

# Synthesis of Re–Ru heterobimetallic polyhydride complexes. Study of the influence of ligands bonded to the monometallic precursors on the nature of the isolated binuclear complexes

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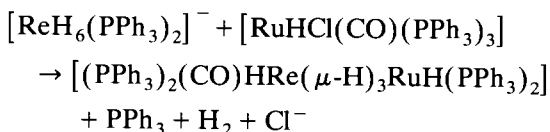
## Abstract

The reaction of  $K [H_6ReL_2]$  with  $[RuHCl(CO)(PPh_3)_{3-x}\{P(OPr^i)_3\}_x]$  ( $L_2 = (PMePh_2)_2$ , dppe,  $(AsPh_3)_2$ , or  $(PPh_3)_2$ ;  $x = 0, 1$  or  $2$ ) leads to  $[L_2(CO)HRe(\mu-H)_3RuH(PPh_3)_{2-y}\{P(OPr^i)_3\}_y]$  ( $x = 0$  or  $1, y = 0$ ;  $x = 2, y = 1 (L_2 = PPh_3)$ ) in a first step. Under the reaction conditions most of these complexes react rapidly with the liberated phosphine giving  $[L_2(CO)Re(\mu-H)_3Ru(PPh_3)_{3-y}\{P(OPr^i)_3\}_y]$  ( $L_2 = (PMePh_2)_2$  or dppe,  $y = 0$ ;  $L_2 = (PPh_3)_2, y = 1$ ) as the only isolable complexes. The structure of  $[(PMePh_2)_2(CO)Re(\mu-H)_3Ru(PPh_3)_3]$  has been established by X-ray structure analysis. The complex  $[(PPh_3)_2(CO)Re(\mu-H)_3Ru(PPh_3)_2(P(OPr^i)_3)]$  reacts with molecular hydrogen under pressure to generate  $[L_2(CO)HRe(\mu-H)_3RuH(PPh_3)(P(OPr^i)_3)]$  as the sole product.

**Keywords:** Ruthenium; Rhenium; X-ray structure; Hydrido complexes; Binuclear complexes

## 1. Introduction

In a recent publication [1] we have shown that  $[(CO)(PPh_3)_2HRe(\mu-H)_3RuH(PPh_3)_2]$  (**1**) is obtained easily at room temperature by the reaction of  $[RuHCl(CO)(PPh_3)_3]$  with  $[ReH_6(PPh_3)_2]^-$  according to the equation shown.



This reaction proceeds with loss of triphenylphosphine and molecular hydrogen, which is unexpected as the final product is an unsaturated 30-electron complex. To check the influence of the ligands bonded to rhenium or ruthenium on the structure of the reaction products, we have extended the study to the cases where triphenylphosphine on rhenium or ruthenium has been replaced by ligands of different steric or

electronic properties. In the case of rhenium these are triphenylarsine, methyl-diphenylphosphine or bis(diphenylphosphino)ethane (dppe) and in the case of ruthenium the complexes  $[RuHCl(CO)(PPh_3)_{3-x}\{P(OPr^i)_3\}_x]$  ( $x = 1$  or  $2$ ) have been used. We report here the results of this study.

## 2. Results and discussion

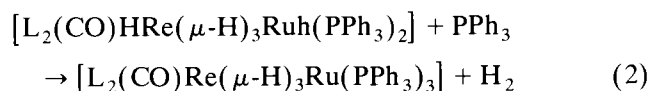
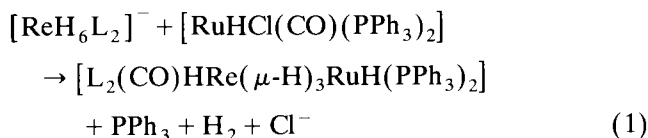
### 2.1. Reactivity of $[K][ReH_6L_2]$ towards $[RuHCl(CO)(PPh_3)_3]$ $L_2 = (PMePh_2)_2$ or dppe

Compared to the reaction of the rhenium complex with triphenylphosphine, this reaction is slow, and heating at  $40^\circ C$  is necessary to cause completion. The IR spectra of the isolated complexes **2** ( $L = PMePh_2$ ) and **3** ( $L = dppe$ ) are very similar in the  $\nu(CO)$ -stretching region ( $1810\text{ cm}^{-1}$  (**2**),  $1815\text{ cm}^{-1}$  (**3**)) but these values are quite different from the value observed for **1** ( $1865\text{ cm}^{-1}$ ) suggesting the formation of a compound of different structure. This is corroborated by the  $^{31}P$   $\{^1H\}$  NMR spectra, which show, at room temperature,

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in either case two signals in the ratio 3:2, the signal of intensity three being in the region of resonance of the triphenylphosphine bonded to ruthenium. In the  $^1\text{H}$  NMR spectrum at room temperature, a broad doublet is observed in the hydride region for the two complexes, and in the case of **2** it is possible, by comparison with the methyl resonance of the diphenylmethylphosphine, to determine that three hydride ligands are present. This is corroborated by the  $^1\text{H}$  NMR spectrum of **3** at 183 K which shows two broad resonances in the ratio 2:1. All these data are consistent with the formulation  $[(\text{CO})(\text{L})_2\text{Re}(\mu\text{-H})_3\text{Ru}(\text{PPh}_3)_3]$  for **2** and **3**. This has been confirmed by an X-ray structure determination for **2** which will be discussed later. These molecules are fluxional, and their fluxionality can be accounted for by a rotation of the three bridging hydrides relative to the fixed  $\text{Re}(\text{CO})\text{L}_2$  and  $\text{Ru}(\text{PPh}_3)_3$  moieties, as in complexes  $[(\text{CO})(\text{PPh}_3)_2\text{HRe}(\mu\text{-H})_3\text{RhL}_2]$  [2].

To obtain an insight about the mechanism of formation of **2** and **3**, the reaction was monitored by IR spectroscopy. In each case a new  $\nu(\text{CO})$  absorption is observed in the first minutes of the reaction (at  $1860\text{ cm}^{-1}$  during the synthesis of **2** and at  $1865\text{ cm}^{-1}$  during the synthesis of **3**) but the  $\nu(\text{CO})$  absorptions of **2** and **3** gradually grow at their expense. This is consistent with the transient formation of complexes with structures similar to that of **1**, and the subsequent displacement of one molecule of hydrogen by triphenylphosphine. We have observed a similar reaction between acetonitrile and **1** [3]. Eqs. (1) and (2) summarize our observations.



Complex **1** does not react with triphenylphosphine under the same conditions. The reason for this difference of reactivity is not clear, but may be a result of less steric crowding around rhenium.

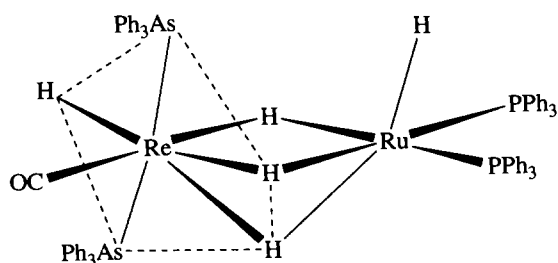


Fig. 1. Proposed structure for complex **4**.

## 2.2. Reactivity of $K[\text{ReH}_6(\text{AsPh}_3)_2]$ towards $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$

$K[\text{ReH}_6(\text{AsPh}_3)_2]$  reacts with the ruthenium complex in the same way as its triphenylphosphine analogue. The reaction proceeds at room temperature leading to  $[(\text{CO})(\text{AsPh}_3)_2\text{HRe}(\mu\text{-H})_3\text{RuH}(\text{PPh}_3)_2]$  (**4**) in good yield. This complex is characterized by a  $\nu(\text{CO})$  absorption at  $1855\text{ cm}^{-1}$ . At room temperature the  $^1\text{H}$  NMR spectrum is also very similar to **1** in the hydride region: we observed a singlet at  $-4.49\text{ ppm}$  for the hydride terminally bonded to rhenium, a triplet for the terminal hydride bonded to ruthenium at  $-17.98\text{ ppm}$  ( $J_{\text{PH}} = 33\text{ Hz}$ ) and a broad resonance at  $-6.14\text{ ppm}$ , these signals being in the ratio of intensity 1:1:3. On lowering the temperature to 193 K the spectrum develops to five signals of the same intensity (see experimental section) confirming a structure similar to that of **1**. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum a single resonance at 71.3 ppm is observed at room temperature, characteristic of the two phosphines bonded to ruthenium. It changes to an AB spectrum at 193 K. We propose the structure shown in Fig. 1 for **4**, similar to the structure of **1** established by X-ray analysis [1].

## 2.3. Reactivity of $K[\text{ReH}_6(\text{PPh}_3)_2]$ toward $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_{3-x}\{\text{P}(\text{OPr}^i)_3\}_x]$ ( $x = 1$ or $2$ )

To investigate the influence of the ligands to ruthenium on the course of the reaction with  $K[\text{ReH}_6(\text{PPh}_3)_2]$  we have chosen to replace progressively the triphenylphosphine by a ligand with a different electronic property and which is known to stabilize bimetallic polyhydrides complexes,  $\text{P}(\text{OPr}^i)_3$  [4].

Starting from  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$  the progressive replacement of triphenylphosphine is possible by changing the stoichiometry and the temperature of the reaction. This procedure has been developed for the synthesis of similar triphenyl phosphite derivatives [5].

At room temperature, the action of one equivalent of triisopropyl phosphite leads to the selective formation of  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2\text{P}(\text{OPr}^i)_3]$  (**5**). The structure of this complex has been deduced from  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data (see experimental section) which show, as expected, that the triisopropyl phosphite has replaced the triphenylphosphine *trans* to the hydride. This structure is shown in Fig. 2.

In boiling THF, **5** reacts with one equivalent of triisopropyl phosphite to give  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)\text{P}(\text{OPr}^i)_3]$  which, from the spectroscopic data (see experimental section), appears to be a mixture of two isomers **6a** and **6b**. In **6a**, the major product of the reaction (80%), the remaining triphenylphosphine is *trans* to a triisopropyl phosphite and in **6b** the phosphine is *trans* to hydride, the two phosphites being

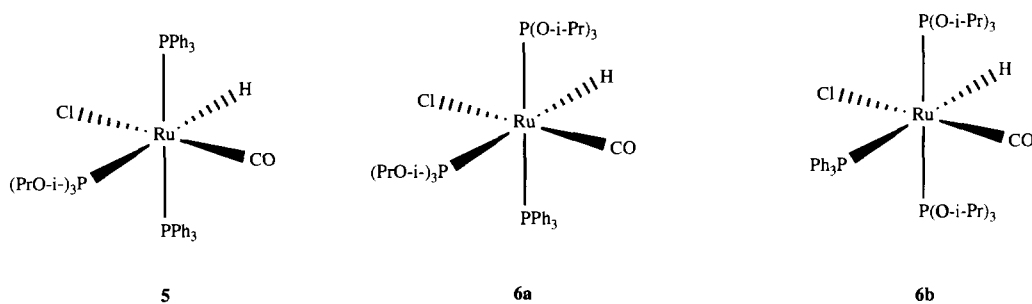


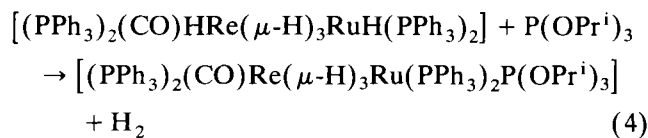
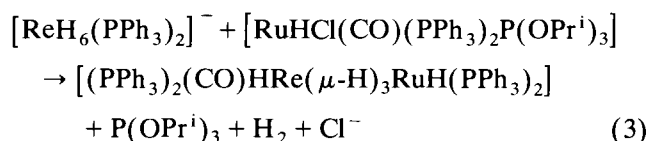
Fig. 2. Structures of complex 5 and the isomers of complex 6.

*trans*. The structures of the two isomers are shown in Fig. 2.

### 2.3.1. Reaction of $K[ReH_6(PPh_3)_2]$ with $[RuHCl(CO)(PPh_3)_2P(OPr^i)_3]$

The reaction has to be conducted at 60°C and a red compound 7 is isolated. IR spectrum in the  $\nu(CO)$ -stretching region shows an absorption at 1800  $cm^{-1}$  which suggests the formation of a complex with structure similar to that 2 and 3. This is supported by NMR data. Indeed in the  $^{31}P\{^1H\}$  NMR spectrum at room temperature, three signals are observed in the ratio of intensity 1:2:2, a triplet at 146.3 ppm ( $J = 40$  Hz) characteristic of phosphite, a doublet at 50.1 ppm ( $J = 40$  Hz) characteristic of two triphenylphosphines bonded to ruthenium, and a broad signal at 37.9 ppm characteristic of two phosphines bonded to rhenium. The  $^1H$  NMR spectrum shows in the hydride region two broad resonances in the 1/2 ratio of intensity 1:2 in the hydride region. On lowering the temperature to 183 K these signals change to three doublets and from selective phosphorus decoupling experiments it appears that one hydride is *trans* to phosphite, the other two being *trans* to the triphenylphosphines bonded to ruthenium. These results are consistent with a formulation  $[(CO)(PPh_3)_2Re(\mu-H)_3Ru(PPh_3)_2(P(OPr^i)_3)]$ .

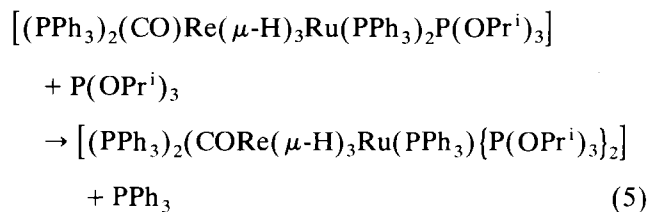
Monitoring the reaction by IR spectroscopy shows an intermediate absorption at 1865  $cm^{-1}$ , which is consistent with the transient formation of 1. This has been confirmed by  $^1H$  NMR spectra. The formation of 7 results from successive reactions (Eqs. (3) and (4)):



This has been confirmed by the reaction of 1 with a slight excess of triisopropyl phosphite in boiling THF which leads to the same complex 7 in good yield. In

addition we have also observed that with a large excess of the phosphite under the same conditions, a second triphenylphosphine is displaced leading to  $[(CO)(PPh_3)_2Re(\mu-H)_3Ru(PPh_3)(P(OPr^i)_3)_2](8)$ , which has been identified by the spectroscopic data. A  $\nu(CO)$  absorption is observed at 1810  $cm^{-1}$  and at room temperature the  $^1H$  NMR spectrum in the hydride region shows two broad doublets in the ratio of intensity 2:1. On lowering the temperature to 183 K these resonances change to three doublets in the ratio of intensity 1:1:1. At room temperature the  $^{31}P\{^1H\}$  NMR spectrum shows three signals in the ratio 2:1:2, a broad resonance at 142 ppm for the phosphites, a triplet at 52 ppm ( $J = 47$  Hz) for the phosphine bonded to ruthenium, and a broad resonance at 40.1 ppm for the phosphines bonded to rhenium. Lowering the temperature to 183 K induces the splitting of the phosphite resonance into a triplet at 149 ppm and an unresolved multiplet at 134 ppm. The signal of the phosphine bonded to ruthenium is a doublet of triplets centred at 55.8 ppm, and the phosphines bonded to rhenium appear as a broad signal at 44.7 ppm and a doublet at 42.4 ppm.

Monitoring the reaction by IR spectroscopy shows that the synthesis of 8 involves the transient formation of 7 and that it results from the successive reactions shown in the Eqs. (4) and (5).



These results give interesting informations about the mechanism of formation and the reactivity of complex 1. The ligand on the mononuclear ruthenium complex which is displaced during the condensation with the rhenium anion is *trans* to the hydride. Furthermore, the ease of displacement of molecular hydrogen in complex 1 appears to be governed by the bulk of the incoming group. It does not occur with triphenylphosphine (cone angle 145°[6]) or diphenylmethylphosphine

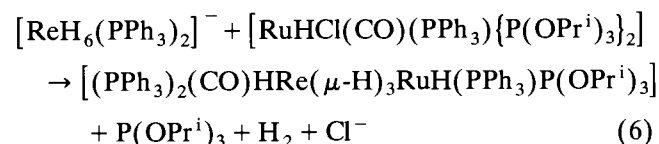
(cone angle  $136^\circ$ ) but it does occur with triisopropyl phosphite (cone angle  $130^\circ$ ).

### 2.3.2. Reaction of $K[ReH_6(PPh_3)_2]$ with $[RuHCl(CO)(PPh_3)\{P(OPr^i)_3\}_2]$

The reaction occurs at  $65^\circ\text{C}$  in THF and leads to a red product **9**, the structure of which has been deduced from spectroscopic data.

In the IR spectrum **9** shows a  $\nu(\text{CO})$  absorption at  $1849\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum at room temperature gives evidence for five hydride ligands with a triplet at  $-4.43\text{ ppm}$  ( $J = 48.7\text{ Hz}$ ), a broad resonance centred at  $-6.60\text{ ppm}$ , and a triplet at  $-18.09\text{ ppm}$  ( $J = 35.8\text{ Hz}$ ), in the ratio of intensity 1:3:1. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at the same temperature shows three signals in the ratio of intensity 1:1:2, a doublet at  $159.7\text{ ppm}$  ( $J = 55.2\text{ Hz}$ ) for the phosphite, a doublet at  $78.1\text{ ppm}$  ( $J = 55.2\text{ Hz}$ ) for the phosphine bonded to ruthenium, and an unresolved multiplet at  $35.2\text{ ppm}$  for the two phosphines bonded to rhenium. On lowering the temperature to  $193\text{ K}$  the broad resonance observed at room temperature at  $-6.60\text{ ppm}$  in the  $^1\text{H}$  NMR spectrum splits into two unresolved multiplets at  $-5.02\text{ ppm}$  and  $-7.77\text{ ppm}$  and a doublet at  $-7.90\text{ ppm}$  ( $J = 69.2\text{ Hz}$ ). At the same temperature the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a splitting of the resonance of the phosphines bonded to rhenium into two multiplets centred at  $38.9\text{ ppm}$  and  $37.5\text{ ppm}$ . All these data are consistent with the formulation  $[(\text{CO})-(\text{PPh}_3)_2\text{HRe}(\mu\text{-H})_3\text{RuH}(\text{PPh}_3)\{\text{P}(\text{OPr}^i)_3\}]$  for **9**, similar to that of **1** [1] and **4** and shown in Fig. 3.

The reaction of formation of **9** is presented by eq. (6).



The reason for the inertness of **9** toward liberated triisopropyl phosphite is not clear. We have observed that **9** reacts with the more bulky triphenylphosphine leading to **7**. Moreover the expected product **8** of the reaction of **9** with triisopropyl phosphite has been obtained, but by the displacement of triphenylphos-

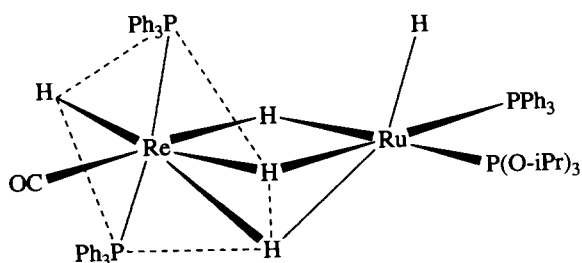


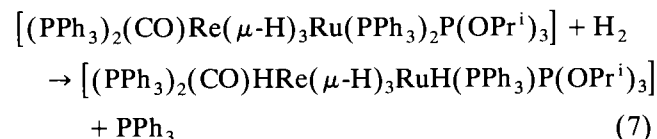
Fig. 3. Proposed structure for complex **9**.

phine from the trihydride complex  $[(\text{CO})((\text{PPh}_3)_2\text{Re}(\mu\text{-H})_3(\text{PPh}_3)_2\text{P}(\text{OPr}^i)_3)]$  (see above).

### 2.4. Reactivity of **7** toward molecular hydrogen and tetrafluoroboric acid

#### 2.4.1. Reaction with molecular hydrogen

We have shown earlier that **7** results from the reaction of **1** with triisopropyl phosphite with loss of molecular hydrogen. So we checked if the reaction of molecular hydrogen with **7** regenerates **1**, or generates **9** or a mixture of the two complexes. It is necessary to work under a pressure of  $50\text{ atm}$  of dihydrogen to observe the complete conversion of **7**. Spectroscopic data of the product isolated at the end of the reaction are identical to that of **9**. This result shows that the displacement of triphenylphosphine is selective and the observed reaction is represented by eq. (7).



#### 2.4.2. Reaction with tetrafluoroboric acid

The reaction of tetrafluoroboric acid with **7** leads to the rapid formation of a new complex which has been isolated after replacement of  $[\text{BF}_4]$  by  $[\text{BPh}_4]$ . This complex **10** has a  $\nu(\text{CO})$  absorption at  $1881\text{ cm}^{-1}$ , a shift of  $81\text{ cm}^{-1}$  compared to **7**, consistent with a protonation reaction. This is confirmed by the  $^1\text{H}$  NMR spectrum at room temperature in the hydride region which shows three signals in the ratio of intensity 1:2:2, a triplet at  $-5.12\text{ ppm}$  ( $J = 56.4\text{ Hz}$ ) characteristic of a terminal hydride bonded to rhenium [1], a doublet at  $-6.38\text{ ppm}$  ( $J = 80.6\text{ Hz}$ ), and a complex multiplet at  $-7.44\text{ ppm}$ . In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum three resonances in the ratio of intensity 1:2:2 are observed, showing that reaction has occurred without ligand displacement. The main change in the  $^1\text{H}$  NMR spectrum on lowering the temperature to  $193\text{ K}$  is the splitting of the multiplet of intensity two into two broad doublets at  $-6.87\text{ ppm}$  ( $J = 10\text{ Hz}$ ) and  $-8.14\text{ ppm}$  ( $J = 30\text{ Hz}$ ) and in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum five resonances are now observed. Selective phosphorus decoupling experiments confirm that the triplet at  $-5.12\text{ ppm}$  results from coupling with phosphines bonded to rhenium and that the other hydrides are coupled with ligands to ruthenium. All these data are consistent with the formulation  $[(\text{CO})((\text{PPh}_3)_2\text{HRe}(\mu\text{-H})_3\text{Ru}(\text{PPh}_3)_2\text{P}(\text{OPr}^i)_3)][\text{BPh}_4]$  for **10**, and we propose the structure shown in Fig. 4. The cation is fluxional in solution, and the phenomenon is similar to that observed for  $[(\text{CO})((\text{PPh}_3)_2\text{Re}(\mu\text{-H})_3\text{RuH}(\text{PPh}_3)_2(\text{CH}_3\text{CN}))]$  [3] with the exchange of two bridging hydrides, the third being unaffected. We propose the

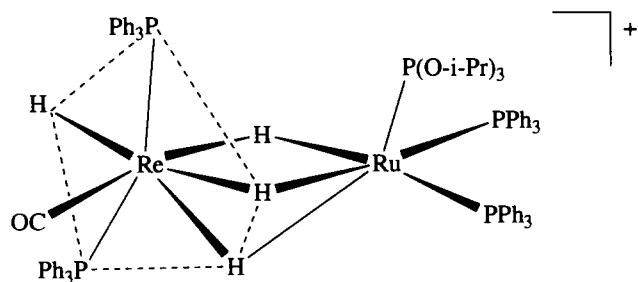


Fig. 4. Proposed structure for complex 10.

same mechanism, an exchange through intermediates with terminal hydrides on rhenium or ruthenium, the dinuclear skeleton being maintained by the third bridging hydride. A similar mechanism was proposed for the fluxionality of  $[\text{Ph}(\text{PET}_3)\text{Pt}(\mu\text{-H})_2\text{IrH}(\text{PET}_3)_3]^+$  [7].

### 2.5. X-ray crystal structure of complex 2

A perspective view of the core of complex 2 is given in Fig. 5, along the labelling scheme. Bond lengths and bond angles of interest are gathered in Table 1. The structure consistent with the spectroscopic data, consists of a dinuclear ReRu unit in which the two metals are bridged by three hydride ligands which were not directly located, but their positions were calculated by the program HYDEX [8]. The overall structure can be described as the union of two distorted octahedra sharing the H(1)H(2)H(3) face. The rhenium atom is bonded to two methylphenylphosphines and a carbonyl group, and the ruthenium atom is surrounded by the three triphenylphosphines. The electronic unsaturation of 2 is reflected by the Re–Ru distance (2.595(1) Å) which is similar to the value found for the isoelectronic complex  $[(\text{CO})(\text{PPh}_3)_2\text{HRe}(\mu\text{-H})_3\text{RuH}(\text{PPh}_3)_2]$  (2.593(2) Å) [1] and is shorter than the value found for the isostructural 32-electron complex  $[(\text{CO})(\text{PPh}_3)_2\text{Re}(\mu\text{-H})_2(\mu\text{-NCHPh})\text{Ru}(\text{PhCN})(\text{PPh}_3)_2]$  (2.654(1) Å)

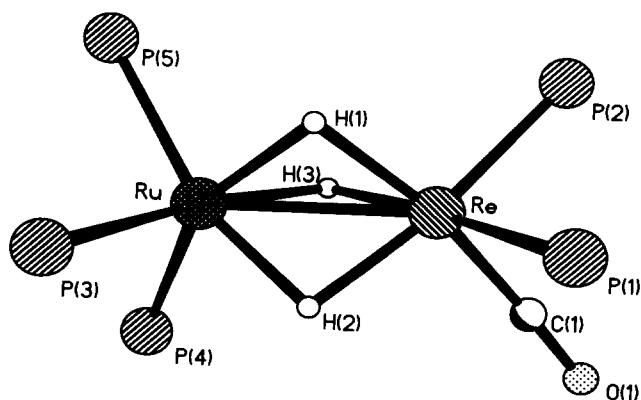


Fig. 5. Perspective view of the core of complex 2, showing the labelling scheme.

Table 1

Selected bond lengths (Å) and angles (°) for  $[(\text{CO})(\text{PMePh}_2)_2\text{Re}(\mu\text{-H})_3\text{Ru}(\text{PPh}_3)_3]$

Re(1)–C(1)	1.84(1)	P(2)–C(41)	1.84(1)
Re(1)–P(2)	2.303(3)	P(2)–C(51)	1.84(1)
Re(1)–P(1)	2.320(3)	P(2)–C(61)	1.84(1)
Re(1)–Ru(1)	2.595(1)	P(3)–C(71)	1.85(1)
Ru(1)–P(3)	2.344(3)	P(3)–C(81)	1.85(1)
Ru(1)–P(5)	2.373(3)	P(3)–C(91)	1.86(1)
Ru(1)–P(4)	2.403(3)	P(4)–C(101)	1.87(1)
P(1)–C(11)	1.85(1)	P(4)–C(111)	1.86(1)
P(1)–C(21)	1.83(1)	P(4)–C(121)	1.87(1)
P(1)–C(31)	1.84(1)	P(5)–C(131)	1.86(1)
C(1)–O(1)	1.19(2)	P(5)–C(141)	1.84(1)
		P(5)–C(151)	1.86(1)
P(3)–Ru–P(5)	97.2(1)	P(3)–Ru–P(4)	101.0(1)
P(3)–Ru–Re	120.5(1)	P(5)–Ru–P(4)	107.0(1)
P(5)–Ru–Re	119.17(8)	P(4)–Ru–Re	109.71(7)
C(1)–Re–P(2)	87.4(4)	C(21)–P(1)–C(31)	98.4(6)
C(1)–Re–P(1)	85.6(4)	C(21)–P(1)–C(111)	101.7(6)
C(1)–Re–Ru	125.2(2)	C(31)–P(1)–C(111)	102.3(6)
P(2)–Re–P(1)	93.9(1)	C(61)–P(2)–C(41)	100.5(6)
P(2)–Re–Ru	126.51(9)	C(61)–P(2)–C(51)	99.2(6)
P(1)–Re–Ru	125.81(8)	C(41)–P(2)–C(51)	98.4(5)
C(81)–P(3)–C(71)	100.2(5)	C(81)–P(3)–C(91)	98.5(5)
C(71)–P(3)–C(91)	100.3(5)	C(111)–P(4)–C(121)	100.8(6)
C(111)–P(4)–C(101)	97.9(6)	C(121)–P(4)–C(101)	100.0(5)
C(141)–P(5)–C(151)	102.7(5)	C(141)–P(5)–C(131)	96.6(5)
C(151)–P(5)–C(131)	99.3(5)	O(1)–C(1)–Re	177(1)

[3]. This is consistent with a formal Re–Ru triple bond expected for a 30-electron dinuclear species.

### 3. Experimental details

All reactions were performed under dinitrogen with standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 200 ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) and WM 250 ( $^1\text{H}$ ,  $^{31}\text{P}$ ) instruments. Variable-temperature and selective-decoupling experiments were carried out on the WM 250 machine. Elemental analyses were performed in our laboratory for C and H. Complexes  $[\text{ReH}_7\text{L}_2]$  were synthesised by an adaptation of the procedure used for the synthesis of  $[\text{ReH}_7(\text{PPh}_3)_2]$  [9], starting from  $[\text{ReOCl}_3\text{L}_2]$  synthesized by ligand exchange from  $[\text{ReOCl}_3(\text{AsPh}_3)_2]$  [10].

#### 3.1. Synthesis of $[(\text{CO})(\text{PMePh}_2)_2\text{Re}(\mu\text{-H})_3\text{Ru}(\text{PPh}_3)_3]$ (2)

To a solution of 0.2 g (0.34 mmol) of  $[\text{ReH}_7(\text{PMePh}_2)_2]$  in 30 ml of THF was added an excess of KH, and the solution was stirred for 1 h giving a yellow solution. The solution was then filtered to eliminate the excess of KH and added to 0.35 g (0.36 mmol) of  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ . After stirring at 40°C for 2 h, the red-brown solution was evaporated to dryness. The

residue was dissolved in toluene (10 ml) and chromatographed on neutral alumina (activity 3). Elution with a 5:1 Et<sub>2</sub>O:hexane mixture allowed the isolation of a dark-red fraction. After evaporation of the solution under vacuum, recrystallisation of the residue from the same solvent mixture at 0°C gave 0.3 g of **2** as dark-red crystals (60%).

Anal. Calc. for C<sub>81</sub>H<sub>74</sub>OP<sub>5</sub>ReRu: C, 64.62; H, 4.95. Found: C, 64.32; H, 4.89%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1810 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 1.47 (broad, Me), -6.98 (bd, *J* = 28 Hz, 3H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR: 49.2 (PPh<sub>3</sub>), 18.9 (PMePh<sub>2</sub>) ppm.

### 3.2. Synthesis of [(CO)(dppe)Re(μ-H)<sub>3</sub>Ru(PPh<sub>3</sub>)<sub>3</sub>] (**3**)

To a solution of 0.2 g (0.34 mmol) of [ReH<sub>7</sub>(dppe)] in 30 ml of THF was added an excess of KH, and the solution was stirred for 1 h giving a yellow solution. The solution was then filtered to eliminate the excess of KH and added to 0.35 g (0.36 mmol) of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>]. After stirring at 40°C for 2 h, the red-brown solution was evaporated to dryness. The residue was dissolved in toluene (10 ml) and chromatographed on neutral alumina (activity 3). Elution with a 4:1 Et<sub>2</sub>O:hexane mixture allowed the isolation of a dark-red fraction. After evaporation of the solution under vacuum, recrystallisation of the residue from the same solvent mixture at 0°C gave 0.4 g of **3** as dark-red crystals (80%).

Anal. Calc. for C<sub>81</sub>H<sub>72</sub>OP<sub>5</sub>ReRu: C, 64.70; H, 4.83. Found: C, 64.54; H, 4.61%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1815 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 2.14 (multiplet, CH<sub>2</sub>), -6.01 (broad d, *J* = 28 Hz, 3H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR: 68.2 (q, *J* = 4 Hz, dppe), 52.2 (t, *J* = 4 Hz, PPh<sub>3</sub>) ppm.

### 3.3. Synthesis of [(CO)(AsPh<sub>3</sub>)<sub>2</sub>HRe(μ-H)<sub>3</sub>RuH(PPh<sub>3</sub>)<sub>2</sub>] (**4**)

To a solution of 0.4 g (0.5 mmol) of [ReH<sub>7</sub>(AsPh<sub>3</sub>)<sub>2</sub>] in 60 ml of THF was added an excess of KH, and the solution was stirred for 1 h giving a yellow solution. The solution was then filtered to eliminate the excess of KH and added to 0.52 g (0.55 mmol) of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>]. After stirring at room temperature for 2 h, the orange solution was evaporated to dryness. The residue was dissolved in toluene (5 ml) and chromatographed on neutral alumina (activity 3). Elution with a 4:1 Et<sub>2</sub>O:hexane mixture allowed the isolation of a dark-red fraction. After evaporation of the solution under vacuum, recrystallisation of the residue in the same solvent mixture at 0°C gave 0.5 g of **4** as orange crystals (65%).

Anal. Calc. for C<sub>73</sub>H<sub>65</sub>As<sub>2</sub>OP<sub>2</sub>ReRu: C, 60.16; H, 4.5. Found: C, 59.73; H, 4.28%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1815 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances:

-4.49 (s, 1H), -6.14 (b, 3H), -17.98 (t, *J* = 33 Hz) ppm (298 K); -4.66 (s, 1H), -5.15 (s, 1H), -7.04 (d, *J* = 19.7 Hz, 1H), -8.71 (d, *J* = 36.1 Hz), -18.32 (t, *J* = 30.7 Hz, 1H) ppm (193 K)(CD<sub>2</sub>Cl<sub>2</sub> sol). <sup>31</sup>P{<sup>1</sup>H} NMR: 71.3 ppm (298 K). 72.7 (AB system, *J* = 31.6 Hz), 72.2 (AB system, *J* = 31.6 Hz) ppm (193 K).

### 3.4. Synthesis of [RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>P(OPr<sup>i</sup>)<sub>3</sub>] (**5**)

To a solution of 2 g (2.1 mmol) of [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] in 20 ml of toluene was added 0.5 ml (2 mmol) of P(OPr<sup>i</sup>)<sub>3</sub>, and the solution was stirred for 0.5 h. The solution was evaporated to dryness and the residue was washed five times with 10 ml of hexane to eliminate the liberated triphenylphosphine. The remaining solid was dried under vacuum giving 1.6 g of **5** as a grey solid (85%).

Anal. Calc. for C<sub>46</sub>H<sub>52</sub>ClO<sub>4</sub>P<sub>3</sub>Ru: C, 61.50; H, 5.83. Found: C, 61.73; H, 6.03%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1950 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 4.65 (m, 3 H, OCH), 1.10 (d, *J* = 6.1 Hz, 18 H), -5.20 (dt, *J*<sub>1</sub> = 15.5 Hz, *J*<sub>2</sub> = 168.2 Hz, 1H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR: 138.1 (t, *J* = 24.7 Hz), 38.9 (d, *J* = 24.7 Hz) ppm.

### 3.5. Synthesis of [RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>{P(OPr<sup>i</sup>)<sub>3</sub>}<sub>2</sub>] (**6a**, **6b**)

To a solution of 1.6 g (1.6 mmol) of [RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>P(OPr<sup>i</sup>)<sub>3</sub>] in 20 ml of THF was added 0.44 ml (1.8 mmol) of P(OPr<sup>i</sup>)<sub>3</sub> and the solution was heated under reflux for 0.25 h. The solution was evaporated to dryness and the residue was dissolved in 3 ml of methanol leading to a white precipitate which was dried under vacuum. 0.8 g (53%).

Anal. Calc. for C<sub>37</sub>H<sub>58</sub>ClO<sub>7</sub>P<sub>3</sub>Ru: C, 52.64; H, 6.92. Found: C, 52.48; H, 6.34%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1957 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 5.03 (m, 6 H, OCH), 1.23 (m, 36H), -5.94 (ddd, *J*<sub>1</sub> = 21.3 Hz, *J*<sub>2</sub> = 25.3 Hz, *J*<sub>3</sub> = 153.7 Hz **6a**), -7.25 (dt, *J*<sub>1</sub> = 25.2 Hz, *J*<sub>2</sub> = 104.2 Hz, **6b**) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR. **6a**: 142.6 (dd, *J*<sub>1</sub> = 40 Hz, *J*<sub>2</sub> = 32 Hz), 136.7 (dd, *J*<sub>3</sub> = 450.7 Hz, *J*<sub>2</sub> = 32 Hz), 34.6 (dd, *J* = 40 Hz, *J* = 450.7 Hz) ppm **6b**: 137.8 (d, *J* = 28 Hz), 19.7 (t, *J* = 28 Hz) ppm.

### 3.6. Synthesis of [(CO)(PPh<sub>3</sub>)<sub>2</sub>Re(μ-H)<sub>3</sub>Ru(PPh<sub>3</sub>)<sub>2</sub>P(OPr<sup>i</sup>)<sub>3</sub>] (**7**)

(a) From [ReH<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub>] and **5**

To a solution of 0.4 g (0.56 mmol) of [ReH<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub>] in 40 ml of THF was added an excess of KH, and the solution was stirred for 1 h giving a yellow solution. The solution was then filtered to eliminate the excess of KH and added to 0.5 g (0.56 mmol) of [RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>P(OPr<sup>i</sup>)<sub>3</sub>]. After stirring at 60°C for 1 h, the red solution was evaporated to dryness. The residue was dissolved in toluene (5 ml) and chromatographed

on neutral alumina (activity 3). Elution with a 1:1 THF:Et<sub>2</sub>O mixture allowed the isolation of a dark-red fraction. After evaporation of the solution under vacuum, recrystallisation of the residue in a toluene/hexane solvent mixture at 0°C gave 0.5 g of **7** as dark-red crystals (56%).

Anal. Calc. for C<sub>82</sub>H<sub>84</sub>O<sub>4</sub>P<sub>5</sub>ReRu: C, 62.51; H, 5.37. Found C, 62.12; H, 5.38%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1800 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 5.12 (bs, 3H), 1.27 (bs, 18H), -5.34 (bs, 1H), -8.52 (bs, 2H) ppm (297 K); 5.18 (m, 3H), 1.22 (m, 18H), -5.41 (d,  $J_{\text{P1H}} = 93.1$  Hz, 1H), -8.02 (d,  $J_{\text{P2H}}$  or  $J_{\text{P3H}} = 46.5$  Hz, 1H), -8.85 (d,  $J_{\text{P2H}}$  or  $J_{\text{P3H}} = 48.5$ , 1H) ppm (183 K)(CD<sub>2</sub>Cl<sub>2</sub> sol.). <sup>31</sup>P{<sup>1</sup>H} NMR: 142.3 (P<sub>1</sub>, t,  $J_1 = 40$  Hz), 50.1 (P<sub>2</sub> + P<sub>3</sub>, dd,  $J_2 = 4$  Hz,  $J_1 = 40$  Hz), 37.9 (P<sub>4</sub> + P<sub>5</sub>) ppm (297 K); 146.3 (P<sub>1</sub>, t,  $J = 34$  Hz), 51.5 (P<sub>2</sub>, m), 49.7 (P<sub>3</sub>, m), 41 (P<sub>4</sub>, m), 40.6 (P<sub>5</sub>, m) ppm (183 K).

(b) From [(CO)(PPh<sub>3</sub>)<sub>2</sub>HRe(μ-H)<sub>3</sub>RuH(PPh<sub>3</sub>)<sub>2</sub>] and P(OPr<sup>i</sup>)<sub>3</sub>

To a solution of 0.1 g (0.07 mmol) of [(CO)(PPh<sub>3</sub>)<sub>2</sub>HRe(μ-H)<sub>3</sub>RuH(PPh<sub>3</sub>)<sub>2</sub>] in 15 ml of THF was added 0.04 ml of P(OPr<sup>i</sup>)<sub>3</sub> and the solution was heated under reflux for 2 h. The solution was then evaporated to dryness. The residue was recrystallised from a toluene/hexane solvent mixture at 0°C giving 0.07 g of **7** as dark-red crystals (60%).

### 3.7. Synthesis of [(CO)(PPh<sub>3</sub>)<sub>2</sub>Re(μ-H)<sub>3</sub>Ru(PPh<sub>3</sub>)<sub>2</sub>]{P(OPr<sup>i</sup>)<sub>3</sub>}<sub>2</sub> (**8**)

To a solution of 0.1 g (0.07 mmol) of [(CO)(PPh<sub>3</sub>)<sub>2</sub>HRe(μ-H)<sub>3</sub>RuH(PPh<sub>3</sub>)<sub>2</sub>] in 15 ml of THF was added 0.3 ml of P(OPr<sup>i</sup>)<sub>3</sub> (1.2 mmol) and the solution was heated under reflux for 2 h. The solution was then evaporated to dryness. The residue was dissolved in hexane and cooled to 0°C, giving 0.07 g of **8** as dark-red crystals (63%).

Anal. Calc. for C<sub>73</sub>H<sub>90</sub>O<sub>7</sub>P<sub>5</sub>ReRu: C, 57.62; H, 5.96. Found: C, 57.52; H, 5.49%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1810 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 5.12 (m, 6H), 1.29 (bm, 36H), -6.21 (b, 2H), -8.60 (b, 1H) ppm (297 K); 4.76 (m, 6H), 0.73 (m, 36H), -6.34 (d,  $J_{\text{P1H}} = 95.2$  Hz, 1H), -7.41 (d,  $J_{\text{P2H}} = 78.6$  Hz, 1H), -8.58 (d,  $J_{\text{P3H}} = 37.7$  Hz, 1H), ppm (183 K) (CD<sub>2</sub>Cl<sub>2</sub> sol). <sup>31</sup>P{<sup>1</sup>H} NMR: 142.0 (P<sub>1</sub> + P<sub>2</sub>, b), 52 (P<sub>3</sub>, t,  $J = 47$  Hz), 40.1 (P<sub>4</sub> + P<sub>5</sub>) ppm (297 K); 149 (P<sub>1</sub>, t,  $J_{\text{P1P2}} = J_{\text{P1P3}} = 48$  Hz), 134 (P<sub>2</sub>, bm), 55.8 (P<sub>3</sub>, dt,  $J_{\text{P3P4}} = 14.6$ ,  $J_{\text{P1P3}} = 48$  Hz), 44.7 (P<sub>4</sub>, bs), 42.4 (P<sub>5</sub>, d,  $J = 23.7$  Hz) ppm (183 K).

### 3.8. Synthesis of (CO)(PPh<sub>3</sub>)<sub>2</sub>HRe(μ-H)<sub>3</sub>RuH(PPh<sub>3</sub>)<sub>2</sub>(P(OPr<sup>i</sup>)<sub>3</sub>) (**9**)

To a solution of 0.4 g (0.56 mmol) of ReH<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub> in 40 ml of THF was added an excess of KH, and the solution was stirred for 1 h giving a yellow solution.

The solution was then filtered to eliminate the excess of KH and added to 0.5 g (0.56 mmol) of RuHCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(P(OPr<sup>i</sup>)<sub>3</sub>)<sub>2</sub>. The mixture was stirred at 70°C temperature for 1 h the orange solution was evaporated to dryness. The residue was dissolved in toluene (5 ml) and chromatographed on neutral alumina (activity 3). Elution with a 1:1 THF:Et<sub>2</sub>O mixture allowed the isolation of a red fraction. After evaporation of the solution under vacuum, recrystallisation of the residue in the same solvent mixture at 0°C gave 0.6 g of **9** as red crystals (68%).

Anal. Calc. for C<sub>64</sub>H<sub>71</sub>O<sub>4</sub>P<sub>4</sub>ReRu: C, 58.44; H, 5.44. Found: C, 58.63; H, 5.22%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1849 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) except phenyl resonances: 4.84 (m, 3H), 1.17 (m, 18H), -4.43 (t,  $J = 48.7$  Hz, 1H), -6.6 (b, 3H), -18.09 (t,  $J = 35.8$  Hz, 1H) ppm (297 K); 4.31 (m, 3H), 0.72 (m, 18H), -4.82 (t,  $J_{\text{P3H}} = J_{\text{P4H}} = 51.2$  Hz, 1H), -5.02 (b, 1H), -7.77 (b, 1H), -7.90 (d,  $J_{\text{P1H}} = 69.2$  Hz), -18.5 (t,  $J_{\text{P1H}} = J_{\text{P2H}} = 34.6$  Hz, 1H) ppm (193 K) (CD<sub>2</sub>Cl<sub>2</sub> sol). <sup>31</sup>P{<sup>1</sup>H} NMR: 159.7 (d,  $J = 55.2$  Hz), 78.1 (d,  $J = 55.2$  Hz), 35.2 (b) ppm (297 K); 163.7 (P<sub>1</sub>, d,  $J_{\text{P1P2}} = 54.9$  Hz), 82.9 (P<sub>2</sub>, ddd,  $J_{\text{P2P4}} = 4$  Hz,  $J_{\text{P2P3}} = 12$  Hz,  $J_{\text{P1P2}} = 54.9$  Hz), 38.9 (P<sub>3</sub>,

Table 2

Experimental data for X-ray study of compound [(CO)(PMePh<sub>2</sub>)<sub>2</sub>Re(μ-H)<sub>3</sub>Ru(PPh<sub>3</sub>)<sub>3</sub>]

Formula	C <sub>81</sub> H <sub>74</sub> O <sub>5</sub> ReRu
$F_w$ , amu	1505.62
$a$ , Å	16.387(1)
$b$ , Å	17.527(2)
$c$ , Å	13.156(1)
$\alpha$ , °	90.20(2)
$\beta$ , °	100.31(1)
$\gamma$ , °	86.51(1)
$V$ , Å <sup>3</sup>	3710(1)
$Z$	2
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.333
Space group	$P\bar{1}$
$t$ , °C	22
Radiation	Mo K $\alpha$ , $\lambda(\text{Mo K}\alpha_1) = 0.7093$ Å
Linear abs coeff, cm <sup>-1</sup>	18.67
Transmission factors <sup>a</sup>	0.72–0.99
Receiving aperture, mm	4.0 × 4.0
Take-off angle, deg	3.0
Scan speed, deg min <sup>-1</sup>	variable, 2–8
Scan mode	$\omega/2\theta$
Scan range, °	0.75 below K $\alpha_1$ to 0.75 above K $\alpha_2$
$2\theta$ limit, °	2–46
Number of collected data	10283
Number of data used in final refinement, $F_o^2 > 4\sigma(F_o^2)$	7614
Final number of variables	402
$R$ (on $F_o$ , $F_o^2 > 3\sigma(F_o^2)$ ) <sup>b</sup>	0.0469
$R_w$ (on $F_o$ , $F_o^2 > 3\sigma(F_o^2)$ ) <sup>c</sup>	0.0691
Error in observ. of unit weight, $e^2/4.7$	

<sup>a</sup>  $\psi$ -scan method; <sup>b</sup>  $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ ; <sup>c</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / (\sum w|F_o|^2)]^{1/2}$ , unit weights.

Table 3

Fractional atomic coordinates and isotropic or equivalent temperature factors ( $\text{\AA}^2 \times 100$ ) with e.s.d.'s in parentheses ( $U_{\text{eq}} = 1/3$  trace  $U$ ) for  $[(\text{CO})(\text{PMePh}_2)_2\text{Re}(\mu\text{-H})_3\text{Ru}(\text{PPh}_3)_3]$

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Re	0.22003(3)	0.84616(3)	0.30681(4)	3.68(3)
Ru	0.21725(6)	0.69902(5)	0.28592(7)	3.40(5)
H(1)	0.21830	0.76560	0.39110	
H(2)	0.28850	0.77070	0.26990	
H(3)	0.14980	0.78090	0.23690	
P(1)	0.3257(2)	0.9108(2)	0.4052(3)	4.5(2)
P(2)	0.1158(2)	0.9273(2)	0.3497(3)	4.4(2)
P(3)	0.3301(2)	0.6186(2)	0.3651(2)	3.4(2)
P(4)	0.2117(2)	0.6662(2)	0.1074(2)	2.4(1)
P(5)	0.1114(2)	0.6341(2)	0.3449(2)	3.1(2)
C(1)	0.2273(8)	0.9144(8)	0.203(1)	5.3(8)
O(1)	0.2338(7)	0.9567(6)	0.1345(8)	7.9(7)
C(12)	0.381(1)	0.9640(9)	0.608(1)	7.3(4)
C(13)	0.381(1)	0.964(1)	0.715(2)	9.2(6)
C(14)	0.333(1)	0.919(1)	0.759(1)	8.0(5)
C(15)	0.286(1)	0.8707(9)	0.698(1)	7.0(4)
C(16)	0.2852(8)	0.8683(8)	0.593(1)	5.7(4)
C(11)	0.3324(8)	0.9138(7)	0.547(1)	4.8(3)
C(21)	0.3374(9)	1.0109(8)	0.375(1)	5.8(4)
C(32)	0.450(1)	0.8740(9)	0.294(1)	7.3(5)
C(33)	0.530(1)	0.848(1)	0.280(2)	8.8(5)
C(34)	0.587(1)	0.821(1)	0.360(1)	8.7(5)
C(35)	0.569(1)	0.817(1)	0.455(1)	8.6(5)
C(36)	0.4891(9)	0.8423(9)	0.472(1)	7.1(4)
C(31)	0.4300(8)	0.8720(7)	0.392(1)	5.2(3)
C(42)	0.1587(8)	1.0402(8)	0.500(1)	5.7(3)
C(43)	0.1721(9)	1.1143(9)	0.535(1)	7.3(4)
C(44)	0.161(1)	1.173(1)	0.465(1)	8.8(5)
C(45)	0.140(1)	1.161(1)	0.361(1)	8.9(5)
C(46)	0.1258(9)	1.0862(8)	0.325(1)	6.9(4)
C(41)	0.1342(8)	1.0253(7)	0.3948(9)	4.8(3)
C(52)	0.0193(9)	0.9261(8)	0.147(1)	5.5(4)
C(53)	-0.0507(9)	0.9444(9)	0.073(1)	6.8(4)
C(54)	-0.117(1)	0.9848(9)	0.100(1)	7.6(5)
C(55)	-0.117(1)	1.008(1)	0.200(1)	8.2(5)
C(56)	-0.046(1)	0.9898(9)	0.273(1)	7.0(4)
C(51)	0.0237(8)	0.9492(7)	0.249(1)	5.0(3)
C(61)	0.0643(8)	0.8918(8)	0.452(1)	5.7(4)
C(72)	0.4526(8)	0.5285(8)	0.281(1)	5.4(3)
C(73)	0.5155(9)	0.5175(9)	0.225(1)	7.1(4)
C(74)	0.543(1)	0.5790(9)	0.180(1)	7.3(4)
C(75)	0.509(1)	0.6514(9)	0.191(1)	7.2(4)
C(76)	0.4454(8)	0.6619(8)	0.247(1)	5.6(4)
C(71)	0.4159(7)	0.6001(7)	0.2920(9)	4.3(3)
C(82)	0.4743(9)	0.6491(8)	0.512(1)	5.6(4)
C(83)	0.5156(9)	0.6678(8)	0.610(1)	6.0(4)
C(84)	0.4711(9)	0.6944(8)	0.683(1)	5.9(4)
C(85)	0.3863(9)	0.7016(8)	0.661(1)	6.2(4)
C(86)	0.3447(9)	0.6832(7)	0.563(1)	5.4(3)
C(81)	0.3884(7)	0.6559(7)	0.4867(9)	4.0(3)
C(92)	0.2723(8)	0.4714(7)	0.341(1)	4.9(3)
C(93)	0.2593(9)	0.3989(8)	0.371(1)	5.9(4)
C(94)	0.2889(9)	0.3734(9)	0.470(1)	6.8(4)
C(95)	0.3349(9)	0.4200(8)	0.539(1)	6.1(4)
C(96)	0.3506(8)	0.4932(8)	0.508(1)	5.4(3)
C(91)	0.3183(7)	0.5203(7)	0.4101(9)	4.2(3)
C(102)	0.1496(9)	0.5509(8)	-0.036(1)	5.6(4)
C(103)	0.154(1)	0.4790(9)	-0.080(1)	7.5(5)
C(104)	0.216(1)	0.427(1)	-0.043(1)	8.5(5)
C(105)	0.277(1)	0.444(1)	0.039(1)	8.0(5)
C(106)	0.2730(9)	0.5160(8)	0.083(1)	6.1(4)

Table 3 (continued)

Atom	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
C(101)	0.2090(8)	0.5692(7)	0.048(1)	4.8(3)
C(112)	0.3367(9)	0.6606(9)	-0.021(1)	6.7(4)
C(113)	0.398(1)	0.692(1)	-0.065(1)	8.6(5)
C(114)	0.418(1)	0.765(1)	-0.047(1)	8.9(5)
C(115)	0.377(1)	0.809(1)	0.017(1)	8.2(5)
C(116)	0.3167(9)	0.7787(8)	0.063(1)	6.5(4)
C(111)	0.2950(8)	0.7035(8)	0.045(1)	5.3(3)
C(122)	0.0407(9)	0.6987(8)	0.047(1)	6.2(4)
C(123)	-0.033(1)	0.7338(9)	-0.009(1)	7.5(4)
C(124)	-0.029(1)	0.7860(9)	-0.084(1)	7.8(5)
C(125)	0.043(1)	0.802(1)	-0.103(1)	8.4(5)
C(126)	0.119(1)	0.7671(9)	-0.050(1)	7.0(4)
C(121)	0.1170(8)	0.7144(7)	0.0273(9)	4.7(3)
C(132)	-0.0169(9)	0.7449(8)	0.265(1)	5.6(4)
C(133)	-0.0981(9)	0.7758(9)	0.241(1)	7.0(4)
C(134)	-0.160(1)	0.7374(9)	0.268(1)	7.4(4)
C(135)	-0.143(1)	0.671(1)	0.320(1)	7.7(5)
C(136)	-0.0617(9)	0.6398(9)	0.346(1)	6.5(4)
C(131)	0.0028(8)	0.6773(7)	0.3166(9)	4.6(3)
C(142)	0.0854(8)	0.5119(7)	0.212(1)	4.9(3)
C(143)	0.0639(9)	0.4398(8)	0.178(1)	6.2(4)
C(144)	0.0411(9)	0.3901(9)	0.247(1)	7.1(4)
C(145)	0.0392(9)	0.4108(9)	0.347(1)	6.9(4)
C(146)	0.0609(8)	0.4828(8)	0.379(1)	5.8(4)
C(141)	0.0855(7)	0.5351(7)	0.3127(9)	4.4(3)
C(152)	0.1718(9)	0.5739(9)	0.549(1)	6.5(4)
C(153)	0.192(1)	0.581(1)	0.658(1)	7.8(5)
C(154)	0.168(1)	0.646(1)	0.701(1)	8.2(5)
C(155)	0.124(1)	0.7053(9)	0.646(1)	7.4(4)
C(156)	0.1028(9)	0.6979(8)	0.537(1)	6.1(4)
C(151)	0.1278(8)	0.6336(7)	0.489(1)	4.9(3)

ddd,  $J_{\text{P1P3}} = 3.5$  Hz,  $J_{\text{P2P3}} = 12$  Hz,  $J_{\text{P3P4}} = 21.5$  Hz), 37.5 ( $\text{P}_4$ , dd,  $J_{\text{P2P4}} = 4$ ,  $J_{\text{P3P4}} = 21.5$  Hz) ppm (183 K).

### 3.9. Protonation of $(\text{CO})(\text{PPh}_3)_2\text{Re}(\mu\text{-H})_3\text{Ru}(\text{PPh}_3)_2\text{P}(\text{OPr}^i)_3$ , synthesis of **10**

To 0.15 g of **7** dissolved in 10 ml of dichloromethane was added 12  $\mu\text{l}$  of  $\text{HBF}_4$  (one equivalent). The solution turned orange and after 5 min of stirring the solution was evaporated under vacuum. The residue was dissolved in a small amount of acetone and 0.04 g of  $\text{Na}[\text{BPh}_4^-]$  was added. After elimination of acetone under vacuum the product was recrystallised from a  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  mixture and 0.16 g of **10** were isolated as orange crystals (88%).

Anal. Calc. for  $\text{C}_{106}\text{H}_{105}\text{BO}_4\text{P}_5\text{ReRu}$ : C, 67.15; H, 5.58. Found: C, 66.73; H, 5.38%. IR  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ : 1851  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) except phenyl resonances: 5.16 (m, 3H), 1.49 (d,  $J = 5.3$  Hz, 18H), -5.12 (t,  $J = 56.4$  Hz, 1H), -6.38 (d,  $J = 80.6$  Hz, 1H), -7.44 (m, 2H) ppm (294 K); 5.04 (m, 3H), 1.29 (d,  $J = 5.1$  Hz, 18H), -5.45 (t,  $J_{\text{P4H}} = J_{\text{P5H}} = 55.9$  Hz, 1H), -6.42 (d,  $J_{\text{P1H}} = 81.8$  Hz, 1H), -6.87 (d,  $J_{\text{P2H}}$  or  $J_{\text{P3H}} = 10$  Hz, 1H), -8.14 (bd,  $J_{\text{P2H}}$  or  $J_{\text{P3H}} = 30$  Hz) ppm (183 K).  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR: 136.9 ( $\text{P}_1$ , t,  $J = 45.4$  Hz), 46.4 ( $\text{P}_2 + \text{P}_3$ , d,  $J = 45.4$  Hz), 29.8 ( $\text{P}_4 + \text{P}_5$ ) ppm (297 K). 140.9 ( $\text{P}_1$ , t,



$J = 47.3$  Hz), 50.2 ( $P_2$ , dd,  $J = 47.3$  Hz; 38.9 Hz), 47.3 ( $P_3$ , dd,  $J = 47.3$  Hz; 38.9 Hz), 35.8 ( $P_4$ , s), 29.6 ( $P_5$ , s) ppm (193 K).

### 3.10. Crystallographic Studies

Crystals of **2** suitable for X-ray diffraction were grown in an ether/hexane mixture. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22°C. Cell constants were obtained by the least-squares refinement of the settings angles of 25 reflections in the range  $20^\circ < 2\theta$  (Mo- $K\alpha_1$ )  $< 24^\circ$ . All calculations were performed on a Micro Vax 3400. Data reductions were carried out using the SDP crystallographic package [11]. The intensities were corrected from absorption by using the empirical  $\Psi$ -scan method [12]. Table 2 shows further crystallographic informations.

The structure was solved by using the SHELXS-86 program [13] and refined by using the SHELX-76 program [14]. The positions of the Re, Ru, and P atoms were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of the full-matrix least-squares refinement and difference electron density syntheses. Atomic scattering factors were taken from the standard tabulations [15]. Anomalous dispersion terms for the Re, Ru, and P atoms were included in the calculated structure factors [16]. Re, Ru, P, C(1), and O(1) atoms were allowed to vibrate anisotropically. Hydrogen atoms attached to the phenyls rings and to the methyl groups were entered in idealised positions ( $C-H = 0.97$  Å). The scattering factors for the hydrogen atoms were taken from Stewart et al. [17].

The three bridging hydrides were not located in the final Fourier difference map. Their positions were calculated by the use of the program HYDEX [8] which clearly showed three energy minima around the metal centres. These energy minima have been refined and subsequently attributed to the bridging hydrides H(1), H(2), and H(3). The hydrides were finally introduced into the last cycle of refinement, at the positions given by HYDEX, with fixed coordinates and thermal parameters arbitrarily set to  $0.06$  Å<sup>2</sup>.

Final atomic coordinates and thermal parameters ( $U_{eq} \times 100$ ) for non-hydrogen atoms are given in Table 3. Thermal parameters for atoms which were refined anisotropically and hydrogen positions are from the Cambridge Crystallographic Data Centre.

## 4. Conclusion

This study of the influence of ligands to rhenium or ruthenium on the coupling reaction between  $[ReH_6-$

$L_2]^-$  and  $[RuHCl(CO)(PPh_3)_{3-x}\{P(OPr^i)_3\}_x]$  has shown some of the factors governing the structure of the final product and gives some insight into the mechanism of the reaction. In all the cases the first step is the formation of  $[(CO)(L)_2HRe(\mu-H)_3RuH(PPh_3)_{2-x}\{P(OPr^i)_3\}_x]$  with liberation of the ligand in *trans* to the hydride in  $[RuHCl(CO)(PPh_3)_{3-x}\{P(OPr^i)_3\}_x]$ . At the temperature needed for the reaction, and depending on the bulk of the liberated phosphite and the crowding around the pentahydride complex, the final product isolated is  $[(CO)(L)_2Re(\mu-H)_3Ru(PPh_3)_{3-x}\{P(OPr^i)_3\}_x]$  which results from the displacement of molecular hydrogen by the liberated phosphite.

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