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Synthesis and alkyne-coupling chemistry of cyclomanganated 1- and 3-acetylindoles, 3-formylindole and analogues

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Abstract

The syntheses are reported of new cyclomanganated indole derivatives (1-acetyl-κ*O*-indolyl-κC^2)dicarbonylbis(trimethylphosphite)manganese (**2**), (1-methyl-3-acetyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese (**4**), (3-formyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese (**5a**) and (1-methyl-3-formyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese (**5b**). The unusually complicated crystal structure of **5b** has been determined, the first for a cyclomanganated aryl aldehyde.

The preparations of a mitomycin-related pyrrolo-indole and related products by thermally promoted and oxidatively (Me_3NO) initiated alkyne-coupling reactions of the previously known complex (1-acetyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese (**1**) are reported for different alkynes and solvents. X-ray crystal structures are reported for the dimethyl acetylenedicarboxylate coupling product of **1** (dimethyl 1-methyl-l-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate; **6a**), and an unusually-cyclised triple insertion product **8** from the coupling of acetylene with **4**, in which a cyclopentadiene moiety is η^3-allyl-coordinated to Mn through only one double bond and an exocyclic carbon, but which rearranges on heating to an η^5-cyclopentadienyl complex.

Keywords: Cyclometallation; Manganese; Indoles; Alkyne coupling

1. Introduction

Coupling of alkynes with orthomanganated aryl ketones to form 1*H*-inden-1-ols has been reported by us [1,2] and by Liebeskind's group [3], as have the corresponding alkyne-coupling reactions of orthomanganated *N*,*N*-diphenylhydrazones of acetophenone and benzaldehyde to form indenylhydrazines [4]. Cambie et al. [5] subsequently used these methods to prepare new steroid-related compounds using substrates derived from the natural product podocarpic acid.

We have reported in a review [6] the initial finding [7] of an equivalent reaction of dimethyl acetylenedicarboxylate (DMAD) with the *N*-acetyl-coordinated manganated indole **1** [(1-acetyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese] to form (Scheme 1) the carbinolamine **6a** (dimethyl 1-hydroxy-1-methylpyrrolo[1,2a]indole-2,3-dicarboxylate) whose pyrrolo-indole skeleton matches that of the mitomycin group of antibiotics [8].

Because there is renewed interest in the synthesis of this class of polycyclic indole derivative [9] we report more general alkyne-coupling chemistry of **1**, its $Mn(CO)_2[P(OMe)_3]_2$ analogue **2**, and the related 2-$Mn(CO)_4$ derivatives of 3-acetylindole and *N*-methyl-3-acetylindole (**3**, **4**). The report also includes the synthesis of the new cyclomanganated indole derivatives **2**, **4**, **5a** and **5b**. The complex crystal structure of **5b** is reported

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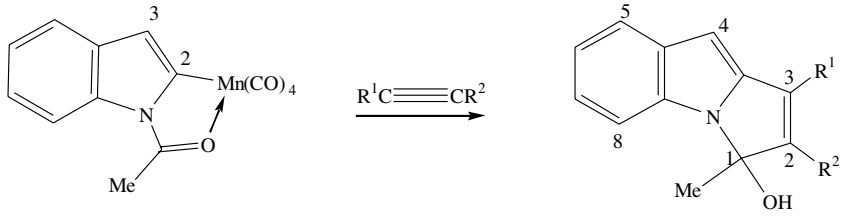


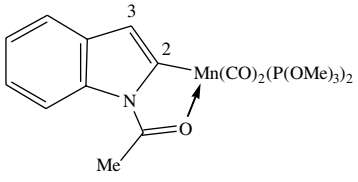
1

6a $R^1 = R^2 = CO_2Me$

6b $R^1 = R^2 = Ph$

Scheme 1.

as well as those of the DMAD coupling product **6a** from **1** and an unusually cyclised triple-acetylene-insertion product from **4**.



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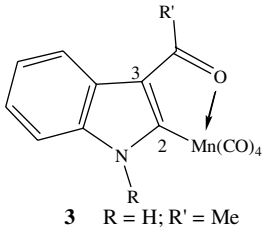


3 R = H; R' = Me
4 R = R' = Me
5a R = R' = H
5b R = Me; R' = H

2. Results and discussion

2.1. Cyclomanganation reactions

Cyclomanganation at the 2-position of indole is routinely achieved for 3-acetyl-1-methylindole employing the standard reaction with $PhCH_2Mn(CO)_5$ in heptane under reflux, as applied earlier to 1-acetyl-, 1-benzoyl- and 3-acetyl-indole [10]. Similarly compounds **5a** and **5b** were formed from 3-formylindole and its 1-methyl analogue. These are notable because an aldehyde group is directing the cyclometallation reaction, which is relatively rare in contrast to the many ketone examples [6]. We note that benzaldehyde does not cyclomanganate under these conditions, though 4-methoxy- and 4-dimethylamino-benzaldehyde do so [10]. This unpredictability occurs again here with only a low yield of **5a** (17%) but a respectable one for **5b** (68%). There are no previous reports of X-ray crystallographically characterized cyclomanganated aryl aldehydes, so that of **5b** is reported below.

These new compounds complement cyclomanganated 1-acetylindole (**1**) and 3-acetylindole (**3**) as substrates which are functionalised at the 2-position of the indole nucleus, which is important because electrophilic substitution, the common entry to aryl functionalisation, occurs with a strong preference for the 3-position in indoles.

2.2. Alkyne coupling chemistry

Results for alkyne-coupling reactions are summarized in Table 1, which, to serve its purpose as a general reactivity guide, covers some reactions which are unsuccessful under conditions in which cyclomanganated acetophenones (cf. [2]) would normally give good yields. For the reactions of **1** with various alkynes, the usual product is of the pyrrolo-indole type **6**, accompanied by varying amounts of 1-acetylindole arising from simple demetallation (entries 1–12, 14–22).

As discussed previously [1–3], the reactions are presumed to involve coordination of alkyne to a vacant coordination site after loss of one CO ligand, achieved thermally [1,2] or by oxidation with trimethylamine oxide [3], followed by insertion of alkyne to give an alkenyl-Mn product (Scheme 2 for the case of *N*-acetylindole). Addition of the manganated carbon to the adjacent acetyl carbonyl group gives the *O*-manganated precursor of the product, which with adventitious proton source on workup or chromatography provides the neutral product (carbinolamine **6** in the case of *N*-acetylindole).

Under thermal activation, by heating under reflux for the stated periods, generally much poorer yields are achieved here with the 2-$Mn(CO)_4$ derivative of *N*-acetylindole than for the 2-$Mn(CO)_4$ derivative of acetophenone, with significant material loss through demetallation of starting material in part responsible. Yields for thermal activation with **1** are really only acceptable for synthesis with diphenylacetylene and then only when using petroleum spirit or benzene as solvent (entries 5 and 6).

2-Hexyne, which gives acceptable indenol yields with cyclomanganated acetophenone [2], fails altogether to do so with **1** under thermal activation (entries 9–12).

With oxidative activation using trimethylamine oxide in acetonitrile at room temperature, even more demetallation of starting compound generally occurs. Nevertheless, better yields of coupling product are obtained for **1** with dimethyl acetylenedicarboxylate (DMAD; entry 16) than for thermal activation (entry 3), although the reverse applies for diphenylacetylene (entries 20 and 7). Similar comparisons apply for reactions conducted in other solvents with these two alkynes. It should be noted that for **1**, when non-polar solvents have been employed instead of acetonitrile for Me_3NO activations (benzene, petroleum spirit, and carbon

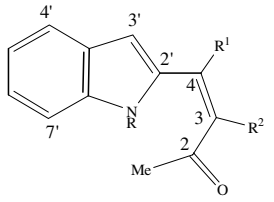
Table 1
Products from alkyne-coupling reactions

Entry	Reactant (activation)	Alkyne (R^1, R^2) (1.4 mol)	Solvent (reaction time)	Yield%	
				Coupling product	Demetallation product[a]
1	**1** (Thermal[b])	CO_2Me, CO_2Me	Pet. sp.[c] (5 h)	15 (**6a**)	27
2			C_6H_6 (24 h)	1	0
3			MeCN (2.5 h)	18	4
4			CCl_4 (2.5 h)	14	7
5		Ph, Ph	C_6H_6 (4 h)	61 (**6b**)	13
6			Pet. sp.[c] (5 h)	64	10
7			MeCN (5 h)	22	62
8			CCl_4 (4 h)	–	25
9		Me, Pr	C_6H_6 (22 h)	0	45[d]
10			Pet. sp.[c] (23 h)	0	31[d]
11			MeCN (2.5 h)	0	81[d]
12			CCl_4 (4 h)	0	42[d]
13		H, H (saturated[e])	C_6H_6 (2 h)	16 (**7a**)	–
14	**1** (Me_3NO[f])	CO_2Me, CO_2Me	Pet. sp.[c] (24 h[g])	15 (**6a**)	27
15			C_6H_6 (22 h)	61	22
16			MeCN (8 h)	61	15
17			CCl_4 (24 h[g])	33	20
18			MeOH (20 h[g])	18	43
19		Ph, Ph	C_6H_6 (24 h[g])	30 (**6b**)	62
20			MeCN (3 h)	7	40
21		Me, Pr	C_6H_6 (24 h[g])	–	26
22			MeCN (3 h[h])	–	81
23	**1** (Li_2PdCl_4[i])	CO_2Me, CO_2Me	MeCN (8 h)	5 (**6a**)	13
24	**2** (Thermal[b])	CO_2Me, CO_2Me	Pet. sp.[b] (30 h)	n.r.[j]	
25			MeCN (28 h)	n.r.[j]	
26	(Me_3NO[f])		MeCN (27 h.)	(87% **2** recov.)	8
27	**3** (Thermal[b])	Ph, Ph	Pet. sp.[c] (7 h)	18 (**6b**)	
28		CO_2Me, CO_2Me	Pet. sp.[c] (26 h)	–	
29		Me, Pr	Pet. sp.[c] (6 h)	–	
30	**4** (Thermal[b])	Ph, Ph	Pet. sp.[c] (24 h)	43 (**7b**)	
31		CO_2Me, CO_2Me	Pet. sp.[c] (24 h)	–	23
32		H,H (saturated[e])	Pet. sp.[c] (6 h)	17 (**8**)[k]	
33	(Me_3NO[f])	Ph, Ph	MeCN (3 h)	53 (**7b**)	18
34		CO_2Me, CO_2Me	MeCN (3 h)	–	

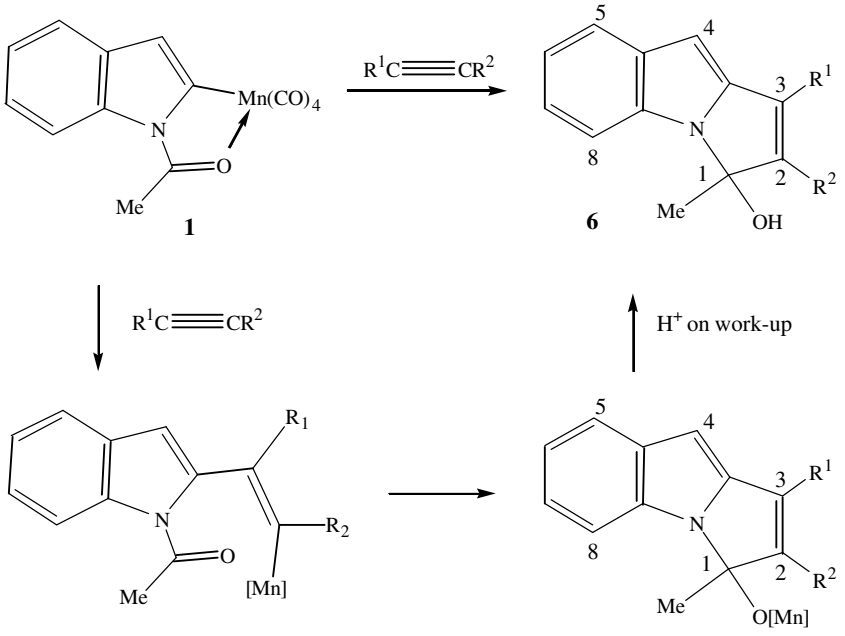
[a] *N*-acetylindole from **1** and **2**; 3-acetyl-*N*-methylindole from **4**.
[b] Under reflux.
[c] B.p. 60–80 °C.
[d] 5–8% unreacted **1** in this series of reactions.
[e] Acetylene at saturation by continuous bubbling through reaction solution under reflux.
[f] Oxidative activation with Me_3NO (1.5 mol); room temperature.
[g] Plus 40 min reflux for completion.
[h] Under reflux throughout.
[i] With added Li_2PdCl_4 (1 mol) under reflux.
[j] Only unreacted **2** detectable by IR.
[k] See text for structure.

tetrachloride), incomplete solubilisation of Me_3NO was observed and after initial reaction at room temperature for 24 h, IR normally indicated some residual manganated reactant, so reaction mixtures were heated under reflux for an additional 40 min to ensure complete reaction (entries 14, 17, 19, 21). As for thermal activation, 2-hexyne again fails to give an indenol with Me_3NO activation either in benzene (entry 21) or acetonitrile, even under reflux (entry 22). Attempted activation with Pd(II) using Li_2PdCl_4 in MeCN failed for **1** with DMAD (entry 23), the yield of **6a** (5%) being negligible by comparison with that using Me_3NO activation in the same solvent.

When **1** was reacted with acetylene (entry 13), no derivative of type **6** was detected. Instead, a 16% yield was obtained of a mono-insertion product **7a**, in which the acetyl group has been transferred to the alkene side-chain, presumably via the breakdown of an initial carbinolamine product like **6a**.



7a R = R^1 = R^2 = H
7b R = Me; R^1 = R^2 = Ph



Scheme 2. Metal ligands omitted at intermediate stages (symbol [Mn]).

To see whether the reactivity could be changed by altering the coordination geometry around the manganese atom, a substituted derivative of **1** was synthesized by thermal reaction with excess trimethylphosphite to give the disubstituted compound **2**. Characterisation data is given in the experimental section, where the single ^{31}P resonance, and the two equally intense ν(CO) bands both indicate that the two phosphine ligands are mutually *trans*, together with *cis* CO groups. This is the same pattern as was found for the crystallographically characterized di-phosphite substituted compound derived from cyclomanganated triphenylphosphine sulfide [11].

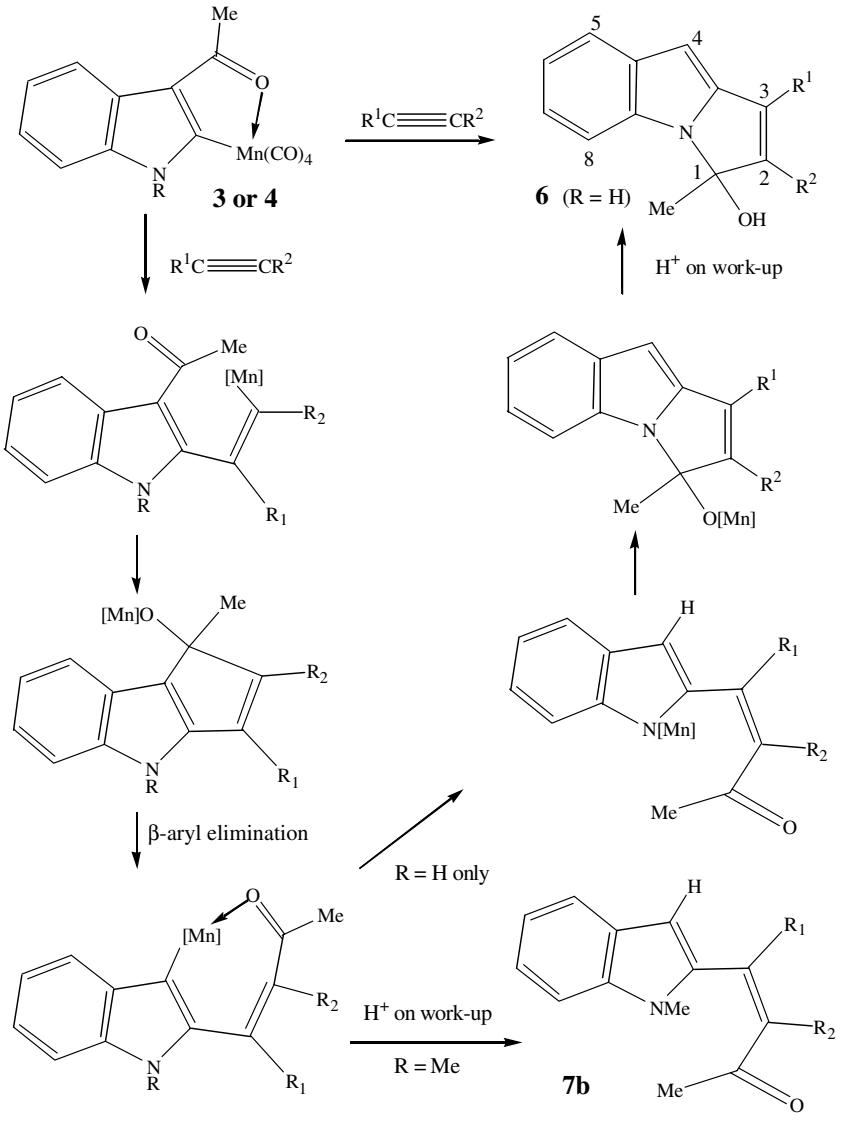
Replacement of two of the metal carbonyl ligands by trimethylphosphite to give the complex **2** serves only to deactivate the Mn center to coupling, at least for the case of DMAD tested. Notably, even the use of Me_3NO for activation resulted in no reaction and since **2** was recovered in 87% yield (entry 26), little if any oxidation of carbonyl ligand occurs. Since replacement of two CO ligands by the poorer π-accepting phosphite ligands will increase the Mn–CO bond order for the remaining CO ligands, this suggests that the reactivity of Me_3NO with strongly coordinated CO is simply lost. It seems unlikely that alkyne would not coordinate if a metal coordination site were available as we have observed electron-deficient alkene (methyl acrylate) insertion in the complex of 3-acetyl-2, 5-dimethylthiophene cyclometallated by $Mn(CO)_2[P(OMe)_3]_2$ under thermal conditions [12].

The 3-acetylindole complex **3** fails to give clean coupled product with DMAD or 2-hexyne (entries 28, 29) but for diphenylacetylene in petroleum spirit, the same coupled product **6b** as from the 1-acetyl complex **1** (entry 6) is unexpectedly obtained, though in comparatively low yield (entry 27). Possibly this occurs (Scheme 3) through cyclisation then deacetylation at C3 by β-aryl-elimination followed by proton transfer to C(3) from N(1) and recyclisation at the latter to give the O[Mn] precursor of **6b** (Scheme 3).

The analogous *N*-methyl-3-acetylindole complex **4** with diphenylacetylene also results in deacetylation at C-3 to form the non-cyclisable enone product **7b**, presumably with the stereochemistry shown (Scheme 3; 43%), and this yield is improved to 53% with Me_3NO activation (entry 33). Again, however, DMAD does not couple successfully without Me_3NO (entry 31) or with it (entry 34). Possibly the bulkier phenyl substituents encourage cyclisation to form the two fused 5-membered rings required for the deacetylation to occur, a form of the Thorpe-Ingold effect [13].

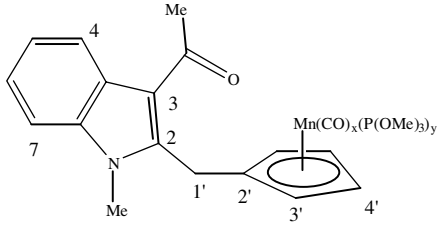
When there are no alkyne substituents (acetylene; under continuous flow: see experimental), complex **4** does give an alternative interesting triple insertion/cyclisation product **8** (17%; entry 32) in which the metal is coordinated to both the oxygen atom of the acetyl group and to an η^3-allyl group which is part of a methylene–cyclopentadiene group attached at the 2-position of the original indole. This five-membered cyclic species has presumably been formed by triple-insertion of C_2H_2, possibly as shown in Scheme 4. Cyclic products from triple acetylene insertion and cyclisation have been seen before with cyclomanganated aryl ketones [2] but in those cases six-membered ring η^5-cyclohexadienyl complexes were formed. In the current case, steric crowding by the 1- and 3-substituents on the indole ring may restrict cyclisation to the alternative mode involving metal-mediated hydride migration as indicated in Scheme 4. A similar mechanism was proposed for an analogous triple insertion of C_2H_2 to give the ruthenium complex **10** [14].

The product **8** is not thermally stable and on heating achieves what is presumably energetically optimal

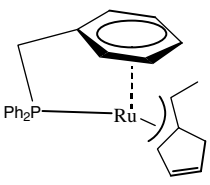


Scheme 3. Metal ligands omitted at intermediate stages: symbol [Mn].

coordination as the cyclopentadienyl complex **9a** (**9b** on heating in the presence of trimethyl phosphite). Possibly **8** is the product of kinetic control and when heated it reverts to its precursor (see Scheme 4) from which **9a** is formed as the product of thermodynamic control by an alternative Mn-mediated hydride migration from the cyclopentadienyl to benzylic carbon (position 1′) of **9a**. Thermally promoted migration of this general type has long been known for *endo*-H in π-cyclohexadienylMn(CO)$_3$ complexes [15].



9a x = 3 y = 0
9b x = 2 y = 1

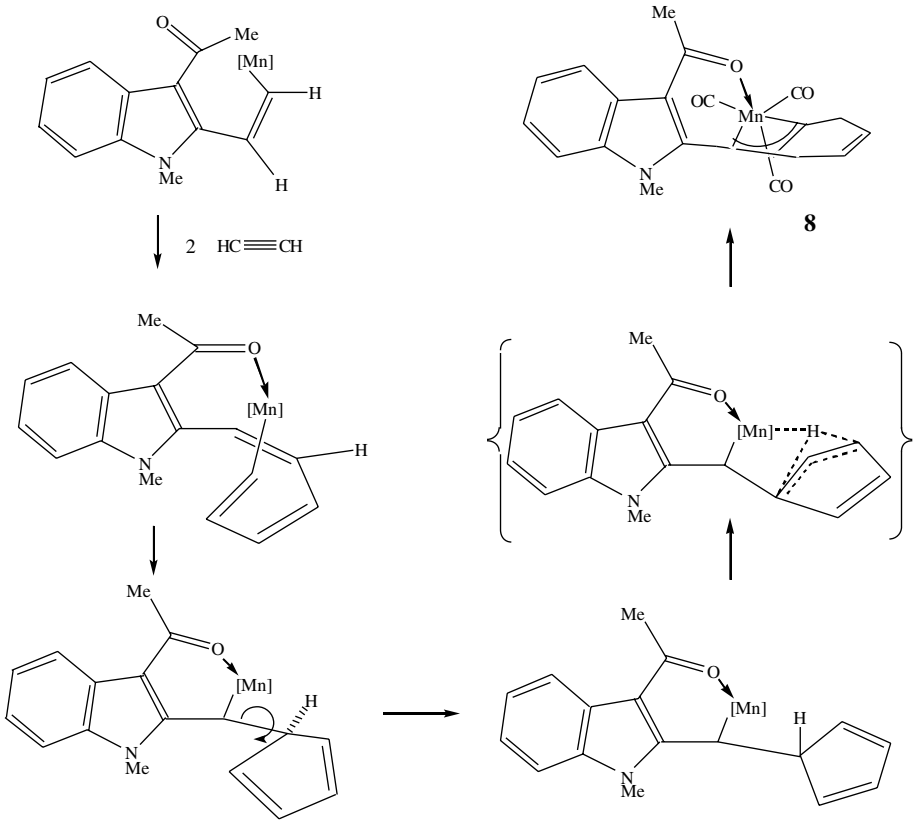


10

2.3. Crystal structures

2.3.1. (1-Methyl-3-formyl-κO-indolyl-κC^2)tetracarbonyl manganese (**5b**)

This is the first structural determination for an ortho-manganated aldehyde. The analysis was complicated by twinning of the crystal and pseudo-symmetry, but a sensible refinement was ultimately achieved for the four independent molecules in the asymmetric unit. The structure of one of the molecules is presented in Fig. 1. It has the expected Mn(CO)$_4$ group attached at C(2) (systematic numbering) of the indole ring and to the formyl oxygen atom to give a five-membered ring. This manganacyclic ring is planar, and the average Mn–C and Mn–O bond lengths [2.003(11) and 2.071(8) Å] conform to the usual pattern of the former being shorter than the latter. The C–Mn–O 'bite' angle of 79.9° and the C–O–Mn angle of 112.9° are similar to those in the ketone examples, suggesting close parallels. Nothing in the structural



Scheme 4. Proposed route to π-allyl complex **8**. The structure in brackets represents a transition state for hydride migration (metal ligands are omitted in intermediates: symbol [Mn]).

features can explain why cyclomanganation of aldehydes is generally less predictable than for aryl ketones.

2.3.2. Dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate (*6a*)

This structure was determined to confirm that insertion of the alkyne and cyclisation had occurred to give a pyrrolo-indole skeleton (Fig. 2). The determination was limited by a weakly diffracting crystal but overall features are clear, the key finding being that the reaction of **1** with alkynes does give the tricyclic core of the mitomycin group of antibiotics. Two other pyrrolo-indole derivatives have been structurally characterized [16], and the present example matches parameters with those of

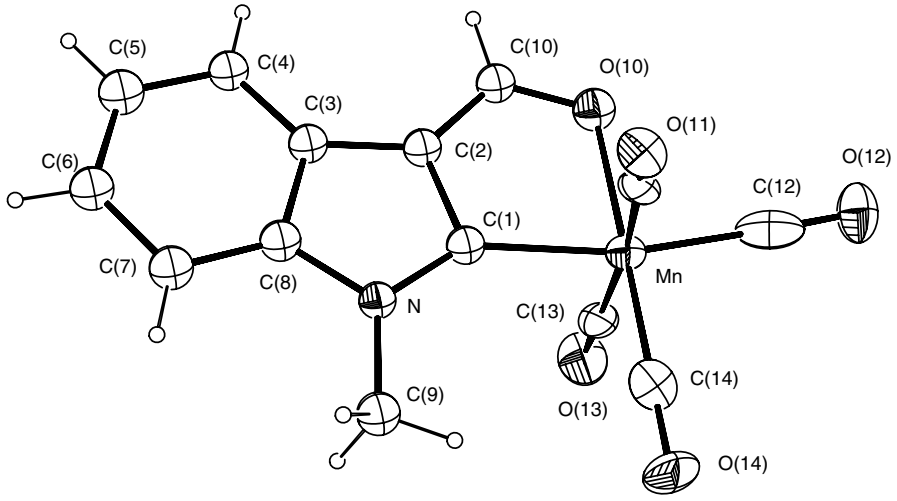


Fig. 1. The structure of one of the independent molecules of (1-methyl-3-formyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese (**5b**). Bond parameters (averaged over all four independent molecules) include: bond lengths (Å) Mn(1)–C(1) 2.003(11), Mn(1)–O(10) 2.071(8), C(10)–O(10) 1.265(14), C(1)–C(2) 1.43(2), C(2)–C(10) 1.36(2); bond angles (°): C(1)–Mn(1)–O(10) 79.9(4), Mn(1)–O(10)–C(10) 112.9(7).

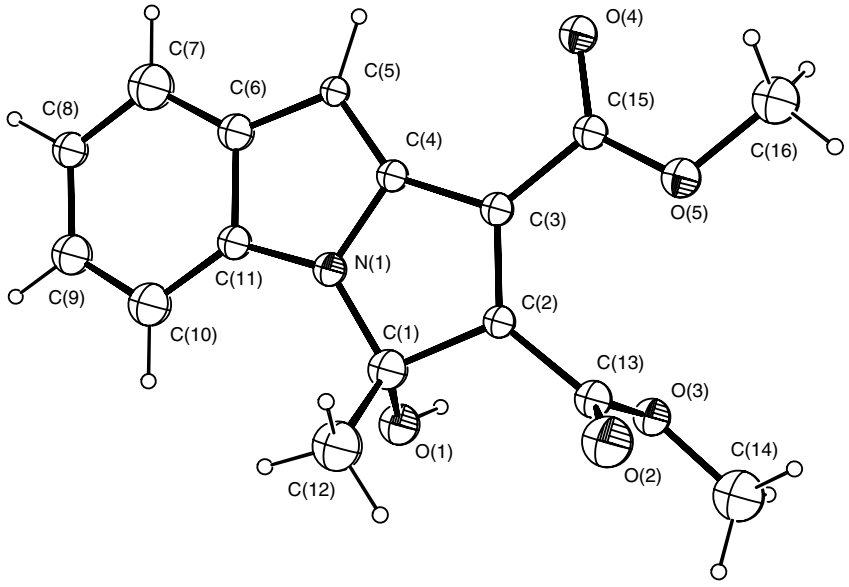


Fig. 2. The structure of dimethyl 1-methyl-l-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate (**6a**). Bond parameters include: bond lengths (Å) N(1)–C(1) 1.474(17), N(1)–C(4) 1.401(16), N(1)–C(11) 1.370(17), C(4)–C(5) 1.32(2), C(1)–C(2) 1.53(2), C(2)–C(3) 1.36(2), C(3)–C(4) 1.44(2), C(1)–O(1) 1.406(18); bond angles (°) C(1)–N(1)–C(4) 114(1), C(1)–N(1)–C(11) 136(1), N(1)–C(1)–C(2) 98(1).

the earlier determinations, within the precision of the determination.

2.3.3. The η^3-allyl complex *8*

The crystal structure determination revealed the molecule shown in Fig. 3. There is a $Mn(CO)_3$ group that has remained coordinated to the 3-acetyl group of the indole. It is also η^3-coordinated to an allyl moiety that is part of a methylene–cyclopentadiene group attached at C(2) of the indole. This group has clearly been formed by linking of three molecules of C_2H_2 as discussed earlier. For the allyl group the exocyclic C(8)–C(9) bond is significantly longer, 1.442(6) Å, than the internal one C(9)–C(10), 1.376(6) Å, with the manganese atom closest to the external carbon atom. This is a similar pattern to that observed in the related ruthenium compound **10** where again the cyclopentadiene-allyl ligand was formed in situ by trimerisation of acetylene [14].

2.3.4. Conclusion

There are now four routes that have been observed for reactions of cyclomanganated ketones with alkynes: (i) monoinsertion followed by addition across the C=O bond to form a five-membered ring as for **6a**; (ii) monoinsertion followed by acetyl-group migration to form an enone group as in **7b**; (iii) triple insertion and cyclisation to give a six-membered η^5-cyclohexadienyl manganese complex; (iv) triple insertion and cyclisation to a five-membered ring

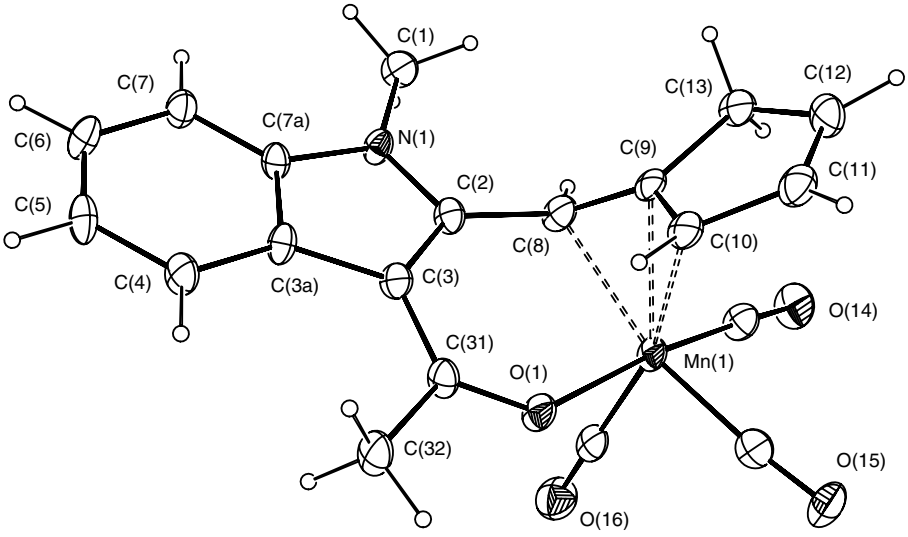


Fig. 3. The structure of the η^3-allyl manganese complex **8**. Bond parameters include: bond lengths (Å) Mn(1)–O(1) 2.052(3), Mn(1)–C(8) 2.145(4), Mn(1)–C(9) 2.155(4) Mn(1)–C(10) 2.280(5), C(31)–O(1) 1.260(5), C(8)–C(9) 1.442(6), C(9)–C(10) 1.376(6), C(9)–C(13) 1.520(6), C(10)–C(11) 1.461(6), C(11)–C(12) 1.336(7), C(12)–C(13) 1.490(7); bond angles (°) Mn(1)–O(1)–C(31) 132.8(3), C(8)–C(9)–C(10) 128.4(4).

methylene–cyclopentadienyl group as for **8**. So far (ii) and (iv) have only been observed with the acetyl-indoles, as reported herein, for reasons that are not yet apparent. It is clear that these reactions have potential for the synthesis of complex hetero-polycyclic compounds from simple starting materials.

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 (in chloroform) were recorded on a Digilab FTS-45 FTIR instrument and NMR spectra on a Bruker AC300 instrument in $CDCl_3$; primed numbers used on structures for convenience to distinguish NMR signals of H or C atoms are not associated with systematic numbering; nor are systematic numbers used in labeling atoms in crystal structure diagrams. Electrospray mass spectrometry (ESMS) was carried out on a VG Platform II machine, with MeOH as mobile phase.

Benzylpentacarbonylmanganese was prepared by the standard method of Closson et al.[17], m.p. 36–37 °C (lit., 37.5–38.5 °C [17]), IR ($CHCl_3$): ν(CO) 2108 (m), 2012 (vs, br), 1993 (s) cm^{-1}.

To prepare 1-methyl-3-acetylindole, 3-acetylindole (1.00 g, 6.28 mmol), potassium carbonate (4.42 g, 32.0 mmol) and methyl iodide (0.51 mL, 8.19 mmol) were heated under reflux in dry acetone (70 mL) overnight. The solution was filtered and volatiles removed under vacuum. The residue was dissolved in ether (40 mL), washed successively with water (50 mL), aqueous NaOH (20 mL; 2 mol L^{-1}), and water (50 mL), then dried over $MgSO_4$. After filtering, the ether was removed to give 1-methyl-3-acetylindole as a creamy brown crystalline solid (0.90 g, 83%), m.p. 108–109 °C (lit. 108 °C [18]). ^1H NMR: δ 8.37 (m, 1H, H-4), 7.66 (s, 1H, H-2), 7.30 (m, 3H, H-5, H-6, H-7), 3.81 (s, 3H, 1-CH_3), 2.50 (s, 3H, 3-$COCH_3$). ^{13}C NMR: δ 193.0 (s, 3-COMe) 137.5 (s, C-7a), 135.9 (d, C-2), 126.2 (s, C-3a), 123.3 (d, C-5 or C-6), 122.5 (d, C-4, C-5 or C-6), 116.8 (s, C-3), 109.7 (d, C-7), 33.4 (q, N-CH_3), 27.6 (q, $COCH_3$). GCMS: m/z 173 (M^+).

3.2. Preparation of cyclomanganated complexes

3.2.1. The standard cyclomanganation procedure is as described for 1-acetylindole: (1-acetyl-κO-indolyl-κC^2)-tetracarbonylmanganese (*1*)

1-Acetylindole (313 mg, 1.96 mmol) and $PhCH_2Mn(CO)_5$ (630 mg, 2.20 mmol) were dissolved in heptane (40 mL) and the solution degassed and flushed with nitrogen twice. After heating under reflux under nitrogen for 90 min, the heptane was removed under vacuum. P.l.c. (1:4 v/v CH_2C1_2/petroleum spirit) gave a broad yellow band which yielded **1** (439 mg, 69%), recrystallised from petroleum spirit as yellow plates, m.p. (dec.) 148 °C (1it. 112 °C [10]). IR ($CHC1_3$): ν(CO) 2090 (m), 2007 (vs, br), 1946 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.52 (d, $J = 8.0$ Hz, 1H, H-7), 7.42 (d, $J = 7.5$ Hz, 1H, H-4), 7.26 (m, 1H, H-5), 7.12 (m, 1H, H-6), 6.84 (s, 1H, H-3), 2.79 (s, 3H, 1-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDC1_3$): δ 220.1 (s, br, CO), 212.3 (s, br, CO), 209.8 (s, br, $2 \times$ CO), 178.4 (s, 1-*C*OMe), 172.6 (s, C-2), 137.6 (s, C-7a), 137.2 (s, C-3a), 124.7 (d, C-5), 121.9 (d, C-3), 121.3 (d, C-6), 118.5 (d, C-4), 112.1 (d, C-7), 22.8 (q, CO*C*H_3).

3.2.2. (1-Acetyl-κO-indolyl-κC^2)dicarbonylbis(trimethylphosphite)manganese (*2*)

(1-Acetyl-κ*O*-indolyl-κC^2)tetracarbonylmanganese (**1**; 203 mg, 0.623 mmol), and trimethylphosphite (0.37 mL, 3.14 mmol) were added to nitrogen-saturated heptane. The solution was heated under reflux for 5 h and the heptane was removed under vacuum. The yellow residue gave by p.l.c. (1:2 ethyl acetate/hexane) **2** (294 mg, 91%) as a yellow solid which crystallised from CH_2Cl_2/pentane as yellow blocks, m.p. 133–134 °C. Anal. Found: C, 41.93; H, 4.99; N, 2.66; $C_{18}H_{26}O_9MnNP_2$ calcd: C, 41.79; H, 5.07; N, 2.71%. IR ($CHCl_3$): ν(CO) 1948 (s), 1869 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.46 (d, $J = 8.0$ Hz, 1H, H-7), 7.30 (d, $J = 7.7$ Hz, 1H, H-4), 7.16 (m, 1H, H-5), 6.95 (m, 1H, H-6), 6.83 (t, $^4J_{PH} = 4.1$ Hz, 1H, H-3), 3.54 (t, $^3J_{PH} = 5.3$ Hz, 18H, $P(OCH_3)_3$), 2.71 (s, 3H, 1-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 228.5 (s, $^2J_{PC} = 33.8$ Hz, br, CO), 220.0 (s, $^2J_{PC} = 27.9$ Hz, br, CO), 188.1 (s, $^2J_{PC} = 36.4$ Hz, C2), 176.4 (s, *C*OMe), 138.0 (s, C-7a), 137.0 (s, C-3a), 123.6 (d, C-5), 120.7 (d, $^3J_{PC} = 5.5$ Hz, C-3), 118.9 (d, C-6), 117.0 (d, C-4), 111.6 (d, C-7), 51.7 (q, $P(OCH_3)_3$), 22.6 (q, CO*C*H_3). ^{31}P NMR (36.23 MHz) ($CDC1_3$): δ 179.0. ESMS: m/z 518 $(M + H)^+$.

3.2.3. (3-Acetyl-κO-indolyl-κC^2)tetracarbonylmanganese (*3*)

Prepared similarly to **1** was **3** (81%), yellow needles from chloroform/pentane, m.p. (dec.) 144 °C. The compound was previously [19] isolated only as an oil. Anal. Found: C, 51.97; H, 2.21; N, 4.32; $C_{14}H_8O_5NMn$ calcd: C, 51.71; H, 2.48; N, 4.31%. IR ($CHCl_3$): ν(CO) 2092 (m), 2010 (vs, br), 1943 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDC1_3$): δ 9.47 (s, br, 1H, NH), 7.64 (d; $J = 7.4$ Hz, 1H, H-4), 7.41 (d, $J = 8.2$ Hz, 1H, H-7), 7.21 (m, 2H, H-5, H-6), 2.65 (s, 3H, $COCH_3$). ^{13}C NMR (75.47 MHz) ($CDC1_3$): δ 220.2 (s, br, CO), 212.6 (s, br, CO), 210.8 (s, C-2), 209.7 (s, br, $2 \times$ CO), 201.9 (s, *C*OMe), 143.7 (s, C-7a), 129.5 (s, C-3), 126.5 (s, C-3a), 122.2 (d, C-5), 121.9 (d, C-6), 117.3 (d,*C*4), 110.5 (s, C-7), 25.0 (q, CO*C*H_3).

*3.2.4. (1-Methyl-3-acetyl-κO-indolyl-κC²)tetracarbonylmanganese (**4**)*

Prepared similarly from 3-acetyl-1-methylindole was **4** (84%), yellow blocks from $CHCl_3$/pentane, m.p. 142–144 °C. Anal. Found: C, 53.26; H, 2.67; N, 4.14; $C_{15}H_{10}O_5NMn$ calcd: C, 53.12; H, 2.97; N, 4.13%. IR ($CHCl_3$): ν(CO) 2091 (m), 2010 (vs), 1943 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 7.60 (m, 1H, H-4), 7.35 (m, 1H, H-7), 7.23 (m, 2H, H-5, H-6), 4.05 (s, 3H, 1-CH_3), 2.61 (s, 3H, 3-$COCH_3$). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.7 (s, br, CO), 213.3 (s, br, CO), 212.1 (s, C-2), 209.7 (s, br, 2 × CO), 200.7 (s, *C*OMe), 144.8 (s, C-7a), 127.7 (s, C-3), 127.0 (s, C-3a), 122.1 (d, C-5), 121.5 (d, C-6), 117.2 (s, C-4), 109.5 (d, C-7), 35.7 (q, 1-CH_3), 24.8 (q, CO*C*H_3).

*3.2.5. (3-Formyl-κO-indolyl-κC²)tetracarbonylmanganese (**5a**)*

Similarly prepared from $PhCH_2Mn(CO)_5$ and indole-3-carboxaldehyde under reflux in heptane but only in low yield after 19 h was **5a** (17%), yellow needles from diethyl ether/pentane, m.p. 148–149 °C. Anal. Found: C, 50.43; H, 1.89; N, 4.55; $C_{13}H_6O_5NMn$ calcd.: C, 50.19; H, 1.94; N, 4.50%. IR ($CHCl_3$): ν(CO) 2094 (m), 2012 (vs, br), 1947 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 9.66 (s, br, 1H, H-1), 9.29 (s, 1H, CHO) 7.68 (m, 1H, H-4), 7.40 (m, 1H, H-7), 7.21 (m, 2H, H-5, H6). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 220.8 (s, br, CO), 215.9 (s, C-2), 212.7 (s, br, CO), 209.4 (s, br, 2 × CO), 190.2 (d, CHO), 143.8 (s, C-7a), 131.8 (s, C-3), 126.3 (s, C-3a), 122.8 (d, C-5 or C-6), 122.6 (d, C-5 or C-6), 117.9 (d, C-4), 110.6 (d, C-7).

*3.2.6. (1-Methyl-3-formyl-κO-indolyl-κC²)-tetracarbonylmanganese (**5b**)*

Similarly prepared from $PhCH_2Mn(CO)_5$ and 1-methylindole-3-carboxaldehyde over 75 min was **5b** (68%), orange blocks from $CHCl_3$/pentane, m.p. 118–120 °C. Anal. Found: C, 51.82; H, 2.09; 4.36; $C_{14}H_8O_5NMn$ calcd: C, 51.71; H, 2.48; N, 4.31%. IR ($CHCl_3$): ν(CO) 2093 (m), 2012 (vs, br), 1947 (s) cm^{-1}. ^1H NMR (300.13 MHz) ($CDCl_3$): δ 9.19 (s, 1H, CHO), 7.65 (m, 1H, H-4), 7.34 (m, 1H, H-7), 7.24 (m, 2H, H-5, H-6), 4.08 (s, 3H, CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 221.4 (s, br, CO), 216.5 (s, C-2), 213.2 (s, br, CO), 209.3 (s, br, 2 × CO), 188.7 (d, CHO), 144.9 (s, C-7a), 130.1 (s, C-3), 127.0 (s, C-3a), 122.7 (d, C-5 or C-6), 122.3 (d, C-5 or C-6), 117.6 (d, C-4), 109.6 (d, C-7), 35.7 (q, 1-CH_3). The single crystal X-ray structure analysis of **5b** is reported below.

3.3. Coupling reactions of alkynes with cyclomanganated compounds

3.3.1. Standard methods

3.3.1.1. Thermally promoted. The orthomanganated compound (100 mg) and alkyne (1.2–2.2 mol equiv.) 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, variously from 2 h to several days, the extent of reaction being monitored by thin layer chromatography and/or IR spectroscopy. At the completion of reaction the solvent was removed under vacuum and the residue subjected to p.l.c. with ethyl acetate/petroleum spirit as eluent. Minor bands were not extracted.

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 (ca. 20 mL) for the duration of the reaction. As it is known that (at 4 °C) 20 mL of benzene dissolves about 0.55 mmol mL^{-1} of acetylene, and 20 mL of cyclohexane (a model for petroleum spirit) about 0.35 mmol mL^{-1} [20], acetylene would be in continuous large excess of the manganated complex (<0.5 mmol in 20 mL solvent) were the reactions run at this temperature, but we can find no data on acetylene solubility in benzene or alkanes nearer their boiling points. Irrespective of its molar excess at any time, however, acetylene is continuously replenished as it reacts.

3.3.1.2. Oxidatively induced with Me_3NO. The standard method is as in Section 3.3.1.1 except that only the orthomanganated compound was dissolved initially. After flushing with nitrogen, trimethylamine-*N*-oxide (ca. 1.4 mol equiv.) was added and the solution was stirred under nitrogen for 15 min (development of an intense yellow colour). The alkyne was then added and the mixture was stirred at ambient temperature for 3–24 h. The extent of reaction was monitored by thin layer chromatography; if any orthomanganated compound still remained after 24 h the solution was heated under reflux for approximately an extra 40 min, by which time t.l.c. showed the reaction to be complete.

*3.3.2. Thermally promoted reactions of (1-acetyl-κO-indolyl-κC²)tetracarbonylmanganese (**1**)*

*3.3.2.1. With dimethyl acetylenedicarboxylate to form dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate (**6a**).* Following the standard procedure above, **1** (81 mg, 0.25 mmol) and DMAD (60 mg, 0.42 mmol) under reflux in petroleum spirit for 5 h followed by p.l.c. (1:3 ethyl acetate/petroleum spirit) gave 1-acetylindole (11 mg, 27%) and **6a** (12 mg, 15%), a yellow oil which crystallised from CH_2C1_2/petroleum spirit as yellow needles, m.p. 98–99 °C. ^1H NMR (300.13 MHz) ($CDC1_3$): δ 7.63 (d, $J = 8.0$ Hz, 1 H, H-4′), 7.53 (d, $J = 8.2$ Hz, 1H, H-7′), 7.26 (t, $J = 8.2$ Hz, 1H, H-6′), 7.11 (t, $J = 8.0$, 1H, H-5′), 6.60 (s, 1H, H-3′), 3.92 (s, 3H, $COOCH_3$), 3.87 (s, 3H, $COOCH_3$), 3.44 (s, 1H, 1-OH), 1.95 (s, 3H, 1-CH_3). ^{13}C NMR (75.47 MHz) ($CDCl_3$): δ 163.0 (s, COOMe), 162.9 (s, COOMe), 140.6 (s, C-2), 137.0 (s, C-3), 134.4 (s, C-7a′), 132.9 (s, C-3a′),132.6 (s, C-2′), 124.4 (d, C-6′), 122.9 (d, C-4′), 120.6 (d, C-5′), 110.6 (d, C-7′), 99.8 (d, C-3′), 90.2 (s, C-1), 52.9 (q, OCH_3), 52.6 (q, OCH_3), 24.1 (q, 1-CH_3). The single crystal X-ray structure determination of **6a** is reported below.

Corresponding outcomes in other solvents for the reflux period stated: benzene (24 h): 1% **6a**; MeCN (2.5 h): 18% **6a** and 4% 1-acetylindole; CCl_4 (2.5 h) 14% **6a** and 14% 1-acetylindole.

*3.3.2.2. With diphenylacetylene to form 1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole (**6b**).* Following the standard procedure for DMAD in Section 3.3.2.1 but using 1:4 ethyl acetate/petroleum spirit for p.l.c., **1** (105 mg, 0.322 mmol) and diphenylacetylene (82 mg, 0.459 mmol) in benzene under reflux over 4 h gave **6b** (66 mg, 61%) as an off-white solid which crystallised from CH_2C1_2/pentane as chunky cream crystals, m.p. 183–184 °C. ^{1}H NMR (300.13 MHz) ($CDC1_3$): δ 7.62 (d, $J = 7.9$ Hz, 1H, H-4′), 7.57 (d, $J = 8.0$ Hz, 1H, H-7′), 7.50 (m, 4H, Ar-H), 7.35 (m, 6H, Ar-H), 7.22 (m, 1H, H-6′), 7.11 (m, 1H, H-5′), 6.41 (s, 1H, H3′), 2.78 (s, br, 1H, 1-OH), 1.82 (s, 3H, 1-CH_3). ^{13}C NMR (75.47 MHz)($CDC1_3$): δ 145.3 (s), 143.3 (s), 133.7 (s), 133.3 (s), 133.2 (s), 132.9 (s), 131.5 (s), 129.3 (d), 129.0 (d), 128.6 (d), 128.5 (d), 128.4 (d), 128.3 (s), 128.1 (d), 122.6 (d, C-6′), 121.9 (d, C-4′), 119.9 (d, C-5′), 110.1 (d, C-7′), 95.3 (d, C-3′), 91.6 (s, C-1), 23.8 (q, 1-CH_3). Also obtained was 1-acetylindole (7 mg, 13%).

Corresponding outcomes in other solvents for the reflux period stated: petroleum spirit (5 h): 64% **6b** and 10% 1-acetylindole; MeCN (5 h): 22% **6b** and 62% 1-acetylindole; CCl_4 (4 h) **6b** not formed; 25% 1-acetylindole.

*3.3.2.3. With 2-hexyne: attempted preparation of 1-methyl-l-hydroxy-2,3-diethyllpyrrolo[1,2a]-indole (**6b**).* The standard procedure for DMAD in Section 3.3.2.1 was unsuccessful in giving any coupling product. Apart from small quantities of residual **1** the only material separated by p.l.c. using 1:4 ethyl acetate/petroleum spirit was demetallated product 1-acetylindole: Benzene (22 h): 7% residual **1** plus 45% 1-acetylindole; petroleum spirit (23 h): 8% **1** and 31% 1-acetylindole; MeCN (2.5 h): 8% **1** and 81% 1-acetylindole; CCl_4 (22 h): 5% **1** and 42% 1-acetylindole.

*3.3.2.4. With acetylene to form 4-(indol-2-yl)but-3-en-2-one (**7a**).* **1** (139 mg, 0.427 mmol) and excess acetylene (continuous flow) under reflux in benzene (40 mL) over 2 h gave $Mn_2(CO)_{10}$ (3 mg, 5%) and **7a** (13 mg, 16%) as a yellow oi1, identified only by spectra: MS (M^+) 185. ^{1}H NMR: δ 7.22 (m, 4H, H-4-7), 6.80 (s, 1H, H-3), 6.76 (d, $J = 12.3$ Hz, 1H, H-1′), 6.12 (d, $J = 12.6$ Hz, 1H, H-2′), 2.35 (s, 3H, CH_3). ^{13}C NMR: δ 199.4 (C=O), 137.4 (C-7a), 134.4 (C-2), 133.9 (C-1′), 128.1 (C-3a), 125.3, 121.5, 120.3, 120.1 (C-4,5,6,2′), 112.4, 112.3 (C-3,7), 31.7 (CH_3). ^{1}H NMR data match those previously reported for 4-(indol-2-yl)but-3-en-2-one [21].

*3.3.3. Me_3NO-activated reactions of (1-acetyl-κO-indolyl-κC^2)tetracarbonylmanganese (**1**)*

*3.3.3.1. With dimethyl acetylenedicarboxylate to form dimethyl1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate (**6a**).* Following the standard procedure above, **1** (107 mg, 0.328 mmol), Me_3NO (36 mg, 0.483 mmol) and DMAD (0.057 mL, 0.464 mmol) in benzene at ambient temperature for 22 h then under reflux for 40 min gave **6a** (60 mg, 61%) and 1-acetylindole (12 mg, 22%).

Corresponding outcomes in other solvents for the reflux period stated: petroleum spirit (24 h + 40 min reflux): 50% **6a** and 9% 1-acetylindole; MeCN (8 h): 61% **6a** and 15% 1-acetylindole; CCl_4 (24 h + 40 min reflux): 33% **6a** and 10% 1-acetylindole; MeOH (24 h + 40 min reflux): 18% **6a** and 43% 1-acetylindole.

*3.3.3.2. With diphenylacetylene to form 1-methyl-1-hydroxy-2,3-diphenylpyrrolo[1,2a]-indole-2,3-dicarboxylate (**6b**).* Following the standard procedure in Section 3.3.2.1, **1** (103 mg, 0.316 mmol), Me_3NO (37 mg, 0.490 mmol) and diphenylacetylene (87 mg, 0.485 mmol) in benzene at ambient temperature for 22 h then under reflux for 40 min gave **6b** (32 mg, 30%) and 1-acetylindole (31 mg, 62%).

Corresponding outcome: MeCN (3 h ambient): 7% **6b** plus 80% 1-acetylindole.

3.3.3.3. With 2-hexyne. The standard procedure in Section 3.3.2.1 applied to 2-hexyne in both benzene and in acetonitrile, gave no analogues of **6**, only 1-acetylindole (52% in benzene; 81% in acetonitrile).

3.3.4. Attempted Pd(II)-promoted coupling reaction of (1-acetyl-κO-indolyl-κC^2)tetracarbonylmanganese and dimethyl acetylenedicarboxylate

$PdC1_2$ (61 mg, 0.343 mmol) and LiCl (61 mg, 1.44 mmol) were stirred in dry acetonitrile (15 mL) for 2 h to solubilise the $PdC1_2$ as $Li_2[PdC1_4]$. **1** (108 mg, 0.332 mmol) and DMAD (0.057 mL, 0.464 mmol) were added and the mixture was heated under reflux for 20 h. The mixture was filtered to remove black precipitate, the filtrate passed through a short silica column and solvent evaporated. P.l.c. (1:3 ethyl acetate/petroleum spirit) gave dimethyl 1-methyl-l-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate (**6a**; 6 mg, 5%) and 1-acetylindole (7 mg, 13%).

*3.3.5. Reactions of (1-acetyl-κO-indolyl-κC^2)dicarbonylbis-(trimethylphosphite)manganese (**2**) with DMAD*

2 and DMAD (1.4 mol) under reflux in petroleum spirit (30 h) or acetonitrile (28 h) showed by t.l.c. only unreacted orthomanganated ketone.

When the reaction was repeated in acetonitrile at ambient temperature but with 1.4 mol Me_3NO for 27 h, p.l.c. (1:2 hexane/ethyl acetate) gave unreacted **2** (87%) and 1-acetylindole (8%).

*3.3.6. Thermally promoted reactions of (3-acetyl-κO-indolyl-κC^2)tetracarbonylmanganese (**3**) in petroleum spirit*

The manganocycle **3** (104 mg, 0.320 mmol) and diphenylacetylene (82 mg, 0.462 mmol) under reflux in petroleum spirit for 7 h gave by p.l.c. (1:4 ethyl acetate/petroleum spirit) 1-methyl-l-hydroxy-2,3-diphenylpyrrolo[1,2a]indole (**6b**; 20 mg, 18%).

For the corresponding reaction with DMAD (after 26 h) and 2-hexyne (6 h), t.l.c. showed the presence of unreacted starting material and no other major organic products.

*3.3.7. Reactions of (1-methyl-κO-acetyl-2-indolyl-κC^2) tetracarbonylmanganese (**4**)*

3.3.7.1. With diphenylacetylene. **4** (103 mg, 0.303 mmol] and diphenylacetylene (82 mg, 0.461 mmol) under reflux in petroleum spirit over 24 h gave 4-(1-methyl-2-indolyl)-3,4-diphenylbut-3-en-2-one (presumably the *Z*-isomer **7b**; 46 mg, 43%) which crystallized from $CHC1_3$/pentane as chunky yellow crystals, m.p. 160–162 °C. Anal. Found: M^+ 351.1620; $C_{25}H_{21}NO$ calcd: M, 351.1623. ^{1}H NMR (300.13 MHz) ($CDC1_3$): δ 7.63 (d, $J = 7.8$ Hz, 1H, H-4′), 7.25–6.99 (m, 13H, Ar–H), 6.68 (s, 1H, H-3′), 3.34 (s, 3H, N-CH_3), 2.09 (s, 3H, $COCH_3$). ^{13}C NMR (75.47 MHz) ($CDC1_3$): δ 205.2 (s, *C*OMe), 146.0 (s), 139.2 (s), 138.6 (s),138.2 (s), 137.4 (s), 135.1 (s), 130.5 (d, Ar–C), 130.2 (d, Ar–C), 128.6 (d, ArC), 128.3 (d, Ar–C), 128.0 (d, Ar–C), 127.8 (s), 122.7 (d, Ar–C), 121.1 (d, C4′), 119.9. (d, Ar–C), 109.5 (d, Ar–C), 106.7 (d, C-3′), 31.1 (q, CO*C*H_3), 30.8 (q, 1′-CH_3).

4 (102 mg, 0.302 mmol), Me_3NO (35 mg, 0.462 mmol) and diphenylacetylene (77 mg, 0.434 mmol) at ambient temperature in acetonitrile for 3 h gave **7b** (57 mg, 53%) and 1-methyl-3-acetylindole (9 mg, 18%).

3.3.7.2. With DMAD. **4** (100 mg, 0.296 mmol] and DMAD (0.055 mL, 0.448 mmol) under reflux in petroleum spirit for 24 h gave unreacted η^2-(1-methyl-3-acetyl-2-indolyl)tetracarbonylmanganese (26 mg, 26%) and 1-methyl-3-acetylindole (12 mg, 23%).

3**4** (104 mg, 0.308 mmol), Me_3NO (35 mg, 0.469 mmol) and DMAD (0.057 mL, 0.464 mmol) were stirred at ambient temperature in acetonitrile for 3 h. The residue was chromatographed (p.l.c. 1:1 ethyl acetate/petroleum spirit) to give several minor bands that were not identified.

3.3.7.3. With acetylene. **4** (200 mg, 0.303 mmol) under reflux in acetylene-saturated petroleum spirit for 6 h followed by p.l.c. (1:4 ethyl acetate/petroleum spirit) gave the cyclopentene-fused allyl complex **8** (39 mg, 17%) which crystallised from chloroform/pentane as chunky orange crystals, m.p. 135–137 °C. IR ($CHC1_3$): *v* (CO) 2013 (s), 1932 (s, br), 1899 (s, br) cm^{-1}. ^{1}H NMR (300.13 MHz) ($CDC1_3$): δ 7.65 (d, $J = 7.3$ Hz, 1H, H-4), 7.37 (d, $J = 7.5$ Hz, 1H, H-7), 7.30 (m, 2H, H-5, H-6), 6.77 (d, $J = 4.8$ Hz, 1H), 6.15 (d, $J = 4.8$ Hz, 1H), 5.11 (s, 1H), 4.06 (s, 3H), 3.59 (d, $J = 22.5$ Hz, 1H), 3.41 (s, 1H), 3.20 (d, $J = 22.5$ Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (75.47 MHz) ($CDC1_3$): δ 223.2 (s), 222.7 (s), 221.8 (s), 194.3 (s), 153.8 (s), 137.4 (s), 136.4 (d), 128.5 (d), 125.8 (s), 123.0 (d), 122.8 (d), 120.0 (d), 110.0 (d), 95.7 (d), 48.6 (t), 43.2 (d), 30.4 (q), 29.9 (q). This compound (**8**) was identified by a single crystal X-ray structure analysis as reported below.

*3.4. Rearrangement reactions of **8***

3.4.1. In heptane under reflux

8 (46 mg, 0.117 mmol) was heated under reflux in heptane (15 mL) for 24 h. The residue was chromatographed (p.l.c. 1:3 ethyl acetate/petroleum spirit) to give (1-methyl-3-acetyl-2-indolylmethylcyclopentadienyl)tricarbonylmanganese (**9a**; 24 mg, 52%) as an opaque oil, identified spectrally only. MS: MH^+ 390.0543; $C_{20}H_{17}O_4NMn$ calcd.: MH, 390.0538. IR ($CHC1_3$): *v*(CO) 2021 (s), 1937 (vs, br). ^{1}H NMR (300.13 MHz) ($CDC1_3$): δ 7.92 (m, 1H, H-4), 7.40 (m, 1H, H-7), 7.30 (m, 2H, H-5, H-6), 4.87 (t, $J = 2.1$ Hz, 2H, H-3′ or H-4′), 4.57 (t, $J = 2.1$ Hz, 2H, H-3′ or H-4′), 4.24 (s, 2H, H-1′), 3.83 (s, 3H, N–CH_3), 2.73 (s, 3H, $COCH_3$). ^{13}C NMR (75.47 MHz) ($CDC1_3$): δ 224.9 (s, CO), 194.3 (s, COMe), 145.1 (s, C-2), 136.8 (s, C-7a), 125.9 (s, C-3a), 122.7 (d, C-5 or C-6), 122.4 (d, C-5 or C-6), 120.8 (d, C-4), 114.1 (s, C-3), 110.2 (d, C-7), 100.9 (s, C-2), 84.4 (d, C-3′ or C-4′), 81.2 (d, C-3′ or C-4′), 31.9 (q, CH_3), 30.0 (q, CH_3), 24.4 (t, C-1′). ESMS: *m*/*z* 407 $(M + NH_4)^+$, 390 $(M + H)^+$.

3.4.2. In the presence of P(OMe)$_3$

8 (20 mg, 0.051 mmol) and trimethylphosphite (50 mL, 0.424 mmol) under reflux in heptane (10 mL) for 4.5 h followed by p.l.c. (3:7 ethyl acetate/petroleum spirit) gave (1-methyl-3-acetyl-2-indolylmethylcyclopentadienyl)dicarbonyl(trimethylphosphite)manganese (**9b**; 12 mg, 50%) as a yellow oi1, identified by spectra only. MS: M^+, 485.0807; $C_{22}H_{25}O_6NPMn$ calcd.: M, 485.0800. IR ($CHC1_3$): *v*(CO) 1946 (s), 1877 (s). ^{1}H NMR (300.13 MHz) ($CDC1_3$): δ 7.93 (m, 1H, H-4′), 7.36 (m, 1H, H-7), 7.30 (m, 2H, H-5, H-6), 4.65 (m, 2H, H-3′ or H-4′), 4.34 (m, 2H, H-3′ or H-4′), 4.27 (s, 2H, H-1′), 3.86 (s, 3H, N–CH_3), 3.60 (d, $^3J_{PH} = 11.6$ Hz, 9H, $P(OCH_3)_3$), 2.71 (s, 3H, $COCH_3$); ^{13}C NMR (75.47 MHz) ($CDC1_3$): δ 230.0 (s, CO), 229.5 (s, CO), 194.2 (s, COMe), 146.2 (s, C-2), 136.8 (s, C-7a), 126.1 (s, C-3a), 122.4 (d, C-5 or C-6), 122.2 (d, C-5 or C-6), 120.8 (d, C-4), 113.8 (s, C-3), 110.1 (d, C7), 98.9 (s, C-2′), 82.2 (d, C-3′ or C-4′), 80.6 (d, C-3′ or C-4′), 51.6 (q, $P(OCH_3)_3$), 31.8 (q, CH_3), 30.4 (q, CH_3), 24.7 (*t*, C-1′). ^{31}P NMR (36.23 MHz) ($CDC1_3$): δ 209.9. ESMS: *m*/*z* 486 $(M + H)^+$.

4. Single crystal X-ray structure determinations

For all structures data were collected on a Nicolet R3 diffractometer using standard procedures. Data were corrected for absorption using an empirical method based on a series of φ-scans for **8**.

*4.1. (1-Methyl-3-formyl-κO-indolyl-κC^2)-tetracarbonylmanganese (**5b**)*

Crystal data: $C_{14}H_8MnNO_5$, M_r 325.15, monoclinic, space group $P2_1$, $a = 9.656(2)$ Å, $b = 11.966(2)$ Å, $c = 23.486(5)$ Å, $\beta = 101.78(3)°$, $V = 2656.5(9)$ Å^3, $D_{calc} = 1.626$ g cm^{-3}, $Z = 8$, μ(Mo Kα) = 1.014 mm^{-1}, orange

crystals from $CHCl_3$/pentane, size $0.72 \times 0.40 \times 0.28$ mm^3, $F(000) = 1312$, $T = 159$ K. Total data 7748, unique data 4912, (R_{int} 0.0013), $4° < 2\theta < 50°$.

The structure was crystallographically complex. It was initially solved in space group $P2_1/a$, although it was apparent there were numerous significant violations of the extinctions associated with the *a*-glide plane. This partial solution led to an R_1 value of 0.28 for 2626 low angle data with $|F_o| > 4\sigma|F_o|$, but could not be further developed. The data could also be indexed in an orthorhombic lattice, but systematic absences (weaknesses) did not correspond to any known space group. Twinning was suspected, by which reflections hkl and $-hkh + l$ were overlapped, as a consequence of the relationship $2a^* \cos\beta^* = c^*$. With the addition of one parameter, α, describing the twinning and upon minimising the function $\Sigma_{hkl} w_{hkl}(|F_o|^2 - |F_c|^2)^2$, where $|F_c|^2 = \alpha|F_{hkl}|^2 - (1 - \alpha)|F_{-hkh+l}|^2$, the value of R_1 dropped to 0.18. With the inclusion of most of the missing atoms, the value dropped to 0.11. However, one of the two crystallographically independent molecules was translationally disordered. The constraint of an *a*-glide plane was dropped, leading to four crystallographically independent molecules in space group $P2_1$ (non-standard setting x, y, z and $1/2 - x$, $1/2 + y$, $-z$), where one pair of molecules (the sets headed by Mn′ and Mn″) was very closely related by a pseudo *a*-glide, while the second pair of molecules (formerly disordered) now were ordered in well separated sites (the sets of atoms headed by Mn and Mn*). On further refinement the value of R_1 dropped to 0.048. About eight missing hydrogen atoms were readily apparent in a difference Fourier map (calculated from data de-twinned using the current value of α). The penultimate R_1 value for a model with only the Mn and carbonyl oxygen atoms anisotropic was 0.036. In breaking the pseudosymmetry, and in space group $P2_1$ with unequal twin components, there are several possible relative orientations of the four independent molecules. The combination originally selected led to a false minimum; performing an *a*-glide operation on each of the non-pseudo-*a* glide related molecules (the sets of atoms headed by Mn and Mn2) led to the parameters reported here as final. Final refinements (on F_o^2) were on all data, with manganese and carbonyl oxygen and carbon atoms allowed anisotropic displacement parameters, leading to final values of R_1 and wR_2 of 0.0453 and 0.1224, respectively, and to a final value for the twinning parameter, α, of 0.296(3). All calculations were with SHELXS -86 and SHELXL-93 [22].

4.2. Dimethyl 1-methyl-1-hydroxypyrrolo[1,2a]-indole-2,3-dicarboxylate (**6a**)

Only a weakly diffracting crystal was found, so the structure determination is of low precision, but confirms the overall geometry. *Crystal data*: $C_{16}H_{15}NO_5$, M_r 301.29, monoclinic, space group $P2_1/c$, $a = 11.400(10)$ Å, $b = 6.674(5)$ Å, $c = 19.960(10)$ Å, $\beta = 108.59(2)°$, $V = 1439.4(18)$ Å^3, $D_{calc} = 1.39$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 0.104 mm^{-1}, yellow crystals from CH_2Cl_2/petroleum spirit, size $0.20 \times 0.16 \times 0.08$ mm^3, $F(000) = 632$, $T = 138$ K. Unique data 1873, $4° < 2\theta < 45°$, $R_1 = 0.0758$, [482 data with $I > 3\sigma(I)$], residual $\Delta e \leqslant |0.39|$ e Å^{-3}.The structure was solved by direct methods and developed and refined routinely using the SHELX programmes with hydrogen atoms included in calculated positions, except for the hydroxyl hydrogen which was fixed in the position located in a penultimate difference map.

4.3. The allyl-cyclopentadiene complex **8**

Crystal data: $C_{20}H_{16}NO_4Mn$, M_r 389.28, monoclinic, space group $P2_1/n$, $a = 12.109(2)$ Å, $b = 8.443(2)$ Å, $c = 17.227(3)$ Å, $\beta = 97.66(3)°$, $V = 1745.6(6)$ Å^3, $D_{calc} = 1.48$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 0.781 mm^{-1}, yellow crystals from CH_2Cl_2/petroleum spirit, size $0.62 \times 0.50 \times 0.24$ mm^3, $F(000) = 800$, $T = 130$ K. $T_{max,min}$ 0.790, 0.618. Unique data 3075, $4° < 2\theta < 50°$, $R_1 = 0.0594$ [$I > 3\sigma(I)$], $wR_2 = 0.1539$ (all data), residual $\Delta e \leqslant |0.96|$ e Å^{-3}. The structure was solved and refined routinely.

5. Supplementary material

Full details of the structure determinations have been deposited with the Cambridge Crystallographic Data Centre as CCDC 282598-282600 for **5b**, **6a** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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