



The hydrogenation reaction of $[\text{Ru}_3(\text{CO})_{10}(\text{C}_6\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{F}_5)_2]$: Migration of a C_6F_5 group from a phosphorus to a ruthenium atom. X-ray crystal structures of $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})\{\mu_2\text{-}(\text{C}_6\text{F}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$, $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_3(\eta^1\text{-C}_6\text{F}_5)\{\mu_3\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$ and $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu_3\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$

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ABSTRACT

The reaction of $[\text{Ru}_3(\text{CO})_{10}(\text{C}_6\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{F}_5)_2]$ (**1**) with hydrogen in toluene produced four compounds. These compounds were characterized spectroscopically and structurally. Some experiments were carried out to determine the relationship between the different reaction products. The first two compounds (**2** and **3**) show μ -phosphide groups bridging metal–metal bonds, produced by the rupture of a P– C_6F_5 bond; **2** also shows a C_6F_5 ring bonded in a η^1 fashion to one of the metal atoms. In both compounds the remaining part of the diphosphine ligand is coordinated in the traditional terminal form. The structure of compounds **4** and **5** show a μ_3 -phosphinidene group where both aromatic rings bonded to the phosphorus atom have been eliminated. Compound **4** also has a C_6F_5 ring bonded to a ruthenium atom.

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1. Introduction

The reactions of carbonyl metal clusters with hydrogen have been of interest to chemists for many years [1] given the potential application of these complexes to serve as catalysts in several processes that involve hydrogen additions [2]. The use of phosphine derived complexes revealed some differences with those of the unsubstituted carbonyl complexes [3], and these observations prompted other studies of the reactions of phosphine substituted clusters [4]. Some of these reactions showed that reaction pathways that transform the phosphine ligands are frequently observed [4,5] including activation of P–C bonds [6].

On the other hand, the introduction of fluorine substituents to the ligands coordinated to metal ions can have a large effect on the chemical and structural properties of the resulting complexes [7]. For example, the electronic characteristics of phosphines have been observed to affect the H–H distances in $\text{Ru}(\text{H}_2)$ complexes and the presence of fluorinated groups is one of the ways to change electronic characteristics [8]. An increase in the Lewis acidity of a metal center by the introduction of fluorine substituents, has been

shown to increase the activity of the metal complex as a catalyst in the Baeyer–Villiger oxidation of ketones [9]. The withdrawing character of fluorine as well as its larger size in comparison with hydrogen, could therefore cause differences in the reactivities of species such as $[\text{Ru}_3(\text{CO})_{10}\text{L}]$ (L = diphosphine). The fluorine substituted derivative of bis(diphenylphosphino)ethane, $[\text{Ru}_3(\text{CO})_{10}\{\text{C}_6\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{F}_5)_2]$, has been reported to have higher catalytic activity for the hydroformylation of ethylene and propylene than the non-fluorinated compound [10].

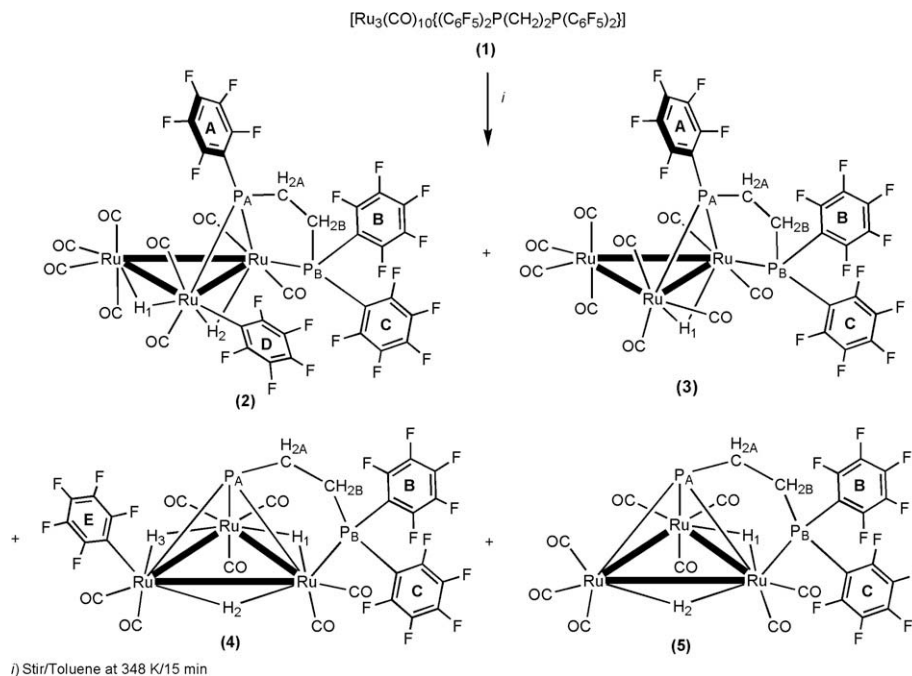
In this work, we describe the spectroscopic and structural characterization of the products of the reaction of $[\text{Ru}_3(\text{CO})_{10}\{\text{C}_6\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{F}_5)_2]$ with hydrogen.

2. Results and discussion

When the reaction between compound **1**, $[\text{Ru}_3(\text{CO})_{10}\{\text{C}_6\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{F}_5)_2]$, with hydrogen was carried out in toluene at 348 K for 15 min, four new compounds, **2** ($[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\eta^1\text{-C}_6\text{F}_5)\{\mu_2\text{-}(\text{C}_6\text{F}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$), **3** ($[\text{Ru}_3(\text{CO})_9(\mu\text{-H})\{\mu_2\text{-}(\text{C}_6\text{F}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$), **4** ($[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_3(\eta^1\text{-C}_6\text{F}_5)\{\mu_3\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$) and **5** ($[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu_3\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$) were obtained in yields of 17%, 40%, 18% and 5%, respectively (Scheme 1). The four compounds were characterized by

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Scheme 1.

spectroscopic techniques and by single crystal X-ray diffraction analysis. The ³¹P NMR spectra of compounds **2** and **3** are very similar. While **2** shows two singlets at 46.9 and 95.8 ppm, the resonance of **3** were observed at 40.7 and 101.6 ppm. The signals at higher frequency in each compound suggest a lower shielding from the metal atoms, consistent with the presence of a phosphido group bridging two of the metal atoms. These values are observed at lower frequency than those reported for other bridging phosphido groups [11,12], but this can be explained by the presence of the fluorine atoms on the aromatic rings bonded to the phosphorus atoms. This behavior has been observed in other compounds containing fluorine substituents, such as the free ligands and the corresponding complexes [Ru₃(CO)₁₀L] (L = dppe and dfpe) [10,13].

The hydride region of the ¹H spectrum of **2** shows two signals indicating the presence of two hydride ligands. Both hydrides couple to both phosphorus atoms. By using heteronuclear irradiation experiments, the signal multiplicity and coupling constants to both phosphorus atoms in the compound were determined (Table 1). On the other hand the corresponding spectrum for **3** only shows one complex signal at -18.10 ppm. After decoupling experiments (Fig. 1), the pattern of the signal can be described as a pair of doublets of triplets due to coupling to each of the two different phosphorus atoms of the diphosphine and to the *ortho* fluorine atoms on the ring bonded to the phosphido group.

More important changes in the spectroscopic results of compound **2**; when compared with data for compound **1** were observed in the ¹⁹F spectrum which shows 15 different signals. The signals in the *ortho*, *para* and *meta* regions suggest the presence of three different aromatic rings on the diphosphine ligand. In addition to these signals, the spectrum shows the presence of 5 other signals; two at higher frequencies (-103 and -105 ppm), and three at lower frequencies (-158.9, -161 and -164 ppm) than those of the rings. After the analysis of a two dimensional COSY experiment, we propose that these signals are due to an additional aromatic ring where all fluorine atoms are non-equivalent. A fluorine substituted aromatic ring coordinated to a cobalt atom through a sigma bond, was reported to have similar fluorine chemical shifts [14]. Sigma coordinated phenyl rings are not common

but there are several examples in the literature [15]. We therefore propose for complex **2** the structure shown in Scheme 1 where there has been a rupture of a P-C bond but the ring was trapped by one of the metal atoms. This is supported by crystallographic studies described below.

The ¹⁹F spectrum of compound **3** shows three signals in each of the regions for the *ortho*, *meta* and *para* fluorine atoms indicating the presence of three different rings.

A crystal obtained from a mixture of complexes **2** and **3** was studied by X-ray crystallography which revealed that both compounds co-crystallized in the asymmetric unit. Even though co-crystallization occurs frequently, we only found a previous report of this behavior for a carbonyl cluster complex [16]. The poor quality of the crystal did not allow a good refinement but it is possible to observe (Fig. 2) that compound **2** has a phosphido group, having only one C₆F₅ group, bridging one of the metal-metal bonds [Ru(1)-Ru(2)] of the triangle while the other phosphorus atom of the ligand, is bonded to one of the same metal atoms, Ru(1). A C₆F₅ group is also bonded to the other metal atom bridged by the phosphido group, Ru(2). The positions of the two hydride atoms in **2** are proposed based on the Ru-Ru distances. Considering that the μ₂-P group donates 3 electrons and the C₆F₅ group gives one electron, one gets that **2** is a 48 electron precise cluster. The other molecule in the asymmetric unit shows a similar structure but does not contain the sigma bonded aryl ring.

Ruthenium cluster compounds showing sigma bonded aryl rings have been previously reported [15b,15c], as products from the reactions of phosphine substituted derivatives, but in those cases the aryls were non-substituted phenyl rings.

A structure of compound **3** was also determined by single crystal X-ray diffraction analysis. The molecular structure of **3** is shown in Fig. 3 while some selected bond distances and angles are given in Table 2.

As indicated from the spectroscopic evidence, compound **3** has a triangular metal framework containing a phosphido group bridging an edge of the triangular Ru₃ cluster. The phosphorus atom of the phosphido (P(1) in Fig. 3) is bonded to a C₆F₅ group and to the ethylene group that connects to the other phosphorus atom

Table 1
¹H, ³¹P and ¹⁹F NMR data for **2–5**.

Compound	¹ H δ (ppm) / J (Hz)	³¹ P δ (ppm) / [² J _{31P–31P}]	¹⁹ F δ (ppm) / J (Hz) [³ J _{19F_p–19F_m}], [³ J _{19F_o–19F_m}]
2	3.12 (dddd) (1H) (CH _{2A}), ² J _{1H–31P_A} = 44.5, ³ J _{1H–31P_B} = 14.9, ² J _{1H–1H} = 14.9, ³ J _{1H–1H} = 5.5	96.1 (s) (P _A)	–103.0 F _o (dbr) (1F) (D), {19.2}
	2.15 (dm) (1H) (CH _{2B}), ² J _{1H–31P_B} = 62.7, 2.06 (m) (2H) (CH _{2A,B})	46.9 (s) (P _B)	–105.1 F _o (dbr) (1F) (D), {19.2}
	–16.29 (ddm) (1H) (H ₁) ² J _{1H–31P_A} = 24.7, ² J _{1H–31P_B} = 11.0		–125.1 F _o (dbr) (1F) (A) {18.5}
	–18.80 (br) (H ₂) ² J _{1H–31P_A} = 8.3 ^a		–125.4 F _o (br) (2F) (B)
			–125.9 F _o (dbr) (1F) (A) {18.5}
			–132.9 F _o (dbr) (2F) (C) {18.5}
			–145.1 F _p (t) (1F) (B), [20.8]
			–147.0 F _p (t) (1F) (C), [20.8]
			–148.5 F _p (t) (1F) (A), [20.8]
			–157.8 F _m (t) (2F) (C), [20.8]
			–158.2 F _m (t) (2F) (B), [20.8]
			–158.6 F _m (t) (1F) (A), [23.1]
			–158.9 F _p (t) (1F) (D), [20.8]
			–159.5 F _m (t) (1F) (A), [23.1]
			–161.1 F _m (t) (1F) (D), [23.1]
			–164.4 F _m (t) (1F) (D), [23.1]
3	3.26 (dddd) (1H) (CH _{2A}), ² J _{1H–31P_A} = 46.2, ³ J _{1H–31P_A} = 14.3, ² J _{1H–1H} = 14.3, ³ J _{1H–1H} = 5.5	101.6 (s) (P _A)	–126.2 F _o (dm) (1F) (A), {23.8}
	2.49 (dm) (1H) (CH ₂), ² J _{1H–31P_B} = 556.6	40.7 (s) (P _B)	–127.3 F _o (d) (3F) (A, B), [20.1]
	2.05 (m) (2H) (CH _{2A,B})		132.6 F _o (d) (2F) (C), {20.1}
	–18.10 (ddt) (1H) (H ₁) ² J _{1H–31P_A} = 27.0, ² J _{1H–31P_B} = 11.1, ⁵ J _{1H–31F_o} = 5.5		–145.6 F _p (tt) (1F) (B), [20.8], ⁴ J _{19F_p–19F_o} = 4.5
			–147.2 F _p (tt) (1F) (C), [20.8], ⁴ J _{19F_p–19F_o} = 4.6
			–148.9 F _p (tm) (1F) (A), [21.0]
			–157.7 F _m (m) (2F) (B)
			–158.1 F _m (m) (2F) (C)
			–159.2 F _m (ddd) (1F) (A), [23.8], [21.0],
			⁴ J _{19F_m–19F_m} = 8.9
			–159.5 F _m (ddd) (1F) (A), [23.8], [21.0],
			⁴ J _{19F_m–19F_m} = 8.9
4	4.86 (ddd) (1H) (CH _{2A}), ² J _{1H–31P_A} = 39.6, ³ J _{1H–31P_B} = 12.1, ² J _{1H–1H} = 12.1	308.0 (m,br) (P _A)	–102.0 F _o (br) (2F) (E)
	3.32 (ddd) (1H) (CH _{2B}), ² J _{1H–31P_B} = 61.6, ³ J _{1H–31P_A} = 6.0, ² J _{1H–1H} = 14.3	19.3 (br) (P _B)	–127.3 F _o (br) (1F) (B)
	3.10 (ddd) (1H) (CH _{2B}), ² J _{1H–31P_B} = 13.2, ³ J _{1H–31P_A} = 6.6, ² J _{1H–1H} = 14.3		–128.2 F _o (br) (1F) (B)
	2.93 (ddd) (1H) (CH _{2A}) ² J _{1H–31P_A} = 12.8, ³ J _{1H–31P_B} = 6.6, ² J _{1H–1H} = 12.1		–132.7 F _o (br) (2F) (C)
	–17.10 (dd) (1H) (H ₂), ² J _{1H₂–31P_B} = 57.0, ³ J _{1H₂–31P_A} = 15.5		–143.9 F _p (t) (1F) (B), [20.8]
	–18.42 (d) (1H) (H ₃), ³ J _{1H₃–31P_A} = 16.0		–146.1 F _p (t) (1F) (C), [20.8]
	–19.90 (br) (1H) (H ₁)		–157.0 F _m (t) (2F) (C), {18.5}
			–157.5 F _m (td) (2F) (B) [23.2], ⁴ J _{19F_m–19F_m} = 9.3
		–161.2 F _p (t) (1F) (E), [18.5]	
		–163.8 F _m (tm) (1F) (E) [23.2]	
5	4.74 (ddd) (1H) (CH _{2A}), ² J _{1H–31P_A} = 41.3, ³ J _{1H–31P_B} = 12.0, ² J _{1H–1H} = 12.0	322.5 (d) (P _A)	–127.3 F _o (br) (2F) (B)
	3.15 (dm) (1H) (CH _{2B}), ² J _{1H–31P_B} = 37.0,	19.9 (d) (P _B) [19.0]	–132.9 F _o (d) (2F) (C), {16.9}
	3.12 (br) (1H) (CH _{2B})		–145.0 F _p (t) (1F) (B), [20.7]
	3.08 (br) (1H) (CH _{2A})		–146.6 F _p (t) (1F) (C), [20.7]
	–17.91 (ddd) (1H) (H ₂), ² J _{1H₂–31P_B} = 45.5, ³ J _{1H₂–31P_A} = 14.1, ² J _{1H₂–1H₁} = 2.7		–158.2 F _m (t) (2F) (C), {16.9}
	–19.84 (dddtt) (1H) (H ₁), ² J _{1H₁–31P_A} = 16.8, ³ J _{1H₁–31P_B} = 9.6, ² J _{1H₁–1H₂} = 2.7,		–158.8 F _m (m) (2F) (B)
	⁵ J _{1H₂–19F_o} = 2.8, ⁵ J _{1H₂–19F_o} = 3.0		

In CDCl₃. s = singlet, d = doublet, m = multiplet. br = broad *o*, *ortho*; *p*, *para*; *m*, *meta*.^a Obtained on selective heteronuclear irradiation at P_B.

(P(2)), which is terminally bonded to one of the ruthenium atoms bridged by the phosphido group. There is a hydride ligand; found in a Fourier density map; bridging the same bond than the phosphido group. The structure is identical to that observed in the co-crystal of **2** and **3**.

The metal–metal bond bridged by the phosphido group and by the hydride, shows a longer bond length (2.9273(10) Å) than the other two metal–metal bonds in the triangle (2.8468(10) Å and 2.8423(11) Å). This lengthening of the bridged metal–metal bond had also been observed in the structurally similar compounds [Ru₃(μ-H)(CO)₁₀(μ₂-P(C₆H₅)H)] [23] and [Os₃(μ-H)(CO)₁₀(μ₂-P(C₆H₅)H)] [17]. The value of M–M distances when these edges are dibridged, is dependent on the nature of the two bridging groups [17].

The Ru(2)–P(1) distance is shorter than the Ru(1)–P(1) (2.311(2) vs. 2.337(2) Å). This is probably due to the presence of the chain of the diphosphine since in [Ru₃(μ-H)(CO)₁₀(μ₂-P(C₆H₅)H)] [17], the phosphido group is bonded symmetrically to both metal atoms with an average Ru–P distance of 2.3385 Å.

The terminally bonded phosphine group shows a Ru(2)–P(2) bond length of 2.303(2) Å, shorter than the value observed in compound **1** (av. distance is 2.331 Å) [15]. The fact that both Ru–P bonds involving Ru(2) are shorter, is probably a consequence of the formation of the metallacycle with the phosphido group. The P(2)–Ru(2)–P(1) angle (85.10(6)°) is similar to that observed in other Ru-diphosphine coordinated in a chelating mode [20]. The Ru–P lengths in **3** are also similar to the chelated phosphine derivatives reported by Puga et al. [20].

Atom P(1) is 1.805 Å above the plane formed by the three metal atoms, with the planes Ru(1)–Ru(2)–Ru(3) and Ru(1)–Ru(2)–P(1) forming an angle of 110.30(5)° which indicates that P(1) is oriented towards the external side of the metal triangle. This value is larger than the one observed in similar compounds [17,20], presumably in order to accommodate the remaining atoms of the diphosphine ligand. The dihedral angle formed by the diphosphine, P(1)–C(1)–C(2)–P(2), is smaller than the one observed in **1** (–37.6(6)° against –103.2 (av)°). The structure is the same as the molecule observed in the co-crystal formed with compound **2** described above. As in

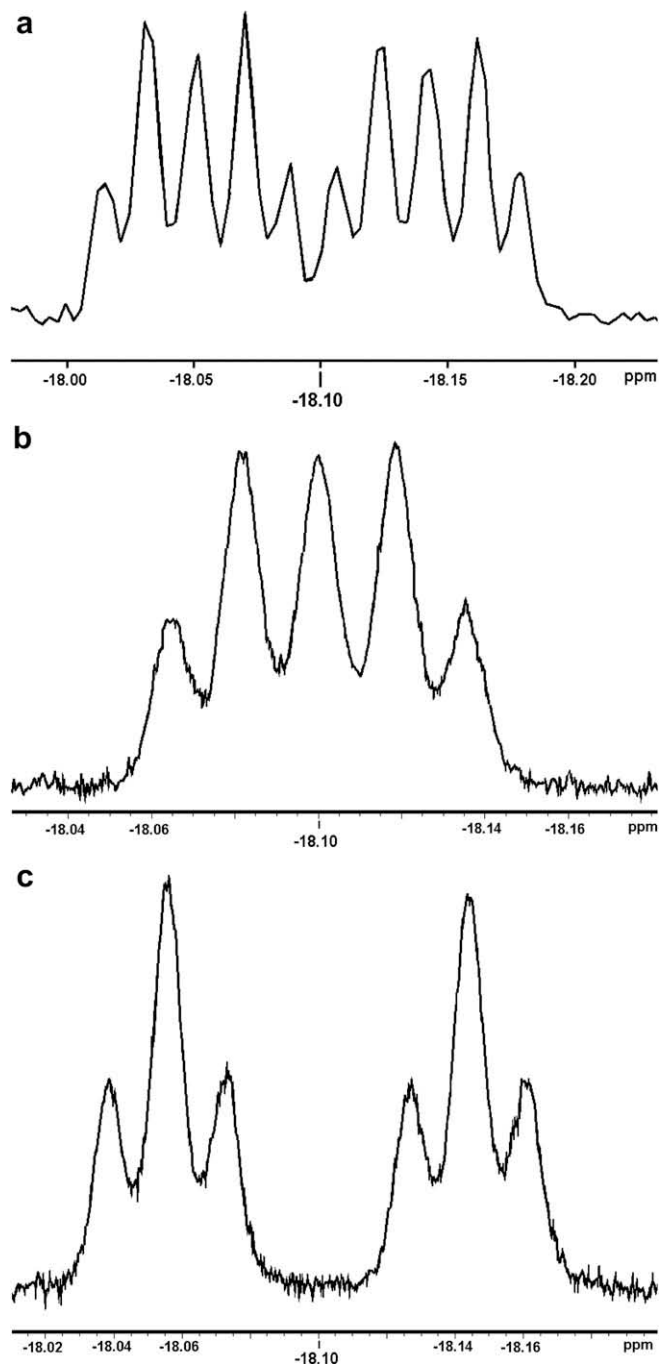


Fig. 1. ^1H NMR spectra for compound **3**. Hydride region. (a) Normal. (b) Irradiation at $\delta^{31}\text{P} = 101.6$ ppm. (c) Irradiation at $\delta^{31}\text{P} = 40.7$ ppm. 20 dB irradiation power.

compound **2**, the chelating diphosphorus ligand donates 5 electrons so that **3** also has 48 electrons.

NMR data for compounds **4** and **5** indicate important similarities to that of compounds **1–3**. The ^{31}P spectra of both **4** and **5**, again show two signals, doublets, at 308.0 and 29.3 ppm and 322.5 and 19.9 ppm, respectively. The signals at lower frequency are assigned to terminal phosphorus atoms of the phosphine ligands (P_2) while the ones at higher frequency are assigned to phosphinidene species (P_1 in Scheme 1), bridging the three metal atoms. There are several reports in the literature of (μ_3 -PR) groups in ruthenium clusters [17,18,21]. In these examples, the ^{31}P chemical shift has been observed to occur between 270 and 282 ppm. However, there are no examples where the bridging phosphorus

atom is part of a chelating chain and this could affect the chemical shift. The similarities in ^{31}P chemical shifts observed in both compounds suggest that the diphosphorus ligands have similar chemical environments.

The ^{19}F spectrum of **4** shows 3 signals with similar chemical shifts to the one assigned to the fluorine atoms in ring D in compound **2**; so these signals were assigned to the fluorine atoms in ring E in Scheme 1. There are also signals assigned to rings B and C, Table 1.

The ^{19}F spectrum of **5** shows two signals in each of the regions suggesting the presence of two different aromatic rings. It is important to point out that the signal assigned to the *ortho* fluorine atoms in one of the rings is broad suggesting a dynamical process. In these compounds, there is ring rotation through the P–C bond causing averaging of the inequivalent *ortho* and the inequivalent *meta* fluorine atoms which leads to averaged signals for both pairs of atoms. Compounds **2**, **3** and **4**, have shown well defined fluorine signals so compound **5** is unusual and a variable temperature study was carried out.

An analysis of the results of the low temperature spectra indicate that in one of the rings, the rotation about the P–C bond is slower than for the other ring. This could be due to larger steric effects, or possibly, due to an interaction of one of the *ortho* fluorine atoms with one of the methylenic hydrogen atoms. Broad signals for *ortho* and *meta* fluorine atoms have also been observed in some transition metal pentafluorophenyl complexes [22], and this has been attributed to a combination of steric and electronic factors; however, only steric factors could be important in compound **5**. The spectrum of compound **4** at room temperature is similar to that of **5** at -50°C suggesting greater steric hindrance in **4** with respect to the rotation about the P–C(aryl) bonds.

The ^1H NMR spectrum of compound **4** shows three signals in the hydride region, at -17.1 (dd), -18.42 (d) and -19.9 (br) ppm; the multiplicity of these signals is due to couplings to the phosphorus atoms in the complex. The corresponding spectrum of compound **5** shows two signals at low frequencies, at -17.91 and -19.84 ppm. The first signal in complex **5**, (H_1) is a pair of doublets of doublets while the other signal shows a complicated coupling pattern. After selective decoupling experiments, the coupling pattern for the signal at lower frequency (H_2) was recognized as a pair of doublets of doublets of triplets of triplets by coupling to both phosphorus atoms, the other hydride ligand and two *ortho* fluorine atoms on different rings.

Single crystals of compounds **4** and **5** were obtained and were studied by X-ray diffraction. The molecular structures are shown in Figs. 4 and 5, respectively. Selected bonds and angles are given in Table 2. Compound **4** contains two independent molecules in the asymmetric unit; both are essentially identical and only one of the two molecules is shown in Fig. 4. Selected bond lengths and angles for the second molecule are included in Table 2 for comparative purposes.

The structures of both compounds are formed by triangles of metal atoms with a μ_3 -phosphinidene group bonded to the triangles and the other phosphorus group bonded to one metal atom: In the case of compound **4** there is also a C_6F_5 group bonded to one of the ruthenium atoms.

The metal triangles in compound **4** are equilateral with all three metal–metal bonds showing values around 2.97 Å, consistent with the presence of three hydride groups bridging all three edges. In the case of compound **5**, two of the ruthenium–ruthenium bonds; Ru(1)–Ru(2) and Ru(1)–Ru(3); are longer (average = 2.9468 Å), than the other one, Ru(2)–Ru(3) (2.8413(18) Å). This indicates that the two hydride ligands detected in the ^1H NMR spectrum are bridging the two long edges of the triangle.

The M–P distances in phosphinidene groups bound to a metal triangle, reported in the literature, show a general pattern of two

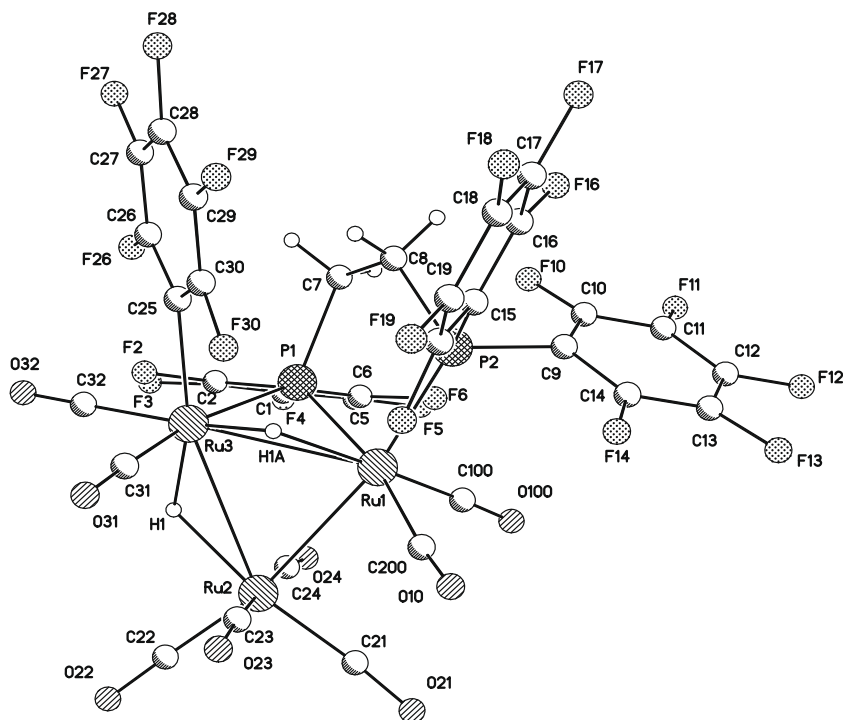


Fig. 2. Molecular structure of compound 2.

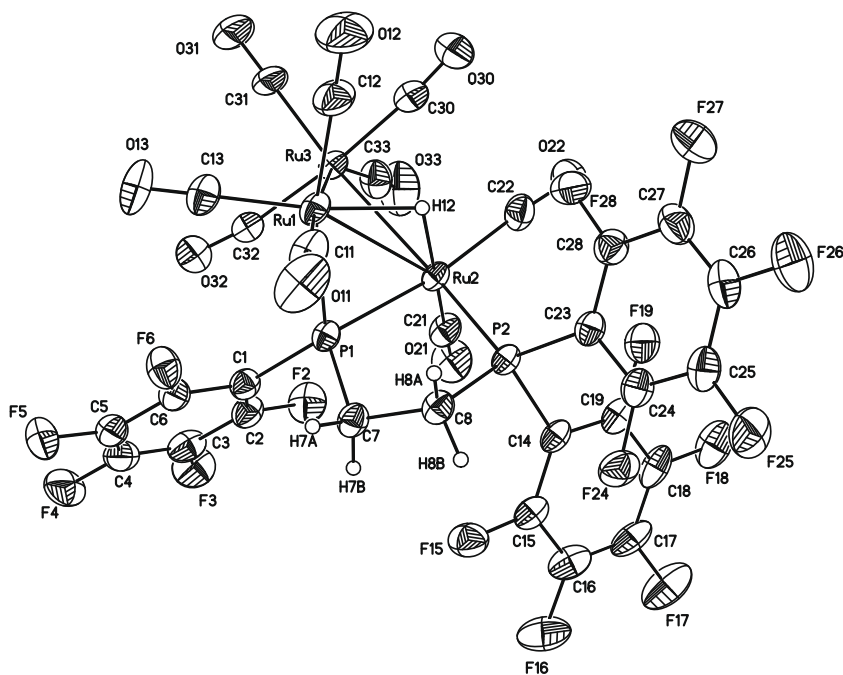


Fig. 3. Molecular structure of compound 3.

short and one longer bonds [18,23]. Compound 4 shows the same pattern having Ru– μ_3 -P distances between 2.286(2) and 2.306(3) Å for the shorter distances and 2.331(2) and 2.340(3) Å for the longer distances. The same trend appears to be present in complex 5 where values are 2.2792 (18), 2.2870(16) and 2.3060(14) Å. In the compounds reported in the literature; [Ru₃(μ -H)₂(CO)₉(μ_3 -P(C₆H₅))] [23] and [Ru₃(μ -H)₂(CO)₉(μ_3 -P(p-CH₃OC₆H₄))] [18], the longer M–P bond distance was observed for the ruthenium atom bearing two hydride ligands. The same is observed in compound

5; however, compound 4 has three hydrides and the differences in M–P distances can not be attributed to this factor. The long Ru–P bond length observed in compound 3 shows a similar value to the long ones observed in compound 4.

The Ru–P bond distances to the terminally-coordinated, phosphorus atoms, show a larger distance in one of the molecules of 4 with values of 2.331(2), and 2.335(2) Å while in compound 5 the corresponding value is 2.3125(15) Å. The similarity in the Ru–P distances, in the bridging and the terminal cases, is different

Table 2

Some selected bond lengths (Å) and angles (°).

	2^a	3	4	5
Ru(1)–Ru(2)	2.861(2)	2.9274(10)	2.9728(10), 2.9658(10)	2.9521(6)
Ru(2)–Ru(3)	2.336(7)	2.8470(10)	2.9799(10), 2.9737(11)	2.8389(7)
Ru(1)–Ru(3)	2.929(3)	2.8419(11)	2.9653(11), 2.9802(11)	2.9434(6)
Ru(1)–P(1)	2.320(10)	2.3378(16)	2.334(3), 2.340(3)	2.3060(14)
Ru(2)–P(1)	–	2.3122(17)	2.301(2), 2.306(3)	2.2792(18)
Ru(3)–P(1)	2.338(7)	–	2.292(2), 2.286(2)	2.2870(16)
Ru–P(2)	2.305(7)	2.3030(15)	2.335(2), 2.331(2)	2.3125(15)
Ru–C(1)	^b	–	2.164(6), 2.179(5)	–
P(1)–Ru(1)–Ru(2)	87.50(17)	50.60(4)	49.62(6), 49.82(6)	49.52(4)
P(1)–Ru(1)–Ru(3)	51.33(17)	84.88(5)	49.51(6), 49.11(6)	49.86(4)
P(2)–Ru(2)–Ru(3)	–	161.37(4)	131.33(6), 131.27(7)	131.98(4)
P(2)–Ru(2)–Ru(1)	–	102.69(4)	96.76(6), 96–01(6)	96.43(4)
C(1)–Ru(3)–Ru(1)	^b	–	149.5(2), 147.64(17)	–
C(1)–Ru(3)–Ru(2)	^b	–	95.9(2), 99.12(8)	–

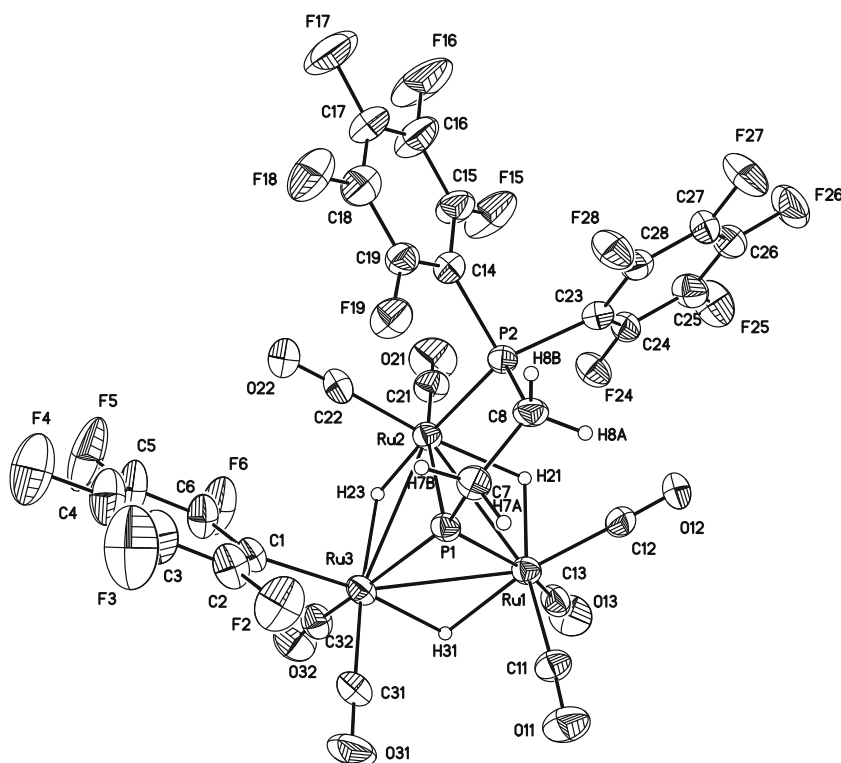
^a Non-hydrogen atoms refined isotropically.^b Due to the bad quality of the data, these values are not meaningful.

to other cases where differences had been observed [19]. The Ru–C(aryl) distances in compound **4**, are 2.164(6) Å and 2.179(5) Å. These values are in the same range than those Ru–C(aryl) bonds already reported [15a,15b]. Both **4** and **5** have 48 electrons considering that each μ_3 -P group donates 4 electrons, so they are saturated.

As a consequence of the formation of the phosphinidene group, the diphosphine ligand adopts a different conformation. While the P–C–P torsion angle in compound **1** is 103.2°(av), the value in compounds **4** and **5** is close to 40°, very similar to the value observed in compound **3**. The angles between the P(C₆F₅)₂ group and the metal–metal bonds also reflect the greater conformational strain of the ligand in compounds **4** and **5**. While in complex **1**, the P–Ru–Ru angles are in the range of 100 and 155°, in compounds **4** and **5**, these values fall either close to 96° or closer to 130°. The corresponding values in compound **3** resemble those in **1**.

An analysis of the reaction products shown in Scheme 2 suggests that the addition of hydrogen promotes the oxidative addi-

tion of dfppe ligand and formation of a σ -bond from a C₆F₅ ring to a ruthenium atom to give compound **2**, since the termolysis of compound **1** alone does not show any appreciable reaction under the same, or more drastic conditions than the ones used for the hydrogenation reaction. Compound **2** subsequently transforms to give compound **3**, this transformation involves the loss of pentafluorobenzene, observed spectroscopically by ¹⁹F NMR, in the reaction of compound **2** in toluene-*d*₈ under CO atmosphere at 348 K made in a J. Young-type NMR tube. In the same experiment we did not observe formation of compound **4**. However, the reaction of **2** in toluene at 348 K in the presence of a hydrogen purge afforded compound **4** in a very low yield. Hence the cleavage of the Ru–C(C₆F₅) bond must be easier to occur; under the reaction conditions; than that of the P–C(C₆F₅) to form **3** instead of **4**. The experiments also showed that compound **3** continues reacting with hydrogen to form compounds **4** and **5** (by purging gas at 348 K in toluene). The transformation from **3** to **4** involves the rupture of P–C(C₆F₅)

**Fig. 4.** Molecular structure of compound **4**.

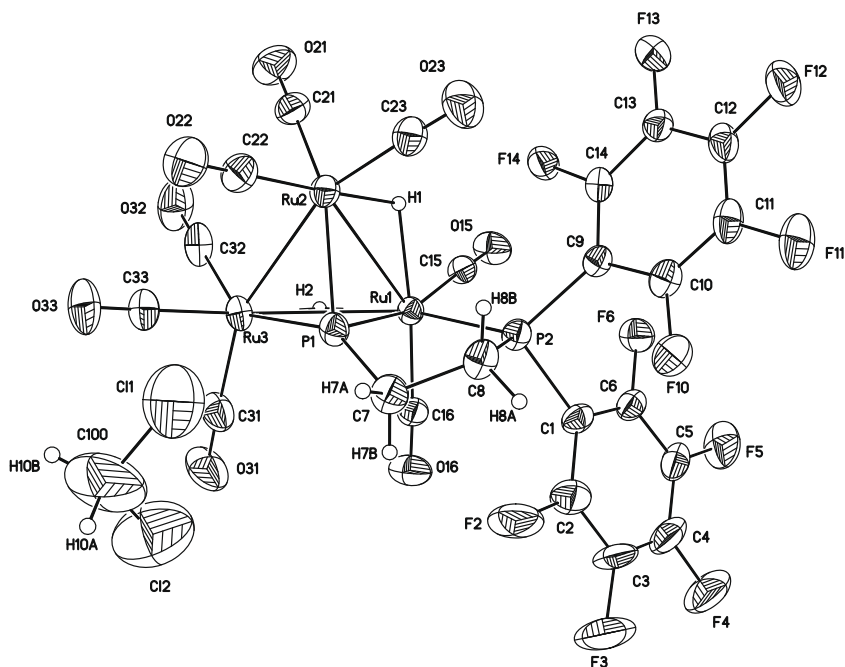


Fig. 5. Molecular structure of compound 5.

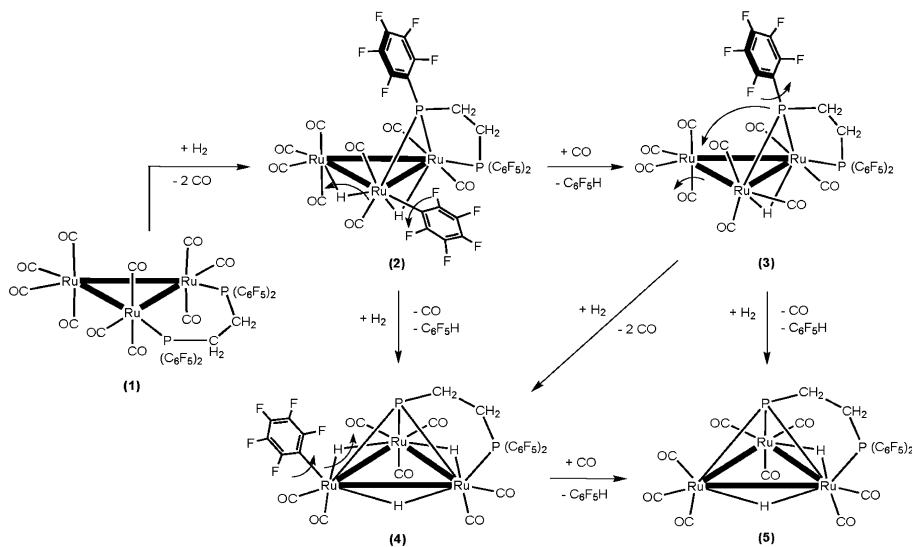
bond and the formation of a new Ru–C(C₆F₅) σ -bond. In a new experiment, the reaction of **4** in toluene at 348 K in the presence of a carbon monoxide purge yields **5**; therefore, the final step involves loss of C₆F₅H (also detected spectroscopically) to give compound **5**, as it is shown in Scheme 2.

The isolation of two derivatives containing σ -bonded C₆F₅ rings to ruthenium atoms, might suggest a larger stability of this bond in comparison with that of a Ru–C₆H₅. This could be explained in terms of stronger $d\pi$ – $p\pi$ interactions, as had been previously proposed [22], in a system containing metals in low oxidation states.

It is important to compare the reactivity of the fluorinated diphosphine complex and the dppe derivative with hydrogen [24]. With dppe derivative at 80 °C and 20 bar; two products were isolated: [Ru₃(μ -H)(μ -3-PPhCH₂PPh₂)(CO)₉] and [Ru₄(μ -H)₄(CO)₁₀-(dppe)]. The trinuclear derivative is a common product in hydroge-

nation reactions of derivatives containing mono- and bidentate phosphines. Formation of a phosphido derivative was observed in the reaction of [Ru₃(CO)₈(dppm)₂] [19] and for the dfppe complex. However, no tetranuclear derivative is formed; under the reaction conditions studied in the case of compound **1**. It is possible that the remaining part of the bidentate phosphine, makes the addition of other metal fragments more difficult and thus the formation of larger clusters would require higher energies.

The dppe complex did not yield a phosphinidene derivative although the corresponding dppm compound, [Ru₃(CO)₁₀(dppm)] did yield a phosphinidene complex, but in that case one of the P–CH₂ bonds was cleaved to form [Ru₃(μ -H)₂(μ -3-PPh)(CO)₈(PMePh₂)] [24]. Therefore, to our knowledge, compounds **4** and **5** are the first examples of phosphinidene complexes with a bridging diphosphine ligand as the source of the (μ -3-PR) group.



Scheme 2.

Table 3
Crystallographic data for compounds **3–5**.

	2	3	4	5
Empirical formula	C ₃₄ H ₆ O ₈ F ₂₀ P ₂ Ru ₃ · C ₂₉ H ₅ F ₁₅	C ₂₉ H ₅ F ₁₅ O ₉ P ₂ Ru ₃ · CHCl ₃	C ₂₈ H ₈ F ₁₅ O ₇ P ₂ Ru ₃ · CHCl ₃	C ₂₂ H ₆ F ₁₀ O ₈ P ₂ Ru ₃ · CH ₂ Cl ₂
Formula weight	2435.0025	1266.85	1153.16	1038.34
Crystal size (mm)	0.075 × 0.05 × 0.025	0.56 × 0.44 × 0.22	0.15 × 0.09 × 0.05	0.10 × 0.05 × 0.03
Crystal colour and shape	Red plates	Orange blocks	Orange flakes	Yellow plates
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions				
<i>a</i> (Å)	21.1830(8)	8.850(2)	12.3381 (2)	12.0003(3)
<i>b</i> (Å)	12.5479(5)	13.435(3)	15.7359(3)	17.4947(5)
<i>c</i> (Å)	28.7569(13)	17.361 (3),	19.3578(6)	15.9204(5)
α (°)		104.99(3)	92.723(1)	
β (°)	93.519(2)	94.00(3)	92.251(1)	105.93(1)
γ (°)		93.58(3)	101.762(2)	
Volume (Å ³)	7629.2(5)	1982.2(7)	3670.66(15)	3214.00(16)
<i>Z</i>	4	2	4	4
Density (calc.) (Mg/m ³)	2.119	2.093	2.087	2.146
Absorption coefficient (mm ⁻¹)	1.393	1.467	1.534	1.760
<i>F</i> (000)	4656	1198		1984
Radiation and wavelength	Mo K α , λ = 0.71073 Å	Mo K α , λ = 0.71073 Å	Mo K α , λ = 0.71073 Å	Mo K α , λ = 0.71073 Å
Scan type	ω - ϕ	ω	ω - ϕ	$\omega/2\theta$
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)
2 θ range for collection (°)	5.90–54.00	4.46–49.94	6.10–54.78	4.22–55.86
Index ranges	–13 ≤ <i>h</i> ≤ 25; –15 ≤ <i>k</i> ≤ 10; –36 ≤ <i>l</i> ≤ 25	–10 ≤ <i>h</i> ≤ 0; –15 ≤ <i>k</i> ≤ 15; 0 ≤ <i>l</i> ≤ 19	–15 ≤ <i>h</i> ≤ 15; –20 ≤ <i>k</i> ≤ 20; –19 ≤ <i>l</i> ≤ 24	–15 ≤ <i>h</i> ≤ 15; –21 ≤ <i>k</i> ≤ 23; –20 ≤ <i>l</i> ≤ 20
Reflections collected	18635	7293	31787	23240
Independent reflections	12363 (.1640)	6967 (.010)	16274 (.0947)	7581 (.001)
[<i>R</i> _(int)]				
Observed reflections (<i>F</i> > 4 σ (<i>F</i>))	2892	3921	9130	4414
<i>R</i> _{final} ; <i>R</i> _{all data}	0.1345; 0.4337	0.0421; 0.0628	0.0677; 0.1398	0.0484; 0.1117
<i>R</i> _w _{final} ; <i>R</i> _w _{all data} ^a	0.2285; 0.3484	0.1161; 0.1292	0.1849; 0.2492	0.1042; 0.1318
GOF	0.950	1.029	0.897	0.996
Maximum, minimum peaks (e Å ⁻³)	0.745; –0.831	0.900; –0.877	2.052; –1.376	0.645; –0.639

$$^a w^{-1} = \sigma^2 F_o^2 + (0.1275P)^2, \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

3. Conclusions

The hydrogenation of the trinuclear ruthenium cluster derived from the bulky bis[di(pentafluoro)phenylphosphine] yields trinuclear products containing μ_2 -phosphide and μ_3 -phosphinidene derivatives where the phosphorus atoms are still a part of the bridging chelating ligand. The NMR characterization of these compounds shows the effect of this type of structure on ³¹P chemical shifts. The formation of metal- σ -aryl rings as intermediates in the formation of the phosphide and phosphinidene compounds was also observed. These intermediates are the first examples of cluster compounds containing fluorinated aryl compounds with direct bonds to the metal core.

4. Experimental

4.1. General procedures and materials

All reactions were carried out under nitrogen atmosphere. Commercial TLC plates (silica gel 60 F254, Merck Co.) were used to monitor the progress of the reactions and to isolate the products. All chemicals were purchased from Strem or Sigma–Aldrich Companies and were used without further purifications. Solvents were dried prior to use by standard techniques. Infrared spectra were recorded in cyclohexane solutions in a GX Perkin–Elmer 16F FT-IR spectrometer. NMR spectra were obtained using a JEOL Eclipse 400 and Bruker Advance DPX-300 spectrometers, with ¹H and ¹³C spectra relative to SiMe₄, ³¹P spectra relative to 85% aq. H₃PO₄ and ¹⁹F spectra referred to CFCl₃. All spectra were obtained in CDCl₃. Elemental analyses were obtained in a Perkin–Elmer ser-

ies II Analyzer 2400 and ThermoFinnigan Model Flash 1112 equipments. Melting points were taken in a MEL-TEMP II fusiometer and report without correction. Mass spectra were obtained in an Agilent Technologies ESI-TOF equipment in the negative detective mode at Washington University.

4.2. Synthesis of [Ru₃(CO)₁₀{(C₆F₅)₂P(CH₂)₂P(C₆F₅)₂}] (**1**) using [Ph₂CO⁻] as catalyst

The procedure for the synthesis of compound **1** is similar to the one described for the preparation of [Ru(CO)₁₀{Ph₂P(CH₂)₂PPh₂}] [25]; Ru₃(CO)₁₂ (50 mg, 0.078 mmol) was dissolved in THF (15 mL), 8 drops of [Ph₂CO⁻] catalyst were added to the solution, followed by the addition of (C₆F₅)₂P(CH₂)₂P(C₆F₅)₂ (65 mg, 0.086 mmol), the solution was treated, dropwise, with additional [Ph₂CO⁻], (8–10 drops), until the Ru₃(CO)₁₂ was totally consumed. The reaction proceeds quantitatively and the red product **1** obtained is spectroscopically the same as that described in the literature [10].

4.3. Synthesis of compounds [Ru₃(CO)₈(μ -H)₂(η^1 -C₆F₅)-{ μ_2 -(C₆F₅)PCH₂CH₂P(C₆F₅)₂}] (**2**), [Ru₃(CO)₉(μ -H)-{ μ_2 -(C₆F₅)PCH₂CH₂P(C₆F₅)₂}] (**3**), [Ru₃(CO)₇(μ -H)₃(η^1 -C₆F₅)-{ μ_3 -PCH₂CH₂P(C₆F₅)₂}] (**4**) and [Ru₃(CO)₈(μ -H)₂-{ μ_3 -PCH₂CH₂P(C₆F₅)₂}] (**5**)

A solution of [Ru₃(CO)₁₀{(C₆F₅)₂P(CH₂)₂P(C₆F₅)₂}] (**1**) (30 mg, 0.022 mmol) in toluene (15 mL) was heated at 348 K for 15 min in the presence of a hydrogen purge. The solvent was then removed under vacuum and the residue was redissolved in CHCl₃

(2 mL) and separated by preparative TLC plates using hexane/chloroform (80:20) as eluent. The first band (bright yellow) was identified as compound $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2\{\mu_3\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$ (**5**) (3.8 mg, 18%), a second band (orange-yellow) contained compounds **2** and **3**, a third yellow fraction corresponds to compound $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_3(\eta^1\text{-C}_6\text{F}_5)\{\mu_3\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$ (**4**) (1.1 mg, 5%). The second band was separated again by preparative TLC using hexane/chloroform (93:7) as eluent. After repeated chromatography the mixture was separated into two bands, the second one (yellow-orange) was identified as compound $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})\{\mu_2\text{-}(\text{C}_6\text{F}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$ (**3**) (10.2 mg, 40%) and the first band (yellow) was identified as compound $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\eta^1\text{-C}_6\text{F}_5)\{\mu_2\text{-}(\text{C}_6\text{F}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]$ (**2**) (5.0 mg, 17%).

A similar procedure was used to repeat the hydrogenation reaction of $[\text{Ru}_3(\text{CO})_{10}\{(\text{C}_6\text{F}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{F}_5)_2\}]$ (**1**) (15 mg, 0.011 mmol) at 348 K increasing the reaction time to 30 min. The same separation procedure yielded compounds, **5** (2.5 mg, 23%), **4** (0.9 mg, 7%), **3** (7.0 mg, 55%) and **2** (1.5 mg, 10%).

Analytical and spectroscopic data for compound 2: $\text{C}_{34}\text{H}_6\text{O}_8\text{F}_{19}\text{-P}_2\text{Ru}_3$ (1287.5). Melting point: 147–149 °C. IR (cyclohexane): $\nu(\text{CO})$ 2114(m), 2078(w), 2062(vs), 2056(m), 2044(s), 2038(s), 2016(w), 1990(m), 1966(w), 1942(w) cm^{-1} . Mass spectrometry FAB: m/z (relative intensity): 1258 (15) (M–H,CO)⁺, 1202.5 (68), 1174.5 (43), 1146.5 (100), 1118.6 (34), 1089.7 (35). NMR data: ¹H: 3.12(dddd) (1H) (CH_{2A}), ² $J_{\text{H-}^{31}\text{P}_A} = 44.5$, ³ $J_{\text{H-}^{31}\text{P}_B} = 14.9$, ² $J_{\text{H-}^1\text{H}} = 14.9$, ³ $J_{\text{H-}^1\text{H}} = 5.5$; (CH_{2A}), ² $J_{\text{H-}^{31}\text{P}_A} = 44.5$, ² $J_{\text{H-}^1\text{H}} = 14.9$, ² $J_{\text{H-}^1\text{H}} = 14.9$, ³ $J_{\text{H-}^1\text{H}} = 5.5$; –16.29 (ddm) (1H) (H₁) ² $J_{\text{H-}^{31}\text{P}_A} = 24.7$, ³ $J_{\text{H-}^{31}\text{P}_B} = 11.0$; –18.80 (br) (H₂) ² $J_{\text{H-}^{31}\text{P}_A} = 8.3$. ³¹P: 96.1 (s) (P_A), 46.9 (s) (P_B).

It was not possible to get appropriate elemental analyses for this compound because it converts to compound **3**.

Analytical and spectroscopic data for compound 3: $\text{C}_{29}\text{H}_5\text{O}_9\text{F}_{15}\text{-P}_2\text{Ru}_3$ (1147.5): Microanalysis: Calc.: C, 30.36; H, 0.44. Expt.: C, 30.13; H, 0.30. Melting point: 135–138 °C. Mass spectrometry: ESI m/z of the most intense peak in the isotopic pattern: 1149. IR (cyclohexane): $\nu(\text{CO})$ 2092(s), 2052(vs), 2038(s), 2028(sh), 2012(m), 2000(m), 1996(sh), 1988(m) cm^{-1} .

Analytical and spectroscopic data for compound 4: $\text{C}_{27}\text{H}_7\text{O}_7\text{F}_{15}\text{-P}_2\text{Ru}_3$ (1093.5): Microanalysis: Calc.: C, 27.72; H, 0.63. Expt.: C, 29.20; H, 1.07 (the analyses for this compound was repeated several times but we believe the results are not very good because it changes to compound **5**). Mass spectrometry: ESI m/z of the most intense peak in the isotopic pattern: 1093. IR (cyclohexane): $\nu(\text{CO})$ 2104(m), 2090(w), 2082(w), 2047(vs, br), 2025(w), 2007(m, br), 1968 (sh, br) cm^{-1} .

Analytical and spectroscopic data for compound 5: $\text{C}_{22}\text{H}_6\text{O}_8\text{F}_{10}\text{-P}_2\text{Ru}_3$ (953.4): Microanalysis: Calc.: C, 27.72; H, 0.63. Expt.: C, 27.33; H, 0.76. Melting point: 148–150 °C. IR (cyclohexane): $\nu(\text{CO})$ 2082(m), 2055(sh), 2043(vs), 2005(s), 1989(sh, br), 1970(w) cm^{-1} .

4.4. X-ray structural determination

Suitable crystals of compounds **2–5** were obtained by slow evaporation of CHCl_3 /hexane solutions, at low temperature (5 °C). All crystals were mounted on glass fibers. Crystal data and details of the structures are listed in Table 3. Crystals containing both **2** and **3**; as co-crystals; were very small and the large number of atoms in the asymmetric unit combined with the crystal size, did not allow a good refinement of the structure. Only the ruthenium, phosphorus and carbon atoms of the methylene groups were refined anisotropically. Other non-hydrogen atoms were only refined isotropically. Hydrogen atoms were placed in fixed positions.

Data for compounds **3** and **5** were collected in a CAD4 Enraf-Nonius while those of compound **4** were measured in a Kappa CCD Nonius diffractometer (Bruker). Data collection and cell

dimensions determination for compounds **3** and **5** were carried out using the CAD4 EXPRESS software [26]. In the case of compound **4**, data collection and cell dimensions determination and refinement were carried out using Collect, Nonius BV, 1997–2000 and the Otwinowski and Minor method [27].

A semi-empirical absorption correction method (SADABS) was applied in all cases. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the methylene groups were fixed at idealized positions and these were refined. Hydride groups were observed in Fourier difference maps and their positions refined. Crystals of **4** had to be cut to the appropriate size and this produced microfractures which affected some structure factor values, thus affecting the general refinement and the *R* value is relatively high. All calculations were carried out using the SHELX-97 package [28].

5. Supplementary material

CCDC 706659, 705660 and 706661 contain the supplementary crystallographic data for **3**, **4** and **5**. 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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