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Journal of Organometallic Chemistry 634 (2001) 157–166

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Regioisomeric preferences in the orthomanganation of *meta*-substituted acetophenones and isopropyl benzoates, and application of iodo-demanganation with iodine chloride to the synthesis of 2-iodo-3-*O*-substituted and other *ortho*-iodo arylcarbonyl compounds

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Received 21 May 2001; accepted 28 July 2001

Abstract

Synthesis is reported of regioisomeric *ortho*-[$Mn(CO)_4$] derivatives of aryl ketones (2-chlorothioxanthen-9-one and 3′,4′-methylenedioxyacetophenone) and esters (isopropyl 3-methoxy- and 3-acetoxy-benzoate), as well as of the single *ortho*-[$Mn(CO)_4$] products from methyl 4-methoxy- and 3,5-dimethoxy-benzoate. Factors influencing the preference for manganation at the crowded positions *ortho* to the C=O in *meta*-substituted aryl ketones and esters are considered. The frequency of the lowest energy metal carbonyl stretching mode is useful in the structural assignment of the regioisomers. Isopropyl 2-iodo-3-methoxy- and 2-iodo-3-acetoxy-benzoates are obtained by reaction of iodine chloride to replace the $Mn(CO)_4$ group at the crowded 2-position of the corresponding orthomanganated 3-*O*-substituted benzoate esters. *ortho*-Iodoacetophenones were prepared likewise, without α-iodination, some with iodine in crowded positions (2′-iodo-3′-methoxy-, -3′,4′-methylenedioxy- and -3′,4′,5′-trimethoxy-acetophenone), others with *O*-protected 2′-hydroxy groups (2′-benzyloxy- and 2′-*t*-butyldimethylsilyloxy-3′,4′-dimethoxy-6′-iodobenzene and 2′-*t*-butyldimethylsiloxy-6′-iodobenzene). Potential general synthetic routes to derivatives of 2-iodo-3-hydroxy-, 2-iodo-3,4-dihydroxy-, and 2-iodo-6-hydroxy-aryl carbonyl compounds are indicated. The corresponding routes to 3-iodo-4-acetyl-2,5-dimethylthiophene and 3-iodo-2-acetylthiophene are also reported.

Keywords: Manganese; Cyclometallation; Metallacycle; Iodination; *o*-Iodoacetophenones; *o*-Iodobenzoic acid esters

1. Introduction and outline of current study

As first reported by Kaesz' group [1,2], aryl ketones can be cyclomanganated in the *ortho* position ('orthomanganation') with the tetracarbonylmanganese [$Mn(CO)_4$] group by reaction with methylpentacarbonylmanganese [1] or benzylpentacarbonylmanganese [2] (e.g. Scheme 1). The reactions are envisaged as involving prior coordination of $RMn(CO)_4$ to the ketone carbonyl, which delivers the substituting group to the adjacent ring position with release of RH. Intramolecular delivery may explain why steric constraints are not overriding in the 3′-substituted acetophenone series [1b,3]: with 3′-OMe (**1a**) [1b,3], 3′-F (**1b**) [3] and 3′-Cl (**1c**) [3], manganation occurs at the sterically crowded 2′-position to form isomer **2**, in preference to reaction at the 6′-position to form **3**. The product preference is reversed, but only a little, with bulky 3′-Br (**1d**) [3]. In contrast, for 3′-Me (**1e**), orthomanganation occurs almost exclusively at 6′-C [1b,3] and for 3′-CF_3 (**1f**) no substitution is detected in the crowded 2′-position [3], although the net yield (of the other isomer) is very low (11%) in this case. The preference for the sterically crowded site in the 3′-OMe case (**1a**) was suggested in the unpublished work [2] possibly to arise from the coordination of a lone pair on OMe in stabilising a complex such as that proposed in **4** with Mn held close to C-2 immediately prior to its

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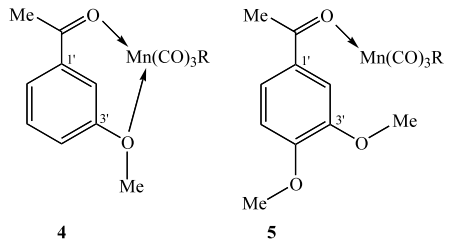
0022-328X/01/$ - see front matter
PII: S0022-328X(01)01174-3

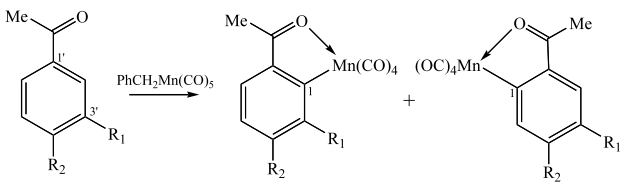
release as a 16-electron Ar–$Mn(CO)_3(R)$ species for oxidative addition at C-2. Reversal of the product ratio in the case of 3′,4′-dimethoxyacetophenone (**1g**) [4] would be consistent with inability of the 3′-OMe to effectively present a lone pair to the metal because the Me group on 3′-O would be rotated towards the metal coordination site so as to reduce the steric interaction with the 4′-OMe, as indicated in structure **5**; equally of course steric hindrance at the 2′-position would thereby be increased, though this is not an overriding limitation to reaction as the ease of orthomanganation of 3′,4′,5′-trimethoxyacetophenone [4,5] indicates. A steric component must nevertheless be invoked if the donor theory is to be extended to explain why the halo groups promote 2′-substitution, because fluorine, the poorest donor but smallest halogen, is the best *ortho*-directing group (**1b** vs. **1c** and **1d**). This suggests a reasonable alternative to the donor theory, which is that the 2′-position is activated to manganation by inductively electron-withdrawing groups in the 3′-position, with overlaying steric effects playing a role.



4 **5**

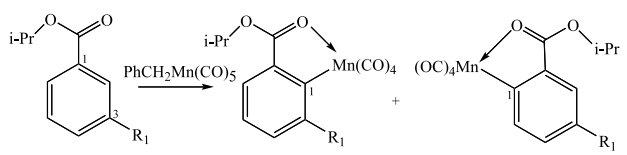
We now report on orthomanganation in the crowded position of other aryl carbonyl compounds including 3′,4′-methylenedioxyacetophenone (**1h**; Scheme 1) and *meta*-substituted isopropyl benzoates (Scheme 2). Also reported is orthomanganation of methyl 4-methoxybenzoate and methyl 3,5-dimethoxybenzoate.

The ease of subsequent replacement of $Mn(CO)_4$ by iodine using iodine chloride as first reported by us for orthomanganated 3′,4′,5′-trimethoxyacetophenone [5] is applied here, with particular interest in iodination at the manganated 2-position in 3-*O*-substituted benzoate esters (**7**) because this gives otherwise elusive crowded iodo compounds (**9**; Scheme 3) with applications in drugs synthesis (see Section 2). Also reported are the ICl reactions of the new orthomanganated ketone **2h** and of some other orthomanganated ketones we have previously synthesised [4] (refer to structures **15a**–**20a** in Section 2). They include examples chosen to check the success of routes to *ortho*-iodination products (**16b**–**18b**) of *O*-benzyl- and *O*-silyl-protected 2′-hydroxyacetophenones in the face of the restriction that orthomanganation of 2′-hydroxyacetophenones with a free OH group is unsuccessful [10], and, in the heteroaromatic area, of the acetylthiophene derivatives **19a** and **20a**.



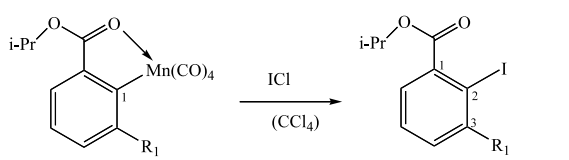
1	(R_1)	(R_2)	[reference]	**2** (% yield)	**3** (%yield)
a	OMe	H	[3]([7])	63 (62)	31 (23)
b	F	H	[3]	70	15
c	Cl	H	[3]([this study])	47 (42)	39 (37)
d	Br	H	[3]	27	38
e	Me	H	[3]	-	77
f	CF_3	H	[3]	-	11
g	OMe	OMe	[4]	20	60
h	O-CH_2-O		[this study]	86	~4

Scheme 1.



6 a R_1 = OMe **7 a** R_1 = OMe **8 a** R_1 = OMe
b R_1 = OC(O)Me **b** R_1 = OC(O)Me **b** R_1= OC(O)Me

Scheme 2.



7 a R_1 = OMe **9 a** R_1 = OMe
b R_1 = OC(O)Me **b** R_1= OC(O)Me

Scheme 3.

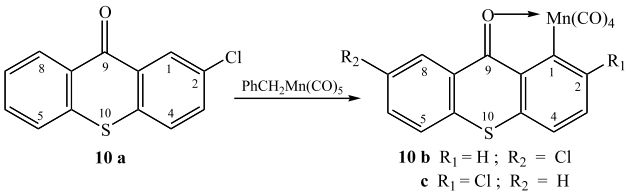
2. Results and discussion

2.1. Orthomanganation reactions

2.1.1. Ketones

Yields and isomer ratios for orthomanganation with $PhCH_2Mn(CO)_5$ were similar to those reported elsewhere in the cases of 3′-methoxyacetophenone [1b] and of 3′-chloroacetophenone [3] (Scheme 1). For comparison with the 3′-Cl case, we tested 2-chlorothioxanthen-9-one (**10a**; Scheme 4) in which the choice is between sites in different rings, and found the reaction to slightly favour the unsubstituted ring (C-8 over crowded C-1) but the ratio (**10b**–**10c**) was close to 1:1 as in the 3′-chloroacetophenone case.

For comparison with the 3′-methoxy (**1a**) and 3′,4′-dimethoxy (**1g**) cases, we studied 3′,4′-methylenedioxyacetophenone (**1h**) in which the donor lone pair on 3′-O



Scheme 4.

is locked into an orientation appropriate for the proposed [2] metal coordination (indicated in intermediate **11**; cf. **4**) at the now sterically less crowded 2′-position: the ca. 20:1 preference for substitution in the 2′-position now is much more dominant than for the 3′-OMe (**1a**) case itself. This reveals some consistency in the trend in ratio across the series 3′,4′-methylenedioxy (20:1), 3′-methoxy (2:1) and 3′,4′-dimethoxy (1:3), irrespective of whether it is a donor effect or an inductive effect of the 3′-substituent, modified by steric influence, which is primarily responsible for the directive effect.

2.1.2. Esters

An early unpublished report [2] showed that, whereas orthomanganation of methyl benzoate is very inefficient, with isopropyl benzoate an 85% yield is obtained. Therefore, although we did find as reported here that two methyl esters, methyl 4-methoxybenzoate and methyl 3,5-dimethoxybenzoate, gave good yields (74 and 87%, respectively) of their orthomanganation products **12a** and **12b**, isopropyl esters were used in the present 3-substituted benzoate study with the intention of maximising yields prior to iodination (see below).

Isopropyl 3-methoxybenzoate (**6a**) undergoes manganation with $PhCH_2Mn(CO)_5$ (Scheme 2) in 53% yield at the 2-position to form **7a** and 39% at the 6-position to form **8a**, the ratio being similar to that for 3′-methoxyacetophenone (**1a**). The effect of reduced donor ability of the 3-O atom was tested with the reaction of isopropyl 3-acetoxybenzoate (**6b**) in which the aryl-O in $O–COCH_3$ will be a weaker donor than that in $O–CH_3$ because of the electron-withdrawing effect of the acetyl group. However, with a similar overall yield (89%), an even stronger preference (8:1) for manganation in the site adjacent to the substituent group (**7b**) showed that lone pair donor ability of the oxygen atom bonded to the 3-position is not paramount in determining the reactivity. On first sight, this would seem to support the alternative theory, that the directive effect of the 3-substituent is an inductive one, because $O–COCH_3$ will be a better $-I$ group with respect to C-2 than $O–CH_3$. It is possible, however, that the 3-$OCOCH_3$ group coordinates with Mn via the carbonyl oxygen thereby promoting a more favourable arrangement [six-membered ring in the proposed intermediate (**13**) vs. the apparently less favourable four-membered (cf. **4**)] for it to attack at C-2. Any such coordination is not, however, retained in the product (see Section 2.2).

2.2. Infrared spectra including structural assignment of orthomanganation regioisomers

If assistance in manganation at the 2-position is provided by the acetate carbonyl (**13**), the metal is nevertheless coordinated in the final product by only the benzoate ester C=O, as shown by the large shift (122 cm^{-1}) in its $\nu_{C=O}$ relative to parent non-metalated ester and by the minor effect on the acetate carbonyl (9 cm^{-1} shift in $\nu_{C=O}$). Similar large metal-induced shifts in $\nu_{C=O}$ of all the coordinating ketone and ester groups in the cyclometalated ring are observed for all the other complexes, as has previously been discussed [1b,6]. However, more subtle diagnostic data lie in the metal carbonyl stretching frequencies. As typical of previously reported *cis*-$L_2Mn(CO)_4$ complexes [1b,6], three metal carbonyl bands are observed. Four bands are predicted for *cis*-$L_2M(CO)_4$ with local C_{2v} symmetry but for orthomanganated derivatives the middle two bands are commonly accidentally degenerate [1b], though there are occasional exceptions, as in the manganated isopropyl esters **7a** and **7b** studied here. It is the lowest frequency band in the range 1940–60 cm^{-1} which has empirical diagnostic value. It is consistently noted that the crowded isomer formed by manganation at the acetophenone 2′-position has a lowest frequency $\nu_{C=O}$ value which is higher than that in the isomer manganated in the remote 6′-position. The magnitude of the shift is similar (10–16 cm^{-1}) across the range of halogens (**2b**–**d** vs. **3b**–**d**) and the oxygen substituents OMe (**2a** vs. **3a**, **2g** vs. **3g**) and $–OCH_2O–$ (**2h** vs. **3h**); it applies also to the esters **7a** versus **8a**. The one exception is with the acetoxy group in the isopropyl 3-acetoxybenzoate case where the shift is only 4 cm^{-1} (**7b** vs. **8b**). The shift is consistent enough to suggest that it may be used diagnostically as a guide to structural assignment in other cases, i.e. the isomer with the lowest $\nu_{C=O}$ is likely to be the uncrowded (6′-manganated) isomer. Such generality is supported by a similar shift (12 cm^{-1}) with the manganated 2-chlorothioxanthen-9-one isomers (**10c** vs. **10b**) when the metal is in alternative rings adjacent to, or remote from, Cl. Related to this case and that for 3′,4′-dimethoxyacetophenone is the result for 2,4,5-triethoxybenzophenone which was found to give ca. 30% substitution at the 6-position adjacent to the 4,5-diethoxy grouping and ca. 60% at the 2′-position in the unsubstituted ring [7]. In this case, a shift of 8 cm^{-1} was observed, but because the products could not be separated, the direction of the shift is not definite. It should be noted that the shift as a guide to regioisomer structure applies only where the substituent is electronegative halogen or oxygen; the small shift in the case of the isomeric manganated 3′-methylacetophenones (**2e**, prepared using $MeMn(CO)_5$ [1b], and **3e**), is in the reverse direction.

2.3. NMR spectra

Structural assignments based on chemical shifts and coupling constants are well established for proton and carbon NMR spectra [1b,6], allowing for unambiguous structural assignment of isomers in the present study (see Section 3).

^{13}C-NMR metal carbonyl signals are broadened, probably because of coupling with ^{17}O and ^{55}Mn quadrupoles [8], allowing them to be easily distinguished from the coordinated ketone carbonyl. The signal at lowest field (ca. 220 ppm) is consistently to lower field in the uncrowded isomer but by only a bare 1–2 ppm, so this shift is likely to be much less reliable in structural diagnosis than the carbonyl frequency shift in the infrared.

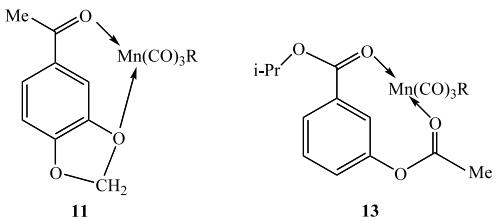
2.4. Synthesis of 3-substituted-2-iodoarylcarbonyl compounds

Iodination to replace manganese (iodo-demanganation) at the sterically crowded manganation sites in the ketone complexes (**2a**, **2h**) and the ester complexes (**7a**, **7b**) was tested using the electrophilic reagent iodine chloride in carbon tetrachloride [5] to see how well it competed with iodo-deprotonation at other uncrowded positions available, especially those activated to electrophilic substitution. Reactions were quite slow at room temperature and some were incomplete on workup (see Section 3) so increasing the reaction time and/or the reagent concentrations employed in this initial standard survey should allow improved yields in their cases. The important finding from this initial study was that in almost all cases iodine was substituted specifically into the manganated positions, even if strongly sterically crowded, and this strongly enhances the value of this synthetic route.

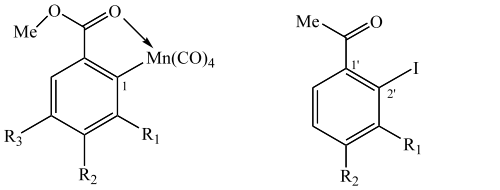
2.4.1. Orthomanganated 3-substituted acetophenones with ICl

For the 3′-methoxyacetophenone case (**2a**), an excellent 89% yield of the product iodinated in the crowded manganated position (**14a**) is obtained.

The one exception to specificity in iodination site was found in the case of the 2′-manganated 3′,4′-methylenedioxyacetophenone (**2h**) which gave 2′-iodo-3′,4′-methylenedioxyacetophenone (**14b**; 63%) but also a small amount (12%) of product of iodination at either the 5′- or the 6′-position, with replacement of $Mn(CO)_4$ at the 2′-position by H. Application of standard substituent increments [9] on proton or carbon signals was indecisive in assignment between the 5′- and 6′-isomers. The presence of two activating oxygen substituents in the aromatic ring would increase the reactivity with electrophiles at the unsubstituted 5′- and 6′-positions, and the HCl produced may be responsible for protiodemanganation at the manganated carbon; it is possible that this happens to some extent before the complete reaction, i.e. some of the wayward iodination may occur at the 5′- or 6′-site subsequent to demetalation. From the final product ratio, the manganated carbon is at least five times the more reactive with ICl, but a better fix on the relative reactivities (and possibly a better yield of 2′-iodinated product) might in future be obtained by carrying out the reaction in the presence of a trap for HCl, e.g. propylene oxide. In the case of the ketones, another possible proton-releasing reaction is iodination at the reactive α-carbon of the $COCH_3$ group. However, there was no sign of α-iodo contaminant here, nor in the 2′-iodo-3′,4′,5′-trimethoxyacetophenone formed from orthomanganated 3′,4′,5′-trimethoxyacetophenone (**15a**) as described in Section 2.4.3. This contrasts with the occurrence of some α-bromination in the corresponding reaction with Br_2 [6,10].



11 **13**



12 a R_2 = OMe; R_1 = R_2 = H
b R_1 = R_3 = OMe; R_2 = H

14 a R_1 = OMe; R_2 = H
b R_1, R_2 = OCH_2O

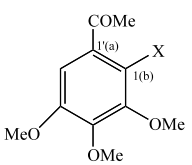
2.4.2. Orthomanganated esters with ICl

Of particular synthetic value in the present study is the highly specific route to 2-iodo-3-hydroxybenzoate derivatives, as represented by **9a** and **9b**. Under the non-optimised conditions used in this exploratory study, **9a** was obtained in 74% yield with recovery of 18% unreacted **7a**, and **9b** in a yield of 49% with recovery of 35% unreacted **7b**. Clearly the yields should be improved with longer reaction times and/or higher reactant concentrations. Such iodo compounds have been important as precursors of many bioactive compounds obtained via aryl–aryl coupling reactions at the crowded iodo-substituted carbon, e.g. a synthesis of the antibiotic gilvocarcin [11] incorporated a multi-step synthesis of 2-iodo-3-methoxy-5-methylbenzyl alcohol [12], followed by oxidation to 2-iodo-3-methoxy-5-methylbenzoic acid. Esterification with a C-glycosidic-α-naphthol allowed for the key intramolecular Pd(II)-promoted coupling of the naphthyl β-carbon to

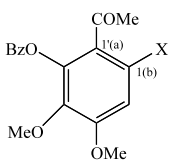
the iodinated aryl carbon. A similar coupling strategy exists in the Jourdan–Ullmann condensation of 3-substituted-2-iodobenzoic acids with 2-aminophenylacetic acids to form analogues of the colon tumour active agent xanthenone-4-acetic acid [13]. When electrophilic nitration at the crowded 2-position of 3-hydroxybenzoic acids competes well with substitution in the much less crowded but similarly activated 4- and 6-positions, reaction with HNO_3 may provide a relatively straightforward entry to 2-iodo compounds via amino and diazonium intermediates, but the manganation route may be preferred for its mild reaction conditions and when directive effects of other ring substituents are likely to influence the orientation of nitration. In this context, it should be noted that the orthomanganated complexes are air-stable compounds which can be chromatographed and handled without any special precaution.

2.4.3. Synthesis of other ortho-iodo aryl methyl ketones

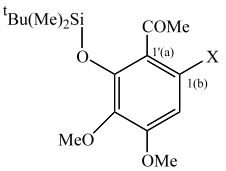
A selection of aryl methyl ketones iodinated at positions not generally accessible by direct electrophilic substitution, which would generally favour the position *meta* to the ketone group, have been synthesised (**15b**–**20b**). The reactions were carried out under standardised conditions in this initial survey and yields have not been optimised. The reactions are slow (days at room temperature; see Section 3) but this is more than compensated for by the specificity of the site of iodination. There is some potential in the manganation route to *ortho*-iodination of 2′-*O*-protected-acetophenones (**16a**–**18a**) to provide a source of new 6′-iodinated-2′-hydroxyacetophenones after removal of the protective group. The thiophene derivatives **19b** and **20b** may have applications in aryl coupling reactions in the heteroaromatic area.



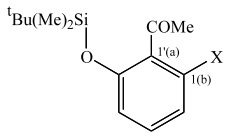
15 a X= $Mn(CO)_4$
b X = I



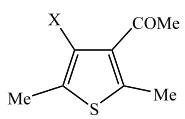
16 a X= $Mn(CO)_4$
b X = I



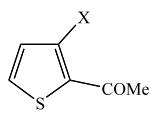
17 a X= $Mn(CO)_4$
b X = I



18 a X= $Mn(CO)_4$
b X = I



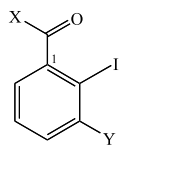
19 a X= $Mn(CO)_4$
b X = I



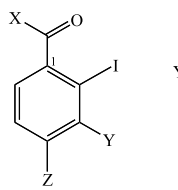
20 a X= $Mn(CO)_4$
b X = I

2.5. Summary: potential synthetic applications of the manganation–iodination sequence

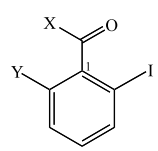
Based on the current results, the manganation–iodination route to 3-substituted-2-iodophenylcarbonyl compounds should be applicable to the synthesis of many types of compounds not accessible by direct iodination as indicated in **21**, including the 3-OH case by removal of acetyl or other protective group. Likewise acetal- or ketal-protected 3,4-dihydroxy systems analogous to the methylenedioxy compound **2h** should allow entry by removal of the protective group to 3,4-di-OH and otherwise di-*O*-substituted compounds as indicated by **22** in both the ketone and ester series (the latter convertible to carboxylic acid by hydrolysis), with the proviso that iodination may also lead to some 5′- or 6′-iodo isomer as observed with **2h**. 6′-Iodo-2′-hydroxyacetophenone derivatives and the corresponding 6-iodo-2-hydroxybenzoates (**23**) should also be generally accessible by these routes, subject to limitations with the specificity of iodination when there are additional ring substituents.



21 X = R, OR, OH
Y = OR, OCOR, OH, etc.



22 X = R, OR, OH
Y,Z = $OC(R)_2O$
or Y = Z = OH, etc.



23 X = R, OR, OH
Y= OH, etc.

3. Experimental

3.1. General

Infrared spectra were recorded in hexane in a Digilab FTS-45 instrument and mass spectra in a Varian MAT CH5 spectrometer. NMR spectra in $CDCl_3$ with Me_4Si internal standard were recorded in a Bruker AC-300; for a few compounds spectral assignments could not be unambiguously assigned to all signals and in these cases the symbols * or # are used to denote pairs of alternative assignments. Elemental analyses were carried out at the University of Otago Microanalytical Laboratory. Preparative chromatography was carried out on 1 mm layers of silica (Merck Kieselgel $60PF_{254+}$ 366).

Benzylpentacarbonylmanganese was prepared from $Mn_2(CO)_{10}$ by the standard method [14]. Syntheses of orthomanganated complexes other than those below has been previously described [4]. New complexes were prepared using $PhCH_2Mn(CO)_5$ and organic substrates under reflux in heptane under nitrogen, normally over 2–3 h, followed by chromatographic purification as described in the illustrative example for **10** below. Organic reagents were sourced from Aldrich with the exception of the benzoate esters which were prepared without yield optimisation from 3-hydroxybenzoic acid as follows.

3.2. Synthesis of esters

3.2.1. Isopropyl 3-hydroxybenzoate

3-Hydroxybenzoic acid (30 g, 0.217 mol), isopropyl alcohol (170 ml, 2.17 mol) and conc. H_2SO_4 (2.7 ml) were heated under reflux for 18.5 h. After removal of excess alcohol the residue was added to water (100 ml) and extracted with Et_2O (40 ml, 2×10 ml). The Et_2O solution was washed with saturated $NaHCO_3$ solution, then water and dried over $MgSO_4$. Solvent removal and recrystallisation from hot EtOH gave *isopropyl 3-hydroxybenzoate* as white chunky crystals, m.p. 55.5–57 °C. ^{1}H-NMR: δ 7.61 (1H, dt, $^3J_{6,5} = 7.9$ Hz, $^4J_{6,4} = {}^4J_{6,2} = 1.3$ Hz, H-6), 7.55 (1H, dd, $^4J_{2,4} = 2.7$ Hz, $^4J_{2,6} = 1.3$ Hz, H-2), 7.30 (1H, t, $^3J_{5,4} = {}^3J_{5,6} = 7.9$ Hz, H-5), 7.04 (1H, ddd, $^3J_{4,5} = 7.9$ Hz, $^4J_{4,2} = 2.7$ Hz, $^4J_{4,6} = 1.3$ Hz, H-4), 5.39 (1H, s, br, 3-OH), 5.24 (1H, m, $^3J = 6.2$ Hz, 1-COOC*H*$(CH_3)_2$), 1.36 (6H, d, $^3J = 6.2$ Hz, 1-COOCH(C*H*$_3)_2$). ^{13}C-NMR: δ 166.9 (s, 1-*C*OOCH$(CH_3)_2$), 156.2 (s, C-3), 131.9 (s, C-1), 129.7 (d, C-5), 121.7 (d, C-6), 120.4 (d, C-4), 116.5 (d, C-2), 69.2 (d, 1-COO*C*H$(CH_3)_2$), 21.9 (q, 1-COOCH(*C*H$_3)_2$).

3.2.2. Isopropyl 3-methoxybenzoate

Isopropyl 3-hydroxybenzoate (4 g, 0.022 mol), K_2CO_3 (6.06 g, 0.044 mol) and MeI (2.75 ml, 0.044 mol) were heated under reflux in acetone (AR, 100 ml) overnight. The solution was filtered and after removal of solvent the residue was added to water (100 ml) and extracted with Et_2O (1×40 ml, 2×20 ml). The Et_2O solution was washed successively with NaOH (2 mol l^{-1}) and water, and dried over $MgSO_4$. Solvent removal gave *isopropyl 3-methoxybenzoate* as a colourless liquid (3.20 g, 75%), pure by ^{1}H-NMR. ^{1}H-NMR: δ 7.62 (1H, dt, $^3J_{6,5} = 8.0$ Hz, $^4J_{6,4} = {}^4J_{6,2} = 1.2$ Hz, H-6), 7.55 (1H, dd, $^4J_{2,4} = 2.7$ Hz, $^4J_{2,6} = 1.2$ Hz, H-2), 7.32 (1H, t, $^3J_{5,6} = {}^3J_{5,4} = 8.0$ Hz, H-5), 7.07 (1H, ddd, $^3J_{4,5} = 8{:}0$ Hz, $^4J_{4,2} = 2.7$ Hz, $^4J_{4,6} = 1.2$ Hz, H-4), 5.24 (1H, m, $^3J = 6.2$ Hz, 1-COOC*H*$(CH_3)_2$), 3.83 (3H, s, 3-OCH3), 1.36 (6H, d, $^3J = 6.2$ Hz, 1-COOCH(C*H*$_3)_2$). ^{13}C-NMR: δ 165.9 (s, 1-*C*OOCH$(CH_3)_2$), 159.6 (s, C-3), 132.3 (s, C-1), 129.3 (d, C-5), 121.9 (d, C-6), 119.0 (d, C-4), 114.1 (d, C-2), 68.4 (d, 1-COO*C*H$(CH_3)_2$), 55.3 (q, 3-OCH$_3$), 21.9 (q, 1-COOCH(*C*H$_3)_2$).

3.2.3. Isopropyl 3-acetoxybenzoate

Isopropyl 3-hydroxybenzoate (4.16 g, 0.023 mol) and Ac_2O (3.27 ml, 0.035 mol) were stirred overnight in Py (10 ml). The residue was poured into water (100 ml) and extracted with Et_2O (40 ml, 2×20 ml). The combined Et_2O extract was washed with HCl (2 mol l^{-1}), NaOH (2 mol l^{-1}), then water, and dried over $MgSO_4$. Ether removal gave *isopropyl 3-acetoxybenzoate* as a very pale yellow liquid (4.05 g, 79%), pure by ^{1}H-NMR. ^{1}H-NMR: δ 7.91 (1H, dt, $^3J_{6,5} = 7.9$ Hz, $^4J_{6,4} = {}^4J_{6,2} =$ 1.2 Hz, H-6), 7.73 (1H, dd, $^4J_{2,4} = 2.5$ Hz, $^4J_{2,6} = 1.2$ Hz, H-2), 7.43 (1H, t, $^3J_{5,6} = {}^3J_{5,4} = 7.9$ Hz, H-5), 7.26 (1H, ddd, $^3J_{4,5} = 7.9$ Hz, $^4J_{4,2} = 2.5$ Hz, $^4J_{4,6} = 1.2$ Hz, H-4), 5.24 (1H, m, $^3J = 6.3$ Hz, 1-COOC*H*$(CH_3)_2$), 2.31 (3H, s, 3-OCOCH$_3$), 1.35 (6H, d, $^3J = 6.3$ Hz, 1-COOCH$(CH_3)_2$). ^{13}C-NMR: δ 169.3 (s, 3-O*C*OCH$_3$), 165.1 (s, 1-COOCH$(CH_3)_2$), 150.6 (s, C-3), 132.5 (s, C-1), 129.3 (d, C-5), 127.0 (d, C-6), 126.1 (d, C-4), 122.8 (d, C-2), 68.8 (d, 1-COO*C*H$(CH_3)_2$), 21.9 (q, 1-COOCH(*C*H$_3)_2$), 21.1 (q, 3-OCO*C*H$_3$).

3.3. Orthomanganation reactions

3.3.1. Standard method for orthomanganation

2-Chlorothioxanthene-9-one (**10a**, 0.126 g, 0.511 mmol) and $PhCH_2Mn(CO)_5$ (0.175 g, 0.613 mmol) were dissolved in heptane (AR, 25 ml) and the solution degassed and flushed with nitrogen several times. After refluxing under nitrogen for 90 min, the heptane was removed under vacuum. The resultant orange solid was dissolved in CH_2Cl_2 and chromatographed on silica plates with 1:10 v/v Et_2O–petroleum spirit; b.p. 60–80 °C as the eluent. A broad bright orange band was extracted to give η^2-(7-chlorothioxanthen-9-on-1-yl)tetracarbonylmanganese (**10b**) (0.108 g, 51%) which was crystallised from petroleum spirit as orange feathers, m.p. 143.5–145 °C. Anal. Found: C, 49.29; H, 1.62. Calc. for $C_{17}H_6O_5ClMnS$: C, 49.48; H, 1.47%. IR: ν(CO) 2083 (m), 1997 (vs, br), 1946 (s). ^{1}H-NMR: δ 8.52 (1H, dd, $^4J_{8,6} = 2.1$ Hz, $^5J_{8,5} = 0.9$ Hz, H-8), 8.14 (1H, dd, $^3J_{2,3} = 7.1$ Hz, $^4J_{2,4} = 1.0$ Hz, H-2), 7.64–7.63 (2H, m, H-5,6), 7.51 (1H, dd, $^3J_{3,4} = 8.0$ Hz, $^3J_{3,2} = 7.1$ Hz, H-3), 7.39 (1H, dd, $^3J_{4,3} = 8.0$ Hz, $^3J_{4,2} = 1$ Hz, H-4). ^{13}C-NMR: δ 221.0 (s, br, CO), 213.2 (s, br, CO), 211.2 (s, $2 \times$ CO), 194.3 (s, C-9), 193.5 (s, C-1), 139.9 (s, C-4a), 139.0 (d, C-2), 138.2 (s, C-10a), 137.1 (s, C-9a), 133.4 (d, C-6), 132.8 (s, C-7), 132.5 (d, C-3), 128.9 (s, C-8a), 128.9 (d, C-8), 127.5 (d, C-5), 120.2 (d, C-4). A second band yielded η^2-(1-(2-chlorothioxanthen-9-on-1-yl)tetracarbonylmanganese [(**10c**); 82 mg, 39%) which crystallised from petroleum spirit as yellow needles, m.p. 136 °C (dec.). Anal. Found: C, 49.51; H, 1.26. Calc. for $C_{17}H_6O_5ClMnS$: C, 49.48; H, 1.47%. IR: ν(CO) 2085 (m), 1999 (vs, br), 1958 (s). ^{1}H-NMR: δ 8.53 (1H, dt, $^3J_{8,7} = 8.2$ Hz, $^4J_{8,6} = {}^5J_{8,5} = 0.9$ Hz, H-8), 7.72–7.69 (2H, m, H-5,6), 7.61 (1H, d, $^3J_{3,4} = 8.4$ Hz, H-3), 7.56–7.51 (1H, m, H-7), 7.35 (1H, d, $^3J_{4,3} = 8.4$ Hz, H-4). ^{13}C-NMR: δ 219.6 (s, br, CO), 214.8 (s, br, CO), 210.6 (s, $2 \times$ CO), 194.7 (s, C-9), 189.3 (s, C-1), 146.2 (s, C-2), 139.4 (s, C-10a), 138.1 (s, C-9a), 137.9 (s, C-4a), 133.4 (d, C-6), 133.3 (d, C-3), 129.8 (d, C-8), 127.8 (s, C-8a), 126.7 (d, C-7), 126.0 (d, C-5), 122.4 (d, C-4).

The following orthomanganated complexes were similarly prepared and purified.

From 3′-chloroacetophenone (**1c**; 179 mg, 1.158 mmol) and $PhCH_2Mn(CO)_5$ (397 mg, 1.389 mmol) under reflux overnight were obtained:

(i) η^2-(2-Acetyl-6-chlorophenyl)tetracarbonylmanganese [(**2c**); 156 mg, 42%] which crystallised from hexane–Et_2O as small yellow–orange regular crystals, m.p. 106–107.5 °C (lit. 105–107 °C [3]). IR: ν(CO) 2088 (m), 1998 (vs, br), 1961 (s). ^{1}H-NMR: δ 7.73 (1H, d, $^3J_{3,4} = 7.6$ Hz, H-3), 7.53 (1H, d, $^3J_{5,4} = 7.6$ Hz, H-5), 7.12 (1H, t, $^3J_{4,3} = {}^3J_{4,5} = 7.6$ Hz, H-4), 2.60 (3H, s, 2-COCH$_3$). ^{13}C-NMR: δ 219.7 (s, br, CO), 217.2 (s, 2-COCH$_3$), 210.8 (s, br, 2 × CO), 189.9 (s, C-1), 149.5 (s, C-6), 146.4 (s, C-2), 134.6 (d, C-5), 129.5 (d,C-3), 125.8 (d, C-4), 25.1 (q, 2-CO*C*H$_3$); one metal carbonyl signal not observed. (ii) η^2-(2-acetyl-4-chlorophenyl)-tetracarbonylmanganese [(**3c**); 137 mg, 37%] which crystallised from hexane–Et_2O as small yellow–orange regular crystals, m.p. 131–133 °C (lit. 132–134 °C [3]. IR: ν(CO) 2085 (m), 1997 (vs, br), 1949 (s). ^{1}H-NMR: δ 88.02 (1H, d, $^3J_{6,5} = 7.9$ Hz, H-6), 7.81 (1H, d, $^4J_{3,5} = 2.1$ Hz, H-3), 7.39 (1H, dd, $^3J_{5,6} = 7.9$ Hz, $^4J_{5,3} = 2.1$ Hz, H-5), 2.61 (3H, s, 2-COCH$_3$). ^{13}C-NMR: δ 221.0 (s, br, CO), 216.2 (s, 2-*C*OCH$_3$), 211.0 (s, br, 2 × CO), 191.6 (s, C-1), 146.4 (s, C-2), 142.4 (d, C-6), 133.7 (d, C-5), 130.9 (d, C-3), 130.5 (s, C-4), 24.7 (q, 2-CO*C*H$_3$); one metal carbonyl signal not observed.

From 3′,4′-methylenedioxyacetophenone (**1h**, 145 mg, 0.883 mmol) and PhCH$_2$Mn(CO)$_5$ (303 mg, 1.060 mmol) under reflux over 2.5 h were obtained:

(i) η^2-(6-Acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese [(**2h**); 251 mg, 86%] which crystallised from hexane–Et_2O as yellow feathers, m.p. 121–122.5 °C. Anal. Found: C, 47.30; H, 2.19. Calc. for $C_{13}H_7O_7Mn$: C, 47.30; H, 2.14%. IR: ν(CO) 2086 (m), 1997 (vs), 1960 (s). ^{1}H-NMR: δ 7.58 (1H, d, $^3J_{5,4} = 8.0$ Hz, H-5), 6.67 (1H, d, $^3J_{4,5} = 8.0$ Hz, H-4), 6.09 (2H, s, 2-OCH$_2$O-3), 2.53 (3H, s, 6-COCH$_3$). ^{13}C-NMR: δ 219.9 (s, br, CO), 213.4 (s, 6-COCH$_3$), 211.0 (s, br, 2 × CO), 163.1 (s, C-1), 157.9 (s, C-2), 149.8 (s, C-3), 141.2 (s, C-6), 129.4 (d, C-5), 105.4 (d, C-4), 100.7 (t, 2-OCH$_2$O-3), 24.2 (q, 6-CO*C*H$_3$); one metal carbonyl signal not observed. MS; m/z: 330 (6.7, [P$^+$]), 274 (7.5, [P$^+$ − 56], [P$^+$ − 2CO]), 246 (15.0, [P$^+$ − 84], [P$^+$ − 3CO]), 218 (100, [P$^+$ − 112], [P$^+$ − 4CO]). (ii) η^2-(2-Acetyl-4,5-methylenedioxyphenyl)tetracarbonylmanganese [(**3h**); 11 mg, ∼4%) as a yellow oil. IR: ν(CO) 2082 (m), 1997 (vs, br), 1944 (s).

From isopropyl 3-methoxybenzoate (**6a**; 319 mg, 1.64 mmol) and PhCH$_2$Mn(CO)$_5$ (564 mg, 1.97 mmol) under reflux over 5 h were obtained:

(i) η^2-(2-Methoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese [(**7a**); 313 mg, 53%] which crystallised from hexane–Et_2O as yellow needles, m.p. 82.5–83.5 °C. IR: ν(CO) 2083 (m), 1993 (vs), 1955 (s). ^{1}H-NMR: δ 7.38 (1H, d, $^3J_{5,4} = 7.6$ Hz, H-5), 7.12 (1H, t, $^3J_{4,3} = {}^3J_{4,5} = 7.6$ Hz, H-4), 6.91 (1H, d, $^3J_{3,4} = 7.6$ Hz, H-3), 5.20 (1H, m, $^3J = 6.2$ Hz, 6-COOC*H*(CH$_3$)$_2$), 3.85 (3H, s, 2-OCH$_3$), 1.35 (6H, d, $^3J = 6.2$ Hz, 6-COOCH(C*H*$_3$)$_2$). ^{13}C-NMR: δ 220.6 (s, br, CO), 214.3 (s, br, CO), 211.9 (s, br, 2 × CO), 179.9 (s, C-1), 170.9 (s, 6-*C*OOCH(CH$_3$)$_2$), 167.6 (s, C-2), 136.4 (s, C-6), 125.5 (d, C-4), 121.7 (d, C-5), 113.8 (d, C-3), 72.1 (d, 6-COO*C*H(CH$_3$)$_2$), 55.5 (q, 2-OCH$_3$), 21.8 (q, 6-COOCH(*C*H$_3$)$_2$). (ii) η^2-(4-Methoxy-2-isopropoxycarbonylphenyl)tetracarbonylmanganese [(**8a**); 229 mg, 39%] a yellow oil which failed to crystallise. IR: ν(CO) 2083 (m), 1994 (vs), 1991 (s), 1944 (s). ^{1}H-NMR: δ 67.82 (1H, d, $^3J_{6,5} = 8.1$ Hz, H-6), 7.28 (1H, d, $^4J_{3,5} =$ 2.6 Hz, H-3), 7.15 (1H, dd, $^3J_{5,6} = 8.1$ Hz, $^4J_{5,3} = 2.6$ Hz, H-5), 5.23 (1H, m, $^3J = 6.2$ Hz, 2-COOC*H*(CH$_3$)$_2$), 3.83 (3H, s, 4-OCH$_3$), 1.35 (6H, d, $^3J = 6.2$ Hz, 2-COOCH(C*H*$_3$)$_2$). ^{13}C-NMR: δ 221.5 (s, br, CO), 213.0 (s, br, CO), 212.1 (s, br, 2 × CO), 179.6 (s, C-1), 171.5 (s, 2-*C*OOCH(CH$_3$)$_2$), 157.5 (s, C-4), 141.2 (d, C-6), 135.2 (s, C-2), 122.6 (d, C-5), 113.1 (d, C-3), 72.3 (d, 2-COO*C*H(CH$_3$)$_2$), 55.4 (q, 4-OCH$_3$), 21.8 (q, 2-COOCH(*C*H$_3$)$_2$).

From isopropyl 3-acetoxybenzoate (**6b**; 385 mg, 1.73 mmol) and PhCH$_2$Mn(CO)$_5$ (595 mg, 2.08 mmol) under reflux over 3 h were obtained:

(i) η^2-(2-Acetoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese [(**7b**); 533 mg, 79%] a yellow oil which failed to crystallise. Anal. Found: C, 49.74; H, 3.53. Calc. for $C_{16}H_{13}O_8Mn$: C, 49.50; H, 3.38%. IR: ν(CO) 2090 (m), 2006 (s), 1994 (s), 1948 (s). ^{1}H-NMR: δ 7.65 (1H, m, second order coupling, H-5), 7.21–7.15 (2H, m, second order coupling, H-3,4), 5.23 (1H, m, $^3J = 6.2$ Hz, 6-COOC*H*(CH$_3$)$_2$), 2.30 (311, s, 2-OCOCH$_3$), 1.36 (6H, d, $^3J = 6.2$ Hz, 6 COOCH(C*H*$_3$)$_2$). ^{13}C-NMR: δ 220.9 (s, br, CO), 213.5 (s, br, CO), 210.5 (s, br, 2 × CO), 179.7 (s, C-1), 172.6 (s, 2-O*C*OCH$_3$), 170.6 (s, 6-*C*OOCH(CH$_3$)$_2$), 160.4 (s, C-2), 137.1 (s, C-6), 127.5 (d, C-5), 127.0 (d, C-4), 125.5 (d, C-3), 72.7 (d, 6-COOCH(CH$_3$)$_2$), 21.8 (q, 6-COOCH(CH$_3$)$_2$), 21.1 (q, 2-OCOCH$_3$). (ii) η^2-(4-Acetoxy-2-isopropoxycarbonylphenyl)tetracarbonylmanganese [(**8b**); 69 mg, 10%], a yellow oil which failed to crystallise. IR: ν(CO) 2083 (m), 1995 (s, br), 1944 (s). ^{1}H-NMR: δ 7.93 (1H, d, $^3J_{6,5} = 8.0$ Hz, H-6), 7.46 (1H, d, $^4J_{3,5} = 2.4$ Hz, H-3), 7.17 (1H, dd, $^3J_{5,6} = 8.0$ Hz, $^4J_{5,3} = 2.4$ Hz, H-5), 5.23 (1H, m, $^3J = 6.2$ Hz, 2-COOC*H*(CH$_3$)$_2$), 2.31 (3H, s, 4-OCOCH$_3$), 1.35 (6H, d, $^3J = 6.2$ Hz, 2-COOCH(C*H*$_3$)$_2$). ^{13}C-NMR: δ 221.2 (s, br, CO), 212.7 (s, br, CO), 211.5 (s, br, 2 × CO), 180.2 (s, C-1), 179.3 (s, 4-O*C*OCH$_3$), 169.7 (s, 2-*C*OOCH(CH$_3$)$_2$), 148.1 (s, C-4), 141.4 (d, C-6), 135.6 (s, C-2), 127.2 (d, C-5), 121.6 (d, C-3), 72.6 (d, 2-COO*C*H(CH$_3$)$_2$), 21.8 (q, 2-COOCH(*C*H$_3$)$_2$), 21.2 (q, 4-OCO*C*H$_3$).

From methyl 4-methoxybenzoate (113 mg, 0.68 mmol)) and PhCH$_2$Mn(CO)$_5$ (233 mg, 0.82 mmol) under reflux over 3 h was obtained η^2-(5-methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese (**12a**, 226 mg, 74%) which crystallised from hexane–Et_2O as yellow feathers, m.p. 105–107 °C. Anal. Found: C, 46.83; H, 2.69. Calc. for $C_{13}H_90_7Mn$: C, 47.01; H,

2.73%. IR: ν(CO) 2085 (m), 1996 (vs, br), 1944 (s). ^{1}H-NMR: δ 7.66 (1H, d, $^3J_{3,4} = 88$ Hz, H-3), 7.45 (1H, d, $^4J_{6,4} = 2.3$ Hz, H-6), 6.63 (1H, dd, $^3J_{4,3} = 8.8$ Hz, $^4J_{4,6} = 2.3$ Hz, H-4), 3.93 (3H, s, 2-COOCH$_3^*$), 3.92 (3H, s, 5-OCH$_3^*$). ^{13}C-NMR: δ 221.4 (s, br, CO), 213.2 (s, br, CO), 212.0 (s, br, 2 × CO), 187.8 (s, C-1), 179.9 (s, 2-COOCH$_3$), 163.9 (s, C-5), 130.7 (d, C-3), 127.0 (s, C-2), 124.2 (d, C-6), 111.4 (d, C-4), 55.3 (q, 5-OCH$_3$), 53.9 (q, 2-COOCH$_3$). MS; m/z: 332 (4.2, [P$^+$]), 276 (4.2, [P$^+$ − 2CO]), 248 (17.5, [P$^+$ − 3CO]), 220 (100, [P$^+$ − 4CO]).

From methyl 3,5-dimethoxybenzoate (134 mg, 0.683 mmol) and PhCH$_2$Mn(CO)$_5$ (234 mg, 0.82 mmol) under reflux over 2.75 h was obtained η^2-(2,4-dimethoxy-6-methoxycarbonylphenyl)tetracarbonylmanganese (**12b**, 247 mg, 87%) which crystallised from hexane–Et$_2$O as orange blocks, m.p. 108–109 °C. Anal. Found: C, 46.44; H, 2.87. Calc. for $C_{14}H_{11}O_8Mn$: C, 46.43; H, 3.06%. IR: ν(CO) 2084 (m), 1992 (vs, br), 1954 (s). ^{1}H-NMR: δ 6.92 (1H, d, $^4J_{5,3} = 2.1$ Hz, H-5*), 6.60 (1H, d, $^4J_{3,5} = 2.1$ Hz, H-3*), 3.95 (3H, s, 6-COOCH$_3^{\#}$), 3.82 (3H, s, 2-OCH$_3^{\#}$), 3.80 (3H, s, 4-OCH$_3^{\#}$). ^{13}C-NMR: δ 220.8 (s, br, CO), 214.3 (s, br, CO), 211.9 (s, br, 2 × CO), 180.4 (s, 6-COOCH$_3$), 168.1 (s, C-2*), 161.1 (s, C-1*), 159.4 (s, C-4), 134.8 (s, C-6), 104.5 (d, C-5$^{\#}$), 104.3 (d, C-3$^{\#}$), 55.5 (q, 2- and 4-OCH$_3$), 54.2 (q, 6-COO*C*H$_3$). MS; m/z: 362 (2.6, [P$^+$]), 306 (1.9, [P$^+$ − 2CO]), 278 (13.3, [P$^+$ − 3CO]), 250 (100, [P$^+$ − 4CO]).

3.4. Iodo-demanganation reactions with ICl

The standard iodination method is described here for the preparation of 2′-iodo-3′,4′,5′-trimethoxyacetophenone (**15b**) [5] and other preparations follow in numerical order of iodination product:

η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (**15a**; 0.151 g, 0.40 mmol) was dissolved in nitrogen-saturated CCl_4 (2 ml). A freshly prepared solution of ICl (0.065 g, 0.40 mmol) in nitrogen-saturated CCl_4 (2 ml) was added. The flask was stoppered and left at room temperature for 4 days after which time the colour of ICl had disappeared and an orange precipitate was visible. The solid was removed by filtration: it was identified by IR as mainly [IMn(CO)$_4$]$_2$ [15]. The filtrate solvent was removed under vacuum, and the residue chromatographed on a silica layer (3:7 Et$_2$O–light petroleum, b.p. 60–80 °C) to give 2′-iodo-3′,4′,5′-trimethoxyacetophenone (**15b**; 0.125 g, 93%) as a colourless oil. Recrystallisation from hexane gave white needles, m.p. 54 °C. Anal. Found: C, 39.31; H, 3.90. Calc. for $C_{11}H_{13}IO_4$: C, 39.35; H, 3.97%. ^{1}H-NMR: δ 6.75 (s, 1H, 6′-H), 3.86 (s, 3H, OCH$_3$), 3.84 (s, 6H, 2 × OCH$_3$), 2.58 (s, 3H, COCH$_3$). ^{13}C-NMR: δ 202.0 (s, CO), 153.8 (s, 3′-C), 153.5 (s, 5′-C), 147.8 (s, 4′-C), 141.0 (s, 1′-C), 107.8 (d, 6′-C), 79.8 (s, 2′-C), 60.93 (q, OCH$_3$).

η^2-(2-Methoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese (**7a**) was reacted similarly with ICl for 6 days to give 18% recovery of **7a** and 74% isopropyl 2-iodo-3-methoxybenzoate (**9a**), a colourless oil. ^{1}H-NMR: δ 7.29 (1H, t, $^3J_{5,4} = {}^3J_{5,6} = 7.9$ Hz, H-5), 7.14 (1H, dd, $^3J_{6,5} = 7.9$ Hz, $^3J_{6,4} = 1.3$ Hz, H-6), 6.86 (1H, dd, $^3J_{4,5} = 7.9$ Hz, $^4J_{4,6} = 1.3$ Hz, H-4), 5.25 (1H, m, $^3J = 6.3$ Hz, 1-COOC*H*(CH$_3$)$_2$), 3.85 (3H, s, 3-OCH$_3$), 1.37 (6H, d, $^3J = 6.3$ Hz, 1-COOCH(C*H*$_3$)$_2$). ^{13}C-NMR: δ 167.3 (s, 1-*C*OOCH(CH$_3$)$_2$), 158.6 (s, C-3), 139.8 (s, C-1), 129.3 (d, C-5), 122.0 (d, C-6), 112.7 (d, C-4), 86.2 (s, C-2), 69.7 (d, 1-COO*C*H(CH$_3$)$_2$), 56.8 (q, 3-OCH$_3$), 21.9 (q, 1-COOCH(*C*H$_3$)$_2$). MS; m/z: 278 ([P$^+$ − C(CH$_3$)$_2$]).

η^2-(2-Acetoxy-6-isopropoxycarbonylphenyl)tetracarbonylmanganese (**7b**) was reacted similarly with ICl for 3 days, giving 35% recovery of **7b** and isopropyl 2-iodo-3-acetoxy-2-iodobenzoate (**9b**; 49%), a colourless oil. ^{1}H-NMR: δ 7.53 (1H, dd, $^3J_{6,5} = 7.9$ Hz, $^4J_{6,4} = 1.5$ Hz, H-6), 7.36 (1H, t, $^3J_{5,4} = {}^3J_{5,6} = 7.9$ Hz, H-5), 7.15 (H, dd, $^3J_{4,5} = 7.9$ Hz, $^4J_{4,6} = 1.5$ Hz, H-4), 5.25 (1H, m, $^3J = 6.3$ Hz, 1-COOC*H*(CH$_3$)$_2$), 2.36(H, s, 3-OCOCH$_3$), 1.37 (6H, d, $^3J = 6.3$ Hz, 1-COOCH(C*H*$_3$)$_2$). ^{13}C-NMR: δ 168.5 (s, 3-O*C*OCH$_3$), 166.1 (s, 1-*C*OOCH(CH$_3$)$_2$), 152.1 (s, C-3), 138.9 (s, C-1), 129.1 (d, C-5), 127.8 (d, C-6), 125.3 (d, C-4), 91.6 (d, C-2), 69.9 (d, 1-COO*C*H(CH$_3$)$_2$), 21.9 (q, 1-COOCH(*C*H$_3$)$_2$), 21.3 (q, 3-OCO*C*H$_3$). MS; m/z: 289 ([P$^+$ − OCH(CH$_3$)$_2$]).

η^2-(6-Acetyl-2-methoxyphenyl)tetracarbonylmanganese (**2a**) was reacted similarly with ICl for 5 days to give 2′-iodo-3′-methoxyacetophenone (**14a**; 0.103 g, 89%), a colourless oil. Anal. Found: C, 39.63; H, 3.36; I, 46.05. Calc. for $C_9H_90_2I$: C, 39.16; H, 3.29; I, 45.97%. ^{1}H-NMR: δ 7.31 (1H, t, $^3J_{5',4'} = {}^3J_{5',6'} = 8.0$ Hz, H-5′), 6.88 (1H, dd, $^3J_{6',5'} = 8.0$ Hz, $^4J_{6',4'} = 1.1$ Hz, H-6′), 6.84 (1H, dd, $^3J_{4',5'} = 8.0$ Hz, $^4J_{6',4'} = 1.1$ Hz, H-4′), 3.87 (3H, s, 3′-OCH$_3$), 2.56 (3H, s, H-2). ^{13}C-NMR: δ 203.4 (s, C-1), 158.3 (s, C-3), 148.0 (s, C-1′), 129.8 (d, C-5′), 119.5 (d, C-6′), 112.1 (d, C-4′), 83.0 (s, C-2′), 56.8 (q, 3′-OCH$_3$), 30.1 (q, C-2). MS; m/z: 276 [P$^+$].

η^2-(6-Acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese (**2h**) was reacted similarly with ICl for 5 days, giving 12% recovery of **2h** and a mixture containing 2′-iodo-3′,4′-methylenedioxyacetophenone (**14b**; 63% from **2h** by ^{1}H-NMR) and either the 5′- or 6′-iodo isomer of 3′,4′-methylenedioxyacetophenone (12% from **2h**). The major and expected isomer 2′-iodo-3′,4′-methylenedioxyacetophenone (**14b**) was obtained pure by fractional crystallisation from benzene–heptane as white crystals, m.p. 114 °C. Anal. Found: C, 37.34; H, 2.77; I, 43.62. Calc. for $C_9H_7O_3I$: C, 37.27; H, 2.43; I, 43.75%. ^{1}H-NMR: δ 7.29 (1H, d, $^3J_{6',5'} = 8.1$ Hz, H-6′), 6.77 (1H, d, $^3J_{5',6'} = 8.1$ Hz, H-5′), 6.10 (2H, s, 3′-OCH$_2$O-4′), 2.59 (3H, s, COCH$_3$). ^{13}C-NMR: δ

198.0 (s, C-1), 151.1 (s, C-3′*), 148.3 (s, C-4′*), 134.7 (s, C-1′), 125.6 (d, C-6′), 107.4 (d, C-5′), 101.0 (t, 3′-OCH_2O-4′), 69.9 (s, C-2′), 28.8 (q, C-2). MS; m/z: 290 [P^+].

The other isomer could not be obtained pure from the crystallisation residue. It had the following spectral characteristics which did not allow distinction between the 5′- and 6′-iodinated isomer of 3′,4′-(methylenedioxy)acetophenone: ^{1}H-NMR: δ 7.35 (1H, s), 7.04 (1H, s), 5.99 (2H, s, $-CH_2-$), 2.52 (3H, s, $-COCH_3$). ^{13}C-NMR: δ 199.7 (s, $-COCH_3$), 150.3 (s), 148.2 (s), 136.3 (s), 120.4 (d), 109.0 (d), 102.4 (t), 81.5 (s), 29.2 (q, $-COCH_3$).

η^2-(2-Acetyl-3-benzyloxy-4,5-dimethoxyphenyl)tetracarbonylmanganese (**16a**) was reacted and worked up similarly after 4 days even though the colour of ICl had not fully disappeared. Bands of the preparative layer silica plate were unreacted orthomanganated ketone (30%) and 2′-benzyloxy-3′,4′-dimethoxy-6′-iodoacetophenone (**16b**; 63%), white crystals, m.p. 86.5–87.5 °C. Anal. Found: C, 49.64; H, 4.33. Calc. for $C_{17}H_{17}IO_4$: C, 49.53; H, 4.16%. ^{1}H-NMR: δ (s, br, 5H, PhH), 7.09 (s, 1H, 5′-H), 5.03 (s, 2H, OCH_2PhPhP), 3.86 (s, 6H, $2 \times OCH_3$), 2.43 (s, 3H, $COCH_3$). ^{13}C-NMR: δ 202.6 (s, CO), 154.4 (s, 4′-C), 149.0 (s, 2′-C), 142.4 (s, 3′-C), 136.5 (s, 1′-C), 128.2 (d, Ph), 128.0 (d, Ph), 118.3 (d, 5′-C), 81.7 (s, 6′-C), 76.2 (t, OCH_2Ph), 60.74 (q, OCH_3), 56.19 (q, OCH_3), 31.02 (q, $COCH_3$).

η^2-(2-Acetyl-3-*t*-butyldimethylsiloxy-4,5-dimethoxyphenyl)tetracarbonylmanganese (**17a**) was reacted similarly with ICl to give 2′-*t*-butyldimethylsiloxy-3′,4′-dimethoxy-6′-iodoacetophenone (**17b**; 95%), white crystals, m.p. 86.5–87.5 °C. Anal. Found: C, 44.11; H, 5.83. Calc. for $C_{16}H_{25}IO_4Si$: C, 44.04; H, 5.83%. ^{1}H-NMR: δ 7.10 (s, 1H, 5′-H), 3.92 (s, 3H, OCH_3PhP), 3.86 (s, 3H, OCH_3), 2.56 (s, 3H, $COCH_3$), 0.97 (s, 9H, *t*-Bu–H), 0.16 (s, 6H, Me_2Si). ^{13}C-NMR: δ 203.1 (s, CO), 154.2 (s, 4′-C), 145.8 (s, 2′-C), 140.2 (s, 3′-C), 133.6 (s, 1′-C), 116.3 (d, 5′-C), 82.3 (s, 6′-C), 60.4 (q, OCH_3), 56.2 (q, OCH_3), 31.4 (q, $COCH_3$), 25.8 (q, $[CH_3]_3C$)), 18.4 (s, $[CH_3]_3C$), −4.36 (q, $[CH_3]_2Si$).

η^2-(2-Acetyl-3-*t*-butyldimethylsiloxyphenyl)tetracarbonylmanganese (**18a**) was reacted similarly with ICl, but because a preliminary test reaction had indicated very sluggish reaction, the solution was exposed to strong sunlight for 6 h and then left to stand for 15 h. There was 43% recovery of unreacted manganated compound and a 45% yield of 2′-*t*-butyldimethylsiloxy-6′-iodoacetophenone (**18b**), a colourless oil, >95% pure by NMR, but which would not crystallise. ^{1}H-NMR: δ 7.43 (dd, $J = 7.0$, 1.5 Hz, 1H, Ar–H), 6.90 (m, 2H, Ar–HPhP), 2.54 (s, 3H, $COCH_3$), 0.97 (s, 9H, *t*-Bu–H), 0.23 (s, 6H, Me_2Si). ^{13}C-NMR: δ 203.8 (s, CO), 151.8 (s, 2′-C), 139.3 (s, 1′-C), 131.6 (d, 4′-C*), 130.7 (d, 5′-C*), 118.6 (d, 3′-C), 90.1 (s, 6′-C), 30.8 (q, $COCH_3$), 25.5 (q, $[CH_3]_3C$)), 18.0 (s, $[CH_3]_3C$), −4.36 (q, $[CH_3]_2Si$).

η^2-(2,5-Dimethyl-4-acetylthien-3-yl)tetracarbonylmanganese (**19a**) was reacted similarly with ICl for 24 h to give 3-acetyl-2,5-dimethyl-4-iodothiophene (**19b**) as a white solid (100%). Recrystallisation from hexane gave fine white needles, m.p. 45.5–46.5 °C. Anal. Found: C, 34.53; H, 3.11. Calc. for C_8H_9IOS: C, 34.30; H, 3.24%. ^{1}H-NMR: δ 2.62 (s, 3H, CH_3PhP), 2.55 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 198.2 (s, CO), 141.6 (s, 5-C), 140.3 (s, 2-C), 136.0 (s, 3-C*), 31.5 (q, $COCH_3$), 18.1 (q, 5-CH_3), 15.2 (q, 2-CH_3), (arylC–I signal obscured under solvent signal). ^{13}C-NMR (CD_3COCD_3): δ 198.0 (s, CO), 142.7 (s, 5-C), 140.2 (s, 2-C*), 136.6 (s, 3-C*), 79.3 (s, 4-C), 31.5 (q, $COCH_3$), 18.1 (q, 5-CH_3), 14.9 (q, 2-CH_3); methyl ketone quartet obscured beneath solvent signal.

η^2-(2-Acetylthieny-3-yl)tetracarbonylmanganese (**20a**) was reacted similarly with ICl for 24 h to give 2-acetyl-3-iodothiophene (**20b**) [16] as a pale yellow solid (75%). Recrystallisation from hexane gave white crystals, m.p. 59–60 °C. Anal. Found: C, 28.52; H, 2.02. Calc. for C_6H_5IOS: C, 28.59; H, 2.02%. ^{1}H-NMR: δ 7.45 (d, $J = 4.8$ Hz, 1H, 5-HPhP), 7.25 (d, $J = 4.8$ Hz, 1H, 4-H), 2.67 (s, 3H, $COCH_3$). ^{13}C-NMR: δ 189.6 (s, CO), 140.3 (s, 2-C), 139.6 (d, 4-C), 132.9 (d, 5-C), 83.6 (s, 3-C), 29.5 (q, $COCH_3$).

Acknowledgements

Research funding support from the Research Committee of the University of Waikato is gratefully acknowledged, as is the scholarship support from the William Georgetti Foundation to J.M.C.

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