

# Chemistry of vinylidene complexes. XVI. Crystal and molecular structure of the novel tetranuclear $\mu_2$ - $\mu_3$ -bis-vinylidene complex $(\eta^2\text{-dppe})\text{PdMn}(\mu_3\text{-C=CHPh})\text{PdMn}(\mu\text{-C=CHPh})(\text{CO})_4\text{Cp}_2$ $\star, \star\star, \star\star\star, \star\star\star\star$

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## Abstract

The crystal and molecular structure of the novel tetranuclear complex  $(\eta^2\text{-dppe})\text{PdMn}(\mu_3\text{-C=CHPh})\text{PdMn}(\mu\text{-C=CHPh})(\text{CO})_4\text{Cp}_2$  (**5**) has been investigated. The metal core of **5** is a bent chain Pd(2)–Mn(2)–Pd(1)–Mn(1). The bond distances and angles are Mn(1)–Pd(1) 2.6025(6), Pd(1)–Mn(2) 2.8913(5), Mn(2)–Pd(2) 2.6463(4) Å, Mn(1)–Pd(1)–Mn(2) 140.2(2)°, Pd(1)–Mn(2)–Pd(2) 69.6(1)°. Complex contains two bridging vinylidene ligands coordinated to metal atoms in different ways. The C=C bond lengths are 1.347(4) and 1.372(4) Å in the  $\mu_2(\eta^1, \eta^1)\text{-C=CHPh}$  and  $\mu_3(\eta^1, \eta^1, \eta^2)\text{-C=CHPh}$  ligands, respectively. The  $\eta^2$ -dppe ligand is coordinated to the Pd(2) atom to form the chelate cycle. Each of Mn(1) and Mn(2) atoms is bonded with the  $\eta^5\text{-C}_5\text{H}_5$  ring and two CO groups.

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**Keywords:** Vinylidene complexes; Heterometallic complexes; Palladium; Manganese; Crystal structure

## 1. Introduction

One of the major properties of vinylidene complexes, resulting from their unsaturation, is the ability to add new metal containing fragments.

Earlier, we have shown for the first time [2,3] that the trimetal  $\mu_3$ -vinylidene clusters of the C type can be obtained by the consecutive assembling of the MM'M'' core, starting from mononuclear vinylidene complex A, via stages (a) and (b) in Scheme 1.

The addition of the [PtL<sub>2</sub>] groups (L = PPh<sub>3</sub>, P(OR)<sub>3</sub>) to Cp(CO)<sub>2</sub>Mn=C=CHPh (A) resulted in the formation of dimetal complexes Cp(CO)<sub>2</sub>MnPt( $\mu\text{-C=CHPh}$ )L<sub>2</sub> (B) [4], the following reactions of which with Fe<sub>2</sub>(CO)<sub>9</sub> gave a series of trimetal clusters CpMnFePt( $\mu_3\text{-C=CHPh}$ )(CO)<sub>6</sub>L and CpMnFePt( $\mu_3\text{-C=CHPh}$ )(CO)<sub>5</sub>L<sub>2</sub> (C) [3]. The products of addition of ironcarbonyl fragment to Cp(CO)<sub>2</sub>MnPt( $\mu\text{-C=CHPh}$ )( $\eta^2\text{-dppm}$ ) (1) [5] were a triangular cluster CpMnFePt( $\mu_3\text{-C=CHPh}$ )( $\mu\text{-dppm}$ )(CO)<sub>5</sub> (C) and its derivative CpMnFePt( $\mu_3\text{-C=CHPh}$ )(CO)<sub>5</sub>[ $\eta^1\text{-Ph}_2\text{-PCH}_2\text{P(=O)Ph}_2$ ] (2) with a metal core in the form of the Mn–Fe–Pt chain (C') [6] (see Scheme 1).

Palladium-containing vinylidene complexes are more rare than those containing platinum [7]. Only two types of vinylidene palladium derivatives, viz. “A-frame” complexes X<sub>2</sub>MPd( $\mu\text{-C=CR}_2$ )( $\mu\text{-dppm}$ )<sub>2</sub> (X = Cl, Br, I; M = Ni, Pd; R = H, Cl) [8] without direct metal–metal bonds, as well as [(PhC≡C)PdPt( $\mu\text{-C=CHPh}$ )(PEt<sub>3</sub>)<sub>4</sub>]<sup>+</sup>[PF<sub>6</sub>]<sup>−</sup> [9]

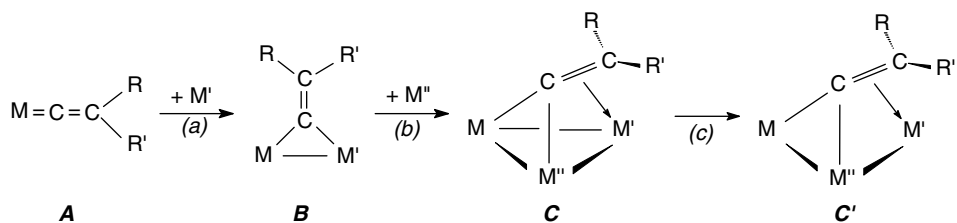
<sup>☆</sup> For Part XV, see Ref. [1].

<sup>☆☆</sup> dppm = Ph<sub>2</sub>P(CH<sub>2</sub>)PPh<sub>2</sub>; dppe = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>; dppp = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>; Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; Cp' =  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ .

<sup>★</sup> In a crystal **5** · 0.5C<sub>6</sub>H<sub>6</sub> · 0.5Et<sub>2</sub>O (**5a**).

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Scheme 1.

with the Pd–Pt bond, were described before the beginning of our work.

Complex  $\text{Cp}(\text{CO})_2\text{MnPd}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$  (**3**) was obtained from the reaction between  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}$  and  $\text{Pd}(\text{PPh}_3)_4$  [10,11]. By substitution of the  $\text{PPh}_3$  ligands in complex **3** for diphosphines dppe, dppp, complexes  $\text{Cp}(\text{CO})_2\text{MnPd}(\mu\text{-C}=\text{CHPh})(\eta^2\text{-dppe})$  (**4**) [11] and  $\text{Cp}(\text{CO})_2\text{MnPd}(\mu\text{-C}=\text{CHPh})(\eta^2\text{-dppp})$  (**4a**) [1] were prepared in 90% yields. Treatment of complexes **4** and **4a** with  $\text{Fe}_2(\text{CO})_9$  resulted in the formation of the first palladium-containing vinylidene clusters  $(\eta^2\text{-dppe})\text{PdFe}_3(\mu_4\text{-C}=\text{CHPh})(\text{CO})_9$  [11] and  $(\eta^2\text{-dppp})\text{PdFe}_3(\mu_4\text{-C}=\text{CHPh})(\text{CO})_9$  [1,12], the latter being studied by the X-ray method [12].

Recently, from reaction between complex **3** and dppe, we have unexpectedly isolated the tetranuclear bis-vinylidene complex  $(\eta^2\text{-dppe})\text{PdMn}(\mu_3\text{-C}=\text{CHPh})\text{PdMn}(\mu\text{-C}=\text{CHPh})(\text{CO})_4\text{Cp}_2$  (**5a**) of a novel type along with the major dinuclear product **4**. The structure of the solvate  $\mathbf{5} \cdot 0.5\text{C}_6\text{H}_6 \cdot 0.5\text{Et}_2\text{O}$  (**5a**) has been resolved by the X-ray single crystal analysis and described herein. The comparison of geometrical parameters of an open cluster **5** with those of the known complexes with the Pd–Mn, Pt–Mn bonds, and also with parameters of  $\mu_3$ -vinylidene clusters possessing metal cores in the form of a triangle and an open chain has been carried out.

## 2. Results

The reaction between  $\text{Cp}(\text{CO})_2\text{MnPd}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$  (**3**) and dppe (Scheme 2) was carried out in benzene solution at 20 °C for 1 h. Crystallization from ether gave orange fine-crystalline  $\text{Cp}(\text{CO})_2\text{MnPd}(\mu\text{-C}=\text{CHPh})(\eta^2\text{-dppe})$  (**4**)

in 90% yield and some few good formed dark-red (almost black) crystals of solvate  $[(\eta^2\text{-dppe})\text{PdMn}(\mu_3\text{-C}=\text{CHPh})\text{-PdMn}(\mu\text{-C}=\text{CHPh})(\text{CO})_4\text{Cp}_2] \cdot 0.5\text{C}_6\text{H}_6 \cdot 0.5\text{Et}_2\text{O}$  (**5a**).

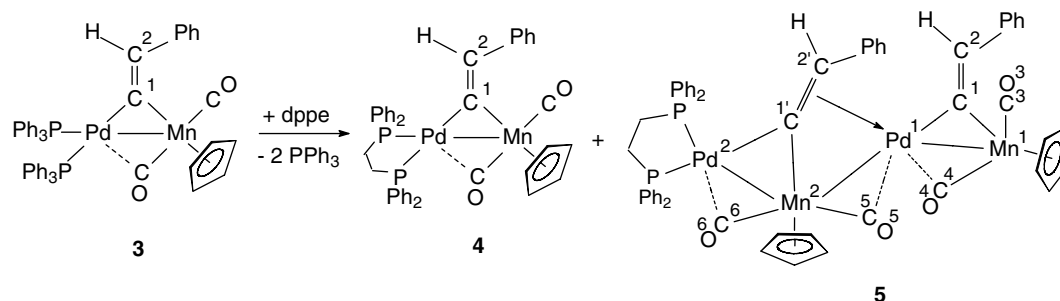
The structure of complex **5** is shown in Fig. 1. The selected bond lengths and angles are given in Table 2.

Complex **5** contains a metal core as four-membered chain of alternating palladium and manganese atoms, Pd(2)–Mn(2)–Pd(1)–Mn(1), with two vinylidene ligands coordinated to it, *viz.*  $\mu_2\text{-C}=\text{CHPh}$  and  $\mu_3\text{-C}=\text{CHPh}$ , and four carbonyl groups. The Pd(2) atom is included in an chelate cycle formed by the  $\eta^2\text{-dppe}$  ligand. Each of manganese atoms is coordinated by the  $\eta^5\text{-C}_5\text{H}_5$  ring.

The central fragment [Pd(2)–Mn(2)–Pd(1)–Mn(1)] of the molecule **5** contains two Pd–Mn bonds (Pd(2)–Mn(2) 2.6463(4) Å and Pd(1)–Mn(1) 2.6025(6) Å), which are much stronger than the third bond Pd(1)–Mn(2) (2.8913(5) Å). Earlier, the Pd–Mn bond lengths were observed in an interval 2.58–2.83 Å [13], e.g. in  $\text{Pd}_2\text{Mn}(\mu_2\text{-dppm})_2(\mu_2\text{-CO})(\mu_3\text{-CO})[\text{Mn}(\text{CO})_5]$  (**6**) [14] and in  $[(\text{OC})\text{Pd}(\mu\text{-NC})\text{Mn}(\text{Cp}')(\text{CO})_2]_4$  (**7**) [15].

The distances Pd(1)···Pd(2) 3.1572(3) Å and Mn(1)···Mn(2) 5.166(3) Å are nonbonding. Such a linear arrangement of metal atoms in tetranuclear vinylidene complexes was not observed before. The Pd(2)–Mn(2)–Pd(1)–Mn(1) chain in molecule **5** is strongly bent: the angles are Pd(2)–Mn(2)–Pd(1) 69.36(1)° and Mn(2)–Pd(1)–Mn(1) 140.17(2)°.

The most interesting feature of molecule **5** is the presence of two bridging vinylidene ligands with different types of coordination. The  $\mu_2\text{-C}(1)=\text{C}(2)\text{HPh}$  ligand bridges the Mn(1)–Pd(1) bond. The  $\mu_3\text{-C}(1')=\text{C}(2')\text{HPh}$  ligand is  $\sigma$ -bonded with the Mn(2) and Pd(2) atoms and  $\eta^2$ -coordinated to the Pd(1) atom.



Scheme 2.

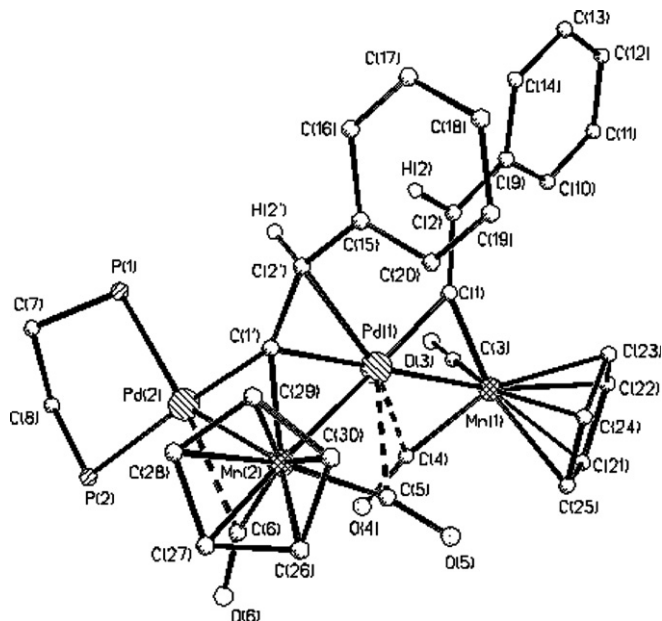


Fig. 1. Molecular structure of  $(\eta^2\text{-dppe})\text{PdMn}(\mu_3\text{-C}\equiv\text{CHPh})\text{PdMn}(\mu\text{-C}\equiv\text{CHPh})(\text{CO})_4\text{Cp}_2$  (**5**) (the Ph rings in the dppe ligand and the H atoms are omitted).

The distances from the  $\mu\text{-C}(1)$  atom to the Mn(1) and Pd(1) atoms are 1.891(3) Å and 2.010(3) Å, respectively. The  $\text{C}(1)=\text{C}(2)$  bond length is 1.347(4) Å. The angles are

Table 1  
Crystallographic data and parameters of refinement for structure of  $(\eta^2\text{-dppe})\text{PdMn}(\mu_3\text{-C}\equiv\text{CHPh})\text{PdMn}(\mu\text{-C}\equiv\text{CHPh})(\text{CO})_4\text{Cp}_2 \cdot 0.5\text{C}_6\text{H}_6 \cdot 0.5\text{Et}_2\text{O}$  (**5a**)

Molecular formula	$\text{C}_{61}\text{H}_{54}\text{Mn}_2\text{O}_{4.5}\text{P}_2\text{Pd}_2$
Formula weight	1243.66
Color, shape	Dark red, prism
Dimension	$0.30 \times 0.20 \times 0.10$
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ (Å)	10.4432(4)
$b$ (Å)	14.2046(6)
$c$ (Å)	18.9740(8)
$\alpha$ (°)	106.109(1)
$\beta$ (°)	95.741(1)
$\gamma$ (°)	102.181(1)
$V$ (Å <sup>3</sup> )	2605.3(2)
$Z$	2
$F(000)$	1
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.585
Radiation, $\lambda$ (Mo-K $\alpha$ ) (Å)	0.71072
Linear absorption, $\mu$ (cm <sup>-1</sup> )	12.64
$T_{\text{min}}/T_{\text{max}}$	0.732/0.993
$2\theta$ Range (°)	1.61–28.50
Completeness of dataset (%)	97.3
Measured	30796
Unique	12838 ( $R(\text{int}) = 0.0376$ )
With $[I > 2\sigma(I)]$	8913
Parameters	682
Final $R_1(F_{\text{hkl}})$	0.0384
$wR_2(F_{\text{hkl}}^2)$	0.0776
GOF	1.000
$\rho_{\text{max}}/\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.093/–0.530

Table 2  
Selected bond distances (Å) and bond angles (°) in molecule **5**

Bond distances (Å)			
Pd(1)–C(1)	2.010(3)	Pd(1)–Mn(1)	2.6025(6)
Pd(1)–C(1')	2.116(3)	Pd(1)–Mn(2)	2.8913(5)
Pd(1)–C(2')	2.343(3)	Pd(2)–Mn(2)	2.6463(4)
Pd(1)–C(4)	2.276(4)	Pd(2)–C(1')	2.043(3)
Pd(1)–C(5)	2.468(3)	Pd(2)–P(1)	2.3221(8)
Mn(1)–C(1)	1.891(3)	Pd(2)–P(2)	2.3612(8)
Mn(1)–C(3)	1.765(3)	Pd(2)–C(6)	2.302(3)
Mn(1)–C(4)	1.815(3)	C(1)–C(2)	1.347(4)
Mn(2)–C(5)	1.812(3)	C(1')–C(2')	1.372(4)
Mn(2)–C(6)	1.822(3)	C(2')–C(15)	1.483(4)
Mn(2)–C(1')	1.925(3)	C(2)–C(9)	1.470(4)
C(3)–O(3)	1.166(4)	C(5)–O(5)	1.162(4)
C(4)–O(4)	1.165(4)	C(6)–O(6)	1.180(4)
Bond angles (°)			
Mn(1)–Pd(1)–Mn(2)	140.17(2)	Pd(2)–Mn(2)–Pd(1)	69.36(1)
C(1)–Pd(1)–C(4)	84.8(1)	C(3)–Mn(1)–C(4)	88.1(2)
C(1)–Pd(1)–C(1')	133.1(1)	C(3)–Mn(1)–C(1)	87.8(1)
C(1)–Pd(1)–C(2')	98.5(1)	C(4)–Mn(1)–C(1)	102.7(1)
C(1)–Pd(1)–C(5)	138.9(1)	C(3)–Mn(1)–Pd(1)	108.2(1)
C(1')–Pd(1)–C(4)	135.2(1)	C(4)–Mn(1)–Pd(1)	58.8(1)
C(1)–Pd(1)–Mn(1)	46.2(1)	C(1)–Mn(1)–Pd(1)	50.14(9)
C(1')–Pd(1)–Mn(1)	176.20(7)	C(5)–Mn(2)–C(6)	86.8(1)
C(4)–Pd(1)–C(2')	160.9(1)	C(5)–Mn(2)–C(1')	104.1(1)
C(1')–Pd(1)–C(5)	79.6(1)	C(6)–Mn(2)–C(1')	105.8(1)
C(4)–Pd(1)–C(5)	82.8(1)	C(5)–Mn(2)–Pd(2)	114.4(1)
C(2')–Pd(1)–C(5)	105.8(1)	C(6)–Mn(2)–Pd(2)	58.61(9)
C(4)–Pd(1)–Mn(1)	43.05(9)	C(1')–Mn(2)–Pd(2)	50.09(8)
C(2')–Pd(1)–Mn(1)	144.61(7)	C(5)–Mn(2)–Pd(1)	58.00(9)
C(5)–Pd(1)–Mn(1)	102.84(8)	C(6)–Mn(2)–Pd(1)	93.07(9)
C(1)–Pd(1)–Mn(2)	164.95(9)	C(1')–Mn(2)–Pd(1)	47.02(9)
C(1')–Pd(1)–Mn(2)	41.72(7)	C(2)–C(1)–Mn(1)	150.4(3)
C(4)–Pd(1)–Mn(2)	107.30(9)	C(2)–C(1)–Pd(1)	125.3(3)
C(2')–Pd(1)–Mn(2)	73.17(7)	Mn(1)–C(1)–Pd(1)	83.6(1)
C(5)–Pd(1)–Mn(2)	38.50(8)	C(2')–C(1')–Mn(2)	145.2(2)
C(1')–Pd(2)–C(6)	86.7(1)	C(2')–C(1')–Pd(2)	131.0(2)
C(1')–Pd(2)–P(1)	100.23(8)	Mn(2)–C(1')–Pd(2)	83.6(1)
C(6)–Pd(2)–P(1)	172.78(7)	C(2')–C(1')–Pd(1)	81.4(2)
C(1')–Pd(2)–P(2)	173.41(8)	Mn(2)–C(1')–Pd(1)	91.3(1)
C(6)–Pd(2)–P(2)	88.39(7)	Pd(2)–C(1')–Pd(1)	98.8(1)
P(1)–Pd(2)–P(2)	84.53(3)	C(1')–C(2')–Pd(1)	63.2(2)
C(1')–Pd(2)–Mn(2)	46.28(8)	C(15)–C(2')–Pd(1)	109.4(2)
C(6)–Pd(2)–Mn(2)	42.49(7)	O(3)–C(3)–Mn(1)	178.7(3)
P(1)–Pd(2)–Mn(2)	143.49(2)	O(4)–C(4)–Mn(1)	165.1(3)
P(2)–Pd(2)–Mn(2)	127.79(2)	O(4)–C(4)–Pd(1)	116.8(3)
C(1')–Pd(2)–Pd(1)	41.47(9)	Mn(1)–C(4)–Pd(1)	78.1(1)
O(5)–C(5)–Mn(2)	160.9(3)	O(6)–C(6)–Mn(2)	156.1(2)
O(5)–C(5)–Pd(1)	115.5(2)	O(6)–C(6)–Pd(2)	124.8(2)
Mn(2)–C(5)–Pd(1)	83.5(1)	Mn(2)–C(6)–Pd(2)	78.9(1)

Mn(1)–C(1)–Pd(1) 83.6(1)°, Mn(1)–C(1)–C(2) 150.4(3)° and Pd(1)–C(1)–C(2) 125.3(3)°.

The  $\mu_2\text{-C}(1)=\text{C}(2)\text{HPh}$  ligand is located almost in the plane of the Pd(1)Mn(1)[ $\mu\text{-C}(1)$ ] carbodimetallacycle. The dihedral angle between the Pd(1)Mn(1)C(1) and C(1)C(2)–C(9) planes is only 5.2°. The phenyl substituent is slightly turned relative to the C(1)C(2)C(9) plane: the torsion angle C(1)–C(2)–C(9)–C(10) is 14.0(5)°.

As compared with the  $\mu_2\text{-C}(1)=\text{C}(2)\text{HPh}$  ligand, the second vinylidene  $\mu_3\text{-C}(1')=\text{C}(2')\text{HPh}$  is more distant from metal atoms: the bond lengths are Mn(2)–C(1') 1.925(3) and Pd(2)–C(1') 2.043(3) Å. The C(1')=C(2') bond

(1.372(4) Å) in  $\mu_3$ -vinylidene ligand is also longer. The angles are Mn(2)–C(1')–Pd(2) 83.6(1)°, Mn(2)–C(1')–C(2') 145.2(2)° and Pd(2)–C(1')–C(2') 131.0(2)°.

The vinylidene  $\mu_3$ -C(1')=C(2')HPh is  $\eta^2$ -coordinated to the Pd(1) atom asymmetrically, since the bond lengths are Pd(1)–C(1') 2.116(3) and Pd(1)–C(2') 2.343(3) Å; the angles are C(1')–C(2')–Pd(1) 63.2(2)° and C(2')–C(1')–Pd(1) 81.4(2)°.

The phenyl ring of the second vinylidene C(1')=C(2')HPh is more noticeably rotated relative to the planes of carbodimetallacycle and C(1')=C(2')–C(15) than that of the first vinylidene. The dihedral angle between the Pd(2)Mn(2)C(1') and C(1')C(2')C(15) planes is 11.6°. The torsion angle C(1')–C(2')–C(15)–C(20) is 35.7(5)°. The variation of the mutual disposition of the Ph groups with respect to double bond in the C=CHPh ligands is mainly the consequence of a different type of coordination of the above ligands to metal atoms, namely  $\mu_2$ -C(1)=C(2)HPh and  $\mu_3, \eta^2$ -C(1')=C(2')HPh. In addition, it should be noted that the analysis of intermolecular contacts has not revealed the presence of any shortened interactions.

Only one of four carbonyl groups, namely C(3)O(3), is terminal (the bond lengths are C(3)–O(3) 1.166(4) and Mn(1)–C(3) 1.765(3) Å, the angle Mn(1)–C(3)–O(3) is 178.7(3)°). The other three CO ligands are semi-bridging. The bond lengths C(4)–O(4) and C(5)–O(5) are nearly identical (av. 1.164 Å), the C(6)–O(6) bond is elongated to 1.180(4) Å. The bonds between Mn and semi-bridging CO are in the interval of 1.812–1.822 Å; the angles Mn–C–O are 156.1–165.1°.

In contrast to the Mn–C=O groups, the geometrical parameters of the Pd–C=O fragments change significantly. The distances Pd(1)–C(4) 2.276(4) and Pd(2)–C(6) 2.302(3) Å are markedly shorter than Pd(1)–C(5) 2.468(3) Å. The Pd–C–O angles are from 115.5(2)° to 124.8(2)°.

The intra-bridging bond angles Mn(1)–C(4)–Pd(1) 78.1(1)° and Mn(2)–C(6)–Pd(2) 78.9(1)° are somewhat smaller than Mn(2)–C(5)–Pd(1) 83.5(1)° in a fragment, where the weakest Mn(2)–Pd(1) and Pd(1)–C(5) bonds are present. The similar geometrical features of bridging Pd–C(O)–M fragments are typical for other complexes, such as **6** (M = Mn) [14] and Pd<sub>2</sub>M<sub>2</sub>( $\mu_3$ -CO)<sub>2</sub>( $\mu_2$ -CO)<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>Cp<sub>2</sub> (M = Cr, Mo, W) [16].

Either of the Mn(1) and Mn(2) atoms in complex **5** is coordinated to the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> ligands in an usual mode. The Mn(1)–C(Cp) and Mn(2)–C(Cp) bond lengths are 2.148 Å on average.

The Pd(2) atom forms a chelate cycle with  $\eta^2$ -Ph<sub>2</sub>P(1)CH<sub>2</sub>CH<sub>2</sub>P(2)Ph<sub>2</sub> (dppe). The bond lengths are Pd(2)–P(1) 2.3221(8) Å and Pd(2)–P(2) 2.3612(8) Å. The P(1)–Pd(2)–P(2) angle is equal to 84.53(3)°.

### 3. Discussion

The mechanism of formation of complex **5** is not clear. However, it is undoubtedly, that **5** is a derivative of dinuclear complex **4**.

The structure of tetranuclear molecule **5** can be described as consisting of two parts, *viz.* group [Cp(CO)<sub>2</sub>Mn(1)Pd(1)–( $\mu$ -C=CHPh)] (*fragment 1*) and molecule Cp(CO)<sub>2</sub>Mn(2)–Pd(2)( $\mu$ -C=CHPh)( $\eta^2$ -dppe) (**4**) (*fragment 2*). Formally, the formation of fragment (*1*) could be supposed to be a result of removal of ligand  $\eta^2$ -dppe from complex **4**. However, comparison of the properties of complexes **3** and **4** [11] indicates that  $\eta^2$ -dppe in complex **4** is bound with the Pd atom appreciably stronger than the PPh<sub>3</sub> ligands in complex **3**. Therefore, it is more realistic to suppose, that fragment (*1*) arose as a result of eliminating of two PPh<sub>3</sub> ligands from complex **3** and then it was attached to complex **4** (see Scheme 2).

Fragments (*1*) and (*2*) in **5** are connected with each other by means of  $\pi$ -bonding of the C(1')=C(2')HPh ligand with the Pd(1) atom, by interaction between the Mn(2) and Pd(1) atoms and by interaction between the Pd(1) atom and semi-bridging carbonyl C(5)O(5) group, linked to the Mn(2) atom (about the Mn(2)–Pd(1) bond see below).

The central part of both fragments (*1*) and (*2*) is the methylenedimetallacyclopropane  $\overline{\text{MnPd}(\mu\text{-C=CHPh})}$  system.

The parameters of the triangular Mn(1)Pd(1)[ $\mu$ -C(1)] system in complex **5** are close to those of the analogous MnPt( $\mu$ -C<sup>1</sup>) system in complex Cp(CO)<sub>2</sub>MnPt( $\mu$ -C<sup>1</sup>=C<sup>2</sup>HPh)( $\eta^2$ -dppm) (**1**) [17]. At the same time, a greater difference between the angles Mn(1)–C(1)–C(2) 150.4(3)° and Pd(1)–C(1)–C(2) 125.3(3)° and between the C(1)–Pd(1) and C(1)–Mn(1) bond lengths show that the Mn(1)Pd(1)[ $\mu$ -C(1)=C(2)] system of complex **5** is less symmetrical than the analogous MnPt( $\mu$ -C=C) system in complex **1**. Apparently, the  $\mu_2$ -C(1)=C(2)HPh ligand in **5** is bonded with the Pd(1) atom weaker than  $\mu$ -C=CHPh with the Pt atom in complex **1**.

The C(1)=C(2) bond length (1.347(4) Å) in  $\mu_2$ -vinylidene ligand of complex **5** is close to the typical C=C distance (1.35 Å) in the known [2,7] dinuclear  $\mu$ -vinylidene complexes, such as complex **1** [17], [Cp(CO)<sub>2</sub>Mn]<sub>2</sub>( $\mu$ -C=CHPh) [18], Cp(CO)<sub>2</sub>MnRh( $\mu$ -C=CHPh)(Acac)(CO) [19] and [Cp(CO)<sub>2</sub>MnCu( $\mu$ -C=CHPh)( $\mu$ -Cl)]<sub>2</sub> [20].

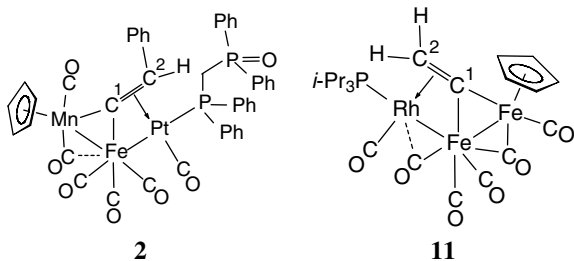
The structure of fragment (*2*) is close to that found for fragment (*1*). However, all bonds in the Mn(2)Pd(2)C(1') triangle and the C(1')=C(2') bond (1.372(4) Å) are elongated in comparison with corresponding bonds in system Mn(1)Pd(1)[ $\mu_2$ -C(1)=C(2)HPh] of fragment (*1*). The C=C distances in the most of described earlier  $\mu_3$ -vinylidene clusters vary from 1.36 to 1.43 Å [2,7].

It is interesting to compare the geometry of the fragment formed as a result of  $\eta^2$ -coordination of the C(1')=C(2')HPh ligand to the Pd(1) atom, with geometry of similar fragments in the known  $\mu_3$ -vinylidene complexes having metal cores in the form of a chain (*C'*) or a triangle (*C*).

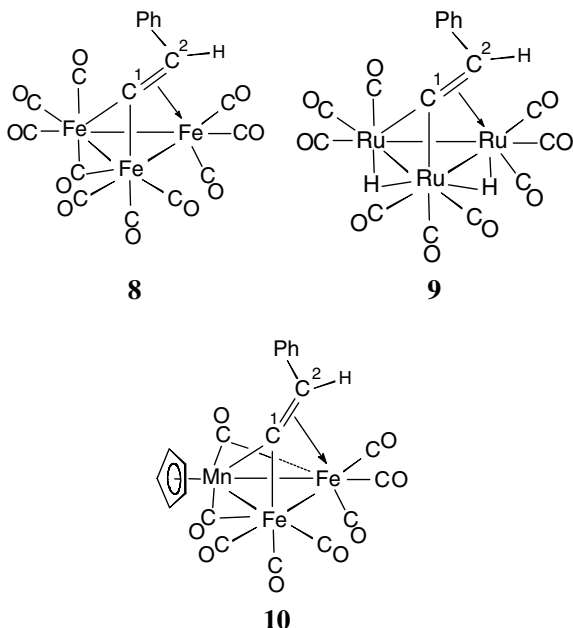
For structural characterization of  $\mu_3$ - and  $\mu_4$ -vinylidene complexes, in our earlier work [1,12], we used a degree of asymmetry of  $\eta^2$ -bonding of the C<sup>1</sup>=C<sup>2</sup>RR' ligand with the metal atom M, which was defined as an absolute value of difference between the M–C<sup>2</sup> and M–C<sup>1</sup> bond lengths and designated as  $\Delta d = |(M-C^2) - (M-C^1)|$ .

In complex **5** the distances Pd(1)–C(1') and Pd(1)–C(2') differ substantially and  $\Delta d$  is 0.227 Å.

At the same time, for two described earlier  $\mu_3$ -vinylidene complexes **2** [6] and (*i*-Pr<sub>3</sub>P)RhFe<sub>2</sub>( $\mu_3$ -C<sup>1</sup>=C<sup>2</sup>H<sub>2</sub>)( $\mu$ -CO)<sub>2</sub>(CO)<sub>4</sub>Cp (**11**) [21], which metal cores are the Mn–Fe–Pt or Fe–Fe–Rh chains (type C'), the practically symmetric  $\eta^2$ -bonding of vinylidene with M atom is observed, and  $\Delta d$  values are rather small (from 0.00 to 0.05 Å). It is significant that in these complexes, the Pt and Rh atoms  $\eta^2$ -coordinated by vinylidenes C=CHR, adopt slightly distorted square-planar geometry.



On the contrary, for  $\mu_3$ -vinylidene clusters with triangular metal core (type C), for instance **8** [22] and **9** [23], the interaction of the M atom with the vinylidene C<sup>2</sup> atom is considerably weaker than that with the C<sup>1</sup> atom. The  $\Delta d$  value for complexes of this type is equal to av. 0.25 Å. In these complexes, the M atoms  $\eta^2$ -coordinated by vinylidenes C=CHR, adopt an octahedral coordination environment.



The most pronounced asymmetry of  $\pi$ -bonding of vinylidene with M was found by us for two independent molecules of triangular cluster **10**, where  $\Delta d$  is equal to 0.58 and 0.45 Å [1].

Consequently, the geometry of the [ $\eta^2$ -C(1')=C(2')]-Pd(1) fragment in complex **5** differs from that of similar fragments in the C' type complexes with an open trimetal chain, but it is close to the geometry of the ( $\eta^2$ -C<sup>1</sup>=C<sup>2</sup>)M fragments in the triangular C complexes, where the M atom is weaker bonded to the C<sup>2</sup> atom than to the C<sup>1</sup> atom of vinylidene.

Probably, a weak interaction between the Pd(1) and C(2') atoms in complex **5** is explained by the fact that the Pd(1) atom is 'overloaded' by the ligands, which give rise to significant steric repulsion.

Complex **5** can be considered as a combination of three tetraatomic cycles Pd(2)C(1')Mn(2)C(6), Pd(1)C(1')Mn(2)-C(5) and Pd(1)C(1)Mn(1)C(4), formed by metals coupled with the carbon atoms of carbonyl and vinylidene ligands. All three cycles are extremely flattened, since the average deviations of atoms are equal to  $\pm 0.15$ ,  $\pm 0.083$  and  $\pm 0.21$  Å, respectively. It is a noteworthy fact that the Pd(1)C(1')Mn(2)C(5) cycle in combination with the Pd(1)C(1)Mn(1)C(4) cycle forms a common strongly flattened system (the atomic deviations are equal to  $\pm 0.36$  Å). The dihedral angle between the plane of this system and the plane of the Pd(2)C(1')Mn(2)C(6) cycle is 96.8°.

The dihedral angle between the Pd(1)C(1)Mn(1)C(4) cycle and the Cp ring [C(21)–C(25)] is equal to 35.7°. The dihedral angle between the Pd(2)C(1')Mn(2)C(6) cycle and the Cp ring [C(26)–C(30)] is 38.4°.

A square-planar coordination of the Pd(2) atom is formed by two P atoms of  $\eta^2$ -dppe and two carbon atoms of the C(6)O(6) and C(1')=C(2')HPh ligands.

A coordination polyhedron of the Pd(1) atom is strongly deformed. Assuming the C(1), C(4), C(5) atoms and midpoint (Mv) of the C(1')=C(2') bond to be functional atoms in the coordination polyhedron of the Pd(1) atom, one can consider it to be a tetrahedron with dihedral angle Pd(1)C(1)C(4)/Pd(1)(Mv)C(5) equal to 44.3°. Such a polyhedron is atypical for the Pd atom.

Summarizing the data presented above, one can draw the following conclusion concerning an interaction between the Pd(1) and Mn(2) atoms.

Indeed, the Pd(1)–Mn(2) distance (2.8913(5) Å) in complex **5** is longer than all known distances 2.58–2.83 Å [13] in complexes with the Pd–Mn bonds.

As it was noted above, molecule **5** consists of two dinuclear fragments, *viz.* [Cp(CO)<sub>2</sub>Mn(1)Pd(1)( $\mu$ -C=CHPh)] (*fragment 1*) and [Cp(CO)<sub>2</sub>Mn(2)Pd(2)( $\mu$ -C=CHPh)( $\eta^2$ -dppe)] (*fragment 2*). It is important to emphasize that the fragment (2) exists as an autonomous molecule **4** whereas the fragment (1) is not capable to exist independently.

If to admit the absence of the Pd(1)–Mn(2) bond, it would be difficult to explain, due to what the heavy and bulky fragments [Cp(CO)<sub>2</sub>Mn(1)Pd(1)( $\mu$ -C=CHPh)] and [Cp(CO)<sub>2</sub>Mn(2)Pd(2)( $\mu$ -C=CHPh)( $\eta^2$ -dppe)] are incorporated with each other into the tetranuclear molecule **5**. The results presented show that both  $\pi$ -bond between the Pd(1) atom and vinylidene C(1')=C(2') group, as well as

semi-bridging interaction between Pd(1) and carbonyl group C(5)O(5) are too weak.

Therefore, it is reasonable to postulate that the metal core in **5** is the Pd(2)–Mn(2)–Pd(1)–Mn(1) chain with some elongated internal Mn(2)–Pd(1) distance. Possibly, weakening of the Mn(2)–Pd(1) bond is caused by steric repulsion between the ligands linked to the Mn(2) and Pd(1) atoms.

#### 4. Conclusions

The structure of complex **5** is unique due to the presence of a chain of alternating Pd and Mn atoms, as well as due to the presence of two vinylidene ligands with different ( $\mu_2$  and  $\mu_3$ ) coordination modes.

Earlier Braunstein et al. described the structure of complex [(OC)Pd( $\mu$ -NC)Mn(Cp')(CO)<sub>2</sub>]<sub>4</sub> (**7**), which incorporates two symmetric Mn–Pd–Pd–Mn chains non-connected with each other [15].

As far as we know, the number of complexes with two vinylidene ligands is limited to three compounds, and all of them contain  $\mu_2, \eta^1, \eta^1$ -C=CHR ligands. The dinuclear complex [CpFe(CO)]<sub>2</sub>( $\mu$ -C=CH<sub>2</sub>)<sub>2</sub> is characterized by a mass spectrum only [24]. The structure of trinuclear bis-vinylidene complex [Cp(CO)<sub>2</sub>Mn]<sub>2</sub>Mo[ $\mu$ -C=C(H)COOMe]<sub>2</sub>(CO)<sub>2</sub> which contains the Mn–Mo–Mn chain and two bridging carbomethoxyvinylidene ligands, coordinated to the metal atoms by an identical mode, has been determined [25]. In dinuclear complex Ir<sub>2</sub>( $\mu$ -C=CH<sub>2</sub>)( $\mu$ -C=CHPh)( $\mu$ -dppm)<sub>2</sub>(CO)<sub>2</sub>I<sub>2</sub> two different vinylidene ligands bridge the Ir–Ir bond and are in a *trans*-position to each other [26].

Complex ( $\eta^2$ -dppe)PdMn( $\mu_3$ -C=CHPh)PdMn( $\mu$ -C=CHPh)(CO)<sub>4</sub>Cp<sub>2</sub> (**5**) represents the first organometallic compound containing the Pd–Mn–Pd–Mn chain, and at the same time, the first example of compound in which two coordination types of vinylidene complexes are present in one molecule, *viz.* **B** type with the symmetric  $\mu_2$ -coordination of vinylidene and **C'** type with  $\mu_3$ -vinylidene ligand.

#### 5. Experimental

##### 5.1. Preparation of Cp(CO)<sub>2</sub>MnPd( $\mu$ -C=CHPh)( $\eta^2$ -dppe) (**4**) and ( $\eta^2$ -dppe)PdMn( $\mu_3$ -C=CHPh)PdMn( $\mu$ -C=CHPh)(CO)<sub>4</sub>Cp<sub>2</sub> (**5**)

A mixture of Cp(CO)<sub>2</sub>MnPd( $\mu$ -C=CHPh)(PPh<sub>3</sub>)<sub>2</sub> (**3**) (578 mg, 0.6 mmol) and dppe (305 mg, 0.7 mmol) in 20 ml of benzene was stirred at 20 °C for 1 h. Then the resulting brown solution was filtered through a ca. 1 cm alumina pad, and the filtrate was evaporated under reduced pressure. Two milliliter of ether were added to the oily residue, and the mixture was cooled to –15 °C. The precipitated crystals were separated from the mother liquor, washed with cooled ether and hexane, and dried. The orange fine-crystalline Cp(CO)<sub>2</sub>MnPd( $\mu$ -C=CHPh)(dppe) (**4**) (442 mg, 90%) was obtained. Several dark-red (almost black) good formed crystals of the solvate [( $\eta^2$ -dppe)-

PdMn( $\mu_3$ -C=CHPh)PdMn( $\mu$ -C=CHPh)(CO)<sub>4</sub>Cp<sub>2</sub>] · 0.5 C<sub>6</sub>H<sub>6</sub> · 0.5Et<sub>2</sub>O (**5a**) were found in addition to the main product **4** and chosen for X-ray diffraction study.

##### 5.2. X-ray crystallographic study of [ $\mu_3$ - $\eta^1, \eta^1, \eta^2$ -(phenyl)ethenylidene]-[ $\mu_2$ - $\eta^1, \eta^1$ -(phenyl)ethenylidene]-tris( $\mu_2$ -carbonyl)-carbonyl-bis( $\eta^5$ -cyclopentadienyl)-[ $\eta^2$ -bis(diphenylphosphino)ethane-*P, P'*]-di-palladium-dimanganese(3Pd–Mn) 0.5 benzene 0.5 diethyl ether solvate (**5a**)

Single-crystal X-ray diffraction experiments for **5** · 0.5C<sub>6</sub>H<sub>6</sub> · 0.5Et<sub>2</sub>O (**5a**) were carried out with a SMART 1000 CCD area detector, using graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å,  $\omega$ -scans with a 0.3° step in  $\omega$  and 10 s per frame exposure,  $\theta = 1.61$ – $30.06^\circ$ ) at 110 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N<sub>2</sub> gas cryostat. Reflection intensities were integrated using SAINT software [27] and semi-empirical method SADABS [28]. The structure was solved by direct method and refined by the full-matrix least-squares method against  $F^2$  in anisotropy approximation. The solvate molecules C<sub>6</sub>H<sub>6</sub> and Et<sub>2</sub>O share the same position in the unit cell and were refined with site occupancy factors equal to 0.5, the C<sub>6</sub>H<sub>6</sub> was refined as rigid model approximation.

All hydrogen atoms were placed in the geometrically calculated positions and included in the refinement using the riding model approximation with the  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the methyne and methylene groups and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl groups, where the  $U_{\text{eq}}(\text{C})$  is the equivalent isotropic temperature factor of the carbon atom bonded to the corresponding H atom.

Details of crystal data, data collection and structure refinement parameters for **5a** are given in Table 1. All calculations were performed on an IBM PC/AT using the SHELXTL software [29].

CCDC 257160 contains the supplementary crystallographic data for **5a**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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