



Chemistry of vinylidene complexes. XXIII. Binuclear rhenium–palladium vinylidene bridged complexes, their reactions with diiron nonacarbonyl[☆]

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ABSTRACT

The reaction of $[\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}]$ (**1**) with $[\text{Pd}(\text{PPh}_3)_4]$ followed by the treatment of resulting $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2]$ (**2**) with diphosphines (dppe, dppp) gave new complexes $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{dppe})]$ (**3**) and $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{dppp})]$ (**4**). Treatment of the synthesized complexes with $[\text{Fe}_2(\text{CO})_9]$ led to mixtures of $[\text{Cp}(\text{CO})_2\text{ReFe}(\mu\text{-C}=\text{CHPh})(\text{CO})_4]$ (**5**), $[(\text{dppe})\text{PdFe}_2(\text{CO})_8]$ (**6**), $[\text{CpReFe}_2(\mu_3\text{-C}=\text{CHPh})(\text{CO})_8]$ (**7**), $[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{dppe})]$ (**8**) and of **5**, $[(\text{dppp})\text{PdFe}_2(\text{CO})_8]$ (**9**), $[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{dppp})]$ (**10**), respectively. The main products of both reactions were trinuclear μ_3 -vinylidene clusters **8** and **10**. Reactions of the trinuclear μ_3 -vinylidene ReFePd clusters **8** and **10** with $\text{Fe}_2(\text{CO})_9$ were also studied. New complexes were characterized by IR, ^1H , ^{13}C , ^{31}P NMR spectroscopy and cyclic voltammetry. The structure of $[\text{CpReFe}_2(\mu_3\text{-C}=\text{CHPh})(\text{CO})_8]$ was determined by single-crystal X-ray diffraction.

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Introduction

Heterometallic compounds have received considerable attention and are of current research interest largely because of their important role in organometallic synthesis and catalysis [1–6]. In this context, the interaction between metal cores and ligands in heterometallic complexes has been widely investigated [7,8]. For instance, it has been shown that mixed-metal clusters offer the possibility of activation of small molecules, as a consequence of the cooperativity effects of the several metal centers working in concert [9].

A variety of methods for the construction of heterometallic compounds have been developed [10]. One of the methods is a consecutive addition of unsaturated metal-containing fragments to

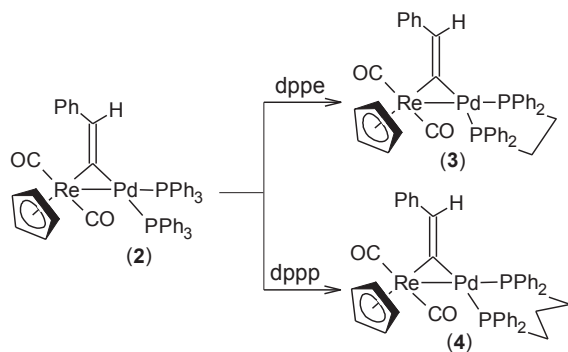
mononuclear complexes with unsaturated hydrocarbon ligands [11–18]. In particular, it has been shown that mononuclear vinylidene complexes of the type $\text{M}=\text{C}=\text{CR}_2$ can be used as building blocks for preparation of heteronuclear compounds [13,14]. A wide variety of heterometallic vinylidene complexes [14,19–22] and clusters [13,14] containing MM' , MM'_2 and $\text{MM}'\text{M}''$ cores were prepared by this method.

At the same time, in spite of the eminent role of palladium in organometallic synthesis and homogenous catalysis, heterometallic vinylidene compounds containing palladium are rare. The heterometallic A-frame complexes of the type $[\text{Cl}_2\text{PdNi}(\mu\text{-C}=\text{CR}_2)(\mu\text{-dppm})]$ ($\text{R} = \text{H}, \text{Cl}$) were synthesized by treating vinyl nickel complex with $[\text{Pd}(\text{PPh}_3)_4]$ and dppm [23]. The cationic μ -vinylidene complex $[\text{PdPt}(\mu\text{-C}=\text{CHPh})(\text{PhC}\equiv\text{C})(\text{PET}_3)_4]\text{PF}_6$ was obtained by the reaction of $[(\text{PET}_3)_2\text{Pd}(\text{C}\equiv\text{CPh})_2]$ and $[\text{trans-Pt}(\text{H})(\text{PET}_3)_2(\text{acetone})]\text{PF}_6$ [24]. The synthesis of binuclear μ -vinylidene complexes of the types $[\text{Cp}(\text{CO})_2\text{MnPd}(\mu\text{-C}=\text{CHPh})(\text{L})]$ ($\text{L} = (\text{PPh}_3)_2, \text{dppe}, \text{dppp}$) were reported [25,26]. The reactions of these MnPd

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Scheme 1.

complexes with $[\text{Fe}_2(\text{CO})_9]$ resulted in the tetranuclear μ_4 -vinylidene clusters $[(\text{P}-\text{P})\text{PdFe}_3(\mu_4\text{-C}=\text{CHPh})(\text{CO})_9]$ ($\text{P}-\text{P} = \text{dppe}, \text{dppp}$). Homonuclear complexes of palladium represent a more wide variety. The series of binuclear A-frame complexes of the types $[\text{X}_2\text{Pd}_2(\mu\text{-C}=\text{CR}_2)(\mu\text{-dppm})_2]$ ($\text{R} = \text{H}, \text{Cl}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{C}\equiv\text{CPh}, \text{NCS}, \text{O}_2\text{CMe}, \text{C}\equiv\text{C}_6\text{H}_4\text{Me-}p, \text{C}\equiv\text{CCMe}_2(\text{OH}), \text{C}\equiv\text{NC}_6\text{H}_4\text{Me-}p$) were studied in the eightieth [27–29]. The unusual asymmetric μ -vinylidene PdPd complex $[(\text{PPh}_3)\text{ClPd}\{\mu\text{-}[\text{C}=\text{C}(\text{H})\text{-N}=\text{CPh}_2]\}\text{PdCl}_2(\text{PPh}_3)_2]$ was obtained by the oxidative addition of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene [30].

Our group studied reactions of binuclear RePd μ -vinylidene complexes with $[\text{Fe}_2(\text{CO})_9]$ to reveal a possible use of mononuclear rhenium vinylidene complex $[\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}]$ (**1**) as building block for the preparation of heteronuclear compounds containing MM' , MM'_2 and $\text{MM}'\text{M}''$ cores. In this paper, we describe new bi- and tri-metallic vinylidene clusters containing palladium, derived from complex **1**.

Results and discussion

Synthesis of $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{dppe})$ (**3**) and $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{dppp})$ (**4**)

We previously reported the reaction of **1** with $[\text{Pd}(\text{PPh}_3)_4]$ (ether, 20 °C, 20 min) that gave the binuclear complex $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{PPh}_3)_2]$ (**2**) in 90% yield [31]. The reactions of **2** with bis-phosphines (dppe and dppp) result in PPh_3 displacement to yield two new binuclear, μ -vinylidene complexes **3** and **4**, which contain chelate diphosphine ligands at a Pd atom (Scheme 1).

These compounds are stable yellow crystalline solids, soluble in benzene and dichloromethane. Complexes **3** and **4** slowly decompose in solution.

NMR and IR study of complexes **3** and **4**

The IR and the ^1H , ^{13}C and ^{31}P NMR data for complexes **3** and **4** were obtained. The NMR signals of complexes **3** and **4** were assigned on the basis of ^1H , ^{13}C and ^1H , $^{31}\text{P}\{^1\text{H}\}$ correlations measured through HSQC and HMQC experiments, respectively.

The signals of C^1 and C^2 vinylidene atoms in the ^{13}C NMR spectra and the signals of vinylidene protons $=\text{C}^2\text{H}$ in the ^1H NMR spectra are in the ranges typical for heteronuclear μ -vinylidene complexes (Table 1) [11,14,24]. It should be noted that the signals of C^1 vinylidene atoms of palladium-containing complexes **3** and **4** are downfield shifted by approximately 15 ppm in comparison to those of corresponding RePt complexes [32]. The ^{31}P NMR spectra of complexes **3** and **4** show two signals corresponding to two non-equivalent phosphorus nuclei. The low-field signals are assigned to the P^1 atom *trans* to the $\mu\text{-C}=\text{CHPh}$ ligand (Table 1). The assignments of the P^1 and P^2 signals were made by analogy with previously published works [25,32–34].

The IR spectra of both complexes **3** and **4** show two $\nu(\text{CO})$ bands that are attributed to the carbonyl groups at a Re atom. The position of these bands indicates that CO ligands are non-equivalent. The first high-frequency $\nu(\text{CO}_t)$ band is terminal. The low-frequency $\nu(\text{CO}_{\text{sb}})$ band is semibridging due to the influence of the adjacent Pd atom. Previously [32] the weak $\text{Pt} \rightarrow \text{CO}_{\text{sb}}$ interaction in the binuclear μ -vinylidene RePt complexes in comparison to the MnPt complexes [34] was found. Noteworthy there are no significant changes in the $\nu(\text{CO})$ frequencies on going from RePt to RePd complexes, indicating the weak $\text{Pd} \rightarrow \text{CO}_{\text{sb}}$ interaction in **3** and **4**. The $\nu(\text{C}=\text{C})$ bands of bridging vinylidene ligand are observed at 1544 cm^{-1} (**3**) and 1550 cm^{-1} (**4**), respectively.

At 298 K, the ^{13}C NMR spectrum of **4** shows one broad CO resonance. The CO signals in the spectrum of complex **3** are broadened so much that they were not detected. To understand the origin of the carbonyl groups resonance broadness, a variable temperature study of **4** was undertaken. The broad resonances of CO groups sharpen progressively upon cooling. At 213 K, two well-resolved CO signals appear at 203.6 and δ 208.8 ppm, which are attributed to the CO_t and the CO_{sb} , respectively (Table 1). Upon warming these signals broaden and coalesce at 308 K into a single sharp line (Fig. 1). An explanation of this observation can be a site exchange of two carbonyl groups of the $[\text{Cp}(\text{CO})_2\text{Re}]$ fragments. The same pattern was observed for the μ -vinylidene RePt complexes in our previous work [32]. Earlier, the presence of several isomers in solutions of dinuclear complexes $[\{\text{Cp}(\text{CO})\text{Fe}\}_2(\mu\text{-C}=\text{CH}_2)(\mu\text{-CO})]$ [35] and $[\{\text{Cp}(\text{CO})\text{Ru}\}_2(\mu\text{-CO})(\mu\text{-CMe}_2)]$ [36] was explained by rotation of the metal-containing fragments around the metal–metal bond. The dynamic bridge-terminal carbonyl exchange in

Table 1
IR and NMR (δ , ppm [J , Hz]) spectroscopic data for the $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{L})]$ ($\text{L} = \text{dppe}$ (**3**), dppp (**4**)).

	IR ^a , $\nu(\text{CO})$, cm^{-1}	NMR ^b							
		^{13}C				^1H		^{31}P	
		$\mu\text{-C}^1=\text{C}^2\text{HPh}$	C_5H_5	CO^c	$=\text{C}^2\text{HPh}$	C_5H_5	P^1	P^2	
3	1909 s, 1833 m, br	247.2 d $^2J_{\text{PC}} = 53.7$	138.4 d $^3J_{\text{PC}} = 9.8$	86.1 s	203.9 s, 216.1 s	7.02 dd $^4J_{\text{PH}} = 17.4$ $^4J_{\text{PH}} = 21.4$	5.20 s	36.72 d $^2J_{\text{PP}} = 14.0$	31.02 d $^2J_{\text{PP}} = 14.0$
4	1921 s, 1854 m, br	245.0 d $^2J_{\text{PC}} = 54.8$	138.0 d $^3J_{\text{PC}} = 11.5$	85.5 s	203.6 s, 208.8 s	6.12 dd $^4J_{\text{PH}} = 18.5$ $^4J_{\text{PH}} = 21.2$	4.88 s	12.18 d $^2J_{\text{PP}} = 19.1$	3.52 d $^2J_{\text{PP}} = 19.1$

^a In CH_2Cl_2 solution.

^b In CD_2Cl_2 solution.

^c The CO signals are recorded at -60 °C.

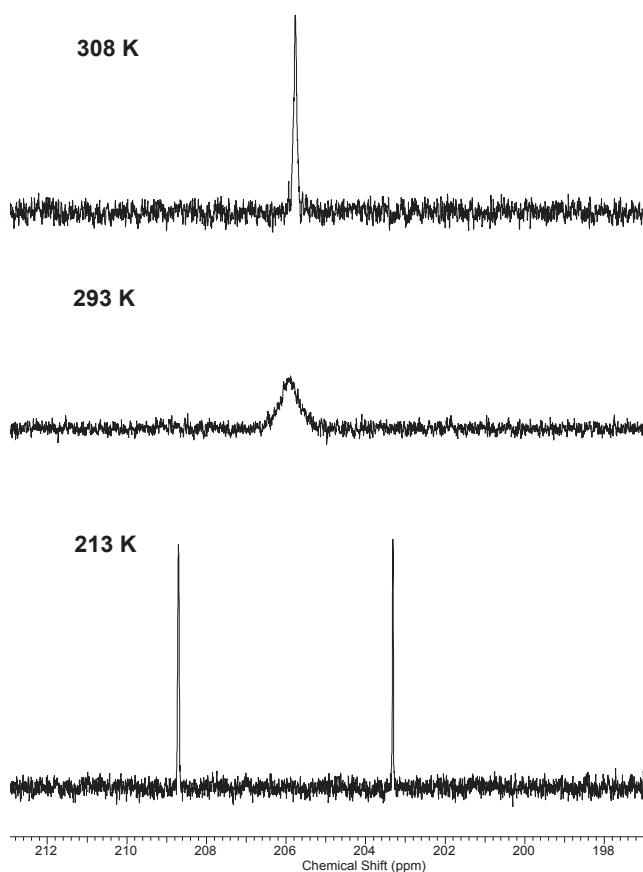
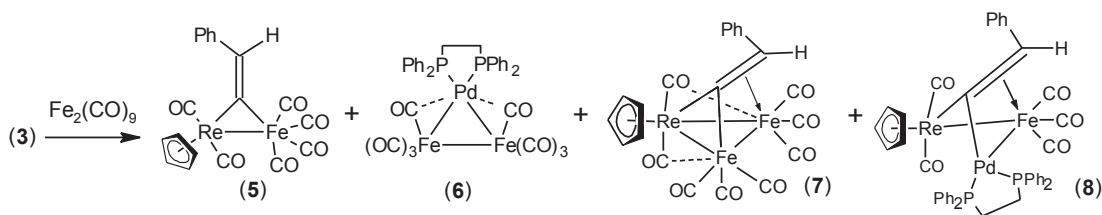
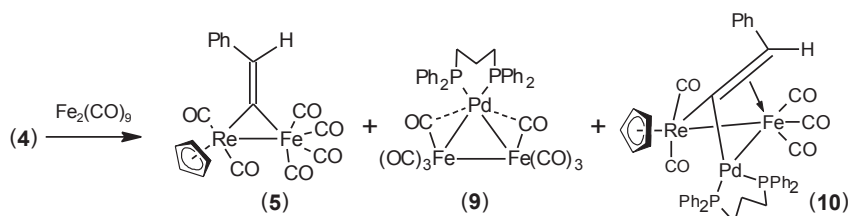


Fig. 1. The variable temperature ^{13}C NMR spectrum of **4** in CD_2Cl_2 solution.

solutions of $[(\eta^5\text{-dienyl})\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Fe}, \text{Ru}$, dienyl, $=\text{C}_5\text{H}_5$, $\text{CH}_3\text{C}_5\text{H}_4$, indenyl and tetrahydroindenyl) [37,38] and $[\text{Cp}(\text{CO})_2\text{MnPt}(\mu\text{-CS})(\text{PMePh}_2)_2]$ [39] was also associated with rotation around the metal–metal bond.



Scheme 2.



Scheme 3.

Reactions of complexes $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{P}-\text{P})]$
($\text{P}-\text{P} = \text{dppe}$ (**3**), dppp (**4**) with $\text{Fe}_2(\text{CO})_9$)

The treatment of complexes **3** and **4** with $[\text{Fe}_2(\text{CO})_9]$ (1:5 molar ratio) in benzene at room temperature gave mixtures of products, which were isolated by column chromatography. The reaction of complex **3** gave four complexes: **5** (yield 12%), **6** (yield 24%), **7** (yield 19%) and **8** (yield 42%) (Scheme 2).

Three complexes were isolated from the reaction mixture of complex **4**: **5** (yield 39%), **9** (yield 20%) and **10** (yield 40%) (Scheme 3).

The orange binuclear complex **5**, as well as the dark-violet trinuclear clusters **6** and **9** were identified earlier [25,26,40]. New complexes **7**, **8** and **10** were characterized by IR and NMR spectra. The NMR signals of these complexes were assigned on the basis of ^1H , ^{13}C and ^1H , $^{31}\text{P}\{^1\text{H}\}$ correlations measured through HSQC and HMQC experiments. The molecular structure of **7** was established by X-ray crystallography.

Trinuclear μ_3 -vinylidene clusters $[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{dppe})]$ (**8**) and $[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{dppp})]$ (**10**)

New trinuclear μ_3 -vinylidene clusters **8** and **10** were isolated as dark-green crystalline solids, which are soluble in benzene, diethyl ether and dichloromethane. Both complexes are quite stable in the solid state under argon, but gradually degrade in solution. Therefore, our attempts to grow X-ray quality crystals failed and both compounds were characterized only by IR and NMR spectra (Table 2).

Compounds **8** and **10** exist in solution as mixtures of two isomers, as revealed by the appearance of several peaks in duplicate in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The presence of two isomers was clearly revealed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which displayed two sets of two doublets resonances in ratio of 5:1 (**8**) and 1:1 (**10**). The peaks of isomers of both complexes in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are of similar ratios of ca. 5:1 (**8**) and 1:1 (**10**) (Tables 2 and 3). At temperatures below -40°C the ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show approximately the same isomers ratios for both complexes.

The presence of μ_3 -vinylidene ligand in **8** and **10** was indicated by their NMR spectra. The signals of C^1 and C^2 atoms of the vinylidene ligand in the ^{13}C NMR spectra and resonances of the

Table 2

IR, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , ppm [J , Hz]) spectroscopic data for the **8** and **10**. Chemical shifts of second isomers are marked with an asterisk (*).

IR ^a , $\nu(\text{CO})$, cm^{-1}	NMR ^b			
	^1H		^{31}P	
	$=\text{C}^2\text{HPh}$	C_5H_5	p^1	p^2
8 2005 s, 1940 s, 1914 m.br, 1856 m.br	6.99 dd	5.16 s	50.03 d	41.62 d
	$^4J_{\text{HP}} = 9.9$	$^*5.37$ s	$^2J_{\text{PP}} = 64.2$	$^2J_{\text{PP}} = 64.2$
	$^4J_{\text{HP}} = 3.2$		$^*49.70$ d	$^*38.57$ d
	$^*6.98$ s		$^2J_{\text{PP}} = 66.2$	$^2J_{\text{PP}} = 66.2$
10 2009 s, 1941 s, 1913 m.br, 1856 m.br	6.11 dd	5.01 s	4.43 d	-2.99 d
	$^4J_{\text{HP}} = 2.8$	$^*5.32$ s	$^2J_{\text{PP}} = 95.6$	$^2J_{\text{PP}} = 95.6$
	$^4J_{\text{HP}} = 11.1$		$^*4.18$ d	$^* -4.92$ d
	$^*6.66$ dd		$^2J_{\text{PP}} = 106.0$	$^2J_{\text{PP}} = 106.0$
	$^4J_{\text{HP}} = 7.7$			
	$^4J_{\text{HP}} = 6.2$			

^a In C_6H_{12} solution.

^b In CD_2Cl_2 solution.

vinylidene protons $=\text{C}^2\text{H}$ in the ^1H NMR spectra were found in the ranges typical for trinuclear complexes with μ_3 -vinylidene ligands (Tables 2 and 3) [11,14].

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **8** and **10** show two doublets for each isomers, their chemical shifts and coupling constants indicate that palladium atoms in both isomers are chelated by phosphorus atoms of the diphosphine ligands (Table 2). Such δ and J_{PP} values are within the ranges observed earlier for the clusters containing iron, palladium atoms and diphosphine ligands [14,25,26,41–43].

Two resonances (209.72 and 210.38) of carbonyl groups at the iron atom of the major isomer are observed in the ^{13}C NMR spectrum of complex **8** at ambient temperature. However, at the same temperature, signals of CO groups at the rhenium atom are broadened. Two distinct broad singlets at 214.9 and 217.7 ppm of these two CO can be detected only at -60°C . The signals of Re–CO and Fe–CO groups of the minor isomer of **8** were also detected at the same temperature (-60°C) (Table 3). In the ^{13}C NMR spectrum of cluster **10** at $+25^\circ\text{C}$ we observed two set of CO signals of $[\text{Fe}(\text{CO})_3]$ groups of both isomers. The ^{13}C NMR spectrum of **10** also shows two signals of the rhenium bonded carbonyl groups for both isomers at 216.2 and 213.2 ppm, which appear as a broad singlet and a broad doublet.

The NMR data for both isomers of **8** and **10** are very similar and show that there are small differences in their geometry. According to the NMR data, the vinylidene ligands in both isomers of **8** and **10** are coordinated to the ReFePd core in a μ_3 - η^2 -mode. The differences between two isomers may arise from two different orientations of H and Ph substituents at C^2 atom of vinylidene ligand relative to a $\text{C}^1\text{C}^2\text{Fe}$ plane (Scheme 4).

Table 3

^{13}C NMR spectroscopic data (δ , ppm [J , Hz]) for the **8** and **10**. Chemical shifts of second isomers are marked with an asterisk (*).

	$\mu\text{-C}^1=\text{C}^2\text{HPh}$		C_6H_5	Re–CO ^b	Fe–CO ^b	C_5H_5
	C^1	C^2	C_{ipso}			
8	264.3 d	106.1 d	142.6 dd	214.9 br. s	210.8 s	89.2 s
	$^2J_{\text{CP}} = 6.7$	$^3J_{\text{CP}} = 24.0$	$^4J_{\text{CP}} = 3.6$	217.7 br. s	211.1 s	$^*88.4$ s
		$^*104.3$ d	$^4J_{\text{CP}} = 3.6$	$^*218.6$ s	$^*207.8$ s	
		$^3J_{\text{CP}} = 24.0$			$^*208.3$ s	
10	265.1 dd	105.6 dd	143.4 dd	216.2 br	208.1 s	88.0 s
	$^2J_{\text{CP}} = 1.9$	$^3J_{\text{CP}} = 2.2$	$^4J_{\text{CP}} = 3.5$	$^*213.2$ d, br	211.7 s	$^*89.1$ s
	$^2J_{\text{CP}} = 8.4$	$^3J_{\text{CP}} = 24.9$	$^4J_{\text{CP}} = 3.5$	$^4J_{\text{CP}} = 19.1$	$^*208.7$ s	
	$^*249.9$ s	$^*111.2$ dd	$^*141.2$ s, br		$^*209.3$ s	
		$^3J_{\text{CP}} = 20.8$				

^aIn CH_2Cl_2 solution.

^bThe CO signals of **8** is recorded at -60°C .

The ^1H NMR spectrum of **10** shows two signals of vinylidene protons $=\text{C}^2\text{H}$ for two isomers at δ 6.11 and 6.66 ppm appearing as doublets of doublets with $^4J_{\text{HP}}$ coupling constants of 2.8, 11.1 and 7.7, 6.2 Hz, respectively. The large difference between coupling constants in the case of the first isomer may indicate that vinylidene proton occupies an opposite side of the molecule from the $[\text{Pd}(\text{dppp})]$ fragment (**b**). Vice versa, the similarity of coupling constants of the second isomer indicates that the vinylidene proton is placed on the same side relatively to the $[\text{Pd}(\text{dppp})]$ fragment (**a**). Thus, the clusters **8** and **10** consist of two diastereomers according to NMR data. A similar type of isomerism was found earlier for the series of trinuclear μ_3 -vinylidene complexes of the type $[\text{MCoFe}(\mu_3\text{-C}=\text{CHR})(\text{CO})_6]$ ($\text{M} = \text{NiCp}, \text{MoCp}(\text{CO})_2, \text{WCp}(\text{CO})_2$; $\text{R} = \text{Me}, \text{Ph}, ^t\text{Bu}$) [44].

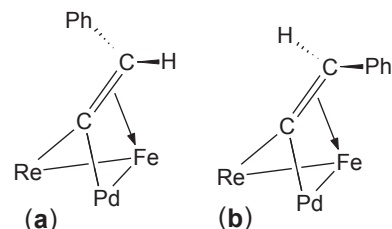
Reactivity of **8** and **10** toward $[\text{Fe}_2(\text{CO})_9]$

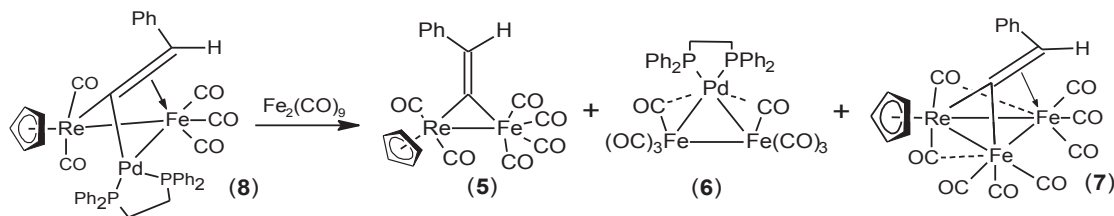
We examined the influence of a reaction time and a ratio of starting compounds on the yield of products in the reactions of binuclear complexes **3** and **4** with $[\text{Fe}_2(\text{CO})_9]$. These experiments showed that the yields of reaction products depend on these parameters. For example, if the approximate molar ratio of binuclear RePd complexes and $[\text{Fe}_2(\text{CO})_9]$ is 1:1 and the reaction time is reduced to 1 h, the yields of trinuclear ReFePd clusters grow from 42% to 66% (**8**) and from 40% to 53% (**10**), whereas the yields of other products decrease. On the basis of these observations, we proposed that a reactivity of μ_3 -vinylidene clusters **8** and **10** toward $[\text{Fe}_2(\text{CO})_9]$ is the cause of such dependence. In order to confirm this hypothesis, reactions between the ReFePd clusters and $[\text{Fe}_2(\text{CO})_9]$ were studied. A treatment of compounds **8** and **10** with $[\text{Fe}_2(\text{CO})_9]$ in benzene at room temperature leads to the mixture of products (Schemes 5 and 6). For the reaction of **8**, the yields of binuclear complex **5**, trimetallic clusters **6** and **7** are 3, 32 and 61%, respectively. For the reaction of **10**, the yields of binuclear complex **5** and trimetallic clusters **9** are 59 and 35%, respectively (the low yield of this reaction may result from an instability of the cluster **10** in solution).

According to the obtained results, two parallel pathways could be proposed for the reactions of binuclear RePd complexes **3** and **4** with $[\text{Fe}_2(\text{CO})_9]$. The first pathway is a replacement of $[\text{Pd}(\text{P}-\text{P})]$ moiety by Fe-containing fragment that gives transmetallation products **5**, **6** and **9**. The second one is the formation of μ_3 -vinylidene ReFePd clusters, which further react with $[\text{Fe}_2(\text{CO})_9]$ to give the additional transmetallation products **5**, **6**, and **7** (in the case of **8**) and **5** and **9** (in the case of **10**). So, the dependence of relative yields of reaction products on the ratio of the starting compounds and reaction time can be accounted for by the reactivity of clusters **8** and **10** toward $[\text{Fe}_2(\text{CO})_9]$.

$[\text{CpReFe}_2(\mu_3\text{-C}=\text{CHPh})(\text{CO})_8]$ (**7**)

Initially, the trinuclear μ_3 -vinylidene cluster **7** was isolated from the reaction mixture of complex **3** and $[\text{Fe}_2(\text{CO})_9]$ in 19% yield. However, the treatment of cluster **8** with $[\text{Fe}_2(\text{CO})_9]$ gave **7** in 73%

**Scheme 4.**



Scheme 5.

yield. Thus, complex **7** is supposed to be a product of reaction of cluster **8** with $\text{Fe}_2(\text{CO})_9$ (Scheme 5). It should be noted that **7** wasn't isolated from the reaction mixture of cluster **10** and $[\text{Fe}_2(\text{CO})_9]$ (Scheme 6). This complex slowly decomposes in solution. The IR spectrum of **7** in CH_2Cl_2 shows six carbonyl bands 2063s, 2020vs, 1993s, 1958m, 1921w and 1874w cm^{-1} . The $\nu(\text{CO})$ bands at 1921 and 1874 cm^{-1} are attributed to semibridging carbonyl groups.

The signals of the phenylvinylidene ligand in the ^1H and ^{13}C NMR spectra are observed in the ranges typical for μ_3 -vinylidene complexes [11,14]. The resonance of the vinylidene proton $=\text{CHPh}$ was found in the ^1H NMR spectra as low-field singlet at δ 6.93. In the ^{13}C NMR spectrum the signals of the C^2 and C^1 atoms of the $\text{C}=\text{CHPh}$ group are observed at δ 99.9 and 265.9 ppm, respectively. One singlet signal at δ 211.6 corresponds to the $\text{Fe}-\text{CO}$ groups, and the signals at δ 201.2 and 202.8 correspond to the CO groups at the Re atom. Both the ^1H and ^{13}C NMR spectra of **7** display one set of signals, indicating that it exists in solution as only one form.

The presence of two crystallographically independent molecules in a unit cell of **7** was established by the X-ray diffraction study. The molecular structure of one of these molecules is shown in Fig. 2. The two molecules of **7** differ slightly in the bond lengths and the angles.

The core of cluster **7** consists of an isosceles triangle of two iron atoms and rhenium atom. The two $\text{Re}-\text{Fe}$ bonds are semibridged by C_3O_3 and C_4O_4 carbonyl ligands. Three terminal CO ligands coordinate each iron atoms. The ReFe_2 triangle is capped by the phenylvinylidene ligand. The length of $\text{C}1=\text{C}2$ bond is slightly shorter (Fig. 2) than that of trinuclear complexes with μ_3 -phenylvinylidene ligand [14]. In contrast to the analogous compound $[\text{CpMnFe}_2(\mu_3-\text{C}=\text{CHPh})(\text{CO})_8]$ [26], the vinylidene ligand in **7** is not disordered over the ReFe_2 metal core but is unsymmetrically coordinated to the Fe2 atom (the average difference between $\text{Fe}2-\text{C}1$ and $\text{Fe}2-\text{C}2$ bond distances is 0.3 Å).

As mentioned above, $\text{C}3\text{O}3$ and $\text{C}4\text{O}4$ carbonyl groups at the Re atom are semibridging due to interaction with the Fe1 and Fe2 atoms, respectively. The $\text{Re}-\text{C}3\text{O}3$ and $\text{Re}-\text{C}4-\text{O}4$ bond angles for both molecules are less than 170° .

Compound **7** is the second example in which the $\mu_3-\eta^2$ -vinylidene ligand is coordinated to the triangular ReFe_2 core. The other known example is $[(\text{CO})_5\text{Re}-\text{ReFe}_2(\mu_3-\text{C}=\text{CHPh})(\text{CO})_9(\mu-\text{CO})]$ cluster [45] containing a $\text{Re}-\text{ReFe}_2$ metal core of "triangle-with-spike" type where the ReFe_2 fragment is coordinated by the μ_3 -phenylvinylidene ligand. The other examples containing the ReFe_2

metal core, but without μ_3 -vinylidene ligand, include carbyne complexes $[(\eta^5-\text{C}_9\text{H}_7)(\mu-\text{CO})\text{ReFe}_2(\mu_3-\text{C}-\text{C}_6\text{H}_4\text{Me}-4)(\mu-\text{NO})(\text{CO})_5]$ [46], $[\text{Cp}(\mu-\text{CO})_2\text{ReFe}_2(\mu_3-\text{C}-\text{C}_6\text{H}_5)(\mu-\text{H})(\text{CO})_6]$ [47] and 2-mercaptobenzothiolato capped cluster $[\text{ReFe}_2(\text{CO})_8(\mu-\text{CO})_2(\mu_3-\text{C}_7\text{H}_4\text{NS}_2)]$ [48].

Electrochemical study

The redox properties of complexes **2**, **3**, **4**, **8**, **10**, **5**, and **7** were also studied by cyclic voltammetry at a platinum and a glassed carbon (GC) electrodes and a controlled-potential electrolysis at a Pt-electrode in the acetonitrile solution. Potentials are given versus $\text{Ag}/0.1\text{ M AgNO}_3$ in MeCN (they can be converted to V versus SCE by adding 0.337 V).

The binuclear complexes **3** and **4** show at the Pt-electrode two similar irreversible oxidation stages at very negative potentials of the first stage ($E_{1/2} = -0.23$ and 0.34 V) as compared to complex **2** ($E_{1/2} = -0.07$ and 0.33 V).

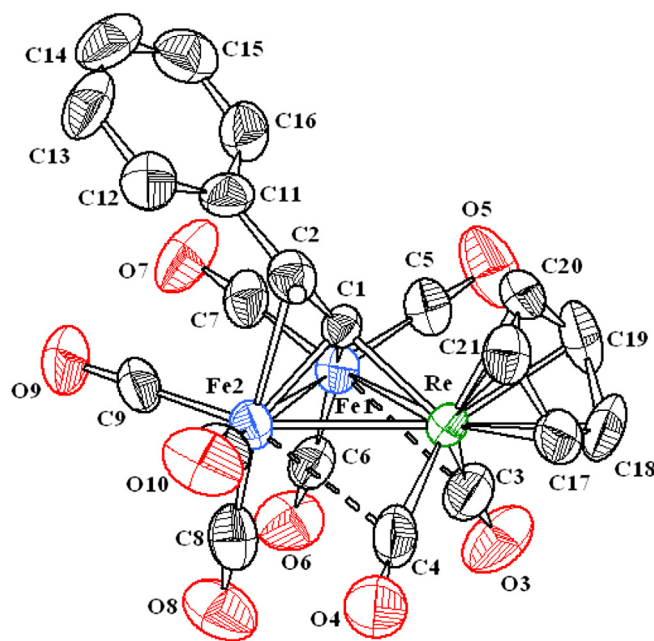
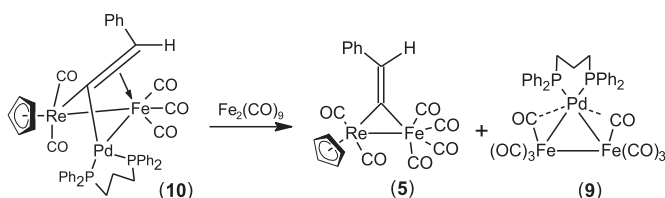


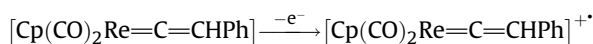
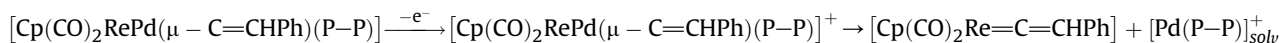
Fig. 2. Molecular structure of $[\text{CpReFe}_2(\mu_3-\text{C}=\text{CHPh})(\text{CO})_8]$ (**7**) with atom labels and 50% probability displacement ellipsoids for non-H atoms. All hydrogen atoms except H of the vinylidene ligand are omitted for clarity. The selected interatomic distances (Å) and angles (deg): (molecule A) $\text{Re}(1)-\text{Fe}(1) = 2.756(1)$, $\text{Re}(1)-\text{Fe}(2) = 2.799(1)$, $\text{Fe}(1)-\text{Fe}(2) = 2.580(2)$, $\text{Re}(1)-\text{C}(1) = 2.079(7)$, $\text{Fe}(1)-\text{C}(1) = 1.862(7)$, $\text{Fe}(2)-\text{C}(1) = 1.957(8)$, $\text{Fe}(2)-\text{C}(2) = 2.280(8)$, $\text{Re}(1)-\text{C}(3) = 1.915(10)$, $\text{Re}(1)-\text{C}(4) = 1.904(10)$, $\text{C}(1)-\text{C}(2) = 1.352(11)$, $\text{Re}-\text{C}(3)-\text{O}(3) = 166.38(86)$, $\text{Re}-\text{C}(4)-\text{O}(4) = 167.34(86)$, (molecule B) $\text{Re}(1)-\text{Fe}(1) = 2.745(2)$, $\text{Re}(1)-\text{Fe}(2) = 2.783(1)$, $\text{Fe}(1)-\text{Fe}(2) = 2.587(2)$, $\text{Re}(1)-\text{C}(1) = 2.080(7)$, $\text{Fe}(1)-\text{C}(1) = 1.856(8)$, $\text{Fe}(2)-\text{C}(1) = 1.949(7)$, $\text{Fe}(2)-\text{C}(2) = 2.243(8)$, $\text{Re}(1)-\text{C}(3) = 1.929(11)$, $\text{Re}(1)-\text{C}(4) = 1.906(10)$, $\text{C}(1)-\text{C}(2) = 1.343(11)$, $\text{Re}-\text{C}(3)-\text{O}(3) = 165.38(93)$, $\text{Re}-\text{C}(4)-\text{O}(4) = 170.76(87)$.



Scheme 6.

The half wave oxidation potential value of the second oxidation stage of **2–4** coincides with the redox potential value of **1** ($E_{1/2} = 0.33$ V) [49,50]. The formation of **1** after one-electron oxidation of complexes **2–4** was confirmed by the controlled-potential electrolysis and by a chemical oxidation with FcBF_4 . Thus, the one-electron oxidation of complexes **2–4** results in a cleavage of the Re–Pd and Pd–vinylidene bonds affording complex **1**.

Based on the obtained data, the following schemes of the redox reactions of complexes **2–4** are proposed:



In contrast to the binuclear complexes, the electrochemical behavior of the trinuclear μ_3 -vinylidene clusters ($[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{P-P})]$ [P–P = dppe (**8**), dppp (**10**)] depends on the diphosphine ligand nature (dppe or dppp).

The complexes **8** and **10** are oxidized at the GC electrode in several stages at $E_{1/2} = -0.28, -0.13, 0.10, 0.45$ V (Fig. 3a) and $-0.36, -0.15, 0.41$ V (Fig. 3b) and are reduced in a one-electron stage at $E_{1/2} = -1.92$ and -1.82 V, respectively (at Pt electrode: $E_{1/2}^{\text{ox}} = -0.28, -0.12, 0.08, 0.46$ V and $-0.38, -0.23, 0.07, 0.37$ V; $E_{1/2}^{\text{red}} = -1.94$ and -1.85 V, respectively). The first and the second oxidation and the reduction waves of the complexes were found to

be electrochemically quasi-reversible (Fig. 3a, peak A₁, A₂, A₅; b, peak B₁, B₂, B₄).

The sums of two first oxidation waves of **8** and **10** correspond to one-electron waves. Moreover, the ratios of waves' heights are 5:1 for complex **8** (Fig. 3a, peaks A₁ and A₂) and 1:1 for **10** (Fig. 3b, peaks B₁ and B₂). These splitting patterns are apparently caused by the presence of isomers in solutions of the complexes [51]. The presence of isomers in solutions of **8** and **10** was confirmed by NMR spectroscopy and discussed above.

The potential value of the fourth oxidation wave of **8** (Fig. 3a, peak A₄) is close to the $E_{1/2}$ value (0.45 V) of the first oxidation wave of **7** (Fig. 3c, peak C₁) and the $E_{1/2}$ value (0.50 V) of the second oxidation wave of $[\text{Pd}(\text{dppe})_2]$. For complex **10** the potential value of the third oxidation wave (Fig. 3b, peak B₃) is close to the $E_{1/2}$ value (0.41 V) of the first oxidation wave of **5** (Fig. 3d, peak D₁) and to the $E_{1/2}$ value (0.45 V) of the first oxidation wave of **7** (Fig. 3c, peak C₁). However, IR spectra of the reaction mixture obtained by exhaustive controlled-potential electrolysis performed at the potential close to one-electron oxidation wave of **8** and **10** for 1 h or by the chemical oxidation with FcBF_4 showed the presence of two complexes $[\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}]$ and $[(\text{P-P})\text{PdFe}_2(\text{CO})_8]$ [P–P = dppe (**6**), dppp (**9**)]. Therefore, based on the electrochemical and IR obtained data, the following schemes of the redox reactions of complexes **8** and **10** can be proposed:

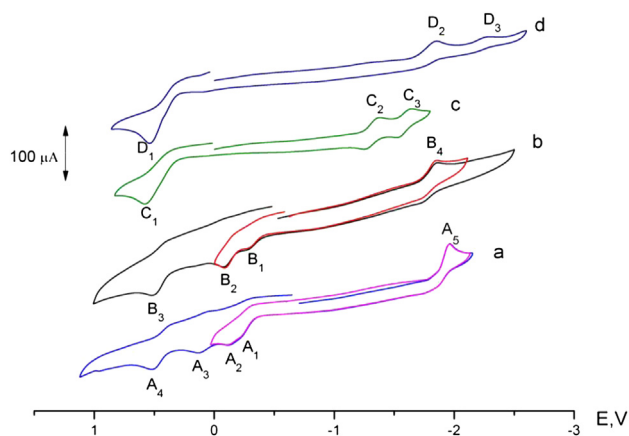
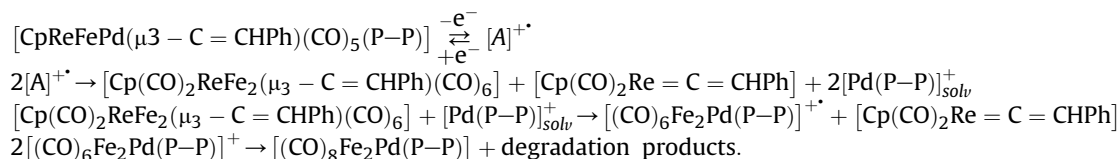


Fig. 3. The cyclic voltammograms of $[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{dppe})]$ (**8**) (a), $[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{dppp})]$ (**10**) (b), $[\text{CpReFe}_2(\mu_3\text{-C}=\text{CHPh})(\text{CO})_8]$ (**7**) (c), $[\text{Cp}(\text{CO})_2\text{ReFe}(\mu\text{-C}=\text{CHPh})(\text{CO})_4]$ (**5**) (d) at GC-electrode in MeCN (0.1 M Et_4NBF_4 , C = 2 mM, scan rate 25 V s^{-1} , potentials vs. $\text{Ag}/0.1 \text{ M AgNO}_3$ in MeCN).

Thus, under CV conditions one-electron oxidation of clusters **8** and **10** leads to the formation of complex **7** and Pd-containing fragments that subsequently undergo further reactions resulting in $[\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}]$ and $[(\text{P-P})\text{PdFe}_2(\text{CO})_8]$ [P–P = dppe (**6**), dppp (**9**)].

Conclusion

The spectroscopic and electrochemical features of RePd μ -vinylidene complexes and ReFePd μ_3 -vinylidene clusters, as well as the spectroscopic and structural features of new ReFe₂ cluster are described.

The present study shows that the reactions of the μ -vinylidene complexes $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{dppe})]$ (**3**) and $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C}=\text{CHPh})(\text{dppp})]$ (**4**) with $[\text{Fe}_2(\text{CO})_9]$ proceed by two parallel pathways. The first pathway is a replacement of $[\text{Pd}(\text{P-P})]$ moiety by Fe-containing fragment that gives transmetalation products **5**, **6** and **9**. The second one results in the trinuclear μ_3 -vinylidene clusters ($[\text{CpReFePd}(\mu_3\text{-C}=\text{CHPh})(\text{CO})_5(\text{P-P})]$ (P–P = dppe (**8**), dppp (**10**))), which are able to further react with $[\text{Fe}_2(\text{CO})_9]$. The trinuclear μ_3 -vinylidene ReFePd clusters **8** and **10** therefore are not the final products of the reactions of **3** and **4**

with $[\text{Fe}_2(\text{CO})_9]$ and they might be considered as quite stable intermediate clusters.

The electrochemical study of clusters **8** and **10** revealed that, one-electron oxidation lead to ReFe_2 cluster and Pd-containing fragments that subsequently undergo further reactions with formation of $[\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}]$ and $[(\text{P}-\text{P})\text{PdFe}_2(\text{CO})_8]$ [$\text{P}-\text{P} = \text{dppe}$ (**6**), dppp (**9**)].

Experimental

General considerations

All operations and manipulations were carried out under an argon atmosphere. Solvents were purified by distillation from appropriate drying agents and stored under argon. The course of reactions were monitored by TLC on Silufol plates and IR spectroscopy. Neutral alumina was used for column chromatography. 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). The X-ray data were obtained with the SMART APEX II diffractometer (Bruker AXS, Germany). The starting complexes of $[\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}]$ (**1**) [50], $[\text{Pd}(\text{PPh}_3)_4]$ [52] and $[\text{Fe}_2(\text{CO})_9]$ [53] were prepared according to the described methods. Preparation of $[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{PPh}_3)_2]$ (**2**) was described in Ref. [31].

$[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{dppe})]$ (**3**)

Dppe (50 mg, 0.126 mmol) was added to a solution of $[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{PPh}_3)_2]$ (**2**) (109 mg, 0.105 mmol) in 10 mL of benzene and reaction mixture was stirred for 30 min. The resulting solution was filtered through 0.5 cm of alumina and concentrated to 3 mL *in vacuo*. Addition of 3 mL of hexane gave after 2 h at 5 °C orange crystals which were collected, washed with a mixture of hexane:diethyl ether (1:1) and dried *in vacuo* at 20 °C. Yield: 83 mg, 87%.

Anal. Found: C, 53.72; H, 3.51%. Calc. for $\text{C}_{41}\text{H}_{35}\text{O}_2\text{P}_2\text{PdRe}$ (914.30): C, 53.81; H, 3.83%.

IR (CH_2Cl_2 , cm^{-1}): 1909s, 1833m, br (ν_{CO}); (KBr, cm^{-1}): 1897s, 1829s (ν_{CO}).

^1H NMR (CD_2Cl_2 , +25 °C) δ , ppm [J, Hz]: 2.52 and 2.30 (m, br, 4H, P-CH₂); 5.20 (s, 5H, C₅H₅); 6.97 (m, 1H, H_{para}=C²HC₆H₅); 7.02 (dd, 1H, $^4J_{\text{PH}} = 17.4$, $^4J_{\text{PH}} = 21.4$, =C²HPh); 7.15–7.74 (m, 20H, P-C₆H₅ and 4H, =C²HC₆H₅).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ , ppm [J, Hz]: 27.4 (dd, P-CH₂, $^1J_{\text{PC}} = 24.7$; $^2J_{\text{PC}} = 15.2$); 29.2 (dd, P-CH₂, $^1J_{\text{PC}} = 26.2$; $^2J_{\text{PC}} = 18.1$); 86.1 (s, 5C, C₅H₅); 123.7 (s, C_{para}=C²HC₆H₅); 125.5 (s, C_{meta}=C²HC₆H₅); 127.7 (s, C_{ortho}=C²HC₆H₅); 128.5–133.8 (m, PC₆H₅); 138.4 (d, $^3J_{\text{PC}} = 9.8$, =C²HPh); 141.4 (dd, $^4J_{\text{PC}} = 15.5$, $^4J_{\text{PC}} = 15.5$, C_{ipso}=C²HC₆H₅); 247.2 (d, $^2J_{\text{PC}} = 53.7$, $\mu\text{-C}^1$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60 °C) δ , ppm [J, Hz]: 27.1–29.3 (m, P-CH₂-CH₂-P); 86.4 (s, 5C, C₅H₅); 123.9 (s, C_{para}=C²HC₆H₅); 125.2 (s, C_{meta}=C²HC₆H₅); 127.9 (s, C_{ortho} of =C²HC₆H₅); 128.7–135.1 (m, PC₆H₅); 137.9 (s, =C²HPh); 141.0 (s, C_{ipso}=C²HC₆H₅); 203.9 (s, CO_t); 216.1 (s, CO_{sb}), 246.2 (s, $\mu\text{-C}^1$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ , ppm [J, Hz]: 31.02 (d, P², $^2J_{\text{PP}} = 14.0$); 36.72 (d, P¹, $^2J_{\text{PP}} = 14.0$).

$[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{dppp})]$ (**4**)

Dppp (57 mg, 0.14 mmol) was added to a solution of $[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{PPh}_3)_2]$ (**2**) (98 mg, 0.09 mmol) in 14 mL of diethyl ether. The mixture after being stirred for 30 min was dried *in vacuo*. A bright-yellow residue was dissolved in

hexane–benzene mixture (1:1) and chromatographed on an alumina column (8 × 2 cm). The column was eluted initially with hexane–benzene (2:1) mixture and subsequently with benzene. The first colorless eluate contained PPh₃ and dppp. The second yellow major band, after removal of solvent and crystallization from benzene–hexane mixture (1:1), afforded yellow microcrystals of **4**. Yield: 71 mg, 85%.

Anal. Found: C, 54.09; H, 3.76%. Calc. for $\text{C}_{42}\text{H}_{37}\text{O}_2\text{P}_2\text{PdRe}$ (928.33): C, 54.29; H, 3.99%.

IR (CH_2Cl_2 , cm^{-1}): 1921s, 1854m, br (ν_{CO}); (KBr, cm^{-1}): 1910s, 1844s (ν_{CO}), 1550 ($\nu_{\text{C}=\text{C}}$).

^1H NMR (CD_2Cl_2 , +25 °C) δ , ppm [J, Hz]: 1.85 (br, -CH₂-); 2.64 (br, P-CH₂-); 4.88 (s, 5H, C₅H₅); 6.12 (dd, 1H, $^4J_{\text{PH}} = 18.5$, $^4J_{\text{PH}} = 21.2$, =C²HPh), 6.93–7.12 (m, 5H, =C²HC₆H₅); 7.34–7.64 (m, 20H, PC₆H₅).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ , ppm [J, Hz]: 19.9 (s, -CH₂-); 29.4–30.0 (m, P-CH₂-); 85.5 (s, 5C, C₅H₅); 123.5 (s, C_{para}=C²HC₆H₅); 125.7 (s, C_{meta}=C²HC₆H₅); 127.5 (s, C_{ortho}=C²HC₆H₅); 128.1–133.5 (m, PC₆H₅); 137.4 (d, $^3J_{\text{PC}} = 11.1$, =C²HPh); 141.1 (t, $^4J_{\text{PC}} = 16.4$, C_{ipso}=C²HC₆H₅); 205.0 (br, 2CO); 245.7 (d, $^2J_{\text{PC}} = 56.2$, $\mu\text{-C}^1$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60 °C) δ , ppm [J, Hz]: 18.9 (s, -CH₂-); 28.3 (d, $^1J_{\text{PC}} = 19.7$, -CH₂-P); 29.8 (d, $^1J_{\text{PC}} = 17.9$, P-CH₂); 85.8 (s, 5C, C₅H₅); 123.7 (s, C_{para}=C²HC₆H₅); 125.5 (s, C_{meta}=C²HC₆H₅); 127.8 (s, C_{ortho}=C²HC₆H₅); 127.1–136.8 (m, PC₆H₅); 138.0 (d, $^3J_{\text{PC}} = 11.5$, =C²HPh); 140.7 (dd, $^4J_{\text{PC}} = 16.5$ Hz, $^4J_{\text{PC}} = 14.5$, C_{ipso}=C²HC₆H₅); 203.6 (s, CO_t); 208.8 (s, CO_{sb}); 245.0 (d, $^2J_{\text{PC}} = 54.8$, $\mu\text{-C}^1$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ , ppm [J, Hz]: 12.18 (d, P², $^2J_{\text{PP}} = 19.1$); 3.52 (d, P¹, $^2J_{\text{PP}} = 19.1$).

Reaction of $[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{dppe})]$ (**3**) with $[\text{Fe}_2(\text{CO})_9]$

$[\text{Fe}_2(\text{CO})_9]$ (146 mg, 0.4 mmol) was added to the solution of $[\text{Cp}(\text{CO})_2\text{RePd}(\mu-\text{C}=\text{CHPh})(\text{dppe})]$ (**3**) (82 mg, 0.09 mmol) in 15 mL of benzene. A reaction mixture was stirred for 3 h at 20 °C and then was transferred via cannula into 50 mL flask. The solvent was removed *in vacuo* and the residue was dissolved in hexane–benzene mixture (2:1) and chromatographed on an alumina column (15 × 2 cm). Four main fractions were subsequently eluted with petroleum ether, petroleum ether:benzene (7:3) and (3:2) mixtures and finally with benzene.

The first light-brown fraction, after evaporation of solvent, gave 6 mg (12%) of bright-orange complex $[\text{Cp}(\text{CO})_2\text{ReFe}(\mu-\text{C}=\text{CHPh})(\text{CO})_4]$ (**5**). This compound was identified by IR spectra [40].

The second rose fraction was eluted with petroleum ether:benzene (7:3). Evaporation of the solvent and crystallization of the crude product from hexane gave 15 mg (24%) of $[\text{Cp}(\text{CO})_2\text{ReFe}_2(\mu-\text{C}=\text{CHPh})(\text{CO})_6]$ (**7**) as red crystals.

IR (CH_2Cl_2 , cm^{-1}): 2063s, 2020vs, 1993s, 1958m, 1921w, 1874w (ν_{CO}); (KBr, cm^{-1}): 2063s, 2015vs, 1996s, 1981s, 1919m, 1901w, 1869w (ν_{CO}).

^1H NMR (CD_2Cl_2 , +25 °C) δ , ppm [J, Hz]: 5.61 (s, 5H, C₅H₅); 6.93 (s, =C²HPh); 7.29 (dd, $^3J_{\text{HH}} = 7.4$, H_{para} of C=C²HC₆H₅); 7.38 (dd, $^3J_{\text{HH}} = 7.7$, H_{meta} of C=C²HC₆H₅); 7.62 (d, $^3J_{\text{HH}} = 7.3$, H_{ortho} of C=C²HC₆H₅).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , +25 °C) δ , ppm [J, Hz]: 89.7 (s, C₅H₅); 99.9 (s, C¹=C²HPh); 127.4 (s, C_{para} of C=CHC₆H₅); 128.0 (s, C_{ortho} of C=CHC₆H₅); 128.6 (s, C_{meta} of C=CHC₆H₅); 143.7 (s, C_{ipso} of C=CHC₆H₅); 201.2, 202.8 (s, Re-CO); 211.6 (s, Fe-CO); 265.9 (s, C¹=C²HPh).

The third violet fraction, after removal of solvent, afforded 14 mg (18%) of dark-violet cluster $[(\text{dppe})\text{PdFe}_2(\text{CO})_8]$ (**6**) identified by IR spectra [26].

The fourth green fraction, after evaporation of solvent and crystallization of the crude product from benzene–hexane mixture

(1:1), afforded 40 mg (42%) dark-green microcrystals of [CpReFePd(μ_3 -C=CHPh)(CO)₅(dppe)] (**8**).

Anal. Found: C, 50.09; H, 3.32%. Calc. for C₄₄H₃₅O₅P₂PdReFe (1054.18): C, 50.27; H, 3.48%.

IR (C₆H₁₂, cm⁻¹): 2005s, 1940s, 1914m.br, 1856m.br (ν_{CO}); (KBr, cm⁻¹): 1995, 1927, 1904, 1845 (ν_{CO}).

¹H NMR (CD₂Cl₂, +25 °C) δ , ppm [J, Hz].

Isomer A: 1.79 (m, 2H, P-CH₂-); 2.45 (m, 1H, P-CH₂-); 2.52 (m, 1H, P-CH₂-); 5.16 (s, 5H, C₅H₅); 6.99 (dd, ⁴J_{HP} = 9.9, ⁴J_{HP} = 3.2, 1H, =C²HPh); 6.74 (dd, ³J_{HH} = 7.4, ³J_{HH} = 7.6, 2H, H_{meta} of C=C²HC₆H₅); 7.12 (d, ³J_{HH} = 7.6, 2H, H_{ortho} of C=C²HC₆H₅); 7.85 (dd, ³J_{HH} = 7.4, ³J_{HH} = 7.4, 1H, H_{para} of C=C²HC₆H₅); 6.71–7.71 (m, 20H, P-C₆H₅).

Isomer B: 1.54 (m, 1H, P-CH₂-); 1.63 (m, 1H, P-CH₂-); 2.45 (m, 1H, P-CH₂-); 2.68 (m, 1H, P-CH₂-); 5.37 (s, 5H, C₅H₅); 6.98 (s, 1H, =C²HPh); 6.71–7.85 (m, 20H, P-C₆H₅ and 5H, =C²HC₆H₅).

¹³C{¹H} NMR (CD₂Cl₂, +25 °C) δ , ppm [J, Hz].

Isomer A: 29.0 (dd, ¹J_{PC} = 28.4, ²J_{PC} = 15.9, P-CH₂); 31.7 (dd, ¹J_{PC} = 23.6, ²J_{PC} = 30.4, P-CH₂); 89.2 (s, C₅H₅); 106.1 (d, ³J_{CP} = 24.0, C¹=C²HPh); 124.5 (s, C_{para} of C=CHC₆H₅); 126.8 (s, C_{meta} of C=CHC₆H₅); 127.6 (unresolved m, C_{ortho} of C=CHC₆H₅); 124–132 (P-C₆H₅); 142.6 (dd, ⁴J_{CP} = 3.6, ⁴J_{CP} = 3.6, C_{ipso} of C=CHC₆H₅); 209.72, 210.38 (s, Fe-CO); 216.77 (s, br Re-CO); 264.3 (d, ²J_{CP} = 6.7, C¹=C²HPh).

Isomer B: 29.5 (s, -(CH₂)₂-); 88.4 (s, C₅H₅); 104.3 (d, ³J_{CP} = 24.0, C¹=C²HPh); 124–132 (m, C=CHC₆H₅ and PC₆H₅); 216.5 (s, Re-CO).

³¹P{¹H} NMR (CD₂Cl₂) δ , ppm [J, Hz].

Isomer A: 41.62 (d, P², ²J_{PP} = 64.2); 50.03 (d, P¹, ²J_{PP} = 64.2).

Isomer B: 38.57 (d, P², ²J_{PP} = 66.2); 49.70 (d, P¹, ²J_{PP} = 66.2).

Reaction of [Cp(CO)₂RePd(μ -C=CHPh)(dppp)] (**4**) with [Fe₂(CO)₉]

[Fe₂(CO)₉] (202 mg, 0.55 mmol) was added to the solution of [Cp(CO)₂RePd(μ -C=CHPh)(dppp)] (**4**) (106 mg, 0.11 mmol) in 15 mL of benzene. The reaction mixture was stirred for 3 h at 20 °C and then was transferred via cannula into 50 mL flask. The solvent was removed *in vacuo* and the residue was dissolved in hexane–benzene mixture (2:1) and chromatographed on an alumina column (11 × 2 cm). Three main fractions were subsequently eluted with petroleum ether, petroleum ether:benzene (3:2) mixture and finally with benzene.

The first light-brown fraction, after evaporation of solvent, gave 25 mg (39%) of bright-orange complex [Cp(CO)₂ReFe(μ -C=CHPh)(CO)₄] (**5**). This compound was identified by IR spectra [40].

The second violet fraction was eluted with petroleum ether:benzene (3:2). Evaporation of the solvent gave 19 mg (20%) of dark-violet cluster [(dppp)PdFe₂(CO)₈] (**9**) identified by IR spectra [12].

Evaporation of the solvent from the third green fraction and crystallization of the crude product from benzene–hexane mixture (1:1) afforded 47 mg (40%) dark-green microcrystals of [CpReFePd(μ_3 -C=CHPh)(CO)₅(dppp)] (**10**).

Anal. Found: C, 50.55; H, 3.46%. Calc. for C₄₅H₃₇O₅P₂PdReFe (1068.21): C, 50.81; H, 3.58%.

IR (C₆H₁₂, cm⁻¹): 2009s, 1941s, 1913m.br, 1856m.br (ν_{CO}); (KBr, cm⁻¹): 1997, 1928, 1903, 1844.

¹H NMR (CD₂Cl₂, +25 °C) δ , ppm [J, Hz].

Isomer A: 1.51 (m, 2H, P-CH₂-); 2.09 (m, 1H, -CH₂-); 2.30 (m, 1H, -CH₂-); 2.40 (m, 1H, P-CH₂-); 2.43 (m, 1H, P-CH₂-); 5.01 (s, 5H, C₅H₅); 6.11 (dd, ⁴J_{HP} = 2.8, ⁴J_{HP} = 11.1, 1H, =C²HPh); 6.7–7.2 (m, 5H, =C²HC₆H₅); 6.85–7.60 (m, 20H, P-C₆H₅).

Isomer B: 1.95 (m, 2H, P-CH₂-); 2.10 (m, 1H, P-CH₂-); 2.11 (m, 2H, -CH₂-); 2.52 (m, 1H, P-CH₂-); 5.32 (s, 5H, C₅H₅); 6.66 (dd, ⁴J_{HP} = 7.7, ⁴J_{HP} = 6.2, 1H, =C²HPh); 6.7–7.2 (m, 5H, =C²HC₆H₅); 6.85–7.60 (m, 20H, P-C₆H₅).

¹³C{¹H} NMR (CD₂Cl₂, +25 °C) δ , ppm [J, Hz].

Isomer A: 18–31 (m, -CH₂- and P-CH₂-); 89.1 (s, C₅H₅); 105.6 (dd, ³J_{CP} = 2.2, ³J_{CP} = 24.9, C¹=C²HPh); 123–135 (m, =CHC₆H₅ and

P-C₆H₅); 143.4 (dd, ⁴J_{CP} = 3.5, ⁴J_{CP} = 3.5, C_{ipso} of C=CHC₆H₅); 208.1, 211.7 (s, Fe-CO); 216.2 (s, br Re-CO); 265.1 (dd, ²J_{CP} = 1.9, ²J_{CP} = 8.4, C¹=C²HPh).

Isomer B: 18–31 (m, -CH₂- and P-CH₂-); 88.0 (s, C₅H₅); 111.2 (dd, ³J_{CP} = 20.8, C¹=C²HPh); 124–135 (m, C=CHC₆H₅ and PC₆H₅); 141.2 (s, br, C_{ipso} of C=CHC₆H₅); 208.7, 209.3 (s, Fe-CO); 213.2 (d, br, ³J_{CP} = 19.1, Re-CO); 249.9 (s, br, C¹=C²HPh).

³¹P{¹H} NMR (CD₂Cl₂) δ , ppm [J, Hz].

Isomer A: -2.99 (d, P², ²J_{PP} = 95.6); 4.43 (d, P¹, ²J_{PP} = 95.6).

Isomer B: -4.92 (d, P², ²J_{PP} = 106.0); 4.18 (d, P¹, ²J_{PP} = 106.0).

Reaction of [CpReFePd(μ_3 -C=CHPh)(CO)₅(dppe)] (**8**) with [Fe₂(CO)₉]

[Fe₂(CO)₉] (84 mg, 0.23 mmol) was added to the solution of [CpReFePd(μ_3 -C=CHPh)(CO)₅(dppe)] (**8**) (67 mg, 0.06 mmol) in 10 mL of benzene. A reaction mixture was stirred for 3 h at 20 °C and then was transferred via cannula into 50 mL flask. The solvent was removed *in vacuo* and the residue was dissolved in hexane–benzene mixture (2:1) and chromatographed on an alumina column (9.5 × 2 cm). The three main fractions were subsequently eluted with petroleum ether, petroleum ether:benzene (7:3) and (3:2) mixtures.

The first light-brown fraction, after evaporation of solvent, gave 1 mg (3%) of bright-orange complex [Cp(CO)₂ReFe(μ -C=CHPh)(CO)₄] (**5**). This compound was identified by IR spectra [40].

The second rose fraction was eluted with petroleum ether:benzene (7:3). Evaporation of the solvent and crystallization of the crude product from hexane gave 25 mg (61%) of [Cp(CO)₂ReFe₂(μ -C=CHPh)(CO)₆] (**7**) as red crystals.

The third violet band, after evaporation of the solvent gave 16 mg (32%) of dark-violet cluster [(dppe)PdFe₂(CO)₈] (**6**) identified by IR spectra [26].

Reaction of [CpReFePd(μ_3 -C=CHPh)(CO)₅(dppp)] (**10**) with [Fe₂(CO)₉]

[Fe₂(CO)₉] (58 mg, 0.16 mmol) was added to solution of [CpReFePd(μ_3 -C=CHPh)(CO)₅(dppp)] (**10**) (30 mg, 0.03 mmol) in 5 mL of benzene. A reaction mixture was stirred for 3 h at 20 °C and then was transferred via cannula into 50 mL flask. The solvent was removed *in vacuo* and the residue was dissolved in hexane–benzene mixture (2:1) and chromatographed on an alumina column (6 × 2 cm). The three main fractions were subsequently eluted with petroleum ether, petroleum ether:benzene (7:3) and (3:2) mixtures.

The first light-brown fraction, after evaporation of solvent, gave 10 mg (59%) of bright-orange complex [Cp(CO)₂ReFe(μ -C=CHPh)(CO)₄] (**5**). This compound was identified by IR spectra [40].

The third violet fraction, after evaporation of the solvent gave 9 mg (35%) of dark-violet cluster [(dppp)PdFe₂(CO)₈] (**9**) identified by IR spectra [26].

X-ray diffraction studies of [CpReFe₂(μ_3 -C=CHPh)(CO)₈] (**7**)

C₂₁H₁₁O₈Fe₂Re, monoclinic, P2₁/c, a = 15.757(1), b = 14.5172(9), c = 19.282(1) Å, β = 97.091(1)°, V = 4377.1(5) Å³, Z = 8. The experimental data were collected using dark-violet fragment of a crystal, dimensions of 0.21 × 0.16 × 0.09 mm, with a SMART Apex II diffractometer (Bruker SMART 4K CCD area detector, graphite monochromator, Mo K α radiation, λ = 0.71073 Å, $2\theta \leq 52.8^\circ$); 36294 reflections were obtained at 293 K, 8957 unique. The experimental completeness is 99.8%. Absorption corrections ($\mu_{\text{Mo}} = 6.87 \text{ mm}^{-1}$) have been applied using multiscan procedure [55], $R_{\text{int}} = 0.093$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 , using SHELXTL program [56]. Hydrogen atoms have been placed in calculated positions and

taken into account in the final stages of refinement in the “riding model” approximation. Refinement converged at a final $R1 = 0.0439$ for 4874 reflections with $F_o > 4\sigma_{F_o}$ and 0.107 for all 8957 data; $wR_2 = 0.0888$, $\text{GoF} = 0.974$, 577 refined parameters.

Electrochemical study

Electrochemical measurements were carried out in acetonitrile solutions with 0.1 M $[\text{Et}_4\text{N}][\text{BF}_4]$ as supporting electrolyte under an argon atmosphere at room temperature. Cyclic voltammograms were recorded on an IPC-Pro M potentiostat with computer software using a three-electrode system. The working electrode was a platinum electrode of 1 mm diameter or a glassed carbon (GC) electrode of 3 mm diameter. The reference electrode was $\text{Ag}/0.1 \text{ M AgNO}_3$ in MeCN and the auxiliary electrode was platinum wire. Controlled-potential electrolysis were carried out with the IPC-Pro potentiostat using three-electrode system with a working platinum electrode of 4 mm diameter.

Appendix A. Supplementary material

CCDC 984728 (7) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2014.07.024>.

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