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Cyclometallated compounds of manganese(I) with 1-methylphenylimidazoles

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Abstract

Cyclometallated complexes of magnanese(I) with 1-methylphenylimidazoles have been prepared. IR and ^{1}H NMR spectroscopic studies show they are octahedral complexes in which the imidazole ligand is bound to the metal through the nitrogen and phenyl C(6) atoms. When the imidazole ligand with two phenyl groups at the C(2′) and C(4′) atoms is used, both possible cyclometallated compounds are obtained.

Introduction

Cyclometallation reactions with aromatic heterocycles have been widely studied [1], but those involving phenylimidazoles have received little attention [2–4]. The present paper describes the preparation and structural characterization of cyclometallated compounds of manganese(I) with six different phenylimidazoles.

Experimental

Solvents were dried and degassed by standard methods. Elemental analyses were carried out with a Perkin–Elmer Elemental Analyzer 240-B. IR spectra were run as cyclohexane solutions or as Nujol mulls between cesium iodide plates in a Perkin–Elmer 180 spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker WM 250 spectrometer with $Si(CH_3)_4$ as internal standard.

Synthesis of the compounds

$MeMn(CO)_5$ [5] and 2,4-diphenylimidazole [6,7] were prepared as previously described. 1-methyl-2,4-diphenylimidazole was made by treating a solution of

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Table 1

Analytical data, melting points and some IR absorptions for the complexes

Complex	M.p. [a] (°C)	Analysis (Found (calcd.) (%))			IR: ν(CO)(cm^{-1}) [b]
		C	H	N	
Ia	151–153	52.2	3.1	8.8	2080vs, 1989vs, 1977vs, 1937vs
		(51.9)	(2.8)	(8.6)	
IIb	160–162	51.9	2.8	8.4	2078m, 1993vs, 1978vs, 1937vs
		(51.9)	(2.8)	(8.6)	
IIIa, IIIb	160–162	61.0	3.2	6.7	2078m, 1992vs, 1985vs, 1943vs
		(60.0)	(3.3)	(7.0)	
IVa	172–174	60.1	3.3	6.8	2078m, 1987vs, 1982vs, 1942vs
		(60.0)	(3.3)	(7.0)	
Vb	164–166	59.9	3.3	6.6	2078s, 1988vs, 1975vs, 1932vs
		(60.0)	(3.3)	(7.0)	
VIa, VIb	166–168	65.5	3.5	5.9	2077m, 2070m, 1986vs, 1977vs, 1938vs
		(65.4)	(3.6)	(5.9)	

[a] With decomposition. [b] In cyclohexane solutions; vs, very strong; s, strong; m, medium.

2,4-diphenylimidazole in dioxane with potassium followed by methyl iodide [7]. 1-Methyl-4-phenylimidazole, 1-methyl-2,5-diphenylimidazole, 1-methyl-4,5-diphenylimidazole and 1-methyl-2,4,5-triphenylimidazole were obtained by treating the corresponding imidazole with n-butyllithium followed by methyl iodide [7,8].

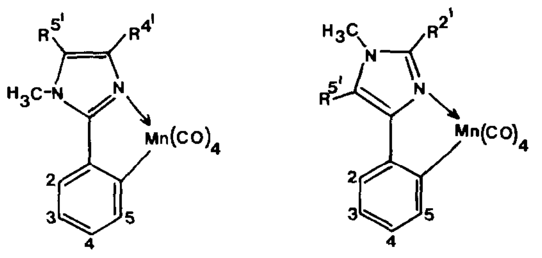
$[(OC)_4\overline{Mn\{MeN\text{-}C(C_6H_4)=N}\text{-}CH=CH\}]$

A solution of 1-methyl-2-phenylimidazole (0.160 g, 1.01 mmol) and $MeMn(CO)_5$ (0.200 g, 0.95 mmol) in dry benzene (15 cm^3) was refluxed for 2 h under dry nitrogen. The cooled solution was column chromatographed on silica gel. Elution with benzene gave the desired product, which was recrystallised from dichloromethane/n-hexane to give a yellow air-sensitive solid. Yield 0.256 g (83%).

The remaining complexes were prepared analogously (Elemental analysis and physical data are given in Table 1).

Results and discussion

The phenylimidazole ligands used in this work react readily with $MeMn(CO)_5$ to give the corresponding cyclometallated complexes in which the ligand is bound to the metal center through the pyridinic nitrogen of the imidazole ring and the phenyl C(6) atoms, except in the case of the 1-methyl-5-phenylimidazole ligand where the large distance between these two atoms inhibits the formation of the analogous cyclometallated compounds. The complexes are octahedral with a structure similar to that reported earlier [2] (see Fig. 1). The IR spectra in cyclohexane solution show four bands in the region 2100–2000 cm^{-1} due to ν(C=O) stretching vibrations and their relative intensities are in accordance with the proposed structure [9] (see Table 1 and Fig. 2). In the case of complexes VIa and VIb more than four carbonyl stretching frequencies appear because there are two possible metallation sites and a mixture of compounds is produced. The ^{1}H NMR spectrum of complex Vb shows that the signals due to protons 2, 3 and 4 of the metallated phenyl ring are shifted to low frequency (highfield) with respect to the free ligand (see Table 2); this shift



a

b

	$R^{4'}$	$R^{5'}$
Ia	H	H
IIIa	C_6H_5	H
IVa	H	C_6H_5
VIa	C_6H_5	C_6H_5

	$R^{2'}$	$R^{5'}$
IIb	H	H
IIIb	C_6H_5	H
Vb	H	C_6H_5
VIb	C_6H_5	C_6H_5

Fig. 1. Where there are more than one phenyl ring their numbering is analogous to that shown in a or b.

could be due to (a) the influence of the phenyl ring at position 5′ of the imidazole ring and (b) π-back-bonding from the metal to the phenyl ring bound to it. We think the latter is more likely since in complexes with only one phenyl ring this shift is still observed. The shift is smaller than that observed for similar palladium(II) complexes [10], since manganese(I) is not as electron rich as palladium(II) and furthermore it is bound to four π-acceptor carbonyl groups. However, the H(5)

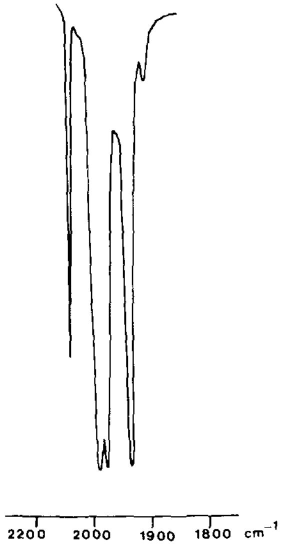


Fig. 2. IR spectrum of Vb, in cyclohexane solution.

Table 2

^{1}H NMR data for the ligands and complexes [a,b]

Complex [c]	N-CH_3	2′	4′	5′	2	3	4	5	6	Others
I	3.71s	–	7.07d	6.92d	7.62dd	← 7.36–7.49 →			7.62dd	–
Ia	3.96s	–	6.96s	6.83s	7.63dd	7.15td	7.23td	7.99dd	–	–
II	3.70s	7.46s		7.38d	7.76dd	7.27td	7.16tt	7.27td	7.76dd	–
IIb	3.76s	7.51s	–	6.06s	7.37dd	← 7.07–7.18m →		7.89dd	–	–
III	3.77s	–		7.26s	7.69dd 7.83dd	← 7.20–7.50m →			7.69dd 7.83dd	7.20–7.50m
IIIa	4.04s	–	–	6.76s	7.60dd	← 7.09–7.80m →		7.96dd	–	–
IIIb	3.54s	–	–	7.08s	← 7.09–7.60m →			7.82dd	–	–
IV	3.69s	–	7.22s	–	7.72dd	← 7.34–7.49m →			7.72dd	7.34–7.49m
IVa	3.94s	–	7.03s	–	7.73dd	← 7.13–7.28 →		8.02dd	–	–
V	3.49s	7.57s	–	–	← 7.14–7.50m →					–
Vb	3.50s	7.62s	–	–	6.96dd	6.83td	7.06td	7.88dd	–	–
VI	3.56s	–	–	–	7.55dd 7.75dd	← 7.10–7.50m →			7.55dd 7.75dd	7.10–7.50m
VIa	3.90s	–	–	–	7.70	[d]	[d]	8.05dd	–	–
VIb	3.25s	–	–	–	6.96dd	6.85td	7.08td	7.89dd	–	–

[a] Chemical shifts: δ(ppm) to highfield of Si(CH$_3$)$_4$; in CDCl$_3$ solution. [b] s, singlet; d, doublet, dd, double doublet, td, triplet of doublets, tt, triplet of triplets, m, multiplet, b, broad. [c] The numbers indicate the positions of the protons on the imidazole ring (2′, 4′, 5′) and the phenyl ring (2, 3, 4, 5, 6) as they are indicated in Fig. 1. [d] Very complex multiplet.

signal is strongly shifted towards high frequency owing to the anisotropic effect of the carbonyl triple bond, as has been observed before [2,11]. The ^{1}H NMR spectra for complexes IIb and Vb show that the $\delta(\text{N}-\text{C}H_3)$ value is close to that for the free ligand (see Table 2). In complexes Ia and IVa, where metallation takes place on a phenyl ring in position 2′ of the imidazole ring, the N-CH_3 signal is shifted to high frequency by ca. 0.25 ppm as a result of the twisting upon metallation of the phenyl ring initially co-planar with the imidazole ring, so that the methyl group falls into the deshielding zone of the phenyl ring. In complexes derived from ligands III and VI, where there are two phenyl rings in positions 2′ and 4′ of the imidazole ring, the ^{1}H NMR spectra show two singlets ca. 4.0–3.2 ppm for the N-CH_3 protons corresponding to the two possible isomers. In each case the weakest signal, ca. 4.0 ppm in IIIa and VIa, is ascribed to the isomer cyclometallated through the phenyl ring in position 2′ of the imidazole ring. The other signal, δ 3.54 (IIIb) and 3.25 (VIb) ppm, is shifted towards low frequency due to the phenyl ring in position 2′ of the imidazole ring, now perpendicular because of the steric effects, producing a shielding of the N-CH_3 protons. This effect has been observed with cyclometallated complexes of palladium(II) [10].

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