Synthesis and reactivity of [(η^6-[3$_2$](1,3)Cyclophane)Mn(CO)$_3$][BF$_4$]

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Abstract

The manganese cyclophane complex, [(η^6-[3$_2$](1,3)cyclophane)Mn(CO)$_3$][BF$_4$] **2**, was prepared by the reaction of [[3$_2$](1,3)-cyclophane] **1** with Mn(CO)$_5$FBF$_3$. Reaction of **2** with NaBH$_3$CN yielded the cyclohexadienyl manganese complex [(η^5-6H-[3$_2$](1,3)cyclophane)Mn(CO)$_3$] **3**. Interestingly, treatment of **3** with Mn(CO)$_5$FBF$_3$ gave the bis-manganese complex (η^6, η^5-6H-[3$_2$](1,3)cyclophane)[Mn(CO)$_3$]$_2$[BF$_4$] **4**. When NaBH$_3$CN was treated with **4**, [(η^5,η^5-6H,6′H-[3$_2$](1,3)cyclophane)Mn(CO)$_3$] **5** was isolated as yellow crystals. The structure of compounds **2** and **3** were determined by single-crystal X-ray crystallography.
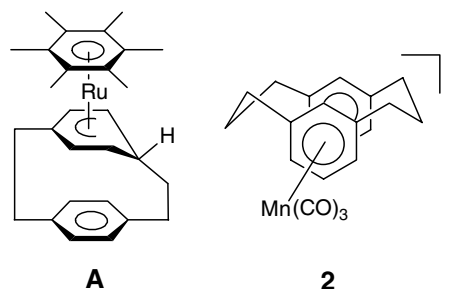© 2004 Elsevier B.V. All rights reserved.

Keywords: Cyclophane; Manganese compound; Nucleophilic addition

1. Introduction

Cyclophane has strong π-electron donating ability due to the transannular π–π interaction of the facing aromatic rings. Thus cyclophane has been used as either a monodentate or bidentate ligand for transition metals [1] and lanthanides [2]. The complexation of transition metals to cyclophane ligands has attracted considerable interest, with the main focus on synthetic studies aimed at one-dimensional polymers consisting of alternating cyclophane and metal complex units [3] and also on reactivity studies of the benzene deck of the cyclophane ligand. Recently, we reported that the cycloaddition of [3$_4$](1,2,4,5)cyclophane with dicyanoacetylene gave barrelenophane [4]. We also found that multi-bridged [3$_n$]cyclophanes(n = 3 [5] and 4 [6]) underwent photochemical reactions in solution to give polycyclic cage compounds with novel skeletons. Boekelheide et al. [7]

reported that the protonation of [(η^6-hexamethylbenzene)(η^4-[2$_2$](1,4) cyclophane)]ruthenium(0) gives a cyclophane ruthenium complex (**A**) containing a cyclohexadienyl anion deck. In an attempt to pursue further studies on thereactivity of the benzene deck of the cyclophane ligand, we envisioned that the cationic manganese complex of type **2** would be a good candidate because a variety of nucleophiles are known to add to the arene ring in (arene)Mn(CO)$_3^+$ to yield the corresponding cyclohexadienyl complex [8].

A   **2**

Recently, Welton and co-workers reported the manganese carbonyl cyclophane complex, [([2,2]paracyclophane)Mn(CO)$_3$]$^+$ using the ionic liquid system

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[bmim]Cl-AlCl$_3$ ([bmim]$^+$ = 1-butyl-3-methylimidazolium cation) in low yield [1e]. [3$_2$](1,3)Cyclophane (**1**) has attracted much interest due to the ease of its preparation [4] and flexibility [9]. For studying the reactivity of the benzene deck, more flexible manganese cyclophane complexes such as **2** are required. Here we report the efficient synthesis of the manganese complex **2** and its reactivity.

2. Results and discussion

Since the arenetricarbonylmanganese salts of the type [(arene)Mn(CO)$_3$]$^+$ were first obtained by Coffield et al. [11] from the arene, manganese pentacarbonyl halide and aluminum halide, Pauson et al. [12] developed a general synthetic method of [(arene)Mn(CO)$_3$]$^+$ complexes by treatment of Mn(CO)$_5$OClO$_3$ with arenes. We envisioned that the latter method could be applicable to the synthesis of the [(η^6-[3$_2$](1,3)cyclophane)Mn(CO)$_3$]$^+$ complex. Indeed, this proved to be the case. The manganese cyclophane complex **2** was readily prepared by the reaction of the cyclophane with Mn(CO)$_5$FBF$_3$ in CH$_2$Cl$_2$ (Eq. (1)). Standard workup and crystallization from CH$_2$Cl$_2$ gave (η^6-[3$_2$](1,3)cyclophane)Mn(CO)$_3$]-[BF$_4$] (**2**) in 91% yield as a yellow crystalline solid which is relatively stable to air. Our efforts to prepare (η^6,η^6-[3$_2$](1,3)cyclophane)[Mn(CO)$_3$]$_2$[BF$_4$]$_2$ by changing the reaction conditions and molar ratio were not successful. Compound **2** is moderately soluble in CH$_2$Cl$_2$ and THF.

$$\text{1} \quad + \quad \text{Mn(CO)}_5\text{Br} \quad \xrightarrow{\text{AgBF}_4} \quad \text{2} \qquad (1)$$
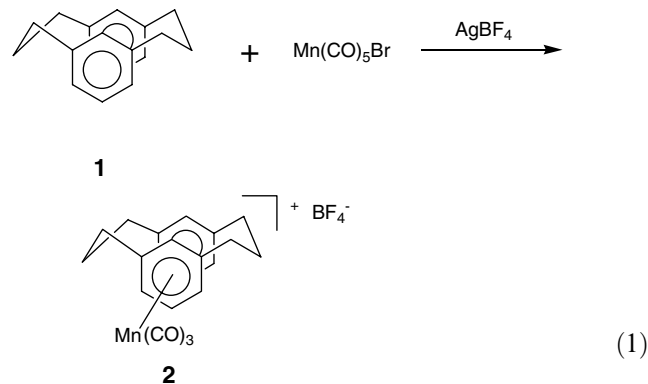
However, acetonitrile displaces cyclophane yielding [(CH$_3$CN)$_3$Mn(CO)$_3$][BF$_4$]. The structure of **2** is evident from its simple ^{1}H-NMR spectrum in which the two sets of three types of aromatic protons appear as the expected patterns. The downfield shifts of the ^{1}H-NMR signals of the metal-bound aromatic protons (δ 7.44, 7.02 and 6.91) as compared with those of free cyclophane (δ 6.74, 6.63 and 6.17) are *ca.* 0.4–0.7 ppm. A similar situation was observed for the Fe(II) and Ru(II) complexes of [3$_n$]cyclophanes [1b,13]. Thus the ^{1}H-NMR chemical shifts of the metal-bound aromatic hydrogens are strongly influenced by the anisotropy effect of the metal. The infrared spectrum exhibits the ex-
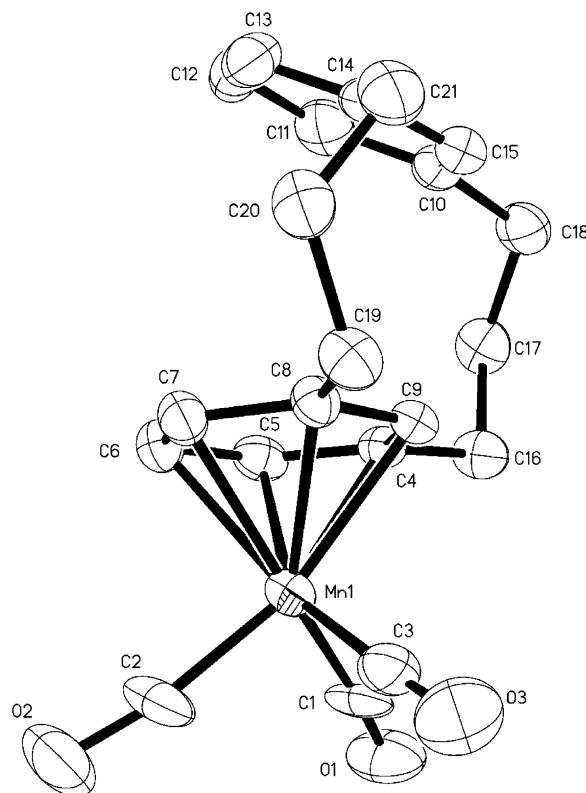

Fig. 1. X-ray crystal structure of **2** with 30% probability thermal ellipsoid depicted. All hydrogen atoms, disordered three carbonyl groups and BF$_4^-$ are omitted for clarity.

pected three bands in the terminal CO stretching region. The structure of **2**, unambiguously established by single-crystal analysis, is shown in Fig. 1. Crystallographic data and processing parameters are depicted in Table 1. The bond lengths of Mn–C(O) ranging from 1.76(2) Å to 1.79(2)′ are remarkably short than those of other arene complexes bearing Mn(CO)$_n$ moiety (1.804(2)–1.872(3) Å) [9]. However, the bond lengths of Mn–C(O) where disordered carbonyl groups are from 1.813(18) to 1.871(19) Å. These results illustrated that the average bone length of Mn–C(O) for **2** could be approximately 1.80 Å, which was close to value reported for the areneMn(CO)$_3^+$ and other derivatives [9,10]. The two phenyl rings (C4–C9 and C10–C15) are not parallel but are tilted by an angle of 26.33°. This value is a little bit larger than that of a similar tilting (24°) of the two aromatic rings of [3$_2$](1,3)cyclophane **1** [9]. The trimethylene bridges assume the same chair–chair conformation as in the case of the parent **1** [9,10]. The cyclophane ring is symmetrical across a mirror plane, which coincides with a pseudo-mirror plane of the entire molecule containing the atoms C6, C9, C12, C15, Mn1 and C1.

The reactivity of π-organic molecules such as arenes is drastically altered upon coordination to a transition metal. In particular, cyclic π-hydrocarbons when coor-

Table 1
Crystallographic data for compound **2** and **3**

	2	**3**
Formula	$C_{21}H_{20}BF_4O_3Mn$	$C_{21}H_{21}O_3Mn$
Formula weight	462.12	376.32
Crystal dimensions (mm^3)	$0.40 \times 0.36 \times 0.28$	$0.44 \times 0.40 \times 0.28$
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*
a (Å)	31.138(3)	28.004(2)
b (Å)	8.6959(15)	7.988(1)
c (Å)	16.445(3)	20.356(1)
β (°)	116.507(8)	128.232(4)
V ($Å^3$)	4112.7(11)	3677.1(5)
Z	8	8
D_{calcd} ($g\,cm^{-3}$)	1.493	1.398
μ (mm^{-1})	0.697	0.754
F(0 0 0)	1888	1568
2θ	4.9–49.98	3.5–50
Number of reflections collected	3612	3200
Number of unique reflections	3539 [$R_{int} = 0.0313$]	3133 [$R_{int} = 0.0201$]
R, R_w	0.0808, 0.2327	0.0293, 0.0745
Goodness of fit	1.148	1.086
Maximum peak, hole (e $Å^{-3}$)	0.577/−0.476	0.212/−0.204

dinated to cationic organometallic fragments undergo facile nucleophilic addition reactions [14]. To check the reactivity of the metal-bound aromatic ring, we attempted the nucleophilic addition of compound **2** with hydride. Reaction of **2** with a mild hydride nucleophile such as $NaBH_3CN$ gave attack at the benzene deck of cyclophane to yield $[(\eta^5\text{-}6H\text{-}[3_2](1,3)\text{cyclophane})Mn(CO)_3]$ **3** (Eq. (2)).

$$\mathbf{2} \xrightarrow{\ NaBH_3CN\ } \mathbf{3} \qquad (2)$$
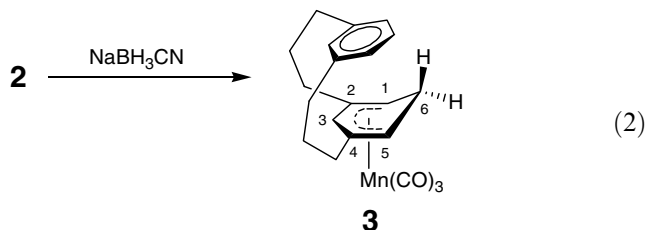
However, a stronger hydride donor, such as $LiAlH_4$, led to decomposition. The structure of **3** is readily assigned evident from its ^1H-NMR spectrum. The ^1H-NMR spectrum of the product exhibited two resonances at 2.83 and 1.48 ppm as a multiplet and a doublet of doublet. The assignment of **3** as 6-*endo* (δ 2.83) and 6-*exo* proton (δ 1.48) is based upon a comparison of its ^1H-NMR spectrum with those for known manganese analogues [15]. The cyclohexadienyl structure in **3** was confirmed by the molecular structure of **3**. The molecular structure of **3** is shown in Fig. 2. Crystallographic data are given in Table 1 and selected bond lengths and angles are given in Table 2. The five unsaturated carbon atoms (C4, C5, C6, C7 and C8) of the cyclohexadienyl cyclophane are essentially planar (maximum deviation
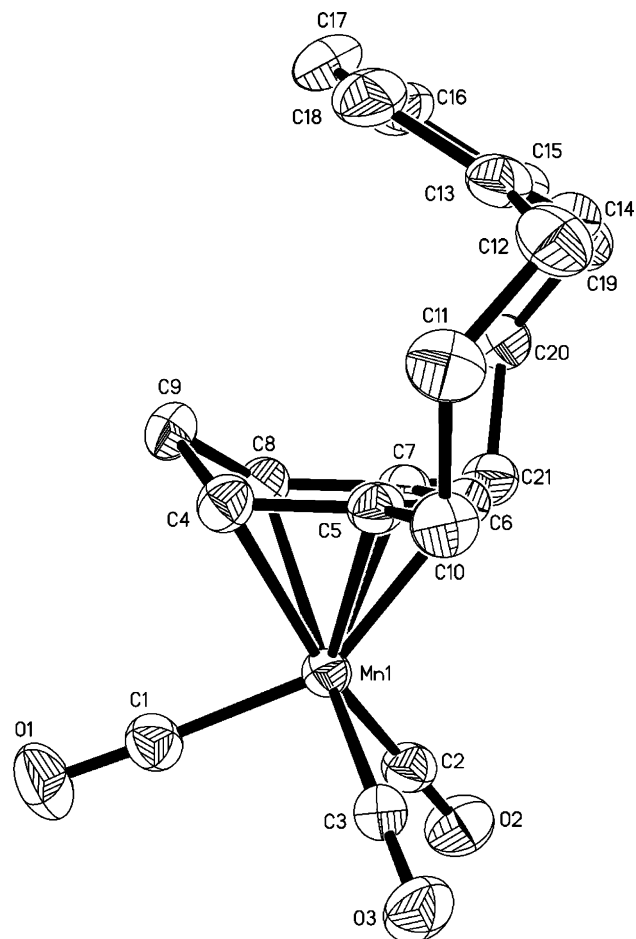

Fig. 2. X-ray crystal structure of **3** with 30% probability thermal ellipsoid depicted.

0.0087 Å). The C9 atom lies 0.560(3) Å above this plane, with respect to which the phenyl group has a dihedral angle of 30.82(9)°, a typical value for cyclohexadienyl complexes [16]. The increased electron density on the metal in **3** compared to **2** is evidenced by the shorter Mn–CO distances in **3**. Although Boekelheide et al. [7]. have reported that reaction of (6-hexamethylbenzene)-$(\eta^4\text{-}[2_2](1,4)\text{cyclophane})$ruthenium with hydrochloric acid gives (6-hexamethyl-benzene)$(\eta^5\text{-}3H\text{-}[2_2](1,4)\text{cyclophane})$ruthenium(II) hydrogen dichloride, compound **3** apparently is the first example of preparing a $[(\eta^5\text{-}6H\text{-}[3_2](1,3)\text{cyclophane})Mn(CO)_3]$ complex [15,16]. There are a few instances of hydride addition yielding a mixture of *exo* and *endo* products [17]. Thus, a brief study of reaction with sodium cyanoborodeuteride was undertaken to confirm whether the hydride donor adds to **2** *exo* or *endo* to the manganese. Treatment of **2** with 1.4 equivalents of sodium cyanoborodeuteride resulted in the disappearance of the 6-*endo* hydrogen peak (δ 2.38) and the appearance of the expected 6-*exo* hydrogen peak at 1.45 ppm with a triplet pattern. This result demonstrates that a hydride donor adds to **3** stereospecifically

Table 2
Selected bond distances (Å) and angles (°) for **2** and **3**

2

Mn1–C1	1.76(2)	Mn1–C3	1.79(2)
Mn1–C2	1.763(19)	Mn1–C6	2.171(6)
Mn1–C9	2.181(6)	Mn1–C5	2.185(6)
Mn1–C4	2.205(6)	Mn1–C7	2.195(6)
Mn1–C8	2.231(6)	C4–C16	1.521(9)
C8–C19	1.515(9)	C10–C18	1.491(10)
C14–C21	1.504(11)	C16–C17	1.531(9)
C17–C18	1.528(10)	C19–C20	1.535(10)
C20–C21	1.538(11)		
C5–C4–C9	118.6(5)	C5–C4–C16	121.2(6)
C9–C4–C16	120.2(6)	C9–C8–C7	118.9(5)
C9–C8–C19	121.1(6)	C7–C8–C19	120.0(6)
C4–C16–C17	112.7(6)	C18–C17–C16	116.6(6)
C17–C18–C10	115.6(6)	C20–C19–C8	112.8(6)
C19–C20–C21	115.5(6)	C20–C21–C14	113.6(6)

3

Mn1–C3	1.790(2)	Mn1–C2	1.802(2)
Mn1–C1	1.806(2)	Mn1–C6	2.110(2)
Mn1–C5	2.170(2)	Mn1–C7	2.178(2)
Mn1–C4	2.216(2)	C4–C5	1.390(3)
C4–C9	1.508(3)	C5–C6	1.417(3)
C5–C10	1.515(3)	C6–C7	1.422(3)
C7–C8	1.398(3)	C7–C21	1.508(3)
C8–C9	1.498(3)		
C3–Mn1–C2	88.5(1)	C3–Mn1–C1	95.0(1)
C2–Mn1–C1	96.9(1)	C4–C5–C6	118.3(2)
C4–C5–C10	121.2(2)	C6–C5–C10	120.4(2)
C8–C7–C6	117.1(2)	C8–C7–C21	121.4(2)
C6–C7–C21	120.7(2)	C8–C9–C4	103.9(2)

endo to the metal. The fact that the hydride has been added *endo* to the benzene deck of the cyclophane ligand suggests that addition of hydride leads to the direct attack to the coordinated cyclophane ligand. Such hydride addition to coordinated arenes was found in the case of several other manganese complexes [18].

As addition to the arene ring of an [(arene)Mn(CO)$_3$]$^+$ cation occurs with a variety of nucleophiles to yield the corresponding cyclohexadienyl complexes [19], we attempted the addition reaction of carbon donor nucleophiles such as MeMgBr and PhMgBr. However, no reaction was observed in both cases due to steric bulkiness.
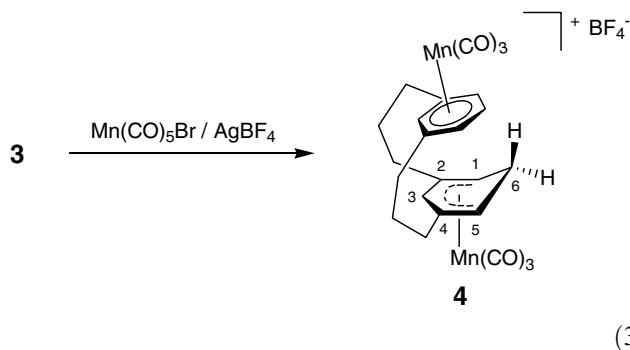
The addition of excess Mn(CO)$_5$FBF$_3$ to cyclophane may represent a possible route to (η^6,η^6-[3$_2$](1, 3)cyclophane)[(Mn(CO)$_3$)]$_2$[BF$_4$]$_2$. However, such addition did not occur under any conditions tried. On the other hand, treatment of **3** with Mn(CO)$_5$FBF$_3$ gave the (η^6,η^5-6H-[3$_2$](1,3)cyclophane)[Mn(CO)$_3$]$_2$[BF$_4$] **4** (Eq. (3)), whose structure is readily established by ^{1}H- and ^{13}C-NMR spectra, and IR spectroscopy. The ^{1}H-NMR spectrum of **4** shows five peaks at 7.42, 7.31, 7.00, 6.91 and 5.04 ppm due to the hydrogen atoms of the benzene deck of the cyclophane ligand. The down field chemical shift (δ 7.42, 7.00 and 6.91) of these η^6aromatic cyclophane protons are consistent with prior observation of Ru and Os cyclophane compounds. In addition, two resonances due to the *endo* and *exo* protons were detected at 3.28 and 1.83 ppm, respectively. The ^{13}C-NMR spectrum of **4** also shows eight peaks due to the carbon atoms of the benzene deck of the cyclophane ligand, together with three resonances due to the carbon atom of the carbonyl ligands. The infrared spectrum of **4** shows the six stretching modes of v(CO). The three peaks at 2073, 2032 and 2004 cm^{-1} are assigned to the carbonyl stretching modes of the η^6-cyclophane compound.

The (η^6,η^5-6H-[3$_2$](1,3)cyclophane)[Mn(CO)$_3$]$_2$[BF$_4$] **4** was found to be a good reactant for an additional hydride addition reaction on the benzene deck of the cyclophane ligand. When 1.4 equivalents of NaBH$_3$CN was treated with **4**, the (η^5,η^5-6H,6$'H$-[3$_2$](1,3)cyclophane)[Mn(CO)$_3$]$_2$ **5** was isolated as yellow crystals in 67% yield (Eq. (4)). The initial assignment of the structure for **5** was based on the symmetry of its ^{1}H-NMR spectrum, only two cyclophane cyclohexadienyl protons signals with two separated singlets at δ 7.26 and 5.42, in addition to two resonances at δ 3.24 and 1.54, due to the *endo*- and *exo*-hydrogen atoms.

In the cyclophane cyclohexadienyl region of the ^{13}C-NMR spectrum of **5**, four resonances at δ 136.2, 125.8, 101.5 and 84.9 were present.

(4)
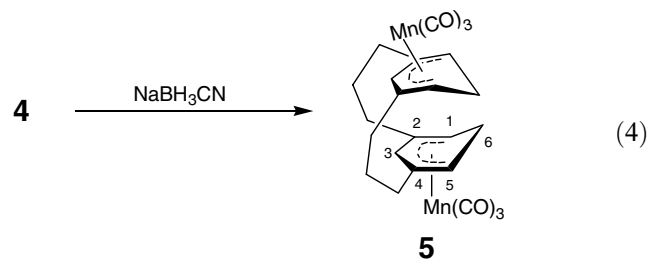
The infrared spectrum of **5** shows the three stretching modes of v(CO) at 2002, 1922 and 1909 cm^{-1}, which are similar to those of (cyclohexadienyl)Mn(CO)$_3$ complexes. These results clearly show that the electrophilic activation of a π-hydrocarbon by coordination to a transition-metal moiety is requisite for nucleophilic addition to the benzene deck of cyclophane.

(3)

In conclusion, we have detailed the synthesis and characterization of $[(\eta^6\text{-}[3_2](1,3)\text{cyclophane})Mn(CO)_3]$ $[BF_4]$. We have shown that the conversion of the manganese mediated benzene deck of cyclophane to coordinated cyclohexadienyl can be a facile procedure. We have also demonstrated that hydride addition to a cyclophane occurs stereospecifically *endo* to the metal. In addition, the reaction of $[(\eta^5\text{-}6H\text{-}[3_2](1,3)\text{cyclophane})\text{-}Mn(CO)_3]$ with $Mn(CO)_5BF_4$ gave rise to $(\eta^6,\eta^5\text{-}6H\text{-}[3_2](1,3)\text{cyclophane})[Mn(CO)_3]_2[BF_4]$.

3. Experimental

All experiments were performed under a nitrogen atmosphere in a vacuum atmospheres drybox or using standard Schlenk techniques. THF and ether were distilled from sodium benzophenone. Dichloromethane and hexane were distilled over CaH_2, ^1H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00 and 75.44 MHz, respectively. Chemical shifts were referenced relative to TMS. IR spectra were recorded on a Biorad FTS-165 spectrometer and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

The chemicals, $NaBH_3CN$, $NOBF_4$ and $AgBF_4$ were purchased from Aldrich and $Mn_2(CO)_{10}$ was purchased from Strem Chemicals. $[3_2](1,3)$Cyclophane [4] and $Mn(CO)_5Br$ [19] were prepared according to the known procedures.

3.1. Synthesis of $[(\eta^6\text{-}[3_2](1,3)Cyclophane)Mn(CO)_3]$ $[BF_4]$ (2)

A solution of $Mn(CO)_5Br$ (280 mg, 1.02 mmol) and $AgBF_4$ (198 mg, 1.02 mmol) in CH_2Cl_2(15 ml) was stirred at reflux temperature for 1 h. The precipitate of silver bromide was removed by filtration. To the filtrate was added 240 mg (1.02 mmol) of $[3_2](1,3)$cyclophane at room temperature. The mixture was refluxed for 2 h. Filtration and cooling at -5 °C yielded **2** as yellow crystals in 91% yield (420 mg). M.p. 213–215 °C (dec). ^1H-NMR (CD_3COCD_3): δ 7.44 (1H, s, C(1)H), 7.02 (1H, t, $J_{HH} = 6.9$ Hz, C(4)H), 6.91 (2H, d, $J_{HH} = 6.9$ Hz, C(3 and 5)H), 6.74 (1H, s, C(1')H), 6.63 (1H, t, $J_{HH} = 6.6$ Hz, C(4')H), 6.17 (2H, d, $J_{HH} = 6.6$ Hz, C(3' and 5')H), 3.03 (4H, m, CH_2), 2.78 (4H, m, CH_2), 2.51 (2H, m, CH_2). $^{13}C\{H\}$-NMR(CD_3COCD_3): δ 217.05, 209.12, 142.09, 135.85, 130.35, 127.73, 124.88, 101.99, 101.27, 96.34, 35.93, 35.23, 31.61. IR (KBr pellet; cm^{-1}): ν 3057(w), 2939(m), 2855(w), 2075(s), 2027(s), 1999(s), 1606(w), 1549(w), 1530(w), 1488(w), 1463(w), 1441(m), 1419(w), 1337(w), 1284(w), 1241(w), 1206(w), 1062(s), 921(w), 882(w), 786(w), 704(w), 647(m), 606(m), 519(m). Anal. Calc. for $C_{21}H_{20}BF_4O_3Mn$: C, 54.58; H, 4.36. Found: C, 54.24; H, 4.14.

3.2. Synthesis of $[(\eta^5\text{-}6H\text{-}[3_2](1,3)Cyclophane)Mn(CO)_3]$ (3)

A 1.4:1 mole excess of sodium cyanoborohydride was added via syringe to a stirred suspension of the manganeses complex **2** (640 mg) in ether (50 ml) at 0 °C. After 4 h, the excess $NaBH_3CN$ was destroyed with several drops of dilute HCl. The precipitated sodium salts were filtered. The clear yellow filtrate was evaporated. The residue was chromatographed on silica gel with hexane as eluent ($R_f = 0.2$). Evaporation of the solvent gave the product **3** as a yellow solid in 60% yield (310 mg). M.p. 137–138 °C. ^1H-NMR (C_6D_6): δ 7.41(1H, s, C(6)H), 7.09 (1H, s, C(14)H), 6.88 (1H, t, $J_{HH} = 7.5$ Hz, C(17)H), 6.52 (2H, d, $J_{HH} = 7.5$ Hz, C(4 and 8)H), 5.00 (2H, t, C(16 and 18)H), 3.04 (4H, m, CH_2), 2.83 (1H, m, $H^{6\text{-endo}}$), 2.68 (4H, m, CH_2), 2.34 (4H, m, CH_2), 1.48 (1H, dd, $J = 5.8$, 4.8 Hz, $H^{6\text{-exo}}$). $^{13}C\{H\}$-NMR(C_6D_6): δ 208.94, 205.80, 141.59, 136.51, 127.73, 127.19, 125.73, 144.46, 84.86, 52.19, 37.70, 36.55, 29.32. IR (KBr pellet; cm^{-1}): ν 3028(w), 2931(m), 2848(w), 2817(w), 2003(s), 1928(s), 1895(s), 1606(w), 1487(w), 1436(m), 1388(w), 1346(w), 1261(m), 1224(w), 1093(m), 1045(m), 1022(m), 912(w), 708(m), 698(w), 663(m), 636(m), 603(m), 522(m), 495(w). Anal. Calc. for $C_{21}H_{21}O_3Mn$: C, 67.02; H, 5.61. Found: C, 67.36; H, 5.44.

3.3. Synthesis of $(\eta^6,\eta^5\text{-}6H\text{-}[3_2](1,3)Cyclophane)$ $[Mn(CO)_3]_2[BF_4]$ (4)

A solution of $Mn(CO)_5Br$ (186 mg, 0.67 mmol) and $AgBF_4$ (132 mg, 0.67 mmol) in CH_2Cl_2 (20 ml) was stirred at reflux temperature for 1 h. The precipitate of silver bromide was removed by filtration. To the filtrate was added 170 mg (0.45 mmol) of $[(\eta^5\text{-}6H\text{-}[3_2](1,3)\text{cyclophane})Mn(CO)_3]$. The mixture was refluxed for 8 h. Filtration and cooling at -5 to -10 °C yielded **4** as yellow crystals in 41% yield (527 mg). M.p. 289–291 °C (dec). ^1H-NMR (CD_3COCD_3): δ 7.42(1H, s, C(1)H), 7.31 (1H, s, C(7)H), 7.00 (1H, t, $J_{HH} = 8.1$ Hz, C(4)H), 6.91 (2H, d, $J_{HH} = 8.1$ Hz, C(3 and 5)H), 5.04 (2H, t, C(9 and 11)H), 3.28 (1H, m, $H^{6\text{-endo}}$), 2.88 (4H, m, CH_2), 2.52 (4H, m, CH_2), 2.36 (2H, m, CH_2), 1.83 (1H, dd, $J = 6.0$, 5.0 Hz, $H^{6\text{-exo}}$). $^{13}C\{H\}$-NMR(CD_3COCD_3): δ 216.69, 208.72, 205.22, 142.15, 135.92, 130.45, 127.81, 124.87, 102.06, 96.43, 70.62, 36.04, 35.35, 34.66. IR (KBr pellet; cm^{-1}): ν 3091(w), 3058(w), 2933(m), 2856(w), 2073(s), 2032(s), 2004(s), 1944(s), 1932(s), 1917(s), 1610(w), 1548(w), 1446(m), 1417(w), 1353(w), 1330(w), 1286(w), 1242(w), 1207(w), 1058(s), 877(w), 790(w), 731(w), 642(s), 607(s), 520(m), 459(w). Anal. Calc. for $C_{24}H_{21}BF_4O_6Mn_2$: C, 47.87; H, 3.51. Found: C, 47.44; H, 3.32.

3.4. Synthesis of $(\eta^5, \eta^5\text{-}6H, 6'H\text{-}[3_2](1,3)Cyclophane)[Mn(CO)_3]_2$ (5)

To a stirred solution of **4** (53 mg, 0.088 mmol) in ether (30 ml) at 0 °C was added $NaBH_3CN$ (0.13 mmol). The solution was warmed to room temperature and stirred for 3 h. The solution was evaporated to dryness and extracted with hexane. Concentration of the hexane extract and cooling at −5 to −10 °C yielded **5** as yellow crystals in 67% yield (30 mg). M.p. 170–173 °C. ^{1}H-NMR ($CDCl_3$): δ 7.26(2H, s, *cyclohexadienyl*), 5.42 (4H, t, *cyclohexadienyl*), 3.24 (2H, m, $H^{6\text{-endo}}$), 2.82 (8H, m, CH_2), 2.03 (4H, m, CH_2), 1.54 (2H, dd, J = 5.8, 5.0 Hz, $H^{6\text{-exo}}$). ^{13}C{H}-NMR($CDCl_3$): δ 207.26, 204.82, 136.15, 125.77, 101.54, 84.92, 45.68, 37.12. IR (KBr pellet; cm^{-1}): ν 3022(w), 2925(m), 2848(w), 2002(s), 1922(s), 1909(s), 1438(w), 1386(w), 1352(w), 1325(w), 1230(w), 904(w), 786(w), 663(m), 632(m), 609(m), 524(m), 445(w), 414(w). Anal. Calc. for $C_{24}H_{22}O_6Mn_2$: C, 55.83; H, 4.28. Found: C, 55.66; H, 4.11.

3.5. X-ray crystallography

All X-ray data of compounds **2** and **3** were collected with a Siemens P4 diffractometer equipped with a Mo Kα ($\lambda = 0.71073$) X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 28 reflections in the range $3.5° < 2\theta < 50°$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were collected for Lorenz and polarization effects and empirically corrected with ψ-scan data. All calculations were carried out with the SHELXL-96 or SHEXTL program [20]. The crystals of **2** and **3** belong to the monoclinic space group $C2/c$, uniquely determined by systematic absences. The structure was solved by a combination of the direct method and the difference Fourier methods. In the case of **2**, disordered three carbonyl groups and two fluorine atoms of BF_4^- were observed. The disordered carbonyl groups were modeled successfully and their contributions in structural factors were also included. All non-hydrogen atoms in compounds **2** and **3** were refined anisotropically. All hydrogen atoms of **2** were included in calculated position with isotropic thermal parameters 1.2 times those of attached atoms. The crystallographic data for **2** and **3** are given in Table 1.

4. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 226387 and 226388 for compounds **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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