Indenols, indenones and (arylcyclohexadienyl)Mn(CO)$_3$ π-complexes from the thermally promoted reactions of alkynes with *ortho*-Mn(CO)$_4$ aryl ketone, amide, ester and aldehyde derivatives

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Dedicated to colleague and mentor Professor Ken Mackay on the occasion of his 70th birthday

Abstract

Thermally promoted reactions of a range of alkynes with the orthomanganated acetophenone (η^2-2-acetylphenyl)Mn(CO)$_4$ generally give 1*H*-inden-1-ols in good yield; effects of substituents and solvent on these reactions are reported, along with the crystal structure of 1-methyl-2,3-diphenyl-1*H*-inden-1-ol. The corresponding orthomanganated benzophenone similarly gives the indenol with diphenylacetylene but by exception, orthomanganated 3-acetylthiophene with phenylacetylene reacts via triple alkyne insertion and cyclisation, shown by crystal structure determination of the π-complex product [(1,2,3,4,5-η)-2-(3-acetylthien-2-yl)-1,3,5-triphenylcyclohexadienyl]tricarbonylmanganese. Corresponding orthomanganated derivatives of *N*,*N*-dimethylbenzamide, methyl 3,4,5-trimethoxybenzoate and 4-dimethylaminobenzaldehyde all give indenones with diphenylacetylene, but with (excess) acetylene only the aldehyde gives an indenone, the amide and ester giving instead [(1,2,3,4,5-η)-6-arylcyclohexadienyl]Mn(CO)$_3$ complexes. ^{1}H NMR analysis of these complexes shows H at C6 to be on the same face of the cyclohexadienyl ring as Mn(CO)$_3$ (*endo*-6-H; *exo* 6-aryl) as expected from three successive *syn* additions of alkyne at metallated carbon followed by intramolecular *syn* addition of alkene in the final cyclisation stage.
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1. Introduction

Cyclomanganated aryl ketones were first shown to couple with alkynes at the metalated *ortho*-carbon to form 1*H*-inden-1-ols (**2**; Scheme 1) via activation at the metal center by oxidative decarbonylation with trimethylamine oxide in acetonitrile [1] or by thermal activation in benzene [2]. We expanded the latter communication in a review, reporting thermal activation to be applicable also to the formation of indenones from cyclomanganated aryl amides, esters and some aldehydes [3]. The cyclopentannulation method has been applied to preparation of ring C aromatic steroidal analogues from orthomanganated ketone derivatives of the natural product podocarpic acid [4] and to the formation of 1-indenylhydrazines through alkyne-coupling reactions of cyclomanganated *N*,*N*-diphenylhydrazones of acetophenone and benzaldehyde [5]. We now report more fully on factors influencing the outcome of the thermally promoted reactions, including

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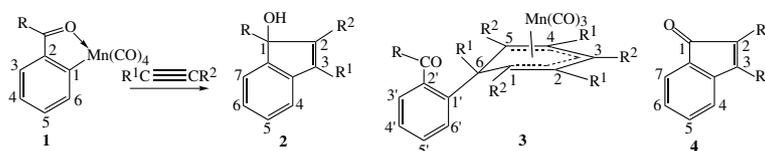
Scheme 1. Alternative products from alkyne-coupling reactions.

the competing formation in some cases of π-cyclohexa-dienyltricarbonylmanganese complexes, products of triple alkyne insertion not so far reported from the oxidative activation method, and the X-ray crystal structural determination of one such complex.

2. Results and discussion

Products and yields under a range of conditions are summarized in the Table 1. Likely routes to products, in the case of **2** as suggested earlier [1,2], are indicated in Scheme 2, which for space excludes the presumed initial coordination of alkyne to a vacant coordination site

on the metal prior to *syn*-addition (step (i)). The proposed route to cyclohexadienyl complexes **3** involves a sequence of successive *syn* additions (steps (i), (iii) (vi)) which would lead as shown to R^1 at C6 being on the same face of the cyclohexadienyl complex as the Mn moiety (*endo* position).

2.1. 1H-inden-1-ol formation

Results indicate a useful general route to indenols, which is not significantly sterically limited if the 85% yield of 1,2,3-triphenylindenol (**2j**; entry 20: Table 1) is any guide. The ready availability of substituted acetophenones, and the range of alkynes that could be used, means

Table 1
Products from alkyne-coupling reactions

Entry	Reactant	Alkyne R^1, R^2 (mol/mol reactant)	Solvent (reflux period/h)	Yield/% (Product[a])
1	**1a** (R = Me)	Ph, Ph (1.1)	C$_6$H$_6$ (8)	98 (**2a**)
2		(1.5)	Pet. sp.[b] (7)	90
3		(1.5)	MeCN (3)	78
4		(1.5)	CCl$_4$ (3)	57
5		(1.1)	MeOH (18)	51[c]
6		H, H (satd)[d]	C$_6$H$_6$ (18)	64 (**2b**)
7		Pr, Pr (1.1)	C$_6$H$_6$ (18)	51 (**2c**)
8		SiMe$_3$, SiMe$_3$ (1.1)	C$_6$H$_6$ (64)	9 (**2d**)
9		CO$_2$Me, CO$_2$Me (1.5)	C$_6$H$_6$ (4.5)	67 (**2e**)
10		(1.5)	Pet. sp.[b] (24)	54
11		(1.5)	MeCN (1)	91
12		(1.5)	CCl$_4$ (3)	87
13		H, Ph (1.1)	C$_6$H$_6$ (3)	43 (**2f**) + 3 (**3a**)[e]
14		(3.0)	C$_6$H$_6$ (3.5)	84 (**2f**) + 14 (**3a**)[e]
15		H, SiMe$_3$ (3.5)	C$_6$H$_6$ (2)	82 (**2g**)
16		Me, Pr (0.7)	C$_6$H$_6$ (22)	51[f] (ca. 2:1 **2h:2i**)[g]
17		(0.7)	MeCN (3.5)	38[f] (ca. 2:1 **2h:2i**)[g]
18		(0.7)	CCl$_4$ (7)	36[f] (ca. 2:1 **2h:2i**)[g]
19		(1.8)	Pet. sp.[b] (5)	60 (ca. 3:1 **2h:2i**)[g]
20	**1b**: R = Ph	Ph, Ph (1.1)	C$_6$H$_6$ (18)	85 (**2j**)
21	**1c**: R = NMe$_2$	Ph, Ph (1.1)	C$_6$H$_6$ (1)	56 (**4a**)
22		H, H (satd[d])	C$_6$H$_6$ (2)	55 (**3b**)
23	**1d**: R = OMe; 4,5,6-(OMe)$_3$	Ph, Ph (1.1)	C$_6$H$_6$ (1)	100 (**4b**; 4,5,6-(OMe)$_3$)
24		H, H (satd[d])	C$_6$H$_6$ (7)	36 (**3c**; 4′,5′,6′-(OMe)$_3$)
25	**1e**: R = H; 5-NMe$_2$	Ph, Ph (1.1)	C$_6$H$_6$ (9)	46 (**4c**; 5-NMe$_2$)
26		H, H (satd[d])	C$_6$H$_6$ (3.5)	20 (**4d**; 5-NMe$_2$)
27	3-Ac-2-thienyl-Mn(CO)$_4$ (**5**)	Ph, H	C$_6$H$_6$ (8)	(**6**)

[a] Product R, R$_1$, R$_2$ groups as for reactants; other substituents as indicated.
[b] Petroleum spirit; b.p. 60–80 °C.
[c] Demetallated reactant (acetophenone) also formed (22%).
[d] Acetylene-saturated reaction solution by continuous bubbling of acetylene gas.
[e] Indefinite structural assignment; see discussion section π-*Cyclohexadienyl complexes.*
[f] Based on alkyne as limiting reagent.
[g] **2h** (R, R$_1$ = Me, R$_2$ = Pr) and **2i** (R, R$_2$ = Me, R$_1$ = Pr) are chromatographically inseparable; ratio by ^{1}H NMR.
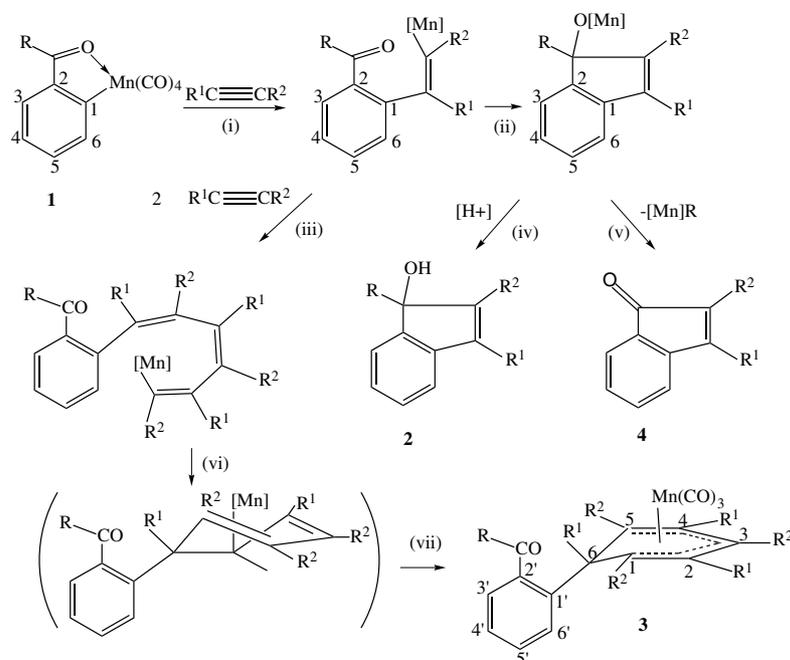
Scheme 2. Routes to alternative products. Metal ligands are omitted at intermediate stages: symbol [Mn].

that this reaction can generate specifically substituted 1-methylinden-1-ols, from which, for example, benzoful-venes can easily be obtained by elimination of water under acidic conditions. There is current interest in potential applications of a novel thermoreversible solid-state non-radical polymerisation of a benzofulvene [6].

Other factors for consideration from the current study are as follows.

2.1.1. Solvent

These thermally promoted reactions proceed in good or reasonable yield in most solvents studied (products **2a**, **2e**, **2h/i**: entries 1–5, 9–12, 16–19) though protic solvents may promote unwanted demetallation of the parent manganated ketone (**2a**; entry 5 for MeOH). Reactions proceeded fastest in acetonitrile where tested (products **2a**, **2e**, **2h/i**; entries 3, 11 and 17) but not to an extent that this would normally be an issue in synthesis; if this is a polarity effect it is not a strong one as, where determined, rates in CCl$_4$ (c.f entries 3,4; 11,12; 17,18) and petroleum spirit (17 and 19) are not a lot slower.

In the case of 2-hexyne, which is unsymmetrical but with similarly sized groups on the triple bond, there is no marked solvent effect on regioselectivity (**2h**:**2i**: entries 16–19).

2.1.2. Alkyne substituent groups

The smaller alkyne substituent is attached either exclusively (H in a number of cases) or preferentially (Me vs. *n*-Pr in the **2h/i** case; entries 16–19) at the 3-position in the indenol next to what was the metalated aryl

carbon in the parent ketone, possibly reflecting a steric bias in the orientation of alkyne coordination to metal (not shown Scheme 2) prior to insertion. Similar regio-specificity was observed for mono-substituted acetylenes when the coordination site is freed by CO oxidation with trimethylamine oxide rather than thermally [1], except in the case of 1-hexyne (12% of the 3-butylindenol isomer), though alkynes of the form RC$_2$CO$_2$Et inserted with the ester group adjacent to the aromatic ring, irrespective of the size of the other acetylene substituent (R = Me, Et, cyclohexyl), suggesting a possible electronic effect.

2.1.3. Triple-insertion-cyclisation sequences

Formation of [(1,2,3,4,5-η)-6-arylcyclohexadienyl]-Mn(CO)$_3$ products (**3**; see Scheme 2) is the only detected reaction for acetylene in some cases (entries 22 and 24) but is not observed at all in others (entries 6 or 26). Triple insertion competes weakly with indenol formation for phenylacetylene (entries 13 and 14) and is not observed at all for disubstituted acetylenes. Steric limitation on successive insertion (steps iii; Scheme 1) or cyclisation (step vi) may be responsible for the latter. There is further discussion in the section *Cyclohexadie-nyl complexes* below.

2.2. Indenone formation

This has been tested for in the current exploratory study only with diphenylacetylene but formation of inde-nones (**4a**, **4b** and **4c**) with the orthomanganated second-ary amide (**1c**), ester (**1d**), and aldehyde (**1e**; entries 21, 23, 25 and 26) indicates useful general routes to

indenones. The reaction presumably occurs from the initial mono-insertion product either stepwise through the carbonyl addition intermediate as shown in Scheme 2 (steps [ii] and [v]), or directly, the carbonyl substituent (amide, alkoxide or hydride) being eliminated with Mn. No solvent or substituent effects have been studied. For acetylene itself in excess (saturation), the orthomanganated aldehyde (1e) gives indenone, though in poor yield (entry 26), and none of the indenol expected by analogy with the ketone (1a; entry 6), while the ester and amide substrates (1c and 1d) give cyclohexadienyl complexes (entries 22 and 24), not indenones. This raises the question of whether the addition step to form the indenone precursor (step [ii], Scheme 2) is slowed in the case of amide or ester carbonyl relative to the more electrophilic aldehyde (or ketone) carbonyl group, limiting competition with successive insertion (steps [iii]). However continuous replenishment of acetylene to saturation level may also work in favour of multiple insertion.

Since the initial reports [1,2] of indenol and indenone formation from alkynes and o-manganated aryl ketones, the first analogous reaction reported for another ortho-metalated arylcarbonyl system was that for orthopalladiated acetophenone and benzaldehyde derivatives, which included the formation of indenone 4b [7]. Later an analogous catalytic (palladium acetate) route to 1H-inden-1-ols (including 2a and 2c) directly from alkyne and o-bromoacetophenone was reported [8] for conditions very similar to those reported much earlier [9] for Pd(OAc)$_2$-catalysed indenone synthesis from ortho-iodobenzaldehyde and diaryl ketones. More recently, high-yield cobalt-catalysed formation of 1H-inden-1-ols (including 2a and 2c) has been reported [10] for alkynes with o-iodoacetophenone using Co(Ph$_2$PCH$_2$CH$_2$PPh$_2$)I$_2$ and zinc in acetonitrile at 80 °C; unsymmetrical alkynes gave similar regiochemistry patterns to those reported here.

Murai's closely related Ru-catalysed alkyne coupling ortho to arylketone groups [11], which could provide a better catalysed pathway to indenols by a similar sequence of steps to those for the formation of 2 in Scheme 2, gives instead routine alkenylation without cyclisation, though, as a single exception, 1-methyl-3-phenyl-2-trimethylsilyl-1H-benz[e]inden-1-ol was reported as a byproduct from the reaction of 1-acetylnaphthalene and 1-phenyl-2-trimethylsilylacetylene in the presence of RuH$_2$(CO)(PPh$_3$)$_3$ as catalyst [12].

2.3. Cyclohexadienyl complexes

A (cyclohexadienyl)Mn(CO)$_3$ complex was first detected as a very minor product (3%) for the reaction of 1a with phenyacetylene in a 1.1 molar excess (entry 13; Table 1). Raising the alkyne excess to 3 molar provided sufficient product (14%; entry 14) for NMR spectroscopy, but multiple signals indicated the presence of other isomers or decomposition, and further attempts at purification were unsuccessful. The primary product is suggested to be 3a (3; R^1 = H; R^2 = Ph), assuming successive syn additions of coordinated alkyne (steps [i] and [iii]; Scheme 2) and alkene (step [vi]). Diagnostic NMR assignments became possible when cyclohexadienyl complexes were obtained in quantity as the only products: 3b obtained pure from acetylene and the o-manganated benzamide (entry 22), and 3c from the benzoate ester complex (entry 24). Their NMR data may be compared with those of complexes such as 8a,b (obtained from nucleophilic carbonyl addition by (4-substituted-phenyl)MgBr to the oxo group of [(1,2,3,4,5-η)-6-oxocyclohexadienyl]-Mn(CO)$_3$, followed by oxyanion acetylation with acetic anhydride [13]) and [(1,2,3,4,5-η)-6-phenylcyclohexadienyl]Mn(CO)$_3$ complexes such as 9a which were obtained using Stille and related Pd-promoted synthetic methodology on [(1,2,3,4,5-η)-1-chlorocyclohexadienyl]-Mn(CO)$_3$ complexes [14].

According to the implicit syn-syn-syn-syn-addition sequence of formation of cyclohexadienyl complex (3; Scheme 2), the C–H bond at C6 (C-R^1 in Scheme 2) should be in the same direction on the face of the π-complex as the Mn(CO)$_3$ moiety (endo-H orientation). To confirm this stereochemistry for 3b (entry 22) and 3c (entry 24), the chemical shifts for H6 (3.91 and 4.41 ppm) and coupling constants (with H5: J = 5.9 and 5.4 Hz) can be considered. They are consistent with signals of the endo-H in complexes 8a (4.54 ppm; J = 6.6 Hz) and 8b (4.40 ppm; J = 6.2 Hz) and other acetoxy-substituted complexes [13], as well as of the endo-H in 9a (4.47; J = 6 Hz) [14b]. However, for definitive assignment of H6 as endo, data for 6-unsubstituted cyclohexadienyl complexes (e.g. 9b [13b]) need to be considered. Chemical shift does not allow a definite distinction between endo vs. exo H as although the latter are often at least 0.5 ppm higher field (e.g. 3.19 for endo-H vs. 2.48 for exo-H in 9b) this is not always so [14b]. However, the coupling constant of endo-H6 to H5 is routinely about 5–6 Hz (6 Hz in the case of 9b) while that for exo-H6 to H5 is not reported so is presumably quite small: the signal for the exo-H is reported as a simple doublet (geminal coupling to endo-H of about 15 Hz). A much less favourable torsion angle for coupling of exo-H6 to H5 than applies for endo-H6 is borne out by the solid state structure of the related cyclohexadienyl complex 6 (see below). In 6, the substituent bond at C5 is C–Ph rather than C–H, but for an indicative torsion angle between this bond and the C6-exo-H and C6-endo-H bonds in these complexes generally, it is an adequate model. As noted in the caption to its crystal structure diagram (Fig. 2; note the different atom numbering scheme), the torsion angle between C(5)–Ph and the exo C–H is 87.5°, while for the endo C–H it is 33.1°.

The first is close to 90° and so correlates well according to the Karplus equation with the coupling constant of near-zero between H5 and exo-H6 as inferred in the above discussion on **9b**. The second (33°) is likewise consistent with a coupling constant of 5–6 Hz. Torsion angles of C6-H and C5-H will of course vary with substituent on C5 or C6 but the crystal structure data when linked to the concordant coupling constants across the compounds **3b**, **3c**, **8a**, **8b**, **9a** and **9b** provides strong support for the assignment of the single H6 in **3b** and **3c** as *endo* rather than *exo* and thereby for the successive *syn* addition sequence proposed in Scheme 2.
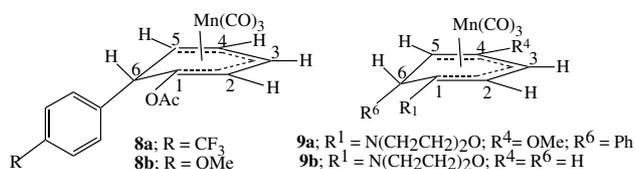
Only cyclohexadienyl product was obtained from the reaction of phenylacetylene with orthomanganated 3-acetylthiophene (**5**; entry 27), possibly because cyclisation to form the indenol equivalent (cf. step [ii] in Scheme 2) may be limited by the requirement to fuse two five-membered rings; this may also be the reason that diphenylacetylene unexpectedly gave an intractable product and no indenol with **5** (not shown in Table 1). However, the crude product from phenylacetylene showed complex line-broadened NMR spectra indicating decomposition. A crystalline product was fortuitously obtained after two successive silica plate chromatograms, followed by crystallization from hexane. The compound was unstable when dissolved in chloroform and NMR data could not be obtained for line broadening effects. However, the compound was pure in the crystalline state and its X-ray crystal structure was determined as the complex **6**. Most likely, **7** is initially formed, as for **3** in Scheme 2, but undergoes prototropic rearrangement to **6** while the reaction solution is still under reflux or with heat on solvent removal: isomerisation through thermally promoted Mn-mediated *endo*-H migration in similar (cyclohexadienyl)Mn(CO)$_3$ complexes has been reported by Pauson [15] and this supports the *endo*-6H isomer **7**, stereochemically analogous to **3a** and **3b**, as the likely primary cyclisation product and precursor of isolated **6**. Although **6** may be considered to be more stable than **7** on the grounds that all four aryl groups are conjugated to the delocalised π-system of the cyclohexadienyl ring, the solid state structure of **6** (see below) shows that all the aryl rings are at large dihedral angles to the planar η^5-coordinated part of the cyclohexadienyl ring so that the level of stabilization by increased conjugation in solution is questionable.
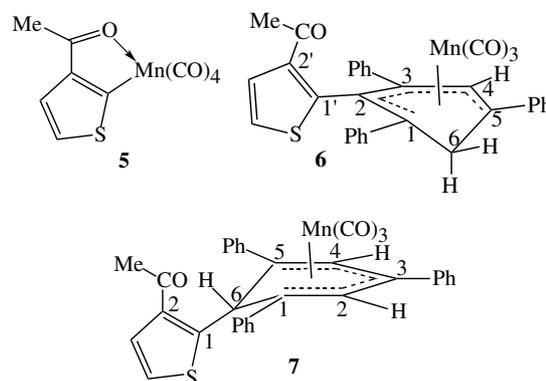
2.4. X-ray crystallography

2.4.1. Structure of 1-methyl-2,3-diphenyl-1H-inden-1-ol (2a; Fig. 1)

Molecules of **2a** pack in the crystal as tetrameric aggregates, linked by a slightly puckered square arrangement of four ···O–H···O hydrogen bonds about the crystallographic 4$_2$ axis. The indene skeleton is planar, with the two peripheral phenyl rings twisted from this plane to form dihedral angles of 53° in each case (Fig. 1). This precludes extended delocalisation so the C–C bonds fall into normal ranges, with C(2)–C(3) an unperturbed double bond (1.347(4) Å). The C(1)–O(1) bond [1.453(4) Å] is longer than usual (range 1.388–1.454 Å, average 1.427 Å, for the 25 related examples in the CCDC database) and the C(10)–C(1)–O(1) angle is small [105.9(3)°] compared with the database range of 106–109° [16], presumably to accommodate the hydrogen bonding.

There are only three previous examples of structurally characterised 1H-inden-1-ol derivatives:
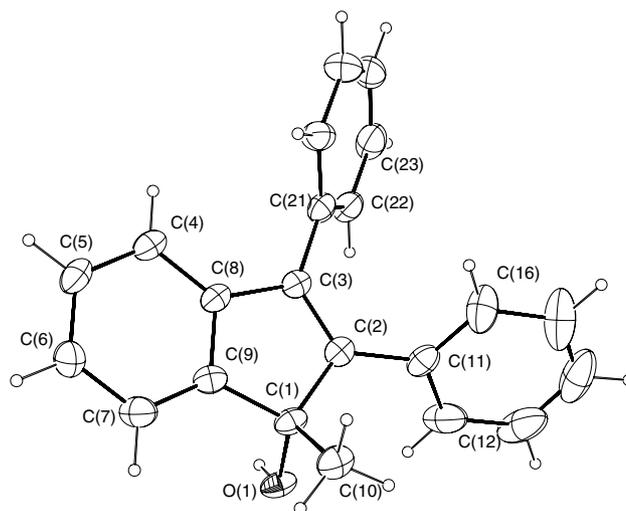
Fig. 1. Molecular structure of 1-methyl-2,3-diphenyl-1H-inden-1-ol (**2a**). Selected bond lengths (Å): C(1)–O(1) 1.453(4), C(1)–C(10) 1.530(4), C(1)–C(2) 1.548(4), C(2)–C(3) 1.347(4), C(3)–C(8) 1.488(4).

1-phenyl-2-p-tosyl [17], 1-methyl-2-carboethoxy-3-p-tolyl [18], and the benzoindenol 1-methyl-3-phenyl-2-trimethylsilyl-1H-benz[e]inden-1-ol [12].

2.4.2. Structure of [(1,2,3,4,5-η)-2-(3-acetylthien-2-yl)-1,3,5-triphenylcyclohexadienyl]tricarbonylmanganese (6; Fig. 2)

The structure determination of **6** showed all four aryl groups to be bonded to unsaturated carbons in the η^5-coordinated cyclohexadienyl ring. The phenyl rings attached to C(2), C(4) and C(6) (Fig. 2 numbering) are orientated at dihedral angles to the η^5-ring of 61°, 40° and 66°, respectively, and for the thiophene ring at C(1) the angle is 70°. The five metal-coordinated cyclohexadienyl carbon atoms, C(1)–C(4) and C(6) (Fig. 2 numbering), are coplanar to within ±0.03 Å, with the manganese atom 1.709 Å from this plane and individual Mn–C distances in the range 2.136–2.289 Å. These are towards the longer end of the range observed for other η^5-cyclohexadienyl manganese molecules for which structures are available, presumably reflecting the crowded nature of the ring in **6**. The methylene carbon, C(5), is tilted out of the ring and does not interact at all with the manganese, as expected.

3. Experimental

3.1. General

Petroleum spirit (b.p. 60–80 °C) and all other solvents in preparative and chromatographic work were

of analytical grade. Other commercial reagents were used without purification. Dimethyl acetylenedicarboxylate is abbreviated as DMAD in the text. P.l.c. refers to preparative layer chromatography on silica (Merck Kieselgel 60PF$_{254}$: $200 \times 200 \times 2$ mm) and t.l.c. to thin layer chromatography on foil-backed silica (Merck Kieselgel 60PF$_{254}$). Infrared spectra (chloroform solvent) were recorded on a Digilab FTS-45 FTIR instrument and NMR spectra (CDCl$_3$) on a Bruker AC300 instrument. Number labels used on structures for assigning NMR signals of H or C atoms are not necessarily associated with systematic numbering, nor are those in the X-ray crystal structure diagrams.

Benzylpentacarbonylmanganese was prepared by the standard method of Closson et al. [19]. It had m.p. 36–37 °C (lit. 37.5–38.5 °C [19]); IR (CHCl$_3$): ν(CO) 2108 (m), 2012 (vs, br), 1993 (s) cm^{-1}.

3.2. Preparation of orthomanganated complexes

Orthomanganated acetophenone (**1a**) was synthesized by the standard method previously reported [20] as were the corresponding complexes of benzophenone (**1b**) [21], N,N-dimethylbenzamide (**1c**) [22] and 4-dimethylaminobenzaldehyde (**1e**) [22]. The same method with minor variations was applied as follows to the synthesis of η^2-(2-methoxycarbonyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**1d**).

Methyl 3,4,5-trimethoxybenzoate (0.162 g, 0.717 mmol) and benzylpentacarbonylmanganese (0.246 g, 0.860 mmol) were dissolved in freshly distilled heptane
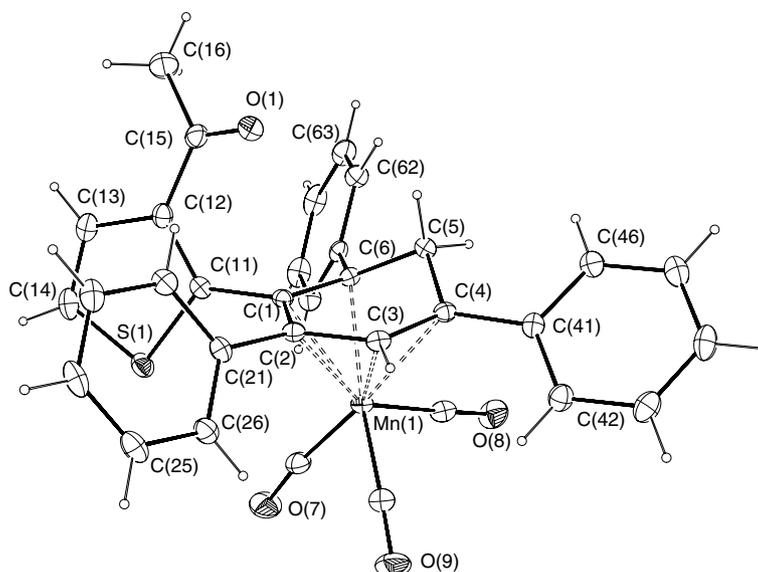
Fig. 2. Molecular structure of [(1,2,3,4,5-η)-2-(3-acetylthien-2-yl)-1,3,5-triphenylcyclohexadienyl]tricarbonylmanganese (**6**). Selected bond lengths (Å): Mn(1)–C(1) 2.191(2), Mn(1)–C(2) 2.154(2), Mn–C(3) 2.136(2), Mn(1)–C(4) 2.289(2), Mn(1)–C(6) 2.239(2), C(1)–C(2) 1.434(3), C(1)–C(6) 1.415(3), C(2)–C(3) 1.425(3), C(3)–C(4) 1.403(3), C(4)–C(5) 1.515(3), C(5)–C(6) 1.518(3). Selected torsion angles: C(41)–C(4)–C(5)–H(5-*exo*)-87.5°; C(41)–C(4)–C(5)–H(5-*endo*) 33.1°.

(30 mL) and the solution degassed and flushed with nitrogen several times. After refluxing under nitrogen for 2 h, heptane was removed under vacuum, and the yellow solid dissolved in dichloromethane (5 mL). Deactivated neutral alumina (3 g, activity IV) was added and the mixture shaken vigorously while the solvent was evaporated under vacuum. The absorbed product was transferred onto a column of neutral alumina (2 × 15 cm; activity IV). Elution with hexane removed a trace of unreacted benzylpentacarbonyl-manganese and as the polarity of the eluent was gradually increased with dichloromethane, a bright yellow fraction was collected. It yielded η^2-(2-methoxycarbonyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**1d**; 0.247 g, 73%). M.p. 121–125 °C. IR v(CO) (CH$_2$Cl$_2$) 2082 (m), 1991 (vs, br), 1940 (s). ^{1}H NMR: δ 7.16 (s, 1H, s, H 3), 4.01 (s, 3H), 3.95 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C NMR: (CDCl$_3$) δ 220.5 (s, br), 213.8 (s, br), 211.7 (s), 179.6 (s), 166.3 (s), 160.5 (s), 151.6 (s), 148.5 (s), 128.2 (s), 109.1 (d), 60.7 (q), 60.0 (q), 56.1 (q), 54.2 (q). MS: m/e 392 (10.7), 308 (19.0), 280 (100.0), 250 (47.1), 223 (30.6), 195 (8.3), 192 (8.3), 162 (6.2), 140 (11.8), 55 (12.5).

3.3. General procedure for thermally promoted coupling reactions of alkynes with orthomanganated compounds

The orthomanganated compound (ca. 100 mg) and alkyne (1.1–1.5 mol equivalent) were dissolved in solvent (20 mL; analytical grade), and the solution was degassed and flushed with nitrogen several times. The mixture was heated under reflux under nitrogen, the extent of reaction being monitored by thin layer chromatography and/or IR spectroscopy. At completion, solvent was removed under vacuum and the residue subjected to p.l.c. on a silica-layered plate (200 × 200 × 2 mm) or a rotating silica plate by use of a Chromatotron, with ethyl acetate/petroleum spirit or dichloromethane/petroleum spirit as eluent.

In the cases of reactions with acetylene the same procedure was used except that acetylene was continuously replenished by bubbling it through the reaction solution for the duration of the reaction. The concentration of acetylene at saturation is unknown as the only literature data on acetylene solubility we can trace is at equilibration with 1 atmosphere acetylene gas at 4 °C [23] at which temperature benzene dissolves about 0.55 mmol/mL of acetylene, and cyclohexane (the best available hydrocarbon match for petroleum spirit in the reported study) about 0.35 mmol/mL acetylene. In relation to the amount of manganated complex used here (<0.05 mmol/mL solvent) these concentrations represent large excesses of acetylene, but the solubility of acetylene will be significantly lower at the b.p. of benzene or petroleum spirit and also at less than 1 atmosphere (nitrogen was

also passed through the reaction solution for air exclusion).

3.4. Reactions of η^2-(2-acetylphenyl)tetracarbonyl-manganese (1a)

3.4.1. With diphenylacetylene to form 1-methyl-2,3-diphenylinden-1-ol (2a)

Following the procedure above, **1a** (0.104 g, 0.364 mmol) and diphenylacetylene (0.067 g, 0.376 mmol) under reflux in benzene for 8 h followed by p.l.c. (2:3 dichloromethane/petroleum spirit) gave Mn$_2$(CO)$_{10}$ (0.026 g) and 1-methyl-2,3-diphenylinden-1-ol (**2a**; 0.107 g, 98%], which crystallised from CH$_2$Cl$_2$/petroleum spirit as white crystals, m.p. 145–146 °C (lit. [1] 143 °C).

Corresponding yields of **2a** in other solvents for the reflux period stated (1.5 mol excess of PhC$_2$Ph): petroleum spirit (7 h) 90%; MeCN (3 h) 78%; CCl$_4$ (3 h) 57%; MeOH (18 h) 51% (plus 22% acetophenone).

3.4.2. With acetylene to form 1-methylinden-1-ol (2b)

1a (0.103 g, 0.360 mmol) and acetylene (continuous saturation) under reflux in benzene over 18 h gave Mn$_2$(CO)$_{10}$ (0.010 g, 18%) and **2b** (0.034 g, 64%) as thin white needles, m.p. 93–96 °C (lit. [24] 96–98 °C). Anal. Calc. for C$_{10}$H$_{10}$O: C, 82.16; H, 6.89. Found: C, 81.44; H, 7.10%. MS (m/z): 146 (M$^+$). ^{1}H NMR: δ 7.41 (m, 4H, H4-7), 6.65 (d, J = 5.6 Hz, 1H, H2), 6.32 (d, J = 5.6 Hz, 1H, H3), 2.10 (br s, 1H, OH), 1.61 (s, 3H, CH$_3$). ^{13}C NMR: δ 149.4 (C7a), 143.0 (C2), 141.2 (C3a), 130.1(C3), 128.4, 126.4 (C6,7), 121.6, 121.5 (C4,5), 82.3 (C1), 23.7 (CH$_3$). The only previous preparation of **1a** that we are aware of involved the reaction of 1-methylinden-1-yllithium with oxygen [24].

3.4.3. With 4-octyne to form 1-methyl-2,3-dipropylinden-1-ol (2c)

1a (0.111 g, 0.388 mmol) and 4-octyne (60 μL, 0.409 mmol) under reflux in benzene over 18 h gave Mn$_2$(CO)$_{10}$ (0.009 g, 15%) and **2c** (0.046 g, 51%) as colourless square plates, m.p. 79.5–81 °C (lit. [11,12]: no m.p. reported). Anal. Calc. for C$_{16}$H$_{22}$O: C, 83.43; H, 9.63. Found: C, 83.31; H, 9.61%. MS (m/z): 230 (M$^+$). ^{1}H NMR: δ 7.18 (m, 4H, H4-7), 2.42 (t, J = 6.4 Hz, 2H, H1′ or 1″), 2.33 (t, J = 7.3 Hz, 2H, H1′ or 1″), 1.58 (m, 4H, H2′, 2″), 1.54 (s, 3H, 1-CH$_3$), 1.00 (t, J = 7.3 Hz, 3H, 3′ or 3″-CH$_3$), 0.98 (t, J = 7.3 Hz, 3H, 3′ or 3″-CH$_3$). ^{13}C NMR: δ 149.6 (C7a), 148.0 (C2), 143.0 (C3a), 136.5 (C3), 128.0, 125.1 (C6,7), 121.2, 118.8 (C4,5), 82.5 (C1), 27.4, 27.2 (C1′,1″), 23.6 (1-CH$_3$), 22.8, 21.7 (C2′,2″), 14.7, 14.3 (C3′,3″).

3.4.4. With bis(trimethylsilyl)acetylene to form 1-methyl-2,3-bis(trimethylsilyl)inden-1-ol (2d)

1a (0.108 g, 0.378 mmol) and bis(trimethylsilyl)acetylene (0.068 g, 0.399 mmol) under reflux in benzene over 64 h gave $Mn_2(CO)_{10}$ and some unreacted **1a** as an inseparable mixture (0.030 g) and 1-methyl-2,3-bis(trimethylsilyl)inden-1-ol (**2d**; 0.008 g, 9%) as white granules, m.p. 125–128 °C, identified by spectra only: MS (m/z): 290 (M^+). ^1H NMR: δ 7.35 (m, 4H, H4-7), 2.61 (s, 1H, OH), 1.60 (s, 3H, 1-CH$_3$), 0.41 (s, 9H, Si–CH$_3$), 0.38 (s, 9H, Si–CH$_3$).

3.4.5. With dimethyl acetylenedicarboxylate to form dimethyl 1-hydroxy-1-methylindene-2,3-dicarboxylate (2e)

1a (0.105 g, 0.368 mmol) and dimethyl acetylenedicarboxylate (DMAD) (0.097 g, 0.684 mmol) under reflux in benzene for 4.5 h gave after p.l.c. (1:3 ethyl acetate/petroleum spirit) dimethyl 1-hydroxy-1-methylindene-2,3-dicarboxylate (**2e**; 64 mg, 67%) as a colourless oil, identified by spectra only. HRMS: Anal. Calc. for $C_{14}H_{14}O_5$: M, 262.0841. Found: M^+, 262.0840. ^1H NMR: δ 7.48–7.26 (m, 4H, Ar–H), 3.92 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$), 3.92 (s, br, 1H, 1-OH), 1.69 (s, 3H, 1-CH$_3$). ^{13}C NMR: δ 165.0 (s, C=O), 164.9 (s, C=O), 149.3 (s), 141.4 (s), 140.3 (s), 136.3 (s), 129.6 (d), 129.1 (d), 123.1 (d), 122.6 (d), 82.0 (s, C-1), 52.5 (q, OCH$_3$), 52.2 (q, OCH$_3$), 24.8 (q, 1-CH$_3$).

Yields in other solvents for the reflux period stated (1.5 mol excess of DMAD): petroleum spirit (24 h) 54% **2e** and 11% unreacted **1a**; MeCN (1 h) 91% **2e**; CCl$_4$ (3 h) 87% **2e**.

3.4.6. With phenylacetylene to form 1-methyl-2-phenylinden-1-ol (2f) and cyclohexadienyl complex 3a

1a (0.090 g, 0.315 mmol) and phenylacetylene (0.104 mL, 0.947 mmol) under reflux in benzene over 3.5 h gave 1-methyl-2-phenylinden-1-ol (**2f**; 0.059 g, 84%) as a white solid, m.p. 123–125 °C (lit. [1] 123–125 °C). Anal. Calc. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.49; H, 6.24%. MS (m/z): 222 (M^+). A separate fraction yielded a yellow brown oil (0.027 g) tentatively identified as a cyclohexadienyltricarbonylmanganese complex by IR (2015(s), 1939 (br, s) cm^{-1}) and by MS (m/z 564; c.f M^+ for **3a**). NMR gave multiple signals indicative of **3a** and isomerisation or decomposition product (c.f preparation of **6** in section (f) below) and no attempts to further purify this minor product were successful.

3.4.7. With (trimethylsilyl)acetylene to form 1-methyl-2-(trimethylsilyl)inden-1-ol (2g)

1a (0.110 g, 0.386 mmol) and (trimethylsilyl)acetylene (200 µL, 1.415 mmol) under reflux in benzene over 2 h gave 1-methyl-2-(trimethylsilyl)inden-1-ol (**2g**; 0.069 g,

82%) as colourless square plates, m.p. 104.5–105 °C (1it. [1] 103–105 °C). Anal. Calc. for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.50; H, 8.44%. MS (m/z): 218 (M^+). ^1H NMR: δ 7.08 (m, 4H, H4-7), 6.71 (s, 1H, H3), 1.47 (s, 3H, 1-CH$_3$), 0.17 (s, 9H, Si–CH$_3$). ^{13}C NMR: δ 157.2 (C2), 152.9 (C7a), 141.6 (C3a), 139.9 (C3), 128.3, 126.4 (C6,7), 121.6, 121.1(C4,5), 86.9 (C1), 25.0 (1-CH$_3$), −0.44 (Si–CH$_3$).

3.4.8. With 2-hexyne to form 1,3-dimethyl-2-propylinden-1-ol (2h) and 1,2-dimethyl-3-propylinden-1-ol (2i)

1a (111 mg, 0.387 mmol] and 2-hexyne (0.031 mL, 0.276 mmol) under reflux in benzene for 22 h gave after p.l.c. (1:1 CH$_2$Cl$_2$/petroleum spirit) an inseparable mixture of 1,3-dimethyl-2-propylinden-1-ol (**2h**) and 1,2-dimethyl-3-propylinden-1-ol (**2i**) as a white solid (28 mg; 51%). Integration of the proton methyl singlets showed the ratio **2h**:**2i** to be approximately 2:1. Assignments were made by nOe of aryl 4-H (δ 7.10) by irradiation of 3-CH$_3$ (δ 1.88) in **2h** and of 1-CH$_3$ (δ 1.47) by irradiation of 2-CH$_3$ (δ 1.89) in **2i**.

2h: ^1H NMR: δ 7.37 (d, 1H, J = 7.6 Hz, Ar–H), 7.26 (m, 1H, Ar–H), 7.14 (m, 2H, Ar–H), 2.34 (m, 2H, CH$_2$CH$_2$CH$_3$), 1.98 (s, 3H, 3-CH$_3$), 1.59 (m, 2H, CH$_2$CH$_2$CH$_3$), 1.51 (s, 3H, 1-CH$_3$), 1.00 (t, 3H, J = 7.4 Hz, CH$_2$CH$_2$CH$_3$). ^{13}C NMR: δ 149.2 (s), 147.8 (s), 143.8 (s), 132.3 (s), 128.3 (d, Ar-C), 125.4 (d, Ar-C), 121.1 (d, Ar-C), 118.4 (d, ArC), 82.6 (s, C-1), 27.0 (t, 2-CH$_2$CH$_2$CH$_3$), 23.4 (q, 1-CH$_3$), 22.8 (t, 2 CH$_2$CH$_2$CH$_3$), 14.7 (q, 2-CH$_2$CH$_2$CH$_3$), 10.4 (q, 3-CH$_3$). GCMS: m/z 202 (M^+).

2i: ^1H NMR: δ 7.40 (d, 1H, J = 7.5 Hz, Ar–H), 7.25 (m, 1H, Ar–H), 7.14 (m, 2H, Ar–H), 2.34 (m, 2H, 3-CH$_2$CH$_2$CH$_3$), 1.89 (s, 3H, 2-CH$_3$), 1.59 (m, 2H, CH$_2$CH$_2$CH$_3$), 1.47 (s, 3H, 1-CH$_3$), 0.94 (t, 3H, J = 7.4 Hz, 3-CH$_2$CH$_2$CH$_3$). ^{13}C NMR: δ 149.5 (s), 144.4 (s), 143.2 (s), 135.3 (s), 128.2 (d, Ar-C), 125.1 (d, Ar-C), 121.4 (d, Ar-C), 118.7 (d, Ar-C), 81.9 (s, C1), 27.0 (t, CH$_2$CH$_2$CH$_3$), 23.1 (q, 1-CH$_3$), 21.6 (t, 3-CH$_2$CH$_2$CH$_3$), 14.1 (q, 3-CH$_2$CH$_2$CH$_3$), 9.0 (q, 2-CH$_3$). GC–MS: m/z 202 (M^+).

Yields in other solvents for the reflux period stated (1.3 mol excess of **1a** over 2-hexyne as above): MeCN (3.5 h) 38%; CCl$_4$ (7 h) 36% (ca. 2:1 ratio **2h**:**2i** as in benzene for both solvents). In petroleum spirit (using 1.7 molar excess of 2-hexyne over **1a**) (5 h) 60%; with ca. 3:1 ratio **2h**:**2i**.

3.5. Reaction of η^2-(2-benzoylphenyl)tetracarbonylmanganese (1b) with diphenylacetylene to form 1,2,3-triphenylinden-1-ol (2j)

1b (0.122 g, 0.350 mmol) and diphenylacetylene (0.065 g, 0.365 mmol) in benzene under reflux over

18 h gave Mn$_2$(CO)$_{10}$ (0.010 g, 18%) and **2j** (0.107 g, 85%) as a colourless oil, pure by NMR, identified by NMR only [8]. ^{1}H NMR: δ 7.90 (m, 19H). ^{13}C NMR: δ 150.9 (C7a), 147.6 (C2), 142.7 (C3a), 141.7 (C1′), 140.5 (C3), 134.8 (C1″), 133.9 (C1‴), 129.5, 129.2, 128.7, 128.4, 127.8, 127.2, 127.0 (C2′–6′,2″–6″,2‴–6‴), 125.1 (C6,7), 123.2, 121.0 (C4,5), 87.0 (C1).

3.6. Reactions of η^2-(2-N,N-dimethylamidophenyl) tetracarbonylmanganese (1c)

3.6.1. With diphenylacetylene to form 2,3-diphenylindenone (4a)

1c (0.108 g, 0.343 mmol) and diphenylacetylene (0.062 g, 0.348 mmol) under reflux in benzene over 1 h gave Mn$_2$(CO)$_{10}$ (0.012 g, 22%) and **4a** (0.054 g, 56%) as red needles, m.p. 152–156 °C (lit. 152–153 °C [25]. Anal. Calc. for C$_{21}$H$_{14}$O: C, 89.33; H, 5.00. Found: C, 89.61; H, 5.01%. MS (*m/z*) 282 (M$^+$).

3.6.2. With acetylene to form [(1,2,3,4,5-η)-6-(2-dimethylamidophenyl)cyclohexadienyl]tricarbonyl-manganese (3b)

1c (0.110 g, 0.349 mmol) and acetylene (continuous saturation) under reflux in benzene over 2 h gave the *endo*-6H isomer of **3b** (0.070 g, 55%), as yellow needles, m.p. 61–65 °C (dec.). Anal. Calc. for C$_{18}$H$_{16}$MnNO$_4$: C, 59.19; H, 4.42; N, 3.83. Found: C, 58.90; H, 4.36; N, 3.80%. MS (*m/z*): 309 (M$^+$ – 2CO). IR: 2017(s), 1930(s), 1640(m) cm^{-1}. ^{1}H NMR: δ 7.27 (td, *J* = 7.6 and 1.4 Hz, 1H, H4′ or 5′), 7.18 (td, *J* = 7.5 and 1.3 Hz, 1H, H4′ or 5′), 7.08 (dd, *J* = 7.8 and 1.2 Hz, 1H, H3′ or 6′), 7.05 (dd, *J* = 7.5 and 1.4 Hz, 1H, H3′ or 6′), 5.75 (tt, *J* = 5.3 and 1.3 Hz, 1H, H3), 4.97 (br t, *J* = 5.5 Hz, 2H, H2,4), 3.91 (t, *J* = 5.9 Hz, 1H, H6), 3.38 (br t, *J* = 6.3 Hz, 2H, H1,5), 3.18 (s, 3H, NCH$_3$), 2.80 (s, 3H, NCH$_3$). ^{13}C NMR: δ 222.6 (CO), 171.1 (C=O), 142.9 (C2′), 133.7 (C1′), 128.8, 126.9, 126.6, 125.6 (C3′–6′), 96.5 (C2,4), 79.2 (C3), 57.1 (C1,5), 38.7 (NCH$_3$), 36.5 (C6), 34.5 (NCH$_3$).

3.7. Reactions of η^2-(2-methoxycarbonyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (1d)

3.7.1. With diphenylacetylene to form 2,3-diphenyl-4,5,6-trimethoxyindenone (4b)

1d (0.098 g, 0.250 mmol) and diphenylacetylene (0.048 g, 0.269 mmol) under reflux in benzene over 1 h gave Mn$_2$(CO)$_{10}$ (0.002 g, 5%) and **4b** (0.098 g, 100%) as a maroon solid, m.p. 124–126 °C (lit. [7b] 121–122 °C). Anal. Calc. for C$_{24}$H$_{20}$O$_4$: C, 77.40; H, 5.41. Found: C, 77.39; H, 5.57%. MS (*m/z*) 372 (M$^+$). ^{1}H NMR: δ 7.34 (s, 5H, ArH), 7.16 (s, 5H, ArH), 7.08 (s, 1H, H7), 3.89 (s, 6H, 4,5-OCH$_3$), 3.29 (s, 3H, 6-OCH$_3$). ^{13}C NMR: δ 195.3 (C=O), 156.2 (C5), 154.3 (C3), 149.3, 147.7 (C4,6), 134.6 (C7a), 132.3 (C3a),

130.9 (C1″), 129.8, 128.9 (C1′), 128.4, 127.8 (C2′,3′,5′,6′,2″,3″,5″,6″), 127.2 (C4,4′), 126.2 (C2), 105.0 (C7), 61.0 (4,5-OCH$_3$), 56.5 (6-OCH$_3$).

3.7.2. With acetylene to form [(1,2,3,4,5-η)-6-(2-methoxycarbonyl-4,5,6-trimethoxy phenyl)cyclohexadienyl]tricarbonylmanganese (3c)

1d (0.110 g, 0.280 mmol) and acetylene under reflux in benzene over 7 h gave Mn$_2$(CO)$_{10}$ (0.004 g, 9%) and a yellow oil (0.045 g) assigned by spectra only as the 6-*endo*-H isomer **3c** (36%). MS (*m/z*) 386: (M$^+$ – 2CO). ^{1}H NMR: δ 6.70 (s, 1H, H2′), 5.74 (t, *J* = 4.7 Hz, 1H, H3), 4.87 (t, *J* = 6.1 Hz, 2H, H2,4), 4.44 (t, *J* = 5.6 Hz, 1H, H6), 4.07 (t, *J* = 7.9 Hz, 2H, H1,5), 3.91 (OCH$_3$), 3.82 (OCH$_3$), 3.53 (OCH$_3$). ^{13}C NMR: δ 222.1 (CO), 169.6 (C=O), 152.6 (C5′), 151.8 (C6′), 144.6 (C4′), 131.6 (C2′), 126.2 (C1′), 107.8 (C3′), 96.7 (C2,4), 79.2 (C3), 60.6 (OCH$_3$), 60.5 (OCH$_3$), 58.7 (C1,5), 55.9 (OCH$_3$), 52.2 (CO$_2$*C*H$_3$), 34.9 (C6).

3.8. Reactions of η^2-(2-formyl-5-dimethylaminophenyl) tetracarbonylmanganese (1e)

3.8.1. With diphenylacetylene to form 2,3-diphenyl-5-dimethylaminoindenone (4c)

1e (0.181 g, 0.574 mmol) and diphenylacetylene (0.103 g, 0.578 mmol) under reflux in benzene over 9 h gave Mn$_2$(CO)$_{10}$ (0.032 g, 36%) and **4c** (0.086 g, 46%) as a maroon solid, m.p. 213–218 °C. Anal. Calc. for C$_{23}$H$_{19}$NO: C, 84.89; H, 5.88; N, 4.30. Found: C, 84.99; H, 5.58; N, 4.38%. MS (*m/z*): 325 (M$^+$). ^{1}H NMR: δ 7.39 (s, 5H, ArH), 7.26 (s, 5H, ArH), 6.45 (br d, *J* = 12 Hz, 1H, H6), 3.04 (s, 6H, NCH$_3$). ^{13}C NMR: δ 194.7 (C=O), 154.3 (C5), 152.0 (C3), 148.2 (C3a), 134.3, 133.3 (C1′,1″), 131.4 (C2), 130.0, 128.7, 127.8, 127.4 (C2′–6′,2″–6″), 125.2 (C7), 117.9 (C7a), 108.2 (C6), 106.5 (C4), 40.4 (NCH$_3$).

3.8.2. With acetylene to form 5-dimethylaminoindenone (4d)

1e (0.138 g, 0.438 mmol) and acetylene (continuous saturation) under reflux in benzene (40 mL) over 3.5 h gave Mn$_2$(CO)$_{10}$ (0.004 g, 6%) and **4d** (0.015 g, 20%) as a red oil, assigned only by ^{1}H NMR: δ 7.73 (d, *J* = 8.9 Hz, 1H, H7), 7.34 (d, *J* = 5.7 Hz, 1H, H2), 6.43 (d, *J* = 2.3 Hz, 1H, H4), 6.26 (dd, *J* = 8.8 and 2.9 Hz, 1H, H6), 5.84 (d, *J* = 5.8 Hz, 1H, H3), 3.06 (s, 6H, NCH$_3$).

3.9. Reaction of η^2-(3-acetylthien-2-yl)tetracarbonyl-manganese (5) with phenylacetylene to form [η^5-2-(3-acetylthien-2-yl)-1,3,5-triphenylcyclohexadienyl]tricarbonylmanganese (6)

η^2-(3-Acetylthien-2-yl)tetracarbonylmanganese (**5**; 0.136 g, 0.47 mmol) and phenylacetylene (0.240 g,

2.3 mmol) were heated under reflux in benzene for 8 h. Rotary evaporation gave a dark oil which by p.l.c. (1:10 diethyl ether/petroleum spirit) gave a broad band yielding an orange oil. Further p.l.c. (1:10 ethyl acetate/petroleum spirit) gave one major band (R_f = 0.34) which was extracted with dichloromethane. Solvent removal gave an orange crystalline solid (168 mg) which was unstable in solution preventing NMR characterization, but which by crystallisation from hexane under refrigeration provided a sample of [η^5-2-(3-acetylthien-2-yl)-1,3,5-triphenylcyclohexa-dienyl]tricarbonylmanganese (**6**) as pure orange crystals, stable in the solid state and characterized by X-ray crystal structure analysis.

3.10. X-ray crystallography

For both structures, data were collected on a Nicolet R3 diffractometer using standard procedures and software. Structures were solved by direct methods and developed and refined (on F^2) routinely using the SHELX programmes [26].

3.10.1. 1-Methyl-2,3-diphenyl-1H-inden-1-ol (2a)
Colourless crystals were obtained from petroleum spirit. *Crystal data:* $C_{22}H_{18}O$, M_r 298.39, tetragonal, space group $P4_2/n$, a = 11.900(2), c = 24.250(8) Å, V = 3434.0(5) Å^3, D_{calc} = 1.154 g cm^{-3}, Z = 8, μ (Mo Kα) = 0.069 mm^{-1}, size 0.64 × 0.34 × 0.10 mm^3, $F(000)$ = 1264, T = 173 K. Total data 2448, unique data 2204 (R_{int} = 0.0455), 4° < 2θ < 45°, R_1 ($I > 2\sigma(I)$) = 0.0538, wR_2 (all data) = 0.1227, GoF = 1.005, residual Δe +0.15/−0.18 e Å^{-3}.

3.10.2. [(1,2,3,4,5-η)-2-(3-Acetylthien-2-yl)-1,3,5-triphenylcyclohexadienyl]tricarbonylmanganese (6)
Orange crystals were obtained from hexane. *Crystal data*: $C_{33}H_{23}MnO_4S$, M_r 570.51, monoclinic, space group $P2_1/n$, a = 11.172(3), b = 21.168(6), c = 11.533(3) Å, β = 94.15(2)°, V = 2720.3(13) Å^3, D_{calc} = 1.393 g cm^{-3}, Z = 4, μ (Mo Kα) = 0.599 mm^{-1}, size 0.76 × 0.50 × 0.36 mm^3, $F(000)$ = 1176, T = 193 K. Total data 5780, unique data 5345 (R_{int} = 0.0425), 4° < 2θ < 52°, R_1 ($I > 2\sigma(I)$) = 0.0380, wR_2 (all data) = 0.0934, GoF = 1.037, residual Δe +0.36/−0.35 e Å^{-3}.

4. Supplementary material

Full details of the structure determinations have been deposited with the Cambridge Crystallographic Data Centre as CCDC 263454 (**2a**) and CCDC 263453 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk).

Acknowledgement

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