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Ortho-manganated arenes in synthesis

V *. *Ortho*-manganation of *N*-acyl heteroaromatics, benzamides and substituted benzaldehydes. Crystal structure of (η^2-*O,C*-1-acetyl-2-indolyl)tetracarbonylmanganese

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Abstract

1-Benzoylpyrrole has been shown to react with $PhCH_2Mn(CO)_5$ in refluxing heptane to *ortho*-manganate the heterocyclic ring to give (η^2-*O,C*-1-benzoyl-2-pyrrolyl)tetracarbonylmanganese in good yield. Similarly prepared were the corresponding derivatives of *N*-acetylpyrrole and of *N*-acetyl- and *N*-benzoyl-indole. *N,N*-Dialkylbenzamides could also be *ortho*-manganated in good yields, but not the parent benzamide. Benzaldehydes also react provided that they contain *p*-MeO or *p*-Me_2N substituents. The structure of (η^2-*O,C*-1-acetyl-2-indolyl)tetracarbonylmanganese has been determined by X-ray diffraction.

Introduction

The *ortho*-manganation of aromatic ketones with alkylpentacarbonylmanganese reagents is well established for benzenoid- and hetero-arenes [1–4], e.g. eq. 1.

$$PhCH_2Mn(CO)_5 + CH_3C(O)C_6H_5 \rightarrow 2\text{-}CH_3C(O)\overline{C_6H_4Mn}(CO)_4 + PhCH_3 \quad (1)$$

Extension to other *O*-donor aromatic substrates is not straightforward; thus aryl ethers do not undergo the corresponding reaction at all [5], methyl benzoate can be *ortho*-manganated only very inefficiently [5], and quinones react quite differently [5], while other reagents containing the C=O functionality do not seem to have been examined previously. We are currently exploring the use of *ortho*-manganated arenes in synthesis [6], and to provide a wider range of substrates we now report the results of our studies of the *ortho*-manganation of *N*-acyl-heteroaromatics, benzamides, and substituted benzaldehydes.

* For Part IV see preceding paper [1].

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Experimental

General procedures are given in the preceding paper [1]. Chromatographic separations were carried out on a Harrison Research Inc. Chromatotron using a 1 mm plate and CH_2Cl_2/petroleum spirit (60–80 °C) 1/4 as eluent. n-Butyllithium (Merck, 15% in hexane, 1.6 mol l^{-1}), the starting amines, amides, and substituted benzaldehydes (BDH), were used as received. Benzaldehyde was purified by an established procedure [7]. *N,N*-Dimethylbenzamide was prepared as described by Johnstone and Rose [8].

Preparation of N-acetylindole. Indole (0.413 g, 3.52 mmol) was dissolved in THF (15 ml) and cooled to 0 °C in an ice bath. n-Butyllithium (2.2 ml, 1.6 mol l^{-1}, 3.52 mmol) was added dropwise under a stream of nitrogen over 15 min. Stirring was continued for a further 30 min at 0 °C. Acetic anhydride (0.35 ml, 3.71 mmol) was added dropwise during 5 min. The solution was allowed to warm to room temperature, then stirred for a further 30 min. The mixture was poured into water (5 ml), and extraction with ethyl acetate (2 × 30 ml) was followed by drying of the extract ($MgSO_4$) and evaporation under reduced pressure to give a brown oil (0.557 g). The oil was chromatographed with CH_2Cl_2/hexane (1/1) to give a colourless oil (0.398 g, 71%). Similarly prepared were *N*-benzoylindole, *N*-acetylpyrrole, *N*-benzoylpyrrole, *N*-acetylimidazole, *N,N*-diethylbenzamide, *N*-benzoylpyrrolidine, *N,N*-diphenylbenzamide, N,N,-diethylacetamide and *N*-acetylpiperidine.

Ortho-manganation of N-acetylindole. A solution of $PhCH_2Mn(CO)_5$ (0.136 g, 0.475 mmol) and *N*-acetylindole (0.081 g, 0.509 mmol) in heptane (25 ml) was refluxed for 4 h. After cooling, the heptane was removed under vacuum. The residue was chromatographed to give a yellow solid (0.105 g, 68%), which was recrystallised from petroleum spirit to give yellow plates of **3**, m.p. 112 °C (dec.). (Found: C, 51.76; H, 2.44; N, 4.22, MS(P^+) 325; $C_{14}H_8NO_5Mn$ calcd.: C, 51.71; H, 2.48; N 4.31%, *M* 325. IR: 2087(m), 2003(vs), 1944(s), 1586(m), 1566(m). ^1H NMR: δ 7.31 (m, 4H, C_6H_4), 6.83 (s, 1H, H(-3)), 2.74 (s, 1H, CH_3).

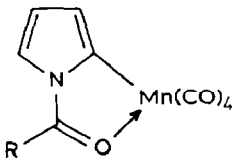
Ortho-manganation of N-acetylpyrrole. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.257 g) and *N*-acetylpyrrole (0.098 g) with 5 h. reflux was **1**, 0.095 g, 36%, m.p. 102 °C. (Found: C, 43.70; H, 2.12; N, 5.03%, MS(P^+) 275; $C_{10}H_6NO_5Mn$ calcd.: C, 43.66; H, 2.20; N, 5.09%, *M* 275. IR: 2087(m), 2000(vs), 1953(s), 1596(m), 1550(m) cm^{-1}. ^1H NMR: δ 7.30, 6.54 6.44 (br s, 1H each, H(ring)), 2.54 (s, 1H, CH_3).

Ortho-manganation of N-benzoylpyrrole. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.174 g) and *N*-benzoylpyrrole (0.107 g) with 1.5 h. reflux was **2** as a non-crystallising oil after chomatography, 0.122 g, 59%. MS(P^+) 337. IR: 2087(m), 2000(m), 1952(s), 1586(m), 1562(m) cm^{-1}. ^1H NMR: δ 7.60 (br, s, 5H, C_6H_5), 7.76(m, 1H), 7.46(m, 1H), 6.56(s, 1H).

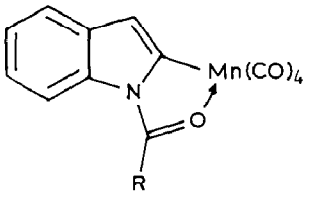
Ortho-manganation of N-benzoylpyrrole. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.174 g) and *N*-benzoylpyrrole (0.107 g) with 1.5 h. reflux was **2** as a non-crystallising oil after chomatography, 0.122 g, 59%. MS(P^+) 337. IR: 2087(m), 2000(m), 1952(s), 1586(m), 1562(m) cm^{-1}. ^1H NMR: δ 7.60 (br, s, 5H, C_6H_5), 7.76(m, 1H), 7.46(m, 1H), 6.56(s, 1H).

A similar reaction with *N*-acetylimidazole gave no manganated product.

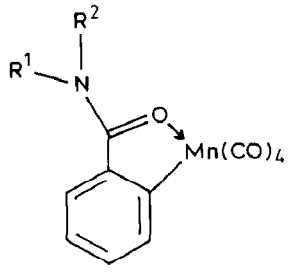
Ortho-manganation of N,N-dimethylbenzamide. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.160 g) and $C_6H_5C(O)NMe_2$ (0.142 g) with 5 h. reflux was **5**,



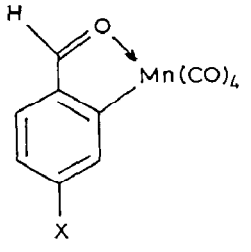
(**1**: R = CH_3 ;
2: R = C_6H_5)



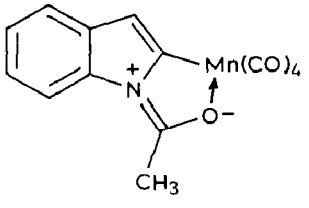
(**3**: R = CH_3 ;
4: R = C_6H_5)



(**5**: $R^1 = R^2 = CH_3$;
6: $R^1 = R^2 = CH_2CH_3$;
7: $R^1, R^2 = (CH_2)_4$)



(**8**: X = OCH_3 ;
9: X = NMe_2)



(**10**)

0.176 g, 100%, m.p. 120–125 °C (dec.). (Found: C, 49.38; H, 3.08; N, 4.37, MS(P^+) 315; $C_{13}H_{10}NO_5Mn$ calcd.: C, 49.52; H, 3.20; N, 4.44%, *M* 315. IR: 2076(m), 1986(vs), 1924(s), 1575(m), 1566(m) cm^{-1}. ^1H NMR: δ 8.05, 7.73, 7.27 (all br, 4H, H(ring)), 3.30 (s, 6H, NCH_3).

Ortho-manganation of N,N-diethylbenzamide. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.116 g) and $C_6H_5C(O)NEt_2$ (0.173 g) with 4 h reflux was **6**, 0.047 g, 33%, m.p. 96-99 °C (dec.). (Found: C, 52.36; H, 4.14; N, 4.08, MS(P^+) 343; $C_{15}H_{14}NO_5Mn$ calcd.: C, 52,49; H, 4.11; N, 4.08%; *M* 343. IR: 2076(m), 1986(vs), 1932(s), 1573(m), 1559(m) cm^{-1}. ^1H NMR: δ 8.02, 7.60 (all br, 4H, H(ring)), 3.63 (br, 4H, NCH_2), 1.33 (br, 6H, CH_3).

Ortho-manganation of N-benzoylpyrrolidine. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.135 g) and $C_6H_5C(O)N(CH_2)_4$ (0.097 g) with 5 h. reflux was **7**, 0.124 g,

77%, m.p. 88–93°C (dec.). (Found: C, 52.74; H, 3.44; N, 4.08, MS(P^+) 341; $C_{15}H_{12}NO_5Mn$ calcd.: C, 52.80; H, 3.54; N, 4.10%, *M* 341. IR: 2076(m), 1986(vs), 1927(s), 1574(m), 1559(m). ^{1}H NMR: δ 8.01(d), 7.74(d), 7.20(m) (4H, H(ring)), 3.63 (t, 4H, NCH_2), 1.42 (br s, 4H, CH_2).

Attempts to *ortho*-manganate *N*,*N*-di-iso-propylbenzamide by the same method gave only traces of expected product, and *N*,*N*-diphenylbenzamide underwent no *ortho*-manganation.

Ortho-manganation of p-methoxybenzaldehyde. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.127 g) and 4-$MeOC_6H_4CHO$ (0.062 g) with 4.5 h reflux was **8**, 0.044 g, 33%, as an oil. MS(P^+) 302; IR: 2083(m), 1996(vs), 1944(s), 1581(m), 1574(m) cm^{-1}. ^{1}H NMR: δ 9.26 (s, 1H, C*H*O), 7.85 (d, *J* 8.8 Hz, 1H, H(3)), 7.60(s, 1H, H(6)), 6.72 (d, *J* 8.8 Hz, 1H, H(4), 3.97 (s, 3H, OCH_3).

Various attempts to *ortho*-manganate unsubstituted benzaldehyde were unsuccessful.

Ortho-manganation of p-(dimethylamino)benzaldehyde. Similarly prepared from $PhCH_2Mn(CO)_5$ (0.114 g) and 4-$(Me_2N)C_6H_4CHO$ (0.062 g) with 7.5 h reflux was **9**, 0.077 g, 61%, m.p. 124–128°C. (Found: C, 49.92; H, 3.35; N, 4.40, MS(P^+) 315; $C_{13}H_{10}NO_5Mn$ calcd.: C, 49.54; H, 3.20; N, 4.44%, *M* 315. IR: 2079(m), 1991(vs), 1935(s), 1588(m), 1562(m) cm^{-1}. ^{1}H NMR: δ 8.99(s, 1H, CHO), 7.70(d, *J* 8.7 Hz, 1H, H(3)), 7.29 (s, 1H, H(6)), 6.46 (dd, *J* 8.7,2.1 Hz, 1H, H(4)), 3.20 (s, 6H, N-CH_3).

X-ray crystal structure of (η^2-1-acetyl-2-indolyl)tetracarbonyl-manganese (3). Preliminary precession photography showed triclinic symmetry. Intensity data were collected on an Enraf–Nonius CAD4 automatic four circle diffractometer using monochromated Mo-K_α X-rays.

Table 1

Positional parameters for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese.

Atom	*x*	*y*	*z*
Mn	0.20924 (5)	0.31846 (4)	0.16923 (3)
C(1)	0.2653 (3)	0.1299 (3)	0.2432 (2)
C(2)	0.3241 (3)	−0.0073 (3)	0.2118 (2)
C(3)	0.3248 (3)	−0.0865 (2)	0.3264 (2)
C(4)	0.3743 (3)	−0.2276 (3)	0.3476 (2)
C(5)	0.3612 (3)	−0.2702 (3)	0.4716 (3)
C(6)	0.3001 (3)	−0.1748 (3)	0.5744 (3)
C(7)	0.2497 (3)	−0.0330 (3)	0.5574 (2)
C(8)	0.2630 (3)	0.0093 (2)	0.4325 (2)
N	0.2254 (2)	0.1428 (2)	0.3810 (2)
C(9)	0.1636 (3)	0.2733 (2)	0.4353 (2)
O(1)	0.1424 (2)	0.3713 (2)	0.3617 (1)
C(10)	0.1233 (3)	0.3022 (3)	0.5762 (2)
C(11)	−0.0147 (4)	0.2158 (3)	0.1351 (2)
O(11)	−0.1420 (3)	0.1453 (3)	0.1075 (2)
C(12)	0.2730 (4)	0.2588 (3)	0.0056 (3)
O(12)	0.3142 (4)	0.2179 (3)	−0.0996 (2)
C(13)	0.1417 (4)	0.5018 (3)	0.1313 (3)
O(13)	0.1000 (4)	0.6144 (2)	0.1079 (2)
C(14)	0.4479 (4)	0.3893 (3)	0.1958 (3)
O(14)	0.5947 (3)	0.4273 (3)	0.2060 (3)

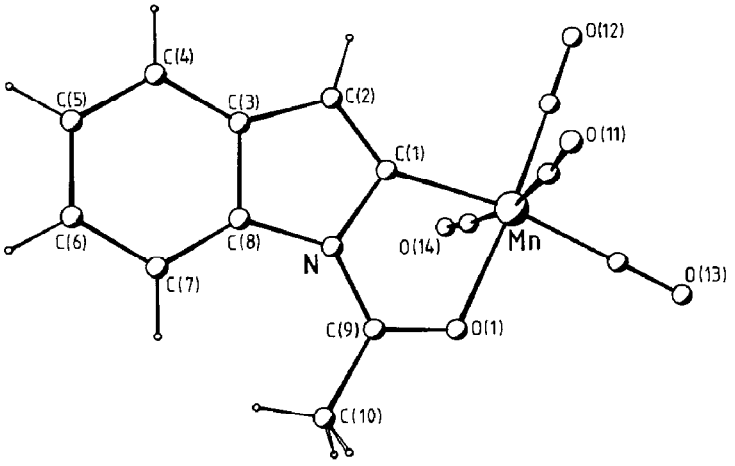


Fig. 1. The structure of (η^2-(O,C)-1-acetyl-2-indolyl)tetracarbonylmanganese (3).

Crystal data: $C_{14}H_8MnNO_5$, M 325.16, triclinic, space group $P\bar{1}$, a 7.451(1), b 8.963(3), c 10.389(2) Å, α 96.01(2), β 87.27(1), γ 94.99(2)°, U 686.9 Å^3. D_c 1.57 g cm^{-3} for $Z = 2$ $F(000)$ 328, μ(Mo-K_α) 9 cm^{-1}, T 23°C. Intensity data in the range $2 < 2\theta < 52°$ were collected using a θ–2θ scan technique. Minimum and maximum transmission factors of 0.9729 and 0.9991 respectively were applied based on a series of azimuthal scans.

A total of 3114 unique reflections were collected and those 2596 for which $I > 2\sigma(I)$ were used in all calculations. The position of the manganese atom was located by Patterson methods, and all other non-hydrogen atoms were found in

Table 2

Selected Bond Parameters for η^2-(1-acetyl-2-indolyl)tetracarbonylmanganese.

Bond lengths (Å).			
Mn–C(1)	2.012(2)	Mn–O(1)	2.054(2)
C(1)–C(2)	1.345(3)	C(2)–C(3)	1.449(3)
Mn–C(11)	1.865(3)	Mn–C(12)	1.783(3)
Mn–C(13)	1.846(3)	Mn–C(14)	1.860(3)
N–C(1)	1.443(3)	N–C(8)	1.416(3)
N–C(9)	1.353(3)	C(9)–O(1)	1.249(3)
C(9)–C(10)	1.481(3)		

(Corresponding distances in *N*-acetyl-3-methylindole [11] are: N–C(1) 1.40; N–C(8) 1.41; N–C(9) 1.38; C(9)–O(1) 1.20; C(1)–C(2) 1.33; C(2)–C(3) 1.43.)

Bond angles (°).			
C(1)–Mn–O(1)	79.2(1)	C(1)–Mn–C(11)	85.1(1)
C(1)–Mn–C(12)	96.2(1)	C(1)–Mn–C(13)	169.6(1)
C(1)–Mn–C(14)	87.1(1)	C(1)–N–C(9)	117.2(2)
C(1)–N–C(8)	109.9(2)	C(8)–N–C(9)	132.9(2)
N–C(9)–O(1)	117.3(2)	N–C(9)–C(10)	122.4(2)
N–C(1)–C(2)	106.5(2)	C(1)–C(2)–C(3)	110.1(2)
Mn–C(1)–N	110.1(1)	Mn–C(1)–C(2)	143.4(2)
C(1)–C(9)–O(1)	120.3(2)	Mn–O(1)–C(9)	116.2(1)

subsequent difference maps. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were assigned to calculated positions. The refinement converged at $R = 0.035$, $R_w = 0.0414$ where $w = [\sigma^2(F) + 0.008F^2]^{-1}$. Calculations were performed using SHELX-76 [9]. Final atom coordinates are given in Table 1, selected bond parameters in Table 2, while the structure is illustrated in Fig. 1.

Results and discussion

By the procedure previously employed for *ortho*-manganating aromatic ketones [1,2], *N*-acetylpyrrole was treated with $PhCH_2Mn(CO)_5$ to give the corresponding complex **1**, with the tetracarbonylmanganese group attached to the ligand via Mn–O and Mn–C bonds. For *N*-benzoylpyrrole two *ortho*-manganation products are possible; the first arising from attack at the *ortho* carbon of the pyrrole ring, and the second from attack at the phenyl ring. We observed only the first of these, i.e. compound **2**, indicating that the pyrrole ring is more reactive than the phenyl ring despite the fact that **2** contains the strained combination of two five-membered rings fused together. These reactions are closely parallelled by those of the larger heterocycles, *N*-acetyl- and *N*-benzoyl-indole, which give **3** and **4**, respectively; for the benzoyl derivative there are three potential sites for the metallation, in the five-membered ring at C(1), the six-membered indole ring at C(7), and the phenyl ring. Attack at only the first of these is observed, and this again presumably reflects the relative reactivities of the different C–H bonds in the substrate. There is an important distinction between the *ortho*-manganated species **1**–**4**, which contain a five-membered ring made up from two carbon atoms and one each of Mn, O and N, and the previously described species derived from ketones where the ring has three carbon atoms and one each of oxygen and manganese. The *N*-acyl-pyrroles and -indoles therefore have the potential for forming unusual heterocyclic ring assemblies via the reactions established for other *ortho*-manganated compounds [6].

Benzamides are another class of compound in which the C=O function is suitably positioned for *ortho*-manganation. The parent compound $H_2NC(O)C_6H_5$ does not give rise to any identifiable organometallic product on treatment with $PhCH_2Mn(CO)_5$ in refluxing heptane. However the substituted analogues $R_2NC(O)C_6H_5$, (R = Me, Et, $(CH_2)_4$) react straightforwardly to give the *ortho*-manganated derivatives **5**–**7**. The yield in the case of R = Me is essentially quantitative, while that for the R = Et is lower, presumably because of increased crowding adjacent to the C=O group, since the yield is also good for the R = $(CH_2)_4$ example, where the steric constraints are smaller . When R = Pr^i only traces of an analogous complex were detected, and with R = Ph no *ortho*-manganation at all was observed.

For the benzamides the possibility of different *ortho*-manganation products again arises, since there are now two potential donor atoms (the O of the C=O group, and the N of the amide group) suitably positioned to encourage *ortho*-manganation to give either *O,C* or *N,C* chelated organic groups, each with a five-membered ring. Although the N,C-type ring is produced [3] with azobenzenes, imines and amines (e.g. with *N,N*-dimethylbenzylamine [10]) under similar conditions, there was no evidence for other than *O,C* coordination with the benzamides studied in the present work. There is of course considerable lowering of lone pair density on the nitrogen of amides through delocalisation on to the oxygen atom.

Attempts to *ortho*-manganate benzaldehyde with $PhCH_2Mn(CO)_5$ were unsuccessful. Although the mechanisms of *ortho*-manganation reactions are not known, a sequence involving coordination of the O-donor to manganese with subsequent attack at an *ortho* C–H seems reasonable. On this basis it has been suggested that the donor ability of the C=O group is important, and that the C–O stretching frequency of this may be a useful guide as to whether a compound is a suitable substrate [4,5] since it should reflect any enhanced lone pair density on the oxygen (for instance resulting from delocalisation from the aryl ring). Benzaldehyde has a high C=O stretching frequency (1700 cm^{-1}) compared with substrates that are readily *ortho*-metallated, so it was of interest to examine substituted benzaldehydes with lowered ν(CO) frequencies in order to test the correlation between this parameter and reactivity. We find that both *p*-methoxybenzaldehyde (ν(CO) 1685 cm^{-1}) and *p*-(dimethylamino)benzaldehyde (ν(CO) 1660 cm^{-1}) react under the usual conditions to give the *ortho*-manganated derivatives **8** and **9**. This does not necessarily mean that it is the donor ability of the C=O group that is the important factor, since substituents on the aromatic ring that increase the electron density on the acyl group, and hence lower the C=O stretching frequency, may also enhance the reactivity of the ring to attack by the metal. However, it does show that there is a useful empirical guide which predicts that substrates for orthomanganation should have $\nu(CO) < 1700\ cm^{-1}$.

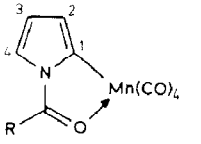
It is generally recognised that cyclomanganation of aliphatic ketones is not possible. This conclusion is based on experiments with substrates having ν(CO) values above 1700 cm^{-1}, which raises the question of whether it is a lack of O-donor strength which leads to non-reaction. To test this, the aliphatic substrate *N*-acetylpiperidine which as an amide has ν(CO) at 1652 cm^{-1} was refluxed in heptane with $PhCH_2Mn(CO)_5$, but no cyclometallation was observed, confirming that attack at a sp^3 carbon is not favoured, at least for amides with an apparently good donor oxygen atom.

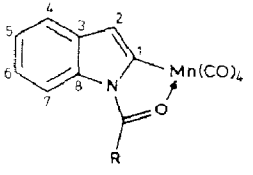
The infrared spectra of **1**–**9** give the expected pattern of three peaks in the carbonyl-stretching region [1,2]. For the *N*-acyl complexes **1**–**4** all the peaks are shifted to higher frequencies by about 15 cm^{-1} when compared to other *ortho*-manganated species. This results from the presence of the electronegative nitrogen atom in the metallocycle and emphasises the point that these complexes are significantly different from *ortho*-manganated aryl ketones. All the species show two peaks in the 1500–1600 cm^{-1} region arising from vibrations associated with the C=O group and the aromatic ring(s), with the lower energy of the two being predominantly from the ketone group, having been shifted about 150 cm^{-1} from the value found for the free ligand (cf. ref. 2).

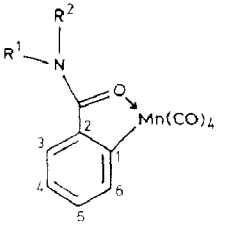
The ^1H NMR data for the new complexes, given in the experimental section, are unremarkable. The ^{13}C data is presented in Table 3, together with the corresponding values for the free ligands. The *N*-acyl-pyrrole and -indole species, and the benzamides, all show signals arising from the C=O carbon atom in the region 177–180 ppm, which is ca. 20 ppm to higher field than those for phenyl ketones [1] or for the benzaldehyde derivatives **8**, **9**. Similarly the carbon atom bonded to the manganese atom is observed in the δ 160–175 region for the *N*-acyl complexes, and at ca. δ 185 for the benzamides, whereas values above δ 190 are more usual for previously studied examples. The smaller δ values observed for complexes **1**–**7** can be directly attributed to the nitrogen atom bonded to the C=O group **5**–**7**, and adjacent to both

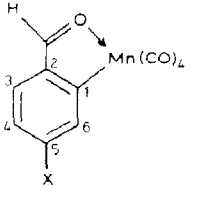
Table 3. ^{13}C shifts of the orthomanganated complex and corresponding free ligand [a]

	C=O	C–Mn	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C≡O	Other
1	178.9	162.6	124.7	120.4	120.7	–	–	–	–	210.0, 216.5	19.9(CH_3)
	(167.4)	(118.9)	(112.8)	(112.8)	(118.9)	–	–	–	–	–	(21.8)(CH_3)
2	177.3	163.3	125.0	120.8	122.8	–	–	–	–	210.1, 212.4	133.2(1′), 128.8(2′,6′), 129.3(3′5′), 130.3(4′)
	(167.3)	(121.0)	(112.9)	(112.9)	(121.0)	–	–	–	–	–	(133.0)(1′), (128.2)(2′,6′), (129.2)(3′,5′), (131.9)(4′)
3	178.4	172.5	112.1	137.2	121.8	121.2	118.5	124.6	137.5	209.8, 219.3 220.2	22.6(CH_3)
	(168.4)	(125.0)	(108.6)	(123.3)	(124.7)	(120.5)	(116.1)	(130.1)	(135.2)	–	(23.4)(CH_3)
4	177.5	172.7	113.0	137.7	122.9	120.8	118.2	124.9	137.9	209.8, 212.2 212.4	132.5(1′), 127.8(2′,6′), 128.9(3′,5′), 131.7(4′)
	(162.4)	(124.2)	(101.6)	(120.2)	(121.3)	(119.2)	(111.1)	(128.1)	(135.6)	–	(134.2)(1′), (128.4)(2′,6′), (130.0)(3′,5′), (132.5)(4′)
5	179.7	185.6	141.6	128.9	138.2	130.9	122.8	–	–	212.4	39.3, 40.4 (N–CH_3)
	(170.9)	(126.5)	(135.9)	(126.5)	(127.8)	(128.9)	(127.8)	–	–	–	(34.8) (38.8) (N–CH_3)
6	179.1	185.3	141.9	127.6	138.1	130.8	123.0	–	–	212.5	44.3 (N–CH_2), 13.4 (CH_3)
	(169.9)	(125.2)	(136.2)	(125.2)	(127.3)	(127.6)	(127.3)	–	–	–	(38.9) (43.8) (N–CH_2), (12.4) (CH_3)
7	177.2	185.0	141.6	123.0	139.0	128.0	123.0	–	–	212.8	23.3, 26.9(β), 49.2, 49.7(α)
	(168.5)	(126.2)	(136.2)	(126.2)	(127.2)	(128.8)	(127.0)	–	–	–	(23.4) (25.4)(β), (45.2) (48.5)(α)
8	199.8	196.9	135.8	134.8	121.5	153.5	108.6	–	–	212.4, 213.0 214.1	40.1(N–CH_3)
	(190.1)	(131.7)	(125.1)	(131.7)	(110.9)	(154.2)	(110.9)	–	–	–	(39.9) (N–CH_3)
9	204.0	200.3	140.5	135.3	124.7	164.5	112.2	–	–	211.3, 212.9	55.6 (O–CH_3)
	(190.0)	(131.2)	(129.4)	(131.2)	(113.7)	(164.0)	(113.7)	–	–	–	(54.9) (O–CH_3)









[a] In parentheses (the numbering is not systematic but is chosen to allow direct comparison of corrsponding signals in the metallated analogues).

carbon atoms in question for **1–4**, since there are similar trends for the free ligands. For all *ortho*-manganated complexes there is a general pattern of the C=O ^{13}C signal shifting from the free ligand value by 10–15 ppm to higher field, while the Mn–C carbon similarly shifts by 40–60 ppm on coordination to the metal.

The structure of the *ortho*-manganated *N*-acetylindole complex **3** was determined by X-ray crystallography in order to compare the novel nitrogen-containing metallocyclic ring with the equivalent fragment of cyclometallated ketones. The structure is illustrated in Fig. 1. The molecule is planar except for the mutually *trans* CO(11) and CO(14), with no other non-hydrogen atom more than 0.06 Å from the least-squares plane. The $Mn(CO)_4$ group is coordinated to the acetyl oxygen atom and the *ortho* carbon atom of the five-membered ring. The strain imposed by fusing two five-membered rings together is reflected in Mn–C(1)–C(2) and C(9)–N–C(8) angles of 143 and 132°, respectively, but the compound is nevertheless prepared in yields comparable with those for less-strained analogues.

A comparison of the bond parameters found for **3** with those of *N*-acetyl-3-methylindole * (Table 2) shows that coordination has led to the shortening of the N–C(9) bond, and lengthening of the C(9)–O(1), the C(1)–N and the C(1)–C(2) bonds. All this is consistent with delocalised π-bonding over the metallocycle ring, with a major redistribution of the nitrogen lone pair from the arene ring into the N–C(9) bond, to compensate for the withdrawal of electron density from C(9) arising from coordination at the acyl oxygen atom (i.e. there is a strong contribution from resonance form **10**). The Mn–C(1) distance of 2.012 Å is the shortest yet recorded for an *ortho*-manganated acyl-arene [1,12], indicating substantial π bonding for this bond, while the C=O distance is at the longer end, and the Mn–O at the shorter end, of the respective ranges found in related molecules. The geometry of the metallocycle ring of **3** is therefore fully consistent with an enhanced delocalised π bonding interaction arising from the presence of the nitrogen atom in the ring. The other bond parameters of the arene ring are unremarkable, while the relative Mn–CO distances and C–Mn–C angles of the $Mn(CO)_4$ group fall into the pattern established for other *ortho*-manganated compelexes [1,12].

Conclusion

Ortho-manganation of benzamides and benzaldehydes is not as general as that of acetophenones, success being dependent on the nature of the substituents on N (benzamides) or on the ring (benzaldehydes). Nevertheless the products obtained have the potential for introduction at the *ortho* position of substituents such as those we have reported for acetophenones, namely halogen [13], HgCl [14] or various carbon functions from alkenes [6,15]. Similar functionalisation at the even less accessible 2-position of indoles (which normally have a chemistry dominated by electrophilic attack at the 3-position) should prove useful.

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* Also known as *N*-acetylskatole [11] The crystal structure of *N*-acetylindole was not available on Cambridge Crystallographic Data Centre file (March, 1987).

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