Dalton Transactions

PAPER

View Article Online
View Journal



Cite this: DOI: 10.1039/c5dt04624f

# A straightforward access to ruthenium-coordinated fluorophosphines from phosphorous oxyacids†

Fuencisla Delgado Calvo,[a] Vincenzo Mirabello,‡[a] Maria Caporali,*[a] Werner Oberhauser,[a] Kolio Raltchev,[b] Konstantin Karaghiosoff[b] and Maurizio Peruzzini*[a]

Received 25th November 2015,
Accepted 22nd December 2015

DOI: 10.1039/c5dt04624f

www.rsc.org/dalton

The transformation of phosphorous oxyacids into the corresponding fluorophosphines was mediated by $[RuCp(PPh_3)_2Cl]$ under mild reaction conditions using a soft deoxofluorinating agent. The reaction is selective, proceeds with high yields and can be extended to a wide range of phosphorous oxyacids once coordinated to the ruthenium synthon $[RuCp(PPh_3)_2]^+$ as their hydroxyphosphine tautomer. Deoxofluorination of phenylphosphinic acid was also mediated by $[RuCp^R(CH_3CN)_3]PF_6$, where $Cp^R$: Cp = $C_5H_5$, Cp* = $C_5Me_5$, and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$. X-Ray single crystal structures of the two new derivatives, $[RuCp(PPh_3)_2\{PhP(OH)_2\}]CF_3SO_3$ and $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{PhP(OH)_2\}]$ have been determined.

## Introduction

Phosphorus halides, especially chlorides, are of great interest in many genres of organic and inorganic chemistry, and represent the key-materials for the manufacturing of several organophosphorus compounds.[1] Among P-halides, fluorophosphines, $PR_xF_y$ (R = organyl group; $x + y = 3$) have been less considered as ligands towards transition-metals in spite their dual function being good σ-donating and strong π-accepting ligands at the same time thus showing great ability to stabilize transition metals in several oxidation states, including the lowest ones.[2] For instance, phosphorus trifluoride ($PF_3$) as a ligand has very similar π-acceptor properties to carbon monoxide. The respective Tolman electronic parameters[3] are 2111 $cm^{-1}$ and 2128 $cm^{-1}$. While complexes bearing carbon monoxide are well-known, and fluorophosphines have been reported as ligands for hydroformylation,[4] the development of new methods and reagents for the synthesis of fluorophosphines is presently scarcely explored.[5] Up to now very few applications of fluorophosphines in catalysis have been described, owing to their instability with respect to the redox disproportionation.[6] It is known indeed that difluorophosphines $RPF_2$ decompose giving $RPF_4$ and RP. Recently, Pringle and his group have prepared remarkably stable fluorophosphines based on both phospha-adamantane cages and phosphabicycles, which proved to be suitable ligands for hydroformylation and hydrocyanation reactions once coordinated to rhodium and nickel, respectively.[4]

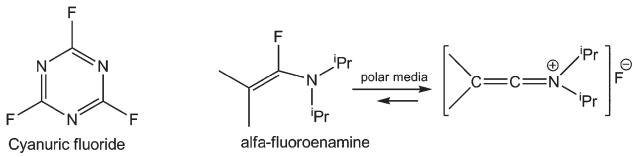
Tri-fluorophosphine complexes of different metals (Pt, Ni) were prepared and characterised more than sixty years ago by Chatt[7] and G. Wilkinson[8] respectively, using highly drastic conditions, starting from the suitable metal precursor in the presence of high pressure of gaseous $PF_3$ (50–250 atm) and high temperature (above 100 °C). Afterwards, J. F. Nixon,[9] prepared analogous complexes of different platinum group metals following a similar procedure. Trying to avoid the use of highly toxic $PF_3$, fluorophosphines have been prepared starting from different chlorophosphines by chlorine–fluorine exchange, using a fluoride salt, such as $NEt_3{\cdot}HF$,[10] $SbF_3$,[11] or NaF[12] as fluorinating agent for the displacement reaction. Lithiation of chlorodifluorophosphines with aryl lithium has allowed the synthesis of a variety of aryl difluorophosphines.[13] Triorganotin(IV) fluorides have been shown to be capable of fluorinating chlorophosphines under very mild conditions.[14]

Conversion of phosphorous oxyacids to the corresponding fluorinated derivatives is another method to achieve fluorinated phosphines.[15] The reaction is based on the use of α-fluoroenamines or cyanuric fluoride, *i.e.* 2,4,6, trifluoro-[1,3,5] triazine, as reagents to bring about the fluoride transfer to phosphorus as shown in Scheme 1. Both reactions are very efficient and almost quantitative, but they encompass the use

[a]Istituto di Chimica dei Composti Organometallici, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy. E-mail: maria.caporali@iccom.cnr.it
[b]Department Chemie und Biochemie, Ludwig-Maximilians University Muenchen, Butenandtstrasse 5, 81377 – Munich, Germany

†Electronic supplementary information (ESI) available. CCDC 1415725 and 1415724. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04624f

‡Present address: Department of Chemistry, University of Bath, Claverton Down, BA2 7AY, UK.



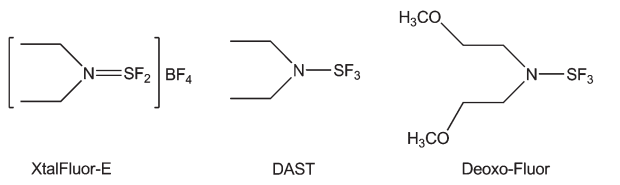

**Scheme 1** Fluorinating agents used for delivering fluoride to phosphorous oxyacids.

of liquid reagents, are very sensitive to hydrolysis, and are corrosive and toxic. In this way, the fluoro derivatives can be prepared without using chloro compounds as intermediates which is the case in most synthetic methods.

Following the observation that low-valent phosphorous hydroxyphosphines, such as $P(OH)_3$, $PH(OH)_2$ and $PH_2(OH)$, can coordinate to $[RuCp(PPh_3)_2]^+$, forming hydroxyphosphine ruthenium complexes of the general formula, $[RuCp(PPh_3)_2\{PH_x(HO)_y\}]^+$ ($x + y = 3$; $x = 0, 1, 2$), *via* ruthenium-promoted tautomerization of the corresponding phosphorous oxyacid ($H_3PO_3$, $H_3PO_2$ and $H_3PO$),[16,17] we were intrigued by the possibility to prepare different fluorophosphines by selective fluorination of the P–OH functional group.

To the best of our knowledge, the deoxofluorination reaction has been traditionally used to convert organic substrates such as alcohols, ketones or carboxylic acids into their fluorinated derivatives. To this purpose $SF_4$ was used, which is a highly toxic gas, difficult to handle and usually requiring drastic reaction conditions, as high temperature. Therefore its use for synthesis is nowadays limited. Middleton synthesized diethylaminosulfur trifluoride, DAST,[18] (Scheme 2) a liquid reagent, which is an alternative to the gaseous $SF_4$. Lal *et al.*[19] reported the synthesis of Deoxo-Fluor, (bis(2-methoxyethyl) aminosulfur trifluoride) a thermally stable fluorinating reagent, that easily converts alcohol into alkyl fluorides, ketones into *gem*-difluorides and carboxylic acids to acid fluorides. DAST and Deoxo-Fluor are commonly used as deoxofluorinating agents for organic substrates, even if they are fuming liquids, difficult to handle in humid environments and violently reactive in contact with water. Markovskii *et al.*[20] modified DAST upon reaction with $BF_3{\cdot}Et_2O$ to give the corresponding dialkylaminodifluorosulfinium tetrafluoroborate salt $[R_2NSF_2]BF_4$ (R = ethyl or morpholine), which were later on commercialized as XtalFluor-E and XtalFluor-M, respectively. The advantage of these reagents is their safer and more cost-efficient preparation. Unlike DAST and Deoxo-Fluor, they do not generate highly corrosive free HF and can be used with standard borosilicate glassware. Moreover, they are stable solids, and easily manageable which led to their successful application for the deoxofluorination of oxo-substrates.[21]

Neither XtalFluor-E, nor the other deoxofluorinating reagents (Scheme 2) have been used to fluorinate hydroxyphosphines.




**Scheme 2** Deoxofluorinating agents.

## Results and discussion

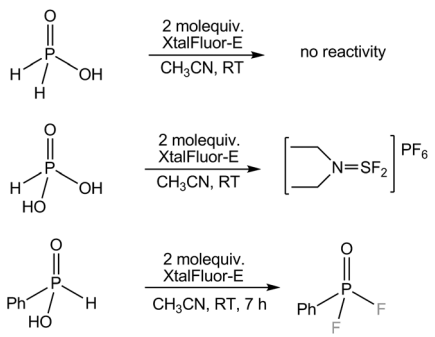
In a first attempt we tried the deoxofluorination of three different phosphorous oxyacids (*i.e.* $H_3PO_2$, $H_3PO_3$ and PhP(O)(OH)(H)) by using one or two equivalents of XtalFluor-E® in acetonitrile at room temperature. As a result, no reaction was observed with $H_3PO_2$, whereas $H_3PO_3$ gave unexpectedly the anion $PF_6^-$ ($^{31}P$ NMR septuplet at −146.2 ppm, $^1J_{PF}$ = 706 Hz) as the only phosphorus containing species. However when phenyl phosphinic acid was reacted with XtalFluor-E the corresponding difluorophosphine oxide was obtained in quantitative yield (Scheme 3), and its identity confirmed by NMR and ESI-MS.[22]

Attempts to reduce the difluorophosphine oxide to the corresponding phosphine, by DIBAL (DIBAL = di-isobutyl-aluminiumhydride) or by the more basic $nBu_3P$ led to decomposition of the fluorophosphine oxide, which was not further studied.

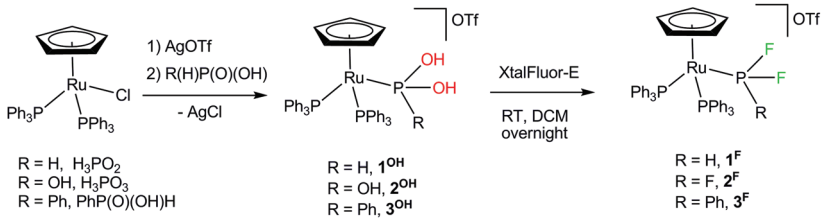
Exploiting the capability of the organometallic fragment $[RuCp(PPh_3)_2]^+$ to stabilize phosphorous oxyacids in the form of their corresponding hydroxyphosphine tautomers,[17] we coordinated the oxyacids reported in Scheme 3 to $[RuCp(PPh_3)_2]^+$ (*i.e.* $[RuCp(PPh_3)_2\{HP(OH)_2\}]OTF$ ($\mathbf{1^{OH}}$), $[RuCp(PPh_3)_2\{P(OH)_3\}]OTf$ ($\mathbf{2^{OH}}$), $[RuCp(PPh_3)_2\{P(OH)_3\}]PF_6$ ($\mathbf{2^{OH'}}$) and $[RuCp(PPh_3)_2\{PhP(OH)_2\}]OTf$ ($\mathbf{3^{OH}}$) ($OTf = OSO_2CF_3$) (Scheme 4).

$\mathbf{1^{OH}}$ and $\mathbf{2^{OH}}$ are known compounds,[17a] while $\mathbf{3^{OH}}$ was prepared following the same synthetic procedure as reported for the former complexes.

The molecular structure of $\mathbf{3^{OH}}$ was confirmed by a single crystal X-ray structure analysis, showing the $[RuCp(PPh_3)_2\{PhP(OH)_2\}]^+$ cation and one triflate anion in the asymmetric unit. The ORTEP-diagram of $\mathbf{3^{OH}}$ exhibits hydrogen bond inter-




**Scheme 3**




**Scheme 4** Synthesis of the Ru-coordinated oxyacids.

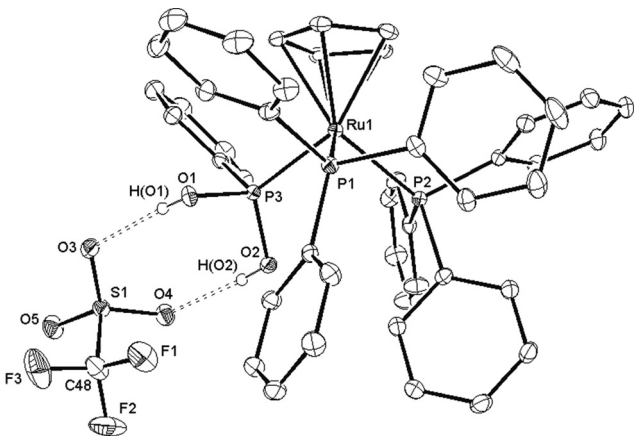



**Fig. 1** ORTEP-diagram of $\mathbf{3}^{OH}$ $CCl_2$ with 30% probability ellipsoids. Hydrogen atoms, except for O(1) and O(2) are omitted for clarity. Selected bond length (Å) and angles (°): Ru(1)–P(1), 2.3670(7); Ru(1)–P(2), 2.3408(7); Ru(1)–P(3), 2.2745(7); Ru–centroid(Cp), 1.8959; O(3)–H(O1), 2.0401; O(4)–H(O2), 2.0177; P(1)–Ru(1)–P(2), 98.20(2); P(1)–Ru(1)–P(3), 97.74(2); P(2)–Ru(1)–P(3), 96.37(2).

actions between both OH units of the coordinated hydroxyphosphine and two of the triflate oxygen atoms (Fig. 1).

Compounds $\mathbf{2}^{OH'}$ and $\mathbf{3}^{OH}$ were quantitatively deoxofluorinated upon reaction with an equimolar amount of XtalFluor-E, giving the corresponding fluorophosphine complexes $[RuCp(PPh_3)_2(PF_3)]PF_6$. ($\mathbf{2}^{F'}$) and $[RuCp(PPh_3)_2(PhPF_2)]OTf$ ($\mathbf{3}^{F}$), respectively (Scheme 4). Noticeably, the deoxofluorination of $\mathbf{2}^{OH}$ needs a three times excess of XtalFluor-E to be completed. In the absence of further experimental evidences for the counter anion effect on the deoxyfluorination we speculate that hydrogen bond interactions between the triflate anion and the hydroxyl groups of the coordinated $P(OH)_3$, as observed for $\mathbf{3}^{OH}$ in the solid state, may hamper the accessibility of hydroxyl groups by the fluoride.

Any attempt to de-coordinate the fluorophenyl phosphine ligand from the ruthenium centre by reaction of $\mathbf{3}^{F}$ with a more basic phosphine such as PTA (1,3,5-triaza-7-phosphaadamantane) or CO pressure, failed. On the other hand, the deoxofluorination of Ru-coordinated $P(OH)_3$ to give metal coordinated $PF_3$ represents an easy and safe method to generate Ru-coordinated $PF_3$ circumventing the usage of $PF_3$ which is a very toxic and hazardous gas. For comparison, it is worth noticing that the generation of $PF_3$ on laboratory scale usually involves the reaction of $PCl_3$ with HF gas,[23] $SbF_3$,[24] $AsF_3$ [25] or $ZnF_2$.[26] Alternatively it can be synthesized by the dropwise addition of $PBr_3$ to excess powdered $SbF_3$.[27]

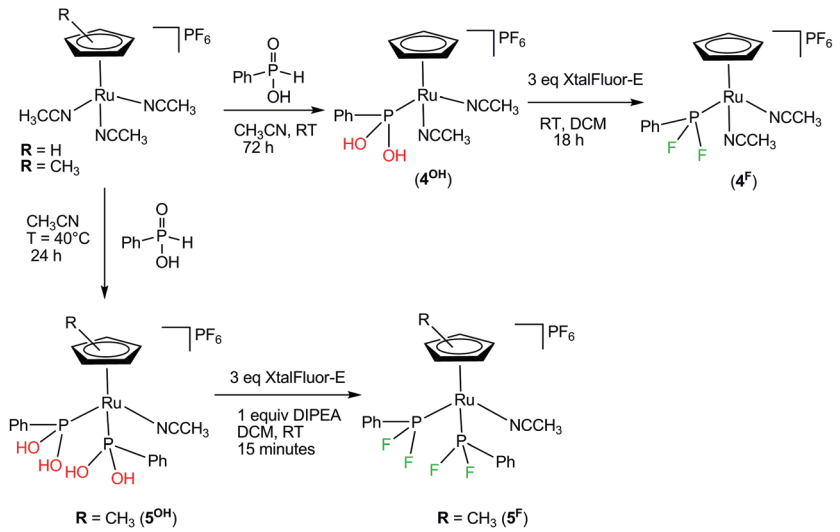
We tried further mono-cationic Ru-precursors of the general formula $[RuCp^R(CH_3CN)_3]PF_6$ where (R = H, $CH_3$).[28,29] This latter Ru-precursor species is characterized by three coordinating acetonitrile molecules, which can be easily replaced by a stronger coordinating ligand. Attempts to coordinate $H_3PO_2$ and $H_3PO_3$ to the ruthenium center failed, even after a prolonged heating and only the starting material was recovered. Unlike $H_3PO_2$ and $H_3PO_3$, phenylphosphinic acid was capable of displacing coordinated acetonitrile in $[RuCp^R(CH_3CN)_3]PF_6$ and after optimization of the reaction conditions two new, analytically pure (*i.e.* proved by ESI-MS and multinuclear NMR spectroscopy) complexes of the formula $[RuCp(CH_3CN)_2\{PhP(OH)_2\}]PF_6$ ($\mathbf{4}^{OH}$) and $[Ru(C_5Me_5)(CH_3CN)\{PhP(OH)_2\}_2]PF_6$ ($\mathbf{5}^{OH}$) were isolated (Scheme 5).

Interestingly in case of $[RuCp(CH_3CN)_3]PF_6$ only one phenylphosphinic acid coordinates to Ru, while the replacement of Cp by $C_5Me_5$ leads to the coordination of two molecules of phenylphosphinic acid.

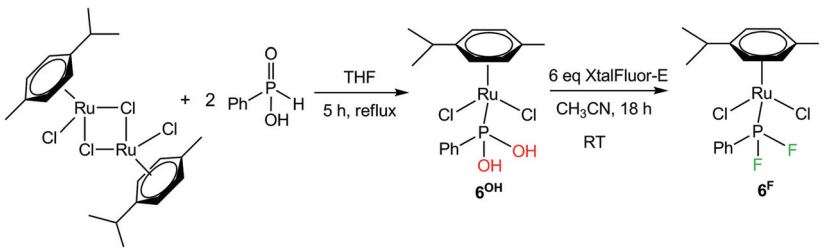
The reaction of $(\mathbf{4/5})^{OH}$ with a three-fold excess of fluorinating reagent gave the corresponding Ru-complexes $(\mathbf{4/5})^{F}$, respectively, bearing the fluorinated phosphine (Scheme 5). The deoxofluorination of $(\mathbf{4/5})^{OH}$ occurred with completely different kinetics, observing under identical experimental conditions with the former compound a very sluggish reaction (*i.e.* reaction time of 18 h for complete conversion), while $\mathbf{5}^{OH}$ reacted rapidly (15 min) in the presence of di-isopropylamine (DIPEA).

We coordinated phenylphosphinic acid also to the neutral $[Ru(\eta^6\text{-}(p\text{-cymene})Cl_2]$ moiety upon reaction of the former with the Ru-dimer[30] $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$, giving the neutral mononuclear Ru-species of the formula $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{PhP(OH)_2\}]$ ($\mathbf{6}^{OH}$) (Scheme 6). The latter dimer Ru-complex is known indeed to form mononuclear complexes by cleavage of the chloride bridges in the presence of a two-electron donor ligand. In this context it has been found that trihalophosphine ligands such as $PF_3$ were successfully coordinated to $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]$.[27] The coordination of one molecule of the tautomer of phenylphosphinic acid to Ru in $\mathbf{6}^{OH}$ was proved by a single crystal X-ray structure analysis, an ORTEP-plot of which is shown in Fig. 2.

$H_3PO_2$ and $H_3PO_3$ did not react with $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ even after a prolonged reaction time of 48 hours, which is




**Scheme 5** Coordination of phenylphosphinic acid to $[RuCp^{R}(CH_3CN)_3]PF_6$ followed by deoxofluorination.




**Scheme 6** Preparation of complexes $\mathbf{6^{OH}}$ and $\mathbf{6^{F}}$.

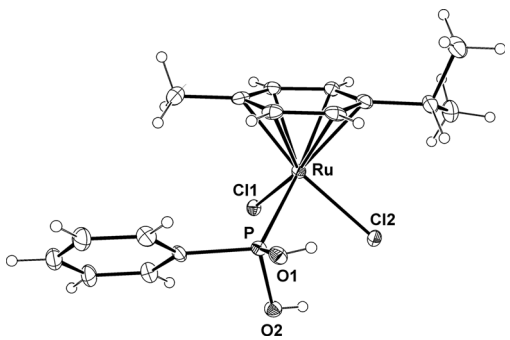



**Fig. 2** ORTEP-diagram of $\mathbf{6^{OH}}$ with 30% probability ellipsoids. Hydrogen atoms, except for O(1) and O(2), are omitted for clarity. Selected bond length (Å) and angles (°): Ru(1)–P(1), 2.2969(9); Ru(1)–Cl(1), 2.4245(8); Ru(1)–Cl(2), 2.4275(9); Ru(1)–centroid(Cp), 1.7045; P(1)–Ru(1)–Cl(1), 87.27(3); P(1)–Ru(1)–Cl(2), 82.78(3).

the consequence of the electron poor metal center not capable of stabilizing. In fact, within the Ru-precursors employed, only $[RuCp(PPh_3)_2]OTf$ was suitable to coordinate the tautomers of hypophosphorous and phosphorous acid.[15] The deoxofluorination of $\mathbf{6^{OH}}$ was carried out first in dichloromethane with a six times excess of fluorinating agent (*i.e.* XtalFluor-E) under reflux for several hours. With these experimental conditions only a mixture of fluorinated Ru-species were obtained, according to $^{31}$P NMR monitoring. By changing the reaction medium to acetonitrile and using a six-fold excess of fluorinating reagent, the desired derivative $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PhPF_2)]$ ($\mathbf{6^{F}}$) was obtained in high yield after 18 hours at room temperature (Scheme 6).

This experimental result is in agreement with theoretical[31] and experimental studies based on photoelectron spectroscopy,[32] and $^{13}$C NMR spectroscopy carried out on a series of $NiL(CO)_3$ complexes)[33] (L = trihalophosphine ligands), which showed the π-acceptor properties of $PF_3$ to be similar to CO and its basicity (σ donor) resembles that of $PEt_3$.

The diphosphine complex $\mathbf{5^{F}}$ displays second order $^{31}$P and $^{19}$F spectra, see Fig. 3 and 4, respectively. The two fluorine atoms at each phosphorus atom in $\mathbf{5^{F}}$ are diastereotopic, forming together with the two phosphorus atoms an AA′BB′XX′ (A, B: $^{19}$F, X: $^{31}$P) spin system. In fact in the $^{19}$F NMR spectrum we observed two distinct multiplets at $\delta = -53.9$ and $\delta = -49.3$ ppm. The values of the coupling constants $^{n}J$(PF) and $^{n}J$(PP) were confirmed by comparison with the simulated $^{31}$P NMR spectrum and are summarized in Table 1S, see ESI.†

Actually, we found out that this in-equivalence was already observed in transition metal complexes bearing two difluoro-

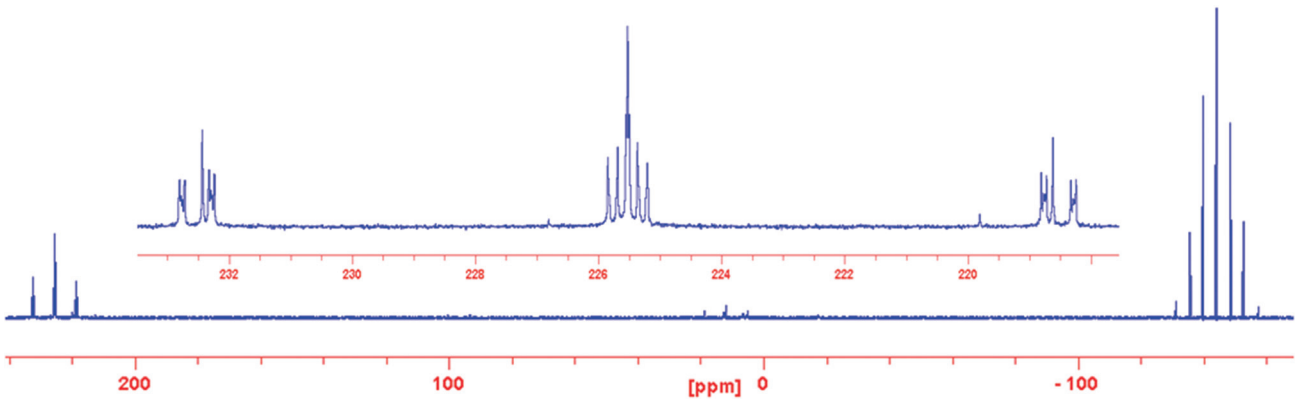



Fig. 3 $^{31}P\{^{1}H\}$ NMR of $\mathbf{5^F}$ in $CD_3OD$ with inset enlarging the signal at 225.8 ppm.

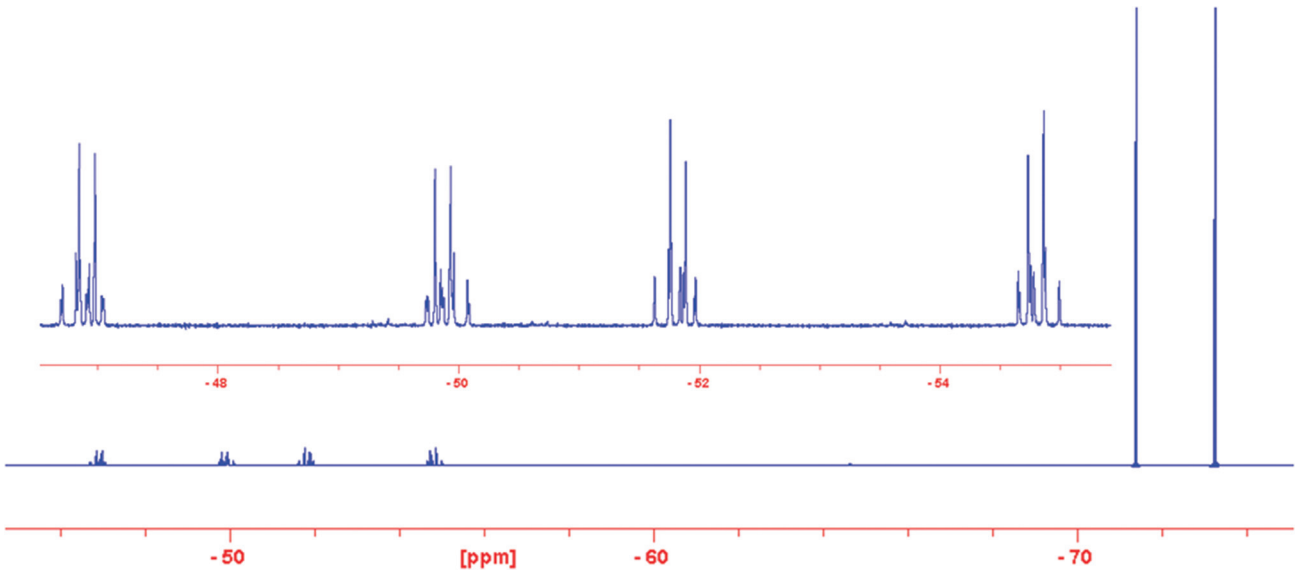



Fig. 4 $^{19}F\{^{1}H\}$ NMR of $\mathbf{5^F}$ $CD_3OD$ with inset enlarging the low field multiplets.

Table 1 $^{19}F$ and $^{31}P$ chemical shifts and relative coupling constants in $CD_2Cl_2$ solution at 25 °C of the fluorophosphine complexes

| Complex | | $\delta(^{19}F)$ | $\delta(^{31}P)$ | $^{1}J(PF)$ Hz | $^{2}J(PP)$ Hz | $^{3}J(PF)$ Hz |
|---|---|---|---|---|---|---|
| $[RuCp(PPh_3)_2(HPF_2)]^+$ | $\mathbf{1^F}$ | 4.6 | 225.1 | 1088.3 | 56.6 | 7.6 |
| $[RuCp(PPh_3)_2(PF_3)]^+$ | $\mathbf{2^F}$ | 4.5 | 144.8 | 1301.6 | 72.4 | — |
| $[RuCp(PPh_3)_2(PhPF_2)]^+$ | $\mathbf{3^F}$ | −34.2 | 227.4 | 1087.3 | 55.9 | 7.4 |
| $[RuCp(CH_3CN)_2(PhPF_2)]^+$ | $\mathbf{4^F}$ | −51.6 | 224.8 | 1147.8 | — | — |
| $[Ru(\eta^5\text{-}C_5Me_5)(CH_3CN)(PhPF_2)_2]^+$ | $\mathbf{5^F}$[a] | −53.9(m)<br>−49.3(m) | 225.8 | −1117.9, 1143.7 | 78.4 | [b] |
| $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PhPF_2)]$ | $\mathbf{6^F}$ | −58.5 | 215.1 | 1156.9 | | |

[a] Acetone-$d_6$. [b] See Table 1S (ESI).

phosphine ligands.[34] On this regard, Schmutzler *et al.*[35] described these symmetrical higher order spin systems invoking a virtual coupling between $^{31}P$ and $^{19}F$ nuclei, and reported the absolute value of the direct coupling constant $J(PF)$ as the sum of two coupling constants $|^{1}J_{PF} + {}^{3}J_{PF}|$. In Table 1 $^{31}P$ and $^{19}F$ chemical shifts and relative coupling constants are summarised for all the fluoro derivatives. Values of $^{1}J_{PF}$ are particularly diagnostic since they give a hint about the nature of the P–F bond order.[27] Indeed, we observed a remarkable variation of $^{1}J_{PF}$, going from 1087 Hz to 1300 Hz, which depends both

on the number of fluorine atoms bonded to phosphorus and also on the kind of substituents on the same phosphorus atom.[36] Free gaseous $PF_3$ has $^1J_{PF}$ of 1403 Hz (ref. 27) (as absolute value), once it is coordinated to ruthenium in $\mathbf{2^F}$ the value goes down to 1301.6 Hz. A similar trend is observed for $PhPF_2$, being $^1J_{PF}$ equal to 1169 Hz for the free ligand[13] while in the series of complexes $\mathbf{3^F}$–$\mathbf{6^F}$ there is a lowering to 1087.3 Hz in $\mathbf{3^F}$. The decrease of the coupling constant may account for a reduction of the phosphorus–fluorine bond order. For instance, the σ- and π-components for the dative bond of $PF_3$ toward a transition metal, operate in the same synergic way observed for carbon monoxide, therefore the π-component is expected to be favoured in trifluorophosphine complexes, in comparison to complexes bearing the ligands $PhPF_2$ or $HPF_2$, because of the presence of three highly electronegative fluorine atoms.[27]

Indeed, examining the Ru–P distance in the crystal structure of Ru–$PF_3$ complexes,[27] it is interesting to see that this distance is very much shorter (2.184 Å) than the Ru–$PPh_3$ distance (average 2.34 Å), which is consistent with the stronger π-bonding ability of $PF_3$ in comparison to triphenylphosphine.

## Conclusions

We present in this work a new way to synthesize a fluorophosphine ligand, using the commercial salt XtalFluor-E® as the fluorine source, thus avoiding the use of highly toxic and unstable fluorinating agents. Phosphorous oxyacids as phosphinic, phenyl phosphinic and phosphonic acids, are the starting materials of choice and the procedure of deoxofluorination here applied for the first time to phosphorous oxyacids, represents an efficient and mild methodology for their transformation into the corresponding fluorophosphines, once coordinated to ruthenium as their tautomer counterpart, *i.e.* hydroxy-phosphanes.

A series of half-sandwich Ru(II) complexes bearing the desired fluorophosphine ligands were prepared and fully characterized by multinuclear NMR. Their synthesis was not trivial, since the working conditions, as solvent, amount of XtalFluor-E® reaction time and temperature, had to be tuned each time to get complete selectivity in the desired product. A dramatic change in $^1J$(P–F) has been observed either changing the ancillary ligand or substituting one atom of fluorine by an hydrogen or a phenyl ring, suggesting that subtle electronic effects are operating.

## Experimental section

### General details

All reactions and manipulations were carried out under nitrogen using standard Schlenk glassware and techniques. Dichloromethane was purified by distillation over $CaH_2$. THF was purified by distillation over sodium wire and benzophenone. Acetonitrile, diethyl ether and *n*-pentane were purified by passing them over two columns filled with molecular sieves (4 Å) (LabMaster MBRAUN MD SPS). *n*-Hexane, $H_3PO_3$, $H_3PO_2$ in water solution 50% w/w, PhP(O)(OH)H, diethylaminodiflurosulfinium tetrafluoroborate salt, (commercial name XtalFluor-E) were used as purchased from Aldrich. Dichloromethane-$d_2$, acetone-$d_6$ and $CD_3OD$ (Aldrich) were pretreated with three freeze–thaw pump cycles before use and kept under an inert atmosphere. Literature methods were used for the preparation of the following compounds: $[RuCp(PPh_3)_2\{HP(OH)_2\}]CF_3SO_3$ ($\mathbf{1^{OH}}$) $[RuCp(PPh_3)_2\{P(OH)_3\}]CF_3SO_3$ ($\mathbf{2^{OH}}$), $[RuCp(PPh_3)_2\{P(OH)_3\}]PF_6$ ($\mathbf{2^{OH'}}$)[17] $[RuCp(CH_3CN)_3]PF_6$[28] $[RuCp^*(CH_3CN)_3]PF_6$,[29] and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ [30a].

Solution multinuclear NMR spectra were recorded on a Bruker Avance 300 and 400 MHz spectrometer. $^1H$ and $^{13}C$ chemical shifts are referenced to tetramethylsilane (TMS), $^{31}P$ chemical shifts are referenced to 85% $H_3PO_4$, $^{19}F$ chemical shifts are referenced to $CFCl_3$ (376.5 MHz). ESI-MS spectrum were recorded by direct introduction of the samples at 5 μl $min^{-1}$ flow rate in an LTQ-Orbitrap high-resolution mass spectrometer (Thermo, San Jose, CA, USA), equipped with a conventional ESI source. The working conditions comprised the following: spray voltage 4 kV, capillary voltage 3 V, capillary temperature 220 °C, tube lens 120 V. The sheath and auxiliary gases were set, respectively, at 10 (arbitrary units) and 3 (arbitrary units). For acquisition, Xcalibur 2.0. software (Thermo) and IT analyser were used. IR spectra were recorded with a Perkin Elmer spectrometer in KBr disks. Diffraction data were collected with an Oxford Diffraction CCD diffractometer, using Mo-Kα radiation ($\lambda$ = 0.71069 Å) and corrected for Lorentz and polarization effects. Absorption corrections were performed using the XABS2 program.[37a] All the structures were solved by direct methods using SHELXS-97[37b] and refined by full-matrix least-squared methods against $F^2$ using the WINGX[37c] software package. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were added at calculated positions and refined applying a riding model with isotropic $U$ values depending on the $U_{eq.}$ of the adjacent carbon atom.

**Synthesis of $[RuCp(PPh_3)_2\{PhP(OH)_2\}]CF_3SO_3$ ($\mathbf{3^{OH}}$).** To a suspension of $[RuCp(PPh_3)_2Cl]$ (250 mg, 0.344 mmol) and $AgCF_3SO_3$ (90 mg, 0.350 mmol) in a mixture of $CH_2Cl_2$ (15 ml) and THF (7 ml) was added phenylphosphinic acid (49 mg, 0.344 mmol). The resulting slurry was stirred at room temperature for 2 hours. The precipitated AgCl was filtered off and yellow microcrystals of $[RuCp(PPh_3)_2\{PhP(OH)_2\}]CF_3SO_3$ were obtained by adding 20 ml of $Et_2O$ and bubbling nitrogen gas for *ca* 30 minutes to evaporate the solvent. Yield: 84%. Crystals suitable for X-ray analysis were obtained by layering petroleum ether (30 ml) over the $CH_2Cl_2$/THF solution. $^1H$ NMR (400 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 8.3 (bs, 2H, $PhP(OH)_2$) = 7.7–6.6 (m, 35H, Ph), 4.3 (m, 5H, $C_5H_5$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 147.6 (t, $^2J_{PAPB}$ = 56 Hz, 1P, $P_A$), 42.2 (d, $^2J_{PAPB}$ = 56 Hz, 2P, $P_B$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 133.9 (s, $CH_{ar}$), 130.1 (s, $CH_{ar}$), 129.9 (s, $CH_{ar}$), 129.0 (d, $^1J_{CP}$ = 12.5 Hz, $C_q$), 127.9 (m, $C_q$), 87.3 (s, $C_5H_5$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 3058 (broad, OH), 1223 (s, $CF_3SO_3$) 887, 847 (s, P–OH).

**Synthesis of $[RuCp(PPh_3)_2(HPF_2)]CF_3SO_3$ ($1^F$).** $[RuCp(PPh_3)_2\{HP(OH)_2\}]CF_3SO_3$ (250.0 mg, 0.276 mmol) and $[Et_2NSF_2]BF_4$ (126.0 mg, 0.552 mmol, 2 eq.) were charged in a schlenk tube and dissolved in $CH_2Cl_2$ (15 ml). The resulting suspension was stirred at room temperature overnight and finally cooled down (*ca* −78 °C). A white crystalline compound precipitated out from the solution and the yellow supernatant was cannulated into a 50 ml schlenk flask and $[RuCp(PPh_3)_2(HPF_2)]CF_3SO_3$ was obtained as a yellow microcrystalline solid by cooling the solution down (*ca* 0 °C) and adding 50 ml of $Et_2O$. Yield: 86%. Anal. Calcd for $C_{42}H_{36}F_5P_3SO_3Ru$: C, 55.45; H, 3.99. Found: C, 55.20; H, 3.82. ESI-MS ($C_{41}H_{36}F_2P_3Ru$) calcd $[M + H]^+$: *m*/*z* = 761.1; found: *m*/*z* = 761.1. $^1H$ NMR (400.13 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 8.7 (dt, $^1J_{H-PA}$ = 465.2 Hz, $^2J_{H-F}$ = 63.0 Hz, 1H, *H*$PF_2$), 7.6–6.7 (m, 30H, $CH_{ar}$), 4.9 (s, 5H, $C_5H_5$) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 225.1 (tt, $^1J_{PAF}$ = 1088.3 Hz, $^2J_{PAPB}$ = 56.6 Hz, 1P, $P_A$), 40.2 (dt, $^2J_{PAPB}$ = 56.6 Hz, $^3J_{PF}$ = 7.6 Hz, 2P, $P_B$) ppm. $^{31}P$ NMR (161.9 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 225.1 (ttd, $^1J_{H-PA}$ = 465.2 Hz, 1P, $P_A$) 40.2 (dt, $^2J_{PAPB}$ = 56.6 Hz, $^3J_{PF}$ = 7.6 Hz, 2P, $P_B$) ppm. $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 4.6 (d, $^1J_{PAF}$ = 1088.3 Hz, $PF_2$), −78.9 (s, $CF_3SO_3^-$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 133.1 (t, $^2J_{CP}$ = 5.3 Hz, $CH_{ar}$), 131.2 (m, $C_q$), 128.8 (s, $CH_{ar}$), 128.9 (t, $^3J_{CP}$ = 5.2 Hz, $CH_{ar}$), 89.3 (s, $C_5H_5$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 2464 (w, P–H), 1275 (s, $CF_3SO_3$), 819 (s, P–F).

**Synthesis of $[RuCp(PPh_3)_2(PF_3)]CF_3SO_3$ ($2^F$).** $[RuCp(PPh_3)_2\{P(OH)_3\}]CF_3SO_3$ (250.0 mg, 0.271 mmol) and $[Et_2N{=}SF_2]BF_4$ (497.0 mg, 2.168 mmol, 8 eq.) were charged in a schlenk tube (100 ml) and dissolved in $CH_2Cl_2$ (15 ml). The resulting suspension was stirred at room temperature overnight and finally cooled down (*ca* −78 °C). A white crystalline compound precipitated out of the solution, presumably a salt by-product of the reaction. The yellow surnatant was cannulated into a 50 ml schlenk flask and $[RuCp(PPh_3)_2(PF_3)]CF_3SO_3$ was obtained as yellow microcrystals by adding 20 ml of $Et_2O$ and bubbling nitrogen gas for *ca* 30 minutes. $[RuCp(PPh_3)_2(PF_3)]CF_3SO_3$ is air stable in solution for a long time. Yield: 94%. Anal. Calcd for $C_{42}H_{35}F_6P_3SO_3Ru$: C, 54.37; H, 3.80. Found: C, 54.26; H, 3.45. ESI-MS ($C_{41}H_{35}F_3P_3Ru$) calcd for $[M + H]^+$: *m*/*z* = 779.1; found: *m*/*z* = 779.1. $^1H$ NMR (400.0 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 7.6–6.8 (m, 30H, $CH_{ar}$), 4.9 (m, 5H, $C_5H_5$) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 144.8 (qt, $^1J_{PAF}$ = 1301.6 Hz, $^2J_{PAPB}$ = 72.4 Hz, 1P, $P_A$), 37.3 (d, $^2J_{PAPB}$ = 72.4 Hz, $2P_B$) ppm. $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 4.5 (d, $^1J_{PF}$ = 1301.6 Hz, $PF_3$), −78.7 (s, $CF_3SO_3^-$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 134.3 (m, $C_q$), 133.1 (t, $^2J_{CP}$ = 5.3 Hz, $CH_{ar}$), 131.3 (m, $CH_{ar}$), 128.9 (t, $^3J_{CP}$ = 5.2 Hz, $CH_{ar}$), 89.4 (s, $C_5H_5$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 1263 (s, $CF_3SO_3$), 864 (s, P–F).

**Synthesis of $[RuCp(PPh_3)_2(PF_3)]PF_6$ ($2^{F'}$).** $[RuCp(PPh_3)_2\{P(OH)_3\}]PF_6$ (250.0 mg, 0.272 mmol) and $[Et_2N{=}SF_2]BF_4$ (187.2 mg, 0.817 mmol, 3 eq.) were charged in a schlenk tube and dissolved in $CH_2Cl_2$ (15 ml). The resulting suspension was stirred at room temperature over night and finally cooled down (*ca* −78 °C). A white crystalline compound precipitated out of the solution, presumably a salt by-product of the reaction. The yellow surnatant was cannulated into a 50 ml schlenk flask and $[RuCp(PPh_3)_2(PF_3)]PF_6$ was obtained as yellow microcrystals by adding 20 ml of $Et_2O$ and bubbling nitrogen gas for *ca* 30 minutes. $[RuCp(PPh_3)_2(PF_3)]PF_6$ is air stable in solution for a long time. Yield: 93%.

**Synthesis of $[RuCp(PPh_3)_2(PhPF_2)]CF_3SO_3$ ($3^F$).** $[RuCp(PPh_3)_2\{PhP(OH)_2\}]CF_3SO_3$ (250.0 mg, 0.255 mmol) and $[Et_2NSF_2]BF_4$ (233.6 mg, 1.02 mmol, 4 eq.) were charged in a schlenk tube (100 ml) and dissolved in $CH_2Cl_2$ (20 ml). The resulting suspension was stirred at room temperature for overnight and finally cooled down (*ca* −78 °C) for 2 hours. A white crystalline compound precipitated and the yellow solution was cannulated into a 50 ml schlenk flask. The solution was concentrated to 10 ml by evaporating the solvent under reduced pressure. $[RuCp(PPh_3)_2(PhPF_2)]CF_3SO_3$ was obtained as yellow microcrystalline solid by adding 50 ml $Et_2O$. Yield: 90%. Anal. Calcd for $C_{48}H_{40}F_5P_3SO_3Ru$: C, 58.41; H, 4.09. Found: C, 58.13; H, 4.19. ESI-MS ($C_{47}H_{40}F_2P_3Ru$) calcd for $[M + H]^+$: *m*/*z* = 837.1; found: *m*/*z* = 836.8. $[M]^+$. $^1H$ NMR (400.13 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 7.7–6.5 (m, 45H, Ph), 4.9 (s, 5H, $C_5H_5$) ppm. $^{31}P\{^1H\}$ NMR (161.97 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 220.8 (tt, $^1J_{PAF}$ = 1087.3 Hz, $^2J_{PAPB}$ = 55.9 Hz, 1P, $P_A$, $PF_2$), 38.6 (dt $^2J_{PAPB}$ = 55.9 Hz, $^3J_{PF}$ = 7.4 Hz, 2P, $P_B$) ppm. $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = −34.2 (d, $^1J_{PAF}$ = 1087.3 Hz, $PF_2$), −79.0 (s, $CF_3SO_3^-$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 133.8 (t, $^2J_{CP}$ = 5.2 Hz, $CH_{ar}$), 131.5 (s, $CH_{ar}$), 129.1 (t, $^3J_{CP}$ = 5.0 Hz, $CH_{ar}$), 127.7 (dt, $^1J_{CP}$ = 13.8 Hz, $^2J_{CF}$ = 3.0 Hz, $C_q$), 89.7 (s, $C_5H_5$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 1263 (s, $CF_3SO_3$), 801 (s, P–F).

**Synthesis of $[RuCp^*(CH_3CN)_3]PF_6$.** The compound was prepared by a modification of the published procedure.[3]

To a solution of $[RuCp^*Cl_2]_2$ (350.0 mg, 1.139 mmol) in acetonitrile (10 ml) was added zinc dust (149.0 mg, 2.279 mmol). After stirring 1 hour at room temperature, dry $KPF_6$ (318.0 mg, 1.608 mmol) was added. The mixture was stirred for 16 hours at room temperature, afterwards the solvent was evaporated to dryness. To the solid residue was added $CH_2Cl_2$ (20 ml) and the surnatant was cannulated into a schlenk tube and evaporated to dryness affording a brown-yellow solid. Yield: 78%. $^1H$ NMR (400.0 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 2.4 (bs, 9H, $CH_3CN$), 2.3 (s, 15H, Cp*) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 298 K): $\delta$ = −144.8 (sept, 1P, $PF_6$, $^1J_{PF}$ = 701.6 Hz) ppm.

**Synthesis of $[RuCp(CH_3CN)_2\{PhP(OH)_2\}]PF_6$ ($4^{OH}$).** $[RuCp(CH_3CN)_3]PF_6$ (300.0 mg, 0.691 mmol) and PhP(O)(H)(OH) (98.1 mg, 0.691 mmol) were charged in a schlenk tube (100 ml) and dissolved in $CH_3CN$ (60 ml). The resulting yellow solution was stirred at room temperature for three days. The solution was concentrated to dryness under reduced pressure and the solid residue was washed three times, each with 15 mL of pentane. A mustard solid was obtained and dried under vacuum. Yield: 74%. Anal. Calcd for $C_{15}H_{18}F_6P_2N_2O_2Ru$: C, 33.58; H, 3.38. Found: C, 33.41; H, 3.25. ESI-MS ($C_{15}H_{18}N_2O_2PRu$) calcd for $[M + H]^+$: *m*/*z* = 391.0; found: *m*/*z* = 390.9. $^1H$ NMR (400.1 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 7.8–7.5 (m, 5H, Ph), 4.6 (s, 5H, $C_p$), 2.3 (s, 6H, $CH_3CN$). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 151.3 (s, 1P), −143.7 (sept, $PF_6$,

$^1J_{PF}$ = 701.6 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 142.1 (d, $^1J_{PC}$ = 64.1 Hz, $C_q$), 130.9 (d, $^2J_{CP}$ = 1.9 Hz, $CH_{ar}$), 129.2 (d, $^2J_{CP}$ = 13.4 Hz, $CH_{ar}$), 128.7 (d, $^3J_{CP}$ = 10.4 Hz, $CH_{ar}$), 127.3 (s, $CH_3CN$), 77.6 (d, $^2J_{CP}$ = 2.7 Hz, $C_5H_5$), 4.1 (s, $CH_3CN$). IR (KBr, $cm^{-1}$): $\nu$ = 2263 (w, CN), 1113, (broad, $P(OH)_2$), 836 (s, $PF_6$).

**Synthesis of $[RuCp^*(CH_3CN)\{PhP(OH)_2\}_2]PF_6$ ($5^{OH}$).** $[RuCp^*(CH_3CN)_3]PF_6$ (100.0 mg, 0.198 mmol, 1 eq.) and PhP(O)(H)(OH) (28.1 mg, 0.198 mmol, 1 eq.) were charged in a schlenk tube (50 ml) and dissolved in $CH_3CN$ (20 ml). The resulting solution was stirred at 40 °C for 24 hours. The solution was concentrated to a small volume and were added in the order, 1 ml of toluene and 50 ml of pentane to precipitate the final product. $[RuCp^*(CH_3CN)\{PhP(OH)_2\}_2]PF_6$ was obtained as yellow-brown solid after filtration under nitrogen and was dried in vacuum. Yield: 52%. Anal. Calcd for $C_{24}H_{32}F_6P_3NO_4Ru$: C, 40.80; H, 4.57. Found: C, 40.57, H, 4.78. ESI-MS ($C_{24}H_{32}NO_4P_2Ru$) calcd for $[M + H]^+$ $m/z$ = 562.1; found: $m/z$ = 562.1; calcd for $[M - PhP(OH)_2]^+$ $m/z$ = 420.1; found: $m/z$ = 419.8. $^1H$ NMR (300.1 MHz, $CD_3OD$, 295 K): $\delta$ = 7.8 (m, 4H, $H_{ar}$), 7.5 (m, 6H, $H_{ar}$), 2.5 (s, 3H, $CH_3CN$), 1.4 (s, 15H, $C_5Me_5$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CD_3OD$, 295 K): $\delta$ = 153.5 (s, 1P), −144.5 (sept, $^1J_{PF}$ = 707.9 Hz, $PF_6$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_3OD$, 295 K): $\delta$ = 142.8 (t, $^1J_{CP}$ = 30.3 Hz, $C_q$), 131.4 (s, $CH_{ar}$), 130.8 (t, $^2J_{CP}$ = 6.4 Hz, $CH_{ar}$), 129.0 (t, $^3J_{CP}$ = 4.7 Hz, $CH_{ar}$), 127.0 (s, $CH_3CN$), 94.4 (s, $C_5Me_5$), 9.5 (s, $C_5Me_5$) 3.6 (s, $CH_3CN$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 2962 (s, OH), 2267 (w, CN), 836 (s, $PF_6$).

The reaction was repeated using a ratio complex/ligand 1 : 2 as follows: $[RuCp^*(CH_3CN)_3]PF_6$ (350.0 mg, 0.6925 mmol, 1 eq.) and PhP(O)(H)(OH) (196.8 mg, 1.385 mmol, 2 eq.) were charged in a schlenk tube and dissolved in $CH_3CN$ (30 ml). The resulting solution was stirred at 40 °C for 24 hours. The solution was concentrated to dryness, the solid residue was rinsed with pentane, than dichloromethane and diethyl ether (ratio 2 : 1) were added to precipitate the pure product. $[RuCp^*(CH_3CN)\{PhP(OH)_2\}_2]PF_6$ was obtained as yellow solid after filtration under nitrogen and was dried in vacuum. Yield: 71%.

The NMR data are the same as above.

**Synthesis of $[RuCp(CH_3CN)_2(PhPF_2)]PF_6$ ($4^F$).** $[RuCp(CH_3CN)_2\{PhP(OH)_2\}]PF_6$ (100.0 mg, 0.187 mmol) and Xtal-Fluor-E (128.3 mg, 0.560 mmol, 3 eq.) were charged in a schlenk tube and dissolved in $CH_2Cl_2$ (30 ml). The resulting solution was stirred at room temperature for 18 hours and afterwards the reaction mixture was kept in the freezer at −30 °C overnight. A white crystalline compound precipitated out and the yellow solution was cannulated into a schlenk flask. The solution was concentrated to a small volume and 50 ml of diethyl ether were added. The desired complex precipitated out of the solution as brown-yellow solid. Yield: 68%. Anal. Calcd for $C_{15}H_{16}F_8N_2P_2Ru$: C, 33.41; H, 2.99. Found: C 33.10; H, 2.83. ESI-MS ($C_{15}H_{16}F_2N_2PRu$) calcd for $[M + H]^+$: $m/z$ = 395.0; found: $m/z$ = 394.7. $^1H$ NMR (300.1 MHz, $CD_2Cl_2$, 298 K): $\delta$ = 7.8–7.6 (m, 5H, Ph), 4.9 (s, 5H, $C_5H_5$), 2.3 (s, 6H, $CH_3CN$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 224.9 (t, $^1J_{PF}$ = 1147.8 Hz, $PF_2$), −144.4 (sept, $^1J_{PF}$ = 711.2 Hz, $PF_6$) ppm. $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = −52.1 (d, $^1J_{FP}$ = 1147.4 Hz, $PhPF_2$), −72.6 (d, $^1J_{FP}$ = 711.2 Hz, $PF_6$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 134.0 (d, $^2J_{CP}$ = 2.2 Hz, $CH_{ar}$), 129.8 (dt, $^1J_{CP}$ = 17.9 Hz, $^2J_{CF}$ = 3.6 Hz, $C_q$), 129.5 (s, $CH_{ar}$), 129.3 (s, $CH_{ar}$), 128.7 (s, $CH_3CN$), 79.9 (d, $^2J_{CP}$ = 2.4 Hz, $C_5H_5$), 4.3 (s, $CH_3CN$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 2228 (w, CN), 839 (bs, $PF_2$, $PF_6$).

**Synthesis of $[RuCp^*(CH_3CN)(PhPF_2)_2]PF_6$ ($5^F$).** $[RuCp^*(CH_3CN)\{PhP(OH)_2\}_2]PF_6$ (190.0 mg, 0.269 mmol) and Xtal-Fluor-E (184.8 mg, 0.868 mmol, 3 eq.) were charged in a schlenk tube (50 ml). In another schlenk and dissolved in $CH_2Cl_2$ (14 ml). The resulting solution was stirred at room temperature for 15 min. The solution was dried by evaporating the solvent under reduced pressure. Afterwards the reaction mixture was kept at −78 °C for 2 hours. A white crystalline compound precipitated out and the brownish solution was cannulated into a schlenk flask. The solution was dried and the remaining oil was washed with diethyl ether and pentane several times until a brownish solid was obtained. Yield: 63%. Anal. Calcd for $C_{24}H_{28}F_{10}NP_3Ru$: C, 40.35; H, 3.95. Found: C, 39.92; H, 3.91. ESI-MS($C_{24}H_{28}F_4NP_2Ru$) calcd For $[M + H]^+$: $m/z$ = 570.1; found: $m/z$ = 570.1. $^1H$ NMR (300.1 MHz, $CD_3OD$, 298 K): $\delta$ = 7.9–7.5 (m, 10H, *Ph*), 2.4 (s, 3H, $CH_3CN$), 1.3 (s, 15H, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CD_3OD$, 295 K, see Fig. 1S in ESI† for the labeling): $\delta$ = 225.9 (second order multiplet, Px and Px′), −141.4 (spt, $^1J_{PF}$ = 707.6 Hz, 1P, $PF_6$) ppm. $^{19}F$ NMR (376.5 MHz, $CD_3OD$, 295 K): $\delta$ = −49.3 (second order multiplet, $F_A$ and $F_{A'}$), −53.9 (second order multiplet, $F_B$ and $F_{B'}$), −73.9 (d, $^1J_{FP}$ = 707.8 Hz, $PF_6$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CD_3OD$, 295 K): $\delta$ = 135.1 (s, $CH_3CN$), 133.5 (d, $^4J_{CP}$ = 2.6 Hz, $CH_{ar}$), 132.4 (d, $^3J_{CP}$ = 10.0 Hz, $CH_{ar}$), 130.4 (d, $^2J_{CP}$ = 11.4 Hz, $CH_{ar}$), 129.6 (d, $^1J_{CP}$ = 15.0 Hz, $C_q$), 128.9 (s, $CH_3CN$), 100.3 (s, $C_5Me_5$), 9.8 (s, $C_5Me_5$) 3.5 (s, $CH_3CN$) ppm.

$^1H$ NMR (400.1 MHz, $(CD_3)_2CO$, 298 K): $\delta$ = 7.8–7.7 (m, 10H, *Ph*), 2.5 (s, 3H, $CH_3CN$), 1.8 (s, 15H, $CH_3$) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$, 295 K, see Fig. 1S in ESI† for the labeling): $\delta$ = 227.5 (second order multiplet, Px and Px′), −144.4 (spt, $^1J_{PF}$ = 707.5 Hz, 1P, $PF_6$) ppm. $^{19}F$ NMR (376.5 MHz, $(CD_3)_2CO$, 295 K): $\delta$ = −48.3 (second order multiplet, $F_A$ and $F_{A'}$), −53.4 (second order multiplet, $F_B$ and $F_{B'}$), −72.4 ($^1J_{FP}$ = 708.2 Hz, $PF_6$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2CO$, 253 K): $\delta$ = 135.5 (dt, $^1J_{CP}$ = 50.4 Hz, $^2J_{CF}$ = 14.3 Hz, $C_q$), 135.0 (s, $CH_{ar}$), 131.1 (s, $CH_{ar}$), 130.1 (s, $CH_{ar}$), 129.6 (s, $CH_3CN$), 99.5 (s, $C_5Me_5$), 9.6 (s, $C_5Me_5$) 4.2 (s, $CH_3CN$) ppm. IR (KBr, $cm^{-1}$): $\nu$ = 2229 (w, CN), 814 (s, $PF_2$), 843 (s, $PF_6$).

**Synthesis of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{PhP(OH)_2\}]$ ($6^{OH}$).** To a suspension of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (250.0 mg, 0.816 mmol) in THF (50 ml) was added phenylphosphinic acid (232.0 mg, 1.632 mmol) as a solid. The solution was refluxed for 5 hours, afterwards the reaction mixture was cooled down to room temperature and concentrated to small volume by evaporating the solvent under reduced pressure. $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{PhP(OH)_2\}]$ was obtained as an orange solid by adding 50 ml of pentane. Yield: 78%. Crystals suitable for X-ray analysis were obtained by cooling down to 4 °C a solution of the complex in dichloromethane and allowing a slow diffusion of pentane.

Anal. Calcd for $C_{16}H_{21}Cl_2PO_2Ru$: C, 42.87; H, 4.72. Found: C, 42.81; H: 4.56. $^1$H NMR (300.0 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 7.9 (m, 1H, C$H_{ar}$), 7.7 (m, 4H, C$H_{ar}$), 5.2 (s, 4H, C$H_{ar}$, *p*-cymene), 2.6 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, C$H$(C$H_3$)$_2$), 2.0 (s, 3H, C$H_3$), 1.1 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C$H_3$)$_2$) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 147.6 (s) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 136.9 (d, $^1J_{CP}$ = 88.5 Hz, $C_q$), 132.1 (s, $CH_{ar}$), 130.3 (d, $^2J_{CP}$ = 12.1 Hz $CH_{ar}$), 128.8 (d, $^3J_{CP}$ = 11.6 Hz, $CH_{ar}$), 105.6 (s, $C_q$), 98.1 (s, $C_q$), 90.0 (d, $^2J_{CP}$ = 5.7 Hz, $CH_{p\text{-cym}}$), 88.2 (d, $^2J_{CP}$ = 5.7 Hz, $CH_{p\text{-cym}}$), 30.3 (s, *C*H(CH$_3$)$_2$), 21.5 (s, CH(*C*H$_3$)$_2$),18.3 (s, C$H_3$-ring) ppm. IR (KBr, cm$^{-1}$): $\nu$ = 3065 (broad, OH), 858 (s, P–OH).

**Synthesis of [Ru(η$^6$-*p*-cymene)Cl$_2$(PhPF$_2$)] (6$^F$).** [Ru(η$^6$-*p*-cymene)Cl$_2${PhP(OH)$_2$}] (100.0 mg, 0.223 mmol) and [Et$_2$NSF$_2$]BF$_4$ (467.2 mg, 1.338 mmol, 6 eq.) were charged in a schlenk tube and dissolved in $CH_3CN$ (40 ml). The solution was stirred at room temperature for 18 hours. The solution was dried by evaporating the solvent under reduced pressure. The solid residue was re-dissolved in dichloromethane and cooled down (*ca* −78 °C) to allow the precipitation of excess of fluorinating agent. After filtration under nitrogen, pentane was added to the filtrate and the desired product precipitated out from the solution. The brown solid was recovered by filtration under inert atmosphere. Yield: 80%. Anal. Calcd for $C_{16}H_{19}F_2Cl_2PRu$: C, 42.49; H, 4.23. Found: C, 42.57; H, 4.11. ESI-MS ($C_{18}H_{22}ClF_2NPRu$) calcd for $[M - Cl + CH_3CN]^+$: *m*/*z* = 458.0; found: *m*/*z* = 457.8; calcd for $[M - Cl]^+$: *m*/*z* = 417.0; found: *m*/*z* = 417.1. $^1$H NMR (300.0 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 7.9–7.7 (m, 5H, $CH_{ar}$), 5.6 (d, $^3J_{HH}$ = 6.0 Hz, 2H, C$H_{ar}$, *p*-cymene), 5.5 (d, $^3J_{HH}$ = 6.0 Hz, 2H, C$H_{ar}$, *p*-cymene), 3.8 (sept, $^3J_{HH}$ = 6.0 Hz, 1H, C$H$(CH$_3$)$_2$), 2.5 (s, 3H, C$H_3$), 1.3 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH(C$H_3$)$_2$) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 215.1 (t, $^1J_{PF}$ = 1156.1 Hz, $PF_2$) ppm. $^{19}$F NMR (376.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = −58.6 (d, $^1J_{FP}$ = 1159.0 Hz, $PHPF_2$) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, $CD_2Cl_2$, 295 K): $\delta$ = 135.2 (bs, $CH_{ar}$), 130.0 (d, $^2J_{CP}$ = 12.3 Hz, $CH_{ar}$), 129.4 (dt, $^1J_{CP}$ = 15.7 Hz, $^2J_{CF}$ = 3.7 Hz $C_q$), 127.1 (d, $^3J_{CP}$ = 11.6 Hz, $CH_{ar}$), 102.2 (s, $C_q$), 97.6 (s, $C_q$), 79.3 (s, $CH_{p\text{-cym}}$), 78.4 (s, $CH_{p\text{-cym}}$), 31.8 (s, *C*H(CH$_3$)$_2$), 22.2 (s, CH(*C*H$_3$)$_2$), 20.8 (s, C$H_3$-ring) ppm. IR (KBr, cm$^{-1}$): $\nu$ = 801 (s, P–F).

### X-Ray crystallographic data collection and refinement of the structures

Crystals, suitable for a single crystal X-ray structure analysis were obtained by layering petroleum ether and $CH_2Cl_2$/THF (**3$^{OH}$**·$CCl_2$) or by slow diffusion of *n*-pentane into a $CH_2Cl_2$ solution of **6$^{OH}$** at 277 K. Diffraction intensity data were collected at 150 K on an Oxford Xcalibur 3 or Xcalibur PX diffractomerts, using graphite-monochromated Mo $K_\alpha$ and Cu $K_\alpha$ radiation respectively. Cell refinement, data reduction, and empirical absorption correction were carried out with the Oxford diffraction software and SADABS, respectively.[37a] All structure determination calculations were performed with the WINGX package,[37b] with SIR-97,[37c] SHELXL-97[37d] and ORTEP-3 programs.[37e] The structure was solved by direct methods and refined by full-matrix $F^2$ refinement. Final refinements based on $F^2$ were carried out with anisotropic thermal parameters for all non-hydrogen atoms, which were included using a riding model with isotropic *U* values 20% larger than those of the adjacent carbon atoms. The crystal structure of **3$^{OH}$** CCl2, showed one disordered $CH_2Cl_2$ molecule (*i.e.* the corresponding carbon atom showed two positions of equal occupancy) in the asymmetric unit. Hence the hydrogen atoms attached to this carbon atom were omitted ($CCl_2$). CCDC reference number for **3$^{OH}$**·$CCl_2$:1415725 and **6$^{OH}$**: 1415724. Crystallographic data for **3$^{OH}$**·$CCl_2$ and **6$^{OH}$** are reported in Table 2.

**Table 2** Crystallographic data for **3$^{OH}$**·$CCl_2$ and **6$^{OH}$**

| | **3$^{OH}$**·$CCl_2$ | **6$^{OH}$** |
|---|---|---|
| Formula | $C_{49}H_{42}Cl_2F_3O_5P_3RuS$ | $C_{16}H_{21}Cl_2O_2PRu$ |
| Formula weight | 1064.77 | 448.27 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| *a* (Å) | 12.5099(2) | 12.4787(2) |
| *b* (Å) | 13.2579(2) | 11.3676(1) |
| c (Å) | 28.0827(6) | 13.2916(2) |
| $\beta$ (°) | 96.283(2) | 107.962(1) |
| *V* (Å$^3$) | 4629.68(14) | 1793.56(4) |
| *Z* | 4 | 4 |
| *T*/K | 150(2) | 150(2) |
| $D_c$ (g cm$^{-3}$) | 1.528 | 1.660 |
| Crystal size (mm) | 0.30 × 0.25 × 0.20 | 0.20 × 0.20 × 0.10 |
| $\mu$ (mm$^{-1}$) | 0.662 | 10.687 |
| 2$\Theta$ range (°) | 8.26–57.80 | 10.46–144.12 |
| Total reflections | 10 671 | 3481 |
| Unique reflections ($R_{int}$) | 10 653 (0.04) | 3473 |
| Observed reflections [$I > 2\sigma(I)$] | 9192 | 3222 |
| Parameters | 594 | 210 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ 0.0413, w$R_2$ 0.1066 | $R_1$ 0.0429, w$R_2$ 0.1131 |
| Max., min, $\Delta\rho$ (e Å$^{-3}$) | 1.553, −1.439 | 0.987, −0.893 |
| Goodness of fit on $F^2$ | 1.045 | 1.043 |

## Acknowledgements

We thank the European Union (Marie Curie ITN SusPhos, Grant Agreement No. 317404) for financial support.

## References

1 D. E. C. Corbridge, *Phosphorus 2000. Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, NL, 2000.
2 For a review describing the first examples of $PF_3$ metal complexes, see: T. Kruck, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 53–67.
3 (*a*) H. Stammreich, K. Kawai, O. Sala and P. Krumholz, *J. Chem. Phys.*, 1961, **35**, 2168–2174; (*b*) H.-R. Jaw and J. I. Zink, *Inorg. Chem.*, 1988, **27**, 3421–3424.
4 N. Fey, M. Garland, J. P. Hopewell, C. L. McMullin, S. Mastroianni, A. Guy Orpen and P. G. Pringle, *Angew. Chem., Int. Ed.*, 2012, **51**, 118–122.

5 (*a*) M. Nivsarkar, A. K. Gupta and M. P. Kaushik, *Tetrahedron Lett.*, 2004, **45**, 6863; (*b*) B. Nawrot, M. Sobczak and S. Antoszczyk, *Org. Lett.*, 2002, **4**, 1799.
6 (*a*) O. Stelzer, *Chem. Ber.*, 1974, **107**, 2329–2340; (*b*) M. Pabel, A. C. Willis and S. B. Wild, *Inorg. Chem.*, 1996, **35**, 1244–1249; (*c*) L. Riesel and J. Haenel, *J. Fluorine Chem.*, 1988, **38**, 335–340.
7 J. Chatt, *Nature*, 1950, **165**, 637.
8 G. Wilkinson, *J. Am. Chem. Soc.*, 1951, **73**, 5501–5502.
9 J. F. Nixon and R. Swain, *Platinum Met. Rev.*, 1975, **19**, 22–29.
10 D. W. Allen and B. J. Walker, *Organophosphorus Chem.*, 1997, 23.
11 R. J. Clark, H. Belefant and S. M. Williamson, *Inorg. Synth.*, 1990, **28**, 310.
12 O. Stelzer and R. Schmutzler, *Inorg. Synth.*, 1978, **18**, 173–179.
13 L. Heuer and R. Schmutzler, *J. Fluorine Chem.*, 1988, **39**, 197–216.
14 P. Švec, P. Novák, M. Nádvorník, Z. Padělková, I. Císařová, L. Kolářová, A. Růžička and J. Holeček, *J. Fluorine Chem.*, 2007, **128**, 1390–1395.
15 (*a*) R. Wärme, L. Juhlin and L. Trogen, *Phosphorus, Sulfur Silicon*, 2008, **183**, 483–486; (*b*) R. Wärme and L. Juhlin, *Phosphorus, Sulfur Silicon*, 2010, **185**, 2402–2408.
16 For reviews on the coordination chemistry of phosphinous acids and related compounds, see: (*a*) D. M. Roundhill, R. P. Sperline and W. B. Beaulieu, *Coord. Chem. Rev.*, 1978, **26**, 263–279; (*b*) B. Walther, *Coord. Chem. Rev.*, 1984, **60**, 67–105; (*c*) T. Appleby and J. D. Woollins, *Coord. Chem. Rev.*, 2002, **235**, 121–140.
17 (*a*) D. N. Akbayeva, M. Di Vaira, S. S. Costantini, M. Peruzzini and P. Stoppioni, *Dalton Trans.*, 2006, 389–395; (*b*) D. Yakhvarov, M. Caporali, L. Gonsalvi, S. Latypov, V. Mirabello, I. Rizvanov, W. Schipper, O. Sinyashin, P. Stoppioni and M. Peruzzini, *Angew. Chem., Int. Ed.*, 2011, **50**, 5370–5373; D. Yakhvarov, M. Caporali, L. Gonsalvi, S. Latypov, V. Mirabello, I. Rizvanov, W. Schipper, O. Sinyashin, P. Stoppioni and M. Peruzzini, *Angew. Chem., Int. Ed.*, 2012, **51**, 2533; (*c*) G. Manca, M. Caporali, A. Ienco, M. Peruzzini and C. Mealli, *J. Organomet. Chem.*, 2014, **760**, 177–185.
18 W. J. Middleton, *J. Org. Chem.*, 1975, **40**, 574.
19 (*a*) G. S. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic and H. Cheng, *J. Org. Chem.*, 1999, **71**, 7048; (*b*) G. S. Lal, *Chem. Commun.*, 1999, 215.
20 L. N. Markovskii, V. E. Pashinnik and E. P. Saenko, *Zh. Org. Khim.*, 1977, **13**, 1116.
21 (*a*) F. Beaulieu, L.-P. Beauregard, G. Courchesne, M. Couturier, F. LaFlamme and A. L'Hereux, *Org. Lett.*, 2009, **11**, 5050–5053; (*b*) A. L'Hereux, F. Beaulieu, C. Bennet, D. R. Bill, S. Clayton, F. LaFlamme, M. Mirmehrabi, S. Tadayon, D. Tovell and M. Couturier, *J. Org. Chem.*, 2010, **75**, 3401–3411; (*c*) M. Couturier and A. L'Hereux, *US* 2012/0108801 A1, 2012.
22 O. Farooq, *J. Chem. Soc., Perkin Trans. 1*, 1998, 839–840.
23 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York, 2nd edn, 1963, vol. 1, pp. 189–190.
24 H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, 1939, **61**, 2927–2934.
25 C. J. Hoffman, *Inorg. Synth.*, 1953, **4**, 149–150.
26 A. A. Williams, *Inorg. Synth.*, 1957, **5**, 95–97.
27 A. M. A. Boshaala, S. J. Simpson, J. Autschbach and S. Zheng, *Inorg. Chem.*, 2008, **47**, 9279–9292.
28 E. P. Kundig and F.-R. Monnier, *Adv. Synth. Catal.*, 2004, **346**, 901–904.
29 B. Steinmetz and W. A. Schenk, *Organometallics*, 1999, **18**, 943–946.
30 (*a*) M. A. Bennet, T. N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1981, **21**, 74–75; (*b*) V. Cadierno, P. Crochet, S. E. Garcìa-Garrido and J. Gimeno, *Dalton Trans.*, 2004, 3635–3641.
31 (*a*) M. P. Mitoraj and A. Michalak, *Inorg. Chem.*, 2010, **49**, 578–582; (*b*) T. Leyssens, D. Peeters, A. Guy Orpen and J. N. Harvey, *Organometallics*, 2007, **26**, 2637–2645.
32 L. W. Yarbrough and M. B. Hall, *Inorg. Chem.*, 1978, **17**, 2269–2275.
33 M. G. Bodner, M. P. May and L. E. McKinney, *Inorg. Chem.*, 1980, **19**, 1951–1958.
34 J. D. Warren and R. J. Clark, *Inorg. Chem.*, 1970, **9**, 373–379.
35 L. Heuer, M. Sell and R. Schmutzler, *Polyhedron*, 1987, **6**, 1295–1307.
36 J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, 1964, **20**, 1835–1842.
37 (*a*) G. M. Sheldrick, *SADABS. Program for Empirical Absorption Corrections*, University of Göttingen, Germany, 1986; (*b*) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838; (*c*) A. Altomare, M. C. Burla, M. Cavalli, G. L. Cascarano, C. Giacovazzo, A. Gagliardi, G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119; (*d*) G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997; (*e*) M. N. Burnett and C. K. Johnson, ORTEP-3, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.