Unusual Migration of Manganese to an Arene *via* Protonation of an Agostic $\eta^{3:CH}$-Cyclohexenyl Complex†

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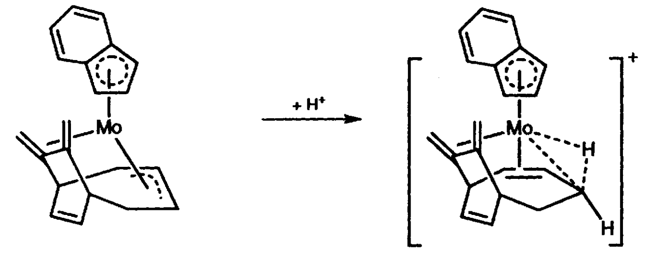
Treatment of the agostic compound $[Mn(\eta^{3:CH}\text{-}C_6H_8Ph)(CO)_3]$ **1a** with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 gave the arene complex $[Mn\{\eta^6\text{-}C_6H_5(C_6H_9)\}(CO)_3][BF_4]$ **2** *via* migration of the metal from the cyclohexenyl ring to the aryl substituent. Reaction of **2** with the nucleophiles triphenylphosphine and methylmagnesium chloride respectively gave the substitution product $[Mn\{\eta^6\text{-}C_6H_5(C_6H_9)\}(CO)_2(PPh_3)][BF_4]$ **3** and the addition product $[Mn\{\eta^5\text{-}C_6H_5Me(C_6H_9)\}(CO)_3]$ **4** as a mixture of isomers. The crystal structure of complex **2** has been determined: triclinic, space group $P\bar{1}$, $a = 9.399(3)$, $b = 10.644(2)$, $c = 8.979(1)$ Å, $\alpha = 93.03(1)$, $\beta = 116.39(2)$, $\gamma = 79.45(3)°$, $R = 0.057$ for 1316 independent reflections.

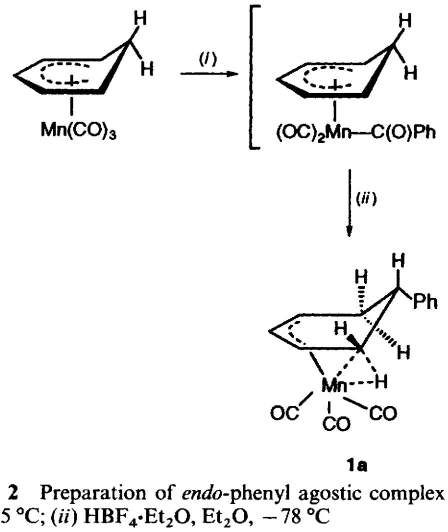
The reactions of η^3-allyl complexes with proton sources has been studied in detail by many groups and generally lead to cleavage of the metal–carbon bond and release of an olefin.[1] In contrast, protonation of cyclic allyl ligands such as the η^3-cyclohexenyl group are rare, and of the few known examples (*i*) (η^3-cyclohexenyl)tris(trifluorophosphine)rhodium(I) reacts with HCl to give $[\{RhCl(PF_3)_2\}_2]$, PF_3, and the decomplexed cyclohexene[1e] and (*ii*) CF_3SO_3H adds to the indenyl derivative $[Mo(C_{12}H_{13})(\eta^5\text{-}C_9H_7)]$ giving an olefin which remains bonded to molybdenum *via* an agostic interaction[2] (Scheme 1). A detailed review of the syntheses and reactions of agostic C–H complexes has been published[3] and these species are finding increasing applications in catalytic processes involving olefins.[4]

Our interest in this area stems from our studies on the intramolecular coupling of polyene ligands and carbon-based ligands, in which we have reported the migration of alkyl and aryl groups from an acyl group to the *endo* face of a cyclohexadienyl ring forming *endo*-phenyl- and -methyl-substituted agostic cyclohexenyl complexes **1**[5] (Scheme 2). This reaction involves the protonation of an acyl complex and we have observed that an excess of protons in the reaction mixture leads to lower yields of **1** and the formation of unidentified salts.

Herein we describe the synthesis and characterization of one of these salts from the reaction of $[Mn(\eta^{3:CH}\text{-}C_6H_8Ph)(CO)_3]$ **1a** with $HBF_4 \cdot Et_2O$. The product is a stable arene complex which results from protonation of the cyclohexenyl ring and migration of the metal to the pendant phenyl moiety. An X-ray crystallographic study on the new cationic complex, and its subsequent reactions with triphenylphosphine and methylmagnesium chloride, are described.



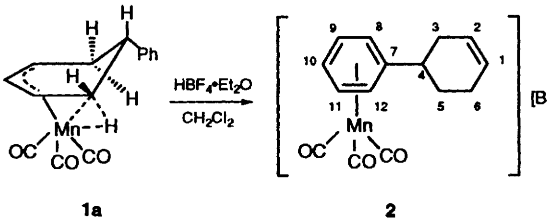
Scheme 1 Protonation of a cyclic allyl ligand in which the olefin remains bonded to the metal *via* an agostic C–H–M interaction[2]



Scheme 2 Preparation of *endo*-phenyl agostic complex **1a**. (*i*) LiPh, Et_2O, 25 °C; (*ii*) $HBF_4 \cdot Et_2O$, Et_2O, −78 °C

Results and Discussion

Protonation of Cyclohexenyl Agostic Managanese Complexes.—The addition of a slight excess of tetrafluoroboric acid–diethyl ether complex to **1a** in dichloromethane leads to protonation of the cyclohexenyl ring and migration of the metal to the phenyl substituent at C(5). The product, tricarbonyl[(1–6-η)-(cyclohex-3-enyl)benzene]manganese(I) tetrafluoroborate **2**, was isolated as a pale yellow solid in 88% yield [equation (1)].



(1)

Complex **2** was characterized *via* elemental analysis, ^1H, ^{13}C NMR (Table 1) and IR spectroscopy. The structure was also

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Proton and ^{13}C NMR data for complexes **2–4**[a]

Complex	δ(^1H)	δ(^{13}C)[b]
2	1.6–2.6 (6 H, br m, $H^{3,5,6}$), 3.03 (1 H, s, H^4), 5.77 (2 H, s, $H^{1,2}$), 6.85 (5 H, m, Ph)	25.4, 29.6, 32.3 ($C^{3,5,6}$), 38.7 (C^4), 99.5–103.5 (C^{8-12}), 125.8 (C^7), 128.0 ($C^{1,2}$), 216.3 (CO)
3	1.7–2.6 (6 H, m, CH_2), 2.90 (1 H, H^4), 5.75 (1 H, H^1 or H^2), 6.00 (1 H, H^1 or H^2), 6.2–6.5 (5 H, m, Ph), 7.4–7.8 (15 H, m, PPh_3)	25.5, 29.5, 32.4 ($C^{3,5,6}$), 38.6 (C^4), 96.4–101.5 (C^{8-12}), 122.2 (C^7), 126.2, 127.8 ($C^{1,2}$), 129–136 (PPh_3), 224.5 (d, J_{CP} = 28 Hz, CO)
4a, **4b**	0.06, 0.07 (d, Me), 1.0–2.0 (m, cyclohexenyl), 2.1 (m, H^6), 2.65 (m, $H^{1,5}$), 4.15 (dd, H^4), 5.00, 5.04 (d, H^3), 5.6 (m, cyclohexenyl)[c]	24.5, 24.9 (Me), 27.8, 28.0, 28.1, 28.2, 30.9, 31.0 (cyclohexenyl), 32.2, 32.7 (C^6), 38.7 (cyclohexenyl CH), 55.6, 55.8, 56.5, 59.5 ($C^{1,5}$), 77.9, 78.6 (C^3), 93.9, 94.2 (C^4), 119.3, 119.4 (C^2), 126.0, 126.1, 127.0, 127.2 (cyclohexenyl), 223.9 (CO)[c]
4c	0.09 (d, Me), 1.0–2.0 (m, cyclohexenyl), 2.15 (m, H^6), 2.58 (t, $H^{1,5}$), 4.20, 4.24 (d, $H^{2,4}$), 5.6 (m, cyclohexenyl)[c]	25.6 (Me), 27.8, 30.3, 31.1 (cyclohexenyl), 33.9 (C^6), 37.9 (cyclohexenyl CH), 56.7, 59.1 ($C^{1,5}$), 94.0 ($C^{2,4}$), 106.9 (C^3), 126.3, 126.9 (cyclohexenyl), 223.9 (CO)[c]
4d, **4e**	0.17, 0.19 (d, Me), 1.0–2.0 (m, cyclohexenyl), 2.2 (m, H^6), 2.49 (m, H^5), 3.95, 4.05 (d, H^2), 4.14 (m, H^4), 4.92 (dd, H^3), 5.6 (m, cyclohexenyl)[c]	25.7, 26.4 (Me), 27.6, 28.7, 28.8, 30.0, 30.1, 33.3 (cyclohexenyl), 33.6, 34.2 (C^6), 39.4, 40.4 (cyclohexenyl CH), 54.3, 56.3 (C^5), 76.5 (C^3), 88.1 (C^1), 93.1, 93.5, 94.7 ($C^{2,4}$), 125.5, 125.6, 126.1, 126.3 (cyclohexenyl), 224.5 (CO)[c]

[a] The atom labelling for NMR assignments is that shown in equations (1)–(3). In [$^2H_6$]acetone at 25 °C. [b] ^{13}C-{^1H} spectra. [c] In C_6D_6.

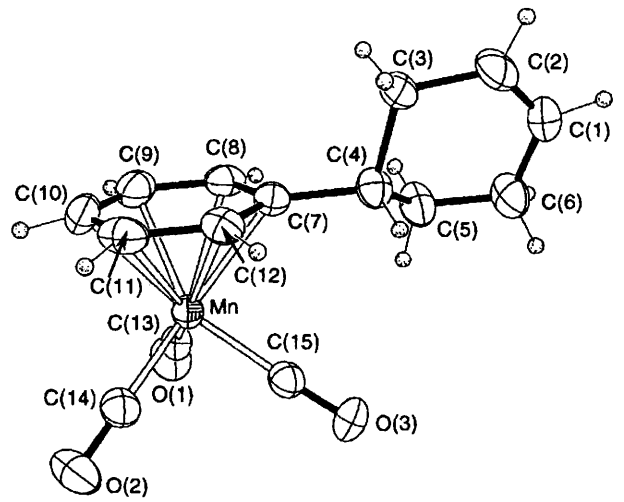
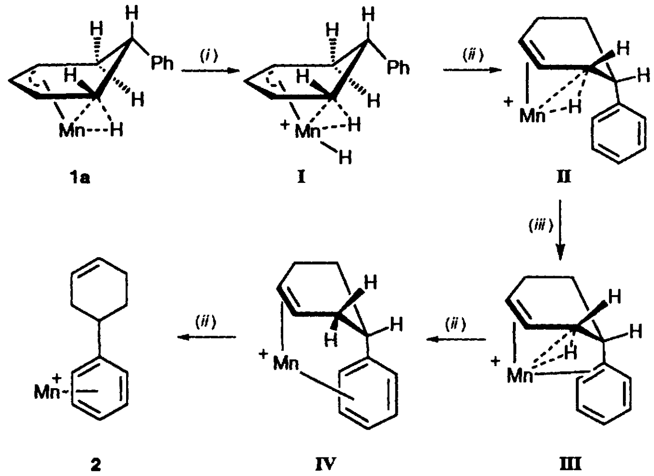


Fig. 1 The molecular structure of the cation of complex **2**



Scheme 3 Proposed mechanism for the formation of complex **2**; carbonyls omitted. (*i*) H^+ Addition; (*ii*) hydrogen migration; (*iii*) η^2-arene co-ordination; (*iv*) η^2- to η^4-arene slip; (*v*) η^4- to η^6-arene slip

confirmed by an X-ray crystallographic study and a drawing of the molecular structure is shown in Fig. 1, with fractional atomic coordinates and selected bond lengths and angles listed in Tables 2 and 3 respectively. No unusual features are present and the structure merely confirms the expected piano-stool geometry at manganese as well as the presence of the cyclohex-3-enyl substituent on the arene ring. The tetrafluoroborate counter ion is however highly disordered.

The formation of complex **2** prompted us to investigate the protonation of other cyclohexenyl complexes containing agostic M–C–H bonds. Therefore, the reactions of [Mn($\eta^{3:CH}$-C_6H_8R)$(CO)_3$] (R = Me **1b** or CH_2Ph **1c**)[6] with $HBF_4 \cdot Et_2O$ at −78 °C were performed. In each case, IR evidence for a cationic tricarbonyl species was obtained [R = Me, ν(CO)$_{max}$ 2080 and 2021; R = CH_2Ph, ν(CO)$_{max}$ 2079 and 2022 cm^{-1}]. However, addition of diethyl ether or hexane to the reaction solutions gave orange oils rather than crystalline salts. These species decomposed within a few minutes at room temperature as evidenced by the absence of any CO absorptions in their CH_2Cl_2 IR spectra. Gas chromatography–mass spectrometry of the mother-liquors revealed the presence of the organic cyclohexenes, but these were not isolated.

The instability of these latter cations is surprising and suggests they are different to **2** even though the benzyl derivative has a phenyl ring suitably placed to capture the metal centre. One possible explanation is that an unsaturated carbon is required adjacent to the cyclohexenyl ring to facilitate metal migration. Thus, the complex [Mn($\eta^{3:CH}$-C_6H_8R)$(CO)_3$] **1d** [R = *cis*/*trans*-C(Me)=CHMe], prepared from [Mn(η^4-C_6H_8)$(CO)_3$]$^-$ and *cis*/*trans*-Br(Me)C=CCHMe,[6] was treated with $HBF_4 \cdot Et_2O$ at −78 °C. As in the case of the benzyl species, a cation was detected by IR spectroscopy [ν(CO)$_{max}$ 2083 and 2024 cm^{-1}], but no salt could be isolated. From these results it is clear that many of the agostic cyclohexenyl species can be protonated to give cationic complexes but that only the phenyl-substituted species forms an isolable salt.

Mechanism for the Formation of Complex **2**.—A proposed mechanism for the protonation of [Mn($\eta^{3:CH}$-C_6H_8Ph)$(CO)_3$] **1a** is outlined in Scheme 3. Proton addition to the co-ordinated hydrocarbon ring occurs indirectly *via* initial electrophilic attack at the metal centre to form a cationic 18-electron manganese hydride intermediate **I**. Hydrogen migration to either end of the η^3-allylic group, *i.e.* olefin insertion into the metal–hydrogen bond, would give a co-ordinatively unsaturated η^2-bonded intermediate **II**. The unsaturation at the metal in **II** could then be relieved by η^2-phenyl co-ordination forming **III**, and subsequent decomplexation of the agostic C–H bond with a change in co-ordination of the aryl ring from η^2 to η^4 to give **IV**. Final decomplexation of the olefin and η^6 co-ordination of the arene would then yield **2**. Another possibility is that protonation occurs at the co-ordinated hydrocarbon ring giving **II** directly, with η^2 to η^4 to η^6 phenyl co-ordination to form **2**. None of the proposed intermediates is observed in the IR spectrum of the

Table 2 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Mn	2605(1)	1752(1)	1525(1)
O(1)	5825(6)	527(5)	4012(7)
O(2)	3110(7)	370(6)	−1185(7)
O(3)	1133(6)	−352(5)	1915(6)
B	545(1)	285(1)	805(1)
F(1)*	399(1)	326(1)	794(1)
F(2)*	628(1)	371(1)	806(2)
F(3)*	530(1)	210(1)	675(1)
F(4)*	648(2)	219(2)	935(2)
F(5)*	545(2)	347(1)	675(2)
F(6)*	572(2)	383(2)	921(2)
F(7)*	402(2)	278(2)	766(3)
F(8)*	629(3)	182(2)	880(3)
C(1)	−1841(9)	2904(8)	499(1)
C(2)	−222(1)	3867(8)	394(1)
C(3)	−1285(8)	4017(7)	301(1)
C(4)	−217(8)	2753(7)	2956(8)
C(5)	633(9)	2086(8)	466(1)
C(6)	−540(10)	1836(8)	524(1)
C(7)	869(8)	3030(6)	2208(8)
C(8)	2416(8)	3288(7)	3196(8)
C(9)	338(1)	3564(7)	2490(10)
C(10)	2810(10)	3596(7)	800(10)
C(11)	1260(10)	3347(7)	−243(9)
C(12)	289(8)	3069(7)	476(9)
C(13)	4590(9)	992(7)	3057(9)
C(14)	2935(9)	909(7)	−110(10)
C(15)	1732(8)	438(7)	1767(8)

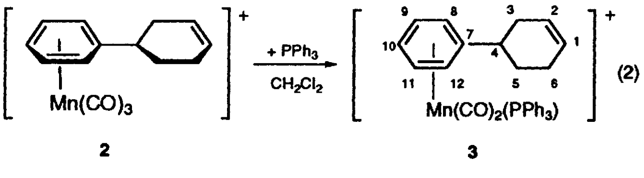
* The BF_4^- group is disordered; F(1)–F(4) have an occupancy of 0.587 and F(5)–F(8) one of 0.413.

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

Mn–C(13)	1.819(7)	Mn–C(14)	1.793(8)
Mn–C(15)	1.813(8)	Mn–C(7)	2.209(7)
Mn–C(8)	2.189(6)	Mn–C(9)	2.172(7)
Mn–C(10)	2.170(8)	Mn–C(11)	2.186(8)
Mn–C(12)	2.197(7)	O(1)–C(13)	1.131(7)
O(2)–C(14)	1.158(8)	O(3)–C(15)	1.138(8)
C(1)–C(2)	1.32(1)	C(1)–C(6)	1.46(1)
C(2)–C(3)	1.49(1)	C(3)–C(4)	1.537(9)
C(4)–C(5)	1.516(9)	C(5)–C(6)	1.48(1)
C(7)–C(8)	1.397(9)	C(4)–C(7)	1.522(9)
C(7)–C(4)–C(3)	108.5(6)	C(7)–C(4)–C(5)	115.9(5)
C(1)–C(2)–C(3)	123.5(7)	C(2)–C(3)–C(4)	112.0(6)
C(3)–C(4)–C(5)	110.0(6)	C(4)–C(5)–C(6)	111.2(6)
C(5)–C(6)–C(1)	114.8(7)	C(2)–C(1)–C(6)	122.4(8)
Mn–C(15)–O(3)	177.3(6)	Mn–C(13)–O(1)	179.6(7)
Mn–C(14)–O(2)	178.4(7)		

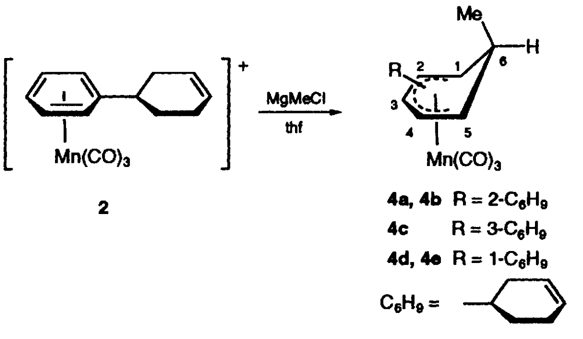
reaction mixture, however the observation that [Mn($\eta^{3:CH}$-C_6H_8R)$(CO)_3$], [R = *cis*/*trans*-C(Me)=CHMe] gives a transient cationic tricarbonyl species suggests an intermediate similar to **III** may be involved.

Reaction of Complex **2** *with Nucleophiles*.—Complex **2** undergoes reactions typical of η^6-arene manganese complexes. Thus, addition of an excess of triphenylphosphine to dichloromethane solutions of **2** gives dicarbonyl[(1–6-η)-(cyclohex-3-enyl)benzene](triphenylphosphine)manganese(I) tetrafluoroborate **3** [equation (2)]. Complex **3** was isolated as a bright yellow solid in 91% yield and characterized by elemental analysis, ^1H, ^{13}C NMR and IR spectroscopy (Table 1).



(2)

In contrast to the reaction with PPh_3, addition of methylmagnesium chloride to complex **2** in tetrahydrofuran (thf) produces the cyclohexadienyl species [Mn{η^5-$C_6H_5Me(C_6H_9)$}$(CO)_3$] **4a**–**4e** as a yellow oil in 49% yield. The product is a mixture of five isomers which result from the addition of a methyl group to the arene ring of **2** at positions *ortho*, *meta* and *para* to the cyclohex-3-enyl substituent [equation (3)]. Five isomers are observed because, of the three regioisomers, two are pairs of diastereomers. Complete separation of these species using column chromatography on alumina was not possible since they co-elute with hexane. However, if the eluate is collected as three fractions, each contains varying amounts of **4a**–**4e**. The first has **4a**, **4b** and **4c** in approximately equal amounts, the second has mostly **4a**, **4b** with some **4c**, whereas the third fraction has equal amounts of **4a**, **4b** and **4d**, **4e** and a trace of **4c**. This partial separation and the ^1H–^1H (COSY) two-dimensional correlation NMR spectrum of each fraction allowed the determination of the structure of each isomer. The relative amounts of the isomers, estimated from the integrals of the ^1H NMR spectra, were **4a**, **4b** (50), **4c** (40) and **4d**, **4e** (10%).



(3)

Isomers **4a**, **4b** are diastereomers of tricarbonyl[(1–5-η)-2-(cyclohex-3-enyl)-6-(*exo*-methyl)cyclohexa-1,3-dienyl]manganese(I), and show two distinct doublets in the ^1H NMR spectrum at δ 5.00 and 5.04 for H^3 of each diastereomer. As expected, a doublet of doublets is observed at δ 4.15 for H^4. The presence of these signals can only be consistent with the 2-substituted compounds. Isomer **4c** is the 3-substituted species and shows two doublets at δ 4.20 and 4.24 for $H^{2,4}$ but no signals around δ 5.0 as would be expected for H^3. The last two isomers are diastereomers of the product resulting from addition of MgMeCl *ortho* to the cyclohexenyl substituent. These (**4d**, **4e**) show signals as expected for two diastereomers of the *ortho* adduct (*e.g.* a doublet of doublets for H^3, and two doublets and a doublet of doublets for H^2, H^4, *etc.*). Five superimposed signals assigned to the methyl groups of all the isomers appear at δ 0.06 and 0.07 for **4a**, **4b**, 0.09 for **4c** and 0.17 and 0.19 for **4d**, **4e**. In addition, complex signals are seen for the cyclohexenyl substituent and for the remaining cyclohexadienyl protons. Analysis of the ^{13}C NMR spectra confirmed the assigned structures and these data are also presented in Table 1. Addition of the methyl group at the 1, 2 and 3 positions has precedent in many reactions of tricarbonyl(arene)manganese(I) species with carbanions,[7] although the observation in our reaction of two diastereomers for both the 1- and 2-substituted adducts is less common. The diastereoisomerism arises from the chirality of the cyclohex-3-enyl substituent and C(6) for 2,6 and 1,6 disubstitution of the ring. The 3,6 isomer has a plane of symmetry which renders C(6) achiral.

Conclusion

We have demonstrated that *endo*-phenyl-substituted agostic cyclohexenyl complexes of manganese undergo a novel protonation reaction in which the metal migrates to the pendant aryl ring forming a cationic arene complex **2**. This complex undergoes reactions with nucleophiles similar to those of known tricarbonyl(η-arene)manganese(I) cations. The addition of methylmagnesium chloride to **2** gives five isomeric products, four of which correspond to two diastereomeric pairs due to the chirality at the cyclohex-3-enyl substituent and C(6) of the cyclohexadienyl ring. The crystal structure of **2** has been determined.

Experimental

Reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried over sodium–benzophenone (thf, diethyl ether) or CaH_2 (hexane, CH_2Cl_2) and were freshly distilled prior to use. Manipulations of air-sensitive solids were performed inside a Braun MB 150 inert-atmosphere glove-box containing a nitrogen atmosphere. Reagents were used as supplied by Aldrich (Milwaukee, WI). Infrared spectra were recorded on a Nicolet 5ZDX FT instrument operated in the transmittance mode and all NMR spectra on a Varian VXR-400S NMR Fourier-transform spectrometer. Gas chromatography-mass spectrometry (GC–MS) was performed using a Hewlett-Packard HP5890 gas chromatograph connected to a Finnegan Mat Incos 50 mass spectrometer (70 eV, *ca.* 1.12×10^{-17} J). Column chromatography used alumina (150 mesh, standard grade, activated, neutral; Aldrich). Microanalyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). Complexes **1a**–**1d** were prepared from the appropriate adaptations of the literature procedures.[5,6]

Tricarbonyl[(1–6-η)-(*cyclohex*-3-*enyl*)*benzene*]*manganese*(I) *Tetrafluoroborate* **2**.—To a stirred solution of complex **1a** (0.255 g, 0.86 mmol) in CH_2Cl_2 (25 cm^3) was added a slight excess of $HBF_4{\cdot}Et_2O$. The reaction was monitored using IR spectroscopy until the only observable CO-containing species was $[Mn\{\eta^6\text{-}C_6H_5(C_6H_9)\}(CO)_3]$ **2**. The volume of the solution was reduced (by *ca.* 25%) *in vacuo* and the product precipitated by addition of an excess of diethyl ether. The mother-liquors were removed by cannula and the precipitate washed several times with diethyl ether and dried *in vacuo*. Recrystallization, by dissolution in the minimum volume of CH_2Cl_2, filtration through Celite® and reprecipitation with diethyl ether gave $[Mn\{\eta^6\text{-}C_6H_5(C_6H_9)\}(CO)_3][BF_4]$ **2** as a pale yellow solid. Yield 0.29 g, 88%. IR (CH_2Cl_2): $\nu(CO)_{max}$ 2080 and 2019 cm^{-1} (Found: C, 46.40; H, 3.25. $C_{15}H_{14}BF_4MnO_3$ requires C, 46.90; H, 3.65%).

Dicarbonyl[(1–6-η)-(*cyclohex*-3-*enyl*)*benzene*](*triphenylphosphine*)*manganese*(I) *Tetrafluoroborate* **3**.—Triphenylphosphine (0.50 g, 1.88 mmol) was added to a stirred solution of complex **2** (0.41 g, 1.07 mmol) in CH_2Cl_2 (20 cm^3). The reaction was monitored by IR spectroscopy and warmed in a water-bath (*ca.* 35 °C) until all of **2** had been consumed (*ca.* 1.75 h). The solution was reduced in volume (to 3–5 cm^3) and the product precipitated with diethyl ether. Removal of the mother-liquor using a cannula and washing several times with diethyl ether gave a crude residue which was recrystallized from CH_2Cl_2–diethyl ether as for **2**. The product $[Mn\{\eta^6\text{-}C_6H_5(C_6H_9)\}(CO)_2(PPh_3)][BF_4]$ was obtained as a bright yellow powder. Yield 0.60 g, 91%. IR (CH_2Cl_2): $\nu_{max}(CO)$ 2003 and 1959 cm^{-1} (Found: C, 62.50; H, 4.65. $C_{32}H_{29}BF_4MnO_2P$ requires C, 62.15; H, 4.75%).

Tricarbonyl[(1–5-η)-(*cyclohex*-3-*enyl*)-6-(exo-*methyl*)*cyclohexadienyl*]*manganese*(I) **4a**–**4e**.—Methylmagnesium chloride (1.25 equivalents of a 3.0 mol dm^{-3} solution in thf) was added to a stirred solution of complex **2** (0.30 g, 0.78 mmol) in thf (75 cm^3) at −78 °C. The mixture was warmed to room temperature over 0.5 h and a few drops of 0.1 mol dm^{-3} HCl were added to destroy the excess of MgMeCl and precipitate magnesium salts. Dissolution of the residue in CH_2Cl_2 and chromatography on alumina eluting with hexane gave a yellow solution. Evaporation of the solvent *in vacuo* afforded a mixture of the three isomers of $[Mn\{\eta^5\text{-}C_6H_5Me(C_6H_9)\}(CO)_3]$ as a yellow oil. Yield 0.12 g, 49%. IR (hexane): $\nu(CO)_{max}$ 2017, 1946 and 1934 cm^{-1}.

Crystal Structure Determination of Complex **2**.—Crystals for an X-ray diffraction study were grown by slow diffusion (2–3 d) of hexane into a CH_2Cl_2 solution of the salt.

Crystal data. $[C_{15}H_{14}MnO_3]^+BF_4^-$, $M = 384.02$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.399(3)$, $b = 10.644(2)$, $c = 8.979(1)$ Å, $\alpha = 93.03(1)$, $\beta = 116.39(2)$, $\gamma = 79.45(3)°$, $U = 790.6(3)$ Å^3, $Z = 2$, $D_c = 1.61$ g cm^{-3}, 17 °C, $F(000) = 388.0$.

Twenty-five reflections ($45.0 \leqslant \theta \leqslant 60.0°$) were used to refine the cell parameters using filtered Cu-Kα (1.5418 Å) radiation on an AFC5R Rigaku rotating-anode system. The yellow prism ($0.25 \times 0.30 \times 0.45$ mm) had a linear absorption coefficient of 7.321 mm^{-1}. Data ($5.0 \leqslant 2\theta \leqslant 120.1°$; $0 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$, $-10 \leqslant l \leqslant 9$) were collected with three standards taken every 150 data points (1.48% decay, correction applied). 2513 Reflections were recorded and 1316 had $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz polarization, and for absorption by an empirical ψ scan ($T_{min} = 0.409$, $T_{max} = 1.000$).

The structure was solved by direct methods using TEXSAN[8] and refined by full-matrix least squares using σ weights. The BF_4^- group was found to be disordered, and the best model consists of four fluorines [F(1)–F(4)] arranged tetrahedrally around the boron with ≈60% occupancy and another four [F(5)–F(8)] making up another tetrahedron and accounting for the other ≈40% occupancy. The ring hydrogen-atom positions were calculated in their geometric positions; the remaining hydrogen atoms were found in difference maps. After refinement of the heavier atoms, all the hydrogen atoms were recalculated and left at these positions. At the end of the refinement, $R = 0.057$, $R' = 0.058$, goodness of fit = 1.72, maximum $\Delta/\sigma = 0.084$, largest difference peak = 0.49, largest difference hole = -0.28 e Å^{-3}. The atomic scattering factors were taken from ref. 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are grateful to the Donors of the Petroleum Research Fund administered by the American Chemical Society and to the Rutgers Research Council for financial support and to Dr. John Cheng of this department for assistance in obtaining NMR spectra.

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Received 7th October 1994; *Paper* 4/06113F