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Ortho-manganated arenes in synthesis

IV *. *Ortho*-manganation of substituted acetophenones and of heteroaromatic methyl ketones. The crystal structures of two cyclometallated acetylthiophene derivatives

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Abstract

A range of acetophenones containing methoxy, methyl and bromo substituents on the ring have been *ortho*-manganated with $PhCH_2Mn(CO)_5$ in refluxing heptane to give substituted complexes of the type $MeC(\overline{O})C_6H_4\overline{Mn}(CO)_4$ in good yields. Similarly prepared were the *ortho*-manganated complexes derived from 2-acetylthiophene, 3-acetyl-2,5-dimethylthiophene, 2-acetyl-*N*-methylpyrrole, 2-acetylfuran and 3-acetylindole. All new complexes were fully characterised by normal methods, including ^{13}C NMR spectra, the first reported for *ortho*-manganated ketones, and X-ray crystal structures are described for the two thiophene derivatives, η^2-(2-acetyl-3-thienyl)tetracarbonylmanganese and η^2-(3-acetyl-2,5-dimethyl-4-thienyl)tetracarbonylmanganese.

Introduction

Cyclometallation reactions provide an important method for activating specific sites in substituted arenes [1]. The cyclometallation of arylketones using alkylpentacarbonylmanganese reagents, e.g. eq. 1, was established by Kaesz and co-workers [2–4]. In their pioneering work they optimised conditions for the *ortho*-manganation

$$PhCH_2Mn(CO)_5 + CH_3C(O)C_6H_5 \rightarrow 2\text{-}CH_3C(\overline{O})C_6H_4\overline{Mn}(CO)_4 + PhCH_3 \quad (1)$$

of a range of acetophenone and benzophenone derivatives and characterised the products [3], with X-ray structure for key species [4]. Since then it has become apparent that only manganese reagents, and the more expensive and less reactive

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rhenium reagents, can directly cyclometallate aromatic substrates where the guiding donor atom is oxygen. Metal reagents such as $Pd(OAc)_2$ or $NiCp_2$ which react smoothly with aromatic compounds with *N*-donor sites [1] do not give corresponding cyclometallated aryl ketones, nor do $PhCH_2Co(CO)_4$ or $PhCH_2Fe(CO)_2Cp$ [5].

We recently showed that cyclomanganated aryl ketones are useful intermediates in the synthesis of a number of novel organic and organometallic compounds [6,7]. To provide starting materials for these reactions we have extended Kaesz's earlier work to other arenes containing C=O groups. In this paper we describe reactions of substituted acetophenones, and of heteroaromatic methyl ketones, and a report of concurrent studies with *N*-acyl aromatics and benzamides appears in the following paper [15].

Experimental

Ortho-manganation reactions were carried out under an inert atmosphere, but subsequent work-up involved no special precautions. Column chromatography was performed using neutral alumina (activity V) unless other wise specified. Spectrometers used were: Perkin–Elmer 180 (infrared, recorded as CH_2Cl_2 solutions unless specified, accurate to ± 1 cm^{-1}); Jeol FX90Q (NMR, recorded in $CDCl_3$); Varian CH5 (mass spectra). For the ^{13}C NMR data, the signal arising from the ketone C is marked *, while that from the carbon attached to manganese is flagged with *. $PhCH_2Mn(CO)_5$ was prepared by the literature method [8]. The Bu^tMe_2Si-protected substrates used to prepare **8** and **9** were synthesised from the corresponding hydroxyacetophenones by a standard procedure [9], and the *O*-benzyl ketone (for **7**) using benzyl chloride and base. Other arenes were purchased from Aldrich. $MeC(O)C_6H_4Mn(CO)_4$ (**1**) and the 5-methoxy substituted analogue **2** were prepared in 85 and 86% yield respectively using Kaesz's method [3]. Other new derivatives were prepared similarly, and details are given only for an illustrative example.

*Preparation of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**).* A heptane (15 ml) solution of $PhCH_2Mn(CO)_5$ (0.28 g, 0.98 mmol) and 3′,4′,5′-trimethoxyacetophenone (0.20 g, 0.95 mmol) was refluxed under nitrogen for 1.5 h. The heptane was removed under vacuum and CH_2Cl_2 (5 ml) and alumina (3 g) were added to the bright yellow residue. The mixture was shaken while being pumped to dryness. The absorbed product was transferred to an alumina column (2×15 cm); elution with hexane removed unchanged $PhCH_2Mn(CO)_5$ (trace) while increasing proportions of CH_2Cl_2 eluted a yellow band of η^2-(2-acetyl-4,5,6-trimethoxyphenyl)tetracarbonylmanganese (**4**), isolated as bright yellow crystals, 0.33 g, 86%. IR: ν(CO) (hexane) 2080(m), 1993(vs), 1987(vs), 1953(s) cm^{-1}; ^1H NMR: δ 7.26 (s, 1H, H(3)) 4.07, 3.91, 3.89 (all s, 3H each, OMe) 2.58 (s, 3H, $C(O)CH_3$). ^{13}C NMR: δ 220.1(s), 214.3 *(s), 213.8(s), 211.5(s), 172.9 *(s), 160.6(s), 151.3(s), 149.1(s), 138.5(s), 111.4(d), 60.9(q), 60.0(q), 56.3(q), 24.7(q). Mass spectrum: *m/e* 376 (P^+).

*Preparation of η^2-(2-acetyl-3,4,5,-trimethoxyphenyl)tetracarbonylmanganese (**3**).* This was prepared similarly in 80% yield from 2′,3′,4′-trimethoxyacetophenone. IR: 2080(m), 1990(vs), 1932(m). ^1H NMR: δ 7.26 (s, 1H, H(6)), 4.06, 4.05, 3.85 (all s, 3H each, OMe), 2.65 (s, 3H, $C(O)CH_3$). ^{13}C NMR: δ 220.9 (s, br), 213.4 * (s, br), 211.7 (s, br), 211.3 (s, br), 191.3 * (s), 158.9 (s), 157.4 (s), 138.1 (s), 131.4 (s), 117.4 (d), 60.8 (q, br), 56.2 (q), 29.3 (q). Mass spectrum: *m/e* 376 (P^+).

Preparation of η^2-(2-acetyl-4,5-dimethoxyphenyl)tetracarbonylmanganese (5) and η^2-(2-acetyl-5,6-dimethoxyphenyl)tetracarbonylmanganese (6). By the standard method, 3′,4′-dimethoxyacetophenone was *ortho*-manganated with $PhCH_2Mn(CO)_5$. The crude product was chromatographed on silica gel plates, with ether/petroleum spirit (1/9) as eluant, to give both possible isomers, the less-congested **5** in 60% yield (^{1}H NMR: δ 7.50, 7.30 (each s, 1H, H(3) and H(6)), 4.06, 3.89 (each s, 3H, OMe), 2.54 (s, 3H, $C(O)CH_3$), and the more congested **6** in 20% yield (^{1}H NMR: δ 7.70 (d J 8.4 Hz, 1H, H(3)), 6.75(d, J 8.4 Hz, 1H, H(4)), 3.97, 3.85 (s, 3H each, OMe), 2.52 (s, 3H, $C(O)CH_3$).

Preparation of η^2-(2-acetyl-3-benzyloxy-4,5-dimethoxyphenyl)tetracarbonylmanganese (7). In the standard procedure 2′-benzyloxy-3′,4′-dimethoxyacetophenone was *ortho*-manganated, and its product purified by column chromatography on neutral alumina (activity III) to give **7** in 90% yield. IR: 2079(m), 1991(vs), 1932(m). ^{1}H NMR: δ 7.35 (s, br, 6H, C_6H_5 + H(6)), 5.26 (s, 2H, OCH_2), 4.00, 3.83 (s, 3H each, OMe), 2.46 (s, 3H, $C(O)CH_3$).^{13}C NMR: 220.9 (s, br), 213.5 ★ (s), 212.9 (s, br), 211.5 (s, br), 191.2 ☆ (s), 158.8 (s), 156.2 (s), 138.3 (s), 136.8 (s), 131.9 (s), 128.4 (d, br), 117.5 (d), 75.7 (t), 60.8 (q), 56.1 (q), 29.5 (q). Mass spectrum: m/e 452 (P^+).

Preparation of η^2-(2-acetyl-3-t-butyldimethylsiloxyphenyl)tetracarbonylmanganese (8). This was prepared similarly in 86% yield after chromatography on silica plates. IR: 2079(m), 1990(vs), 1933(m). ^{1}H NMR: 7.50 (d, J 7.4 Hz, 1H, H(6)), 7.60 (m, 1H, H(5)), 6.48 (d, J 8.1 Hz, 1H, H(4)), 2.62 (s, 3H, $C(O)CH_3$), 0.96 (s, 9H, $C(CH_3)_3$), 0.31 (s, 6H, SiMe). ^{13}C NMR: 220.9 (s), 215.5 ★ (s), 213.1 (s, br), 211.7 (s, br), 195.7 ☆ (s), 160.3 (s), 136.3 (s), 134.7 (d), 133.7 (d), 114.3 (d), 31.0 (q), 26.1 (q), 18.8 (s), −3.5 (q). Mass spectrum: m/e 332 (P^+).

Preparation of η^2-(2-acetyl-3-t-butyldimethylsiloxy-4,5-dimethoxyphenyl)tetracarbonylmanganese (9). This was prepared similarly in 80% yield. IR: 2079(m), 1990(vs), 1931(m). ^{1}H NMR: δ 7.27 (s, 1H, H(6)), 4.07, 3.77 (s, 3H each, OMe), 2.67 (s, 3H, $C(O)CH_3$), 0.95 (s, 9H, $C(CH_3)_3$), 0.31 (s, 6H, SiMe). ^{13}C NMR: δ 220.8 (s, br), 212.7 ★ (s, br), 211.8 (s, br), 191.1 ☆ (s), 158.6 (s), 153.7 (s), 136.6 (s), 131.6 (s), 115.9(d), 60.4 (q), 56.0 (q), 29.5 (q), 26.2 (q), 19.2 (s), −2.9 (q). Mass spectrum: m/e 476 (P^+).

Preparation of η^2-(2-acetyl-3,5-dimethylphenyl)tetracarbonylmanganese (10). The standard procedure was used with 2′,4′-dimethylacetophenone and $PhCH_2Mn(CO)_5$. The crude product was chromatographed on silica plates, with ether/petroleum spirit (1/20) as eluant to give **10** in 56% yield; m.p. 122.5–124°C. (Found: C, 53.49; H, 3.53. $C_{14}H_{11}MnO_5$ calcd.: C, 53.52; H, 3.53%). IR (hexane): 2078(m), 1990(vs), 1941(m) cm^{-1}. ^{1}H NMR: δ 7.73, 6.75 (s, 1H each, H(4) + H(6)), 2.35, 2.57 (s, 3H, 3-Me + 5-Me), 2.65 (s, 3H, C(O)Me). ^{13}C NMR: δ 221.0 (s), 215.5 ★ (s), 213.1 (s), 211.9(s), 195.7 ☆ (s), 144.2 (s), 142.3 (s), 142.2 (s), 140.1 (d), 129.7 (d), 31.0 (q), 23.5 (q), 21.6 (q). Mass spectrum: m/e 314 (P^+).

Preparation of η^2-(2-acetyl-5-bromophenyl)tetracarbonylmanganese (11). Similarly *p*-bromoacetophenone was *ortho*-manganated in 96% yield; m.p. 116–120°C. (Found: C, 39.45; H, 1.70. $C_{12}H_6O_5BrMn$ calcd.: C, 39.49; H, 1.66%). IR (hexane): 2083(m), 1996(vs), 1949(m) cm^{-1}. ^{1}H NMR: δ 8.22 (d, J 1.79 Hz, 1H, H(6)), 7.68 (d, J 8.06 Hz, 1H, H(3)), 7.30 (dd, J 8.06, 1.79 Hz, 1H, H(4)), 2.59 (s, 3H, C(O)Me). ^{13}C NMR: δ 220.3 (s), 216.0 ★ (s), 212.5 (s), 210.7 (s), 196.5 ☆ (s), 143.8 (s), 143.5 (d), 132.1(d), 131.7 (s), 127.3 (d), 24.7 (q). Mass spectrum: m/e 366 (P^+).

Preparation of η^2*-(2-acetylthien-3-yl)tetracarbonylmanganese (12).* In the standard procedure, 2-acetylthiophene was *ortho*-manganated to give **12** in 75% yield. IR: 2085(m), 1998(vs), 1942(m). ^{1}H NMR: δ 8.10 (d, J 4.8 Hz, 1H, H(5)), 7.75 (d, J 4.8 Hz, 1H, H(4)), 2.25 (s, 3H, C(O)Me). ^{13}C NMR: δ 221.2 (s), 213.0 (s), 210.4 (s), 208.0 ★ (s), 204.3 ☆ (s), 141.7 (s), 138.9 (d), 138.6 (d), 25.0 (q). Mass spectrum: m/e 292 (P^+). The X-ray crystal structure is reported below.

Preparation of η^2*-(2-acetyl-1-methylpyrrol-3-yl)tetracarbonylmanganese (13).* This was prepared similarly from 2-acetyl-1-methylpyrrole in 28% yield after chromatography on silica plates. IR: 2079(m), 1990(vs), 1930(m). ^{1}H NMR: δ 7.07 (d, J 1.8 Hz, 1H, H(5)), 6.59 (d, J 1.8 Hz, 1H, H(4)), 3.88 (s, 3H, NMe), 2.49 (s, 3H, C(O)Me). Mass spectrum: m/e 289 (P^+).

Preparation of η^2*-(2-acetylfuran-3-yl)tetracarbonylbonylmanganese (14).* This was made in the usual way from 2-acetylfuran in 18% yield. IR: 2089(m), 2000(vs), 1944(m). ^{1}H NMR: δ 7.79 (d, J 1.1 Hz, 1H, H(5)), 7.05 (d, J 1.1 Hz, 1H, H(4)), 2.46 (s, 3H, C(O)Me). Mass spectrum: m/e 276 (P^+).

Preparation of η^2*-(3-acetyl-2,5-dimethylthien-4-yl)tetracarbonylmanganese (15).* This was prepared similarly from 3-acetyl-2,5-dimethylthiophene, in 70% yield. IR: 2078(m), 1987(vs), 1930(m). ^{1}H NMR: δ 2.73, 2.50, 2.48 (all s, 3H, Me). ^{13}C NMR: δ 222.3 (s), 213.6 (s), 211.7 (s), 205.6 ★, 166.0 ☆ (s), 151.3 (s), 147.1 (s), 134.6 (s), 27.2(q), 16.6 (q), 15.5 (q). Mass spectrum: m/e 320 (P^+). The X-ray crystal structure is reported below.

Preparation of η^2*-(3-acetylindol-2-yl)tetracarbonylmanganese (16).* This was prepared similarly from 3-acetylindole, and purified by preparative liquid chromatography (PLC) silica, in 90% yield. IR: 2089 (w), 1998 (vs), 1937 (s). ^{1}H NMR: δ 9.57 (s, br, 1H, N–H), 7.59 (m, br, 1H, ArH), 7.22 (m, br, 3H, ArH) 2.64 (s, 3H, C(O)Me). ^{13}C NMR: 212.7 (s), 210.9 ★ (s), 209.8 (s), 201.9 ☆ (s), 143.8 (s), 129.5 (s), 126.5 (s), 122.2 (d), 121.8 (d), 117.3 (d), 110.5 (d), 24.9 (q). Mass spectrum: m/e 325 (P^+).

X-ray crystal structure of ***12***

Yellow plates of the *ortho*-manganated 2-acetylthiophene derivative **12** were obtained from ether/hexane. Preliminary precession photography indicated monoclinic symmetry, with systematic absences appropriate for space group $C2/c$ or Cc. Cell constants and intensity data were obtained on an Enraf–Nonius CAD4 diffractometer.

Crystal data: $C_{10}H_5O_5MnS$, M 292.15, monoclinic, space group $C2/c$, a 25.855(3), b 5.863(1), c 16.952(3) Å, β 116.58(1)°, U 2298.2 Å^3, D_c 1.62 g cm^{-1} for $Z = 8$, $F(000)$ 1120, μ(Mo-K_α) 13 cm^{-1}, T 23°C. Total unique data 2779 in range $2° < 2\theta < 56°$, 1446 data with $I > 2\sigma(I)$ (after correction for Lorentz, polarisation, and absorption effects) used for all calculations. The structure was solved by automatic Patterson interpretation (SHELXS-86) and routinely developed. In the final cycle of least-squares full-matrix refinement all non-hydrogen atoms were treated anisotropically and hydrogen atoms were included in their calculated positions with common isotropic temperature factors. At convergence $R = 0.0366$, $R_w = 0.0336$ with $w = [\sigma^2(F) + 0.00025F_0^{2-}]^{-1}$, with no final shifts greater than 0.3σ. A final difference map showed no feature greater than ± 0.28 e Å^{-3}.

X-ray crystal structure of ***15***

Yellow rhombs of the *ortho*-manganated 3-acetyl-2,5-dimethylthiophene derivative **15** were obtained from ether/hexane. Preliminary precession photography

Table 1

Final positional parameters for (η^2-2-acetyl-3-thienyl)tetracarbonylmanganese (**12**)

Atom	x	y	z	Atom	x	y	z
Mn	0.14183(2)	−0.0497(1)	0.79885(4)	C(7)	0.0740(2)	0.1082(7)	0.7315(3)
S	0.07852(5)	−0.0971(2)	1.0039(1)	C(8)	0.1164(2)	−0.2691(8)	0.7174(3)
C(1)	0.1000(1)	−0.1595(7)	0.8684(2)	C(9)	0.1843(2)	0.0977(8)	0.7503(3)
C(2)	0.1132(1)	−0.0193(7)	0.9413(2)	C(10)	0.2032(2)	−0.2379(8)	0.8693(3)
C(3)	0.0460(2)	−0.3149(9)	0.9335(3)	O(1)	0.1705(1)	0.1895(5)	0.8992(2)
C(4)	0.0606(2)	−0.3321(8)	0.8657(3)	O(7)	0.0313(1)	0.1917(6)	0.6885(2)
C(5)	0.1522(2)	0.1642(8)	0.9564(2)	O(8)	0.1001(1)	−0.4120(6)	0.6656(2)
C(6)	0.1736(2)	0.3184(9)	1.0337(3)	O(9)	0.2103(1)	0.1889(7)	0.7211(2)
				O(10)	0.2391(1)	−0.3591(6)	0.9108(2)

Table 2

Final positional parameters for (η^2-3-acetyl-2,5-dimethyl-4-thienyl)tetracarbonylmanganese (**15**)

Atom	x	y	z	Atom	x	y	z
Mn	0.1604(2)	0.2289(1)	0.5687(1)	O(4)	0.363(1)	0.3814(9)	0.6032(6)
S	0.0994(3)	0.1159(2)	0.7874(1)	C(5)	−0.031(1)	0.0767(8)	0.5978(6)
C(1)	0.300(1)	0.1365(9)	0.5676(6)	O(5)	0.0113(9)	0.1259(6)	0.5497(4)
O(1)	0.387(1)	0.0813(9)	0.5691(5)	C(6)	0.028(1)	0.0988(7)	0.6633(5)
C(2)	0.173(1)	0.257(1)	0.4790(1)	C(7)	0.006(1)	0.0577(8)	0.7248(6)
O(2)	0.184(1)	0.2746(8)	0.4233(5)	C(8)	0.175(1)	0.1962(8)	0.7270(6)
C(3)	0.022(1)	0.3175(8)	0.5877(6)	C(9)	0.129(1)	0.1778(7)	0.6644(5)
O(3)	−0.059(1)	0.3731(7)	0.6002(6)	C(10)	−0.2099(7)	0.0034(5)	0.5672(3)
C(4)	0.285(1)	0.3208(9)	0.5884(7)	C(11)	−0.085(1)	−0.027(1)	0.7452(7)
C(12)	0.280(1)	0.2659(9)	0.7525(7)				

Table 3

Bond length and bond angles for (η^2-2-acetyl-3-thienyl)tetracarbonylmanganese (**12**)

Bond lengths (Å)			
Mn–C(1)	2.030(4)	Mn–O(1)	2.069(3)
Mn–C(7)	1.856(4)	Mn–C(8)	1.784(5)
Mn–C(9)	1.853(4)	Mn–C(10)	1.862(4)
S–C(2)	1.729(4)	S–C(3)	1.692(5)
C(1)–C(2)	1.392(5)	C(1)–C(4)	1.421(5)
C(2)–C(5)	1.418(5)	C(3)–C(4)	1.366(6)
C(5)–C(6)	1.480(5)	C(5)–O(1)	1.263(4)
Bond angles (°)			
C(1)–Mn–C(7)	85.0(2)	C(1)–Mn–C(8)	96.6(2)
C(7)–Mn–C(8)	88.0(2)	C(1)–Mn–C(9)	168.9(2)
C(7)–Mn–C(9)	94.5(2)	C(8)–Mn–C(9)	94.5(2)
C(1)–Mn–C(10)	87.8(2)	C(7)–Mn–C(10)	171.8(2)
C(8)–Mn–C(10)	89.0(2)	C(9)–Mn–C(10)	93.3(2)
O(1)–Mn–C(1)	79.9(2)	O(1)–Mn–C(7)	93.4(2)
O(1)–Mn–C(8)	176.1(2)	O(1)–Mn–C(9)	89.0(2)
O(1)–Mn–C(10)	89.1(2)	C(2)–S–C(3)	89.8(2)
Mn–C(1)–C(2)	110.2(3)	Mn–C(1)–C(4)	140.1(3)
C(2)–C(1)–C(4)	109.7(3)	S–C(2)–C(1)	113.6(3)
S–C(2)–C(5)	127.7(3)	C(1)–C(2)–C(5)	118.7(3)
S–C(3)–C(4)	114.3(3)	C(1)–C(4)–C(3)	112.6(4)
C(2)–C(5)–C(6)	125.3(4)	C(2)–C(5)–O(1)	115.5(4)
O(1)–C(5)–C(6)	119.1(4)		

Table 4

Bond parameters for (η^2-3-acetyl-2,5-dimethyl-4-thienyl)tetracarbonylmanganese, 15

Bond lengths (Å)			
Mn–C(1)	1.860(3)	Mn–C(2)	1.838(3)
Mn–C(3)	1.853(3)	Mn–C(4)	1.786(3)
Mn–C(9)	2.039(2)	Mn–O(5)	2.055(2)
S–C(7)	1.701(3)	S–C(8)	1.748(3)
C(6)–C(7)	1.383(3)	C(6)–C(9)	1.454(3)
C(8)–C(9)	1.365(3)	C(5)–C(10)	1.496(3)
C(7)–C(11)	1.498(3)	C(8)–C(12)	1.498(3)
C(5)–O(5)	1.251(3)	C(1)–O(1)	1.131(4)
C(2)–O(2)	1.133(4)	C(3)–O(3)	1.133(4)
C(4)–O(4)	1.145(4)		
Bond angles (°)			
C(2)–Mn–C(1)	94.7(1)	C(3)–Mn–C(1)	169.6(1)
C(3)–Mn–C(2)	95.6(1)	C(4)–Mn–C(1)	90.5(1)
C(4)–Mn–C(2)	91.7(1)	C(4)–Mn–C(3)	88.1(1)
C(9)–Mn–C(1)	83.8(1)	C(9)–Mn–C(2)	170.3(1)
C(9)–Mn–C(3)	86.2(1)	C(9)–Mn–C(4)	97.9(1)
O(50–Mn–C(1)	90.8(1)	O(5)–Mn–C(2)	90.6(1)
O(5)–Mn–C(3)	90.2(1)	O(5)–Mn–C(4)	177.3(1)
O(5)–Mn–C(9)	79.8(1)	C(7)–S–C(8)	93.8(1)
C(6)–C(5)–O(5)	117.0(2)	C(10)–C(5)–O(5)	117.8(2)
C(10)–C(5)–C(6)	125.1(2)	C(5)–O(5)–Mn	117.3(2)
C(7)–C(6)–C(5)	130.3(2)	C(9)–C(6)–C(5)	114.3(2)
C(9)–C(6)–C(7)	114.9(2)	C(6)–C(7)–S	109.4(2)
C(11)–C(7)–S	119.3(1)	C(11)–C(7)–C(6)	131.3(2)
C(9)–C(8)–S	111.2(2)	C(12)–C(8)–S	117.7(2)
C(12)–C(8)–C(9)	131.1(2)	C(6)–C(9)–Mn	111.0(2)
C(8)–C(9)–Mn	138.3(2)	C(8)–C(9)–C(6)	110.7(2)

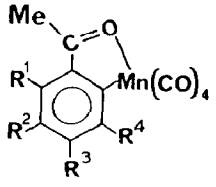
indicated orthorhombic symmetry, with systematic absences uniquely defining the space group *Pbca*. Cell constants and intensity data were obtained with a Nicolet XRD P3 diffractometer.

Crystal data: $C_{12}H_9O_5MnS$, M 320.20, orthorhombic, space group *Pbca*, a 9.601(2), b 13.913(3), c 19.918(10) Å, U 2660 Å^3, D_c 1.55 g cm^{-1} for $Z = 8$, $F(000)$ 1288, μ(Mo-K_α) 9.57 cm^{-1}, T −135 °C. Total data 3434 in range $5° < 2\theta < 55°$, 2758 data with $I > 2\sigma(I)$ after correction for Lorentz, polarisation and absorption effects used for all calculations. The structure was solved by direct methods (MULTAN [10]) and routinely developed. In the final cycle of least-squares full-matrix refinement Mn, S, and O atoms were treated anisotropically and hydrogen atoms were included in their calculated positions with common isotropic temperature factors. At convergence $R = 0.0495$, $R_w = 0.0611$ with $w = [\sigma^2(F) + 0.0008\ F_0^{2-}]^{-1}$, with no final shifts greater than 0.5σ.

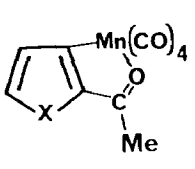
For both structures the refinement was carried out with SHELX-76 [11]. Final positional parameters are given in Tables 1 and 2, and selected bond parameters in Tables 3 and 4. Tables of thermal parameters, hydrogen atom positions, and structure factors can be obtained from the authors (BKN).

Results and discussion

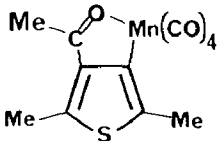
Previous work by Kaesz and co-workers has shown that *ortho*-manganation of substituted acetophenones using $PhCH_2Mn(CO)_5$ occurs readily according to eq. 1 in refluxing heptane during 1–2 hours [3], and our present syntheses of compounds **1–11** were designed mainly to extend the range of compounds available for further reactions. Some points are worth emphasising, however. The experimental procedures are straightforward, and yields are generally very good; yields are best when there are π-donor substituents on the arene. The ready *ortho*-manganation of *p*-bromoacetophenone (to give **11**) shows that halogen groups on the arene ring do not interfere with the reaction, so can be used to maintain potential reaction sites for elaboration following use of the *ortho*-manganated position. 2′-Hydroxyacetophenones do not react, presumably because the intramolecular hydrogen bonding removes the keto group as a potential donor to the metal atom, but protection of the hydroxy group with Bu^tMe_2Si or $PhCH_2$ allows the reaction to proceed (compounds **7–9**). Reaction of 3′,4′-dimethoxyacetophenone gives rise to two isomers **5** and **6**, depending on which of the two *ortho* C–H bonds is replaced



	R^1	R^2	R^3	R^4
(1)	H	H	H	H
(2)	H	H	OMe	H
(3)	OMe	OMe	OMe	H
(4)	H	OMe	OMe	OMe
(5)	H	OMe	OMe	H
(6)	H	H	OMe	OMe
(7)	OCH_2Ph	OMe	OMe	H
(8)	$OSiMe_2Bu^t$	H	H	H
(9)	$OSiMe_2Bu^t$	OMe	OMe	H
(10)	Me	H	Me	H
(11)	H	H	Br	H



(12) X = S
(13) X = N-CH_3
(14) X = O



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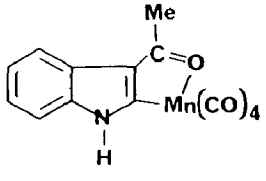


(16)

by the metal. The less sterically congested **5** is preferentially formed, in a ratio of 3/1 over **6** in which the manganese is adjacent to an OMe group. This contrasts with the results in the related reaction of 3′-methoxyacetophenone (originally reported with $MeMn(CO)_5$ [3], but we have obtained the same result with $PhCH_2Mn(CO)_5$), for which the attack occurs mainly at the C–H bond adjacent to the OMe, a preference attributed to the electronic properties of the substituent [3]. Presumably a similar electronic preference would be present during the preparation of **5** and **6**, but is countered by the increased steric constraints resulting from the 4′-methoxy groups preventing the 3′-methoxy bending away from the 2′-site. Such steric crowding is obviously not very severe, since even the highly substituted 3′,4′,5′-trimethoxyacetophenone can be efficiently *ortho*-manganated.

More novel are our results with heteroaromatic substrates. Kaesz found that *ortho*-manganation of acetylferrocene proceeded in only low yield, attributed to the strain of fusing two 5-membered rings together [12]. This however did not prove to be a difficulty for acetylthiophenes, which were observed to undergo very efficient *ortho*-manganation to give the 5-membered metallocyclic ring fused to either the 2,3 side (**12**) or the 3,4 side (**15**) of the thiophene ring, depending on the substrate used. The structures of these derivatives do not indicate excessive strain for either of these derivatives (see below). With the analogues 2-acetyl-1-methylpyrrole and 2-acetylfuran the corresponding *ortho*-manganated species **13** and **14** were isolated, but in only 28 and 18% yields, respectively. This may reflect the lower aromaticity of these heteroaromatic species compared with thiophene, although 3-acetylindole reacted in the pyrrole ring to produce **16** in high yield. There is no interference from the N–H bond of the indole.

All the new complexes reported are yellow, crystalline, air-stable substances which are readily soluble in polar organic solvents but less so in hexane. They were straightforwardly characterised by spectroscopy. In the carbonyl-stretching region there are generally three strong bands at about 2080, 1990 and 1935 cm^{-1}, with the middle one of these being a composite of two separate bands which are sometimes just resolved. The mass spectra of the compounds were unremarkable, giving clear parent ions, with subsequent stepwise loss of CO. Clean ^1H NMR spectra were obtained for all species and provided a useful guide to purity. The ^{13}C NMR spectra of *ortho*-manganated complexes have not been previously discussed, and so are considered here in more detail. The *ortho*-manganated derivatives generally show four signals around δ 200 ppm. Three of these are broad (intensity ratio 1/1/2) and are assigned to the four terminal CO groups on the manganese, while the remaining sharp peak (flagged with an * in the Experimental section) can be assigned to the acetyl carbon which has been shifted by 12–21 ppm to lower field from the value for the free ligand. This assignment is supported by the spectrum of $MeC(\overline{O})\overline{C_6H_5}MnCO)_3PPh_3$ [12], which shows three broad ^{13}C signals strongly coupled to phosphorus (J 17–22 Hz) and a sharp signal only weakly coupled (3 Hz) [5]. For the tetracarbonyl species further assignment can be made on the basis that CO groups with the lowest CO force constant (most back-bonding) give rise to the highest ^{13}C chemical shift [13]. Structural studies on *ortho*-manganated aryl ketones [4,14] show that Mn–CO bond lengths decrease going from the CO ligands *trans* to each other, to the CO *trans* to the aryl carbon, to the CO *trans* to the ketone O. The lowest-field signal therefore arises from the carbon opposite to the oxygen atom, the next lowest from that opposite to the carbon atom, with the highest field signal

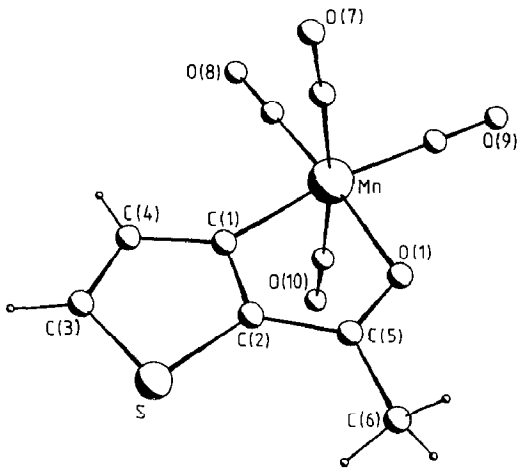


Fig. 1. The structure of *ortho*-managanated 2-acetylthiophene (**12**).

assigned to the two equivalent CO ligands. The signal from the aryl-carbon atom bonded to manganese was generally found in the range 190–210 ppm, although that of **4** was at 172 ppm, and that of **15** at 166.0 ppm. Comparison with the spectra of the free ketones shows that coordination shifts the signal of the carbon attached to manganese (marked with a * in the experimental section) by 62–74 ppm to lower field, those on either side by 9–14 ppm to lower field, with only small shifts for the remaining aryl carbon signals.

The structures of two *ortho*-manganated thiophene derivatives **12** and **15** were determined to investigate the effects of fusing two five-membered rings together. The geometry of the *ortho*-manganated 2-acetylthiophene is shown in Fig. 1. The molecule consists of two coplanar five-membered heterocycles with essentially octahedral coordination about the manganese atom, although the small "bite" of the chelating ligand gives rise to a C(1)–Mn–O(1) angle of 79.9°, and the out-of-plane *trans*-CO ligands lean towards the weaker π-acceptor ligands, as expected. There seems to be little evidence of strain in the molecule, with the C(4)–C(1)–Mn angle of 140° the only parameter significantly different from normal values. The bond lengths show that coordination of the organic group leads to: (i) lengthening of the C(5)–O(1) and C(1)–C(2) bonds; and (ii) shortening of the C(2)–C(5) and S–C(3) bonds. This can be explained in terms of the resonance forms **17**. The Mn–C(1) distance of 2.030(4) Å appears to be shorter than expected for a single bond (> 2.1 Å [4]), suggesting that there is significant multiple bonding. An extensively delocalised π bonding system over both rings is therefore indicated.

The structure of **15** is shown in Fig. 2. Again the molecule is planar except for the two *trans*-CO ligands and the coordination about manganese is similar to that in **12**. The C(9)–Mn–O(5) angle is 79.8° which appears characteristic of these five-membered manganacyclic rings [4]. For this molecule there is some evidence of strained geometry; both C(5)–C(6)–C(7) and Mn–C(9)–C(8) angles are larger than expected (130.3 and 138.3°, respectively) and the methyl groups are also bent towards the sulphur atom to give C(6)–C(7)–C(11) and C(9)–C(8)–C(12) angles of about 131°. These distortions probably arise more from the crowding in the tetrasubstituted ring than from difficulties in combining two five-membered rings. The variations in C–C

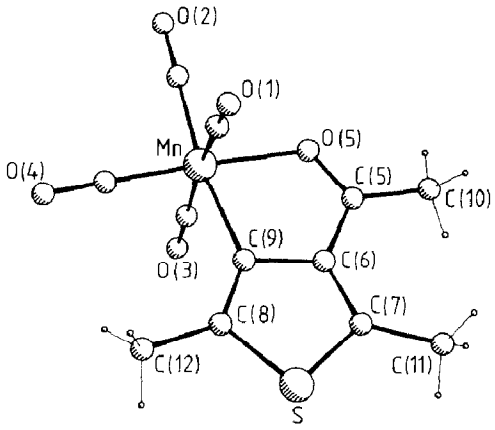
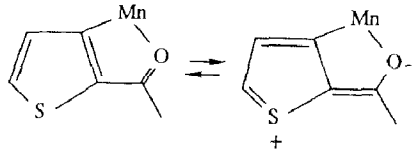


Fig. 2. The structure of the *ortho*-managanated 3-acetyl-2,5-dimethylthiophene (**15**).

bond lengths within the molecule can be understood in terms of contributions from both resonance forms **18**, but again a delocalised π-bonding network over the whole planar framework is indicated. For both of the structures reported here the Mn–CO distances vary. The carbonyl ligand *trans* to the Mn–O bond is the shortest, that opposite the Mn–C(aryl) bond is next shortest, with the two equivalent Mn–CO bonds above and below the plane of the molecule the longest. This is a common feature in *ortho*-manganated complexes [4,14] arising from the relative π-bonding properties of the coordinated atoms, and is also reflected in the ^{13}C NMR shifts for the carbonyl carbon atoms (see above).

A comparison of the structures **12** and **15**, containing two five-membered rings, with that of the *ortho*-manganated acetophenone **1**, containing fused six- and five-membered rings [4], shows that the metallocyclic ring is very similar in all three



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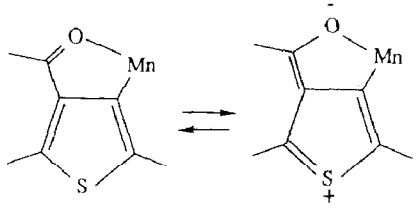

(18)

species. The longer C–O and shorter adjacent C–C distances in the thiophene complexes may indicate slightly greater delocalisation for these compared with that in the phenyl analogue, but other bond parameters compare closely. The problems encountered [12] in *ortho*-manganation of acetylferrocene and related metallocycles may therefore not arise from the strain of fusing two small rings together, but rather relate to electronic factors.

Acknowledgements

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