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Reactions of orthomanganated aryl ketones with SO_2: synthesis and structural characterisation of a novel six-membered metallocyclic ring and a new route to aryl sulfonates

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Abstract

SO_2 inserts into the Mn–C bond of orthometallated derivatives of substituted acetophenones, benzophenone or 2-acetylthiophene to give complexes **2** which have six-membered metallocyclic rings incorporating an S-sulfinate group. The X-ray structural determinations of two examples of the new species **2** show the ring to be strongly puckered. Some of the complexes **2** undergo a facile conversion to a dimeric species **3**, shown by an X-ray structure analysis to have been formed from two molecules of **2** by mutual displacement of a CO ligand from one Mn atom by an S=O group from the other molecule. This provides a six-membered Mn–S–O–Mn–S–O core to the molecule. Oxidative demetallation of the SO_2-inserted species **2** with H_2O_2 gives the corresponding aryl-sulfinates or -sulfonates.

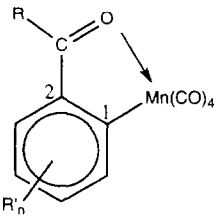
Keywords: Manganese; Metallocycle; Aryl sulfonates; Aryl ketones; Crystal structure

1. Introduction

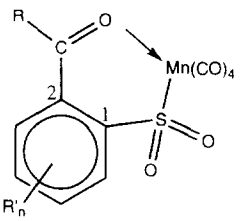
The reaction of aromatic ketones with $PhCH_2Mn(CO)_5$ to give orthomanganated derivatives of type **1** has proved to be very general [1]. The manganese derivatives have in turn been shown to have applications in organic synthesis. Thus, reactions with alkenes give both coupled and cyclised products [2], reactions with alkynes lead to cyclopenta-annulation species [3], while organic isocyanates give phthalimidines [4]. For all of these reactions reasonable mechanisms can be proposed which involve insertion of the unsaturated species into the Mn–C bond as a key step.

To extend the range of this type of reaction, we turned our attention to SO_2. The insertion of SO_2 into the metal–carbon bond of coordinatively saturated transition metal alkyls and aryls has been systematically studied [5]. Insertion can, in principle, generate several types of linkage. Although the usual product is an S-sulfinate, reactions may also give O-alkyl-S-sulfoxylates, O-sulfinates or O,O′-sulfinates [5]. Specifically, for $RMn(CO)_5$ (R = Me, Et, CH_2Ph) compounds, SO_2 was found [6] to insert readily into the metal–alkyl carbon bond to yield the S-sulfinato complexes $RS(O)_2Mn(CO)_5$. In contrast, the aryl species $PhMn(CO)_5$ gave an insertion product only under forcing conditions and in low yields [6].

This earlier chemistry indicated that insertion of SO_2 into the Mn–C bond of orthomanganated aryl ketones might provide a useful method for introducing a sulfur



(1)



(2)

1a. R = Me R'_n = 5-OMe
1b. R = Me R'_n = H
1c. R = Me R'_n = 5-Cl
1d. R = Me R'_n = 3,4,5-$(OMe)_3$
1e. R = Ph R'_n = H

2a. R = Me R'_n = 5-OMe
2b. R = Me R'_n = H
2c. R = Me R'_n = 5-Cl
2d. R = Me R'_n = 3,4,5-$(OMe)_3$
2e. R = Ph R'_n = H

Scheme 1.

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functionality into the *ortho* position of an aromatic ring. This paper describes some of these insertion reactions, and subsequent rearrangements and oxidations of the insertion products.

2. Experimental details

NMR spectra were recorded in $CDCl_3$ as solvent. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on either a Bruker AC300 instrument or a Jeol FX-90Q instrument. Full NMR assignments were made using 2D-COSY, XHCORR, BIRDTRAP, XHBIRD and NOE experiments. IR spectra were recorded in solution cells (KBr windows) with CH_2Cl_2 as solvent (unless otherwise stated) on a Digilab FTS-45 FTIR instrument. Electron impact mass spectra were recorded on a Varian MAT CH5 instrument, while electrospray mass spectra (ESMS) were recorded on a VG Platform II mass spectrometer using CH_3CN:H_2O (1:1) as solvent. The cyclomanganated aryl ketones were prepared by routes described earlier [7]. Sulfur dioxide (BDH Chemicals) was used as supplied. Preparative layer chromatography (PLC) was carried out on 1 mm layers of silica gel (Merck Kieselgel 60).

2.1. Reactions with SO_2

2.1.1. Reaction of η^2-(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (1a) with SO_2

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (**1a**) (200 mg, 0.633 mmol) was placed in an ampoule fitted with a ground glass joint. The ampoule was attached to a conventional vacuum line and evacuated. Liquid SO_2 (ca. 10 ml), which had been degassed by two freeze–pump–thaw cycles, was condensed into the ampoule. This was sealed and placed in a Carius tube maintained at 55 °C overnight. The ampoule was opened and the excess SO_2 allowed to evaporate in the fume hood. The residue was extracted with dichloromethane, and an IR spectrum showed complete conversion to the SO_2 insertion product η^2-(2-acetyl-5-methoxyphenylsulfonyl)tetracarbonylmanganese (**2a**). Recrystallisation from dichloromethane/pentane at 4 °C afforded small yellow plates, 84% yield, m.p. 115 °C (dec.). ESMS: m/e 381 $(M + H)^+$. IR: ν(CO) 2111(m), 2039(s), 2020(s), 1986(s) cm^{-1}. ^{1}H-NMR: δ 7.84 (2H, br, s), 7.04 (1H, br, s), 4.02 (3H, s, 5-OCH_3), 2.77 (3H, s, 2-$COCH_3$). ^{13}C-NMR: δ 214.6 (s, br, C ≡ O), 210.0 (s, 2-$COCH_3$), 209.1 (s, br, C ≡ O), 205.8 (s, br, 2 × C ≡ O), 166.0 (s, C-5), 154.3 (s, C-1), 135.2 (d, C-3), 123.6 (s, C-2), 117.2 (d, C-4), 105.8 (d, C-6), 56.4 (q, 5-OCH_3), 29.5 (q, 2-$COCH_3$). The compound was further characterised by X-ray crystallography (see below).

2.1.2. Reaction of η^2-(2-acetylphenyl)tetracarbonylmanganese (1b) with SO_2

Similarly, SO_2 (10 ml) was condensed onto η^2-(2-acetylphenyl)tetracarbonylmanganese (**1b**) (200 mg, 0.699 mmol), and the solution was maintained over night at 55 °C. After opening of the ampoule and evaporation of excess SO_2, an IR spectrum of the residue showed complete conversion to the SO_2 insertion product η^2-(2-acetylphenylsulfonyl)tetracarbonylmanganese (**2b**) by the absence of the reactant peaks at 2083(m), 1996(vs), 1948(s) cm^{-1} and the appearance of new peaks at 2112(m), 2040(s), 2020(s), 1980(s) cm^{-1}. The compound could only be obtained as an oil which failed to crystallize. IR: ν(CO) 2112(m), 2040(s), 2020(s), 1980(s) cm^{-1}.

2.1.3. Reaction of η^2-(2-acetyl-5-chlorophenyl)tetracarbonylmanganese (1c) with SO_2

Similarly, SO_2 (10 ml) was condensed onto η^2-(2-acetyl-5-chlorophenyl)tetracarbonylmanganese (**1c**) (188 mg, 0.59 mmol) and the solution was maintained for 140 h at 58 °C. The ampoule was opened and excess SO_2 was allowed to evaporate. An IR spectrum of the residue showed that there was still unreacted starting complex present, together with a new compound (ν(CO) 2113(m), 2042(vs), 2018(s), 1992(s) cm^{-1}), which was tentatively assigned as the insertion product η^2-(2-acetyl-5-chlorophenylsulfonyl)tetracarbonylmanganese (**2c**). Attempts to isolate a pure sample by crystallisation were unsuccessful because of slow decomposition.

2.1.4. Reaction of η^2-(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (1d) with SO_2

η^2-(2-Acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (**1d**) (235 mg, 0.63 mmol) was sealed in an ampoule with SO_2 (ca. 10 ml). After 24 h at 55 °C the SO_2 was allowed to evaporate. An IR spectrum of the residue run immediately in CH_2Cl_2 gave peaks at 2109(m), 2037(s), 2017(s), 1984(s), characteristic of the SO_2-inserted product **2d**. Attempted recrystallisation from CH_2Cl_2/pentane gave orange crystals which were shown to be bis[η^2-(2-acetyl-3,4,5-trimethoxyphenylsulfonyl)tricarbonylmanganese] (**3a**), ν(CO) 2046(vs), 1974(s), 1934(s) cm^{-1}. Anal. Found: C, 37.77; H, 3.15; S, 7.18. $C_{29}H_{26}Mn_2O_{18}S_2 \cdot CH_2Cl_2$ Calc.: C, 38.30; H, 3.10; S, 7.05%. ESMS: m/e 825 $(M + H)^+$. The compound was fully characterised by X-ray crystallography (see below).

The reaction of the isomeric η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese under the same conditions failed to give a detectable (by IR) insertion product.

2.1.5. Reaction of η^2-(benzoylphenyl)tetracarbonylmanganese (1e) with SO_2

Similarly, η^2-(benzoylphenyl)tetracarbonylmanganese (**1e**) (268 mg, 0.77 mmol) and SO_2 (ca. 10 ml)

were left for 14 h at 50 °C. The ampoule was opened after cooling in ice and the SO_2 was evaporated at 0 °C. An IR spectrum of the residue run immediately in CH_2Cl_2 gave peaks at 2110(m), 2039(s), 2019(s), 1987(s) cm^{-1}, which could be assigned to the SO_2-inserted product **2e**. This was supported by an ESMS peak at m/e 454 $(M + CH_3CN + H)^+$. However, attempts to isolate and completely characterise the product were hampered by ready conversion to a species with ν(CO) 2047(vs), 1971(s), 1936(s), which was assigned as bis[η^2-(2-benzoylphenylsulfonyl)tricarbonylmanganese] (**3b**) by comparison with the related complex derived from orthomanganated 3,4,5-trimethoxyacetophenone.

2.1.6. Reaction of η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (4) with SO_2

SO_2 (10 ml) and η^2-(2-acetylthien-3-yl)tetracarbonylmanganese (**4**) (115 mg, 0.394 mmol) at 55 °C for 24 h gave, after recrystallisation from CH_2Cl_2/pentane, small light-orange crystals of η^2-(2-acetylthien-3-yl-sulfonyl)tetracarbonylmanganese (**5**), yield 74%, m.p. 119 °C (dec.). IR: ν(CO) 2115(m), 2040(s), 2027(s), 1987(s) cm^{-1}. Anal. Found: C, 33.14; H, 1.43; S, 17.80. $C_{10}H_5S_2O_7Mn$ Calc.: C, 33.72; H, 1.41; S, 18.00%. ^{1}H-NMR: δ 7.84 (2H, m, aryl-H), 2.75 (3H, s, $-CH_3$). ^{13}C-NMR: δ 214.3 (s, C ≡ O), 208.6 (s, C ≡ O), 205.2 (s, br, 2 × C ≡ O), 202.0 (s, 2-$COCH_3$), 160.3 (s, C-3), 137.9 (d, C-5), 133.3 (s, C-2), 124.7 (d, C-4), 30.2 (q, 2-$COCH_3$). The compound was further characterised by X-ray crystallography (see below).

2.2. Oxidation reactions

2.2.1. Oxidation of η^2-(2-acetyl-5-methoxyphenylsulfonyl)tetracarbonylmanganese (2a) with H_2O_2

2.2.1.1. Under neutral conditions. η^2-(2-Acetyl-5-methoxyphenylsulfonyl)tetracarbonylmanganese (**2a**) (105 mg, 0.276 mmol) in MeOH (40 ml) was treated with excess H_2O_2 (10 ml of 30 vol.%). A vigorous reaction ensued and a black precipitate (presumably MnO_2) formed. After 20 min the solution was filtered and the solvent removed under vacuum. A sample of the cream colored residue was examined by ESMS, which showed peaks corresponding to both the 2-acetyl-5-methoxybenzene-sulfinate (**6a**) and -sulfonate (**7a**) species. The rest of the solid residue was redissolved in MeOH and treated with excess CH_2N_2 in ether to form the methyl esters. Chromatography (PLC, 1:4 ethyl acetate/petroleum spirit) gave two main bands.

Band 1 (R_f 0.17) was methyl 2-acetyl-5-methoxybenzenesulfinate (**8a**), (9 mg, 14%). GCMS m/e 228 (M^+), 213 $[M-Me]^+$, 197 $[M-OMe]^+$, 182 $[M-OMe-Me]^+$. ESMS: m/e 229 $[MH]^+$. ^{1}H-NMR: δ 7.90 (1H, d, $^3J_{3,4}$ = 8.3 Hz, H-3), 7.85 (1H, s, H-6), 7.07 (1H, d, $^3J_{3,4}$ = 8.3 Hz, H-4), 3.95 (3H, s, OMe), 3.77 (3H, s, OMe), 2.60 (3H, s, Me). ^{13}C-NMR: δ 197.07 (s, C=O) 163.68 (s, C-5), 149.98 (s, C-1), 127.60 (s, C-2), 133.12 (d, C-3), 117.20 (d, C-4), 109.79 (d, C-6), 56.04 (q, OMe), 54.79 (q, OMe), 27.41 (q, Me).

Band 2 (R_f 0.25) was methyl 2-acetyl-5-methoxybenzenesulfonate (9a) (7 mg, 10%). GCMS m/e 244 (M^+), 229 $[M-Me]^+$, 213 $[M-OMe]^+$, 165 $[M-SO_2Me]^+$. ^{1}H-NMR: δ 7.47 (1H, d, $^4J_{6,4}$ = 2.5 Hz, H-6), 7.36 (1H, d, $^3J_{3,4}$ = 8.5 Hz, H-3), 7.16 (1H, dd, $^3J_{3,4}$ = 8.5 Hz, $^4J_{4,6}$ = 2.51 Hz, H-4), 3.90 (3H, s, OMe), 3.85 (3H, s, OMe), 2.60 (3H, s, Me). ^{13}C-NMR: δ 201.59 (s, C=O) 160.43 (s, C-5), 134.67, 133.59 (s, C-1, C-2), 128.76 (d, C-3), 119.26 (d, C-4), 114.84 (d, C-6), 56.84 (q, OMe), 55.99 (q, OMe), 31.28 (q, Me).

The reaction was repeated with slow addition of H_2O_2 over 90 min at 0 °C. Removal of solvent, methylation and GCMS examination showed exclusively methyl 2-acetyl-5-methoxybenzenesulfonate (**9a**), although the yield was not determined.

2.2.1.2. With intermediate filtration. The reaction was repeated at room temperature, except that after filtration the solution was treated with a further 6 ml of H_2O_2. Work-up as above and examination of the solid residue by ESMS indicated that only the sulfonate (**7b**) was present, with no sulfinate peaks.

2.2.1.3. Under acid conditions. In MeOH which had been acidified with HCl, the reaction with H_2O_2 at room temperature followed the same course with the exception that no black precipitate formed. Work-up, methylation and GCMS examination of the crude product indicated it to be two mono-chlorinated isomers of methyl 2-acetyl-5-methoxybenzenesulfonate in 60:40 ratio.

2.2.2. Oxidation of η^2-(2-benzoylphenylsulfonyl)tetracarbonylmanganese (2e) with H_2O_2

For these studies the crude residue left after the removal of SO_2 from the insertion reaction with **1e** was used directly, since pure samples were not accessible by recrystallisation (see above).

2.2.2.1. At room temperature. η^2-(2-Benzoylphenylsulfonyl)tetracarbonylmanganese (**2e**) (97 mg, 0.235 mmol) in MeOH (40 ml) was treated with H_2O_2 (10 ml, 30 vol.%). After 20 min, when the vigorous reaction had subsided, the solution was filtered and evaporated to give a cream residue. A sample was shown to contain 2-benzoylbenzenesulfinate anion (**6b**) by ESMS (m/e 245, M^-). The bulk of the residue was methylated with CH_2N_2 and chromatographed on PLC plates, as above, to give one major band of methyl 2-benzoylbenzenesulfinate (**8b**) (14 mg, 23%). GCMS: m/e 260 (M^+), 229 $[M-OMe]^+$, 105 $[PhCO]^+$. ^{1}H-NMR: δ 8.2-7.4

(9H, m, aryl), 3.56 (3H, s, OMe). ^{13}C-NMR: δ 195.2 (s, C=O), 145.60 (s, C-1), 137.21 136.89 (s, C-2, C-1′), 133.57, 131.49, 131.16, 130.06 (all d, unassigned), 130.19 (d, C-2′, C-6′), 128.63 (d, C-3′, C-5′), 125.64 (d, C-6), 53.32 (q, OMe).

The reaction was repeated but with addition of further H_2O_2 (6 ml) after the filtration step. Removal of solvent left a white solid which was shown to contain 2-benzoylbenzenesulfonate (**7b**) by ESMS (m/e 261 M^-).

2.2.2.2. At 0 °C. The reaction was repeated, except that the addition of H_2O_2 was over 25 min while the mixture was cooled in an ice bath. Work-up and methylation, followed by chromatography as before, gave one major band of methyl 2-benzoylbenzenesulfonate (**9b**) (12 mg, 18%). GCMS: m/e 276 (M^+), 199 $[C_6H_4C(O)SO_2Me]^+$, 105 $[PhCO]^+$. ^{1}H-NMR: δ 8.2–7.4 (9H, m, aryl), 3.78 (3H, s, OMe). ^{13}C-NMR: δ 194.89 (s, C=O), 140.33 (s, C-1), 136.30 s, 133.90 d, 133.59 s, 133.37 d, 130.02 d, 129.86 d, 128.17 d (unassigned), 130.12 (d, C2′, C6′), 128.50 (d, C3′, C5′), 53.32 (q, OMe).

2.3. X-ray structures

2.3.1. Structure of η^2-(2-acetyl-5-methoxyphenylsulfonyl)tetracarbonylmanganese (2a)

Yellow plates were obtained on crystallisation by vapor diffusion of pentane into a saturated dichloromethane solution of **2a** at 4 °C. Preliminary precession photography indicated triclinic symmetry, $P\bar{1}$ was assumed to be the space group and this was confirmed by the successful refinement. Intensity data were obtained on an Enraf-Nonius CAD4 automatic four-circle diffractometer with Mo Kα X-rays at 23 °C.

Crystal data: $C_{13}H_9MnO_8S$, $M_r = 380.23$, triclinic, space group $P\bar{1}$, $a = 6.426(1)$, $b = 9.045(4)$, $c = 13.767(2)$ Å, $\alpha = 97.37(2)°$, $\beta = 103.16(1)°$, $\gamma = 78.45(2)°$, $V = 760.6(4)$ Å^3, $D_{calc} = 1.66$ g cm^{-3}, $Z = 2$, $F(000) = 384$, μ(Mo Kα) = 1.04 mm^{-1}. Crystal size $0.7 \times 0.5 \times 0.78$ mm^3. A total of 2798 reflections in the range $0° < \theta < 25°$ was collected, of which 2576 were unique. These were corrected for Lorentz and polarisation effects and for linear absorption by a ψ scan method ($T_{max, min}$ 1.00, 0.78). The position of the Mn atom was located from a Patterson map, and all other non-hydrogen atoms were located in a subsequent difference map phased on the Mn atom. In the final cycle of full-matrix least-squares refinement based on F^2, all non-hydrogen atoms were assigned anisotropic temperature factors and H atoms were included in their calculated positions with common isotropic temperature factors for each type. The refinement converged with $R_1 = 0.0401$ [for 2392 data with $I > 2\sigma(I)$], $R_1 = 0.0427$, $wR_2 = 0.1092$, GOF = 1.085 (all data) and with no parameter shifting more than 0.001σ. A final difference map was featureless bar a ripple of electron density around the manganese atom, ± 0.8 e Å^{-3}. Table 1 lists final positional parameters, Table 2 selected bond parameters, and Figs. 1 and 2(a) give views of the molecule.

Table 1
Atomic coordinates and equivalent isotropic displacement parameters for η^2-(2-acetyl-5-methoxyphenylsulfonyl)tetracarbonylmanganese (**2a**)

Atom	x	y	z	U_{eq}
Mn(1)	1.0411(1)	0.2375(1)	0.3237(1)	0.032(1)
S(1)	0.7825(1)	0.0900(1)	0.2954(1)	0.035(1)
O(1)	1.4077(3)	0.4114(2)	0.3773(2)	0.057(1)
O(2)	0.7227(3)	0.5064(2)	0.2571(2)	0.063(1)
O(3)	1.0895(4)	0.1664(8)	0.1102(2)	0.072(1)
O(4)	0.9589(4)	0.3282(3)	0.5314(2)	0.063(1)
O(5)	1.2417(2)	0.0475(2)	0.3735(1)	0.035(1)
O(6)	0.7564(3)	0.0412(2)	0.3882(2)	0.050(1)
O(7)	0.5797(3)	0.1439(2)	0.2265(2)	0.054(1)
O(8)	0.7130(4)	−0.3621(3)	0.0278(2)	0.059(1)
C(1)	1.2743(4)	0.3427(3)	0.3553(2)	0.040(1)
C(2)	0.8494(4)	0.4020(3)	0.2840(2)	0.044(1)
C(3)	1.0782(4)	0.1882(3)	0.1910(2)	0.043(1)
C(4)	0.9907(4)	0.2897(3)	0.4544(2)	0.041(1)
C(5)	1.2626(4)	−0.0904(3)	0.3479(2)	0.033(1)
C(6)	1.4526(4)	−0.1898(3)	0.4069(2)	0.042(1)
C(7)	1.1136(4)	−0.1565(3)	0.2641(2)	0.034(1)
C(8)	0.8979(4)	−0.0850(3)	0.2309(2)	0.033(1)
C(9)	0.7596(4)	−0.1492(3)	0.1524(2)	0.038(1)
C(10)	0.8345(5)	−0.2877(3)	0.1043(2)	0.043(1)
C(11)	1.0484(5)	−0.3599(3)	0.1351(2)	0.048(1)
C(12)	1.1832(4)	−0.2961(3)	0.2145(2)	0.043(1)
C(13)	0.4924(6)	−0.2915(4)	−0.0087(3)	0.067(1)

Table 2
Selected bond lengths (Å) and angles (deg) for η^2-(2-acetyl-5-methoxyphenylsulfonyl)tetracarbonylmanganese (**2a**)

Bond lengths			
Mn(1)–S(1)	2.270(1)	Mn(1)–O(5)	2.024(2)
Mn(1)–C(1)	1.873(3)	Mn(1)–C(2)	1.789(3)
Mn(1)–C(3)	1.881(3)	Mn(1)–C(4)	1.884(3)
C(5)–C(7)	1.468(4)	S(1)–O(6)	1.459(2)
S(1)–O(7)	1.462(2)	S(1)–C(8)	1.820(3)
Bond angles			
S(1)–Mn(1)–O(5)	83.5(1)	Mn(1)–O(5)–C(5)	136.4(2)
S(1)–Mn(1)–C(1)	173.8(1)	S(1)–Mn(1)–C(2)	93.2(1)
S(1)–Mn(1)–C(3)	90.0(1)	S(1)–Mn(1)–C(4)	88.3(1)
O(5)–Mn(1)–C(1)	90.4(1)	O(5)–Mn(1)–C(2)	175.7(1)
O(5)–Mn(1)–C(3)	93.6(1)	O(5)–C(5)–C(7)	123.1(2)
O(5)–Mn(1)–C(4)	88.2(1)	C(1)–Mn(1)–C(2)	92.8(1)
C(5)–C(7)–C(8)	122.5(2)	C(1)–Mn(1)–C(3)	91.7(1)
C(1)–Mn(1)–C(4)	90.1(1)	C(2)–Mn(1)–C(3)	89.0(1)
S(1)–C(8)–C(7)	121.3(2)	C(2)–Mn(1)–C(4)	89.0(1)
C(3)–Mn(1)–C(4)	177.4(1)	Mn(1)–S(1)–O(6)	111.8(1)
Mn(1)–S(1)–O(7)	115.9(1)	Mn(1)–S(1)–C(8)	104.7(1)
O(6)–S(1)–O(7)	115.0(1)	O(6)–S(1)–C(8)	103.4(1)
O(7)–S(1)–C(8)	104.2(1)		

2.3.2. Structure of η^2-(2-acetylthien-3-ylsulfonyl)tetracarbonylmanganese (5)

Orange crystals of **5** were obtained from CH_2Cl_2/pentane. The space group $P2_1/c$ was assigned from precession photography. Intensity data and accurate cell parameters were obtained on a Seimens P4 automatic four-circle diffractometer with Mo Kα X-rays at −143 °C.

Crystal data: $C_{10}H_5MnO_7S_2$, $M_r = 356.20$, monoclinic, space group $P2_1/c$, $a = 12.654(3)$, $b = 7.171(5)$, $c = 15.011(5)$ Å, $\beta = 110.96(2)°$, $V = 1272(1)$ Å^3, $D_{calc} = 1.86$ g cm^{-3}, $Z = 4$, $F(000) = 712$, μ(Mo Kα) = 1.39 mm^{-1}. Crystal size $0.48 \times 0.46 \times 0.44$ mm^3. A total of 2113 reflections in the range $2° < \theta < 29°$ was collected, of which 1978 were unique. These were corrected for Lorentz and polarisation effects and for linear absorption by a ψ scan method ($T_{max, min}$ 0.43, 0.36). The structure was solved by direct methods and routinely developed. In the final cycle of full-matrix least-squares refinement based on F^2, all non-hydrogen atoms were assigned anisotropic temperature factors and H atoms were included in their calculated positions with common isotropic temperature factors for each type. The refinement converged with $R_1 = 0.056$ [for 1513 data with $I > 2\sigma(I)$], $R_1 = 0.0798$, $wR_2 = 0.1678$, GOF = 1.089 (all data) and with no parameter shifting more than 0.001σ. The largest peak in a final difference map was 0.76 e Å^{-3} adjacent to the manganese atom.

Table 3 lists final positional parameters, Table 4 selected bond parameters and Fig. 2(b) shows a perspective view of the molecule.

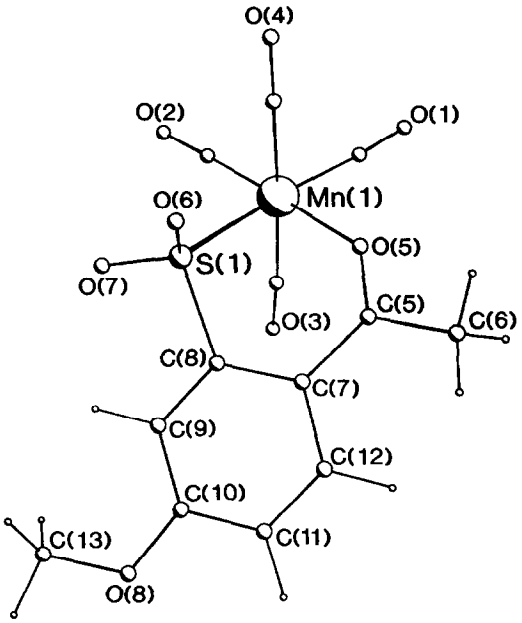


Fig. 1. The structure of the SO_2-inserted product **2a** derived from orthomanganated 5′-methoxyacetophenone.

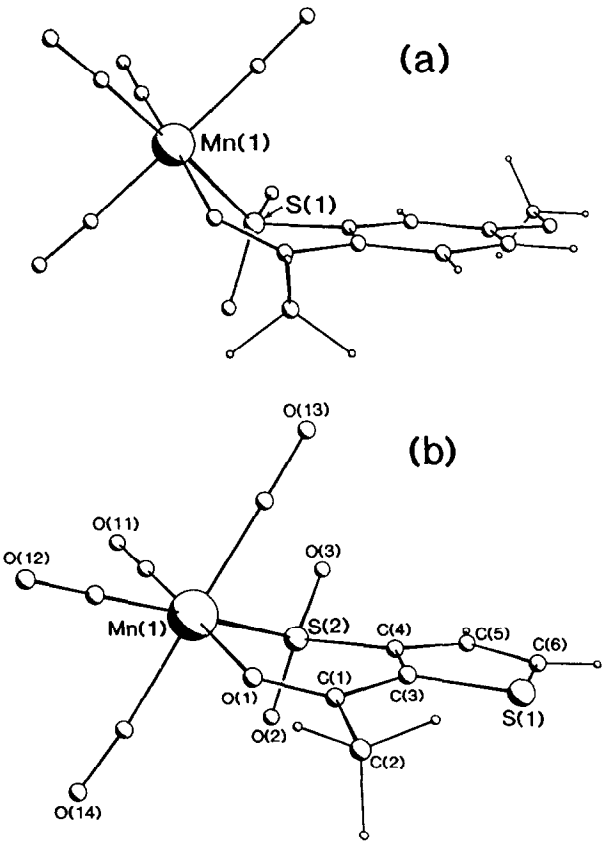


Fig. 2. Side views of the SO_2-inserted species showing the degree of ring puckering: (a) **2a** from orthomanganated 5′-methoxyacetophenone; (b) **4** from orthomanganated 2-acetylthiophene.

2.3.3. Structure of bis[η^2-(2-acetyl-3,4,5-trimethoxyphenylsulfonyl)tricarbonylmanganese] (3a)

An orange square-pyramidal crystal was obtained from CH_2Cl_2/pentane. Preliminary precession photog-

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for η^2-(2-acetylthien-3-ylsulfonyl)tetracarbonylmanganese (**5**)

Atom	x	y	z	U_{eq}
Mn(1)	0.1620(1)	0.1802(2)	0.9507(1)	0.025(1)
S(1)	0.4445(1)	−0.2649(3)	0.9689(2)	0.029(1)
S(2)	0.3056(1)	0.1615(2)	1.0957(1)	0.024(1)
O(1)	0.2159(3)	0.0471(7)	0.8457(4)	0.028(1)
O(2)	0.3665(3)	0.3242(7)	1.1015(4)	0.034(1)
O(3)	0.2970(3)	0.1108(7)	1.2043(4)	0.030(1)
O(11)	0.0811(4)	0.3813(9)	1.1000(5)	0.045(2)
O(12)	−0.0273(4)	0.2147(9)	0.7622(4)	0.048(2)
O(13)	0.1045(4)	−0.1789(9)	1.0292(5)	0.055(2)
O(14)	0.2178(4)	0.5510(10)	0.8864(5)	0.060(2)
C(1)	0.2847(5)	−0.0567(10)	0.8531(6)	0.028(2)
C(2)	0.2917(5)	−0.1352(11)	0.7480(6)	0.032(2)
C(3)	0.3567(5)	−0.1045(9)	0.9623(6)	0.023(2)
C(4)	0.3720(5)	−0.0309(9)	1.0675(5)	0.021(2)
C(5)	0.4534(5)	−0.1025(11)	1.1525(6)	0.029(2)
C(6)	0.4990(5)	−0.2311(11)	1.1100(6)	0.031(2)
C(11)	0.1129(5)	0.3015(12)	1.0426(6)	0.035(2)
C(12)	0.0457(5)	0.1988(11)	0.8322(6)	0.032(2)
C(13)	0.1274(5)	−0.0449(13)	0.9977(6)	0.036(2)
C(14)	0.2017(6)	0.4077(11)	0.9084(6)	0.036(2)

Table 4
Selected bond lengths (Å) and angles (deg) for η^2-(2-acetylthien-3-yl-sulfonyl)tetracarbonylmanganese (**5**)

Bond lengths			
Mn(1)–C(12)	1.864(8)	Mn(1)–C(13)	1.876(10)
Mn(1)–C(14)	1.883(8)	Mn(1)–C(11)	1.913(9)
Mn(1)–O(1)	2.152(5)	Mn(1)–S(2)	2.287(2)
S(1)–C(3)	1.578(6)	S(1)–C(6)	1.994(8)
S(2)–O(2)	1.384(5)	S(2)–O(3)	1.710(6)
S(2)–C(4)	1.745(7)	O(1)–C(1)	1.119(8)
O(11)–C(11)	1.217(10)	O(12)–C(12)	1.129(9)
O(13)–C(13)	1.153(10)	O(14)–C(14)	1.119(10)
C(1)–C(3)	1.602(10)	C(1)–C(2)	1.707(11)
C(3)–C(4)	1.609(11)	C(4)–C(5)	1.419(10)
C(5)–C(6)	1.362(11)		
Bond angles			
C(12)–Mn(1)–C(13)	102.1(3)	C(12)–Mn(1)–C(14)	80.3(3)
C(13)–Mn(1)–C(14)	177.6(3)	C(12)–Mn(1)–C(11)	107.8(3)
C(13)–Mn(1)–C(11)	86.6(4)	C(14)–Mn(1)–C(11)	92.5(4)
C(12)–Mn(1)–O(1)	71.5(3)	C(13)–Mn(1)–O(1)	94.1(3)
C(14)–Mn(1)–O(1)	86.8(3)	C(11)–Mn(1)–O(1)	179.1(3)
C(12)–Mn(1)–S(2)	179.2(3)	O(1)–Mn(1)–S(2)	108.60(13)
C(3)–S(1)–C(6)	86.9(4)	O(2)–S(2)–O(3)	110.1(3)
C(4)–S(2)–Mn(1)	95.9(2)	C(1)–O(1)–Mn(1)	131.3(6)
O(1)–C(1)–C(3)	112.5(7)	S(1)–C(3)–C(4)	110.1(5)
C(1)–C(3)–C(4)	139.3(5)	C(5)–C(4)–S(2)	109.0(6)
C(3)–C(4)–S(2)	126.8(4)		

raphy indicated monoclinic symmetry, with systematic absences defining $P2/n$. Intensity data were obtained on a Seimens P4 four-circle diffractometer with Mo K α X-rays at −141 °C.

Crystal data: $C_{28}H_{26}Mn_2O_{18}S_2 \cdot CH_2Cl_2$, M_r = 909.43, monoclinic, space group $P2/n$, a = 11.674(7), b = 12.455(7), c = 12.394(8) Å, β = 97.40(4)°, V = 1787(2) Å^3, D_{calc} = 1.69 g cm^{-3}, Z = 2, $F(000)$ = 924, $\mu(Mo\ K\alpha)$ = 1.05 mm^{-1}. Crystal size 0.78 × 0.56 × 0.52 mm^3. A total of 2460 reflections in the range $2° < \theta < 22.5°$ was collected, of which 2316 were unique. These were corrected for Lorentz and polarisation effects and for linear absorption by the empirical method of SHELXA. The structure was solved by direct methods. A penultimate difference map showed electron density which was assigned to a poorly-ordered CH_2Cl_2 molecule of crystallisation (the presence of which was also indicated by microanalysis). Refinement based on F^2 included all non-hydrogen atoms with anisotropic temperature factors, and H atoms in their calculated positions. Convergence gave R_1 = 0.0797 [for 1937 data with $I > 2\sigma(I)$], R_1 = 0.0970, wR_2 = 0.1823, GOF = 1.171 (all data) and with no parameter shifting more than 0.003σ. Maximum final features were +0.59/−0.56 e Å^{-3}. Table 5 lists final positional parameters, Table 6 selected bond parameters, and the structure is illustrated in Fig. 3.

For all the structure studies the SHELX programs were used [8]. Tables of hydrogen atom coordinates and thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Table 5
Atomic coordinates and equivalent isotropic displacement parameters for bis[η^2-(2-acetyl-3,4,5-trimethoxyphenylsulfonyl)tricarbonylmanganese] (**3a**)

Atom	x	y	z	U_{eq}
Mn(1)	0.0988(1)	0.7053(1)	0.1302(1)	0.022(1)
S(1)	0.1249(2)	0.6871(2)	0.3134(2)	0.022(1)
O(1)	0.2697(5)	0.7426(5)	0.1280(5)	0.023(1)
O(2)	0.1071(6)	0.5803(5)	0.3575(6)	0.036(2)
O(3)	−0.1162(6)	1.0338(5)	0.3177(5)	0.032(2)
O(4)	−0.2179(5)	0.9595(5)	0.4995(5)	0.024(2)
O(5)	−0.1715(5)	0.7627(5)	0.5737(5)	0.028(2)
O(7)	0.0970(5)	0.8652(5)	0.1679(5)	0.019(1)
O(11)	−0.1508(6)	0.6689(5)	0.1277(6)	0.035(2)
O(12)	0.0558(6)	0.7412(6)	−0.1104(6)	0.038(2)
O(13)	0.1119(6)	0.4717(5)	0.0971(6)	0.038(2)
C(1)	0.0152(7)	0.7715(7)	0.3594(8)	0.022(2)
C(2)	−0.0045(7)	0.8770(7)	0.3202(7)	0.021(2)
C(3)	−0.0870(7)	0.9390(7)	0.3671(7)	0.021(2)
C(4)	−0.1406(8)	0.8979(7)	0.4526(8)	0.024(2)
C(5)	−0.1168(7)	0.7924(7)	0.4901(7)	0.021(2)
C(6)	−0.0388(7)	0.7299(7)	0.4416(7)	0.019(2)
C(7)	0.0621(8)	0.9215(7)	0.2377(8)	0.023(2)
C(8)	0.0918(8)	1.0388(7)	0.2356(8)	0.027(2)
C(11)	−0.0534(9)	0.6843(7)	0.1298(8)	0.028(2)
C(12)	0.0743(8)	0.7299(8)	−0.0187(9)	0.029(2)
C(13)	0.1117(8)	0.5623(8)	0.1087(9)	0.029(2)
C(31)	−0.1517(9)	1.1249(7)	0.3746(8)	0.032(2)
C(41)	−0.3358(8)	0.9421(8)	0.4579(9)	0.035(3)
C(51)	−0.1457(9)	0.6571(8)	0.6171(9)	0.035(3)
Cl(1)	0.2037(4)	0.5775(3)	0.6298(5)	0.090(1)
C(91)	0.1840(15)	0.5242(18)	0.7294(21)	0.125(8)

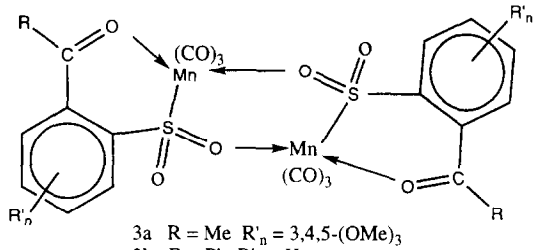
3. Results and discussion

3.1. Reactions of orthometallated complexes with SO_2

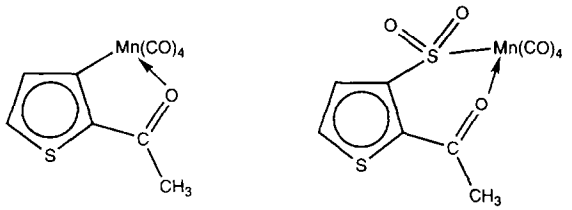
There was ready insertion of SO_2 into the Mn–C_{aryl} bond of orthomanganated aryl ketones **1a–e**, **4** to give

Table 6
Selected bond lengths (Å) and angles (deg) for bis[η^2-(2-acetyl-3,4,5-trimethoxyphenylsulfonyl)tricarbonylmanganese] (**3a**)

Bond lengths			
Mn(1)–O(7)	2.046(6)	Mn(1)–O(1)	2.052(6)
Mn(1)–S(1)	2.263(3)	S(1)–O(2)	1.464(7)
S(1)–O(1)	1.513(6)	S(1)–C(1)	1.805(9)
O(7)–C(7)	1.223(10)		
Bond angles			
C(11)–Mn(1)–C(13)	87.5(4)	C(11)–Mn(1)–C(12)	89.7(4)
C(13)–Mn(1)–C(12)	91.2(4)	O(7)–Mn(1)–O(1)	79.7(2)
O(7)–Mn(1)–S(1)	82.7(2)	O(1)–Mn–S(1)	91.8(2)
O(2)–S(1)–O(1)	112.4(4)	O(2)–S(1)–C(1)	105.7(4)
O(1)–S(1)–C(1)	98.5(4)	O(2)–S(1)–Mn(1)	117.3(3)
O(1)–S(1)–Mn(1)	115.6(3)	C(1)–S(1)–Mn(1)	104.5(3)
S(1)–O(1)–Mn(1)	128.5(4)	C(7)–O(7)–Mn(1)	137.2(6)



3a R = Me R'_n = 3,4,5-$(OMe)_3$
3b R = Ph R'_n = H



(4) (5)

Scheme 2.

the corresponding S-sulfinato complexes **2a–e**, **5** incorporating a six-membered chelate ring. The reactions were carried out by sealing the two reactants in an ampoule which was held at 50–55 °C for 12–24 h. The mild heating was necessary since no reaction occurred at room temperature; this parallels the observations with alkyne coupling where heating, or other means of initiation, was needed [3]. Work-up was particularly straightforward, since the reactions were essentially quantitative for the substrates given above (except for **1c** which reacted only sluggishly), and simply allowing the excess SO_2 to evaporate left the raw product. Only for **2a** and **5** were purified compounds isolated; **2b** and **2c** could not be recrystallised, while **2d** or **2e** underwent conversion on attempted crystallisation to give the dimeric species **3a** or **3b** (see below). However, all were readily identified by comparison with the well-characterised examples **2a** and **5**. In particular, SO_2 insertion is signalled by a shift to higher frequencies by 20–50 cm^{-1} for the ν(CO) frequencies of the $Mn(CO)_4$ unit, although the overall pattern of the spectrum is similar to that of the starting complex.

The insertion reaction appears to be reversible, since a ^{13}C-NMR spectrum of a sample of **2a** in $CDCl_3$ left over night indicated reversion of around 25% of the product to the orthomanganated precurser by extrusion of SO_2. No such reversion was observed when the S-sulfinato complexes were stored at low temperature, either in the crystalline form or in solution. The reversibility for the cyclomanganated species contrasts with observations with non-cyclic $RS(O)_2Mn(CO)_5$, where no elimination of SO_2 could be induced [6]. Hence, both insertion and de-insertion for Mn–C bonds appear to be more facile for the cyclometallated compounds.

The efficient insertion of SO_2 into the $Mn–C_{aryl}$ bond of the orthomanganated ketone contrasts with the sluggish insertion of SO_2 into the $Mn–C_{aryl}$ bond of $PhMn(CO)_5$ reported by Hartman and Wojcicki [6]. This is possibly due to increased electron density at the aryl carbon for the orthomanganated compound as a result of coordination to manganese by the oxygen which is not a π-acceptor ligand.

The insertion of SO_2 into M–C bonds is believed to involve an electrophilic cleavage process, involving backside electrophilic attack of SO_2 at the α-carbon [6]. A similar reaction scheme can also be envisaged for the insertion of SO_2 into the $Mn–C_{aryl}$ bond of orthomanganated ketones. Consistent with this, η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese did not react with SO_2, whereas the 3,4,5-trimethoxy-sub-

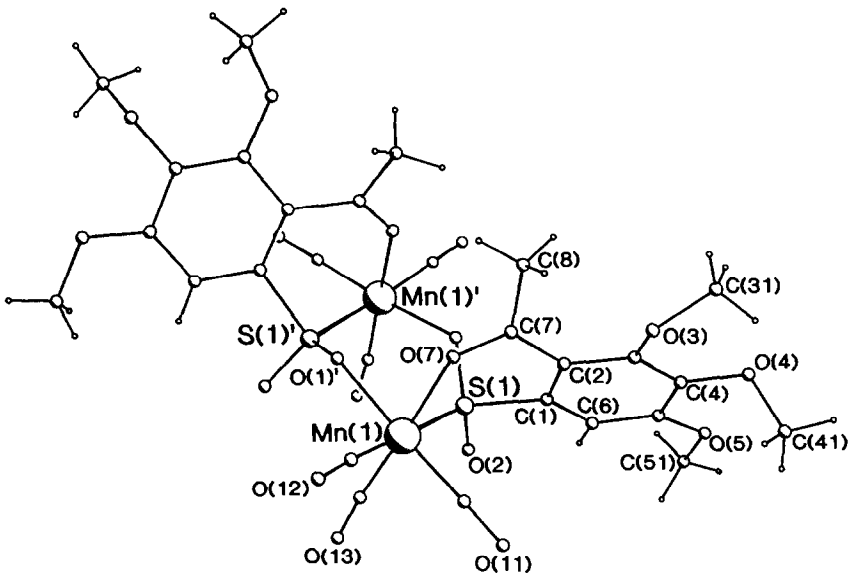


Fig. 3. The structure of the dimeric complex bis[η^2-(2-acetyl-3,4,5-trimethoxyphenylsulfonyl)tricarbonylmanganese] (**3a**).

stituted example did; substituents adjacent to the Mn–C bond apparently hinder attack. The comparatively sluggish reaction of the 5-chloro derivative **1c** can also be explained, since although chloro substituents are *ortho /para* directing, like methoxy groups, they are deactivating with respect to electrophilic aromatic substitution.

3.2. Structures of SO_2-inserted compounds 2a and 5

Insertion of SO_2 into the Mn–C_{aryl} bond of orthomanganated aryl ketones leads to the formation of a six-membered metallocyclic ring which differs considerably in geometry from that of its five-membered precursor.

Orthomanganated compounds incorporating a five-membered chelate ring exhibit remarkably constant geometry within the metallocycle, which is invariably planar. In contrast, the metallocyclic ring of **2a** shows considerable deviation from planarity (see Fig. 2(a)). The ring can be defined by two planes: plane 1 comprising the atoms C(5)C(7)C(8)S(1), and plane 2 defined by the atoms S(1)Mn(1)O(5)C(2)O(2)C(1)O(1), with a dihedral angle between the planes of 50.1(1)°. This pronounced fold presumably arises from the requirement for the S atom to assume tetrahedral geometry.

Coordination about the manganese atom is essentially octahedral, distortions from ideal geometry being far less pronounced than for cyclomanganated species with five-membered rings. The axial carbonyls are essentially perpendicular to the plane defined by the equatorial ligands about manganese, with deviation from 90° of only 2.6°. This contrasts with most other C_{ax}–Mn–C_{ax} bond angles reported for orthomanganated complexes, where the folding of the axial carbonyls towards the ring carbon bonded to manganese is usually very pronounced. C_{ax}–Mn–C_{ax} bond angles of about 169° are typical for these compounds [7,9]. The six-membered ring in **2a** allows a wider chelate bite (83.5(1)°) than is found for species with a five-membered chelate ring (78–80°).

The C(5)–O(5)–Mn bond angle of 136.4(2)° in **2a** deviates considerably from that expected for ideal sp^2 hybridised geometry. This opening of the bond angle suggests an increase in s-character in the C(5)–O(5) and O(5)–Mn bonds, which would account for some shortening within these bonds. The Mn–O distance is the shortest yet reported for a cyclomanganated complex.

The SO_2 group withdraws electron density from manganese. This is evident from the shift to higher wavenumbers in the metal–carbonyl region of the IR spectrum, the longer Mn–CO distances in this compound, and the upfield shift in the ^{13}C-NMR resonances of the metal–carbonyls compared with the orthomanganated precursor.

The Mn–S distance in **2a** of 2.270(1) Å is considerably shorter than that reported for the six-membered cyclic S-sulfinate $(OC)_4MnPPh_2(CH_2)_3SO_2$, 2.312(2) Å, where the other donor atom is phosphorus [10]. The C(5)–O(5) bond length of 1.233(3) Å is around 0.03 Å longer than the uncoordinated carbonyl distance in free acetophenone [11], and is identical to that reported for **1b** [9a]. Whereas this decrease in double bond character has been rationalised by π-delocalisation over the entire metallocycle for **1b**, for **2a** the lengthening of the C=O bond must arise from the σ-donation to the Mn atom since extensive π-delocalisation will be precluded by the non-planarity of the ring.

The structure of the second example of an SO_2 insertion product **5** is shown in Fig. 2(b). This differs in that it has a five-membered thiophene ring fused to the six-membered metallocyclic ring. Although the crystal structure appears to be well-determined (reasonable *R* values, unambiguous space group assignment, sensible absorption correction, low residual electron density), an examination of bond parameters suggests caution. In particular, the two S=O distances are 1.38 and 1.71 Å (compared with values of ca. 1.46 Å for **2a**), and the S–C distances in the thiophene ring are also unrealistically different (1.58 and 1.99 Å, cf. 1.7 Å expected [7b]). The most likely explanation is that there is some unresolved disorder in this part of the molecule, a conclusion supported by moderate (though not excessive) anisotropy in the thermal ellipsoids. Despite these reservations, it is clear that the overall features are similar to those noted above for **2a**, except that the folding of the metallocyclic ring is much less (Fig. 2(b)). The dihedral angle between the plane defined by the Mn atom and the four atoms in the equatorial positions, and the plane defined by S(2)C(4)C(3)C(1)-O(1), is 26° compared with 50° for the equivalent angle in **2a**. This suggests that the six-membered rings are quite flexible, with a conformation dictated by crystal packing forces.

3.3. The formation of dimeric compounds 3

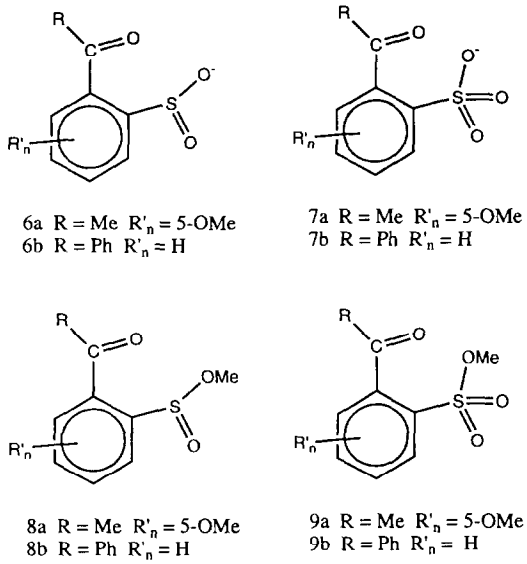
As mentioned above, attempted recrystallisation of the crude SO_2-inserted species from reaction with orthometallated trimethoxyacetophenone or benzophenone gave rise to a different species which showed a carbonyl-region IR spectrum consistent with an $Mn(CO)_3$ unit. Identification came from an X-ray structure determination of the trimethoxyacetophenone example **3a**. Fig. 3 shows that it is a dimer, lying on a crystallographic two-fold axis, made up from two molecules of **2d** which have each lost one CO ligand and accepted a pair of electrons from one of the sulfur-bonded oxygen atoms on the other molecule. The dimer is therefore held together by a six-membered Mn–S–O–Mn–S–O

ring. The geometry about the manganese atoms is essentially octahedral, with variations of up to 6° from 90°. The metallocyclic rings involving the arene are strongly puckered, as discussed above for **2a**; the dihedral angle between the planes defined by S(1)C(1)C(2)C(7) and S(1)Mn(1)O(7) in **3a** is 53°, compared with 50° for the corresponding unit in **2a**. The only other significant difference is in the Mn–O (ketone) distances, which are 2.046(6) Å in **3a** vs. 2.023(2) Å in **2a**. The Mn–O (sulfinate) distance is longer at 2.052(6) Å, suggesting that it is a poorer donor than the ketone oxygen atom. The S=O distances are 1.464(7) and 1.513(6) Å respectively for the free and coordinated groups.

The formation of this dimer under such mild conditions is unexpected, since displacement of CO from $Mn(CO)_4$ groups usually requires elevated temperatures or chemical aids such as Me_3NO; the SO_2 group must be providing strong labilisation of a *cis*-CO group to allow dimerisation at ambient temperature. Both the trimethoxyacetophenone and benzophenone derivatives underwent this dimerisation so readily that recrystallisation of the initially formed tetracarbonyl monomer was not possible. However, the monomeric $Mn(CO)_4$ derivatives from acetophenone, 5′-methoxyacetophenone or 2-acetylthiophene, were stable under the same conditions.

3.4. Oxidation of the S-sulfinate complexes

The reaction of the cyclic manganese-S-sulfinate **2a** with H_2O_2 in MeOH at ambient temperature gave a mixture of the 2-acetyl-5-methoxybenzene-sulfinate **6a** and -sulfonate **7a** anions, presumably as the Mn^{2+} salts. These were identified from the ESMS spectra of the crude product, and also by GCMS and NMR spectroscopy on the neutral methyl esters after derivatisation with CH_2N_2. The presence of the sulfinate despite the addition of excess H_2O_2 can be attributed to incomplete oxidation. Reaction led to the formation of a black solid, attributed to MnO_2, which is known to efficiently catalyse the decomposition of H_2O_2 [12]. To check the possibility that H_2O_2, even though in excess, was being decomposed by MnO_2 before it could complete the oxidition of the sulfinate complex, the reaction was repeated after acidification with HCl to prevent MnO_2 formation; this produced sulfonate products but was accompanied by ring-chlorination reactions (H_2O_2 is a sufficiently strong oxidising agent to convert Cl^- to Cl_2). The oxidation reaction could be made specific for the sulfonate **7a** by either adding the H_2O_2 very slowly at reduced temperatures, or by filtering off the MnO_2 after the first phase of the reaction and adding a second aliquot of H_2O_2 to convert any sulfinate to sulfonate. Although yields under these modified conditions were not determined, the methods are certainly specific for sulfonate.



Scheme 3.

These observations with **2a** were mirrored with the benzoyl species **2e**, where rapid addition of H_2O_2 at room temperature gave mainly 2-benzoylbenzenesulfinate **6b**, with lesser amounts of the corresponding sulfonate **7b**. Carrying out the reaction with slow addition at low temperature, or with an intermediate filtration step, again made the reaction selective for the sulfur(VI) species **7b**, which was isolated and characterised as the methyl ester **9b**.

Preliminary reactions of orthomanganated 2-acetyl-5-methoxybenzenesulfinate (**2a**) with excess I_2, or of the benzoyl complex **2d** with ceric ammonium nitrate, indicated these oxidising agents could also be used to induce oxidative demetallation to the sulfonate anions, but H_2O_2 is the reagent of choice because of the simplicity of work-up and the low cost.

4. Conclusions

SO_2 inserts into the Mn–C bond of orthometallated aryl ketones provided the site is not blocked by an immediately adjacent substituent. The stability of the six-membered metallocycle species varies somewhat unpredictably, since some are readily isolable while others undergo a facile dimerisation. From the limited number of examples so far examined it is not yet possible to rationalise these differences.

Oxidative demetallation of the SO_2-inserted species provides a new synthetic route to benzene-sulfonates or -sulfinates under mild conditions.

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