrangement under Fischer–Hafner conditions. Alkyl group rearrangements have previously been found in connection with the synthesis of $[(\eta^6\text{-arene})_2Fe]^{+2}$.[32] During a Fischer–Hafner synthesis of $[(\eta^6\text{-}C_6H_5CMe_3)Mn(CO)_3]^+$, Chung[13] noted byproduct formation of the 1,3-di-*tert*-butylbenzene complex. Such rearrangements in the presence of Lewis acids proceed by a retro Friedel–Crafts mechanism.[33] Durene is especially prone to this, as evidenced in the Jacobsen rearrangement.[34] This fact can be understood since the *meta* arrangement is recognized as the thermodynamically preferred for polyalkylated aromatics.[33]

A final factor which may influence coordination must be considered for aromatics with heteroatom substituents. Lone pair-bearing heteroatoms attached to the arene could preferentially coordinate to the metal in a σ-fashion, yielding products analogous to the known $[Mn(CO)_3(solvent)_3]^+$, solvent = acetone, CH_3CN, or THF.[8,21c,35] This phenomenon was not observed in the current study, however. In fact a number of substrates, such as phenol, DBT, and the β-ketoarenes, which have accessible lone pairs, were successfully coordinated in an η^6-fashion.

Comments on the Individual Methods. No one of the three coordination methods is clearly the reaction of choice in all cases, although the TFA anhydride technique usually gives the best product yields for acid-insensitive substrates. The comments which follow address the pros and cons of each technique.

The Fischer–Hafner synthesis is conveniently carried out and does not require inert atmosphere. Yields are high for most hydrocarbon substrates. This method is not recommended for polyalkylated arenes, however, due to retro Friedel–Crafts rearrangements. In fact other investigators have noted rearrangements of even monoalkylated aromatics.[13,32] The method is useful for ethers and nonconjugated carbonyl arenes but not for phenol. A general difficulty inherent with this reaction stems from the formation of the product as an insoluble oil beneath the cyclohexane solvent. This makes it impossible to monitor the progress of the reaction by infrared spectroscopy, although the visible formation of this layer is a qualitative indicator. An exception occurs in the use of haloaromatic solvent.

The TFA anhydride method utilizes the harshest conditions. Trifluoroacetic anhydride is not a particularly convenient solvent, as it is both moderately expensive and produces irritating fumes. Particular caution must be exercised during the evaporation of this liquid. Many arenes are unstable under the strongly Bronsted acidic conditions. Efforts were made to modify the method, reducing the amount of TFA anhydride by adding CH_2Cl_2 solvent. Unfortunately, the desired reaction did not occur under these conditions.

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Table 7. Crystal and Structure Refinement Data for $[(\eta^6\text{-}C_6H_5CH_2COCH_2Ph)Mn(CO)_3]BF_4$

empirical formula	$C_{18}H_{14}BF_4MnO_4$
fw	436.04
temp	298(2) K
wavelength	0.710 73 Å
cryst system	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 12.5429(12)$ Å
	$b = 12.465(2)$ Å
	$c = 12.109(2)$ Å
	$\beta = 106.128(10)°$
V	1818.8(5) Å^3
Z	4
D(calcd)	1.592 mg m^{-3}
abs coeff	0.787 mm^{-1}
F(000)	880
cryst size	0.52 × 0.46 × 0.45 mm
θ range for data collcn	2.35–25.01°
index ranges	$-14 \le h \le 14, -14 \le k \le 1, -1 \le l \le 14$
no. of reflcns collcd	4015
no. of indpdt reflcns	3174 ($R_{int} = 0.0311$)
refinement method	full-matrix least squares on F^2
data/restraints/params	3174/0/253
goodness-of-fit	1.008
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0570$, w$R2 = 0.1609$
R indices (all data)	$R1 = 0.0753$, w$R2 = 0.1793$
largest diff peak and hole	0.899 and −0.376 e Å^{-3}

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters U(eq)^a (Å$^2 \times 10^3$) for $[(\eta^6\text{-}C_6H_5CH_2COCH_2Ph)Mn(CO)_3]BF_4$

atom	x	y	z	U(eq)
Mn(1)	1938(1)	8853(1)	2180(1)	41(1)
O(1)	3883(2)	10951(2)	5467(3)	56(1)
O(2)	3265(3)	8829(3)	512(3)	81(1)
O(3)	247(3)	7466(3)	667(3)	82(1)
O(4)	787(3)	10797(3)	1056(3)	86(1)
C(1)	3312(3)	9420(3)	3614(3)	45(1)
C(2)	3475(3)	8322(3)	3421(3)	51(1)
C(3)	2642(4)	7574(3)	3394(3)	55(1)
C(4)	1649(4)	7930(3)	3586(3)	54(1)
C(5)	1480(3)	9000(3)	3787(3)	48(1)
C(6)	2313(3)	9767(3)	3811(3)	43(1)
C(7)	2128(3)	10935(3)	4038(4)	53(1)
C(8)	2991(3)	11377(3)	5072(3)	46(1)
C(9)	2666(4)	12401(3)	5542(4)	60(1)
C(10)	3614(3)	12918(3)	6417(4)	53(1)
C(11)	4220(4)	13749(3)	6116(5)	69(1)
C(12)	5133(5)	14169(5)	6944(8)	101(2)
C(13)	5432(5)	13759(6)	8052(7)	97(2)
C(14)	4834(5)	12981(6)	8327(5)	83(2)
C(15)	3932(4)	12564(4)	7532(4)	66(1)
C(16)	2742(4)	8850(3)	1145(4)	56(1)
C(17)	887(4)	8002(4)	1238(4)	57(1)
C(18)	1212(4)	10045(4)	1491(4)	59(1)
B(1)	1497(5)	4673(6)	2548(8)	92(2)
F(1)	1681(11)	4854(8)	1527(8)	306(6)
F(2)	2517(4)	4743(5)	3118(7)	191(3)
F(3)	1104(3)	3699(3)	2490(6)	158(2)
F(4)	827(4)	5445(4)	2553(6)	177(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

A recurring byproduct of the TFA anhydride method is $[Mn(CO)_6]^+$ with its signature infrared band around 2100 cm^{-1}. This compound is the product of disproportionation of $[Mn(CO)_5]^+$ or possibly represents carbonyl abstraction from $[Mn_2(CO)_{10}]$. It is usually evident at roughly constant concentrations throughout the synthesis and is not eliminated by longer reflux intervals nor by rapid flushing with nitrogen. Fortunately, it is not found above trace amounts in most isolated products. Nevertheless, significant levels of $[Mn(CO)_6]^+$ were present in the bromobenzene and phenol products.

There are several very positive aspects of the TFA anhydride technique. It does not require an inert atmosphere, and the progress of the reaction is readily monitored by diluting a drop of the reaction mixture in CH_2Cl_2 and observing the infrared spectrum. Finally and most importantly, this method is useful with a relatively wide range of arenes and usually provides the best product yields.

The silver(I) method is without a doubt the mildest of the three reactions. It is the method of choice for acid-sensitive arenes. Reaction progress is conveniently monitored by IR spectroscopy. However, it is best carried out under inert atmosphere and in the dark. Yields can also be unpredictable and are notably low for halide-bearing aromatics.

X-ray Crystallographic Study of the 1,3-Diphenylacetone Complex. Since the β-phenylketones represent a new substrate for coordination to $[Mn(CO)_3]^+$, a single crystal X-ray structure was sought. Suitable crystals of the 1,3-diphenylacetone complex were grown by diffusion of diethyl ether into a concentrated acetone solution of the complex. Solution of the monoclinic structure was accomplished by direct methods. Crystallographic data are listed in Table 7, fractional nonhydrogen atom coordinates in Table 8, and selected bond lengths and angles in Table 9. A thermal ellipsoid drawing of the cation is shown in Figure 3. The refined $\omega R2$ factor was higher than desirable due to extensive disorder which was present in the BF_4^- anion. Modeling of the disorder in the present case was unsuccessful. Nevertheless, the structure of the cation was reasonable and showed no significant disorder. Its general configuration was the expected piano stool with the arene substituent adopting a nearly *syn* eclipsed position with respect to the carbonyl ligands. The metal tripod is rotated about 12° from the eclipsed conformation. The metal carbonyls are approximately linear. The six carbons of the coordinated arene ring were found to be planar by least squares analysis, with the maximum deviation being 0.0066 Å. The metal atom lies within 0.0026 Å from a line projected perpendicular to the ring centroid. The structure of the side chain reflects the lack of conjugation. The carbonyl-bearing plane (C(7), C(8), C(9), O(1)) lies at a 52° angle to the coordinated ring, with the carbonyl pointing away from the metal fragment. The carbonyl plane produces an angle of 78° with the noncoordinated ring and the two ring planes are almost perpendicular to one another (86°).

Conclusions

The coordination of aromatic molecules to $[Mn(CO)_3]^+$ has been investigated and found to be moderately general in scope. Although the three synthetic methods are successful for most arenes, the TFA anhydride method usually resulted in the highest product yields. Substrates bearing electron-donating substituents such as alkyl, alkoxy, and hydroxy may be coordinated in high yield. Fused ring aromatic systems in which a lone pair-bearing heteroatom is directly attached to the fused benzene ring can also be metalated. Arenes bearing mild acceptor groups, such as aryls, chlorides, or nonconjugated carbonyl groups, can be coordinated as well. No direct evidence has been found for competitive coordination to manganese by heteroatoms. Unusual substitution reactions of aryl halides have been found

Table 9. Selected Bond Lengths and Angles in $[(\eta^6\text{-}C_6H_5CH_2COCH_2Ph)Mn(CO)_3]BF_4$

Bond Lengths (Å)			
Mn(1)—C(16)	1.813(5)	Mn(1)—C(17)	1.819(5)
Mn(1)—C(18)	1.824(4)	Mn(1)—C(4)	2.167(4)
Mn(1)—C(3)	2.182(4)	Mn(1)—C(5)	2.185(4)
Mn(1)—C(2)	2.191(4)	Mn(1)—C(1)	2.196(3)
Mn(1)—C(6)	2.216(4)	O(1)—C(8)	1.211(5)
O(2)—C(16)	1.139(6)	O(3)—C(17)	1.123(5)
O(4)—C(18)	1.134(5)	C(1)—C(6)	1.408(5)
C(1)—C(2)	1.412(6)	C(2)—C(3)	1.394(6)
C(3)—C(4)	1.402(6)	C(4)—C(5)	1.383(6)
C(5)—C(6)	1.411(5)	C(6)—C(7)	1.510(5)
C(7)—C(8)	1.514(6)	C(8)—C(9)	1.499(5)
C(9)—C(10)	1.501(5)	C(10)—C(15)	1.370(6)
C(10)—C(11)	1.391(6)	C(11)—C(12)	1.398(9)
C(12)—C(13)	1.387(10)	C(13)—C(14)	1.324(9)
C(14)—C(15)	1.369(7)	B(1)—F(2)	1.277(8)
B(1)—F(4)	1.280(8)	B(1)—F(3)	1.305(8)
B(1)—F(1)	1.338(11)		
Bond Angles (deg)			
C(16)—Mn(1)—(18)	89.3(2)	C(16)—Mn(1)—C(17)	90.7(2)
C(18)—Mn(1)—C(17)	90.3(2)	C(16)—Mn(1)—C(4)	142.0(2)
C(18)—Mn(1)—C(4)	128.5(2)	C(17)—Mn(1)—C(4)	86.1(2)
C(16)—Mn(1)—C(3)	105.4(2)	C(18)—Mn(1)—C(3)	164.3(2)
C(17)—Mn(1)—C(3)	94.8(2)	C(4)—Mn(1)—C(3)	37.6(2)
C(16)—Mn(1)—C(5)	161.8(2)	C(18)—Mn(1)—C(5)	96.8(2)
C(17)—Mn(1)—C(5)	106.4(2)	C(4)—Mn(1)—C(5)	37.0(2)
C(3)—Mn(1)—C(5)	67.6(2)	C(16)—Mn(1)—C(2)	85.5(2)
C(18)—Mn(1)—C(2)	142.5(2)	C(17)—Mn(1)—C(2)	126.8(2)
C(4)—Mn(1)—C(2)	66.9(2)	C(3)—Mn(1)—C(2)	37.2(2)
C(5)—Mn(1)—C(2)	79.2(2)	C(16)—Mn(1)—C(1)	94.7(2)
C(18)—Mn(1)—C(1)	106.4(2)	C(17)—Mn(1)—C(1)	162.5(2)
C(4)—Mn(1)—C(1)	79.4(2)	C(3)—Mn(1)—C(1)	67.7(2)
C(5)—Mn(1)—C(1)	67.10(14)	C(2)—Mn(1)—C(1)	37.5(2)
C(16)—Mn(1)—C(6)	126.6(2)	C(18)—Mn(1)—C(6)	86.8(2)
C(17)—Mn(1)—C(6)	142.5(2)	C(4)—C(1)—C(6)	67.2(2)
C(3)—Mn(1)—C(6)	80.2(2)	C(5)—Mn(1)—C(6)	37.38(14)
C(2)—Mn(1)—C(6)	67.37(14)	C(1)—M(1)—C(6)	37.20(13)
C(6)—C(1)—C(2)	120.2(4)	C(6)—C(1)—Mn(1)	72.1(2)
C(2)—C(1)—Mn(1)	71.0(2)	C(3)—C(2)—C(1)	120.7(4)
C(3)—C(2)—Mn(1)	71.1(2)	C(1)—C(2)—Mn(1)	71.4(2)
C(2)—C(3)—C(4)	118.6(4)	C(2)—C(3)—Mn(1)	71.8(2)
C(4)—C(3)—Mn(1)	70.6(2)	C(5)—C(4)—C(3)	121.4(4)
C(5)—C(4)—C(1)	72.2(2)	C(3)—C(4)—Mn(1)	71.8(2)
C(4)—C(5)—C(6)	120.6(4)	C(4)—C(5)—Mn(1)	70.8(2)
C(6)—C(5)—Mn(1)	72.5(2)	C(1)—C(6)—C(5)	118.5(4)
C(1)—C(6)—C(7)	121.1(4)	C(5)—C(6)—C(7)	120.5(3)
C(1)—C(6)—Mn(1)	70.7(2)	C(5)—C(6)—Mn(1)	71.0(2)
C(7)—C(6)—Mn(1)	130.7(3)	C(6)—C(7)—C(8)	113.0(3)
O(1)—C(8)—C(9)	122.9(4)	O(1)—C(8)—C(7)	122.5(3)
C(9)—C(8)—C(7)	114.6(3)	C(8)—C(9)—C(10)	112.8(3)
C(15)—C(10)—C(11)	117.9(4)	C(15)—C(10)—C(9)	120.9(4)
C(11)—C(10)—C(9)	121.2(5)	C(12)—C(11)—C(10)	119.3(6)
C(11)—C(12)—C(13)	120.2(6)	C(14)—C(13)—C(12)	119.6(5)
C(13)—C(14)—C(15)	121.1(6)	C(10)—C(15)—C(14)	121.9(5)
O(2)—C(16)—Mn(1)	178.2(4)	O(3)—C(17)—Mn(1)	179.0(4)
O(4)—C(18)—Mn(1)	178.1(4)	F(2)—B(1)—F(4)	120.5(7)
F(2)—B(1)—F(3)	113.5(7)	F(4)—B(1)—F(3)	117.5(5)
F(2)—B(1)—F(1)	94.8(8)	F(4)—B(1)—F(1)	99.2(8)
F(3)—B(1)—F(1)	105.4(8)		

to occur during hydrolysis in the presence of aluminum chloride. Further investigation of the reactivity of new $[(\eta^6\text{-arene})Mn(CO)_3]^+$ species is in progress.

Experimental Section

HPLC grade dichloromethane was purchased from Aldrich and was distilled from CaH_2. Acetone was distilled from P_4O_{10}. Cyclohexane and benzene were distilled from CaH_2. Hexane was stored over sodium ribbon. All aromatic ligands were purchased from Aldrich and used as received. Decacarbonyldimanganese was purchased from Strem. Pentacarbonylmanganese bromide[36] was prepared according to the literature, using cyclohexane solvent, rather than CS_2 or CCl_4. Anhydrous aluminum chloride was purchased from Aldrich and kept in an argon-filled drybox to prevent hydrolysis. Silver tetrafluoroborate was purchased from Aldrich and was stored in a desiccator between use. Trifluoroacetic anhydride was purchased from Aldrich. Tetrafluoroboric acid, aqueous (50%) and etherate (54%), was purchased from Fluka.

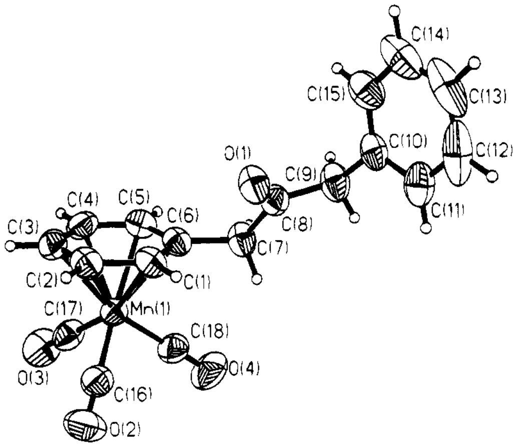

Figure 3. Thermal ellipsoid drawing of the cation in $[(\eta^6\text{-}C_6H_5CH_2COCH_2Ph)Mn(CO)_3]BF_4$ at the 50% probability level.

Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR using a liquid cell with CaF_2 windows, and ^1H- and ^{13}C-NMR spectra were collected using a General Electric QE-300 spectrometer. All arene salts were crystallized by slow diffusion of ether into acetone or CH_2Cl_2 solutions prior to NMR analysis. This was done to remove trace amounts of paramagnetic manganese salts. Decomposition points were recorded using a Thomas Hoover Unimelt apparatus and are reported without correction. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN.

Representative procedures for each of the three synthetic methods are given below. Infrared bands are labeled as follows: s, strong; m, medium; w, weak; br, broad.

Preparation of $[(\eta^6\text{-}C_6H_5OPh)Mn(CO)_3]PF_6$ by the Fischer–Hafner Method. $[Mn(CO)_5Br]$ (1.46 g, 5.30 mmol), $AlCl_3$ (2.03 g, 15.2 mmol), and $(C_6H_5)_2O$ (5 mL, 30 mmol) were refluxed for 14 h in 50 mL of cyclohexane under a $CaCl_2$ drying tube. As the reaction progressed, the cyclohexane changed from orange to almost colorless. Simultaneously, a red oil formed beneath the solvent. After cooling to 0 °C, the solvent was decanted and the oil treated with 20 mL of ice water. A yellow aqueous solution was formed. This was washed with diethyl ether and the ether back-extracted with water. The combined aqueous layer was treated with a solution of NH_4PF_6 (1.20 g, 7.35 mmol in 5 mL of H_2O). The yellow precipitate was collected and redissolved in acetone. It was precipitated using ether to give a pale yellow powder (2.12 g, 4.68 mmol, 88% yield).

Preparation of $[(\eta^6\text{-}2\text{-}ClC_6H_4Mn(CO)_5)Mn(CO)_3]PF_6$ by the Fischer–Hafner Method. $[Mn(CO)_5Br]$ (1.53 g, 5.55 mmol) and $AlCl_3$ (1.85 g, 13.9 mmol) were dissolved in 50 mL of o-$C_6H_4Cl_2$, and the solution was heated to 75 °C with stirring under N_2. After 4 h the mixture was a clear red color and IR revealed that the starting bromide complex (2135 (w), 2048 (s), 2006 (m) cm^{-1}) had been converted to $[Mn(CO)_5]^+$ (2153 (w), 2073 (s), 2035 (m) cm^{-1}). Heating was continued for a total of 27 h. The mixture was cooled to 25 °C, and an IR spectrum showed the dichlorobenzene product (2089 (s), 2046 (s, br) cm^{-1}). The mixture was further cooled to 0 °C and treated with 20 mL of ice water. A yellow aqueous solution was formed. This was washed with ether and the ether back-extracted with water. The combined aqueous layer was treated with a solution of NH_4PF_6 (0.994 g, 6.10 mmol in 5 mL of H_2O). A yellow precipitate was collected and redissolved

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(36) Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160.

in acetone. It was precipitated using ether to give a pale yellow powder which was identified as the bimetallic product by spectroscopy and elemental analysis (0.471 g, 0.798 mmol, 29% yield).

Preparation of [(η^6-C_6H_5OH)Mn(CO)$_3$]BF$_4$ by the Silver(I) Method. [Mn(CO)$_5$Br] (0.801 g, 2.91 mmol) and AgBF$_4$ (0.615 g, 3.16 mmol) were mixed in 40 mL of CH_2Cl_2, and the solution was thoroughly degassed using N_2. The mixture was placed in a foil-wrapped Schlenk flask and was refluxed under N_2 for 1 h. The IR spectrum of the cloudy yellow-orange solution was indicative of the [Mn(CO)$_5$]$^+$ ion (2137 (w), 2051 (s), 2007 (m) cm^{-1}). CH_2Cl_2 (8 mL) containing 2.04 g (21.7 mmol) of C_6H_5OH and a drop of $HBF_4{\cdot}OEt_2$ was injected through the side arm, and the mixture was refluxed for an additional 4.5 h. The use of acid is necessary only for the preparation of the phenol product. The IR spectrum revealed the desired arene product (2072 (s), 2016 (s, br) cm^{-1}). The solution was immediately cooled to room temperature. The solution was filtered through a bed of Celite. The Celite was washed with acetone until all the yellow color was removed. The CH_2Cl_2/acetone mixture was concentrated to about 10 mL *in vacuo* and was precipitated with ether. The yellow precipitate was collected and redissolved in acetone. It was precipitated using ether to give a pale yellow powder (0.638 g, 2.00 mmol, 69% yield).

Preparation of [(η^6-dibenzothiophene)Mn(CO)$_3$]BF$_4$ by the TFA Anhydride Method. TFA anhydride (15 mL) was cooled to 0 °C, and dibenzothiophene (2.09 g, 11.3 mmol) was added with stirring. [Mn$_2$(CO)$_{10}$] (0.350 g, 0.898 mmol) was added. The solution developed a brownish color. Finally aqueous HBF$_4$ (4 mL, 50% solution) was added. *Caution*: Exothermic reaction. After 1 min, the lemon-colored solution underwent exothermic reaction, refluxing briefly despite the ice bath. After this occurred the mixture was allowed to warm to room temperature and was refluxed for 4 h. The color became golden brown. An IR was taken by diluting a drop of the mixture in CH_2Cl_2. Product was evident (2077 (s), 2025 (s, br) cm^{-1}). The mixture was cooled and the solvent removed *in vacuo*. The bright yellow residue was then dissolved in 10 mL of 1:1 acetone/CH_2Cl_2, and the product was precipitated by the addition of ether. The bright yellow precipitate was collected and redissolved in acetone, and the mixture was filtered. It was precipitated using ether to give a bright yellow powder (0.656 g, 1.60 mmol, 89% yield).

X-ray Diffraction Study of [(η^6-$C_6H_5CH_2COCH_2Ph$)Mn(CO)$_3$]BF$_4$. Suitable crystals were grown by diffusion of diethyl ether into an acetone solution of the compound at 25 °C. One of the transparent yellow block-shaped crystals was selected (0.52 × 0.46 × 0.45 mm) and was glued to a glass fiber. X-ray data collection was carried out at 25 °C using a Siemens P4 single crystal diffractometer (Mo Kα radiation, 0.710 73 Å) controlled by XSCANS software. ω scans were used for data collection, at variable speeds from 10 to 60° min^{-1}. Three standard reflections were measured after every 97 reflections; no systematic decrease in intensity was observed. Data reduction included profile fitting and an empirical absorption correction based on separate azimuthal scans for seven reflections (maximum and minimum transmission, 0.441 and 0.399). The structure was determined by direct methods and refined initially by use of programs in the SHELXTL 5.1 package, which were also used for all figures. About half of the hydrogen atoms appeared in a difference map, and each was introduced in an ideal position, riding on the atom to which it is bonded. They were refined with isotropic temperature factors 20% greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters. Final refinement on F^2 was carried out using SHELXL 93.[37]

Acknowledgment is made to the Thomas F. and Kate Miller Jeffress Memorial Trust, to the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF No. 26521-GB1), and to the College of William and Mary for support of this research. The X-ray equipment was purchased with assistance from an instrument grant from the National Science Foundation (CHE-8206423) and a grant from the National Institutes of Health (RR-06462).

Supplementary Material Available: Tables of H coordinates and *U* values, anisotropic thermal parameters, torsion angles, and least squares planes and a unit cell diagram (6 pages). Ordering information is given on any current masthead page.

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[37] Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.