Novel (η⁶-arene)-ruthenium(II) complexes containing bis(iminophosphorano)methanide and methandiide ligands

Victorio Cadierno *, Josefina Díez, Joaquín García-Álvarez, José Gimeno *

*Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles"
(Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain*

Abstract

The novel bis(iminophosphorano)methanes $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (**1a**), Et (**1b**)) have been obtained by oxydation of dppm with the corresponding thiophosphorylated azides $(RO)_2P(=S)N_3$. Deprotonation of **1a,b** with KH generates the methanide species $KCH[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (**2a**), Et (**2b**)). The ruthenium(II) dimer $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ reacts with **2a,b** to afford the cationic complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}C,N,S\text{-}CH[P\{=NP(=S)(OR)_2\}Ph_2]_2)]^+$ (R = Ph (**3a**), Et (**3b**)), via selective $\kappa^3\text{-}C,N,S$-coordination of the bis(iminophosphorano)methanide anions to ruthenium. The structure of $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}C,N,S\text{-}CH[P\{=NP(=S)(OEt)_2\}Ph_2]_2)][PF_6]$ (**3b**) has been confirmed by single-crystal X-ray crystallography. Deprotonation of complexes **3a,b** with NaH leads to the neutral carbene derivatives $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}C,N\text{-}C[P\{=NP(=S)(OR)_2\}Ph_2]_2)]$ (R = Ph (**4a**), Et (**4b**)).
© 2005 Elsevier B.V. All rights reserved.

Keywords: Bis(iminophosphorano)methane; Bis(iminophosphorano)methanide; Bis(iminophosphorano)methandiide; Ruthenium; Carbene complexes

1. Introduction

Oxidation of the two phosphorus atoms of bis(diphenylphosphino)methane (dppm) with organic azides (RN_3), by means of the Staudinger reaction [1], has been successfully applied to the preparation of several bis(iminophosphorano)methane derivatives $CH_2\{P(=NR)Ph_2\}_2$ (see for example [2]). The presence of two highly polarized P=N groups in these compounds results in an enhanced acidity of the methylenic hydrogen atoms, and consequently deprotonation reactions to afford the corresponding bis(iminophosphorano)methanide anions (**A**; see Chart 1) can easily take place [3]. The coordination chemistry of these monoanions has been the subject of several studies over the last few years due to their topological similarity with the well-known β-diketiminate ligands **B** [4]. As expected, bis(iminophosphorano)methanides **A** have proven to be versatile chelating ligands being able to adopt $\kappa^2\text{-}N,N$ (**C**; Zn, Fe, Ge and group 13 complexes) (see for example [5]), $\kappa^2\text{-}C,N$ (**D**; Rh, Ir, Pd and Pt complexes) (see for example [6]) or $\kappa^3\text{-}N,C,N$ (**E**; V, Co, Rh, Ir, Ni, Mn, Fe, U, Y and lanthanide complexes) (see for example [7]) coordination modes, depending on the nature of the metal fragment (Chart 1).

In this context, the groups of Cavell [8] and Stephan [9] have also reported the synthesis and structural characterization of the dilithiomethandiide dimer $[Li_2C\{P(=NSiMe_3)Ph_2\}_2]_2$, as the result of the double deprotonation of the PCH_2P backbone of the bis(iminophosphorano)methane derivative $CH_2\{P(=NSiMe_3)Ph_2\}_2$.

---
* Corresponding authors. Tel.: +34 985 103 461; fax: +34 985 103 446.
  E-mail addresses: jgh@uniovi.es (J. Gimeno), vcm@uniovi.es (V. Cadierno).
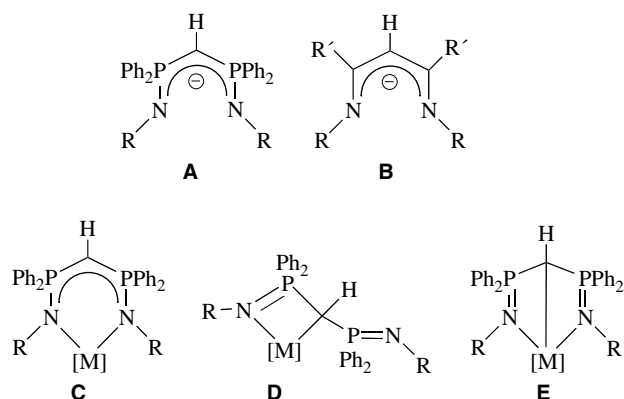
Chart 1. Structure of the anions **A** and **B**, and coordination modes of **A**.

Interestingly, the coordination of this dianionic unit to a metal fragment leads to unique "pincer" (**F**) or bridged (**G**) carbene complexes (see Chart 2). Thus, pincer-type structures **F** have been found in some complexes of group

4 metals [10], samarium [11], and molybdenum [12], while bimetallic species **G** are known for chromium [13], aluminum [5b,14] and group 14 metals [15]. The synthesis and reactivity of the platinum–carbene complex **H** [16] and the bis(germavinylidene) **I** [5f,12,15] has been also reported.

In contrast, very few ruthenium complexes containing bis(iminophosphorano)methanide anions **A** have been described in the literature (see Chart 3). Recently, we and others have reported the only examples known to date, namely: (i) the cationic complex [Ru(η^6-p-cymene)(κ^3-N,C,N-CH{P(=NPh)Ph$_2$}$_2$)][Cl] (**J**) in which the bis(iminophosphorano)methanide ligand displays a symmetric κ^3-N,C,N-coordination mode [17] and (ii) complexes of the type **K** and **L** (R = Ph, Et) in which N-phosphorylated bis(iminophosphorano)methanide anions are acting as unsymmetrical κ^2-C,N (**K**) or κ^3-C,N,O (**L**) chelate ligands [18]. Significantly, the latter complexes have shown to be good precursors of nucleophilic carbenes **M** via deprotonation of the methinic
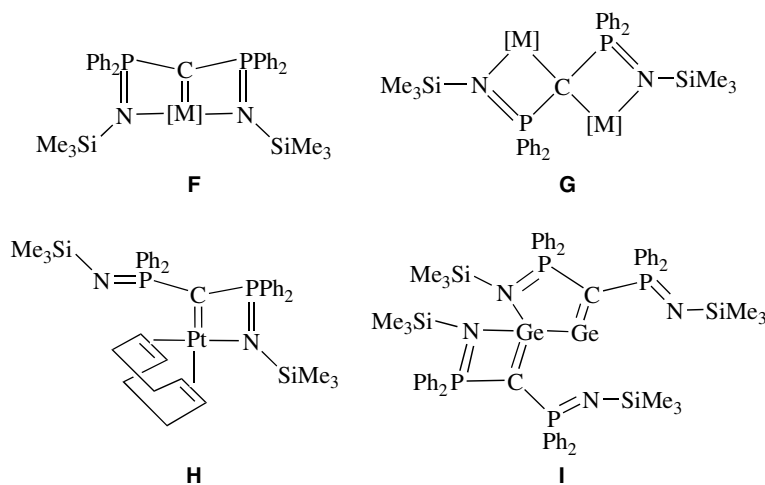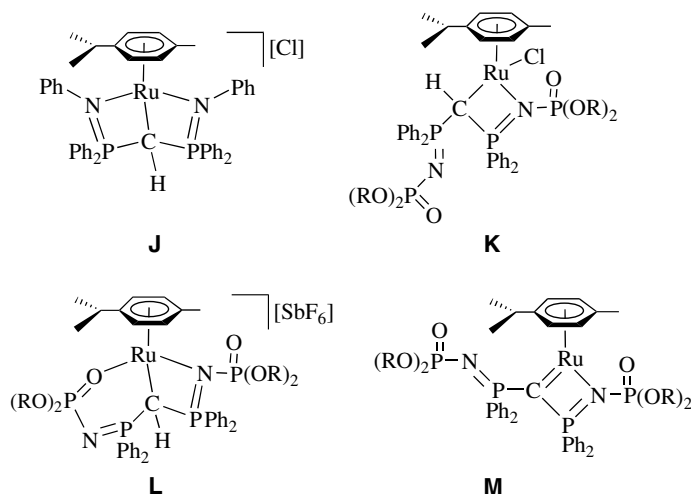

Chart 2. Structure of the carbenic species **F–I**.

Chart 3. Ruthenium(II) complexes containing bis(iminophosphorano)methanide and methandiide ligands.

PCHP hydrogen atom [18]. To the best of our knowledge, they are the sole examples of ruthenium complexes containing bis(iminophosphorano)methandiide ligands.

As an extension of our previous studies, mainly devoted to explore the scope of this synthetic approach to ruthenium–carbene complexes, in this paper we report: (i) the synthesis of the novel *N*-thiophosphorylated bis(iminophosphorano)methanes $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph, Et), (ii) the reactions of their methanide anions with the ruthenium(II) dimer [{Ru-(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] giving rise to thiophosphorylated ruthenacarbobicycles, and (iii) the synthesis of novel carbene derivatives of the type **M**.

2. Results and discussion

2.1. Synthesis of the N-thiophosphorylated bis(iminophosphorano)methane ligands $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (**1a**), Et (**1b**))

The novel *N*-thiophosphorylated bis(iminophosphorano)methane ligands **1a,b** have been readily prepared by treating dppm with two equivalents of the corresponding azides $(RO)_2P(=S)N_3$ in THF at room temperature (see Scheme 1).

Compounds **1a,b** have been isolated as air-stable white solids in high yields (90% and 84%, respectively). They are soluble in chlorinated solvents, THF and diethyl ether, and are insoluble in apolar solvents such as *n*-pentane or hexanes. Characterization of **1a,b** was straightforward following their analytical and spectroscopic data (details are given in Section 4). The most remarkable features of the NMR spectra are: (i) ($^{31}P\{^1H\}$ NMR) The presence of two multiplets with equal relative intensities (**1a:** 10.95 ($Ph_2P=N$) and 51.23 ($(PhO)_2P=S$) ppm; **1b:** 9.14 ($Ph_2P=N$) and 59.07 ($(EtO)_2P=S$) ppm; AA′ XX′ spin system). These chemical shifts can be compared with those described in the literature for related bis(iminophosphoranes) $CH_2[P-(=NR)Ph_2]_2$ [2] and thiophosphorylated species $R_3P=NP(=S)(OR)_2$ (see for example [19]). And, (ii) (^1H and $^{13}C\{^1H\}$ NMR) both proton and carbon resonances of

the methylenic PCH_2P group which appear as triplet signals at ca. 5 and 23 ppm, respectively, due to the coupling with the two equivalent $Ph_2P=N$ phosphorus atoms (ca.$^2J_{HP}$ = 15 Hz and $^1J_{CP}$ = 56 Hz).

2.2. Synthesis of the anionic bis(iminophosphorano)methanide species $KCH[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (**2a**), Et (**2b**))

The reaction of **1a,b** with an excess of potassium hydride, in THF at room temperature, consumes only one equivalent of KH to give the moisture-sensitive bis(iminophosphorano)methanide potassium salts $KCH-[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (**2a**), Et (**2b**)) in almost quantitative yields (see Scheme 2) [20]. No evidence for further deprotonation of these ligands was observed even when LDA or organolithium reagents were used.
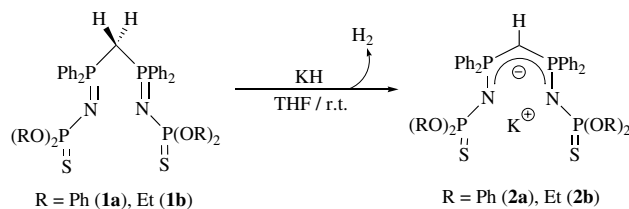
Compounds **2a,b** have been characterized by multinuclear NMR spectroscopic techniques (see Section 4 for details). As previously reported for other bis(iminophosphorano)methanides [3,18]: (i) The ^{31}P resonances of the $Ph_2P=N$ groups in **2a,b** are downfield shifted ($\Delta\delta$ ca. 8 ppm) relative to their parent bis(iminophosphorano)methanes **1a,b** (in contrast, slight high-field shifts ($\Delta\delta$ ca. −2 ppm) are observed for the thiophosphoryl units (RO)P=S). (ii) The methine PCHP proton appears in the ^1H NMR spectra as a broad signal at 1.42–2.02 ppm (instead of the expected triplet because of coupling with the equivalent $Ph_2P=N$ phosphorus nuclei). And, (iii) the methine carbon resonates in the $^{13}C\{^1H\}$ NMR spectra as a well-defined triplet (ca. $^1J_{CP}$ = 140 Hz) at ca. 20 ppm.

2.3. Reactions of the bis(iminophosphorano)methanide anions 2a,b with [{Ru(η^6-p-cymene)(μ-Cl)Cl}$_2$]

The treatment of [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] with **2a,b** in refluxing THF affords selectively the cationic derivatives [Ru(η^6-*p*-cymene)(κ^3-*C,N,S*-CH[P{=NP-(=S)(OR)$_2$}Ph$_2$]$_2$)][Cl] (R = Ph (**3a**), Et (**3b**)) (see Scheme 3). These air-stable complexes have been isolated as the corresponding hexafluorophosphate salts, in 54 (**3a**) and 49% (**3b**) yield, via a classical Cl$^-$/PF$_6^-$ exchange
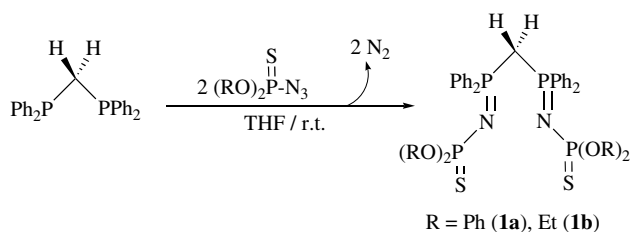
Scheme 1. Synthesis of the *N*-thiophosphorylated bis(iminophosphorano)methanes **1a,b**.

Scheme 2. Synthesis of the *N*-thiophosphorylated bis(iminophosphorano)methanides **2a,b**.

using $NaPF_6$ in a mixture $CH_2Cl_2/MeOH$ at room temperature.

Compounds **3a,b** have been characterized by elemental analyses, conductance measurements (1:1 electrolytes; $\Lambda_M = 107$ (**3a**) and 120 (**3b**) Ω^{-1} cm^2 mol^{-1}), and IR and NMR spectroscopy (details are given in Section 4), the latter supporting the diastereoselective formation of an unsymmetric metallabicycle (two stereogenic centers are formed, i.e. the ruthenium atom and the PCHP carbon). The most relevant spectroscopic data concern the methine PCHP resonances: (i) (^1H NMR) A doublet of doublets (**3a**; $^2J_{HP} = 11.8$ and 7.9 Hz) or multiplet (**3b**) at ca. 4.3 ppm. And, (ii) ($^{13}C\{^1H\}$ NMR) a well-resolved dddd signal at ca. −8 ppm ($^1J_{CP} = 55.7–62.4$ Hz; $^3J_{CP} = 10.6–17.8$ Hz).

Moreover, the structure of complex **3 b** was unambiguously confirmed by a single-crystal X-ray diffraction study (a $R_{Ru}S_C/S_{Ru}R_C$ racemic mixture is present). An ORTEP-type drawing of the molecular structure of the $R_{Ru}S_C$ enantiomer is shown in Fig. 1, and selected bond distances and angles are listed in the caption. The coordination sphere around ruthenium consists of the η^6-*p*-cymene ring, the methinic PCHP carbon, the nitrogen atom of one of the –P=N–P=S arms, and the sulphur atom of the second one, disposed with a classical three-legged piano-stool geometry. In accord, the values of the interligand angles N(2)–Ru–C(27), C(27)–Ru–S(1), and N(2)–Ru–S(1), and those between the centroid of the *p*-cymene ring C* and the legs, are typical of a pseudo-octahedron. In spite of the unsymmetrical
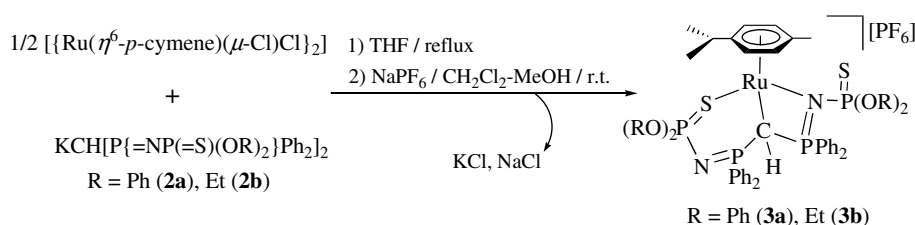
Scheme 3. Coordination of the bis(iminophosphorano)methanides **2a,b** to a (η^6-arene)-Ru(II) fragment.
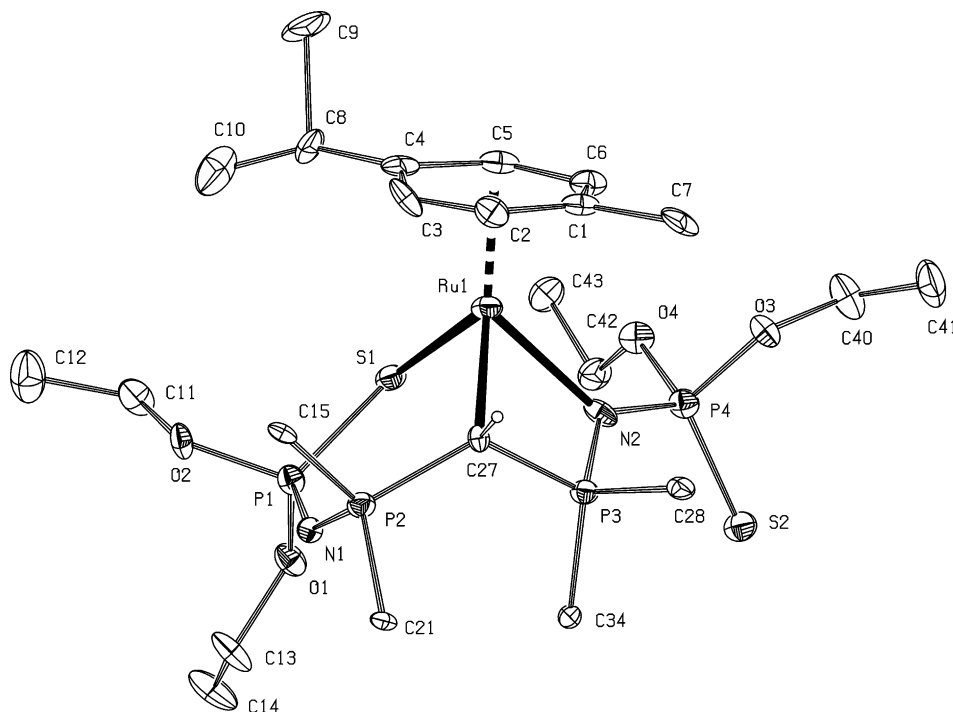

Fig. 1. ORTEP-type view of the structure of **3b** showing the crystallographic labeling scheme. Hexafluorophosphate anion, phenyl groups of the ligand and hydrogen atoms (except that on the C(27) carbon) have been omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Selected bond distances (Å) and angles (°): Ru–N(2) = 2.163(11); Ru–C(27) = 2.160(13), Ru–S(1) = 2.445(4); Ru–C* = 1.6852(5); C(27)–P(2) = 1.825(12); P(2)–N(1) = 1.547(9); N(1)–P(1) = 1.568(10); P(1)–S(1) = 1.998(5); P(1)–O(1) = 1.597(9); P(1)–O(2) = 1.586(9); C(27)–P(3) = 1.756(12); P(3)–N(2) = 1.607(9); N(2)–P(4) = 1.632(11); P(4)–S(2) = 1.929(5); P(4)–O(3) = 1.599(9); P(4)–O(4) = 1.571(9); C*–Ru–N(2) = 130.82(2); C*–Ru–C(27) = 129.35(3); C*–Ru–S(1) = 125.71(2); N(2)–Ru–C(27) = 71.5(4); N(2)–Ru–S(1) = 85.5(3); C(27)–Ru–S(1) = 96.7(3); Ru–C(27)–P(3) = 93.2(6); C(27)–P(3)–N(2) = 97.2(6); P(3)–N(2)–Ru = 97.6(5); P(3)–N(2)–P(4) = 132.4(7); N(2)–P(4)–S(2) = 117.1(4); Ru–N(2)–P(4) = 129.7(5); Ru–C(27)–P(2) = 120.5(6); C(27)–P(2)–N(1) = 115.8(6); P(2)–N(1)–P(1) = 136.4(6); N(1)–P(1)–S(1) = 118.4(4); P(1)–S(1)–Ru = 113.07(18). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5) and C(6)).

κ^3-*C*,*N*,*S*-coordination of the bis(iminophosphorane)methanide ligand, only slight differences in the bond distances within the two $-$Ph$_2$P$=$N$-$P($=$S)(OEt)$_2$ frameworks are observed (ca. ±0.07 Å). This fact, along with the similarity between the formal single and double PN bonds (from 1.547(9) to 1.632(11) Å), is indicative of an extensive π-electronic delocalization within both Ph$_2$P$=$N-P($=$S)(OEt)$_2$ arms of the ligand. A similar trend was previously observed in the X-ray structure of the related *N*-phosphorylated complex [Ru(η^6-*p*-cymene)(κ^3-*C*,*N*,*O*-CH[P{$=$NP($=$O)(OPh)$_2$}Ph$_2$]$_2$)][SbF$_6$] [18]. The Ru–C(27) bond length (2.160(13) Å) shows the expected value for a ruthenium–carbon single bond [21].

The formation of complexes **3a,b**, containing two fused six- and four-membered ruthenacarbocycles, contrast with our previous results using the closely related *N*-phosphorylated sodium salts NaCH[P{$=$NP-($=$O)(OR)$_2$}Ph$_2$]$_2$ [18] which lead instead to neutral complexes [RuCl(η^6-*p*-cymene)(κ^2-*C*,*N*-CH[P{$=$NP-($=$O)OR)$_2$} Ph$_2$]$_2$)] (**K** in Chart 3). Nevertheless, the corresponding cationic derivatives [Ru(η^6-*p*-cymene)-(κ^3-*C*,*N*,*O*-CH[P{$=$NP($=$O)(OPh)$_2$}Ph$_2$]$_2$)][SbF$_6$] (**L** in Chart 3) were prepared via coordination of the phosphoryl group after chloride abstraction. All attempts to isolate or detect the analogous κ^2-*C*,*N*-thiophosphoryl derivatives containing the four-membered ruthenacarbocycle of the type **K** have been unsuccessful. All these results indicate how the nature of the P$=$N substituents can modify the binding preferences of this type of ligands. This is also assessed by the formation of complex [Ru(η^6-*p*-cymene)(κ^3-*N*,*C*,*N*-CH{P($=$NPh)Ph$_2$}$_2$)]-[Cl] (**J** in Chart 3), recently reported by Caulton and co-workers [17], in which the analogous methanide anion [CH{P($=$NPh)Ph$_2$}$_2$]$^-$ shows a symmetric κ^3-*N*, *C*,*N*-coordination mode forming a fused two four-membered ruthenacarbocycle.

*2.4. Synthesis of ruthenium(II) carbene complexes [Ru(η^6-p-cymene)(κ^2- C,N-C[P{$=$NP($=$S)-(OR)$_2$}Ph$_2$]$_2$)] (R = Ph (**4a**), Et (**4b**))*

Following the synthetic route for the preparation of carbene complexes **M** (see Chart 3) [18], the treatment of the cationic complexes [Ru(η^6-*p*-cymene)(κ^3-*C*,*N*,*S*-CH[P{$=$NP($=$S)(OR)$_2$}Ph$_2$]$_2$)][Cl] (R = Ph (**3a**), Et (**3b**)) with an excess of NaH (ca. 10 equiv.), in THF at

room temperature, generates the novel carbene derivatives [Ru(η^6-*p*-cymene)(κ^2-*C*,*N*-C[P{$=$NP($=$S)(OR)$_2$}-Ph$_2$]$_2$)] (R = Ph (**4a**), Et (**4b**)) (see Scheme 4). They have been isolated as air-stable violet solids in good yields (80–83%).

Analytical and spectroscopic data (IR, and ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) of complexes **4a,b** support the proposed formulation. In particular, the ^{31}P{^{1}H} NMR spectra show the presence of four chemically inequivalent phosphorus nuclei. The downfield chemical shift observed for one of the two Ph$_2$P$=$N phosphorus resonances (**4a**: 66.02 ppm (dd, $^2J_{PP}$ = 96.7 and 23.0 Hz); **4b**: 60.49 ppm (dd, $^2J_{PP}$ = 84.7 and 14.1 Hz)) confirms its coordination to the metal center forming part of the four-membered ruthenacarbocycle (the uncoordinated Ph$_2$P$=$N units resonate at ca. 12 ppm). The ^{1}H and ^{13}C{^{1}H} NMR spectra clearly confirm the deprotonation of bis(iminophosphorano)methanide ligands by the disappearance of the characteristic methinic PCHP signals. As previously observed for the related compounds [Ru(η^6-*p*-cymene)(κ^2-*C*,*N*-C[P{$=$NP($=$O)(OR)$_2$}Ph$_2$]$_2$)] (**M**) [18], the carbenic Ru$=$C carbon resonances of complexes **4a,b** fall within the aromatic signals region being overlapped. Only in the case of **4b** this resonance could be identified by using ^{13}C{^{1}H} APT experiments (δ_C 128.59 ppm).

3. Concluding remarks

In this paper, we have shown that the sequential double deprotonation of the methylenic backbone of the readily available bis(iminophosphorano)methanes CH$_2${P($=$NR)Ph$_2$}$_2$ [2] is a general route for the preparation of metallacyclic ruthenium–carbene complexes. It is also shown the versatile coordination ability of the methanide species {CH[P{$=$NP($=$X)(OR)$_2$}Ph$_2$]$_2$}$^-$ (X = O,S), which display κ^2-*C*,*N*- or κ^3-*C*,*N*,*X*-coordination modes depending on the presence of both P$=$O or P$=$S groups in the partner iminophosphorane. Current studies aimed at exploring the reactivity and synthetic applications of the unusual metallacyclic carbene complexes [Ru]$=$C{P($=$NR)Ph$_2$}P($=$NR)Ph$_2$ are now in progress.
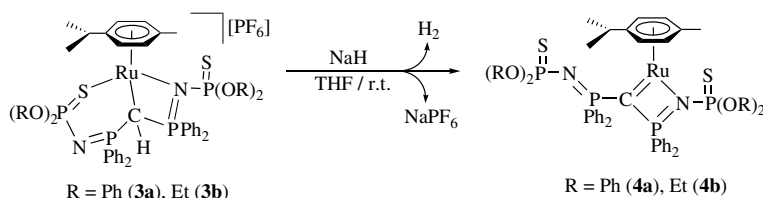
Scheme 4. Synthesis of the novel carbene-ruthenium(II) complexes **4a,b**.

4. Experimental

4.1. General information

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers with the exception of compounds $(RO)_2P(=S)N_3$ (R = Et, Ph) [22] and $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ [23] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol was used as the matrix. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standards. DEPT experiments have been carried out for all the compounds reported.

4.2. Synthesis of $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (1a), Et (1b))

A solution of bis(diphenylphosphino)methane (0.384 g; 1 mmol) in THF (40 ml) was treated with the corresponding azide $(RO)_2P(=S)N_3$ (2.2 mmol) for 10 h at room temperature. The solvent was then removed under reduced pressure to give a colorless oil which was washed with *n*-pentane (3 × 20 ml) and dried in vacuo to afford compounds **1a,b** as white solids. **(1a):** Yield: 90% (0.820 g); Anal. Calcd for C$_{49}$H$_{42}$O$_4$P$_4$N$_2$S$_2$ (910.90 g mol^{-1}): C, 64.61; H, 4.65; N, 3.07. Found: C, 64.59; H, 4.58; N, 3.19%; IR (KBr) v = 468 (w), 501 (s), 517 (w), 548 (w), 605 (w), 625 (m), 691 (s), 736 (s), 759 (m), 775 (m), 834 (s), 890 (vs), 910 (vs), 1027 (m), 1108 (m), 1195 (vs), 1269 (s), 1440 (m), 1459 (w), 1485 (s), 1591 (m), 2857 (w), 2885 (w), 3056 (w) cm^{-1}; ^{31}P$\{^1$H$\}$ NMR (CDCl$_3$) δ = 10.95 (m, Ph$_2$P=N), 51.23 (m, (PhO)$_2$P=S) ppm (AA$'$ XX$'$ spin system); ^{1}H NMR (CDCl$_3$) δ = 5.02 (t, 2H, $^2J_{HP}$ = 15.1 Hz, PCH$_2$P), 7.11–7.44 (m, 28H, Ph), 7.68–7.79 (m, 12H, Ph) ppm; ^{13}C$\{^1$H$\}$ NMR (CDCl$_3$) δ = 23.85 (t, $^1J_{CP}$ = 57.1 Hz, PCH$_2$P), 121.28–132.30 (m, Ph), 151.80 (d, $^2J_{CP}$ = 9.3 Hz, C$_{ipso}$ of OPh) ppm. **(1b):** Yield: 84% (0.604 g); Anal. Calcd. for C$_{33}$H$_{42}$O$_4$P$_4$N$_2$S$_2$ (718.72 g mol^{-1}): C, 55.15; H, 5.89; N, 3.90. Found: C, 55.20; H, 5.86; N, 3.89%; IR (KBr) v = 498 (s), 517 (w), 551 (w), 590 (w), 691 (m), 721 (m), 757 (m), 810 (m), 959 (s), 1037 (s), 1109 (m), 1174 (w), 1231 (vs), 1386 (w), 1437 (m), 1486 (w), 1591 (w), 2981 (m), 2979 (m), 3053

(w) cm^{-1}; ^{31}P$\{^1$H$\}$ NMR (CDCl$_3$) δ = 9.14 (m, Ph$_2$P=N), 59.07 (m, (EtO)$_2$P=S) ppm (AA$'$ XX$'$ spin system); ^{1}H NMR (CDCl$_3$) δ = 1.18 (t, 12H, $^3J_{HH}$ = 7.1 Hz, OCH$_2$CH$_3$), 3.90 (m, 8H, OCH$_2$CH$_3$), 5.31 (t, 2H, $^2J_{HP}$ = 15.4 Hz, PCH$_2$P), 7.26–7.49 (m, 12H, Ph), 7.78–7.85 (m, 8H, Ph) ppm; ^{13}C$\{^1$H$\}$ NMR (CDCl$_3$) δ = 15.95 (d, $^3J_{CP}$ = 8.7 Hz, OCH$_2$CH$_3$), 22.59 (t, $^1J_{CP}$ = 55.3 Hz, PCH$_2$P), 61.82 (d, $^2J_{CP}$ = 5.8 Hz, OCH$_2$CH$_3$), 128.18–131.99 (m, Ph) ppm.

4.3. Synthesis of $KCH[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Ph (2a), Et (2b))

A solution of the corresponding bis(iminophosphorano)methane **1a,b** (0.45 mmol) in THF (30 ml) was treated, at room temperature, with KH (0.180 g, 4.5 mmol) for 30 min. The resulting suspension was filtered through Kieselguhr and the filtrate evaporated to dryness giving **2a,b** as colorless oils in almost quantitative yield. **(2a):** ^{31}P$\{^1$H$\}$ NMR (C$_6$D$_6$) δ = 18.83 (m, Ph$_2$P=N), 48.31 (m, (PhO)$_2$P=S) ppm (AA$'$ XX$'$ spin system); ^{1}H NMR (C$_6$D$_6$) δ = 2.02 (br, 1H, PCHP), 6.87–7.35 (m, 28H, Ph), 8.04 (m, 12H, Ph) ppm; ^{13}C$\{^1$H$\}$ NMR (C$_6$D$_6$) δ = 17.78 (t, $^1J_{CP}$ = 138.3 Hz, PCHP), 122.06–138.19 (m, Ph), 152.88 (d, $^2J_{CP}$ = 9.3 Hz, C$_{ipso}$ of OPh) ppm. **(2b):** ^{31}P$\{^1$H$\}$ NMR (C$_6$D$_6$) δ = 17.65 (m, Ph$_2$P=N), 57.55 (m, (EtO)$_2$P=S) ppm (AA$'$ XX$'$ spin system); ^{1}H NMR (C$_6$D$_6$) δ = 0.94 (t, 12H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH$_3$), 1.42 (br, 1H, PCHP), 3.72 (m, 8H, OCH$_2$CH$_3$), 7.00–7.19 (m, 12H, Ph), 8.03–8.10 (m, 8H, Ph) ppm; ^{13}C$\{^1$H$\}$ NMR (C$_6$D$_6$) δ = 18.22 (d, $^3J_{CP}$ = 8.7 Hz, OCH$_2$CH$_3$), 20.31 (t, $^1J_{CP}$ = 140.9 Hz, PCHP), 63.91 (d, $^2J_{CP}$ = 7.0 Hz, OCH$_2$CH$_3$), 132.39–140.70 (m, Ph) ppm. Compounds **2a,b** were too sensitive to moisture to give satisfactory elemental analyses.

4.4. Synthesis of $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-} C,N,S\text{-}CH[P\{=NP(=S)(OR)_2\}Ph_2]_2)][PF_6]$ (R = Ph (3a), Et (3b))

To a solution of $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ (0.092 g, 0.15 mmol) in 30 ml of THF was added, at room temperature, the corresponding bis(iminophosphorano)methanide compound **2a,b** (0.45 mmol), and the reaction mixture refluxed for 1 h. The solvent was then removed under vacuum, the crude product extracted with dichloromethane (ca. 20 ml), and the extract filtered. The resulting solution was treated, at room temperature, with a solution of NaPF$_6$ (0.252 g, 1.5 mmol) in 10 ml of methanol for 3 h. The solvents were then removed under vacuum, the crude product extracted with dichloromethane (ca. 20 ml), and the extract filtered. Concentration of the resulting solution (ca. 5 ml) followed by the addition of a mixture diethyl ether/hexanes (ca. 50 ml; 1:1 v/v) precipitated an orange

solid, which was washed with a mixture diethyl ether/ hexanes (3×30 ml; 1:1 v/v) and dried in vacuo. **(3a):** Yield: 54% (0.209 g); Anal. Calcd for $RuC_{59}H_{55}F_6$-$P_5O_4N_2S_2 \cdot 1/5CH_2Cl_2$ (1307.13 g mol^{-1}): C, 54.40; H, 4.27; N, 2.14. Found: C, 54.48; H, 4.18; N, 2.17%; Conductivity (acetone, 20 °C) 107 Ω^{-1} cm^2 mol^{-1}; IR (KBr) v = 557 (m), 689 (m), 729 (w), 768 (w), 842 (s), 919 (s), 1024 (w), 1111 (m), 1130 (m), 1161 (m), 1191 (s), 1287 (w), 1438 (m), 1488 (s), 1570 (m), 2860 (w), 2960 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$) δ = 28.49 (ddd, $^2J_{PP}$ = 18.6 and 4.7 Hz, $^4J_{PP}$ = 3.1 Hz, Ph$_2$P=N), 43.08 (d, $^2J_{PP}$ = 18.6 Hz, (PhO)$_2$P=S—Ru), 60.65 (dd, $^2J_{PP}$ = 27.6 and 4.7 Hz, Ru—N=PPh$_2$), 66.89 (dd, $^2J_{PP}$ = 27.6 Hz, $^4J_{PP}$ = 3.1 Hz, Ru—NP(=S)(OPh)$_2$) ppm; ^1H NMR (CD$_2$Cl$_2$) δ = 0.83 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 1.04 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH-(CH$_3$)$_2$), 1.90 (s, 3H, CH$_3$), 2.16 (m, 1H, CH(CH$_3$)$_2$), 4.21 (dd, 1H, $^2J_{HP}$ = 11.8 and 7.9 Hz, PCHP), 4.31 and 4.59 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 5.40 (br, 2H, CH of *p*-cymene), 6.70–8.32 (m, 40H, Ph) ppm; $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$) δ = −8.16 (dddd, $^1J_{CP}$ = 55.7 and 55.7 Hz, $^3J_{CP}$ = 17.8 and 10.9 Hz, PCHP), 18.24 (s, CH$_3$), 19.93 and 23.26 (s, CH(CH$_3$)$_2$), 30.45 (s, CH(CH$_3$)$_2$), 77.43, 82.17, 83.24 and 84.45 (s, CH of *p*-cymene), 98.14 and 113.84 (s, C of *p*-cymene), 120.02–135.22 (m, Ph), 151.05 (d, $^2J_{CP}$ = 12.1 Hz, C$_{ipso}$ of OPh), 151.12 (d, $^2J_{CP}$ = 7.6 Hz, C$_{ipso}$ of OPh), 151.34 (d, $^2J_{CP}$ = 6.8 Hz, C$_{ipso}$ of OPh), 152.10 (d, $^2J_{CP}$ = 8.3 Hz, C$_{ipso}$ of OPh) ppm. **(3b):** Yield: 49% (0.161 g); Anal. Calcd for $RuC_{43}H_{55}F_6P_5O_4N_2S_2$ (1097.98 g mol^{-1}): C, 47.04; H, 5.05; N, 2.55. Found: C, 47.33; H, 5.21; N, 2.53%; Conductivity (acetone, 20 °C) 120 Ω^{-1} cm^2 mol^{-1}; IR (KBr) v = 487 (w), 531 (w), 557 (s), 596 (w), 655 (w), 691 (m), 752 (s), 840 (s), 912 (m), 958 (s), 1026 (s), 1110 (s), 1159 (m), 1264 (m), 1285 (m), 1388 (w), 1438 (s), 1473 (w), 1588 (w), 2901 (w), 2928 (w), 2978 (m), 3059 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR ((CD$_3$)$_2$CO) δ = 26.27 (ddd, $^2J_{PP}$ = 17.8 and 3.4 Hz, $^4J_{PP}$ = 5.1 Hz, Ph$_2$P=N), 51.29 (d, $^2J_{PP}$ = 17.8 Hz, (EtO)$_2$P=S—Ru), 64.68 (dd, $^2J_{PP}$ = 23.8 and 3.4 Hz, Ru—N=PPh$_2$), 69.80 (dd, $^2J_{PP}$ = 23.8 Hz, $^4J_{PP}$ = 5.1 Hz, Ru—NP(=S)(OEt)$_2$) ppm; ^1H NMR ((CD$_3$)$_2$CO) δ = 1.15 and 1.50 (t, 3H each, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH$_3$), 1.21–1.28 (m, 12H, CH(CH$_3$)$_2$ and OCH$_2$CH$_3$), 2.15 (s, 3H, CH$_3$), 3.06 (m, 1H, CH(CH$_3$)$_2$), 3.65, 3.87 and 4.03 (m, 2H each, OCH$_2$CH$_3$), 4.30 (m, 3H, OCH$_2$CH$_3$ and PCHP), 4.64 and 5.39 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 5.06 (br, 2H, CH of *p*-cymene), 7.17–8.44 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR ((CD$_3$)$_2$CO) δ = −8.09 (dddd, $^1J_{CP}$ = 62.4 and 62.4 Hz, $^3J_{CP}$ = 17.2 and 10.6 Hz, PCHP), 15.96 (d, $^3J_{CP}$ = 5.2 Hz, OCH$_2$CH$_3$), 16.01 (d, $^3J_{CP}$ = 6.0 Hz, OCH$_2$CH$_3$), 16.07 and 16.12 (d, $^3J_{CP}$ = 4.8 Hz, OCH$_2$CH$_3$), 18.21 (s, CH$_3$), 21.25 and 22.33 (s, CH(CH$_3$)$_2$), 30.62 (s, CH(CH$_3$)$_2$), 63.51 (d, $^2J_{CP}$ = 8.5 Hz, OCH$_2$CH$_3$), 63.60 (d, $^2J_{CP}$ = 10.0 Hz, OCH$_2$CH$_3$), 63.65 (d, $^2J_{CP}$ = 5.2

Hz, OCH$_2$CH$_3$), 64.24 (d, $^2J_{CP}$ = 7.5 Hz, OCH$_2$CH$_3$), 79.09, 82.18, 83.32 and 84.19 (s, CH of *p*-cymene), 99.60 and 110.67 (s, C of *p*-cymene), 125.25–135.56 (m, Ph) ppm.

4.5. Synthesis of [Ru(η⁶-p-cymene)(κ²-C,N-C[P{=NP(=S)(OR)₂}Ph₂]₂)] (R = Ph (4a), Et (4b))

A solution of the corresponding cationic complex [Ru(η^6-*p*-cymene)(κ^3-*C*,*N*,*S*-CH[P{=NP(=S)(OR)$_2$}-Ph$_2$]$_2$)][PF$_6$] **3a,b** (0.1 mmol) in 30 ml of THF was treated, at room temperature, with NaH (0.024 g, 1 mmol) for 3 h. The solvent was then removed under vacuum, the crude product extracted with diethyl ether (ca. 50 ml), and the extract filtered. Concentration of the resulting solution (ca. 2 ml) followed by the addition of hexanes (ca. 50 ml) precipitated a violet solid, which was filtered, washed with hexanes (3×20 ml) and dried in vacuo. **(4a):** Yield: 80% (0.092 g); Anal. Calcd for Ru-$C_{59}H_{54}O_4P_4N_2S_2$ (1144.17 g mol^{-1}): C, 61.93; H, 4.76; N, 2.45. Found: C, 62.00; H, 4.48; N, 2.20%; IR (KBr) v = 498 (w), 531 (w), 617 (w), 688 (s), 768 (m), 804 (s), 909 (m), 1024 (s), 1101 (s), 1159 (m), 1195 (s), 1261 (s), 1434 (m), 1488 (s), 1590 (m), 2924 (w), 2962 (w), 3047 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ = 12.72 (ddd, $^2J_{PP}$ = 96.7 and 27.0 Hz, $^4J_{PP}$ = 9.8 Hz, Ph$_2$P=N), 47.71 (d, $^2J_{PP}$ = 27.0 Hz, (PhO)$_2$P=S), 61.00 (dd, $^2J_{PP}$ = 23.0 Hz, $^4J_{PP}$ = 9.8 Hz, Ru—NP(=S)(OPh)$_2$), 66.02 (dd, $^2J_{PP}$ = 96.7 and 23.0 Hz, Ru—N=PPh$_2$) ppm; ^1H NMR (C$_6$D$_6$) δ = 1.11 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 1.96 (s, 3H, CH$_3$), 2.24 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 5.48 and 5.59 (d, 2H each, $^3J_{HH}$ = 5.9 Hz, CH of *p*-cymene), 6.85–7.90 (m, 40H, Ph) ppm; $^{13}C\{^1H\}$ NMR (C$_6$D$_6$) δ = 19.33 (s, CH$_3$), 23.46 (s, CH(CH$_3$)$_2$), 31.34 (s, CH(CH$_3$)$_2$), 79.11 and 81.97 (s, CH of *p*-cymene), 87.17 and 98.69 (s, C of *p*-cymene), 121.61–136.44 (m, Ph and PCP), 153.32 (d, $^2J_{CP}$ = 9.3 Hz, C$_{ipso}$ of OPh) ppm. **(4b):** Yield: 83% (0.079 g); Anal. Calcd for $RuC_{43}H_{54}O_4P_4N_2S_2$ (952.00 g mol^{-1}): C, 54.25; H, 5.72; N, 2.94. Found: C, 54.01; H, 5.61; N, 2.89%; IR (KBr) v = 479 (w), 531 (w), 556 (w), 690 (m), 748 (m), 801 (s), 911 (w), 948 (m), 1024 (s), 1102 (s), 1152 (m), 1261 (s), 1387 (w), 1436 (m), 1460 (w), 2855 (w), 2931 (w), 2951 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR (C$_6$D$_6$) δ = 11.59 (ddd, $^2J_{PP}$ = 84.7 and 29.3 Hz, $^4J_{PP}$ = 9.8 Hz, Ph$_2$P=N), 55.44 (d, $^2J_{PP}$ = 29.3 Hz, (EtO)$_2$P=S), 60.49 (dd, $^2J_{PP}$ = 84.7 and 14.7 Hz, Ru—N=PPh$_2$), 70.23 (dd, $^2J_{PP}$ = 14.7 Hz, $^4J_{PP}$ = 9.8 Hz, Ru—NP(=S)(OEt)$_2$) ppm; ^1H NMR (C$_6$D$_6$) δ = 1.01 and 1.21 (t, 6H each, $^3J_{HH}$ = 6.9 Hz, OCH$_2$CH$_3$), 1.16 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 2.10 (s, 3H, CH$_3$), 2.61 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 4.04 (m, 8H, OCH$_2$CH$_3$), 5.41 and 5.47 (d, 2H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 6.94–7.94 (m, 20H, Ph) ppm; $^{13}C\{^1H\}$ NMR (C$_6$D$_6$) δ = 15.98 and 16.29 (d,

$^3J_{CP}$ = 8.8 Hz, OCH_2CH_3), 19.35 (s, CH_3), 23.41 (s, $CH(CH_3)_2$), 31.07 (s, $CH(CH_3)_2$), 61.43 (d, $^2J_{CP}$ = 5.6 Hz, OCH_2CH_3), 61.93 (d, $^2J_{CP}$ = 4.8 Hz, OCH_2CH_3), 79.10 and 81.80 (s, CH of *p*-cymene), 89.01 and 99.89 (s, C of *p*-cymene), 127.21–138.14 (m, Ph), 128.59 (m, PCP) ppm.

4.6. X-ray crystal structure determination of $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-} C,N,S\text{-}CH[P\{=NP(=S)\text{-}(OEt)_2\}Ph_2]_2)]$ $[PF_6]$ (**3b**)

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of the complex in dichloromethane. Data collection, crystal and refinement parameters are collected in Table 1. Diffraction data were recorded at 200 K on a Nonius Kappa CCD single-crystal diffractometer using Cu Kα radiation. Crystal-detector distance was fixed at 29 mm and a total of 1365 frames were collected using the oscillation method, with 2° oscillation and 45 s exposure time per frame. Data collection strategy was calculated with the program Collect [24]. Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack [25].

The software package WINGX was used for space group determination, structure solution and refinement [26]. The structure was solved by Patterson methods using the program DIRDIF [27]. Absorption correction was applied by means of SORTAV [28]. Full-matrix least-squares refinement on F^2 was carried out with SHELXL-97 [29]. All non-H atoms were anisotropically refined. The H atoms were geometrically placed and their coordinates were refined riding on their parent atoms. The final cycle of full-matrix least-squares refinement based on 6077 reflections and 569 parameters converged to a final value of R_1 ($F^2 > 2\sigma (F^2)$) = 0.0585. The function minimized was $[\sum w(F_o^2 - F_c^2)/ \sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$ with $\sigma^2(F_o^2)$ from counting statistics and $P = \text{Max}(F_o^2 + 2F_c^2)/3$. The maximum shift-to-esd ratio in the last full-matrix least-squares cycle was 0.000. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [30]. Geometrical calculations were made with PARST [31]. The crystallographic plots were made with PLATON [32].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 250207 for compound **3b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033;

Table 1
Crystal data and structure refinement for **3b**

Empirical formula	$RuC_{43}H_{55}F_6P_5O_4N_2S_2$
Formula weight	1097.93
Temperature (K)	200(2)
Wavelength (Å)	1.5418
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	
a (Å)	15.339(5)
b (Å)	18.192(7)
c (Å)	18.931(7)
α (°)	90
β (°)	106.18(2)
γ (°)	90
Volume (Å³)	5073(3)
Z	4
Density (calculated) (g cm⁻³)	1.437
Absorption coefficient (mm⁻¹)	5.305
F (0 0 0)	2256
Crystal size (mm)	$0.1 \times 0.075 \times 0.025$
Theta range for data collection (°)	3.86–67.98
Index ranges	$-16 \leqslant h \leqslant 17$
	$-20 \leqslant k \leqslant 20$
	$-21 \leqslant l \leqslant 21$
Reflections collected/unique	27372/6077 [*R*(int) = 0.110]
Completeness to theta = 67.98°	73.5%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6077/0/569
Goodness-of-fit on F^2	1.003
R_1^a [$I > \sigma I$]	0.0585
wR_2^a [$I > \sigma I$]	0.1213
R_1 (all data)	0.1181
wR_2 (all data)	0.1457
Largest difference peak and hole (e Å⁻³)	0.383 and −0.517

^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] H. Staudinger, J. Meyer, Helv. Chim. Acta 2 (1919) 635.
[2] (a) A.M. Aguiar, H.J. Aguiar, T.G. Archibald, Tetrahedron Lett. 27 (1966) 3187;
(b) V.A. Gilyarov, V.Y. Kovtun, M.I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim. 5 (1967) 1159;
(c) V.Y. Kovtun, V.A. Gilyarov, M.I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim. 11 (1972) 2612;
(d) R. Appel, I. Ruppert, Z. Anorg. Allg. Chem. 406 (1974) 131;

(e) P. Imhoff, R. van Asselt, C.J. Elsevier, K. Vrieze, K. Goubitz, K.F. van Malssen, C.H. Stam, Phosphorus, Sulfur and Silicon 47 (1990) 401.

[3] (a) Bis(iminophosphorano)methanes are readily mono-deprotonated by alkali metal hydrides and amides, and organolithium reagents. See Ref. [2e] and: R.P. Kamalesh Babu, K. Aparna, R. McDonald, R.G. Cavell, Inorg. Chem. 39 (2000) 4981;
(b) R.P. Kamalesh Babu, K. Aparna, R. McDonald, R.G. Cavell, Organometallics 20 (2001) 1451;
(c) M.T. Gamer, P.W. Roesky, Z. Anorg. Allg. Chem. 627 (2001) 877.

[4] β-Diketiminato anions have received special attention as stable and robust ancillary ligands for a large variety of metal fragments. For a review, see: L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.

[5] (a) A. Kasani, R. McDonald, R.G. Cavell, Organometallics 18 (1999) 3775;
(b) K. Aparna, R. McDonald, M. Ferguson, R.G. Cavell, Organometallics 18 (1999) 4241;
(c) C.M. Ong, P. McKarns, D.W. Stephan, Organometallics 18 (1999) 4197;
(d) R.G. Cavell, K. Aparna, R.P. Kamalesh Babu, Q. Wang, J. Mol. Catal. A 189 (2002) 137;
(e) M.S. Hill, P.B. Hitchcock, J. Chem. Soc., Dalton Trans. (2002) 4694;
(f) W.-P. Leung, C.-W. So, Z.-X. Wang, J.-Z. Wang, T.C.W. Mak, Organometallics 22 (2003) 4305;
(g) M.S. Hill, P.B. Hitchcock, S.M.A. Karagouni, J. Organomet. Chem. 689 (2004) 722;
(h) M.S. Hill, P.B. Hitchcock, J. Organomet. Chem. 689 (2004) 3163.

[6] (a) P. Imhoff, C.J. Elsevier, J. Organomet. Chem. 361 (1989) C61;
(b) P. Imhoff, R. van Asselt, J.M. Ernsting, K. Vrieze, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, A.P.N. Kentgens, Organometallics 12 (1993) 1523;
(c) M.W. Avis, K. Vrieze, H. Kooijman, N. Veldman, A.L. Spek, C.J. Elsevier, Inorg. Chem. 34 (1995) 4092;
(d) M.W. Avis, K. Vrieze, J.M. Ernsting, C.J. Elsevier, N. Veldman, A.L. Spek, K.V. Katti, C.L. Barnes, Organometallics 15 (1996) 2376.

[7] (a) P. Imhoff, J.H. Gülpen, K. Vrieze, W.J.J. Smeets, A.L. Spek, C.J. Elsevier, Inorg. Chim. Acta 235 (1995) 77;
(b) S. Al-Benna, M.J. Sarsfield, M. Thornton-Pett, D.L. Ormsby, P.J. Maddox, P. Brès, M. Bochmann, J. Chem. Soc., Dalton Trans. (2000) 4247;
(c) M.T. Gamer, S. Dehnen, P.W. Roesky, Organometallics 20 (2001) 4230;
(d) G. Aharonian, K. Feghali, S. Gambarotta, G.P.A. Yap, Organometallics 20 (2001) 2616;
(e) G. Aharonian, S. Gambarotta, G.P.A. Yap, Organometallics 20 (2001) 5008;
(f) M.T. Gamer, P.W. Roesky, J. Organomet. Chem. 647 (2002) 123;
(g) P. Wei, D.W. Stephan, Organometallics 21 (2002) 1308;
(h) M.J. Sarsfield, M. Helliwell, D. Collison, Chem. Commun. (2002) 2264;
(i) P. Wei, D.W. Stephan, Organometallics 22 (2003) 601;
(j) D.J. Evans, M.S. Hill, P.B. Hitchcock, Dalton Trans. (2003) 570;
(k) M.S. Hill, P.B. Hitchcock, Chem. Commun. (2003) 1758;
(l) M.S. Hill, P.B. Hitchcock, Dalton Trans. (2003) 4570.

[8] (a) A. Kasani, R.P. Kamalesh Babu, R. McDonald, R.G. Cavell, Angew. Chem. Int. Ed. 38 (1999) 1483;
(b) M. Klobukowski, S.A. Decker, C.C. Lovallo, R.G. Cavell, J. Molec. Struct. (Theochem) 536 (2001) 189.

[9] C.M. Ong, D.W. Stephan, J. Am. Chem. Soc. 121 (1999) 2939.

[10] (a) R.G. Cavell, R.P. Kamalesh Babu, A. Kasani, R. McDonald, J. Am. Chem. Soc. 121 (1999) 5805;
(b) R.P. Kamalesh Babu, R. McDonald, S.A. Decker, M. Klobukowski, R.G. Cavell, Organometallics 18 (1999) 4226;
(c) R.P. Kamalesh Babu, R. McDonald, R.G. Cavell, Chem. Commun. (2000) 481;
(d) R.P. Kamalesh Babu, R. McDonald, R.G. Cavell, Organometallics 19 (2000) 3462.

[11] K. Aparna, M. Ferguson, R.G. Cavell, J. Am. Chem. Soc. 122 (2000) 726.

[12] W.-P. Leung, C.-W. So, J.-Z. Wang, T.C.W. Mak, Chem. Commun. (2003) 248.

[13] A. Kasani, R. McDonald, R.G. Cavell, Chem. Commun. (1999) 1993.

[14] (a) K. Aparna, R. McDonald, R.G. Cavell, J. Am. Chem. Soc. 122 (2000) 9314;
(b) R.G. Cavell, K. Aparna, R.P. Kamalesh Babu, Q. Wang, J. Mol. Catal. A 189 (2002) 137.

[15] W.-P. Leung, Z.-X. Wang, H.-W. Li, T.C. Mak, Angew. Chem. Int. Ed. 40 (2001) 2501.

[16] (a) N.D. Jones, G. Lin, R.A. Gossage, R. McDonald, R.G. Cavell, Organometallics 22 (2003) 2832;
(b) G. Lin, N.D. Jones, R.A. Gossage, R. McDonald, R.G. Cavell, Angew. Chem. Int. Ed. 42 (2003) 4054.

[17] C. Bibal, M. Pink, Y.D. Smurnyy, J. Tomaszewski, K.G. Caulton, J. Am. Chem. Soc. 126 (2004) 2312.

[18] V. Cadierno, J. Díez, J. García-Álvarez, J. Gimeno, M.J. Calhorda, L.F. Veiros, Organometallics 23 (2004) 2421.

[19] (a) C. Larré, B. Donnadieu, A.M. Caminade, J.P. Majoral, Eur. J. Inorg. Chem. (1999) 601;
(b) V. Maraval, R. Laurent, B. Donnadieu, A.M. Caminade, J.P. Majoral, Synthesis (2003) 389;
(c) V. Cadierno, P. Crochet, J. Díez, J. García-Álvarez, S.E. García-Garrido, S. García-Granda, J. Gimeno, M.A. Rodríguez, Dalton Trans. (2003) 3240;
(d) We note that J.P. Majoral and co-workers have widely used the Staudinger reaction between tricoordinated phosphorus atoms and functionalised thiophosphoryl azides to design a large variety of dendrimers containing P=N—P=S linkages. For recent overviews, see:J.P. Majoral, A.M. Caminade, V. Maraval, Chem. Commun. (2002) 2929;
(e) J.P. Majoral, A.M. Caminade, R. Laurent, P. Sutra, Heteroatom. Chem. 13 (2002) 474;
(f) A.M. Caminade, V. Maraval, R. Laurent, J.P. Majoral, Curr. Org. Chem. 6 (2002) 739;
(g) A.M. Caminade, V. Maraval, R. Laurent, C.O. Turrin, P. Sutra, J. Leclaire, L. Griffe, P. Marchand, C. Baudoin-Dehoux, C. Rebout, J.P. Majoral, C. R. Chimie 6 (2003) 791;
(h) A.M. Caminade, J.P. Majoral, Acc. Chem. Res. 37 (2004) 341.

[20] We note that the treatment of **1a,b** with an excess of NaH (10 equiv.), in THF at room temperature, leads to incomplete reactions even after 24 h.

[21] (a) E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984;
(b) This Ru–C bond length compares well to that found in the structure of $[Ru(\eta^6$-p-cymene)(κ^3-C,N,O-CH[P{=NP(=O)-(OPh)_2}Ph_2])]$ [SbF$_6$] (2.228(5) Å). See Ref. [18].

[22] A.A. Khodak, V.A. Gilyarov, M.I. Kabachnik, Zh. Obshch. Khim. 44 (1974) 27.

[23] M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.

[24] Collect, Nonius BV, Delft, 1997–2000.

[25] Z. Otwinowski, W. Minor, Meth. Enzymol. 276 (1997) 307.

[26] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[27] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF Program System, Technical Report of the Crystallo-

graphic Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1999.

[28] R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33.

[29] G.M. Sheldrick, SHELXL97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

[30] International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, 1974. (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

[31] M. Nardelli, Comput. Chem. 7 (1983) 95.

[32] A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, University of Utrecht, The Netherlands, 2000.