



# Chemistry of vinylidene complexes. XX. Intramolecular carbonylation of vinylidene on the MnFe center: Spectroscopic and structural study. X-ray structure of the new trimethylenemethane type MnFe complex<sup>☆,☆☆</sup>

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## ABSTRACT

Reactions of  $\text{Fe}_2(\text{CO})_9$  with  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}$  (**1**) and  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}=\text{CHPh}$  (**3**) gave the heterometallic trimethylenemethane complexes  $\eta^4\text{-}[\text{C}(\text{Mn}(\text{CO})_2\text{Cp})(\text{CO})\text{CHPh}]\text{Fe}(\text{CO})_3$  (**2**) and  $\eta^4\text{-}[\text{C}(\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp})(\text{CO})\text{CHPh}]\text{Fe}(\text{CO})_3$  (**4**), respectively. The formation of the benzylideneketene  $[\text{PhHC}=\text{C}=\text{C}=\text{O}]$  fragment included in complexes **2** and **4** occurs via intramolecular coupling of the carbonyl and vinylidene ligands. The structures of **3** and **4** were determined by single crystal XRD methods. The influence of the nature of the L ligands at the Mn atom on the structural and spectroscopic characteristics of  $\eta^4\text{-}[\text{C}(\text{Mn}(\text{CO})(\text{L})\text{Cp})(\text{CO})\text{CHPh}]\text{Fe}(\text{CO})_3$  ( $\text{L} = \text{CO}$  (**2**),  $\text{PPh}_3$  (**4**)) is considered. According to the VT  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, complex **2** reversibly transforms in solution into  $\mu\text{-}\eta^1\text{:}\eta^1\text{-vinylidene}$  isomer  $\text{Cp}(\text{CO})_2\text{MnFe}(\mu\text{-C}=\text{CHPh})(\text{CO})_4$  (**2a**), whereas complex **4** containing the  $\text{PPh}_3$  ligand is not able to a similar transformation.

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## 1. Introduction

Transition metal complexes containing vinylidene ligands  $\text{C}=\text{CRR}'$  ( $\text{R}$  and  $\text{R}' = \text{H}$ , alkyl, aryl, etc.) attract attention due to their use in stoichiometric syntheses of organometallic compounds and valuable organic substances, as well as due to their participation as intermediates in many catalytic processes [1–12].

The reactions of the second metal atom  $\text{M}'$  addition to the mononuclear  $\text{LM}=\text{C}=\text{CHR}$  complexes represent a common method for dinuclear heterometallic  $\mu\text{-vinylidene}$  complexes synthesis [1–6]. A wide series of dinuclear  $\mu\text{-vinylidene}$  complexes with the  $\text{Mn-M}'$  ( $\text{M}' = \text{Mo}$ ,  $\text{W}$ ,  $\text{Mn}$ ,  $\text{Fe}$ ,  $\text{Rh}$ ,  $\text{Pd}$ ,  $\text{Pt}$ ,  $\text{Cu}$ ) [2,3,13,14],  $\text{Re-M}'$  ( $\text{M}' = \text{Pd}$ ,  $\text{Pt}$ ) [1] and  $\text{Rh-M}'$  bonds ( $\text{M}' = \text{Cr}$ ,  $\text{Mn}$ ,  $\text{Fe}$ ) [6a,15] have been obtained based on the corresponding complexes  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHR}$  ( $\text{R} = \text{Ph}$  (**1**),  $\text{COOMe}$ ),  $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$  and  $\text{Cp}(i\text{-Pr}_3\text{P})\text{Rh}=\text{C}=\text{CHR}$  ( $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{Ph}$ ).

As a rule, the  $[\text{Fe}(\text{CO})_4]$  fragment adds to the  $\text{M}=\text{C}^1$  bond ( $\text{M} = \text{Mn}$ ,  $\text{Rh}$ ) of the mononuclear vinylidene  $\text{LM}=\text{C}^1=\text{C}^2\text{HR}$  or allenylidene  $\text{LM}=\text{C}^1=\text{C}^2=\text{C}^3\text{R}_2$  complex to form the triangular  $\text{MFe}(\mu\text{-C}^1)$  system, but does not participate in any other interactions with the organic part of the molecule. The syntheses of the stable  $\text{Cp}(\text{CO})_2\text{MnFe}[\mu\text{-C}=\text{C}(\text{H})\text{COOMe}](\text{CO})_4$ ,  $\text{Cp}(\text{CO})_2\text{MnFe}[\mu\text{-C}=\text{C}=\text{CPh}_2](\text{CO})_4$  [14],  $\text{Cp}(i\text{-Pr}_3\text{P})\text{RhFe}(\mu\text{-C}=\text{CHR})(\mu\text{-CO})(\text{CO})_3$  and  $(i\text{-Pr}_3\text{P})\text{RhFe}_2(\mu_3\text{-C}=\text{CHR})(\mu\text{-CO})_2(\text{CO})_4\text{Cp}$  ( $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{Ph}$ ) [15] complexes can be mentioned as examples.

In contrast, the addition of the  $[\text{Fe}(\text{CO})_4]$  fragment to  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}$  (**1**) resulted not in the expected  $\mu\text{-vinylidene}$   $\text{Cp}(\text{CO})_2\text{MnFe}(\mu\text{-C}=\text{CHPh})(\text{CO})_4$  (**2a**), but in its isomer  $\eta^4\text{-}[\text{C}(\text{Mn}(\text{CO})_2\text{Cp})(\text{CO})\text{CHPh}]\text{Fe}(\text{CO})_3$  (**2**) including the benzylideneketene fragment  $[\text{PhHC}=\text{C}=\text{C}=\text{O}]$  [16]. This reaction was the first example of the vinylidene carbonylation by intramolecular vinylidene-carbonyl coupling on a metal center, and complex **2** appeared to be the first heterometallic congener of trimethylenemethane (TMM) transition metal complexes.

Complex **2** was also obtained by the reaction between  $\text{Cp}(\text{CO})_2\text{Mn}(\eta^2\text{-HC}\equiv\text{CPh})$  and  $\text{Fe}_2(\text{CO})_9$  in low yield [17]. The formation of **2** was observed during the action of  $\text{Fe}_2(\text{CO})_9$  on

<sup>☆</sup> For Part XIX, see Ref. [1].

<sup>☆☆</sup> Abbreviations: Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; TMM = trimethylenemethane; VT = variable temperature; XRD = X-ray diffraction.

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$\text{Cp}(\text{CO})_2\text{MnRh}(\mu\text{-C}\equiv\text{CHPh})(\text{Acac})(\text{CO})$  [18] or  $[\text{Cp}(\text{CO})_2\text{MnCu}(\mu\text{-C}\equiv\text{CHPh})(\mu\text{-Cl})_2]_2$  [19] occurring with the substitution of the Rh or Cu fragments by  $[\text{Fe}(\text{CO})_4]$ .

Complex  $\eta^4\text{-}\{\text{C}[\text{Fe}(\text{CO})_3(\text{Et}_3\text{P})](\text{CO})\text{CH}_2\}\text{Fe}(\text{CO})_2(\text{Et}_3\text{P})$  incorporating the vinylideneketene fragment  $[\text{H}_2\text{C}=\text{C}=\text{C}=\text{O}]$  has also been reported [20]. Its crystal structure corresponds to the “TMM type”, but in solution the complex is in equilibrium with the  $\mu$ -vinylidene isomer  $\text{Fe}_2(\mu\text{-C}\equiv\text{CH}_2)(\text{CO})_6(\text{PEt}_3)_2$ .

The  $\mu$ -vinylidene complex  $\text{Mn}_2(\text{CO})_8[\mu\text{-C}^1=\text{C}^2(\text{H})\text{C}(\text{OEt})=\text{O}]$  containing the  $\text{EtOC}=\text{O}$  substituent at the  $\text{C}^2$  atom has been formed by UV-irradiation of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{HC}\equiv\text{COEt}$  in hexane solution saturated with carbon monoxide [21]. Various methods have been investigated to obtain complexes containing the  $\eta^1$ -vinylidene  $\text{C}^1=\text{C}^2(\text{C}=\text{O})\text{RR}'$  ( $\text{R} = \text{Me}, \text{Ph}, \text{CHPh}_2, \text{OMe}, \text{etc.}$ ) ligands [22]. However, these complexes can not be attributed to vinylidene carbonylation products in the strict sense of the word.

The intramolecular vinylidene carbonylation has been observed on the diplatinum center [23]. The action of  $\text{PPh}_3$  on  $(\text{C}_6\text{F}_5)_2\text{-(C}^3\text{O)-Pt}_2(\mu\text{-C}^1=\text{C}^2\text{HPh})(\text{PPh}_3)_2$  resulted in the unusual complex  $(\text{C}_6\text{F}_5)_2(\text{PPh}_3)\text{Pt}[(\eta^3\text{-PhC}^2\text{HC}^1\text{C}^3\text{O})\text{Pt}(\text{PPh}_3)_2]$ , in which the benzylideneketene  $[\text{PhC}^2\text{H}=\text{C}^1=\text{C}^3=\text{O}]$  ligand serves as  $\eta^3$ -allylic ligand on one of the Pt atoms, and forms a  $\text{C}^1\text{-Pt}$   $\sigma$ -bond with the second Pt. The formation of benzylideneketene  $[\text{PhC}^2\text{H}=\text{C}^1=\text{C}^3=\text{O}]$  is a result of the C-C coupling of the  $\text{C}^3\text{O}$  and  $\mu\text{-C}^1=\text{C}^2\text{HPh}$  ligands.

The vinylidene carbonylation reactions do not have common features, as it follows from the above rare examples. At the same time, the intra- and intermolecular carbonylation reactions of carbenes and carbynes on mono-, di- and polymetal centers resulting in the formation of free ketenes, coordinated  $\eta^2$ -ketene,  $\eta^1$ - and  $\eta^2$ -ketenyl groups, are quite common and have been intensively investigated [24–31]. The formation of ketene ligands by insertion of CO into the metal-carbene bond is considered to be the key step in useful synthetic reactions such as Dötz's benzanulation reaction [24] and other carbon chain growth processes. In addition, the interest in carbonylation reactions is caused by the organometallic compounds participating in similar reactions considered as models of probable intermediates in the Fischer-Tropsch process [8,32,33].

Recently, we have briefly reported [3,34] that the hetero-trimethylenemethane form of complex **2**,  $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})_2\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$ , exists in solutions in equilibrium with the  $\mu$ -vinylidene form  $\text{Cp}(\text{CO})_2\text{MnFe}(\mu\text{-C}\equiv\text{CHPh})(\text{CO})_4$  (**2a**) (Scheme 1).

That is the evidence of the reversibility of the intramolecular carbonyl-vinylidene coupling for this system.

In this article we describe the synthesis of the new hetero-nuclear TMM complex  $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$  (**4**), formed from the irreversible intramolecular vinylidene carbonylation by treatment of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}\equiv\text{CHPh}$  (**3**) with  $\text{Fe}_2(\text{CO})_9$ , and its investigation by XRD and spectroscopic methods. The structure of the initial compound **3** has also been solved by X-ray single crystal analysis. The interconversion of the complexes **2** and **2a** caused by the reversible carbonylation of the vinylidene ligand and decarbonylation of the benzylideneketene in the absence of the electron donor ligand  $\text{PPh}_3$  at the Mn atom has been studied by VT NMR spectroscopy.

## 2. Results and discussion

The synthetic routes employed for preparation of complexes **2–4** are shown in Scheme 1. The complexes were characterized by the IR and NMR spectroscopy. The structures of **3** and **4** were solved via the single crystal X-ray technique.

### 2.1. Syntheses of $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})_2\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$ (**2**) and $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$ (**4**)

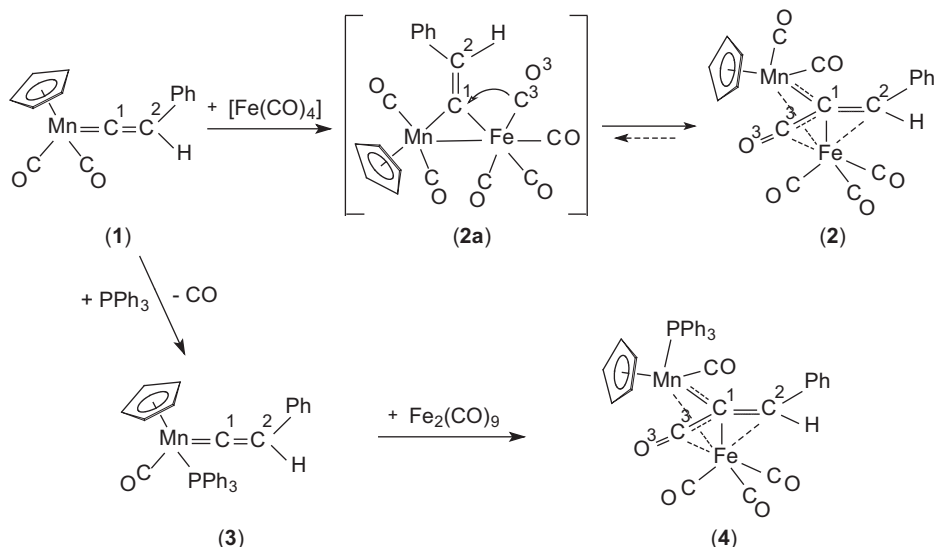
The reaction of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}\equiv\text{CHPh}$  (**3**) with  $\text{Fe}_2(\text{CO})_9$  in benzene at 20 °C for 3 h resulted in the formation of  $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$  (**4**) (Scheme 1).

The new compound **4** was isolated in 70% yield as the stable black crystals easily soluble in polar and moderately soluble in nonpolar organic solvents.

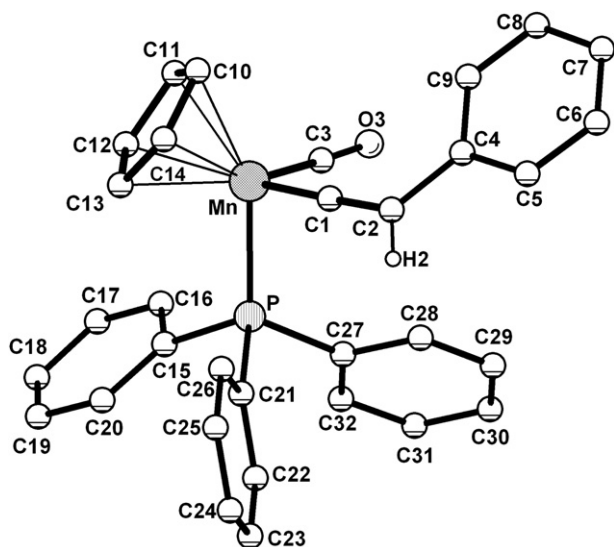
Complex **2** was synthesized earlier from complex **1** and  $\text{Fe}_2(\text{CO})_9$  (Scheme 1) and characterized by the X-ray, IR and mass spectrometry data [16]. The ion peaks at  $m/z$  130 belonging to the benzylideneketene ion  $[\text{PhCH}=\text{C}=\text{C}=\text{O}]^+$  were found in the mass spectra of complexes **2** and **4**.

### 2.2. X-ray diffraction study of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}\equiv\text{CHPh}$ (**3**)

Complex **3** was synthesized earlier [13] by the photochemical reaction of  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}\equiv\text{CHPh}$  (**1**) with  $\text{PPh}_3$ . The structure of **3** was proposed on the base of the IR, NMR and elemental analysis data [13,35].



Scheme 1.



**Fig. 1.** Molecular structure of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}=\text{CHPh}$  (**3**). Hydrogen atoms of  $\text{C}_5\text{H}_5$  and  $\text{C}_6\text{H}_5$  groups are omitted for clarity. Selected interatomic distances (Å) and bond angles ( $^\circ$ ):  $\text{Mn}=\text{C}(1)$  1.752(2);  $\text{C}(1)=\text{C}(2)$  1.328(3);  $\text{C}(2)-\text{C}(4)$  1.486(3);  $\text{Mn}-\text{C}(3)$  1.769(3);  $\text{Mn}-\text{P}$  2.2378(7);  $\text{C}(3)-\text{O}(3)$  1.157(3);  $\text{Mn}-\text{Cp}$  2.150(2);  $\text{Mn}-\text{C}(1)-\text{C}(2)$  178.6(2);  $\text{C}(1)-\text{C}(2)-\text{C}(4)$  125.7(2);  $\text{Mn}-\text{C}(3)-\text{O}(3)$  177.9(3);  $\text{C}(1)-\text{Mn}-\text{C}(3)$  91.4(1);  $\text{C}(1)-\text{Mn}-\text{P}$  91.34(7);  $\text{C}(3)-\text{Mn}-\text{P}$  89.29(9).

Whereas the  $[\text{Fe}(\text{CO})_4]$  unit adds to complex **3** to give **4**, no addition of  $[\text{CuCl}]$  and  $[\text{Pt}(\text{PPh}_3)]$  fragments occurs, contrary to complex **1**. We have supposed that the bulky  $\text{PPh}_3$  ligand at the Mn atom hinders this joining.

The X-ray diffraction study of a single crystal was performed to determine the structure of **3** (Fig. 1). The selected crystallographic data are given in Table 1.

The structures of the  $[\text{Cp}(\text{CO})\text{Mn}=\text{C}=\text{CHPh}]$  fragments in complexes **1** [36] and **3** are similar. The  $\text{Mn}-\text{C}(1)-\text{C}(2)$  angle in **3** is more near to linear one than that in **1** ( $174(2)^\circ$ ). The  $\text{Mn}=\text{C}(1)$  bond in **3** is substantially longer and the  $\text{C}(1)=\text{C}(2)$  bond in **3** is slightly shorter than the similar bonds in **1** (1.68(2) and 1.34(3) Å, respectively).

In contrast to **1**, where the metallaallene  $\text{Mn}=\text{C}(1)=\text{C}(2)$  system is weakly shielded by other ligands and can easily be attacked even by bulky reagents [3], the  $\text{Mn}=\text{C}(1)=\text{C}(2)$  system of complex **3** is strongly shielded by the  $\text{PPh}_3$  ligand on the one side, and by phenyl group on the other side.

The facile formation of **4** from **3** can be explained by assumption that the first step of the reaction of **3** with  $\text{Fe}_2(\text{CO})_9$  is the  $\eta^2$ -coordination of the  $[\text{Fe}(\text{CO})_4]$  fragment to the  $\text{C}(1)=\text{C}(2)$  bond. The following intramolecular carbonylation within an intermediate **4a** results in the final product **4** (Scheme 2).

The possibility of the intermediate **4a** formation in this reaction was shown by the quantum chemical DFT-B3LYP calculations [37a].

**Table 1**

Crystallographic data and refinement details for complexes **3** and **4**.

Complex	<b>3</b>	<b>4</b>
Empirical formula	$\text{C}_{32}\text{H}_{26}\text{MnOP}$	$\text{C}_{36}\text{H}_{26}\text{FeMnO}_5\text{P} \times 0.5(\text{C}_6\text{H}_{14})$
Colour	Dark red	Black
Formula weight	512.44	723.41
<i>T</i> (K)	296	288
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.674 (1)	11.132 (7)
<i>b</i> (Å)	10.060 (1)	11.439 (7)
<i>c</i> (Å)	16.134 (2)	15.281 (9)
$\alpha$ ( $^\circ$ )	104.748 (2)	105.767 (7)
$\beta$ ( $^\circ$ )	99.377 (2)	97.754 (8)
$\gamma$ ( $^\circ$ )	101.054 (1)	102.599 (7)
<i>V</i> (Å <sup>3</sup> )	1302.5 (3)	1788 (2)
$\rho_c$ (g/cm <sup>−3</sup> )	1.307	1.344
<i>Z</i>	2	2
$\mu$ (MoK $\alpha$ ) (mm <sup>−1</sup> )	0.591	0.845
<i>N</i> <sub>tot</sub>	10993	14173
<i>N</i> <sub>uniq</sub> ( <i>R</i> <sub>int</sub> )	5610 (0.0169)	6985 (0.0283)
$2\theta_{\text{max}}$ ( $^\circ$ )	54	52
<i>R</i> <sub>1</sub>	0.0402	0.0502
<i>wR</i> <sub>2</sub>	0.1204	0.1575
Goof	1.015	1.015
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$	−0.22/0.52	−0.41/0.71

### 2.3. X-ray diffraction study of $\eta^4\text{-}[\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}]\text{Fe}(\text{CO})_3$ (**4**)

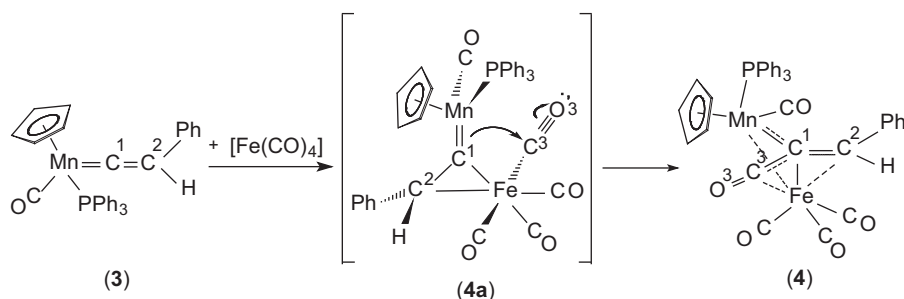
The structure of **4** is shown in Fig. 2. The main crystallographic data are given in Table 1. The selected geometrical parameters of **2** and **4** are given in Table 2.

The benzyldeneketene  $[\text{PhC}^2\text{H}=\text{C}^1=\text{C}^3=\text{O}^3]$  together with the  $[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}]$  group form the unusual organometallic ligand  $\{\text{C}^1[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{C}^3\text{O}^3)\text{C}^2\text{HPh}\}$  which is  $\eta^4$ -coordinated to the Fe atom.

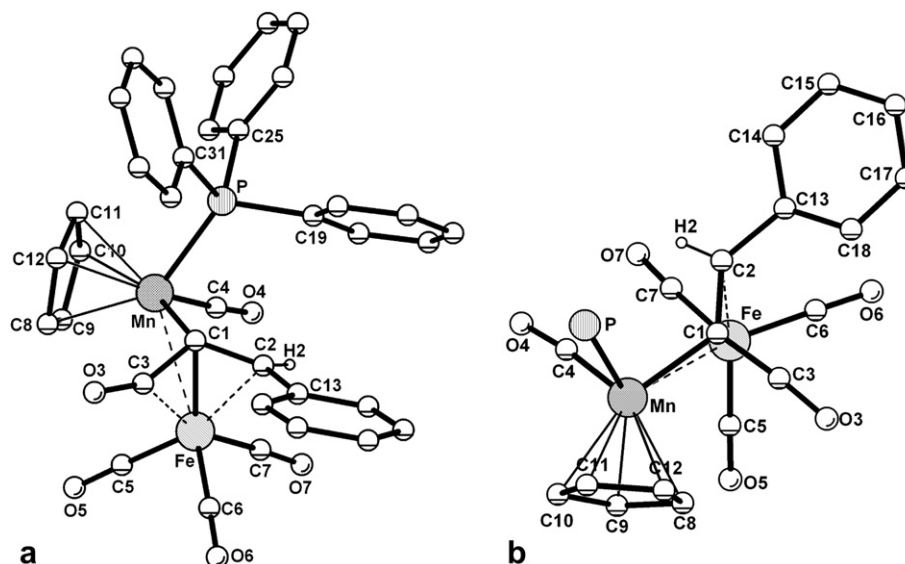
The structure of **4** is similar to that of **2** [16] and classical TMM complexes  $\eta^4\text{-}[\text{C}(\text{CH}_2)_3]\text{Fe}(\text{CO})_3$  [38] and  $\eta^4\text{-}[\text{C}(\text{CH}_2)_2(\text{CHPh})]\text{Fe}(\text{CO})_3$  [39] (Scheme 3).

The  $\{\text{C}(1)(\text{Mn})[\text{C}(3)\text{O}](\text{C}(2)\text{HPh})\}$  fragment in **2** is an almost planar conjugated system, and the central  $\text{C}(1)$  atom is displaced from the  $\text{MnC}(2)\text{C}(3)$  plane by 0.10 Å opposite to the Fe atom [16]. In the molecules  $\eta^4\text{-}[\text{C}(\text{CH}_2)_3]\text{Fe}(\text{CO})_3$  [38] and  $\eta^4\text{-}[\text{C}(\text{CH}_2)_2(\text{CHPh})]\text{Fe}(\text{CO})_3$  [39] such displacement is 0.3 Å. The  $\text{C}(1)$  atom in complex **4** is displaced from the  $\text{MnC}(2)\text{C}(3)$  plane by 0.302 Å.

The Fe atom attached to the  $\eta^4\text{-}[\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}]$  fragment of **4** has octahedral configuration which is typical for the trimethylenemethane iron complexes. The methylene groups in  $\eta^4\text{-}[\text{C}(\text{CH}_2)_3]\text{Fe}(\text{CO})_3$  [38] and  $\eta^4\text{-}[\text{C}(\text{CH}_2)_2(\text{CHPh})]\text{Fe}(\text{CO})_3$  [39] are in a staggered conformation in relation to the CO groups. The  $\text{Fe}(\text{CO})_3$  and  $\text{C}(1)\text{MnC}(2)\text{C}(3)$  fragments of **2** and **4** (see Fig. 2b) are also mutually staggered. The axis of the  $\text{Fe}(\text{CO})_3$  group, having the  $\text{C}_{3v}$



**Scheme 2.**



**Fig. 2.** Molecular structure of  $\eta^4$ -[C[Mn(CO)(PPh<sub>3</sub>)Cp](CO)CHPh]Fe(CO)<sub>3</sub> (**4**). Two perspectives (a) and (b). Hydrogen atoms of C<sub>5</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub> groups in both perspectives, and Ph groups of the PPh<sub>3</sub> ligand in (b) are omitted for clarity.

local symmetry, coincides with the Fe–C(1) bond in all four compounds.

Therefore, the compound **4** belongs to the type of heterometallic trimethylenemethane complexes where the “trimethylenemethane” system is created by the isolobal replacement of one of the [CH<sub>2</sub>] groups by [C(3)=O(3)], the second [CH<sub>2</sub>] – by the [Mn(CO)(PPh<sub>3</sub>)Cp] group, and the phenylmethylene [CHPh] is the third substituent at the central C(1) atom.

The  $\eta^4$ -[C[Mn(CO)(PPh<sub>3</sub>)Cp](CO)CHPh] group in **4** contains the somewhat shorter C(1)–C(2), C(1)–C(3) and Mn–C(1) bonds than the corresponding bonds in the molecule **2** (Table 2). The bond distance C(3)=O(3) of the benzylideneketene fragment PhC(2)H=C(1)=C(3)=O(3) in complex **4** is somewhat longer than that in **2**. The Mn–Fe distance 2.846(2) Å in complex **4** is longer than this distance 2.760(4) Å in complex **2**. The Mn–C<sup>1</sup>–C<sup>3</sup> angle in complex **4** is 17° less than the similar angle in molecule **2**. These features of the complex **4** geometry can apparently be explained by the

presence of the PPh<sub>3</sub> ligand which is very bulky and possesses the stronger electron-donating ability, compared with the CO group at the Mn atom in complex **2**.

#### 2.4. Spectroscopic study of $\eta^4$ -[C[Mn(CO)<sub>2</sub>Cp](CO)CHPh]Fe(CO)<sub>3</sub> (**2**) and $\eta^4$ -[C[Mn(CO)(PPh<sub>3</sub>)Cp](CO)CHPh]Fe(CO)<sub>3</sub> (**4**)

The differences in behavior of complexes **2** and **4** in solutions revealed by IR and NMR spectroscopy are considered in this section.

The IR spectrum of complex **4** in cyclohexane solution contains five bands in the  $\nu$ (CO) region, one of which, at 1835 cm<sup>−1</sup>, is attributed to the C<sup>3</sup>=O<sup>3</sup> group, that is consistent with the structure found in the solid state (Fig. 2). A similar band of the C<sup>3</sup>=O<sup>3</sup> group at 1844 cm<sup>−1</sup> has been found in the IR spectrum of **2** [16]. Unlike complex **4**, the IR spectrum of **2** contains the increased number of the  $\nu$ (CO) bands (8 bands instead of 6) (Table 3). The IR spectrum of the  $\mu$ -vinylidene complex Cp(CO)<sub>2</sub>MnFe( $\mu$ -C=CHCOOMe)(CO)<sub>4</sub> [14] which contains five  $\nu$ (CO) bands from 2090 to 1930 cm<sup>−1</sup> is given in Table 3 for comparison.

The <sup>1</sup>H NMR spectrum of complex **4** in *d*<sub>6</sub>-acetone solution contains the doublet signal of the cyclopentadienyl ligand protons at  $\delta$  4.57 ppm (<sup>3</sup>J<sub>PH</sub> = 2.05 Hz). A similar signal of the C<sub>5</sub>H<sub>5</sub> protons at  $\delta$  4.65 ppm (<sup>3</sup>J<sub>PH</sub> = 1.15 Hz) is observed for the initial compound **3** [35]. The singlet signal of the proton C<sup>2</sup>H of **4** is observed at  $\delta$  3.27 ppm. It should be noted that the <sup>1</sup>H NMR spectrum of the TMM complex  $\eta^4$ -[C<sup>1</sup>(C<sup>3</sup>H<sub>2</sub>)<sub>2</sub>(C<sup>2</sup>HPh)]Fe(CO)<sub>3</sub> contains the C<sup>2</sup>HPh proton resonance at  $\delta$  4.28 ppm [39].

The signal of the central C<sup>1</sup> atom of complex **4** is observed in the <sup>13</sup>C NMR spectrum at  $\delta$  101.60 ppm with <sup>2</sup>J<sub>PC</sub> = 34.04 Hz. The signal of the carbonyl group Mn–CO at  $\delta$  241.51 ppm has the similar value of the coupling constant <sup>2</sup>J<sub>PC</sub> = 39.59 Hz. The signal of C<sup>2</sup> at  $\delta$  73.49 ppm has a considerably smaller constant <sup>3</sup>J<sub>PC</sub> = 2.77 Hz.

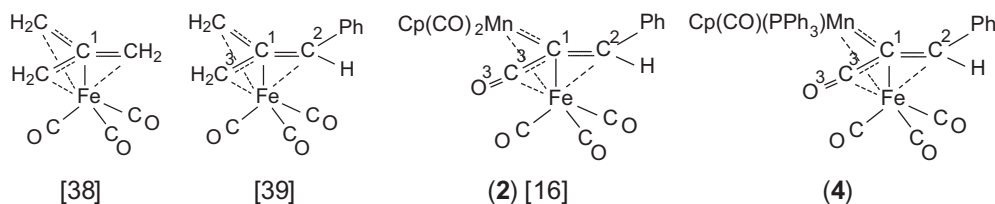
The chemical shifts of the proton C<sup>2</sup>H and carbon C<sup>1</sup> signals of complexes **2** and **4** (Table 3) are close to the corresponding signals in the NMR spectra of the known complexes (TMM)Fe(CO)<sub>3</sub> [40–42]. The signals of the C<sup>2</sup>HR proton of the TMM complexes with various R substituents are in the range of  $\delta$  2.8–4.8 ppm and the signals of C<sup>1</sup> in the <sup>13</sup>C NMR spectra are near  $\delta$  100 ppm.

The <sup>31</sup>P NMR spectrum of complex **4** contains a signal at  $\delta$  87.57 ppm which is close to the value of  $\delta$  89.8 ppm for the initial complex **3** [35].

**Table 2**  
Selected bond lengths (Å) and angles (°) for complexes **2** and **4**.

	<b>2</b> [16]	<b>4</b>
Bond lengths (Å)		
Mn–Fe	2.760 (4)	2.846 (2)
Mn–C1	2.03 (2)	2.012 (4)
C1–C2	1.44 (2)	1.409 (5)
C1–C3	1.45 (2)	1.410 (5)
C3=O3	1.16 (2)	1.190 (5)
Fe–C1	2.00 (1)	2.017 (4)
Fe–C2	2.22 (1)	2.141 (4)
Fe–C3	2.08 (2)	2.066 (4)
Mn–P	–	2.303 (2)
C4–O4	1.17 (2)	1.164 (4)
Mn–C4	1.79 (2)	1.776 (4)
Mn–Cp (av.)	2.18 (2)	2.175 (2)
Bond angles (°)		
Mn–C1–C2	124.8 (1)	125.3 (3)
Mn–C1–C3	124.4 (1)	107.2 (3)
C2–C1–C3	119.8 (1)	116.5 (3)
Fe–C1–Mn	86.3 (6)	89.9 (2)
Fe–C1–C2	86.3 (6)	75.0 (2)
Fe–C1–C3	72.1 (1)	71.7 (2)
C1–C3–O3	152.5 (2)	151.2 (4)





Scheme 3.

The behavior of **2** in  $\text{CD}_2\text{Cl}_2$  solution was investigated by the NMR spectroscopy in the temperature range from  $-60$  to  $+30$  °C.

The  $^1\text{H}$  NMR spectrum of **2** at  $-60$  °C containing one set of signals at  $\delta$  4.99 ( $\text{C}_5\text{H}_5$ ), 4.25 ( $\text{C}^2\text{H}$ ) is consistent with the structure of **2** found in the solid state [16]. Gradual warming of the solution up to  $+10$  °C leads to the appearance of the new additional signals at  $\delta$  4.94 ( $\text{C}_5\text{H}_5$ ) and 8.22 ppm ( $=\text{C}^2\text{H}$ ) in a 5:1 ratio of their integral intensity (Fig. 3). A significant broadening of the signals at  $\delta$  4.99 ( $\text{C}_5\text{H}_5$ ), 4.27 ( $\text{C}^2\text{H}$ ) and 4.94 ( $\text{C}_5\text{H}_5$ ), 8.23 ( $=\text{C}^2\text{H}$ ) ppm is observed and the third set of narrow signals at 4.79 and 8.29 ppm appears additionally at  $+22$  °C.

The additional signals at  $\delta$  8.23 and 8.29 are in the region typical for the signals of the vinylidene ligand  $\mu\text{-C}=\text{CHPh}$  protons [3], indicating the formation of the  $\mu$ -vinylidene complex  $\text{Cp}(\text{CO})_2\text{MnFe}(\mu\text{-C}=\text{CHPh})(\text{CO})_4$  (**2a**) in solution.

Cooling down to  $-60$  °C leads to the disappearance of the additional signals of the  $\mu$ -vinylidene complex **2a**.

The data obtained allow us to conclude that the cleavage of the  $\text{C}^1\text{--C}^3$  bond of the benzylideneketene [ $\text{PhC}^2\text{H}=\text{C}^1=\text{C}^3=\text{O}^3$ ] fragment and reversible formation of dinuclear  $\mu$ -vinylidene complex **2a** occur when complex **2** is dissolved.

A similar dynamic process has been observed earlier [20] by  $^1\text{H}$  NMR spectroscopy for the TMM complex  $\eta^4\text{-}\{\text{C}[\text{Fe}(\text{CO})_3(\text{PET}_3)](\text{CO})\text{-CH}_2\}\text{Fe}(\text{CO})_2(\text{PET}_3)$  which is in equilibrium with the  $\mu$ -vinylidene isomer in solution (Scheme 4).

Some reversible cleavage reactions of the  $\eta^2$ -coordinated ketene  $\text{R}_2\text{C}=\text{C}=\text{O}$  into the carbene  $\text{R}_2\text{C}$  and CO ligands on the metal centers Ir, Mn,  $\text{MnCo}_2$  have been reported [30,31a] (Scheme 5).

The presence of two signals at  $\delta$  8.23 ppm (broad singlet) and 8.29 ppm (narrow singlet) (Fig. 3) in the  $^1\text{H}$  NMR spectrum of **2** in solution indicates that two isomeric forms of  $\mu$ -vinylidene complex **2a** (**E** and **Z**) appear, which differ in the orientation of the Ph and H substituents at the vinylidene  $\text{C}^2$  atom (Scheme 6).

The rates of the interconversion between TMM complex **2** and each of the **2a-E** and **2a-Z** forms are different. The signal set of one of isomers **2a** in the  $^1\text{H}$  NMR spectrum is not observed upon heating of the solution up to  $+10$  °C, but appears only at  $+22$  °C. It is noteworthy that the lines of the proton signals for each isomer of **2a**

at  $+22$  °C have different widths (Fig. 3). The wide signals of the TMM form **2** and one of isomers **2a** indicate a rapid interconversion between these forms. Narrower signals of another isomer **2a** demonstrate a slower interconversion with the TMM form of **2**.

According to the quantum chemical DFT-B3LYP calculations, the energy barriers of the conversions **2**  $\rightarrow$  **2a-E** and **2**  $\rightarrow$  **2a-Z** are 25 and 12 kcal/mol, respectively [37b]. On the base of these data and the VT NMR data, the set of broad signals at  $\delta$  4.94 ( $\text{C}_5\text{H}_5$ ) and 8.23 ( $\text{C}^2\text{H}$ ) may be attributed to the **2a-Z** isomer, and the set of narrow signals at  $\delta$  4.79 and 8.29 to the **2a-E** isomer.

The final equilibrium between complex **2** and isomers **2a-Z** and **2a-E** in the 3.7:1.3:1 ratio, respectively, was observed after warming the solution up to  $+22$  °C for 2 h.

As follows from the above data, the interconversion of the **E** and **Z** isomers of the **2a** form occurs through the TMM form **2**, as shown in Scheme 6. It is additionally confirmed by quantum chemical calculations [37b] which reveal that the energy barrier of the direct interconversion between **2a-Z** and **2a-E** amounts to 27 kcal/mol.

Besides characteristic signals of the trimethylenemethane form at  $\delta$  95.84 ( $\text{C}^1$ ) and 76.30 ( $\text{C}^2$ ) ppm, the  $^{13}\text{C}$  NMR spectrum of **2** also contains two additional signal sets. A broad singlet at  $\delta$  249.02 and a narrow singlet at 253.91 correspond to the  $\mu\text{-C}^1$  atoms of the vinylidene isomers **2a-Z** and **2a-E**, respectively (Table 3).

On the contrary, no evidence of the formation of a compound with the bridging coordination of the vinylidene ligand from  $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$  (**4**) was found from the IR and NMR spectroscopic data.

### 3. Conclusion

The interaction of  $\text{Fe}_2(\text{CO})_9$  with  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}$  (**1**) and  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}=\text{CHPh}$  (**3**) resulted in the formation of heterometallic trimethylenemethane complexes  $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})_2\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$  (**2**) and  $\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{CO})\text{CHPh}\}\text{Fe}(\text{CO})_3$  (**4**), respectively, due to the intramolecular carbonylation of the bridging phenylvinylidene ligand on the dinuclear MnFe center. The crystal and molecular structures of complexes **3** and **4** were

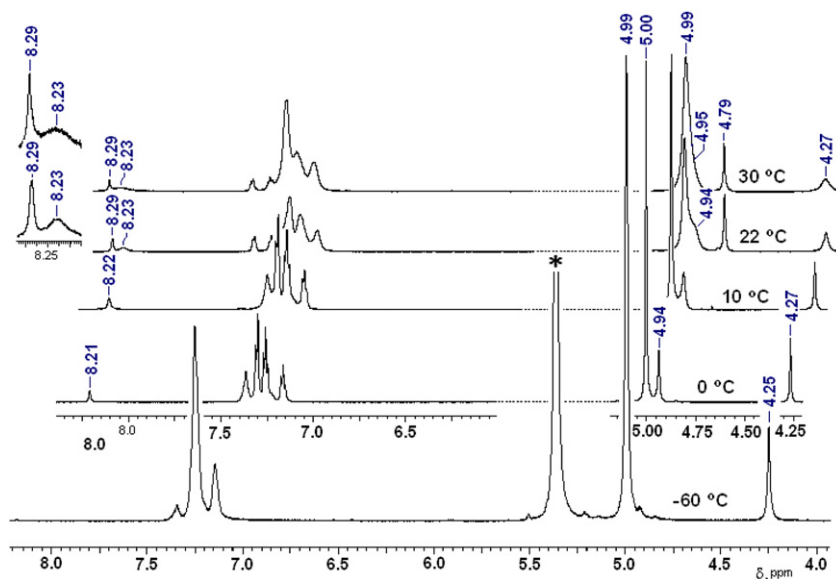
**Table 3**  
The IR and NMR data for dinuclear complexes with the Mn–Fe bonds.

Complex	NMR spectrum, $\delta$ , ppm, J, Hz			IR spectrum, ( $\text{C}_6\text{H}_{12}$ ), $\text{cm}^{-1}$
	$^1\text{H}$	$^{13}\text{C}$	$^{31}\text{P}$	
$\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})_2\text{Cp}](\text{C}^3\text{O}^3)\text{C}^2\text{HPh}\}\text{Fe}(\text{CO})_3$ ( <b>2</b> ) <sup>a</sup>	4.25s ( $\text{C}^2\text{H}$ ), 4.99s ( $\text{C}_5\text{H}_5$ )	95.84s ( $\text{C}^1$ ) 76.30s ( $\text{C}^2$ )	—	2085, 2055, 2000, 1971, 1917, 1875, 1851 ( $\text{C}\equiv\text{O}$ ), 1844 ( $\text{C}^3=\text{O}^3$ )
$\text{Cp}(\text{CO})_2\text{MnFe}(\mu\text{-C}^1=\text{C}^2\text{HPh})(\text{CO})_4$ ( <b>2a-Z</b> ) <sup>b</sup>	8.23s ( $\text{C}^2\text{H}$ ), 4.94s ( $\text{C}_5\text{H}_5$ )	249.02s ( $\mu\text{-C}^1$ ) 142.62s ( $\text{C}^2$ )	—	
$\text{Cp}(\text{CO})_2\text{MnFe}(\mu\text{-C}^1=\text{C}^2\text{HPh})(\text{CO})_4$ ( <b>2a-E</b> ) <sup>b</sup>	8.29s ( $\text{C}^2\text{H}$ ), 4.79s ( $\text{C}_5\text{H}_5$ )	253.91s ( $\mu\text{-C}^1$ ) 141.29s ( $\text{C}^2$ )	—	
$\eta^4\text{-}\{\text{C}[\text{Mn}(\text{CO})(\text{PPh}_3)\text{Cp}](\text{C}^3\text{O}^3)\text{C}^2\text{HPh}\}\text{Fe}(\text{CO})_3$ ( <b>4</b> ) <sup>c</sup>	3.27s ( $\text{C}^2\text{H}$ ), 4.57d ( $\text{C}_5\text{H}_5$ , $^3J_{\text{PH}} = 2.05$ Hz)	101.60d ( $\text{C}^1$ , $^2J_{\text{PC}} = 34.04$ Hz), 73.49d ( $\text{C}^2$ , $^3J_{\text{PC}} = 2.77$ Hz)	87.57	2042, 1989, 1965, 1885 ( $\text{C}\equiv\text{O}$ ), 1835 ( $\text{C}^3=\text{O}^3$ ) 2090, 2040, 2015, 1975, 1930
$\text{CpMnFe}(\mu\text{-C}=\text{CHCOOMe})(\text{CO})_6$ [14]	—	—	—	

<sup>a</sup> The NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$  solution at  $-60$  °C.

<sup>b</sup> The ratio of the **2a-Z** and **2a-E** isomers is 1.3:1 at  $+22$  °C.

<sup>c</sup> The NMR spectrum of **4** in  $d_6$ -acetone solution.



**Fig. 3.** Variable temperature  $^1\text{H}$  NMR spectra of  $\eta^4\text{-[C}^1\text{[Mn(CO)}_2\text{Cp]([C}^3\text{O}^3\text{)]C}^2\text{HPh]Fe(CO)}_3\text{ (2)}$  and isomers  $\text{Cp(CO)}_2\text{MnFe}(\mu\text{-C=CHPh})(\text{CO})_4\text{ (2a-Z and 2a-E)}$  in  $\text{CD}_2\text{Cl}_2$  solution. The asterisk marks the signal of  $\text{CH}_2\text{Cl}_2$ .

determined by X-ray single crystal analysis. The influence of the nature of ligands  $\text{L} = \text{CO}$ ,  $\text{PPh}_3$  at the Mn atom on the structural and spectroscopic characteristic of complexes  $\eta^4\text{-[C[Mn(CO)(L)Cp]([CO-CHPh])Fe(CO)}_3\text{ (2, 4)}$  has been studied.

The equilibrium between TMM form **2** and two dinuclear  $\mu$ -vinylidene forms  $\text{Cp(CO)}_2\text{MnFe}(\mu\text{-C=CHPh})(\text{CO})_4\text{ (2a-Z and 2a-E)}$  has been ascertained by VT NMR spectroscopy. The data obtained allow us to conclude that the cleavage of the benzylideneketene [ $\text{PhCH=C=O}$ ] fragment into the vinylidene  $\text{PhCH=C}$  and CO groups and reversible formation of dinuclear  $\mu$ -vinylidene complexes **2a-Z** and **2a-E** from complex **2** occur in solution.

In contrast to **2**, complex **4** containing the  $\text{PPh}_3$  ligand at the Mn atom was shown to exist in solution only as TMM form by the NMR and IR spectroscopy.

## 4. Experimental

### 4.1. General considerations

All operations were carried out in an argon atmosphere. Absolute solvents saturated with argon were used. Complexes  $\text{Cp(CO)}_2\text{Mn=C=CHPh}$  (**1**) and  $\text{Cp(CO)(PPh}_3\text{)Mn=C=CHPh}$  (**3**) were prepared as described in Ref. [13]. The course of reaction was followed by means of TLC on Silufol plates and IR spectroscopy. Physico-chemical characteristics were obtained in the Krasnoyarsk Regional Centre of Research Equipment, Siberian Branch of the Russian Academy of Science. The IR spectra were recorded on the Vector 22 Infrared Fourier spectrometer (Bruker, Germany). The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained using NMR spectrometer AVANCE III 600 DPX (Bruker, Germany). The X-ray data were obtained with the SMART APEX II autodiffractometer (Bruker, Germany).

#### 4.1.1. Preparation of $\eta^4\text{-[C[Mn(CO)}_2\text{Cp]([CO)CHPh]Fe(CO)}_3\text{ (2)}$

A mixture of  $\text{Cp(CO)}_2\text{Mn=C=CHPh}$  (**1**) (0.550 g, 2 mmol) and  $\text{Fe}_2(\text{CO})_9$  (0.690 g, 2 mmol) in hexane (20 ml) was stirred at  $20^\circ\text{C}$  for 5 h. The reaction mixture was concentrated to a volume of  $\sim 10$  ml and filtered from the precipitated complex **2**. The filtrate was chromatographed on the silica column. The wide brown zone was eluted with hexane–ether (25:1) mixture. The eluate was evaporated in vacuum; the solid residue was combined with **2** precipitated from the reaction mixture and crystallized from hexane–ether (1:1) mixture. The brown acicular crystals of  $\eta^4\text{-[C[Mn(CO)}_2\text{Cp]([CO)CHPh]Fe(CO)}_3\text{ (2)}$  were isolated (0.386 g, 43% yield).

IR ( $\text{C}_6\text{H}_{12}$ ),  $\nu(\text{CO})$  2087w, 2060s, 2034w, 2001vs, 1987sh, 1977vs, 1928m, 1854vw  $\text{cm}^{-1}$ . Ref.: ( $\text{CH}_2\text{Cl}_2$ ),  $\nu(\text{CO})$  2086, 2055, 2029sh, 2000, 1970, 1918 ( $\text{C=O}$ ), 1844 ( $\text{C=O}$ )  $\text{cm}^{-1}$  [16].

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-60^\circ\text{C}$ ):  $\delta$  4.25 (s, 1H,  $\text{C}^2\text{H}$ ); 4.99 (s, 5H,  $\text{C}_5\text{H}_5$ ); 7.14–7.34 (m, 5H,  $\text{C}_6\text{H}_5$ ).

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $+22^\circ\text{C}$ ):  $\delta$  76.30 (s,  $\text{C}^2$ ); 89.45 (s,  $\text{C}_5\text{H}_5$ ); 95.84 (s,  $\text{C}^1$ ); 125.00–128.40 (m,  $\text{C}_6\text{H}_5$ ); 145.59 (s,  $\text{C}_{\text{ipso}}$  of  $\text{C}^2\text{HC}_6\text{H}_5$ ); 198.17 (s,  $\text{C}^3=\text{O}^3$ ); 211.11 (s, br,  $\text{Fe(CO)}_3$ ); 230.30 (s, br,  $\text{Mn(CO)}_2$ ).

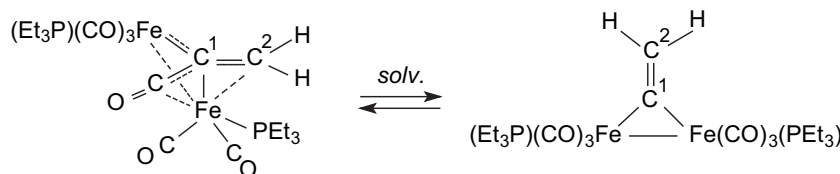
Isomer  $\text{Cp(CO)}_2\text{MnFe}(\mu\text{-C=CHPh})(\text{CO})_4\text{ (2a-Z)}$ :

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $+22^\circ\text{C}$ ):  $\delta$  4.94 (s,  $\text{C}_5\text{H}_5$ ); 7.14–7.34 (m, 5H,  $\text{C}_6\text{H}_5$ ); 8.23 (s,  $=\text{C}^2\text{H}$ ).

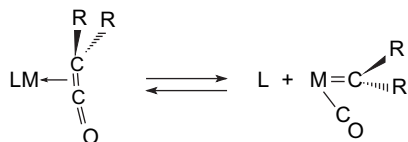
$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $+22^\circ\text{C}$ ):  $\delta$  88.28 (s,  $\text{C}_5\text{H}_5$ ); 125.00–128.40 (m,  $\text{C}_6\text{H}_5$ ); 142.62 (s,  $=\text{C}^2\text{HPh}$ ); 146.87 (s,  $\text{C}_{\text{ipso}}$  of  $=\text{C}^2\text{HC}_6\text{H}_5$ ); 204.52 and 208.43 (s,  $\text{Fe(CO)}_4$ ); 234.08 (s, br,  $\text{Mn(CO)}_2$ ); 249.02 (s, br,  $\text{C}^1$ ).

Isomer  $\text{Cp(CO)}_2\text{MnFe}(\mu\text{-C=CHPh})(\text{CO})_4\text{ (2a-E)}$ :

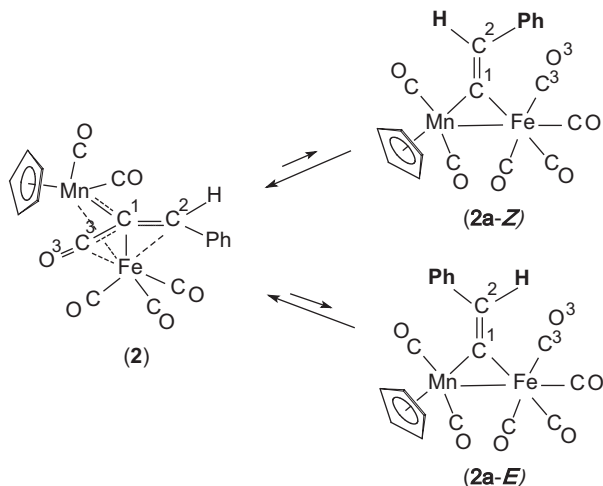
$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $+22^\circ\text{C}$ ):  $\delta$  4.79 (s,  $\text{C}_5\text{H}_5$ ); 7.41 (tr, 2H,  $H_{\text{meta}}$  of  $=\text{C}^2\text{HC}_6\text{H}_5$ ,  $J_{\text{HH}} = 7.61$ ); 7.53 (d, 2H,  $H_{\text{ortho}}$  of  $=\text{C}^2\text{HC}_6\text{H}_5$ ,  $J_{\text{HH}} = 6.93$ );  $H_{\text{para}}$  of  $=\text{C}^2\text{HC}_6\text{H}_5$  overlapping with  $\text{C}_6\text{H}_5$  signals of **2** and isomer **2a-Z**; 8.29 (s,  $=\text{C}^2\text{H}$ ).



**Scheme 4.**



Scheme 5.



Scheme 6.

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , +22 °C):  $\delta$  88.72 (s,  $\text{C}_5\text{H}_5$ ); 125.59, 127.16 and 128.22 (s,  $\text{C}_{\text{para}}$ ,  $\text{C}_{\text{meta}}$ ,  $\text{C}_{\text{ortho}}$  of  $=\text{C}^2\text{HC}_6\text{H}_5$ ); 141.29 (s,  $=\text{C}^2\text{HPh}$ ); 148.23 (s,  $\text{C}_{\text{ipso}}$  of  $=\text{C}^2\text{HC}_6\text{H}_5$ ); 204.62 and 208.17 (s,  $\text{Fe}(\text{CO})_4$ ); 229.05 and 235.23 (s,  $\text{Mn}(\text{CO})_2$ ); 253.91 (s,  $\text{C}^1$ ).

#### 4.1.2. Preparation of $\eta^4\text{-[C[Mn(CO)(PPh}_3\text{)Cp](CO)CHPh]Fe(CO)}_3$ (**4**)

A mixture of  $\text{Cp(CO)(PPh}_3\text{)Mn=C=CHPh}$  (**3**) (0.050 g, 0.098 mmol) and  $\text{Fe}_2(\text{CO})_9$  (0.073 g, 0.200 mmol) in benzene (10 ml) was stirred for 3 h. The solution was filtered through alumina pad and the solvent was evaporated in vacuum. The residue was dissolved in 5 ml of hexane–benzene (4:1) mixture and chromatographed on an alumina column ( $l = 80$  mm,  $d = 15$  mm). Pale-yellow zone was eluted with hexane–benzene (4:1) mixture and wide brown zone was eluted with hexane–benzene (2:1) mixture sequentially. Removal of solvents from the first fraction gave pale-yellow crystals of  $\text{Fe(CO)}_4(\text{PPh}_3)$  (0.013 g). (IR ( $\text{CH}_2\text{Cl}_2$ ),  $\nu$  (CO): 2054, 1974, 1941  $\text{cm}^{-1}$ ). After removal of solvent from the second fraction and crystallization from hexane, 0.048 g (70%) of black crystals  $\eta^4\text{-[C[Mn(CO)(PPh}_3\text{)Cp](CO)CHPh]Fe(CO)}_3$  (**4**) were isolated.

Anal. Found: C, 72.32; H, 3.80; Mn, 8.15; Fe, 8.27%.  $\text{C}_{36}\text{H}_{26}\text{PMnFeO}_5$ . Anal. Calc: C, 72.35; H, 3.82; Mn, 8.20; Fe, 8.23%.

IR ( $\text{C}_6\text{H}_{12}$ )  $\nu$ (CO), 2042s, 1989s, 1965m, 1885w, 1835w  $\text{br cm}^{-1}$ .

Mass spectrum (EI, 70 eV)  $m/z$ : 438 [ $\text{C}_5\text{H}_5(\text{CO})\text{MnP}(\text{C}_6\text{H}_5)_3$ ] $^+$ , 382 [ $\text{C}_5\text{H}_5\text{MnP}(\text{C}_6\text{H}_5)_3$ ] $^+$ , 262 [ $\text{P}(\text{C}_6\text{H}_5)_3$ ] $^+$ , 148 [ $\text{C}_5\text{H}_5\text{MnCO}$ ] $^+$ , 130 [ $\text{C}_6\text{H}_5\text{CHCCO}$ ] $^+$ , 120 [ $\text{C}_5\text{H}_5\text{Mn}$ ] $^+$ , 102 [ $\text{C}_6\text{H}_5\text{C}_2\text{H}$ ] $^+$ , 55 [ $\text{Mn}$ ] $^+$ .

$^1\text{H}$  NMR ( $d_6$ -acetone):  $\delta$  3.27 (s, H,  $\text{C}^2\text{H}$ ); 4.57 (d, 5H,  $\text{C}_5\text{H}_5$ ,  $^3J_{\text{PH}} = 2.05$ ); 6.85–7.13 [m, 5H,  $\text{C}^2\text{HC}_6\text{H}_5$ ]; 7.49–7.79 [m, 15H,  $\text{P}(\text{C}_6\text{H}_5)_3$ ].

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_6$ -acetone):  $\delta$  73.51 (d,  $\text{C}^2$ ,  $^3J_{\text{PC}} = 2.77$  Hz); 90.14 (s,  $\text{C}_5\text{H}_5$ ); 101.60 (d,  $\text{C}^1$ ,  $^2J_{\text{PC}} = 34.04$  Hz); 124.52 (s,  $\text{C}_{\text{meta}}$  of  $\text{C}^2\text{HC}_6\text{H}_5$ ); 125.56 (s,  $\text{C}_{\text{para}}$  of  $\text{C}^2\text{HC}_6\text{H}_5$ ); 128.05 (s,  $\text{C}_{\text{ortho}}$  of  $\text{C}^2\text{HC}_6\text{H}_5$ ); 128.42 (d,  $\text{C}_{\text{meta}}$  of  $\text{PPh}_3$ ,  $^3J_{\text{PC}} = 9.39$  Hz); 130.17 (d,  $\text{C}_{\text{para}}$  of  $\text{PPh}_3$ ,  $^4J_{\text{PC}} = 2.05$  Hz); 133.48 (d,  $\text{C}_{\text{ortho}}$  of  $\text{PPh}_3$ ,  $^2J_{\text{PC}} = 8.71$  Hz); 136.19 (d,  $\text{C}_{\text{ipso}}$  of  $\text{PPh}_3$ ,  $J_{\text{PC}} = 42.20$  Hz); 147.36 (s,  $\text{C}_{\text{ipso}}$  of  $\text{C}^2\text{HC}_6\text{H}_5$ ); 204.03 (s,  $\text{C}^3=\text{O}^3$ ); 211.16 (m,  $\text{Fe}(\text{CO})_3$ ); 241.51 (d,  $\text{Mn}(\text{CO})$ ,  $^2J_{\text{PC}} = 39.59$  Hz).

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_6$ -acetone):  $\delta$  87.56 (s,  $\text{Mn-PPh}_3$ ).

4.3. X-ray diffraction studies of ( $\eta^5$ -cyclopentadienyl)-(carbonyl)-(triphenylphosphine)-[ $\eta^1$ -(phenyl)ethynylidene]-manganese (**3**) and 2,2,2,2- $\eta^4$ -[[(1- $\eta^5$ -cyclopentadienyl)-(1-carbonyl)-(1-triphenylphosphine)-2- $\eta^1$ -manganese]-(2- $\eta^1$ -phenylmethylene)-(2- $\eta^1$ -carbo)-(1,2- $\eta^1, \eta^1$ -methane)]-(2,2,2-tricarbonyl)-iron( $\text{Mn-Fe}$ ) (**4**)

The intensity data were collected with Bruker SMART APEX II X-ray area-detector diffractometer,  $\text{MoK}\alpha$ -radiation, for single crystals of complexes **3** and **4**. The sample of **4** was cooled to obtain the sufficient number of data. Absorption corrections have been introduced via multi-scan method [43]. The structures were solved and refined in the anisotropic approximation of non-hydrogen atoms using [44]. All hydrogen atoms were placed in geometrically idealized locations and refined as riding. All phenyl cycles were preserved in the idealized form during the refinement procedure. The Cp cycle also was idealized in both cases with Mn–C distance of average value and the distance was preserved with the *esd* of 0.002 Å.

There are the solvent molecules (hexane) in the crystal of **4**. These molecules are arranged in the inversion centers in the middle of the *c*-axis, what indicates the presence of alone hexane molecule in the crystal cell. The molecule was also idealized over interatomic distances and angles, but the torsion angles were free for some variations during the refinement.

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#### Appendix. A. Supplementary material

The supplementary crystallographic data for compounds **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 781985 and 781984, correspondingly. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk> or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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