Synthesis and spectroscopic (^{1}H NMR, ESR) characterization of new aryloxy–Mn(II) complexes: steric control over *O*– vs. phenyl–π-coordination of ArO^- ligands (ArO^- = $C_6H_5O^-$, 4-methyl-$C_6H_4O^-$, 3,5-dimethyl-$C_6H_3O^-$, 2,6-di-*tert*-butyl-$C_6H_3O^-$, 2,6-dimethyl-$C_6H_3O^-$) to the "Mn(II)Cp" moiety, and their reactivity with carbon dioxide

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Abstract: The coordination chemistry of phenoxide ligands, such as $C_6H_5O^-$, 4-(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$, 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$, 2,6-$(CH_3)_2$-$C_6H_3O^-$, to Mn(II) has been investigated because of the possible implication of Mn(II)–phenoxide complexes as intermediates in the phenylphosphate carboxylase enzyme, a protein which catalyses the selective carboxylation of phenylphosphate to 4-OH-benzoic acid using CO_2. We report here the synthesis and characterization of $[CpMn(\mu\text{-}OAr)(THF)]_2$ (ArO = $C_6H_5O^-$, 4-(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$, 2,6-$(CH_3)_2$-$C_6H_3O^-$) and $[CpMn(\eta^5\text{-}ArO)]$ (ArO = 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$ and 2,6-$(CH_3)_2$-$C_6H_3O^-$) complexes, the first examples of mixed-sandwich complexes with Cp and phenate as π-ligands. The latter bear the 2,6-substituted phenoxide π-coordinated to the $[Mn(Cp)]^+$ moiety. The different mode of bonding of the phenoxide ligands to Mn(II), substantiated by ^{1}H NMR and electron spin resonance (ESR) spectroscopy, is controlled by the steric hindrance of substituents at the 2- and 6-position. The reactivity of the π-bonded ligand towards CO_2 is also reported as a quite rare example of nucleophilic attack at the cumulene by the ring-carbon of the phenoxide, which is driven by electron density localization at the 4-position generated upon π-coordination to Mn(II).

Key words: Mn(II)-complexes, phenoxide ligands, ^{1}H NMR spectroscopy, ESR spectroscopy, reaction with carbon dioxide.

Résumé : On a étudié la chimie de coordination des ligands phénolates, tels que $C_6H_5O^-$, 4(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$, 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$ et 2,6-$(CH_3)_2$-$C_6H_3O^-$, avec le Mn(II) en raison de l'implication possible des complexes Mn(II)-phénolates comme intermédiaires dans l'enzyme carboxylase du phosphate de phényle, une protéine qui catalyse la carboxylation sélective du phosphate de phényle en 4-HO-C_6H_4-C(O)OH à l'aide de CO_2. On a synthétisé et caractérisé les complexes $[CpMn(\mu\text{-}OAr)(THF)]_2$ (ArO = $C_6H_5O^-$, 4(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$ et 2,6-$(CH_3)_2$-$C_6H_3O^-$) et $[CpMn(\eta^5\text{-}ArO)]$ (ArO = 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$ et 2,6-$(CH_3)_2$-$C_6H_3O^-$), le premier exemple d'un complexe sandwiche mixte comportant un Cp et un phénate comme ligands π. Dans le dernier, le phénolate 2,6-disubstitué est fixée par une coordination π à la partie $[Mn(Cp)]^+$. Les différents modes de fixation des ligands phénolates au Mn(II), tels que confirmés par RMN du ^{1}H et par spectroscopie RPE, sont contrôlés par l'encombrement stérique des substituants en positions 2 et 6. On a aussi déterminé la réactivité des ligands fixés d'une façon π vis à vis du CO_2; il s'agit d'un rare exemple d'attaque nucléophile au niveau du cumulène par l'atome de carbone du cycle du phénolate alors que celle-ci est amenée par la localisation de la densité électronique en position 4 sous l'influence d'une coordination π avec le Mn(II).

Mots clés : complexes du Mn(II), ligands phénolates, spectroscopie RMN du ^{1}H, spectroscopie RPE, réaction avec le bioxyde de carbone.

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

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Introduction

Phenol and its derivatives have been shown to act as ligands to transition metal systems (1) through either the *O*-atom or the phenyl π-electron system. Bulky substituents in both 2- and 6-position of the phenyl ring, as well as an unsaturated coordination of the metal, may force π-phenyl bonding to the metal center (2). Such a situation has been structurally documented for diamagnetic Rh(I) complexes (3). Although both diamagnetic and paramagnetic phenoxide-complexes are extensively described in the literature, no examples of phenoxide π-coordination to a paramagnetic center have been reported to date.

Iron(III) complexes bearing phenol or substituted phenols, which are exclusively η^1–*O*-bonded, have been extensively studied as model compounds of catechol oxidase (4). The importance of Mn(II) systems in several biosystems (5) and in material science has prompted investigatations of complexes or clusters bearing the η^1–*O*-bonded phenoxide anion (6). Only a single case of π-bonded phenate to Mn(I) is reported in the literature (7). Despite this interest practically no reports are available in the literature that describe both modes of bonding of phenol and (or) its substituted forms to manganese(II).

Very recently we have extracted a phenol carboxylase enzyme from the anaerobic bacteria *Thauera aromatica* (8). The extracted enzyme was supported onto an organic matrix and shown to catalyse very selectively the conversion of phenylphosphate into 4-OH-benzoic acid in mesophilic conditions (9) with significant turnover frequency (TOF) and turnover number (TON). While information about the structure of the active site is still not available, it is known that the enzymatic activity is Mn(II) dependent (8) and that if the enzyme is incubated with phenol this activity is strongly retained. This finding prompted us to investigate the coordination of phenol and its derivatives to Mn(II) in order to gain information about the relevance of the mode of bonding to reactivity. Therefore, we decided to investigate the reaction of $Mn(Cp)_2$ with C_6H_5OH, 4-(CH_3)-C_6H_4OH, 3,5-$(CH_3)_2$-C_6H_3OH, 2,6-(*tert*-butyl)$_2$-C_6H_3OH, and 2,6-$(CH_3)_2$-C_6H_3OH.

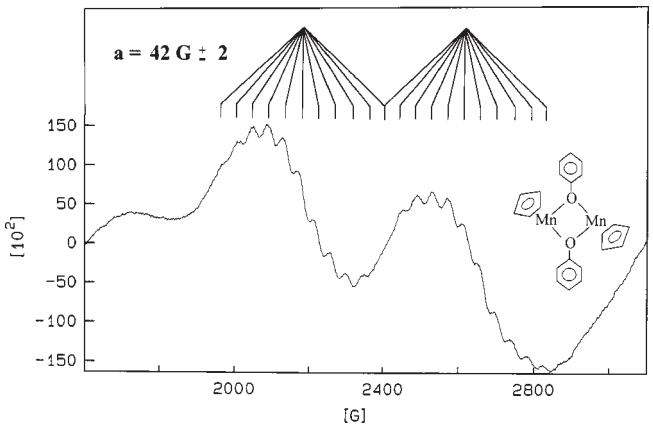
In this paper, we report the synthesis of complexes of the formula [CpMn(ArO)(THF)] (ArO = $C_6H_5O^-$, 4-(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$, 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$, and 2,6-$(CH_3)_2$-$C_6H_3O^-$), which are quite rare examples of paramagnetic complexes bearing one Cp and one phenoxide ligand. The different mode of bonding of phenoxide anion to Mn(II) is substantiated by ^{1}H NMR, electron spin resonance (ESR), and IR spectroscopy, and by the reactivity of Mn–phenoxides with CO_2. A unique example of ring carboxylation of phenol derivatives to substituted 4-OH-benzoic acid under ambient conditions, which is fully mimetic of the above mentioned biological carboxylation of phenol, is also reported.

Results and discussion

Synthesis and characterization of the [Cp(THF)Mn(μ-*O*-C_6H_5)]$_2$ complex (1)

Cp_2Mn reacts with PhOH (in THF) in a 1:1 molar ratio at room temp to afford a white solid (**1**), which separates quantitatively from the reaction mixture (eq. [1]). This reaction is very clean and can be followed by GC that allowed the reaction stoichiometry to be determined for eq. [1].

Fig. 1. ESR sectrum of [Cp(THF)Mn(μ-*O*-C_6H_5)]$_2$ (in THF, *T*= 77 K, mod amplitude: 2.299 G, frequency: 9.4247866 GHz, power: 2.00e + 01 mW).



[1] $2Cp_2Mn + 2C_6H_5OH \xrightarrow[298K]{THF} [Cp(THF)Mn(\mu\text{-}O\text{-}C_6H_5)]_2 + 2C_5H_6$

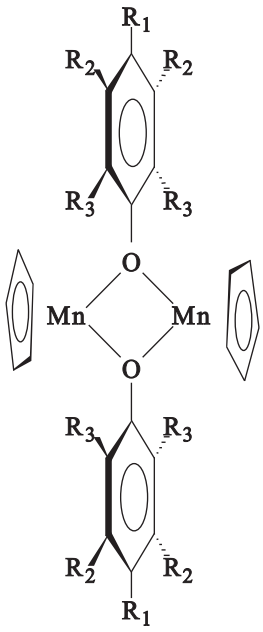
GC analysis of the reaction solution after precipitation of the solid, shows that one mol of C_5H_6 per mol of Cp_2Mn is released after addition of phenol. Residual phenol is not found in solution.

Complex **1** is very oxygen- and moisture-sensitive. The white solid is pyrophoric and could not be correctly characterized by conventional elemental analysis techniques. In spite of this, it was possible to ascertain its composition by acidolysis of the compound and quantitative determination, via GC, of the ligands released (see *Experimental*). Analysis of **1**, by this methodology, ascertained that Cp and PhO^- are coordinated to the metal in a 1:1 ratio and that one mol of solvent (THF) per mol of Cp and PhO^- is also present in the metal coordination sphere. Quantitative determination of Mn was achieved by atomic absorption after acidolysis of the compound in aqueous solution and was determined to be present in a 1:1 ratio with the other ligands (PhOH, Cp, THF). When **1** was suspended in pentane under continuous stirring for approximately two days, the analysis of the recovered compound, after acidolysis, still gave a 1:1:1:1 ratio for Cp, THF, phenol, and Mn, respectively, indicating that the THF ligand remains quite strongly bound to the metal when the solid is suspended in non-coordinating solvents.

Complex **1** has been also characterized by spectroscopic techniques (ESR, IR, ^{1}H NMR) and by magnetic measurements. The IR spectrum (Nujol™ suspension) shows bands at 1587 (s, (C=C)) and 1260 (m, (C-O)) cm^{-1}. The ESR spectrum of **1** (Fig. 1), measured at 77 K in frozen THF, shows several not well resolved absorptions in the range 0–5000 G.

The two transitions in the range 1800–2800 G show an hyperfine structure consisting of 11 lines with a hyperfine coupling constant of 42 ± 2 G, in which the intensities follow quite well the 1:2:3:4:5:6:5:4:3:2:1 ratio. The observed value (42 G) is approximately half the value (85–90 G) found for monomeric complexes (10). Preliminary theoreti-

Fig. 2. Proposed structure of dimeric Mn-complexes.



Compound **1** $R_1 = H, R_2 = H, R_3 = H$
Compound **2** $R_1 = CH_3, R_2 = H, R_3 = H$
Compound **3** $R_1 = H, R_2 = CH_3, R_3 = H$
Compound **5** $R_1 = H, R_2 = H, R_3 = CH_3$

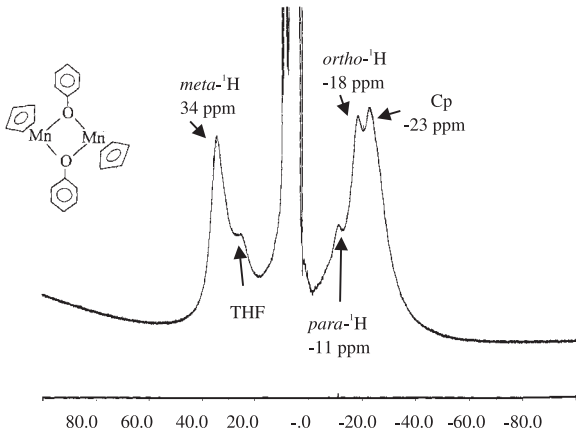
cal calculations[2] also support the presence of a dimeric system. The above reported spectral features indicate the presence of two ^{55}Mn centers ($I = 5/2$) with strong electron spin exchange interaction through the bridging *O*-bonded phenoxide ligands. Such features are common to other Mn(II)-complexes bearing *O*-bridging ligands (11). The proposed structure for compound **1** is shown in Fig. 2 and accounts for a 17 electron-system.

Complex **1** has a magnetic moment of $\mu_{eff} = 5.35\ \mu_B$ per Mn atom measured at room temp and $4.54\ \mu_B$ at 80 K. The product $(\chi_m \cdot \theta)$ is almost constant over the entire range of temperature. This value may indicate the presence of high spin antiferromagnetically coupled Mn(II) centers (12).

Unfortunately, it was not possible to obtain the ^{13}C NMR spectrum of **1**. The ^1H NMR spectrum of **1** (Fig. 3), however, shows a very complex pattern with broad signals (half-widths of ca. 4 kHz) at 34, 24, –11, –18, and –23 ppm. The ^1H NMR spectra reported throughout this paper are quite rare examples of proton NMR spectra of Mn(II) complexes, for which very often it is reported that it was not possible to obtain the ^1H NMR spectrum due to sensivity reasons.

The observed pattern in the ^1H NMR spectra strongly indicates the dominance of the spin density polarisation effect through the aromatic ring (5). As the integral and the chemical shifts were not helpful for the assignment of the resonances for the phenoxide, THF, and Cp protons, a systematic study of the ^1H NMR spectra of half-sandwich Mn(II) complexes with *ortho*-, *meta*-, and *para*-substituted phenols ($4\text{-}(CH_3)\text{-}C_6H_4OH$, $3,5\text{-}(CH_3)_2\text{-}C_6H_3OH$, $2,6\text{-}(tert\text{-butyl})_2\text{-}C_6H_3OH$), and $2,6\text{-}(CH_3)_2\text{-}C_6H_3OH$) was undertaken. This study was reputed useful for the following reasons. (*i*) As

Fig. 3. ^1H NMR spectrum of $[Cp(THF)Mn(\mu\text{-}O\text{-}C_6H_5)]_2$ in THF-d_8, $T = 298$ K.



documented in the literature, the ^1H NMR signals of CH_3-protons attached to aromatic systems in paramagnetic complexes are narrower with respect to the signals of protons directly attached to the carbon atoms of the phenyl ring and, thus, they can be more easily recognized in the spectrum. (*ii*) If strong spin density polarisation is taking place through the aromatic ring, the substitution of H with a CH_3 group is expected to significantly shift the proton resonance. This feature is often very helpful in proton assignment.

In fact, a comparative analysis of the variation of the CH_3-proton shifts with the position of the substituents in the ring made possible the assignment of almost all resonances for the complexes with the different ligands listed above; the results are reported in Table 1.

On the basis of the total spectral assignments for the complexes bearing coordinated phenoxide and its substituted forms, we can, for complex **1**, attribute the signal at 34 ppm to phenolate-*meta*-protons and the signals at –18 and –11 ppm to the phenolate *ortho*- and *para*-protons, respectively. The signal at –23 ppm is assigned to the coordinated Cp protons. This value is in agreement with the data reported in the literature for half-sandwich complexes with facial coordination of the Cp ligand (13). The band at 24 ppm is assigned to the coordinated THF molecule. When the spectrum was registered in THF-d_8 this signal was not observed, because of the exchange with the deuterated solvent. By adding small amounts of THF directly to the solution in the NMR tube, the resonance at 24 ppm did finally appear.

Reaction of Cp_2Mn with $4\text{-}CH_3\text{-}C_6H_4OH$

The reaction of Cp_2Mn with $4\text{-}(CH_3)\text{-}C_6H_4OH$ in a 1:1 molar ratio in THF affords compound **2**, which is soluble in THF and can be separated from a very concentrated solution.

$$[2] \quad 2Cp_2Mn + 2(4\text{-}CH_3\text{-}C_6H_4OH) \xrightarrow[298\ K]{THF} [Cp(THF)Mn(\mu\text{-}O\text{-}4\text{-}(CH_3)\text{-}C_6H_4)]_2 + 2C_5H_6$$

[2] V. Minin. Kurnakov Institute of General and Inorg. Chem. of the Russian Academy of Sciences, Moscow, Russia (personal communication).

Table 1. ^{1}H NMR data for Mn-complexes.

	H-*ortho*	H-*meta*	H-*para*	Cp
[Cp(THF)Mn(μ-C_6H_5)]$_2$ (**1**)	–18	34	–11	–23
[Cp(THF)Mn(μ-*O*-4-(CH_3)-C_6H_4)]$_2$ (**2**)	n.a.	26[a]	31 (CH_3)	–26
[Cp(THF)Mn(μ-*O*-3,5-(CH_3)$_2$-C_6H_3)]$_2$ (**3**)	–2	–5 (CH_3)	–18	–26
[CpMn(η^5–2,6-(*tert*-butyl)$_2$-C_6H_3O)] (**4**)	10 (*t*-Bu)	31	–22	3
[Cp(THF)Mn(μ-*O*-2,6-(CH_3)$_2$-C_6H_3)]$_2$ (**5**)	28 (CH_3)	35	–18	–29
[CpMn(η^5–2,6-(CH_3)$_2$-C_6H_3O)] (**6**)	–24 (CH_3)	25	–18	2

Note: n.a. = not assigned.
[a]Tentative assignment.

In this case, GC analysis of the reaction solution is not helpful for monitoring the amount of Cp released upon the reaction of Cp_2Mn with 4-(CH_3)-C_6H_4OH. In fact, because the product is soluble in the reaction solvent, the GC technique cannot distinguish the free Cp in solution from that generated upon decomposition of the complex in the injector. It was, however, possible to follow the reaction by monitoring the IR spectrum of the reaction solution. In fact, just minutes after the addition of 4-CH_3-(C_6H_4)OH, the band at 3600 cm^{-1} due to the free phenol ν(OH) completely disappears, allowing one to conclude that the added substituted phenol has completely reacted with Mn(II). Complex **2** was analyzed by GC and atomic absorption analysis after acidolysis of the solution (see *Experimental*) and shown to bear Mn in a 1:1 ratio to Cp, THF, and 4-(CH_3)-C_6H_4OH. The analytical data do not change if complex **2** is suspended in pentane (even for 2 days), indicating that THF is always strongly bound to the metal. The ESR spectrum of **2** measured at 77 K, as a frozen THF solution, is very similar to that of **1**, including the presence of the 11 line hyperfine structure for bands in the range 1800–2800 G with hyperfine coupling of 42 ± 2 G. These features suggest a dimeric structure for complex **2**, with μ-*O*-bonded phenoxide ligands. The ^{1}H NMR spectrum of **2** shows only two intense signals at 31 and –26 ppm, assigned to the CH_3-*para*-protons of the phenoxide ligand and the cyclopentadienyl protons, respectively. The shift towards lower fields of the CH_3-*para*-phenoxide protons is in agreement to what is observed for CH_3-*para*-protons of 4-(CH_3)-$C_6H_4O^-$ coordinated to Fe(III)–salen complexes (5), and the observed value of –26 ppm, is in the correct range for Cp protons. The signals of the *ortho*- and *meta*-protons of the phenoxide ligand are probably obscured by the two large signals reported above. The structure for compound **2** is shown in Fig. 2.

Reaction of Cp_2Mn with 3,5-(CH_3)$_2$-C_6H_3OH

The reaction of Cp_2Mn with 3,5-dimethylphenol (1:1 molar ratio) in THF closely matches the reaction reported for **2**. A white powder is isolated from a very concentrated solution, which was analyzed to be [Cp(THF)Mn(μ-*O*-3,5-(CH_3)$_2$-C_6H_3)]$_2$ (**3**).

[3] $$2Cp_2Mn + 2(3,5\text{-}(CH_3)_2\text{-}C_6H_3OH) \xrightarrow[298\ K]{THF} [Cp(THF)Mn(\mu\text{-}O\text{-}3,5(CH_3)_2\text{-}C_6H_3)]_2 + 2C_5H_6$$

THF is strongly bound as shown by the stability of **3** in pentane even for a long period of time (2 days).

The ESR spectrum of **3** in frozen THF solution at 77 K consists of bands in the range 1800–2800 G, with a hyperfine structure comprised of 11 lines, and hyperfine coupling of 42 ± 2 G. A dimeric structure is also assigned to complex **3** (Fig. 2).

The ^{1}H NMR spectrum of compound **3** in THF-d_8 shows that the CH_3-*meta*-protons (–5 ppm) and the Cp protons (–26 ppm) almost overlap the signals found at –2.5 and –18 ppm, which are assigned to the *para*- and *ortho*-phenoxide protons, respectively, in the dimeric μ-*O*-bonded phenoxide complex (compound **3**, Fig. 2). This is in agreement with a negative spin density delocalization on the CH_3-*meta*-protons of the μ-*O*-coordinated phenoxide anion and confirms the spectral analogies between Mn(II)– and Fe(III)–phenoxide complexes (5). In fact, the pattern of the isotropic shifts of CH_3-*meta*- or *para*-protons in compound **3** or **2,** respectively, is very similar to what observed for (salen)Fe(III) – methyl-substituted-phenoxide complexes, and demonstrates the presence of a strong spin polarization through the aromatic ring. On this basis, a positive spin density delocalization is expected and revealed for protons of CH_3-group *ortho*- or *para*- in the phenoxide ligand, as found also in relevant (salen)Fe(III) complexes.

Reaction of Cp_2Mn with 2,6-(*tert*-butyl)$_2$-C_6H_3OH

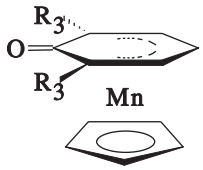
When Cp_2Mn is reacted in anhydrous THF with 2,6-(*tert*-butyl)$_2$-C_6H_3OH in a 1:1 molar ratio a white solid product (**4**) is isolated. (eq. [4])

[4] $$Cp_2Mn + 2,6\text{-}(tert\text{-butyl})_2\text{-}C_6H_3OH \xrightarrow[298\ K]{THF} [CpMn(\eta^5\text{–}2,6\text{-}(tert\text{-butyl})_2\text{-}C_6H_3O)] + C_5H_6$$

Again, the reaction cannot be followed by GC analysis because of the solubility of the reaction product, but can be isolated and analyzed by GC after acidolysis. The ligands (Cp, THF, and 2,6-(*tert*-butyl)$_2$-C_6H_3OH) are determined to be in a 1:1:1 reciprocal ratio and each in 1:1 ratio to Mn. If **4** is suspended in pentane for 12 h, analysis of the solid shows that THF has been released almost quantitatively (less than 5% of product still contains coordinated THF, as demonstrated by GC analyses).

The ESR spectrum of **4** measured at 77 K, in a frozen THF solution, shows only one large signal at g = 2.003 G due to a low spin Mn(II) with a six line hyperfine structure. The coupling constant (A = 85 ± 3 G) and the six lines clearly indicate the presence of a monomeric species (10). When 2,6-(*tert*-butyl)$_2$-C_6H_3OH is added in a 1:1 ratio to a

Fig. 4. Proposed structure of monomeric [CpMn(η^5–2,6-(*tert*-butyl)$_2$-C_6H_3O)].



R_3 = *t*-Bu; Compound **4**
R_3 = CH_3; Compound **6**

solution of Cp_2Mn and the ESR spectrum of the reaction mixture is measured at low temperature (80 K) with time, several changes are observed. Immediately after the addition of 2,6-(*tert*-butyl)$_2$-C_6H_3OH, a complex pattern of signals appears, similar to that observed for compounds **1**–**3**. If the solution is allowed to warm to room temp, and after 30 min the spectrum is repeated at low temperature (80 K), one single signal is observed as specified above. These features indicate the initial formation of a high spin species (most probably, the *O*-bonded phenoxide complex is the kinetic product), which in a short time converts into a low spin species. The complex bearing the phenol moiety π-bonded to the metal is the thermodynamic product.

Since, Cp_2Mn and substituted cyclopentadienyl manganocenes show a spin cross-over effect at temperature close to room temp that depends on the matrix that contains the compound, a detailed analysis of the dependence of the high spin ⇄ low spin equilibrium for **4** is in progress.

Complex **4** is soluble enough in benzene at room temp for preparing a 1×10^{-2} M solution, which was not possible for dimeric compounds described above, to allow for molecular mass determination of **4** by cryoscopy (14). The molecular mass of **4** was found to be 355 g mol^{-1} (calculated 325 g mol^{-1}), thus, confirming the monomeric structure of the complex. The ^{1}H NMR of **4** in THF-d_8 shows a signal at 10 ppm for the *tert*-butyl-protons. As the *tert*-butyl-protons are one C—C bond further away from the aromatic ring with respect to the CH_3-protons, the slight shift to lower fields confirms that in this complex the same mechanism of spin density delocalization is operative as described for the other complexes in this paper. The signal due to Cp protons overlaps with that of the solvent and is found around 3 ppm. The ^{1}H NMR spectrum of **4** in C_6D_6 shows the same features of that measured in THF-d_8, demonstrating that both benzene and THF do not coordinate to the metal center and, thus, validates the cryoscopic measurement of the molecular mass made in C_6H_6. The monomeric structure of **4**, as shown by ESR and cryoscopic measurements, can be explained by considering a π-coordination of the aromatic ring to the metal center (Fig. 4).

A single *O*-bonded phenoxide to the CpMn moiety should, in fact, give a coordinatively unsaturated 13e$^-$ species. While in the literature, one example of a dimeric Mn–phenoxide complex (15) which formally accounts for 11e$^-$, is reported, all known momeric cyclopentadienyl complexes account for 17–19e$^-$.

Reaction of Cp_2Mn with 2,6-$(CH_3)_2$-C_6H_3OH

The reaction of Cp_2Mn with 2,6-$(CH_3)_2$-C_6H_3OH in a 1:1 molar ratio in THF affords a mixture of solid products. Analysis shows the ligands and Mn to all be in a 1:1 ratio. However, the suspension of the white solid in pentane for 12 h allows for isolation of a powder showing, after acidolysis, a Cp:THF:phenoxide ratio of 1:0.5:1, indicating that THF is released from the coordination sphere even in non-coordinating solvents. Such finding must be related to a possible change of the coordination mode of the ligand.

Spectroscopic data of the white solid clearly show the presence of two products (**5** and **6**) (see discussion below) formed according to eq. [5]:

$$[5]\quad 3Cp_2Mn + 3(2,6\text{-}(CH_3)_2\text{-}C_6H_3OH) \xrightarrow[298\ K]{THF} [Cp(THF)Mn(\mu\text{-}O\text{-}2,6\text{-}(CH_3)_2\text{-}C_6H_3)]_2 + [CpMn(\eta^5\text{-}2,6\text{-}(CH_3)_2\text{-}C_6H_3O)] + 3C_5H_6$$

Such data can be rationalized considering the features of complexes **1**–**4** described above. The ESR spectrum of the reaction product measured at 77 K in a frozen THF solution shows a quite complex pattern of signals, only in part similar to the ESR spectrum of compound **1**. The most important differences are related to: (*i*) the absence of the hyperfine structures in the bands in the range 1800–2800 G; and (*ii*) the presence of hyperfine splitting in the region of 500 G. In this region a six-line pattern is observed. Such a hyperfine structure suggests the presence of a monomeric species, as found for complex **4**. The analysis of the ^{1}H NMR spectrum (in THF-d_8) shows two broad and partially overlapping signals at 35 and 28 ppm. One very broad strong signal appears at –28 ppm with two less intense signals in the high field region at –18 and –24 ppm. The signals at 28 and –24 ppm are easily recognized as CH_3-protons on the basis of their half-width of ca. 1 kHz. The signal at 28 ppm is assigned to CH_3-protons of a dimeric compound (compound **5**, Fig. 1). The difference in the absolute value of the isotropic shift for the *tert*-butyl-protons of compound **4** compared with the CH_3-protons of compound **6** is due to the absence of the strong hyperconjugation effect operative in the case of the CH_3-protons. While the presence of the CH_3-proton signal at 28 ppm is in agreement with the above discussed pattern, the signal at –24 ppm deviates strongly if a μ-*O*-structure is considered. The latter signal is assigned to a species bearing the *O*-2,6-$(CH_3)_2$-C_6H_3 moiety π-coordinated to the Mn(II) center. The signals at 35 and –18 ppm are assigned to the *meta*- and *para*-protons, respectively, of compound **5**. The Cp ligand in this complex is found at –29 ppm. In **6** the Cp signal is shifted to lower field (2 ppm), and partially overlaps with the solvent signal.

Both the ESR and ^{1}H NMR spectra and the analytical data support the conclusion that two products (**5** and **6**) are formed as shown in eq. [5]. The experimental evidence that half of the coordinated THF is released after suspension of the solid in pentane, indicates that approximately half of the solid is a species in which THF is not strongly bound to the metal and can be removed by the action of a non-coordinating solvent. By simply taking into account electron-counting, compound **5** can reach a 17e$^-$ configuration by being a dimer with a molecule of THF in the coordination

sphere. The monomeric species (**6**), which on the basis of the analytical data is composed of Mn, Cp, and phenoxide in 1:1:1 ratio, does not need THF to reach the $17e^-$ configuration as it bears the π-coordinated phenoxide ligand. In compound **6**, the presence of two methyl groups in the 2- and 6-positions, forces the η^5-coordination of the substituted phenoxide, but the steric hindrance is not such to afford the π-coordination as the only form, as observed in the case of **4**. Attempts to isolate compounds **5** and **6** as pure solids have been done. By crystallization from benzene or toluene it is possible to obtain a compound richer in **6**, but not totally free of **5**. The interconversion (**5** ⇄ **6**) is not operating at room temp or lower.

Reaction of 4 and 6 with CO_2

When complex **4** (or **6**) is exposed to CO_2, 4-OH-3,5-di-*tert*-butyl-benzoic acid (or 4-OH-3,5-dimethyl-benzoic acid) is isolated (yield ca. 10%). When Mn-complexes bearing *O*-bonded phenols are used, ring-carboxylation is not observed. The behaviour of μ-*O*- and π-bonded phenols can be explained by taking into account that the π-coordination forces electron-dislocation in the 4-position to facilitate nucleophilic attack on CO_2. This produces the ring carboxylation, as also observed for similar Rh-complexes (4*a*), and benzene electro-carboxylation, via electron-transfer, to the ring coordinated Cr(0)-system upon electrochemical reduction of the metal center (16). Conversely, the μ-*O*-bonded phenols undergo CO_2 insertion into the Mn—O bond. Subsequent acidolysis produces the semi-carbonate (ROC(O)OH), which promptly decomposes into ROH and CO_2.

Experimental

General procedure

Unless otherwise stated, all reactions and manipulations were conducted under a nitrogen (N_2) atmosphere by using vacuum-line techniques. Samples for ESR studies were prepared using a Brown glove-box under N_2 atmosphere. All solvents were dried as described in the literature (17) and stored under nitrogen. FT-IR spectra were recorded using a Bruker 113V Fourier transform interferometer. Frequencies are accurate to ±1 cm^{-1}. Solid samples were studied as Nujol™ mulls (Nujol™ was previously dried on sodium wires and bubbled with argon). GC analyses were performed with a Dani 3800 gas chromatograph equipped with a FID detector and a packed SE30 column. Quantitative Mn determination was performed with an PerkinElmer 3110 atomic absorption spectrometer equipped with Mn lamp.

NMR spectra were recorded using a AM 500 Bruker spectrometer. ESR spectra were recorded at 9.4247866 GHz (power = 2.00×10^1 mW) on a Bruker ESP300E spectrometer, which has a 100 kHz magnetic field modulation and is equipped with a Bruker NMR gaussmeter (ER 035M) and a Hewlett–Packard microwave frequency counter (HP 5350B).

Acidolysis, GC, and atomic absorption analysis of compounds

All described compounds were pyrophoric and could not be analysed by conventional analytical techniques. The following methodology allowed for compositional analysis: (*i*) 20–30 mg of the compound, carefully weighted out of the contact with air, was put in a Schlenck tube cooled to 0°C with an ice water bath and, under vigorous stirring, was added dry toluene (2 mL) previously saturated with dry, gaseous HCl. A brown solid immediately separated. After deposition of the solid, the liquid fraction was analysed by GC using a temperature program, which allowed for the separation of cyclopentadiene (1.07 min), THF (1.72 min), toluene (7.8 min), and phenols (C_6H_5OH, 10.40 min; 4-CH_3-C_6H_4OH, 12.38 min; 3,5-$(CH_3)_2$-C_6H_3OH, 14.5 min; 2,6-(*tert*-butyl)$_2$-C_6H_3OH, 15.3 min; 2,6-$(CH_3)_2$-C_6H_3OH, 12.87 min). (*ii*) Alternatively, the solid sample was treated with a large (>100 molar ratio) excess of propionic acid. The solution was analysed by the same GC procedure (propionic acid retention time is 5.5 min in the reaction conditions and does not interfere with other species).

For the quantitative determination of Mn, the following procedure was applied: to 15–20 mg of carefully weighted compound was put in a Schlenck tube under N_2 and was added, under vigorous stirring, distilled water (2 mL) and concentrated H_2SO_4 (analytical grade) (1 mL). The light pink solution obtained was quantitatively transferred into a 50 mL analytical flask and diluted with distilled water. The solution was then analysed by atomic absorption spectroscopy.

Synthesis of [Cp(THF)Mn(μ-*O*-C_6H_5)]$_2$ (1)

To a solution of Cp_2Mn (400 mg, 2.1 mmol) in anhydrous THF (30 mL) under a N_2 atmosphere was added, with vigorous stirring, phenol (200 mg, 2.1 mmol) dissolved in THF (10 mL). A white solid immediately precipitated. After stirring for 1 h, the mixture was filtered and the white solid washed with THF (10 mL), pentane (20 mL), and finally dried in vacuo. The compound was isolated in 95% yield. The GC and atomic absorption analysis, carried out after acidolysis of **1** (as previously described), revealed the presence of Cp, THF, phenol, and Mn in a 1:1:1:1 ratio.

Compound **1** was suspended in anhydrous pentane (30 mL) under a N_2 atmosphere with vigorous stirring for 2 days. The solvent was eliminated and the complex washed and dried in vacuo. Analysis, after acidolysis, of the isolated product showed the same composition as reported above. FT-IR (Nujol/KBr) (cm^{-1}): (PhO-ligand) 1587 (vs) (C=C), 1260 (m) (C-O), 753 (s) (γC-H), 693 (s) (γC-H); (cyclopentadienyl ligand) 1025 (vs) (δC-H), 1006 (s) (δC-H), 760 (s) (γC-H). ^{1}H NMR (THF-d_8) δ: 34 (H-*meta*), –11 (H-*para*), –18 (H-*ortho*), –23 (Cp).

Synthesis of [Cp(THF)Mn(μ-*O*-4-(CH_3)-C_6H_4)]$_2$ (2) and [Cp(THF)Mn(μ-*O*-3,5-(CH_3)$_2$-C_6H_3)]$_2$ (3)

(*i*) A solution of 4-CH_3-C_6H_4OH (292 mg, 2.7 mmol) dissolved in anhydrous THF (15 mL) was added to Cp_2Mn (500 mg, 2.7 mmol) in THF (35 mL) (under N_2 atmosphere) with stirring. The resulting mixture was stirred for 4 h and then concentrated in vacuo to 5–7 mL. A light-brown solid separated from the solution and the organic phase was removed. The solid was washed anhydrous THF (2 × 5 mL), anhydrous pentane (10 mL), and dried in vacuo. The compound, isolated as a grey powder in 90% yield, was determined to be [Cp(THF)Mn(μ-*O*-4-(CH_3)-C_6H_4)]$_2$ by GC analysis after acidolysis (as previously described).

Compound **2** was suspended in anhydrous pentane following the same procedure as described for compound **1**. Analysis,

showed that no change had occurred. FT-IR (Nujol/KBr) (cm^{-1}): (4-CH_3-$C_6H_4O^-$ ligand) 1589 (s) (C=C), 1260 (vs) (C-O), 750 (s) (γC-H), 700 (s) (γC-H); (cyclopentadienyl ligand) 1025 (vs) (δC-H), 1006 (s) (δC-H), 770 (s) (γC-H). ^{1}H NMR (THF-d_8) δ: 26 (H-*meta*), 31 (CH_3-*para*), –26 (Cp).

(*ii*) A solution of 3,5-$(CH_3)_2$-C_6H_3OH (278 mg, 2.28 mmol) in anhydrous THF (10 mL) was added, under N_2 flow and vigorous stirring, at room temp to a flask containing Cp_2Mn (420 mg, 2.28 mmol) dissolved in THF (30 mL). The mixture was worked up as described above and [Cp(THF)Mn(μ-*O*-3,5-$(CH_3)_2$-C_6H_3)]$_2$ was isolated in 90% yield.

Compound **3** in anhydrous pentane did not change its composition after two days. FT-IR (Nujol/KBr) (cm^{-1}): (3,5-$(CH_3)_2$-$C_6H_3O^-$ ligand) 1585 (s) (C=C), 1155 (vs) (C-O), 750 (s) (γC-H), 690 (s) (γC-H); (cyclopentadienyl ligand) 1025 (vs) (δ C-H), 1006 (s) (δC-H). ^{1}H NMR (THF-d_8) δ: –5 (CH_3-*meta*), –2 (H-*ortho*), –18 (H-*para*), –26 (Cp).

Synthesis of [CpMn(η^5-2,6-(*tert*-butyl)$_2$-C_6H_3O)] (4)

A solution of Cp_2Mn (300 mg, 1.62 mmol) dissolved in anhydrous THF (20 mL) under a N_2 atmosphere was added to 2,6-(*tert*-butyl)$_2$-C_6H_3OH (334 mg, 1.62 mmol) dissolved in THF (10 mL). The mixture was stirred for 4 h and then worked up as for **2**. A white solid compound was isolated in 90% yield which analysis, after acidolysis, showed Cp, THF, 2,6-(*tert*-butyl)$_2$-C_6H_3OH, and Mn to be in a 1:1:1:1 ratio. Compound **6** was suspended in anhydrous pentane (30 mL) and stirred for 12 h. The solvent was eliminated and the product obtained was dried in vacuo. The analysis after acidolysis of the obtained complex showed Cp, THF, phenoxide, and Mn to be in a 1:0.05:1:1 ratio. FT-IR (Nujol/KBr) (cm^{-1}): (2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$ ligand) 1575 (s) (C=O and C=C), 1181 (vs) (C-O), 840 (m) (γC-H), 610 (m) (γC-H); (cyclopentadienyl ligand) 1000 (s) (δC-H), 775 (s) (γC-H). ^{1}H NMR (THF-d_8) δ: 31 (H-*meta*), –22 (H-*para*), 10 (*t*-Bu-*ortho*), 3 (Cp).

Synthesis of [Cp(THF)Mn(μ-*O*-2,6-$(CH_3)_2$-C_6H_3)]$_2$ (5) and [CpMn(η^5-2,6-$(CH_3)_2$-C_6H_3O)] (6)

To a solution of Cp_2Mn (450 mg, 2.4 mmol) in THF (35 mL) was added 297 mg (2.4 mmol) of 2,6-$(CH_3)_2$-C_6H_3OH dissolved in 10 mL of the same solvent. The mixture was stirred for 4 h and then worked up as for **2**. A white powder was isolated in 90% yield. GC analysis, carried out after acidolysis, revealed the presence of Cp, THF, 2,6-$(CH_3)_2$-C_6H_3OH, and Mn in a 1:1:1:1 ratio. The white solid obtained was suspended in anhydrous pentane (30 mL) under N_2 atmosphere with vigorous stirring for 12 h. The solvent eliminated and the complex dried in vacuo. Analysis, after acidolysis, of the obtained product showed the Cp, THF, phenoxide, and Mn in a 1:0.5:1:1 ratio. FT-IR (Nujol/KBr) (cm^{-1}): (2,6-$(CH_3)_2$-$C_6H_3O^-$ ligand) 1585(s) (C=O and C=C), 1250 (vs) (C-O), 750(s) (γC-H), 690(s) (γ C-H); (cyclopentadienyl ligand) 1025(w) (δC-H), 995(s) (δC-H), 760(s) (γC-H).

Crystallization from benzene–pentane allowed separating almost pure samples of **5** and **6**. ^{1}H NMR (THF-d_8) δ: (compound **5**) 35 (H-*meta*), –18 (H-*para*), 28 (CH_3-*ortho*), –29 (Cp); (compound **6**) 25 (H-*meta*), –18 (H-*para*), –24 (CH_3-*ortho*), 2 (Cp).

Reaction of 4 and 6 with CO_2

Complex **4** (180 mg, 0.5 mmol) (180 mg (0.7 mmol) for **6**) was dissolved in THF and the solution exposed to 0.1 MPa of CO_2 at room temp. After 6 h stirring, the solution was dried in vacuo and the residual solid treated with BF_3–CH_3OH. Water was added to eliminate the excess of BF_3 and the mixture extracted with diethyl ether. The GC analysis of the resulting ether solution showed the formation of the methyl ester of 4-OH-3,5-(*tert*-butyl)-benzoic acid if starting from **4** (or of 4-OH-3,5-$(CH_3)_2$-benzoic acid if starting from complex **6**).

Conclusions

The results reported above demonstrate that bulky substituents at the 2,6-positions of the phenyl ring may force the η^5-coordination to Mn(II) of substituted phenoxides. Coupling ESR and ^{1}H NMR spectroscopy proved to be a useful tool for structure determination in solution. The η^5-coordination of the phenol prompts the phenyl-ring to a nucleophilic attack of CO_2, which produces the ring carboxylation.

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