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# Orthomanganation of arylhydrazones and related *N*-donor substrates[1]

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**Abstract**

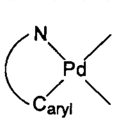
The *N*-phenyl- and *N*,*N*-diphenylhydrazones of benzaldehyde or acetophenone are readily cyclometallated on reaction with $PhCH_2Mn(CO)_5$ to give complexes **3** of the type $(OC)_4\overline{MnC_6H_4C(R^1)=N}NPhR^2$ incorporating a five-membered $\overline{MnC_3N}$ ring. The example with $R^1 = Me$, $R^2 = H$ has been structurally characterised. The similar reaction with the *N*,*N*-diphenylhydrazone of cyclohexanone produces a species with an alternative $\overline{MnC_2N_2}$ ring which was also structurally characterised. A related species $(OC)_4\overline{MnC_6H_4NN}=O$ is formed from *N*-nitrosodiphenylamine. Reactions of compounds **3** from the diphenylhydrazones with alkynes $PhC{\equiv}CPh$ or $Me_3SiC{\equiv}CH$ give *N*′-indenyl-*N*,*N*-diphenylhydrazines in reasonable yields. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Orthometallation; Manganese; Arylhydrazones; Alkyne reactions

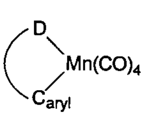
## 1. Introduction

Cyclometallation is now a standard procedure for activating C–H bonds. Michael Bruce provided the first comprehensive review of the area in 1977 [1], and this has provided a useful basis for much of the subsequent work, as demonstrated by the fact that it is still regularly cited 20 years later. Later reviews have covered selected areas of cyclometallation chemistry as the range of substrates and metals involved has increased, and as applications of cyclometallated compounds in synthesis have been increasingly developed [2–9].

The best developed area is probably that involving cyclopalladation of aromatic substrates incorporating an *N*-donor, giving complexes of type **1**. Substituted azobenzenes [10–12], benzylamines [13–19], aryl–pyridines [20,21], *N*-benzylideneamines (imines) [22–29], azines [30,31] and hydrazones [30–33] have all been used to give palladium derivatives, and their reactivities have been studied.



**1**



**2**

D = O, S, Se etc.

We have been developing the chemistry of cyclomanganated complexes of type **2**, especially those derived from aryl ketones and enones where O is the donor atom [9,34,35], and from triphenylphosphine chalcogenides where O, S or Se is also attached to the C-bonded manganese atom [36]. During the course of these studies we noted that there had been little development of cyclomanganation chemistry involving *N*-donor substrates, despite the fact that these were the earliest examples reported for manganese, mainly by Bruce et al. [37–42] who studied benzyl

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[1] Dedicated to Michael Bruce, a good friend and colleague, on the occasion of his 60th birthday.

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amines, aryl–imines and azobenzenes. This has meant that the reactivity of related cyclomanganated and cyclopalladated complexes has rarely been directly compared [30], since palladium does not readily form cyclometallated complexes with the O-donor ketones that represent the best developed chemistry for manganese.

We now report the preparation, structures and selected reactions of new compounds formed by cyclomanganation of *N*-arylhydrazones and related substrates.

## 2. Experimental details

### *2.1. General*

Samples of $PhCH_2Mn(CO)_5$ (m.p. 34–36°C, lit. 37.5–38.5°C [43]), the phenylhydrazones of benzaldehyde (m.p. 155–156°C) and acetophenone (m.p. 105–106°C), the diphenylhydrazones of benzaldehyde (m.p. 114–116°C), acetophenone (m.p. 93–94°C) and cyclohexanone (m.p. 72–74°C) and diphenylnitrosamine [CARE: toxicity hazard, carcinogen] (m.p. 66–67°C) were prepared by standard methods and their purity was established by $^1$H- and $^{13}$C-NMR spectroscopy and by melting points [44]. The *N*-phenylhydrazones were stored under nitrogen at low temperature to minimise their ready autoxidation [45].

### *2.2. Cyclomanganation reactions*

### *2.2.1. Cyclomanganation of benzaldehyde phenylhydrazone*

A sample of PhCH=NNHPh (0.189 g, 0.962 mmol) and $PhCH_2Mn(CO)_5$ (0.295 g, 1.03 mmol) was added to heptane (25 ml). The mixture was degassed and flushed with nitrogen, before bringing to reflux for 2 h. The initially yellow solution changed through orange to deep red. Solvent was removed under vacuum to leave a dark oil. This was dissolved in $CH_2Cl_2$ and alumina (Brockmann grade II) was added. The $CH_2Cl_2$ was removed under vacuum and the residue was transferred to the top of an alumina column. Elution with petroleum spirit gave some $Mn_2(CO)_{10}$, while petroleum spirit/$CH_2Cl_2$ removed a deep orange band of $\eta^2$-(N,C)-2-(*N*-phenylhydrazonomethyl)phenyltetracarbonylmanganese, **3a** (0.267 g, 77%) as an oil which could not be crystallised. IR $\nu$(CO) (heptane, cm$^{-1}$): 2077 m, 1994 s, 1985 vs, 1947 s. $^1$H-NMR: $\delta$ 8.38 (1H, s, H-1), 7.98 (1H, d, $^3J_{6',5'} = 5.37$Hz, H-6′), 7.56–7.03 (13H, m, C–H aromatic). $^{13}$C-NMR: $\delta$ 220.2 (s, $C\equiv O$), 213.7 (s, $C\equiv O$), 211.5 (s, $C\equiv O$), 181.7 (s, C-1′), 173.6 (d, C-1), 145.1 (s, C-1″), 144.7 (s, C-2′), 141.2 (d, C-6′), 130.5 (d, C-3′), 129.6 (d, C-3″,5″), 124.9 (d, C-4″), 124.0 (d, C-4′), 123.4 (d, C-2″,6″).

### *2.2.2. Cyclomanganation of acetophenone phenylhydrazone*

Similarly, PhC(Me)=NNHPh (0.213 g, 1.16 mmol) and $PhCH_2Mn(CO)_5$ (0.332 g, 1.01 mmol) in refluxing heptane (30 ml) for 2 h gave an orange oil which was crystallised from $CHCl_3$ to yield orange crystals of $\eta^2$-(N,C)-2-[1-*N*-phenylhydrazono)ethyl]phenyltetracarbonylmanganese, **3b**, (0.334 g, 87%), m.p. 76–77°C. Anal.: Found C 57.31, H 3.40, N 7.39%; $C_{18}H_{13}N_2O_4Mn$ requires C 57.46, H 3.48, N 7.45%. IR $\nu$(CO) (heptane, cm$^{-1}$): 2071 m, 1988 s, 1980 vs, 1947 s. UV–vis (hexane): $\lambda_{max}$ 340 nm. $^1$H-NMR: $\delta$ 8.01 (1H, d, br, H-6′), 7.67 (1H, d, br, H-3′), 7.34 (2H, t, br, H-3″,5″), 7.25 (2H, d, br, H-2″,6″), 7.06 (1H, t, br, H-4″), 6.66 (1H, t, br, H-5′), 6.05 (1H, t, br, H-4′), 5.30 (1H, s, br, N–H), 2.53 (3H, s, br, H-2). $^{13}$C-NMR: $\delta$ 219.5 (s, $C\equiv O$), 213.5 (s, $C\equiv O$), 212.7 (s, $C\equiv O$), 186.9 (s, C-1′), 180.4 (s, C-1), 145.9 (s, C-1″), 144.7 (s, C-2′), 141.4 (d, C-6′), 131.4 (d, C-3′), 129.6 (d, C-3″,5″), 129.0 (d, C-5′), 123.9 (d, C-4′), 122.3 (d, C-4″), 114.8 (d, C-2″,6″), 15.5 (q, C-2).

### *2.2.3. Cyclomanganation of benzaldehyde diphenylhydrazone*

Similarly, $PhCH=NNPh_2$ (0.304 g, 1.12 mmol) and $PhCH_2Mn(CO)_5$ (0.352g, 1.23 mmol) in refluxing heptane (30 ml) for 2.5 h gave a yellow solid which was recrystallised from $CHCl_3$ to yield a yellow powder of $\eta^2$-(N,C)-2-(*N*,*N*-diphenylhydrazonomethyl)phenyltetracarbonylmanganese, **3c** (0.395 g, 83%), m.p. 105–106°C. Anal.: Found C 62.96, H 3.29, N 6.34%; $C_{23}H_{15}N_2O_4Mn$ requires C 63.03, H 3.45, N 6.39%; $\nu$(CO) (heptane, cm$^{-1}$) 2074 m, 1985 vs, 1950 s. $^1$H-NMR: $\delta$ 7.66–7.09 (16H, m, C–H aromatic), 2.15 (1H, s, H-1). $^{13}$C-NMR: $\delta$ 143.8 (s, C-1″), 136.2 (s, C-1′), 135.6 (d, C-1), 129.8 (d, C-3″,5″), 128.6 (d, C-2′,6′), 128.1 (d, C-4′), 126.4 (d, C-3′,5′), 124.5 (d, C-4″), 122.6 (d, C-2″,6″).

### *2.2.4. Cyclomanganation of acetophenone diphenylhydrazone*

Similarly, $PhC(Me) = NNPh_2$ (0.401 g, 1.40 mmol) and $PhCH_2Mn(CO)_5$ (0.420 g, 1.468 mmol) in refluxing heptane (30 ml) for 2 h gave a dark solution. Work-up gave a major yellow band which was crystallised from petroleum spirit/$CHCl_3$ as a yellow powder of $\eta^2$-(N,C)-2-[1-(*N*,*N*-diphenylhydrazono)ethyl]phenyltetracarb onylmanganese, **3d**, (0.541 g, 86%), m.p. 88–9°C. Anal.: Found C 63.73, H 3.68, N 6.17%; $C_{24}H_{17}N_2O_4Mn$ requires C 63.73, H 3.79, N 6.19%. IR $\nu$(CO) (heptane, cm$^{-1}$): 2071 m, 1988 s, 1980 vs, 1947 s. UV–vis (hexane): $\lambda_{max}$ 362 nm (br). $^1$H-NMR: $\delta$ 7.97–7.13 (15H, m, C–H aromatic), 2.35 (3H, s, H-2). $^{13}$C-NMR: $\delta$ 213.5 (s, $C\equiv O$), 188.7 (s, C-1′), 182.9 (s, C-1), 145.2 (s, C-1′), 143.5 (s, C-1″), 141.4 (d, C-6′), 131.4 (d, C-3′), 129.5 (d, C-3″,5″), 123.9 (d, C-4′), 123.4 (d, C-4″), 120.1 (d, C-2″,6″), 17.0 (q, C-2).

### 2.2.5. Cyclomanganation of cyclohexanone diphenylhydrazone

A sample of $C_6H_{10}NNPh_2$ (0.282 g, 0.986 mmol) and $PhCH_2Mn(CO)_5$ (0.248 g, 0.938 mmol) was heated under reflux in heptane (25 ml) for 2 h. to give a yellow solution. Chromatographic work-up as in Section 2.2.1 gave one major band which was recrystallised from petroleum spirit/$CH_2Cl_2$ as yellow crystals of $\eta^2$-(N,C)-2-($N^2$-cyclohexylidene-$N^1$-phenylhydrazino)phenyltetracarbonylmanganese, **4** (0.379 g, 94%), m.p. 110–112°C. Anal.: Found C 61.19, H 4.36, N 6.40%; $C_{22}H_{19}N_2O_4Mn$ requires C 61.40, H 4.45, N 6.51%. IR $\nu$(CO) (heptane, $cm^{-1}$): 2073 m, 1991 vs, 1977 s, 1940 s. $^1$H-NMR: $\delta$ 7.90–7.82 (1H, m, C–H aromatic), 7.23–6.70 (m, C–H aromatic), 2.99–2.80 (m, C–H cyclohexyl), 1.92–1.43 (m, C–H cyclohexyl). $^{13}$C-NMR: $\delta$ 220.4 (s, C≡O), 214.2 (s, C≡O), 212.4 (s, C≡O), 191.7 (s, C-1), 160.6 (s, C-1′), 151.3 (s, C-2′), 145.0 (s, C-1″), 141.7 (d, C-6′), 129.2 (d, C-3″,5″), 125.8 (d, C-4′), 123.8 (d, C-5′), 121.9 (d, C-4″), 120.4 (d, C-3′), 113.6 (d, C-2″,6″), 38.8 (t, C-6), 32.3 (t, C-2), 26.9 (t, C-4), 26.4 (t, C-5), 24.9 (t, C-3).

### 2.2.6. Cyclomanganation of diphenylnitrosamine

A sample of $Ph_2NNO$ (0.201 g, 1.01 mmol) and $PhCH_2Mn(CO)_5$ (0.303g, 1.06 mmol) in refluxing heptane (30 ml) for 0.5 h gave, after the standard work-up, $\eta^2$-(N,C)-2-[*N*-nitroso-*N*-phenylamino]phenyltetracarbonylmanganese, **5** (0.258 g, 70%). Recrystallisation from petroleum spirit gave orange–brown crystals, m.p. 65–66°C. Anal.: Found C 56.33, H 3.22, N 7.75%; $C_{16}H_9N_2O_5Mn \cdot 0.25Ph_2NH$ requires C 56.17, H 2.85, N 7.23%. IR $\nu$(CO) (heptane, $cm^{-1}$): 2084 m, 2004 s, 2001vs, 1970 s. $^1$H-NMR: $\delta$ 7.93 (1H, d, $^3J_{6',5'} = 1.79$ Hz, H-6′), 7.86 (1H, t, $^3J_{4',5'} = 1.79$ Hz), 7.57–7.51 (3H, m, C–H aromatic), 7.28–6.95 (4H, m, C–H aromatic). $^{13}$C-NMR: $\delta$ 219.7 (s, C≡O), 211.0 (s, C≡O), 210.0 (s, C≡O), 156.4 (s, C-1′), 147.8 (s, C-2′), 141.6 (d, C-6′), 135.1 (s, C-1″), 130.9 (d, C-3′), 130.3 (d, C-3″,5″), 127.5 (d, C-2″,6″), 127.1 (d, C-4′), 124.8 (d, C-4″), 114.8 (d, C-3′). Diphenylamine impurity peaks (ca. 25%): $\delta$ 143.2 (s, C-1), 129.4 (d, C-3,5), 121.1 (d, C-4), 117.9 (d, C-2,6). Electrospray mass spectroscopy, ESMS ($MeCN/H_2O$, 1:1, cone voltage 10V): *m/z* 382 (21%) $[M + NH_4]^+$, 365 (100%) $[M + H]^+$, 336 (13%) $[M + NH_4 - 2CO]^+$, 170 (33%) $[Ph_2NH_2]^+$.

## 2.3. Reactions of orthomanganated complexes with alkynes

### 2.3.1. Reaction of $\eta^2$-(N,C)-2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese, *3c*, with $Ph_2C_2$

Compound **3c** (0.251 g, 0.573 mmol) and $Ph_2C_2$ (0.20 g, 1.12 mmol) were heated under reflux in acetonitrile (25 ml) for 2 h; by this time an IR spectrum showed that all of **3c** had been consumed to be replaced by $\nu$(CO) bands at 2024m, 1982w, 1919 vs $cm^{-1}$. The solvent was removed under vacuum, the residue was dissolved in $CH_2Cl_2$, and alumina (Brockmann grade II) was added. The $CH_2Cl_2$ was pumped off and the resulting powder was transferred to the top of an alumina column (8.0 × 2.5 cm). Elution with petroleum spirit gave unreacted $Ph_2C_2$, identified by NMR. Elution with petroleum spirit:$CH_2Cl_2$ (7:3) gave an orange band which was crystallised from petroleum spirit as an orange powder identified as the indenyl diphenylhydrazine **7a**, (0.133 g, 53%). Anal.: Found C 86.96, H 5.60, N 6.19%; $C_{33}H_{25}N_2$ requires C 87.16, H 5.60, N 6.23%. $^1$H-NMR: $\delta$ 7.33–6.91 (24H, m, C–H aromatic), 4.48 (1H, s, C-1). $^{13}$C-NMR: $\delta$ 148.0 (s), 144.9 (s), 144.6 (s), 141.4 (s), 140.9 (s), 134.8 (s) 134.0 (s), 131.5 (s), 129.4 (d), 129.1 (d) 128.6 (d), 128.4 (d), 127.7 (d), 127.4 (d) 126.0 (d), 124.8 (d), 122.8 (d), 121.3 (d) 121.1 (d), 120.6 (d), 117.9 (d), 64.2 (d).

### 2.3.2. Reaction of $\eta^2$-(N,C)-2-(N,N-diphenylhydrazonomethyl)phenyltetracarbonylmanganese, *3c*, with $Me_3SiC_2H$

Following the same work-up procedure after a 4 h reflux, the major yellow band to be eluted with petroleum spirit:$CH_2Cl_2$ (10:1) was identified spectroscopically as an inseparable 2:1 mixture of the two isomers **7b** and **7c** in total 54% yield. $^1$H-NMR: $\delta$ 7.73–7.08 (15H, m, C–H aromatic), 1.62 (1H, s, C-1), 1.46 (1H, s, C-1), 0.37 (9H, s, $Si(C\underline{H}_3)_3$), 0.24 (9H, s, $Si(C\underline{H}_3)_3$). $^{13}$C-NMR: $\delta$ 143.8 (s), 141.2 (s), 134.2 (s), 133.3 (s), 129.9 (d), 129.1 (d), 127.8 (s), 128.1 (s), 1 (s), 126.7 (s), 126.2 (s), 124.6 (d), 122.6 (d), 121.0 (d), 29.8 (d), 22.8 (d), − 0.7 (q, $Si(\underline{C}H_3)_3$), − 1.17 (q, $Si(\underline{C}H_3)_3$).

### 2.3.3. Reaction of $\eta^2$-(N,C)-[1-(N,N-diphenylhydrazono)ethyl]phenyl-tetracarbonylmanganese, *3d*, with $Ph_2C_2$

This reaction, after a 3 h reflux, gave a major orange band with petroleum spirit:$CH_2Cl_2$ (3:7) which crystallised from petroleum spirit to give the analogous hydrazine **8a**, 42%, m.p. 127°C, identified spectroscopically. $^1$H-NMR: $\delta$ 7.62–7.11 (24H, m, C–H aromatic), 3.06 (3H, s, C-1). $^{13}$C-NMR: $\delta$ 157.7 (s), 149.5 (s), 137.7 (s), 136.0 (s), 131.4 (d), 130.3 (d) 129.9 (d), 129.3 (s), 128.2 (d), 127.6 (d), 127.1 (d) 126.9 (d), 126.5 (d), 126.3 (d), 125.5 (d), 22.76 (q, $\underline{C}H_3$).

### 2.3.4. Reaction of $\eta^2$-(N,C)-[1-(N,N-diphenylhydrazono)ethyl]phenyl-tetracarbonylmanganese, *3d*, with $Me_3SiC_2H$

Following the same procedure, but for a 5 h reflux, the major yellow band to be eluted with petroleum spirit:$CH_2Cl_2$ (3:1) gave an impure yellow oil that could not be further purified, but which NMR spectroscopy suggested contained the hydrazine **8b** as the major component. $^1$H-NMR: δ 7.35–6.89 (15H, m, C–H aromatic), 2.02 (3H, s, C-1), 0.11 (9H, s, Si(C$\underline{\text{H}}_3$)$_3$). $^{13}$C-NMR: δ 168.3 (s), 148.7 (s), 141.9 (d), 139.4 (s), 136.9 (s), 132.8 (d), 129.3 (d), 128.7 (d), 128.2 (d), 127.8 (d), 126.4 (d), 123.4 (d), 121.8 (d), 22.6 (q, C-1), −1.2 (q, Si($\underline{\text{C}}$H$_3$)$_3$). Impurity resonances: δ 129.4 (d), 121.6 (d), 117.9 (d).

### 2.3.5. Unsuccessful reactions

The following reactions were carried out, all of which gave complex mixtures of products which were not able to be characterised:

1. the mono-phenylhydrazones **3a** and **3c** with $Ph_2C_2$,
2. the di-phenylhydrazones **3b** and **3c** with $C_2(COOMe)_2$ and
3. the cyclohexylidene complex **4** with $Ph_2C_2$ or $PhC_2H$.

## 2.4. X-ray crystal structure determinations

Accurate cell parameters and intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer (for **3b** and **5**) or an Enraf-Nonius CAD4 four-circle diffractometer (for **4**) with monochromated Mo–K$_\alpha$ X-rays ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-86 [46]) and the refinement was based on $F^2$ (SHELXL-93 [47]). All non-H atoms were refined anisotropically and H atoms were included in calculated positions.

### 2.4.1. $\eta^2$-2-[1-(N-Phenylhydrazono)ethyl]phenyltetracarbonylmanganese (**3b**)

Orange crystals of **3b** were obtained from $CHCl_3$. Crystal data: $C_{18}H_{13}MnN_2O_4$, $M_r = 376.24$, monoclinic, space group $P2_1/c$, $a = 10.878(2)$, $b = 8.712(2)$, $c = 17.765(4)$ Å, $\beta = 93.78(3)°$, $V = 1679.9(6)$ Å$^3$, $D_{calc.} = 1.488$ g cm$^{-3}$, $Z = 4$, $F(000) = 768$, $\mu$(Mo–K$_\alpha$) = 0.811 mm$^{-1}$, $T_{max}$ 0.79, $T_{min}$ 0.69. Crystal size 0.48 × 0.46 × 0.16 mm$^3$.

A total of 2333 reflections (2197 unique) were collected at −143°C, $4° < 2\theta < 45°$, 1838 with $I > 2\sigma(I)$. The refinement converged with $R_1 = 0.0317$ ($2\sigma$ data), and $R_1 = 0.0430$, $wR_2 = 0.0767$, GoF = 1.047 (all data). Final largest $\Delta/\sigma$ 0.001, largest final feature 0.37 e Å$^{-3}$. Coordinates and selected bond parameters are listed in Tables 1 and 2, respectively, and the structure is illustrated in Fig. 1.

Table 1
Atomic coordinates and equivalent isotropic displacement parameters for $\eta^2$-2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonylmanganese (**3b**)

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Mn(1) | 0.2777(1) | 0.1688(1) | 0.5755(1) | 0.020(1) |
| N(1) | 0.2885(2) | 0.2904(3) | 0.4772(1) | 0.020(1) |
| N(2) | 0.2643(2) | 0.2278(3) | 0.4035(1) | 0.022(1) |
| C(1) | 0.2781(3) | 0.0915(3) | 0.6698(2) | 0.025(1) |
| C(2) | 0.4393(3) | 0.1100(3) | 0.5758(2) | 0.022(1) |
| C(3) | 0.1184(3) | 0.2453(3) | 0.5871(2) | 0.025(1) |
| C(4) | 0.2154(3) | −0.0063(4) | 0.5279(2) | 0.024(1) |
| O(1) | 0.2843(2) | 0.0500(3) | 0.7315(1) | 0.036(1) |
| O(2) | 0.5416(2) | 0.0737(2) | 0.5813(1) | 0.030(1) |
| O(3) | 0.0231(2) | 0.2910(2) | 0.5974(1) | 0.034(1) |
| O(4) | 0.1757(2) | −0.1142(3) | 0.4983(1) | 0.035(1) |
| C(11) | 0.3394(2) | 0.3785(3) | 0.6156(2) | 0.019(1) |
| C(12) | 0.3487(2) | 0.4896(3) | 0.5580(2) | 0.019(1) |
| C(13) | 0.3875(2) | 0.6398(3) | 0.5741(2) | 0.023(1) |
| C(14) | 0.4191(2) | 0.6830(3) | 0.6479(2) | 0.025(1) |
| C(15) | 0.4102(2) | 0.5761(3) | 0.7054(2) | 0.026(1) |
| C(16) | 0.3713(2) | 0.4270(3) | 0.6894(2) | 0.022(1) |
| C(17) | 0.3174(2) | 0.4356(3) | 0.4808(2) | 0.020(1) |
| C(18) | 0.3200(3) | 0.5391(3) | 0.4137(2) | 0.025(1) |
| C(21) | 0.1394(2) | 0.2256(3) | 0.3738(2) | 0.019(1) |
| C(22) | 0.1053(3) | 0.1170(3) | 0.3187(2) | 0.025(1) |
| C(23) | −0.0117(3) | 0.1176(4) | 0.2838(2) | 0.029(1) |
| C(24) | −0.0968(3) | 0.2269(4) | 0.3035(2) | 0.028(1) |
| C(25) | −0.0646(2) | 0.3322(3) | 0.3589(2) | 0.026(1) |
| C(26) | 0.0536(2) | 0.3332(3) | 0.3945(2) | 0.022(1) |

### 2.4.2. $\eta^2$-2-(N$^2$-Cyclohexylidene-N$^1$-phenylhydrazono)phenyltetracarbonylmanganese (**4**)

Orange crystals were obtained by diffusion of pentane into an ether solution of **4** at 4°C.
Crystal data: $C_{22}H_{19}MnN_2O_4$, $M_r = 430.33$, monoclinic, space group $Pn$, $a = 10.529(2)$, $b = 17.959(3)$, $c = 10.924(2)$ Å, $\beta = 94.65(2)°$, $V = 2058.8(6)$ Å$^3$, $D_{calc.} = 1.388$ g cm$^{-3}$, $Z = 4$, $F(000) = 888$, $\mu$(Mo–K$_\alpha$) = 0.671 mm$^{-1}$, $T_{max}$ 1.00, $T_{min}$ 0.96. Crystal size 0.57 × 0.47 × 0.40 mm$^3$.

A total of 3897 unique reflections (3816 unique) were collected at 20°C, $2° < 2\theta < 50°$, 3660 with $I > 2\sigma(I)$.

Table 2
Selected bond parameters for $\eta^2$-2-[1-(N-phenylhydrazono)ethyl]phenyltetracarbonyl-manganese (3b)

| | | | | | |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| Mn(1)–C(11) | 2.058(3) | Mn(1)–N(1) | 2.053(2) | Mn(1)–C(1) | 1.806(3) |
| Mn(1)–C(2) | 1.830(3) | Mn(1)–C(3) | 1.881(3) | Mn(1)–C(4) | 1.851(3) |
| C(11)–C(12) | 1.416(4) | C(12)–C(17) | 1.469(4) | N(1)–C(17) | 1.303(4) |
| N(1)–N(2) | 1.427(3) | | | | |
| Bond angles (°) | | | | | |
| N(1)–Mn(1)–C(11) | 78.5(1) | Mn(1)–N(1)–N(2) | 124.5(2) | | |
| Mn(1)–N(1)–C(17) | 119.2(2) | Mn(1)–C(11)–C(12) | 113.2(2) | | |
| C(11)–C(12)–C(17) | 115.6(2) | Mn(1)–C(11)–C(16) | 130.3(2) | | |
| N(1)–C(17)–C(12) | 113.3(2) | C(2)–Mn(1)–C(3) | 172.1(1) | | |

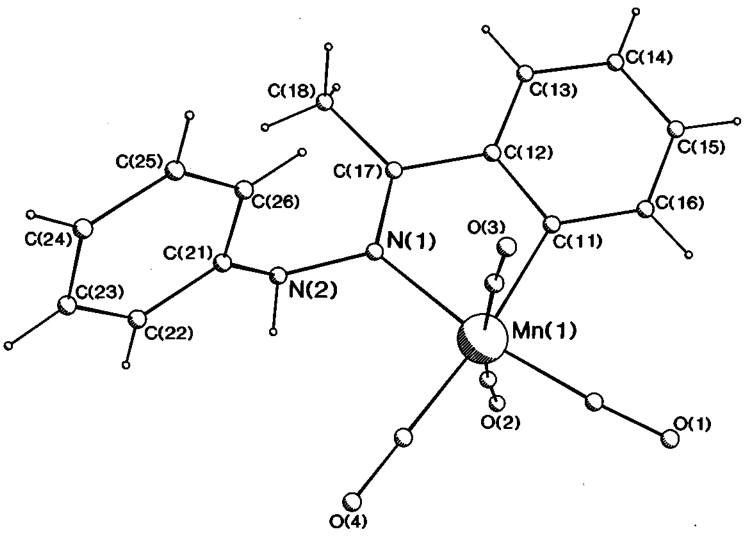


Fig. 1. A PLUTO-plot of the structure of the orthomanganated complex of acetophenone–phenylhydrazone, **3b**.

The refinement converged with $R_1 = 0.0332$ ($2\sigma$ data), and $R_1 = 0.0356$, $wR_2 = 0.0891$, GoF = 1.054 (all data). Final largest $\Delta/\sigma$ 0.001, largest final feature 0.54 e Å$^{-3}$. The Flack $x$ parameter refined to $-0.004(14)$ indicating the correct polarity was chosen. Coordinates and selected bond parameters are listed in Tables 3 and 4, respectively, and the structure is illustrated in Fig. 2.

### 2.4.3. *$\eta^2$-2-($N^1$-Nitroso-$N^1$-phenylamino)phenyltetracarbonylmanganese* (**5**)

Orange crystals were obtained by diffusion of pentane into a $CH_2Cl_2$ solution of **5**.

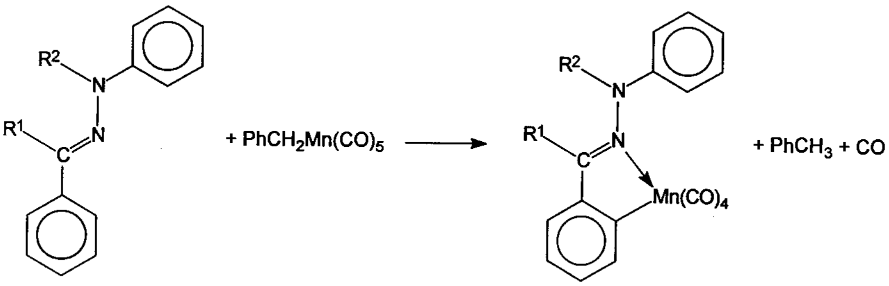
Crystal data: $C_{16}H_9MnN_2O_5$, $M_r = 364.19$, triclinic, space group $P\bar{1}$, $a = 9.677(2)$, $b = 11.55(1)$, $c = 17.53(3)$ Å, $\alpha = 71.45(3)$, $\beta = 94.65(2)$, $\gamma = 88.08(3)$°, $V = 1849(4)$ Å$^3$, $D_{\mathrm{calc.}} = 1.308$ g cm$^{-3}$, $Z = 4$, $F(000) = 736$, $\mu$(Mo–K$_\alpha$) = 0.738 mm$^{-1}$, $T_{\max}$ 0.826, $T_{\min}$ 0.706. Crystal size $0.70 \times 0.28 \times 0.21$ mm$^3$.

A total of 6054 (5670 unique) reflections were collected at $-143$°C, $4° < 2\theta < 48°$, 2186 with $I > 2\sigma(I)$. The structure solved to reveal two independent molecules of the cyclomanganated diphenylnitrosamine. At this stage significant residual electron density was found in the lattice, approximating 0.25 $C_6H_6$ which presumably can be attributed to the co-crystallising $Ph_2NH$ which was also indicated from the NMR and micro-analytical data (see text). However this was not very successfully modelled and combined with the weak data set from a poorly diffracting crystal, the structure was less precisely defined than usual. The refinement converged with $R_1 = 0.1297$ ($2\sigma$ data) and $wR_2 = 0.4514$, GoF = 1.031 (all data). Final largest $\Delta/\sigma$ 0.001, largest final feature 1.86 e Å$^{-3}$. The structure is illustrated in Fig. 3, but no numerical data is presented here because of the low quality of the determination which served mainly to confirm atom connectivity and overall conformation.

## 3. Results and discussion

### 3.1. Syntheses

Cyclomanganation of the mono- and di-phenylhydrazones of benzaldehyde and of acetophenone proceeds smoothly under the normal conditions to give the C,N-bonded five-membered ring metallocycles **3a–3d**, Eq. 1:



**3a** $R^1 = R^2 = H$

**3b** $R^1 = Me$, $R^2 = H$

**3c** $R^1 = H$, $R^2 = Ph$

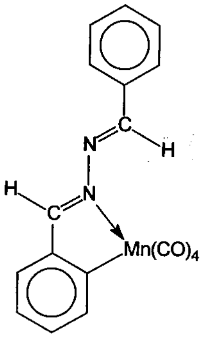
**3d** $R^1 = Me$, $R^2 = Ph$

**Equation 1**

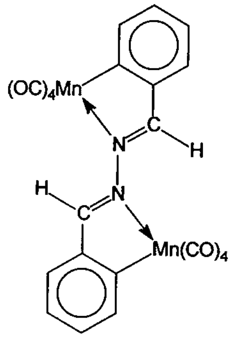
Table 3
Atomic coordinates and equivalent isotropic displacement parameters for $\eta^2$-2-($N^2$-cyclohexylidene-$N^1$-phenylhydrazino)phenyltetracarbonylmanganese (**4**)

| Atom | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| Mn(1) | 0.6901(1) | 0.2879(1) | 0.3640(1) | 0.033(1) |
| N(11) | 0.8262(3) | 0.2760(2) | 0.2355(3) | 0.036(1) |
| N(12) | 0.8331(3) | 0.3428(2) | 0.1640(3) | 0.042(1) |
| C(11) | 0.5557(4) | 0.3107(2) | 0.4481(3) | 0.045(1) |
| C(12) | 0.5966(3) | 0.2143(2) | 0.2764(3) | 0.038(1) |
| C(13) | 0.7702(4) | 0.3731(2) | 0.4298(3) | 0.043(1) |
| C(14) | 0.7560(4) | 0.2276(2) | 0.4893(4) | 0.046(1) |
| O(11) | 0.4691(3) | 0.3283(2) | 0.4973(3) | 0.067(1) |
| O(12) | 0.5397(3) | 0.1731(2) | 0.2179(3) | 0.063(1) |
| O(13) | 0.8108(3) | 0.4253(2) | 0.4722(3) | 0.070(1) |
| O(14) | 0.7902(4) | 0.1910(2) | 0.5694(3) | 0.072(1) |
| C(111) | 0.6182(3) | 0.3550(2) | 0.2226(3) | 0.037(1) |
| C(112) | 0.7071(3) | 0.3716(2) | 0.1392(3) | 0.040(1) |
| C(113) | 0.6725(4) | 0.4094(2) | 0.0298(4) | 0.055(1) |
| C(114) | 0.5487(4) | 0.4354(2) | 0.0073(4) | 0.058(1) |
| C(115) | 0.4607(4) | 0.4213(2) | 0.0903(4) | 0.054(1) |
| C(116) | 0.4953(3) | 0.3808(2) | 0.1964(4) | 0.045(1) |
| C(121) | 0.9395(3) | 0.3891(2) | 0.1960(3) | 0.042(1) |
| C(122) | 1.0439(4) | 0.3637(2) | 0.2699(4) | 0.053(1) |
| C(123) | 1.1515(4) | 0.4082(3) | 0.2924(5) | 0.063(1) |
| C(124) | 1.1588(5) | 0.4770(3) | 0.2409(5) | 0.068(1) |
| C(125) | 1.0549(5) | 0.5030(3) | 0.1700(5) | 0.071(1) |
| C(126) | 0.9450(5) | 0.4610(2) | 0.1479(4) | 0.057(1) |
| C(131) | 0.8900(3) | 0.2210(2) | 0.1986(3) | 0.038(1) |
| C(132) | 0.9691(4) | 0.2229(2) | 0.0896(4) | 0.050(1) |
| C(133) | 0.9337(5) | 0.1589(3) | 0.0020(4) | 0.065(1) |
| C(134) | 0.9399(5) | 0.0845(3) | 0.0674(5) | 0.068(1) |
| C(135) | 0.8556(4) | 0.0842(2) | 0.1732(4) | 0.057(1) |
| C(136) | 0.8908(3) | 0.1478(2) | 0.2628(3) | 0.043(1) |
| Mn(2) | 0.9089(1) | 0.8084(1) | 0.3054(1) | 0.039(1) |
| N(21) | 0.7425(3) | 0.7686(2) | 0.2100(3) | 0.037(1) |
| N(22) | 0.6696(3) | 0.8305(2) | 0.1552(3) | 0.042(1) |
| C(21) | 1.0309(5) | 0.8598(3) | 0.3937(4) | 0.062(1) |
| C(22) | 0.9598(4) | 0.8572(2) | 0.1666(4) | 0.050(1) |
| C(23) | 0.8504(4) | 0.7733(2) | 0.4512(4) | 0.049(1) |
| C(24) | 1.0207(4) | 0.7319(2) | 0.2811(4) | 0.049(1) |
| O(21) | 1.1056(4) | 0.8946(3) | 0.4472(5) | 0.102(2) |
| O(22) | 1.0023(3) | 0.8885(3) | 0.0895(4) | 0.080(1) |
| O(23) | 0.8116(4) | 0.7564(2) | 0.5396(3) | 0.072(1) |
| O(24) | 1.0974(4) | 0.6891(2) | 0.2678(4) | 0.076(1) |
| C(211) | 0.7816(4) | 0.8934(2) | 0.3261(3) | 0.046(1) |
| C(212) | 0.6763(4) | 0.8899(2) | 0.2425(3) | 0.046(1) |
| C(213) | 0.5754(5) | 0.9394(3) | 0.2424(5) | 0.063(1) |
| C(214) | 0.5840(6) | 0.9972(3) | 0.3305(6) | 0.077(2) |
| C(215) | 0.6864(7) | 1.0020(3) | 0.4135(6) | 0.077(2) |
| C(216) | 0.7829(5) | 0.9509(2) | 0.4126(4) | 0.062(1) |
| C(221) | 0.6984(3) | 0.8461(2) | 0.0314(3) | 0.040(1) |
| C(222) | 0.6908(4) | 0.9184(2) | −0.0141(4) | 0.048(1) |
| C(223) | 0.7177(4) | 0.9319(2) | −0.1343(4) | 0.054(1) |
| C(224) | 0.7529(4) | 0.8757(3) | −0.2087(4) | 0.057(1) |
| C(225) | 0.7587(4) | 0.8042(2) | −0.1654(4) | 0.052(1) |
| C(226) | 0.7317(4) | 0.7890(2) | −0.0452(4) | 0.047(1) |
| C(231) | 0.6852(4) | 0.7059(2) | 0.2050(4) | 0.044(1) |
| C(232) | 0.5518(4) | 0.6934(3) | 0.1490(4) | 0.058(1) |
| C(233) | 0.4681(5) | 0.6626(3) | 0.2442(5) | 0.069(1) |
| C(234) | 0.5229(6) | 0.5923(3) | 0.3020(6) | 0.083(2) |
| C(235) | 0.6597(6) | 0.6044(3) | 0.3555(6) | 0.083(2) |
| C(236) | 0.7440(4) | 0.6377(2) | 0.2632(5) | 0.059(1) |

This reaction parallels those used by Sales et al. [30] to prepare the mono- and di-manganated derivatives of the di-azene of benzaldehyde, **3e** and **3f**.



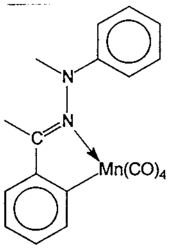
**3e**



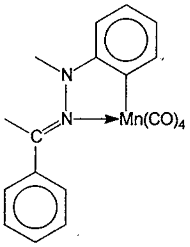
**3f**

Yields of **3a**–**3d** are good and the compounds are readily purified by chromatography. The compounds are closely related to orthomanganated imines, first reported by Bruce et al. [48], with a similar orthomanganated ring [49,50]. There is no interference in the reaction from the N–H group of the mono-phenylhydrazone reactions. One notable difference was that the mono-phenylhydrazone examples **3a** and **3b** were intensely orange while the di-phenylhydrazone examples **3c** and **3d** were light yellow, which is perhaps the reverse of what would be expected. Possibly there is a difference in the orientation of the *N*-bonded phenyl rings in the two classes, limiting delocalisation in the more crowded example.

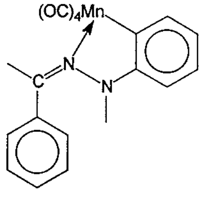
With these substrates there is the possibility of different isomers forming, **6a**–**e**, depending on which N atom coordinates to the manganese, and which aryl C–H becomes the site of metallation.



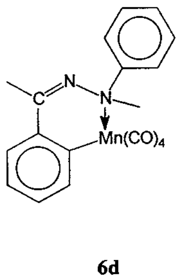
**6a**



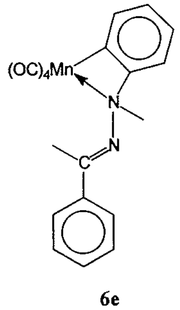
**6b**



**6c**



**6d**



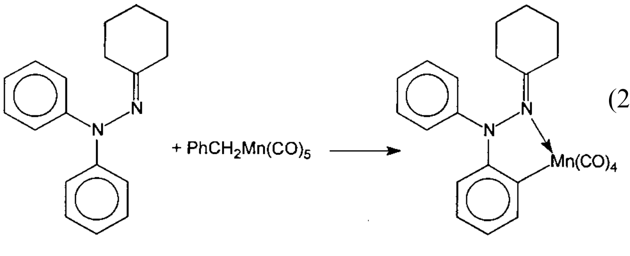
**6e**

Table 4
Selected bond parameters for $\eta^2$-2-($N^2$-cyclohexylidene-$N^1$-phenylhydrazino)phenyltetracarbonylmanganese (**4**)

| | Mol 1 | Mol 2 | | Mol 1 | Mol 2 |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| Mn–N(1) | 2.096(3) | 2.091(3) | Mn–C(11) | 2.055(3) | 2.056(4) |
| Mn–C(1) | 1.796(4) | 1.798(4) | Mn–C(2) | 1.865(4) | 1.867(4) |
| Mn–C(3) | 1.862(4) | 1.863(4) | Mn–C(4) | 1.837(4) | 1.842(4) |
| N(1)–N(2) | 1.437(4) | 1.453(4) | N(1)–C(31) | 1.278(5) | 1.276(5) |
| N(2)–C(12) | 1.429(5) | 1.428(5) | C(11)–C(12) | 1.391(6) | 1.380(6) |
| Bond angles (°) | | | | | |
| C(11)–Mn–N(1) | 77.7(1) | 77.4(1) | C(2)–Mn–C(3) | 169.6(2) | 171.7(2) |
| Mn–N(1)–N(2) | 110.3(2) | 109.7(2) | N(1)–N(2)–C(12) | 108.5(3) | 107.5(3) |
| N(2)–C(12)–C(11) | 117.6(2) | 118.1(3) | Mn–C(11)–C(12) | 113.0(2) | 112.9(4) |
| Mn–N(1)–C(31) | 134.1(2) | 134.2(3) | N(1)–N(2)–C(21) | 115.5(3) | 113.1(3) |

However only one isomer is observed in all of the reactions, shown by an X-ray structure determination of a representative example below to correspond to **6a**. It is generally accepted that five-membered metallocyclic rings are most favoured so it is not surprising that the six- or four-membered species **6d** or **6e** are spurned. Compounds **6c** and **6d** would also only form from the less-favoured *anti* isomer of the starting hydrazones which are only minor components in the starting material. However isomer **6b** includes a five-membered ring and would form from the *syn* isomer of the starting material so it would be a reasonable product to expect. It appears that the more rigid, planar $\overline{\mathrm{MnC_3N}}$ ring of **6a** is preferred to the alternative $\overline{\mathrm{MnC_2N_2}}$ ring of **6b** (these two alternatives have been classified as *endo* and *exo*, respectively, in related palladium examples [32]). Partial delocalisation of $\pi$-electrons within the five-membered ring would be possible for **6a** but not for **6b**, which may also be a factor. It would be interesting to investigate the phenylhydrazones of di-ortho-substituted acetophenones to see if metallation of the $N$-bonded phenyl ring could be directed when the alternative sites are blocked, a strategy that has been successful for cyclopalladiation of the phenylhydrazone of 2,4,6-trimethylbenzaldehyde [32].

To see whether a ring of the type shown in **6b** could be formed when there is no alternative, the orthomanganation of the diphenylhydrazone of cyclohexanone was examined. This too went smoothly (Eq. 2) to give the *exo* complex **4** which indeed does incorporate the novel $\overline{\mathrm{MnC_2N_2}}$ ring.



(2)

**4**

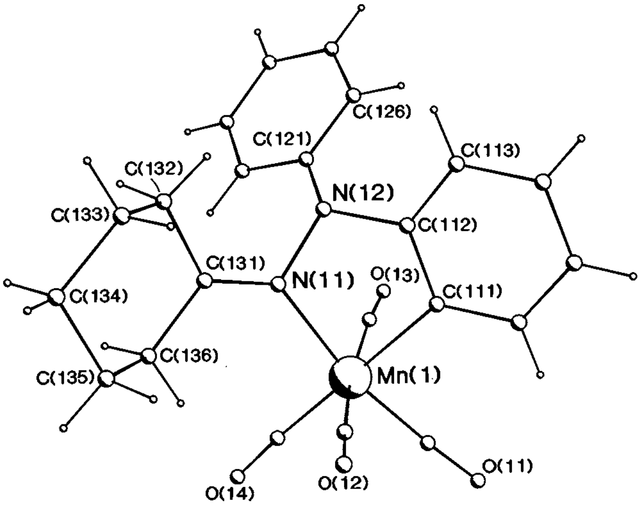


Fig. 2. The structure of the orthomanganated complex **4** derived from the diphenylhydrazone of cyclohexanone. Only molecule 1 of the two independent molecules is shown; the labelling for molecule 2 corresponds directly, with N(11) becoming N(21), etc.

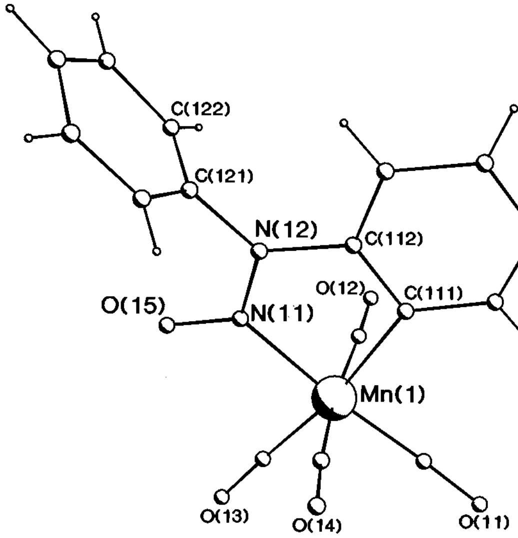
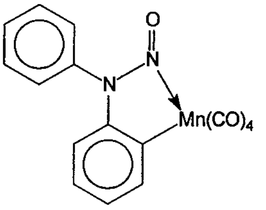


Fig. 3. The structure of the orthomanganated complex **5** derived from diphenylnitrosamine.

This suggests that *exo* isomers of type **6b** would be stable if they were formed, but that the **6a** type products are more favoured.

Finally $Ph_2NNO$ was examined to see if this could be cyclometallated to give the corresponding ring to that in **4**, and this led to compound **5** in reasonable yield.



**5**

Again this is a new type of orthomanganated complex, although analogous Pd species have been prepared from *N*-methyl-*N*-nitrosoanilines [51,52]. Characterisation of **5** was made more difficult by co-crystallisation with an impurity. $^{13}$C-NMR spectroscopy of a sample of **5** after chromatography and recrystallisation showed extra peaks which exactly coincided with those of a genuine sample of $Ph_2NH$, and the presence of this species is consistent with microanalytical data, with the ESMS data (where a $Ph_2NH_2^+$ ion was identified) and with the crystal structure determination where residual electron density associated with phenyl rings was found. There was no $Ph_2NH$ in the starting nitrosamine so it appears that some of the $Ph_2NNO$ is converted to $Ph_2NH$ during the orthometallation procedure. Although there is no doubt that compound **5** was synthesised, leading to an alternative example containing a $\overline{MnC_2N_2}$ ring, we cannot claim to have isolated a pure sample and propose that some $Ph_2NH$ formed during the reaction was not separated from **5** either by chromatography or by recrystallisation.

Overall, however, phenylhydrazones and related species are therefore good substrates for orthomanganation reactions, giving either $\overline{MnC_3N}$ or $\overline{MnC_2N_2}$ rings, depending on the substituents. The compounds are all reasonably stable and can be handled in air without significant decomposition. Indeed the orthomanganated primary phenylhydrazones **3a** and **3c** appear to be less susceptible to autoxidation via the N–H bond than the non-metallated precursors.

### 3.2. Spectroscopy

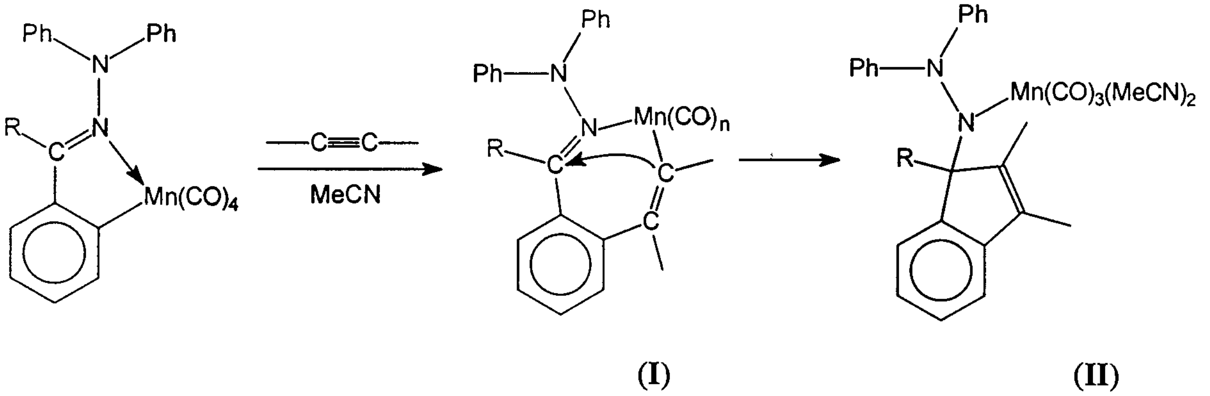
The new compounds gave the expected spectroscopic features. The carbonyl-region IR spectra showed the normal four-band pattern characteristic of the *cis* $L_2Mn(CO)_4$ group, although accidental degeneracy of the middle two bands occurred for compound **3c**. The different type of metallocyclic ring in complex **4** leads to significant differences in the $\nu$(CO) region, with the two strongest peaks separated by 14 $cm^{-1}$ (cf. 0–8 $cm^{-1}$ in other derivatives) and with a particularly low energy absorbance for the lowest frequency band at 1940 $cm^{-1}$ (cf. $>1945$ $cm^{-1}$ for others). Similarly the $^1$H- and $^{13}$C-NMR spectra were straightforward for all of the compounds. The only example to be examined by ESMS, the orthomanganated diphenylnitrosamine **5**, gave clear peaks assignable to $[M+NH_4]^+$ and $[M+H]^+$ ions under standard conditions.

### 3.3. Structure determinations

The structure of the orthomanganated acetophenone–phenylhydrazone **3b** is illustrated in Fig. 1. It contains the expected five-membered ring with the manganese attached to the *ortho*-position of the ring derived from the acetophenone moiety and to the C=N nitrogen atom. The coordination about the manganese atom is essentially octahedral, with the main deviation associated with the C(11)–Mn–N(1) bite angle of 78.5°. The core of the molecule is planar, with the anilino–aryl group twisted to generate a dihedral angle of 77°. The metallocyclic ring is directly analogous to those characterised previously in derivatives of the phenylimines of benzaldehyde [53] and 2-chloroacetophenone [49], and in the di-azine species **3e** and **3f** [30]. The geometry of the corresponding part of the molecules in all these species shows little variation.

The structure analysis of the orthomanganated complex derived from the cyclohexanone–diphenylhydrazone, **4**, revealed two independent molecules in the asymmetric unit. These differed mainly in the relative orientation of the non-coordinated phenyl ring which gave dihedral angles with respect to the chelate ring of 54 and 70°, respectively, in the two molecules. Fig. 2 shows the geometry of molecule 1, which does contain the unique $\overline{MnC_2N_2}$ ring. In contrast to other orthomanganated species, this ring is not planar, but is puckered so that N(12) is 0.23 Å above, and N(11) 0.24 Å below, the least squares plane of the ring. This is presumably to accommodate the $sp^3$ hybridised N(12), which precludes delocalisation of electron density within the metallocyclic unit. Consistent with this, the Mn–N and N–N bonds are longer than those in the imine-derived metallocyclic ring of **3b**. In the analogous $\overline{PdC_2N_2}$ species the ring is much closer to planar with shorter N–N distances [32].

The crystal structure of the orthomanganated diphenylnitrosamine **5** was also determined. Only weakly diffracting crystals could be formed, and a co-crystallising impurity complicated analysis, so that the results can only be used to confirm the overall conformation of the compound. Clearly cyclometallation has occurred to give another example of the $\overline{MnC_2N_2}$ ring found for compound **4**. Here the ring

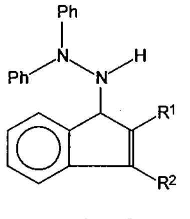


Scheme 1.

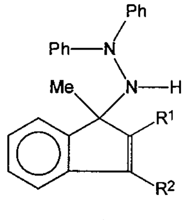
appears to be planar, with shorter Mn–N and N–N bonds than for **4**, but this may be an artifact of the imprecise determination so is not discussed further, other than to note that the same general features were found in the cyclopalladiated *N*-nitroso examples [51,52].

### 3.4. Reactions of orthomanganated hydrazones with alkynes

When the diphenylhydrazone complexes **3c** or **3d** were reacted with the alkynes $Ph_2C_2$ or $Me_3SiC_2H$ the indenyl hydrazines **7a–c** or **8a,b** were isolated in moderate yields after chromatography on alumina.



**7a** $R^1 = R^2 = Ph$
**7b** $R^1 = H, R^2 = SiMe_3$
**7c** $R^1 = SiMe_3, R^2 = H$



**8a** $R^1 = R^2 = Ph$
**8b** $R^1 = SiMe_3, R^2 = H$

Conditions used were reflux in acetonitrile for 2–5 h, since preliminary studies showed this solvent resulted in a cleaner reaction than benzene or heptane. At completion of the reaction, an infrared spectrum of the mixture showed $\nu$(CO) bands with a distinctive pattern associated with a *fac*-$LMn(CO)_3$ fragment. However this proved to be too unstable to characterise and work-up provided only metal-free products, with the indenyl hydrazines the only ones in significant amounts. Compounds **7** and **8** are the expected products by analogy with the reactions of orthomanganated aryl ketones with alkynes [9,54–56], and a similar mechanism can be proposed. The first step will be insertion of the alkyne into the Mn–C bond of the complex **3** to give a seven-membered ring species (**I**); related species have been characterised from the equivalent reactions with orthometallated triphenylphosphite [57] or triphenylphosphine sulphide [58]. The second step will be intra-molecular addition of the new Mn–C bond across the C=N group to form the indene core (**II**) with the Mn group associated as the unidentified $Mn(CO)_3$ species detected by IR. This species presumably achieves an 18-e configuration by coordination of MeCN solvent molecules, since removal of solvent led to decomposition; alternatively intramolecular coordination to electron density from the indene ring would be possible. Protio-demetallation on work-up would lead to the final highly-substituted hydrazine products **7** or **8** (Scheme 1).

In contrast, reactions of the mono-phenylhydrazone complexes **3a** or **3b** with alkynes did not lead to characterised products. Reaction did take place under similar conditions but work-up yielded a multitude of species in low yields and so they were not further investigated. Similarly, no major products were found with the cyclohexylidene complex **4**.

These preliminary investigations into the coupling reactions of the hydrazone complexes therefore show that there are some similarities with the established chemistry for analogous ketone complexes, but they appear to be less generally useful.

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