ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 585 (1999) 68–82

Journal of Organometallic Chemistry

Investigation of the reactivity of the phosphorus–hydrogen bond in $Cp'RuL_1L_2Cl$ complexes with diphenylphosphine ligands

Román Torres-Lubián [a,1], M. Jesús Rosales-Hoz [a], Atta M. Arif [b], Richard D. Ernst [b], M. Angeles Paz-Sandoval [a,*]

[a] *Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado 14-740, Mexico, D.F. 07000, Mexico*

[b] *Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA*

Abstract

Products resulting from the oxidation, chlorination, hydrolysis and ethanolysis of $Cp^*Ru(PHPh_2)_2Cl$ (**1**) are described. Chlorination of the P–H bond in **1** allowed isolation of $Cp^*Ru(PClPh_2)_2Cl$ (**6**) and there is spectroscopic evidence for the presence of $Cp^*Ru(PClPh_2)(PHPh_2)Cl$ (**5**). Hydrolysis of compounds **1** and **5** gave a dihydride complex $[Cp^*Ru(H)_2(OPPh_2)(POHPh_2)]$ (**13**) and cationic species $[Cp^*Ru(PHPh_2)_3]Cl$ (**14**) and $[Cp^*RuPOHPh_2(PHPh_2)_2]Cl$ (**15**). Formation of **14** was confirmed by the synthesis of $[Cp^*Ru(PHPh_2)_3]OTf$ (**14′**) through intermediate $[Cp^*Ru(MeCN)(PHPh_2)_2]OTf$ (**16**) which was obtained from the addition of AgOTf to **1** in MeCN solution. Reaction of $(Cp^*RuCl_2)_2$ (**12**) in EtOH with two equivalents of $PHPh_2$ gave compound **1** and ethanolysis products $Cp^*Ru(POEtPh_2)(PHPh_2)Cl$ (**18**) and $Cp^*Ru(POEtPh_2)_2Cl$ (**11**), while reaction of **12** with diphenylphosphine oxide ($OPHPh_2$) led to the formation of $Cp^*Ru(POHPh_2)_2Cl$ (**7**), which can either be converted to hydride compound $Cp^*Ru(H)(Cl)[(OPPh_2)(POHPh_2)]$ (**10**) or an aromatic ring of its coordinated phosphine will bind to the electrophilic $[Cp^*Ru]^+$ fragment to give compound $[Cp^*Ru[\mu\text{-}(\eta^6\text{-}C_6H_5)POHPh]Cp^*Ru(POHPh_2)Cl]Cl$ (**8**). Based on ^1H- and ^{31}P-NMR spectroscopic data, compounds with two different P-donor ligands have also been prepared, including $Cp^*Ru(POHPh_2)(PHPh_2)Cl$ (**9**), $[Cp^*Ru(POHPh_2)_2(PHPh_2)]OTf$ (**17**) and $Cp^*Ru(POHPh_2)(POEtPh_2)Cl$ (**19**). According to NMR observations, a free radical mechanism is proposed for the chlorination and oxidation reactions. Crystal structures are provided for complexes **6**, **13** and **18**, and a related cationic Cp complex $[CpRu(POHPh_2)(PHPh_2)_2]Cl$ (**20**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Pentamethylcyclopentadienyl; Cyclopentadienyl; Diphenylphosphine

1. Introduction

Significant reactivity of the P–H bond has been established in early transition metal complexes containing secondary and primary phosphines. In some cases, simple loss of H occurs, leading to bridging phosphides [1]. The formation of terminal phosphides has been observed through the oxidative addition of $PHPh_2$ to complexes, such as $Cp^*MoCl(N_2)(PMe_3)_2$, $Cp^*W(H)(Cl)(PMe_3)(\eta^2\text{-}CH_2PMe_2)$ and $Cp^*Ta(Me)_2(\eta^2\text{-}C_2H_4)$, giving the corresponding $Cp^*M(H)(Cl)(PPh_2)(PMe_3)$ [M = Mo, W] and $Cp^*TaMe(PPh_2)(\eta^2\text{-}C_2H_4)$, respectively [2]; or through HCl elimination from complexes $CpMCl(HPR_2)(CO)_2$ or $CpMH(ClPR_2)(CO)_2$ (M = Mo, W; R = alkyl, aryl) [3] to give $CpM(PR_2)(CO)_2$. It has been shown that these species can be isolated because of the 1,2-positioning of the hydrogen and chlorine atoms.

In contrast, there is a paucity of information on ruthenium species; while $Ru(PHRPh)_4Cl_2$ (R = H [4], Ph [5]) complexes have been reported, there are no reports in the literature on reactions of the P–H bond in secondary or primary phosphines complexed with ruthenium. We recently reported the synthesis, properties and crystal structures of pentamethylcyclopentadi-

* Corresponding author. Fax: +525-7477-113.

E-mail address: mpaz@mail.cinvestav.mx (M.A. Paz-Sandoval)

[1] Permanent address: CIQA, Blvd Ing. Enrique Reyna 140, Saltillo, Coahuila 25100, Mexico.

PII: S0022-328X(99)00191-6

enyl– and cyclopentadienyl–ruthenium (II) diphenylphosphine complexes $(C_5R_5)Ru(PHPh_2)_2Cl$ (R = Me, **1**; R = H, **2**) and $(C_5R_5)Ru(PHPh_2)(PPh_3)Cl$ (R = Me, **3**; R = H, **4**) [6] and we now present a study of the chemistry of the P–H bond for compounds **1** and **3**. Preliminary results on the Cp analogous complexes **2** and **4** revealed that the disubstituted compounds **1** and **2** are more reactive than the corresponding complexes with two different P-donor ligands, such as **3** and **4**, respectively, due to the presence of two P–H bonds.

The focus of this study is on the reactivity of the P–H bond in coordinated secondary phosphine complexes of ruthenium, with a goal of obtaining a more detailed understanding of how the chemistry of such species might be changed, and complicated, by the presence of the more reactive P–H bonds. As far as we are aware, this is the first attempt to gain an understanding of the reactivity of the P–H bond in a ruthenium complex. The results we have obtained differ significantly from those obtained in secondary phosphine complexes of Mo, W, Ta, Ir or Rh, and thus provide useful complementary information on the chemical behavior of the rarely used secondary phosphine ligands. In addition, the results serve as a guide to the effects that reaction conditions (solvent, inert atmosphere, etc.) will have on product distributions. In this paper we are more concerned in understanding the chemistry of the starting materials, rather than to obtain efficient methods of synthesis. We are also interested in learning how readily side products are formed, their structures and behaviour, so that one could then design and optimize subsequent studies accordingly. The chemistry of **1** with chloroform, atmospheric oxygen, ethanol and water turns out to be quite versatile, affording new Cp*Ru(II) and Cp*Ru(IV) compounds.

2. Results and discussion

2.1. ^1H- and ^{31}P-NMR studies of compound $Cp^*Ru(PHPh_2)_2Cl$ (1)

(a) On combining compound **1** in a sealed NMR tube with $CDCl_3$ and 1.5 equivalents of DBN (1,5-diazabicyclo[4.3.0]non-5-ene), the formation of compounds $Cp^*Ru(PHPh_2)(PClPh_2)Cl$ (**5**) and $Cp^*Ru(PClPh_2)_2Cl$ (**6**) took place by successive chlorination of both P–H bonds (Scheme 1). Prior to the complete transformation of **1** to **6** after 32 h at room temperature (r.t.), several species were detected by ^{31}P-NMR spectroscopy. Except for **5**, the other species were formed in only trace quantities, and after 3.66 h a ratio of 0.7:1:0.04 for **5**, **6** and **1**, respectively, was observed[2].

A similar experiment, now with the addition of a trace of 1,4-benzoquinone, revealed no evidence of any reaction, suggesting the involvement of free radicals in the previous reaction. Reaction of **1** with DBN in CD_2Cl_2 revealed no chlorination of the P–H bond even after 70 days at r.t.

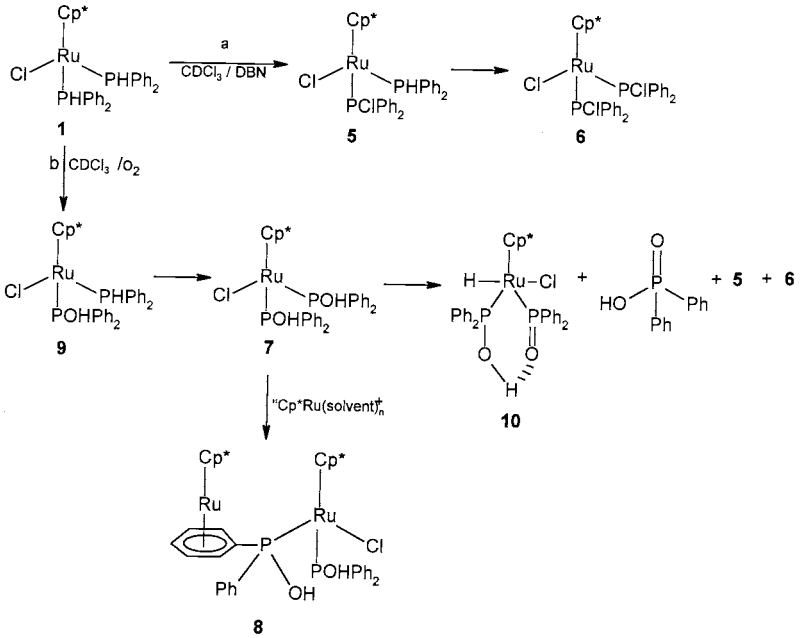
(b) In contrast, in the absence of DBN, reaction of **1** with $CDCl_3$ and air in an open NMR tube led to a complex mixture (Scheme 1) after 30 days with the formation of the following species: **6**, **7** [$Cp^*Ru(POHPh_2)_2Cl$] and **8** {[$Cp^*Ru[\mu\text{-}(\eta^6\text{-}C_6H_5)POHPh]\text{-}Cp^*Ru(POHPh_2)Cl]Cl$} whose identities were confirmed through their isolation from other reactions (vide infra)[3]. Diphenylphosphonic acid ($OPOHPh_2$, ^{31}P $\delta = 33.2$ ppm) and compounds **5**, **9** [$Cp^*RuCl(POHPh_2)(PHPh_2)$] and **10** {$Cp^*Ru(H)(Cl)[(OPPh_2)(POHPh_2)]$} (Scheme 1) are also proposed to be present, based on ^1H- and ^{31}P-NMR spectroscopic data. Furthermore, it was demonstrated that **7** is a precursor of **10**. The intramolecular oxidative addition for **7** occurs slowly, giving after 6.25 h in $CDCl_3$ a mixture of the monohydride compound **10** and compound **7** in a 1:2 ratio, respectively.

(c) Considering the adjacent positions of the chlorine and hydrogen atoms in compound **1**, we decided to check if an elimination of HCl could occur, presumably yielding a terminal phosphide complex in the absence of a chlorinated solvent. An experiment in an open NMR tube involving compound **1** in deuterated toluene was found to lead only to traces of compounds **5**, **6** and **9**, which in contrast could easily be formed in the presence of chloroform.

Even after 7 h at 100°C, compound **1** had undergone little change, while addition of 1.5 equivalents of Et_3N and heating at 100°C for 27 h gave, in traces, the same species **5**, **6** and **9**, along with diphenylphosphine oxide, $OPHPh_2$ (^{31}P $\delta = 19$ ppm). Finally, after 70 h at 100°C an insoluble dark material was found, along with the $OPHPh_2$.

[2] The reaction after 20 min at room temperature showed the following signals [relative intensities]: ^{31}P $\delta = 37.0$, s, [1] **1**; 34.6 (d, 50 Hz), 130.2 (d, 48 Hz), [1], **5**; 132.3, s, [0.25], **6**; 20.0, s, [0.12] and traces at 97.5, d; 80.5, s; 67.5, d; 37.8 (d, 23 Hz); 30.5 (d, 37.8 Hz); 21.8, s; 17.5, s. The minor species were not assigned. The reaction after 3.66 h at room temperature showed signals at: ^{31}P-NMR $\delta = 37.0$, s, [1], **1**; 34.6 (d, 48 Hz), 130.1 (d, 48 Hz), [17], **5**; 132.4, s, [24], **6**; 80.3, s, [0.7]; 37.8 (d, 25.3 Hz) [0.4]; 17.4, s, [0.43]; −2.35, s, [0.4] and signals found in traces at: 28.9, s; 67.5, d; 80.6, s; 110.8, s; 119.7 (d, 25.3 Hz)].

[3] The reaction after 10 days at room temperature showed basically starting material **1** by ^{31}P-NMR: $\delta = 37.2$ ppm [1] and peaks in lower quantities for compounds at °: 33.9, $(OH)P(O)Ph_2$, [0.8]; 130.4 (d, 48 Hz), 34.7 (d, 48 Hz), **5**, [0.7]; 130.2 (d, 53 Hz), 36.3 (d, 53 Hz), **9**, [0.5]; 9.4, s, **10**, [0.12]; 21.5, s, [0.08]; 129.2, s, **7**, [0.05]; 132.4, s, **6**, [0.05]; 29, s, [0.02]. After 17 days the same species are present in a different ratio: 1:2:1.5:1:0.7:0.07:0.23:0.23:0.07, respectively.



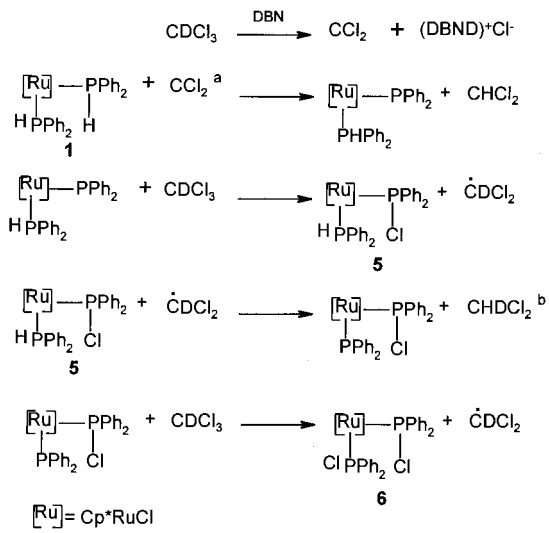
Scheme 1. (a) Products observed during the chlorination reaction of **1** at r.t., in a sealed NMR tube, in $CDCl_3$ with DBN. (b) Products observed during oxidation and chlorination reaction of **1** at r.t. in an unsealed NMR tube, in $CDCl_3$.

As described in Scheme 1, the chemistry of **1** in $CDCl_3$ consists basically of the chlorination and oxidation of the P–H bond. The chlorination could take place through the formation of a carbene from $CDCl_3$ and the base DBN (Scheme 2), while the oxidation could involve the activation of molecular oxygen by free radicals. The oxidation may occur at the coordinated $PHPh_2$, which appears more reasonable compared to other alternatives such as: (i) Initial dissociation of $PHPh_2$ from **1**, giving a coordinatively unsaturated species $Cp^*Ru(PHPh_2)Cl$ followed by oxidation of the free $PHPh_2$ and coordination of the resulting phosphine oxide to the ruthenium atom giving a new OP–Ru bond. This possibility was discarded because compound **1** did not undergo any reaction in the presence of an equivalent of $OPHPh_2$ in refluxing toluene for 4 h. A more polar solvent such as EtOH was also used, but in that case, the product $Cp^*Ru(POEtPh_2)_2Cl$ (**11**) was obtained as a result of the ethanolysis of **1** after 24 h at r.t. (vide infra); (ii) The participation of a coordinatively unsaturated complex which might activate molecular oxygen, has been reported during the oxidation of PPh_3 catalyzed by several organometallic compounds [7]. However, attempts to add oxygen to **1** in toluene-d_8 or in an even more polar solvent were not successful. An isopropanol solution of **1** even after 2 h in the presence of air at r.t. did not give evidence of a $OPHPh_2$ ligand.

2.2. Reaction of $(Cp^*RuCl_2)_2$ (12) and $OPHPh_2$

Due to the large number of products formed during the oxidation of **1** in chloroform, we considered whether some of these species could be prepared directly from the interaction of dimer **12** with the diphenylphosphine oxide (Scheme 3). From the latter reaction, after 1 h in EtOH, compounds **7**, **8** and $OPOEtPh_2$ were indeed obtained.

Considering the mechanism of the conversion of the coordinated phosphine oxide to phosphinite ($OPHR_2$) ligands, it is well known that a tautomeric equilibrium is present for phosphinites and their corresponding



Scheme 2. Proposed free radical mechanism for oxidation of the P–H group in **1**. (a) Carbenes in a triplet state abstract hydrogen or other atoms; in the singlet state they only remove halogens [45]. (b) There is evidence of $CHDCl_2$ formation in the ^{1}H-NMR spectrum.

phosphinous acids ($POHR_2$) [8]. Kinetic studies have supported the fact that the slow step is the tautomerization of the tricoordinated structure $POHR_2$, which is responsible for reactions with electrophiles. Additionally, compound **12** can be regarded as an electrophile which reacts with dienes, [9] σ-donor ligands such as phosphines, [10] and soft [11] or strong [12] nucleophiles such as MeOH and $Na[OP(OEt)_2]$, respectively. Then, we tentatively propose a nucleophilic attack by the phosphorus lone pair of two $POHPh_2$ ligands on one of the ruthenium atoms in compound **12**, giving complex **7**. The formation of compound **8** is attributed to the presence of **7** and a weakly solvated fragment $[Cp^*Ru(solvent)_n]^+$, which has already been observed by Chaudret [13]. The dimeric compound **8** has been characterized based on its similarities to the known $[CpRu[\mu\text{-}(\eta^6\text{-}C_6H_5)PPh_2]CpRu(PPh_3)Cl]Cl$ [14]. Finally, the formation of $OP(OEt)Ph_2$ can be expected to result from a nucleophilic attack of EtOH on the phosphorus atom of the diphenylphosphine oxide under the refluxing conditions used.

2.3. By-products obtained during the synthesis of compound $Cp^*Ru(PHPh_2)_2Cl$ (1)

We reported earlier the preparation of compound **1** in varying yields depending on the starting materials used: Cp*RuLCl, L = COD (90%), L = 1,5-NBD (1.5%), $[Cp^*RuCl]_4$ (75%); $Cp^*Ru(PPh_3)_2Cl$ (67%); $[Cp^*RuCl_2]_2$ (60%); $Cp^*Ru(PPh_3)Cl_2$ (48%) [6]. More recently, we isolated **1** from the last (paramagnetic) compound in 59% yield, as a result of changing the mixture of solvents used in the chromatography (8:2 hexane–diethyl ether). In the following discussions, we will refer exclusively to the species observed or isolated as by-products during the synthesis of **1**.

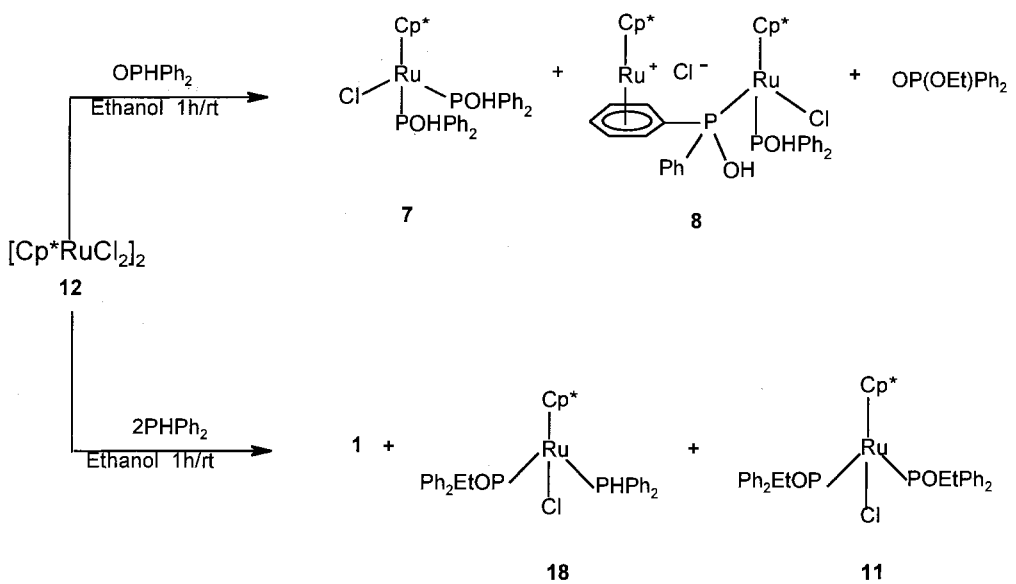
2.3.1. Reaction of $PHPh_2$ with $Cp^*Ru(PPh_3)Cl_2$

The addition of three equivalents of $PHPh_2$ to $Cp^*Ru(PPh_3)Cl_2$ gave a mixture of **1**, **5**, $PHPh_2$ and PPh_3. Chromatography of this mixture on silica gel afforded **1** in 48% yield, along with a dihydride compound $[Cp^*Ru(H)_2(OPPh_2)(POHPh_2)]$ (**13**) in 19% yield and small amounts of compounds $[Cp^*Ru(PHPh_2)_3]Cl$ (**14**) and $[Cp^*Ru(POHPh_2)(PHPh_2)_2]Cl$ (**15**) (Scheme 4).

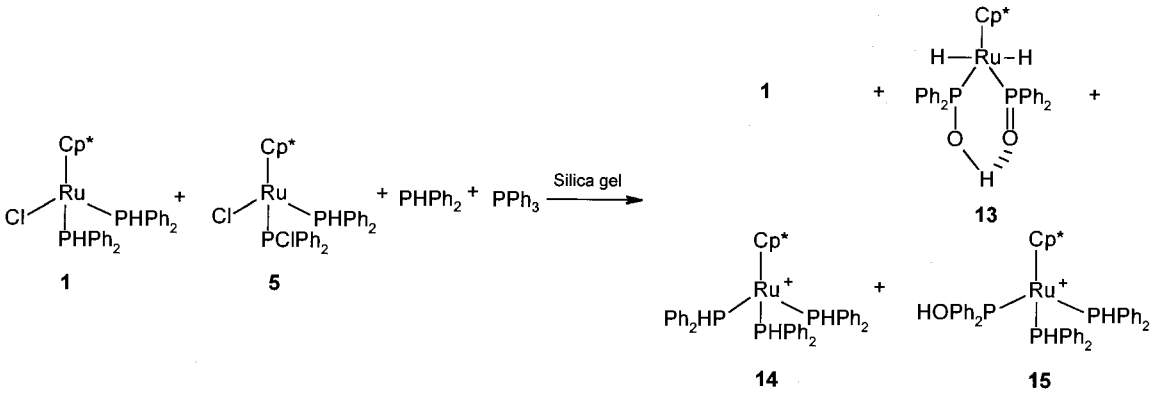
When chromatography was carried out on pure compound **1**, **1** was recovered in 67% yield along with 7% of **13**, showing that hydrolysis of **5** is more facile than that of **1**. Compound **5** was also observed from the reaction of **1** with chloroform (vide supra, **1a**) and it has, as already mentioned, only been characterized by ^1H- and ^{31}P-NMR spectroscopy as was also the case for **14** and **15**.

The formation of **14** and **15** may be rationalized as resulting from the easy dissociation of Cl^- from **1** and **5**, which, in the presence of an excess of $PHPh_2$, would lead to **14** and **15**. In order to confirm this hypothesis we prepared $[Cp^*Ru(PHPh_2)_3]OTf$ (**14′**) from **1** and AgOTf in acetonitrile (Scheme 5).

Precipitation of AgCl gave $[Cp^*Ru(MeCN)(PHPh_2)_2]OTf$ (**16**) cleanly. Addition of 1.2 equivalents of $PHPh_2$ to **16** then afforded **14′** which showed the same ^{31}P- and ^1H-NMR spectra as **14**. An NMR experiment showed that in solution compound **14′** suffers transformation into mono- and disubstituted compounds $[Cp^*Ru(POHPh_2)(PHPh_2)_2]OTf$ (**15′**) and $[Cp^*Ru(POHPh_2)_2(PHPh_2)]OTf$ (**17**), respectively. These compounds were not isolated, but their charac-



Scheme 3.



Scheme 4.

terizations were straightforwardly carried out through ^{1}H- and ^{31}P-NMR spectroscopy.

*2.3.2. Reaction of $PHPh_2$ with $(Cp^*RuCl_2)_2$ (**12**)*

Two equivalents of $PHPh_2$ in EtOH react with dimer **12** affording, according to ^{31}P-NMR, a mixture of three compounds: **1**, $Cp^*Ru(POEtPh_2)(PHPh_2)Cl$ (**18**) and $Cp^*Ru(POEtPh_2)_2Cl$ (**11**) in a 1:0.6:0.1 ratio (Scheme 3). Chromatography on silica gel afforded two fractions: The first one, eluted with hexane/diethyl ether (4:1), contained the unseparated compounds **1**, **11** and **18**. After several recrystallizations, the components of this fraction could be separated, affording pure compounds **11** and **18**. The second minor fraction was eluted with acetone/hexane (1:1) and gave a mixture of products **13** and **19** $[Cp^*Ru(POHPh_2)(POEtPh_2)Cl]$ which arose through hydrolysis of the corresponding compounds **1** and **18**. The small amount of **19** isolated only allowed for its characterization through ^{1}H- and ^{31}P-NMR.

In order to determine if reaction of the P–H group in $PHPh_2$ occurs before or after the formation of compound **1** we carried out two experiments: (i) $PHPh_2$ was mixed with EtOH, showing after 24 h at r.t. mostly $PHPh_2$ with only traces of $OPHPh_2$. After 3 days, this was heated at 60°C for 3 h without change. This result suggested that $PHPh_2$ did not suffer ethanolysis before being coordinated to the ruthenium atom. (ii) Reaction between **1** and EtOH, under a nitrogen atmosphere for 24 h at r.t., showed a complete transformation of **1** to **11** which indicates that the reaction of $PHPh_2$ occurs after formation of **1**. However, it is important to recognize that the ethanolysis is even faster when the dimer **12** is used as the starting material.

2.4. ^{1}H-, ^{13}C- and ^{31}P-NMR studies

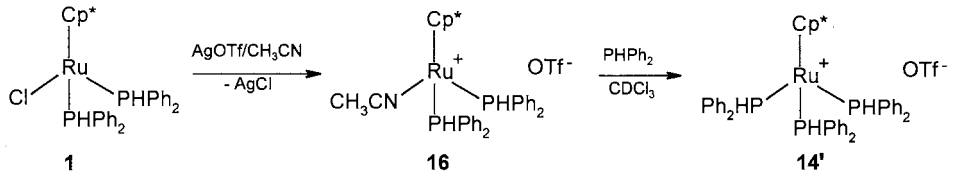
*2.4.1. Compounds $[Cp^*Ru[\mu\text{-}(\eta^6\text{-}C_6H_5)POHPh]Cp^*Ru(POHPh_2)Cl]Cl$ (**8**) and $[Cp^*Ru(H)_2(OPPh_2)(POHPh_2)]$ (**13**)*

Compounds **8** and **13** deserve detailed discussion due to their characteristic NMR patterns. Binuclear **8** is rather similar to $[CpRu(\mu\text{-}\eta^6\text{-}C_6H_5)PPh_2]RuCp(PPh_3)Cl]X$ [X = Cl, BPh_4] [14]. In its ^{31}P-NMR spectrum at 109.25 MHz, **8** in $CDCl_3$ exhibits two signals: a doublet (J_{PP} = 55.5 Hz) and a broad singlet while at 36.22 MHz the broad signal is partially resolved as a broad doublet (J_{PP} = 51.3 Hz)[4]. The same spectrum at −90°C showed two well-defined doublets (J_{PP} = 55.5 Hz). Similarly, **8** in CD_2Cl_2 at r.t. and at 109.25 MHz exhibited a weakly resolved doublet (J_{PP} = 53 Hz). It is not clear whether this behavior is due to a relaxation effect for P1 (–$POHPh_2$) or an electronic effect.

The assignments of P1 (–$POHPh_2$) and P2 (–POHPh) were carried out through ^{31}P–^{1}H heteronuclear correlation. Coupling between *ortho*-hydrogens of the coordinated phenyl ring and P2 showed a $^{3}J_{PH}$ = 6 Hz, while hydrogens from POH functions were found by ^{1}H-NMR to be correlated with P2 (δ = 9.6, d, 5 Hz) and P1 (δ = 8.4, d, 4.5 Hz).

When the chlorine counterion in **8** is replaced by PF_6, a drastic change was detected through ^{1}H- and ^{31}P-NMR spectroscopy. An AB system with substantially different chemical shifts (120.4 and 131.9 ppm) and coupling constants (J_{PP} = 45.4 Hz) was evident from ^{31}P-NMR. Similar behavior has been reported for $[(CH_2)_2S(O)MePt(PPh_2Me)(POHPh_2)]X$ (X = Cl, PF_6) [15], for which the ^{31}P chemical shifts changed from 51.5 (X = Cl) to 67.9 ppm (X = PF_6). This $\Delta\delta$ = 16.4 ppm was attributed to an interaction between the Cl^- and the hydrogen of the $POHPh_2$ ligand. For compound **8**, a similar $\Delta\delta$ = 15 ppm was observed and, according to heteronuclear correlation (^{1}H–^{31}P) data, the hydrogen bonding interaction of Cl is with the OH in P1.

[4] Interestingly, freshly prepared ^{1}H-NMR tube samples afforded broad signals, while after standing a couple of hours, sharper signals were then observed. The same observation has been made by Wilczewski [14a].



Scheme 5.

The ^{1}H-NMR spectrum of **8** showed an asymmetric aromatic ring with five triplets corresponding to the benzene ring π-bonded to Ru[5]. A triplet was observed for the methyl groups of one of the Cp* ligands due to long range coupling ($^4J_{PH} = 1.8$ Hz), while a singlet was found for the Cp* bonded to the cationic ruthenium atom. ^{13}C-NMR spectra showed that the *ortho* and *meta* carbon atoms were exclusively coupled to P2. There was no evidence of coupling for C*i*, even though it has a direct bond to P2. The rest of the resonances for the aromatic ring in the molecule were difficult to assign, in contrast with mononuclear species **1**, **6** and **7**.

The dihydride complex **13** showed in its ^{1}H-NMR spectrum a triplet at −8.38 ppm ($^3J_{PH} = 25$ Hz) for the equivalent terminal hydride ligands, a triplet of triplets at 1.29 ppm ($^4J_{PH} = 0.68$ Hz) for the Cp* ligand, and a singlet at 16.54 ppm (−90°C) for the hydroxy hydrogen atom, which above 0°C was observed as a broad signal. The ^{31}P-NMR spectrum showed a singlet at 116.37 ppm even at −90°C, suggesting a fast exchange of the bridging hydroxy hydrogen between the two phosphorus ligands in solution. The aromatic rings present in the P ligands were also equivalent as shown by ^{13}C-NMR.

2.4.2. NMR tube experiment of compound *4* with $PHPh_2$

In the presence of 5 equivalents of $PHPh_2$ in deuterated toluene, compound **4** was found to lead to the formation of **2**. Following this reaction it was observed that **2** was readily oxidized, giving several products, including compounds $[CpRu(POHPh_2)(PHPh_2)_2]Cl$ (**20**), $[CpRu(POHPh_2)_2(PHPh_2)]Cl$ (**21**) and diphenylphosphonic acid, $OPOHPh_2$.

A few examples of complexes with $POHPh_2$ ligands are known in the literature, namely, $W(CO)_4(POHPh_2)(PPh_2CH_2COR)$ (R = Ph, p-MeC_6H_4) [18] and $PtCl_2(PXR_2)$ (X = OH, R = OEt,Ph, Et) [19].

2.4.3. General spectroscopic trends

The ^{31}P-NMR spectra of Cp and Cp* complexes with two different P-donor ligands showed J_{PP} values around 45–66 Hz, suggesting adjacent P atoms. It has been predicted [20] that J_{PP} should increase as the phosphine π-accepting ability increases. This expected trend was observed for compounds $Cp^*Ru(POHPh_2)(POEtPh_2)Cl$ (**19**) > $Cp^*Ru(PClPh_2)(PHPh_2)Cl$ (**5**) > $Cp^*Ru(POEtPh_2)(PHPh_2)Cl$ (**18**), $[CpRu(POHPh_2)(PHPh_2)_2]Cl$(**20**) > $CpRu(PHPh_2)(PPh_3)Cl$ (**4**) > $[CpRu(POHPh_2)_2(PHPh_2)]Cl$ (**21**) > $[Cp^*Ru(POHPh_2)_2(PHPh_2)]OTf$ (**17**), $[Cp^*Ru(POHPh_2)(PHPh_2)_2]Cl$ (**15**) as a result of the presence of atoms more electronegative than carbon in the phosphine ligands.

A comparison of J_{PP} values and the P1–Ru–P2 bond angles for compounds **3** [42.9 Hz, 91.33(8)°] and **4** [46.7 Hz, 92.26(8)°] suggests that the difference in J_{PP} values may be due to an electronic effect, since the bond angles are very similar [6]. The same trend was found for compounds **20** (47.9 Hz) and **21** (55.5 Hz).

Resonances for the Cp ligand did not show evidence of $^3J_{PH}$ couplings by ^{1}H-NMR, while those for the Cp* ligand appeared as triplets due to $^4J_{PH}$. Similar long-range couplings were reported for compounds $[Cp^*M(PHPh_2)_2Cl]^+$ [M = Rh, $\delta = 1.45$ (t), $^4J_{PH} = 3.8$; M = Ir, $\delta = 1.49$ (t), $^4J_{PH} = 2.5$] [21].

The methylenic hydrogen atoms of the OEt group in compound **11** were observed as a multiplet which, after irradiation of the Me group, afforded a triplet with $J_{PH} = 2.5$ Hz. This virtual coupling has also been detected for aromatic *i*, *o* and *m* carbon atoms of the phosphine ligands through ^{13}C-NMR. Similar couplings were observed for compounds $Cp^*Ru(PHPh_2)_2Cl$ (**1**), $CpRu(PHPh_2)_2Cl$ (**2**), $Cp^*Ru(PClPh_2)_2Cl$ (**6**), $Cp^*Ru(POHPh_2)_2Cl$ (**7**), $[Cp^*Ru(MeCN)(PHPh_2)_2]OTf$ (**16**) and $[CpRu(POHPh_2)(PHPh_2)_2]Cl$ (**20**), as well as for compounds $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+$ and $[(\eta^3\text{-}C_3H_5)Pd(PEt_2Ph)_2]^+$ [22].

The asymmetric compounds $CpRu(PHPh_2)(PPh_3)Cl$ (**4**) and $Cp^*Ru(POEtPh_2)(PHPh_2)Cl$ (**18**) showed three and four chemically non-equivalent rings, respectively, in the aromatic region, while disubstituted compounds **1**, **2**, **6**, **7** and $Cp^*Ru(POEtPh_2)_2Cl$ (**11**) with prochiral Ru and P atoms gave eight signals in the aromatic region: six triplets and two singlets. This fact suggests free rotation of the P–C aromatic ring bonds leading to the corresponding equivalence of the respective *ortho* and *meta* carbon atoms in both rings. Interestingly, $[Cp^*RuPOHPh_2(PHPh_2)_2]Cl$ (**15**) showed virtual cou-

[5] It is interesting to contrast the good resolution obtained for compound **8** with the poorer results for compounds $[CpRu(\mu\text{-}\eta^6\text{-}C_6H_5)PPh_2]RuCp(PPh_3)Cl]X$ [X = Cl, BPh4] [14] $CpRu(\eta^6\text{-}C_6H_5PPh_2)BPh_4$ [14], $CpRu(\eta^6\text{-}C_6H_5)BPh_3$ [16]; $[CpRu(\eta^6\text{-}C_6H_5\text{-}POPh_2]X$ (X = Cl, BPh_4 14a; X = ClO_4 [17]).

pling for the aromatic carbon atoms of the two $PHPh_2$ ligands, while for $POHPh_2$ only doublets were observed, indicating that the coupling only involves one of the P atoms.

2.5. Crystal structures of compounds Cp*Ru(PClPh$_2$)$_2$Cl (6), [Cp*Ru(H)$_2$(OPPh$_2$)(POHPh$_2$)] (13), Cp*Ru(POEtPh$_2$)(PHPh$_2$)Cl (18) and [CpRu(POHPh$_2$)(PHPh$_2$)$_2$]Cl (20)

Selected crystallographic data are summarized in Table 1, and ORTEP diagrams of **20**, **18**, and **13** are displayed in Figs. 1, 2 and 4, respectively. Crystals of compound **6** showed the presence of a disordered molecule of hexane; the refinement was carried out exclusively for the metallic fragment, which is shown in Fig. 3.

2.5.1. Molecular structure of [CpRu(POHPh$_2$)(PHPh$_2$)$_2$]Cl (20)

The molecular structure of cationic complex **20** has a three-legged piano stool geometry with angles near 90° between the phosphine ligands, indicating a pseudo-octahedral ruthenium atom in which the steric interactions for $PHPh_2$ and $POHPh_2$ ligands are very similar. The structure of compound **20** showed disorder as a result of the $POHPh_2$ ligand being present in all three phosphine locations, yielding occupancy values for the oxygen sites of 0.1586 (O1), 0.1566 (O2) and 0.6853 (O3). Thus, P3 has the highest $POHPh_2$ character and the Ru–P3 bond length is similar to the value of 2.274(1)Å in **13**. Selected bond distances and angles are reported in Table 2.

The Ru–C (Cp) distance showed small deviations by the Cp plane from perpendicularity relative to the $Ru–C_{centroid}$ vector (1.890 Å). The latter distance is significantly longer than other $Ru–C_{centroid}$ distances, such as those in **4** (1.841 Å) [6], **18** (1.868 Å), and other Cp [23] and Cp* [6,24] complexes, except for **6** (1.884 Å) and **13** (1.914 Å). This observation may reflect the smaller electron density on the Ru atom due to the presence of the better π acceptor $POHPh_2$ ligand.

2.5.2. Molecular structures of Cp*Ru(PClPh$_2$)$_2$Cl (6) and Cp*Ru(POEtPh$_2$)(PHPh$_2$)Cl (18)

Selected bond distances and bond angles are given in Table 3 for neutral pseudo-octahedral structures **6** and **18**.

From the Cl(1)–Ru–P1, Cl(1)–Ru–P2 and P1–Ru–P2 bond angles for several of the three-legged piano stool structures, it is clear that the increase in the octahedral distortion follows the order: CpRu(PHPh$_2$)(PPh$_3$)Cl(**4**) < Cp*Ru(PHPh$_2$)$_2$Cl (**1**) ≈ Cp*Ru(POEtPh$_2$)(PHPh$_2$)Cl (**18**) < Cp*Ru(PHPh$_2$)(PPh$_3$)Cl(**3**) < Cp*Ru(PClPh$_2$)$_2$Cl (**6**). The corresponding Cl(1)–Ru–P1, Cl(1)–Ru–P2 and P1–Ru–P2 angles for similar Cp complexes [25,26] and pentadienyl derivatives [27], including complexes (η^5-C_nH_m)Ru(PHPh$_2$)(PPh$_3$)Cl [$n=5$, $m=7$, 91.73(3), 96.70(3), 93.34(3); $n=7$, $m=11$, 85.81(2), 85.92(2), 92.45(2)°] [28] allowed us to compare the influence of the phosphine ligands in these 'half sandwich' compounds. Notably, Cp complexes with two different P-donor ligands [25,26] showed no significant difference between their Cl–Ru–P1 and Cl–Ru–P2 angles, while the disubstituted Cp* species **1** [Δ = 6.5°] [6] and **6** [Δ = 3.5°], as well as pentadienyl complexes (η^5-C_5H_7)Ru(PEt$_2$R)$_2$Cl [R = Et Δ = 6.76°; R = Ph Δ = 4.74°] [27] showed important differences between these angles, reflecting the higher steric congestion of the Cp* and the open pentadienyl ligand compared to the analogous Cp species. The same trend has been observed for the mixed Cp species **4** (Δ = 0.84°) [6] and Cp* species **3** (Δ = 8.9°) [6] and **18** (Δ = 6.2°).

As expected from the ligand cone angles, compound **6** (137°) [29] was found to have its three P–Ru–(P,Cl) angles greater than 90°, and a $Ru–Cp^*_{centroid}$ distance longer than that found for **1** or the mixed compounds **3**, **4** and **18**, as a result of the electronegative Cl atom in the phosphine ligands. Thus, a greater angular separation was required for the $PClPh_2$ ligands in **6**. The mean Ru–P2 distance (2.278 Å) in compounds **1**, **3**, **4** and **18** is shorter than the corresponding ones for *trans*-Ru(PHPh$_2$)$_4$Cl$_2$ (Δ = 2.358 Å) [4,30], or (η^5-C_nH_m)Ru(PHPh$_2$)(PPh$_3$)Cl ($n=5$, $m=7$, 2.308 Å; $n=7$, $m=11$, 2.297 Å) [28].

Interestingly, the Ru–P1 and Ru–P2 distances in **6** are shorter than the $Ru–PHPh_2$ distances in **1**, **3**, and **4** even though the cone angle for $PClPh_2$ (137°) is larger than the corresponding one for $PHPh_2$ (128°). This may reflect a predominantly electronic effect, the general shortening observed for π-accepting ligands [31]. The parallel orientation observed for the two aromatic rings in **6** (Fig. 3) likely represents a favorable π–π stacking interaction between the two rings. Some of the resulting non-bonded contacts are: Cl(10)–Cl(20) (3.784 Å), C29–C17 (3.421 Å), C30–C18 (3.590 Å), C31–C19 (3.748 Å), C32–C20(3.746 Å), C33–C21 (3.554 Å) and C34–C22 (3.380 Å), which would thus require the parallel positioning of the aromatic rings.

A shorter Ru–Cl distance was observed for **6** compared to **1**, presumably due to the lower electron density on the ruthenium atom. The C11–P1–C17 (97.5°) and C29–P2–C35 (99.1°) angles in **6** are significantly smaller than those of 101.5° and 104.9° for **1**, reflecting the greater steric crowding experienced on coordination by $PClPh_2$ as compared to $PHPh_2$. The same trend holds for $POEtPh_2$ and $PHPh_2$ in **18**.

In summary, we can conclude that $PClPh_2$ ligands in compound **6** are better π acceptor than $PHPh_2$ and PPh_3 in their analogous complexes (**1**, **3** and **4**) [6]; this

Table 1
Crystal data for **6**, **13**, **18** and **20**

Formula	$C_{34}H_{35}P_2Cl_3Ru$ (**6**) [a]	$C_{34}H_{38}O_2P_2Ru{\cdot}CHCl_3$ (**13**)	$C_{36}H_{41}OP_2ClRu$ (**18**)	$[C_{41}H_{38}OP_3Ru]Cl$ (**20**)
Molecular weight	713.03 [a]	761.08	688.20	775.5
Crystal system	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	*Pbca*
a (Å)	16.717(5)	10.156(4)	10.537(3)	12.150(4)
b (Å)	9.789(2)	10.869(4)	16.367(5)	17.712(2)
c (Å)	23.724(7)	16.718(7)	10.954(4)	33.241(5)
α (°)	90.0	106.44(3)	80.20(2)	90
β (°)	107.59(3)	89.89(3)	113.47(2)	90
γ (°)	90.0	104.25(3)	108.16(2)	90
V (Å^3)	3700.9(1.7)	1711.05	1644.12	7154(3)
Z	4	2	2	8
F(000)	1820 [a]	780	712	3168
Radiation	Mo–K_α ($\lambda = 0.7107$ Å)	Mo ($\lambda = 0.7107$ Å)	Mo ($\lambda = 0.7107$ Å)	Mo–K_α ($\lambda = 0.7107$ Å)
μ (Mo–K_α) (cm^{-1})	9.23	8.07	6.71	6.68
D_{calc} (g cm^{-3})	1.6 [a]	1.477	1.39	1.44
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Δw (°)	0.80 + 0.345 tg θ	0.8 + 0.35 tg θ	0.8 + 0.34 tg θ	0.8 + 0.345 tg θ
θ limit (°)	1–25	1–25	2–25	1–25
Total data	7156	6234	6108	5918
Total unique data	6506	6004	5420	5354
Total observed data $(F_o)^2 > 3\sigma(F_o)^2$	3900	4555	4077	2156
Decay %	0.04	<1	<1	<1
DIFABS corr. range	0.37:1.45	0.93:1.045	0.68:1.0	0.93:1.1
Final R_1 [b]	0.088	0.0374	0.0507	0.039
Final wR_2 [c]	0.099	0.0492	0.0605	0.041 $\omega = 1.0$
No. of refined parameters	390	400	374	434

[a] There are some electron density peaks that suggest a disordered solvent molecule in the lattice. The refinement reported here was obtained excluding the solvent molecule.
[b] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[c] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

is reflected by the increase in the M–$Cp_{centroid}$ distance, perhaps the smaller C–P–C angles and a shortening of the Ru–P bond. However, it is also true that there is not a general increase in the P–C distances, which perhaps reflects only a weak participation of their σ^* bonds in backbonding interactions [31].

*2.5.3. Molecular structure of [Cp*RuH$_2$(OPPh$_2$)(POHPh$_2$)]·CHCl$_3$ (13)*

The complex has a four-legged piano stool geometry (Fig. 4), with the ruthenium atom then formally heptacoordinated. There is also a molecule of chloroform in the unit cell. Selected bond lengths and angles are reported in Table 4.

The angle of 85.58° between the Cp* and P1–Ru–P2 planes represents the greatest deviation from perpendicularity among similar MH_2L_2 complexes [32–39]. The $Cp^*_{centroid}$–Ru distance (1.914 Å) in **13** is similar to that found for some of the dihydride complexes described above [32–35], but significantly longer than those for the pseudo-octahedral Ru(II) compounds Cp*Ru(NBD)Cl, (**1**, **3**, **4**) [6], **18** and **20**. This increase may reflect reduced electron density on the ruthenium(IV) center, due to both its greater charge as well as the presence of oxygenated phosphorus ligands which have good π acceptor properties, and also the increased steric repulsions in **13**. Various electron deficient species, such as the dimers $(Cp^*RuCl_2)_2$ (**12**) (2.191 Å), $[(\eta^5\text{-}C_5Me_4Et)RuCl_2]_2$ (2.191 Å) and $[Cp^*RuBr_2]_2$ (2.194 Å) showed longer $Cp^*_{centroid}$–Ru distances [40] compared to **13**.

The P1–Ru–P2 angle (95.40°) is somewhat similar to that of $[Cp^*FeH_2(dippe)]BF_4$ [37] but even closer to those found for other dihydride compounds without chelating phosphines [32,33,35,36,38,39]. The Ru–P2 distance of 2.274 (1) Å is shorter than that for Ru–P1, 2.291(1) Å, reflecting the better ability of P2 to receive electron density from the metal. To the best of our knowledge, no examples of crystalline ruthenium–hydrogen phosphonate complexes exist. A report on the platinum complex *cis*-$PtH[OPPh_2][POHPh_2](PEt_3)$, prepared by the addition of $OPHPh_2$ to $Pt(PEt_3)_3$, [41] showed quite similar M–P bonding. The O1–O2 separation (2.317 Å) is shorter than the corresponding value for **13** (2.467(4) Å). However, both distances are shorter than the sum of the van der Waals radii, which is indicative of hydrogen bonding involving the two oxygen atoms. Further support for this conclusion is provided by the observation that the two P–O bond lengths (P1–O1, P2–O2) have values between those reported for single (1.60 Å) and double [1.483(2) Å] P–O bonds [41]. However, the

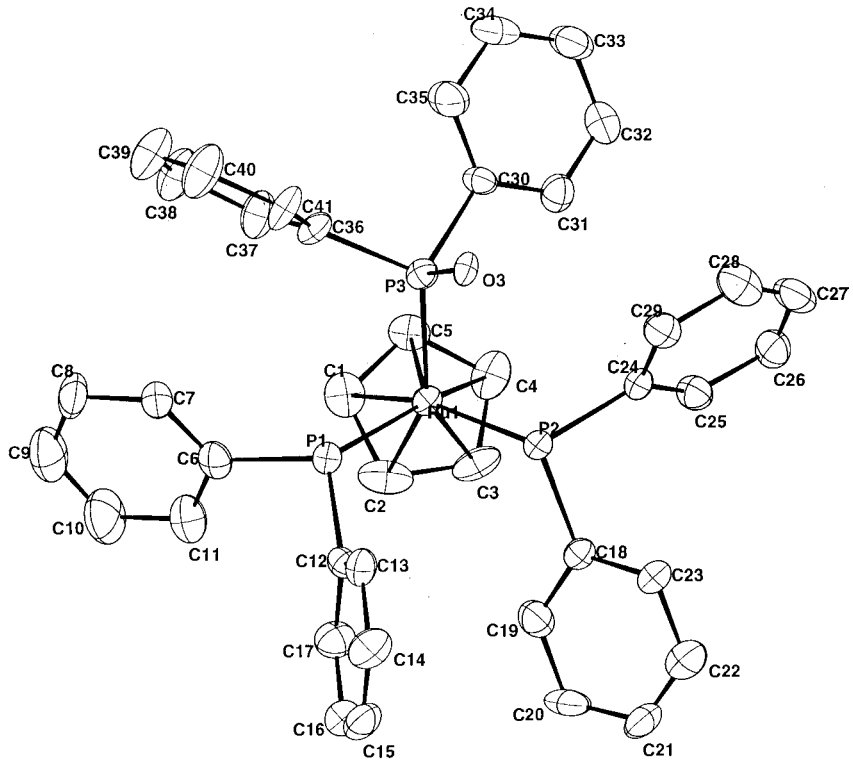


Fig. 1. ORTEP drawing of compound $[CpRu(POHPh_2)(PHPh_2)_2]Cl$ (**20**).

O–H1C distances are not equivalent. Thus, it could be proposed that H1C is covalently bonded to O2 and hydrogen bonded to O1 (Table 4).

3. Experimental

All compounds were prepared under a dry nitrogen atmosphere using conventional vacuum line techniques. Solvents were dried and distilled prior to use by standard methods. Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY and Robertson Microlit Laboratories, Inc., Madison, NJ. Melting points (uncorrected) were obtained on a Mel-Temp apparatus in sealed capillaries. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 16FPC-FT spectrophotometer. Electron-impact mass spectra were recorded on a Hewlett–Packard HP-5990A or a Finnigan MAT95 (FAB) mass spectrometer. ^{1}H-, ^{31}P- and ^{13}C-NMR spectra were recorded at 270, 109.25 and 67.8 MHz on a Jeol GSX-270 spectrometer or at 90, 36.2 and 22.5 MHz on a Jeol FX90Q spectrometer. Spectral standards were TMS (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P).

Purchased reagents, $RuCl_3{\cdot}3H_2O$, $PHPh_2$, C_5Me_5H, Zn (Strem), PPh_3, AgOTf, *n*-BuLi (Aldrich), C_5H_6 (previously cracked from dicyclopentadiene, Eastman Organic Chemicals), silica gel (Merck, 0.04–0.063 mm) were used as supplied. The $(Cp^*RuCl_2)_2$ (**12**) [40], (**1**–**4**) [6], and $OPHPh_2$ [42] reagents were synthesized using literature procedures.

3.1. Synthesis of $Cp^*Ru(PClPh_2)_2Cl$ (6)

Compound **1** (425 mg, 0.66 mmol) was dissolved in $CHCl_3$ (15 mL) under nitrogen, and Et_3N (0.12 mL, 0.86 mmol) was added at ambient temperature. The solution was refluxed for 8 h, without any obvious color change. The $CHCl_3$ was removed under vacuum and hexane extractions afforded an orange–red powder which was recrystallized with $CHCl_3$/hexane. Yield 83.7 mg (17.8%); m.p. 122–125°C. Anal. Calc. for $C_{34}H_{35}Cl_3P_2Ru{\cdot}CHCl_3$: C, 50.50; H, 4.36 Found: C,50.37; H,4.13. ^{1}H-NMR ($CDCl_3$): δ 7.90–6.90 (m, 20H), 1.34 (t, $^4J_{PH} = 2.64$, 15H); ^{31}P{^{1}H}-NMR: δ 132.32 (s); ^{13}C{^{1}H}-NMR: δ 141.07 (*t*, 16.5, *i*), 140.41 (*t*, 15.4, *i*), 132.53 (*t*, 7.7, *o*), 131.13 (*t*, 6.6, *o*), 129.88 (s, *p*), 129.15 (s, *p*), 127.37 (*t*, 5.5, *m*), 127.29 (*t*, 5.5, *m*), 95.65 (s, Cp*), 9.14 (s, Cp*). Mass spectrum (EI + VE, 25 eV): *m*/*z* (%); 714(10) $[M+1]^+$, 729(7), 658(4), 678(2), 544(18), 492(70.5), 472(9), 457(40), 421(8.5), 272(1.7), 236(1.5), 220(100), 183(50.6), 154(77.7), 107(20.0).

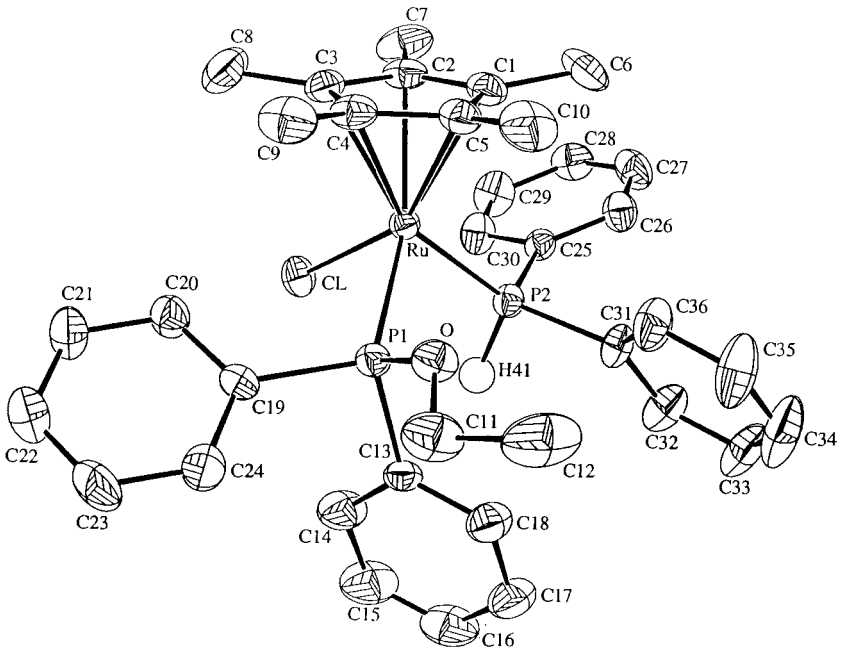


Fig. 2. ORTEP drawing of compound $Cp^*Ru(POEtPh_2)(PHPh_2)Cl$ (**18**).

3.2. Synthesis of $Cp^*Ru(POHPh_2)_2Cl$ (**7**) and $[Cp^*Ru[\mu\text{-}(\eta^6\text{-}C_6H_5)POHPh]Cp^*Ru(POHPh_2)Cl]Cl$ (**8**)

Compound **12** (568 mg, 1.85 mmol) was dissolved in EtOH (20 mL), and $OPHPh_2$ (746 mg, 3.69 mmol) was added to the stirred dark-brown solution at r.t. After 1 h of reflux the wine-red solution was filtered and concentrated to half of its original volume. Compound **8** precipitated as a yellow powder upon overnight cooling to 0°C and it was filtered and recrystallized twice; first, from CH_2Cl_2/hexane and then from $CHCl_3$/hexane. Yield 230 mg (13.1%); m.p. 140–142°C. Anal. Calc. for $C_{44}H_{52}Cl_2O_2P_2Ru_2{\cdot}CH_2Cl_2$: C, 52.33; H,5.23; Cl, 13.73 Found: C, 51.51; H, 4.95; Cl, 12.25. ^{1}H-NMR (CD_2Cl_2): δ 9.6 (d, 5, 1H), 8.4 (d, 4.5, 1H), 8.3 (s, br, 1H), 7.77 (s, br, 1H), 7.65 (t, 8.6, 1H), 7.3–7.5 (m, 2H), 7.0–7.15 (m, 5H), 6.8–6.97 (m, 5H), 6.27 (t, 6, 1H, *o*), 5.86 (t, 6, 1H, *o′*), 5.06 (t, 6, 1H, *m′*), 4.62 (t, 6, 1H, *p*), 4.52 (t, 6, 1H, *m*), 1.48 (s, 15H, Cp*), 1.03 (t, 1.8, 15H, Cp*); $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 117.36 (d, 55.5), 106.15 (br). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 148.51 (d, 28.7, *i*), 140.58 (d, 49.5, *i*), 126.5–128.2 (m), 129.5–132.5 (m), 109.43 (s), 95.31 (s, Cp*), 92.99 (s, Cp*), 86.89 (d, 11), 85.95 (d, 13.2), 85.58 (s), 84.37 (d, 5.6), 82.90 (d, 4.4), 10.67 (s, Cp*), 9.26 (s, Cp*). IR: ν(OH) = 3442, ν(P–OH) = 870. Mass spectrum (20 eV, EI): *m*/*z*(%) 912(4.0) [M^+], 1082(4.56), 926(14.35), 880(9.20), 844(37.9), 833(100.0), 818(83.36), 632(31.36), 544(64.0), 472(9.9), 437(2.0), 361(13.2), 371(25.1), 315(5.0), 78(40.7), 52(3.0). [LR/FAB (3NBA/$CHCl_3$)]: 912(2.6) [M^+], 877(0.5), 709(0.6), 439(7.3), 154(100), 136(68)]. After filtration of **8** the remaining ethanolic solution was reduced in volume, and chromatography on silica gel [7:3 hexane–diethyl ether elution] afforded an orange–yellow powder, which after recrystallization gave 250 mg of **7** (20%). m.p. (dec) 110°C. Anal. Calc. for $C_{34}H_{37}ClO_2P_2Ru$: C, 60.40; H, 5.52. Found: C, 60.88; H, 5.53. ^{1}H-NMR ($CDCl_3$): δ 7.15–7.43 (m, 20H), 4.90 (s, br, 2H), 1.29 (t, 1.8, 15H); $^{31}P\{^1H\}$-NMR: δ 129.23 (s); $^{13}C\{^1H\}$-NMR: δ 142.45 (dd, 23, *i*), 140.23 (dd, 27 *i*), 130.66 (dd, 6.5, *o*), (two overlapped triplets), 129.48 (s, *p*), 129.16 (s, *p*), 127.57 (dd, 5.5, *m*), 127.31 (dd, 4.4, *m*), 91.98 (s, Cp*), 9.66(s, Cp*). IR: ν(O–H) = 3343, ν(P–OH) = 828. Mass spectrum [LR/FAB (3NBA/$CHCl_3$)]: *m*/*z* (%) 676(6.94) [M^+], 641(19.3), 474(10.51), 439(68.2), 422(7.36), 361(13.11), 314(16.32), 236(7.59), 91(52.4), 55(100.0).

3.3. Synthesis of $Cp^*RuH_2(OPPh_2)[POHPh_2]$ (**13**), $[Cp^*Ru(PHPh_2)_3]Cl$ (**14**) and $[Cp^*Ru(POHPh_2)(PHPh_2)_2]Cl$ (**15**)

Compound $Cp^*Ru(PPh_3)Cl_2$ (1.32 g, 2.32 mmol) was partially dissolved in THF (70 mL), and $PHPh_2$ (1.21 mL, 6.96 mmol) was added dropwise with stirring at r.t. The solution was refluxed for 4 h, giving a yellow–orange solution, which was filtered and reduced in vacuo (^{31}P-NMR of the crude product showed a mixture of species **1**, **5**, $PHPh_2$ and PPh_3). The residue was dissolved in a small amount of toluene and chromatography was carried out with a silica gel column (4.5 × 15.5 cm) using hexane, 7:3 hexane–diethyl ether and 1:1 hexane–acetone, giving $PHPh_2$ and PPh_3, **1** (715 mg, 48%), and **13** (295 mg, 20%), respectively. Crystals of **13** for X-ray studies were obtained by liquid diffusion of hexane into a $CHCl_3$ solution. m.p. (dec.) 175°C. Anal.

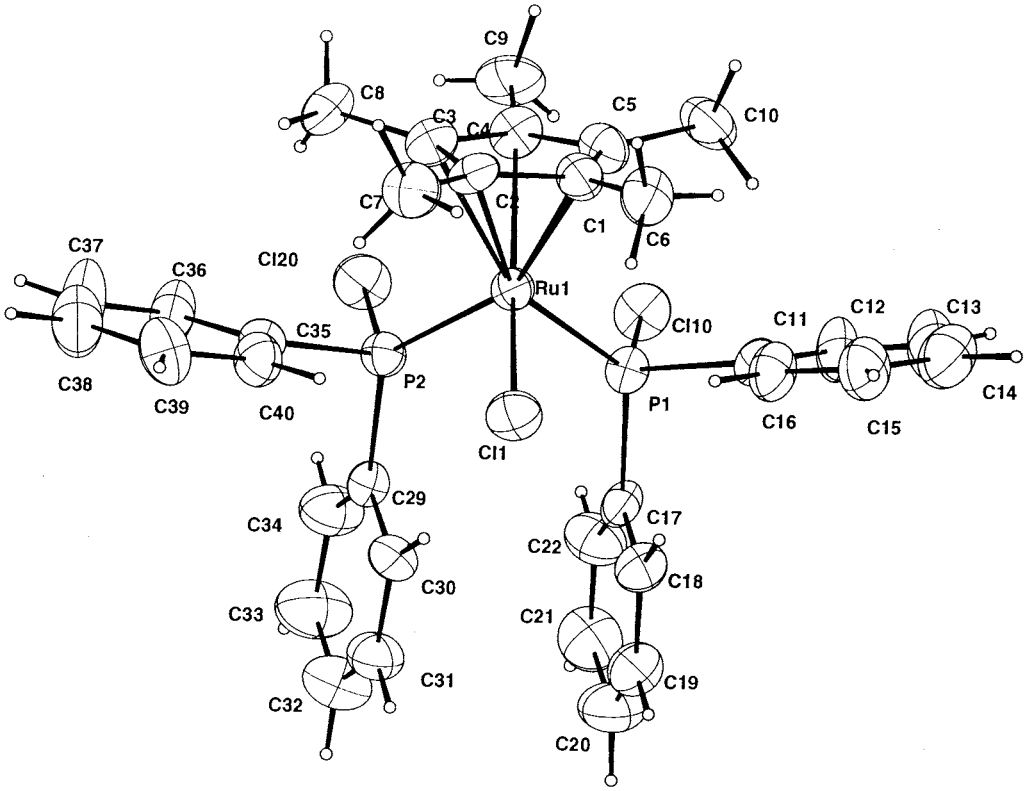


Fig. 3. ORTEP drawing of compound $[Cp^*Ru(PClPh_2)_2Cl$ (**6**).

Calc. for $C_{34}H_{38}O_2P_2Ru$: C, 63.65; H, 5.97 Found: C, 63.80; H, 5.54. ^{1}H-NMR (CD_2Cl_2): δ 16.54 (s, 1H, −90°C), 7.29–7.56 (m, 20H), 1.29 (tt, 0.67, 15H), −8.38 (t, 25, 2H); $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 116.37 (s); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 143.52 (*t*, 65, 2.2, *i*), 131.54 (*t*, 5.5 and two lateral signals of 27.6 Hz, *o*), 129.45 (s, *p*), 127.50 (*t*, 5.5 and two lateral signals of 26.4 Hz, *m*), 98.02 (s, Cp*), 9.10 (s, Cp*). IR ν(OH) = 3564, ν(Ru–H) = 1994, ν(P = O) = 1098, ν(P–OH) = 980 (in accord with Ref. [12]). Mass spectrum [LR/FAB (3NBA/benzene)]: *m*/*z* (%) 641(12.3) [M^+], 439(14.3), 361(4.3), 313(2), 154(100), 136(72.4), 107(21.8), 55(32.2). Final elution of the chromatographic column with an ethanol solution gave a mixture of compounds **14** and **15** in a 1:20 ratio according to a ^{31}P-NMR spectrum. Compound **14** ^{1}H–NMR ($CDCl_3$): δ 7.5–6.8 (m, Ar), 5.83 (s, PH) 1.57 (q, $^4J_{PH} = 1.67$, 15H); ^{31}P-NMR: δ 35.74 (d, $J_{PH} = 370$). Compound **15** ^{1}H-NMR ($CDCl_3$): δ 11.10 (s, br, 1H), 7.65–6.87 (m, 30H), 5.87 (d, PH, $^3J_{PH} = 7.9$), 1.45 (q, $^4J_{PH} = 1.87$, 15H); ^{31}P-NMR: δ 37.39 (d, 42.8, $J_{PH} = 357$, $PHPh_2$), 127.71 (t, 42.8, $POHPh_2$); $^{13}C\{^1H\}$-NMR: δ 140.38 (d, 44.1, *i*), 133.02 (t, 5.5, *o*), 132.94 (t, 5.5, *o*), 132.34 (d, 12.1, *o*), 129.89 (s, *p*), 129.64 (s, *p*), 129.38 (s, *p*), 128.36 (t, 5.5, *m*), 127.60 (d, 9.9, *m*), 95.72 (s, Cp*), 10.07 (s, Cp*). Mass spectrum [LR/FAB (3NBA/$CHCl_3$)]: *m*/*z*(%) 811(2.0) [M^+], 625(16.0), 609(5.0), 439(26.0), 423(26.2), 361(3.62), 313(3.81), 91(36.67), 73(100), 55(75.7), 43(63.4).

3.4. Synthesis of $[Cp^*Ru(PHPh_2)_2(MeCN)]OTf$ (**16**)

To a 10 mL solution of MeCN containing **1** (80 mg, 0.124 mmol) was added 1 equivalent of AgOTf (32 mg, 0.124 mmol) with stirring at r.t. A white–gray precipitate of AgCl began to form immediately. The solution was stirred for 30 min and filtered giving a light yellow solution, which was evacuated to dryness. The oily residue was dried in vacuum, but several attempts to crystallize the oil failed. After treatment with CH_2Cl_2–hexane and MeCN–diethyl ether an oil remained. ^{31}P-NMR showed, however, that the sample of **16** was pure. ^{1}H-NMR (CD_2Cl_2): δ 7.40–6.90 (m, 20H), 5.68 (s, 1H, PH), 2.06 (t, 1.7, 3H), 1.42 (t, $^4J_{PH} = 2.5$, 15H); ^{31}P-NMR: δ 33.92 (d, $J_{PH} = 358.1$). $^{13}C\{^1H\}$-NMR: δ 138.86

Table 2
Selected bond distances and angles for **20**

Bond distances (Å)		Bond angles (°)	
RuCp* [a]	1.890	P1–Ru1–P2	90.64(9)
Ru1–P1	2.295(3)	P1–Ru1–P3	88.80(1)
Ru1–P2	2.268(3)	P2–Ru1–P3	89.20(1)
Ru1–P3	2.282(3)	Ru1–P1–O1	115.7(13)
P1–O1	1.59(3)	Ru1–P2–O2	117.5(13)
P2–O2	1.56(4)	Ru1–P3–O3	119.7(3)
P3–O3	1.607(8)		

[a] Cp* denotes the centroid of the ring.

Table 3
Selected bond distances and angles for **6** and **18**

Bond distances (Å)			Bond angles (°)		
	6	**18**		**6**	**18**
Ru1–Cl(1)	2.439(3)	2.450(2)	Cl(1)–Ru1–P1	95.8(1)	90.38(6)
Ru1–P1	2.255(3)	2.273(2)	Cl(1)–Ru1–P2	92.3(1)	84.21(6)
Ru1–P2	2.239(3)	2.273(3)	P1–Ru1–P2	93.5(1)	91.40(6)
P1–C11	1.83(1)	1.831(6)	Ru1–P1–C11	115.8(4)	119.3(2)
P1–C17	1.83(1)	1.849(7)	Ru1–P1–C17	127.7(4)	116.1(2)
P2–C29	1.85(1)	1.840(6)	C11–P1–C17	97.5(5)	100.4(3)
P2–C35	1.82(1)	1.816(6)	Ru1–P2–C29	124.8(4)	116.3(2)
P2–H2	–	1.387(56)	Ru1–P2–C35	116.9(4)	122.0(2)
P1–Cl(10)	2.086(4)	–	C29–P2–C35	99.1(5)	103.6(3)
P2–Cl(20)	2.089(4)	–	Ru1–P1–Cl(10)	111.7(2)	–
P1–O	–	1.637(5)	Cl(10)–P1–C11	100.8(4)	–
O–C41	–	1.403(9)	Cl(10)–P1–C17	99.2(4)	–
C41–C42	–	1.50(1)	Ru1–P2–Cl(20)	112.3(2)	–
Ru–Cp* [a]	1.884	1.868	Cl(20)–P2–C29	99.2(4)	–
			Cl(20)–P2–C35	100.5(4)	–
			Ru1–P1–O	–	110.1(2)
			O–P1–C11	–	103.9(3)
			O–P1–C17	–	105.5(3)
			P1–O–C41	–	128.8(5)

[a] Cp* denotes the centroid of the ring.

(t, 4.4, *o*), 132.39 (t, 4.4, *o*), 132.12 (t, 21.0, *i*), 130.97 (t, 22.6, *i*), 130.69 (s, *p*), 130.44 (s, *p*), 129.26 (t, 4.4, *m*), 129.09 (t, 4.4, *m*), 126.68 (s, OTf–), 92.04 (s, Cp*), 9.36 (s, Cp*), 4.32 (s, Me). The signal for the quaternary carbon of MeCN was not observed.

3.5. Synthesis of $Cp^*Ru(POEtPh_2)_2Cl$ (**11**) $Cp^*Ru(POEtPh_2)(PHPh_2)Cl$ (**18**), and $Cp^*Ru(POHPh_2)(POEtPh_2)$ (**19**)

Compound **12** (300 mg, 0.96 mmol) was dissolved in dry ethanol (15 mL), and $PHPh_2$ (0.34 mL, 1.92 mmol) was added dropwise with stirring at r.t. The solution changed from dark-brown to yellowish-green. After the solution had stirred for 1 h the ^{31}P-NMR spectrum of the crude product showed a mixture of species **1**, **11**, and **18** in a 1:0.05:0.35 ratio, respectively, and no evidence of free $PHPh_2$. The solution was then filtered and evaporated to dryness. The yellow powder was re-dissolved in $CHCl_3$ and filtered again, leading to its separation from a black residue. Successive recrystallizations with CH_2Cl_2–hexane afforded the crystalline compound **18** in very low yield, m.p. 165–175°C. ^{1}H-NMR ($CDCl_3$): δ 7.00–7.62 (m, 20H), 6.31 (d, $J_{PH} = 362.2$), 3.62–3.76 (m, 1H, CH_2), 3.36–3.51 (m, 1H, CH_2), 1.42 (t, $^4J_{PH} = 2$, 15H), 1.19 (t, 7.0, Me); ^{31}P-NMR: δ 137.67 (d, 47.9, $POEtPh_2$), 35.49 (d, 47.9, $PHPh_2$, $J_{PH} = 363$); ^{13}C{^{1}H}-NMR: δ 138.33 (d, 40.8, *i*), 137.87 (d, 34.1, *i*), 135.06 (d, 36.3, *i*), 134.97 (d, 35.2, *i*), 134.54 (d, 9.9, *o*), 133.44 (d, 12.2, *o*), 132.60 (d, 8.8, *o*), 131.28 (d, 11, *o*), 129.36 (s, *p*), 128.59 (s, *p*), 127.82 (d, 8.9, *m*), 127.32 (d, 8.8, *m*), 127.09 (d, 9.9, *m*), 126.94 (d, 8.8, *m*), 90.38 (s, Cp*), 62.15 (d, 7.7, OCH_2), 16.29 (d, 8.8, Me), 9.71 (s, Cp*). Mass spectrum [LR/FAB (3NBA/$CHCl_3$)]: *m*/*z*(%); 688(30.69) [M^+], 653(72.78), 502(35.20), 467(29.95), 457(7.82), 437(5.63), 422(25.9), 314, 231(7.16), 154(100), 136(69.62). Compound **11** was subsequently isolated from the mother liquor after several recrystallizations with hexane at −5°C. Yield: 10 mg (18%) m.p. 154–160°C. ^{1}H-NMR ($CDCl_3$): δ 7.00–7.55 (m, 20H), 3.38–3.50 (m, CH_2, 4H), 1.30 (t, $^4J_{PH} = 1.5$, 15H), 1.01 (t, 7.0, Me, 6H); ^{31}P{^{1}H}-NMR: δ 139.19 (s); ^{13}C{^{1}H}-NMR: δ 132.54 (t, 5.5, *o*), 132.33 (t, 5.5, *o*), 128.85 (s, *p*), 128.04 (s, *p*), 127.05 (t, 4.4, *m*), 126.92 (t, 4.4, *m*), 91.92 (s, Cp*), 62.37 (t, 5.5, OCH_2), 16.26 (t, 3.3, Me), 9.32 (s, Cp*). Mass spectrum [LR/FAB (3NBA/$CHCl_3$)]: *m*/*z*(%) 732(1.55) [M^+], 697(58.68), 467(23.28), 422(4.6), 154(100), 136(64.43).

Attempts to separate compounds **1**, **11** and **18** by column chromatography on elution with 4:1 hexane–diethyl ether were not successful. However, when a 1:1 hexane–acetone mixture was used, a mixture of hydrolysis products **13** and **19** was obtained. The compound $Cp^*RuCl(POHPh_2)(POEtPh_2)$ (**19**) was characterized by NMR from the reaction mixture. ^{1}H-NMR ($CDCl_3$): δ 7.12–7.80 (m), 6.05 (s, br, OH), 3.40–3.50 (m, CH_2), 1.29 (t, $^4J_{PH} = 1.97$, Cp*), 1.15 (t, 7.0, Me); ^{31}P{^{1}H}-NMR: δ 146.2 (d, 65.6), 135.0 (d,65.6).

3.6. NMR tube reactions[6]

(a) Compound **1** (30 mg, 0.047 mmol) was dissolved in $CDCl_3$ (0.5 mL), in the presence of 1.5 equivalents of

[6] Only Cp or Cp* hydrogens are assigned because most of the samples discussed in this section were not isolated.

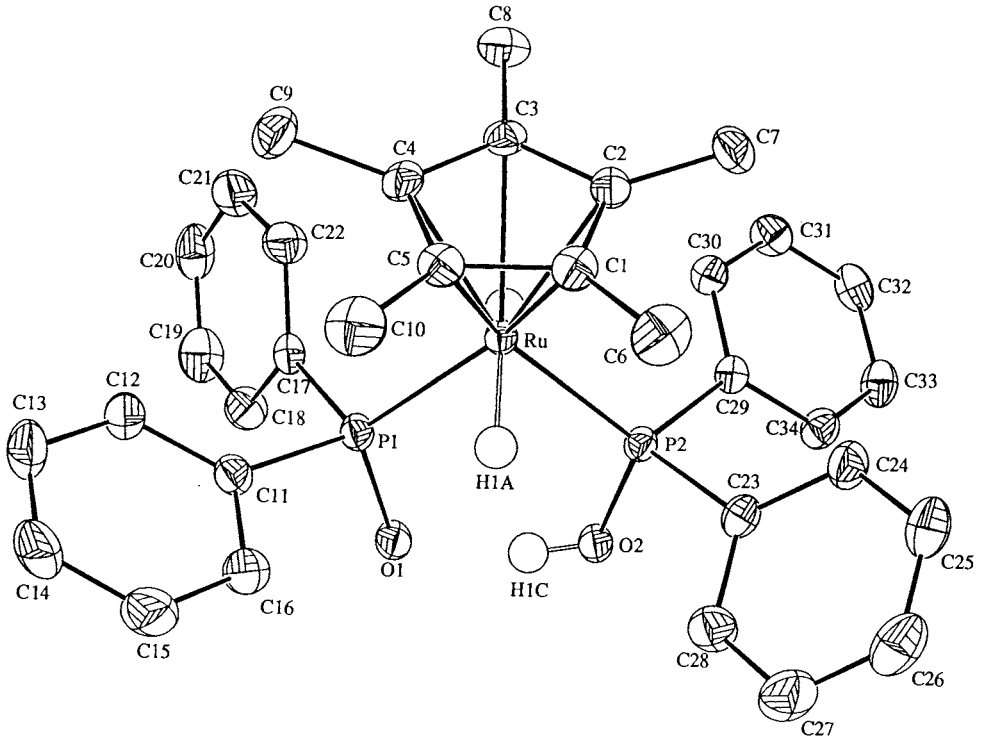


Fig. 4. ORTEP drawing of compound $[Cp^*Ru(H)_2(OPPh_2)(POHPh_2)]$ (**13**).

DBN (8.68 mg, 8.64 μL, 0.07 mmol) and the NMR tube was sealed under vacuum. After 20 min at r.t. the formation of **5** [^{1}H-NMR: δ 1.45 (t, 1.98, Cp*), 5.99 (d, 368, $PHPh_2$); ^{31}P-NMR: δ 34.7 (d, 50, $J_{PH} = 368$), 130.4 (d, 50)] was observed, yielding a 1:1 mixture with **1**, while after 220 min the ratio changed to 17:1. Longer reaction times afforded compound **6** preferentially.

(b) Compound **3** (30 mg, 0.042 mmol) was dissolved in $CDCl_3$ (0.5 mL) at r.t. in a non-sealed NMR tube. Subsequently a complex mixture of products was observed from which compounds **1**, **5**, **9** [^{31}P{^{1}H}-NMR: δ 36.3 (d, 53), 130.2 (d, 53)] and **10** [^{1}H-NMR: δ −6.99 (t, 22.8, Ru–H), 1.42 (s, Cp*); ^{31}P{^{1}H}-NMR: δ 89.4 (s)] were observed in ratios of (1:0.7:0.5:0.12), (1:1.5:1:0.7) and (0:0.4:0.12:0.03) after 10, 17 and 30 days, respectively.

(c) Compound **4** (30 mg, 0.046 mmol) was dissolved in deuterated toluene (0.5 mL) and five equivalents of $PHPh_2$ (43 mg, 40 μL, 0.231 mmol) were added. The reaction mixture was heated in an NMR tube for 67 h at 100°C. After cooling the NMR tube sample at r.t., pale yellow crystals of **20** precipitated. The crystals were filtered, giving: ^{1}H-NMR ($CDCl_3$): δ 6.95–7.40 (m, 30H, Ar), 6.10 (s, 1H, OH), 5.01 (s, 5H, Cp); ^{31}P-NMR: δ 33.57 (d, 47.9, $J_{PH} = 395.5$, $PHPh_2$) 125.0 (t, 47.9, $POHPh_2$). After 8 days the NMR tube at r.t. contained a crystalline mixture of **21** and diphenylphosphonic acid, $OPOHPH_2$ in a 1:1 ratio. The precipitated mixture was filtered and the isolated solid **21** showed: [^{1}H-NMR ($CDCl_3$): δ 7.0–7.8 (m, 30H, Ar), 6.38 (t, 6.11, 1H, $PHPh_2$), 4.95 (s, 5H, Cp). ^{31}P{^{1}H}-NMR: δ 37.8 (t, 45.4), 126.63 (d, 45.4)]. $HOP(O)Ph_2$ [^{31}P{^{1}H}-NMR ($CDCl_3$): δ 33.67 ppm].

(d) Compound **16** (30 mg, 0.047 mmol) was dissolved in $CDCl_3$ (0.5 mL) in the presence of 1.2 equivalents of $PHPh_2$ (10.4 mg, 9.7 μL, 0.056 mmol) giving **14′** [^{1}H-NMR: δ 5.83 (s, $PHPh_2$), 1.55 (q, 1.67, Cp*); ^{31}P-NMR: δ 36.0 (d, $J_{PH} = 368$)]. **14′** oxidizes in the

Table 4
Selected bond distances and angles for **13**

Bond distances (Å)		Bond angles (°)	
Ru–Cp* [a]	1.914(5)	H1A–Ru–HIB	126.0(3)
Ru–H1A	1.34(4)	P1–Ru–P2	95.40(4)
Ru–H1B	1.47(4)	O1–H1C–O2	166.0(5)
Ru–P1	2.291(1)	P1–Ru–H1A	72.0(2)
Ru–P2	2.274(1)	P1–Ru–H1B	72.0(2)
P1–O1	1.543(3)	P2–Ru–H1A	71.0(2)
P2–O2	1.572(3)	P2–Ru–H1B	74.0(2)
P1–C11	1.831(4)	Ru–P1–O1	115.0(1)
P1–C17	1.826(4)	Ru–P2–O2	114.4(4)
P2–C23	1.808(4)	Ru–P2–C23	114.4(1)
P2–C29	1.824(4)	Ru–P2–C29	118.4(1)
O1–H1C	1.65(5)	O2–P2–C23	101.8(2)
O2–H1C	0.83(5)	O2–P2–C29	103.4(2)
O1–O2 [b]	2.467(4)		
H1A–H1B [b]	2.507(52)		

[a] Cp* denotes the centroid of the ring.
[b] Non-bonded contacts.

presence of air, to give compounds **15′** [^{1}H-NMR: δ 1.44 (q, 1.87, Cp*); ^{31}P-NMR: δ 37.1 (d, 43, $J_{PH} = 368$), 130.6 (t, 43)] and **17** [^{1}H-NMR: δ 1.40 (q, 1.46, Cp*); ^{31}P-NMR: δ 42.3 (t, 43, $J_{PH} = 362$), 136.2 (d, 43)].

3.7. X-ray structure determinations of *6*, *13*, *18*, and *20*

Suitable single crystals for X-ray structure determinations were obtained by vapor diffusion of *n*-hexane into a CH_2Cl_2 solution of **20** at r.t. and after recrystallization of **18** from CH_2Cl_2/hexane and **6** and **13** from $CHCl_3$/hexane. Selected crystals of the compounds were mounted in capillary tubes and set up on a CAD4 Enraf–Nonius diffractometer. Experimental conditions as well as crystallographic data are given in Table 1. Two standard reflections were monitored periodically and showed no change during data collection. Calculation for structures **6** and **20** were carried out using the CRYSTALS [43] program, adapted to a PC. The structures of **13** and **18** were solved and refined using the SHELX programs. An empirical absorption correction (DIFABS [44]) was applied for compounds **6** and **20**. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were placed in idealized position and not refined. Unit weights were used in the refinement of **6** and **20**.

The structure of compound **6** showed extra electron density presumably due to a disordered hexane molecule. However, attempts to properly assign the atoms were not successful. The structure of compound **13** also show a solvent molecule, $CHCl_3$ which was refined. The hydrogen atom H1C was found in a Fourier map and its position refined. The structure of compound **20** showed a statistical disorder in the positioning of the oxygen atoms bonded to phosphorus. Occupancy values in the three positions were refined obtaining values of 0.68, 0.15 and 0.15 for the three locations.

4. Supplementary material

The supplementary material includes a list of the positional parameters and their standard deviations, a complete list of bond lengths and angles, anisotropic displacement parameters, the calculated fractional coordinates of the hydrogen atoms, and a list of observed and calculated structure factors. This is available on request from the authors (M.A.P.S.). A copy of the CIF for each structure is also available (CCDC deposit numbers: 116934 **13**; 116935 **18**; 116936 **6**; 116937 **20**).

Acknowledgements

This work was supported in part by grants from the Consejo Nacional de Ciencia y Tecnología (CONACYT), México and the National Science Foundation. J.R.T.L. would like to thank CONACYT for a grant and M.A.P.S. would like to thank M. Cervantes for assistance with some syntheses and Professor Robert J. Angelici for helpful comments.

References

[1] A.J. Carty, S.A. MacLaughlin, D. Nucciarone, in: J.G. Verkade, L.D. Quin (Eds.), Stereochemistry of Metal Complexes: Phosphido Bridging Ligands, VCH, Florida, 1987, p. 559.
[2] R.T. Baker, J.C. Calabrese, R.L. Harlow, I.D. Williams, Organometallics 12 (1993) 830.
[3] (a) A. Fried, W. Malisch, M. Schmeusser, U. Weis, Phosphorus, Sulfur and Silicon 65 (1992) 75. (b) K. Jorg, W. Malisch, W. Reich, A. Meyer, U. Schubert, Angew. Chem. Int. Ed. Engl. 25 (1986) 92.
[4] A.J. Blake, N.R. Champness, R.J. Forder, C.S. Framton, C.A. Frost, G. Reid, R.H. Simpson, J. Chem. Soc. Dalton Trans. (1994) 3377.
[5] (a) J.R. Sanders, J. Chem. Soc. A (1971) 2991. (b) J.R. Sanders, J. Chem. Soc. Dalton Trans. (1972) 1333; (1973) 743.
[6] R. Torres-Lubián, M.A. Paz-Sandoval, J. Organometal. Chem. 532 (1997) 17.
[7] (a) J. Halpern, A. Sen, J. Am. Chem. Soc. 99 (1977) 8337. (b) B.W. Graham, K.R. Laing, C.J. O'Connor, W.R. Roper, J. Chem. Soc. Dalton Trans. (1972) 1237. (c) F.J. Arnáiz, R. Aguado, J. Chem. Educ (1995) A196.
[8] A.J. Kirby, S.G. Warren, The Organic Chemistry of Phosphorus, Elsevier, New York, 1967, p. 21.
[9] A. Salzer, D. Nietlispach, H.U. Hund, H.W. Bosch, Organometallics 11 (1992) 2087.
[10] (a) N. Oshima, H. Suzuki, Y. Moro-Oka, Chem. Lett. (1984) 1161. (b) T.D. Tilley, R.H. Grubbs, J.E. Bercaw, Organometallics 3 (1984) 274.
[11] U. Köelle, J. Kossakowski, R. Boese, J. Organomet. Chem. 378 (1989) 449.
[12] U. Köelle, T. Ruther, N.L. Narvor, U. Englert, W. Kläui, Angew. Chem. Int. Ed. Engl. 33 (1994) 991.
[13] B. Chaudret, Bull. Soc. Chim. Fr. 132 (1995) 268.
[14] (a) T. Wilczewski, J. Organomet. Chem. 382 (1990) 431. (b) T. Wilczewski, J. Organomet. Chem. 297 (1985) 331.
[15] I.J.B. Lin, J.S. Lai, C.W. Liu, Organometallics 9 (1990) 530.
[16] R.J. Haines, A.L. Du Preez, J. Organometal. Chem. 84 (1975) 357.
[17] L.A. Oro, R. Usón, M.A. Ciriano, M.M. Naval, M.C. Apreda, C. Foces-Foces, F.H. Cano, S. Garcia-Blano, J. Organomet. Chem. 256 (1983) 331.
[18] S. Al-Jibori, M.Hall, A.T. Hutton, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1984) 863.
[19] D.E. Berry, K.A. Beveridge, G.W. Bushnell, K.R. Dixon, Can. J. Chem. 63 (1985) 2949.
[20] J.G. Verkade, R.E. McCarley, D.G. Hendricker, R.W. King, Inorg. Chem. 4 (1965) 228.
[21] M. Esteban, A. Pequerul, D. Carmona, F.J. Lahoz, A. Martin, L.A. Oro, J. Organometal. Chem. 402 (1991) 421.
[22] D.E. Axelson, C.E. Hollaway, J. Chem. Soc. Chem. Commun. (1973) 455.
[23] P. Seiler, J.D. Dunitz, Acta Crystallogr. Sect. B Struct. Sci. 36 (1980) 2946.
[24] M.O. Albers, D.C. Liles, D.J. Robinson, A. Shaver, E. Singleton, M.B. Wiege, J.C.A. Boeyens, D.C. Levendis, Organometallics 5 (1986) 2321.

[25] M.I. Bruce, F.S. Wong, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1981) 1398.
[26] M.E. Cucullu, L. Luo, S.P. Nolan, P.J. Fagan, N.L. Jones, J.C. Calabrese, Organometallics 14 (1995) 289.
[27] J.R. Bleeke, D.J. Rauscher, Organometallics 7 (1988) 2328.
[28] M.A. Paz-Sandoval, O. Pérez-Camacho, R.D. Ernst, A.M. Arif, unpublished results.
[29] P.B. Dias, M.E. Minas de Piedade, J.A. Martinho Simoes, Co-ordination Chem. Rev. 135/136 (1994) 737 and references therein.
[30] E.B. McAslan, A.J. Blake, T.A. Stephenson, Acta Crystallogr. Sect. C 45 (1989) 1811.
[31] R.D. Ernst, J.W. Freeman, L. Stahl, D.R. Wilson, A.M. Arif, B. Nuber, M.L. Ziegler, J Am. Chem. Soc. 117 (1995) 5075.
[32] W.A. Herrmann, H.G. Theiler, E. Herdtweck, P. Kiprof, J. Organometal. Chem. 367 (1989) 291.
[33] J.S. Ricci, T.F. Koetzle, M.J. Fernandez, P.M. Maitlis, J.C. Green, J. Organometal. Chem. 299 (1986) 383.
[34] F.R. Lemke, L. Brammer, Organometallics 14 (1995) 3980.
[35] L. Brammer, W.T. Klooster, F.R. Lemke, Organometallics 15 (1996) 1721.
[36] M. Rottink, R.J. Angelici, J. Am. Chem. Soc. 115 (1993) 7267.
[37] M. Jiménez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 13 (1994) 3330.
[38] W.D. Jones, J.A. Maguire, Organometallics 6 (1987) 1301.
[39] B.K. Campion, R.H. Heyn, T.D. Tilley, J. Chem. Soc. Chem. Commun. (1992) 1201.
[40] U. Koelle, J. Kossakowski, N. Klaff, L. Wesemann, U. Englert, G.E. Heberich, Angew. Chem. Int. Ed. Engl. 30 (1991) 690.
[41] L-B. Han, N. Choi, M. Tanaka, Organometallics 15 (1996) 3259 and references therein.
[42] M.M. Rauhut, H.A. Currier, J. Org. Chem. 26 (1961) 4626.
[43] D.J. Watkin, J.R. Carruthers, P.W. Betteridge, Crystals. An advanced Crystallographic Program System; Chemical Crystallography Laboratory, University of Oxford; England, 1994.
[44] N. Walker, D. Stuart, Acta Crystallogr. 39 (1983) 158.
[45] J. March, Advanced Organic Chemistry. Reactions, Mechanisms and Structure, 4th ed., John Wiley, New York, 1992, p. 202.