

# Reactions of orthomanganated aryl ketones with PhNSO and related species: a new route to orthomanganated imines

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## Abstract

PhN=S=O reacts with some orthomanganated acetophenones to replace the ketone oxygen with a Ph–N group, so generating the corresponding orthomanganated imine. No insertion into the Mn–C bond was observed, in contrast to analogous reactions of SO<sub>2</sub>. The related PhS(O)<sub>2</sub>N=S=O or (PhS(O)<sub>2</sub>N=)<sub>2</sub>S did not react under the same conditions. The X-ray crystal structure of one of the new imine complexes, η<sup>2</sup>-3-chloro-2-[1-(*N*-phenylimino)ethyl]phenyltetracarbonylmanganese, was determined.

**Keywords:** Manganese; Carbonyl; Orthometallation; Imines; Crystal structure

## 1. Introduction

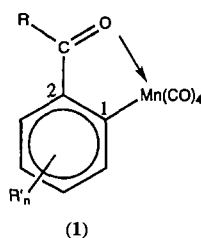
We have recently reported on the reactions of orthomanganated aryl ketones of type **1** [1] with SO<sub>2</sub>, in which insertion into the Mn–C<sub>aryl</sub> bond gave new metallocyclic species incorporating Mn–S(O)<sub>2</sub>–C units (e.g. **2**) [2]. As an extension to this work we have now turned to the SO<sub>2</sub>-mimics R–N=S=O and R–N=S=N–R [3], which are also known to insert into metal–carbon σ-bonds, but which have been much less studied [4]. The coordination chemistry of these iminoxosulphuranes with Ru, Os, Rh and Ir complexes has been thoroughly examined by Herberhold and Hill who defined different coordination modes [5], but only rarely found insertion into an M–C bond [6]. The cleanest insertion reactions are those of R'S(O)<sub>2</sub>N=S=O or [R'S(O)<sub>2</sub>N=]<sub>2</sub>S with Cp(CO)<sub>2</sub>FeR or Cp(CO)<sub>3</sub>MR (M = Mo, W) complexes, giving initially N-bonded species [7,8]. In manganese carbonyl chemistry, the only reported examples appear to be the reaction between MeMn(CO)<sub>5</sub> and the cumulene MeS(O)<sub>2</sub>NSO which afforded an insertion product, stable only at low temperature, assigned as

(OC)<sub>5</sub>Mn{N[S(O)<sub>2</sub>Me]S(O)Me} [8]. Insertion of [MeS(O)<sub>2</sub>N]<sub>2</sub>S into the Mn–C bond of MeMn(CO)<sub>4</sub>L (L = CO, PPh<sub>3</sub>) yielded L(OC)<sub>3</sub>Mn{[NS(O)<sub>2</sub>Me]S(Me)N}S(O)<sub>2</sub>Me via an initial insertion reaction [8]. Similar reactions of aryl-manganese compounds do not seem to have been examined previously.

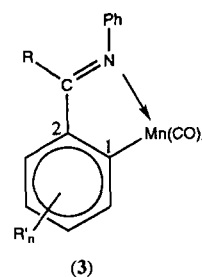
## 2. Experimental details

NMR spectra were recorded in CDCl<sub>3</sub> as solvent. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker AC300 instrument while infrared spectra were recorded in solution cells (KBr windows) with hexane as solvent (unless otherwise stated) on a Digilab FTS-45 FTIR instrument. The cyclomanganated aryl ketones were prepared by routes described earlier [1,9] and the cumulenes *N*-sulphonylaniline (PhN=S=O) [10], *N*-sulphonylbenzene-sulphonamide (PhS(O)<sub>2</sub>N=S=O) and the disulphonylsulphodiimide ([PhS(O)<sub>2</sub>N]<sub>2</sub>S) [11] were prepared by established literature methods. Reactions were conducted under a dry nitrogen atmosphere in anhydrous solvents. Preparative layer chromatography (PLC) was carried out on 1 mm layers of silica gel (Merck Kieselgel 60), and thin layer chromatography (TLC) on the same support.

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- 1a. R = Me R'n = H  
 1b. R = Me R'n = 3,4,5-(OMe)<sub>3</sub>  
 1c. R = Me R'n = 3-Cl  
 1d. R = Me R'n = 5-OMe  
 1e. R = OMe R'n = 5-OMe  
 1f. R = Me R'n = 5,6-OCH<sub>2</sub>O-

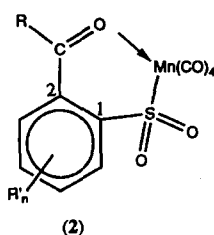


- 3a. R = Me R'n = H  
 3b. R = Me R'n = 3,4,5-(OMe)<sub>3</sub>  
 3c. R = Me R'n = 3-Cl  
 3d. R = Me R'n = 5-OMe

## 2.1. Reactions with PhNSO

### 2.1.1. Reaction of $\eta^2$ -(2-acetylphenyl)tetracarbonylmanganese (1a) with PhNSO

A degassed solution of  $\eta^2$ -(2-acetylphenyl)tetracarbonylmanganese (1a) (208 mg, 0.727 mmol) in benzene (8 ml) was treated with PhNSO (0.41 ml, 3.64 mmol) and the mixture was heated under reflux in nitrogen for 1 h. An infrared spectrum showed a pattern of metal carbonyl stretches which matched those of the starting material but with small shifts to lower frequencies, indicating that a reaction had gone to completion. The benzene was removed under vacuum and the resultant yellow oil was dissolved in dichloromethane and chromatographed on silica plates (1:10 ether–petroleum spirit eluant) to yield  $\eta^2$ -2-[1-*N*(phenylimino)ethyl]phenyltetracarbonylmanganese (3a), (53 %), m.p. 108–110 °C. Anal. Found: C, 60.12; H, 3.62; N, 4.01. C<sub>18</sub>H<sub>12</sub>MnNO<sub>4</sub>. Calc.: C, 59.85; H, 3.35; N, 3.88%. IR:  $\nu$ (CO) 2074 (m), 1985 (vs), 1947 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  8.06 (1H, *d*, <sup>3</sup>*J*<sub>6,5</sub> = 7.4 Hz, H-6), 7.66 (1H, *d*, <sup>3</sup>*J*<sub>3,4</sub> = 7.4 Hz, H-3), 7.48 (2H, *t*, <sup>3</sup>*J*<sub>3',2'</sub> = <sup>3</sup>*J*<sub>3',4'</sub> = <sup>3</sup>*J*<sub>5',4'</sub> = <sup>3</sup>*J*<sub>5',6'</sub> = 7.6 Hz, H-3',5'), 7.36 (1H, *t*, <sup>3</sup>*J*<sub>5,4</sub> = <sup>3</sup>*J*<sub>5,6</sub> = 7.4 Hz, H-5), 7.30 (1H, *t*, <sup>3</sup>*J*<sub>4',3'</sub> = <sup>3</sup>*J*<sub>4',5'</sub> = 7.6 Hz, H-4'), 7.21 (1H, *t*, <sup>3</sup>*J*<sub>4,3</sub> = <sup>3</sup>*J*<sub>4,5</sub> = 7.4 Hz, H-4), 6.95 (2H, *d*, <sup>3</sup>*J*<sub>2',3'</sub> = <sup>3</sup>*J*<sub>6',5'</sub> = 7.6 Hz, H-2',6'), 2.24 (3H, *s*, 2-C(NPh)CH<sub>3</sub>). <sup>13</sup>C NMR:  $\delta$  220.4 (*s*, br, C≡O), 214.1 (*s*, br, C≡O), 212.6 (*s*, br, 2 × C=O), 183.1 (*s*, 2-C=NPh), 182.3 (*s*, C-1), 152.9 (*s*, C-1'), 148.8 (*s*, C-2), 141.5 (*d*, C-6), 131.3 (*d*, C-5), 129.8 (*d*, C-3',5'), 128.9 (*d*, C-3), 126.3



(*d*, C-4'), 123.5 (*d*, C-4), 121.2 (*d*, C-2',6'), 17.9 (*q*, 2-C(NPh)CH<sub>3</sub>).

### 2.1.2. Reaction of $\eta^2$ -(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (1b) with PhNSO

Similarly,  $\eta^2$ -(2-acetyl-3,4,5-trimethoxyphenyl)tetracarbonylmanganese (1b); 215 mg, 0.572 mmol) and PhNSO (0.32 ml, 2.86 mmol) in benzene (8 ml) were heated for 3 h. The solvent was removed under vacuum and PLC (diethyl ether–petroleum spirit (1:10) as the eluant) gave a broad yellow band of  $\eta^2$ -3,4,5-trimethoxy-2-[1-*N*(phenylimino)ethyl]phenyltetracarbonylmanganese (3b); 285 mg, 60%), m.p. 113–114.5 °C. Anal. Found: C, 55.88; H, 4.15; N, 3.17. C<sub>21</sub>H<sub>18</sub>MnNO<sub>7</sub>. Calc.: C, 55.89; H, 4.02; N, 3.17%. IR:  $\nu$ (CO) 2073 (m), 1985 (vs), 1942 (s) 1566 (w), 1536 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.42 (2H, *t*, <sup>3</sup>*J*<sub>3',2'</sub> = <sup>3</sup>*J*<sub>3',4'</sub> = <sup>3</sup>*J*<sub>5',4'</sub> = <sup>3</sup>*J*<sub>5',6'</sub> = 7.6 Hz, H-3',5'), 7.23 (1H, *t*, <sup>3</sup>*J*<sub>4',3'</sub> = <sup>3</sup>*J*<sub>4',5'</sub> = 7.6 Hz, H-4'), 7.23 (1H, *s*, H-6), 6.89 (2H, *d*, <sup>3</sup>*J*<sub>2',3'</sub> = <sup>3</sup>*J*<sub>6',5'</sub> = 7.6 Hz, H-2',6'), 4.00 (3H, *s*, -OCH<sub>3</sub>), 3.96 (3H, *s*, -OCH<sub>3</sub>), 3.85 (3H, *s*, -OCH<sub>3</sub>), 2.32 (3H, *s*, 2-C(NPh)CH<sub>3</sub>). <sup>13</sup>C NMR:  $\delta$  220.4 (*s*, br, C≡O), 214.1 (*s*, br, C≡O), 212.3 (*s*, br, 2 × C=O), 182.9 (*s*, 2-C=NPh), 178.8 (*s*, C-1), 155.8 and 155.7 (*s*, C-3, C-5), 153.3 (*s*, C-1'), 138.8 (*s*, C-2), 133.7 (*s*, C-4), 129.7 (*d*, C-3',5'), 125.9 (*d*, C-4'), 121.6 (*d*, C-2',6'), 118.1 (*d*, C-6), 61.0 (*q*, 5-OCH<sub>3</sub>), 60.7 (*q*, 4-OCH<sub>3</sub>), 55.9 (*q*, 3-OCH<sub>3</sub>), 21.6 (*q*, 2-C(NPh)CH<sub>3</sub>).

No reaction was observed in the reaction of (1b) with PhNSO in benzene at room temperature, nor in refluxing dichloromethane over 150 min.

### 2.1.3. Reaction of $\eta^2$ -(2-acetyl-3-chlorophenyl)tetracarbonylmanganese (1c) with PhNSO

Similarly,  $\eta^2$ -(2-acetyl-3-chlorophenyl)tetracarbonylmanganese (1c) (174 mg, 0.542 mmol) and PhNSO (0.31 ml, 2.71 mmol) under reflux in benzene (8 ml) over 2 h afforded  $\eta^2$ -3-chloro-2-[1-*N*(phenylimino)ethyl]phenyltetracarbonylmanganese (3c), (62%), m.p. 109–109.5 °C. Anal. Found: C, 54.77; H, 2.79; N, 3.66. C<sub>18</sub>H<sub>11</sub>ClMnNO<sub>4</sub> Calc.: C, 54.64; H,

2.80; N, 3.54%. IR:  $\nu(\text{CO})$  2076 (m), 1989 (vs), 1950 (s)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  7.89 (1H, *m*, H-6), 7.46 (2H, *t*,  $^3J_{3',2'} = ^3J_{3',4'} = ^3J_{5',4'} = ^3J_{5',6'} = 7.4$  Hz, H-3',5'), 7.28 (1H, *t*,  $^3J_{4',3'} = ^3J_{4',5'} = 7.4$  Hz, H-4'), 7.18 (2H, *m*, H-4,5), 6.88 (2H, *d*,  $^3J_{2',3'} = ^3J_{6',5'} = 7.4$  Hz, H-2',6'), 2.51 (3H, *s*, 2-C(NPh)CH<sub>3</sub>).  $^{13}\text{C NMR}$ :  $\delta$  219.7 (*s*, br, C=O), 213.2 (*s*, br, C=O), 211.8 (*s*, br, 2 × C≡O), 186.9 (*s*, 2-C=NPh), 184.1 (*s*, C-1), 153.3 (*s*, C-1'), 143.8 (*s*, C-2), 139.8 (*d*, C-6), 135.4 (*s*, C-3), 131.0 (*d*, C-5), 130.0 (*d*, C-3',5'), 127.4 (*d*, C-4), 126.4 (*d*, C-4'), 121.0 (*d*, C-2',6'), 24.3 (*q*, 2-C(NPh)CH<sub>3</sub>).

This compound was further characterised by an X-ray crystal structure determination (see below).

#### 2.1.4. Reaction of $\eta^2$ -(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**1d**) with PhNSO

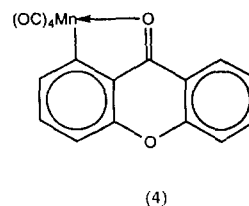
Similarly,  $\eta^2$ -(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**1d**) (200 mg, 0.633 mmol) and PhNSO (0.36 ml, 3.17 mmol) under reflux in benzene (8 ml) over 2 h afforded  $\eta^2$ -5-methoxy-2-[1-*N*(phenylimino)ethyl]phenyltetracarbonylmanganese (**3d**), (47%), m.p. 131–133 °C. Anal. Found: C, 58.55; H, 3.65; N, 3.59. C<sub>19</sub>H<sub>14</sub>MnNO<sub>5</sub>. Calc.: C, 58.33; H, 3.61; N, 3.58%. IR: (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu(\text{CO})$  2073 (m), 1985 (vs), 1935 (s)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  7.59 (1H, *d*,  $^3J_{3,4} = 7.9$  Hz, H-3), 7.55 (1H, *s*, H-6), 7.44 (2H, *t*,  $^3J_{3',2'} = ^3J_{3',4'} = ^3J_{5',4'} = ^3J_{5',6'} = 7.4$  Hz, H-3',5'), 7.26 (1H, *t*,  $^3J_{4',3'} = ^3J_{4',5'} = 7.4$  Hz, H-4'), 6.92 (2H, *d*,  $^3J_{2',3'} = ^3J_{6',5'} = 7.4$  Hz, H-2',6'), 6.69 (1H, *d*,  $^3J_{4,3} = 7.9$  Hz, H-4), 3.93 (3H, *s*, 5-OCH<sub>3</sub>), 2.17 (3H, *s*, 2-C(NPh)CH<sub>3</sub>).  $^{13}\text{C NMR}$ :  $\delta$  220.4 (*s*, br, C=O), 214.2 (*s*, br, C=O), 212.7 (*s*, br, 2 × C=O), 185.4 (*s*, 2-C=NPh), 181.6 (*s*, C-1), 161.4 (*s*, C-5), 153.0 (*s*, C-1'), 142.0 (*s*, C-2), 130.1 (*d*, C-3), 129.7 (*d*, C-3',5'), 126.1 (*d*, C-4'), 125.3 (*d*, C-6), 121.6 (*d*, C-2',6'), 109.9 (*d*, C-4), 55.2 (*q*, 5-OCH<sub>3</sub>), 17.8 (*q*, 2-C(NPh)CH<sub>3</sub>).

#### 2.1.5. Reaction of $\eta^2$ -(5-methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese (**1e**) with PhNSO

Reaction of  $\eta^2$ -(5-methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese (**1e**); 138 mg, 0.416 mmol) and PhNSO (0.23 ml, 2.08 mmol) in refluxing benzene (8 ml) after 5.5 h showed no bands in the metal carbonyl region by infrared spectroscopy. TLC indicated no major organic products, and therefore the reaction was abandoned.

#### 2.1.6. Reaction of $\eta^2$ -4-(dibenzosuberonyl)tetracarbonylmanganese (**4**) with PhNSO

$\eta^2$ -4-(Dibenzosuberonyl)tetracarbonylmanganese (**4**); 412 mg, 1.10 mmol [12] and PhNSO (0.62 ml, 5.51 mmol) were refluxed in benzene (8 ml) for 5 h. Infrared spectroscopy of the crude reaction mixture showed only Mn<sub>2</sub>(CO)<sub>10</sub> in the metal carbonyl region, and therefore the reaction was abandoned.



#### 2.1.7. Reaction of phenylpentacarbonylmanganese with PhNSO

Phenylpentacarbonylmanganese (203 mg, 0.76 mmol) and PhNSO (0.09 ml, 0.82 mmol) were stirred in benzene (5 ml) for 2 h. Infrared spectroscopy and TLC showed no sign of reaction so the reaction mixture was refluxed overnight. An infrared spectrum and TLC indicated only the starting materials.

#### 2.2. Attempted reactions with PhS(O)<sub>2</sub>NSO

##### 2.2.1. Reaction of $\eta^2$ -(2-acetyl-5-methoxyphenyl)tetracarbonylmanganese (**1d**) with PhS(O)<sub>2</sub>NSO

$\eta^2$ -(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (**1d**); 127 mg, 0.40 mmol) and PhS(O)<sub>2</sub>NSO (245 mg, 1.20 mmol) were stirred in benzene (6 ml) for 40 min, after which time there was no sign of reaction by TLC or infrared spectroscopy in the metal carbonyl region. The mixture was refluxed for 1 h and then evaporated to dryness under reduced pressure. An infrared spectrum of the residue showed only starting material (**1d**).

Similarly, no compounds were isolated from attempted reactions of PhS(O)<sub>2</sub>NSO with  $\eta^2$ -(2-acetyl-5-chlorophenyl)tetracarbonylmanganese (**1c**) nor with PhMn(CO)<sub>5</sub>.

#### 2.3. X-ray crystal structure determination of $\eta^2$ -3-chloro-2-[1-(*N*-phenylimino)ethyl]phenyltetracarbonylmanganese (**3c**)

Yellow prismatic crystals were obtained by recrystallisation from chloroform–hexane (1:10) at –20 °C. Preliminary precession photography indicated monoclinic symmetry with systematic absences appropriate for the space group *P*2<sub>1</sub>/*c*. Intensity data and cell parameters were obtained on a Nicolet P3 four-circle diffractometer at –105 °C with monochromated Mo K $\alpha$  radiation.

##### 2.3.1. Crystal data

C<sub>18</sub>H<sub>11</sub>ClO<sub>4</sub>MnN, *M*<sub>r</sub> = 395.69, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 8.564(2), *b* = 21.544(6), *c* = 10.055(4) Å,  $\beta$  = 111.98(2)°, *U* = 1720.3(9) Å<sup>3</sup>, *D*<sub>calc</sub> = 1.53 g cm<sup>–3</sup>, *Z* = 4, *F*(000) = 800,  $\mu(\text{Mo K}\alpha)$  = 0.944 mm<sup>–1</sup>. Crystal size 0.76 × 0.66 × 0.36 mm<sup>3</sup>. A

Table 1  
Final positional parameters for  $\eta^2$ -3-chloro-2-[1-(*N*-phenylimino)ethyl]phenyltetracarbonylmanganese (3c)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mn(1)	0.7975(1)	0.3816(1)	1.0595(1)	Cl(1)	0.1168(1)	0.3009(1)	0.8097(1)
N(1)	0.6191(2)	0.3905(1)	0.8578(2)	C(1)	0.5888(3)	0.3468(1)	1.0848(2)
C(2)	0.4440(3)	0.3423(1)	0.9559(2)	C(3)	0.2988(3)	0.3146(1)	0.9613(2)
C(4)	0.2900(3)	0.2945(1)	1.0893(2)	C(5)	0.4288(3)	0.3015(1)	1.2148(2)
C(6)	0.5768(3)	0.3263(1)	1.2128(2)	C(7)	0.4676(3)	0.3698(1)	0.8301(2)
C(8)	0.3319(3)	0.3758(1)	0.6839(2)	C(9)	0.6649(3)	0.4204(1)	0.7497(2)
C(10)	0.6564(3)	0.4847(1)	0.7381(2)	C(11)	0.7150(3)	0.5139(1)	0.6432(2)
C(12)	0.7832(3)	0.4796(1)	0.5622(2)	C(13)	0.7912(3)	0.4156(1)	0.5744(2)
C(14)	0.7304(3)	0.3858(1)	0.6674(2)	C(15)	0.8303(3)	0.2999(1)	1.0224(2)
C(16)	0.9694(3)	0.4144(1)	1.0111(2)	C(17)	0.7306(3)	0.4564(1)	1.1107(2)
C(18)	0.9372(3)	0.3703(1)	1.2435(2)	O(15)	0.8452(2)	0.2480(1)	1.0063(2)
O(16)	1.0771(2)	0.4345(1)	0.9848(2)	O(17)	0.6851(2)	0.5005(1)	1.1472(2)
O(18)	1.0251(2)	0.3626(1)	1.3614(1)				

total of 4559 reflections in the range  $4 < 2\theta < 50^\circ$  was collected, corresponding to 3020 unique reflections. These were corrected for Lorentz and polarisation effects and for linear absorption by a  $\Psi$  scan method ( $T_{\max, \min} = 0.90, 0.72$ ). All non-hydrogen atoms were located using the TREF direct methods option of SHELXS-86 [13]. In the final cycle of full-matrix least squares refinement based on  $F^2$  (SHELXL-93 [13]) all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions. The refinement converged with  $R_1 = 0.0289$  (for 2620 data with  $I > 2\sigma(I)$ ),  $R_1 = 0.0358$ ,  $wR_2 = 0.0725$ , GoF = 1.009 (all data), with no parameter shifting more than  $0.001\sigma$ . The final difference map showed no peak or trough of electron density greater than  $0.30 \text{ e } \text{Å}^{-3}$ . Table 1 gives final positional parameters, selected bond parameters are listed in Table 2, and a view of the structure is presented in Fig. 1. A complete list of bond lengths and angles and tables of anisotropic displace-

Table 2  
Selected bond lengths (Å) and angles (deg) for  $\eta^2$ -3-chloro-2-[1-(*N*-phenylimino)ethyl]phenyltetracarbonylmanganese (3c)

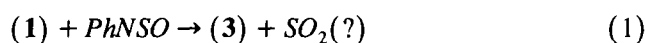
Bond lengths			
Mn(1)–N(1)	2.041(2)	Mn(1)–C(1)	2.040(2)
Mn(1)–C(15)	1.843(2)	Mn(1)–C(16)	1.854(2)
Mn(1)–C(17)	1.848(2)	Mn(1)–C(18)	1.804(2)
Cl(1)–C(3)	1.750(2)	N(1)–C(7)	1.300(3)
N(1)–C(9)	1.439(3)	C(1)–C(2)	1.422(3)
C(2)–C(7)	1.477(3)		
Bond angles			
N(1)–Mn(1)–C(1)	78.1(1)	N(1)–Mn(1)–C(15)	90.2(1)
N(1)–Mn(1)–C(16)	94.4(1)	N(1)–Mn(1)–C(17)	90.0(1)
N(1)–Mn(1)–C(18)	173.7(1)	C(1)–Mn(1)–C(15)	83.2(1)
C(1)–Mn(1)–C(16)	172.4(1)	C(1)–Mn(1)–C(17)	84.7(1)
N(1)–C(7)–C(2)	113.5(2)	C(1)–Mn(1)–C(18)	95.7(1)
C(15)–Mn(1)–C(16)	96.6(1)	C(15)–Mn(1)–C(17)	167.6(1)
C(15)–Mn(1)–C(18)	89.2(1)	C(16)–Mn(1)–C(17)	95.7(1)
C(16)–Mn(1)–C(18)	91.9(1)	C(17)–Mn(1)–C(18)	89.3(1)
Mn(1)–N(1)–C(7)	119.8(1)	Mn(1)–C(1)–C(2)	114.7(1)
C(1)–C(2)–C(7)	113.7(2)		

ment parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

### 3. Results and discussion

#### 3.1. Reactions with PhNSO

Reaction of PhNSO with a number of orthomanganated acetophenones led to the formation of the corresponding orthomanganated imine, according to Eq. (1).



Presumably the other product is  $SO_2$ , although this was not specifically observed. There was no indication

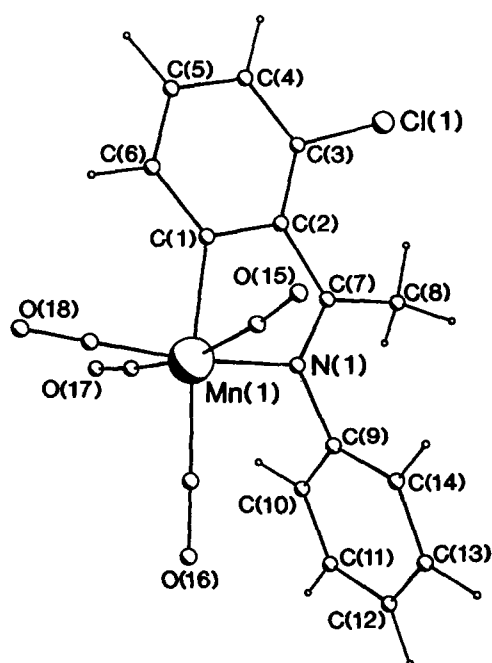
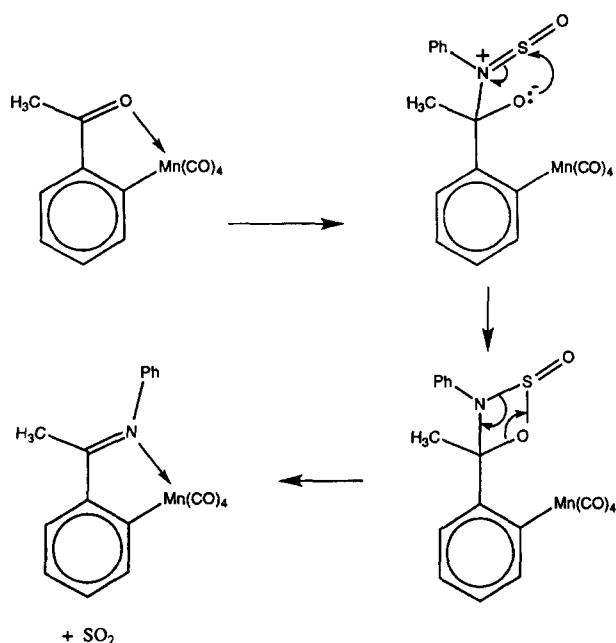


Fig. 1. The structure of  $\eta^2$ -3-chloro-2-[1-(*N*-phenylimino)ethyl]phenyltetracarbonylmanganese (3c).



at all of insertion into the Mn–C bond, in direct contrast to the corresponding  $\text{SO}_2$  reactions [2]. A possible mechanism for the reaction is given in Scheme 1.

Clearly, attack at the carbonyl functional group of complexes of type **1** by PhNSO takes precedence over that at the Mn–C bond. This is possibly due to the fact that for PhNSO the nitrogen atom is a better nucleophile than the oxygen in  $\text{SO}_2$  [3]. The carbon atom of the donor carbonyl group would be particularly susceptible to nucleophilic attack, through coordination of the oxygen to the manganese atom. The driving force for the reaction would be the release of  $\text{SO}_2$ , and the replacement in the metallocyclic ring of the better donor atom N for the O atom.

It has been reported that PhNSO reacts with benzaldehyde on heating to give benzylideneaniline [11]. However, the corresponding reaction with free acetophenone does not give an imine [12], reflecting the greater susceptibility for aldehydes to undergo nucleophilic attack compared with ketones. Hence, coordination of the carbonyl group by manganese is necessary to polarise the ketone carbonyl so it becomes susceptible to nucleophilic attack by PhNSO.

An alternative reaction involving the hydrolysis of the moisture-sensitive PhNSO to  $\text{PhNH}_2$  followed by nucleophilic attack at the ketone carbon can be precluded since the reactions were conducted under anhydrous conditions, and reaction of aniline with orthomanganated acetophenone does not give the corresponding imine complex under the same conditions as those employed for the reactions studied herein [14].

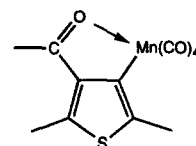
This imine-forming reaction of orthomanganated compounds with PhNSO is reasonably general for sub-

strates derived from acetophenone. Thus, most of the acetophenones studied, **1a–1d**, afforded the corresponding orthomanganated imine in reasonable yield. However,  $\eta^2$ -(6-acetyl-2,3-methylenedioxyphenyl)tetracarbonylmanganese (**1f**) failed to yield the expected product for reasons that are not obvious. Reaction with PhNSO was observed for  $\eta^2$ -(4-acetyl-2,5-dimethylthien-3-yl)tetracarbonylmanganese (**5**), though the resulting product, assumed to be the imine, proved to be unstable. However, the related  $\eta^2$ -(2-acetylthien-3-yl)tetracarbonylmanganese did not react under the same conditions. Benzophenone systems are also not reactive if the polycyclic example,  $\eta^2$ -4-(dibenzosuberonyl)tetracarbonylmanganese (**4**) is typical of this class of substrate. Steric effects might be responsible in this case, but not for the preceding examples of lack of ketone reactivity.

The orthomanganated ester,  $\eta^2$ -(5-methoxy-2-methoxycarbonylphenyl)tetracarbonylmanganese (**1e**), also failed to react with PhNSO. This can be attributed to the lower reactivity of esters compared with ketones towards nucleophiles. It is noteworthy that there is no reaction at the Mn–C bond even when, as in this case, the alternative reaction at the C=O group does not take place, so there is a genuine lack of reactivity towards PhNSO and not a diversion to a faster reaction site. This conclusion was also indicated by examination of the corresponding reaction of PhNSO with  $\text{PhMn}(\text{CO})_5$  to see if an insertion into an Mn–C<sub>aryl</sub> bond could be achieved in the absence of a competitive site for attack. Again, in this case, no reaction was observed. This is perhaps not unexpected, as aryl–metal bonds are generally less reactive than alkyl–metal bonds towards insertion reactions, as shown by the different behaviour of  $\text{PhMn}(\text{CO})_5$  and  $\text{MeMn}(\text{CO})_5$  towards  $\text{SO}_2$  [15].

### 3.2. Attempted reactions with $\text{PhS}(\text{O})_2\text{NSO}$ and $[\text{PhS}(\text{O})_2\text{N}]_2\text{S}$

Attempted reaction of *N*-sulphonylsulphonamide or the disulphonylsulphur diimide with orthomanganated *p*-methoxyacetophenone (**1e**) was unsuccessful under the conditions employed. This is consistent with the assumption that the reactions described above with PhNSO occur by nucleophilic attack since the increased



(5)

electron withdrawal by the sulphonamide group would appreciably decrease the nucleophilic character of the nitrogen atom. Note that these reagents are more reactive than PhNSO in electrophilic reactions involving the sulphur atom [16].

### 3.3. X-ray structure of $\eta^2$ -3-chloro-2-[1-(N-phenylimino)ethyl]phenyltetracarbonylmanganese **3c**

This is the first crystal structure of a cyclomanganated imine derived from an aryl ketone, although the structure of the cyclomanganated imine formed from the Schiff base benzylideneaniline [17,18], has been described.

In the complex **3c**, the manganese atom is coordinated in a distorted octahedral configuration with the chelate ligand and two carbonyl ligands in the equatorial plane, while the axial positions are occupied by the other two carbonyl ligands. The organic ligand is bound via a metal–nitrogen bond and a metal–carbon  $\sigma$ -bond to the ortho position of the chlorine substituted phenyl ring.

The chelate five-membered ring, Mn–N–C(7)–C(2)–C(1), is only slightly puckered, deviating from planarity by about 0.3 Å. The two phenyl rings are each essentially planar, with the aniline phenyl ring (C(9)–C(14)) twisted by 131.81(8)° from the chelate plane and with the chlorine-substituted phenyl ring (C(1)–C(6)) giving rise to a corresponding dihedral angle of 21.40(5)°.

The coordination about the manganese atom is distorted octahedral, the principal distortions being related to the chelate bite angle of 78.1(1)° and to the non-linearity of the C(15)–Mn–C(17) vector. The latter distortion involves an angular displacement of C(15) and C(17) away from C(16) and towards C(1), with a resulting C(17)–Mn–C(15) angle of 167.6(1)°. The C=N bond is lengthened upon coordination to manganese, from 1.237(3) Å in the related free imine benzylideneaniline [19] to 1.300(3) Å, while the C(2)–C(7) bond length appears to be shortened slightly (1.477(3) Å in **3c** compared with 1.496(3) Å in the free imine [19]). The Mn–C(1) and Mn–N distances are at the shorter end of ranges found in related molecules [20], but are otherwise unremarkable.

The overall structure is consistent with  $\pi$ -delocalised bonding over the chelate ring, analogous to that described for other orthomanganated arenes for which structures have been determined; there is some theoretical backing for this model [21]. Following the pattern established for O-donor orthomanganated complexes, some variation in the individual Mn–C $\equiv$ O bond lengths is observed, the shortest being to the carbonyl trans to the donor atom, in this case a nitrogen. A comparison of the <sup>13</sup>C-NMR M–C $\equiv$ O resonances for **3c** and those for the corresponding orthomanganated acetophenone **1c**

[12] reveal little variation in chemical shift between these two compounds, suggesting that in these compounds the O and N atoms have similar bonding properties.

## 4. Conclusion

The sulphur-imine reagents show no tendency to insert into the Mn–C bonds of orthomanganated aryl ketones, so differ markedly from SO<sub>2</sub> in this respect. The conversion of the orthomanganated acetophenones into the corresponding phenyl-imines with PhNSO is interesting, since it is the first example found in which coordination to the manganese directs reaction to the ketone group rather than to the Mn–C bond. However the reaction is unlikely to find application in synthesis, since imines, readily prepared from the aryl ketones, should undergo straightforward cyclometallation under the usual conditions, although so far only imines derived from aldehydes appear to have been examined directly [18].

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