Synthesis and Reactions of Acyl(cyclohexadienyl)manganates†

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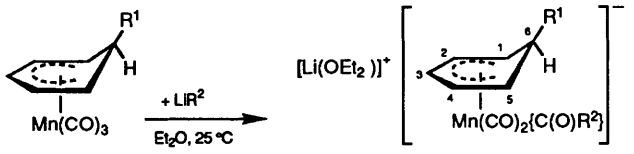
The cyclohexadienyl complexes $[Mn(\eta^5\text{-}C_6H_6R^1)(CO)_3]$ **1** (R^1 = *exo*-H, Me or C_6H_4Me-4) react with LiR^2 (R^2 = Me or Ph) to give acylmetalates $[Li(OEt_2)][Mn(\eta^5\text{-}C_6H_6R^1)(CO)_2\{C(O)R^2\}]$ **2**. Complex **2** (R^1 = Me, R^2 = Ph) has been characterised by an X-ray crystallographic study: orthorhombic, space group $P2_12_12_1$, a = 9.113(2), b = 14.491(8), c = 32.803(9) Å, R = 0.064 for 1458 independent reflections. Protonation of **2** with HBF_4·Et_2O induces an aryl- or alkyl-group transfer to the *endo* face of the cyclohexadienyl ring yielding the new agostic cyclohexenyl complexes $[Mn(\eta^{3:C\prime\prime}C_6H_7R^1R^2)(CO)_3]$ **3**. The cyclohexenyl ligands can be decomplexed from the metal *via* treatment of **3** with 1,2-bis(diphenylphosphino)ethane (dppe) in tetrahydrofuran to afford mixtures of substituted cyclohexa-1,3-dienes and $[MnH(CO)_3(dppe)]$. The acylmetalates **2** react with $[NO][BF_4]$ at −78 °C to give $[Mn(\eta^5\text{-}C_6H_6R^1)(CO)(NO)\{C(O)R^2\}]$ which decompose at room temperature to form the *trans*-disubstituted acylcyclohexadienes $C_6H_6R^1[C(O)R^2]$. Reaction of **2** with electrophiles $SiMe_3Cl$, $[Me_3O][BF_4]$ or $[Et_3O][BF_4]$ results in O alkylation and formation of stable carbene complexes $[Mn(\eta^5\text{-}C_6H_6R^1)(CO)_2\{C(OE)R^2\}]$ (E = $SiMe_3$, Me or Et).

The stereo- and regio-specific functionalisation of co-ordinated cyclohexadienyl ligands is now well documented[1–4] and has been utilised in the synthesis of both complex natural products[1] as well as simple disubstituted cyclohexadienes.[2–4] Noteworthy in this field is the work of Pearson and co-workers[1] on the $[Fe(\eta^5\text{-}C_6H_6R)(CO)_3]^+$ system,[1] that of the Kuendig group[2] with $[Cr(\eta^5\text{-}C_6H_6R)(CO)_3]^-$, the results of Sweigart and co-workers[3] using $[Mn(\eta^5\text{-}C_6H_6R)(CO)_{2-x}L_x(NO)]^+$ (L = phosphine), and Brookhart's transformation of co-ordinated arenes into cyclohexadienes *via* cyclohexenyl derivatives.[4] In general, stereocontrol in the carbon–carbon bond-forming process has been achieved through either the *exo* addition of nucleophiles to the polyenyl ligand,[1,3] or by attack of an electrophile at the metal prior to its migration to the *endo* face of the ring.[2,4]

Our interest in this area is the synthesis of cyclohexadienyl complexes with a functional organic group as one of the auxiliary ligands, which can be stereo- or regio-specifically transferred to the *endo* face of the C_6 ligand. Herein we report the syntheses and intramolecular coupling reactions of complexes possessing both acyl or carbene moieties as well as a cyclohexadienyl ligand. A portion of this work has been previously communicated.[5]

Results and Discussion

Synthesis of Acylmetalates.—The cyclohexadienyl complexes $[Mn(\eta^5\text{-}C_6H_6R^1\text{-}exo)(CO)_3]$ (R^1 = H **1a**,[6] Me **1b**[7] or C_6H_4-Me-4 **1c**) react with phenyl- and methyl-lithium in diethyl ether to give the acylmetalates $[Li(OEt_2)][Mn(\eta^5\text{-}C_6H_6R^1)(CO)_2\{C(O)R^2\}]$ **2a**–**2e** (R^2 = Ph or Me) as air-sensitive orange crystalline solids (Scheme 1). This addition proceeds in quantitative yield (as observed by IR spectroscopy), precipitating **2** as a $[Li(OEt_2)]^+$ salt which can be isolated in up to 90% yield. The new acylmetalates were characterised using ^1H, ^{13}C NMR and IR spectroscopy (Table 1) and show a distinctive ^{13}C NMR resonance around δ 315 assigned to the acyl carbonyl carbon.



1a R^1 = H
1b R^1 = Me
1c R^1 = C_6H_4Me-4

2a R^1 = H, R^2 = Ph
2b R^1 = H, R^2 = Me
2c R^1 = Me, R^2 = Ph
2d R^1 = Me, R^2 = Me
2e R^1 = C_6H_4Me-4, R^2 = Ph

Scheme 1

The formation of **2** is similar to the well known Fischer acyl syntheses,[8] and demonstrates that carbanions can readily be added to the neutral cyclohexadienylmanganese species **1**. Since complexes **1b** and **1c** result from alkylation of benzenetricarbonylmanganese(I) hexafluorophosphate,[7b] the synthesis of **2** also shows that two carbanions can be sequentially added to the cationic arene complex. In earlier studies only hydride anion[4,9] could be added to **1** forming a cyclohexadiene complex $[Mn(\eta^4\text{-}C_6H_8)(CO)_3]^-$, although a recent report has described the addition of carbanions to C^2 of the dienyl ligand in related tricarbonyl(η^5-pentadienyl)manganese complexes.[10]

The $[Li(OEt_2)]^+$ salts of complexes **2** are very oxygen sensitive and often ignite upon exposure to air. A more stable salt (decomposition in air, 2–3 h) can be prepared *via* metathesis of the $[Li(OEt_2)]^+$ salts with $[N(PPh_3)_2]Cl$ in water. Crystals of the $[N(PPh_3)_2]^+$ salt of **2c**, grown by slow diffusion of hexane into a CH_2Cl_2 solution of the salt, were used for an X-ray crystallographic study. A drawing of the anion is shown in Fig. 1 and fractional atomic coordinates and selected bond lengths and angles are listed in Tables 2 and 3. The structure reveals a piano-stool geometry typical of many manganese half-sandwich compounds, and confirms the *exo* stereochemistry of the methyl group. The benzoyl ligand lies beneath the dienyl fragment rather than the less sterically demanding C(6) carbon, with the phenyl group directed away

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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

Complex	δ(^1H)[b]	δ(^{13}C)[b,c]
2a	0.47 [O(CH$_2$*Me*)$_2$], 1.69 (1 H, br s, H^6 *exo*), 2.21 (3 H, br, H^{1}H^5 and H^6 *endo*), 2.58 [O(*CH$_2$*Me)$_2$], 3.86 (2 H, br s, H^{2}H^4), 5.11 (1 H, br s, H^3) and 6.61 (5 H, m, Ph)	16.2 (C^6), 46.3 (C^{1}C^5), 79.4 (C^3), 99.9 (C^{2}C^4), 124.4, 129.5 and 156.9 (Ph), 236.6 (CO), 318.6 (*C*OPh)[d]
2b	1.07 [O(CH$_2$*Me*)$_2$], 2.03 (1 H, br s, H^6 *exo*), 2.2 (5 H, br H^{1}H^5 and Me), 2.46 (1 H, br s, H^6 *endo*), 3.39 [O(*CH$_2$*Me)$_2$], 4.13 (2 H, br s, H^{2}H^4) and 5.35 (1 H, br s, H^3)[d]	27.2 (C^6), 36.0 (Me), 54.2 (C^{1}C^5), 80.6 (C^3), 98.0 (C^{2}C^4), 236.4 (CO), 309.7 (*C*OMe)
2c	0.41 (3 H, d, *J* 6, Me), 0.87 [6 H, br s, O(CH$_2$*Me*)$_2$], 2.57 (1 H, br s, H^6 *endo*), 3.0 [6 H, br, H^{1}H^5 and O(*CH$_2$*Me)$_2$], 4.27 (2 H, br s, H^{2}H^4) and 5.44 (1 H, br s, H^3), 7.01 and 7.55 (5 H, br m, Ph)	15.5 [O(CH$_2$*Me*)$_2$], 27.9 (Me), 30.9 (C^6), 59.5 (C^{1}C^5), 66.1 [O(*CH$_2$*Me)$_2$], 79.9 (C^3), 98.2 (C^{2}C^4), 123.9, 128.5 and 157.0 (Ph), 237 (CO), 336 (br, *C*OPh)
2c[e]	0.21 (3 H, d, *J* 6, Me), 2.32 (1 H, m, H^6 *endo*), 2.55 (2 H, t, *J* 6, H^{1}H^5), 4.08 (2 H, t, *J* 6, H^{2}H^4), 5.26 (1 H, t, *J* 6, H^3), 6.9–7.7 {35 H, br m, Ph and [N(PPh$_3$)$_2$]$^+$}[f]	28.8 (Me), 31.2 (C^6), 55.2 (C^{1}C^5), 78.3 (C^3), 98.3 (C^{2}C^4), 125.1, 126.7, 128.9 and 155.9 (Ph), 126.9 {dd, *J*(^{31}PC) 84 and 12, *ipso* [N(PPh$_3$)$_2$]$^+$}, 129.9, 131.1, 132.8, 134.0 and 135.3 {br, [N(PPh$_3$)$_2$]$^+$}, 238.4 (CO), 293.4 (*C*OPh)[f]
2e	1.21 [6 H, br t, *J* 6, O(CH$_2$*Me*)$_2$], 2.30 (3 H, s, C$_5$H$_4$*Me*), 3.33 [4 H, br d, *J* 6, O(*CH$_2$*Me)$_2$], 3.54 (2 H, br s, H^{1}H^5), 4.16 (1 H, br s, H^6 *endo*), 4.64 (2 H, br t, H^{2}H^4), 5.60 (1 H, br s, H^3), 7.25 (2 H, br s, C$_6$H$_4$Me), 7.39 (5 H, br s, Ph), 7.84 (2 H, br s, C$_5$H$_4$Me)	15.2 [O(CH$_2$*Me*)$_2$] 20.9 (C$_6$H$_4$*Me*), 40.1 (C^6), 59.4 (C^{1}C^5), 65.8 [O(*CH$_2$*Me)$_2$], 80.4 (C^3), 99.2 (C^{2}C^4), 123.5, 126.1, 128.9, 135.4, 146.6, 156.0 (C$_6$H$_4$Me, Ph), 236.9 (CO), 332 (br, *C*OPh)

[a] The atom labelling for NMR assignments is that shown in Scheme 1; [Li(OEt$_2$)]$^+$ salts unless stated otherwise. [b] In C$_6$D$_6$ at 25 °C; *J* in Hz. [c] ^{1}H-Decoupled spectra. [d] In [^{2}H$_8$]tetrahydrofuran at 15 °C. [e] As the [N(PPh$_3$)$_2$]$^+$ salt. [f] In [^{2}H$_6$]acetone.

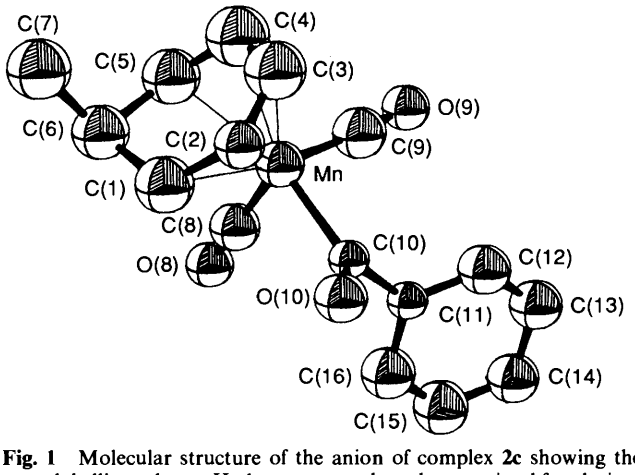
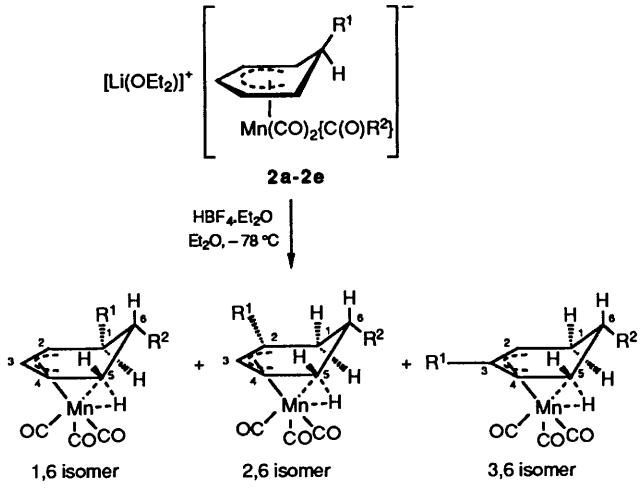


Fig. 1 Molecular structure of the anion of complex **2c** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity



Scheme 2 **3a** R^1 = H, R^2 = Ph; **3b** R^1 = H, R^2 = Me; **3c** R^1 = Me, R^2 = Ph; **3d** R^1 = Me, R^2 = Me; **3e** R^1 = C$_6$H$_4$Me-4, R^2 = Ph; **3a(D)** = [Mn(η$^{3:CH}$-C$_6$D$_7$R^{1}R^2)(CO)$_3$] R^1 = H, R^2 = Ph

from the cyclohexadienyl ring. The asymmetric orientation of three ligands beneath the cyclohexadienyl ligand, although unexpected given steric considerations, has also been observed for other [Mn(η^5-dienyl)(CO)$_{3-x}$L$_x$] and [Mn(η^4-diene)(CO)$_{3-x}$L$_x$] complexes.[11]

Synthesis of endo-*Substituted Cyclohexenyl Complexes.*—Dropwise addition of HBF$_4$·Et$_2$O to complexes **2a–2e**, or even excess of water to **2a**, results in protonation of the cyclohexadienyl ring and phenyl or methyl migration from the acyl group to the *endo* face of the C$_6$ ligand. This remarkable transformation leads to new η$^{3:CH}$-cyclohexenyl complexes [Mn(η$^{3:CH}$-C$_6$H$_7$R^{1}R^2)(CO)$_3$] **3** that have one agostic *endo* C–H bond and an *endo*-R^2 group at C^6 (Scheme 2). When the reaction is done at −78 °C using HBF$_4$·Et$_2$O, followed by slow warming to room temperature, **3** can be isolated as orange oils or solids in 45–95% yields. The cyclohexenyl species are formed as mixtures of the three possible regioisomers that can result from disubstitution of a cyclohexenyl ring (Table 4). For **3a** and **3b** all regioisomers are identical, although a labelling study (see later) shows both 1,6 and 2,6 isomers are formed for **3a**. For **3c** the 1,6 isomer can be separated from the remaining 2,6 and 3,6 species, but complexes **3d** and **3e** could only be characterised as mixtures of the 1,6, 2,6 and 3,6 isomers.*

Complex **3b** has also been prepared by a different route reported by Brookhart *et al.*[4a,c] and was characterised by comparison of its ^1H NMR spectrum with that reported. Compounds **3a** and **3c–3e** were characterised using ^1H, ^{13}C NMR, and IR spectroscopy (Table 5), and show both ^1H and ^{13}C NMR data consistent with structures in which the *endo*-methyl or -phenyl group adopts the position furthest from the metal allyl fragment, namely C^6. All the cyclohexenyl derivatives undergo the well defined fluxional processes reported for **3b** and [Mn(η$^{3:CH}$-C$_6$H$_9$)(CO)$_3$][4a] shown in Scheme 3.

Process A interchanges structures **I** and **II** *via* a 16-electron species **III**. This occurs rapidly at room temperature and results in an averaged ^1H NMR resonance for the two *endo* H^1 and H^5 protons. For **3a**, the signal at δ −5.72 (2 H) is assigned to *endo*-H^1 and *endo*-H^5 being the average of the normal (expected at *ca.* δ 1.0) and agostic (expected at *ca.* δ −13) environments for these protons. Process B is much slower and involves 1,4 H shifts *via* metal hydride intermediates **VI** and **VII**. This leads to species **IV** or **V** in which only an agostic environment is experienced by the *endo*-H^{1}H^5 protons. This latter process is

* The 1,6, 2,6 and 3,6 labelling of isomers for **3** is used rather than 4,5-, 1,5- and 2,5- to remain consistent with labelling adopted in the schemes and NMR signal assignments for all compounds reported throughout.

Table 2 Non-hydrogen atomic coordinates for complex **2c**

Atom	*x*	*y*	*z*
Mn	1.379 5(4)	0.548 2	−0.087 9(1)
P(1)	1.022 8(6)	0.079 1(3)	−0.102 0(2)
P(2)	1.048 8(6)	0.091 7(3)	−0.190 8(2)
N(1)	1.027(2)	0.126 2(9)	−0.145 6(6)
O(8)	1.630(2)	0.513(1)	−0.037 9(5)
O(9)	1.350(4)	0.357(1)	−0.112 3(6)
O(10)	1.531(2)	0.660(1)	−0.146 6(5)
C(1)	1.358(3)	0.692(2)	−0.063 4(9)
C(2)	1.274(3)	0.677(2)	−0.098 6(8)
C(3)	1.166(4)	0.609(2)	−0.101 0(8)
C(4)	1.147(4)	0.553(2)	−0.068(1)
C(5)	1.230(3)	0.570(2)	−0.033 9(8)
C(6)	1.287(4)	0.670(2)	−0.022 5(7)
C(7)	1.159(4)	0.730(2)	−0.008 4(7)
C(8)	1.533(3)	0.530(2)	−0.057 1(7)
C(9)	1.364(4)	0.435(2)	−0.103 0(7)
C(10)	1.512(2)	0.583(2)	−0.132 5(6)
C(11)	1.618(2)	0.509(2)	−0.149 9(8)
C(12)	1.589(3)	0.436(2)	−0.176 4(8)
C(13)	1.696(4)	0.384(1)	−0.190 9(8)
C(14)	1.841(3)	0.398(3)	−0.179 1(9)
C(15)	1.871(3)	0.463(2)	−0.152(1)
C(16)	1.762(4)	0.522(2)	−0.140 5(7)
C(21)	1.197(2)	0.069(1)	−0.081 1(5)
C(22)	1.238(3)	0.002(2)	−0.050 8(8)
C(23)	1.380(3)	0.008(2)	−0.036 0(8)
C(24)	1.482(3)	0.071(2)	−0.046(1)
C(25)	1.439(3)	0.135(2)	−0.073(1)
C(26)	1.313(3)	0.131(1)	−0.090 5(6)
C(31)	0.934(2)	−0.032(1)	−0.100 4(6)
C(32)	0.782(3)	−0.027(1)	−0.097 8(7)
C(33)	0.698(3)	−0.105(2)	−0.099 1(8)
C(34)	0.766(3)	−0.187(2)	−0.107 5(6)
C(35)	0.919(3)	−0.192(1)	−0.111 2(7)
C(36)	0.998(2)	−0.114(1)	−0.107 6(7)
C(41)	0.925(2)	0.156(1)	−0.070 0(6)
C(42)	0.909(3)	0.136(1)	−0.028 2(7)
C(43)	0.835(3)	0.196(2)	−0.003 7(8)
C(44)	0.773(3)	0.271(2)	−0.019 6(8)
C(45)	0.787(3)	0.295(1)	−0.059 5(9)
C(46)	0.871(3)	0.236(1)	−0.085 0(6)
C(51)	0.884(3)	0.089(1)	−0.216 6(5)
C(52)	0.754(3)	0.116(1)	−0.198 1(7)
C(53)	0.611(3)	0.121(2)	−0.217 8(7)
C(54)	0.610(3)	0.099(1)	−0.257 9(8)
C(55)	0.735(3)	0.072(1)	−0.277 5(7)
C(56)	0.869(3)	0.069(1)	−0.257 0(9)
C(61)	1.140(3)	−0.019(1)	−0.196 6(7)
C(62)	1.062(3)	−0.098(1)	−0.207 8(8)
C(63)	1.132(3)	−0.178(1)	−0.207 5(9)
C(64)	1.284(3)	−0.184(1)	−0.196 8(7)
C(65)	1.357(3)	−0.106(1)	−0.183 2(8)
C(66)	1.285(3)	−0.023(1)	−0.184 7(8)
C(71)	1.157(3)	0.175(1)	−0.216 0(7)
C(72)	1.177(3)	0.259(1)	−0.197 9(6)
C(73)	1.253(3)	0.330(1)	−0.216 6(8)
C(74)	1.306(3)	0.316(1)	−0.256 1(7)
C(75)	1.289(3)	0.235(1)	−0.274 8(8)
C(76)	1.213(3)	0.162(1)	−0.256 3(9)

Table 3 Selected bond distances (Å) and angles (°) for the anion of complex **2c**

Mn–C(1)	2.24(2)	Mn–C(2)	2.12(2)	Mn–C(3)	2.17(3)
Mn–C(4)	2.22(3)	Mn–C(5)	2.25(2)	Mn–C(8)	1.74(2)
Mn–C(10)	1.96(2)	O(8)–C(8)	1.11(2)	O(9)–C(9)	1.17(2)
O(10)–C(10)	1.22(2)	C(1)–C(2)	1.40(3)	C(1)–C(6)	1.52(3)
C(2)–C(3)	1.38(3)	C(3)–C(4)	1.37(3)	C(4)–C(5)	1.37(3)
C(5)–C(6)	1.58(3)	C(6)–C(7)	1.51(4)	C(10)–C(11)	1.54(3)

C(8)–Mn–C(9)	95(1)	C(8)–Mn–C(10)	89(1)
C(9)–Mn–C(10)	95(1)	O(8)–C(8)–Mn	176(3)
O(9)–C(9)–Mn	178(3)	O(10)–C(10)–Mn	127(2)
O(10)–C(10)–C(11)	114(2)	C(2)–C(1)–C(6)	117(2)
C(1)–C(2)–C(3)	123(2)	C(2)–C(3)–C(4)	118(3)
C(3)–C(4)–C(5)	118(3)	C(4)–C(5)–C(6)	122(3)
C(1)–C(2)–C(3)	123(2)	C(1)–C(6)–C(5)	97(2)
C(1)–C(6)–C(7)	119(2)	C(5)–C(6)–C(7)	110(3)
C(1)–Mn–C(10)	95(1)	C(2)–Mn–C(10)	86(1)
C(3)–Mn–C(10)	108(1)	C(4)–Mn–C(10)	143(1)
C(5)–Mn–C(10)	157(1)		

Table 4 Distribution of isomers for complexes **3**

	Isomers (%)		
Complex	1,6	2,6	3,6
3a(D)′	65	35	0
3c	70	20	10
3d	20	20	60
3e	0	90	10

not significant at room temperature since only small amounts of **IV** and **V** can be detected in the ^{1}H NMR spectra of **3**. For example **3a** shows a small peak at δ −13.3, assigned to the minor isomers **IV** and **V**, that is only 2% the intensity of the signal at δ −5.72.

The symmetric 3,6-disubstituted isomers of complexes **3c–3e** show similar signals to **3a** and **3b** in the high-field region of their ^{1}H NMR spectra. Thus, **3c** (3,6 isomer) shows a signal at δ −5.20 (2 H), **3d** (3,6 isomer) at δ −6.23 (2 H) and **3e** (3,6 isomer) at δ −5.62 (2 H) all of which are assigned to the H^1H^5 *endo* protons in these complexes. The remaining 1,6 and 2,6 isomers show more complex spectra due to asymmetric substitution of the ring. Thus two signals, symmetrically displaced about δ −5.5, are observed, each of which is the average of the two possible environments for H^1 *endo* or H^5 *endo*. For example, the 1,6 isomer of **3c** shows signals at δ −6.45 (1 H) and −4.19 (1 H), with signals for the 2,6 isomer appearing at δ −6.97 (1 H) and −3.50 (1 H). Similar spectra were obtained by Brookhart and Lukacs[4d] for the *exo*-methylcyclohexenyl complex [Mn($\eta^{3:CH}$-C_6H_8Me)$(CO)_3$] **4**. Complex **4** was found to undergo fluxional processes A and B with the latter involving a complete 'walk' around the ring by the metal. Complexes **3a–3e** only undergo a partial 'walk' since the *endo*-methyl or -phenyl group does not migrate to the metal when adjacent to the allyl carbons (structures **IV** and **V** in Scheme 3).

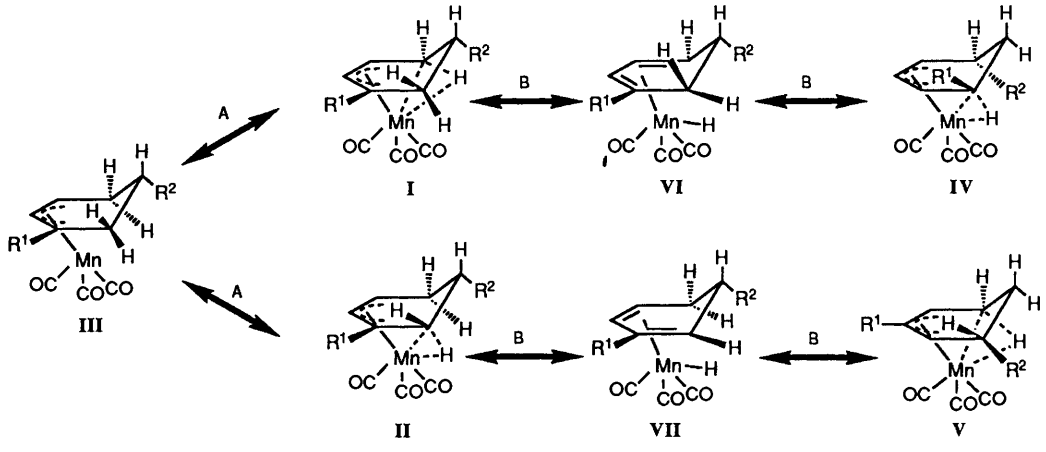
A more detailed analysis of the chemical shifts of the *endo*-H^1H^5 protons allows the determination of the ratio of **I** to **II** for the asymmetric isomers of complexes **3c–3e**. Thus, by analogy with the data reported[4d] for **4**, the following approximate ratios and chemical shift assignments can be made; **3c** (1,6), **I**:**II** = 42:58, δ −6.45 (**II**), −4.19 (**I**); **3c** (2,6), **I**:**II** = 39:61, δ −6.97 (**II**), −3.50 (**I**); **3d** (1,6), **I**:**II** = 48:52, δ −6.5 (**II**), −6.0 (**I**); **3d** (2,6), **I**:**II** = 43:57, δ −7.20 (**II**), −5.23 (**I**); **3e** (2,6), **I**:**II** = 23:77, δ −9.5 (**II**), −1.3 (**I**).

The ^{13}C NMR data for complexes **3a–3c** are consistent with the structures shown and are comparable with those reported for **4** and other related cyclohexenyl complexes.[4] Noteworthy is $^1J(CH_{endo})$ for C^1 and C^5 of 110 Hz, which represents an average between the M–H–C agostic form [expected ^1J(CH) of 85 Hz] and a normal sp^3-hybridised C–H coupling of *ca.* 135 Hz. This average is due to the rapid decomplexation and recomplexation of the *endo*-CH groups *via* process A (Scheme 3).

Table 5 Proton and ^{13}C NMR data for cyclohexenyl complexes **3a–3e**[a]

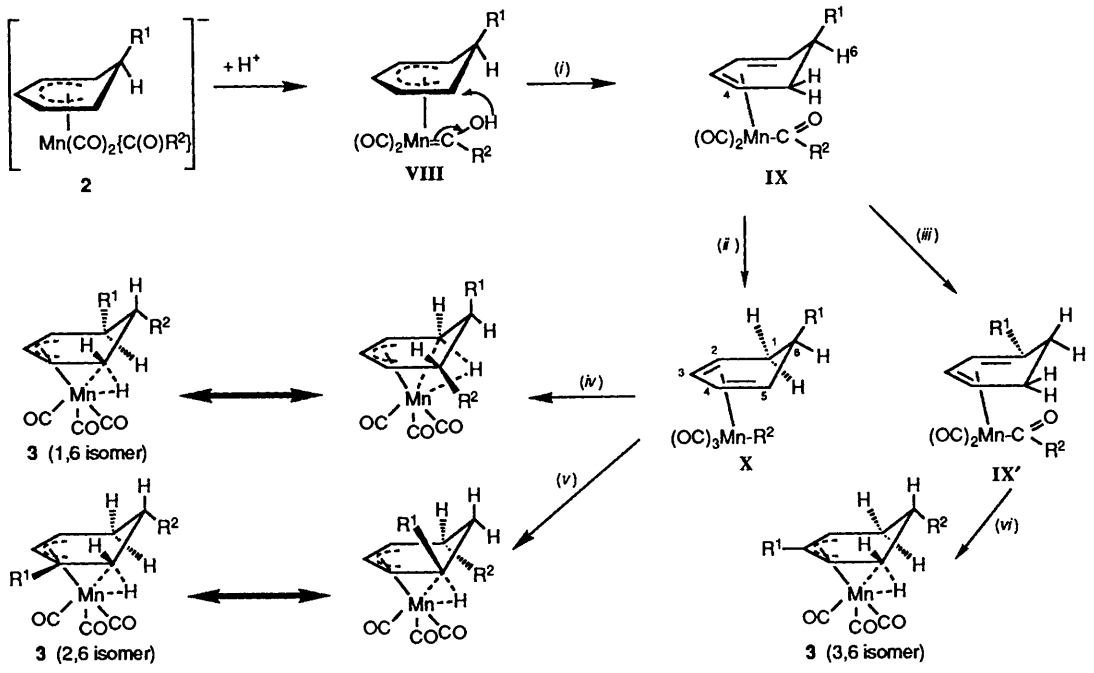
Complex	$\delta(^1H)$[b]	$\delta(^{13}C)$[b]
3a	−5.72 (2 H, br s, H^1H^5 *endo*), 1.20 (2 H, d, H^1H^5 *exo*), 1.35 (1 H, m, H^6 *exo*), 4.06 (2 H, br s, H^2H^4), 4.50 (1 H, t, H^3), 6.80 (5 H, m, Ph)	29.2 (C^1C^5), 34.9 (C^6), 69.2 (C^2H^4), 94.3 (C^3), 127.4 (m, Ph), 144.0 (*ipso* Ph) and 222.3 (CO)[c]
3b[d]		29.2 (dd, *J* 141 and 109, C^1C^5), 34.9 (d, *J* 135, C^6), 69.2 (d, *J* 167, C^2C^4), 94.3 (d, *J* 167, C^3), 127.4 (m, Ph), 144.0 (s, *ipso* Ph)
3c	−6.45 (1 H, br dd, H^1H^5 *endo*), −4.19 (1 H,	20.3 (Me), 32.3 (C^5), 35.6 (C^1), 41.8 (C^6), 68.6 and 76.2 (C^2C^4), 93.2 (C^3), 127.1,
(1,6 isomer)	br dd, H^1H^5 *endo*), 0.87 (3 H, d, *J* 7, Me), 1.43 (1 H, m, H^6 *exo*), 1.63 (1 H, dt, *J* 16 and 5, H^5 *exo*), 4.43 (2 H, br m, H^2H^4), 4.87 (1 H, br m, H^3), 7.0–7.9 (5 H, m, Ph)	128.5, 130.2 and 142.7 (Ph), 222 (CO)[c]
(2,6 isomer)	−6.97 (1 H, br dd, *J* 15 and 8.5, H^1H^5 *endo*), −3.50 (1 H, br dd, *J* 15 and 8.5, H^1H^5 *endo*), 1.6–2.0 (3 H, m, $H^1H^5H^6$ *exo*), 2.29 (3 H, s, Me), 4.25 (1 H, br s, H^4), 5.10 (1 H, br d, H^3), 6.9–7.6 (5 H, m, Ph)	20.3 (q, *J* 127, Me), 32.3 (dd, *J* 142 and 102, C^5), 35.6 (d, *J* 104, C^1), 41.8 (d, *J* 132, C^6), 68.6 (d, *J* 170, C^2 or C^4), 76.2 (d, *J* 170, C^2 or C^4), 93.2 (d, *J* 166, C^3), 127.1, 128.5, 130.2 and 142.7 (m, Ph), 222 (CO)
		22.5 (Me), 31.0 (br, C^1C^5), 35.1 (C^6), 64.1 (C^4), 86.3 (C^2), 94.0 (C^3), 127–130 (Ph), 142.5 (*ipso* Ph), 222 (br, CO)[c]
		22.5 (q, *J* 127, Me), 31.0 (br dd, *J* 136 and 108, C^1C^5), 35.1 (d, *J* 134, C^6), 64.1 (d, *J* 170, C^4), 86.3 (s, C^2), 94.0 (d, *J* 164, C^3), 127–130 (m, Ph), 142.5 (s, *ipso* Ph), 222 (CO)
(3,6 isomer)	−5.20 (2 H, br s, H^1H^5 *endo*), 1.51 (2 H, br d, *J* 16, H^1H^5 *exo*), 1.80 (1 H, br m, H^6 *exo*), 2.03 (3 H, s, Me), 4.76 (2 H, br m, H^2H^4), 6.9–7.6 (5 H, m, Ph)	22.1 (Me), 28.2 (C^1C^5), 38.3 (C^6), 69.6 (C^2C^4), 109.3 (C^3), 127–130 (Ph), 142.9 (*ipso* Ph), 222 (br, CO)[c]
		22.1 (q, *J* 127, Me), 28.2 (dd, *J* 138 and 108, C^1C^5), 38.3 (d, *J* 128, C^6), 69.6 (d, *J* 166, C^2C^4), 109.3 (s, C^3), 127–130 (m, Ph), 142.9 (s, *ipso* Ph), 222 (CO)
cis	−12.83 (1 H, m, H^1 *endo*), 0.33 (3 H, d, Me), 0.50 (1 H, dd, *J* 16 and 7, H^6 *exo*), 1.76 (1 H, m, H^1 *exo*), 1.95 (1 H, m, H^5 *exo*), 3.42 (1 H, m, H^2), 4.49 (1 H, m, H^4), 4.73 (1 H, m, H^3), 6.37 (2 H, m, Ph), 6.94 (3 H, m, Ph)	15.5 (C^1), 19.8 (Me), 36.4 (C^5), 39.7 (C^6), 73.8 (C^2 or C^4), 75.9 (C^2 or C^4), 93.9 (C^3), 124.9, 126.7, 129.3 (Ph), 140.4 (*ipso* Ph) and 223.5 (CO)[c]
		15.5 (dd, *J* 149 and 85, C^1), 19.8 (q, *J* 124, Me), 36.4 (d, *J* 127, C^5), 39.7 (d, *J* 127, C^6), 73.8 (d, *J* 179, C^2 or C^4), 75.9 (d, *J* 170, C^2 or C^4), 93.9 (d, *J* 166, C^3), 124.9 (m, Ph), 126.7 (m, Ph), 129.3 (m, Ph), 140.4 (s, *ipso* Ph), 223 (CO)
3e	−9.5 (1 H, br dd, *J* 16 and 8, H^1H^5 *endo*),	19.6 (C_6H_4Me), 30.2 and 31.7 (C^1C^5), 33.8 (C^6), 63.9 (C^4), 87.6 (C^2), 90.0 (C^3),
(2,6 isomer)	−1.3 (1 H, br dd, *J* 16 and 8, H^1H^5 *endo*), 0.61 (1 H, m, H^5 *exo*), 1.40 (1 H, m, H^6 *exo*), 1.65 (1 H, d, *J* 16, H^1 *exo*), 1.91 (3 H, s, C_6H_4Me), 3.55 (1 H, br dd, H^4), 5.07 (1 H, d, *J* 7.5, H^3), 6.2–7.4 (9 H, m, aryl)	125–144 (Ph and C_6H_4Me), 223 (br, CO)[c]
(3,6 isomer)	−5.62 (2 H, br s, H^1H^5 *endo*), 0.67 (2 H, m, H^1H^5*exo*), 1.75 (3 H, s, C_6H_4Me), 2.03 (1 H, br m, H^6 *exo*), 4.41 (2 H, br s, H^2H^4), 6.2–7.4 (9 H, m, aryl)	19.5 (C_6H_4Me), 27.0 (C^1C^5), 34.6 (C^6), 65.4 (C^2C^4), 108.3 (C^3), 125–144 (Ph and C_6H_4Me), 220 (br, CO)[c]
3d[e]	−6.5 (1 H, br s, H^1 or H^5 *endo*), −6.0 (1 H, br s, H^1 or H^5 *endo*), 0.19 (3 H, d, *J* 7, Me, *endo*), 0.75 (1 H, m, H^6 *exo*), 0.90 (3 H, d, *J* 7,	
(1,6 isomer)	C^1Me *exo*), 1.0 (1 H, br d, H^5 *exo*), 4.50 (2 H, br m, H^2H^4), 4.75 (1 H, dd, H^3)	
(2,6 isomer)	−7.20 (1 H, br s, H^1 or H^5 *endo*), −5.23 (1 H, br s, H^1 or H^5 *endo*), 0.17 (3 H, d, *J* 7, Me *endo*), 0.6 (1 H, br m, H^6 *exo*), 0.94 (3 H, s, C^2Me), 1.05–1.2 (2 H, H^1H^5 *exo*), 3.8 (1 H, br s, H^4), 4.6 (1 H, br d, H^3)	
(3,6 isomer)	−6.23 (2 H, br s, H^1H^5 *endo*), 0.20 (1 H, br m, H^6 *exo*), 0.22 (3 H, d, *J* 7, Me *endo*), 1.12 (2 H, m, H^1H^5 *exo*), 1.59 (3 H, s, C^3Me), 3.91 (2 H, br s, H^2H^4)	

[a] The atom labelling for NMR assignments is that shown in Schemes 2 and 5. [b] In C_6D_6 at 25 °C; *J* in Hz. [c] ^1H-Decoupled spectrum. [d] Data for complex **3b** were identical to those previously reported in refs. 4*a* and 4*c*. [e] ^1H NMR only in [$^2H_8$]toluene.



Scheme 3 Dynamic processes for complexes **3a–3e**. For brevity only the 2,6 isomer of complex **3** is depicted in Scheme 3, although the same fluxionality is seen for the 1,6 and 3,6 species

Mechanism for the Formation of Complexes **3** *and Labelling Studies*.—The conversion of complexes **2** into **3** is a novel transformation involving protonation of the cyclohexadienyl ring, deinsertion of the acyl CO ligand and migration of an alkyl or aryl group to the *endo* face of the ring. We suggest this reaction proceeds as outlined in Scheme 4 with initial H^+ addition to the acyl oxygen forming a hydroxycarbene derivative **VIII**. Protonation of an acyl ligand giving a hydroxycarbene complex has precedent in the reaction of HBF_4 with $[Re(\eta^5\text{-}C_5H_5)\{C(O)Ph\}(NO)(PPh_3)]$,[12] and as described later



Scheme 4 (*i*) Proton migration; (*ii*) deinsertion of CO; (*iii*) migration of H^6 to C^4; (*iv*) migration of R^2 to C^5; (*v*) migration of R^2 to C^2; (*vi*) deinsertion of CO followed by migration of R^2

we have shown that alkylation of **2** with $[Me_3O][BF_4]$ occurs at the acyl oxygen to give deep red carbene complexes. Indeed, the addition of $HBF_4{\cdot}Et_2O$ to **2a** at −78 °C initially gives a deep red species which slowly transforms into pale orange **3a** upon warming to room temperature. We propose that this latter transformation proceeds *via* hydrogen-atom transfer to the *endo* face of the ring in **VIII** forming a 16-electron diene/acyl derivative **IX**. Deinsertion of the acyl CO in **IX** would then give **X**, with subsequent migration of the alkyl or aryl group resulting in **3**.

As shown, the added proton becomes an *endo*-hydrogen on C^1 or C^5, and the R^2 group can migrate to either C^5 or to C^2 in **X** to give 1,6 and 2,6 isomers respectively. In order for the 3,6 species to form, a rearrangement must occur that allows migration of R^2 to a position that is both a terminal diene carbon akin to C^2 or C^5 and is also 1,4 with respect to R^1. We propose that the intermediate **IX** may undergo a 1,3-H shift of H^6 *endo* forming **IX′**, which then transforms to the 3,6 isomer *via* CO deinsertion and migration as for **X**. Similar hydrogen-atom shifts in η^4-diene and η^5-dienyl complexes are known.[13] Alternatively, the 3,6 isomer may form from **X** by direct migration of R^2 to C^4.

To investigate both the stereochemistry of the protonation and the regiochemistry of R^2 migration, the following experiments were performed. First, the perdeuterio complex $[Mn(\eta^5\text{-}C_6D_7)(CO)_3]$ **1a(D)** was treated with LiPh and protonated to give **3a(D)**. The ^1H NMR spectrum of **3a(D)** shows signals at δ 6.8–7.5 (5 H) and −5.80 (2 H) assigned to the phenyl and *endo*-H^1H^5 protons respectively. Therefore, the addition of H^+ to **2** cannot occur from direct *exo* protonation of the ring, but must arise either from initial *endo* addition or attack at the metal and its ancillary ligands. Moreover, integration of the *endo*-H^1H^5 proton signals suggests 2 equivalents of H^+ are added and implies exchange of *endo*-deuterons for the excess of protons in solution. This could occur *via* a metal hydride species similar to that involved in the conversion of **IX** to **IX′**, or those in dynamic process B (structures **VI** and **VII**, Scheme 3).

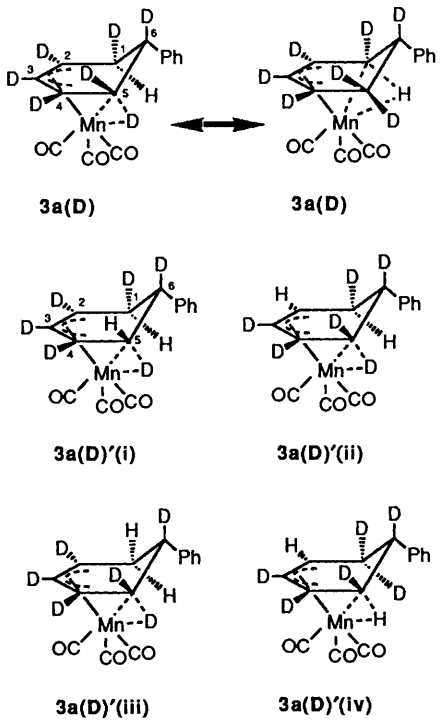
A second labelling experiment was performed to probe whether complex **3a** exists as 1,6, 2,6 and 3,6 isomers, with respect to an *exo* substituent at C^6. Thus, **3a(D)′** was synthesised from $[Mn(\eta^5\text{-}C_6D_6H\text{-}exo)(CO)_3]$,* and shows four ^1H NMR signals in addition to the phenyl protons. A singlet at δ 4.06 and a doublet at δ 1.20 (total 1 H) are assigned to protons H^2 in structure **3a(D)′(ii)** and *exo*-H^1 or -H^5 in **3a(D)′(i),(iii)**. The remaining two signals at δ −5.75 (d) and −5.90 (s) (total 2 H) are assigned to *endo*-H^1H^5 in all the possible isomers **3a(D)′(i)–(iv)**. The former is assigned to isomer **3a(D)′(iii)** since this shows coupling to *exo*-H^5, whereas the latter is assigned to the remaining three isomers, none of which has two geminal protons. Noteworthy is the fact that **3a(D)′(i)** is the expected 1,6 isomer based upon the proposed mechanism, and that the alternative observed 1,6 isomer, **3a(D)′(iii)**, can only be formed *via* intermolecular D/H exchange. Similarly, **3a(D)′(ii)** is the expected 2,6 isomer and therefore **3a(D)′(iv)** must also derive from intermolecular H/D exchange.† That intermolecular H/D exchange occurs is further supported by the integration of the two signals to two protons (see earlier), and also by the fact that **3a(D)′(i)** and **3a(D)′(iii)**, or **3a(D)′(ii)** and **3a(D)′(iv)**, cannot interconvert by any known intramolecular dynamic process such as those shown in Scheme 3. Confirmation of the formation of both 1,6 and 2,6 isomers was provided by the $^{13}C\text{-}\{^1H\}$ NMR data for **3a(D)′** which show two H-substituted carbon atoms, C^2 and C^1 or C^5.

Decomplexation of Cyclohexa-1,3-dienes from Complexes **3**.—Earlier studies by Brookhart and co-workers[4] have demonstrated that treatment of $[Mn(\eta^{3:CH}\text{-}C_6H_9)(CO)_3]$ with KH gives $[Mn(\eta^4\text{-}C_6H_8)(CO)_3]^-$ **5** which can be converted into either cyclohexa-1,3-diene by exposure to oxygen or *endo*-substituted derivatives of **3** by reaction with electrophiles.

The cyclohexenyl species **3a–3e** behave similarly (Scheme 5). For example, reaction of **3a** with KH followed by (*i*) addition of dry O_2 gave 5-phenylcyclohexa-1,3-diene **6a**[14] and (*ii*) addition

* Formed from $[Mn(\eta\text{-}C_6D_6)(CO)_3]^+$ and $[NBu^n_4][BH_4]$ in tetrahydrofuran (thf).

† It should be noted that unlike **3a(D)′(iii)** the signals for H^1H^5 *endo* in **3a(D)′(iv)** are identical to those for isomers (i) and (ii). Therefore the existence of **3a(D)′(iv)** is not confirmed in this experiment.



of methyl iodide gave $[Mn\{\eta^{3:CH}\text{-}C_6H_7(endo\text{-}Me)(endo\text{-}Ph)\}(CO)_3]$ *cis*-**3c**. Subsequent treatment of *cis*-**3c** with KH and O_2 gave *cis*-5-methyl-6-phenylcyclohexa-1,3-diene *cis*-**6c**. The new dienes were spectroscopically characterised (Table 6), and **6a** was also characterised as its adduct with tcne (tetracyanoethene).

Using 1,2-*bis*(*diphenylphosphino*)*ethane* (*dppe*). The two-step process described above can be replaced with a one-step decomplexation procedure using dppe. Thus, if 1 equivalent of dppe is added to thf solutions of complexes **3** a red colour develops (10–15 min) and monitoring by IR spectroscopy reveals the only metal-containing species to be $[MnH(CO)_3(dppe)]$ **7**.[15] Precipitation of **7** with hexane and work-up of the mother-liquors gave the cyclohexadienes in good yield. In contrast to the KH/O_2 procedure, the use of dppe leads to specific isomers of the dienes. For example, reaction of the 1,6 isomer of **3c** with dppe gives 1-methyl-6-phenylcyclohexa-1,3-diene **6c**′ as the major organic product, and similar treatment of the 2,6 isomer of **3e** gives 6-phenyl-2-tolylcyclohexa-1,3-diene **6e** (Scheme 6). When the KH/O_2 procedure was performed on **3c** (1,6 isomer) an approximate 1:1 mixture of the two possible products, **6c**′ and *trans*-5-methyl-6-phenylcyclohexa-1,3-diene *trans*-**6c**, was observed. This latter result is consistent with Brookhart's results[4e] that attribute the ratios of isomers formed using KH and O_2 to the isomer distribution in **3** [*e.g.* for **3c** (1,6 isomer) the relative ratio of species **I** and **II** is 42:58 (*ca.* 1:1)].

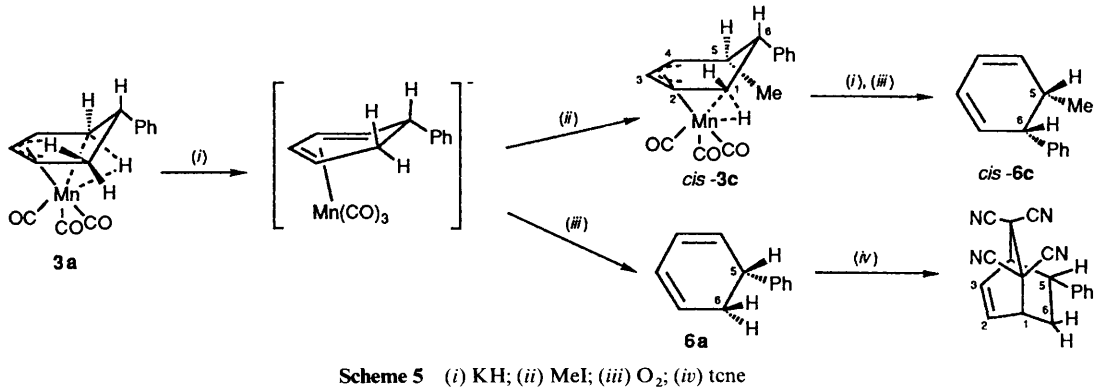
Using dppe as the decomplexation reagent, dienes were isolated from the 1,6 and 2,6 isomers of complex **3c** and the 2,6 isomer of **3e**. The decomplexed diene from **3d** (3,6 isomer) was isolated as a mixture of its *endo* and *exo* adducts with tcne. In all cases other minor isomers of the dienes (< 10% total) were detected using gas chromatography–mass spectrometry (GC–MS) but could not be separated from the major species.

A proposed mechanism of the reaction of complexes **3** with dppe is shown in Scheme 7 and allows a rationalisation for the regiospecificity of diene decomplexation. Initial addition of dppe to **3** displacing the agostic C–H bond has precedent in the reactions of $[Mn(\eta^{3:CH}\text{-}C_6H_9)(CO)_3]$ with trimethyl phosphite and carbon monoxide.[4c] Chelation of the bidentate phosphine in intermediate **XI** concomitant with a change from η^3 to σ co-ordination of the cyclohexenyl ring gives **XII**. β-Elimination of the diene from **XII** results in the observed products. Close monitoring of the reaction (IR spectroscopy) at low temperature reveals a tricarbonyl species [$\nu_{max}(CO)/cm^{-1}$ 1987, 1911 and 1893 (thf)] prior to formation of complex **7**. Upon warming to room temperature these bands disappear while those for **7** [$\nu_{max}(CO)/cm^{-1}$ 1995 and 1915; $\nu_{max}(Mn\text{–}H)/cm^{-1}$ 2013] increase in intensity. We believe the intermediate tricarbonyl to be either **XI**, if the rate-limiting step is the η^3- to σ-co-ordination change, or **XII** if β elimination is rate limiting.

From this mechanism it is clear that regiocontrol arises from the η^3 to σ slip of the cyclohexenyl ring, such that the metal becomes σ bonded to C^2 rather than C^4. For the 1,6 isomer of **3c** this places the metal adjacent to the methyl-substituted carbon C^1, and β elimination leads to 1-methyl-6-phenylcyclohexa-1,3-diene. In the 2,6 isomers of both **3c** and **3e** the metal shifts to the substituted carbon C^2 and β elimination gives 2-methyl-6-phenylcyclohexa-1,3-diene **6c**″ and 6-phenyl-2-tolylcyclohexa-1,3-diene **6e** respectively. Two possible explanations for the selective decomplexation reactions are (*i*) the metal has a preference for σ co-ordination to the most substituted carbon (C^2), or (*ii*) the chelation of dppe is directed such that the incoming PPh_2 group displaces the least-substituted allyl terminus. The latter appears more likely on steric grounds even though the intermediate **XII** is more sterically congested than if the metal were attached to the least-hindered allyl carbon (C^4). It is also possible that formation of such a sterically crowded intermediate drives the unusual β-elimination reaction.

Alternative mechanisms involving the minor isomers of complexes **3** (**IV** and **V**, Scheme 3) are possible, however these species are not significant at room temperature (^1H NMR data) and the initial adduct with dppe forms immediately upon adding the reagent at −78 °C.

Reaction of Acylmetalates **2** *with* $[NO][BF_4]$.—Addition of $[NO][BF_4]$ to a CH_2Cl_2 solution of the $[N(PPh_3)_2]^+$ salt of complex **2c** at −78 °C resulted in the formation of moderate

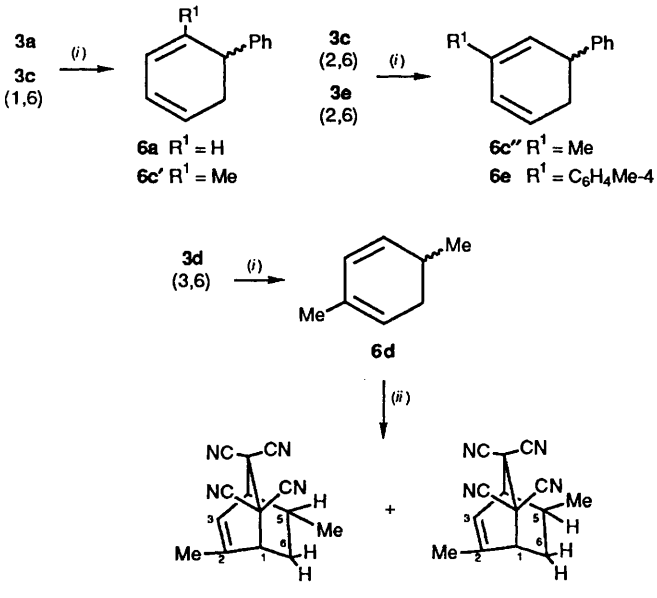


Scheme 5 (*i*) KH; (*ii*) MeI; (*iii*) O_2; (*iv*) tcne

Table 6 NMR spectral data for dienes **6**[a]

Compound	δ(^{1}H)
6a[b]	2.32 (1 H, m, H^6), 2.47 (1 H, m, H$^{6'}$), 3.6 (1 H, m, H^5), 5.8 (2 H, m, H^{1}H^4), 5.94 (1 H, m, H^2), 6.04 (1 H, m, H^3), 7.3 (5 H, m, Ph)
(tcne adduct)	1.88 (1 H, ddd, *J* 15, 6 and 6, H^6), 2.76 (1 H, ddd, H$^{6'}$), 3.59 (2 H, m, H^{4}H^5), 3.69 (1 H, m, H^1), 6.59 (1 H, t, H^3), 6.87 (1 H, t, *J* 8, H^2), 7.17 (5 H, m, Ph)
cis-**6c**	0.90 (3 H, d, Me), 2.63 [1 H, m, *J*(H^{5}H^6) 9, H^5], 3.68 (1 H, m, H^6), 5.7 (1 H, m, H^1), 5.9 (2 H, m, H^{2}H^4), 6.07 (1 H, m, H^3), 7.2 (5 H, m, Ph)
	[c] 14.2 (Me), 33.9 (C^5), 44.9 (C^6), 123.0, 124.3, 126.4 and 129.6 (C$^{1-4}$), 128.1, 129.0 and 132.8 (Ph) and 140.8 (*ipso* Ph)
6c′	1.80 (3 H, s, Me), 2.26 (1 H, m, H^5), 2.39 (1 H, m, H$^{5'}$), 3.55 (1 H, br m, H^6), 5.49 (1 H, br s, H^4), 5.90 (2 H, m, H^{2}H^3), 7.2 (5 H, m, Ph)
trans-**6c**	0.99 (3 H, d, *J* 7, Me), 2.51 (1 H, m, H^5), 3.22 (1 H, m, H^6), 5.7–6.1 (4 H, m, H$^{1-4}$), 7.2 (5 H, m, Ph)
6c″	2.13 (1 H, m, H^5), 2.30 (3 H, s, Me), 2.96 (1 H, m, H$^{5'}$), 3.49 (1 H, br m, H^6), 4.87 (2 H, br m, H^{1}H^4), 6.15 (1 H, m, H^3), 7.2 (5 H, m, Ph)
tcne adduct of **6d**	0.9 (2 H, br m, H^6 or H$^{6'}$), 0.98 (6 H, dd, 2 × Me), 1.1 (2 H, m, H^6 or H$^{6'}$), 2.04 (6 H, br s, 2 × Me), 2.40 (2 H, br m, H^5), 3.0–3.5 (4 H, m, H^{1}H^4), 6.15 (1 H, d, H^3), 6.23 (1 H, br s, H^3)
6e	2.16 (3 H, s, C$_6$H$_4$*Me*), 2.40 (2 H, m, H^{5}H$^{5'}$), 3.50 (1 H, dt, H^6), 5.86 (1 H, dt, H^1), 5.94 (1 H, dd, H^4), 6.43 (1 H, d, H^3), 7.0 (2 H, d, C$_6$*H*$_4$Me), 7.35 (2 H, d, C$_6$*H*$_4$Me), 7.18 (5 H, m, Ph)

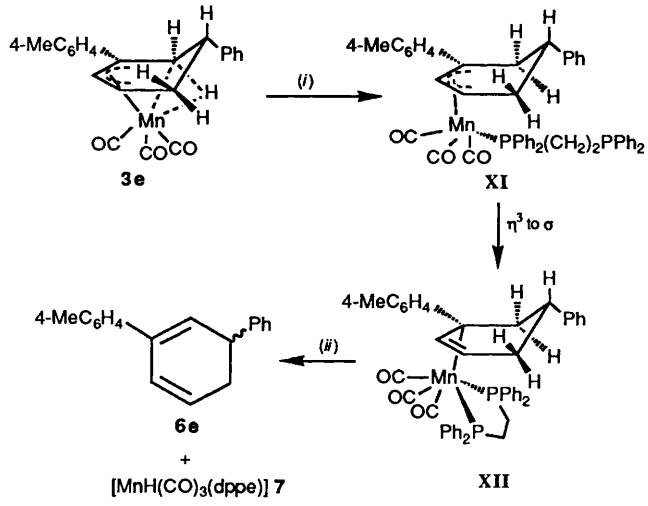
[a] The atom labelling for NMR assignments is that shown in Schemes 5 and 6. Proton NMR data in $CDCl_3$ unless stated otherwise; *J* in Hz. [b] Data for compound **6a** are identical to those previously reported.[14] [c] ^{13}C-{^1H} NMR spectrum in C_6D_6.



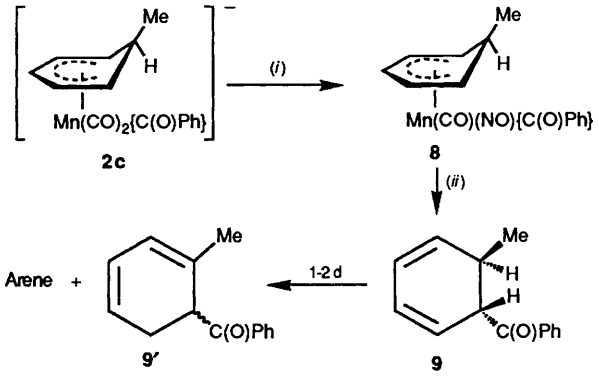
Scheme 6 (*i*) +dppe, −[MnH(CO)$_3$(dppe)]; (*ii*) +tcne

yields of [Mn(η^5-C$_6$H$_6$Me)(CO)(NO){C(O)Ph}] **8**, Scheme 8.* Complex **8** was isolated following low-temperature chromatography on alumina as an orange crystalline solid in 40–46% yield. Characteristic features of its spectroscopic data (Table 7) include two resonances in the ^{13}C NMR spectrum at δ 231.3 (CO) and 263.3 (acyl CO), as well as three IR absorptions at

* Similar Acylnitrosylcyclohexadienyl complexes have been briefly reported by Sweigart and co-workers.[3a]



Scheme 7 (shown for 2,6 isomer of **3e**) (*i*) dppe; (*ii*) β elimination



Scheme 8 (*i*) [NO][BF$_4$], [N(PPh$_3$)$_2$][NO$_2$], CH_2Cl_2, −78 °C; (*ii*) 25 °C, CH_2Cl_2, 12 h

2009 [ν$_{max}$(CO)], 1741 [ν$_{max}$(NO)] and 1607 [ν$_{max}$(acyl)] cm^{-1}. Optimal yields of **8** were obtained when [N(PPh$_3$)$_2$][NO$_2$] was added to the reaction mixture. The use of [N(PPh$_3$)$_2$][NO$_2$] with [NO][BF$_4$] as a nitrosylating reagent has been reported by Geoffroy and co-workers[16] in the synthesis of related manganese nitrosyl α-ketoacyl complexes.

Complex **8** is thermally sensitive in solution and at room temperature eliminates the acyldiene C$_6$H$_6$Me[C(O)Ph] **9**. Diene **9** was characterised from two-dimensional correlation spectroscopy (COSY) ^1H NMR and high-resolution mass spectroscopic data and has a *trans* orientation of the methyl and benzoyl groups [*J*(H^{5}H^6) = 12 Hz]. The diene undergoes slow transformation (1–2 d) to an isomer **9′** *via* a 1,3-H shift as well as aromatisation in air to 2-methylbenzophenone (Scheme 8).

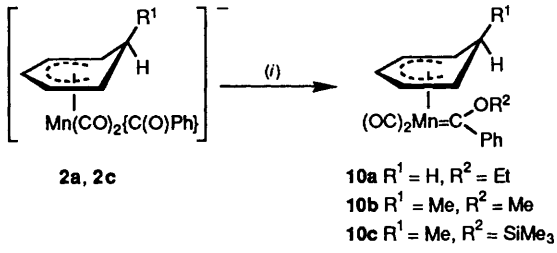
Complex **8** reacts with triphenylphosphine at −10 °C to form a new carbonyl nitrosyl derivative [1958, ν$_{max}$(CO); 1686 cm^{-1}, ν$_{max}$(NO)], but this product is extremely thermally sensitive and readily decomposes to **9**. Repeated attempts to obtain satisfactory NMR data failed, although the ^1H NMR data did suggest two isomers of a complex of **9** may be formed, possibly by phosphine-induced migration of the benzoyl ligand to the cyclohexadienyl ring.

Cyclohexadienyl Carbene Complexes.—The acylmetalates **2** can be alkylated at the acyl oxygen to form carbene complexes **10** (Scheme 9). Thus, treatment of **2a** with [Et$_3$O][BF$_4$] in diethyl ether gave a 50% yield of the carbene complex [Mn(η^5-C$_6$H$_7$)(CO)$_2${C(OEt)Ph}] **10a**. Similarly, [Mn(η^5-C$_6$H$_6$Me)(CO)$_2${C(OMe)Ph}] **10b** and [Mn(η^5-C$_6$H$_6$Me)(CO)$_2${C(OSiMe$_3$)Ph}] **10c** were prepared from **2c** and [Me$_3$O][BF$_4$] and SiMe$_3$Cl respectively. The carbene complexes were characterised by IR, ^1H and ^{13}C NMR spectroscopy (Table 7) and show distinctive ^{13}C signals at *ca.* δ 335 assigned to the carbene

Table 7 Proton and ^{13}C NMR data for complexes **8** and **10**[a]

Complex	δ(^{1}H)	δ(^{13}C)[b]
8	0.46 (3 H, br s, Me), 2.40 (1 H, br s, H^6 *endo*), 3.56 (1 H, br s, H^1 or H^5), 4.41 (1 H, br s, H^1 or H^5), 4.88 (2 H, br s, H^2H^4), 6.30 (1 H, br s, H^3), 7.2–7.6 (5 H, br m, Ph)[c]	27.1 (Me), 28.8 (C^6), 68.9 and 75.0 (C^1C^5), 90.1 and 97.4 (C^2C^4), 108.0 (C^3), 126.9–130.7 (Ph), 147.2 (*ipso* Ph), 231.3 (CO), 263.3 (*C*OPh)[c]
10a	1.17 (3 H, t, *J* 7, OCH_2Me), 1.85 (1 H, d, *J* 11, H^6 *exo*), 2.49 (3 H, m, H^1H^5 and H^6 *endo*), 4.18 (2 H, t, *J* 5.5, H^2H^4), 4.80 (2 H, q, *J* 7, OCH_2Me), 5.2 (1 H, t, *J* 5.5, H^3) and 7.0–7.3 (5 H, m, Ph)	15.1 (OCH_2CH_3), 24.6 (C^6), 50.9 (C^1C^5), 73.8 (OCH_2CH_3), 81.2 (C^3), 100.7 (C^2C^4), 124.2, 127.4 and 128.7 (Ph), 153.0 (*ipso* Ph), 230 (CO), 338 [*C*(OEt)Ph]
10b	0.38 (3 H, d, *J* 7, Me), 2.55 (1 H, m, H^6 *endo*), 2.95 (2 H, t, *J* 6, H^1H^5), 4.20 (2 H, t, *J* 6, H^2H^4), 4.35 (3 H, s, OMe), 5.18 (1 H, t, *J* 6, H^3) and 7.1–7.3 (5 H, m, Ph)	22.6 (Me), 27.6 (C^6), 59.8 (C^1C^5), 64.1 (OMe), 81.5 (C^3), 98.5 (C^2C^4), 124.1, 127.3 and 128.5 (Ph), 154.0 (*ipso* Ph), 229.4 (CO), 339.2 [*C*(OMe)Ph]
10c	0.02 (9 H, br s, $OSiMe_3$), 0.31 (3 H, br s, Me), 2.35 (1 H, br s, H^6 *endo*), 3.10 (2 H, br s, H^1H^5), 4.24 (2 H, br m, H^2H^4), 5.34 (1 H, br s, H^3) and 7.21 (5 H, m, Ph)	1.1 ($OSiMe_3$), 28.0 (Me), 30.0 (C^6), 62.4 (C^1C^5), 80.8 (C^3), 101.4 (C^2C^4), 123.3, 126.9 and 128.9 (Ph), 156.2 (*ipso* Ph), 230.2 (CO), 340.8 [*C*($OSiMe_3$)Ph)]

[a] In C_6D_6 at 25 °C unless stated otherwise; *J* in Hz. [b] ^{1}H-Decoupled spectra. [c] In $CDCl_3$ at −30 °C.



2a, 2c **10a** R^1 = H, R^2 = Et; **10b** R^1 = Me, R^2 = Me; **10c** R^1 = Me, R^2 = $SiMe_3$

Scheme 9 (*i*) $[Et_3O]^+$ or $[Me_3O]^+$ or $SiMe_3Cl$

carbon. The complexes are isolated as deep red air-sensitive oils and repeated attempts to obtain satisfactory elemental analyses failed.

In other work[17] we have shown that analogous cycloheptadienylcarbene complexes rearrange *via* a novel dienyl–carbene coupling to form two new C–C bonds between the ring and the carbene ligand. Surprisingly, under a variety of conditions, compounds **10a–10c** do not undergo carbene migration to the ring (*e.g.* refluxing in toluene, irradiation with UV light or addition of PPh_3). We ascribe this lack of reactivity to the instability of cyclohexadienylcarbene adducts, in which coordination of a highly strained bicyclo[3.1.1]heptene ring is required.

Conclusion

We have shown that two carbanions can be sequentially added to benzenetricarbonylmanganese(I) cations to give reactive cyclohexadienylmanganese acylmetalates. One of these, $[N(PPh_3)_2][Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(O)Ph\}]$ **2c** was characterised by an X-ray crystallographic study. The new acylmetalates undergo a novel rearrangement upon protonation forming 1,6-, 2,6- and 3,6-disubstituted $\eta^{3:CH}$ agostic cyclohexenyl derivatives, from which the cyclohexadienes can be isolated *via* treatment with dppe. The new decomplexation procedure is regioselective and possible mechanisms for this and the protonation reaction have been proposed. The acylmetalates react with other electrophiles to form carbene complexes that show no tendency to rearrange like their cycloheptadienyl counterparts. Finally, we have also shown that the new acyl species **2c** reacts with $[NO]^+$ to give a neutral nitrosyl complex **8** that readily eliminates the *trans*-disubstituted acylcyclohexadiene **9** at room temperature.

Experimental

General.—The preparation, purification and reactions of all complexes described were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried over sodium–benzophenone (toluene, benzene, thf, diethyl ether), CaH_2 (hexane, pentane, CH_2Cl_2) or K_2CO_3 (acetone), and were freshly distilled prior to use. Tetrahydrofuran or diethyl ether solutions of organolithium reagents and all other materials were used as supplied by Aldrich (Milwaukee, WI). The complexes $[Mn(\eta^5\text{-}C_6H_6R^1)(CO)_3]$ (R^1 = *exo*-H, Me or C_6H_4Me-4) were prepared using the literature procedures.[6,7b] Infrared spectra were recorded using a Nicolet 5ZDX FT instrument operated in the transmittance mode, NMR spectra on Bruker WP 200 or Varian VXR-400S spectrometers, using the COSY-45 pulse sequence for all two-dimensional work. Gas chromatography–mass spectrometry 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). High-resolution mass spectra were obtained at Hoffman La Roche (Nutley, NJ). Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories (Woodside, NY). The NMR spectroscopic data for most new compounds are displayed in Tables 1 and 4–7.

Syntheses.—Tricarbonyl[6-exo-(4-*tolyl*)*cyclohexadienyl*]*manganese*(I) **1c**. Complex **1c** was prepared using $MgBr(C_6H_4Me\text{-}Br)$ as described for **1b**.[7b] Yield (94%); ν_{max}/cm^{-1}(CO) 2022, 1951 and 1942 (hexane); $\delta_H(CDCl_3)$ 2.27 (3 H, s, Me), 3.47 (2 H, t, *J* 6, H^1H^5), 3.77 (1 H, dd, *J* 6 and 2, H^6), 4.94 (2 H, t, *J* 6, H^2H^4), 5.76 (1 H, dd, *J* 6 and 1, H^3), 6.85 (2 H, d, *J* 7.5, tolyl) and 7.03 (2 H, d, *J* 7.5 Hz, tolyl); $\delta_C(CD_2Cl_2)$ 20.6 (Me), 39.2 (C^6), 58.9 (C^1C^5), 79.5 (C^3), 96.0 (C^2C^4), 123.7, 128.1, 136.5, 144.0 (tolyl) and 223.3 (CO) (Found: C, 62.40; H, 4.35. $C_{16}H_{13}MnO_3$ requires C, 62.35; H, 4.20%).

General procedure for acyldicarbonylcyclohexadienylmanganates **2**. To a stirred pale yellow solution of complex **1** (4–12 mmol) in diethyl ether (20–50 cm^3) at room temperature was added the appropriate organolithium (1.05 equivalents) dropwise by syringe. The product **2** precipitates as bright orange crystals from the resulting dark red solution upon either cooling in ice or upon partial removal (50–70%) of the solvent *in vacuo*. Removal of the remaining mother-liquor *via* cannula, washing with hexane (2×10 cm^3) and drying *in vacuo* gives the acylmetalates **2** as their $[Li(OEt_2)]^+$ salts. These are extremely air sensitive and repeated attempts at obtaining satisfactory elemental analyses proved unsuccessful. Complex **2a**: yield 92%; ν_{max}/cm^{-1}(CO) 1907 and 1803 (Et_2O), 1904, 1801 and 1402 (acyl) (KBr). Complex **2b**: yield 46%; ν_{max}/cm^{-1}(CO) 1908 and 1794 (Et_2O). Complex **2c** as $[Li(OEt_2)]^+$ salt: yield 87%; ν_{max}/cm^{-1}(CO) 1907 and 1805 (Et_2O), 1905, 1806 and 1398 (acyl) (KBr). Complex **2e**: yield 85%; ν_{max}/cm^{-1}(CO) 1904 and 1802 (Et_2O).

Bis(*triphenylphosphoranylidene*)*ammonium benzoyldicarbonyl*(6-exo-*methylcyclohexadienyl*)*manganate*(I), $[N(PPh_3)_2][Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(O)Ph\}]$ **2c**. To a stirred solution of the $[Li(OEt_2)]^+$ salt of complex **2c** (0.67 g, 1.7 mmol) in thf (20 cm^3) was added $[N(PPh_3)_2]Cl$ (0.95 g, 1.65 mmol). After

0.5 h the solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2 (10 cm^3). Filtration through Celite and precipitation of the product with diethyl ether gave $[N(PPh_3)_2][Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(O)Ph\}]\cdot CH_2Cl_2$ as a bright yellow crystalline solid (1.35 g, 92%); ν_{max}/cm^{-1}(CO) 1880 and 1804 (CH_2Cl_2), 1888, 1816 and 1482 (acyl) (KBr) (Found: C, 68.65; H, 5.10; N, 1.75. $C_{52}H_{44}MnNO_3P_2\cdot CH_2Cl_2$ requires C, 68.25; H, 4.95; N, 1.50%). The product is moderately stable in air (1 h), and suitable crystals for an X-ray diffraction study were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the salt.

General procedure for protonation of acyldicarbonylcyclohexadienylmanganates **2**. The acylmetalates **2** were prepared as described above. The resulting deep red diethyl ether solutions, or orange precipitates in deep red mother-liquor, were then cooled to −78 °C and *ca.* 1 equivalent of dry $HBF_4\cdot Et_2O$ was added dropwise using a syringe. Warming to room temperature over 1–2 h resulted in a gradual change in colour from deep red to clear orange. Further warming with a water-bath (35 °C for 10 min) ensured complete conversion into the product. Removal of solvent *in vacuo* and extraction with hexane until no product was detected in the extract (IR spectrum), followed by filtration through Celite and final removal of hexane *in vacuo*, gave crude complexes **3** as either an orange oil or orange crystals.

$[Mn(\eta^{3:CH}\text{-}C_6H_8Ph)(CO)_3]$ **3a**. Using the general procedures above, $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$ **1a** (1 g, 4.58 mmol) was treated with LiPh (4.8 mmol) in diethyl ether to give complex **2a**. Cooling to −78 °C and addition of 20 drops of $HBF_4\cdot Et_2O$ gave crude **3a** (1.3 g, 95%) following work-up. Analytically pure **3a** was obtained following chromatography on neutral alumina (Brockman Activity I, *ca.* 150 mesh) with hexane–diethyl ether (9:1) as eluent. Yield 1.2 g, 88%; ν_{max}/cm^{-1}(CO) 2025, 1944 and 1937 (hexane) (Found: C, 60.7; H, 4.2. $C_{15}H_{13}MnO_3$ requires C, 60.8; H, 4.4%); *m/z* 296 (M^+), 268 (M^+ − CO), 240 (M^+ − 2CO) and 212 (M^+ − 3CO).

Cyclohexenyl complexes **3b–3e**. Complexes **3b–3e** were prepared as described for **3a** using the appropriate cyclohexadienyl precursor **1a–1c** and organolithium reagent. All yields are based on **1a–1c**. Complex **3b**: yield 60%. Complex **3c**. The 1,6 isomer can be separated from the 2,6 and 3,6 species *via* chromatography on alumina eluting with hexane. Yield, all isomers (92%); ν_{max}/cm^{-1}(CO) 2022, 1942 and 1934 (hexane), 2015 and 1919 (CH_2Cl_2); *m/z* 310 (6, M^+), 282 (11, M^+ − CO), 254 (10, M^+ − 2CO), 226 (41, M^+ − 3CO) and 171 [100%, M^+ − $Mn(CO)_3$]. Complexes **3d** and **3e** were characterised as mixtures of isomers: **3d**, yield 43%; ν_{max}/cm^{-1}(CO) 2022, 1941 and 1932 (hexane); *m/z* 248 (3, M^+), 220 (30, M^+ − CO), 192 (7, M^+ − 2CO), 164 (45, M^+ − 3CO), 162 (50, M^+ − 3CO − 2H) and 109 [100%, M^+ − $Mn(CO)_3$]; **3e**, yield 54%; ν_{max}/cm^{-1}(CO) 2023 and 1941 (hexane).

$[Mn\{\eta^{3:CH}\text{-}C_6H_7(endo\text{-}Me)(endo\text{-}Ph)\}(CO)_3]$ *cis*-**3c**. The following procedure is adapted from ref. 4*c*. Potassium hydride (0.25 g, 6.23 mmol) was added to a stirred orange solution of complex **3a** (1.3 g, 4.39 mmol) in thf (40 cm^3). Evolution of gas (H_2) was observed and the solution darkened to a red colour. The deprotonation was complete after 1.5 h {IR of anion $[Mn\{\eta^4\text{-}C_6H_7(endo\text{-}Ph)\}(CO)_3]^-$, ν_{max}/cm^{-1}(CO) 1932, 1841 and 1796 (thf)}. The solution was filtered through Celite into a cold (0 °C) thf solution (10 cm^3) of methyl iodide (3 g, 21.1 mmol) and stirred for 15 min. Warming to room temperature, filtration and removal of thf *in vacuo* gave an oily residue which was extracted with hexane (2 × 20 cm^3). Filtration and removal of solvent, followed by chromatography on alumina eluting with hexane, gave *cis*-**3c** as an orange oil. Yield 1.25 g, 92%; ν_{max}/cm^{-1}(CO) 2025, 1947 and 1936 (hexane); *m/z* 310 (M^+), 282 (M^+ − CO), 254 (M^+ − 2CO) and 226 (M^+ − 3CO).

5-*Phenylcyclohexa*-1,3-*diene* **6a** *and its tcne adduct*. Diene **6a** was prepared from complex **3a** using the published decomplexation procedure:[4c] *m/z* 156.0939 (M^+) and 154.0784 (M^+ − 2H) (Calc. for $C_{10}H_{10}$: 156.0939). The tcne adduct was also prepared as described earlier.[4c]

cis-5-*Methyl*-6-*phenylcyclohexa*-1,3-*diene cis*-**6c**. This diene was prepared from complex *cis*-**3c** using the published decomplexation procedure:[4c] *m/z* 170 (M^+) and 155 (M^+ − Me).

General procedure for the decomplexation of dienes from complexes **3** *using* dppe. One equivalent of dppe was added to a solution of the appropriate complex **3** in thf at room temperature. The orange solution gradually turned red and the reaction was monitored *via* IR spectroscopy until the only observable CO-containing species was $[MnH(CO)_3(dppe)]$ **7** (10–15 min). Precipitation of **7** with hexane, filtration and concentration of the mother-liquors *in vacuo* gave the crude dienes **6** as pale yellow oils. The pure dienes were isolated following chromatography (TLC, silica) eluting with the appropriate CH_2Cl_2–hexane mixture.

Diene **6a**. Using the general procedure described above a thf solution (15 cm^3) of complex **3a** (0.35 g, 1.2 mmol) and dppe (0.47 g, 1.2 mmol) gave compound **6a** (0.15 g, 78%) as a pale yellow oil following TLC [elution CH_2Cl_2–hexane (1:9)]. Data for **6a** prepared in this manner were identical to those reported above and in ref. 14.

1-*Methyl*-6-*phenylcyclohexa*-1,3-*diene* **6c′** *and* 5-*methyl*-6-*phenylcyclohexa*-1,3-*diene trans*-**6c**. As described above a thf solution (15 cm^3) of the 1,6 isomer of complex **3c** (0.52 g, 1.7 mmol) and dppe (0.71 g, 1.8 mmol) gave compound **6c′** (0.21 g, 74%) as a pale yellow oil following TLC [elution CH_2Cl_2–hexane (1:19)]. The sample also contained a small amount of *trans*-**6c** (<15% by GC–MS). Compound **6c′**: *m/z* 170 (100, M^+), 155 (60, M^+ − Me), 141 (33, M^+ − $MeCH_2$), 129 (40, M^+ − MeCHCH), 115 (32, M^+ − $MeCHCHCH_2$), 104 (55, $PhCHCH_2$), 91 (75) and 79 (52%). Compound *trans*-**6c**: *m/z* 170 (62, M^+), 155 (100, M^+ − Me), 141 (19, M^+ − $MeCH_2$), 128 (20, M^+ − $MeCHCH_2$), 115 (23, M^+ − $MeCHCHCH_2$), 91 (50) and 77 (25%).

2-*Methyl*-6-*phenylcyclohexa*-1,3-*diene* **6c″** *and* 3-*methyl*-6-*phenylcyclohexa*-1,3-*diene*. As described above a thf solution (10 cm^3) of a 2:1 mixture of the 2,6 and 3,6 isomers of complex **3c** (0.24 g, 0.8 mmol) and dppe (0.3 g, 0.8 mmol) gave a mixture of compound **6c″** and 3-methyl-6-phenylcyclohexa-1,3-diene that could not be separated using TLC (0.11 g, 84%). The sample also contained small amounts (<5%) of other unidentified isomers of **6c** (detected using GC–MS). Compound **6c″**: *m/z* 170 (100, M^+), 155 (85, M^+ − Me), 142 (60), 141 (48), 129 (33), 128 (31), 115 (50), 102 (8), 91 (98), 79 (45) and 77 (42%). 3-Methyl-6-phenylcyclohexa-1,3-diene: $\delta_H(CDCl_3)$ 2.39 (3 H, s, Me), 4.76 (2 H, br m, H^1H^4) and 5.99 (1 H, br m, H^3); other signals could not be unambiguously assigned due to superposition of peaks due to the 2,6 isomer; *m/z* 170 (75, M^+), 155 (100, M^+ − Me), 141 (12), 128 (20), 115 (30), 102 (6), 91 (80) and 77 (26%).

6-*Phenyl*-2-*tolylcyclohexa*-1,3-*diene* **6e**. This was prepared as described above from the 2,6 isomer of complex **3e**: *m/z* 246 (100, M^+) and 155 (82%, M^+ − tolyl).

2,5-*Dimethylcyclohexa*-1,3-*diene* **6d**. Compound **6d** was prepared as described above from the 3,6 isomer of complex **3d**. The latter was not isolated but treated with tcne to give a mixture of both *endo* and *exo* adducts of **6d**. GC–MS data for **6d**: *m/z* 108 (40, M^+), 93 (100, M^+ − Me), 91 (60) and 77 (43%). Three other isomers (total <8%) of *m/z* 108 derived from **3d** were also present.

$[Mn(\eta^5\text{-}C_6H_6Me)(CO)(NO)\{C(O)Ph\}]$ **8**. The salts $[NO][BF_4]$ (0.08 g, 0.68 mmol) and $[N(PPh_3)_2][NO_2]$ (0.2 g, 0.35 mmol) were added to a stirred cold (−70 °C) solution of $[N(PPh_3)_2][Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(O)Ph\}]$ **2c** (0.55 g, 0.65 mmol) in CH_2Cl_2 (15 cm^3). After stirring for 10 min the solution was warmed to 0 °C and the solvent removed *in vacuo*. Extraction of the orange residue with hexane (30 cm^3) at 0 °C and chromatography on alumina at −20 °C eluting with CH_2Cl_2–hexane (1:3) gave complex **8** as orange microcrystals following removal of solvent at −10 °C. Complex **8** is thermally sensitive both as a solid and in solution. Yield 0.093 g, 46%. IR (CH_2Cl_2): ν_{max}/cm^{-1}(CO) 2009, ν_{max}/cm^{-1}(NO) 1741 and ν_{max}/cm^{-1}(acyl) 1607.

trans-5-*Benzoyl*-6-*methylcyclohexa*-1,3-*diene*, C_6H_6Me-[C(O)Ph] **9**. A CH_2Cl_2 solution (10 cm^3) of complex **8** (0.2 g, 0.06 mmol) was stirred overnight at room temperature. Filtration through Celite to remove black residues and chromatography (TLC, silica) eluting with CH_2Cl_2–hexane (1:3) gave compound **9** as a colourless oil, yield (0.083 g, 65%): ν_{max}/cm^{-1}(acyl) 1683; $\delta_H(CDCl_3)$ 1.07 (3 H, d, *J* 7, Me), 3.08 (1 H, br m, H^6), 3.95 (1 H, dd, *J* 12 and 3, H^5), 5.58 (1 H, dd, *J* 9.5 and 3.5, H^4), 5.76 (1 H, dd, *J* 9 and 3 Hz, H^1), 5.87 (1 H, dd, H^2), 5.97 (1 H, dd, H^3), 7.46 (2 H, dd, Ph), 7.56 (1 H, dd, Ph) and 7.96 (2 H, d, Ph); *m/z* 198.1039 (M^+) (Calc. for $C_{14}H_{14}O$: 198.1044).

6-*Benzoyl*-1-*methylcyclohexa*-1,3-*diene* **9′**. Solutions of compound **9** slowly convert into the arene 2-methylbenzophenone and **9′**. Compound **9′** was separated from the arene *via* TLC on silica: ν_{max}/cm^{-1}(acyl) 1648; $\delta_H(CDCl_3)$ 2.34 (3 H, s, Me), 2.62 (2 H, dd, *J* 9 and 4, $H^5H^{5'}$), 4.12 (1 H, t, *J* 9.5 Hz, H^6), 5.61 (1 H, m, H^4), 5.93 (2 H, m, H^2H^3) and 7.3–8.0 (5 H, m, Ph); *m/z* 198.0938 (M^+) (Calc. for $C_{14}H_{14}O$: 198.1044).

Dicarbonylcyclohexadienyl(*ethoxyphenylcarbene*)*manganese*, $[Mn(\eta^5\text{-}C_6H_7)(CO)_2\{C(OEt)Ph\}]$ **10a**. A cold (−50 °C) solution of complex **2a**, prepared as described earlier from **1a** (0.1 g, 0.46 mmol) and LiPh (0.69 mmol), in diethyl ether (15 cm^3) was treated dropwise with $[Et_3O][BF_4]$ (0.69 mmol from a 1.0 mol dm^{-3} solution in CH_2Cl_2). The red solution was stirred for 1 h and filtered through Celite. Chromatography on alumina eluting with diethyl ether–hexane (1:3) gave a red band which, following removal of solvent *in vacuo*, gave complex **10a** as a red oil. Yield from **1a**: 0.075 g, 50%; ν_{max}/cm^{-1}(CO) 1950 and 1895 (hexane).

Dicarbonyl(*methoxyphenylcarbene*)(6-exo-*methylcyclohexadienyl*)*manganese*, $[Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(OMe)Ph\}]$ **10b**. The salt $[Me_3O][BF_4]$ (0.097 g, 0.65 mmol) was added to a stirred solution of complex **2c**, prepared as described earlier from **1b** (0.1 g, 0.43 mmol) and LiPh (0.65 mmol), in N_2-saturated water (15 cm^3) with pentane (15 cm^3). The pentane layer gradually turned red and was filtered through Celite after 20 min. Chromatography on alumina eluting with diethyl ether–hexane (3:20) gave a red band which, following removal of solvent *in vacuo*, gave complex **10b** as a red oil. Yield based on **1b**: 0.077 g, 55%; ν_{max}/cm^{-1}(CO) 1952 and 1898 (hexane).

Dicarbonyl(6-exo-*methylcyclohexadienyl*)(*phenyltrimethylsiloxycarbene*)*manganese*, $[Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(OSiMe_3)Ph\}]$ **10c**. Chlorotrimethylsilane (0.087 cm^3, 0.65 mmol) was added to a solution of complex **2c**, prepared as described for **10b**, in diethyl ether (15 cm^3) at 0 °C. After stirring for 1 h, the solvent was removed *in vacuo* to give a red oily residue. Extraction with hexane, filtration through Celite and removal of the hexane gave complex **10c** as a red oil. Yield from **1b**: 0.115 g, 70%; ν_{max}/cm^{-1}(CO) 1964 and 1910 (hexane).

Crystal Structure Analysis of $[N(PPh_3)_2][Mn(\eta^5\text{-}C_6H_6Me)(CO)_2\{C(O)Ph\}]$ **2c**.—*Crystal data*. $C_{52}H_{44}MnNO_3P_2$, M = 847.8, orthorhombic, space group $P2_12_12_1$, a = 9.113(2), b = 14.491(8), c = 32.803(9) Å, U = 4332(3) $Å^3$, Z = 4, D_c = 1.30 g cm^{-3}, λ = 0.710 69 Å, μ = 3.76 cm^{-1}, $F(000)$ = 1768, T = 295 K.

A rectangular platelet of complex **2c** (0.23 × 0.45 × 0.80 mm) was mounted inside a glass capillary under nitrogen. Fifteen high-angle reflections were used to calculate the orientation matrix and best cell dimensions. On the basis of the extinct reflections the space group was uniquely determined to be $P2_12_12_1$. Data were collected on a Syntex $P2_1$ diffractometer with a graphite monochromator using Mo-Kα radiation with three check reflections (111, 006, 020) recorded in every 100 reflections (±1.0%). A total of 7025 unique reflections were measured in the θ–2θ scan mode ($3.0 < 2\theta < 60.0°$), of which 1458 had $I > 3\sigma(I)$ and were used in the refinement. After accurate measurement of three pairs of parallel crystal faces, absorption corrections were made (minimum = 1.04, maximum = 1.18). The structure was solved by heavy-atom (Patterson and Fourier difference) methods, and refined by blocked least squares. All non-H atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom and were held unrefined. Final refinement gave residual indices R = 0.064, R' = 0.070, S = 3.1. Final difference electron-density maps showed no features outside the range 0.34 to −0.40 e $Å^{-3}$. Since molecule **2c** crystallises in space group $P2_12_12_1$, a discrepancy test[18] between the two possible enantiomers was performed. The molecule as presented has the correct handedness at least to the 99.5% confidence level.

Calculations were made using local[19] and SHELX[20] programs. Complex neutral-atom scattering factors were taken from ref. 21.

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

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References

1 A. J. Pearson, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, London, 1982, vol. 8, pp. 939–1011; A. J. Pearson, in *Chemistry of the Carbon–Metal Bond*, eds. F. R. Hartley and S. Patai, Wiley, Chichester, 1987, vol. 4, ch. 10.
2 E. P. Kuendig, G. Bernardinelli, R. Liu and A. Ripa, *J. Am. Chem. Soc.*, 1991, **113**, 9676; E. P. Kuendig, M. Inage and G. Bernardinelli, *Organometallics*, 1991, **10**, 2921; E. P. Kuendig, A. F. Cunningham, jun., P. Paglia, D. P. Simmons and G. Bernardinelli, *Helv. Chim. Acta*, 1990, **73**, 386; E. P. Kuendig, *Pure Appl. Chem.*, 1985, **57**, 1855.
3 R. D. Pike, W. J. Ryan, N. S. Lennhoff, J. Van Epp and D. A. Sweigart, *J. Am. Chem. Soc.*, 1990, **112**, 4798; R. D. Pike, W. J. Ryan, G. B. Carpenter and D. A. Sweigart, *J. Am. Chem. Soc.*, 1989, **111**, 8535; Y. K. Chung, D. A. Sweigart, N. G. Connelly and J. B. Sheridan, *J. Am. Chem. Soc.*, 1985, **107**, 2388.
4 (*a*) M. Brookhart, W. Lamanna and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **104**, 2117; (*b*) W. Lamanna and M. Brookhart, *J. Am. Chem. Soc.*, 1981, **103**, 989; (*c*) M. Brookhart, W. Lamanna and A. R. Pinhas, *Organometallics*, 1983, **2**, 638; (*d*) M. Brookhart and A. Lukacs, *Organometallics*, 1983, **2**, 649; (*e*) M. Brookhart and A. Lukacs, *J. Am. Chem. Soc.*, 1984, **106**, 4161.
5 R. S. Padda, J. B. Sheridan and K. Chaffee, *J. Chem. Soc., Chem. Commun.*, 1990, 1226.
6 G. Winkhaus, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1961, 3807.
7 (*a*) P. L. Pauson and J. A. Segal, *J. Chem. Soc., Dalton Trans.*, 1975, 1677; (*b*) Y. K. Chung, P. G. Williard and D. A. Sweigart, *Organometallics*, 1982, **1**, 1053.
8 E. O. Fischer and A. Maasbol, *Chem. Ber.*, 1967, **100**, 2445.
9 P. Bladon, G. A. M. Munro, P. L. Pauson and C. A. L. Mahaffy, *J. Organomet. Chem.*, 1981, **221**, 79.
10 B. C. Roell, jun. and K. F. McDaniel, *J. Am. Chem. Soc.*, 1990, **112**, 9004.
11 S. D. Ittel, J. F. Whitney, Y. K. Chung, P. G. Williard and D. A. Sweigart, *Organometallics*, 1988, **7**, 1323; N. G. Connelly, M. J. Freeman, A. G. Orpen, A. R. Sheehan, J. B. Sheridan and D. A. Sweigart, *J. Chem. Soc., Dalton Trans.*, 1985, 1019; Y. K. Chung, E. P. Honig, W. T. Robinson, D. A. Sweigart, N. G. Connelly and S. D. Ittel, *Organometallics*, 1983, **2**, 1479.
12 W. E. Buhro, A. Wong, J. H. Merrifield, G.-Y. Lin, A. C. Constable and J. A. Gladysz, *Organometallics*, 1983, **2**, 1852.
13 G. A. M. Munro and P. L. Pauson, *J. Chem. Soc., Chem. Commun.*, 1976, 134.
14 H. J. Reich and S. Wollowitz, *J. Am. Chem. Soc.*, 1982, **104**, 7051.
15 D. J. Kuchynka, C. Amatore and J. K. Kochi, *J. Organomet. Chem.*, 1987, **328**, 133.
16 S. L. Bassner, J. B. Sheridan, C. Kelley and G. L. Geoffroy, *Organometallics*, 1989, **8**, 2121.

17 C. Wang, M. G. Lang, J. B. Sheridan and A. L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 3236.
18 W. A. Hamilton, *Acta Crystallogr.*, 1965, **18**, 502.
19 R. A. Lalancette, P. A. Vanderhoff and H. W. Thompson, *Acta Crystallogr., Sect. C*, 1990, **46**, 1682.
20 G. M. Sheldrick, SHELX 76 System of Computing Programs, Cambridge, 1976.
21 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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