



Chemistry of vinylidene complexes. XXI. Synthesis, spectroscopic and structural study of the RePt and MnPt μ -vinylidene complexes [☆]

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ABSTRACT

Reaction of $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$ (**1**) with $\text{Pt}(\text{PPh}_3)_4$ and subsequent treatment of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (**2**) with diphosphines $\text{P-P} = \text{dppe}$, dppp afforded new complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{P-P})$ (**4**, **5**). The structures of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (**5**) and $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (**10**) have been determined by single crystal XRD. The influence of the nature of $\text{M} = \text{Re}$, Mn and $\text{L}_2 = (\text{PPh}_3)_2$, dppm , dppe , dppp at the Pt atom on the structural, IR and ^1H , ^{13}C and ^{31}P NMR spectroscopic characteristics of complexes $\text{Cp}(\text{CO})_2\text{M}(\text{Pt}(\mu\text{-C}=\text{CHPh})(\text{L}_2))$ (**2–5**, **7–10**) is considered.

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1. Introduction

Heterometallic complexes containing bridging vinylidene ligands $\mu\text{-C}=\text{CRR}'$ (R and $\text{R}' = \text{H}$, alkyl, aryl, etc.) may be used as building blocks for heteronuclear clusters synthesis, as precursors of new heterometallic materials, and in catalysis [2–5].

Tens of bimetallic μ -vinylidene complexes with the Mn-M bonds ($\text{M} = \text{Mo}$, W [6], Mn [7–10], Fe [11], Rh [12,13], Pd [14], Pt [15], Cu [16]) were synthesized using mononuclear complexes $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHR}$ ($\text{R} = \text{Ph}$, COOMe , $\text{CH}[\text{O}(\text{CH}_2)_3\text{O}]$) or $\text{Cp}(i\text{-Pr}_3\text{P})\text{Rh}=\text{C}=\text{CHR}$ ($\text{R} = \text{H}$, Me , Ph) and fragments containing the second metal M .

On the contrary, the number of known dinuclear μ -vinylidene complexes with the Re-M bonds is limited to several rare examples. In the seventies, synthesis of $\text{Cp}_2(\text{CO})_4\text{MnRe}(\mu\text{-C}=\text{CHPh})$ decomposing at 20°C through the Mn-Re bond cleavage has been

Abbreviations: Cp, $\eta^5\text{-C}_5\text{H}_5$; CO_{sb} , semibridging CO group; CO_t , terminal CO group; dppm , $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$; dppe , $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$; dppp , $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$; VT, variable temperature; XRD, X-ray diffraction.

[☆] For Part XX, see Ref. [1].

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reported [17]. Recently [18,19], starting from $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$ (**1**), we have obtained three stable complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$, $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (**2**) and $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{dppm})$ (**3**).

Dinuclear complexes with the Re-M bonds ($\text{M} = \text{Cr}$, Mo , W [20–22], Fe [23,24], Pt [20,25–28]) supported by carbene ligands $\mu\text{-CH}_2$, $\mu\text{-CHPh}$, $\mu\text{-C}(\text{OMe})\text{Ph}$, $\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}$ represent a more wide variety. The majority of them are the RePt complexes.

These complexes attract attention due to rhenium catalytic properties. Bimetallic RePt catalysts are employed in industrial processes of oil reforming to produce high-octane fuel [29]. Organometallic compounds with the Re-Pt bond are used in the simulation of processes occurring on a metal surface. The RePt complexes are expected to be effective in homogeneous catalysis.

Rhenium-containing complexes provoke also the academic interest. The Re atom has a greater size than the Mn atom [30,31] and is more electron rich, that is a prerequisite for preparation of heterometallic clusters with specific properties and structures. Recently [32], we have synthesized an unusual μ_3 -vinylidene cluster $\text{CpReFePt}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_6(\text{PPh}_3)$ containing trimetallic chain core Re-Fe-Pt originated from dinuclear complex **2**.

In this article we describe the syntheses of dinuclear μ -vinylidene complexes containing the Re-Pt bonds and their investigation by

XRD and spectroscopic methods. The influence of the nature of metals $M = \text{Re}$, Mn and ligands $L_2 = (\text{PPh}_3)_2$, dppm , dppe , dppp at the Pt atom on the structure and spectroscopic characteristics of complexes $\text{Cp}(\text{CO})_2\text{MPt}(\mu\text{-C=CHPh})(L_2)$ is discussed.

2. Results and discussion

2.1. Syntheses of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{P-P})$ (**2–5**)

Recently [18,19], we have shown that the reaction of $\text{Cp}(\text{CO})_2\text{Re-e=C=CHPh}$ (**1**) with $\text{Pt}(\text{PPh}_3)_4$ gave the dinuclear complex $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**2**) (90% yield), which transformed into $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppm})$ (**3**) (74% yield) by treating with dppm .

New complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{P-P})$ ($\text{P-P} = \text{dppe}$ (**4**), dppp (**5**)) containing chelate ligands $\eta^2\text{-P-P}$ at the Pt atom were obtained by the action of bis-phosphines dppe and dppp on complex **2** (benzene, 20 °C, 1–3 h, 94% yields) (Scheme 1).

Complexes **2–5** are stable orange crystalline solids well soluble in benzene, CH_2Cl_2 . In solution these complexes slowly decompose.

Earlier, starting from $\text{Cp}(\text{CO})_2\text{Mn-e=C=CHPh}$ (**6**), the series of MnPt complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**7**) [15], $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppm})$ (**8**), $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppe})$ (**9**) and $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppp})$ (**10**) [33] was synthesized. However, X-ray structures of these MnPt complexes were not known at that time.

2.2. X-ray diffraction study of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppp})$ (**5**) and $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppp})$ (**10**)

Crystallographic data and parameters of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**2**) [34], $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dppm})$ (**3**) [19], $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**7**) [35] and $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dppm})$ (**8**) [36] were recently reported.

Single crystal XRD data of new complex $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dppp})$ (**5**) and its manganese analogue $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppp})$ (**10**) are considered in more detail here. Molecular structures of **5** and **10** are shown in Figs. 1 and 2.

Crystallographic data for complexes **5** and **10** are given in Table 1. Selected geometrical parameters of **5** and **10** are given in Table 2.

The central fragment of $\text{Cp}(\text{CO})_2\text{MPt}(\mu\text{-C=CHPh})(\text{dppp})$ ($M = \text{Re}$ (**5**), Mn (**10**)) is the carbodimetallacycle

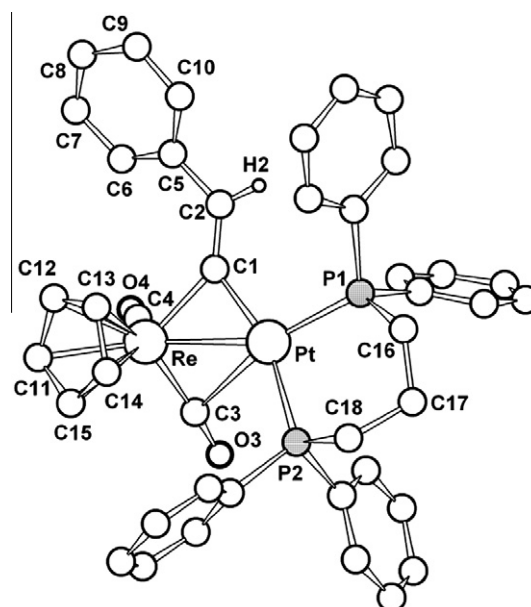
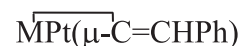


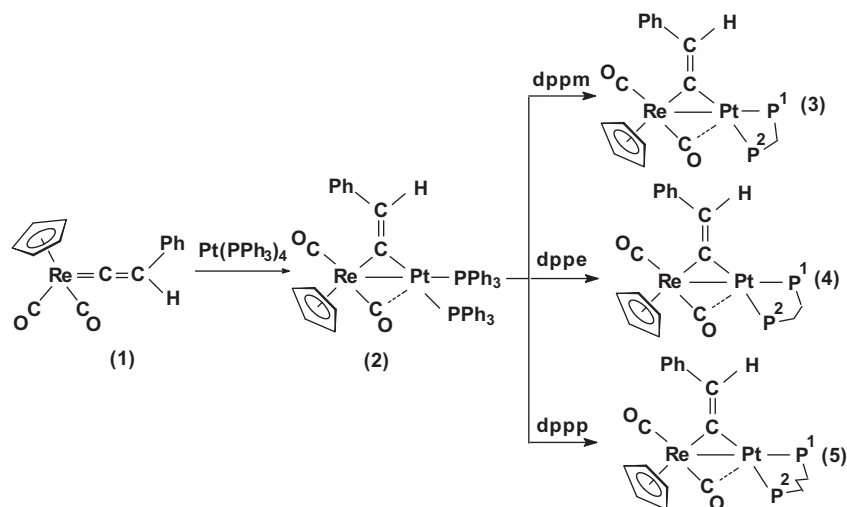
Fig. 1. Molecular structure of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppp})$ (**5**).



formed from bridging phenylvinylidene and two metal atoms. The M atoms are bound to η^5 -cyclopentadienyl ligands, terminal (C4O4), and semibridging (C3O3) carbonyl groups. Chelate bis-(diphenylphosphine)propane ligand is η^2 -coordinated to the Pt atom.

The core fragments $[\text{MPt}(\mu\text{-C=CHPh})]$ ($M = \text{Re}$, Mn) of complexes **2–5** and **7–10** are very similar. The slight distortion of planar structure of the $\overline{\text{MPt}(\mu\text{-C=CHPh})}$ system is observed in all molecules. The deviation of the C2 atom from the $\overline{\text{Re-Pt-C1}}$ carbodimetallacycle plane is 0.16(1) Å in complex **2**, 0.28(2) Å in **3** and 0.17(2) Å in **5**. The C2 atom deviates from the $\overline{\text{Mn-Pt-C1}}$ plane by 0.148 Å in **7** [35], by 0.144 Å in **8** [36] and by 0.13(2) Å in **10**.

Dihedral angles between the $\overline{\text{MPtC1}}$ ($M = \text{Re}$, Mn) and C1C2C5 planes are 9.7° on average. Torsion angles C1–C2–C5–C6 are given in Table 2.



Scheme 1.

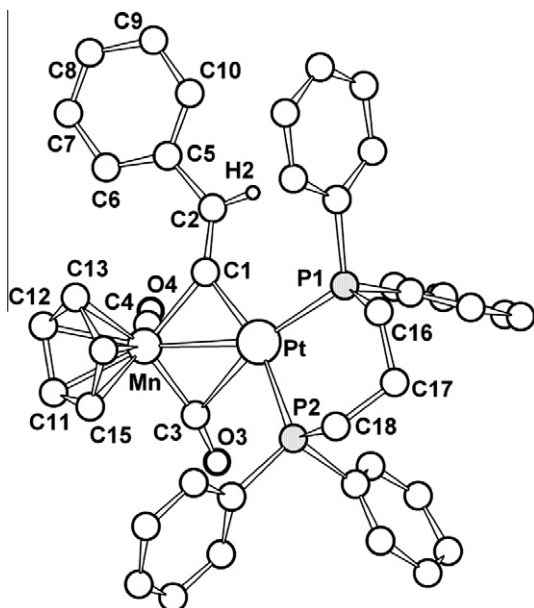


Fig. 2. Molecular structure of $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppp})$ (**10**).

Table 1
Crystallographic data and parameters of structure refinement for complexes **5** and **10**.

Complex	5	10
Empirical formula	$\text{C}_{42}\text{H}_{37}\text{O}_2\text{P}_2\text{PtRe}\cdot 2(\text{C}_6\text{H}_6)$	$\text{C}_{42}\text{H}_{37}\text{O}_2\text{P}_2\text{PtMn}\cdot \text{CH}_2\text{Cl}_2$
Formula weight	1173.16	970.61
Colour	Orange	Orange
Crystal size (mm)	$0.41 \times 0.28 \times 0.22$	$0.30 \times 0.20 \times 0.05$
<i>T</i> (K)	223	298
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	10.9757(7)	17.861(3)
<i>b</i> (Å)	10.8158(7)	10.941(2)
<i>c</i> (Å)	38.663(3)	21.091(4)
β (°)	95.121(1)	107.407(2)
<i>V</i> (Å ³)	4571.4(5)	3933(1)
ρ_c (g/cm ⁻³)	1.705	1.639
<i>Z</i>	4	4
μ (Mo K α) (mm ⁻¹)	5.813	4.127
<i>N</i> _{tot}	30212	10374
<i>N</i> _{uniq} (<i>R</i> _{int})	7186 (0.07)	6171 (0.11)
$2\theta_{\text{max}}$ (°)	48.0	48.0
<i>N</i> _{par}	513	460
<i>R</i> ₁	0.049	0.040
<i>wR</i> ₂	0.130	0.067
Goodness-of-fit (GOF) on <i>F</i> ₂	1.171	0.780
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$ (e Å ³)	-2.79/1.22	-0.76/0.95

Since the Re atom size (covalent atomic radius is 1.51 Å [30,31]) is greater than that of the Mn atom (1.38 Å [30], 1.39 Å [31]), the Re–Pt and Re– μ -C1 bonds in complexes **2**, **3**, **5** are significantly longer than the Mn–Pt and Mn– μ -C1 bonds of corresponding complexes **7**, **8**, **10** (Table 2).

The lengths of the Pt–C1 bonds in complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{L}_2)$ (*M* = Mn, Re) are almost independent on the nature of ligands *L*₂ = (PPh₃)₂, dppm, dppp and lie in the interval between 1.976(7) Å (in **3**) and 2.008(4) Å (in **2**).

The C1=C2 bond lengths are in the typical interval of 1.33–1.36 Å for binuclear μ -vinylidene complexes [3]. Vinylidene ligand μ -C1=C2HPh deviates from Re or Mn atoms towards Pt: the Re–C1–C2 and Mn–C1–C2 angles (av. 141°) are increased as compared

to the Pt–C1–C2 angles (av. 134°). The P1–Pt–P2 angles in complexes **3** and **8** with dppm (av. 73°), in **5** and **10** with dppp (av. 94°), in **2** and **7** with two PPh₃ (av. 103°) are close to the standard values [37].

Each of molecules **2–5**, **7–10** contains two carbonyl groups in different coordination modes. Terminal group C4O4 together with atom *M* = Mn or Re forms an almost linear chain with the *M*–C4–O4 angle from 174° to 179°. The *M*–C3–O3 system including the second carbonyl group is bent. The *M*–C3–O3 angles and Pt–C3 distances depend on the nature of *M* atoms and *L*₂ ligands.

The *M*–C3–O3 angle of Mn and Re complexes with dppm is smaller than that of complexes with *L*₂ = (PPh₃)₂ and dppp (Table 2). At the same time, the *M*–C3–O3 angles of Re complexes are larger than those in corresponding Mn analogues. The largest *M*–C3–O3 angle (173(1)°) was found in **5**, and the smallest (153.3(6)°) in **8**.

Both Re and Mn complexes containing dppm ligand have the shortest Pt–C3 distances. The Pt–C3 distance is longer in all Re complexes than in the Mn analogues: it increases in **2** versus **7** on 0.325 Å, in **3** versus **8** on 0.18 Å, in **5** versus **10** on 0.26 Å.

These data indicate that the interaction between the Pt atom and C3O3 group in complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{L}_2)$ is considerably weaker than in $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{L}_2)$.

Thus, in contrast to $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dppm})$ (**8**) [36] with asymmetric bridging C3O3 group, only weak semibridging interaction Pt → C3O3 is observed in $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppp})$ (**10**). The C3O3 groups in $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**2**) and $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppp})$ (**5**) are rather terminal.

The weakening of the Pt → C3O3 interaction in rhenium complexes is probably caused by less effective overlap of the Pt atomic orbital with the C3≡O3 orbitals due to larger distance between them.

2.3. IR study of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{L}_2)$ (**2–5**)

The IR spectra of complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{L}_2)$ (*M* = Mn, Re) (see [15,33] and Section 4) contain $\nu(\text{C=C})$ bands of the bridging phenylvinylidene in the interval of 1553–1541 cm⁻¹ typical for dinuclear μ -vinylidene complexes [3].

The $\nu(\text{CO})$ frequencies of the known rhenium carbonyl complexes are lower than those of manganese analogs due to stronger electron-donor power of the Re atom in comparison with the Mn atom. It can be seen from $\nu(\text{CO})$ for mononuclear complexes $\text{CpM}(\text{CO})_2(\text{L})$ (*M* = Mn, Re; *L* = CO, PPh₃, $\eta^2\text{-PhC}\equiv\text{CH}$, $\eta^1\text{-C=CHPh}$) listed in Table 3. The $\nu(\text{CO})$ of the low-frequency bands for dinuclear complexes $[\text{Cp}(\text{CO})_2\text{MM}']_2(\mu\text{-C=CHPh})$ decrease sequentially in the order of $\text{MM}' = \text{Mn}_2 > \text{MnRe} > \text{Re}_2$ [8,17,38].

The inverse tendency has been found for complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{L}_2)$ (*M* = Re, Mn): the $\nu(\text{CO})$ frequencies increase for Re complexes in comparison with the Mn analogs [19].

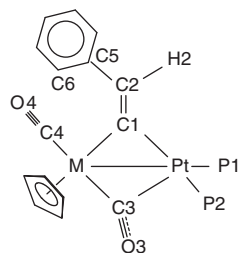
The high-frequency shift of $\nu(\text{CO}_t)$ bands for Re complexes is not too large, viz. 2–11 cm⁻¹ in the case of *L*₂ = (PPh₃)₂, dppe and dppp. The $\nu(\text{CO}_t)$ band of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dppm})$ (**3**) is even low-frequency shifted for 7 cm⁻¹ compared to that of $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dppm})$ (**8**).

But increase in the low-frequency $\nu(\text{CO}_{sb})$ bands attributed to semibridging carbonyl groups, which are under influence of the adjacent Pt atom, is especially noticeable (Table 3). The $\nu(\text{CO}_{sb})$ frequency for complex **2** is higher than that for **7** by 20 cm⁻¹, for **3** than **8** by 5 cm⁻¹.

The greatest increase of $\nu(\text{CO}_{sb})$ of RePt complexes in relation to MnPt analogs has been observed for complexes with *L*₂ = dppe and dppp (Table 3). The $\nu(\text{CO}_{sb})$ frequencies of **4** and **5** are higher than those of **9** and **10** by 55 cm⁻¹ and 31 cm⁻¹, respectively.

Table 2Comparison of geometric parameters of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (**2**) [34], $\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (**3**) [19], $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (**5**) and $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (**10**).

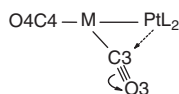
	M = Re/Pt ₂			M = Mn/Pt ₂		
	(PPh ₃) ₂ (2)	dppm (3)	dppp (5)	(PPh ₃) ₂ (7)	dppm (8)	dppp (10)
Bond length (Å)						
M–Pt	2.7360(3)	2.7306(7)	2.7251(6)	2.6344(4)	2.607(1)	2.644(1)
M–C1	2.083(5)	2.090(8)	2.10(1)	1.972(3)	1.924(7)	1.966(8)
Pt–C1	2.008(4)	1.976(7)	2.00(1)	2.006(3)	1.991(6)	1.998(8)
C1=C2	1.351(6)	1.35(1)	1.34(2)	1.327(4)	1.363(9)	1.36(1)
C2–C5	1.497(5)	1.48(1)	1.45(2)	1.486(3)	1.469(9)	1.47(1)
Pt–P1	2.272(1)	2.265(2)	2.250(3)	2.2745(7)	2.280(2)	2.274(2)
Pt–P2	2.375(1)	2.353(2)	2.318(3)	2.3548(8)	2.331(2)	2.344(2)
M–C3	1.905(6)	1.92(1)	1.91(1)	1.811(3)	1.826(8)	1.82(1)
M–C4	1.883(6)	1.88(1)	1.86(2)	1.761(4)	1.775(8)	1.78(1)
Pt–C3	2.722(5)	2.392(9)	2.71(1)	2.397(3)	2.212(7)	2.454(9)
C3–O3	1.163(6)	1.18(1)	1.15(1)	1.159(3)	1.189(8)	1.153(9)
C4–O4	1.171(6)	1.16(1)	1.18(1)	1.160(4)	1.154(8)	1.153(9)
Bond angle (°)						
M–C1–Pt	83.9(2)	84.3(3)	83.3(5)	82.9(1)	83.5(3)	83.7(3)
C1–Pt–M	49.2(1)	49.6(2)	49.9(3)	47.99(8)	47.2(2)	47.7(2)
M–C1–C2	141.6(4)	137.9(7)	140.4(10)	141.0(2)	143.3(5)	140.7(7)
Pt–C1–C2	133.5(4)	135.1(6)	135.2(9)	135.2(2)	132.5(5)	135.0(6)
C1–C2–C5	132.0(4)	129.6(8)	131(1)	131.9(3)	126.4(6)	131.3(8)
P1–Pt–P2	102.99(4)	72.91(7)	94.8(1)	102.31(3)	72.83(6)	93.95(9)
P1–Pt–C1	96.0(1)	102.8(2)	103.3(3)	98.76(8)	102.7(2)	104.1(2)
P1–Pt–M	144.89(3)	151.30(5)	153.17(9)	144.90(2)	149.17(5)	151.44(7)
P2–Pt–C1	159.0(1)	170.8(2)	160.4(3)	154.04(8)	169.4(2)	158.2(2)
P2–Pt–M	110.78(3)	132.89(5)	111.45(7)	112.78(2)	135.32(5)	114.48(7)
C1–Pt–C3	82.1(3)	91.0(3)	82.9(8)	84.2(1)	89.1(3)	84.5(3)
M–C3–O3	171.5(5)	159.6(7)	173(1)	166.0(3)	153.3(6)	164.3(9)
Pt–C3–O3	118.2(4)	122.5(7)	116.5(8)	117.7(2)	126.8(5)	120.9(8)
M–C4–O4	177.6(6)	175.4(8)	174(1)	178.9(4)	176.3(6)	179.5(10)
M–C3–Pt	70.0(2)	77.7(3)	69.8(3)	76.1(1)	79.8(3)	74.8(3)
Dihedral angle MPtC1/C1C2C5 (°)						
	9.6(6)	12(1)	10(2)	11.3(4)	6.2	6.9(9)
Torsion angle C1–C2–C5–C6 (°)						
	–175.3(5)	–32(1)	–29(2)	–152.5(3)	–36.7	16(1)

**Table 3**

IR data for mono- and dinuclear carbonyl complexes of manganese and rhenium.

Complex	$\nu(\text{CO}), \text{cm}^{-1}$	$\Delta\nu^a$	Ref.
$\text{CpM}(\text{CO})_2(\text{L})^b$			
$\text{CpMn}(\text{CO})_3$	2034 s, 1949 vs	–	[8]
$\text{CpRe}(\text{CO})_3$	2028 s, 1935 vs	–	[38]
$\text{CpMn}(\text{CO})_2(\text{PPh}_3)$	1946 s, 1880 s	–	[8]
$\text{CpRe}(\text{CO})_2(\text{PPh}_3)$	1930 s, 1859 s ^c	–	[39]
$\text{CpMn}(\text{CO})_2(\eta^2\text{-PhC}\equiv\text{CH})$	1981 s, 1921 s	–	[8]
$\text{CpRe}(\text{CO})_2(\eta^2\text{-PhC}\equiv\text{CH})$	1980 s, 1911 s	–	[38]
$\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}$ (6)	2009 s, 1955 s	–	[8]
$\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$ (1)	2003 s, 1938 s	–	[38]
$[\text{Cp}(\text{CO})_2\text{MM}']_2(\mu\text{-C}=\text{CHPh})^b$			
$[\text{Cp}(\text{CO})_2\text{Mn}]_2(\mu\text{-C}=\text{CHPh})$	1983 m, 1953 vs, 1928 s	–	[8]
$\text{Cp}_2(\text{CO})_4\text{MnRe}(\mu\text{-C}=\text{CHPh})$	1983 m, 1952 vs, 1920 s	–	[17]
$[\text{Cp}(\text{CO})_2\text{Re}]_2(\mu\text{-C}=\text{CHPh})$	1983 m, 1953 vs, 1916 s	–	[38]
$\text{Cp}(\text{CO})_2\text{MPt}[\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}](\text{L}_2)$ ($M = \text{Mn}, \text{Re}$) ^b			
$\text{Cp}(\text{CO})_2\text{MnPt}[\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}](\text{PMe}_3)_2$	1869 s, 1813 s	56	[25]
$\text{Cp}(\text{CO})_2\text{RePt}[\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}](\text{PMe}_3)_2$	1885 s, 1827 s	58	[25]
$\text{Cp}(\text{CO})_2\text{MnPt}[\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}](\text{PMe}_2\text{Ph})_2$	1861 s, 1797 s ^c	64	[26]
$\text{Cp}(\text{CO})_2\text{RePt}[\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}](\text{PMe}_2\text{Ph})_2$	1882 s, 1827 s	55	[25]
$\text{Cp}(\text{CO})_2\text{MPt}(\mu\text{-C}=\text{CHPh})(\text{L}_2)$ ($M = \text{Mn}, \text{Re}$) ^c			
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (7)	1924 s, 1838 m, br	86	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (2)	1933 s, 1858 m, br	75	d
$\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (8)	1902 s, 1768 m, br	134	[33]
$\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (3)	1895 s, 1773 m, br	122	d
$\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppe})$ (9)	1906 s, 1784 m, br	122	[33]
$\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppe})$ (4)	1908 s, 1839 m, br	69	d
$\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppp})$ (10)	1913 s, 1822 m, br	91	[33]
$\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppp})$ (5)	1924 s, 1853 m, br	71	d

^a The value of the splitting between the stretching absorption bands of the terminal (CO_t) and semibridging (CO_{sb}) groups, $\Delta\nu = \nu(\text{CO}_t) - \nu(\text{CO}_{sb})$.^b In cyclohexane solution.^c In CH_2Cl_2 solution.^d The present work.



Scheme 2.

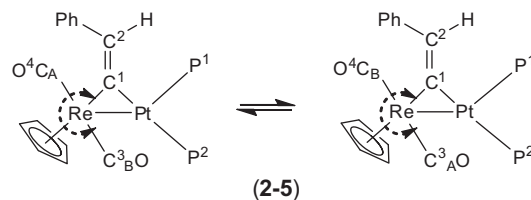
It should be noted that the higher $\nu(\text{CO})$ frequencies for μ -carbene complexes $\text{Cp}(\text{CO})_2\text{RePt}[\mu\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}](\text{L})_2$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}$) in comparison with the MnPt analogs (Table 3) were observed 30 years ago by Stone and coworkers [25], however this phenomenon was not discussed.

Earlier [33,40], we have proposed to use the magnitude of the splitting between the stretching vibration bands of two carbonyl groups $\Delta\nu = \nu(\text{CO}_t) - \nu(\text{CO}_{sb})$ for estimating the degree of semibridging interaction in complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{L}_2)$ (Scheme 2).

The smooth changing of the $\text{C}3\text{O}3$ group coordination mode from terminal in $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)(\text{CO})$ ($\Delta\nu = 67 \text{ cm}^{-1}$) to semibridging in $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (**7**) ($\Delta\nu = 86 \text{ cm}^{-1}$) and then to bridging in $\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (**8**) ($\Delta\nu = 134 \text{ cm}^{-1}$) was revealed [40]. This conclusion was afterwards confirmed by XRD of **7** [35] and **8** [36].

On going from $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{L}_2)$ (**7–10**) to the corresponding analogs $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{L}_2)$ (**2–5**), the $\Delta\nu$ value decreases in all cases (Table 3). This can indicate the weaker $\text{Pt} \rightarrow \text{C}3\text{O}3$ interaction in RePt complexes in comparison with MnPt analogs.

This conclusion is in accordance with the elongation of distances between the Pt atom and $\text{C}3\equiv\text{O}3$ group in rhenium complexes **2, 3, 5** in comparison with manganese analogs **7, 8, 10**, occurring consentaneously with the lengthening of the Re–Pt bonds in comparison with the Mn–Pt bonds (see Section 2.2, Table 2).



(2-5)

Scheme 3.

2.4. NMR study of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{L}_2)$ (**2–5**)

In the ^{13}C NMR spectra of complexes **2–5**, the C^1 vinylidene atoms resonate at δ 232–235 ppm. These are upfield shifted by 30–40 ppm in comparison with corresponding MnPt complexes **7–10** (Table 4). The resonances at δ 136–139 ppm of the C^2 vinylidene atom of complexes **2–5** are upfield shifted only by 3–4 ppm. In the spectra of the known dinuclear complexes, μ -vinylidene ligand appears as signals at δ 235–295 (C^1) and 120–150 (C^2) ppm [3]. The magnitudes of the Pt– C^1 and P– C^1 coupling constants for RePt complexes **2–5** are close to those found previously [33] for MnPt analogs **7–10**.

Earlier, we have reported that the ^{13}C NMR spectra of complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{L}_2)$ (**7–10**) contain two signals in the range δ 229–253 ppm that belong to two carbonyl groups [33]. The narrow signal at high field was attributed to terminal CO_t group, and the second, broad signal at low field – to semibridging CO_{sb} group. The greatest downfield shift (by 22.45 ppm) of the CO_{sb} group signal versus CO_t has been observed for $\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (**8**) (Table 4) with the strongest $\text{Pt} \rightarrow \text{CO}_{sb}$ interaction.

In contrast to MnPt complexes **7–10**, the ^{13}C NMR spectrum of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (**2**) at +25 °C contains two broad CO signals, and spectrum of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{dppm})$

Table 4
 $^{13}\text{C}\{^1\text{H}\}$ NMR data (δ , ppm [J, Hz]) for complexes $\text{Cp}(\text{CO})_2\text{MPt}(\mu\text{-C}=\text{C}^2\text{HPh})(\text{L}_2)$ ($\text{M} = \text{Mn}, \text{Re}; \text{L}_2 = (\text{PPh}_3)_2, \text{dppm}, \text{dppe}, \text{dppp}$).

Complex ^a	$\mu\text{-C}^1=\text{C}^2\text{HC}_6\text{H}_5$		C_5H_5	CO_t^b	CO_{sb}^b	Ref.
	C^1	C^2				
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (7)	264.30 d $^1J_{\text{PtC}} = 857$ $^2J_{\text{PtC}} = 61.4,$ 2.5	141.25 s, br $^2J_{\text{PtC}} = 115$ $^3J_{\text{PtC}} = 7$	84.19 s	229.84 s	233.75 br	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2$ (2)	232.24 d $^1J_{\text{PtC}} = 821.61$ $^2J_{\text{PtC}} = 65.25$	138.25 t $^2J_{\text{PtC}} = 96.16$ $^3J_{\text{PtC}} = 4.00$	85.70 s	203.41s	205.49 s	c
$\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (8)	271.14 d $^1J_{\text{PtC}} = 735.0$ $^2J_{\text{PtC}} = 61.0$	141.20 d $^2J_{\text{PtC}} = 93.0$ $^3J_{\text{PtC}} = 13.0$	86.17 s	229.97s	252.42 d	[33]
$\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C}=\text{CHPh})(\mu\text{-CO})(\text{dppm})$ (3) ^d	234.38 d $^2J_{\text{PtC}} = 62.50$	136.05 d $^2J_{\text{PtC}} = 90.40$ $^3J_{\text{PtC}} = 8.45$	87.71 s	205.59 s	230.32s, br	c
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{dppe})$ (9)	269.75 d $^2J_{\text{PtC}} = 63.0$	141.63 br	85,61 s	230.34 s	238.90 br	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{dppe})$ (4)	234.57dd $^1J_{\text{PtC}} = 764.05$ $^2J_{\text{PtC}} = 66.46,$ 3.27	138.34 dd $^2J_{\text{PtC}} = 101.38$ $^3J_{\text{PtC}} = 2.91$ 5.11	86.31 s	204.90 s	216.04s, br	c
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (10)	265.96 d $^1J_{\text{PtC}} = 818.0$ $^2J_{\text{PtC}} = 63.0$	140.48 br $^2J_{\text{PtC}} = 112.0$	83.50 s	229.77s	236.99 br	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (5)	233.41dd $^1J_{\text{PtC}} = 813.79$ $^2J_{\text{PtC}} = 65.55,$ 2.59	137.61 t $^2J_{\text{PtC}} = 104.99$	85.61s	203.31 s	208.70 s	c

^a The spectra in CD_2Cl_2 (**2–5**) and CDCl_3 (**7–10**) solutions.

^b The CO signals of **2–5** at -60 °C.

^c The present work.

^d The spectrum of **3** is recorded at -60 °C.

Table 5The data of the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (δ , ppm [J, Hz]) for complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}\equiv\text{C}^1\text{HPh})(\text{L}_2)$ ($\text{M} = \text{Mn, Re}$; $\text{L}_2 = (\text{PPh}_3)_2, \text{dppm}, \text{dppe}, \text{dppp}$).

Complex	^1H ^a		^{31}P ^{b,c}				Ref.
	$\equiv\text{C}^2\text{H}$		P^1	P^2	$^1\text{J}(\text{PtP}^1)$	$^1\text{J}(\text{PtP}^2)$	
	δ	δ					
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}\equiv\text{CHPh})(\text{PPh}_3)_2$ (7)	7.92 t $^3J_{\text{PH}} 25.6$ $^4J_{\text{PH}} 12.5$	4.12 s	43.50 d $^2J_{\text{PP}} 17$	4414	27.40 d $^2J_{\text{PP}} 17$	2607	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}\equiv\text{CHPh})(\text{PPh}_3)_2$ (2)		4.81 s	39.29 d $^2J_{\text{PP}} 21.58$	4609	28.14 d $^2J_{\text{PP}} 21.58$	2607	e
$\text{Cp}(\text{CO})\text{MnPt}(\mu\text{-C}\equiv\text{CHPh})(\mu\text{-CO})\text{-}(\text{dppm})$ (8)	8.33 t $^3J_{\text{PH}} 23.2$ $^4J_{\text{PH}} 15.3$	4.68 s	-8.60 d $^2J_{\text{PP}} 32$	3261	-17.40 d $^2J_{\text{PP}} 32$	2177	[33]
$\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C}\equiv\text{CHPh})(\mu\text{-CO})\text{-}(\text{dppm})$ (3) ^f	7.91 t $^4J_{\text{PH}} 17.52$	5.35 s	-12.84 d $^2J_{\text{PP}} 18.2$	3512	-16.35 d $^2J_{\text{PP}} 18.2$	2242	e
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}\equiv\text{CHPh})(\text{dppe})$ (9)	8.27 t $^3J_{\text{PH}} 24.9$ $^4J_{\text{PH}} 11.7$	4.49 s	52.10 d $^2J_{\text{PP}} 33$	3815	49.40 d $^2J_{\text{PP}} 33$	2545	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}\equiv\text{CHPh})(\text{dppe})$ (4)	8.02 dd $^3J_{\text{PH}} 20.83$ $^4J_{\text{PH}} 13.14$ $^4J_{\text{PH}} 14.29$	5.09 s	49.20 d $^2J_{\text{PP}} 36.34$	4267	51.89 d $^2J_{\text{PP}} 36.34$	2493	e
$\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}\equiv\text{CHPh})(\text{dppp})$ (10)		4.18 s	18.20 d $^2J_{\text{PP}} 3$	4030	10.70 d $^2J_{\text{PP}} 3$	2365	[33]
$\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}\equiv\text{CHPh})(\text{dppp})$ (5)	7.17 dd $^3J_{\text{PH}} 17.66$ $^4J_{\text{PH}} 13.19$ $^4J_{\text{PH}} 15.42$	4.82 s	14.77 d $^2J_{\text{PP}} 6.24$	4285	9.90 d $^2J_{\text{PP}} 6.24$	2312	e

^a The ^1H NMR spectra in CD_2Cl_2 (**2–5**), C_6D_6 (**7**) and CDCl_3 (**8–10**) solutions.^b The ^{31}P NMR spectra in CD_2Cl_2 (**2–5**), C_6D_6 (**7**) and CDCl_3 (**8–10**) solutions.^c P^1 – *trans* to $\text{M} = \text{Mn, Re}$; P^2 – *trans* to $\mu\text{-C}\equiv\text{C}^2\text{HPh}$.^d The $\equiv\text{C}^2\text{H}$ signal is masked by resonances of phenyl groups.^e The present work.^f The ^1H and ^{31}P NMR spectra of **3** are recorded at -60°C .

(**5**) contains only one broad CO signal. The CO signals in spectra of complexes **3** and **4** at $+25^\circ\text{C}$ are broadened so much that they were not detected. This can be explained if the assumption is made that the $[\text{Cp}(\text{CO})_2\text{Re}]$ fragment rotates around the Re–Pt bond, and the site exchange of two CO groups is occurred (Scheme 3).

Earlier, the presence of several isomers in solutions of dinuclear complexes $[\text{Cp}(\text{CO})\text{M}]_2(\mu\text{-C}\equiv\text{CRR}')(\mu\text{-CO})$ ($\text{M} = \text{Fe, Ru}$) [41,42] and $[\text{CpFe}(\text{CO})_2]_2$ [43] has been explained by rotation of metal-containing fragments around metal–metal bond.

Two well-defined CO signals in the ^{13}C NMR spectra of all complexes **2–5** appeared at -60°C (Table 4).

The signals of CO_t group in the ^{13}C spectra of complex (**2**) with monodentate phosphorous ligands and complexes (**3–5**) with chelate diphosphines ligands are observed in the narrow interval of δ 203–206 ppm. However the signals of the CO_{sb} group of complexes **3** and **4** are deeply shifted to the low field, so that in the spectrum of (**3**) the broadened signal of CO_{sb} is seen at δ 230.32 ppm, and that of (**4**) lies at 216.04 ppm. The chemical shifts of the CO_{sb} group of the complexes **2** and **5** are close and observed at δ 205.49 ppm and 208.70 ppm, respectively, thus such signal positions can be accounted for by the decreasing of the semibridging nature of the $\text{Pt} \rightarrow \text{C}3\text{O}3$ interaction in these complexes.

In the ^1H NMR spectra of complexes with the $\mu\text{-C}\equiv\text{C}^2\text{HPh}$ ligand, the resonance of vinylidene proton $\equiv\text{C}^2\text{H}$ is usually observed at δ 6.5–8.5 ppm [3]. The signals of the $\equiv\text{C}^2\text{H}$ protons of complexes **2–5** are observed in the same interval (Table 5).

The ^{31}P NMR spectra of complexes **2–5** and **7–10** each show two signals of non-equivalent phosphorus nuclei (Table 5). Previously [15,33], for complexes $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C}\equiv\text{CHPh})(\text{PR}_3)_2$ the low-field signal having a large coupling constant J_{PtP} (e.g. 4414 Hz for **7**) was assigned to the P^1 atom in *trans*-position to the Mn atom, and the high-field signal having considerably smaller coupling constant J_{PtP} (e.g. 2607 Hz for **7**) was assigned to the P^2

atom (*trans* to $\mu\text{-C}\equiv\text{CHPh}$). Assignment of the P^1 and P^2 signals for complexes **2–5** was performed similarly.

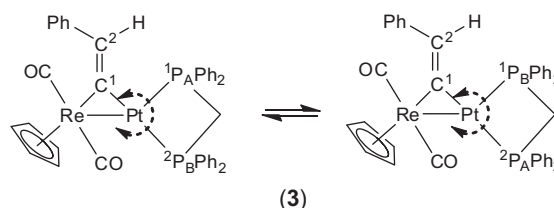
Unlike spectra of MnPt complexes **7–10** and RePt complexes **2, 4, 5**, the ^{31}P NMR spectrum of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}\equiv\text{CHPh})(\text{dppm})$ (**3**) at $+25^\circ\text{C}$ contains broad signals without coupling constant between the P^1 and P^2 nuclei.

The ^1H NMR spectrum of complex **3** at $+25^\circ\text{C}$ shows methylene protons of dppm (δ 4.44) and vinylidene proton (δ 8.00) as broad signals. Phenyl protons of dppm were also observed as two broad signals (δ 7.45 and 7.72). At the same time, three narrow signals at δ 6.99, 7.20 and 7.33 attributed to *para*-, *meta*- and *ortho*-protons of vinylidene phenyl group were observed.

This broadening of signals can be explained by $[\text{Pt}(\text{dppm})]$ fragment rotation around the Re–Pt bond, accompanied by site exchange of phosphorus atoms (Scheme 4). The similar rotation of the $[\text{Pd}(\text{PPh}_3)_2]$ fragment in $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}\equiv\text{CHPh})(\text{PPh}_3)_2$ around the Re–Pd bond we observed earlier [19].

Dynamic behaviour of complex **3** was confirmed by VT NMR study. The ^{31}P NMR spectrum of **3** at -60°C contains two doublets: for P^1 at δ -12.84 and for P^2 at δ -16.35 with coupling constants $^2J_{\text{PP}} = 18.20$ Hz and $J_{\text{PtP}} = 3512$ and 2242 Hz, respectively.

The ^1H NMR spectrum of **3** at -60°C shows vinylidene proton as a triplet signal at δ 7.91 with coupling constant $^4J_{\text{PH}} = 17.52$ Hz

**Scheme 4.**

and two methylene protons of dpmm as two signals at δ 4.33 and 4.54 with vicinal constants $J_{\text{PH}} = 9.9$ Hz and 9.3 Hz, respectively, and geminal constant $J_{\text{HH}} = 15.8$ Hz.

Thus, the site exchange processes are not observed in solution of complex **3** at -60 °C, and the ^1H and ^{31}P NMR spectra correspond with the structure found for **3** in the solid state [19].

3. Conclusions

New complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppe})$ and $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppp})$ obtained by treatment of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ with diphosphines dppe and dppp were added to the set of μ -vinylidene complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PR}_3)_2$. The structures of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppp})$ and $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{dppp})$ were determined by single crystal XRD.

A comparison of XRD, IR and NMR data for series $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{L}_2)$ ($\text{L}_2 = (\text{PPh}_3)_2$, dpmm, dppe, dppp) and synthesized earlier manganese analogs $\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-C=CHPh})(\text{L}_2)$ has been carried out to reveal an influence of the nature of Mn and Re atoms and L_2 ligands at the Pt atom on the complexes characteristics. The Re and Mn atoms sizes have been shown to influence not only on the geometry of complexes, but also on the IR spectra in the $\nu(\text{CO})$ region and on the ^{13}C NMR spectra in the region of chemical shifts of carbonyl groups. The elongations of the Re–Pt bond and the distance between the Pt atom and semibridging CO group, due to the greater size of Re atom, give rise to the weakening of semibridging Pt \rightarrow CO interaction in all RePt complexes in comparison with MnPt analogs. This structural feature accounts for appreciable increase of the $\nu(\text{CO})$ frequencies in the IR spectra and upfield shift of the CO signals in the ^{13}C NMR spectra of RePt complexes in comparison with MnPt analogs. Electron-donor ability of the Re atom is revealed by appreciable upfield shift of $\mu\text{-C}^1$ signals in the ^{13}C NMR spectra of complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C}^1\text{=C}^2\text{HPh})(\text{L}_2)$ relative to the corresponding MnPt analogs.

Rotation of $[\text{Cp}(\text{CO})_2\text{Re}]$ and $[\text{PtP}_2]$ fragments around the Re–Pt bond in solutions of complexes $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{P})_2$ has been shown by VT NMR investigation.

4. Experimental

4.1. General considerations

All synthetic operations and manipulations with organometallics were carried out under an argon atmosphere. Solvents were purified by distillation from drying agents and stored under argon. Complexes $\text{Cp}(\text{CO})_2\text{Re}=\text{C=CHPh}$ (**1**) [44] and $\text{Pt}(\text{PPh}_3)_4$ [45] were prepared according to the known methods. Preparations of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**2**) [18,19] and $\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dpmm})$ (**3**) [19] have been previously described. Neutral alumina was used for column chromatography. The course of reactions was followed by 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 Sciences. The IR spectra were recorded on the Vector 22 Infrared Fourier spectrometer (Bruker, Germany). The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained using NMR spectrometer AVANCE III 600 DPX (Bruker, Germany) at $+25$ and -60 °C. The X-ray data were obtained with the SMART APEX II autodiffractometer (Bruker, Germany).

The NMR data for **2** and **3** obtained using AVANCE 200 DPX spectrometer at 20 °C have been published earlier [18,19]. Refined IR and NMR data for **2** and **3** and VT NMR data for complexes **2–5** are given here.

4.1.1. IR and NMR data for $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**2**)

IR (CH_2Cl_2 , cm^{-1}): 1933s, 1858 m, br (ν_{CO}); (KBr, cm^{-1}): 1922s, 1857 m (ν_{CO}), 1545 m ($\nu_{\text{C=C}}$).

^1H NMR (CD_2Cl_2 , $+25$ °C) δ : 4.81 (s, 5H, C_5H_5); 6.96 (t, 1H, $J_{\text{PH}} = 6.00$ Hz, H_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.05 (d, 2H, H_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.11 (t, 2H, H_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.16–7.69 (m, 30H, PC_6H_5 and 1H, $=\text{C}^2\text{H}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , $+25$ °C) δ : 85.70 (s, C_5H_5); 123.32 (s, C_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 125.92 (s, C_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 127.39–135.32 (m, PC_6H_5); 127.59 (s, C_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 138.25 (t, $^2J_{\text{PtC}} = 96.16$ Hz, $^3J_{\text{PC}} = 4.00$ Hz, $=\text{C}^2\text{H}$); 143.67 (dd, $^3J_{\text{PtC}} = 51.70$ Hz, $^4J_{\text{PC}} = 13.20$ Hz, $^4J_{\text{PC}} = 7.90$ Hz, C_{ipso} of $=\text{C}^2\text{C}_6\text{H}_5$); 204.48 (br, CO); 202.78 (br, CO); 232.24 (d, $^1J_{\text{PtC}} = 821.61$ Hz, $^2J_{\text{PC}} = 65.25$ Hz, $\mu\text{-C}^1$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60 °C) δ : 86.05 (s, C_5H_5); 123.52 (s, C_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 125.47 (s, C_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 127.66–134.87 (m, PC_6H_5); 128.83 (s, C_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 138.31 (t, $^2J_{\text{PtC}} = 104.30$ Hz, $=\text{C}^2\text{H}$); 143.20 (dd, $^4J_{\text{PC}} = 14.08$ Hz, $^4J_{\text{PC}} = 5.98$ Hz, C_{ipso} of $=\text{C}^2\text{C}_6\text{H}_5$); 203.41 (s, CO); 205.49 (s, CO); 232.92 (d, $^2J_{\text{PC}} = 65.33$ Hz, $\mu\text{-C}^1$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , $+25$ °C) δ : 28.14 (d, $^1J_{\text{PtP}} = 2607$ Hz, $^2J_{\text{PP}} = 21.58$ Hz, P^2); 39.29 (d, $^1J_{\text{PtP}} = 4609$ Hz, $^2J_{\text{PP}} = 21.58$ Hz, P^1).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60 °C) δ : 27.92 (d, $^1J_{\text{PtP}} = 2592$ Hz, $^2J_{\text{PP}} = 20.33$ Hz, P^2); 39.35 (d, $^1J_{\text{PtP}} = 4621$ Hz, $^2J_{\text{PP}} = 20.33$ Hz, P^1).

4.1.2. IR and NMR data for $\text{Cp}(\text{CO})\text{RePt}(\mu\text{-C=CHPh})(\mu\text{-CO})(\text{dpmm})$ (**3**)

IR (CH_2Cl_2 , cm^{-1}): 1895s, 1773 m, br (ν_{CO}); (KBr, cm^{-1}): 1895s, 1768 m, br (ν_{CO}), 1541 ($\nu_{\text{C=C}}$).

^1H NMR (CD_2Cl_2 , $+25$ °C) δ : 4.44 (br, 2H, P– CH_2 –P); 5.32 (s, 5H, C_5H_5); 6.99 (t, 1H, $J_{\text{PH}} = 6.01$ Hz, H_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.20 (t, 2H, H_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.33 (t, 2H, H_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.45 (br, P(C_6H_5) $_2$); 7.72 (br, P(C_6H_5) $_2$); 8.00 (s, br, 1H, $=\text{C}^2\text{H}$).

^1H NMR (CD_2Cl_2 , -60 °C) δ : 4.33 (dt, 1H, $^2J_{\text{PH}} = 9.88$ Hz, $J_{\text{HH}} = 15.83$ Hz, P– CH_2 –P); 4.54 (dt, 1H, $^2J_{\text{PH}} = 9.27$ Hz, $J_{\text{HH}} = 15.83$ Hz, P– CH_2 –P); 5.35 (s, 5H, C_5H_5); 6.96 (t, 1H, $J_{\text{PH}} = 7.26$ Hz, H_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.18 (t, 2H, H_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.26 (d, 2H, H_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.35–7.89 (m, 20H, P(C_6H_5) $_2$); 7.91 (t, 1H, $J_{\text{PH}} = 17.52$ Hz, $=\text{C}^2\text{H}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , $+25$ °C) δ : 46.18 (s, br, P– CH_2 –P); 87.18 (s, C_5H_5); 123.56 (s, C_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 125.78 (s, C_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 128.33 (s, C_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 128.64–133.07 (m, PC_6H_5); 136.62 (t, $^2J_{\text{PtC}} = 91.22$ Hz, $=\text{C}^2\text{H}$); 143.87 (s, C_{ipso} of $=\text{C}^2\text{C}_6\text{H}_5$); 233.35 (s, $\mu\text{-C}^1$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60 °C) δ : 46.76 (t, $^1J_{\text{PC}} = 29.37$ Hz, P– CH_2 –P); 87.71 (s, C_5H_5); 123.72 (s, C_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 125.46 (s, C_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 127.84 (s, C_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 128.36–133.58 m (PC_6H_5); 136.05 (d, $^2J_{\text{PtC}} = 90.4$ Hz, $^3J_{\text{PC}} = 8.45$ Hz, $=\text{C}^2\text{H}$); 143.46 (dd, $^4J_{\text{PC}} = 16.50$ Hz, C_{ipso} of $=\text{C}^2\text{C}_6\text{H}_5$); 205.59 (s, CO $_t$); 230.32 (s br, CO $_{\text{sb}}$); 234.38 (d, $^2J_{\text{PC}} = 62.50$ Hz, $\mu\text{-C}^1$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , $+25$ °C) δ : 14.29 (br, $^1J_{\text{PtP}} = 2190$ Hz, P^2); 10.16 (br, $^1J_{\text{PtP}} = 3650$ Hz, P^1).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60 °C) δ : 16.35 (d, $^1J_{\text{PtP}} = 2242$ Hz, $^2J_{\text{PP}} = 18.20$ Hz, P^2); 12.84 (d, $^1J_{\text{PtP}} = 3512$ Hz, $^2J_{\text{PP}} = 18.20$ Hz, P^1).

4.1.3. Preparation of $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppe})$ (**4**)

A mixture of complex **2** (0.140 g, 0.124 mmol) and dppe (0.060 g, 0.151 mmol) in benzene (20 ml) was stirred for 3 h. The reaction mixture was filtered through ~ 0.5 cm alumina pad, filtrate was concentrated *in vacuo* to a volume of ~ 2 ml, and then diethyl ether (3 ml) was added. The solution was stored at 5 °C for 12 h. The resulting bright-orange crystals were washed with diethyl ether (2×2 ml) and hexane-diethyl ether (1:1) mixture. Complex $\text{Cp}(\text{CO})_2\text{RePt}(\mu\text{-C=CHPh})(\text{dppe})$ (**4**) was obtained in the yield of 0.116 g (94%).

Anal. Calc. for $\text{C}_{41}\text{H}_{35}\text{O}_2\text{P}_2\text{PtRe}$ (1002.96): C, 49.10; H, 3.49. Found: C, 49.56; H, 3.72%.

IR (CH_2Cl_2 , cm^{-1}): 1908s, 1839 m, br (ν_{CO}); (KBr, cm^{-1}): 1901s, 1829s (ν_{CO}), 1553 ($\nu_{\text{C=C}}$).

^1H NMR (CD_2Cl_2 , +25 °C) δ : 2.41 (br, 4H, $\text{P}(\text{CH}_2)_2\text{P}$); 5.09 (s, 5H, C_5H_5); 7.00 (tt, 1H, $J_{\text{PH}} = 7.29$ Hz, H_{para} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.18 (t, 2H, $J_{\text{PH}} = 5.58$ Hz, H_{meta} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.31 (d, 2H, H_{ortho} of $=\text{C}^2\text{C}_6\text{H}_5$); 7.49–7.85 (m, 20H, C_6H_5); 8.02 (dd, 1H, $^4J_{\text{PH}} = 13.14$ Hz, $^4J_{\text{PH}} = 14.29$ Hz, $^3J_{\text{PH}} = 20.83$ Hz, $=\text{C}^2\text{H}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ : 31.68 (dd, $^2J_{\text{PC}} = 36.47$ Hz, $^2J_{\text{PC}} = 15.88$ Hz, $\text{P}-\text{CH}_2-$); 29.67 (dd, $^2J_{\text{PC}} = 12.18$ Hz, $^2J_{\text{PC}} = 34.07$ Hz, $-\text{CH}_2-\text{P}$); 86.31 (s, 5C, C_5H_5); 123.46 (s, C_{para} of $=\text{C}^2\text{HC}_6\text{H}_5$); 125.83 (s, C_{meta} of $=\text{C}^2\text{HC}_6\text{H}_5$); 127.66 (s, C_{ortho} of $=\text{C}^2\text{HC}_6\text{H}_5$); 128.27–133.43 (m, PC_6H_5); 138.34 (dd, $^2J_{\text{PC}} = 101.38$ Hz, $^3J_{\text{PC}} = 2.91$ Hz, $^3J_{\text{PC}} = 5.11$ Hz, $=\text{C}^2\text{HPh}$); 144.61 (dd, $^4J_{\text{PC}} = 8.69$ Hz, $^4J_{\text{PC}} = 13.93$ Hz, $C_{\text{ipso}} = \text{C}^2\text{HC}_6\text{H}_5$); 234.57 (dd, $^2J_{\text{PC}} = 3.27$ Hz, $^2J_{\text{PC}} = 66.46$ Hz, $^1J_{\text{PC}} = 764.05$ Hz, $\mu-\text{C}^1$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , –60 °C) δ : 30.92–32.25 (m, $\text{P}-\text{CH}_2-\text{CH}_2-\text{P}$); 86.60 (s, 5C, C_5H_5); 123.65 (s, C_{para} of $=\text{C}^2\text{HC}_6\text{H}_5$); 125.46 s, C_{meta} of $=\text{C}^2\text{HC}_6\text{H}_5$); 127.96 (s, C_{ortho} of $=\text{C}^2\text{HC}_6\text{H}_5$); 128.88–135.55 (m, PC_6H_5); 137.91 (s, $=\text{C}^2\text{HPh}$); 144.19 (s, $C_{\text{ipso}} = \text{C}^2\text{HC}_6\text{H}_5$); 204.90 (s, CO); 216.04 (s, br, CO), 234.26 (s, $\mu-\text{C}^1$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ : 49.20 (d, $^1J_{\text{PtP}} = 4267$ Hz, $^2J_{\text{PP}} = 36.34$ Hz, P^1); 51.89 (d, $^1J_{\text{PtP}} = 2493$ Hz, $^2J_{\text{PP}} = 36.34$ Hz, P^2).

4.1.4. Preparation of $\text{Cp}(\text{CO})_2\text{RePt}(\mu-\text{C}=\text{CHPh})(\text{dppp})$ (**5**)

A solution of $\text{Cp}(\text{CO})_2\text{RePt}(\mu-\text{C}=\text{CHPh})(\text{PPh}_3)_2$ (**2**) (0.115 g, 0.102 mmol) in benzene (20 ml) was treated with dppp (0.046 g, 0.112 mmol) and stirred at 20 °C for 1 h. The obtained solution was filtered through ~ 0.5 cm alumina pad and the solvent was evaporated *in vacuo*. The residue was dissolved in hexane–benzene (2:1) mixture and chromatographed on an alumina column. The first zone was eluted with hexane–benzene (2:1) mixture and gave 4 mg of PPh_3 and dppp. The second broad yellow zone was eluted with hexane–benzene (1:2) mixture. After removal of the solvent and crystallization of the residue from hexane–diethyl ether (2:1) mixture, bright-yellow crystals $\text{Cp}(\text{CO})_2\text{RePt}(\mu-\text{C}=\text{CHPh})(\text{dppp})$ (**5**) (0.098 g, 94%) were isolated.

Anal. Calc. for $\text{C}_{42}\text{H}_{37}\text{O}_2\text{P}_2\text{PtRe}$ (1016.99): C, 49.61; H, 3.60. Found: C, 49.78; H, 3.51%.

IR (CH_2Cl_2 , cm^{-1}): 1924s, 1853 m, br (ν_{CO}); (KBr, cm^{-1}): 1922s, 1856s (ν_{CO}), 1547 ($\nu_{\text{C}=\text{C}}$).

^1H NMR (CD_2Cl_2 , +25 °C) δ : 1.92 (br, $-\text{CH}_2-$); 2.57 (br, PCH_2-); 4.82 (s, 5H, C_5H_5); 6.99 (m, 1H, $=\text{C}^2\text{HC}_6\text{H}_5$); 7.13 (d, 4H, $=\text{C}^2\text{C}_6\text{H}_5$); 7.17 (dd, 1H, $^3J_{\text{PH}} = 17.66$ Hz, $^4J_{\text{PH}} = 13.19$ Hz, $^4J_{\text{PH}} = 15.42$ Hz, $=\text{C}^2\text{HC}_6\text{H}_5$); 7.37–7.62 (m, 20H, PC_6H_5).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ : 19.93 (s, $-\text{CH}_2-$); 29.64 (dd, $^2J_{\text{PC}} = 29.24$ Hz, $\text{P}-\text{CH}_2$); 29.24 (dd, $^2J_{\text{PC}} = 28.83$ Hz, $\text{P}-\text{CH}_2$); 85.61 (s, 5C, C_5H_5); 123.31 (s, C_{para} of $=\text{C}^2\text{HC}_6\text{H}_5$); 126.11 (s, C_{meta} of $=\text{C}^2\text{HC}_6\text{H}_5$); 127.60 (s, C_{ortho} of $=\text{C}^2\text{HC}_6\text{H}_5$); 128.45–133.75 (m, PC_6H_5); 137.61 (t, $^2J_{\text{PC}} = 104.99$ Hz, $=\text{C}^2\text{HC}_6\text{H}_5$); 143.96 (dd, $^4J_{\text{PC}} = 8.18$ Hz, $^4J_{\text{PC}} = 14.64$ Hz, $J_{\text{PC}} = 40.04$ Hz, C_{ipso} of $=\text{C}^2\text{HC}_6\text{H}_5$); 205 (br, 2CO); 233.41 (dd, $^2J_{\text{PC}} = 2.59$ Hz, $^2J_{\text{PC}} = 65.55$ Hz, $J_{\text{PC}} = 813.79$ Hz, $\mu-\text{C}^1$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , –60 °C, 600 Hz) δ : 19.01 (s, $-\text{CH}_2-$); 29.79–30.17 (m, $\text{P}-\text{CH}_2$); 85.80 (s, 5C, C_5H_5); 123.69 (s, C_{para} of $=\text{C}^2\text{HC}_6\text{H}_5$); 125.47 (s, C_{meta} of $=\text{C}^2\text{HC}_6\text{H}_5$); 127.84 (s, C_{ortho} of $=\text{C}^2\text{HC}_6\text{H}_5$); 127.84–136.65 (m, PC_6H_5); 137.91 (s, $=\text{C}^2\text{HC}_6\text{H}_5$); 140.70 (d, $^4J_{\text{PC}} = 15.43$ Hz, C_{ipso} of $=\text{C}^2\text{HC}_6\text{H}_5$); 203.31 (s, CO); 208.70 (s, CO); 245.03 (dd, $^2J_{\text{PC}} = 3.02$, $^2J_{\text{PC}} = 54.33$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ : 9.90 (d, $^3J_{\text{PP}} = 6.24$ Hz, $J_{\text{PtP}} = 2312$ Hz, P^2); 14.77 (d, $^3J_{\text{PP}} = 6.24$ Hz, $J_{\text{PtP}} = 4285$ Hz, P^1).

4.2. X-ray diffraction study of $\text{Cp}(\text{CO})_2\text{RePt}(\mu-\text{C}=\text{CHPh})(\text{dppp})$ (**5**)

Bright-yellow crystals of (1,1-dicarbonyl)-(1- η^5 -cyclopentadienyl) $-\mu-[1-\eta^1,2-\eta^1-(\text{phenyl})\text{ethenylidene}]-[2-\eta^2-\text{bis}(\text{diphenylphosphine})\text{propane-PP}']-\text{rheniumplatinum}$ (*Re-Pt*) (**5**) were obtained from a hexane–benzene (2:1) mixture. For reducing thermal vibrations of atoms and to collect enough number of experi-

mental data we were reluctant to cool the sample down to 223 K. The absorption has been taken into account using multi-scan method, SADABS utility [46]. The structure was solved by direct methods and refined using the SHELXTL programs [47]. The unit cell of the crystal contains four molecules of **5** and eight molecules of benzene. All hydrogen atoms, except H2, and benzene molecules were refined in idealized states. The η^5 -cyclopentadienyl ligand was refined as “variable metric” rigid group.

4.3. X-ray diffraction study of $\text{Cp}(\text{CO})_2\text{MnPt}(\mu-\text{C}=\text{CHPh})(\text{dppp})$ (**10**)

Bright-yellow crystals of (1,1-dicarbonyl)-(1- η^5 -cyclopentadienyl)- $\mu-[1-\eta^1,2-\eta^1-(\text{phenyl})\text{ethenylidene}]-[2-\eta^2-\text{bis}(\text{diphenylphosphine})\text{propane-PP}']-\text{manganeseplatinum}$ (*Mn-Pt*) (**10**) were obtained from methylene dichloride. The selected sample possessed the twinned composition, so the experimental data were preprocessed using the “CELL_NOW” utility [48]. The structure was solved by direct methods and refined using the SHELXTL programs [47]. The hydrogen atoms and the η^5 -cyclopentadienyl ligand were refined like in previous case. The unit cell of the crystal contains four molecules of **10** and four molecules of methylene dichloride.

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Appendix A. Supplementary material

CCDC 831323 and 831322 contain the supplementary crystallographic data for compounds **5** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2012.06.038>.

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