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Orthomanganated arenes in synthesis

VIII *. Mono- and dicyclomanganation of diacetyl benzenes

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Abstract

1,3-Diacetylbenzene reacts with $PhCH_2Mn(CO)_5$ in refluxing heptane to give the mono- and di-cyclomanganated complexes η^2-(2,4-diacetylphenyl)tetracarbonylmanganese (1) and η^2,η^2-4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese) (2). Corresponding cyclomanganated compounds are also formed by 1,4-diacetylbenzene. Infrared studies and a crystal structure determination of 2, indicate little interaction between the two manganese groups attached to the same ring.

Introduction

The C=O functional group is a generally useful one for directing the cyclomanganation of arenes [1–4], as for example in eq. 1.

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

Among the substrates that have given cyclomanganated derivatives are acetophenones [2–4], benzophenones [2], acetylthiophenes [4], *N*-acetylindole [5], *N*,*N*-dimethylbenzamides [5], and aryl esters [6] and aldehydes [5]. The reactions take place under mild conditions (refluxing heptane) and mostly give high yields. The cyclomanganated species are of interest in that they provide substrates for a number of synthetically useful reactions, including Pd-catalysed coupling with alkenes [7] and cyclisation reactions with alkynes [3,8].

So far, only singly manganated species have been reported. Multi-metallated arenes with more than one transition metal linked to a single ring are rare. Other than examples from cluster chemistry with benzyne type ligands bridging two or

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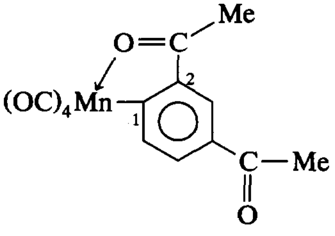
more metal atoms, the only well-characterised examples appear to be di(vanadocene)benzene [9], anthraquinone di-cyclometallated with $Re(CO)_4$ groups [2], and the recently reported di-cyclopalladation products of diacetylbenzene dioximes [10].

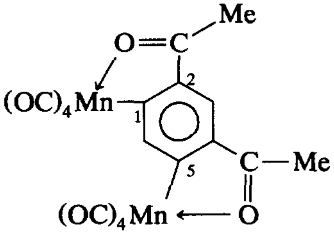
We now report ortho-manganation of 1,3- and 1,4-diacetylbenzene and the crystal structure of the di-manganated species from 1,3-diacetylbenzene.

Results and discussion

The reaction of 1,3-diacetylbenzene with one equivalent of $PhCH_2Mn(CO)_5$ proceeds smoothly to give a mixture of the mono-metallated **1** and the dimetallated **2**, with 46% of the manganese incorporated into **1** and 44% into **2**. The reaction is a stepwise one since, in a separate experiment, **1** reacted with an equivalent amount of $PhCH_2Mn(CO)_5$ to give 69% of **2**. Only one isomer for each of **1** and **2** was observed. This is not unexpected, since the alternative isomers would involve the $Mn(CO)_4$ group entering at the sterically crowded site between the two acetyl groups.

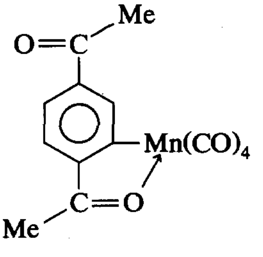


(1)

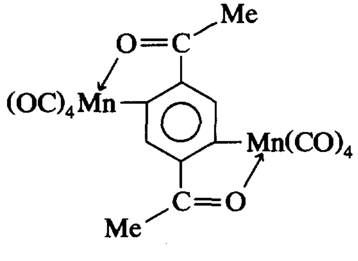


(2)

Similarly, on treatment with $PhCH_2Mn(CO)_5$, 1,4-diacetylbenzene gives a mixture of the mono-manganated **3** and the di-manganated **4** in a 2:1 ratio. Once again only the less sterically crowded di-manganated isomer is formed.



(3)



(4)

These reactions suggest that the acetyl groups are acting independently of each other, and that the first manganation of the ring has little effect on the subsequent reactivity of the second site.

The physical and spectroscopic properties of the new derivatives **1–4** match those of previously reported orthomanganated arenes [1–5]. The carbonyl region infrared spectra for both the mono- and di-metallated compounds give the familiar

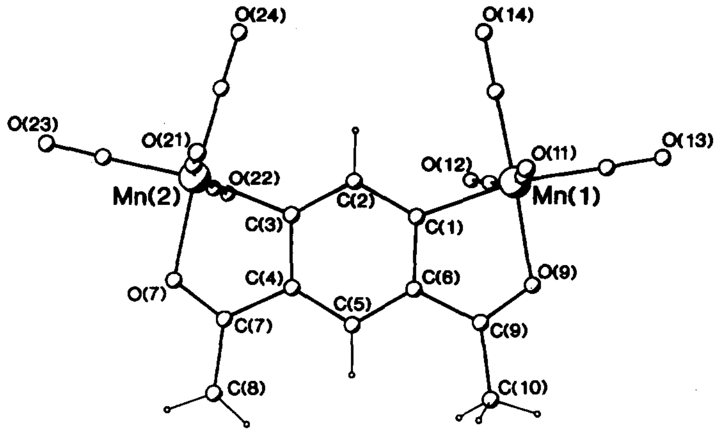
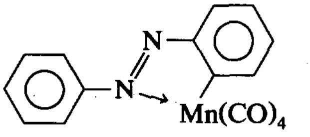


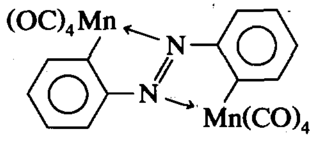
Fig. 1. A view of η^2,η^2-4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese) (**2**) perpendicular to the least-squares plane through the core of the molecule.

four-band pattern, showing no significant coupling of vibrations between the two $Mn(CO)_4$ groups in **3** or **4**.

Bruce *et al.* [11] have studied the mono- and di-manganation of azobenzene, which gives compounds **5** and **6**. They have shown that **6** reacts with azobenzene to



(5)



(6)

give **5** in high yield, demonstrating the intermolecular transfer of a $Mn(CO)_4$ group. To see if a similar process could occur with the acetylbenzenes, **2** was refluxed with 1,3-diacetylbenzene in heptane. After 2.5 h, 31% of **2** remained, 35% of **1** was present and 33% of the free ligand had been consumed. While this is consistent with some $Mn(CO)_4$ transfer, the alternative interpretation based on partial demetallation of **2** cannot be excluded because of the relatively low yields; certainly any intermolecular exchange is less clean and efficient than was observed for the azobenzene system.

The X-ray crystal structure of **2** was determined for comparison with those of mono-manganated arenes; orthomanganated acetophenone provides a particularly useful basis for comparison [12]. The structure is illustrated in Fig. 1. The molecule has near *mm* symmetry, and is essentially planar apart from the axial CO ligands on each manganese atom, with no other atom more than 0.25 Å from the least-squares plane. There is a slight twisting of the Mn(1) and Mn(2) manganacycle rings by 3.6° and 2.1°, respectively, from the plane of the central arene ring. The coordination about each Mn is distorted-octahedral, with an acute $O-Mn-C_{aryl}$ angle of 80° induced by the "bite" of the ligand. The axial carbonyl groups lean towards the aryl ring, reflecting the different π-bonding characteristics of the arene group and the CO ligand trans to it. These features have also been found for other orthomanganated arenes for which structures are available [1].

A detailed comparison of the five-membered manganacycle rings of **2** with that found for orthomanganated acetophenone [12], shows close similarities with perhaps a slightly longer C–O (1.251(4), *cf.* 1.244(3) Å) and a slightly shorter $Mn-C_{arene}$ (2.036(3), *cf.* 2042(2) Å) distance for **2**. The C–C bond that the manganacycle shares with the benzene ring [C(1)–C(6) or C(3)–C(4)] is also longer in **2** (1.421(5) Å) than the equivalent bond in orthomanganated acetophenone (1.406(3) Å). This observation suggests that **2** can be regarded as an organometallic pseudo-analogue of anthracene, where the internal C–C bonds of the three linked rings are also relatively long [13]. Overall the bond variations observed for **2** are consistent with delocalised π interactions represented by the resonance forms **2a** and **2b**, but the small differences between the manganacycle rings of **2** and of orthomanganated acetophenone suggest the overall interaction between the two manganese groups is not great. This is consistent with the infrared data discussed above, and with the observed similar reactivity towards manganation of **1** and free 1,3-diacetylbenzene.


(2a) **(2b)**

It thus appears that the two manganese groups in **2** and **4** are acting essentially independently of each other, which in turn suggests that the reactions established for mono-manganated arenes [1] should provide a useful basis for predicting the reactions of the di-metallated species.

Experimental

$PhCH_2Mn(CO)_5$ was prepared by the standard method [14] and acetylbenzenes were purchased (Aldrich) and used as received. Reactions were performed under nitrogen, but subsequent work-up and handling of the air-stable products required no special precautions. Instrumentation and general methods have been described elsewhere [4,5].

Reaction of 1,3-diacetylbenzene with $PhCH_2Mn(CO)_5$

A heptane solution of 1,3-diacetylbenzene (103 mg, 0.635 mmol) and $PhCH_2Mn(CO)_5$ (156 mg, 0.545 mmol) was refluxed for 1.5 h. The mixture was cooled and the solvent was removed under vacuum. The residue was chromatographed on silica-gel with CH_2Cl_2/petroleum spirit (60–80°C fraction) as eluent. The more mobile yellow band was identified as η^2-(2,4-diacetylphenyl)tetracarbonylmanganese (**1**) (82 mg, 46% of the manganese), while the slower moving component was η^2,η^2-4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese) (**2**) (59 mg, 44% of the manganese).

For **1**: yellow crystals, m.p. 140–141°C. Anal. Found: C, 51.52; H, 2.74%, M_r (mass spectrum, M^+) 328. $C_{14}H_9MnO_6$ calc.: C, 51.24; H, 2.76%; M_r 328.16. IR (hexane): 2085m, 2000s, 1951s, 1693w, 1591w cm^{-1} NMR ($CDCl_3$): ^1H: δ 8.40 (s, H3), 8.25 (d, $J = 7.6$ Hz, H6), 7.91 (d, $J = 7.6$ Hz, H5), 2.72 (s, CH_3). ^{13}C: δ 220.6, 212.4, 210.5 (CO), 217.2 (C=O–Mn), 205.1 (C1), 197.2 (C=O), 145.6 (C2), 141.6 (C6), 133.8 (C4), 131.9 (C5), 129.9 (C3), 26.4, 24.8 (CH_3).

For **2**: yellow crystals, m.p. *ca* 175°C (dec). Anal. Found: C, 43.94; H, 1.58%; M_r (mass spectrum, M^+) 494. $C_{18}H_8Mn_2O_{10}$ calc.: C, 43.75; H, 1.63%; M_r 494.13. IR (hexane): 2085m, 2076w, 1999s, 1952m, 1548w cm^{-1} NMR ($CDCl_3$): ^1H: δ 9.00 (s, H3), 8.05 (s, H6), 2.64 (s, CH_3s). ^{13}C: δ 220.5, 212.8, 211.2 (CO), 215.6 (C=O), 207.6 (C1,5), 155.8 (C6), 141.5 (C2,4), 130.9 (C3), 24.0 (CH_3). The compound was further characterised by X-ray crystallography (see below).

Reaction of 1,4-diacetylbenzene with $PhCH_2Mn(CO)_5$

Similarly, 1,4-diacetylbenzene (63 mg, 0.388 mmol) and $PhCH_2Mn(CO)_5$ (107 mg, 0.374 mmol) were refluxed in heptane for 3 h. The mixture was cooled and the solvent removed under vacuum. Chromatography as above gave η^2-(2,5-diacetylphenyl)tetracarbonylmanganese (**3**) (52 mg, 42%), and η^2,η^2-(2,5-diacetylphenyl)bis-1,4-(tetracarbonylmanganese) (**4**) (20 mg, 22%).

For **3**: orange crystals, m.p. 97–99°C. Anal. Found: C, 51.27; H, 2.76. $C_{14}H_9MnO_6$ calc.: C, 51.24; H, 2.76%. IR (hexane): 2084m, 1998s, 1949s, 1697w, 1589w cm^{-1} NMR ($CDCl_3$): ^1H: δ 8.56 (d, $J = 1.6$ Hz, H6), 7.93 (d, $J = 8.0$ Hz, H3), 7.69 (dd, $J = 8.0$, 1.6 Hz, H4), 2.67 (s, CH_3). ^{13}C: δ 220.7, 212.5, 210.8 (CO), 217.1 (C=O–Mn), 199.2 (C=O), 194.2 (C1), 148.1 (C2), 140.3 (C6), 139.5 (C5), 131.5 (C3), 123.6 (C4), 27.2, 25.0 (CH_3).

For **4**: red solid, m.p. *ca* 120°C (dec). Anal. Found: C, 44.55; H, 1.59. $C_{18}H_8Mn_2O_{10}$ calc.: C, 43.75; H, 1.63%. IR (hexane): 2080m, 1999s, 1947m, 1579w cm^{-1}. NMR ($CDCl_3$): ^1H: δ 8.48 (s, H3,6), 2.77 (s, CH_3). ^{13}C: δ 221.5, 213.5, 211.3 (CO), 218.7 (C=O), 182.3 (C1,4), 149.4 (C2,5), 143.7 (C3,6), 25.4 (CH_3).

Reaction of 1 with $PhCH_2Mn(CO)_5$

A heptane solution of **1** (106 mg, 0.323 mmol) and $PhCH_2Mn(CO)_5$ (95 mg, 0.332 mmol) was refluxed for 5 h. Work-up gave **2** (110 mg, 69%) and unreacted **1** (7 mg, 7%).

Reaction of 2 with 1,3-diacetylbenzene

A mixture of **2** (49 mg, 0.099 mmol) and 1,3-diacetylbenzene (19 mg, 0.120 mmol) in heptane was refluxed for 2.5 h. Chromatography gave **1** (14 mg, 0.043 mmol), unchanged **2** (15 mg, 31%) and diacetylbenzene (13 mg, 0.080 mmol, 0.039 mmol reacted).

X-Ray crystal structure of η^2,η^2-4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese) (2)

A yellow needle-shaped crystal was obtained from CH_2Cl_2/petroleum spirit. Preliminary precession photography showed no symmetry higher than triclinic. Cell dimensions and intensity data were obtained from a crystal 0.24 × 0.82 × 0.15 mm^3 on a Nicolet P3 four-circle diffractometer with monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å).

Table 1

Final positional parameters for η^2,η^2-4,6-diacetylbenzene-1,3,-bis(tetracarbonylmanganese) (2)

Atom	x	y	z	U_{eq}
Mn(1)	0.33179(6)	0.30468(5)	0.11150(4)	0.020
Mn(2)	0.23523(6)	0.15363(5)	0.65432(4)	0.019
C(1)	0.2742(4)	0.3299(3)	0.2778(3)	0.021
C(2)	0.2723(4)	0.2320(4)	0.3833(3)	0.021
C(3)	0.2400(4)	0.2709(3)	0.4902(3)	0.019
C(4)	0.2080(4)	0.4161(3)	0.4896(3)	0.020
C(5)	0.2072(4)	0.5163(3)	0.3867(3)	0.020
C(6)	0.2387(4)	0.4728(3)	0.2819(3)	0.020
C(7)	0.1750(4)	0.4490(3)	0.6045(3)	0.021
O(7)	0.1701(3)	0.3481(2)	0.6900(2)	0.023
C(8)	0.1547(4)	0.5948(4)	0.6241(3)	0.026
C(9)	0.2401(4)	0.5673(3)	0.1691(3)	0.022
O(9)	0.2798(3)	0.5163(2)	0.0813(2)	0.024
C(10)	0.1924(5)	0.7194(4)	0.1528(3)	0.031
C(11)	0.1275(5)	0.2697(4)	0.1107(4)	0.039
O(11)	0.0034(4)	0.2403(4)	0.1155(4)	0.073
C(12)	0.5309(4)	0.3228(4)	0.1434(3)	0.026
O(12)	0.6489(3)	0.3235(3)	0.1711(2)	0.042
C(13)	0.3872(4)	0.3181(4)	−0.0462(3)	0.026
O(13)	0.4238(3)	0.3249(3)	−0.1426(2)	0.040
C(14)	0.3711(4)	0.1192(4)	0.1444(3)	0.028
O(14)	0.3973(4)	−0.0004(3)	0.1656(3)	0.051
C(21)	0.0383(4)	0.1117(4)	0.6358(3)	0.028
O(21)	−0.0766(3)	0.0822(3)	0.6177(3)	0.050
C(22)	0.4395(4)	0.2042(3)	0.6415(3)	0.022
O(22)	0.5625(3)	0.2363(3)	0.6259(2)	0.038
C(23)	0.2227(4)	0.0738(4)	0.8108(3)	0.030
O(23)	0.2149(4)	0.0221(3)	0.9074(2)	0.053
C(24)	0.3049(4)	−0.0068(4)	0.6114(3)	0.029
O(24)	0.3522(4)	−0.1070(3)	0.5818(3)	0.043

Crystal data

$C_{18}H_8Mn_2O_{10}$, $M_r = 494.13$. Triclinic, space group $P\bar{1}$, $a = 8.774(2)$, $b = 9.782(2)$, $c = 11.898(3)$ Å, $\alpha = 77.25(2)$, $\beta = 82.56(2)$, $\gamma = 85.59(2)°$, $U = 986.4$ Å^3, D_c $1.66 = \text{g cm}^{-3}$ for $Z = 2$, $F(000) = 492$, $\mu(\text{Mo-}K_\alpha) = 12.8$ cm^{-1}, $T = 173$ K. A total of 3865 unique reflections $4° < 2\theta < 52°$ were collected with ω scans and were corrected for absorption by a numerical method based on indexed crystal faces (transmission factors 0.83 max, 0.71 min). Of these 2861 had $I > 3\sigma(I)$ and were used in all calculations. The structure was solved by direct methods. In the final cycles of full-matrix least-squares refinement all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in calculated positions, with a common isotropic temperature factor for each type. Refinement converged with $R = 0.0342$, $R_w = 0.0367$ where $w = [\sigma^2(F) + 0.000622F^2]^{-1}$, with no final shifts greater than 0.3σ and no residual electron density > 0.38 e Å^{-3}. Calculations were performed using the SHELX programs [15]. Final positional parameters are given in Table 1, selected bond parameters in Table 2 and the structure is illustrated in Figure 1. A complete table of bond

Table 2

Selected bond parameters for η^2,η^2-4,6-diacetylbenzene-1,3-bis(tetracarbonylmanganese) (2)

Bond lengths (Å)			
Mn(1)–C(1)	2.042(3)	Mn(2)–C(3)	2.031(3)
Mn(1)–O(9)	2.047(2)	Mn(2)–O(7)	2.062(2)
Mn(1)–C(11)	1.852(4)	Mn(2)–C(21)	1.857(4)
Mn(1)–C(12)	1.865(4)	Mn(2)–C(22)	1.874(4)
Mn(1)–C(13)	1.855(4)	Mn(2)–C(23)	1.845(4)
Mn(1)–C(14)	1.786(4)	Mn(2)–C(24)	1.795(4)
C(7)–O(7)	1.250(4)	C(9)–O(9)	1.253(4)
C(7)–C(8)	1.489(4)	C(9)–C(10)	1.491(5)
C(1)–C(2)	1.400(5)	C(4)–C(5)	1.390(4)
C(1)–C(6)	1.419(5)	C(4)–C(7)	1.461(4)
C(2)–C(3)	1.395(4)	C(5)–C(6)	1.393(4)
C(3)–C(4)	1.425(4)	C(6)–C(9)	1.451(5)
Bond angles (°)			
C(1)–Mn(1)–O(9)	79.9(1)	C(3)–Mn(2)–O(7)	80.1(1)
C(1)–Mn(1)–C(11)	87.4(2)	C(3)–Mn(2)–C(21)	85.6(1)
C(1)–Mn(1)–C(12)	83.1(1)	C(3)–Mn(2)–C(22)	84.1(1)
C(1)–Mn(1)–C(13)	169.2(1)	C(3)–Mn(2)–C(23)	170.8(1)
C(1)–Mn(1)–C(14)	97.5(1)	C(3)–Mn(2)–C(24)	95.3(1)
O(9)–Mn(1)–C(11)	90.8(1)	O(7)–Mn(2)–C(21)	94.9(1)
O(9)–Mn(1)–C(12)	93.6(1)	O(7)–Mn(2)–C(22)	87.3(1)
O(9)–Mn(1)–C(13)	89.8(1)	O(7)–Mn(2)–C(23)	90.8(1)
O(9)–Mn(1)–C(14)	177.2(1)	O(7)–Mn(2)–C(24)	174.3(1)
Mn(1)–C(1)–C(2)	130.5(2)	Mn(2)–C(3)–C(2)	130.6(2)
Mn(1)–C(1)–C(6)	111.6(2)	Mn(2)–C(3)–C(4)	111.7(2)
Mn(2)–O(7)–C(7)	115.9(2)	Mn(1)–O(9)–C(9)	116.3(2)
C(1)–C(6)–C(9)	114.5(3)	C(3)–C(4)–C(7)	114.6(3)
C(4)–C(7)–O(7)	117.2(3)	C(6)–C(9)–O(9)	117.6(3)
C(4)–C(7)–C(8)	123.5(3)	C(6)–C(9)–C(10)	123.5(3)

lengths and angles and lists of thermal parameters and structure factors are available from the authors.

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