



Rhenium carbonyl compounds with (diphenyl)phosphinoalkynes and a sterically hindered phosphinoalkyne

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ABSTRACT

The synthesis and characterization of two series of rhenium carbonyl complexes with P-coordinated phosphinoalkynes are reported. The anionic *fac*-[ReBr₂(CO)₃(Ph₂PC≡CR)]⁻ and neutral *fac*-[ReBr(CO)₃(Ph₂PC≡CR)] (R = Ph, Tol, ^tBu) complexes have been prepared and the crystal structures of *fac*-[ReBr₂(CO)₃(Ph₂PC≡CTol)]⁻ and *fac*-[ReBr(CO)₃(Ph₂PC≡C^tBu)] have been determined by X-ray crystallography, evidencing the presence of the uncoordinated alkyne in all these compounds. The phosphinoalkyne (*o*-Tol)₂PC≡CPh with bulky groups linked to the phosphorus atom was prepared in order to avoid the coordination of two phosphinoalkynes in *cis*-position around the rhenium metal. As a result, surprisingly the complex *fac*-[ReBr(CO)₃((*o*-Tol)₂PC≡CPh)₂] was obtained. The crystal structure of this compound was determined confirming the *cis*-coordination of two bulky phosphinoalkynes in an octahedral rhenium atom. The electronic properties of the uncoordinated alkyne in these new rhenium complexes was analyzed, based on ¹³C NMR data and was compared with reported data on iron complexes. The results obtained indicate that the electronic characteristics of uncoordinated alkynes are similar in both families of complexes. Thus, the different reactivity observed between rhenium and iron complexes is related to the different nature of metallic fragments rather than to electronic features of uncoordinated alkynes.

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1. Introduction

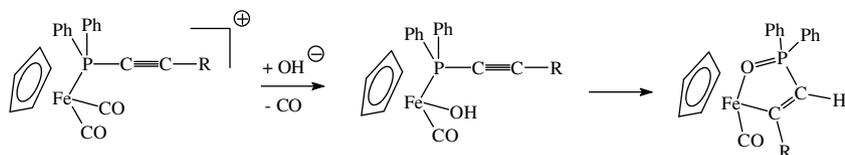
Alkynyl phosphines Ph₂PC≡CR are attracting ligands that have been extensively studied because of their versatile behaviour, resulting from their ability to react via the phosphine and the alkyne functions. The first studies in the 1980s were focused on their capacity to support polynuclear metal clusters by means of phosphido and alkynyl fragments, which were formed after P–C bond cleavage [1]. However, further studies with a broad range of metal complexes have revealed other interesting abilities of these ligands such as the preparation of metal complexes with uncoordinated alkynes [2–4], intramolecular coupling of the alkynyl moieties [5–7], insertion of the triple bond in M–H or M–C bonds [8,9], preparation of heterometallic compounds [6,10–12], or the development of new materials [13]. These ligands can also lead to the formation of metallacycles by means of a reaction between the alkyne and another ligand linked to metal [9,14,15]. We reported some years ago that cationic P-coordinated iron complexes [(C₅H₅)Fe(CO)₂(Ph₂PC≡CR)]⁺ can lead to the formation of metallacycles in mild conditions, giving good yields by the reaction pathway shown in Scheme 1 [15].

Although no further studies have shown if it could be performed with other metals, this reaction has recently attracted our attention again in the course of our work with rhenium carbonyl complexes [16]. The chemistry of the cation [Re(CO)₃(H₂O)₃]⁺ and its homologous technetium-99m complex has become a relevant topic in radiopharmaceutical chemistry [17] after the publication of simple methods that allow the preparation of [^{99m}Tc(CO)₃(H₂O)₃]⁺ starting from [^{99m}TcO₄]⁻ [18]. One of the goals of this field is the search for new stable coordination sets that could be prepared in water medium starting from [^{99m}Tc(CO)₃(H₂O)₃]⁺. The most common approach to this objective has been the replacement of the labile water molecules by other ligands with heteroatoms as oxygen [19], nitrogen [20], phosphorus [21], sulphur [22] or mixed donor atoms [23]. However, there are few examples of substitution reactions of the water molecules by an organometallic fragment. The most relevant studies have been done with cyclopentadienyl [24], and as far as we know no studies have been reported with metallacycles.

Therefore, the main objective of the present work is to prepare new P-coordinated phosphinoalkynes with the fragment *fac*-{Re(CO)₃}⁺. These compounds will be the starting material to study the viability of a reaction similar to Scheme 1 with rhenium carbonyls, which could lead to the formation of stable metallacycles in water medium. The preparation of P-coordinated

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Scheme 1.

phosphinoalkynes can also supply interesting information about the electronic properties of the metal fragment. In a previous paper we reported a relationship between the ^{13}C NMR chemical shift of acetylenic carbons and the donor properties of the phosphine group [3], thus the alkyne can act as a sensor of electronic interaction between phosphorus and metal. Therefore, the analysis of ^{13}C NMR data in P-coordinated rhenium carbonyl phosphinoalkynes will allow us to compare the electronic properties of *fac*- $\{\text{Re}(\text{CO})_3\}^+$ with other previously reported metals fragments.

2. Results and discussion

2.1. Complexes with $\text{Ph}_2\text{PC}\equiv\text{CR}$ ($R = \text{Ph}, \text{Tol}, ^t\text{Bu}$)

In order to prepare P-coordinated complexes with the fragment $\{\text{Re}(\text{CO})_3\}^+$ the anion $[\text{ReBr}_3(\text{CO})_3]^{2-}$ was chosen as starting product. This complex is commonly used in the preparation of complexes with the fragment $\{\text{Re}(\text{CO})_3\}^+$ because bromide ligands are easily substituted by other ligands and using this approach $[\text{ReBr}_2(\text{CO})_3(\text{L})]^-$ complexes ($\text{L} =$ monodentate phosphine) have been reported [21]. The P-coordinated rhenium carbonyl complexes **1–3** (Scheme 2) were prepared by simple addition at room temperature of the phosphinoalkyne to the rhenium precursor in dichloromethane solution in stoichiometric ratio. This reaction was monitored by IR in the $\nu(\text{CO})$ region and by ^{31}P NMR spectroscopy and no significant differences was observed if certain reaction conditions such as temperature, reaction time and phosphine excess were modified. In all cases a main compound was formed, which displayed a sole signal in the ^{31}P NMR spectra between $-24/-27$ ppm with the characteristic shift to low field respect to free ligands ($-32/-34$ ppm) after coordination of the phosphorus atom to the metal. The IR spectra in the $\nu(\text{CO})$ region also is consistent with this hypothesis since in all cases an intense signal is observed around 2175 cm^{-1} , assigned to the uncoordinated alkyne [4,7,11,12] and three bands characteristic of the *fac*- $\{\text{Re}(\text{CO})_3\}^+$ fragment [23a,25]. Unfortunately, all attempts to isolate complexes **1–3** in solid state led to compounds contaminated with $[\text{NEt}_4]\text{Br}$, which is formed in the substitution reaction of bromide by the phosphine (Scheme 2). The isolation of pure complexes **1–3** has been attempted by treatment and recrystallization with a wide range of solvents, as well as the use of Reverse Phase Sep-Pack cartridges, however in all cases the complexes obtained were contaminated by tetraethylammonium bromide. This situation has been previously described in the literature of rhenium carbonyl complexes prepared from $[\text{NEt}_4]_2[\text{ReBr}_3(\text{CO})_3]$ [26]. The best results

were obtained by recrystallization in dichloromethane/toluene which yielded crystals of complexes **1–3** contaminated with small quantities of $[\text{NEt}_4]\text{Br}$. The crystal structure of complex **2** was determined by X-ray diffraction methods (Fig. 1), confirming the proposed structure for these complexes. The ^{13}C NMR spectra of complexes **1–3** also supply relevant information in agreement with the proposed structure since in all cases two doublets can be observed in the 70–120 ppm region assigned to the two acetylenic carbons. The shift observed respect to the free ligands and the increase in the $J_{\text{P-C}}$ coupling constants is characteristic of P-coordinated phosphinoalkynes [3,4,7,11,12].

Once the formation of P-coordinated phosphinoalkyne complexes was corroborated, the next goal was to study the possible reaction between the coordinated phosphinoalkyne and a water molecule linked to the rhenium atom. This was studied by means of the reaction between $[\text{NEt}_4]_2[\text{ReBr}_3(\text{CO})_3]$ with the phosphinoalkyne in water/ethanol medium (Scheme 3). Under these conditions, Re–Br bonds are hydrolysed [27]. This reaction was monitored by IR in the $\nu(\text{CO})$ region and was performed at different temperatures (room temperature and reflux), phosphine/metal ratios (values of 1 or 2) and reaction times. In all cases the observed IR spectra were nearly identical, in agreement with the formation

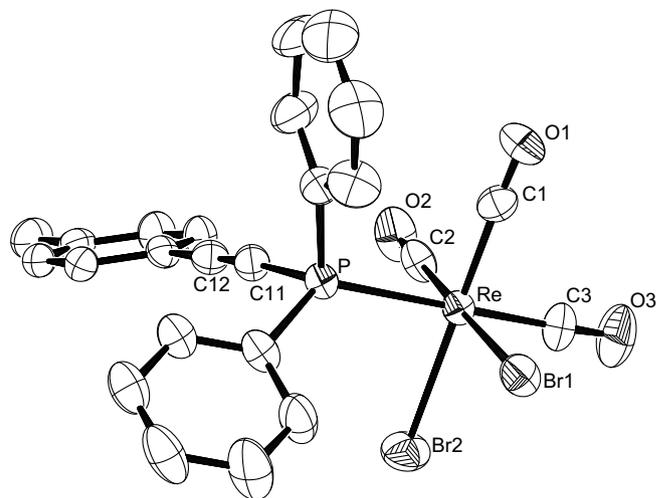
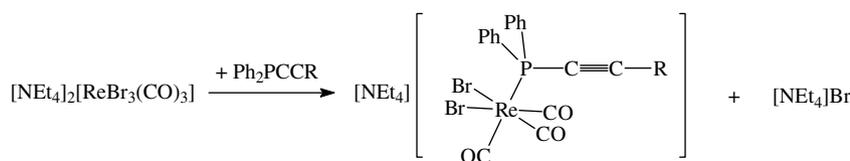
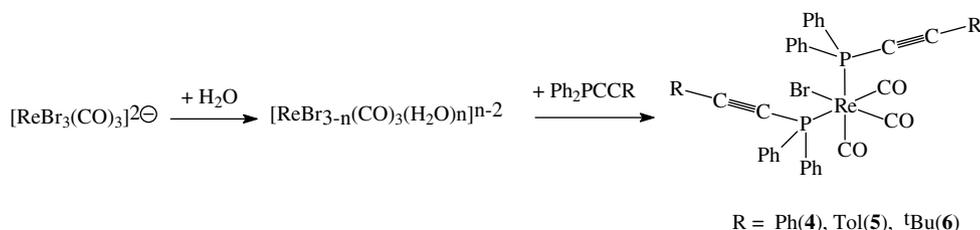


Fig. 1. ORTEP drawing of the anionic fragment *fac*- $[\text{ReBr}_2(\text{CO})_2(\text{Ph}_2\text{PC}\equiv\text{CTol})]^-$ (**2**) with thermal ellipsoids at the 30% probability level, including the atom numbering of selected atoms. All hydrogen atoms have been omitted for clarity.



$R = \text{Ph}(\mathbf{1}), \text{Tol}(\mathbf{2}), ^t\text{Bu}(\mathbf{3})$

Scheme 2.



Scheme 3.

of the same compound in all cases, and the reaction conditions essentially affect the yields of the reaction.

Complexes **4–6** could be isolated by simple addition of water to the reaction medium because the polar medium promotes the precipitation of these compounds. In this case, pure complexes could be isolated in high yield because tetraethylammonium bromide is soluble in ethanol/water medium. The IR spectra of complexes **4–6** are very similar and the $\nu(\text{CO})$ bands are shifted to higher frequencies in comparison with those of complexes **1–3**. This shift is consistent with the expected change between an anionic carbonyl and a neutral carbonyl complex. The signal of the uncoordinated alkyne is observed in a position nearly identical to that of complexes **1–3** but the intensity of this signal visibly increases. This could be related to an increase in the triple bond dipole moment [3]. The ^{31}P NMR spectra show a sole signal in a position similar to those of complexes **1–3** but slightly shifted to low field ($-22/-24$ ppm). These results are consistent with the coordination of phosphorus atom and the existence of free alkyne in complexes **4–6**. This hypothesis is also supported by the ^{13}C NMR spectra that show the signals of the alpha acetylenic carbons with $J_{\text{P-C}}$ couplings higher than 100 Hz, typical values of P-coordinated phosphinoalkynes [3,7,11,12]. These spectra also provided the first evidence of the presence of two phosphinoalkynes coordinated to rhenium in complexes **4–6**. The signals of alpha acetylenic carbons appear as double doublets (**5**: $^1J_{\text{P-C}} = 102.2$ Hz, $^3J_{\text{P-C}} = 7.2$ Hz) and the signals of beta acetylenic carbons as the A part of a second order AXX' system [28]. This split suggest the existence of two phosphorus atoms linked to the metal, a supposition that was corroborated by the MS-ESI of complexes **4–6** that show in all cases a main signal of cation $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})(\text{Ph}_2\text{PCCR})_2]^+$. The crystal structure of complex **6** was determined by X-ray diffraction methods (Fig. 2) and it confirms the presence of the two P-coordinated phosphinoalkynes bonded to the *fac*- $[\text{Re}(\text{CO})_3]^+$ fragment. The coordination set around the metal is completed by a bromide ligand. Hence, the formation and subsequent precipitation of complexes **4–6** can be understood from the perspective that the reaction between the phosphinoalkyne and the hydrolyzed rhenium complex $[\text{ReBr}_{3-n}(\text{CO})_3(\text{H}_2\text{O})_n]^{2-n}$ is visibly different from the reaction with $[\text{ReBr}_3(\text{CO})_3]^{2-}$. In the reaction with the hydrolyzed complex we observed that complexes with two phosphinoalkynes linked to the metal are formed as the main compound in all experiments, even when the phosphine/metal

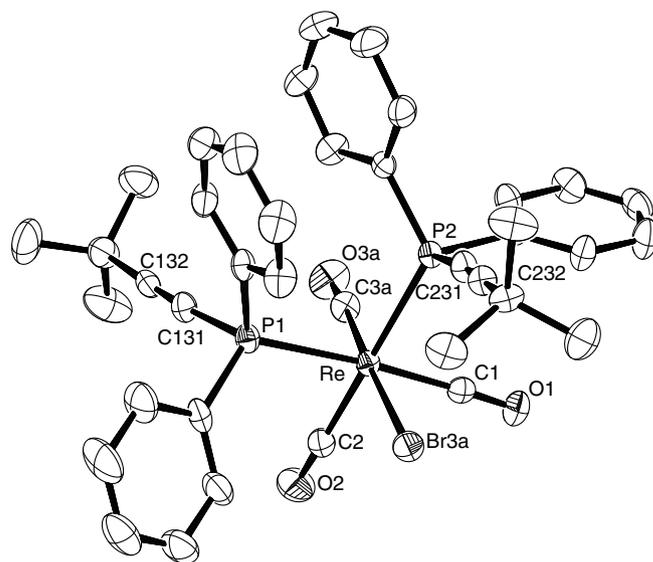
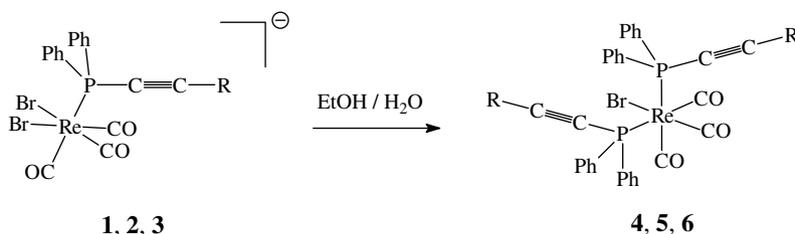


Fig. 2. ORTEP drawing of *fac*- $[\text{ReBr}(\text{CO})_3(\text{Ph}_2\text{PC}\equiv\text{C}^t\text{Bu})_2]$ (**6**) with thermal ellipsoids at the 30% probability level, including the atom numbering of selected atoms. All hydrogen atoms have been omitted for clarity.

ratio value is equal to 1. On the contrary, the reaction with $[\text{ReBr}_3(\text{CO})_3]^{2-}$ led to the substitution of only one bromide by phosphorus for phosphine/metal ratios between 1 and 2. Consequently, the reaction with $[\text{ReBr}_3(\text{CO})_3]^{2-}$ favours the formation of a complex with a phosphine bonded to metal and the reaction with the hydrolyzed complex has a tendency to form the complex with two phosphines linked to metal. The trend to form complexes **4–6** in water medium is reflected by the evolution of the anionic complexes **1–3** in a medium with water. Thus, complexes **1–3** were dissolved in ethanol and water was added to the solution in identical conditions to the preparation of complexes **4–6**. The IR and ^{31}P NMR spectroscopy evidence the fast, nearly quantitative formation of neutral complexes **4–6** as shown in Scheme 4.

Since the formation of the metallacycles shown in Scheme 1 is more favourable in basic medium, the hydrolysis of complexes **1–3** in presence of bases was studied by means of IR and ^{31}P NMR spectroscopy. Experiments using the weak base 2,6-lutidine



Scheme 4.

in acetonitrile/water medium were performed at different reaction times and temperatures. In all studied cases the evolution was similar. Initially, the IR spectrum shows changes in the position of $\nu(\text{CO})$ bands but $\nu(\text{C}\equiv\text{C})$ band remains practically unaltered. After some time, a white precipitate of $[\text{NEt}_4][\text{Re}_2(\text{CO})_6(\mu\text{-OH})_3]$ is formed [29] and the ^{31}P NMR of filtrate shows the characteristic signal of the free phosphinoalkyne ligand. Similar results were found using strong bases as NaOH. These results can be related with the initial substitution of bromide by other ligands present in the reaction medium but the absence of a metallacycle in this step is revealed by the unaltered signal of the uncoordinated alkyne. Subsequent evolution to the formation of the binuclear complex $[\text{Re}_2(\text{CO})_6(\mu\text{-OH})_3]^-$ and free phosphinoalkyne evidence that in the studied reaction conditions this reaction way is more favorable than other possibilities as the metallacycle formation.

2.2. Complexes with $X_2\text{PC}\equiv\text{CPh}$ ($X = o\text{-Tol}$)

Since the reactivity of the hydrolyzed rhenium complex with phosphinoalkynes $\text{Ph}_2\text{PC}\equiv\text{CR}$ showed a propensity to form complexes with two phosphines coordinated to rhenium, we decided to study the same reaction with a sterically hindered phosphinoalkyne by substitution of phenyl groups with bulkier *o*-tolyl groups. The aim was to study if the use of this more sterically hindered phosphine could lead to a different reactivity since this scenario might favour the formation of a complex with a sole phosphine linked to the *fac*- $[\text{Re}(\text{CO})_3]^+$ fragment. The synthesis of $(o\text{-Tol})_2\text{PC}\equiv\text{CPh}$ has been reported [30] but it has been only used in phosphinoalkyne cyclization reactions and, as far as we know, no coordination studies have been reported. Thus, the phosphine $(o\text{-Tol})_2\text{PC}\equiv\text{CPh}$ was synthesized by the same procedure employed for phosphines $\text{Ph}_2\text{PC}\equiv\text{CR}$, but using $(o\text{-Tol})_2\text{PCL}$ instead of Ph_2PCL . This phosphine $(o\text{-Tol})_2\text{PC}\equiv\text{CPh}$ was crystallized in ethanol and was obtained in good yield after crystallization (60%). The IR spectrum of this phosphine shows the characteristic $\nu(\text{C}\equiv\text{C})$ band at 2160 cm^{-1} . The position of the two acetylenic carbons in the ^{13}C NMR spectrum (84.8 and 107.8 ppm) is very similar to that found for $\text{Ph}_2\text{PC}\equiv\text{CPh}$ (85.2 and 107.6 ppm), showing that the electronic properties of the two acetylenic fragments should be comparable. However, the differences around the phosphorus atom are revealed by the ^{31}P NMR spectrum that displays a signal at -46.5 ppm , nearly 14 ppm shifted highfield with respect to $\text{Ph}_2\text{PC}\equiv\text{CR}$ phosphines. This change in behaviour can be related to a higher distortion around the phosphorus atom [31].

The reaction between phosphine $(o\text{-Tol})_2\text{PC}\equiv\text{CPh}$ and the anion $[\text{ReBr}_3(\text{CO})_3]^{2-}$ led to the formation of the respective P-coordinated complex $[\text{ReBr}_2(\text{CO})_3(\text{L})]^-$ (**7**, $\text{L} = (o\text{-Tol})_2\text{PC}\equiv\text{CPh}$), analogous to

complexes **1–3**. The IR spectrum of this complex in the $\nu(\text{CO})$ region is nearly identical to that of complexes **1–3** and the ^{31}P NMR spectra are also very similar (**7**, -21.7 ppm ; **1**, -23.9 ppm), although the free phosphines show resonances at more dissimilar positions as was stated in the previous paragraph. The formation of an anionic complex similar to **1–3** with the phosphine $(o\text{-Tol})_2\text{PC}\equiv\text{CPh}$ confirms that the higher steric hinderance around the phosphorus atom is compatible with the coordination to the fragment $[\text{ReBr}_2(\text{CO})_3]^-$ leading to complex **7**.

The reaction between the phosphine $(o\text{-Tol})_2\text{PC}\equiv\text{CPh}$ and $[\text{NEt}_4]_2[\text{ReBr}_3(\text{CO})_3]$ was performed in water/ethanol, in a similar way to the preparation of complexes **4–6**, with the aim of preparing a complex with a sole phosphinoalkyne bonded to the $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})]^+$ fragment. Unexpectedly, the IR spectrum in the $\nu(\text{CO})$ region of the resulting solution was analogous to that of complexes **4–6**, even with a phosphine/rhenium molar ratio of 1. Complex **8** was isolated from this solution and was characterized by IR, ESI-MS, ^1H , ^{13}C , ^{31}P NMR spectroscopy, and elemental analysis. All data agree with a structure identical to that found for complexes **4–6** with two phosphinoalkyne ligands linked to the $[\text{ReBr}(\text{CO})_3]$ fragment. The most relevant difference was observed in the ^{31}P NMR spectrum. The position of the resonance was similar to those of complexes **4–6** (-23.4 ppm) but the signal was displayed as a more broad band for complex **8** at room temperature. The shape of this signal evolves with temperature and at higher temperatures ($50\text{ }^\circ\text{C}$) a sharp signal is observed. Low-temperature ^{31}P NMR spectroscopic measurements were performed in order to determine if this phenomenon could be associated with the presence of an equilibrium process (Fig. 3). Although at first sight the spectrum at low temperatures resembles an AB system, the asymmetric appearance and the different separation between the two peaks at high field (260 Hz) and low field (289 Hz) rules out this possibility. An alternative possibility to explain the splitting of this signal could be the presence of different conformers in solution. An EXSY ^{31}P - ^{31}P NMR experiment showed correlations between all signals in agreement with this hypothesis. This different behaviour observed in complex **8** with respect to **4–6** could be associated with the presence of the *o*-tolyl groups in **8** that hinder the rotation around the metal–phosphorus bond leading to different conformers, which can be detected by ^{31}P NMR at low temperatures. The ESI-MS of **8** shows a main signal assigned to the cation $[\text{Re}(\text{CO})_3\{(o\text{-Tol})_2\text{PC}\equiv\text{CPh}\}_2]^+$, evidencing the presence of two phosphines linked to the metal atom.

It should be emphasized that complex **7** evolves in ethanol/water medium to complex **8** in an identical manner to that found with complexes **1–3** (Scheme 5). This result shows that the trend to form complexes with two phosphinoalkynes linked to the metal

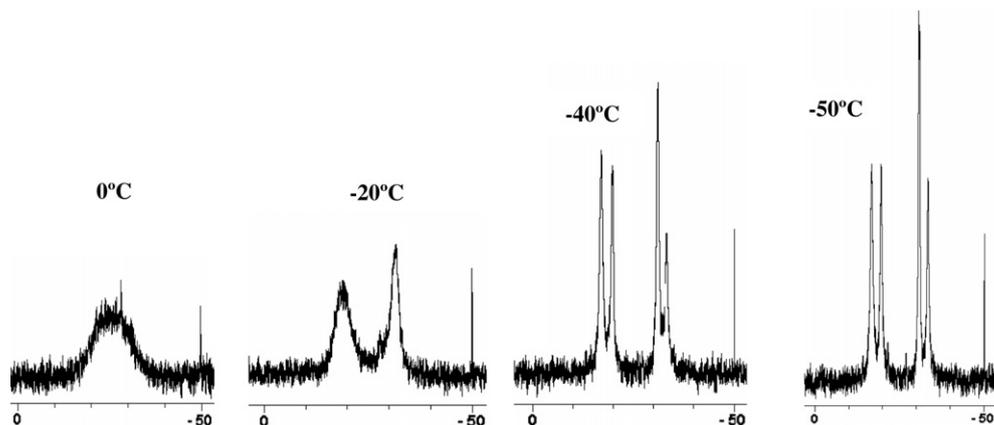
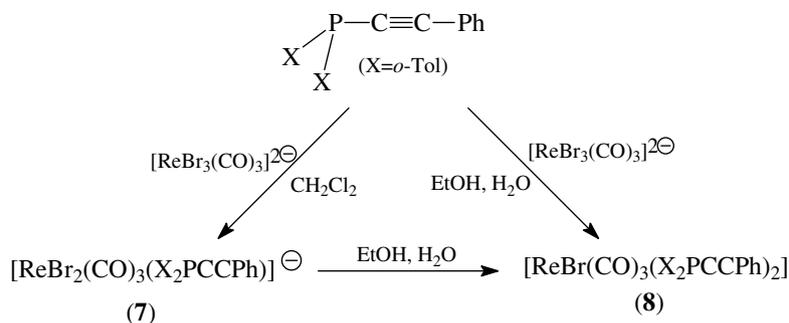


Fig. 3. Low-temperature ^{31}P NMR spectra for complex **8**.



Scheme 5.

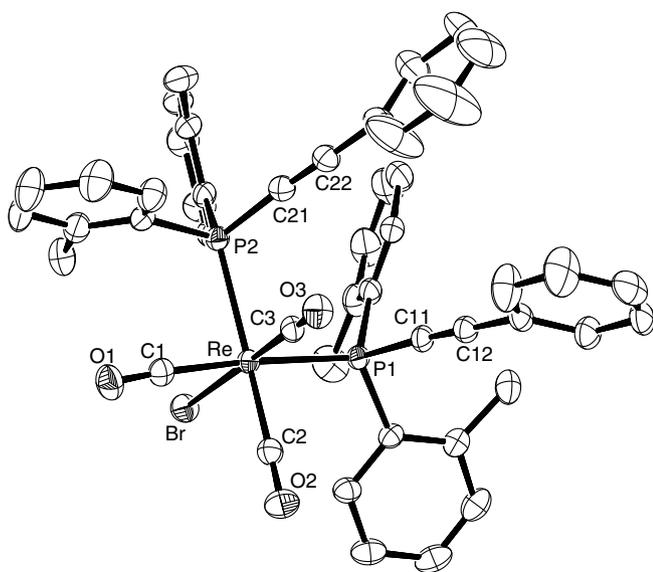


Fig. 4. ORTEP drawing of *fac*-[ReBr(CO)₃(*o*-Tol)₂PC≡Ph]₂ (**8**) with thermal ellipsoids at the 30% probability level, including the atom numbering of selected atoms. All hydrogen atoms have been omitted for clarity.

in ethanol/water media is retained although the phosphine is sterically hindered. Finally, the crystal structure of complex **8** was determined by X-ray diffraction methods (Fig. 4) and it confirmed the presence of the two P-coordinated phosphinoalkynes bonded to the *fac*-[Re(CO)₃]⁺ fragment.

2.3. Crystal structures of complexes **2**, **6** and **8**

Selected bond distances and angles for complexes **2**, **6** and **8** are, respectively, displayed in Tables 1 and 2. Rhenium metal atom presents a slightly distorted octahedral arrangement for the three complexes. The structure of the coordination set around rhenium metal for complex **2** is very similar to the few previously reported complexes [21] that contain a phosphine ligand linked to the anionic fragment *fac*-{ReBr₂(CO)₃}⁻. Complexes with two phosphine ligands linked to the neutral fragment *fac*-{ReBr(CO)₃} have been reported but it should be emphasized that the two phosphines in *cis*-position have never contained bulky groups as in complex **8**. With monodentate phosphines, the reported complexes contain two triarylphosphines [21b,32], alkyldiarylphosphines [33] or 1,3,5-triaza-7-phosphaadamantane [21a]. Another option is the presence of a sole bidentate bis(diphenylphosphine) ligand occupying the two *cis*-positions [33]. The geometric parameters around rhenium metal for complex **6** are very similar to those of previously reported complexes with the coordination set *fac*-[Re-

Table 1
Selected bond distances (Å) for complexes **2**, **6** and **8**

2	6	8
<i>Re-P</i>		
2.4849 (19)	2.4855 (15)/Re-P ₁	2.5132 (12)/Re-P ₁
	2.4856 (15)/Re-P ₂	2.5252 (11)/Re-P ₂
<i>Re-Br</i>		
2.6454 (9)/Re-Br ₁	2.6244 (16)/Re-Br _{3A}	2.6423 (5)
	2.618 (7)/Re-Br _{3B}	
	2.6227 (11)/Re-Br ₂	
<i>Re-C</i>		
1.908 (9)/Re-C ₁	1.937 (6)/Re-C ₁	1.945 (5)/Re-C ₁
1.890 (8)/Re-C ₂	1.955 (7)/Re-C ₂	1.928 (5)/Re-C ₂
1.910 (9)/Re-C ₃	1.895 (11)/Re-C _{3A}	1.917 (5)/Re-C ₃
	1.945 (9)/Re-C _{3B}	
<i>C-O</i>		
1.099(10) (1)/C ₁ -O ₁	1.151 (6)/C ₁ -O ₁	1.135 (6)/C ₁ -O ₁
1.153 (9)/C ₂ -O ₂	1.136 (7)/C ₂ -O ₂	1.149 (5)/C ₂ -O ₂
1.142(11) (1)/C ₃ -O ₃	1.158 (19)/C _{3A} -O _{3A}	1.123 (5)/C ₃ -O ₃
	1.144 (10)/C _{3B} -O _{3B}	
<i>C=C</i>		
1.217(11) (1)/C ₁₁ -C ₁₂	1.189 (7)/C ₁₃₁ -C ₁₃₂	1.200 (6)/C ₁₁ -C ₁₂
	1.181 (7)/C ₂₃₁ -C ₂₃₁	1.179 (6)/C ₂₁ -C ₂₂

Br(CO)₃P₂] [21,32,33]. When comparing these parameters between complexes **6** and **8**, we can see that the substitution of the phenyl groups by the *o*-tolyl groups implies that Re-P bonds are somewhat lengthier and some angle bonds that contain phosphorus are slightly more opened, changes that should be attributed to higher steric hindrance of *o*-tolyl groups. It must be born in mind that, as far as we know, only one structure of an octahedral transition metal complex with two bis(*o*-tolyl)phosphine groups in *cis*-position has been reported [34], and in this case the ligand is a tripodal phosphine.

The structure of *fac*-{Re(CO)₃} fragment in the three complexes (**2**, **6**, **8**) does not differ significantly and it is also similar to previously reported rhenium carbonyl complexes [21,32,33]. The C≡C bond distance is also similar for the three complexes and resembles reported values for other P-coordinated phosphinoalkyne metal complexes [3,4,7,11,12]. This result implies that no relevant structural differences are observed if the phosphinoalkyne is coordinated to the anionic fragment {ReBr₂(CO)₃}⁻ or to the neutral fragment {ReBr(CO)₃}. However, a remarkable difference is observed on comparing the relative positions of the two alkyne fragments between complexes **6** and **8**. In complex **8** the two alkyne fragments are positioned in the same direction, so they are close each other, whereas in complex **6** they are placed in opposite directions and as a result they are far away. This difference is probably a consequence of the steric hindrance between the bulky *o*-tolyl fragments. Although in the present work no significant chemical differences have been observed between complexes **6** and **8**, this

Table 2
Selected bond angles (deg) for complexes **2**, **6** and **8**

2	6	8
<i>P</i> -Re-C		
91.4 (3)/P-Re-C ₁	174.8 (2)/P ₁ -Re-C ₁	175.3 (1)/P ₁ -Re-C ₁
87.0 (2)/P-Re-C ₂	88.7 (2)/P ₁ -Re-C ₂	90.3 (1)/P ₁ -Re-C ₂
176.6 (3)/P-Re-C ₃	93.8 (4)/P ₁ -Re-C _{3A}	91.3 (1)/P ₁ -Re-C ₃
	87.6 (2)/P ₂ -Re-C ₁	87.6 (1)/P ₂ -Re-C ₁
	174.0 (2)/P ₂ -Re-C ₂	168.5 (1)/P ₂ -Re-C ₂
	89.7 (3)/P ₂ -Re-C _{3A}	84.9 (1)/P ₂ -Re-C ₃
<i>P</i> -Re-Br		
94.51 (5)/P-Re-Br ₁	89.90 (5)/P ₁ -Re-Br _{3A}	91.57 (3)/P ₁ -Re-Br
87.85 (5)/P-Re-Br ₂	90.54 (5)/P ₂ -Re-Br _{3A}	96.28 (3)/P ₂ -Re-Br
<i>P</i> -Re-P		
	94.22 (5)/P ₁ -Re-P ₂	96.24 (4)/P ₁ -Re-P ₂
<i>Br</i> -Re-Br		
88.08 (4)/Br ₁ -Re-Br ₂		
<i>C</i> -Re-C		
89.6 (4)/C ₁ -Re-C ₂	90.0 (2)/C ₁ -Re-C ₂	86.3 (2)/C ₁ -Re-C ₂
89.7 (4)/C ₂ -Re-C ₃	84.8 (4)/C ₂ -Re-C _{3A}	85.6 (2)/C ₂ -Re-C ₃
89.4 (4)/C ₁ -Re-C ₃	91.1 (4)/C ₁ -Re-C _{3A}	91.7 (2)/C ₁ -Re-C ₃
<i>C</i> -Re-Br		
89.9 (3)/C ₁ -Re-Br ₁	85.2 (2)/C ₁ -Re-Br _{3A}	85.4 (1)/C ₁ -Re-Br
177.7 (2)/C ₁ -Re-Br ₂	94.8 (2)/C ₂ -Re-Br _{3A}	92.9 (1)/C ₂ -Re-Br
178.4 (2)/C ₂ -Re-Br ₁	176.2 (4)/C _{3A} -Re-Br _{3A}	176.8 (1)/C ₃ -Re-Br
92.4 (2)/C ₂ -Re-Br ₂		
88.8 (3)/C ₃ -Re-Br ₁		
91.5 (3)/C ₃ -Re-Br ₂		
<i>P</i> -C≡C		
171.8(8)/P-C ₁₁ -C ₁₂	172.8 (6)/P ₁ -C ₁₃₁ -C ₁₃₂	175.8(4)/P ₁ -C ₁₁ -C ₁₂
	174.1 (6)/P ₂ -C ₂₃₁ -C ₂₃₂	175.9(4)/P ₂ -C ₂₁ -C ₂₂

feature could lead to design in future attracting strategies to approach alkyne groups in P-coordinated phosphinoalkyne metal complexes.

2.4. ¹³C NMR spectra of acetylenic carbon atoms

As previously mentioned, the analysis of ¹³C NMR resonances of acetylenic carbon in phosphinoalkynes and their P-coordinated metal complexes is a useful tool to compare the electronic properties of metal fragments linked to phosphinoalkynes. The chemical shift differences ($\delta C^2 - \delta C^1$) of acetylenic carbons for different compounds can be related to the triple bond polarization [35],

Table 3
¹³C NMR chemical shift (δ , ppm) for the acetylenic atoms in phosphinoalkynes and P-coordinated phosphinoalkynes

Compound	C ¹	C ²	C ² -C ¹
Ph ₂ PC≡C ² Ph	85.2	107.6	22.4
[ReBr ₂ (CO) ₃ (Ph ₂ PC≡C ² Ph)] ⁻ (1)	83.2	108.3	25.1
[ReBr(CO) ₃ (Ph ₂ PC≡C ² Ph) ₂] (4)	80.0	111.1	31.1
[Fe ₃ (CO) ₉ (CCH ₃)(Ph ₂ PC ¹ ≡C ² Ph)] ^{-a}	87.0	107.1	20.1
[CpFe(CO) ₂ Ph ₂ PC ¹ ≡C ² Ph] ^{†b}	80.3	115.7	35.4
Ph ₂ PC≡C ² Tol	84.3	107.9	23.6
[ReBr ₂ (CO) ₃ Ph ₂ PC ¹ ≡C ² Tol] ⁻ (2)	82.3	108.7	26.4
[ReBr(CO) ₃ (Ph ₂ PC ¹ ≡C ² Tol) ₂] (5)	79.2	111.7	32.5
[Fe ₃ (CO) ₉ (CCH ₃)(Ph ₂ PC ¹ ≡C ² Tol)] ^{-a}	86.1	107.4	21.3
[CpFe(CO) ₂ Ph ₂ PC ¹ ≡C ² Tol] ^{†b}	80.0	116.5	36.5
Ph ₂ PC ¹ ≡C ² - ^t Bu	73.7	118.2	44.5
[NEt ₄][ReBr ₂ (CO) ₃ Ph ₂ PC ¹ ≡C ² - ^t Bu] ⁻ (3)	72.3	119.3	47.0
[ReBr(CO) ₃ (Ph ₂ PC ¹ ≡C ² - ^t Bu) ₂] (6)	69.7	122.1	52.4
[Fe ₃ (CO) ₉ (CCH ₃)(Ph ₂ PC ¹ ≡C ² - ^t Bu)] ^{-a}	75.7	117.7	42.0
[CpFe(CO) ₂ Ph ₂ PC ¹ ≡C ² - ^t Bu] ^{†b}	70.9	127.9	57.0

^a Ref. [36].^b Ref. [3].

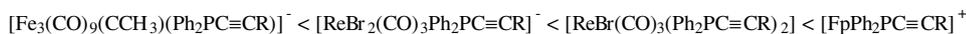
Table 3 displays the ¹³C NMR chemical shifts of the acetylenic atoms for complexes **1–6**, their respective free phosphinoalkynes and the values of a series of cationic [3] and anionic [36] iron complexes for comparison purposes. The P-coordination of a phosphinoalkyne to a metal involves an increase in the C≡C triple bond polarization and the ¹³C resonances of acetylenic carbon atoms C¹ and C² are shifted upfield and downfield, respectively, with regard to that of the corresponding free phosphinoalkyne. Table 3 shows that $\delta C^2 - \delta C^1$ values for the anionic complexes (**1**, **2**, **3**) are nearly six ppm lower than the values for neutral complexes (**4**, **5**, **6**). The same tendency was previously observed when comparing anionic and cationic iron complexes [3] (see Table 3) and is explained by the higher charge on phosphorus atom in the cationic complexes that induces the polarization of the triple bond. On comparing the metal complexes for the three phosphinoalkynes studied (Ph₂PC≡CR; R = Ph, Tol, ^tBu), it can be seen that in all cases the triple bond polarization increases following the same pattern as it is shown in Scheme 6.

(Fp = Fe(CO)₂Cp). The values of $\delta C^2 - \delta C^1$ for the neutral complexes (**4**, **5**, **6**) are only 4.0–4.6 ppm lower than those obtained for the cationic iron complexes [FpPh₂PC≡CR]⁺, that means that the alkyne polarization is not very different between these rhenium and iron compounds. In addition, when complexes **4**, **5**, **6** are in solution in a medium that contains water, the Re-Br bond is probably hydrolyzed to form cationic complexes like [Re(H₂O)(CO)₃(Ph₂PC≡CR)₂]⁺ where the polarization of the C≡C bond should be even higher than in the neutral complexes **4**, **5**, **6**. Consequently, the different chemical behaviour observed between iron and rhenium complexes, namely the iron compounds quickly evolve to form metallacycles while, to date rhenium compounds do not, cannot be attributed to different electron properties of the alkyne fragment.

3. Conclusions

We have examined the reactivity of phosphinoalkynes Ph₂PC≡CR (R = Ph, Tol, ^tBu) with the rhenium carbonyl precursor *fac*-[ReBr₃(CO)₃]²⁻ and the anionic P-coordinated complexes *fac*-[ReBr₂(CO)₃(Ph₂PC≡CR)]⁻ (**1**, **2**, **3**) were formed in all cases. These complexes evolve in an ethanol/water medium to form neutral *fac*-[ReBr(CO)₃(Ph₂PC≡CR)₂] (**4**, **5**, **6**) complexes. The same complexes were obtained by direct reaction between the carbonyl precursor *fac*-[ReBr₃(CO)₃]²⁻ and the respective phosphinoalkyne in ethanol/water medium, independently of whether the metal/phosphine ratio used was one or two. This singular behaviour can be related with a higher tendency of the hydrolyzed complex to form compounds with two phosphorus atoms linked to the metal. The same behaviour has been observed even with the phosphinoalkyne (*o*-Tol)₂PC≡CPh, which contains two bulky *o*-tolyl groups linked to the phosphorus atom. Complex **8** contains two *cis* coordinated (*o*-Tol)₂PC≡CPh ligands, and the bulky groups do not modify substantially the reactivity towards rhenium complexes with respect to Ph₂PC≡CPh ligands. To date, the most significant differences were found in: (1) the different orientation of alkyne fragments in crystal structure of **8** with respect to **6**; (2) the ³¹P NMR spectra of **8** at low temperature that show the presence of different conformers, probably as a result of hindered rotation by bulky groups.

The analysis of ¹³C NMR resonances of acetylenic carbons show that alkyne polarization for neutral complexes (**4**, **5**, **6**) is only slightly lower than the values previously reported for P-coordinated cationic iron complexes, so the electronic properties of alkynes should be comparable for both kind of complexes. However, up to now no reaction that could yield a metallacycle similar to those reported for iron complexes has been observed.



Scheme 6.

4. Experimental

4.1. Synthesis

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin–Elmer 2000 FT spectrometer. The NMR spectra were recorded by the *Servei de Ressonància Magnètica Nuclear de la Universitat Autònoma de Barcelona* on a Bruker AVANCE DPX-250 instrument. Microanalyses were performed by the *Servei de Microanàlisi de l'Institut d'Investigacions Químiques i Ambientals de Barcelona (IIQAB)*. Mass spectra were obtained on an Esquire 3000 with electrospray ionization and an ion trap Bruker Daltonics by *Servei d'Anàlisi Química del Departament de Química de la Universitat Autònoma de Barcelona*. Crystal structure determinations were performed by *Servei de Difracció de Raigs X de la Universitat Autònoma de Barcelona*.

The complex $[\text{NET}_4]_2[\text{ReBr}_3(\text{CO})_3]$ [27a] and the acetylenic phosphines $\text{Ph}_2\text{PC}\equiv\text{CR}$ {R = *p*-tolyl, Ph and ^tBu} [37] were prepared by published procedures.

4.1.1. Synthesis of (*o*-tolyl)₂PC≡CPh

The phosphine (*o*-tolyl)₂PC≡CPh was prepared by using a similar procedure to that reported for Ph₂PC≡CR [37]. To a solution of phenylacetylene (0.45 mL, 4 mmol) in diethyl ether (20 mL) maintained at –78 °C was dropwise added under stirring a solution of butyllithium (2.5 mL, 1.6 M in hexane; 4 mmol) in diethyl ether (20 mL). The solution was stirred for 30 min; then (*o*-tolyl)₂PCL (1 g, 3.9 mmol) in solution in 20 mL of diethyl ether was dropwise added keeping the temperature at –78 °C. This mixture was slowly raised to room temperature and the solution was stirred for additional 1 h. After filtration to remove LiCl, the solution was evaporated to dryness. Crystallization in absolute ethanol gave 0.76 g of product as white solid. Yield: 63%. IR (CH₂Cl₂, cm⁻¹): 2159 (s, C≡C). ¹H NMR ((CD₃)₂CO, 25 °C, δ in ppm): 2.50 (s; CH₃), 7.20–7.70 (m; H_{ar}). ³¹P{¹H} NMR ((CD₃)₂CO, δ in ppm): –46.5 (s). ¹³C{¹H} NMR ((CD₃)₂CO, δ in ppm): 19.9 (s; CH₃), 20.2 (s; CH₃), 84.8 (d, ¹J_{C–P} = 7.9 Hz; ≡C–P), 107.8 (d, ²J_{C–P} = 4.5 Hz; ≡C–C_{ar}), 122.4 (s; C_{ar}–C≡), 125.7–133.2 (m; C_{ar}), 141.4 (d, ¹J_{C–P} = 7.2 Hz; C_{ar}–P). ESI/MS (positive mode, *m/z*): 315.1 [MH⁺].

4.1.2. Synthesis of [NET₄][ReBr₂(CO)₃(X₂PC≡CR)] {(X = R = Ph, **1**), (X = Ph, R = *p*-tolyl, **2**), (X = Ph, R = ^tBu, **3**), (X = *o*-tolyl, R = Ph, **7**)}

A solution of the acetylenic phosphines (0.14 mmol) in CH₂Cl₂ (20 mL) was added to a solution of [NET₄]₂[ReBr₃(CO)₃] (0.1 g, 0.13 mmol) in CH₂Cl₂ (70 mL) and stirred for 3 h at room temperature for complexes **1–3**. This reaction must be performed under reflux for **7**. Next, the reaction mixture was concentrated by evaporation to a few milliliters and toluene was added. The complexes crystallize contaminated with NET₄Br.

4.1.2.1. Complex 1. IR (CH₂Cl₂, cm⁻¹): 2178 (s, C≡C), 2021 (vs, C≡O), 1920 (vs, C≡O), 1884 (vs, C≡O). ¹H NMR ((CD₃)₂CO, δ in ppm): 7.40–8.25 (m; H_{ar}). ³¹P{¹H} NMR ((CD₃)₂CO, δ in ppm): –23.9 (s). ¹³C{¹H} NMR ((CD₃)₂CO, δ in ppm): 83.2 (d, ¹J_{C–P} = 83.8 Hz; ≡C–P), 108.3 (d, ²J_{C–P} = 12.4 Hz, ≡C–C_{ar}), 121.5 (d, *J* = 2.7 Hz; C_{ar}), 127.2–133.7 (m; C_{ar}), 191.5–193.6 (m; CO).

4.1.2.2. Complex 2. IR (CH₂Cl₂, cm⁻¹): 2175 (s, C≡C), 2021 (vs, C≡O), 1921 (vs, C≡O), 1885 (vs, C≡O). ¹H NMR ((CD₃)₂CO, δ in

ppm): 2.37 (s; CH₃), 7.27 (d, ³J_{H–H} = 8.1 Hz; H *meta* position tolyl group), 7.61 (d, ³J_{H–H} = 8.1 Hz; H *ortho* position tolyl group), 7.30–8.20 (m; H_{ar}). ³¹P{¹H} NMR ((CD₃)₂CO, δ in ppm): –24.3 (s). ¹³C{¹H} NMR ((CD₃)₂CO, δ in ppm): 20.4 (s; CH₃), 82.3 (d, ¹J_{C–P} = 85.0 Hz; ≡C–P), 108.7 (d, ²J_{C–P} = 12.8 Hz; ≡C–C_{ar}), 118.5 (d, *J* = 2.9 Hz; C_{ar}), 127.2–133.8 (m; C_{ar}), 140.0 (s; C_{ar}), 191.5–193.6 (m; CO).

4.1.2.3. Complex 3. IR (CH₂Cl₂, cm⁻¹): 2167 (s, C≡C), 2173 (s, C≡C), 2020 (vs, C≡O), 1919 (vs, C≡O), 1884 (vs, C≡O). ¹H NMR ((CD₃)₂CO, δ in ppm): 1.41 (s; CH₃), 7.36–8.15 (m; H_{ar}). ³¹P{¹H} NMR ((CD₃)₂CO, δ in ppm): –26.4 (s). ¹³C{¹H} NMR ((CD₃)₂CO, δ in ppm): 29.5 (s; C–(CH₃)₃), 29.7 (s; CH₃), 72.3 (d, ¹J_{C–P} = 88.3 Hz; ≡C–P), 119.3 (d, ²J_{C–P} = 11.7 Hz; ≡C–C), 127.6–139.7 (m; C_{ar}), 191.5–193.6 (m; CO).

4.1.2.4. Complex 7. IR (CH₂Cl₂, cm⁻¹): 2177 (s, C≡C), 2021 (vs, C≡O), 1919 (vs, C≡O), 1884 (vs, C≡O). ¹H NMR (CD₂Cl₂, δ in ppm): 2.16 (s; CH₃), 7.10–8.60 (m; H_{ar}). ³¹P{¹H} NMR (CD₂Cl₂, δ in ppm): –21.7 (s). ¹³C NMR spectrum could not be obtained because solubility was too low.

4.1.3. Synthesis of [ReBr(CO)₃(Ph₂PC≡CR)₂] {R = *p*-tolyl (**4**), Ph (**5**), ^tBu (**6**)}

To a solution of [NET₄]₂[ReBr₃(CO)₃] (50 mg, 0.07 mmol) in EtOH/H₂O (4 mL:3 mL) was added a solution of the acetylenic phosphines (0.18 mmol) in EtOH (10 mL). The reaction mixture was heated to reflux and water (9 mL) was slowly added during 90 min (1 mL/10 min). After addition was complete, reflux was continued for additional 90 min. A white precipitated was formed, which was filtered, washed with 2 × 5 mL of a cold 50% water: EtOH mixture and recrystallized in toluene/hexane.

4.1.3.1. Complex 4. Yield: 73%. Anal. Calc. for C₄₃H₃₀O₃BrP₂Re: C, 55.97; H, 3.28. Found: C, 55.93; H, 3.14%. IR (CH₂Cl₂ cm⁻¹): 2177 (s, C≡C), 2040 (vs, C≡O), 1964 (vs, C≡O), 1909 (vs, C≡O). ¹H NMR (CDCl₃, δ in ppm): 2.43 (s; CH₃), 7.26 (d, ³J_{H–H} = 8.1 Hz; H *meta* position tolyl group), 7.50 (d, ³J_{H–H} = 8.1 Hz; H *ortho* position tolyl group), 7.42–7.72 (m; H_{ar}). ³¹P{¹H} NMR (CDCl₃, δ in ppm): –21.9 (s). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 21.4 (s; CH₃), 79.2 (dd, ¹J_{C–P} = 103.7 Hz, ³J_{C–P} = 7.2 Hz; ≡C–P), 111.7 (AXX', three lines are observed, ²J_{C–P} + ⁴J_{C–P} = 13.4; ≡C–C_{ar}), 117.9 (d, *J* = 2.1 Hz; C_{ar}), 127.0–134.4 (m; C_{ar}), 140.2 (s; C_{ar}), 187.2–189.0 (m; CO). ESI/MS (positive mode, *m/z*): 889.3 [M–Br+H₂O]⁺.

4.1.3.2. Complex 5. Yield: 80%. Anal. Calc. for C₄₅H₃₄O₃BrP₂Re: C, 56.85; H, 3.60. Found: C, 56.84; H, 3.53%. IR (CH₂Cl₂, cm⁻¹): 2179 (s, C≡C), 2040 (vs, C≡O), 1966 (vs, C≡O), 1909 (vs, C≡O). ¹H NMR (CDCl₃, δ in ppm): 7.10–7.90 (m; H_{ar}). ³¹P{¹H} NMR (CDCl₃, δ in ppm): –21.5 (s). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 80.0 (dd, ¹J_{C–P} = 102.2 Hz, ³J_{C–P} = 7.0 Hz; ≡C–P), 111.1 (AXX', three lines are observed, ²J_{C–P} + ⁴J_{C–P} = 13.8 Hz; ≡C–C_{ar}), 120.9 (s; C_{ar}), 127.0–134.0 (m; C_{ar}), 187.1–190.0 (m; CO). ESI/MS (positive mode, *m/z*): 861.2 [M–Br+H₂O]⁺.

4.1.3.3. Complex 6. Yield: 82%. Anal. Calc. for C₃₉H₃₈O₃BrP₂Re: C, 53.06; H, 4.34. Found: C, 53.11; H, 4.41%. IR (CH₂Cl₂, cm⁻¹): 2211 (s, C≡C), 2171 (s, C≡C), 2039 (vs, C≡O), 1962 (vs, C≡O), 1908 (vs, C≡O). ¹H NMR (CDCl₃, δ in ppm): 1.47 (s; CH₃), 7.26–7.77 (m; H_{ar}). ³¹P{¹H} NMR (CDCl₃, δ in ppm): –23.8 (s). ¹³C{¹H} NMR

Table 4
Crystal data and structure refinement details

	2	6	8 · C₇H₈
Formula	C ₃₂ H ₃₇ Br ₂ NO ₃ PRe	C ₃₉ H ₃₈ BrO ₃ P ₂ Re	C ₅₄ H ₄₆ BrO ₃ P ₂ Re
Formula weight	860.62	882.74	1070.96
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>a</i> (Å)	10.1649(6)	10.4976(6)	13.1572(7)
<i>b</i> (Å)	10.5660(6)	9.7402(6)	14.4084(8)
<i>c</i> (Å)	16.7362(10)	36.753(2)	14.8729(8)
α (°)	94.542(1)	90	109.139(1)
β (°)	90.217(1)	90.474(1)	115.375(1)
γ (°)	106.493(1)	90	90.212(1)
<i>V</i> (Å ³)	1717.5(2)	3757.8(4)	2372.1(2)
<i>Z</i>	2	4	2
<i>D</i> _{calc} (Mg cm ⁻³)	1.664	1.560	1.499
Absorption coefficient (mm ⁻¹)	5.94	4.42	3.51
<i>F</i> (000)	840	1744	1068
Crystal size (mm ³)	0.47 × 0.26 × 0.06	0.54 × 0.46 × 0.05	0.40 × 0.16 × 0.10
θ Range for data collection	2.02–29.07	1.11–29.07	1.63–29.03
Number of reflections collected/unique (<i>R</i> _{int})	11596/7918 (0.0441)	25547/9225 (0.0604)	16631/11105 (0.0207)
Data/restraints/parameters	7918/34/358	9225/26/449	11105/18/504
Goodness-of-fit on <i>F</i> ²	0.962	1.023	1.036
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0609, <i>wR</i> ₂ = 0.1501	<i>R</i> ₁ = 0.0495, <i>wR</i> ₂ = 0.0794	<i>R</i> ₁ = 0.0399, <i>wR</i> ₂ = 0.0966
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0751, <i>wR</i> ₂ = 0.1564	<i>R</i> ₁ = 0.0891, <i>wR</i> ₂ = 0.0903	<i>R</i> ₁ = 0.0505, <i>wR</i> ₂ = 0.1024
Largest difference in peak and hole (e Å ⁻³)	2.31 and -1.50	0.88 and -0.69	0.96 and -0.49

(CDCl₃, δ in ppm): 28.7 (s; C-(CH₃)₃), 30.4 (s; CH₃), 69.7 (dd, ¹*J*_{C-P} = 105.4 Hz, ³*J*_{C-P} = 7.0 Hz; ≡C-P), 122.1 (AXX', three lines are observed, ²*J*_{C-P} + ⁴*J*_{C-P} = 12.4 Hz; ≡C-C_{ar}), 127.2–134.6 (m; C_{ar}), 187.1–189.8 (m; CO). ESI/MS (positive mode, *m/z*): 803.3 [M-Br]⁺.

4.1.4. Synthesis of [ReBr(CO)₃{(o-tolyl)₂PC≡CPh}₂] · C₇H₈ (**8**)

To a solution of [NEt₄]₂[ReBr₃(CO)₃] (0.1 g, 0.13 mmol) in EtOH/H₂O (6 mL:4 mL) was added a solution of (o-tolyl)₂PC≡CPh (0.14 mmol) in EtOH (10 mL). The reaction mixture was heated to reflux and water (20 mL) was slowly added during 100 min (2 mL/min). After addition was complete, reflux was continued for additional 80 min. A white precipitated was formed, which was filtered, washed with 2 × 5 mL of a cold 50% water:EtOH mixture and recrystallized in toluene/hexane.

Yield: 56%. Anal. Calc. for C₅₄H₄₆O₃BrP₂Re: C, 60.56; H, 4.33. Found: C, 60.70; H, 4.28%. IR (CH₂Cl₂, cm⁻¹): 2177 (s, C≡C), 2038 (vs, C=O), 1958 (vs, C=O), 1913 (vs, C=O). ¹H NMR (CDCl₃, δ in ppm): 2.08 (s; CH₃), 2.16 (s; CH₃), 7.00–7.30 (m; H_{ar}), 8.35 (dd, ⁴*J*_{P-H} = 14.4 Hz, ⁴*J*_{H-H} = 7.4 Hz; H *ortho* position tolyl group), 8.45 (dd, ⁴*J*_{P-H} = 14.4 Hz, ⁴*J*_{H-H} = 7.4 Hz; H *ortho* position tolyl group). ³¹P{¹H} NMR (CDCl₃, δ in ppm): -23.4 (s). ¹³C{¹H} NMR (CDCl₃, δ in ppm): 21.5 (s; CH₃), 21.8 (s; CH₃), 82.3 (d, ¹*J*_{C-P} = 88.6 Hz; ≡C-P), 109.4 (d, ²*J*_{C-P} = 11.4 Hz; ≡C-C_{ar}), 121.2 (s; C_{ar}), 124.8–137.3 (m; C_{ar}), 141.2 (d, *J* = 10.4 Hz; C_{ar}), 187.1–189.3 (m; CO). ESI/MS (positive mode, *m/z*): 899.1 [M-Br]⁺.

4.2. X-ray crystallography

Table 4 reports crystal data and structure refinement details for complexes **2**, **6** and **8**. Colorless crystals of these compounds were obtained by slow evaporation from dichloromethane/toluene solutions at room temperature under nitrogen atmosphere. Diffraction data were collected using a SMART Apex CCD area detector diffractometer with Mo K α radiation. Data reduction was carried out using the SAINT program [38] and absorption corrections were applied (SADABS [39]). Structures were solved by direct methods and refined by full-matrix least-squares methods on *F*² for all reflections (SHELXTL [40]).

In **2**, the cation, [NEt₄]⁺, is disordered. Two positions for every methylene and for one methyl groups were considered and the

corresponding site occupation factors were refined. Geometric restraints were applied. These five split atoms were refined with isotropic displacement parameters, *U*, and the rest of non-hydrogen atoms in the structure, with anisotropic *U*_{ij}. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters fixed at 1.5 (methyl H atoms) or 1.2 (the rest) times the *U*_{eq} of the corresponding carbon atoms.

In **6**, the Br and the opposite CO show positional disorder. In Fig. 2, only the main component of disorder (70%) is shown. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters fixed at 1.5 (methyl H atoms) or 1.2 (benzenic H atoms) times the *U*_{eq} of the corresponding carbon atoms.

In **8**, the crystal structure is a 1:1 complex:toluene solvate. The solvent molecule is highly disordered. Two constrained benzene rings and four positions for methyl C atom, partially overlapped, were considered and refined with isotropic displacement parameters. H atoms were not included in this model of disordered solvent. For the complex, non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in calculated positions with isotropic displacement parameters fixed at 1.5 (methyl H atoms) or 1.2 (benzenic H atoms) times the *U*_{eq} of the corresponding carbon atoms.

5. Supplementary material

CCDC 686111, 686112, and 686113 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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