

# Molecular structure of a new tetranuclear $\mu_2:\mu_3$ -bis-vinylidene cluster, $\text{Cp}_2(\text{CO})_4\text{RePd}(\mu\text{-C=CHPh})\text{RePd}(\mu_3\text{-C=CHPh})(\eta^2\text{-dppe})$



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## ABSTRACT

The novel tetranuclear di-vinylidene complex  $\text{Cp}_2(\text{CO})_4\text{RePd}(\mu_2\text{-C=CHPh})\text{RePd}(\mu_3\text{-C=CHPh})(\text{dppe})$  was isolated and characterized by X-ray diffraction. This cluster consists of two RePd fragments linked to each other through the bonding of the palladium atom in the  $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})]$  fragment to the carbonyl and vinylidene ligands in the  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{dppe})$  fragment.

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## 1. Introduction

Heterometallic compounds attract considerable attention, mainly 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 extensively studied [7,8]. A variety of methods for the synthesis of heterometallic compounds have been developed [9]. One of the methods is the consecutive addition of unsaturated metal-containing fragments to mononuclear complexes containing unsaturated hydrocarbyl ligands [10–17]. In particular, mononuclear vinylidene complexes,  $\text{M}=\text{C}=\text{CHR}$ , have been used as building block for the preparation of heteronuclear complexes and clusters containing  $\text{MM}'$ ,  $\text{MM}'_2$  and  $\text{MM}'\text{M}''$  cores [12,13]. At the same time, in spite of the eminent role of palladium in organometallic synthesis and homogenous catalysis, Pd-containing heterometallic vinylidenes are still rare.

Recently [18], we prepared the trinuclear  $\text{ReFePd}$   $\mu_3$ -vinylidene clusters by the conversion of the rhenium vinylidene  $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{CHPh}$  (**1**) into the binuclear  $\text{RePd}$  complex  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{P-P})$  ( $\text{P-P}=\text{dppe}$  (**2**),  $\text{dppp}$  (**3**)) followed by the treatment of **2** and **3** with  $\text{Fe}_2(\text{CO})_9$  to give the trinuclear complex-

es  $\text{CpReFePd}(\mu_3\text{-C=CHPh})(\text{CO})_5(\text{P-P})$  ( $\text{P-P}=\text{dppe}$  (**4**),  $\text{dppp}$  (**5**)). Complexes **4** and **5** are of limited stability and decomposed slowly in solution, which did not allow us to obtain X-ray quality crystals. However, our last attempts to grow crystals of **4** resulted in the unexpected isolation of the tetranuclear complex  $\text{Cp}_2(\text{CO})_4\text{RePd}(\mu\text{-C=CHPh})\text{RePd}(\mu_3\text{-C=CHPh})(\text{dppe})$  (**6**) in a very low yield. We report here on an independent and more convenient route to **6**, as well as its molecular geometry determined by X-ray crystallography.

## 2. Results and discussion

The tetranuclear complex **6** was isolated in a moderate yield as a dark-orange crystalline solid from the reaction of  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$  (**7**) with  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{dppe})$  (**2**) in dichloromethane. The cluster **6** is quite stable in the solid state, but gradually decomposes in solution. It was characterized by IR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. The molecular structure of **6** was established by X-ray diffraction (Fig. 1). Crystal data and refinement parameters are provided in Table 1.

The cluster **6** consists of two parts: the  $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})]$  unit (*fragment 1*) and the  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{dppe})$  unit (*fragment 2*). These two fragments are bonded to each other by the interaction of the Pd1 atom of *fragment 1* with the semi-bridging C505 group of *fragment 2* and by a  $\pi$ -bond

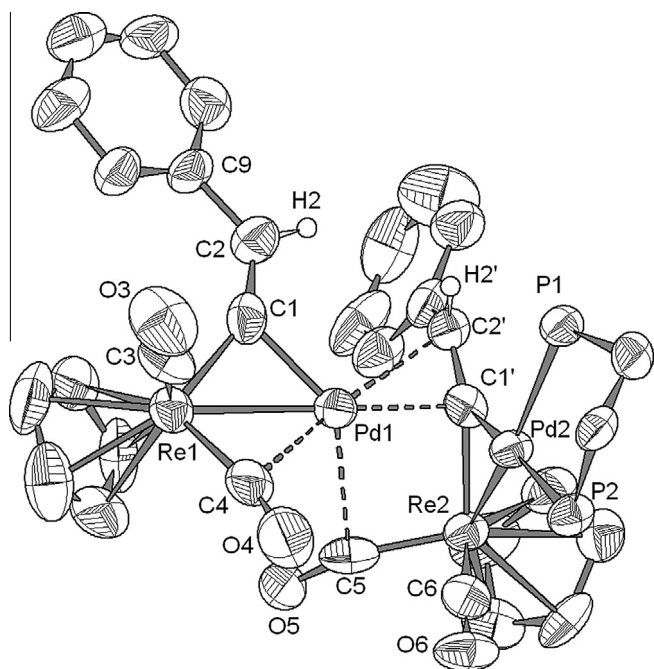
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between Pd1 and the vinylidene group C1'=C2'HPh of *fragment 2*. The metal core of the cluster **6** consists of four alternating rhenium and palladium atoms, Re1–Pd1–Re2–Pd2. The Re1–Pd1 and Re2–Pd2 bond lengths are 2.7136(12) and 2.7690(11) Å, respectively. The Pd1···Re2 distance is 3.0105(11) Å, which is 0.1 Å longer than the sum of the covalent radii of the Pd and Re atoms [19] (Table 2). Only one of four carbonyl groups of **6**, namely C3O3, is terminal (the Re1–C3–O3 bond angle is 175.6(13)° and the Re1–C3 bond length is 1.854(15) Å). Three other CO groups are semi-bridging. Their bond angles are less than 168°, and the Pd1–C4, Pd1–C5, Pd2–C6 bond lengths are 2.423(15), 2.565(12) and 2.495(12) Å, respectively. It should be noted that the structural characteristics of cluster **6** and its manganese analog Cp<sub>2</sub>(CO)<sub>4</sub>MnPd(μ-C=CHPh)MnPd(μ<sub>3</sub>-C=CHPh)(dppe) (**8**) are similar and most of the differences between them can be attributed to the smaller covalent radius of the Mn atom [19].

The cluster **6** contains two vinylidene ligands, which coordinate to the Re1–Pd1–Re2–Pd2 core in two different manners. The C1=C2HPh ligand of *fragment 1* bridges the Re1 and Pd1 atoms in a μ<sub>2</sub>-coordination mode. The rhenium, palladium and bridged carbonyl carbon atoms form a triangle. The Re1–Pd1, Pd1–C1 and Re1–C1 bond lengths are 2.7136(12), 1.992(13) and 1.999(14) Å, respectively. The Re1–C1–Pd1, Pd1–Re1–C1 and Re1–Pd1–C1 bond angles of this triangle are 85.7(6)°, 47.1(4)° and 47.3(4)°, respectively. The μ-C1=C2HPh ligand is located in the plane of the Re1Pd1C1 carbodimetallacycle; the dihedral angle between the Pd1Re1C1 and C1C2C9 planes is 7.9(18)°. These structural parameters of *fragment 1* are close to those of dinuclear μ-vinylidene complexes [12,13,20].

In contrast, the second vinylidene ligand of *fragment 2* coordinates to the Pd1–Re2–Pd2 core in a μ<sub>3</sub>-η<sup>2</sup>:η<sup>1</sup>:η<sup>1</sup> fashion, forming σ-bonds to the Re2 and Pd2 atoms and an unsymmetrical π-bond to the Pd1 atom. The structure of *fragment 2* is close to that of *fragment 1*. The Re2–Pd2, Pd2–C1' and Re2–C1' bond lengths are 2.7690(11), 2.051(10) and 2.030(11) Å, respectively. The Re2–C1'–Pd2, Pd2–Re2–C1' and Re2–Pd2–C1' bond angles of this triangle are 85.5(4)°, 47.6(3)° and 46.9(3)°, respectively. The



**Fig. 1.** Molecular structure of Cp<sub>2</sub>(CO)<sub>4</sub>RePd(μ-C=CHPh)RePd(μ<sub>3</sub>-C=CHPh)(dppe) (**6**). The dppe phenyl groups and all hydrogen atoms, except that of the vinylidene ligand, are omitted for clarity.

**Table 1**  
Crystal data and X-ray experimental details for complex **6**.

Empirical formula	C <sub>56</sub> H <sub>46</sub> O <sub>4</sub> P <sub>2</sub> Pd <sub>2</sub> Re <sub>2</sub> ; CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	1430.07; 84.92
Temperature (K)	296
Crystal system	triclinic
Space group	P $\bar{1}$
<i>a</i> (Å)	10.843(2)
<i>b</i> (Å)	14.494(3)
<i>c</i> (Å)	19.331(4)
$\alpha$ (°)	106.035(2)
$\beta$ (°)	97.323(3)
$\gamma$ (°)	103.626(3)
<i>V</i> (Å <sup>3</sup> )	2776.7(10)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.812
$\mu$ (mm <sup>-1</sup> )	5.180
<i>F</i> (000)	1456
Crystal size (mm <sup>3</sup> )	0.38 × 0.35 × 0.08
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection (°)	51
Reflections collected	21014
Independent reflections [ <i>R</i> <sub>int</sub> ]	10271 (0.0691)
Data/restraints/parameters	10271/3/519
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.998
Final <i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	0.0578
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [all data]	0.1351, 0.1395
$\Delta\rho_{\min}/\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	-1.361/1.446

**Table 2**

Selected interatomic distances (Å) and angles (°) in Cp<sub>2</sub>(CO)<sub>4</sub>RePd(μ-C=CHPh)RePd(μ<sub>3</sub>-C=CHPh)(dppe) (**6**).

Distances (Å)		Angles (°)	
Pd(1)–C(1)	1.992(13)	Re(1)–Pd(1)–Re(2)	138.17(4)
Pd(1)–C(1)′	2.128(11)	C(1)–Pd(1)–Re(1)	47.3(4)
Pd(1)–C(2)′	2.358(11)	C(1)′–Pd(2)–Re(2)	46.9(3)
Re(1)–C(1)	1.999(14)	Pd(2)–Re(2)–Pd(1)	66.56(3)
Re(1)–C(3)	1.854(15)	C(1)–Re(1)–Pd(1)	47.1(4)
Re(1)–C(4)	1.891(14)	C(1)′–Re(2)–Pd(2)	47.6(3)
Re(2)–C(5)	1.838(17)	Re(1)–C(1)–C(2)	148.3(10)
Re(2)–C(6)	1.894(16)	Pd(1)–C(1)–C(2)	124.9(10)
Re(2)–C(1)′	2.030(11)	Re(1)–C(1)–Pd(1)	85.7(6)
Pd(1)–Re(1)	2.7136(12)	C(2)′–C(1)′–Re(2)	143.4(8)
Pd(1)–Re(2)	3.0105(12)	C(2)′–C(1)′–Pd(2)	131.1(9)
Pd(2)–Re(2)	2.7690(11)	Re(2)–C(1)′–Pd(1)	85.5(4)
Pd(2)–C(1)′	2.051(10)	C(2)′–C(1)′–Pd(1)	82.2(7)
C(1)–C(2)	1.377(17)	O(3)–C(3)–Re(1)	175.6(13)
C(1)′–C(2)′	1.345(14)	O(4)–C(4)–Re(1)	168.2(12)
		O(5)–C(5)–Re(2)	164.7(11)
		O(6)–C(6)–Re(2)	162.5(10)

μ-C1'=C2'HPh ligand is located in the plane of the Re2Pd2C1' carbodimetallacycle; the dihedral angle between the Re2Pd2C1' and C1'C2'C15 planes is 9.9(14)°. The C1', C6, P1 and P2 atoms of *fragment 2* almost form one plane, and the deviation of the central Pd2 atom from this plane is only 0.061(5) Å. At the same time, the structural parameters of the [Pd1Re2Pd2(μ<sub>3</sub>-C1'=C2'HPh)] fragment (for instance, the Pd1Pd2Re2, Pd2Pd1Re2 and Pd2Re1Pd1 bond angles) resemble those found for trinuclear μ<sub>3</sub>-vinylidene complexes [13,21]. However, the Pd1···Pd2 (3.1778(14) Å) and Pd1···Re2 (3.0105(12) Å) distances cannot be considered only as non-bonding (they are longer than the sum of the covalent radii of the corresponding metals) [19].

The plane of *fragment 1* is almost perpendicular to that of *fragment 2*. The dihedral angle between the Pd1Re1C1 and Pd2Re2C1' planes is 87.7(3)°. The C=C bond lengths of the vinylidene ligands are 1.377(17) Å for *fragment 1* and 1.345(14) Å for *fragment 2*. They are similar in length to the C=C bonds found in the Pd-containing complexes Cl<sub>2</sub>Pd<sub>2</sub>(μ-C=CCl<sub>2</sub>)(μ-dppm)<sub>2</sub> (1.30(2) Å) [22], Cl<sub>2</sub>PdNi(μ-C=CCl<sub>2</sub>)(μ-dppm)<sub>2</sub> (1.290(14) Å) [23] and (PPh<sub>3</sub>)<sub>2</sub>CIPd{μ-[C=C(H)-N=CPh<sub>2</sub>]}PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.339(4) Å) [24]. The

Re1–Pd1 (2.7136(12) Å) and Re2–Pd2 (2.7690(11) Å) bond lengths are slightly different. Previously, a significant difference between the two Re–Pd bond lengths was observed in the compound  $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})(\text{CO})_3\text{RePd}]_2$  (2.866(1) and 2.666(1) Å) [25]. The Re–Pd bond distances are shorter than those in  $(\eta^5\text{-7-CB}_{10}\text{H}_{11})(\text{CO})_3\text{RePd}(\text{dppe})$  (2.7858(4) Å) [26],  $\text{Re}_2(\text{CO})_8(\mu\text{-SnPh}_2)[\text{Pd}(\text{PBU}^t)_3]_2$  (2.8580(5) Å) [27] and  $[\text{NET}_4][\text{Re}_7(\text{CO})_{21}\{\text{Pd}(\eta^3\text{-PhC}_3\text{-H}_4)\}(\text{C})]$  (2.872(5) Å) [28].

The most reasonable route to the  $\text{Re}_2\text{Pd}_2$  cluster **6** seems to be the coupling of two RePd fragments, one of which is coordinatively unsaturated  $[\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})]$  (*fragment 1*) and the other one is the stable complex **2** (*fragment 2*). The generation of the former by the spontaneous dissociation of triphenylphosphane from  $\text{Cp}(\text{CO})_2\text{RePd}(\mu_2\text{-C=CHPh})(\text{PPh}_3)_2$  (**7**) in the presence of **2** indeed gave **6** in 20% yield (Scheme 1). It is no wonder that the degradation of the trinuclear cluster  $\text{CpReFePd}(\mu_3\text{-C=CHPh})(\text{CO})_5(\text{dppe})$  (**4**) gave only trace amounts of **6**, since generation of both RePd fragments are rather complicated in this case. Indeed, the formation of **2** from **4** requires the elimination of an iron tricarbonyl group, while the generation of *fragment 1* requires abstraction of dppe from **2**, presumably by  $\text{Fe}(\text{CO})_3$ . Note, the mechanism for the formation of **6** from the binuclear  $\mu$ -vinylidene complexes **2** and **7** is similar to that proposed for the manganese analog  $\text{Cp}_2(\text{CO})_4\text{MnPd}(\mu\text{-C=CHPh})\text{MnPd}(\mu_3\text{-C=CHPh})(\text{dppe})$  (**8**).

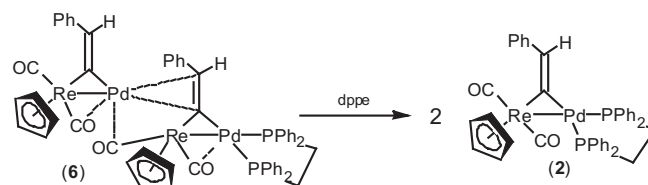
It was found that the interaction between the two fragments of the cluster is labile, and *fragment 1* can be eliminated in the reactions of cluster **6** with diphosphane ligands. Thus, after addition of one equiv. of dppe to a benzene solution of **6**, *fragment 2* is replaced by the diphosphane ligand, giving 2 equiv. of complex **2** quantitatively (IR and TLC monitoring) (Scheme 2).

The tetranuclear complex **6** is a representative example of rare complexes wherein the metal cores consist of alternating metal atoms. Other known examples are  $\text{Cp}_2(\text{CO})_4\text{MnPd}(\mu\text{-C=CHPh})\text{MnPd}(\mu_3\text{-C=CHPh})(\text{dppe})$  [29],  $[\text{Mn}_2\text{Rh}_2(\mu\text{-CC}_6\text{H}_5)(\mu_3\text{-CC}_6\text{H}_5)(\mu\text{-CO})_3(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)_2]$ ,  $[\text{Mn}_3\text{Rh}_2(\mu\text{-CC}_6\text{H}_5)_2(\mu_3\text{-CC}_6\text{H}_5)(\mu\text{-Cl})(\mu\text{-CO})_3(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_3]$ ,  $[\text{Re}_2\text{Rh}_2(\mu\text{-CC}_6\text{H}_5)(\mu_3\text{-CC}_6\text{H}_5)(\mu\text{-CO})_3(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)_2]$  [11] and  $\text{Pd}_2\text{Re}_2(\text{CO})_8(\mu\text{-SnPh}_2)_2(\text{PBU}^t)_2$  [27,30]. Moreover, the presence of two different coordinated vinylidene ligands in one molecule has been reported previously only for the analogous manganese complex  $\text{Cp}_2(\text{CO})_4\text{MnPd}(\mu\text{-C=CHPh})\text{MnPd}(\mu_3\text{-C=CHPh})(\text{dppe})$  [29] and the cluster  $\text{Cp}^*\text{IrOs}_3(\text{CO})_9(\mu_4\text{-C=CHPh})(\mu_3\text{-C=CHPh})$ , where one vinylidene unit is bounded to all four metal atoms and the second one to two osmium atoms and the iridium atom [31].

### 3. Experimental

#### 3.1. Reaction of $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{dppe})$ (**2**) with $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$ (**7**)

$\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{dppe})$  (**2**) (55 mg, 0.06 mmol) was added to a solution of  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{PPh}_3)_2$  (**7**) (62 mg, 0.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL). The reaction mixture was stirred for 7 h at 20 °C. The solvent was evaporated and the residue was washed with hexane (10 mL). The remaining solid was



Scheme 2.

redissolved in a  $\text{CH}_2\text{Cl}_2$ –hexane mixture (10:1). After the solution was allowed to stand at  $-20$  °C for 2 days, a mixture of dark-orange, air-stable crystals of **6** and an undefined violet powder were obtained; these were separated manually (by hand). Yield: 20%.

Anal. Calc. for  $\text{C}_{56}\text{H}_{46}\text{O}_4\text{P}_2\text{Pd}_2\text{Re}_2$  (1430.18): C, 46.99; H, 3.22. Found: C, 46.72; H, 3.45%.

IR (KBr,  $\text{cm}^{-1}$ ): 1917s, 1876s, 1850s, 1813 m ( $\nu_{\text{CO}}$ ).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $+25$  °C)  $\delta$ , ppm [J, Hz]: 1.94 (m, 2H, P- $\text{CH}_2$ -); 2.08 (m, 1H, P- $\text{CH}_2$ -); 2.21 (m, 1H, P- $\text{CH}_2$ -); 4.75 (s, 5H,  $\text{C}_5\text{H}_5$ ); 4.91 (s, 5H,  $\text{C}_5\text{H}_5$ ); 6.75 (s, 1H,  $=\text{C}^2\text{HPh}$ ); 6.93–7.12 (m, 20H,  $\text{PC}_6\text{H}_5$ ); 7.43–7.59 (m, 10H,  $=\text{C}^2\text{HC}_6\text{H}_5$  and  $=\text{C}^2\text{HC}_6\text{H}_5$ ); 7.02 (d, 1H,  $^4J_{\text{PH}} = 7.61$ ,  $=\text{C}^2\text{HPh}$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$ , ppm [J, Hz]: 30.68 (d,  $P^2$ ,  $^2J_{\text{PP}} = 17.8$ ); 35.95 (d,  $P^1$ ,  $^2J_{\text{PP}} = 17.8$ ).

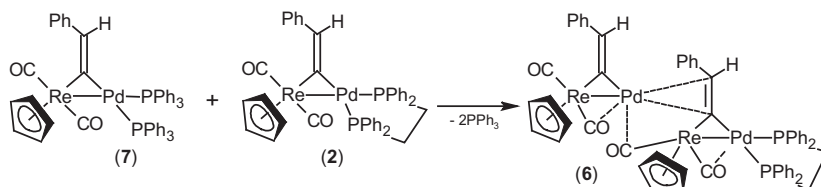
#### 3.2. Reaction of $\text{Cp}_2(\text{CO})_4\text{RePd}(\mu\text{-C=CHPh})\text{RePd}(\mu_3\text{-C=CHPh})(\text{dppe})$ (**6**) with dppe

To 20 mg (0.014 mmol) of **6** dissolved in 5 mL of benzene was added 6 mg (0.015 mmol) of dppe at RT. After stirring for 30 min, the solution changed colour from dark-yellow to bright-yellow. The reaction mixture was filtered through a pad of  $\text{SiO}_2$  ( $0.2 \times 2$  cm). The solvent was evaporated *in vacuo*, and residue was redissolved in a benzene–hexane mixture (1:2). After crystallization for 12 h at  $-20$  °C, complex **2** was obtained (12 mg, 92%) and identified by IR spectroscopy. The formation of  $\text{Cp}(\text{CO})_2\text{RePd}(\mu\text{-C=CHPh})(\text{dppe})$  (**2**) in the reaction mixture was detected by TLC.

IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 1909, 1833 ( $\nu_{\text{CO}}$ ).

#### 3.3. X-ray diffraction studies of $\text{Cp}_2(\text{CO})_4\text{RePd}(\mu\text{-C=CHPh})\text{RePd}(\mu_3\text{-C=CHPh})(\text{dppe})$ (**6**)

$\text{C}_{56}\text{H}_{46}\text{O}_4\text{P}_2\text{Pd}_2\text{Re}_2$ , triclinic,  $P\bar{1}$ ,  $a = 10.843(2)$ ,  $b = 14.494(3)$ ,  $c = 19.331(4)$  Å,  $\alpha = 106.035(2)$ ,  $\beta = 97.323(3)$ ,  $\gamma = 103.626(3)^\circ$ ,  $V = 2776.7(10)$  Å<sup>3</sup>,  $Z = 2$ . The experimental data were collected using a dark-red fragment of a crystal, with dimensions  $0.38 \times 0.35 \times 0.08$  mm, using a SMART Apex II diffractometer (CCD area detector, graphite monochromator, Mo K $\alpha$ -radiation,  $2\theta \leq 51$ ); 21014 reflections were obtained at 296 K, 10271 were unique. The experimental completeness is 99.3%. Absorption corrections ( $\mu_{\text{Mo}} = 5.180 \text{ mm}^{-1}$ ) have been applied using a multi-scan procedure [32],  $R_{\text{int}} = 0.0691$ . The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ , using the



Scheme 1.

SHELXTL program [33]. The solvent ( $\text{CH}_2\text{Cl}_2$ ) molecule was detected in the asymmetric part of the unit cell. Because of strong disordering of the molecule, it was fixed in a perfect form during the refinement. All phenyl rings were idealized and refined as rigid groups; hydrogen atoms were placed in calculated positions and taken into account in the final stages of refinement in the “riding model” approximation. Refinement converged at a final  $R_1$  value of 0.0578 for 5339 reflections with  $F_o > 4\sigma_{F_o}$  and 0.135 for all 10271 data;  $wR2 = 0.1395$ ,  $\text{GooF} = 0.998$ , 519 refined parameters.

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### Appendix A. Supplementary data

CCDC 984706 contain the supplementary crystallographic data for compound **6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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