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Coupling reactions of manganese(I) cyclometallated compounds derived from heterocyclic N-donor ligands with alkynes

Antonio Suárez[a,*], Fernanda Faraldo[a], José M. Vila[b], Harry Adams[c], Alberto Fernández[a], Margarita López-Torres[a], Jesús J. Fernández[a]

[a] *Departamento de Química Fundamental, Universidad de A Coruña, 15071 A Coruña, Spain*
[b] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[c] *Department of Chemistry, The University, Sheffield S3 7HF, UK*

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Abstract

The reaction of PhC≡CPh with cyclomanganated compounds derived from substituted phenylimidazoles gave the seven-membered metallacycles [Mn{2-(CPh=CPh)C_6H_4C=NCH=CHN(Me)}$(CO)_4$] (**1**) and [Mn{2-(CPh=CPh)C_6H_4CN=CHN(Me)C(Ph)}$(CO)_4$] (**2**), with insertion of the alkyne into the Mn–C bond. When an unsymmetrical alkyne such as MeC≡CPh was used, the reaction was not regiospecific and two different isomers were obtained, which could be separated by fractional crystallization, e.g. [Mn{2-(CMe=CPh)C_6H_4CN=CHN(Me)–C(Ph)}$(CO)_4$] (**5**) and [Mn{2-(CPh=CMe)C_6H_4CN=CHN(Me)C(Ph)}$(CO)_4$] (**6**). The compounds were characterized by analytical and spectroscopic techniques, and in the case of **5**, by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Cyclometallation; Nitrogen heterocycles; Insertion; Alkynes

1. Introduction

The metal–carbon bond in cyclometallated compounds, formed upon C–H activation of an organic ligand by transition metals, is fairly reactive towards insertion of unsaturated species. Most of the work previously reported concerns cyclopalladated complexes, and many examples of such compounds have been described as intermediates to novel organometallic and organic compounds [1–3]. Although few examples with other transition metals have been reported, interest in cylomanganated compounds has increased in the past years; however, much of the research is related to chalcogen-donor ligands, especially those with O-donor atoms [4–6].

Alkylmanganese pentacarbonyl complexes react regioselectively with alkynes or alkenes to produce acyl-coordinated manganese complexes [7], but coupling reactions of alkynes with cyclomanganated compounds usually afford demetallation products. Although a reasonable reaction mechanism may be proposed: initial η^2-coordination of the alkyne to the metal center by displacement of a carbonyl group, and subsequent intramolecular insertion into the Mn–C bond, none of the suggested intermediates have been detected, and evidence of their formation is supported by the corresponding final species. Moreover, intermediate metallacycles were initially isolated only in poor yields when *ortho*-manganated triphenylphosphite reacted with phenylacetylene and diphenylacetylene under UV irradiation [8], and only recently has insertion of alkynes into the Mn–C bond been accomplished [9,10]. However, little attention has been directed towards the chemistry of the related cyclomanganated species derived from N-donor ligands, more so when the donor atom is part of an heterocycle [11], and which should nevertheless display a similar behavior. We sought out to develop this chemistry, and in the present communication we report the synthesis, characterization and X-ray crystal structure analysis of a novel Mn(I) *ortho*-metallated insertion compound derived from a substituted phenylimidazole.

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* Corresponding author. Fax: +34-981-167065
E-mail address: lujjfs@udc.es (A. Suárez).

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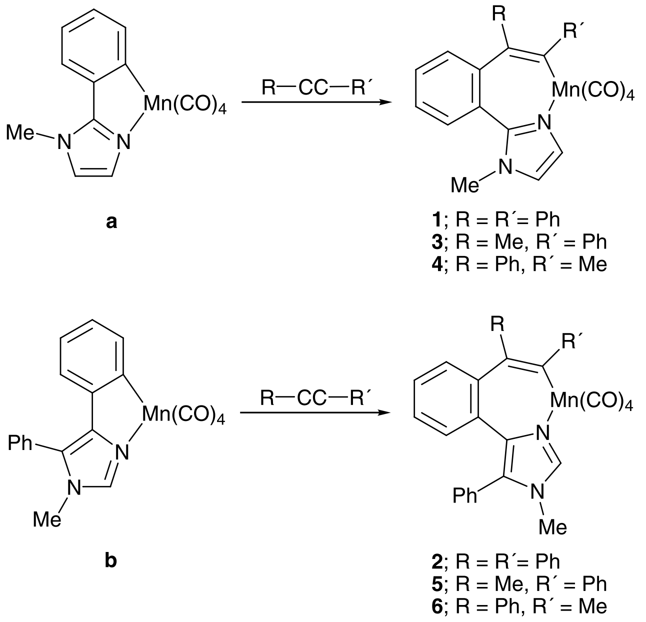
2. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. Benzylpentacarbonylmanganese has proved to be the most efficient starting material in numerous cyclometallation reactions. Treatment of 1-methyl-2-phenylimidazole and 1-methyl-4,5-diphenylimidazole with the manganese(I) complex yielded the corresponding cyclomanganated compounds **a** and **b** [12].

Reaction of **a** or **b** with diphenylacetylene in boiling toluene under argon afforded the seven-membered metallacycle products **1** and **2**, respectively, by insertion of the alkyne into the Mn–C bond, in very good yields (77 and 72%, respectively). The obtained products were air-stable solids and although soluble in common organic solvents decomposed slowly in solution. All the new products gave satisfactory elemental analyses, and IR spectra. Four ν(CO) stretching bands, at 2065–1920 cm^{-1}, were consistent with a $Mn(CO)_4$ unit [13].

Similarly, reaction of **a** or **b** with 1-phenyl-1-propyne gave the isomeric insertion products **3**, **4** (yield 74%), and **5**, **6** (yield 82%), respectively (see Scheme 1). The relative ratios of the isomer species are ca. 1:1 in each case as calculated from the integrals in the ^{1}H-NMR spectrum. Cyclometallation and insertion were confirmed by ^{1}H-NMR and IR spectroscopy. The major feature in the ^{1}H-NMR spectra were two singlets at δ 1.96, δ 1.81 (**3**, **4**) and δ 1.87, δ 1.61 (**5**, **6**) assigned to the alkyne methyl group, which confirmed that the reaction was not regiospecific, in contrast with normal coupling reactions where the major product is the isomer with the bulkier substituent of the inserted product nearest to the metallated ring [14]. The presence of two doublets assigned to the NMe proton resonance in each ^{1}H-NMR spectrum (δ 3.67 and 3.37 for **3**–**4**; δ 3.67 and 3.62 for **5**–**6**) confirmed the existence of two different products. Successful separation of both isomers was achieved by fractional crystallization, albeit only suitable crystals could be grown for **5**. The corresponding ^{1}H-NMR resonance could be unambiguously assigned (Section 3).



Scheme 1.

Other unsaturated derivatives were tested in similar insertion reactions, such as methyl propiolate or 1-butyne, but a untreatable oily mixture was obtained, and no compound could be characterized even when the reaction was performed in the presence of trimethylamine N-oxide.

2.1. Molecular structure of compound 5

Suitable crystals of **5** were grown from a toluene–*n*-hexane solution. The labeling scheme for the complex is shown in Fig. 1. The crystal consists of discrete molecules, separated by normal van der Waals distances. Crystallographic data and selected interatomic distances and angles are listed in Tables 1 and 2. The X-ray crystal structure analysis confirms the product to be the isomer with the alkyne phenyl group attached to the carbon atom bonded to manganese. The manganese atom shows a distorted octahedral geometry and is bonded to four terminal carbonyl groups and to the chelating C, N-ligand.

The seven-membered metallacycle ring in **5** adopts a boat conformation, defined by three planes: (1) C(6)–C(14)–C(15)–C(20) (mean deviation 0.38°), (2) N(2)–C(6)–C(20)–C(21) (mean deviation 3.60°), and (3)

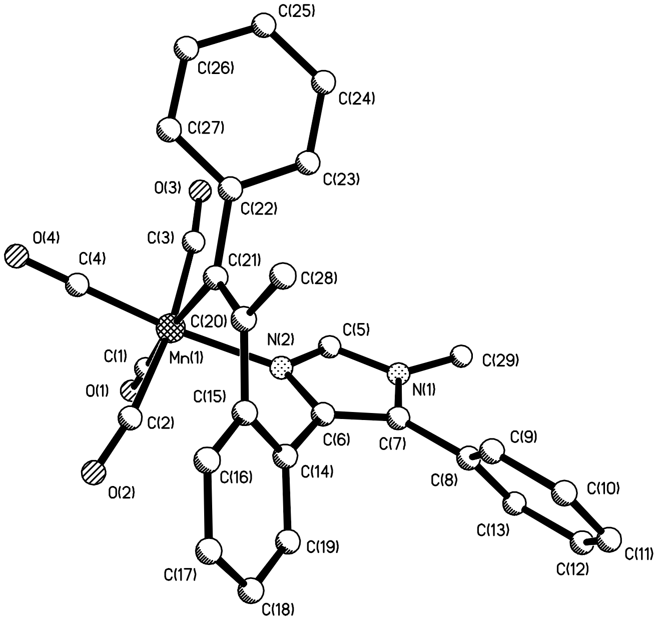


Fig. 1. Crystal structure of complex **5** (hydrogen atoms were omitted for clarity).

Table 1
Crystal and structure refinement data for **5**

Empirical formula	$C_{29}H_{21}MnN_2O_4$
Formula weight	516.42
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.034(2)
b (Å)	23.559(5)
c (Å)	13.519(3
β (°)	98.70(2)
V (Å^3)	2529.3(10)
Z	4
D_{calc} (Mg m^{-3})	1.356
Absorption coefficient (mm^{-1})	0.559
Crystal size (mm)	0.64 × 0.44 × 0.34
θ Range for data collection (°)	1.75–22.50
Index ranges	$-1 < h < 8$, $-1 < k < 25$, $-14 < l < 14$
Reflections collected	4392
Independent reflections	3311 ($R_{int} = 0.0320$)
Data/restraints/parameters	3311/0/325
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0419$, $wR_2 = 0.1048$
R indices (all data)	$R_1 = 0.0572$, $wR_2 = 0.1148$
Largest difference peak and hole (e Å^{-3})	0.238 and −0.203

Table 2
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths (Å)		Bond angles (°)	
Mn(1)–C(1)	1.831(4)	C(1)–Mn(1)–C(2)	88.4(2)
Mn(1)–C(2)	1.867(4)	C(1)–Mn(1)–C(3)	87.6(2)
Mn(1)–C(3)	1.845(4)	C(2)–Mn(1)–C(21)	94.09(14)
Mn(1)–C(4)	1.803(4)	C(3)–Mn(1)–C(21)	90.69(14)
Mn(1)–N(2)	2.061(3)	C(4)–Mn(1)–C(21)	88.53(14)
Mn(1)–C(21)	2.115(3)	N(2)–Mn(1)–C(21)	81.33(11)
N(2)–C(6)	1.395(4)	C(6)–N(2)–Mn(1)	126.5(2)
C(6)–C(14)	1.478(4)	N(2)–C(6)–C(14)	122.2(3)
C(14)–C(15)	1.416(4)	C(15)–C(14)–C(6)	121.6(3)
C(15)–C(20)	1.492(5)	C(14)–C(15)–C(20)	121.0(3)
C(20)–C(21)	1.350(4)	C(21)–C(20)–C(15)	123.4(3)
O(1)–C(1)	1.150(4)	C(20)–C(21)–Mn(1)	125.8(2)
O(2)–C(2)	1.144(4)	C(20)–C(21)–C(22)	118.2(3)
O(3)–C(3)	1.153(4)	C(21)–C(20)–C(28)	123.6(3)
O(4)–C(4)	1.150(4)		

C(21)–Mn–N(2). The dihedral angle between planes 1 and 2 is 46.3°, while that between planes 2 and 3 is 44.9°. There is no indication of strain in the metallacycle ring, which shows normal bond lengths and angles. The C(20)–C(21) distance, 1.350(4) Å, is in agreement with the value for a C=C double bond, while the Mn–C(21) distance of 2.115(3) Å is in accordance with similar Mn–C(sp^2) bonds reported earlier [7,15].

The Mn–CO bond lengths and C–Mn–C bond angles of the $Mn(CO)_4$ moiety show values close to those found in other *ortho*-manganated complexes; however, the Mn–CO bond length *trans* to the imidazole nitrogen, Mn(1)–C(4), is shorter than expected (1.803(4) A vs. 1.83–1.87 Å in the other Mn–CO distances), which arises from the relative π-bonding properties of the coordinated complexes [16]. The Mn–N bond length, 2.061(3) Å, is shorter than the single bond value of 2.09 Å calculated from the covalent radii of N(sp^2), 0.70 Å, and manganese, 1.39 Å [15].

In conclusion, the present work describes the synthesis and isolation of new tetracarbonyl Mn(I) complexes derived from differently substituted imidazoles via coupling reactions with alkynes.

3. Experimental

3.1. General remarks

All manipulations were performed under prepurified argon using standard Schlenk techniques. All solvents were distilled prior to use from appropriate drying agents [17]. $PhCH_2Mn(CO)_5$ was prepared according to procedures described elsewhere [18]. All other chemicals were used as supplied from commercial sources. ^{1}H-NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$, and were recorded on a Bruker AC-200F spectrometer (200.0 MHz for ^{1}H). IR spectra were recorded as chloroform solutions or Nujol mulls on a Perkin–Elmer 1330 spectrophotometer. The synthesis of [Mn{C_6H_4C=NCH=CHN(Me)}$(CO)_4$] (**a**) and [Mn{C_6H_4CN=CHN(Me)C(Ph)}$(CO)_4$] (**b**) was reported in a previous paper from this laboratory [12].

3.2. Preparation of the insertion compounds

3.2.1. [Mn{2-(CPh=CPh)C_6H_4C=NCH=CHN(Me)}$(CO)_4$] (*1*)

To a solution of **a** (130 mg, 0.40 mmol) in dry toluene (ca. 15 cm^3), diphenylacetylene (0.79 mg, 0.79 mmol) was added, and the mixture refluxed under argon for 4 h. After cooling to room temperature (r.t.) and concentrating to low volume under reduced pressure, *n*-hexane was added to precipitate the required product, which was obtained as yellow microcrystals. Yield: 162 mg, 77%. Anal. Found: C, 67.0; H, 4.0; N, 5.1. $C_{27}H_{19}N_2O_4Mn$ requires: C, 66.8; H, 4.0; N, 5.0%. IR: ν(C=O): 2065s, 1979s, 1966s, 1929s. ^{1}H-NMR: 3.81 (s, 3H, NMe). M.p.: 156 °C.

A similar method was used for the preparation of **2**–**6**.

3.2.2. [Mn{2-(CPh=CPh)C_6H_4CN=CHN(Me)C(Ph)}$(CO)_4$] (*2*)

Yield: 72%. Anal. Found: C, 69.7; H, 3.7; N, 4.7. $C_{33}H_{23}N_2O_4Mn$ requires: C, 70.5; H, 3.9; N, 4.8%. IR:

ν(C=O): 2061s, 1976s, 1962s, 1920s. ^{1}H-NMR: 3.50 (s, 3H, NMe). M.p.: 179 °C.

3.2.3. *[Mn{2-(CMe=CPh)C_6H_4C=NCH=CHN(Me)}$(CO)_4$] (**3**), [Mn{2-(CPh=CMe)C_6H_4C=NCH=CHN(Me)}$(CO)_4$] (**4**)*

A reaction time of 8 h was used. The final residue gave a mixture of **3** and **4** in a 1:1 molar ratio as calculated from the integrals in the ^{1}H-NMR spectra. Both compounds could be obtained from the mixture in pure form by fractional recrystallization. The mixture was dissolved in chloroform (ca. 15 cm^3), filtered, *n*-hexane carefully added and the resultant solution kept at −15 °C for 24 h. Yellow crystals of **3** were formed. The chloroform–*n*-hexane solution was evaporated to dryness giving **4** as a yellow solid. Overall yield: 74%. **3**: Anal. Found: C, 62.4; H, 3.6; N, 6.5. $C_{22}H_{17}N_2O_4Mn$ requires: C, 62.7; H, 3.8; N, 6.3%. IR: ν(C=O): 2060s, 1990s, 1968s, 1921s. ^{1}H-NMR: 3.37 (s, 3H, NMe), 1.81 (s, 3H, CMe). M.p.: 172 °C. **4**: Anal. Found: C, 62.3; H, 3.6; N, 6.6. $C_{22}H_{17}N_2O_4Mn$ requires: C, 62.7; H, 3.8; N, 6.3%. IR: ν(C=O): 2060s, 1985s, 1965s, 1928s. ^{1}H-NMR: 3.68 (s, 3H, NMe), 1.96 (s, 3H, CMe). M.p.: 176 °C.

3.2.4. *[Mn{2-(CMe=CPh)C_6H_4CN=CHN(Me)C(Ph)}$(CO)_4$] (**5**), [Mn{2-(CPh=CMe)C_6H_4CN=CHN(Me)C(Ph)}$(CO)_4$] (**6**)*

Overall yield: 82%. **5**: Anal. Found: C, 67.1; H, 3.8; N, 5.5. $C_{28}H_{21}N_2O_4Mn$ requires: C, 67.4; H, 4.1; N, 5.4%. IR: ν(C=O): 2079s, 1984s, 1972s, 1930s. ^{1}H-NMR: 3.67 (s, 3H, NMe), 1.61 (s, 3H, CMe). M.p.: 176 °C. **6**: Anal. Found: C, 67.2; H, 4.0; N, 5.3. $C_{28}H_{21}N_2O_4Mn$ requires: C, 67.4; H, 4.1; N, 5.4%. IR: ν(C=O): 2065s, 1980s, 1965s, 1935s. ^{1}H-NMR: 3.62 (s, 3H, NMe), 1.87 (s, 3H, CMe). M.p.: 179 °C.

3.3. *X-ray structure determination*

For complex **5** three-dimensional, r.t. X-ray data were collected in the range $3.5 < 2\theta < 45.0°$ on a Siemens P4 diffractometer by the omega scan method. 4392 reflections were measured, all of which were corrected for Lorentz and polarisation effects. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0419$ ($wR_2 = 0.1148$ for all 3331 unique data, 325 parameters, mean and maximum δ/σ 0.000, 0.001), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.238 and 1.203 e Å^{-3}. Complex scattering factors were taken from the program package SHELXL93 [19].

4. Supporting information available

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 177060 for compound **5**. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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