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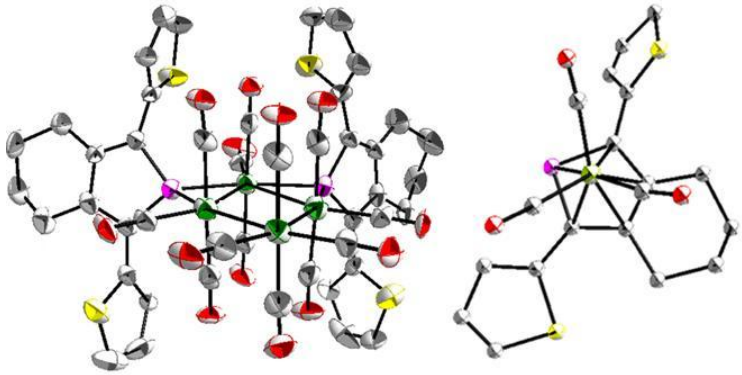

# Reactivity of dirhenium and triruthenium carbonyls toward a biphosphole ligand: M–M, P–P and C–H bonds cleavage

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## Abstract

The reaction of $[Re_2(CO)_8(CH_3CN)_2]$ with bis(2-thienyl)biphosphole in refluxing *n*-octane affords the complex $[Re(CO)_3(\eta^5\text{-}PC_{16}H_{14}S_2)]$ (**1**) where cleavage of the Re–Re and P–P bonds occurs; its molecular structure confirms the formation of a rhenium mononuclear compound with a $\eta^5$-coordinated phospholyl unit and three carbonyl groups oriented in a tripod. On the other hand, bis(2-thienyl)biphosphole reacts with $[Ru_3(CO)_{12}]$ in refluxing cyclohexane to affording two new compounds $[Ru_3(CO)_9(\mu\text{:}\eta^1\text{:}\eta^5\text{-}PC_{16}H_{13}S_2)]$ **(2)** and $[Ru_4(CO)_{13}(\mu\text{:}\eta^1\text{-}PC_{16}H_{14}S_2)_2]$ **(3)**. Spectroscopic data and theoretical studies of **2** suggest the formation of an open Ru3 cluster with two metal–metal bonds bridged by a $(\eta^1\text{:}\eta^5\text{-}PC_{16}H_{13}S_2)$ unit and a C-H bond activation of one of the thienyl substituents. X-ray structure of **3** reveals a novel tetranuclear ruthenium cluster containing 13 terminal carbonyl ligands and two phospholyl units coordinated as μ-phosphide.

**Keywords:** *Biphosphole; metal-metal and phosphorus-phosphorus bonds cleavage; tetranuclear cluster; $\eta^5$-phospholyl complex; C-H activation.*

## 1. Introduction

Heterocyclic π-complexes have been demonstrated to be excellent ligands for asymmetric catalysis [1-5]. Particularly, phosphole ligands have been interesting for the development of complexes with specific applications since they have the ability to act as both σ- and π-donor ligands, sometimes simultaneously (Figure 1). Several phosphole-complexes have been used in catalytic transformations, such as hydroformylation, hydrosilylation or asymmetric allylic substitution [6-9]. They have also been investigated in fields as diverse as OLEDs, WOLEDs and non linear optics [10-12]. Additionally, phospholyl anions (phospholides) obtained from phosphole derivatives have unique electronic properties since they are good π-acceptors and poor σ-donors [13-16]. They are capable of $\eta^1$- and $\eta^5$-coordinating to metal centers (Figure 1) [17]. Particularly, $\eta^5$-phospholyl complexes have been used in numerous catalytic [4, 13, 14, 18-20].

On the other hand, organometallic compounds that incorporate two or more metal sites in close proximity provide access to reaction pathways not available in mononuclear chemistry [21]. This has been manifested, for example, in reversible metal–metal bond cleavage [22, 23], skeletal rearrangement without degradation [24-26] and ligand activation via multisite coordination [27, 28].

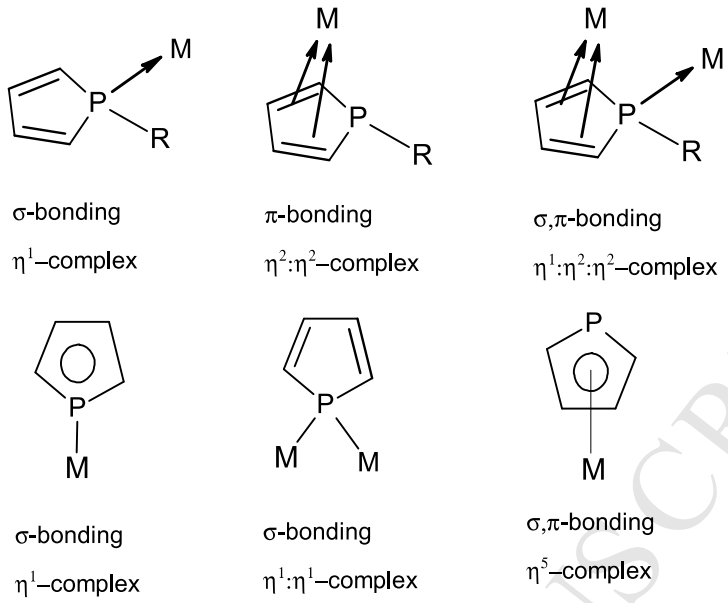


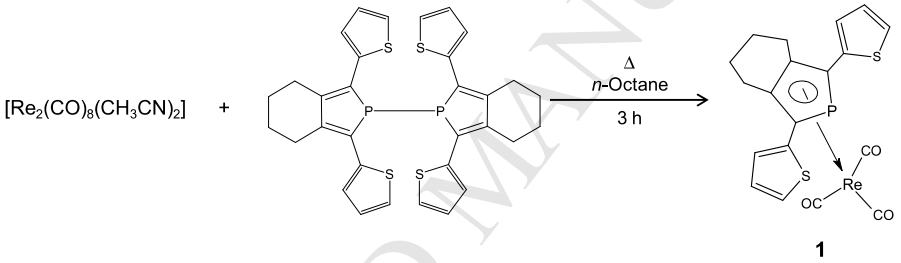

**Figure 1.** Coordination modes of phosphole and phospholyl ligands

In this regard, our studies have been focused on the reactivity of phosphorus derivatives, such as phosphines and phospholes, toward two or more metal centers, and we have found σ,π-complexes, derivatives containing ring-opened ligands, insertion of a phospholide unit into a metal–metal bond and bridging phosphide ligands [27, 29, 30]. Recently, we have studied the reaction of a variety of π-conjugated phosphole ligands with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ finding that the binding mode is restricted to σ-coordination, where electronic properties and steric effects of these phosphole ligands play a role in controlling the final product distribution and giving rise to a variety of isomers [31]. We are convinced that the coordination chemistry of phospholes is still a fertile area for further research. Thus, we have extended the study to the coordination chemistry of biphosphole derivatives on direnium and triruthenium carbonyls.

## 2. Results and discussion

### *2.1. Thermal treatment of [$Re_2(CO)_8(CH_3CN)_2$] with 2,2'-5,5'-tetra(2-thienyl)-1,1'-biphosphole*

The reaction of [$Re_2(CO)_8(CH_3CN)_2$] with biphosphole ligand in refluxing *n*-octane affords one main compound characterized as [$Re(CO)_3(\eta^5\text{-}PC_{16}H_{14}S_2)$] (**1**), (Scheme 1). Its $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ -23.2, which is shifted upfield in comparison to the signal of free ligand (δ -0.1) [32], suggesting that the phosphorus atom is involved in the coordination to the metal center. The $^1H$ NMR spectrum does not show significant differences compared to those of the free ligand. However, in the $^{13}C\{^1H\}$ NMR spectrum, signals for the dienic system are notably upfield shifted, indicating that coordination to the metal center by the dienic system has occurred.




**Scheme 1.** Reaction of [$Re_2(CO)_8(CH_3CN)_2$] with bis(2-thienyl)biphosphole

The molecular structure of compound **1** was determined by single crystal X-ray diffraction studies (See Figure 2, Table 1), which reveals a ($\eta^5$-phospholyl)rhenium complex obtained by cleavage of the Re–Re and P–P bonds of the starting materials. The complex is a rhenium mononuclear with three carbonyl groups in a tripodal orientation and one $\eta^5\text{-}PC_{16}H_{14}S_2$ unit, molecular species with three-legged piano-stool geometry. The $PC_{16}H_{14}S_2$ moiety is coordinated as a phospholide to the rhenium atom [Re1–C1 = 2.36 (1) Å, Re1–C2 = 2.327(8) Å, Re1–C7 = 2.347 (7)Å, Re1–C8 = 2.337 (7) Å, Re1–P1 = 2.530 (3) Å], resulting in a $\eta^5$-complex. Phospholyl ring can be considered planar due to that the phosphorus atom lies 0.073 Å out of the mean plane containing the dienic moiety, and the bond delocalization is evidenced by the small deviation in inter atom distances

[C1–C2 = 1.45(1) Å, C2–C7 = 1.43(1) Å, C7–C8 = 1.42(1) Å, P1–C1 = 1.817(9) Å, P1–C8 = 1.80(1) Å], similar to the reported for the analogous manganese derivative $[Mn(CO)_3(\eta^5\text{-}PC_9H_6)]$ [33].

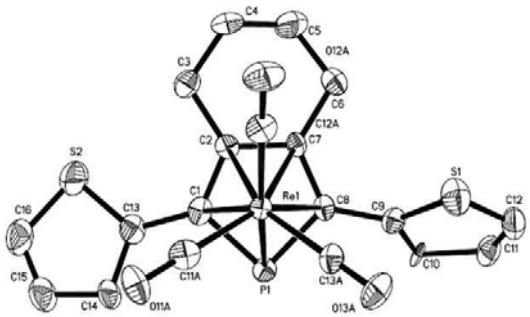
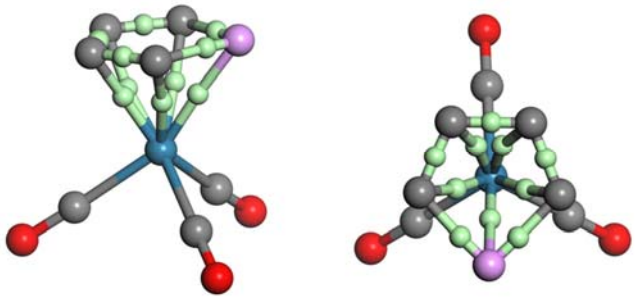



**Figure 2.** Molecular structure of **1**, showing 50% probability ellipsoids. Selected bond lengths (Å) an angles (°): Re1–P1 = 2.530 (3), Re1–C1 = 2.36 (1), Re1–C2 = 2.327 (8), Re1–C7 = 2.347 (7), Re1–C8 = 2.337 (7), P1–C1 = 1.817 (9), P1–C8 = 1.80 (1), C1–C2 = 1.45 (1), C2–C7 = 1.43 (1), C7–C8 = 1.42 (1), C11A–Re1–C12A = 91.5 (4), C11A–Re1–C13A = 90.3 (4), C12A–Re1–C13A = 90.7 (4).

Additionally, the ($\eta^5$-phospholyl)rhenium complex formation is corroborated by the presence of five bond critical points (BCP) between the rhenium atom and each element of the ring structure, as displayed in Figure 3. The electron density distribution of a free atom has spherical symmetry. Once this atom is bound, e.g. to form a molecule or a crystal, the electron density loss its spherical uniformity and this new distribution presents different types of critical points. The topological properties of a molecular or crystal charge distribution are summarized by its critical points (CP) [34]. These are points at which the gradient vector field, $\nabla F(r)$, vanishes. Among them there are maxima, minima and two types of saddle points. Every CP has a characteristic pattern of trajectories or gradient paths of F(r). The trajectories originate and end at critical points. For our purpose we are interested in two of them, the maxima CP which are associated to the nuclear positions, and one type of saddle points which is associated to the bond critical points (BCP). A BCP is found between every pair of neighboring nuclei. It represents both local maxima in two

103 directions and a local minimum in the third direction. The network of nuclei and BCP defines a
104 graph, which describes the atomic connectivity and structure within a molecule or a crystal cell. In
105 Figure 3, top and side views are presented for the molecular graph of the ring coordinated to the
106 metal center, showing a "three legs stool" geometrical arrangement. For a better visualization, the
107 rest of the elements in the structure are omitted. The magnitudes of the electron density over each
108 BCP are similar, varying between 0.36 and 0.38 atomic units, which indicates that the electron
109 density is consistently shared between the metal center and phospholyl ring. Theoretical
110 calculations also indicate that the free energy of formation for compound **1**, based on the
111 stoichiometrically balanced reaction, is +48 kcal/mol (Scheme 1).



112

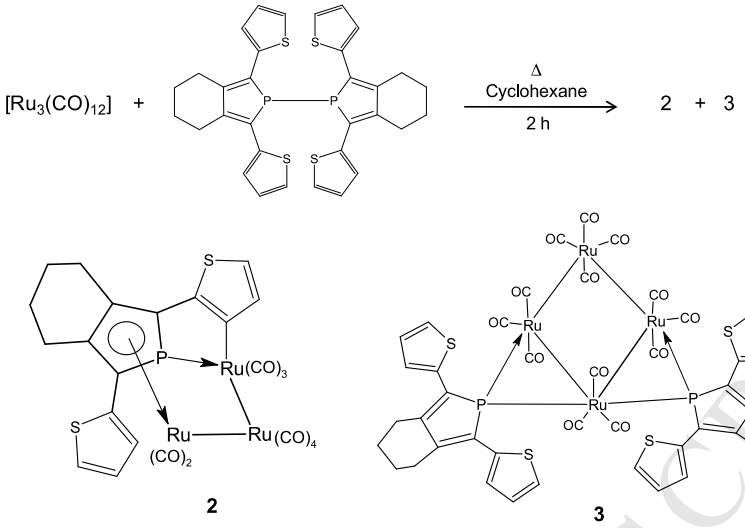
113 **Figure 3**. Molecular graphs (top and side view) of the phosphorus ring coordinated to the metal center in **1**. Gray, red,
114 blue and purple spheres represent C, O, Re and P atoms, respectively. Light green spheres represent the bond critical
115 points (BCPs).

116

117 *2.2 Thermal treatment of [$Ru_3(CO)_{12}$] with 2,2'-5,5'-tetra(2-thienyl)-1,1'-biphosphole*

118 Two new compounds were obtained by reaction of [$Ru_3(CO)_{12}$] with 2,2'-5,5'-tetra(2-thienyl)-1,1'-
119 biphosphole in refluxing cyclohexane, [$Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_{16}H_{13}S_2)$] **(2)** and [$Ru_4(CO)_{13}(\mu:\eta^1\text{-}$
120 $PC_{16}H_{14}S_2)_2$] **(3)** (Scheme 2). The IR spectrum of compound **2** in the carbonyl region is
121 characteristic of a nonacarbonyl trinuclear compound similar to [$Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_4H_2Me_2)(\eta^1\text{-}$
122 $C_6H_5)$] [27]. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at δ 112.2, significantly downfield shifted

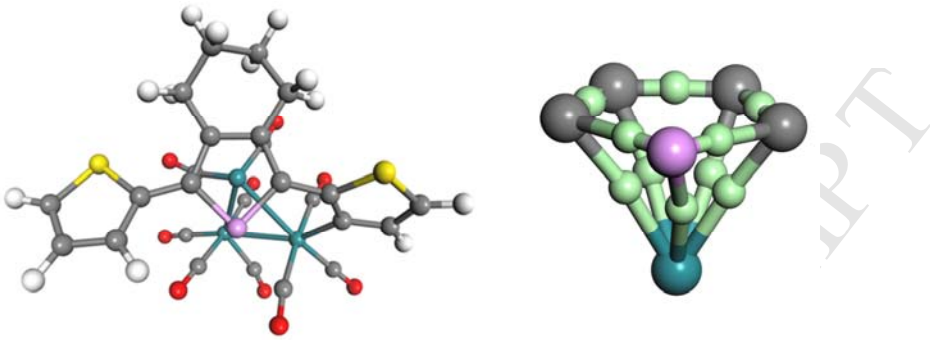
in comparison to the free ligand, similar to that observed for $[Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_4H_2Me_2)(\eta^1\text{-}C_6H_5)]$ [27]. The $^1H$ NMR spectrum of compound **2** shows two sets of signals for the thienyl protons, showing inequivalence between both thienyl rings. Absence of the thienyl proton $H_3$ is also observed, suggesting the occurrence of C-H bond activation. In the $^{13}C$ NMR spectrum, signals assigned to the dienic system of the phosphorus ring are considerably upfieldshifted, similar to those found for $[Re_2(CO)_7(\mu:\eta^1:\eta^2\text{-}PhPC_4H_3Me)]$, $[Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_4H_2Me_2)(\eta^1\text{-}C_6H_5)]$ [27, 29, 30], indicating the coordination of the phospholyl ring to the trinuclear complex. The signal of $C_{3thienyl}$ is downfield shifted, confirming the C-H bond activation. The ESI-MS spectrum of compound **2** displays parent peaks of high intensity corresponding to its molecular ion $[M+H]^+$ at m/z 858.79, which is in agreement with the molecular formula $[Ru_3(CO)_9(PC_{16}H_{13}S_2)]$. Unfortunately, we were unable to obtain suitable crystals of compound **2** for X-ray diffraction analysis, however, based on the spectroscopic data and its comparison with the ruthenium analogue $[Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_4H_2Me_2)(\eta^1\text{-}C_6H_5)]$ [27], the proposed molecular structure of $[Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_{16}H_{13}S_2)]$ (**2**) is the most likely as shown in Scheme 2 . Thus, the structure consists of an open Ru3 cluster with two metal–metal bonds bridged by a $(\eta^1:\eta^5\text{-}PC_{16}H_{13}S_2)$ unit, obtained probably by triple decarbonylation of $[Ru_3(CO)_{12}]$, cleavage of a Ru–Ru and P-P bonds and C-H activation of thienyl ring. Shift to higher values of the IR ν(CO) frequencies as expected for an anionic Ru3 species was not observed for **2**, so an eight-electron donating ligand can be considered in this case, which makes compound **2** a 50-electron cluster where each ruthenium atom has the optimal 18-valence electron configuration.




**Scheme 2.** Reaction of $[Ru_3(CO)_{12}]$ with bis(2-thienyl)biphosphole

With the aim to complement the experimental characterization, theoretical calculations were performed for compound **2**. Several possible conformers were considered, however, only the most stable conformer was taken into account (see Figure 4). Figure 4.a shows that the ligand is coordinated to one of the Ru atoms through a metal-$C_{3thienyl}$ σ-bond and by the phosphorus ring to a second metal center, which is consistent with the propose structure. The coordination by the other two carbons of the thienyl group was considered, but the geometrical stress induced by this arrangement implies the decoordination of the phosphorous ring and/or the P atom with the metal center. In the most stable geometry the phosphorus ring is coordinated in a similar way than compound **1**, through its five atoms (Figure 4.b), confirming the $\eta^5$-coordination and the formation of a ($\eta^5$-phospholyl)ruthenium complex. Magnitudes of the electron density over each BCP between the phosphorus ring and Ru atom vary from 0.41 to 0.49 atomic units, where the smaller value corresponds to the P-Ru interaction. Similar to compound **1**, these BCP values indicate that electron density on the phosphorus ring is noticeably shared with the metal center, which is representative of

159 covalent interactions. The absence of a bond critical point between the two Ru atoms bound to two
160 and three carbonyl ligands, respectively, indicates that the triruthenium structure is open.



161

162 **Figure 4.** a) Most stable geometry for **2**. b) Molecular graph (side view) of the phosphorus ring coordinated to the metal
163 center in **2**. Gray, red, blue, purple, white and yellow spheres represent C, O, Ru, P, H and S atoms, respectively. Light
164 green spheres represent the bond critical points (BCPs).

165

166 The $^{31}P$, $^{1}H$ and $^{13}C$ NMR spectra of **3** suggest that a μ-phosphide coordination of the ligand is
167 obtained; its molecular structure was determined by X-ray diffraction studies of crystals obtained by
168 slow evaporation in a cyclohexane-dichloromethane mixture (See Figure 5, Table 1). The structure
169 reveals a novel tetranuclear ruthenium cluster with 13 terminal carbonyl ligands and two phospholyl
170 units, what are obtained from P-P bond cleavage in the biphosphole ligand. This makes each
171 ruthenium atom have an effective atomic number equal to 54, according to EAN rule. The metal
172 core can be described as a kite with four Ru–Ru bonds, two pairs of almost identical sides [Ru1–
173 Ru2 = 3.137 (1) Å, Ru1–Ru4 = 3.136 (1) Å and Ru4–Ru3 = 2.930 (1), Ru2–Ru3 = 2.920 (1) Å]
174 with angles two pairs similar [Ru2–Ru1–Ru4 = 60.16(2)°, Ru4–Ru3–Ru2 = 65.01(2)° and Ru1–
175 Ru4–Ru3 = 117.25(2)°, Ru1–Ru2–Ru3 = 117.51(2)]. The axial carbonyl groups are eclipsed and
176 both $PC_{16}H_{14}S_2$ moieties are coordinated as μ-phosphides. The two phosphorus atoms are nearly
177 positioned in the same plane of the four ruthenium atoms [0.023 Å (P1) and 0.058 Å (P2)]. The
178 Ru2–P1 [2.344(2) Å] and Ru4–P2 [2.340(2) Å] distances are slightly shorter than Ru1–P1 [2.396(2)

Å] and Ru1–P2 [2.387(2) Å], indicating that Ru1–Ru2 and Ru1–Ru4 edges are asymmetrically bridged by a phospholyl unit. The P1 and P2 atoms lie out of the plane of the diene system (0.094 Å and 0.022 Å respectively), describing the phosphorus rings with an opened envelope-type conformation.

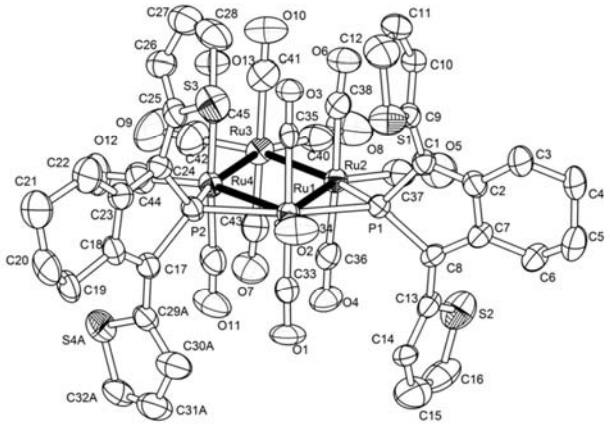



**Figure 5.** Molecular structure of **3**, showing 50% probability ellipsoids. Selected bond lengths (Å) an angles (°): Ru1–Ru2 = 3.137 (1), Ru1–Ru4 = 3.136 (1), Ru4–Ru3 = 2.930 (1), Ru2–Ru3 = 2.920 (1), Ru2–P1 = 2.344(2) Å, Ru4–P2 = 2.340(2), Ru1–P1 = 2.396(2), Ru1–P2 =2.387(2), Ru2–Ru1–Ru4 = 60.16(2), Ru4–Ru3–Ru2 = 65.01(2), Ru1–Ru4–Ru3 = 117.25(2), Ru1–Ru2–Ru3 = 117.51(2).

On the other hand, the molecular graph containing the metal core and its neighbouring atoms for compound **3** is shown in Figure 6. This graph displays two BCPs between each P atom and the two closest ruthenium atoms, corroborating the μ-phosphide coordination of the ligand. Interestingly, and in contrast to the X-ray molecular structure shown in Figure 5, Ru2 and Ru4 are bound while Ru1–Ru2 and Ru1–Ru4 bonds are not present, even though the observed internuclear Ru2–Ru4 distance [3.144(1) Å] is longer than those for Ru1–Ru2 [3.137(1) Å] and Ru1–Ru4 [3.136(1) Å]. As revealed in Figure 6, the BCP electron density value of Ru2–Ru4 bond is found to be smaller (0.174 e/Å$^3$) than the $\rho_{BCP}$ of Ru2–Ru3 and Ru3–Ru4 bonds (0.245 and 0.246 e/Å$^3$, respectively), indicating that no Ru2–Ru4 bond exists. This is consistent with the corresponding internuclear distances found with X-ray diffraction analyses.

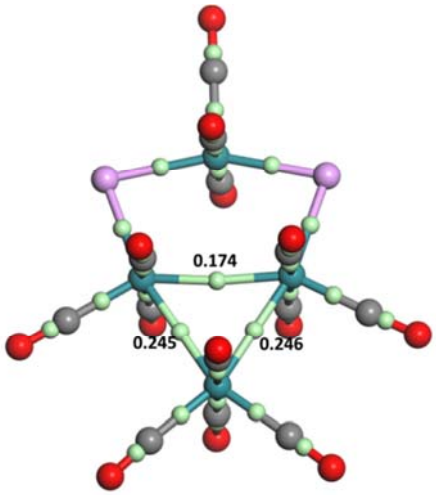



**Figure 6.** Molecular graph for the metal core of **3**.The BCP electron density values for Ru2─Ru4, Ru3─Ru4 and Ru2─Ru3 bonds are given in e/Å$^3$. Bond distances are as presented in Table 1. Gray, red, blue and purple spheres represent C, O, Ru and P atoms, respectively. Light green spheres represent the bond critical points (BCPs).

## 3. Conclusions

A new ($\eta^5$-phospholyl)rhenium complex [Re(CO)$_3$($\eta^5$-PC$_{16}$H$_{14}$S$_2$)] (**1**) was obtained by the rhenium-rhenium and phosphorus-phosphorus bonds cleavage, when [Re$_2$(CO)$_8$(CH$_3$CN)$_2$] reacts with bis(2-thienyl)biphosphole. Additionally, two new ruthenium carbonyl clusters were characterized as [Ru$_3$(CO)$_9$($\mu$:$\eta^1$:$\eta^5$-PC$_{16}$H$_{13}$S$_2$)] **(2)** and [Ru$_4$(CO)$_{13}$($\mu$:$\eta^1$-PC$_{16}$H$_{14}$S$_2$)$_2$] **(3)**, wherein compound **2** represents the second example of a phospholide unit inserted into a metal–metal bond, while compound **3** is the first example of a tetranuclear cluster with two π-conjugated phospholyl units coordinated as μ-phosphides. These results open up the possibility for a facile access to new ruthenium and rhenium complexes with phospholyl units as bridging ligands which can be used in catalytic reactions.

## 4. Experimental section

*4.1 General remarks*

218 $[Re_2(CO)_8(CH_3CN)_2]$ and 2,2'-5,5'-tetra(2-thienyl)-1,1'-biphosphole were synthesized as
219 previously described [32, 35]. $[Ru_3(CO)_{12}]$ was used as supplied by Aldrich Chemical Company.
220 $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded using Bruker Avance AM300 and AM500
221 spectrometers, and assignment of carbon chemical shifts was based on HMBC and HMQC
222 experiment. Infrared spectra were recorded as cyclohexane solutions using a 2 mm $CaF_2$ cell on a
223 Spectrum 100 series Perkin Elmer spectrophotometer. Mass spectra were acquired on a Thermo
224 Scientific TSQ Quantum Ultra AM Triple Quadrupole mass spectrometer employing the Heated
225 Electrospray Ionization (HESI) technique. Routine separation of products in air was by thin-layer
226 chromatography on plates coated with Merck Kieselgel 60 $GF_{254}$.
227
228 *4.2 Reaction of $[Re_2(CO)_8(CH_3CN)_2]$ with 2,2'-5,5'-tetra(2-thienyl)-1,1'-biphosphole*
229 A solution of $[Re_2(CO)_8(CH_3CN)_2]$ (100 mg, 0.147 mmol) and 2,2'-5,5'-tetra(2-thienyl)-1,1'-
230 biphosphole (89 mg, 0.147 mmol) in dry *n*-octane (50mL) was taken to reflux under nitrogen for
231 3h. After evaporation of the solvent, TLC ($SiO_2$) of the brown solid residue
232 (hexane/dichloromethane, 9:1 v/v) gave $[Re(CO)_3(\eta^5\text{-}PC_{16}H_{14}S_2)]$ (**1**) (89% yield). Spectral data for
233 **1**: IR ($\nu_{(CO)}$, cyclohexane): 2026 (s), 1949 (s), 1935 (s) $cm^{-1}$. $^1H$ NMR (500 MHz, $CD_2Cl_2$): δ= 1.93
234 (m, 2H, $CH_2$-$CH_2$-C=C), 2.09 (m, 2H, $CH_2$-$CH_2$-C=C), 3.05 (m, 2H, $CH_2$-C=C), 3.17 (m, 2H, $CH_2$-
235 C=C), 7.03 (d, $^4J_{H5–H3}$ = 1.6 Hz, 2H, $H_{3\ thienyl}$), 7.04 (d, $^3J_{H5–H4}$ = 4.7 Hz, 2H, $H_{4\ thienyl}$), 7.34 (dd,
236 $^3J_{H4–H5}$ = 4.7 Hz, $^4J_{H3–H5}$ = 1.6 Hz, 2H, $H_{5\ thienyl}$). $^{13}C\{^1H\}$ NMR (500 MHz, $CD_2Cl_2$): δ= 22.6 (s,
237 $CH_2$-$CH_2$-C=C), 26.3 (s, $CH_2$-C=C), 109.1 (d, $J_{P–C}$ = 23.0 Hz, $C_\alpha$), 114.6 (d, $^2J_{P–C}$ = 4.9 Hz, $C_\beta$),
238 126.6 (s, $C_{5\ thienyl}$), 127.3 (s, $C_{4\ thienyl}$), 128.5 (d, $^3J_{P–C}$ = 6.8 Hz, $C_{3\ thienyl}$), 136.2 (d, $^2J_{P–C}$ = 20.3 Hz,
239 $C_{2\ thienyl}$), 194.4 (s, M-CO). $^{31}P\ \{^1H\}$ NMR (500 MHz, $CDCl_3$): δ= -23.2 (s). MS: *m/z* 373.24
240 $[M+H]^+$.
241

*4.3 Reaction of [$Ru_3(CO)_{12}$] with 2,2'-5,5'-tetra(2-thienyl)-1,1'-biphosphole*

A solution of [$Ru_3(CO)_{12}$] (100 mg, 0.156 mmol) and 2,2'-5,5'-tetra(2-thienyl)-1,1'-biphosphole (94 mg, 0.156 mmol) in dry cyclohexane (50mL) was taken to reflux under nitrogen for 2h. After evaporation of the solvent, TLC ($SiO_2$) of the brown solid residue (hexane/dichloromethane, 8:2 v/v) gave two compounds [$Ru_3(CO)_9(\mu:\eta^1:\eta^5\text{-}PC_{16}H_{13}S_2)$] **(2)** (19% yield), and [$Ru_4(CO)_{13}(\mu:\eta^1\text{-}PC_{16}H_{13}S_2)_2$] **(3)** (35% yield). Spectral data for **2**: IR ($\nu_{(CO),}$ cyclohexane): 2109 (m), 2063 (s), 2048 (s), 2026 (s), 2016 (m), 1999 (m), 1984 (w), 1949 (w) $cm^{-1}$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ= 2.16 (m, 2H, $CH_2$-$CH_2$-C=C), 2.31 (m, 2H, $CH_2$-$CH_2$-C=C), 2.81 (m, 1H, $CH_2$-C=C), 3.08 (m, 2H, $^*CH_2$-C=C), 3.30 (m, 1H, $CH_2$-C=C), 6.82 (dd, $^3J_{H4–H5}$ = 4.8 Hz, $^3J_{H4–H3}$ = 3.6 Hz, 1H, $H_{4\ thienyl}$), 6.88 (dd, $^3J_{H3–H4}$ = 3.6 Hz, $^4J_{H3–H5}$ = 1.1 Hz, 1H, $H_{3\ thienyl}$), 7.02 (d, $^3J_{H4^*\text{-}H5^*}$ = 4.9 Hz, 1H, $H_{4^*\ thienyl}$), 7.17 (dd, $^3J_{H5–H4}$ = 4.8 Hz, $^4J_{H5–H3}$ = 1.8 Hz, 1H, $H_{5\ thienyl}$), 7.25 (dd, $^3J_{H5^*–H4^*}$ = 4.9 Hz, $^5J_{H5^*–P}$ = 1.3 Hz, 1H, $H_{5^*\ thienyl}$). $^{13}C\{^1H\}$ NMR (300 MHz, $CD_2Cl_2$): δ= 23.0 (s, $CH_2$-$CH_2$-C=C), 23.7 (s, $^*CH_2$-$CH_2$-C=C), 25.4 (d, $^2J_{P–C}$ = 5.3 Hz, $^*CH_2$-C=C), 26.2 (d, $^2J_{P–C}$ = 3.9 Hz, $CH_2$-C=C), 54.5 (s, $C_{6^*\ thienyl}$), 57.2 (s, $C_{6\ thienyl}$), 98.6 (s, $C_{7^*\ thienyl}$), 98.9 (s, $C_{7\ thienyl}$), 127.1 (s, $C_{5^*\ thienyl}$), 127.2 (s, $C_{5\ thienyl}$), 127.7 (s, $C_{4\ thienyl}$), 130.0 (d, $^3J_{P–C}$ = 7.2 Hz, $C_{3\ thienyl}$), 135.6 (s, $C_{2\ thienyl}$) 135.8 (s, $C_{2^*\ thienyl}$), 137.4 (s, $C_{4\ thienyl}$), 160.6 (s, $C_{3^*\ thienyl}$), 195.4 (s, M-CO), 203.2 (s, M-CO), 205.9 (s, M-CO). $^{31}P\ \{^1H\}$ NMR (500 MHz, $CD_2Cl_2$): δ= 112.2 (s). MS: 858.79 *m/z* $[M+H]^+$ . Spectral data for **3**: IR ($\nu_{(CO),}$ cyclohexane): 2105 (w), 2079 (m), 2042 (s), 2015 (m), 1995 (m), 1975 (w) $cm^{-1}$. $^1H$ NMR (500 MHz, $CD_2Cl_2$): δ= 1.73 (m, 4H, $CH_2$-$CH_2$-C=C), 2.44 (m, 4H, $CH_2$-C=C), 6.90 (dd, $^4J_{H5–H3}$ = 1.0 Hz, $^3J_{H4–H3}$ = 3.5 Hz, 2H, $H_{3\ thienyl}$), 6.97 (dd, $^3J_{H5–H4}$ = 5.1 Hz, $^3J_{H3–H4}$ = 3.5 Hz, 2H, $H_{4\ thienyl}$), 7.39 (dd, $^3J_{H4–H5}$ = 5.1 Hz, $^4J_{H3–H5}$ = 1.0 Hz, 2H, $H_{5\ thienyl}$). $^{13}C\{^1H\}$ NMR (500 MHz, $CD_2Cl_2$): δ= 22.8 (s, $CH_2$-$CH_2$-C=C), 28.4 (s, $CH_2$-C=C), 127.2 (s, $C_{4\ thienyl}$), 127.6 (s, $C_{5\ thienyl}$), 129.6 (s, $C_{3\ thienyl}$), 136.4 (s, $C_{2\ thienyl}$), 139.2 (s, $C_\alpha$), 150.3 (s, $C_\beta$), 206.2 (s, M-CO). $^{31}P\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ= 84.4 (s). MS: *m/z* 1371.00 $[M+H]^+$.

*4.4 Crystal structure determination for 1 and 3*

Intensity data were recorded at room temperature on a Rigaku AFC–7S diffractometer equipped with a Mercury CCD detector using monochromated Mo(Kα) radiation (λ = 0.71070 Å). An empirical absorption correction (multi–scan) was applied using the CrystalClear package. The low completeness ratio is due to the experimental setup whereby by the equipment have a\c circle and an added area detector (four-circle diffractometer modified with a CCD). This precludes the collection of some regions of reciprocal lattice space and lowers the completeness. In order to compensate, additional redundant data were measured. The structures were solved by direct methods and refined by full–matrix least–squares on F2 using the SHELXTL–PLUS package. All non hydrogen atoms were refined anisotropically, and hydrogen atoms were added at calculated positions (C–H = 0.93–0.97Å) and refined as riding with $U_{iso}$(H) = 1.2$U_{eq}$. One crystallographically independent dichloromethane molecule located on special positions was found disordered. Attempts were made to model this disorder or split it into two positions, but were unsuccessful. PLATON/SQUEZZE routine was used to correct the data for the presence of two disordered solvent. A potential solvent volume of 461 A^3^ was found. The stoichiometry of the solvent was calculated to be 1 molecule of dichloromethane per formula unit, which results in a total of 125 electrons per unit cell. This molecule was used to calculate expected molecular weight, DXcalc and F(000). Additionally, we have managed to solve the disorder of the S4 atom with a thorough revision of the map of Fourier differences, managing to model not only the disorder of the atom S4 but the complete thienyl group to which it belongs; C29-S4-C30-C31-C32 atoms, which group has a 60.8% disorder. Therefore, considering this disorder we find that the bond distance for the C29-C30 is 1.434 Å, whose distance is inside the maximum (1.819 Å) and minimum (1.053 Å) values and average of 1.343(36) Å for similar structures in a search made with Mogul 1.7.1 build RC2.

Crystal and refinement information for compounds **1** and **3** is showed in Table 1. CCDC 1497908 and 1497909 contain the supplementary crystallographic data for compounds **1** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

**Table 1.** Experimental details for X-ray diffraction collected data and structural refinement for compounds **1** and **3**.

| | **[Re(CO)$_3$($\eta^5$-PC$_{16}$H$_{14}$S$_2$)] (1)** | **[Ru$_4$(CO)$_{13}$($\mu$-PC$_{16}$H$_{13}$S$_2$)$_2$] (3)** |
|---|---|---|
| Chemical formula | $C_{19}H_{14}O_3PReS_2$ | $C_{46.5}H_{31}Cl_3O_{13}P_2Ru_4S_4$ |
| Formula weight | 571.59 | 1498.52 |
| Crystal system, Space group | Triclinic, *P-1* (No. 2) | Triclinic, *P-1* (No. 2) |
| a(A° ), α(°) | 9.746(6), 98.363(9) | 12.058(2), 74.21(3) |
| b(A° ), β(º) | 10.127(5), 111.609(15) | 14.584(3), 71.28(2) |
| c(A° ), γ(º) | 10.340(6), 91.830(18) | 17.487(3), 72.92(2) |
| V(Å$^3$), Z | 934.7(9), 2 | 2729.8(11), 2 |
| dx (g cm$^{-3}$) | 2.031 | 1.823 |
| Crystal size (mm) | 0.05 × 0.14 × 0.16 | 0.44× 0.40 × 0.36 |
| F(000) | 548 | 1470 |
| μ (mm$^{-1}$) | 6.826 | 1.503 |
| θ range (°) | 2.0414 – 27.4333 | 1.254 – 27.573 |
| Reflections Collected | 10362 | 25543 |
| Reflections Unique($R_{int}$) | 3359 | 9350 |
| Reflections With I>2σ(I) | 3084 | 7075 |
| Number of parameters | 235 | 629 |
| R(F$^2$) [$I$>2σ I)] | 0.046 | 0.050 |
| wR(F $^2$) [$I$ >2r(I)] | 0.120 | 0.155 |
| Goodness of fit on F$^2$ | 1.07 | 1.10 |
| Max/min Δρ (e Å$^{-3)}$ | 1.82 – 2.43 | 1.60 – 0.83 |

*4.5 Theoretical calculations*

All structures were optimized using DMol$^3$ [36-38]. This DFT based program permits determination of the relative stability of all studied species based on their electronic structure. The calculations were performed using the Kohn–Sham Hamiltonian with the Perdew–Wang 1991 gradient correction [39] and the double-zeta plus (DNP) numerical basic set [36, 37, 40], which provides good accuracy at a relatively low computational cost. The All Electron core treatment was used for all the atoms. Frequency calculations of the structures showed that all frequencies were positive

indicating that all structures are real minima. The presence and nature of the chemical bonds, has been analyzed using the quantum theory of atoms in molecules (QTAIM) [34] and the AIM-UC code [41].

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($\eta^5$-phospholyl)rhenium complex is obtained from the Re–Re and P–P bonds cleavage.

A phospholyl unit inserted into a M–M bond represents the 2nd example.

A new tetranuclear cluster with two μ-phosphides units is obtained.

A ruthenium tetranuclear cluster with two π-conjugated phospholyl units coordinated as μ-phosphide and a ($\eta^5$-phospholyl)rhenium complex are obtained from M-M and P-P bonds cleavage.