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Journal of Organometallic Chemistry 689 (2004) 4889–4896
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Regioselective cyclomanganation of Schiff bases. An unexpected effect of chloro substituents

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Received 12 May 2004; accepted 3 July 2004
Available online 11 November 2004

Abstract

In this paper we describe the synthesis of new metallacycles by the cyclomanganation reaction of benzyl-benzylidene-amines by using $[MnMe(CO)_5]$ as metallating agent. These ligands can undergo metallation on different aromatic carbon atoms but no important differences have been found in the regioselectivity of the process, that can be related to the electronic effect of the substituents, and in all the cases studied the *endo*-cyclomanganated complexes of *para*-substituted imines have been obtained. The corresponding *exo*-metallacycles were obtained by reaction of $[MnMe(CO)_5]$ on the imine 2,6-$Cl_2C_6H_3CH{=}NCH_2Ph$ and 2,4,6-$Me_3C_6H_2$-$CH{=}NCH_2Ph$, derived from 2,6-dichlorobenzaldehyde and 2,4,6-trimethylbenzaldehyde, respectively.

The results described suggest that the mechanism of the cyclomanganation is similar to that of cyclopalladation and it can be proposed that cyclomanganation takes place by the formation of a four-centered transition state, involving the C–H and Mn–C_{acetyl} bonds, in the acetyl coordination complex formed in the first step of the reaction.

Keywords: Imines; Manganese; Metallacycles; Metallation

1. Introduction

Cyclometallation reactions were one of the first known examples of C–H bond activation and cyclometallated complexes of a wide variety of ligands, containing N, P, As, O or S, as the heteroatom has been described [1]. The cyclopalladation of N-donor ligands has been extensively studied and it has acquired great interest because of the application of the metallacycles in many areas including organic synthesis, homogenous catalysis, the design of new metallomesogenes and antitumoral drugs [2]. In contrast less work has been reported on the cyclomanganation of N-donor ligands. Bruce et al. [3], in early reports, described the cyclomanganation of azobenzene, benzylideneaniline and benzylidenemethylamine and some studies on the cyclomanganation of different amines, imines, hydrazones and azines have been recently reported.

Some of these studies deal with the regioselectivity of the manganation reaction. Bruce et al. [3b] reported that cyclomanganation of azobenzenes takes place in the most electron-rich aromatic ring and they concluded that cyclomanganation reactions with $[MnR(CO)_5]$ occur by a nucleophilic attack of the metal complex. In contrast, a subsequent paper by Sales and coworkers described the impossibility of synthesising any cyclomanganated derivative with azines, containing nitro substituents, and they proposed that the cyclomanganation process takes place by an electrophilic attack of the

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doi:10.1016/j.jorganchem.2004.07.010

manganese compound on the ligand [3f]. Pfeffer et al. [3g] reported the cyclomanganation of tertiary amines and suggested that the manganese complex can react via a multicentered pathway. Finally, a more recent paper by Rourke et al. [3e,4] proposed that the first steps of the cyclomanganation reaction are the migration of the methyl group of the [$MnMe(CO)_5$] complex onto a carbonyl, generating a vacant coordination site, followed by the coordination of the ligand. These authors also propose a final nucleophilic attack by the manganese on the aromatic ring.

In this paper we describe the cyclomanganation reaction of benzyl-benzylidene-amines by using [$MnMe(CO)_5$] as metallating agent. These imines are particularly suitable ligands for the study of the regioselectivity of cyclometallation reactions, since they can undergo metallation on different aromatic carbon atoms.

2. Results and discussion

Scheme 1 shows the cyclomanganated compounds prepared in this work by reaction between benzyl-benzylidene-amines and [$MeMn(CO)_5$] in refluxing octane under an inert atmosphere. These imines can undergo metallation on different carbon atoms, giving organometallic complexes of different structures: *endo*-metallacycles, if the C=N bond is included in the metallacycle, or *exo*-derivatives (see Fig. 1). In addition, imines can exist in *E* or *Z* isomers, but in general, N-aldimines adopt the more stable *E* form [5]. *Endo*- or *exo*-metallacycles can be obtained from imines in *E*-form but *exo*-derivatives can only be formed from the *Z*-isomer.

Overall NMR data showed that with imines **1a**–**1e** only the *endo*-derivative was formed. This finding shows that, in the manganation reaction of imines, the so-called *endo* effect is more important than the electronic effect of substituents. In the case of **1d**, which presents two non-equivalent potential metallation sites (C^2 and C^6), only one isomer was obtained and proton NMR spectrum clearly shows that the metallation occurs in the less hindered C–H bond.

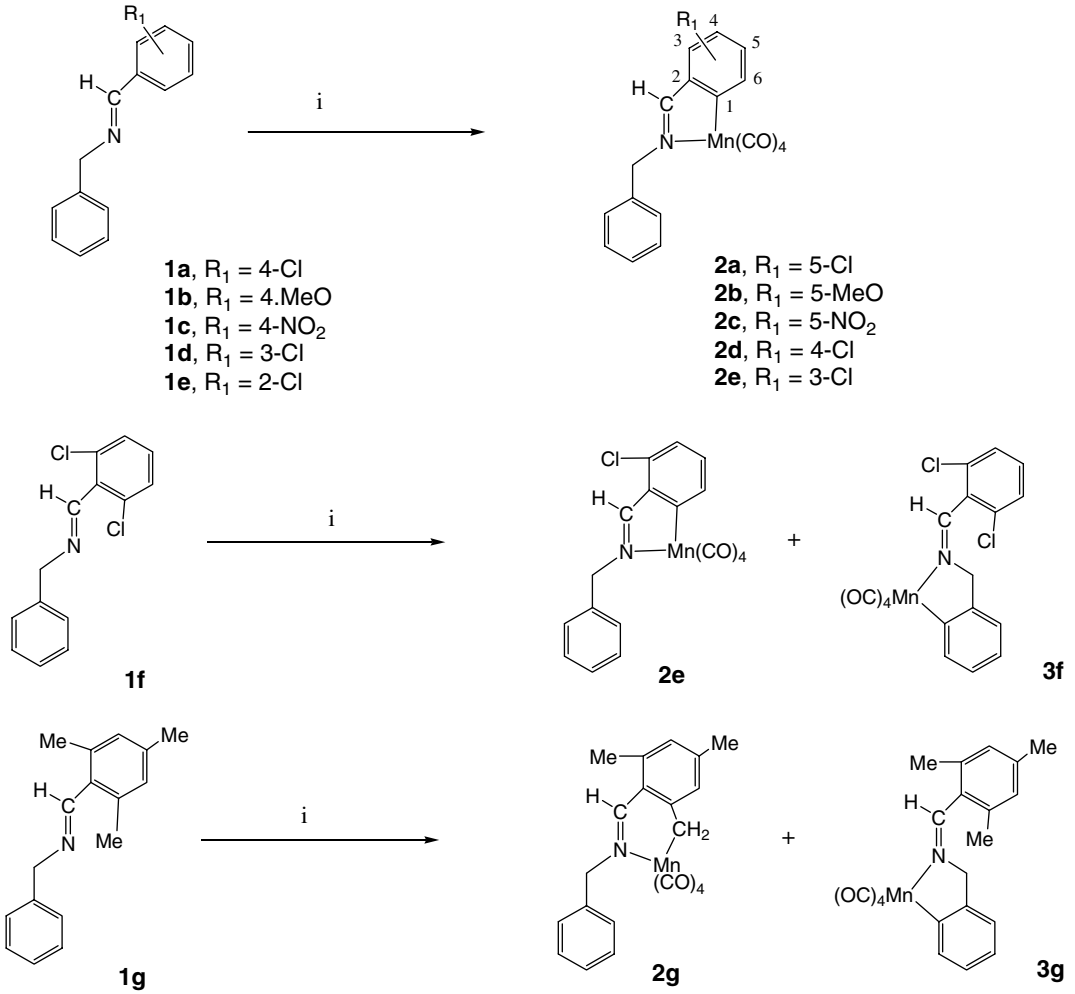
The *endo* effect has been reported for the cyclopalladation of imines [6] and for the oxidative addition of C–X bonds *ortho*-halosubstituted imines to Ni(0), Pd(0), Pt(II) and W(0) complexes [7]. It should be noted that in some cases the oxidative addition of C–F bonds (126 kcal/mol) or C–Cl bonds (96 kcal/mol) to form *endo*-metallacycles takes place in preference to the oxidative addition of C–Br bonds (81 kcal/mol) or C–I bonds (65 kcal/mol) to form *exo*-derivatives.

The aromaticity of the five-membered metallacycle, involving the two conjugated bonds C=C, C=N and the filled *d* orbital of the metal of appropriate symmetry has been proposed to explain the greater stability of *endo*-cyclic compounds [8] and the electrochemical properties of imine-platinum(II) compounds support the electronic delocalization within the metallated system [9]. Some kinetics studies on the cyclopalladation of imines have also been reported [10]. These studies suggest that the cyclopalladation of imines takes place via a first step, the formation of an imine-palladium coordination complex, followed by a second rate-determining step. The formation of a highly ordered transition state in which there is a four centered interaction between the carbon and hydrogen atoms of the C–H bond to be activated, the oxygen atom of the acetato leaving group and the metal explains the kinetic data. The planarity of the PhC=N fragment on the imines facilitates the formation of such intermediate with the *ortho* C–H bond of the methinic phenyl group.

It has been shown that *exo*-metallacycles can be obtained by cyclopalladation of imines if the *ortho* positions of the methinic phenyl ring (which leads to the formation of *endo*-metallacycles) are blocked by substituents such as chlorine atoms [11]. Following and expanding this strategy to prepare *exo*-cyclic imine cyclomanganated derivatives, the action of [$MnMe(CO)_5$] on the imines **1f** and **1g**, derived from 2,6-dichlorobenzaldehyde and 2,4,6-trimethylbenzaldehyde, was studied. When the reaction was performed with imine **1f** two cyclomanganated compounds, **2e** and **3f** were obtained in 1/1 ratio. NMR data showed that **3f** is the *exo*-derivative containing the imine in the *Z* form, obtained by activation of a $C_{aromatic}$–H bond. NMR data also showed that the *endo*-metallacycle **2e** (previously isolated from imine **1e** by activation of a $C_{aromatic}$–H bond) was also obtained, in this case by activation of the *ortho* C–Cl bond of the imine **1f**. The significant amount of compound **3f** formed is not compatible with a nucleophilic attack of Mn complex to C–X bonds, because it is well known that $C_{aromatic}$–Cl bonds are more labile in front to nucleophilic attack than $C_{aromatic}$–H bonds [12]. When the cyclomanganation reaction was performed with imine **1g** the *exo*-metallacycle **3g** was obtained, but the formation of the *endo*-complex **2g**, by activation of a $C_{aliphatic}$–H bond, was also observed. Compound **3g** was fully characterised but, in contrast **2g** is surprisingly unstable and good analytical data were not obtained for this compound.

All the new organometallic compounds obtained were characterised by elemental analysis, IR spectra, and ^1H NMR spectra. In some cases, 2D NMR experiments and positive FAB-mass spectra were carried out to complete the characterisation.

The IR spectra of the carbonyl region showed the expected four-band pattern for the cyclomanganated derivatives and the stretching frequencies can be related to the electronic effect of the substituents. For example the stretching frequencies of the carbonyls in the MeO compound **2b** are 8–10 cm^{-1} lower than those of the chloro substituted derivatives **2a**, **2d** and **2e**. This can



Scheme 1. i: $[MnMe(CO)_5]$, refluxing octane.

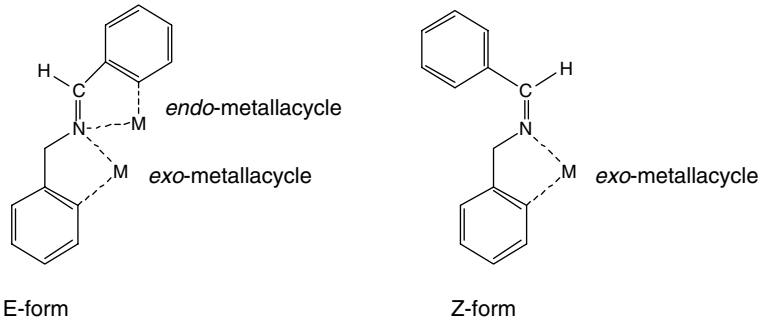


Fig. 1.

be explained in terms of the higher electron density present in the case of the more electron donating MeO group, that increases the back-bonding to carbonyls.

The FAB mass spectra of the manganated complexes showed the signals corresponding to the molecular peak and also exhibited the signals corresponding to ions arising from the usual stepwise loss of carbonyl groups.

The proton NMR spectra provided a conclusive evidence on the metallation position, and also on the *E*/*Z* configuration of the imine. The methinic proton signal in compounds **2a**–**2d** appeared at a δ value close to that of the methinic proton of the free imines, in agreement with an *E* configuration for this ligand. In contrast, this signal appeared shifted to low field in relation to free

imine in **3f** and **3g**. This downfield shift can be explained by the paramagnetic anisotropy of the metal [13] and suggests that the imine, in these compounds, adopt a *Z* configuration in which this proton is close to the metal atom, which minimises steric repulsions [11]. In addition, the coupling between CH_2N and HC=N protons confirms the *Z*-form of the imine in these compounds. For all the compounds containing a chlorine substituent in an *ortho* position on the aromatic ring (**1e**, **1f**, **2e** and **3f**) the HC=N proton resonance appeared at lower fields than for the non-substituted derivatives, indicating an intramolecular interaction between the atoms, as has been found for related palladium and platinum metallacycles [14].

Suitable crystals for the determination of the crystal structure of compound **3g** were grown in hexane solution, at room temperature, and their crystal structure has been determined (Fig. 2). Selected bond lengths and angles are listed in Table 1. The crystal structure is composed of discrete molecules separated by van der Waals distances. The manganese is coordinated in a distorted octahedral disposition and the bond lengths and angles are similar to others previously reported for cyclomanganated complexes [3g,3e]. The metallacycle presents an *exo*-configuration and the imine is in the *Z*-form.

In summary no important differences have been found in the manganation reaction of imines that can be related to the electronic effect of the substituents and in all the cases studied the *endo*-cyclomanganated complexes of *para*-substituted imines have been obtained with similar yields (30–45%), in good agreement with the results previously described for the cyclopalladation of these ligands. These results show that the planarity of the PhC=N fragment on the imines plays a key role on the regioselectivity of the process. This is the first time that it has been shown that the *endo* effect is important in cyclomanganation reactions.

It should be noted that imine **1e**, which contains a chloro substituent in the *ortho* position of the methinic phenyl group, is the only ligand that affords the cyclomanganated complex in high yield (70%). This result cannot be explained by the standard effect of the sustituents. It should be noted that the proton NMR spectrum of this imine shows the existence of an interaction between the *ortho* C–Cl bond and the methinic proton (see above). This CH···Cl interaction reinforces the planarity of the ArCH=N fragment and brings the C–H bond to be activated close to the metal in the intermediate coordination complex, thus making easy the metallation process. This effect have been recently proposed to explain the results obtained in the oxidative addition of C–Cl bonds of imines to $[Pt(dba)_2]$ [15].

All these results suggest that the mechanism of the cyclomanganation reactions can be similar to that of cyclopalladation and, in consequence, cyclomanganation takes place by the formation of a four-centered transition state, involving the C–H and Mn–C_{acetyl} bonds, in

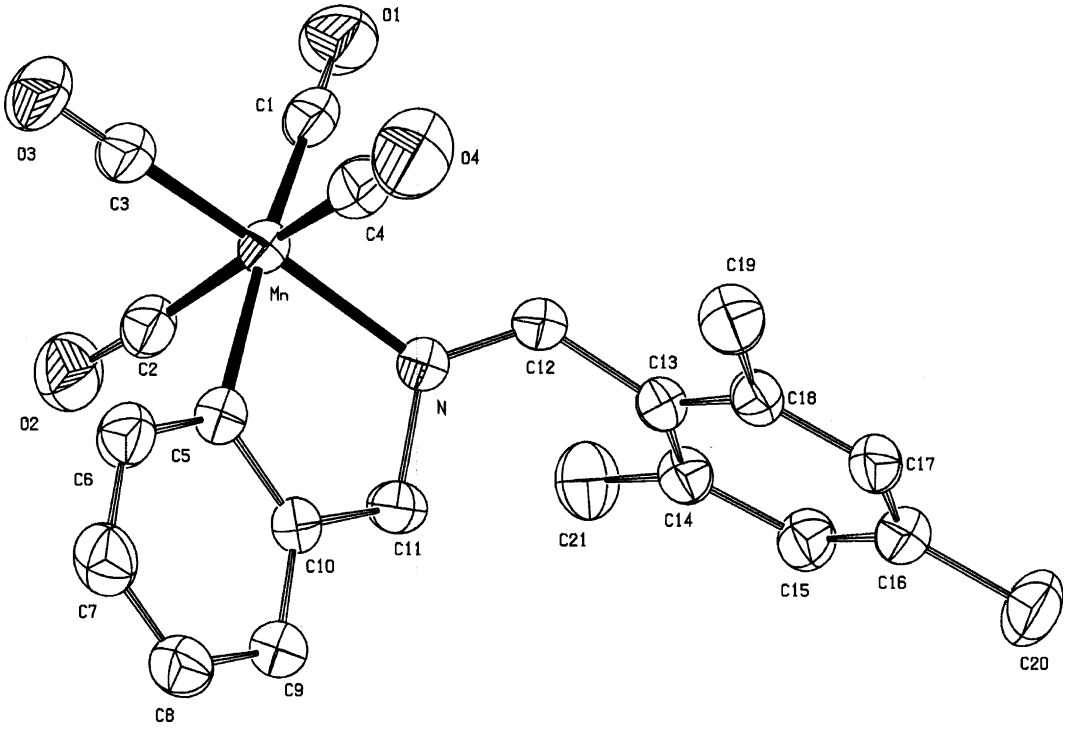


Fig. 2. Molecular structure of compound **3g**.

Table 1
Crystal data and structure refinement for **3g**

Empirical formula	$C_{21}H_{18}MnNO_4$
Formula weight	403.30
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
	$a = 7.0580(10)$ Å, $\alpha = 90°$
	$b = 12.4250(10)$ Å, $\beta = 94.480(10)°$
	$c = 22.0920(10)$ Å, $\gamma = 90°$
Volume (Å^3)	1931.5(3)
Z, calculated density (Mg/m^3)	4, 1.387
Absorption coefficient (mm^{-1})	0.709
F (000)	832
Crystal size (mm)	$0.1 \times 0.1 \times 0.2$
Theta range for data collection	3.22–31.78°
Limiting indices	$-9 \leqslant h \leqslant 0$, $-15 \leqslant k \leqslant 15$, $-32 \leqslant l \leqslant 32$
Reflections collected/unique	40734/3665 [$R_{(int)} = 0.0349$]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3665/0/316
Goodness-of-fit on F^2	1.108
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0502$, $wR_2 = 0.1314$
R indices (all data)	$R_1 = 0.0625$, $wR_2 = 0.1387$
Largest differential peak and hole (e Å^{-3})	0.295 and −0.298

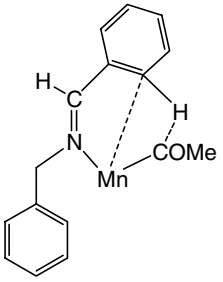


Fig. 3.

the acetyl coordination complex formed in the first step of the reaction (see Fig. 3).

3. Experimental

3.1. General

^{1}H NMR spectra at 200 MHz were recorded in a Varian Gemini 200 spectrometer. Chemical shifts (in ppm) were measured relative to $SiMe_4$. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the *Servei de Recursos Cientifics I Tècnics* (Universitat Rovira i Virgili). Infrared spectra were recorded with a Nicolet 520 FT-IR spectrometer using octane solutions. Mass spectra were recorded on a Fisons VG-Quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzyl-alcohol for FAB analysis and then bombarded with caesium atoms.

3.2. Materials and synthesis

All the reactions were carried out using Schlenk techniques under nitrogen atmosphere. All solvents were dried and degassed by standard methods. All chemicals were of commercial grade and used as received. $[MnMe(CO)_5]$ was prepared according to the procedure described elsewhere [16].

3.3. Synthesis of imines *1a–1f*

A mixture of benzylamine (243 mg, 2.26 mmol) and the corresponding aldehyde (2.26 mmol) was refluxed in ethanol for 3 h. The resulting solution was concentrated in vacuo and the oil obtained was characterised by IR and ^{1}H NMR spectra and was used without further purification.

^{1}H NMR (200 MHz, $CDCl_3$) data for **1a**: $\delta = 4.80$ (s, 2H, CH_2Ph); 7.29–7.39 (m, 5H, aromatic); 7.69 (d, 2H, JHH = 8.4 Hz, aromatic); 8.32 (s, 1H, CH=N).

^{1}H NMR (200 MHz, $CDCl_3$) data for **1b**: $\delta = 3.85$ (s, 3H, CH_3O); 4.79 (s, 2H, CH_2Ph); 6.93 (d, 2H, JHH = 8.2 Hz, aromatic); 7.31–7.35 (m, 5H, aromatic); 7.74 (d, 2H, JHH = 8.2 Hz, aromatic); 8.33 (s, 1H, CH=N).

^{1}H NMR (200 MHz, $CDCl_3$) data for **1c**: $\delta = 4.89$ (s, 2H, CH_2Ph); 7.32–7.38 (m, 5H, aromatic); 7.94 (d, 2H, JHH = 8.6 Hz, aromatic); 8.27 (d, 2H, JHH = 8.4 Hz, aromatic); 8.46 (s, 1H, CH=N).

^{1}H NMR (200 MHz, $CDCl_3$) data for **1d**: $\delta = 4.82$ (s, 2H, CH_2Ph); 7.28–7.38 (m, 6H, aromatic); 7.61 (d, 1H, JHH = 7.6 Hz, aromatic); 7.80 (s, 1H, aromatic); 8.32 (s, 1H, CH=N).

^{1}H NMR (200 MHz, $CDCl_3$) data for **1e**: $\delta = 4.86$ (s, 2H, CH_2Ph); 7.27–7.36 (m, 8H, aromatic); 8.09 (d, 2H, JHH = 8.0 Hz, aromatic); 8.84 (s, 1H, CH=N).

^{1}H NMR (200 MHz, $CDCl_3$) data for **1f**: $\delta = 4.93$ (s, 2H, CH_2Ph); 7.20–7.38 (m, 8H, aromatic); 8.56 (s, 1H, CH=N).

^{1}H NMR (200 MHz, $CDCl_3$) data for **1g**: $\delta = 2.26$ (s, 3H, Me); 2.40 (s, 6H, Me); 4.82 (s, 2H, CH_2Ph); 6.85 (s, 2H, aromatic); 7.27–7.36 (m, 5H, aromatic); 8.70 (s, 1H, CH=N).

3.4. Synthesis of *2a–2g*

Compound $[(CO)_4Mn(5\text{-}ClC_6H_3CH{=}NCH_2Ph)]$ (**2a**). Under an inert atmosphere, $[MeMn(CO)_5]$ (44.8 mg, 0.21 mmol) and ligand **1a** (48.2 mg, 0.21 mmol) were dissolved in octane (15 ml) and refluxed for 2 h. The

solution obtained was eluted by column chromatography over SiO_2, with hexane as eluent to obtain compound **2a** in 42% yield (36 mg).

Characterisation data for **2a**. Anal. (%) Calcd. for $C_{18}H_{11}ClNO_4Mn$: C: 54.64, H: 2.80, N: 3.54. Found: C, 54.4; H, 2.7; N, 3.5. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.91$ (s, 2H, CH_2Ph); 7.12 (dd, 1H, JHH = 8.2 Hz, JHH = 1.8 Hz, H^4); 7.23–7.27 (m H, aromatic); 7.36–7.41 (m, H, aromatic); 7.49 (d, 1H, JHH = 8.2 Hz, H^3); 7.90 (d, 1H, JHH = 1.8 Hz, H^6); 8.35 (s, 1H, CH=N). IR (cm^{-1}): ν(CO) 1949 m, 1986 m, 1999 s, 2079 w. FAB-MS, *m*/*z*: 395 [M], 368 [M–CO], 339 [M–2CO], 311 [M–3CO], 283 [M–4CO].

Compound $[(CO)_4Mn(5\text{-}MeOC_6H_3CH{=}NCH_2Ph)]$ (**2b**). Under an inert atmosphere, $[MeMn(CO)_5]$ (43 mg, 0.20 mmol) and ligand **1b** (46 mg, 0.20 mmol) were dissolved in octane (15 ml) and refluxed for 90 min. The solution obtained was eluted by column chromatography over SiO_2, with hexane–dichloromethane (5–1) as eluent to obtain compound **2b** in 38% yield (30 mg).

Characterisation data for **2b**. Anal. (%) Calcd. for $C_{19}H_{14}NO_5Mn$: C: 58.33, H: 3.61, N: 3.51. Found: C, 58.4; H, 3.6; N, 3.5. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.89$ (s, 3H, MeO); 4.85 (s, 2H, CH_2Ph); 6.65 (dd, 1H, JHH = 8.2 Hz, JHH = 2.3 Hz, H^4); 7.24–7.28 (m, 2H, aromatic); 7.34–7.39 (m, 3H, aromatic); 7.49 (d, 1H, JHH = 2.3 Hz, H^6); 7.53 (d, 1H, JHH = 8.2 Hz, H^3); 8.28 (s, 1H, CH=N). IR (cm^{-1}): ν(CO) 1941 m, 1981 m, 1992 s, 2079 w. FAB-MS, *m*/*z*: 391 [M], 364 [M–CO], 335 [M–2CO], 307 [M–3CO], 279 [M–4CO].

Compound $[(CO)_4Mn(5\text{-}NO_2C_6H_3CH{=}NCH_2Ph)]$ (**2c**). Under an inert atmosphere, $[MeMn(CO)_5]$ (32.8 mg, 0.15 mmol) and ligand **1c** (37.5 mg, 0.15 mmol) were dissolved in octane (15 ml) and refluxed for 3 h. The solution obtained was eluted by column chromatography over SiO_2, with hexane–dichloromethane (5–3) as eluent to obtain compound **2c** in 30% yield (19 mg).

Characterisation data for **2c**. Anal. (%) Calcd. for $C_{18}H_{11}N_2O_6Mn$: C: 53.22, H: 2.73, N: 6.90. Found: C, 53.0; H, 2.5; N, 6.7. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.99$ (s, 2H, CH_2Ph); 7.27–7.29 (m, 2H, aromatic); 7.41–7.48 (m, 3H, aromatic); 7.69 (d, 1H, JHH = 8.2 Hz, H^3); 7.97 (dd, 1H, JHH = 2.0 Hz, JHH = 8.2 Hz, H^4); 8.49 (s, 1H, CH=N); 8.74 (d, 1H, JHH = 2.0 Hz, H^6). IR (cm^{-1}): ν(CO) 1954 m, 1991 m, 1999 s, 2081 w. FAB-MS, *m*/*z*: 407 [M], 379 [M–CO], 351 [M–2CO], 323 [M–3CO], 295 [M–4CO].

Compound $[(CO)_4Mn(4\text{-}ClC_6H_3CH{=}NCH_2Ph)]$ (**2d**). Under an inert atmosphere, $[MeMn(CO)_5]$ (27.4 mg, 0.13 mmol) and ligand **1d** (30 mg, 0.13 mmol) were dissolved in octane (15 ml) and refluxed for 90 min. The solution obtained was eluted by column chromatography over SiO_2, with hexane–dichloromethane (5–0.7) as eluent to obtain compound **2d** in 45% yield (24 mg).

Characterisation data for **2d**. Anal. (%) Calcd. for $C_{18}H_{11}ClNO_4Mn$: C: 54.64, H: 2.80, N: 3.54. Found: C, 56.6; H, 3.0; N, 3.3. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.91$ (s, 2H, CH_2Ph); 7.22–7.26 (m, 3H, aromatic); 7.37–7.40 (m, 3H, aromatic); 7.55 (d, 1H, JHH = 2.0 Hz, H^3); 7.85 (d, 1H, JHH = 7.8 Hz, H^6); 8.34 (s, 1H, CH=N). IR (cm^{-1}): ν(CO) 1946 m, 1985 m, 1997 s, 2078 w. FAB-MS, *m*/*z*: 395 [M], 368 [M–CO], 339 [M–2CO], 311 [M–3CO], 283 [M–4CO].

Compound $[(CO)_4Mn(3\text{-}ClC_6H_3CH{=}NCH_2Ph)]$ (**2e**). Under an inert atmosphere, $[MeMn(CO)_5]$ (27.4 mg, 0.13 mmol) and ligand **1e** (30 mg, 0.13 mmol) were dissolved in octane (15 ml) and refluxed for 1 h. The solvent was removed under vacuum and the solid obtained was eluted by column chromatography over SiO_2, with hexane–dichloromethane (5–0.5) as eluent to obtain compound **2e** in 70% yield (31 mg).

Characterisation data for **2e**. Anal. (%) Calcd. for $C_{18}H_{11}ClNO_4Mn$: C: 54.65, H: 2.80, N: 3.54. Found: C, 54.6; H, 3.0; N, 3.3. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.92$ (s, 2H, CH_2Ph); 7.05 (d, 1H, JHH = 7.9 Hz, H^4); 7.17 (t, 1H, JHH = 7.8, H^5); 7.27–7.31 (m, 2H, aromatic); 7.36–7.44 (m, 3H, aromatic); 7.79 (d, 1H, JHH = 7.2 Hz, H^6); 8.78 (s, 1H, CH=N). IR (cm^{-1}): ν(CO) 1946 m, 1984 m, 1997 s, 2077 w. FAB-MS, *m*/*z*: 395 [M], 368 [M–CO], 339 [M–2CO], 311 [M–3CO], 283 [M–4CO].

Metallation of $2,6\text{-}Cl_2C_6H_3CH{=}NCH_2Ph$. Under an inert atmosphere, $[MeMn(CO)_5]$ (44.8 mg, 0.21 mmol) and ligand **1f** (56.3 mg, 0.21 mmol) were dissolved in octane (15 ml) and refluxed for 2 h. The solution obtained was eluted by column chromatography over SiO_2, with hexane–dichloromethane (5–0.5) as eluent to obtain compound **2e** in the first eluted band and **3f** in the second band in 12% yield in both cases (10 and 11 mg, respectively).

Characterisation data for **3f**. Anal. (%) Calcd. for $C_{18}H_{10}Cl_2NO_4Mn$: C: 50.26, H: 2.34, N: 3.20. Found: C, 50.4; H, 2.4; N, 3.0. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.62$ (d, JHH = 2.6 Hz, 2H, CH_2Ph); 6.89 (d, 1H, JHH = 7.4 Hz, aromatic); 7.00 (t, 1H, JHH = 7.0 aromatic); 7.13 (t, 1H, JHH = 7.2 Hz, aromatic); 7.42 (m, 3H, aromatic); 7.75 (d, 1H, JHH = 7.4 Hz, aromatic); 8.86 (t, JHH = 2.6 Hz 1H, CH=N). IR (cm^{-1}): ν(CO) 1942 m, 1979 m, 1991 s, 2072 w.

Metallation of $2,4,6\text{-}Me_3C_6H_2CH{=}NCH_2Ph$. Under an inert atmosphere, $[MeMn(CO)_5]$ (31.5 mg, 0.15 mmol) and ligand **1g** (34.5 mg, 0.15 mmol) were dissolved in octane (15 ml) and refluxed for 2 h. The solution obtained was eluted by column chromatography over SiO_2, with hexane–dichloromethane (5–2) as eluent to obtain compound **2g** in the first eluted band (12 mg, 20% yield) and **3g** in the second band in 22% yield (14 mg).

Characterisation data for **3g**. Anal. (%) Calcd. for $C_{21}H_{18}NO_4Mn$: C: 62.54, H: 4.50, N: 3.53. Found: C,

Table 2
Selected bond lengths [Å] and angles [°] for **3g**

Mn–C(3)	1.801(3)
Mn–C(1)	1.830(3)
Mn–C(2)	1.843(3)
Mn–C(4)	1.845(3)
Mn–N	2.062(2)
Mn–C(5)	2.069(3)
O(1)–C(1)	1.141(4)
O(2)–C(2)	1.131(4)
O(3)–C(3)	1.137(4)
O(4)–C(4)	1.134(4)
N–C(12)	1.271(3)
N–C(11)	1.473(3)
C(5)–C(6)	1.380(4)
C(5)–C(10)	1.393(4)
C(6)–C(7)	1.393(5)
C(7)–C(8)	1.367(5)
C(8)–C(9)	1.385(4)
C(9)–C(10)	1.388(4)
C(10)–C(11)	1.501(4)
C(3)–Mn–C(1)	93.53(13)
C(3)–Mn–C(2)	87.77(13)
C(1)–Mn–C(2)	93.12(14)
C(3)–Mn–C(4)	87.78(14)
C(1)–Mn–C(4)	98.56(15)
C(2)–Mn–C(4)	167.74(14)
C(3)–Mn–N	173.19(12)
C(1)–Mn–N	92.42(11)
C(2)–Mn–N	95.21(11)
C(4)–Mn–N	88.07(12)
C(3)–Mn–C(5)	94.62(12)
C(1)–Mn–C(5)	170.07(12)
C(2)–Mn–C(5)	81.54(12)
C(4)–Mn–C(5)	87.44(13)
N–Mn–C(5)	79.81(10)
C(12)–N–C(11)	119.6(2)
C(12)–N–Mn	126.47(17)
C(11)–N–Mn	113.32(17)
O(1)–C(1)–Mn	177.1(3)
O(2)–C(2)–Mn	174.0(3)
O(3)–C(3)–Mn	179.1(3)
O(4)–C(4)–Mn	176.1(3)
C(6)–C(5)–C(10)	116.7(3)
N–C(11)–C(10)	108.3(2)
N–C(12)–C(13)	128.7(2)

62.5; H, 4.9; N, 3.5. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.13 (s, 6H, Me); 2.32 (s, 3H, Me); 4.45 (s, 2H, CH_2Ph); 6.86 (d, 1H, JHH = 7.5 H^6); 6.92 (s, 2H, aromatic); 6.98 (t, 1H, JHH = 7.5 H^5); 7.12 (t, 1H, JHH = 7.2 H^4); 7.74 (d, 1H, JHH = 7.2 H^3); 8.99 (s, 1H, CH=N). IR (cm^{-1}): *v*(CO) 1935 m, 1985 s, 2069 w. FAB-MS, *m/z*: 402 [M], 376 [M–CO], 347 [M–2CO], 319 [M–3CO], 292 [M–4CO].

Characterisation data for **2g**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.06 (s, 2H, CH_2Mn); 2.13 (s, 3H, Me); 2.25 (s, 3H, Me); 4.86 (s, 2H, CH_2Ph); 6.58 (s, 1H, aromatic); 6.91 (s, 1H, aromatic); 7.28–7.39 (m, 5H, aromatic); 8.35 (s, 1H, CH=N). IR (cm^{-1}): *v*(CO) 1927 m, 1969 m, 1979 s, 2063 w.

3.5. X-ray crystallography

The crystal data, data collection and refinement parameters for the X-ray structures are listed in Table 2. Data were collected in MAR345 diffractometer with a image plate detector. Unit-cell parameters were determined from 16,264 reflections ($3.22° < \theta < 31.78°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation. 40,734 reflections were measured in the range $3.22° < \theta < 31.78°$). 3665 of which were non-equivalent by symmetry {R_{int} (on I) = 0.034}. 3114 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Lorentz-polarization but not absorption corrections were made.

The structure was solved by Direct methods, using SHELXS computer program [17] and refined by full-matrix least-squares method. The function minimised was $\sum w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0636P)^2 + 1.0799P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f′ and f″ were taken from International Tables of X-Ray Crystallography [18]. All H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor.

4. Supplementary material

Crystallographic data for **3g** have been deposited with the Cambridge Crystallographic data Centre as supplementary publication number: CCCD 238164. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Ministerio de Ciencia y Tecnología and ERDF, European Regional Development Found, (project: BQU2003-00906) and by the Comissionat per a Universitats i Recerca (project: 2001SGR-00054).

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