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Synthesis and reactions of tetracarbonylmanganese complexes of benzoylsilanes

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Abstract

Reactions of benzoylsilane with benzylpentacarbonylmanganese (1) give *ortho*-η^2-manganese complexes in high yield. The derived aldehyde complex can then be formed by fluoride-catalysed desilylation of the acylsilane complex. Coupling reactions of the acylsilane complexes with alkenes or alkynes are reported.

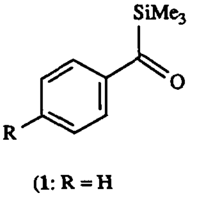
Key words: Manganese; Carbonyl; Silane; Aldehyde; Alkene; Alkyne

1. Introduction

While cyclomanganation of some benzaldehydes carrying electron-donating substituents has been achieved, albeit in low yield [1,2], that of benzaldehyde itself has not been achieved. On the basis of their relatively low ν(C=O) values (*ca.* 1620 cm^{-1}) benzoylsilanes would be expected to undergo facile *ortho* metallation, and since they are synthetic equivalents of aldehydes a study of their cyclomanganation has been carried out in order to circumvent the problem of the low yields from direct manganation of the aldehydes.

2. Results and discussion

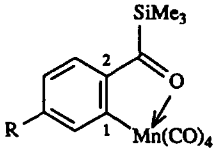
The organic ligands benzoyltrimethylsilane (1) and 4-methoxybenzoyltrimethylsilane (2) were prepared by standard methods [3-6]. On treatment with an equimolar amount (*cf.* [7]; simplified product isolation) of benzylpentacarbonylmanganese(1) (3) in refluxing heptane both 1 and 2 readily underwent cyclomanganation to form the novel *ortho* η^2-manganated complexes 4 (88%) and 5 (93%), respectively. The IR spectra of 4 and 5 showed distinctive C-Si stretching frequencies at 1254-1238 and 845-846 cm^{-1}, and carbonyl absorption at 1576 (*cf.* 1, 1614) and 1581 (cf. 2, 1613) cm^{-1}, respectively. Four bands due to the carbonyl ligands are expected for a *cis*-$L_2Mn(CO)_4$ complex, but only three (2079-2080, 1950-1995, 1933-1943 cm^{-1}) were observed, due to accidental degeneracy of the two absorptions in the central band [8].



(1: R = H
2: R = OMe)

$PhCH_2Mn(CO)_5$

(3)



(4: R = H
5: R = OMe)

The ^{1}H NMR spectrum of 4 contained a singlet at δ 0.40 ppm due to the $SiMe_3$ group, and aromatic resonances at δ 7.18, 7.37, 8.07, and 8.15 ppm were assigned to H(4), H(5), H(6), and H(3), respectively. The ^{13}C NMR spectrum of 4 showed signals at δ 153.4, 196.0, and 253.7 ppm, which were assigned to C(2), C(1), and $COSiMe_3$, respectively. The resonance of the aryl carbon atom (C(1)) bonded to manganese showed a characteristic large shift (68.6 ppm) to lower field

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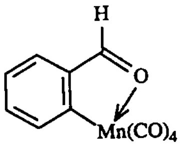
upon coordination, while the signal due to C(2), *ortho* to the C–Mn bond, showed a smaller downfield shift of 12.1 ppm. As expected, the signals due to the remaining aryl carbons and the signal of the ketone carbonyl ligated to manganese each showed differential shifts to lower field. The remaining signals at δ 221.3, 213.3, and 211.7(2C) ppm were assigned to the manganese-bonded carbonyl ligand opposite the ketone carbonyl, to the carbonyl ligand *trans* to the aryl carbon, and to the remaining two carbonyls *trans* to each other, respectively [9,10]. The EI mass spectrum of **4** showed a molecular ion peak at *m/z* 344, accurate mass measurement of which corresponded to the molecular formula $C_{14}H_{13}MnO_5Si$, confirming the composition indicated from microanalysis of a solvate.

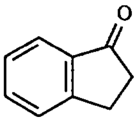
^1H and ^{13}C NMR spectral parameters for **5** were similar to those of **4**.

The acylsilane complex **4** was converted into the previously inaccessible benzaldehyde complex, tetracarbonyl(2-formylphenyl-C^1,O^2)manganese (**6**) (54%) by stirring a solution in THF with a catalytic amount of tetrabutylammonium fluoride (0.2 molar equiv.) [11] and water for 50 min. Use of a stoichiometric amount of $Bu_4N^+F^-$ for 5 min, but without added water, gave a lower yield (26%) of the complex **6**, and after 4 h only a mixture of unidentified products. Protodesilylation of **4** with cesium fluoride (1.1 molar equiv.) and a catalytic amount of 18-crown-6 in THF at room temperature for 23 h gave an even higher yield (69%) of the aldehyde complex **6**. In this reaction, the proton source was presumably water present in the THF. Like that of **4**, the IR spectrum of **6** showed three distinctive Mn–CO stretching frequencies, but it now showed aldehyde absorption (1588 cm^{-1}). The ^1H NMR spectrum showed an aromatic aldehyde proton singlet at δ 9.50 ppm while the ^{13}C NMR spectrum showed the aldehyde carbonyl signal at δ 208.0 ppm.



(6)

Coupling reactions of the complexes **4** and **6** with selected alkenes or alkynes, promoted by oxidative decarbonylation using Me_3NO at room temperature, or by thermally induced decarbonylation, were investigated. A series of reactions with **4** in refluxing heptane, acetonitrile, methanol, tetrahydrofuran, or benzene indicated the latter to be the solvent of choice. Thus, treatment of **4** with methyl propenoate (1.18 molar equiv.) in refluxing degassed dry benzene for 2 h, and then photolytic demetallation of the crude product by irradiation in acetonitrile/chloroform at 350 nm for 2 h followed by addition of water and stirring in air, gave a complicated mixture. Flash chromatography and PLC gave 2,3-dihydro-1*H*-inden-1-one (**7**) (1%), a mixture of the diastereoisomers of methyl 1-trimethylsiloxyindane-2-carboxylate (**8**) (29%), both diastereoisomers of methyl 1-hydroxyindane-2-carboxylate (**9**) (25%), the saturated uncyclized adduct **12** (2%), the indene **13** (2%), and the indenes **14** (13%) and **18** (23%) resulting from incorporation of two molecules of methyl propenoate. Structures were assigned from comparison of the MS obtained from GC-MS with those of the isolated (PLC) products, and from NMR spectra.



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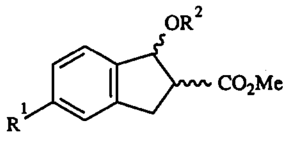
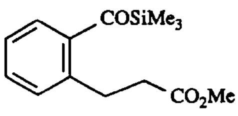
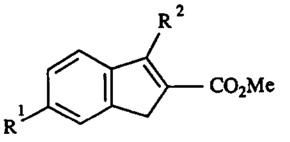


(8: R^1 = H, R^2 = $SiMe_3$
9: R^1 = R^2 = H
10: R^1 = OMe, R^2 = $SiMe_3$
11: R^1 = OMe, R^2 = H)

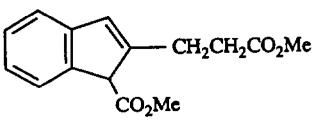


(12)

Thus the product **7** with the lowest retention time on GLC gave an accurate mass measurement of its molecular ion which corresponded to C_9H_8O, and showed cyclopentenone carbonyl absorption (1715 cm^{-1}) in the IR spectrum. The ^1H NMR spectrum contained two two-proton triplets at δ 2.66 (H(3)) and 3.12 (H(2)) ppm. The carbonyl resonance occurred at δ 206.8 ppm in the ^{13}C NMR spectrum, with the C(3) and C(2) methylene carbon resonances at δ 25.6 and



(13: R^1 = R^2 = H
14: R^1 = H, R^2 = $CH_2CH_2CO_2Me$
15: R^1 = OMe, R^2 = H
16: R^1 = OMe, R^2 = $SiMe_3$
17: R^1 = OMe, R^2 = $CH_2CH_2CO_2Me$)



(18)

36.0 ppm, respectively. The remaining signals were in agreement with those reported in the literature [13].

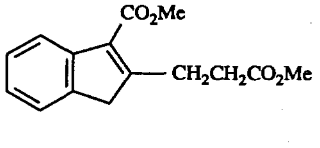
Accurate mass measurement of the molecular ions from the mixture **8** indicated a molecular formula of $C_{14}H_{20}O_3Si$, while the IR spectrum of one of the diastereoisomers (purified by PLC) contained C–Si absorptions (1251, 842 cm^{-1}) and an ester carbonyl stretching frequency (1738 cm^{-1}). In addition to the molecular ion the MS showed intense peaks at m/z 204 $(M - HCO_2Me)$ and 89 $(OSiMe_3^+)$ while the ^1H NMR spectrum showed two singlets at δ 0.22 and 3.76 ppm, corresponding to $OSiMe_3$ and CO_2Me, respectively. The presence of a signal at δ 5.54 ppm (H(1)) confirmed migration of the $SiMe_3$ group from carbon to the benzylic oxygen atom. The ^{13}C NMR spectrum showed signals at δ 0.2 $(OSiMe_3)$, 51.8 $(CO_2\mathit{Me})$, and 174.8 ppm $(\mathit{C}O_2Me)$, methine carbon signals at δ 54.5 (C(2)) and 79.2 ppm (C(1)), and a methylene carbon signal at δ 33.9 ppm (C(3)). The regiochemistry of the proposed structure, wherein methyl propenoate had inserted to give the regioisomer with the bulky ester group tethered at C-2 rather than at C-1, was consistent with that of reported [14] cyclopentaannulated products obtained from various unsymmetrical alkynes.

The stereoisomers of the related 1-indanols **9** gave an accurate mass measurement for the molecular ion (m/z 192) consistent with the formula $C_{11}H_{12}O_3$. Although neither compound was isolated (PLC) from the crude reaction mixture, presumably due to their facile conversion into the alkene **13**, comparison of their mass spectra from GC-MS with that of a mixture of diastereoisomers of methyl 1-hydroxyindane-2-carboxylate isolated from the reaction of tetracarbonyl(2-formylphenyl-C^1,O^2)manganese (**6**) with methyl propenoate (see below) enabled verification of the formation of these alcohols, albeit without definition of their relative stereochemistry.

Compound **12** gave an accurate mass measurement for the molecular ion corresponding to the molecular formula $C_{14}H_{20}O_3Si$. This compound showed two distinct carbonyl absorptions (1738 and 1613 cm^{-1}) which were assigned to the CO_2Me and $COSiMe_3$ groups, respectively, and C–Si stretching frequencies at 1250 and 843 cm^{-1}. In addition to an $SiMe_3$ singlet at δ 0.32 ppm, two two-proton triplets ($J = 7.7$ Hz) were observed in the ^1H NMR spectrum at δ 2.62 $(C\mathit{H}_2CO_2Me)$ and 3.04 ppm $(C\mathit{H}_2CH_2CO_2Me)$, and two corresponding methylene carbon signals were observed at δ 25.9 and 36.0 ppm in the ^{13}C NMR spectrum. Since the $CH_2CH_2CO_2Me$ moiety was still present in this product, cyclization had not occurred. Saturated uncyclized products analogous to **12** have been obtained from reactions of diterpenoid η^2-manganese complexes with methyl propenoate [2].

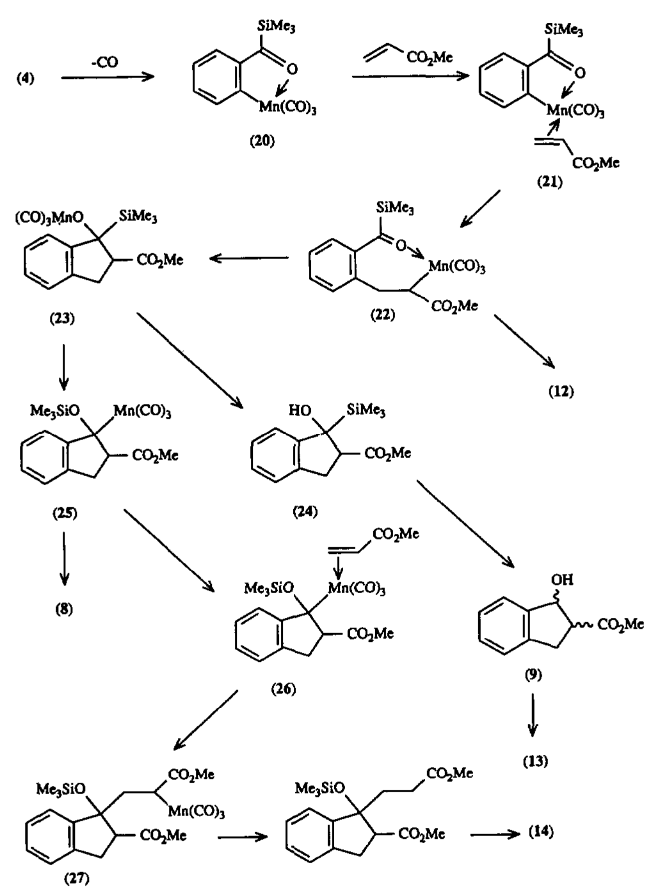
Accurate mass measurement indicated a molecular formula of $C_{11}H_{10}O_2$ for methyl 1*H*-indene-2-carboxylate (**13**), which arises via elimination of water from the indanols **9**. The IR spectrum showed a carbonyl stretching peak indicative of an unsaturated ester (1715 cm^{-1}) while the ^1H NMR spectrum showed a two-proton doublet ($^4J = 1.8$ Hz) at δ 3.65 ppm due to $H(1)_2$, and a one-proton triplet at δ 7.72 ppm due to H(3). The ^{13}C NMR spectrum showed signals at δ 38.3 and 141.2 ppm due to C(1) and C(3), respectively.

The final two compounds isolated (lowest R_f values) each gave a molecular ion whose accurate mass measurement was consistent with the molecular formula $C_{15}H_{16}O_4$. The more volatile (GC) of the two **14**, had an IR spectrum which showed two carbonyl maxima at 1739 and 1705 cm^{-1}, due to an alkyl methyl ester and olefinic methyl ester, respectively. Two two-proton AA′BB′ "triplets" at δ 2.65 $(C\mathit{H}_2CO_2Me)$ and 3.35 ppm $(C\mathit{H}_2CH_2CO_2Me)$ in the ^1H NMR spectrum suggested the presence of a methyl propanoate side-chain. A five-proton singlet at δ 3.67 ppm was due to the indene methylene protons and to $CH_2CH_2CO_2\mathit{Me}$, whose chemical shifts were accidentally coincident, while a three-proton singlet at 3.84 was due to the conjugated 2-$CO_2\mathit{Me}$. The structure was supported by the ^{13}C NMR spectrum which showed methylene carbon signals at δ 21.9 $(\mathit{C}H_2CO_2Me)$, 33.1 $(\mathit{C}H_2CH_2CO_2Me)$, and 38.8 ppm (C(1)), and carbonyl signals at 165.7 and 173.2 due to 2-$\mathit{C}O_2Me$ and $CH_2CH_2\mathit{C}O_2Me$, respectively. This structure was assigned as methyl 3-[3-(methyl 1*H*-indene-2-carboxylate)]propanoate (**14**) and not as its regioisomer **19** on the basis that the first methyl propenoate molecule had inserted to give the regioisomer with the bulkyl ester group tethered at C-2 of the indane derivative [14].



(19)

The remaining product **18** showed only one carbonyl absorption (1738 cm^{-1}, saturated ester) in the IR spectrum while the ^1H NMR spectrum contained two three-proton singlets at δ 3.67 and 3.72 ppm. These data suggested that this product was a regioisomer of the *bis* adduct **14**, and ruled out the possibility of it being **19**. The ^1H NMR signals in the region δ 3.26–3.37 ppm, together with the ^{13}C NMR signals at δ 34.5 and 34.6 ppm, indicated that a $CH_2CH_2CO_2Me$ unit was still present in the product and hence the compound was assigned as the double bond isomer, methyl 3-[2-(methyl 1*H*-indene-1-carboxylate)]propanoate (**18**), an



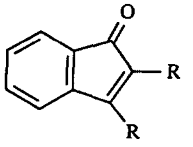
Scheme 1.

assignment supported by other signals in the ^1H and ^{13}C NMR spectra.

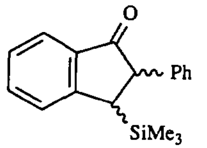
Routes leading to some of these products are shown in Scheme 1. The acylsilane manganese complex **4** is first thermolysed to promote the loss of carbon monoxide to give the coordinatively unsaturated 16-electron species **20**, to which the alkene then coordinates to form the bis η^2 intermediate **21**. Migratory insertion of the olefin into the Mn–C bond of **21** followed by reductive cleavage affords the saturated compound **12**. Alternatively, the intermediate alkylmanganese complex **22** could undergo insertion across the carbonyl group, resulting in cyclization to give the oxymanganese cyclopentaannulated species **23**. This intermediate could undergo reductive cleavage to give **24**, and then desilylation [15] via a Brook rearrangement (1,2 C → O) to give the indanols **9**, and then **13** by elimination of water. Alternatively, the Mn intermediate **23** could undergo a 1,2 Si shift followed by reductive cleavage of **25** to give the trimethylsiloxyindanol derivative **8**. In order to account for the formation of ester **14**, the intermediate **25** could coordinate a second molecule of methyl propenoate to give complex **26**. Migratory insertion of the alkene into the Mn–C bond would afford complex **27**, and then reductive cleavage followed by desilylation and elimination of water would yield the ester **14**. In order to confirm that the products **7–9**, **12–14**, and **18** had in fact resulted from reaction of **4** with methyl propenoate, two blank reactions were performed. First, **4** was refluxed in dry degassed benzene under nitrogen for 2 h. Second, a solution of the uncomplexed acylsilane **1** and methyl propenoate (2 molar equiv.) in dry degassed benzene was refluxed for 2 h and then irradiated at 350 nm for 2 h and worked up as before. In each case TLC analysis indicated the presence of starting materials only.

Reaction of the acylsilane complex **5** with methyl propenoate followed by photolytic demetallation as before also gave a mixture of at least ten components. GC and GC-MS analysis showed the presence of **10** (13%), **15** (28%), **16** (2%), the *cis* and *trans* isomers of **11** (24%, 17%), and **17** (9%).

Reaction of the complex **4** with the symmetrical alkyne diphenylethyne (2.2 molar equiv.) in benzene followed by irradiation and usual workup again gave a number of products, the minor ones of which were not isolated or characterized. PLC afforded 2,3-diphenyl-1*H*-inden-1-one (**28**) (22%), accurate mass measurement of the molecular ion of which confirmed a molecular formula of $C_{21}H_{14}O$. The IR spectrum showed absorption indicative of a cyclopentadienone carbonyl at 1705 cm^{-1}, but the ^1H NMR spectrum was very complicated since all of the hydrogens are aromatic and their signals overlapped. However, seventeen signals, including that of a carbonyl carbon (δ 196.5 ppm) [16], were observed in the ^{13}C NMR spectrum, corresponding to all of the different carbon atoms.

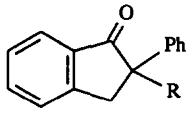


(**28**: R= Ph
29: R = H)

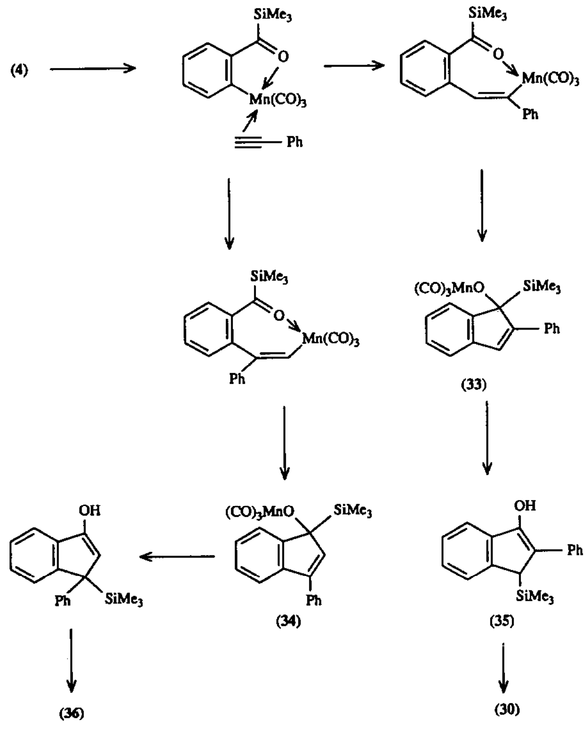


(**30**)

Reaction of the complex **4** with phenylethyne (1.7 molar equiv.) for 8.5 h followed by photolytic oxidative demetallation again gave a large number of products. Flash chromatography and repetitive PLC afforded 2,3-dihydro-2-phenyl-3-trimethylsilyl-1*H*-inden-1-one (**30**), 2-dichloromethyl-2,3-dihydro-2-phenyl-1*H*-inden-1-one (**31**), and 2,3-dihydro-2-hydroxy-2-phenyl-1*H*-inden-1-one (**32**). The trimethylsilylindanono **30** gave



(**31**: R = $CHCl_2$
32: R = OH)



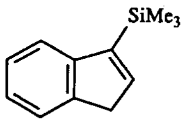
Scheme 2.

an accurate mass measurement of its molecular ion that was correct for $C_{18}H_{20}OSi$. The IR spectrum contained C–Si absorptions (1251, 853 cm^{-1}) and a carbonyl stretching frequency (1714 cm^{-1}), while the ^{1}H NMR spectrum showed a strong signal at δ 0.06 ppm due to the $SiMe_3$ group and one-proton doublets ($J = 2$ Hz) at δ 2.90 (H(3)) and 3.71 ppm (H(2)). Since only a single isomer was isolated, the stereochemistry could not be assigned unequivocally on the basis of $J_{2,3}$, but it is more likely to be *trans* than *cis*. The ^{13}C NMR spectrum showed two resonances due to alkyl methine carbons at δ 39.8 and 56.8 ppm which were assigned to C(3) and C(2), respectively, and a signal at δ 206.4 ppm due to CO. This product was assigned as **30** and not its regioisomer 2,3-dihydro-3-phenyl-2-trimethylsilyl-1H-inden-1-one on the basis of mechanistic considerations as before. Thus, formation of **30** is envisaged to have occurred *via* insertion of the alkyne into the Mn–C bond of a coordinatively unsaturated intermediate (Scheme 2), followed by cyclization to form either **33** or its regioisomer **34**, depending on the regiochemistry of the insertion step. Assuming that the insertion occurs with the bulky phenyl group away from the indane aromatic ring [14], intermediate **33** will be preferred. This 2-phenylindane could then undergo a 1,3-Si shift [17] followed by reductive cleavage of the Mn–O bond to give the indenol **35** which would tautomerize to the observed product **30**. If, however, the alkyne insertion gave regioisomer **34**, the 1,3-Si shift followed by reductive cleavage and tautomerism would give **36**.

The isolation of **31** was unexpected. This compound gave an accurate mass measurement for its molecular ion that was consistent with the formula $C_{16}H_{12}Cl_2O$. The diastereotopic $H(3)_2$ protons gave rise to two doublets, which showed a typically large geminal coupling (17.8 Hz), at δ 3.87 and 4.02 ppm in the ^{1}H NMR spectrum. A singlet at δ 6.58 ppm was assigned to $CHCl_2$. The ^{13}C NMR spectrum contained a methylene carbon signal at δ 34.4 ppm due to C(3), a quaternary carbon resonance at 64.9 due to C(2), and a methine carbon signal at 76.9 due to $CHCl_2$. The regiochemistry was assigned on the basis of Liebeskind's mechanistic rationalisation [14]. Incorporation of the dichloromethyl substituent suggested that reaction of the expected primary cyclization product, 2-phenylindenone, with either a $\cdot CHCl_2$ radical or a $:CCl_2$ carbene had occurred during the photolysis step, in which chloroform had been added to acetonitrile to ensure solubility of the crude mixture.

Accurate mass measurement of the molecular ion of **32** indicated the molecular formula $C_{15}H_{12}O_2$. The IR spectrum showed a broad absorption due to O–H (3398 cm^{-1}), and a carbonyl stretching frequency (1716 cm^{-1}). The ^{1}H NMR spectrum contained two doublets ($J = 17.1$ Hz) due to $H(3)_2$ at δ 3.54 and 3.65 ppm. The ^{13}C NMR spectrum showed methylene and quaternary carbon resonances at δ 44.4 (C(3)) and 81.3 ppm (C(2)). Conclusive proof of the structure was obtained by comparison of the ^{1}H NMR chemical shifts reported for the methylene protons in 2,3-dihydro-2-hydroxy-2-phenyl-1H-inden-1-one [18] and its regioisomer 2,3-dihydro-3-hydroxy-3-phenyl-1H-inden-1-one [19], with those of **32**.

Reaction of the complex **4** with ethene using anhydrous Me_3NO [20] to promote removal of CO at room temperature, followed by photolytic demetallation and flash chromatography of the product gave 1H-inden-3-yltrimethylsilane (**37**) (15%) and 2,3-dihydro-1H-inden-1-one (**7**) (42%). The indenyl silane **37** was isolated as a colourless oil, the IR spectrum of which showed C–Si stretching frequencies (1249, 836 cm^{-1}), and the ^{1}H NMR spectrum of which showed a singlet at δ 0.30 ppm due to the $SiMe_3$ group. A two-proton doublet at δ 3.40 ppm ($^{4}J = 1.7$ Hz) and a one-proton



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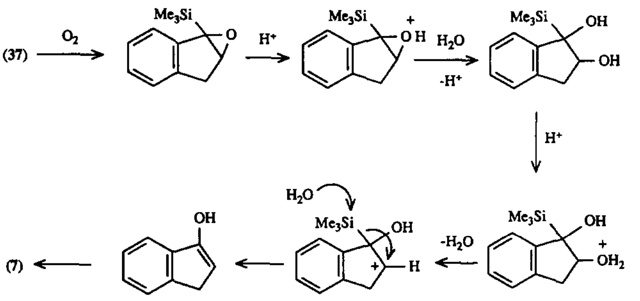
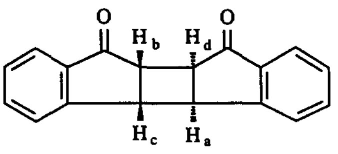


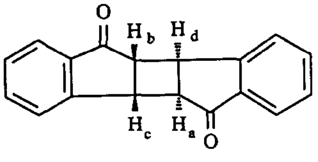
Scheme 3.

triplet at δ 6.75 ppm were assigned to H(1) and H(2), respectively. Conclusive proof of the structure was obtained by comparison of the ^{13}C NMR spectrum with those reported for the three isomeric compounds 1*H*-inden-1-yltrimethylsilane, 1*H*-inden-2-yltrimethylsilane, and 1*H*-inden-3-yltrimethylsilane [22]. The vinyl silane **37** was very air-sensitive, generating **7**, the major product of the manganese-mediated reaction, probably via the sequence shown in Scheme 3.

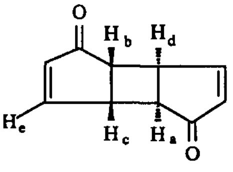
Reaction of the complex **4** with ethyne was carried out under conditions identical to those used for ethene, but, because of the light-sensitive nature of the anticipated indenone product, without photolytic demetallation. Flash chromatography gave 1*H*-inden-1-one (**29**) (19%) and 2,3-dihydro-1*H*-inden-1-one (**7**) (21%). The IR spectrum of the extremely light-sensitive indenone **29** showed an unsaturated carbonyl absorption (1710 cm^{-1}), while the ^1H NMR spectrum contained a doublet at δ 5.89 ppm ($J = 5.96$ Hz) and a doublet of doublets at 7.57 ppm ($J = 5.96$, 0.50 Hz), in addition to the signals due to the aromatic hydrogens. The signal at δ 7.57 ppm was assigned unequivocally to H(3) since ^4J coupling to H(4) is not possible from H(2). The resonances of all of the methine carbons were observed in the ^{13}C NMR spectrum, although all of the signals due to the quaternary carbons were not detected. ^1H NMR analysis of the indenone **29** 1 day later indicated that a complicated mixture had been formed, despite the compound having been kept under nitrogen in the dark at low temperature. Flash chromatography of this mixture gave a solid which had a molecular ion at *m/z* 360 corresponding to the molecular formula $C_{18}H_{12}O_2$, which suggested a dimer of the indenone **29**. The base peak was observed at *m/z* 130, corresponding to the molecular ion of the monomer **29**. The ^1H NMR spectrum contained two doublet of doublet patterns at δ 3.55 and 4.31 ppm ($J = 10.6$, 6.2 Hz), in addition to signals due to the aromatic protons at δ 7.12–7.56 ppm. These data indicated that only one stereoisomer was present. If the dimer had formed *via* a photochemically promoted [2 + 2] cycloaddition four diastereomers are possible, two of which, *viz.* **38** and **39** with a *cis,anti,cis*-stereochemistry, would be expected to be more likely [23]. In the head-to-head dimer, which has a C_2 axis of symmetry, H_b/H_d are chemical shift equivalent (homotopic) as are H_c/H_a. As a result dimer **38** should give rise to two doublets for the cyclobutane hydrogens in the ^1H NMR spectrum. However, in the head-to-tail dimer **39**, which has a centre of symmetry, H_b/H_a are chemical shift equivalent but magnetically inequivalent [24] as are H_c/H_d (AA′XX′ system). Hence two doublet of doublet patterns, each integrating for two cyclobutyl hydrogens, would be expected for this isomer. From these considerations the product was assigned as the head-to-tail dimer **39**. The head-to-tail dimer of cyclopentenone, *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione (**40**) also shows only two sets of ^1H



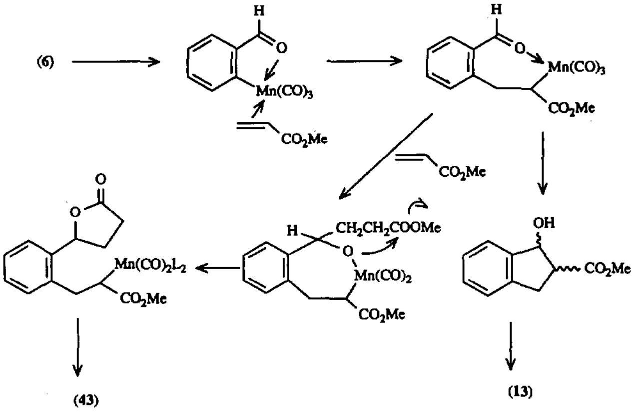
(38)



(39)



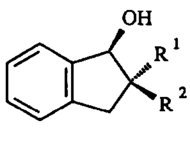
(40)



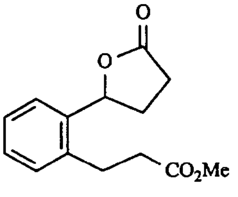
Scheme 4.

NMR patterns for the hydrogens on the cyclobutane ring [25]. In this case the signals due to H_a occurred as a doublet of doublets at δ 2.72 ppm ($J = 5.4$, 2.7 Hz), while the multiplet at δ 3.25 ppm was assigned to H_c which is coupled not only to H_a and H_b but also to H_e.

Reaction of the unsubstituted aldehyde complex **6** with methyl propenoate followed by irradiation and treatment with air and water gave methyl 1*H*-indene-2-carboxylate (**13**) (10%), a mixture (41 : 9) of the diastereoisomers **41** (17%) and **42** (4%) of methyl 1-hydroxyindane-2-carboxylate, and 5-[2-(2-methoxycarbonylethyl)phenyl]-4,5-dihydro-3*H*-furan-2-one (**43**) (9%). Accurate mass measurement of the molecular ions of the mixture of **41** and **42** indicated a molecular formula of $C_{11}H_{12}O_3$. A carbonyl stretching frequency was observed at 1732 cm^{-1} in the IR spectrum. Both the ^1H and ^{13}C NMR spectra showed two sets of signals corresponding to the two diastereoisomers. The major isomer contained two singlets in the ^1H NMR spectra at δ 2.95 and 3.75 ppm which were assigned to the OH and CO_2Me group protons, and a doublet of doublets at δ 3.07 ppm ($J = 14.7$, 7.0 Hz) which was assigned to one H(3) coupling to the geminal H(3) and to H(2). However, the signals due to H(2) and the complementary H(3) could not be assigned individually as they overlapped in the region δ 3.36–3.41 ppm. The resonance due to the benzylic proton H(1) occurred as a doublet at δ 5.31 ppm ($J = 5.4$ Hz). The ^{13}C NMR spectrum of the major isomer showed the methine carbon resonances at δ 49.4 (C(2)) and 75.8 ppm (C(1)), and a carbonyl carbon signal at δ 173.3 ppm. The major isomer **41** was assigned as the *cis* isomer as it showed the C(1), C(2), and 2-CO_2Me resonances upfield of the corresponding signals for the minor *trans* isomer **42**, in accord with the assignment of relative stereochemistry in a pair of related indanols [2].



(41: $R^1 = H, R^2 = CO_2Me$
42: $R^1 = CO_2Me, R^2 = H$)



(43)

Accurate mass measurement of the molecular ion of the bis adduct **43** confirmed the molecular formula $C_{14}H_{16}O_4$. The IR spectrum showed carbonyl maxima at 1771 (γ-lactone) and at 1732 cm^{-1} (alkyl CO_2Me), but the ^1H NMR spectrum was very complicated and no unequivocal assignments could be made. The ^{13}C NMR spectrum contained a methine carbon resonance at δ 78.3 ppm and a methyl carbon signal at δ 51.8 ppm, which were assigned to the lactone CH and CO_2*Me*, respectively. A proposed mechanism for the formation of **13** and **43** is outlined in Scheme 4.

3. Experimental details

For general experimental details, see refs. 27, 28. High field ^1H NMR spectra were recorded at 400.13 MHz and ^{13}C NMR spectra at 100.62 MHz on a Bruker AM 400 instrument operating at 9.2 T. Multiplicities were determined from DEPT spectra.

3.1. Benzoyltrimethylsilane (1)

Benzoyltrimethylsilane was prepared *via* benzyltrimethylsilane [3] and [dibromo(phenyl)methyl]trimethylsilane [4] by heating the latter with silica gel (Riedel-de-Haën 31608, 0.063–0.1 mm) at 50°C with stirring for 1.5 h [5]. The product was flash chromatographed on silica gel (hexanes/ether, 9 : 1) to give benzoyltrimethylsilane as a yellow oil, b.p. 73–78°C at 1.5 mmHg (lit. [29] b.p. 84°C at 2 mmHg). ν_{max} 1614 (C=O), 1251, 841 cm^{-1} (C–Si). δ(H) 0.38 (s, $SiMe_3$); 7.40–7.60 (m, H(3), H(4)); 7.84 (dd, $J = 7.8$, 1.8 Hz, H(2)) ppm. δ(C) 0.2 ($SiMe_3$); 127.4 (C(2)); 128.6 (C(3)); 132.6 (C(4)); 141.3 (C(1)); 235.7 (C=O) ppm.

3.2. Tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]manganese (4)

A solution of $PhCH_2Mn(CO)_5$ [30] (4.1 g, 14.4 mmol) and benzoyltrimethylsilane (2.56 g, 14.4 mmol) in heptane (180 ml, distilled from CaH_2, degassed with argon) was heated under reflux for 2 h under argon, concentrated *in vacuo* to one-third volume, and flash chromatographed (hexanes) on silica gel to give tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]-manganese (4.06 g, 82%) as brown crystals, m.p. 37–40°C, or more commonly as a brown oil. Anal. Found: C, 49.7; H, 4.0%; $M^{+\cdot}$, 343.9915. $C_{14}H_{13}MnO_5Si.(0.1)C_5H_{12}$ calcd.: C, 49.5; H, 4.0%; *M*, 343.9913. ν_{max}(hexanes) 2079sh, 1980v br, 1933br (Mn–C≡O), 1576 (C=O); 1254, 845 (C–Si) cm^{-1}. δ(H) 0.40 (s, $SiMe_3$); 7.18 (t, $J = 7.4$ Hz, H(4)); 7.37 (dt, $J = 7.4$, 1.1 Hz, H(5)); 8.07 (br d, $J = 7.4$ Hz, H(6)); 8.15 (d, $J = 7.4$ Hz, H(3)) ppm. δ(C) -1.7 ($SiMe_3$); 123.6 (C(6)); 133.1 (C(3)); 133.2 (C(5)); 141.7 (C(4)); 153.4 (C(2)); 196.0 (C(1)); 211.7 (2C); 213.3, 221.3 (Mn–C≡O); 253.7 (*C*OSiMe$_3$) ppm. *m/z* 344 (6, M^+), 288 (3, $M - 2CO$), 260 (15, 288 − CO), 232 (91, 260 − CO), 177 (17, 232 − Mn), 104 (11, 177 − $SiMe_3$), 73 (100, $SiMe_3^+$), 55 (25, Mn^+).

3.3. Tetracarbonyl(2-formylphenyl-C^1,O^2)manganese (6)

Tetrabutylammonium fluoride in THF (1 mol l^{-1}, 0.35 ml, 0.35 mmol) was added to a solution of the manganese complex **4** (0.6 g, 1.73 mmol) in THF (15 ml). The orange-brown solution became deep green almost immediately. Water (10 drops) was added slowly and the mixture was stirred at room temperature for 50 min. The mixture was then concentrated *in vacuo* to one-third volume, and the solution was flash chromatographed on silica gel (hexanes/ether, 9 : 1) to give tetracarbonyl(2-formylphenyl-C^1,O^2)manganese (0.25 g, 54%) as orange-brown crystals, m.p. 39–41°C, or more commonly as a brown oil. Anal. Found: $M^{+\cdot}$, 271.9510. $C_{11}H_5O_5Mn$ calcd.: M, 271.9517). ν_{max} (hexanes) 2084sh, 1989v br, 1940br (Mn–C≡O), 1588 (C=O) cm^{-1}. δ(H) 7.22 (td, J_{obs} = 7.66, 0.74 Hz, H(4)); 7.46 (td, J_{obs} = 7.35, 1.33 Hz, H(5)); 7.93 (dd, J_{obs} = 7.60, 0.81 Hz, H(6)); 8.13 (br d, J_{obs} = 7.41 Hz, H(3)); 9.50 (s, CHO) ppm. δ(C) 124.3 (C(4)); 133.6 (C(3)); 134.7 (C(5)); 141.5 (C(6)); 146.7 (C(2)); 196.1 (C(1)); 208.0 (CHO); 211.1 (2C); 212.6, 221.1 (Mn–C≡O) ppm. m/z 272 (9, M^+), 254 (12, $M - H_2O$), 216 (8, M – 2CO), 188 (21, 216 – CO), 160 (100, 188 – CO), 105 (22, 160 – Mn), 55 (58, Mn^+).

An attempt to trap the acyl anion generated from **4** by treatment with $PhCH_2Br$ and then CsF/18-crown-6, gave, after 23 h at room temperature, only the aldehyde complex **6** (69%).

3.4. 4-Methoxybenzoyltrimethylsilane (2)

4-Methoxybenzoyltrimethylsilane was prepared *via* [(4-methoxyphenyl)methyl]trimethylsilane [6] and [dibromo(4-methoxyphenyl)methyl]trimethylsilane as a yellow liquid (lit. [31] b.p. 85°C at 0.1 mmHg). ν_{max} 1613 (C=O), 1261, 843 (C–Si) cm^{-1}. δ(H) 0.37 (s, $SiMe_3$); 3.85 (s, OMe); 6.95 (AA′BB′ “doublet”, J = 8.89, 2.70, 2.07, and 2.02, 2.78 Hz, H(3)); 7.84 (AA′BB′ “doublet”, J = 8.92, 2.70, 2.08 and 2.04, 2.76 Hz, H(2)) ppm. δ(C) (–1.4, $SiMe_3$); 55.2 (OMe); 113.7 (C(3)); 129.7 (C(2)); 135.1 (C(1)); 163.1 (C(4)); 232.6 ($COSiMe_3$) ppm.

3.5. Tetracarbonyl[(2-(5-methoxyphenyl))trimethylsilylmethanone-C^1,O^2]manganese (5)

A solution of $PhCH_2Mn(CO)_5$ (0.41 g, 1.43 mmol) and 4-methoxybenzoyltrimethylsilane (0.31 g, 1.45 mmol) in purified heptane (42 ml, distilled from CaH_2, degassed with argon) was heated under reflux for 70 min under argon. The mixture was then concentrated *in vacuo* to one-third volume, and the solution was flash chromatographed (hexanes) on silica gel to give tetracarbonyl[(2-(5-methoxyphenyl)trimethylsilylmethanone-C^1,O^2]manganese (0.50 g, 93%) as brownish yellow crystals, m.p. 68.5–69.5°C. Anal Found: C, 48.2; H, 4.2%; $M^{+\cdot}$ 374.003. $C_{15}H_{15}MnO_6Si$ calcd.: C, 48.1; H, 4.0%; M, 374.0018. ν_{max} (hexanes) 2080sh, 1995v br, 1943br (Mn–C≡O), 1581 (C=O), 1238, 846 (C–Si) cm^{-1}. δ(H) 0.35 (s, $SiMe_3$); 3.95 (s, OMe); 6.66 (dd, J = 8.6, 2.4 Hz, H(4)); 7.62 (d, J = 2.4 Hz, H(6)); 8.00 (d, J = 8.6 Hz, H(3)) ppm. δ(C) – 1.6 ($SiMe_3$); 55.4 (OMe); 111.1 (C(6)); 124.5 (C(4)); 134.7 (C(3)); 147.7 (C(2)); 162.8 (C(5)); 200.7 (C(1)); 211.9 (2C), 213.6, 221.3, (Mn – C≡O); 247.6 ($COSiMe_3$) ppm. m/z 374 (4, M^+), 290 (12, M – 3CO), 262 (100, 290 – CO), 207 (24, 262 – Mn), 134 (20, 207 – $SiMe_3$), 73 (68, $SiMe_3^+$), 55 (22, Mn^+).

3.6. General procedure for reaction of tetracarbonylmanganese complexes with an alkene or alkyne

A degassed solution of the tetracarbonylmanganese complex was either heated under reflux with the alkene or alkyne in dry benzene under nitrogen, or was stirred with Me_3NO in MeCN under nitrogen at room temperature for 5 min and then treated with the alkene or alkyne. The mixture was then filtered through a plug of silica gel and the eluate and washings (CH_2Cl_2) were concentrated to an oil. A degassed solution of the oil in MeCN–$CHCl_3$ was irradiated at 350 nm while flushing a steady stream of nitrogen through the system. Water (0.5–5 ml) was added and the mixture stirred under a stream of air for 1.5–2 h, and then filtered through a plug of silica gel. The concentrated (*in vacuo*) eluate and washings (CH_2Cl_2) were purified by flash chromatography on silica gel and/or PLC on silica gel.

3.7. Reaction of tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]manganese (4) with methyl propenoate

The complex **4** (1.0 g, 2.90 mmol) was reacted with methyl propenoate (0.31 ml, 3.44 mmol) in benzene (20 ml) for 2 h, followed by irradiation of the crude product in $CHCl_2$ (200 ml) and MeCN (200 ml) for 2 h and then exposure to air and water for 1.5 h. Flash chromatography followed by PLC (hexanes/ether) of the partially purified fractions gave (i) 2,3-dihydro-1*H*-inden-1-one (**7**) as a clear oil (1%). Anal. Found: $M^{+\cdot}$, 132.0575. C_9H_8O calcd.: M, 132.0575). ν_{max} 1715 (C=O) cm^{-1}. δ(H) 2.66 (AA′BB′ “triplet”, J = 5.6, 6.1 Hz, H(3)); 3.12 (AA′BB′ “triplet”, J = 5.6, 6.1 Hz, H(2)); 7.35 (t, J_{obs} = 7.3 Hz, H(6)); 7.46 (d, J_{obs} = 7.6 Hz, H(4)); 7.57 (td, J_{obs} = 7.3, 1.2 Hz, H(5)); 7.74 (d, J_{obs} = 7.7 Hz, H(7)) ppm. δ(C) 25.6 (C(3)); 36.0 (C(2)); 123.5 (C(7)); 126.5 (C(4)); 127.1 (C(6)); 134.4 (C(5)); 136.9 (C(7a)); 155.0 (C(3a)); 206.8 (C(1)) ppm. m/z 132 (100, M^+), 104 (97, M – CO); (ii) 1,2-diphenylethane (an artifact arising from coupling of benzyl radicals generated from traces of residual $PhCH_2Mn(CO)_5$) Anal. Found: $M^{+\cdot}$, 182.1093. $C_{14}H_{14}$ calcd.: M, 182.1096. δ(H) 2.91 (s, CH_2); 7.13–7.31 (m, ArH) ppm. δ(C) 37.9 (CH_2); 125.9, 128.3, 128.4 (aryl *C*H); 141.7 (C(1)) ppm. m/z 182 (27, M^+), 91 (100, $PhCH_2^+$); (iii) a mixture

(2 : 1) of diastereoisomers of methyl 1-trimethylsiloxyindane-2-carboxylate (**8**) as a pale yellow oil (29%). Anal. Found: $M^{+\cdot}$, 264.1172. $C_{14}H_{20}O_3Si$ calcd.: *M*, 264.1182. ν_{max} 1738 (C=O), 1251, 842 (C–Si) cm^{-1}. δ(H) 0.22 (s, $OSiMe_3$); 3.08 (dd, *J* = 14.1, 8.2 Hz, H(3)); 3.18 (ddd, *J* = 8.2, 8.2, 6.6 Hz, H(2)); 3.25 (dd, *J* = 14.1, 8.2 Hz, H(3)); 3.76 (s, CO_2Me); 5.54 (d, *J* = 6.6 Hz, H(1)); 7.16–7.25 (m, ArH) ppm. δ(C) 0.2 ($OSiMe_3$); 33.9 (C(3)); 51.8 (CO_2*Me*); 54.5 (C(2)); 79.2 (C(1)); 124.0 (C(6)); 124.5 (C(4)); 127.1 (C(7)); 128.2 (C(5)); 139.6 (C(3a)); 143.6 (C(7a)); 174.8 (*C*O_2Me) ppm. *m/z* 264 (8, M^+), 249 (16, *M* – Me), 204 (100, *M* – HCO_2Me), 189 (10, 204 – Me), 174 (22, 189 – Me), 159 (18, 174 – Me), 115 (38, $C_9H_7^+$), 89 (84, $OSiMe_3^+$), 73 (64, $SiMe_3^+$); (iv) one stereoisomer of methyl 1-hydroxyindane-2-carboxylate (**9**) (2%); (v) methyl 3-(2-trimethylsilylbenzoyl)propanoate (**12**) as a yellow oil (2%). Anal. Found: $M^{+\cdot}$, 264.1167. $C_{14}H_{20}O_3Si$ calcd.: *M*, 264.1182). ν_{max} 1738 (ester C=O), 1613 ($COSiMe_3$), 1250, 843 (C–Si) cm^{-1}. δ(H) 0.32 (s, $SiMe_3$); 2.62 (t, *J* = 7.7 Hz, C*H*$_2$$CO_2Me$); 3.04 (t, *J* = 7.7 Hz, C*H*$_2$$CH_2CO_2Me$); 3.65 (d, *J* = 1.06 Hz, CO_2Me); 7.07–7.38 (m, ArH) ppm. δ(C) 1.2 ($SiMe_3$); 28.9 (*C*H_2CO_2Me); 36.0 (*C*$H_2CH_2CO_2Me$); 51.5 (CO_2 *Me*); 126.0; 129.9, 130.9, 131.4 (aryl *C*H); 173.4 (*C*O_2Me) ppm; signals due to quaternary C and to *C*$OSiMe_3$ were not observed. *m/z* 264 (3, M^+), 249 (6, *M* – Me), 205 (24, *M* – CO_2Me), 204 (23, *M* – HCO_2Me), 115 (14, $C_9H_7^+$), 89 (34, $OSiMe_3^+$), 73 (100, $SiMe_3^+$); (vi) methyl 1*H*-indene-2-carboxylate (**13**) (2%) as needles, m.p. 68–74°C. Anal. Found: $M^{+\cdot}$, 174.0683. $C_{11}H_{10}O_2$ calcd.: *M*, 174.0681. ν_{max} 1715 (C=O) cm^{-1}. δ(H) 3.68 (d, *J* = 1.8 Hz, H(1)); 3.84 (s, CO_2Me); 7.31–7.37 and 7.49–7.54 (m, ArH); 7.72 (t, *J* = 1.8 Hz, H(3)) ppm. δ(C) 38.3 (C(1)); 51.6 (CO_2*Me*); 123.3 (C(5)); 124.2 (C(4)); 126.8 (C(7)); 127.6 (C(6)); 137.0 (C(2)); 141.2 (C(3)); 142.7 (C(7a)) *; 144.8 (C(3a))*; 165.4 (*C*O_2Me) ppm. *m/z* 174 (55, M^+), 159 (1, *M* – Me), 143 (22, *M* – OMe), 115 (100, *M* – CO_2Me); (vii) *cis* or *trans* methyl 1-hydroxyindane-2-carboxylate (**9**) (23%) (see later); (viii) methyl 3-[3-(methyl-1*H*-indene-2-carboxylate)]propanoate (**14**) as a yellow oil (13%). Anal. Found: $M^{+\cdot}$, 260.1036. $C_{15}H_{16}O_4$ calcd.: *M*, 260.1049. ν_{max} 1739, 1705 (C=O) cm^{-1}. δ(H) 2.65 (AA′BB′ "triplet", *J* = 7.5, 8.5 Hz, C*H*$_2$$CO_2Me$); 3.35 (AA′BB′ "triplet", *J* = 7.5, 8.5 Hz, C*H*$_2$$CH_2CO_2Me$); 3.67 (s, H(1)); 3.67 (s, CO_2*Me*); 3.84 (s, 2-CO_2Me); 7.34–7.58 (m, ArH) ppm. δ(C) 21.9 (*C*H_2CO_2Me); 33.1 (*C*$H_2CH_2CO_2Me$); 38.8 (C(1)); 51.3 (CO_2*Me*); 51.7 (CO_2*Me*); 121.2, 124.2, 126.7, 127.8 (aryl CH); 130.4, 143.7, 143.8, 154.0 (quaternary C); 165.7 (2-*C*O_2Me); 173.2 (*C*O_2Me). *m/z* 260 (25, M^+), 228 (73, *M* – MeOH), 200 (30, *M* – HCO_2Me), 186 (100, *M* – CH_3CO_2Me), 155 (42, 186 – OMe); and (ix) methyl 3-[2-(methyl-1*H*-indene-1-carboxylate)]propanoate (**18**) as a yellow oil (23%). Anal. Found: $M^{+\cdot}$, 260.1037. $C_{15}H_{16}O_4$ calcd.: *M*, 260.1049). ν_{max} 1738 (C=O) cm^{-1}. δ(H) 3.26–3.37 (m, C*H*$_2$$CO_2Me$ and C*H*$_2$$CH_2CO_2Me$); 3.67 (s, CO_2Me); 3.72 (s, CO_2Me); 3.87 (br s, H(1)); 6.26 (td, *J* = 7.5, 2.1 Hz, H(3)); 7.18–7.50 (m, ArH) ppm. δ(C) 34.5 (*C*H_2CO_2Me)*; 34.6 (*C*$H_2CH_2CO_2Me$)*; 45.7 (C(1)); 51.8 (CO_2*Me*); 52.0 (CO_2*Me*); 114.4 (C(3)); 120.4, 124.9, 126.8, 128.4 (aryl CH); 139.5, 142.6, 143.7 (quaternary C); 171.8 (*C*O_2Me); 173.4 (*C*O_2Me) ppm. *m/z* 260 (10, M^+), 228 (29, *M* – MeOH), 201 (26, *M* – CO_2Me), 200 (49, *M* – HCO_2Me), 186 (26, *M* – CH_3CO_2Me), 168 (60, 200 – MeOH), 141 (100, 200 – CO_2Me), 115 (37, $C_9H_7^+$).

The percentage distribution of these products was estimated from GLC data. The temperature of the GC column (HP-20M, polyethylene glycol, 25 m) was set at 80°C for 1.5 min, followed by an increment at a rate of 10°C min^{-1} to 120°C. The temperature was then held constant for 10 min before a second increment at a rate of 3°C min^{-1} to 190°C. The temperature was then held constant for a further 10 min.

The coupling reaction was repeated using either heptane, MeCN, MeOH, or THF as solvent under thermolysis conditions as above, as well as at room temperature in MeCN using Me_3NO to promote loss of CO. Analytical TLC indicated that the same product mixture was obtained in each case, but a longer time was needed for complete reaction.

3.8. *Reaction of tetracarbonyl[(2-(5-methoxyphenyl))trimethylsilylmethanone-C^1,O^2]manganese (5) with methyl propenoate*

Reaction of the complex **5** (84 mg, 0.224 mmol) with methyl propenoate (0.04 ml, 0.449 mmol) in dry benzene (4 ml) for 2.25 h and workup as above followed by GC and GC-MS analyses showed the presence of (i) methyl 5-methoxy-1-trimethylsiloxyindane-2-carboxylate (**10**) (13%). Anal. Found: $M^{+\cdot}$, 294.1314. $C_{15}H_{22}O_4Si$ calcd.: *M*, 294.1287. *m/z* 294 (27, M^+), 279 (32, *M* – Me), 234 (100, *M* – HCO_2Me), 204 (63, *M* – Me_3SiOH), 173 (40, 204 – OMe), 145 (55, 234 – $OSiMe_3$), 89 (40, $OSiMe_3^+$), 73 (68, $SiMe_3^+$); (ii) methyl 6-methoxy-1*H*-indene-2-carboxylate (**15**) (28%). Anal. Found: $M^{+\cdot}$, 204.0772. $C_{12}H_{12}O_3$ calcd.: *M*, 204.0786. *m/z* 204 (80, M^+), 173 (25, *M* – OMe), 145 (100, *M* – CO_2Me); (iii) methyl 6-methoxy-3-trimethylsilyl-1*H*-indene-2-carboxylate (**16**) (2%) (tentative). Anal.

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* May be interchanged.

Found: $M^{+\cdot}$, 276.1174. $C_{15}H_{20}O_3Si$ calcd.: M, 276.1182). m/z 276 (9, M^+), 261 (14, $M-\mathrm{Me}$), 217 (100, $M-\mathrm{CO_2Me}$), 203 (19, $M-\mathrm{SiMe_3}$), 73 (80, $\mathrm{SiMe_3^+}$); (iv) one stereoisomer of methyl 1-hydroxy-5-methoxyindane-2-carboxylate (**11**) (24%). Anal. Found: $M^{+\cdot}$, 222.0896. $C_{12}H_{14}O_4$ calcd.: M, 222.0892. m/z 222 (41, M^+), 204 (23, $M-\mathrm{H_2O}$), 163 (100, $M-\mathrm{CO_2Me}$), 162 (80, $M-\mathrm{HCO_2Me}$); (v) the other stereoisomer of methyl 1-hydroxy-5-methoxyindane-2-carboxylate (**11**) (17%). Anal. Found: $M^{+\cdot}$, 222.0895. $C_{12}H_{14}O_4$ calcd.: M, 222.0892. m/z 222 (58, M^+), 204 (100, $M-\mathrm{H_2O}$), 189 (75, 204 − Me), 145 (67, 204 − $\mathrm{CO_2Me}$); (vi) methyl 3-[3-(methyl 6-methoxy-1*H*-indene-2-carboxylate)]propanoate (**17**) (%). Anal. Found: $M^{+\cdot}$, 290.1174. $C_{16}H_{18}O_5$ calcd.: M, 290.1154. m/z 290 (29, M^+), 259 (22, $M-\mathrm{OMe}$), 258 (29, M-MeOH), 230 (9, $M-\mathrm{HCO_2Me}$), 216 (100, $M-\mathrm{CH_3CO_2Me}$), 185 (18, 216 − OMe).

The percentage composition of the product mixture was estimated from GLC data. The temperature of the GLC column was set at 80°C for 1.5 min, followed by an increment at a rate of 10°C $\mathrm{min^{-1}}$ up to 140°C. The temperature was then subjected to a second increment at a rate of 3°C $\mathrm{min^{-1}}$ up to 170°C, and then a final increment at a rate of 1.5°C $\mathrm{min^{-1}}$ up to 200°C. The temperature was then held constant for a further 20 min.

3.9. Reaction of tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]manganese (4) with diphenylethyne

Reaction of the complex **4** (0.10 g, 0.29 mmol) with diphenylethyne (0.11 g, 0.63 mmol) in dry benzene (4 ml) for 4.5 h, and workup as above followed by PLC (hexanes/ether, 23:2, two elutions) gave 2,3-diphenyl-1*H*-inden-1-one (**28**) (22%) as bright orange crystals, m.p. 147–151°C. Anal. Found: $M^{+\cdot}$, 282.1032. $C_{21}H_{14}O$ calcd.: M, 282.1045. ν_{max} 1705 (C=O) $\mathrm{cm^{-1}}$. δ(H) 7.14 (d, J = 7.21 Hz, ArH); 7.23–7.43 (m, ArH); 7.59 (d, J = 6.71 Hz, ArH) ppm. δ(C) 121.3, 123.0, 127.7, 128.1 (2C); 128.5 (2C); 128.8 (2C); 128.9, 129.3, 130.0 (2C); 133.4 (aryl CH); 129.0, 130.7, 132.4, 132.7, 145.3, 155.3 (aryl quaternary C); 196.5 (C=O) ppm.

3.10. Reaction of tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]manganese (4) with phenylethyne

Reaction of the complex **4** (0.98 g, 2.85 mmol) with phenylethyne (0.54 ml, 4.91 mmol) in benzene (35 ml) for 8.5 h, and irradiation-oxidation of the product in $CHCl_3$ (220 ml) and MeCN (220 ml) for 4 h followed by flash chromatography and then PLC (hexanes/ether) gave (i) 2,3-dihydro-2-phenyl-3-trimethylsilyl-1*H*-inden-1-one (**30**) as a yellow oil. Anal. Found: $M^{+\cdot}$, 280.1283. $C_{18}H_{20}OSi$ calcd.: M, 280.1283. ν_{max} 1714 (C=O), 1251, 853 (C–Si) $\mathrm{cm^{-1}}$. δ(H) 0.06 (s, $\mathrm{SiMe_3}$); 2.90 (d, J = 2 Hz, H(3)); 3.71 (d, J = 2 Hz, H(2)); 7.10–7.43 (m, ArH); 7.59 (t, J = 7.4 Hz, ArH); 7.77 (d, J = 7.7 Hz, ArH) ppm. δ(C) 0.2 ($\mathrm{SiMe_3}$); 39.8 (C(3)); 56.8 (C(2)); 125.0, 125.3, 126.3, 126.9, 127.3 (2 *ortho* C); 128.8 (2 *meta* C); 134.9 (aryl CH); 140.7 (C(7a)); 158.2 (C(3a)); 206.4 (C(1)) ppm. m/z 280 (82, M^+), 265 (10, $M-\mathrm{Me}$), 73 (100, $\mathrm{SiMe_3^+}$); (ii) 2-dichloromethyl-2,3-dihydro-2-phenyl-1*H*-inden-1-one (**31**) as a yellow oil. Anal. Found: $M^{+\cdot}$, 290.0266. $C_{16}H_{12}Cl_2O$ calcd.: M, 290.0265. ν_{max} 1715 (C=O) $\mathrm{cm^{-1}}$. δ(H) 3.87 (d, J = 17.8 Hz, H(3)); 4.02 (d, J = 17.8 Hz, H(3)); 6.58 (s, $\mathrm{CHCl_2}$); 7.25–7.75 (m, ArH) ppm. δ(C) 34.4 (C(3)); 64.9 (C(2)); 76.9 ($\mathrm{CHCl_2}$); 125.3, 126.1, 126.9 (2 *ortho* C); 128.0, 128.3, 128.8 (2 *meta* C); 135.7 (aryl CH); 152.4 (quaternary C) ppm; the other quaternary C were not detected. m/z 290 (31, M^+), 255 (68, $M-\mathrm{Cl}$), 219 (100, 255 − HCl), 191 (55, 219 − CO); (iii) 2,3-dihydro-2-hydroxy-2-phenyl-1*H*-inden-1-one (**32**) as a yellow oil (lit. [18] m.p. 127–128°C). Anal. Found: $M^{+\cdot}$, 224.0841. $C_{15}H_{12}O_2$ calcd.: M, 224.0837. ν_{max} 3398 (O–H), 1716 (C=O) $\mathrm{cm^{-1}}$. δ(H) 3.54 (d, J = 17.1 Hz, H(3)); 3.65 (d, J = 17.1 Hz, H(3)); 7.25–7.30 (m, ArH); 7.45 (t, J_{obs} = 7.6 Hz, H(6)); 7.51 (d, J_{obs} = 7.7 Hz, H(4)); 7.69 (td, J_{obs} = 7.5, 1.2 Hz, H(5)); 7.83 (d, J_{obs} = 7.6 Hz, H(7)) ppm. δ(C) 44.4 (C(3)); 81.3 (C(2)); 124.7 (2 *ortho* C); 125.3, 126.5, 127.8, 128.2, 128.6 (2 *meta* C); 136.1 (aryl CH); 134.4, 142.3, 151.9 (aryl quaternary C); 206.2 (C(1)) ppm. m/z 224 (43, M^+), 207 (3, $M-\mathrm{OH}$), 105 (100, $\mathrm{PhCO^+}$), 77 (34, $\mathrm{Ph^+}$); and a complicated mixture of unidentified products.

3.11. Reaction of tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]manganese (4) with ethene

Reaction of the complex **4** (1.05 g, 3.06 mmol) in MeCN (60 ml) with Me_3NO (0.35 g, 4.59 mmol) gave a red solution. After 5 min at room temperature, the solution was saturated with ethene and stirred under ethene (150–200 kPa) at room temperature for 25 h. Irradiation (MeCN, 300 ml) and oxidation as before followed by flash chromatography (hexanes/ether, 19:1, then 9:1, then 8:2, then 1:1) gave (i) 1*H*-inden-3-yltrimethylsilane (**37**) as a colourless oil (60 mg, 15%). ν_{max} 1249, 836 (C–Si) $\mathrm{cm^{-1}}$. δ(H) 0.30 (s, $\mathrm{SiMe_3}$); 3.40 (d, J = 1.7 Hz, H(1)); 6.75 (t, J = 1.7 Hz, H(2)); 7.13–7.31 (m, H(5), H(6)); 7.49 (d, J = 7.9 Hz, H(4)); 7.49 (d, J = 7.9 Hz, H(7)) ppm. δ(C) −1.1 ($\mathrm{SiMe_3}$); 40.7 (C(1)); 121.9 (C(4)); 123.7 (C(7)); 124.2 (C(6)); 126.5 (C(5)); 144.0 (C(2)); 144.6 (C(7a)); 145.2 (C(3a)); 148.0 (C(3)); (ii) 2,3-dihydro-1*H*-inden-1-one (**7**) as a colourless oil (170 mg, 42%).

On exposure to air **37** gave **7**.

3.12. Reaction of tetracarbonyl[trimethylsilyl(2-phenyl)methanone-C^1,O^2]manganese (4) with ethyne

Reaction of the complex **4** (0.6 g, 1.74 mmol) in MeCN (45 ml) with Me_3NO (0.2 g, 2.62 mmol) and then with ethyne (150–200 kPa) at room temperature for 4.5 h followed by flash chromatography on silica gel (hexanes/ether, 19:1, then 9:1, then 8:2) of the light-sensitive product gave (i) 1*H*-inden-1-one (**29**) as a pale yellow oil (lit. [32] b.p. 63–65°C at 1 mmHg) (44 mg, 19%). ν_{max} 1710 (C=O) cm^{-1}. δ(H) 5.89 (d, *J* = 5.96 Hz, H(2)); 7.06 (d, *J* = 7.14 Hz, ArH); 7.20–7.49 (m, ArH); 7.57 (dd, *J* = 5.96, 0.80 Hz, H(3)) ppm. δ(C) 122.2, 122.7, 127.2, 129.2, 133.7, 149.7 (CH) ppm; the quaternary C were not detected; (ii) 2,3-dihydro-1*H*-inden-1-one (**7**) as a colourless oil (50 mg, 1%).

On exposure to diffuse light, **29** rapidly gave the *cis, anti, cis* dimer **39**. Anal. Found: $M^{+\cdot}$, 260.0831. $C_{18}H_{12}O_2$ calcd.: *M*, 260.0837. δ(H) 3.85 (dd, *J* = 10.6, 6.2 Hz, cyclobutane H α to C=O); 4.31 (dd, *J* = 10.6, 6.2 Hz, cyclobutane H); 7.12–7.56 (m, ArH) ppm. *m/z* 260 (39, M^+), 232 (9, *M* – CO), 130 (100, $C_9H_6O^+$), 102 (23, 130–CO).

3.13. Reaction of tetracarbonyl(2-formylphenyl-C^1,O^2)manganese (6) with methyl propenoate

Reaction of the complex **6** (0.36 g, 1.30 mmol) with methyl propenoate (0.23 ml, 2.55 mmol) in benzene (12 ml) for 2.25 h, and irradiation-oxidation of the product in $CHCl_3$ (60 ml)/MeCN (60 ml) and flash chromatography (hexanes/ether, 9:1, then 8:2, then 1:1, then 3:7, then ether) gave (i) methyl 1*H*-indene-2-carboxylate (**13**) (23 mg, 10%) as white needles, m.p. 68–74°C; (ii) a mixture (41:9) of diastereoisomers of methyl 1-hydroxyindane-2-carboxylate (**41**) and (**42**) (53 mg, 23%) as white crystals, m.p. 35–60°C. Anal. Found: $M^{+\cdot}$, 192.0786. $C_{11}H_{12}O_3$ calcd.: *M*, 192.0786. ν_{max} 3449 (O–H), 1732 (C=O) cm^{-1}. *Cis* isomer **41** (major): δ(H) 2.95 (br s, OH); 3.07 (dd, *J* = 14.7, 7.0 Hz, H(3)); 3.36–3.41 (m, H(2), H(3)); 3.75 (s, CO_2Me); 5.31 (d, *J* = 5.4 Hz, H(1)); 7.21–7.28 (m, ArH); 7.40 (d, *J* = 7.0 Hz, H(7)) ppm. δ(C) 32.7 (C(3)); 49.4 (C(2)); 51.9 (CO_2*Me*); 75.8 (C(1)); 124.9 (C(6)); 125.2 (C(4)); 127.1 (C(7)); 129.0 (C(5)); 141.7 (C(3a))*; 142.5 (C(7a))*; 173.3 (*C*O_2Me) ppm. *m/z* 192 (6, M^+), 174 (100, *M* – H_2O), 159 (12, 174 – Me), 115 (73, 174 – CO_2Me). *Trans* isomer **42** (minor): δ(H) 3.20–3.25 (m, H(3)); 3.43–3.47 (m, H(2) and H(3)); 3.71 (s, CO_2Me); 5.44 (d, *J* = 6.5 Hz, H(1)) ppm. δ(C) 33.0, (C(3)); 52.0 (CO_2*Me*); 54.3 (C(2)); 78.4 (C(1)); 123.9, 124.5, 128.4 (aryl CH); 174.4 (*C*O_2Me) ppm; one aryl CH and both quaternary C were not detected; (iii) 5-[2-(2-methoxy-carbonylethyl)phenyl]4,5-dihydro-3*H*-furan-2-one (**43**) (21 mg, 9%). Anal. Found: $M^{+\cdot}$, 248.1043. $C_{14}H_{16}O_4$ calcd.: *M*, 248.1049. ν_{max} 1771 (lactone C=O), 1732 (ester C=O) cm^{-1}. δ(C) 27.0, 29.0, 30.4, 35.1 (CH_2); 51.8 (CO_2Me); 78.3 (lactone CH); 125.0; 127.1, 128.6, 129.2 (aryl CH); 137.1 (aryl quaternary C) ppm; one quaternary C and both carbonyl C were not detected. *m/z* 248 (19, M^+), 220 (23, *M* – CO), 216 (32, *M* – MeOH), 174 (64, *M* – CH_3CO_2Me), 161 (100, *M* – $CH_2CH_2CO_2Me$), 133 (94, 161 – CO).

An attempt to eliminate water from the crude product using dilute hydrochloric acid was unsuccessful.

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