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Journal of Organometallic Chemistry 617–618 (2001) 681–695

Journal of Organo metallic Chemistry

Synthesis and reactivity of μ-bis(carbene)dimanganese complexes. X-ray structures of $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH_2CH_2(EtO)C{=}\}$, (E)-$\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH{=}CH(EtO)C{=}\}$ and $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}CN(Ph)CH(Ph)CHCHCH(Ph)N(Ph)C{=}\}$

Alain Rabier, Noël Lugan *, René Mathieu

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne 31077 Toulouse, France

Received 12 September 2000; accepted 29 September 2000

Abstract

The carbene anions resulting from in situ deprotonation of the Fischer-type carbene complexes $Cp'(CO)_2Mn{=}C(OEt)CH_2R$ (**1**; **1a**: R = H; **1b**: Me) undergo an oxidative coupling in the presence of Cu(I), Cu(II) or Fe(III) salts to produce the corresponding μ-bis(carbene)dimanganese complexes $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH(R)CH(R)(OEt)C{=}\}$ (**2**; **2a**: R = H; **2b**: Me). Double deprotonation of **2a** gives a dianionic species that undergoes an oxidation in the presence of Fe(III) chloride to afford the μ-bis(vinylcarbene)dimanganese complex (E)-$\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH{=}CH(OEt)C{=}\}$ (**3**). The controlled electro-reduction of the latter gives a radical anion whose ESR spectrum is consistent with a type III Mn^0/Mn^I mixed valence complex. When reacted with BCl_3 followed by benzylideneaniline complex **2** afford a mixture of the mixed μ-(alkylalkoxy carbene/azetidinylidene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH_2CHCH(Ph)N(Ph)C{=}\}$ (**4**) and the μ-bis(azetidinylidene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}CN(Ph)CH(Ph)CHCHCH(Ph)N(Ph)C{=}\}$ (**5**). Complex **4** is the product of a net [2 + 2] cycloaddition reaction between the mixed μ-(alkylalkoxy carbene/carbyne)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH_2CH_2C{\equiv}\}^+$ $[\mathbf{6}]^+$ and the imine, whereas **5** results from a net $2 \times [2+2]$ cycloaddition between the μ-bis(carbyne)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{\equiv}CCH_2CH_2C{\equiv}\}^{2+}$ $[\mathbf{7}]^{2+}$ and imine. The treatment of complex **4** by BCl_3 followed by reaction with benzylideneaniline afford the mixed μ-(vinylidene/azetidinylidene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C{=}CHCHCH(Ph)N(Ph)C{=}\}$ (**8**). Finally, the oxidative coupling-type reaction observed from the alkylalkoxy carbene complex **1** could be extended to the azetidinylidene complex $[Cp'(CO)_2Mn{=}CN(Ph)CHPhCH_2]$ (**10**) to yield **5** in a selective manner. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Carbene complex; Carbene anion; Carbyne complex; Vinylidene complex; Oxidative coupling

1. Introduction

Since their original report in 1964 [1], Fischer-type carbene complexes have been extensively studied and have found widespread applications in organic synthesis. [2]. Due to the electrophilic character of the carbene carbon atoms in this class of complexes adjacent C–H bonds present an enhanced acidity [3]. As a consequence, metal carbene anions are easily generated upon treatment of alkyl carbene complexes with bases [4]. Such a property has been widely utilised to build elaborated carbene side chains of interest in organic synthesis via (i) formation of carbene anion and (ii) reaction with electrophilic organic [2c, 5] or organometallic [6] reagents.

In some aspects, the chemistry of carbene anions is reminiscent to that of organic ester enolates, as in aldol- or aldol condensation-type reaction with aldehydes or ketones [5b, 7] or in cycloaddition reactions with α,β-unsaturated imines [8] for instance. While studying the reactivity of chromium carbene anion $[Li][(CO)_5Cr{=}C(OMe)CH_2]$ toward oxiranes with the aim to prepare oxacyclo carbene complexes, Licandro et al. briefly mentioned the formation of traces the

* Corresponding author. Tel.: +33-561-333171; fax: +33-561-533003.

E-mail address: lugan@lcc-toulouse.fr (N. Lugan).

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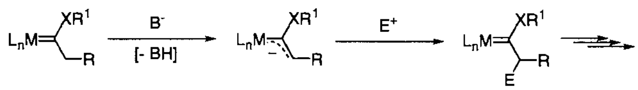
PII: S0022-328X(00)00719-1

Table 1
Oxidative coupling of the carbene anions $[Cp'(CO)_2Mn{=}C(OEt)CH_2R]^-$ ([**1**]$^-$; [**1a**]$^-$: R = H; [**1b**]$^-$: R = Me).

Carbene anion	Oxidising agent	Product (%yield)
[**1a**]$^-$	CuI/O_2 [a,b,d]	**2a** (63)
[**1a**]$^-$	$CuCl_2$ [a,c]	**2a** (49)
[**1a**]$^-$	$CuBr_2$ [a,c]	**2a** (47)
[**1a**]$^-$	CuI_2 [a,c]	**2a** (47)
[**1a**]$^-$	$CuCl_2/O_2$ [a,b,d]	**2a** (68)
[**1a**]$^-$	$FeCl_3$	**2a** (85)
[**1a**]$^-$	electrooxidation [e]	**2a** (42)
[**1b**]$^-$	CuI/O_2 [a,b,d]	**2b** (43)
[**1b**]$^-$	$FeCl_3$ [a,c]	**2b** (65)

[a] Carbene anion generated at −60°C in THF.
[b] 0.5 Equivalent of oxidising agent added at −80°C as a solid.
[c] Equivalent of oxidising agent added at −80°C as a solid.
[d] O_2 bubbled for 30 s at −80°C.
[e] Carbene anion generated at −30°C, anodic oxidation performed at −30°C.



Scheme 1.

μ-bis(carbene)dichromium complex $\{(CO)_5Cr\}_2\{\mu{-}{=}C(OMe)CH_2CH_2(OMe)C{=}\}$ as side product of the reactions [9]. This complex could be seen as the net result of the oxidative coupling of two chromium carbene anions. It was suggested that such a coupling might have been induced by $TiCl_4$ used to pre-activate the oxiranes substrates.

In the course of our investigations of the reactivity of the manganese alkylalkoxy carbene complexes $Cp'(CO)_2Mn{=}C(OEt)CH_2R$ ($Cp' = \eta^5\text{-}MeC_5H_4$) [7c,8,10] and with the support of the above observations, we became interested in determining whether their deprotonated form would indeed undergo an oxidative coupling in the presence of metal salts just as ketone enolates or ester enolates do [11] to afford μ-bis(alkylalkoxy carbene)dimanganese complexes in effective yields [12]. Having in mind that manganese alkylalkoxy carbene can easily be derived into highly reactive cationic alkyl carbyne complexes [13,14], one of our objectives was to further use the incipient dinuclear bis(alkyl carbene) complexes as precursors for dinuclear bis(alky carbyne) complexes, whose reactivity had never been examined.

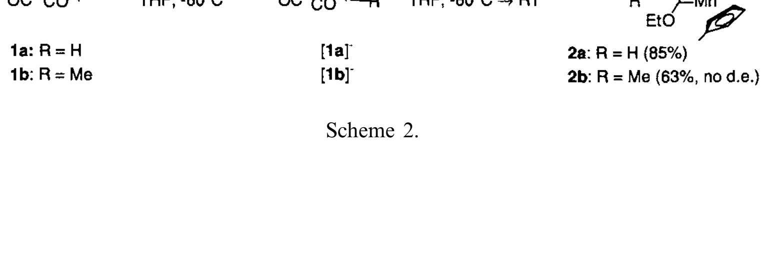
In this paper, we present details of the synthesis of μ-bis(carbene)dimanganese complexes obtained by intermolecular oxidative coupling and oxidation of the manganese carbene anions $[Cp'(CO)_2Mn{=}C(OEt)CHR]^-$ and $[\{Cp'(CO)_2Mn\}_2\{\mu\text{-}C(OEt)CHCH(OEt)C\}]^{2-}$, respectively, and the results of our investigation directed at the synthesis of new dimanganese bis(carbyne) complexes. The solid state structures of $\{Cp'(CO)_2Mn\}_2\{\mu{-}{=}C(OEt)CH_2CH_2(EtO)C{=}\}$, (*E*)-$\{Cp'(CO)_2Mn\}_2\{\mu{-}{=}C(OEt)CH{=}CH(EtO)C{=}\}$ and $\{Cp'(CO)_2Mn\}_2\{\mu{-}{=}CN(Ph)CH(Ph)CHCHCH(Ph)N(Ph)C{=}\}$ are also presented. A preliminary account of part of this work has appeared [15,16].

2. Results and discussion

2.1. Intermolecular oxidative coupling of the carbene anions $[Cp'(CO)_2Mn{=}C(OEt)CHR]^-$ (1)

Cu(I), Cu(II) or Fe(III) salts are commonly used to induce the oxidative coupling of carbanions [11,17]. Examination of the literature shows that the use 0.5 M equivalent of cuprous salt (usually followed by reaction with O_2), or 1 M equivalent of a cupric salt (sometimes followed by reaction with O_2) usually provides the best yields in coupling products. Following procedures directly inspired from organic chemistry, we found that the treatment of a solution the carbene anion $[Cp'(CO)_2Mn{=}C(OEt)CH_2]^-$ ([**1a**]$^-$)-generated in situ by reaction of $Cp'(CO)_2Mn{=}C(OEt)CH_3$ (**1a**) with ^{n}BuLi in THF at −60°C, by either Cu(I) or Cu(II) salts lead to the formation of μ-bis(carbene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu{-}{=}C(OEt)CH_2CH_2(OEt)C{=}\}$ (**2a**) in yields ranged between 42 and 68%, depending on the nature of the copper salt and on the reaction conditions (see Table 1).

Ultimately, it was found that anhydrous Fe(III) chloride is best oxidative coupling reagent for that reaction, affording **2a** in 85% isolated yield (Schemes 1 and 2). Similar treatment of the carbene complex $Cp'(CO)_2\text{-}Mn{=}C(OEt)CH_2Me$ (**1b**) afforded the complex $\{Cp'\text{-}(CO)_2Mn\}_2\{\mu{-}{=}C(OEt)CH(Me)CH(Me)(EtO)C{=}\}$ (**2b**) in 63% yield.



Scheme 2.

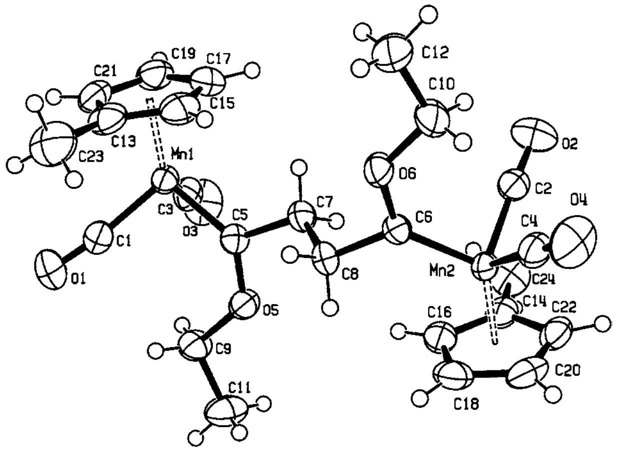


Fig. 1. Perspective view of the complex $\{Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)CH_2CH_2(OEt)C=\}$ (**2a**).

The oxidative coupling of the carbene anion [**1a**]$^-$ could also be induced by electro-oxidation. Cyclic voltamperometry of a solution of the carbene anion [**1a**]$^-$ at -30°C displayed an irreversible oxidation wave at 0.040 V (versus SCE) at a scan speed of 0.1 V s^{-1}. An anodic oxidation of [**1a**]$^-$ conducted at a platinum gauze electrode at -30°C in THF/[$^nBu_4N$][PF_6] medium led to the formation of **2a**, which was isolated in 42% yield.

The complexes **2a** and **2b** were characterised by the usual spectroscopic techniques (see Section 4) and for **2a** by an X-ray diffraction study (see Fig. 1 and below). NMR analysis of **2b**, which bears two asymmetric carbon atoms, shows the compound to form as a 1:1 mixture of the meso form and the dl pair. Attempts to separate the two diastereoisomers by column chromatography remained unsuccessful.

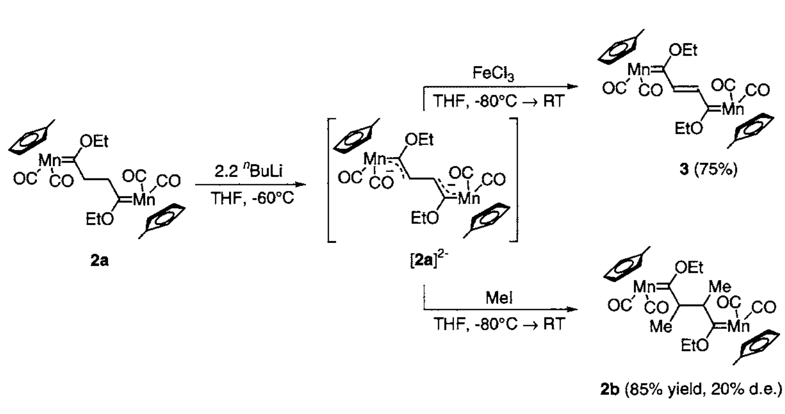
2.2. *Oxidation of the μ-bis(carbene dianion) [$\{Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)CHCH(OEt)C=\}]^{2-}$ ([**2a**]$^{2-}$)*

Saegusa et al. reported that Cu(II) salts can efficiently promote the oxidation of 1,4-diketones dienolates to give olefinic diketones [11c]. Upon consideration of the similarity in the reactivity pattern of organic enolates and carbene anions, we anticipated that an appropriate treatment of the μ-bis(carbene)dimanganese complexes $\{Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)CH(R)CH(R)(EtO)C=\}$ (**2**) could lead to a μ-bis(vinylcarbene)dimanganese species.

Indeed, the treatment of complex $\{Cp'(CO)_2Mn\}_2\{\mu$-$=(OEt)CH_2CH_2(EtO)C=\}$ (**2**) at low temperature with 2.2 M equivalents of ^{n}BuLi followed by addition of 2.2 M equivalents of Cu(II) chloride gave the new μ-bis(vinylcarbene)dimanganese complex $\{Cp'(CO)_2Mn\}_2$-$\{\mu$-$=C(OEt)CH=CH(OEt)C=\}$ (**3**) in 36% yield. Bubbling O_2 for few seconds into the cold solution could significantly improve the yield of **3** (62%). As for the synthesis of **2a**, anhydrous $FeCl_3$ was finally found to be the best oxidative coupling reagent allowing us to recover complex **3** in 75% yield (Scheme 3).

Complex **3** was characterised by the usual spectroscopic techniques and by an X-ray diffraction study. The ^{13}C-NMR spectrum of **3** clearly shows, in addition to the signals due to the ethoxy groups and to the Cp′ ligand, a singlet at 129.1 ppm characteristic of the vinylic carbon atoms. In the ^{1}H-NMR spectrum, the vinylic hydrogen atoms appear as a singlet at 6.85 ppm. A perspective view of complex **3** is given in Fig. 2. Bond distances and bond angles of interest are gathered in Table 2, along with those for **2a**.

The X-ray structure determination reveals an E arrangement of the Cp(′(CO)$_2$Mn fragment relative to the C(7)–C(8) carbon–carbon double bond. Examination of the carbon–carbon bond lengths within the Mn(1)–C(5)–C(7)–C(8)–C(6)–Mn(2) chain deserve some comments. The C(7)–C(8) (C(7)–C(8)=1.323(4) Å) bond is longer than the C=C distance of isolated double bond (1.299 Å [18]) and compares well with the C=C distance found in conjugate systems (1.330 Å [18]). On the other hand the C(5)–C(6)) and C(7)–C(8)) bond are significantly shorter than the corresponding C–C bond in



Scheme 3.

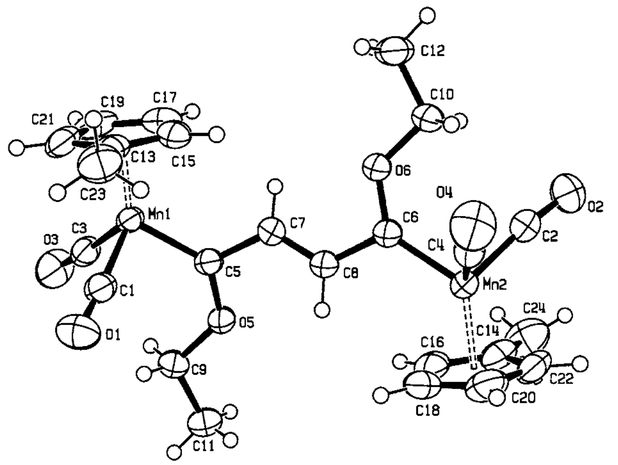


Fig. 2. Perspective view of the complex (*E*)-{Cp′(CO)$_2$Mn}$_2${μ-=C(OEt)CH=CH(OEt)C=} (**3**).

Table 2
Bond distances (Å) and bond angles (°) of interest for compounds **2a** and **3** [a]

	2a	**3**
Bond distances		
Mn(1)–C(1)	1.774(2)	1.777(3)
Mn(1)–C(3)	1.773(2)	1.775(4)
Mn(1)–C(5)	1.885(2)	1.893(3)
C(1)–O(1)	1.155(3)	1.149(4)
C(3)–O(3)	1.155(3)	1.148(5)
C(5)–O(5)	1.334(2)	1.338(4)
C(5)–C(7)	1.523(2)	1.471(4)
C(7)–C(8)	1.540(3)	1.323(4)
Mn(2)–C(2)	1.775(2)	1.775(3)
Mn(2)–C(4)	1.772(2)	1.776(4)
Mn(2)–C(6)	1.880(2)	1.891(3)
C(4)–O(4)	1.150(2)	1.153(6)
C(2)–O(2)	1.153(2)	1.151(4)
C(6)–O(6)	1.346(2)	1.344(3)
C(6)–C(8)	1.521(2)	1.472(4)
Bond angles		
C(1)–Mn(1)–C(3)	91.42(10)	88.6(2)
C(1)–Mn(1)–C(5)	99.73(9)	93.2(1)
C(3)–Mn(1)–C(5)	87.86(9)	97.5(2)
Mn(1)–C(1)–O(1)	173.1(2)	176.8(3)
Mn(1)–C(3)–O(3)	178.9(2)	175.45(3)
O(5)–C(5)–C(7)	103.46(15)	106.4(3)
Mn(1)–C(5)–O(5)	132.37(13)	132.5(2)
Mn(1)–C(5)–C(7)	123.72(13)	120.7(2)
C(5)–C(7)–C(8)	113.82(15)	124.2(2)
C(4)–Mn(2)–C(2)	90.24(9)	90.3(2)
C(4)–Mn(2)–C(6)	95.97(9)	90.4(2)
C(2)–Mn(2)–C(6)	94.17(9)	99.3(1)
Mn(2)–C(4)–O(4)	175.91(19)	179.3(3)
Mn(2)–C(2)–O(2)	177.04(19)	173.9(3)
O(6)–C(6)–C(8)	102.64(15)	106.3(3)
Mn(2)–C(6)–O(6)	132.06(13)	130.9(2)
Mn(2)–C(6)–C(8)	125.17(13)	122.7(2)
C(6)–C(8)–C(7)	108.74(15)	124.9(2)

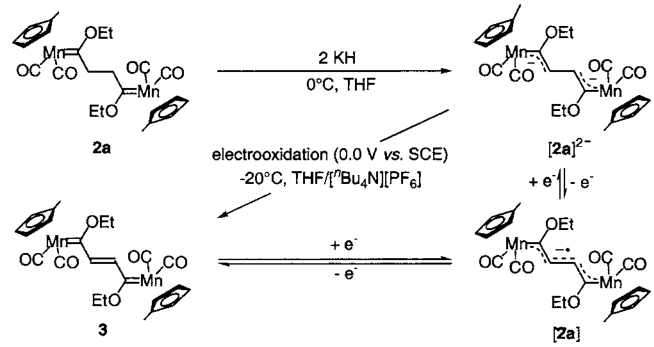
[a] Esd's in parentheses.

complex **2a** (see Table 2). This indicates a substantial delocalisation of the C=C bond within the hydrocarbon link. Yet, the Mn=C bonds are little affected by this phenomenon since both Mn(1)–C(5) and Mn(2)–C(6) bond distances are equal within the experimental error to the Mn=C bonds distances found in complex **2a**.

It is very likely that in the formation of complex **3** proceeds via the intermediacy of a μ-bis(carbene) dianion resulting from a double deprotonation of **2a**, [Li]$_2$[**2a**], followed by an oxidation induced by the Fe(III) salt (or the Cu(II) salt). Though the dianionic complex was not observed due its thermal instability, evidence for its formation was obtained upon treatment with MeI at low temperature, giving complex **2b** in a nearly quantitative yield as a 60:40 mixture of diastereoisomers (Scheme 2).

Efforts to extend the reaction shown on Scheme 3 to complex **2b** failed. Apparently, the hydrogen atoms α to the carbene atom in **2b** are not acidic enough to be removed by ^{n}BuLi. When **2b** was sequentially treated by a slight excess of ^{n}BuLi at −60°C and by MeI, no methylation product could be detected, whereas **2b** was recovered unchanged. In contrast to earlier observations by Casey et al. that even tertiary carbon atom attached to the carbene carbon atom of a chromium Fischer-type carbene complexes can be deprotonated [19], here the Cp′(CO)$_2$Mn fragment we deal with presents a poorer acceptor ability than the (CO)$_5$M (M=Cr, W) fragment and is thus less likely to stabilise tertiary carbanions as those that would form upon deprotonation of **2b**. It is worth noting that attempts to deprotonated **2b** by ^{t}BuLi led to an intricate mixture of compounds.

While seeking the best experimental procedure for the synthesis of **3**, **2a** was deprotonated with the use of KH (Scheme 4). As far as the oxidation reaction is concerned, the reactivity of [K]$_2$ [**2a**] is about the same as [Li]$_2$ [**2a**] as its treatment with $FeCl_3$ (or $CuCl_2/O_2$) at low temperature followed by warming up to room temperature (r.t.) does lead to the formation **3** with a comparable yield. However, the complex [K]$_2$ [**2a**]—



Scheme 4.

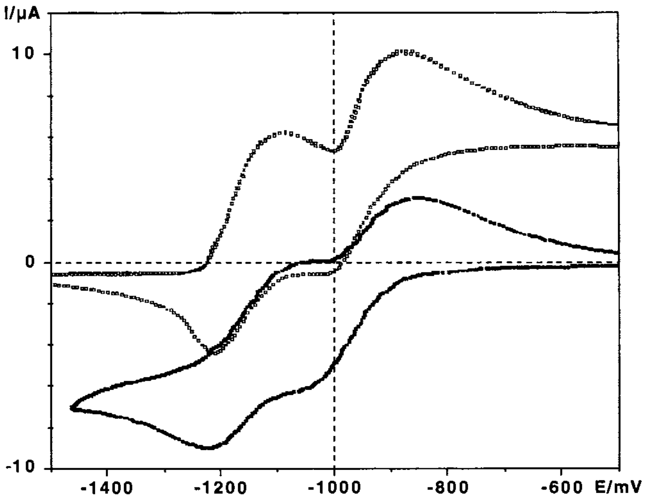


Fig. 3. Cyclic voltammetry of [{Cp′(CO)$_2$Mn}$_2${μ-C(OEt)CHCH-(OEt)C}]$^{2-}$ ([**2a**]$^{2-}$, upper trace) and (*E*)-{Cp′(CO)$_2$Mn}$_2${μ-=C(OEt)CH=CH(OEt)C=} (**3**, lower trace) (−20°C, THF/[^{n}Bu$_4$N]PF$_6$], 0.1 V s^{-1}).

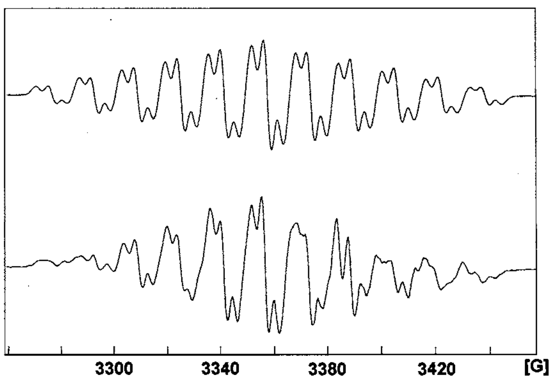


Fig. 4. ESR spectrum (bottom) of [**2a**]$^{•-}$ at 22°C ($g = 2.007$). Simulated spectrum (top) was obtained assuming the unpaired electron was coupled to two equivalent Mn nuclei ($S = 5/2$), and two equivalent H nuclei ($S = 1/2$) with hyperfine coupling constants of $A_{Mn} = 16.2$ G and $A_H = 4.3$ G.

whose IR spectrum shows two bands shifted by 75–100 cm^{-1} with respect to those of **2a**—was found to be much more thermally stable than its lithium analogue. This prompted us to investigate its electrochemical behaviour.

Cyclic voltammetry (CV) of the complex [K]$_2$ [**2a**] at 0°C in THF/[^{n}Bu$_4$N][PF$_6$] medium (scan rate = 0.1 V s^{-1}displays two quasi-reversible one electron oxidation waves at −0.95 and −1.15 V versus Fig. 3, upper trace). Under the same conditions, CV of **3** (Fig. 3, lower trace) shows two quasi-reversible one electron reduction waves at the same potentials as for [**2a**]$^{2-}$. An anodic oxidation of [**2a**]$^{2-}$ at 0.0 V conducted at a platinum gauze electrode at −20°C in THF/[^{n}Bu$_4$N][PF$_6$] medium led to the formation of **3** (Scheme 4).

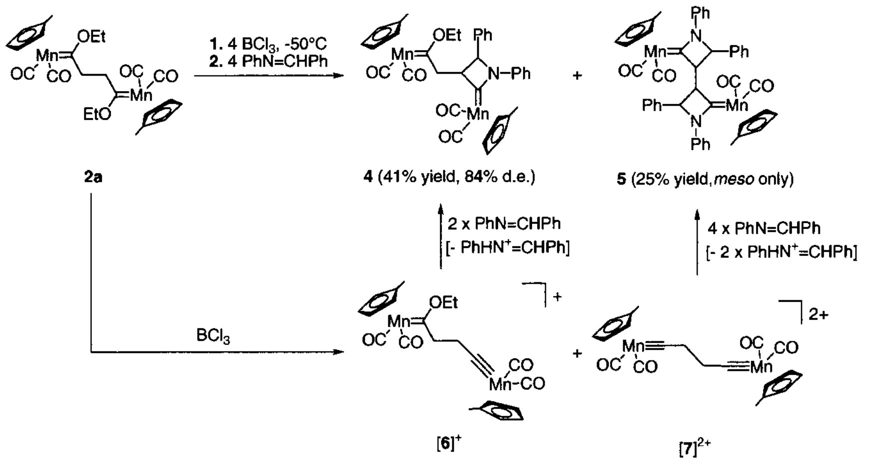
Both controlled reduction of **3** or controlled oxidation of [**2a**]$^{2-}$ on the plateau between the two oxido-reduction waves leads to the formation of the same radical anion [**2a**]$^{-•}$.The r.t. ESR spectrum of this complex shows an hyperfine pattern that consists of an undecet of triplets (Fig. 4). This pattern is consistent with a type III [20] Mn^0/Mn^I mixed-valence complex in which the unpaired electron would be delocalised on the EPR time scale over the two manganese atoms. The electrochemical behaviour of complexes [**2a**]$^{2-}$/**3** is reminiscent of those of closely related dimetal complexes in which a C$_4$ unsaturated hydrocarbon chain spans the two metal centres [21].

*2.3. Synthesis and characterisation of the mixed μ-(alkylalkoxy carbene/azetidinylidene) dimanganese complex {Cp′(CO)$_2$Mn}$_2${μ-=C(OEt)CH$_2$-CHCH(Ph)N(Ph)C=} (**4**) and the μ-bis(azetidinylidene)dimanganese complex {Cp′(CO)$_2$Mn}$_2${μ-=CN(Ph)CH(Ph)CH-CHCH(Ph)N(Ph)C=} (**5**)*

One of our objectives was to use the above μ-bis(alkylalkoxy carbene)dimanganese complexes as precursors of μ-bis(alkyl carbyne)dimanganese complexes. However, when the carbene complex **2a** was reacted with an excess of BCl$_3$ at low temperature-the most typical procedure used for the generation of manganese carbyne complexes [13,14]—the compounds that formed were found to be extremely thermolabile and could not be characterised. We then thought about assaying the formation of dinuclear carbyne complexes by their reaction with *N*-benzylideneaniline. Indeed, some of us previously reported that the cationic alkylcarbyne complexes [Cp′(CO)$_2$Mn≡CCH$_2$R]$^+$ react with imines to produce stable azetidinylidene complexes in high yield through net [2 + 2] cycloaddition reactions [14].

Complex **2a** was thus reacted with an excess of BCl$_3$ and subsequently treated with four M equivalent of N-benzylideneaniline, PhN=CHPh. After chromatographic workup, the two new complexes {Cp′(CO)$_2$Mn}$_2${μ - =C(OEt)CH$_2$CHCH(Ph)N(Ph)C=} (**4**) and {Cp′(CO)$_2$Mn}$_2${μ-=CN(Ph)CH(Ph)CH-CHCH(Ph)N(Ph)C=} (**5**) were isolated in 41 and 25% yield, respectively (Scheme 5).

The structure of complex **4** was inferred from spectroscopic data. The presence of the amino- and the alkoxy-carbene functions within the complex is evidenced in both the IR and ^{13}C-NMR spectra. Indeed, the IR spectrum shows four bands of similar of intensity in the v(CO) region which can be regarded as two sets of two bands. The first set, 1950, 1890 cm^{-1}, is characteristic of the Cp′(CO)$_2$Mn-alkoxy carbene fragment (compare to IR data for **2a** for instance), while



Scheme 5.

the second set, which appears at lower wave numbers, 1935, 1970 cm^{-1}, can be attributed to the Cp′(CO)$_2$Mn-aminocarbene part [14]. The ^{13}C-NMR spectrum also displays two very distinct signals in the carbene carbon region at 337.7 ppm and at 298.9 ppm, which can be attributed to the alkylalkoxy carbene carbon and to the alkylamino carbene carbon, respectively. The ^{1}H-NMR spectrum of **4** indicates the complex forms as a mixture of diastereoisomers. Indeed, the ^{1}H-NMR displays two doublets at 5.58 ppm (J_{HH} = 5 Hz) and 5.27 ppm (J_{HH} = 2 Hz), with an intensity ratio of 8:92. By comparison with the ^{1}H-NMR spectrum of Cp′(CO)$_2$Mn=CN(Ph)CH(Ph)CH(Me) [14], the most intense doublet was assigned to the diastereoisomer in which the benzyl and the methine protons are *trans* to each other. Although we could not obtain a complete data set for the minor isomer (some signals being totally or partially obscured by those of **4**), we tentatively attribute the other doublet to the benzyl proton of the other diastereoisomer (benzyl and the methine protons *cis* to each other).

The second complex isolated from the reaction, {Cp′(CO)$_2$Mn}$_2${μ-=CN(Ph)CH(Ph)CH-CHCH(Ph)N(Ph)C=} (**5**), was characterised both spectroscopically and crystallographically.

A perspective view of complex **5** is given in the Fig. 5. Bond distances and bond angles of interest are gathered in Table 3. The molecule can be described as two azetidinylidene fragments linked together on their α position via the C(5)–C(5)′ carbon–carbon bond. The molecule, that carries four stereogenic centres (C(4), C(5), C(5) #, and C(4) #), could exists under four different diastereomeric forms: two meso forms and four dl pairs. The present molecule possesses a crystallographic inversion centre located in the middle of the C(5)–C(5) # vector (origin of the cell); therefore it is one of the meso form. The Mn=C bond distance (Mn(1)–C(3) = 1.906(6) Å) is equivalent within the experimental error to the Mn=C distance found in the related azetidinylidene complex Cp′(CO)$_2$Mn=CCH$_2$-CH(Ph)N(Ph) (Mn=C = 1.889(4), and 1.894(4) Å for each independent molecule, respectively [14]) and, noticeably, not significantly different from Mn=C bond distances found in compound **2a** or in other manganese alkylalkoxy- or arylalkoxy-carbene complexes [22]. This feature shows that NR$_2$ and OR groups are not different enough in terms of p-donation ability to compete with the Cp′ fragment, which eventually determines the Mn=C bond length. The atoms C(3), C(5), C(5), and N(1), that constitute the four-membered amino carbene cycle, are essentially coplanar [average deviation from least-squares plane is 0.0218 Å with maximum deviation of 0.025 associate with C(4)]. Within the four-membered ring, the C(5)–C(4) and the C(5)–C(3) bond distances are equivalent whilst the N(1)–C(3) distance is significantly shorter than the N(1)–C(4) bond [C(3)–N(1) = 1.348(8) Å; N(1)–C(4) = 1.483(7) Å] thus evidencing substantial p-donation from the nitrogen atom to the carbene carbon atom.

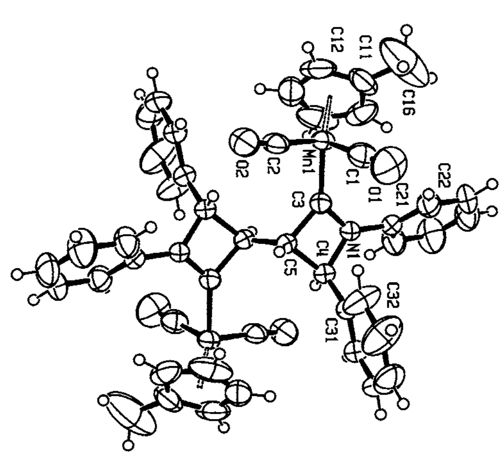


Fig. 5. Perspective view of the complex {Cp′(CO)$_2$Mn}$_2${μ-=CNPhCH(Ph)CHCHCH(Ph)N(Ph)C=} (**5**).

Table 3
Bond distances (Å) and bond angles (°) of interest for compound **5** [a,b]

Bond distances	
Mn(1)–C(2)	1.750(8)
Mn(1)–C(1)	1.758(9)
Mn(1)–C(3)	1.906(6)
Mn(1)–C(12)	2.126(9)
Mn(1)–C(13)	2.131(12)
Mn(1)–C(11)	2.148(9)
Mn(1)–C(15)	2.150(10)
Mn(1)–C(14)	2.155(10)
C(1)–O(1)	1.160(11)
C(2)–O(2)	1.175(9)
C(3)–N(1)	1.348(8)
C(3)–C(5)	1.566(8)
N(1)–C(4)	1.483(7)
C(4)–C(5)	1.565(8)
C(5)–C(5) #	1.535(12)
Bond angles	
C(2)–Mn(1)–C(1)	89.5(4)
C(2)–Mn(1)–C(1)	89.5(4)
C(2)–Mn(1)–C(1)	89.5(4)
C(2)–Mn(1)–C(3)	94.4(3)
C(1)–Mn(1)–C(3)	88.2(3)
Mn(1)–C(1)–O(1)	180.0(7)
Mn(1)–C(2)–O(2)	175.5(6)
N(1)–C(3)–C(5)	90.1(4)
Mn(1)–C(3)–N(1)	133.3(4)
Mn(1)–C(3)–C(5)	136.5(4)
C(3)–N(1)–C(4)	98.1(4)
N(1)–C(4)–C(5)	85.4(4)
C(4)–C(5)–C(5) #	112.7(6)
C(3)–C(5)–C(5) #	113.2(6)
C(3)–C(5)–C(4)	86.3(4)

[a] Esd's in parentheses.
[b] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$.

In solution, the RMN data are consistent with the structure in the solid state. In particular, the methyne fragments appear at 6.13 and 3.75 ppm as singlets as one expected for the meso form shown in Fig. 5 . It is worth noting that no other diastereomer of **5** could be detected in the NMR spectra of the crude reaction mixture yet after filtration on short column of alumina. Under the specific reaction conditions described in Scheme 5, complex **5** thus seems to form in a diastereoselective manner.

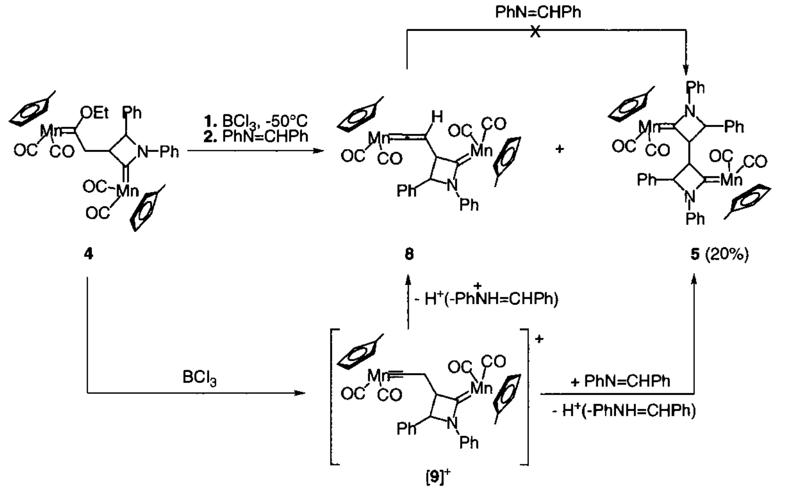
Even though we were unable to clearly identify any of the compounds formed after the initial addition of BCl_3, the nature of the compounds isolated at the end of the reaction sequence strongly suggests that the reaction of BCl_3 and **2a** leads to a mixture of the mixed μ-(carbene-carbyne)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=C(OEt)CH_2CH_2C≡$\}^+$ [**6**]$^+$, and the μ-bis(carbyne)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu$-≡CCH_2CH_2C≡$\}^{2+}$ [**7**]$^{2+}$. Complex **4** can be seen as the result of a formal [2 + 2] cycloaddition reaction between [**6**]$^+$ and PhN=CHPh, whilst **5** would be the reaction product of 2 × [2 + 2] cycloadditions between [**7**]$^{2+}$ and PhN=CHPh, as shown in Scheme 5.

2.4. Synthesis and characterisation of the mixed μ-(vinylidene/azetidinylidene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=C=CHCHCH(Ph)N(Ph)C=} (8)

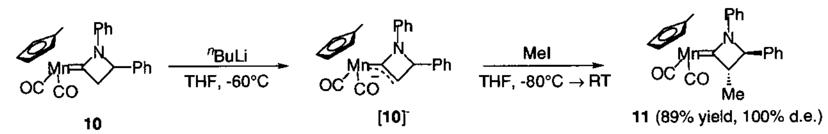
In an attempt to convert the dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu$ - =C(OEt)CH_2CHCH(Ph)N(Ph)C=} (**4**) into the μ-bis(azetidinylidene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=CN(Ph)CH(Ph)CH-CHCH(Ph)N(Ph)C=} (**5**), complex **4** was reacted with BCl_3 followed by PhN=CHPh. Although **5** could indeed be produced in that manner, the major product of the reaction was found to be the mixed μ-(vinylidene/azetidinylidene)dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=C=CHCHCH(Ph)N(Ph)C=} (**8**). At this stage NMR analysis of the mixture showed the compounds **5** and **8** to be present in a 32:68 ratio. Attempts to separate the two complexes remained unsuccessful, extensive chromatographic workup leading to the decomposition of **8**. Only complex **5** could be ultimately isolated in a pure form in 20% yield.

The structure of complex **8** has been inferred from spectroscopic data. As for complex **4**, IR and ^{13}C-NMR spectra of **8** clearly indicate the presence of two different functions in the complex. The IR spectrum shows three bands in the νCO region which can be reduced to two sets of two bands 1998, 1939 cm^{-1}, and 1939, 1875 cm^{-1}. The second set is characteristic of the azetidinylidene moiety (vide supra), while the first set compares well with CO stretches in $Cp'(CO)_2$Mn-vinylidene complexes ($Cp'(CO)_2$Mn=C=CH(Me) (νCO: 1992, 1928 cm^{-1} in CH_2Cl_2). The C=C stretch of the vinylidene moiety is observed at 1646 cm^{-1} ($Cp'(CO)_2$-Mn=C=CH(Me): νCC 1662 cm^{-1} in CH_2Cl_2 [14]). The ^{13}C-NMR spectrum of **8** shows two very distinct signals in the low field region at 372.2 and 297.0 ppm. The first signal can unambiguously be attributed to the α-carbon atom of the vinylidene part [14], while the second one can be assigned to the azetidinylidene carbon atom (vide supra). Other NMR data are in good agreement with the proposed structure.

Considering the nature reaction products, it is very likely that $\{Cp'(CO)_2Mn\}_2\{\mu$-=C(OEt)-CH_2CHCH(Ph)N(Ph)C=} (**4**) react with BCl_3 to afford the carbyne complex $\{Cp'(CO)_2Mn\}_2\{\mu$-≡CCH_2CHCH(Ph)N(Ph)C=} [**9**]$^+$, as shown in Scheme 6. Upon addition of the imine, two reaction pathways would compete: (i) a deprotonation of the carbon atom



Scheme 6.



Scheme 7.

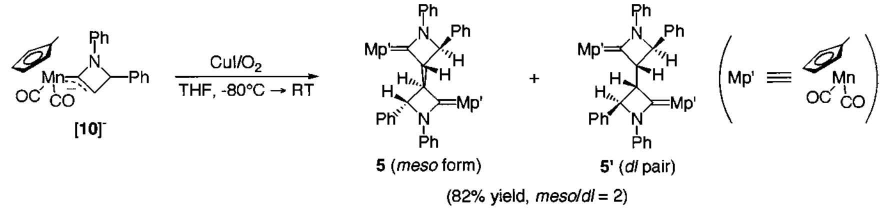
α to the carbyne carbon atom by the imine would lead to **8**, or (ii) the nucleophilic attack of the imine on the carbyne carbon atom would give the adduct $[\mathbf{10}]^+$, which in turn would undergo a deprotonation—likely by the imine present in the medium [14]—to give **5** as the final product. It is worth noting that whereas the vinylidene complex Cp′(CO)$_2$Mn=C=CH(Me) reacts with PhN=CHPh to give the azetidinylidene complex Cp′(CO)$_2$Mn=CN(Ph)CH(Ph)CH(Me) [14], complex **8** do not react with PhN=CHPh neither in the above reaction condition nor at r.t, probably for steric reasons.

2.5. Oxidative coupling of the azetidinylidene anion [Cp′(CO)$_2$Mn=CN(Ph)CHPhCH]$^-$ ([**10**]$^-$)

As noted in Section 2.3, complex **5** can be viewed as the association of two azetidinylidene moieties [Cp′(CO)$_2$Mn=CN(Ph)CH(Ph)CH] linked together on their α position. It was naturally tempting to check whether complex **5** could be synthesised via oxidative coupling of the azetidinylidene anion [Cp′(CO)$_2$Mn=CN(Ph)CH(Ph)CH]$^-$.

In a preliminary experiment aimed at assaying the formation of an azetidinylidene anion, complex Cp′(CO)$_2$Mn=CN(Ph)CHPhCH$_2$ (**10**) [14] was sequentially treated with ^{n}BuLi and methyl iodide. This effectively produced the methylated derivative Cp′(CO)$_2$-Mn=CN(Ph) CHPhCH(Me) (**11**) in almost quantitative yield. In addition, an NMR analysis of the crude reaction mixture showed the methylation reaction to be totally *trans* selective (Scheme 7).

The azetidinylidene anion [Cp′(CO)$_2$Mn=CN-(Ph)CH(Ph)CH]$^-$ [**10**]$^-$ was next allowed to react at low temperature with a suspension 0.6 equivalent of CuI followed by oxygen (Scheme 8). In addition to traces of unreacted complex **10**, the ^{1}H-NMR analysis of the crude reaction mixture indicated the formation two complexes in a 2:1 ratio. As expected, **5** was the most abundant, whereas the minor product **5′** was identified as a stereoisomer of **5**. The structure of **5′** was inferred from the NMR data. The observation of two singlets only in the ^{1}H-NMR spectrum (δ 5.71 and 3.95



Scheme 8.

ppm) for its four methine groups implies that (i) the protons within each of the azetidinylidene rings are *trans* to each other and (ii) the corresponding protons in each of the azetidinylidene rings are magnetically equivalent. Among the six stereoisomers that are distinguishable by NMR—four *dl* pairs and two meso forms—only two have structures compatible with such an NMR spectrum, the meso form **5** (vide supra) and the dl pair **5′** as drawn on Scheme 8.

Considering the structures of **5** and **5′**, it appears that the oxidative coupling of the azetidinylidene rings occurs exclusively in *trans* position relative to the phenyl groups-just like the methylation reaction shown in Scheme 7 — but the overall reaction is poorly stereoselective with respect to the relative configuration of the α carbon atoms of the azetidinylidene rings **3**.

3. Conclusion

In summary, we have shown that carbene anions resulting from in situ deprotonation of manganese alkoxy- or amino-carbene complexes bearing primary or secondary carbon atoms in the α position relative to the carbene carbon atom can undergo intermolecular oxidative coupling in the presence of Cu(I), Cu(II), or Fe(III) to afford μ-bis(carbene)dimanganese complexes in good yield. It has been observed that such an oxidative coupling can also take place in an intramolecular fashion as a manganese μ-bis(carbene)dianion was converted into μ-bis(vinylcarbene)dimanganese upon reaction with a Fe(III) salt.

This type of reaction, a convenient route to carbon-linked bis(carbene)dimetal complexes, is not specific of manganese complexes, since it has been also observed with chromium carbene complexes [16b].

Treatment of the μ-bis(alkylalcoxy carbene)-dimanganese complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH(R)CH(R)(OEt)C{=}\}$ with a Lewis acid gave an extremely labile species. However, subsequent reaction with benzylidene aniline gave evidence for the formation of transient dinuclear alkyl carbyne complexes and allowed the synthesis a series of unusual species such as μ-(alkylalkoxy carbene/carbyne)-, μ-(alkylalkoxy carbene/azetidinylidene)-, μ-(vinylidene/azetidinylidene)- or even μ-bis(azetidinylidene)dimanganese complexes.

4. Experimental

4.1. General

The complexes $Cp'(CO)_2Mn{=}C(OEt)CH_3$ (**1a**) [23], $Cp'(CO)_2Mn{=}C(OEt)CH_2CH_3$ (**1b**), [24]and $Cp'(CO)_2$-$Mn{=}CCH_2CH(Ph)N(Ph)$ (**10**) [14]were prepared by published procedures. Tetrahydrofuran and diethyloxide used for the synthesis were distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following standard procedure, and stored under nitrogen. The following reagent grade chemicals PhN=CH(Ph), BCl_3 (1 M solution in hexane), ^{n}BuLi (1.6 M solution in hexane), $CuCl_2$, $CuBr_2$, CuI_2, CuI, $FeCl_3$, and MeI were obtained from Aldrich and used without further purification. All synthetic manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. A liquid N_2/isopropanol slush bath was used to maintain samples at the desired low temperature. Chromatographic separation of the complexes was performed on alumina (neutral, activity III (Aldrich)). Solution IR spectra were recorded on either Perkin–Elmer 225 or Perkin–Elmer 983G spectrophotometer with 0.1 mm cells equipped with CaF_2 windows. ^{1}H, and ^{13}C spectra were obtained on Brucker AC200 or WM250 spectrometers in C_6D_6 and were referenced to the residual signals of the solvent. Mass spectra were recorded on a Nermag R10-10 mass spectrometer (EI). Microanalysis of C, H, and N elements were performed on a Perkin–Elmer 2400 CHN analyser. Electrochemical studies were carried out on a home-made potensiostat [25].

4.2. Preparation of $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)CH_2CH_2(OEt)C{=}\}$ (**2a**)

4.2.1. Cu(I)/O_2-assisted synthesis

The carbene complex $Cp'(CO)_2Mn{=}C(OEt)CH_3$ (**1a**) (500 mg, 1.9 mmol) was dissolved in 10 ml of THF. The solution was cooled at −60°C and ^{n}BuLi (1.3 ml of a 1.6 M solution in hexane, 2.1 mmol) was added dropwise via syringe. After stirring for 30 min, the solution was cooled to −80°C and CuI (217 mg, 1.1 mmol) was added. When all the solid CuI disappeared (2 h) dry oxygen was bubbled to the solution for 30 s, which caused the orange solution to turn yellow–brown. The solvent was then removed under vacuum while the reaction flask was allowed to reach r.t. The residue was extracted with ether (50 ml) and filtered on a short column of alumina. The filtrate was evaporated to dryness and recrystallisation of the residue from diethyloxide/hexane left complex $\{Cp'(CO)_2Mn\}_2\{\mu\text{-}{=}C(OEt)$-$CH_2CH_2(OEt)C{=}\}$ (**2a**) as an orange microcrystalline compound in 63% yield (315 mg, 0.6 mmol).

4.2.2. Fe(III) assisted synthesis

The carbene anion was generated as above from $Cp'(CO)_2Mn{=}C(OEt)CH_3$ (**1a**) (3 g, 11.5 mmol) in solution in THF (25 ml) and ^{n}BuLi (8 ml of a 1.6 M solution in hexanes, 12.7 mmol). After stirring for 30 min, the solution was cooled to −80°C and anhydrous $FeCl_3$ (2.06 g, 12.7 mmol) was added. The reaction mixture was stirred for 3 h while maintaining the temperature at −80°C. The mixture was warmed to r.t, then filtered on a short column of alumina. The filtrate was evaporated to dryness and recrystallisation of the residue as above afforded complex **2a** in 85% yield (2.5 g, 4.8 mmol).

4.2.3. Synthesis via electrooxidation

The carbene complex $Cp'(CO)_2Mn{=}C(OEt)CH_3$ (**1a**) (306 mg, 1.2 mmol) was dissolved in a Schlenk flask in 50 ml of THF. The solution was cooled at −60°C and ^nBuLi (1.3 ml of a 1.6 M solution in hexane, 2.1 mmol) was added dropwise via syringe. After stirring for 30 min $[^nBu_4N][PF_6]$ (1.93 g, 5 mmol) was added and the mixture was transferred with the use of a cannula to the anodic compartment of electrolysis cell precooled at −30°C. The working electrode was a Pt foil (ca. 16 cm^2), the reference electrode consisted of a SCE separated from the solution by a bridge compartment filled with a solution of the same supporting electrolyte in the same solvent as used in the cell. The counter-electrode was a spiral of Pt wire of ca. 1 cm^2 apparent surface area. The electrolysis was performed at 0.6 V (versus SCE). When one electron was exchanged, the electrolysis was stopped. The electrolysis cell was warmed to r.t, the solution was transferred in a Schlenk flask and evaporated to dryness. The residue was extracted with diethyloxide (2 × 20 ml) and chromatographic workup as above gave complex **2a** in 42% yield (130 mg, 0.25 mmol).

2a: Anal. Calc. for $C_{24}H_{28}Mn_2O_6$: C, 55.17; H, 5.36. Found: C, 55.20; H, 5.44% **IR** (νCO, CH_2Cl_2) 1945, 1880 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 4.66 (q, 4H, $J_{HH} = 7$ Hz, $-OCH_2CH_3$), 4.57–4.33 (m, 8H, $C_5H_4CH_3$), 3.02 (s, 4H, $-CH_2CH_2-$), 1.73 (s, 6H, $C_5H_4CH_3$), 1.19 (t, 6H, $J_{HH} = 7$ Hz, $-OCH_2CH_3$). ^{13}C-NMR (C_6D_6): δ 338.53 (Mn=*C*), 233.6 (Mn–*C*O), 103.7, 87.5, 86.3, ($C_5H_4CH_3$), 72.3 ($-OCH_2CH_3$), 57.9 ($-CH_2CH_2-$), 14.9, 13.6 ($C_5H_4CH_3$ and $-OCH_2CH_3$). MS (EI) *m/z* 522 (M^+).

4.3. Preparation of {Cp′(CO)₂Mn}₂{μ-=C(OEt)CH-(Me)C(Me)(OEt)C=} (2b)

4.3.1. From $Cp'(CO)_2Mn{=}C(OEt)CH_2CH_3$ (1b)

The carbene complex **1b** (630 mg, 2.3 mmol) was dissolved in 10 ml of THF. The solution was cooled at −60°C and ^nBuLi (1.6 ml of a 1.6 M solution in hexane, 2.5 mmol) was added dropwise via syringe. After stirring for 30 min, the solution was cooled to −80°C and $FeCl_3$ (406 mg, 2.5 mmol) was added. The reaction mixture was stirred for 3 h while maintaining the temperature at −80°C. The solution was warmed to r.t. and evaporated to dryness under vacuum. The residue was extracted with ether (50 ml) and filtered on a short column of alumina. The filtrate was evaporated to dryness and recrystallisation of the residue from diethyloxide/hexane gave complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=C(OEt)CH(Me)CH(Me)(OEt)C=} (**2b**) as an orange microcrystalline compound in 65% yield (407 mg, 0.7 mmol). NRM analysis of **2b** showed the complex to form as a 1:1 mixture of the diastereoisomers.

4.3.2. From $\{Cp'(CO)_2Mn\}_2\{\mu$-=C(OEt)-CH_2CH_2(OEt)C=} (2a)

The carbene complex **2a** (261 mg, 0.5 mmol) was dissolved in THF (15 ml). The solution was cooled at −60°C and ^nBuLi (0.69 ml of 1.6 M solution in hexane, 1.1 mmol) was added dropwise via syringe. After stirring for 30 min the solution was cooled to −80°C and an excess of MeI (0.093 ml, 1.5 mmol) was added. The cooling bath was removed to allow the solution to warm to r.t. The THF was evaporated under vacuum, the residue was extracted with ether, and filtered on a short column of alumina. Recrystallisation of the crude product from diethyloxide/hexane gave complex **2b** in 85% yield (240 mg, 0.44 mmol).

2b: Anal. Calc. for $C_{26}H_{32}Mn_2O_6$: C, 56.74; H, 5.86. Found: C, 56.27; H, 5.86% IR (νCO, CH_2Cl_2) 1945, 1880 cm^{-1}. ^{1}H-NMR (C_6D_6, mixture of diastereoisomers **2b** and **2b′**): δ 4.8-4.2 (m, $-OCH_2CH_3$ and $C_5H_4CH_3$), 3.93 (AA′($X_3X'_3$) pattern, 2H, $J_{AA'} = 6.7$ Hz, $J_{AX} = 6.9$ Hz, $-CH(CH_3)CH(CH_3)-$, isomer **2b**), 3.71 (AA′($X_3X'_3$) pattern, 2H, $J_{AA'} = 10.7$ Hz, $J_{AX} = 6.5$ Hz, $-CH(CH_3)CH(CH_3)-$, isomer **2b′**), 1.76 (s, 6H, $C_5H_4CH_3$), 1.75 (s, 6H, $C_5H_4CH_3$), 1.20 (t, 6H, $J_{HH} = 7.0$ Hz, $-OCH_2CH_3$), 1.18 (t, 6H, $J_{HH} = 7.0$ Hz, $-OCH_2CH_3$), 0.96 ((AA′)$X_3X'_3$ pattern, 3H, $-CH(CH_3)CH(CH_3)-$, isomer **2b′**), 0.91 ((AA′)$X_3X'_3$ pattern, 3H, $-CH(CH_3)CH(CH_3)-$, isomer **2b**). **^{13}C-NMR** (C_6D_6, mixture of diastereoisomers): δ 344.4 (Mn=*C*), 233.5, 234.2 (Mn–*C*O), 104.2, 103.2, 88.75–85.9, ($C_5H_4CH_3$), 73.0, 72.7 ($-OCH_2CH_3$), 65.7, 65.5 ($-CH(CH_3)CH(CH_3)-$), 18.3, 18.11, 15.4, 15.2, 14.2 ($C_5H_4CH_3$, $-OCH_2CH_3$ and $-CH(CH_3)CH(CH_3)-$). MS (EI) *m/z* 550 (M^+), 466 (M^+–3CO), 438 (M^+–4CO).

4.4. Preparation of (E)-{Cp′(CO)₂Mn}₂{μ-=C(OEt)CH=CH(OEt)C=} (3)

4.4.1. Fe(III)-assisted synthesis

The complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=C(OEt)CH_2CH_2-(OEt)C=} (**2a**) (260 mg, 0.5 mmol) was dissolved in THF (10 ml). The solution was cooled at −60°C and ^nBuLi (0.68 ml of 1.6 M solution in hexane, 1.1 mmol) was added drop wise via syringe. After stirring for 30 min, the solution was cooled to −80°C and $FeCl_3$ (178 mg, 1.1 mmol) was added. After stirring for 3 h at −80°C the solution was allowed to reach r.t. by removing the cooling bath. The resulting deep purple solution was filtrated on a short column of alumina, the THF was evaporated under vacuum, and the oily residue was dissolved in pure pentane. Compound **3** was obtained as black crystals (195 mg, 75% yield) upon standing of the solution at -30°C overnight.

4.4.2. Synthesis via electrooxydation

THF (20 ml) was slowly introduced via syringe to a Schlenk flask containing $Cp'(CO)_2Mn\}_2\{\mu-=C(OEt)$-$CH_2CH_2(OEt)C=\}$ (**2a**) (260 mg, 0.5 mmol) and KH (45 mg, 1.1 mmol) precooled at 0°C. After IR monitoring showed total disappearance of **2a** [νCO (THF) 1943, 1878 cm^{-1}] to the profit of $[Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)CH_2CH_2(OEt)C=\}]$ $[\mathbf{2a}]^{2-}$ [νCO (THF) 1865, 1780 cm^{-1}], the solution was transferred via cannula to the anodic compartment of electrolysis cell containing a solution of $[^nBu_4N][PF_6]$ (1.93 g, 5 mmol) in THF (20 ml) precooled at -30°C, see section Section 4.2. The electrolysis was performed on the plateau between the two oxido-reduction waves (-1000 mV versus SCE). When one electron was exchanged, the electrolysis was stopped and a 1 ml aliquot of the solution was transferred into an EPR tube for analysis. The electrolysis was resumed at 0.0 mV versus SCE until one more electron was exchanged. At this stage, the electrolysis was stopped and the residue was extracted with diethyloxide (2×20 ml). After chromatographic workup, the complex **3** was isolated 57% yield as a microcrystalline black solid.

3: Anal. Calc. for $C_{24}H_{26}Mn_2O_6$: C, 55.38; H, 5.00. Found: C, 55.27; H, 5.09%. IR (νCO, Et_2O) 1940, 1885 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 6.85 (s, 2H, –*H*C=C*H*–), 4.50 (q, 4H, J_{HH}=7 Hz, –OCH_2CH$_3$), 4.6–4.4 (m, 8H, $C_5H_4CH_3$), 1.64 (s, 6H, $C_5H_4CH_3$), 1.23 (t, 6H, $J_{HH}=7$ Hz, –OCH$_2$CH_3). ^{13}C-NMR (C_6D_6): δ 319.6 (Mn=*C*), 234.5 (Mn–*C*O), 129.1 (s, –H*C*=*C*H–), 105.4, 88.8, 88.0, ($CH_3C_5H_5$), 72.1 (–OCH_2CH$_3$), 15.5, 14.0 ($C_5H_4CH_3$ and –OCH$_2$CH_3). MS (EI) *m*/*z* 520 (M$^+$), 464 (M$^+$ $-$2CO).

*4.5. Reaction of $\{Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)$-$CH_2CH_2(EtO)C=\}$ (**2a**) with BCl_3, followed by N-benzylideneaniline*

Complex **2a** (220 mg, 0.42 mmol) was dissolved in a mixture of dichloromethane (5 ml) and toluene (15 ml). The solution was cooled to -50°C and BCl_3 (1.7 ml of a 1 M solution in hexane, 1.7 mmol) was added dropwise via syringe, which caused deposition of a red oil. After stirring for 20 min, the supernatant was removed with the use of a cannula. The flask was cooled to -80°C, the residue was dissolved in THF (20 ml), and PhN=C(H)Ph (310 mg dissolved in 5 ml of THF, 1.7 mmol) was added with the use of a cannula. After stirring for 2 h at -80°C the solution was allowed to reach r.t. by removing the cooling bath. The THF was removed under vacuum and the residue was extracted with ether (20 ml). The solution was filtered on a short column of alumina, concentrated to ~ 2 ml under vacuum, and chromatographed on alumina. Elution with a 10:1 pentane/diethyloxide mixture gave an orange band containing complex $\{Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)CH_2CHCH(Ph)N(Ph)C=\}$ (**4**), and continued elution with 1:1 pentane/diethyloxide gave a red band of $\{Cp'(CO)_2Mn\}_2\{\mu$-=CN(Ph)CHPhCHCHCHPhN-(Ph)C=$\}$ (**5**). Removal of the solvent from the collected bands gave **4** as an orange oil (112 mg, 41% yield) and **5** a dark orange microcrystalline solid (82 mg, 25% yield). NMR analysis of **4** showed the complex to form as a mixture of two diastereoisomers, **4** and **4′**, in a 8:92 ratio.

4: Anal. Calc. for $C_{35}H_{33}Mn_2NO_5$: C, 63.93; H, 5.06; N, 2.13. Found: C, 66.57; H, 5.59; N, 1.98%. IR (νCO, Et_2O) 1950, 1935, 1890, 1870 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 7.3–6.8 (m, 10H, C_6H_5), 5.27 (d, 1H, $J_{HdHc}=2$ Hz, H_d), 4.8–4.2 (m, 8H, $C_5H_4CH_3$), 4.55 (ABX$_3$ pattern, 2H, $J_{HH}=1$ Hz, $J_{HH(Me)}=7$ Hz, –OCH_2CH$_3$), 4.25 (dd, 1H, $J_{HaHb}=15$ Hz, $J_{HaHc}=4$ Hz, H_a), 3.56 (dd, 1H, $J_{HbHa}=15$ Hz, $J_{HbHc}=12$ Hz, H_b), 3.37 (ddd, 1H, $J_{HcHd}=2$ Hz, $J_{HcHa}=4$ Hz, $J_{HcHb}=12$ Hz, H_c), 1.83 (s, 3H, $C_5H_4CH_3$), 1.72 (s, 3H, $C_5H_4CH_3$), 0.72 (t, 3H, $J_{HH}=7$ Hz, –OCH$_2$CH_3). ^{13}C-NMR (C_6D_6): δ 337.2 (Mn=*C*(OEt)–), 298.9 (Mn=*C*(NPh)–), 234.1(br, Mn–*C*O), 135–120 (m, C_6H_5), 104.0, 101.6, 88.2, 87.1, 84.3, 84.1, 83.7, 82.9 ($C_5H_4CH_3$), 80.2, (–*C*HPh–), 73.3 (–O*C*H$_2$CH$_3$), 63.7 (–*C*HCH$_2$–), 62.2 (–*C*H$_2$–), 14.8, 14.6, 14.1 ($C_5H_4CH_3$ and –OCH$_2$*C*H$_3$). MS (EI) *m*/*z* 657 (M +), 573 (M + –3CO).

4′ (from a mixture of 4/4′): 1H-NMR (C_6D_6): δ 7.3–6.8 (m, 10H, C_6H_5), 5.58 (d, 1H, $J_{HdHc}=5$ Hz, H_d), 1.82 (s, 3H, $C_5H_4CH_3$), 1.62 (s, 3H, $C_5H_4CH_3$), 1.20 (t, 3H, $J_{HH}=7$ Hz, –OCH$_2$CH_3) (due to overlapping with the signals of 4, the –OCH$_2$CH$_3$, $C_5H_4CH_3$, and –CHCH$_2$– groups could not be unambiguously identified).

5: Calc. for $C_{23}H_{16}MnNO_2$: C, 69.70; H, 4.83; N, 3.53. Found: C, 69.39; H, 5.29; N, 3.53%. IR (νCO, Et_2O) 1935, 1865 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 7.6–6.8 (m, 10H, C_6H_5), 6.13 (s, 1H, –C*H*Ph), 4.5–4.2 (m, 4H, $C_5H_4CH_3$), 3.75 (s, 1H, –C*H*–), 1.73 (s, 3H, $C_5H_4CH_3$). ^{13}C-NMR (C_6D_6): δ 296.1 (Mn=*C*(NPh)–), 234.6 (Mn–*C*O), 136.4–122.2 (m, C_6H_5), 102.1, ($C_5H_4CH_3$), 88.9–85.2, ($C_5H_4CH_3$), 78.7 (–*C*HPh–), 65.6 (–*C*H–), 14.3 ($C_5H_4CH_3$). MS (EI) *m*/*z* 792 (M$^+$), 736 (M$^+$ –2CO).

*4.6. Synthesis of $\{Cp'(CO)_2Mn\}_2\{\mu$-$=C(OEt)$-$CH_2CHCH(Ph)N(Ph)C=\}$ (**4**).*

The complex $\{Cp'(CO)_2Mn\}_2\{\mu$-=C(OEt)CH$_2$CH$_2$C-(OEt)=$\}$ (**2a**) (260 mg, 0.5 mmol) was dissolved in a mixture of toluene (5 ml) and hexane (15 ml). The solution was cooled to -50°C, and BCl_3 (1.1 ml of a 1

M solution in hexane, 1.1 mmol) was added dropwise via syringe, which caused deposition of a red oil. After the addition of BCl_3 was complete, the reaction mixture was stirred an additional 15 min, then the supernatant was removed with the use of a cannula. The flask was cooled to −80°C and residue was dissolved in THF (20 ml). To this was added via cannula PhN=C(H)Ph (200 mg dissolved in 5 ml of THF, 1.1 mmol). The reaction flask was allowed the slowly warm to r.t, the THF was removed under vacuum, and the residue was extracted with ether (20 ml). The solution was filtered on a short column of celite, concentrated to ~2ml under vacuum, and chromatographed on alumina. Elution with a 1:1 pentane/diethyloxide mixture gave an orange band containing a mixture of complexes **4**, **4′**, and **5**. At this stage, NMR analysis of the mixture showed the compounds **4**, **4′**, and **5** to be present in a 21:3:1 ratio. The mixture was chromatographied again on a alumina column. Elution with a 10:1 pentane/diethyloxide mixture gave an orange band containing complexes **4** and **4′**. Removal of the solvents from this fraction left complex **4** as a red–orange oil (220 mg, 0.33 mmol, 68% yield, 9:1 mixture of diastereoisomers).

*4.7. Reaction of {Cp′(CO)₂Mn}₂{μ-=C(OEt)-CH₂CHCH(Ph)N(Ph)C=} (**4**) with BCl₃ followed by N-benzylideneaniline*

Complex **4** (220 mg, 0.33 mmol) was dissolved in a mixture of toluene (5 ml) and hexane (15 ml). The solution was cooled to −50°C and BCl_3 (0.66 ml of a 1 M solution in hexane, 0.66 mmol) was added dropwise via syringe, which caused deposition of a red oil. After the addition of BCl_3 was complete, the reaction mixture was stirred an additional 15 min, then the supernatant was removed with the use of a cannula. The flask was cooled to −80°C and the residue was dissolved in THF (20 ml). To this was added via cannula PhN=CHPh (120 mg dissolved in 5 ml of THF, 0.66 mmol). The reaction flask was then allowed to slowly warm to r.t, the THF was removed under vacuum, and the residue was extracted with ether (20 ml). The solution was filtered on a short column of celite, concentrated to ~2ml under vacuum, and chromatographed on a short column of alumina. Elution with a 1:1 pentane/diethyloxide mixture gave an orange band containing a mixture of complexes **5** and {Cp′(CO)$_2$-Mn}$_2${μ-=CCHCHCH(Ph)N(Ph)C=} (**8**). At this stage

Table 4
Experimental data for X-ray study of compounds **2a**, **3** and **5**

	2a	**3**	**5**
Formula	$C_{22}H_{28}Mn_2O_6$	$C_{46}H_{40}Mn_2N_2O$	$C_{24}H_{28}Mn_2O_6$
F_w (amu)	522.36	520.36	792.72
a (Å)	10.047(1)	10.172(6)	10.039(2)
b (Å)	11.404(1)	11.095(3)	8.523(1)
c (Å)	11.460(1)	11.356(3)	22.821(2)
α (°)	106.61(1)	105.42(2)	
β (°)	108.07(1)	93.07(5)	94.56(1)
γ (°)	91.02(1)	108.06(5)	
V (Å^3)	1187.9(3)	1162(1)	1946.5(5)
Z	2	2	4
D_{calc} (g cm^{-3})	1.46	1.46	1.352
Space group	C_i^1-$P1$ (bar)	C_i^1-$P1$ (bar)	C_{2h}^5-$P2_1/n$
T (°C)	22	22	22
Radiation		Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)	
μ(Mo–K$_\alpha$) (cm^{-1})	10.55	10.791	6.663
Transmission factors	1−0.973	1−0.952	1−0.934
Receiving aperture (mm)	4.0×4.0	4.0×4.0	4.0×4.0
Scan speed (deg min^{-1})	variable, 2–5.5	variable, 2–8	variable
Scan mode	$\omega/2\theta$	ω	$\omega/2\theta$
Scan range (°)	0.8	0.9	0.8
2θ limit (°)	2–50	2–48	2–46
Unique data used in final refinment, $Fo^2 > n\sigma(Fo^2)$	4169 ($n=2$)	3407 ($n=3$)	1806 ($n=3$)
Final number of variables	293	289	184
R (on Fo^2, $Fo^2 > 3\sigma(Fo^2)$)	0.026		
R (on Fo^2, $Fo^2 > 3\sigma(Fo^2)$)	0.069		
R (on Fo, $Fo^2 > 3\sigma(Fo^2)$)		0.032	0.032
R_w (on Fo, $Fo^2 > 3\sigma(Fo^2)$)		0.034	0.060

NMR analysis of the mixture showed the compounds **5** and **8** to be present in a 32:68 ratio. Attempts to separate the two complexes have been unsuccessful. However, extensive chromatographic workup lead to the decomposition of compound **8** and complex **5** could be ultimately isolated in a pure form in 20% yield.

8: IR (Et_2O) $\nu_{C=O}$ 1998(m), 1939(s), 1875(m); $\nu_{C=C}$ 1646(*w*) cm^{-1}. ^{1}H-NMR (C_6D_6): δ 7.6–6.8 (m, 10H, C_6H_5), 5.95 (d, 1H, $J_{HdHc}=9$ Hz, =C=C*H*–), 5.40 (d, 1H, $J_{HH}=2$ Hz, –C*H*(Ph)–), 4.7–4.2 (m, 8H, $C_5H_4CH_3$), 3.51 (dd, 1H, $J_{HH}=9$ Hz, 2 Hz, –C*H*CH(Ph)–), 1.88 (s, 3H, $C_5H_4CH_3$), 1.53 (s, 3H, $C_5H_4CH_3$). ^{13}C-NMR (C_6D_6): δ 372.2 (Mn=*C*=C), 297.0 (Mn=*C*(NPh)–), 234.2, 233.7, 228.1, 227.7 (Mn–*C*O), 138–123 (m, C_6H_5), 117.7 (Mn=C=*C*), 106.3, 101.7, 88.2, 87.1, 84.3, 84.1, 83.7, 82.9 ($CH_3C_5H_4$), 80.1, (–*C*HPh–), 60.2 (–*C*HCHPh–), 14.1, 13.4 ($CH_3C_5H_4$). MS (EI) *m*/*z* 611 (M^+).

4.8. Synthesis of $Cp'(CO)_2Mn=CN(Ph)CH(Ph)CH(Me)$ (11)

The azetidinylidene complex $Cp'(CO)_2Mn=CN$-(Ph)CH(Ph)CH_2 (**10**) (400 mg, 1 mmol) was dissolved in THF (15 ml). The solution was cooled at −60°C and ^{n}BuLi (0.69 ml of 1.6 M solution in hexanes, 1.1 mmol) was added dropwise via syringe. After stirring for 30 min the solution was cooled to −80°C and an excess of MeI (0.093 ml, 1.5 mmol) was added. The cooling bath was removed to allow the solution to warm to r.t. The solution was filtered on a short column of alumina, concentrated to ~2 ml under vacuum, and chromatographed on alumina. Elution with a 10:1 pentane/diethyloxide mixture gave an orange band containing traces of $Cp'Mn(CO)_3$ and continued elution with 1:1 pentane/diethyloxide gave a red band of $Cp'(CO)_2Mn=CN(Ph)CHPhCH(Me)$ (**11**). After evaporation of the solvents under high vacuum, complex **11** was isolated as a red oil (365 mg, 0.89 mmol, 89% yield).

Complex **11** was identified by comparison of its NMR spectra with those of an authentic sample of $Cp'(CO)_2Mn=CN(Ph)CH(Ph)CH(Me)$ [14].

4.9. Intermolecular oxidative coupling of the azetidinylidene anion $Cp'(CO)_2Mn=CN(Ph)CH(Ph)CH_2$ ([10]$^-$)

The azetidinylidene complex $Cp'(CO)_2Mn=CN$-(Ph)CH(Ph)CH_2 (**10**, 400 mg, 1 mmol) was dissolved in THF (15 ml). The solution was cooled at −60°C, and ^{n}BuLi (0.69 ml of a 1.6 M solution in hexane, 1.1 mmol) was added dropwise via syringe. After stirring for 30 min the solution was cooled to −80°C and CuI (114 mg, 0.6 mmol) was added. When all of the solid CuI disappeared (2 h) dry oxygen was bubbled to the solution for 30 s. The solvent was then removed under vacuum while the reaction flask was allowed to reach r.t. The residue was extracted with ether (50 ml), and filtered on a short column of alumina. The mixture was chromatographed again on alumina. A first elution with a 1:10 diethyloxide/pentane mixture gave a yellow band containing traces of unreacted **10**. Continued elution with a 1:1 diethyloxide/pentane mixture gave an orange band containing complex **5**. Evaporation of the solvents from that second fraction afforded complex **5** as an orange oil in 74% yield (290 mg, 0.37 mmol). NMR analysis of **5** showed the complex to form in these reaction conditions as a mixture of two diastereoisomers (**5** and **5′**) in a 2:1 ratio. Attempts to separate the two isomers by column chromatography have been unsuccessful.

5′ (from a mixture of **5**/**5′**): ^{1}H-NMR (C_6D_6): δ 7.6–6.8 (m, 10H, C_6H_5), 5.71 (s, 1H, –C*H*Ph), 4.5–4.2 (m, 4H, $CH_3C_5H_4$), 3.95 (s, 1H, –C*H*–), 1.57 (s, 3H, $CH_3C_5H_4$). ^{13}C-NMR (C_6D_6): δ 295.5 (Mn=*C*(NPh)–), 234.4 (Mn–*C*O), 136.4–122.2 (m, C_6H_5), 102.3 ($C_5H_4CH_3$), 88.9–85.2, ($C_5H_4CH_3$), 75.7 (–*C*HPh–), 65.3 (–*C*H–), 14.1 ($C_5H_4CH_3$).

Table 5
Atomic coordinates and equivalent isotropic displacement parameters (Å$^2\times100$) for compound **2a**

Atom	x/a	y/b	z/c	U_{eq}/U_{iso} [a]
Mn(1)	0.4276(1)	0.3122(1)	0.2359(1)	3.3(1)
C(1)	0.3714(2)	0.1738(2)	0.1053(2)	4.8(1)
O(1)	0.3489(2)	0.0816(2)	0.0233(2)	7.9(1)
C(3)	0.3803(2)	0.2418(2)	0.3390(2)	4.4(1)
O(3)	0.3499(2)	0.1976(2)	0.4076(2)	7.1(1)
O(5)	0.1220(1)	0.3325(1)	0.1623(1)	4.2(1)
C(5)	0.2564(2)	0.3821(2)	0.2139(2)	3.3(1)
C(7)	0.2467(2)	0.5181(2)	0.2731(2)	3.8(1)
C(9)	0.0794(2)	0.2027(2)	0.953(2)	4.5(1)
C(11)	0.0773(2)	0.1827(2)	0.0610(3)	6.1(1)
C(13)	0.5845(2)	0.3649(2)	0.1612(2)	5.1(1)
C(15)	0.5452(2)	0.4720(2)	0.2343(2)	5.0(1)
C(17)	0.5794(2)	0.4697(2)	0.3621(2)	5.1(1)
C(19)	0.6403(2)	0.3598(2)	0.3684(2)	5.3(1)
C(21)	0.6444(2)	0.2960(2)	0.2462(2)	5.2(1)
C(23)	0.5758(3)	0.3345(3)	0.0238(3)	7.8(1)
Mn(2)	0.0173(1)	0.7789(1)	0.3160(1)	3.1(1)
C(2)	0.1389(2)	0.8493(2)	0.4730(2)	3.9(1)
O(2)	0.2130(2)	0.8961(2)	0.5769(2)	6.4(1)
C(4)	0.0235(2)	0.9199(2)	0.2806(2)	4.3(1)
O(4)	0.0201(2)	1.0125(2)	0.2590(2)	7.2(1)
O(6)	0.2797(1)	0.7656(1)	0.2499(1)	4.3(1)
C(6)	0.1565(2)	0.7139(2)	0.2462(2)	3.3(1)
C(8)	0.1563(2)	0.5786(2)	0.1761(2)	3.5(1)
C(10)	0.3313(3)	0.8945(2)	0.3128(3)	6.3(1)
C(12)	0.4721(3)	0.9154(2)	0.3071(3)	7.0(1)
C(14)	0.1046(2)	0.6835(2)	0.3969(2)	4.2(1)
C(16)	0.0961(2)	0.6021(2)	0.2820(2)	4.6(1)
C(18)	0.1595(2)	0.6499(2)	0.1797(2)	5.3(1)
C(20)	0.2076(2)	0.7615(2)	0.2323(2)	5.5(1)
C(22)	0.1742(2)	0.7830(2)	0.3655(2)	4.7(1)
C(24)	0.0580(3)	0.6665(2)	0.5279(2)	5.9(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U^{ij} tensor.

Table 6
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 100$) for **3**

Atom	x/a	y/b	z/c	U_{eq}/U_{iso} [a]
Mn(1)	−0.48037(4)	0.81741(4)	0.77177(4)	3.50(2)
C(1)	−0.3642(3)	0.9793(3)	0.8528(3)	4.4(2)
O(1)	−0.2944(3)	1.0854(3)	0.9070(2)	6.1(2)
C(3)	−0.4746(3)	0.7748(3)	0.9115(3)	4.6(2)
O(3)	−0.4779(3)	0.7505(3)	1.0037(2)	7.6(2)
O(5)	−0.2128(2)	0.7632(2)	0.7638(2)	4.6(1)
C(5)	−0.3349(3)	0.7586(3)	0.7094(3)	3.7(2)
C(7)	−0.3360(3)	0.7090(3)	0.5755(3)	3.9(2)
C(9)	−0.1697(3)	0.8111(4)	0.8956(3)	5.3(2)
C(11)	−0.0260(3)	0.8123(4)	0.9211(3)	5.8(2)
C(13)	−0.6050(3)	0.9039(3)	0.6793(3)	4.5(2)
C(15)	−0.5901(3)	0.7936(3)	0.5932(3)	4.7(2)
C(17)	−0.6487(3)	0.6793(4)	0.6302(3)	5.1(2)
C(19)	−0.7018(3)	0.7189(4)	0.7400(4)	6.1(2)
C(21)	−0.6754(3)	0.8571(4)	0.7711(3)	5.5(2)
C(23)	−0.5632(4)	1.0423(4)	0.6716(4)	6.2(2)
Mn(2)	−0.05971(4)	0.73629(4)	0.31305(4)	3.72(2)
C(4)	−0.1145(3)	0.8430(3)	0.2452(3)	4.8(2)
O(4)	−0.1485(3)	0.9133(3)	0.2015(3)	8.0(2)
C(2)	−0.1186(3)	0.6068(3)	0.1711(3)	5.0(2)
O(2)	−0.1446(3)	0.5260(3)	0.0773(3)	7.2(2)
O(6)	−0.3601(2)	0.6482(2)	0.3346(2)	4.5(1)
C(6)	−0.2249(3)	0.6997(3)	0.3857(3)	3.9(2)
C(8)	−0.2237(3)	0.7352(3)	0.5204(3)	4.2(2)
C(10)	−0.4067(3)	0.5978(3)	0.2041(3)	4.4(2)
C(12)	−0.5619(3)	0.5616(4)	0.1864(3)	5.3(2)
C(14)	0.1054(3)	0.6637(4)	0.3573(3)	5.4(2)
C(16)	0.0677(3)	0.7289(4)	0.4676(3)	5.8(2)
C(18)	0.0928(3)	0.8618(4)	0.4731(3)	5.6(2)
C(20)	0.1472(3)	0.8805(4)	0.3659(4)	5.9(2)
C(22)	0.1560(3)	0.7593(4)	0.2945(3)	5.5(2)
C(24)	0.1032(4)	0.5246	0.3184(5)	8.4(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U^{ij} tensor.

Table 7
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 100$) for compound **5**

Atom	x/a	y/b	z/c	U_{eq}/U_{iso} [a]
Mn(1)	0.27074(9)	0.0122(1)	0.10683(4)	4.50(5)
C(1)	0.2660(7)	0.204(1)	0.1350(4)	6.4(5)
O(1)	0.2629(7)	0.3305(8)	0.1536(3)	10.1(5)
C(2)	0.3280(6)	0.0868(9)	0.0420(3)	5.4(4)
O(2)	0.3749(5)	0.1373(7)	0.0004(2)	6.9(4)
C(3)	0.0865(6)	0.0344(7)	0.0808(3)	4.1(4)
N(1)	−0.0266(4)	0.0363(6)	0.1090(2)	4.0(3)
C(4)	−0.1209(6)	0.0802(8)	0.0583(3)	4.4(4)
C(5)	0.0036(6)	0.0699(8)	0.0213(2)	4.1(4)
C(11)	0.387(1)	−0.073(1)	0.1835(4)	7.5(6)
C(12)	0.4479(8)	−0.114(1)	0.1336(5)	8.7(7)
C(13)	0.367(1)	−0.209(1)	0.0999(4)	10.0(8)
C(14)	0.253(1)	−0.234(1)	0.1267(6)	9.1(8)
C(15)	0.2643(9)	−0.149(1)	0.1789(5)	8.3(7)
C(16)	0.441(2)	0.013(2)	0.2336(5)	21.(2)
C(21)	−0.0598(6)	0.0032(8)	0.1671(3)	4.2(1)
C(22)	0.0040(7)	0.0754(8)	0.2155(3)	5.5(2)
C(23)	−0.0308(8)	0.0331(9)	0.2712(3)	6.9(2)
C(24)	−0.1286(8)	−0.074(1)	0.2781(4)	7.9(3)
C(25)	−0.1947(9)	−0.142(1)	0.2296(4)	8.7(3)
C(26)	−0.1599(7)	−0.1032(9)	0.1735(3)	6.4(2)
C(31)	−0.1840(7)	0.2393(8)	0.0641(3)	4.9(2)
C(32)	−0.1067(9)	0.369(1)	0.0748(4)	8.3(3)
C(33)	−0.168(1)	0.517(1)	0.0774(4)	10.6(3)
C(34)	−0.3073(9)	0.526(1)	0.0690(4)	9.0(3)
C(35)	−0.3824(9)	0.399(1)	0.0615(4)	7.3(2)
C(36)	−0.3220(7)	0.2527(9)	0.0584(3)	5.7(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

4.10. X-ray diffraction studies

Crystals of **2a**, **3**, and **5** suitable for X-ray diffraction were obtained through recrystallisation from diethyl ether/pentane mixtures at −15°C. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22°C. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range $24° < 2\theta(\text{Mo–K}_{\alpha1}) < 28°$. Full crystallographic data for the three complexes are gathered in Table 4.

For compound **2a**, calculations were performed on a PC-compatible computer using the WinGX system [26]. The structures were solved by using the SIR-92 program [27], which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXS-97 program [28]. For compound **3** and **5** calculations were performed on a MicroVax 3400. Data reductions were carried out using the SDP crystallographic computing package [29]. The structures were solved by using SHELXS-86 program [30]. All non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELX-76 program [31].

Atomic scattering factors were taken from the usual tabulations [32]. Anomalous dispersion terms for Mn were included in F_c [33]. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealised position (C–H = 0.96 Å; U set to 0.06) and held fixed during refinements. The intensities were corrected from absorption by using the empirical Ψ-scan method [34].

Final atomic coordinates for non-hydrogen atoms for compounds **2a**, **3**, and **5** are given in Tables 5–7, respectively. Lists of structure factor amplitude, anisotropic thermal parameters, and hydrogen atoms positions for the three structures are available from the authors upon request.

5. Supplementary material

Lists of structure factor amplitude, anisotropic thermal parameters, and hydrogen atoms positions for the three structures are available from the authors upon request.

Acknowledgements

Thanks are due to Dr Guy Lavigne, Dr D. de Montauzon and Dr A. Mari for helpful discussions.

References

[1] E.O. Fischer, A. Maasböl, Angew. Chem. Int. Ed. Engl. 3 (1964) 580.

[2] (a) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163. (b) L.S. Hegedus, Tetrahedron 53 (1997) 4105. (c) W.D. Wulff, Organometallics, 17 (1998) 3116. (d) K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187. (e) Z. Dörwald, Metal Carbene in Organic Synthesis, Wiley, New York, 1999. (f) J.W. Herndon, Tetrahedron 56 (2000) 1257.

[3] (a) C.G. Kreiter, Angew. Chem. Int. Ed. Engl. 7 (1968) 390. (b) C.F. Bernasconi, W.T. Sun, J. Am. Chem. Soc. 115 (1993) 12526.

[4] (a) C.P. Casey, R.A. Boggs, R.L. Anderson, J. Am. Chem. Soc. 94 (1972) 8947. (b) P. Veya, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 13 (1994) 214.

[5] (a) C.P. Casey, Chemtech, 1979, p. 378. (b) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Elsevier, Oxford, 12 (1995) 469. (c) D.F. Harvey, Chem. Rev. 96 (1996) 271.

[6] (a) D.W. Macomber, P. Madhukar, R.D. Rogers, Organometallics 8 (1989) 1275. (b) J. Breimair, T. Weidmann, B. Wagner, W. Beck, Chem. Ber. 124 (1991) 2431. (c) C. Kelley, A. W. Kaplan, G. L. Geoffroy, N. Lugan, R. Mathieu, A.L. Rheingold, Inorg. Chim. Acta 198–200 (1992) 601. (d) F. Rose-Munch, C. Susanne, F. Balssa, E. Rose, J. Organomet. Chem. 476 (1994) C25. (e) V. Cadierno, M. Pilar Gamassa, J. Gimeno, J. Borge, S. Garcia-Granda, J. Chem. Soc. Chem. Commun. (1994) 2795. (f) A. Geisbauer, K. Polborn, W. Beck, J. Organomet. Chem. 542 (1997) 205. (g) F. Rose-Munch, C. Le Corre-Susanne, F. Balssa, E. Rose, J. Vaissermann, E. Licandro, A. Papagni, S. Maiorana, W.de Meng, G.R. Stephenson, J. Organomet. Chem. 545–546 (1997) 9.

[7] (a) R. Aumann, H. Heinen, Chem. Ber. 120 (1987) 537. (b) C.S. Yi, G.L. Geoffroy, C.A. White, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 3806. (c) H. Wang, R.P. Hsung, W.D. Wulff, Tetrahedron Lett. 39 (1998) 1849. (d) C. Mongin, N. Lugan, R. Mathieu, Eur. J. Inorg. Chem. (1999) 739.

[8] C. Gimenez, N. Lugan, R. Mathieu, G.L. Geoffroy, J. Organomet. Chem. 517 (1996) 133.

[9] L. Lattuada, E. Licandro, S. Maiorana, H. Molinari, A. Papagni, Organometallics 10 (1991) 807.

[10] (a) C. Mongin, N. Lugan, R. Mathieu, Organometallics 16 (1997) 3873. (b) C. Mongin, K. Gruet, N. Lugan, R. Mathieu, Tetrahedron Lett. 41 (2000) 7341.

[11] (a) T. Kauffmann, D. Kuhlmann, W. Sahm, H. Schrecken, Angew. Chem. Int. Ed. Engl. 7 (1968) 540. (b) M.W. Rathke, A. Lindert, J. Am. Chem. Soc. 93 (1971) 460. (c) Y. Ito, T. Konoike, T. Saegusa, J. Am. Chem. Soc. 97 (1975) 2912. (d) Y. Ito, T. Konoike, T. Harada, T. Saegusa, J. Am. Chem. Soc. 99 (1977) 1487. (e) Y. Kobayashi, T. Taguchi, T. Morikawa, Tetrahdron Lett. (1978) 3555. (f) Y. Kobayashi, T. Tagushi, T. Morikawa, E. Tokuno, S. Sekiguchi, Chem. Pharm. Bull. 28 (1980) 262.

[12] (a) R. Aumann, H. Heinen, Chem. Ber. 120 (1987) 537. (b) D.W. Macomber, M.H. Hung, A.G. Verma, Organometallics 7 (1988) 2072. (c) D.W. Macomber, P. Madhukar, J. Organomet. Chem. 433 (1992) 279. (d) S. Cron, V. Morvan, C. Lapinte, C. J. Chem. Soc. Chem. Commun. (1993) 1611. (e) R. Aumann, B. Jasper, R. Fröhlich, S. Kotila, J. Organomet. Chem. 502 (1995) 137. (f) V. Péron, E. Porhiel, V. Ferrand, H. Le Bozec, J. Organomet. Chem. 539 (1997) 201. (g) H. Wang, W.D. Wulff, J. Am. Chem. Soc. 120 (1998) 10573. (h) E. Kuester, L.S. Hegedus, Organometallics 18 (1999) 5318.

[13] E.O. Fischer, V.N. Postnov, F.R. Kreissl, J. Organomet. Chem. 127 (1977) C19.

[14] M.R. Terry, L.A. Mercado, C. Kelley, G.L. Geoffroy, N. Lugan, P. Nombel, R. Mathieu, B.S. Haggerty, B.E. Owens-Waltermire, A.L. Rheingold, Organometallics 13 (1994) 843.

[15] A. Rabier, N. Lugan, R. Mathieu, G.L. Geoffroy, Organometallics 13 (1994) 4676.

[16] (a) After the preliminary account of part of this work has appeared, Beck et al. reported a parallel study on the synthesis μ-bis(carbene)dichromium complexes and on the reactivity of carbene anions derived from towards organic and organometallic substrates [16b]. (b) A. Geisbauer, S. Mihan, W. Beck, J. Organomet. Chem. 501 (1995) 61.

[17] (a) G.M. Whitesides, J. San Filippo Jr., C.P. Casey, E.J. Panek, J. Am. Chem. Soc. 89 (1967) 5302. (b) A.E. Jukes, Adv. Organomet. Chem. 12 (1974) 215. (c) Th. Kauffman, Angew. Chem. Int. Ed. Engl. 5 (1974) 291.

[18] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2 (1987) S1.

[19] C.P. Casey, W.R. Brunsvold, J. Organomet. Chem. 118 (1976) 309.

[20] M.B. Robin, P. Day, Adv. Inorg. Chem. Radiochem. 10 (1967) 247.

[21] (a) B.A. Etzenhouser, Q. Chen, M.B. Sponsler, Organometallics 13 (1994) 4176. (b) F. Coat, M.A. Guillevic, L. Toupet, F. Paul, C. Lapinte, Organometallics 16 (1997) 5988. (c) M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A.J. Amoroso, A.M. Arif, M. Böhme, G. Frenking, J.A. Gladysz, J. Am. Chem. Soc. 119 (1997) 775.

[22] U. Schubert, Organometallics 1 (1982) 1085.

[23] E.O. Fischer, A. Massböl, Chem. Ber. 100 (1967) 2445.

[24] C. Kelley, N. Lugan, M.R. Terry, G.L. Geoffroy, B.S. Haggerty, A.L. Rheingold, J. Am. Chem. Soc. 114 (1992) 6735.

[25] J.B. Tommasino, Thése de l'Université Paul Sabatier, Toulouse, 1993.

[26] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[27] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343.

[28] G.M. Sheldrick, SHELXS-97, SHELXL-97, CIFTAB-Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[29] Enraf-Nonius, Structure Determination Package, fourth edition, B.A. Frenz & Associated Inc. and Enraf-Nonius: College Station, TX, and Delft, The Netherland, 1981.

[30] G.M. Sheldrick, SHELXS-86: Programm for crystal structure solution, University of Göttingen, Göttingen, Germany, 1986.

[31] G.M. Sheldrick, SHELX-76: Programm for crystal structure determination, University of Cambridge, Cambridge, UK, 1976.

[32] (a) D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol.4, Kynoch Press, Birmingham UK, 1974, (Table 22B). (b) R.F. Stewart, E.R. Davidson, W.T. Simpson, J. Chem. Phys. 42 (1965) 3175. (c) T. Hahn (Ed.), International Tables for Crystallography, vol A, Kluwer Academic, Dordrecht The Netherlands, 1995.

[33] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. 4, Kynoch Press, Birmingham, UK, 1975, p. Table 2.3.1.

[34] A.C.T. North, D.C. Phillips, F.S. Mathew, Acta Crystallogr. A24 (1968) 351.