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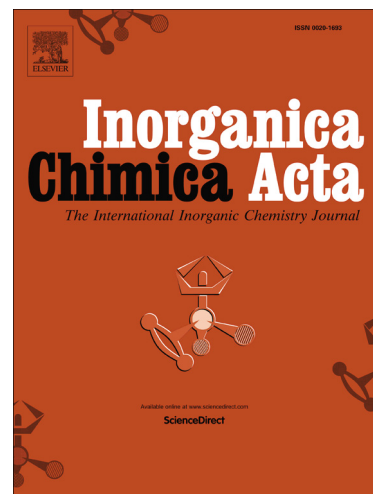
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**High variety of coordination modes of  $\pi$ -conjugated phospholes in dinuclear rhenium carbonyls. Fluxional behavior of  $\sigma,\pi$ -complexes.**

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**Abstract**

A variety of dirhenium carbonyl complexes containing  $\pi$ -conjugated phosphole derivatives were obtained from reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with each of the following phospholes: 2,5-bis(2-thienyl)-1-phenylphosphole (btp), 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp) and 1,2,5-triphenylphosphole (tpp). The  $\pi$ -conjugated phospholes were found to behave as two-, four- or six-electron donor ligands *via*  $\sigma$  or  $\sigma-\pi$  interactions with the metal centers, presenting bridging or chelating coordination modes as determined by spectroscopic methods and single crystal X-ray diffraction analysis. Metal-metal bond cleavage was evidenced when btp was used, leading to a mono-substituted mononuclear complex. Variable-temperature  $^1\text{H}$  NMR studies for  $\sigma,\pi$ -complexes showed a fluxional behavior due to the restricted rotation around the P-C and C-C bonds of the 1,2,5-trisubstituted phosphole ring.

**Keywords:** Rhenium dinuclear;  $\pi$ -conjugated phospholes; chelate and bridge coordination;  $\sigma, \pi$ -complexes, fluxional behavior.

## 1. Introduction

Phosphole ligands display an important role in organometallic and coordination chemistry, owing to their ability to stabilize a great variety of metal complexes [1–7]. Structural diversity of their transition metal complexes has been facilitated by the ability to act as both  $\sigma$ - and  $\pi$ -donor ligands, sometimes simultaneously [8]. Phosphole-complexes have been used in many catalytic transformations of synthetic relevance, such as hydroformylation, hydrosilylation, asymmetric allylic substitution and single and double  $A^3$ -coupling [9–15]. They also have been reported as multifunctional materials for OLEDs [16–19], as well as potent Thioredoxin reductase (TrxR) inhibitors [20–24].

Carbonyl complexes that incorporate two or more metal centers are particularly attractive because of their ability to provide access to catalytic reaction pathways that might not be offered in mononuclear chemistry [25–30], such as reversible metal–metal bond cleavage, skeletal rearrangement without degradation and ligand activation via multisite coordination [31–37].

Due to the versatility of phospholes and metal carbonyl complexes, we have been exploring the interaction of both chemical entities. We have found  $\sigma$ - and  $\sigma, \pi$ -complexes, metal-metal bond cleavage and formation of derivatives where the phosphole ligand have undergone P–P and P–C bonds cleavage, C–H bond activation or partial hydrogenation of phosphorus ring [8,38–42]. Herein, we have studied the reactivity of 2,5-disubstituted phenylphosphole derivatives with  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  to investigate coordination modes that could afford novel types of rhenium complexes. Thus, we report the synthesis and

structural characterization of a new series of phosphole-rhenium complexes from the reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with the  $\pi$ -conjugated phosphole derivatives 2,5-bis(2-thienyl)-1-phenylphosphole (btpp), 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp) and 1,2,5-triphenylphosphole (tpp).

## 2. Experimental

**2.1. General Remarks.** All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. The solvents were previously dried and distilled following standard methods [43].  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ , 2,5-bis(2-thienyl)-1-phenylphosphole (btpp); 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp) and 1,2,5-triphenylphosphole (tpp) were synthesized according to published procedures [44,45]. NMR spectra were recorded on Bruker Avance AM300 and AM500 spectrometers. Assignments of  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were based on COSY, HMQC and HMBC experiments. IR spectra were recorded on a Nicolet 5DXC.

**2.2. Crystal structure determination.** Single crystals suitable for X-ray crystal analysis were obtained by slow evaporation in cyclohexane/dichloromethane mixtures. Single crystal data collection were performed at 100 K for derivative **2**, **6** and **7**, and at 150 K for derivative **1**, **4** and **5** with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Reflections were indexed, Lorentz-polarization corrected and integrated by using DENZO from KappaCCD software package. The data merging process was performed with the program SCALEPACK [46]. Structure determinations were performed by direct methods with the solving program SIR97 [47], that

revealed all the non-hydrogen atoms. SHELXL program [48] was used to refine the structures by full-matrix least-squares based on F<sup>2</sup>. Most non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at idealized positions and refined with isotropic displacement parameters.

In the crystal lattices of derivatives **6** and **7**, one dichloromethane solvent molecule respectively, was found into the asymmetric unit of the corresponding crystals. In all cases, these solvent molecules have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solutions, a process that induce a rapid degradation of the single crystal integrity of the crystals investigated. To slow down this process, the single crystals were coated in paratone oil once removed from the mother solution, mounted at low temperature (150 K) as quickly as possible on the diffractometer goniometer, and then X-ray data collection performed at the same temperature. X-ray crystal structure resolution revealed that the solvent molecules were highly disordered. A correct modeling for disorders on solvent molecules in the crystal lattice of **7** was succeeded but it was more difficult in the case of **6**, leading to a model for this disordered solvent molecule that is associated to large anisotropy displacement parameters. Nevertheless, a correct modeling of this disorder based on the consideration of different CH<sub>2</sub>Cl<sub>2</sub> molecules having different locations and relative occupancies freely refined was not possible. As a result, ALERTs LEVEL A and B appear in the checkCIF report.

For **1**, several carbon atoms could not be refined with anisotropic displacements parameters and where refined with isotropic displacements parameters, which generated ALERTs LEVEL A and B in the checkCIF report.

For **4**, two symmetrically independent molecules were found in the unit cell. In both of them, the thienyl rings were found disordered over two positions. The relative occupancies of these

positions (8 positions in total in the unit cell) were modeled with several atoms for which isotropic displacement parameters had to be applied, generating ALERTs LEVEL A and B in the checkCIF report.

For **7**, the phenyl ring carried by the phosphorus atom of the phosphole ring was found to be disordered over two positions whose relative occupancies were pondareted.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography [49]. CCDC reference numbers 1896642, 1896645, 1896647, 1896644, 1896646, 1896643 contain the supplementary crystallographic data for derivatives **1**, **2**, **4**, **5**, **6** and **7**, respectively. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Center (12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033, e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**2.3. Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with 2,5-bis(2-thienyl)-1-phenylphosphole (btpp).** A solution of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  (100 mg, 0.147 mmol) and btpp (56 mg, 0.147 mmol) in dry cyclohexane (40 mL) was refluxed under nitrogen for 1.5 h. After evaporation of the solvent, preparative TLC ( $\text{SiO}_2$ ) of the yellow residue (heptane: $\text{CH}_2\text{Cl}_2$ , 8:2 v/v) gave five bands:  $[\text{ReH}(\text{CO})_4(\eta^1\text{-btpp})]$  (**1**, 20 mg; 10%);  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-bptt})(\text{CH}_3\text{CN})]$  (**2**, 18 mg, 12%);  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-btpp})]$  (**3**, 34 mg, 23%);  $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-btpp})]$  (**4**, 37 mg, 26%) and  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{S})\text{-btpp})]$  (**5**, 41 mg, 28%). Spectral data for **1**: IR ( $\nu_{\text{CO}}$ , cyclohexane): 2194 w, 2082 m, 1991 s, 1979 s, 1965 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.85 (ddd,  $^4\text{J}(\text{H},\text{H}) = 1.3$  Hz,  $^3\text{J}(\text{H},\text{H}) = 7.0$  Hz,  $^3\text{J}(\text{P},\text{H}) = 7.1$  Hz, 2H, o- $\text{H}_{\text{Ph}}$ ), 7.50 (m, 2H, m- $\text{H}_{\text{Ph}}$ ), 7.50 (m, 1H, p- $\text{H}_{\text{Ph}}$ ), 7.32 (dd,  $^3\text{J}(\text{H},\text{H}) = 3.3$  Hz,  $^3\text{J}(\text{H},\text{H}) = 3.3$  Hz, 2H,  $\text{H}_4$  thienyl), 6.95 (d,  $^3\text{J}(\text{H},\text{H}) = 3.3$  Hz, 2H,  $\text{H}_3$  thienyl), 6.95 (d,  $^3\text{J}(\text{H},\text{H}) = 3.3$  Hz, 2H,  $\text{H}_5$  thienyl), 2.95 (m,

4H, CH<sub>2</sub>-C=C), 1.90 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-C=C), -5.38 (d, <sup>1</sup>J(P,H) = 24.2 Hz, M-H<sub>T</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 144.8 (d, <sup>1</sup>J(P,C) = 13.0 Hz, C<sub>α-P</sub>), 136.1 (d, <sup>2</sup>J(P,C) = 32.2 Hz, C<sub>β-P</sub>), 135.7 (s, C<sub>2</sub> thienyl), 133.6 (s, o-C<sub>Ph</sub>), 133.5 (s, ipso-C<sub>Ph</sub>), 131.7 (d, <sup>4</sup>J(P,C) = 2.8 Hz, p-C<sub>Ph</sub>), 129.2 (d, <sup>3</sup>J(P,C) = 10.0, m-C<sub>Ph</sub>), 127.8 (d, <sup>3</sup>J(P,C) = 6.8 Hz, C<sub>3</sub> thienyl), 126.8 (s, C<sub>4</sub> thienyl), 126.4 (s, C<sub>5</sub> thienyl), 30.0 (d, <sup>3</sup>J(P,C) = 8.8 Hz, CH<sub>2</sub>-C=C), 22.6 (s, CH<sub>2</sub>-CH<sub>2</sub>-C=C). <sup>31</sup>P{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>): δ = + 25.8 (s). Spectral data for **2**: IR (ν<sub>CO</sub>, cyclohexane): 2085 m, 2006 m, 1976 s, 1953 m, 1922 w, 1915 w cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.78 (ddd, <sup>4</sup>J(H,H) = 1.9 Hz, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>3</sup>J(P,H) = 11.8 Hz, 2H, o-H<sub>Ph</sub>), 7.53 (m, 2H, m-H<sub>Ph</sub>), 7.53 (m, 2H, p-H<sub>Ph</sub>), 7.33 (d, <sup>3</sup>J(H,H) = 5.1 Hz, 2H, H<sub>5</sub> thienyl), 6.99 (dd, <sup>3</sup>J(H,H) = 3.8 Hz, <sup>3</sup>J(H,H) = 5.1 Hz, 2H, H<sub>4</sub> thienyl), 6.90 (d, <sup>3</sup>J(H,H) = 3.8 Hz, 2H, H<sub>3</sub> thienyl), 3.03 (m, 4H, CH<sub>2</sub>-C=C), 1.99 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-C=C), 1.91 (s, CH<sub>3</sub>CN). <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 205.7 (d, <sup>1</sup>J(P,C) = 5.5 Hz, M-CO), 199.6 (d, <sup>1</sup>J(P,C) = 6.0 Hz, M-CO), 198.0 (s, M-CO), 143.5 (d, <sup>2</sup>J(P,C) = 13.4 Hz, C<sub>β-P</sub>), 137.0 (d, <sup>2</sup>J(P,C) = 17.7 Hz, C<sub>2</sub> thienyl), 136.5 (d, <sup>1</sup>J(P,C) = 48.2 Hz, C<sub>α-P</sub>), 135.0 (d, <sup>2</sup>J(P,C) = 12.4 Hz, o-C<sub>Ph</sub>), 131.5 (d, <sup>1</sup>J(P,C) = 44.6 Hz, ipso-C<sub>Ph</sub>), 131.1 (d, <sup>4</sup>J(P,C) = 3.2 Hz, p-C<sub>Ph</sub>), 129.1 (d, <sup>3</sup>J(P,C) = 10.6, m-C<sub>Ph</sub>), 127.1 (d, <sup>3</sup>J(P,C) = 5.5 Hz, C<sub>3</sub> thienyl), 127.0 (s, C<sub>4</sub> thienyl), 125.7 (s, C<sub>5</sub> thienyl), 123.6 (s, CH<sub>3</sub>CN), 28.9 (d, <sup>3</sup>J(P,C) = 8.0 Hz, CH<sub>2</sub>-C=C), 22.9 (s, CH<sub>2</sub>-CH<sub>2</sub>-C=C), 22.8 (s, CH<sub>3</sub>CN). <sup>31</sup>P{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>): δ = + 36.0 (s). Spectral data for **3**: IR (ν<sub>CO</sub>, cyclohexane): 2105 m, 2037 w, 1998 s, 1967 m, 1943 m cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.70 (ddd, <sup>4</sup>J(H,H) = 2.0 Hz, <sup>3</sup>J(H,H) = 6.2 Hz, <sup>3</sup>J(P,H) = 8.0 Hz, 2H, o-H<sub>Ph</sub>), 7.60 (m, 2H, m-H<sub>Ph</sub>), 7.60 (m, 2H, p-H<sub>Ph</sub>), 7.35 (d, <sup>3</sup>J(H,H) = 5.1 Hz, 2H, H<sub>5</sub> thienyl), 7.02 (dd, <sup>3</sup>J(H,H) = 3.8 Hz, <sup>3</sup>J(H,H) = 5.1 Hz, 2H, H<sub>4</sub> thienyl), 6.85 (d, <sup>3</sup>J(H,H) = 3.8 Hz, 2H, H<sub>3</sub> thienyl), 3.11 (m, 4H, CH<sub>2</sub>-C=C), 1.98 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-C=C). <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 197.1 (d, <sup>1</sup>J(P,C) = 5.0 Hz, M-CO), 143.6 (d, <sup>2</sup>J(P,C) = 14.4 Hz, C<sub>β-P</sub>), 137.7 (d, <sup>1</sup>J(P,C) = 53.2 Hz, C<sub>α-P</sub>), 136.0 (d, <sup>2</sup>J(P,C) = 18.1



Hz, C<sub>2</sub> thienyl), 132.8 (d, <sup>2</sup>J(P,C) = 12.8 Hz, o-C<sub>Ph</sub>), 131.6 (d, <sup>1</sup>J(P,C) = 43.3 Hz, ipso-C<sub>Ph</sub>), 130.5 (s, p-C<sub>Ph</sub>), 129.2 (d, <sup>3</sup>J(P,C) = 10.7, m-C<sub>Ph</sub>), 127.3 (d, <sup>3</sup>J(P,C) = 6.0 Hz, C<sub>3</sub> thienyl), 126.9 (s, C<sub>4</sub> thienyl), 126.4 (s, C<sub>5</sub> thienyl), 123.6 (s, CH<sub>3</sub>CN), 28.6 (d, <sup>3</sup>J(P,C) = 8.8 Hz, CH<sub>2</sub>-C=C), 22.6 (s, CH<sub>2</sub>-CH<sub>2</sub>-C=C). <sup>31</sup>P{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>): δ = +29.2 (s). Spectral data for **4**: IR (ν<sub>CO</sub>, cyclohexane): 2078 s, 2009 s, 1990 s, 1950 s, 1937 s. cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 30°C): δ = 7.20 (dd, <sup>4</sup>J(H,H) = 1.2 Hz, <sup>3</sup>J(H,H) = 5.0 Hz, 2H, H<sub>5</sub> thienyl), 6.81 (dd, <sup>3</sup>J(H,H) = 3.7 Hz, <sup>3</sup>J(H,H) = 5.0 Hz, 2H, H<sub>4</sub> thienyl), 6.49 (d, <sup>3</sup>J(H,H) = 1.2 Hz, 2H, H<sub>3</sub> thienyl), 3.68 (m, 2H, CH<sub>2</sub><sup>a</sup>-C=C), 3.27 (m, 2H, CH<sub>2</sub><sup>b</sup>-C=C), 2.35 (m, 2H, CH<sub>2</sub><sup>a</sup>-CH<sub>2</sub>-C=C), 2.09 (m, 2H, CH<sub>2</sub><sup>b</sup>-CH<sub>2</sub>-C=C). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -30°C): δ = 7.73 (dd, <sup>3</sup>J(H,H) = 6.6 Hz, <sup>3</sup>J(H,H) = 7.0 Hz, 1H, m<sup>a</sup>-H<sub>Ph</sub>), 7.68 (ddd, <sup>4</sup>J(H,H) = 1.0 Hz, <sup>3</sup>J(H,H) = 6.6 Hz, <sup>2</sup>J(P,H) = 7.3 Hz, 1H, o<sup>a</sup>-H<sub>Ph</sub>), 7.60 (ddd, <sup>4</sup>J(H,H) = 1.0 Hz, <sup>3</sup>J(H,H) = 7.0 Hz, <sup>3</sup>J(H,H) = 7.1 Hz, 1H, p-H<sub>Ph</sub>), 7.49 (dd, <sup>3</sup>J(H,H) = 7.1 Hz, <sup>3</sup>J(H,H) = 7.4 Hz, 1H, m<sup>b</sup>-H<sub>Ph</sub>), 7.33 (ddd, <sup>4</sup>J(H,H) = 1.1 Hz, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>2</sup>J(P,H) = 7.9 Hz, 1H, o<sup>b</sup>-H<sub>Ph</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 196.6 (s, M-CO), 193.1 (s, M-CO), 192.7 (s, M-CO), 187.8 (d, <sup>1</sup>J(P,C) = 10.3 Hz, M-CO), 136.2 (d, <sup>2</sup>J(P,C) = 3.2 Hz, C<sub>2</sub> thienyl), 136.1 (s, p-C<sub>Ph</sub>), 136.0 (s, m-C<sub>Ph</sub>), 132.3 (d, <sup>2</sup>J(P,C) = 2.0 Hz, o-C<sub>Ph</sub>), 132.5 (d, <sup>1</sup>J(P,C) = 7.8 Hz, ipso-C<sub>Ph</sub>), 130.0 (d, <sup>3</sup>J(P,C) = 7.2 Hz, C<sub>3</sub> thienyl), 126.8 (s, C<sub>4</sub> thienyl), 126.1 (s, C<sub>5</sub> thienyl), 95.6 (d, <sup>2</sup>J(P,C) = 7.9 Hz, C<sub>β-p</sub>), 57.6 (d, <sup>1</sup>J(P,C) = 49.1 Hz, C<sub>α-p</sub>), 25.5 (s, CH<sub>2</sub>-C=C), 23.1 (s, CH<sub>2</sub>-CH<sub>2</sub>-C=C). <sup>31</sup>P{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>): δ = -6.6 (s). Spectral data for **5**: IR (ν<sub>CO</sub>, cyclohexane): 2075 s, 2024 s, 1981 s, 1961 m, 1948 m, 1930 s cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.60 (ddd, <sup>4</sup>J(H,H) = 1.3 Hz, <sup>3</sup>J(H,H) = 6.4 Hz, <sup>2</sup>J(P,H) = 8.2 Hz, 2H, o-H<sub>Ph</sub>), 7.47 (m, 2H, m-H<sub>Ph</sub>), 7.47 (m, p-H<sub>Ph</sub>), 7.39 (dd, <sup>4</sup>J(H,H) = 1.1 Hz, <sup>3</sup>J(H,H) = 5.1 Hz, 1H, H<sub>5</sub><sup>a</sup> thienyl), 7.30 (dd, <sup>4</sup>J(H,H) = 0.6 Hz, <sup>3</sup>J(H,H) = 5.6 Hz, 1H, H<sub>5</sub><sup>b</sup> thienyl), 7.19 (ddd, <sup>5</sup>J(P,H) = 2.2 Hz, <sup>3</sup>J(H,H) = 3.7 Hz, <sup>3</sup>J(H,H) = 5.6 Hz, 1H, H<sub>4</sub><sup>b</sup> thienyl), 7.06

(d,  $^3J(\text{H,H}) = 3.7$  Hz, 1H,  $\text{H}_3^{\text{b}}$  thienyl), 7.02 (dd,  $^3J(\text{H,H}) = 3.8$  Hz,  $^3J(\text{H,H}) = 5.1$  Hz, 1H,  $\text{H}_4^{\text{a}}$  thienyl), 6.73 (ddd,  $^4J(\text{H,H}) = 1.2$  Hz,  $^3J(\text{H,H}) = 3.8$  Hz,  $^4J(\text{P,H}) = 1.8$  Hz, 1H,  $\text{H}_3^{\text{a}}$  thienyl), 3.08 (m, 1H,  $\text{CH}_2^{\text{a}'}\text{-C}=\text{C}$ ), 2.93 (m, 1H,  $\text{CH}_2^{\text{b}}\text{-C}=\text{C}$ ), 2.87 (m, 1H,  $\text{CH}_2^{\text{b}'}\text{-C}=\text{C}$ ), 2.73 (m, 1H,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 2.04 (m, 2H,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ), 1.60 (m, 2H,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 201.9$  (s, M-CO), 200.2 (d,  $^1J(\text{P,C}) = 2.3$  Hz, M-CO), 197.9 (d,  $^1J(\text{P,C}) = 9.2$  Hz, M-CO), 194.8 (s, M-CO), 188.9 (d,  $^1J(\text{P,C}) = 10.1$  Hz, M-CO), 186.2 (s, M-CO), 150.7 (d,  $^1J(\text{P,C}) = 11.8$  Hz,  $\text{C}_{\alpha}^{\text{b-p}}$ ), 147.5 (d,  $^2J(\text{P,C}) = 13.6$  Hz,  $\text{C}_2^{\text{b}}$  thienyl), 145.7 (d,  $^2J(\text{P,C}) = 13.2$  Hz,  $\text{C}_{\beta}^{\text{b-p}}$ ), 140.0 (d,  $^4J(\text{P,C}) = 6.11$  Hz,  $\text{C}_5^{\text{b}}$  thienyl), 139.5 (s,  $\text{C}_{\alpha}^{\text{a-p}}$ ), 134.4 (d,  $^2J(\text{P,C}) = 17.1$  Hz,  $\text{C}_2^{\text{a}}$  thienyl), 133.1 (d,  $^2J(\text{P,C}) = 11.8$  Hz, o- $\text{C}_{\text{Ph}}$ ), 131.6 (s, p- $\text{C}_{\text{Ph}}$ ), 130.9 (s,  $\text{C}_4^{\text{b}}$  thienyl), 129.7 (s,  $\text{C}_{\beta}^{\text{a-p}}$ ), 129.3 (s, ipso- $\text{C}_{\text{Ph}}$ ), 129.2 (d,  $^3J(\text{P,C}) = 10.4$  Hz, m- $\text{C}_{\text{Ph}}$ ), 128.6 (d,  $^3J(\text{P,C}) = 4.6$  Hz,  $\text{C}_3^{\text{a}}$ ), 127.8 (d,  $^3J(\text{P,C}) = 7.1$  Hz,  $\text{C}_3^{\text{b}}$ ), 127.4 (s,  $\text{C}_5^{\text{a}}$ ), 127.0 (s,  $\text{C}_4^{\text{a}}$ ), 29.5 (d,  $^3J(\text{P,C}) = 7.0$  Hz,  $\text{CH}_2^{\text{b}}\text{-C}=\text{C}$ ), 28.3 (s,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 22.6 (s,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ), 22.4 (s,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = +25.4$  (s).

**2.3.1. Thermal treatment of 3.** A solution of **3** (20 mg) in 10 mL of cyclohexane was heated to reflux under nitrogen for 6 h. After evaporation of the solvent and TLC work-up on  $\text{SiO}_2$  (eluant heptane:dichloromethane, 8:2 v/v) gave compounds **4** and **5**.

**2.3.2 Photolysis of 3.** A solution of **3** (10 mg) in 5 mL of dried dichloromethane was irradiated with white light, the solution color changed from light yellow to phosphorescent yellow over 4 h. The solvent was removed and TLC work-up on  $\text{SiO}_2$  (eluant heptane:dichloromethane, 7:3 v/v) gave compound **1**.

**2.4. Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp).**

A solution of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  (100 mg, 0.147 mmol) and bpypp (54 mg, 0.147 mmol) in dry cyclohexane (40 mL) was refluxed under nitrogen for 1 h. After evaporation of the solvent, preparative TLC ( $\text{SiO}_2$ ) of the brown residue (heptane: $\text{CH}_2\text{Cl}_2$ , 8:2 v/v) gave two

bands:  $[\text{Re}_2(\text{CO})_8(\eta^1:\eta^1\text{-bpypp})]$  (**6**, 59 mg, 42%) and  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1:\eta^1\text{-bpypp})]$  (**7**, 48 mg, 34%). Spectral data for **6**: IR ( $\nu_{\text{CO}}$ , cyclohexane): 2077 m, 1991 s, 1964 s, 1903 w, 1886 w  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.95 (dd,  $^5\text{J}(\text{H,H}) = 0.5$  Hz,  $^3\text{J}(\text{H,H}) = 5.6$  Hz, 1H,  $\text{H}_6^{\text{b}}$  pyridyl), 8.70 (dd,  $^5\text{J}(\text{H,H}) = 0.7$  Hz,  $^3\text{J}(\text{H,H}) = 5.4$  Hz, 1H,  $\text{H}_6^{\text{a}}$  pyridyl), 7.82 (m, 2H, o- $\text{H}_{\text{Ph}}$ ), 7.82 (dd,  $^3\text{J}(\text{H,H}) = 7.4$  Hz,  $^3\text{J}(\text{H,H}) = 7.8$  Hz, 1H,  $\text{H}_4^{\text{b}}$  pyridyl), 7.72 (dd,  $^3\text{J}(\text{H,H}) = 7.6$  Hz,  $^3\text{J}(\text{H,H}) = 8.0$  Hz, 1H,  $\text{H}_4^{\text{a}}$  pyridyl), 7.64 (ddd,  $^5\text{J}(\text{H,H}) = 0.7$  Hz,  $^4\text{J}(\text{H,H}) = 1.4$  Hz,  $^3\text{J}(\text{H,H}) = 8.0$  Hz, 1H,  $\text{H}_3^{\text{a}}$  pyridyl), 7.57 (ddd,  $^5\text{J}(\text{H,H}) = 0.5$  Hz,  $^4\text{J}(\text{H,H}) = 1.8$  Hz,  $^3\text{J}(\text{H,H}) = 7.8$  Hz, 1H,  $\text{H}_3^{\text{b}}$  pyridyl), 7.31 (m, 2H, m- $\text{H}_{\text{Ph}}$ ), 7.31 (m, 1H, p- $\text{H}_{\text{Ph}}$ ), 7.17 (ddd,  $^4\text{J}(\text{H,H}) = 1.4$  Hz,  $^3\text{J}(\text{H,H}) = 5.4$  Hz,  $^3\text{J}(\text{H,H}) = 7.6$  Hz, 1H,  $\text{H}_5^{\text{a}}$  pyridyl), 7.04 (ddd,  $^4\text{J}(\text{H,H}) = 1.8$  Hz,  $^3\text{J}(\text{H,H}) = 5.6$  Hz,  $^3\text{J}(\text{H,H}) = 7.4$  Hz, 1H,  $\text{H}_5^{\text{b}}$  pyridyl), 3.31 (m, 1H,  $\text{CH}_2^{\text{b}'}\text{-C}=\text{C}$ ), 2.94 (m, 1H,  $\text{CH}_2^{\text{b}'}\text{-C}=\text{C}$ ), 2.94 (m, 2H,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 2.13 (m, 2H,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ), 1.80 (m, 1H,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ), 1.76 (m, 1H,  $\text{CH}_2^{\text{b}'}\text{-CH}_2\text{-C}=\text{C}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 207.2 (s, M-CO), 203.7 (s, M-CO), 203.2 (s, M-CO), 201.1 (s, M-CO), 199.4 (s, M-CO), 197.3 (s, M-CO), 189.1 (s, M-CO), 156.9 (s,  $\text{C}_6^{\text{b}}$  pyridyl), 155.1 (d,  $^2\text{J}(\text{P,C}) = 8.4$  Hz,  $\text{C}_2^{\text{b}}$  pyridyl), 155.0 (d,  $^1\text{J}(\text{P,C}) = 7.5$  Hz,  $\text{C}_\alpha^{\text{a-p}}$ ), 152.5 (d,  $^2\text{J}(\text{P,C}) = 12.8$  Hz,  $\text{C}_2^{\text{a}}$  pyridyl), 149.1 (s,  $\text{C}_6^{\text{a}}$  pyridyl), 147.5 (d,  $^2\text{J}(\text{P,C}) = 7.5$  Hz,  $\text{C}_\beta^{\text{a-p}}$ ), 144.6 (d,  $^2\text{J}(\text{P,C}) = 56.5$  Hz,  $\text{C}_\beta^{\text{b-p}}$ ), 140.9 (d,  $^1\text{J}(\text{P,C}) = 38.2$  Hz,  $\text{C}_\alpha^{\text{b-p}}$ ), 137.1 (s,  $\text{C}_4^{\text{b}}$  pyridyl), 136.3 (s,  $\text{C}_4^{\text{a}}$  pyridyl), 135.6 (d,  $^1\text{J}(\text{P,C}) = 46.8$  Hz, ipso- $\text{C}_{\text{Ph}}$ ), 131.7 (d,  $^2\text{J}(\text{P,C}) = 10.6$  Hz, o- $\text{C}_{\text{Ph}}$ ), 129.7 (s, p- $\text{C}_{\text{Ph}}$ ), 127.9 (d,  $^3\text{J}(\text{P,C}) = 9.9$  Hz, m- $\text{C}_{\text{Ph}}$ ), 123.8 (d,  $^3\text{J}(\text{P,C}) = 6.9$  Hz,  $\text{C}_3^{\text{b}}$  pyridyl), 123.0 (s,  $\text{C}_5^{\text{b}}$  pyridyl), 122.5 (d,  $^3\text{J}(\text{P,C}) = 6.8$  Hz,  $\text{C}_3^{\text{a}}$  pyridyl), 122.0 (s,  $\text{C}_5^{\text{a}}$  pyridyl), 29.6 (d,  $^3\text{J}(\text{P,C}) = 7.9$  Hz,  $\text{CH}_2^{\text{b}'}\text{-C}=\text{C}$ ), 29.0 (d,  $^3\text{J}(\text{P,C}) = 4.6$  Hz,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 23.4 (s,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ), 21.45 [s,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ].  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = + 32.0 (s). Spectral data for **7**: IR ( $\nu_{\text{CO}}$ , cyclohexane): 2065 m, 2012 m, 1968 m, 1937 w, 1903 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 9.20 (d,  $^3\text{J}(\text{H,H}) = 5.2$  Hz, 1H,  $\text{H}_6^{\text{b}}$  pyridyl), 8.54 (d,  $^3\text{J}(\text{H,H}) = 6.0$  Hz,

$^1\text{H}$ ,  $\text{H}_6^{\text{a}}$  pyridyl), 7.71 (dd,  $^3\text{J}(\text{H},\text{H}) = 7.3 \text{ Hz}$ ,  $^3\text{J}(\text{H},\text{H}) = 7.3 \text{ Hz}$ ,  $^1\text{H}$ ,  $\text{H}_4^{\text{b}}$  pyridyl), 7.52 (d,  $^3\text{J}(\text{H},\text{H}) = 7.8 \text{ Hz}$ ,  $^1\text{H}$ ,  $\text{H}_3^{\text{a}}$  pyridyl), 7.50 (m, 2H, o- $\text{H}_{\text{Ph}}$ ), 7.51 (dd,  $^3\text{J}(\text{H},\text{H}) = 6.7 \text{ Hz}$ ,  $^3\text{J}(\text{H},\text{H}) = 7.8 \text{ Hz}$ ,  $^1\text{H}$ ,  $\text{H}_4^{\text{a}}$  pyridyl), 7.34 (m, 2H, m- $\text{H}_{\text{Ph}}$ ), 7.34 (m, 1H, p- $\text{H}_{\text{Ph}}$ ), 7.14 (dd,  $^3\text{J}(\text{H},\text{H}) = 5.2 \text{ Hz}$ ,  $^3\text{J}(\text{H},\text{H}) = 7.3 \text{ Hz}$ ,  $^1\text{H}$ ,  $\text{H}_5^{\text{b}}$  pyridyl), 7.09 (dd,  $^3\text{J}(\text{H},\text{H}) = 6.0 \text{ Hz}$ ,  $^3\text{J}(\text{H},\text{H}) = 6.7 \text{ Hz}$ ,  $^1\text{H}$ ,  $\text{H}_5^{\text{a}}$  pyridyl), 6.78 (d,  $^3\text{J}(\text{H},\text{H}) = 7.3 \text{ Hz}$ ,  $^1\text{H}$ ,  $\text{H}_3^{\text{b}}$  pyridyl), 3.28 (m, 1H,  $\text{CH}_2^{\text{b}}\text{-C}=\text{C}$ ), 3.19 (m, 1H,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 2.84 (m, 1H,  $\text{CH}_2^{\text{b}'}\text{-C}=\text{C}$ ), 2.58 (m, 1H,  $\text{CH}_2^{\text{a}'}\text{-C}=\text{C}$ ), 2.04 (m, 1H,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ), 1.88 (m, 1H,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ), 1.77 (m, 1H,  $\text{CH}_2^{\text{b}'}\text{-CH}_2\text{-C}=\text{C}$ ), 1.77 (m, 1H,  $\text{CH}_2^{\text{a}'}\text{-CH}_2\text{-C}=\text{C}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 207.7$  (s, M-CO), 206.3 (s, M-CO), 202.5 (s, M-CO), 198.7 (d,  $^1\text{J}(\text{P},\text{C}) = 11.1 \text{ Hz}$ , M-CO), 196.3 (d,  $^1\text{J}(\text{P},\text{C}) = 46.3 \text{ Hz}$ , M-CO), 195.8 (s, M-CO), 191.2 (d,  $^1\text{J}(\text{P},\text{C}) = 12.6 \text{ Hz}$ , M-CO), 189.4 (s, M-CO), 158.5 (s,  $\text{C}_6^{\text{b}}$  pyridyl), 157.7 (d,  $^2\text{J}(\text{P},\text{C}) = 10.2 \text{ Hz}$ ,  $\text{C}_2^{\text{b}}$  pyridyl), 152.4 (d,  $^2\text{J}(\text{P},\text{C}) = 13.5 \text{ Hz}$ ,  $\text{C}_2^{\text{a}}$  pyridyl), 149.6 (d,  $^2\text{J}(\text{P},\text{C}) = 9.4 \text{ Hz}$ ,  $\text{C}_{\beta}^{\text{b-p}}$ ), 149.0 (s,  $\text{C}_6^{\text{a}}$  pyridyl), 147.4 (d,  $^2\text{J}(\text{P},\text{C}) = 9.6 \text{ Hz}$ ,  $\text{C}_{\beta}^{\text{a-p}}$ ), 143.5 (d,  $^1\text{J}(\text{P},\text{C}) = 49.3 \text{ Hz}$ ,  $\text{C}_{\alpha}^{\text{b-p}}$ ), 142.9 (d,  $^1\text{J}(\text{P},\text{C}) = 50.4 \text{ Hz}$ ,  $\text{C}_{\alpha}^{\text{a-p}}$ ), 137.9 (s,  $\text{C}_4^{\text{a}}$  pyridyl), 136.0 (s,  $\text{C}_4^{\text{b}}$  pyridyl), 131.6 (d,  $^2\text{J}(\text{P},\text{C}) = 12.4 \text{ Hz}$ , o- $\text{C}_{\text{Ph}}$ ), 130.5 (s, p- $\text{C}_{\text{Ph}}$ ), 128.7 (d,  $^3\text{J}(\text{P},\text{C}) = 10.6 \text{ Hz}$ , m- $\text{C}_{\text{Ph}}$ ), 128.3 (d,  $^1\text{J}(\text{P},\text{C}) = 42.1 \text{ Hz}$ , ipso- $\text{C}_{\text{Ph}}$ ), 126.6 (d,  $^3\text{J}(\text{P},\text{C}) = 3.4 \text{ Hz}$ ,  $\text{C}_3^{\text{b}}$  pyridyl), 123.9 (s,  $\text{C}_5^{\text{a}}$  pyridyl), 123.2 (d,  $^3\text{J}(\text{P},\text{C}) = 5.9 \text{ Hz}$ ,  $\text{C}_3^{\text{a}}$  pyridyl), 121.9 (s,  $\text{C}_5^{\text{b}}$  pyridyl), 29.5 (d,  $^3\text{J}(\text{P},\text{C}) = 8.0 \text{ Hz}$ ,  $\text{CH}_2^{\text{b}}\text{-C}=\text{C}$ ), 26.6 (d,  $^3\text{J}(\text{P},\text{C}) = 6.4 \text{ Hz}$ ,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 22.7 (s,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ), 21.4 (s,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = + 31.4$  (s).

**2.5. Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with 1,2,5-triphenylphosphole (tpp).** A solution of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  (100 mg, 0.147 mmol) and tpp (54 mg, 0.147 mmol) in dry cyclohexane (40 mL) was refluxed under nitrogen for 4 h. After evaporation of the solvent, preparative TLC ( $\text{SiO}_2$ ) of the yellow residue (heptane/ $\text{CH}_2\text{Cl}_2$ , 8:2 v/v) gave three bands:  $\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-tpp})$  (**8**, 54 mg, 38%);  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-tpp})_2]$  (**9**, 89 mg, 45%) and

[Re<sub>2</sub>(CO)<sub>8</sub>(η<sup>1</sup>-tpp)(CH<sub>3</sub>CN)] (**10**, 25 mg, 16%). Spectral data for **8**: IR (ν<sub>CO</sub>, cyclohexane): 2078 m, 2029 w, 2006 s, 1991 s, 1947 w, 1934 m cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -60°C): δ = 7.36 (ddd, <sup>3</sup>J(P,H) = 7.4 Hz, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>3</sup>J(H,H) = 7.4 Hz, 1H, m<sup>b</sup>-H<sub>Ph</sub>), 7.68 (dd, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>2</sup>J(P,H) = 7.2 Hz, 1H, o<sup>b</sup>-H<sub>Ph</sub>), 7.59 (dd, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>3</sup>J(H,H) = 7.4 Hz, 1H, p-H<sub>Ph</sub>), 7.49 (ddd, <sup>3</sup>J(P,H) = 7.6 Hz, <sup>3</sup>J(H,H) = 7.3 Hz, <sup>3</sup>J(H,H) = 7.4 Hz, 1H, m<sup>a</sup>-H<sub>Ph</sub>), 7.36 (dd, <sup>3</sup>J(H,H) = 7.9 Hz, <sup>2</sup>J(P,H) = 7.6 Hz, 1H, o<sup>a</sup>-H<sub>Ph</sub>), 7.26 (dd, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>3</sup>J(P,H) = 7.5 Hz, 1H, H<sub>3</sub><sup>b</sup>), 7.18 (d, <sup>3</sup>J(H,H) = 7.4 Hz, 1H, H<sub>4</sub><sup>a</sup>), 7.18 (d, <sup>3</sup>J(H,H) = 7.4 Hz, 1H, H<sub>4</sub><sup>b</sup>), 6.97 (dd, <sup>3</sup>J(H,H) = 7.4 Hz, <sup>3</sup>J(H,H) = 7.8 Hz, 1H, H<sub>3</sub><sup>a</sup>), 6.97 (d, <sup>3</sup>J(H,H) = 7.5 Hz, 1H, H<sub>2</sub><sup>b</sup>), 6.51 (d, <sup>3</sup>J(H,H) = 7.8 Hz, 1H, H<sub>2</sub><sup>a</sup>), 3.63 (m, 2H, CH<sub>2</sub><sup>a</sup>-C=C), 3.15 (m, 2H, CH<sub>2</sub><sup>b</sup>-C=C), 2.24 (m, 2H, CH<sub>2</sub><sup>a</sup>-CH<sub>2</sub>-C=C), 1.99 (m, 2H, CH<sub>2</sub><sup>b</sup>-CH<sub>2</sub>-C=C). <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -60 °C): δ = 198.2 (s, M-CO), 189.7 (s, M-CO), 188.7 (d, <sup>1</sup>J(P,C) = 10.7 Hz, M-CO), 136.9 (d, <sup>1</sup>J(P,C) = 32.8 Hz, ipso-C<sub>Ph</sub>), 133.6 (s, C<sub>1</sub><sup>a</sup>), 133.5 (s, C<sub>1</sub><sup>b</sup>), 132.7 (s, C<sub>3</sub><sup>a</sup>), 132.5 (d, <sup>3</sup>J(P,C) = 9.3 Hz, C<sub>2</sub><sup>b</sup>), 129.4 (s, o<sup>a</sup>-C<sub>Ph</sub>), 129.4 (s, o<sup>b</sup>-C<sub>Ph</sub>), 129.2 (d, <sup>3</sup>J(P,C) = 7.9 Hz, C<sub>2</sub><sup>a</sup>), 128.9 (s, m<sup>a</sup>-C<sub>Ph</sub>), 128.8 (s, m<sup>b</sup>-C<sub>Ph</sub>), 128.3 (s, C<sub>3</sub><sup>b</sup>), 128.1 (s, C<sub>4</sub><sup>a</sup>), 127.7 (s, C<sub>4</sub><sup>b</sup>), 126.8 (s, p-C<sub>Ph</sub>), 96.8 (d, <sup>2</sup>J(P,C) = 8.1 Hz, C<sub>β</sub>), 63.2 (d, <sup>1</sup>J(P,C) = 49.8 Hz, C<sub>α</sub>), 25.4 (s, CH<sub>2</sub>-C=C), 23.2 (s, CH<sub>2</sub>-CH<sub>2</sub>-C=C). <sup>31</sup>P{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>): δ = -14.0 (s). Spectral data for **9**: IR (ν<sub>CO</sub>, cyclohexane): 2017 w, 1986 w, 1968 s, 1962 s, 1936 w cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.73 (ddd, <sup>4</sup>J(H,H) = 1.4 Hz, <sup>3</sup>J(H,H) = 7.8 Hz, 2H, o-H<sub>Ph</sub>), 7.58 (m, 2H, m-H<sub>Ph</sub>), 7.58 (m, 1H, p-H<sub>Ph</sub>), 7.23 (d, <sup>4</sup>J(H,H) = 2.4 Hz, 2H, H<sub>4</sub>), 7.23 (d, <sup>3</sup>J(H,H) = 7.3 Hz, 2H, H<sub>3</sub>), 7.02 (dd, <sup>4</sup>J(H,H) = 2.4 Hz, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, H<sub>2</sub>), 3.03 (m, 2H, CH<sub>2</sub><sup>a</sup>-C=C), 2.85 (m, 2H, CH<sub>2</sub><sup>b</sup>-C=C), 1.95 (m, 2H, CH<sub>2</sub><sup>a</sup>-CH<sub>2</sub>-C=C), 1.78 (m, 2H, CH<sub>2</sub><sup>b</sup>-CH<sub>2</sub>-C=C). <sup>13</sup>C{<sup>1</sup>H} NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 198.8 (s, M-CO), 145.2 (d, <sup>2</sup>J(P,C) = 14.1 Hz, C<sub>β</sub>), 143.4 (d, <sup>1</sup>J(P,C) = 50.5 Hz, C<sub>α</sub>), 34.9 (d, <sup>2</sup>J(P,C) = 14.1 Hz, C<sub>1</sub>), 132.3 (s, p-C<sub>Ph</sub>), 132.3 (d,

$^3\text{J}(\text{P},\text{C}) = 6.0 \text{ Hz}$ , m- $\text{C}_{\text{Ph}}$ ), 132.0 (s, ipso- $\text{C}_{\text{Ph}}$ ), 130.9 (s, o- $\text{C}_{\text{Ph}}$ ), 129.0 (s,  $\text{C}_2$ ), 128.1 (s,  $\text{C}_3$ ), 127.1 (s,  $\text{C}_4$ ), 27.6 (s,  $\text{CH}_2\text{-C}=\text{C}$ ), 22.8 (s,  $\text{CH}_2\text{-CH}_2\text{-C}=\text{C}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = +33.0$  (s). Spectral data for **10**: IR ( $\nu_{\text{CO}}$ , cyclohexane): 2085 m, 2045 m, 2004 m, 1975 s, 1952 m, 1922 m, 1916  $\text{m cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.70$  (dd,  $^3\text{J}(\text{H},\text{H}) = 8.7 \text{ Hz}$ ,  $^3\text{J}(\text{H},\text{H}) = 8.7 \text{ Hz}$ , 2H, o- $\text{H}_{\text{Ph}}$ ), 7.48 (m, 2H, m- $\text{H}_{\text{Ph}}$ ), 7.48 (m, 1H, p- $\text{H}_{\text{Ph}}$ ), 7.21 (m, 2H,  $\text{H}_4$ ), 7.21 (d,  $^3\text{J}(\text{H},\text{H}) = 7.2 \text{ Hz}$ , 2H,  $\text{H}_3$ ), 7.04 (d,  $^3\text{J}(\text{H},\text{H}) = 7.2 \text{ Hz}$ , 2H,  $\text{H}_2$ ), 2.98 (m, 2H,  $\text{CH}_2^{\text{a}}\text{-C}=\text{C}$ ), 2.83 (m,  $\text{CH}_2^{\text{b}}\text{-C}=\text{C}$ ), 1.87 (m,  $\text{CH}_2^{\text{a}}\text{-CH}_2\text{-C}=\text{C}$ ), 1.74 (s,  $\text{CH}_3\text{CN}$ ), 1.72 (m,  $\text{CH}_2^{\text{b}}\text{-CH}_2\text{-C}=\text{C}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 144.7$  (d,  $^2\text{J}(\text{P},\text{C}) = 14.0 \text{ Hz}$ ,  $\text{C}_{\beta}$ ), 143.0 (d,  $^1\text{J}(\text{P},\text{C}) = 50.1 \text{ Hz}$ ,  $\text{C}_{\alpha}$ ), 34.5 (d,  $^2\text{J}(\text{P},\text{C}) = 13.9 \text{ Hz}$ ,  $\text{C}_1$ ), 132.2 (s, p- $\text{C}_{\text{Ph}}$ ), 132.1 (d,  $^3\text{J}(\text{P},\text{C}) = 6.2 \text{ Hz}$ , m- $\text{C}_{\text{Ph}}$ ), 132.0 (s, ipso- $\text{C}_{\text{Ph}}$ ), 130.2 (s, o- $\text{C}_{\text{Ph}}$ ), 129.5 (s,  $\text{C}_2$ ), 128.0 (s,  $\text{C}_3$ ), 126.5 (s,  $\text{C}_4$ ), 27.1 (s,  $\text{CH}_2\text{-C}=\text{C}$ ), 21.9 (s,  $\text{CH}_2\text{-CH}_2\text{-C}=\text{C}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = +34.5$  (s).

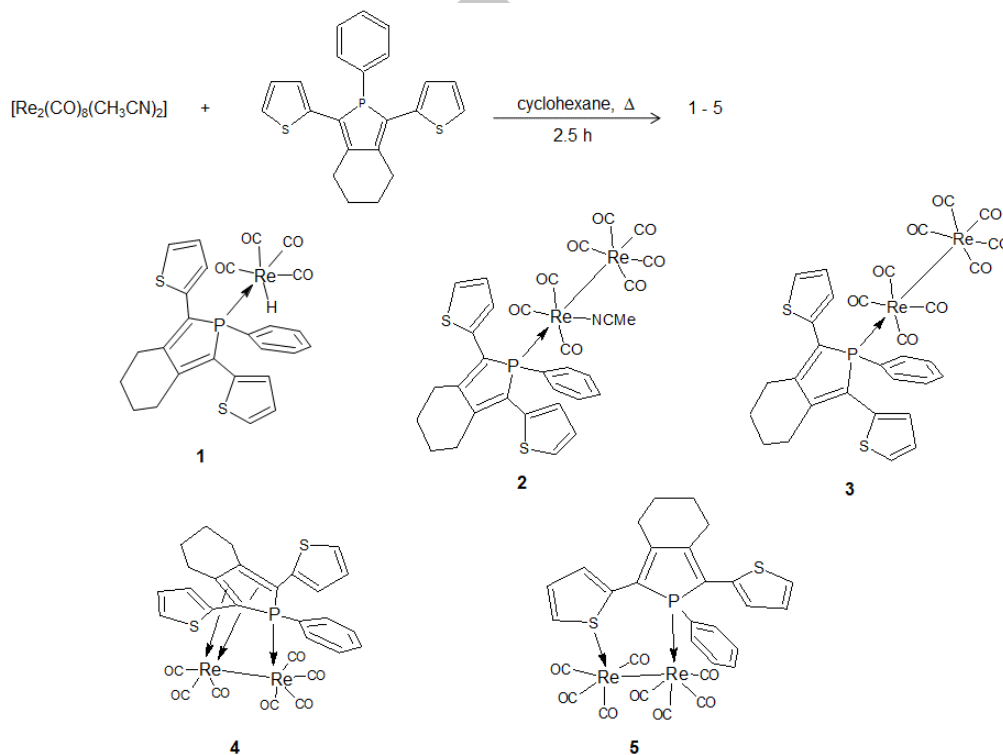
### 3. Results and discussion

#### 3.1. Synthesis and characterization.

Thermal treatment of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with the corresponding phosphole derivative: 2,5-bis(2-thienyl)-1-phenylphosphole (btpp), 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp) and 1,2,5-triphenylphosphole (tpp), led to a variety of  $\sigma$ - and  $\sigma,\pi$ -complexes, including bridging and chelating coordination modes (Scheme 1-3). The variety of products obtained in these reactions were probably influenced by electronic and steric properties of the phosphole derivatives.

##### 3.1.1. Thermal treatment of $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ with 2,5-bis(2-thienyl)-1-phenylphosphole (btpp).

Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with btp<sub>p</sub> in refluxing cyclohexane yielded five compounds characterized as  $[\text{ReH}(\text{CO})_4(\eta^1\text{-btp})]$  (**1**),  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-btp})(\text{CH}_3\text{CN})]$  (**2**),  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-btp})]$  (**3**),  $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1\text{:}\eta^2\text{-btp})]$  (**4**) and  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{S})\text{-btp})]$  (**5**) (Scheme 1). The thermolysis of **3** in refluxing cyclohexane afforded **4** and **5** by decarbonylation, while thermolysis of **2** led to decomposition. Photolysis of **3** in dichloromethane led to the mononuclear complex **1** due to the occurrence of metal-metal bond cleavage, presenting an IR spectrum similar to those found for  $[\text{ReH}(\text{CO})_4(\text{P})]$  (P = PPh<sub>3</sub>, PTh<sub>3</sub>) [50,51]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** showed a singlet at  $\delta$  +25.8 ppm, while  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals were similar to the free ligand. Additionally, the  $^1\text{H}$  NMR spectrum displayed a doublet at  $\delta$  -5.38 ppm ( $J_{\text{H-P}} = 24.2$  Hz) that was assigned to a terminal hydride. Thus, IR and NMR data for **1** are consistent with the proposed structure (Scheme 1), wherein the btp<sub>p</sub> is  $\sigma$ -coordinated to metal center through phosphorus atom.



**Scheme 1.** Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with btp<sub>p</sub>.

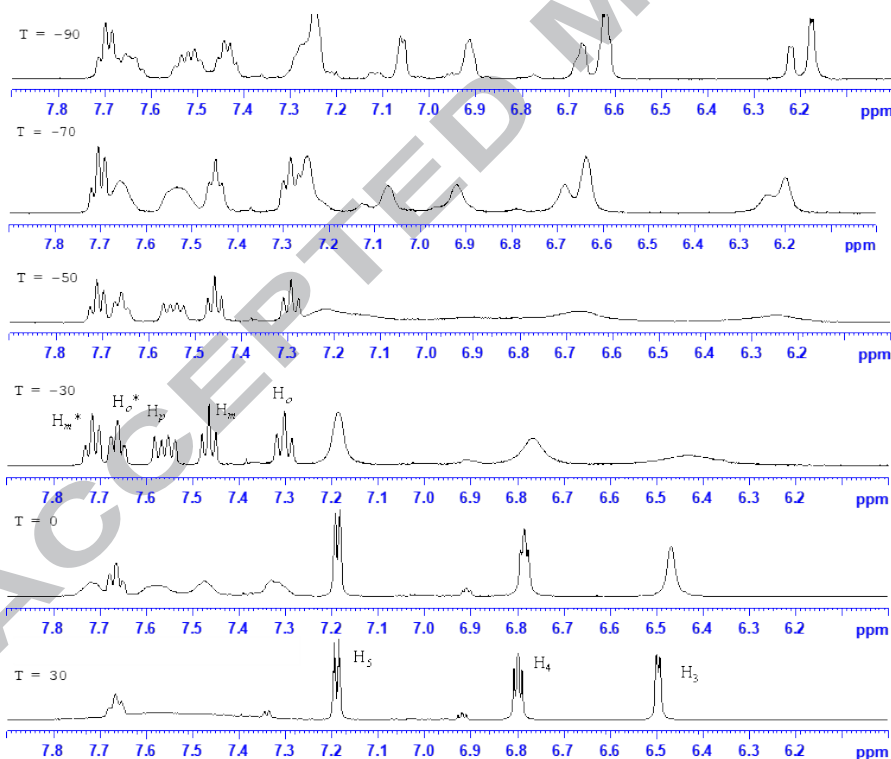
The substitution of one acetonitrile ligand by one btpm molecule on the labile dinuclear  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  yielded compound **2**. Its IR spectrum in the carbonyl stretching region was characteristic of octacarbonyl dinuclear complexes [52,53]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum revealed a singlet at  $\delta = +36.0$  ppm, which was shifted to low field with respect to the free ligand ( $\delta = +12.7$  ppm), suggesting P-bonding of the btpm ligand. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals did not show significant differences with those of the free ligand, and both spectra confirmed the presence of one acetonitrile molecule. Based on these data, the structure of **2** corresponds to a dirhenium octacarbonyl complex containing one acetonitrile and one btpm ligand coordinated to the same rhenium atom (Scheme 1).

The IR  $\nu(\text{CO})$  frequencies for **3** were similar to those found for monosubstituted nonacarbonyl dinuclear complexes  $[\text{Re}_2(\text{CO})_9\text{L}]$  ( $\text{L} = \text{t-BuNC}, \text{PBz}_3, \text{RCN}, \text{PTh}_3$ ) [50,54,55]. The  $^{31}\text{P}\{^1\text{H}\}$  signal showed a chemical shift characteristic of P-bonding ( $\delta = +12.7$  ppm). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra did not show significant variations in comparison to the free ligand, suggesting a  $\eta^1$ -coordination of the btpm ligand. The spectroscopic data of **3** and previously reported results [50,54,55] indicate that the structure shown in Scheme 1 is the most likely.

The dinuclear derivative  $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-btpm})]$  (**4**) presented an IR spectrum in the carbonyl stretching region very similar to  $[\text{M}_2(\text{CO})_7\text{L}]$  ( $\text{M} = \text{Mn}, \text{Re}$ ) [5,6,38]. Its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum exhibited a singlet at  $\delta -6.63$ , upfield shifted in comparison to the free ligand. The room-temperature  $^1\text{H}$  NMR spectrum of **4** showed broad resonances for the phenyl protons, suggesting that a fluxional behavior might be occurring in solution. Additionally, inequivalence of  $\text{CH}_2$  protons was observed. To determine if a fluxional behavior was taking place, a variable-temperature  $^1\text{H}$  NMR was carried out from 30 to  $-90$



°C in CD<sub>2</sub>Cl<sub>2</sub> (Fig. 1). At -30 °C, phenyl protons were clearly observed while the thienyl protons converted to broad signals. At -50 °C, the coalescence of both thienyl group signals was evidenced, which then appeared to be chemically inequivalent at -90 °C. These results suggest that two different fluxional behaviors are in fact taking place in complex **4**. The phenyl and thienyl groups are moving at two different rates around the C-P and C-C bonds, respectively, possibly due to sterically restricted rotations in the complex. This behavior has not been observed for related complexes with 3,4-dimethyl-1-phenyl-phosphole and 3-methyl-1-phenyl-phosphole as ligands, previously reported by our research group [38]. Therefore, the restricted rotation might be associated to steric effects of the bulky btpp ligand. On the other hand, <sup>13</sup>C NMR signals of the phosphole ring were shifted to higher field than the free ligand due to the coordination of the dienic system to one rhenium atom.



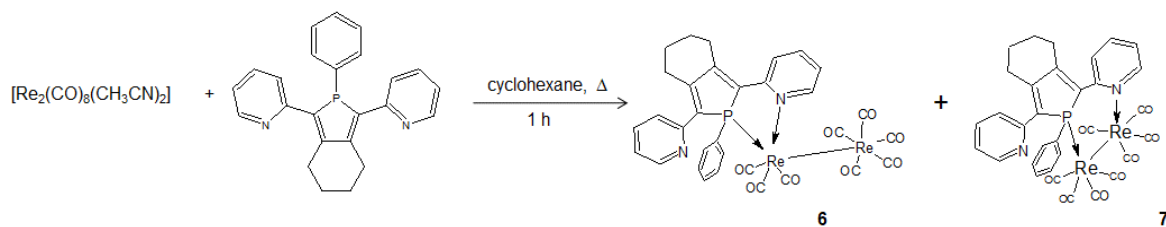
**Fig. 1.** Variable-temperature <sup>1</sup>H NMR spectra of **4** in CD<sub>2</sub>Cl<sub>2</sub>.

The complex  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{S})\text{-btpp})]$  (**5**) showed an IR spectrum similar to  $1,2\text{-eq,eq-}[\text{Re}_2(\text{CO})_8(\text{P}(\text{OMe})_3)_2]$  [56]. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, a singlet characteristic of  $\sigma(\text{P})$ -coordination was observed at  $\delta +25.4$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed two sets of signals for the thienyl rings, suggesting an unsymmetrical coordination of btpp. The first set of signals showed chemical shifts similar to the free ligand while the other set was shifted downfield, indicating a  $\eta^1$ -coordination through one of the sulfur atoms.

### 3.1.2. Thermal treatment of $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ with 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp).

Treatment of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with bpypp in refluxing cyclohexane afforded two structural isomers:  $[\text{Re}_2(\text{CO})_8(\eta^1\text{:}\eta^1\text{-bpypp})]$  (**6**, 42% yield) and  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-bpypp})]$  (**7**, 34% yield) (Scheme 2). Only starting material was isolated when this reaction was performed in refluxing dichloromethane, while that refluxing *n*-octane would lead to decomposition. Thermolysis of **6** and **7** in refluxing cyclohexane led to decomposition products, and  $\sigma,\pi$ -complexes were not observed.

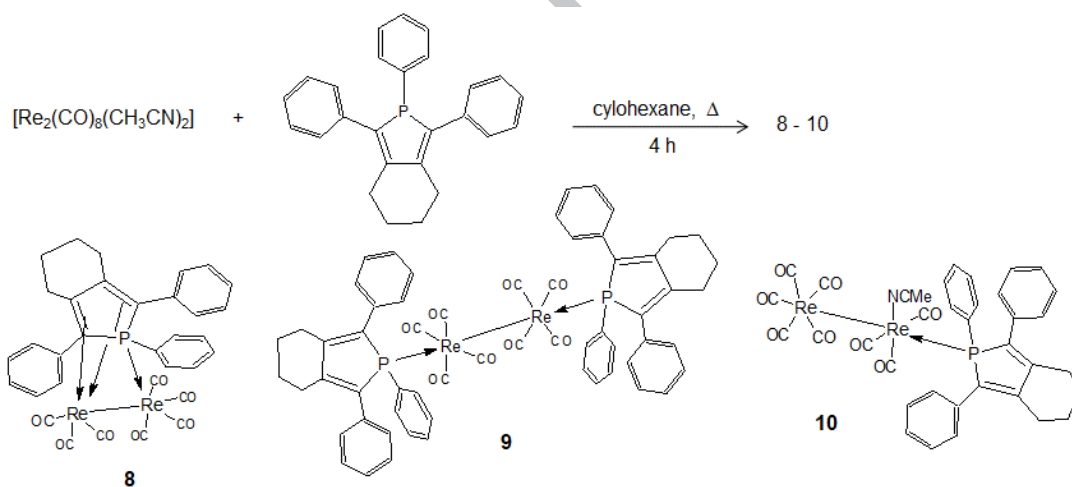
IR spectrum for **6** was closely related to  $1,1\text{-eq,ax-}[\text{M}_2(\text{CO})_8\text{L}]$  [52,57], while the infrared  $\nu(\text{CO})$  frequencies for **7** were consistent with dinuclear complexes  $1,2\text{-eq,eq-}[\text{M}_2(\text{CO})_8\text{L}]$  [58]. The NMR data for both isomers were very similar to each other. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra displayed an unsymmetrical coordination of bpypp, showing two sets of signals for the pyridyl rings, one of them showed chemical shifts similar to the free ligand while the other set was shifted downfield, being this last characteristic of a pyridyl ring coordinated through the nitrogen atom [57,59].



**Scheme 2.** Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with bpypp.

### 3.1.3. Thermal treatment of $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ with 1,2,5-triphenylphosphole (tpp).

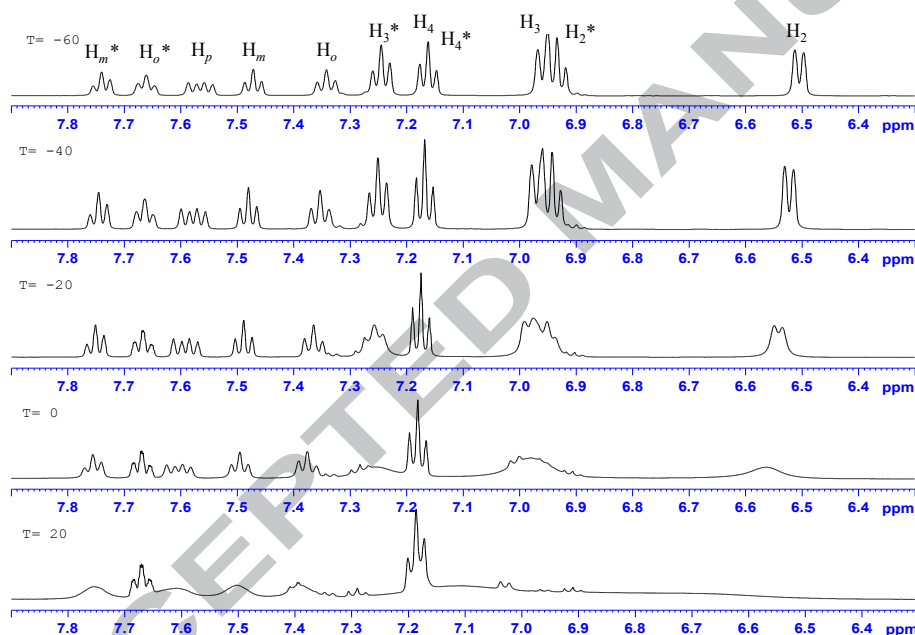
Compounds  $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-tpp})]$  (**8**),  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-tpp})_2]$  (**9**) and  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-tpp})(\text{CH}_3\text{CN})]$  (**10**) were obtained by thermal treatment of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with tpp in refluxing cyclohexane (Scheme 3). The formation of the  $\sigma$ -complex  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-tpp})]$  was not observed even when the reaction was run at lower temperature (e.g. refluxing dichloromethane).



**Scheme 3.** Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with tpp.

Compound **8** presented an IR spectrum very similar to those found for **4** and previously reported heptacarbonyl dinuclear complexes [5,6,38]. Its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed a singlet at  $\delta -13.95$  ppm, suggesting a  $\eta^1$ -coordination through the phosphorus atom

as observed for compound **4**. The  $^{13}\text{C}$  NMR spectrum displayed the phosphole ring carbons shifted upfield compared to the free tpp ligand, indicating a  $\eta^2:\eta^2$ -coordination of the dienic system. As described for compound **4**, the room-temperature  $^1\text{H}$  NMR spectrum of **8** showed broad signals that were linked to a dynamic process in solution where the phenyl groups experience restricted rotation around the P–C and C–C bonds induced by the steric effects of the bulky tpp ligand and its rigid coordination to the dinuclear complex. As seen in Fig. 2, this dynamic process is “frozen” out at  $-60^\circ\text{C}$  and signals of the three phenyl rings are clearly observed.



**Fig. 2.** Variable-temperature  $^1\text{H}$  NMR spectra of **8** in  $\text{CD}_2\text{Cl}_2$ .

Supported by previous reports [50,60], the spectroscopic data for compound **9** clearly indicated the formation of a disubstituted dinuclear complex  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-tpp})_2]$ , formed *via* a step by step substitution of acetonitrile molecules by  $\sigma$ -coordination of tpp ligands through the phosphorus atom.

Finally, compound **10** exhibited spectroscopic data that was closely related to the monosubstituted complex **2** (see experimental section), therefore a similar structure is proposed for **10** (Scheme 3).

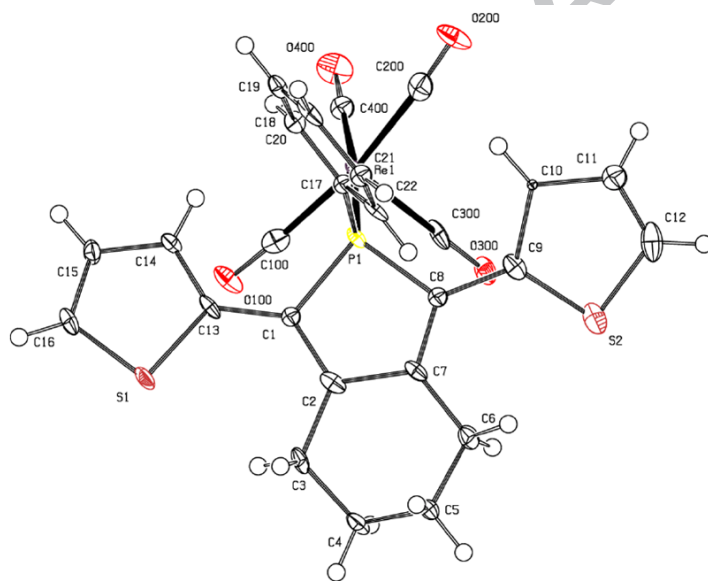
### 3.2. X-ray diffraction analysis.

The structure of **1** was confirmed by single-crystal X-ray diffraction, and its molecular structure is shown in Fig. 3. Selected bond lengths and angles are given in Table 1. The distorted octahedral geometry contains four carbonyls, a btp<sub>p</sub> and hydride ligand (*cis* to btp<sub>p</sub>) binding a rhenium atom. The hydride ligand is not shown in the ORTEP structure, but the reduction of the *trans*-C100–Re1–C200 angle [170.7(5)°] suggests the presence of a hydride ligand in this position as observed for previously reported analogues [50]. The Re–P distance is slightly longer than that for [ReH(CO)<sub>3</sub>(PTh<sub>3</sub>)<sub>2</sub>] [50] [2.461(3) Å versus 2.369(17) Å, respectively], probably due to the presence of the bulkier btp<sub>p</sub> ligand. The phosphorus atom lies out of the main plane that contains the four carbon atoms of the phosphole ring [0.087(1) Å], drawing a ring with an opened envelope-type conformation.

**Table 1.** Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **4**, **5**, **6** and **7**.

[ReH(CO) <sub>4</sub> (η <sup>1</sup> -btp <sub>p</sub> )] ( <b>1</b> )	Re1–P1 = 2.461(3) C100–Re1–C200 = 170.7(5)
[Re <sub>2</sub> (CO) <sub>8</sub> (η <sup>1</sup> -btp <sub>p</sub> )(CH <sub>3</sub> CN)] ( <b>2</b> )	Re1–Re2 = 3.0241(3) Re1–P1 = 2.353(1) Re1–N100 = 2.151(6) Re2–Re1 – P1 = 175.55(4) Re2–Re1 – N100 = 87.0(1)
[Re <sub>2</sub> (CO) <sub>7</sub> (μ-η <sup>1</sup> :η <sup>2</sup> :η <sup>2</sup> -btp <sub>p</sub> )] ( <b>4</b> )	Re1–Re2 = 3.0431(3) Re2–P1 = 2.402(2) Re1–C1 = 2.346(5) Re1–C2 = 2.309(6) Re1–C7 = 2.324(6) Re1–C8 = 2.342(6) C203–Re2–Re1 = 166.8(2)

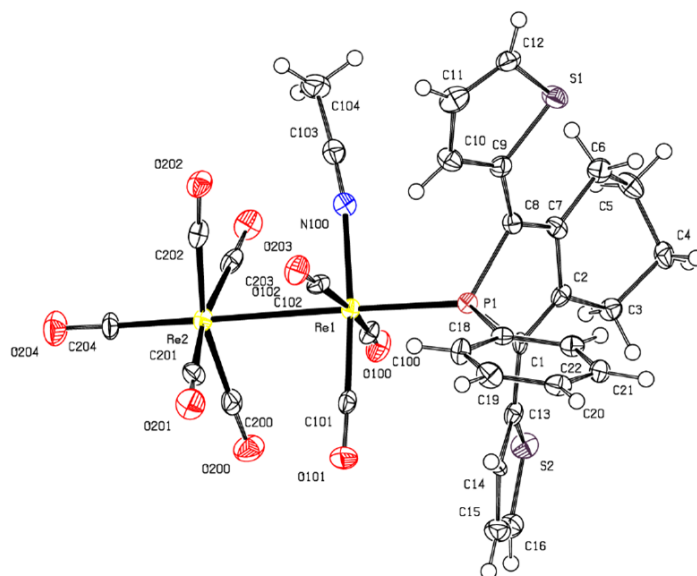
	C103–Re1–Re2 = 162.8(2)
[Re <sub>2</sub> (CO) <sub>8</sub> (μ-η <sup>1</sup> (P):η <sup>1</sup> (S)-btp)] (5)	Re1–Re2 = 3.0578(6) Re–P = 2.447(3) Re2–S1 = 2.469(3) Re2–Re1–P1 = 94.56(7) Re1–Re2–S1 = 82.52(7)
[Re <sub>2</sub> (CO) <sub>8</sub> (η <sup>1</sup> :η <sup>1</sup> -bpypp)] (6)	Re1–Re2 = 3.0859(7) Re1–P1 = 2.441(2) Re1–N1 = 2.251(8) Re2–Re1–P1 = 100.49(6) Re2–Re1–N1 = 91.8(2)
[Re <sub>2</sub> (CO) <sub>8</sub> (μ-η <sup>1</sup> :η <sup>1</sup> -bpypp)] (7)	Re1–Re2 = 3.0442(4) Re1–P1 = 2.425(2) Re2–N1 = 2.252(6) Re1–Re2–N1 = 91.5(1) Re2–Re1–P1 = 87.39(4)



**Fig. 3.** Molecular structure of [ReH(CO)<sub>4</sub>(η<sup>1</sup>-btp)] (1), showing 50% probability ellipsoids.

The single-crystal X-ray diffraction analysis for compound **2** afforded the molecular structure shown in Fig. 4 (selected bond lengths and angles are given in Table 1). The structure shows a dinuclear rhenium complex containing three carbonyls, an acetonitrile and

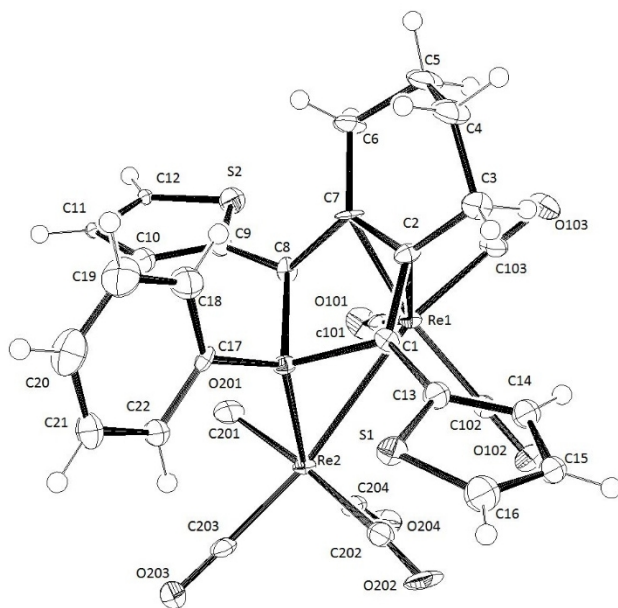
a btpb ligand bound to Re1 and four carbonyl ligands bound to Re2. The btpb ligand is axially coordinated while the acetonitrile occupies an equatorial site. The Re–Re, Re–P and Re–N distances [3.0241(3) Å, 2.353(1) Å and 2.151(6) Å, respectively] are similar to those found for analogue dirhenium derivatives [50,59,61]. The distance between the phosphorus atom and the plane containing the phosphole dienic system [0.136(1) Å] is longer than that observed for **1**.



**Fig. 4.** Molecular structure of  $[\text{Re}_2(\text{CO})_8(\eta^1\text{-btpb})(\text{CH}_3\text{CN})]$  (**2**), showing 50% probability ellipsoids.

The molecular structure of **4** is shown in Fig. 5; selected bond lengths and angles are given in Table 1. The structure shows a  $\sigma,\pi$ -complex where the btpb displays a bridging coordination and behaves as a six-electron donor: two electrons by  $\sigma$ -coordination through the phosphorus atom and four electrons by  $\pi$ -coordination of the phosphole dienic system. The Re–Re distance of 3.0431(3) Å is in concordance with the values found for similar reported complexes [38]. The Re–P bond length [2.402(2) Å] is slightly longer than that for

$[\text{Re}_2(\text{CO})_7(\eta^1:\eta^2:\eta^2\text{-P})]$  [ $\text{P} = 3,4\text{-dimethyl-1-phenylphosphole}$  and  $3\text{-methyl-1-phenylphosphole}$ ] [38], probably due to the bulkier btpb ligand. The phosphorus atom is  $0.320(1)$  Å out of the plane that contains the four carbons of the dienic system, slightly shorter than that reported for analogues  $\sigma,\pi\text{-complexes}$  containing  $3,4\text{-disubstituted phospholes}$  [38].

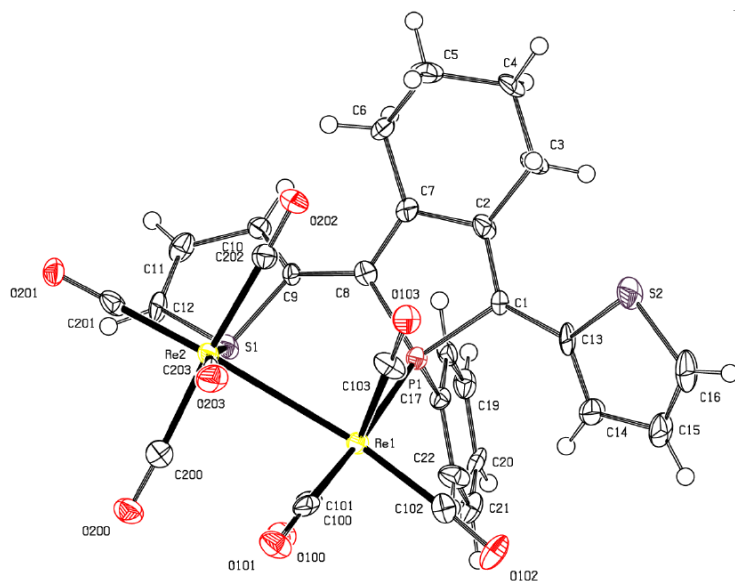


**Fig. 5.** Molecular structure of  $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1:\eta^2:\eta^2\text{-btpb})]$  (**4**), showing 50% probability ellipsoids.

The X-ray diffraction analysis for **5** confirmed the proposed structure previously described. The ORTEP structure is shown in Fig. 6 (bond lengths and angles are given in Table 1). The molecular structure consists of an octacarbonyl dirhenium complex with a btpb ligand that displays a bridging coordination mode and behaves as four-electron donor. The coordination occurs via the phosphorus atom and a sulfur atom from one of the thienyl groups: both groups occupying equatorial sites. The Re–P bond distance [ $2.447(3)$  Å] is somewhat longer than that observed for **1** and **2**, and the Re–S length [ $2.469(3)$  Å] is slightly shorter than that found for  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-SC}_{12}\text{H}_8)]$ ,  $[\text{Re}_2(\text{CO})_7(\eta^1:\eta^1\text{-SC}_8\text{H}_6)(\text{PMe}_3)_3]$  and



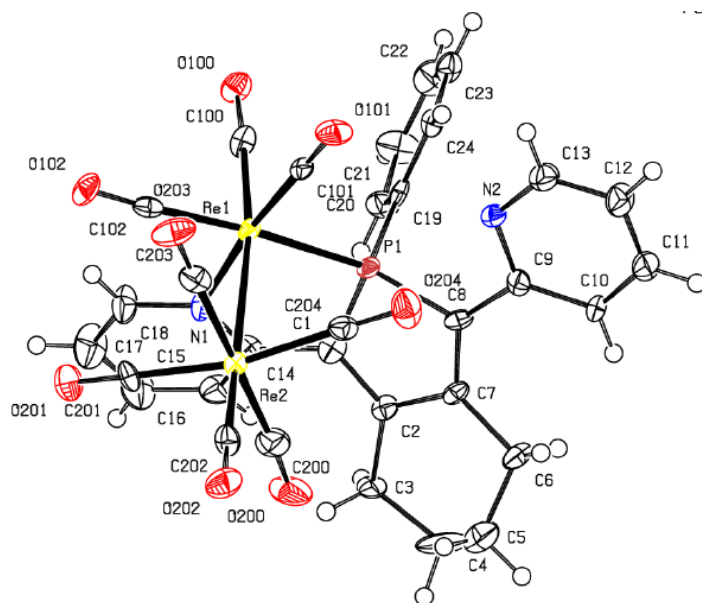
$[\text{Re}_2(\text{CO})_7(\mu(\text{s})-\eta^1\text{-SC}_8\text{H}_6)(\text{PMe}_3)_2]$  [62,63]. The distance between the phosphorus atom and the plane that contains the four carbon atoms of phosphole ring [0.071(1) Å] is shorter than that found for **1**, **2** and **4**. The torsion angle between C3-C4 and C6-C5 bonds is 66(1), which explains the inequivalence among these CH<sub>2</sub> groups on the <sup>1</sup>H NMR.



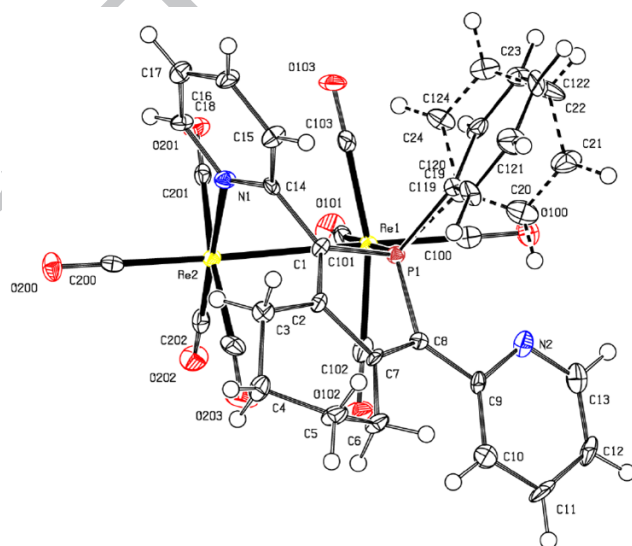
**Fig. 6.** Molecular structure of  $[\text{Re}_2(\text{CO})_8(\mu-\eta^1(\text{P}):\eta^1(\text{S})\text{-btpp})]$  (**5**), showing 50% probability ellipsoids.

The X-ray diffraction analyses for **6** and **7** confirmed the proposed structural isomers. Their molecular structures are showed in the Fig. 7 and 8, respectively. The structures of **6** and **7** show both having the bpypp ligand coordinated through the phosphorus atom and a pyridyl nitrogen atom, however, **6** presents the ligand in a chelating coordination mode while that **7** carries a bridging mode of the ligand. Both structures displayed the phosphorus and nitrogen atoms occupying axial and equatorial sites, respectively. The structure of **6** shows the phosphorus atom at 0.014(1) Å out of plane that contains the four carbon atoms of the dienic system, which is much shorter than those found for **1**, **2**, **4** and **5**, probably due to the

chelating coordination mode. In the structure of **7**, this distance was of 0.062(1) Å, consistent with the value found for **5** whose coordination was also a bridging mode. The Re–N bond distance for both structures are similar [Re1–N1 = 2.251(8) Å (**6**), Re2–N1 = 2.252(6) Å (**7**)], while the Re–P length in **6** [2.441(2) Å] is slightly longer than that found for **7** [2.425(2) Å].



**Fig. 7.** Molecular structure of  $[\text{Re}_2(\text{CO})_8(\eta^1:\eta^1\text{-bpypp})]$  (**6**), showing 50% probability ellipsoids.



**Fig. 8.** Molecular structure of  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-bpypp})]$  (**7**), showing 50% probability ellipsoids.

## Conclusions

This work provided a new example of reactivity between the labile dinuclear  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  and three different  $\pi$ -conjugated phosphole derivatives: 2,5-bis(2-thienyl)-1-phenylphosphole (btp), 2,5-bis(2-pyridyl)-1-phenylphosphole (bpypp), 1,2,5-triphenylphosphole (tpp), which afforded ten new complexes. We found that phosphole ligands undergo  $\sigma$ - or  $\sigma,\pi$ -coordination to the labile rhenium dinuclear, behaving as two-, four- or six-electron donors. When the bidentate coordination of the  $\pi$ -conjugated phospholes occurs, bridging and chelating modes were obtained.  $\sigma,\pi$ -Complexes  $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-P})]$  [P = btp (**4**), tpp (**8**)] presented a fluxional behavior in solution due to the restricted rotation around the P- $C_{\text{ipso-Ph}}$  and C-C bonds of the 2,5-substituents on the phosphole ring, which was associated with steric effects of the bulky phosphole ligands. Additionally, we carried out X-ray diffraction analyses for six compounds (**1**, **2**, **4**, **5-7**), which confirmed the proposed structures.

## Acknowledgements

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## References

- [1] S. Attar, W.H. Bearden, N.W. Alcock, E.C. Alyea, J.H. Nelson, Phosphole complexes of gold(I) halides: comparison of solution and solid-state structures by a combination of solution and CP/MAS phosphorus-31 NMR spectroscopy and x-ray crystallography, *Inorg. Chem.* 29 (1990) 425–433. doi:10.1021/ic00328a017.
- [2] J.J. MacDougall, J.H. Nelson, F. Mathey, Intra- and intermolecular equilibria and their pertinence to the mechanism of cis-trans isomerization of  $L_2PtX_2$  complexes: four- and five-coordinate platinum phosphole complexes, *Inorg. Chem.* 21 (1982) 2145–2153. doi:10.1021/ic00136a005.
- [3] Z. Csók, G. Keglevich, G. Petőcz, L. Kollár, Platinum Complexes of Phospholes with Reduced Pyramidal Character from Steric Crowding, *Inorg. Chem.* 38 (1999) 831–833. doi:10.1021/ic980963n.
- [4] S. Attar, J.H. Nelson, W.H. Bearden, N.W. Alcock, E.B. Milosavljevic, Phosphole complexes of gold (III) halides: Synthesis, structure, electrochemistry and ligand redistribution reactions, *Polyhedron.* 10 (1991) 1939–1949.
- [5] J.M. Rosalky, B. Metz, F. Mathey, R. Weiss, Metal-phosphole and-phospholyl complexes. Crystal and molecular structures of (1-tert-butyl-3, 4-dimethylphosphole) heptacarbonyldimanganese and (3,4-dimethylphospholyl) undecacarbonyltrimanganese, *Inorg. Chem.* 16 (1977) 3307–3311.
- [6] F. Mathey, Reaction des phospholes avec  $Mn_2(CO)_{10}$ . Identification du (dimethyl-3, 4 phospholyl) manganese tricarbonyl, *J. Organomet. Chem.* 93 (1975) 377–388.
- [7] M. Sauthier, F. Leca, L. Toupet, R. Réau, Palladium Complexes of a Novel Family of P,N-Chelates, the 2-(2-Pyridyl)phospholes: Synthesis, Structural Characterization, and Catalytic Activity for Olefin/CO Copolymerization, *Organometallics.* 21 (2002)

1591–1602. doi:10.1021/om011034y.

- [8] A.J. Arce, Y. De Sanctis, M.C. Goite, R. MacHado, Y. Otero, T. Gonzalez, Insertion of a phospholide unit into a metal-metal bond: Synthesis and X-ray structure of  $[\text{Ru}_3(\text{CO})_9(\mu\text{:}\eta^1\text{:}\eta^5\text{-PC}_4\text{H}_2\text{Me}_2)(\eta^1\text{-C}_6\text{H}_5)]$ , *Inorganica Chim. Acta.* 392 (2012). doi:10.1016/j.ica.2012.01.033.
- [9] I. Odinet, T. Körtvélyesi, T. Kégl, L. Kollár, G. Keglevich, Rh complexes of 1-(2,4,6-triisopropylphenyl)-3-methyl-1H-phosphole: preparation and use as catalysts in the hydroformylation of styrene, *Transit. Met. Chem.* 32 (2007) 299–303. doi:10.1007/s11243-006-0166-2.
- [10] G. Mora, B. Deschamps, S. van Zutphen, X.F. Le Goff, L. Ricard, P. Le Floch, Xanthene-Phosphole Ligands: Synthesis, Coordination Chemistry, and Activity in the Palladium-Catalyzed Amine Allylation, *Organometallics.* 26 (2007) 1846–1855. doi:10.1021/om061172t.
- [11] L.K. Peterson, R.S. Dhimi, F. Wada, The Synthesis and Characterization of Rhenium(o)-Nitrile Complexes  $\text{Re}_2(\text{CO})_{9,8}(\text{RCN})_{1,2}$ , *Synth. React. Inorg. Met. Chem.* 13 (1983) 291–303. doi:10.1080/00945718308059334.
- [12] S. Doherty, E.G. Robins, J.G. Knight, C.R. Newman, B. Rhodes, P.A. Champkin, W. Clegg, Selectivity for the methoxycarbonylation of ethylene versus CO-ethylene copolymerization with catalysts based on  $\text{C}_4$ -bridged bidentate phosphines and phospholes, *J. Organomet. Chem.* 640 (2001) 182–196. doi:https://doi.org/10.1016/S0022-328X(01)01180-9.
- [13] J. Hydrio, M. Gouygou, F. Dallemer, J.-C. Daran, G.G.A. Balavoine, New chiral phosphole ligands: their coordination behaviour and application in palladium-catalysed asymmetric allylic substitution, *Tetrahedron: Asymmetry.* 13 (2002) 1097–

1102. doi:[https://doi.org/10.1016/S0957-4166\(02\)00256-2](https://doi.org/10.1016/S0957-4166(02)00256-2).

- [14] G. Keglevich, T. Kégl, T. Chuluunbaatar, B. Dajka, P. Mátyus, B. Balogh, L. Kollár, Hydroformylation of styrene in the presence of rhodium-2,4,6-trialkylphenylphosphole in situ catalytic systems, *J. Mol. Catal. A Chem.* 200 (2003) 131–136. doi:[https://doi.org/10.1016/S1381-1169\(03\)00046-3](https://doi.org/10.1016/S1381-1169(03)00046-3).
- [15] J.R. Cammarata, R. Rivera, F. Fuentes, Y. Otero, E. Ocando-Mavárez, A. Arce, J.M. Garcia, Single and double A<sup>3</sup>-coupling (aldehyde-amine-alkyne) reaction catalyzed by an air stable copper(I)-phosphole complex, *Tetrahedron Lett.* 58 (2017). doi:10.1016/j.tetlet.2017.09.031.
- [16] A.I. Aranda Perez, T. Biet, S. Graule, T. Agou, C. Lescop, N.R. Branda, J. Crassous, R. Réau, Chiral and extended pi-conjugated bis(2-pyridyl)phospholes as assembling N,P,N pincers for coordination-driven synthesis of supramolecular [2,2]paracyclophane analogues, *Chemistry (Easton)*. 17 (2011) 1337–1351. doi:10.1002/chem.201001862.
- [17] P.-A. Bouit, A. Escande, R. Szűcs, D. Szieberth, C. Lescop, L. Nyulászi, M. Hissler, R. Réau, Dibenzophosphapentaphenes: Exploiting P chemistry for gap fine-tuning and coordination-driven assembly of planar polycyclic aromatic hydrocarbons, *J. Am. Chem. Soc.* 134 (2012) 6524–6527.
- [18] H. Chen, W. Delaunay, L. Yu, D. Joly, Z. Wang, J. Li, Z. Wang, C. Lescop, D. Tondelier, B. Geffroy, 2, 2'-Biphospholes: Building Blocks for Tuning the HOMO–LUMO Gap of  $\pi$ -Systems Using Covalent Bonding and Metal Coordination, *Angew. Chemie Int. Ed.* 51 (2012) 214–217.
- [19] J. Crassous, R. Réau,  $\pi$ -Conjugated phosphole derivatives: synthesis, optoelectronic functions and coordination chemistry, *Dalt. Trans.* (2008) 6865–6876.

- [20] S. Urig, K. Fritz-Wolf, R. Réau, C. Herold-Mende, K. Tóth, E. Davioud-Charvet, K. Becker, Undressing of phosphine gold (I) complexes as irreversible inhibitors of human disulfide reductases, *Angew. Chemie Int. Ed.* 45 (2006) 1881–1886.
- [21] M. Deponte, S. Urig, L.D. Arscott, K. Fritz-Wolf, R. Réau, C. Herold-Mende, S. Koncarevic, M. Meyer, E. Davioud-Charvet, D.P. Ballou, Mechanistic studies on a novel, highly potent gold-phosphole inhibitor of human glutathione reductase, *J. Biol. Chem.* 280 (2005) 20628–20637.
- [22] E. Viry, E. Battaglia, V. Deborde, T. Müller, R. Réau, E. Davioud-Charvet, D. Bagrel, A Sugar-Modified Phosphole Gold Complex with Antiproliferative Properties Acting as a Thioredoxin Reductase Inhibitor in MCF-7 Cells, *ChemMedChem Chem. Enabling Drug Discov.* 3 (2008) 1667–1670.
- [23] S. Alfonso, S. González, A.R. Higuera-Padilla, A. Vidal, M. Fernández, P. Taylor, I. Urdanibia, A. Reiber, Y. Otero, W. Castro, A new complex of copper-phosphole. Synthesis, characterization and evaluation of biological activity, *Inorganica Chim. Acta.* 453 (2016). doi:10.1016/j.ica.2016.09.012.
- [24] S. Alfonso-Bueno, P. Taylor, I. Urdanibia, W. Castro, Y. Otero, Studies of the Interaction of Au (I)-Phosphole Complexes with DNA and their Relation to Biological Activity, *J Med Chem Drug Des.* 1 (2018).
- [25] Y. Miyake, Y. Nomaguchi, M. Yuki, Y. Nishibayashi, Synthesis and Reactivity of Diphosphine-Bridged Diruthenium Complexes, *Organometallics.* 26 (2007) 3611–3613.
- [26] E.L. Diz, A. Neels, H. Stoeckli-Evans, G. Süss-Fink, New Ru<sub>3</sub>(CO)<sub>12</sub> derivatives with bulky diphosphine ligands: synthesis, structure and catalytic potential for olefin hydroformylation, *Polyhedron.* 20 (2001) 2771–2780.

- [27] W.M. Alley, I.K. Hamdemir, Q. Wang, A.I. Frenkel, L. Li, J.C. Yang, L.D. Menard, R.G. Nuzzo, S. Özkar, K.A. Johnson, Iridium Ziegler-Type Hydrogenation Catalysts Made from [(1,5-COD)Ir( $\mu$ -O<sub>2</sub>C<sub>8</sub>H<sub>15</sub>)<sub>2</sub>] and AlEt<sub>3</sub>: Spectroscopic and Kinetic Evidence for the Ir<sup>n</sup> Species Present and for Nanoparticles as the Fastest Catalyst, *Inorg. Chem.* 49 (2010) 8131–8147.
- [28] M.D. Fryzuk, Coordinatively unsaturated clusters of rhodium incorporating chelating bidentate ligands. Synthesis of [ {(CH<sub>3</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>}RhH]<sub>4</sub> and [ {(i-C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(Oi-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>}RhH]<sub>2</sub>, *Organometallics*. 1 (1982) 408–409.
- [29] M. Kulzick, R.T. Price, E.L. Muetterties, V.W. Day, A new member of the (HRhL<sub>2</sub>)<sub>x</sub> cluster class:[(μ-H)Rh(1,5-cyclooctadiene)]<sub>4</sub>, *Organometallics*. 1 (1982) 1256–1258.
- [30] B. Fontal, M. Reyes, T. Suárez, F. Bellandi, J.C. Díaz, Catalytic studies with ruthenium clusters substituted with diphosphines: Part I. Studies with Ru<sub>3</sub>(CO)<sub>10</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>), *J. Mol. Catal. A Chem.* 149 (1999) 75–85.
- [31] G. Huttner, J. Schneider, H. Müller, G. Mohr, J. von Seyerl, L. Wohlfahrt, Reversible opening of a trinuclear heterometal cluster, *Angew. Chemie Int. Ed. English*. 18 (1979) 76–77.
- [32] F. Richter, H. Vahrenkamp, Basic cluster reactions. 1. Reversible unfolding of FeCo<sub>2</sub>Mo and FeCo<sub>2</sub>W clusters, *Organometallics*. 1 (1982) 756–757.
- [33] P. Braunstein, Interplay between bridging groups and metal-metal bonds in heterometallic clusters, *Mater. Chem. Phys.* 29 (1991) 33–63.
- [34] M.I. Bruce, J.G. Matison, J.R. Rodgers, R.C. Wallis, Cluster chemistry. Synthesis and X-ray structure of [Ru<sub>5</sub>(CO)<sub>14</sub>(CNBut)<sub>2</sub>], containing an unusual open Ru<sub>5</sub> cluster, *J. Chem. Soc. Chem. Commun.* (1981) 1070–1071.
- [35] D.H. Farrar, P.F. Jackson, B.F.G. Johnson, J. Lewis, J.N. Nicholls, M. McPartlin, A



- high-yield synthesis of  $\text{Ru}_5\text{C}(\text{CO})_{15}$  by the carbonylation of  $\text{Ru}_6\text{C}(\text{CO})_{17}$ ; the X-ray structure analyses of  $\text{Ru}_5\text{C}(\text{CO})_{15}$  and  $\text{Ru}_5\text{C}(\text{CO})_{14}\text{PPh}_3$ , *J. Chem. Soc. Chem. Commun.* (1981) 415–416.
- [36] R.D. Adams, M. Chen, X. Yang, Iridium–Gold Cluster Compounds: Syntheses, Structures, and an Unusual Ligand-Induced Skeletal Rearrangement, *Organometallics*. 31 (2012) 3588–3598.
- [37] A.J. Arce, Y. De Sanctis, J. Manzur, A.J. Deeming, N.I. Powell, Oxidative addition of phenylphosphole: X-ray crystal structures of two ring-opened products  $[\text{Os}_3(\mu^3\text{-PhPC}_4\text{H}_4)(\text{CO})_x]$  where  $x = 8$  or  $9$ , *J. Organomet. Chem.* 408 (1991) C18–C21. doi:[https://doi.org/10.1016/0022-328X\(91\)80111-V](https://doi.org/10.1016/0022-328X(91)80111-V).
- [38] Y. Otero, A. Arce, Y. De Sanctis, R. Machado, M.C. Goite, T. Gonzalez, A. Briceño, High versatility of 3,4-dimethyl-1-phenyl-phosphole and 3-methyl-1-phenyl-phosphole as ligands in the reaction with  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  and  $[\text{Ru}_3(\text{CO})_{12}]$ : X-ray structures of  $[\text{Re}_2(\text{CO})_7(\eta^1:\eta^2:\eta^2\text{-PhPC}_4\text{H}_2\text{Me}_2)]$ ,  $[\text{Re}_2(\text{CO})_7(\eta^1:\eta^2:\eta^2\text{-PhPC}_4\text{H}_3\text{Me})]$  and  $[\text{Ru}_2(\text{CO})_4(\text{PhPC}_4)]$ , *Inorganica Chim. Acta.* 404 (2013) 77–81. doi:<http://dx.doi.org/10.1016/j.ica.2013.04.002>.
- [39] D. Peña, Y. Otero, A. Arce, L. Díaz, Y. De Sanctis, E. Ocando-Mavarez, J.M. García, R. Machado, T. González, Synthesis and characterization of trinuclear osmium clusters containing diallylphosphines as hemilabile ligands: Experimental and theoretical studies of their reactivity with nucleophilic molecules, *J. Organomet. Chem.* 772 (2014). doi:[10.1016/j.jorganchem.2014.08.023](https://doi.org/10.1016/j.jorganchem.2014.08.023).
- [40] Y. Otero, D. Peña, A. Arce, M. Hissler, R. Réau, Y. De Sanctis, E. Ocando-Mavárez, R. Machado, T. González, Fluxional behaviour of phosphole and phosphine ligands on triosmium clusters, *J. Organomet. Chem.* 799–800 (2015).

doi:10.1016/j.jorganchem.2015.08.026.

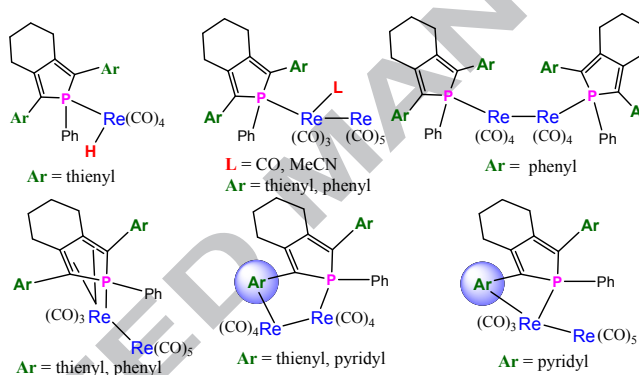
- [41] Y. Otero, D. Coll, A. Arce, D. Peña, F. Fuentes, M. Hissler, R. Réau, R. Machado, T. Gonzalez, E. Ávila, Reactivity of dirhenium and triruthenium carbonyls toward a biphosphole ligand: M–M, P–P and C–H bonds cleavage, *J. Organomet. Chem.* 834 (2017). doi:10.1016/j.jorganchem.2017.02.012.
- [42] Y. Otero, D. Peña, C. Lescop, E. Ávila, A. Arce, M. Hissler, R. Réau, R. Machado, Reaction of carbonyl trinuclear clusters with 2,5-bis(2-thienyl)-1-phenyl-phosphole as a ligand: a new pathway to ruthenacyclopentadiene and cyclopentadienone ruthenium complexes, *New J. Chem.* 42 (2018) 12234–12242. doi:10.1039/C8NJ01442F.
- [43] W.L.F. Armarego, Purification of laboratory chemicals / W.L.F. Armarego and D.D. Perrin, Butterworth Heinemann, Oxford ; Boston, 1996.
- [44] M.I. Bruce, P.J. Low, Expeditious synthesis of  $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$ , *J. Organomet. Chem.* 519 (1996) 221–222. doi:https://doi.org/10.1016/S0022-328X(96)06231-6.
- [45] C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, R. Réau, Phosphole-Containing  $\pi$ -Conjugated Systems: From Model Molecules to Polymer Films on Electrodes, *Chem. Eur. J.* 7 (2001) 4222–4236.
- [46] Z. Otwinowski, W. Minor, [20] Processing of X-ray diffraction data collected in oscillation mode, in: *Methods Enzymol.*, Elsevier, 1997: pp. 307–326.
- [47] A. Altomare, M.C. Burla, M. Camalli, G.L. Casciarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, SIR97: a new tool for crystal structure determination and refinement, *J. Appl. Crystallogr.* 32 (1999) 115–119.
- [48] G.M. Sheldrick, SHELX-97, program for the solution and refinement of crystal structures, Univ. Göttingen, Ger. (1997).

- [49] I.U. of Crystallography, International tables for X-ray crystallography, Kynock Press, 1959.
- [50] M.N. Uddin, M.A. Mottalib, N. Begum, S. Ghosh, A.K. Raha, D.T. Haworth, S. V Lindeman, T.A. Siddiquee, D.W. Bennett, G. Hogarth, E. Nordlander, S.E. Kabir, Carbon–Phosphorus Bond Activation of Tri(2-thienyl)phosphine at Dirhenium and Dimanganese Centers, *Organometallics*. 28 (2009) 1514–1523. doi:10.1021/om801075p.
- [51] N. Flitcroft, J.M. Leach, F.J. Hopton, The reactions of hydridopentacarbonylrhenium with phosphorus-containing ligands, *J. Inorg. Nucl. Chem.* 32 (1970) 137–143. doi:https://doi.org/10.1016/0022-1902(70)80457-2.
- [52] D.L. Morse, M.S. Wrighton, Photochemistry of metal-metal bonded complexes. 5. Cleavage of the MM bond in  $(OC)_5M-M(CO)_3L$  by irradiation into a low-lying M. fwardw. L charge-transfer band, *J. Am. Chem. Soc.* 98 (1976) 3931–3934.
- [53] J.W.M. Van Outersterp, D.J. Stufkens, J. Fraanje, K. Goubitz, A. Vlcek Jr, Synthesis and Characterization of New Dinuclear Complexes  $(CO)_5MnRe(CO)_3(L)$  ( $L = 2,2'$ -Bipyrimidine, 2,3-Bis(2-pyridyl)pyrazine) and Trinuclear Compounds  $(CO)_5MnRe(CO)_3(L)R$  ( $R = Re(Br)(CO)_3, W(CO)_4$ ). Evidence for Asymmetric Distortion of the , *Inorg. Chem.* 34 (1995) 4756–4766.
- [54] R.D. Adams, J.A. Belinski, J. Schierlmann, The ring opening and unusual coupling of 3, 3-dimethylthietane ligands in a dirhenium carbonyl complex, *J. Am. Chem. Soc.* 113 (1991) 9004–9006.
- [55] W.L. Ingham, N.J. Coville, Site selectivity studies on homonuclear metal dimer complexes: Substitution reactions of  $Re_2(CO)_9L$ , *J. Organomet. Chem.* 423 (1992) 51–64. doi:http://dx.doi.org/10.1016/0022-328X(92)83023-B.

- [56] P.O. Nubel, T.L. Brown, Photolysis of dirhenium decacarbonyl in the presence of simple olefins. Thermal reactivity of ( $\mu$ -hydrido)( $\mu$ -alkenyl)dirhenium octacarbonyl compounds, *J. Am. Chem. Soc.* 106 (1984) 644–652.
- [57] R.A. Machado, M.C. Goite, D. Rivillo, Y. De Sanctis, A.J. Arce, A.J. Deeming, L. D’Ornelas, A. Sierralta, R. Atencio, T. González, Reactivity of 2,3-bis(2-pyridyl)pyrazine with  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ : Molecular structures of  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  and  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$ , *J. Organomet. Chem.* 692 (2007) 894–902.
- [58] L. Carlucci, D.M. Proserpio, G. D’Alfonso, 1, 2-eq,eq- $[\text{Re}_2(\text{CO})_8(\text{THF})_2]$ : A Reactive  $\text{Re}_2(\text{CO})_8$  Fragment That Easily Activates H–H and C–H Bonds, *Organometallics*. 18 (1999) 2091–2098.
- [59] R.A. Machado, D. Rivillo, A.J. Arce, L. D’Ornelas, Y. De Sanctis, R. Atencio, T. González, E. Galarza, Synthesis and molecular structure of  $[\text{Re}_2(\mu:\eta^6\text{-C}_{24}\text{H}_{18}\text{N}_4)(\text{CO})_6]$  containing the rtct-tetrakis (2-pyridyl) cyclobutandiyl ligand, derived from the reaction of  $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$  and 1,2-bis(2-pyridyl)ethene, *J. Organomet. Chem.* 689 (2004) 2486–2493.
- [60] D. Peña, Y. Otero, A. Arce, J.M. García, D.S. Coll, E. Ocando-Mavarez, R. Machado, T. González, Synthesis, characterization and reactivity of dinuclear rhenium complexes containing hemilabile phosphines as ligands: X-ray structures of diax- $[\text{Re}_2(\text{CO})_8\kappa^1(\text{P})\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{CN}]_2$ ,  $[\text{Re}_2(\text{CO})_8\{\mu:\kappa^3(\text{P},\text{C},\text{C})\text{-}i\text{Pr}_2\text{NP}(\text{CH}_2\text{CHCH}_2)_2\}]$  and diax- $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)\{\kappa^1(\text{P})\text{-}p\text{-MeOC}_6\text{H}_4\text{P}(\text{CH}_2\text{CHCH}_2)_2\}]$ , *Inorganica Chim. Acta.* 439 (2016). doi:10.1016/j.ica.2015.10.013.
- [61] M.J. Mays, D.W. Prest, P.R. Raithby, Dirhenium complexes containing two, three, and four linked acetylene molecules derived from the reaction of  $[\text{Re}_2(\text{CO})_{10}]$  with  $\text{RC}_2\text{R}$  (R = Ph or Me); the X-ray crystal structure of

$[\text{Re}_2(\text{CO})_4\{(\text{PhCCPh})_3\}(\text{CNCH}_2\text{SO}_2\text{C}_6\text{H}_4\text{Me-p})_2]\cdot\text{CH}_2\text{Cl}_2$ , J. Chem. Soc. Dalt. Trans. (1981) 771–776. doi:10.1039/DT9810000771.

- [62] M.A. Reynolds, I.A. Guzei, R.J. Angelici,  $\text{Re}_2(\text{CO})_{10}$ -Mediated Carbon–Hydrogen and Carbon–Sulfur Bond Cleavage of Dibenzothiophene and 2,5-Dimethylthiophene, Organometallics. 20 (2001) 1071–1078.
- [63] M.A. Reynolds, I.A. Guzei, R.J. Angelici, Organometallic models of catalytic hydrodesulfurization:  $\text{Re}_2(\text{CO})_{10}$ -promoted cleavage of C–S bonds in benzothiophene, Chem. Commun. (2000) 513–514.



$\pi$ -Conjugated phospholes undergo  $\sigma$ - or  $\sigma,\pi$ -coordination to the dirhenium centre.

Phospholes undergo coordination to the dirhenium centre in bridging or chelate modes

Phospholes were found to behave as two-, four- or six-electron donor ligands

$\sigma,\pi$ -Complexes show a fluxional behavior due to the restricted rotation of the ligand

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