Reaction of isocyanides with iminophosphorane-based carbene ligands: Synthesis of unprecedented ketenimine–ruthenium complexes

Victorio Cadierno *, Joaquín García-Álvarez, José Gimeno *, Javier Rubio-García

*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 Ru=C bond of the bis(iminophosphorano)methandiide-based ruthenium(II) carbene complexes [Ru(η^6-p-cymene)(κ^2-C,N-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) undergoes a C–C coupling process with isocyanides to afford ketenimine derivatives [Ru(η^6-p-cymene)(κ^3-C,C,N-C(C=NR')[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et, R' = Bz (**3a**), 2,6-C$_6$H$_3$Me$_2$ (**3b**), Cy (**3c**); R = Ph, R' = Bz (**4a**), 2,6-C$_6$H$_3$Me$_2$ (**4b**), Cy (**4c**)). Compounds **3–4a–c** represent the first examples of ketenimine–ruthenium complexes reported to date. Protonation of **3–4a** with HBF$_4$ · Et$_2$O takes place selectively at the ketenimine nitrogen atom yielding the cationic derivatives [Ru(η^6-p-cymene)(κ^3-C,C,N-C(CNHBz)[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)][BF$_4$] (R = Et (**5a**), Ph (**6a**)).
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1. Introduction

Ketenimines R^{1}N=C=CR^{2}R^3 have been extensively used in organic synthesis as versatile building blocks for the preparation of a large variety of cyclic compounds via inter- or intramolecular cycloaddition reactions [1]. In addition, novel synthetic approaches to carbocyclic and *N*-heterocyclic four-, five- and six-membered rings by using ketenimine complexes of transition-metals have been developed [2]. Although ketenimine complexes can be prepared by direct coordination of free ketenimines to unsaturated metallic fragments [3], the most employed route is based on C–C coupling processes between carbene complexes [M]=CR^{2}R^3 and isocyanides (R^{1}NC) [4,5]. Mainly depending on the electronic properties of the metal fragment, ketenimines can bind to transition-metals either as chelate ligands, via the C=N or C=C π-bonds (**A** and **B** in Chart 1), or as terminal ligands through the nitrogen lone pair (**C** in Chart 1) [2]. We also note that isomerization processes involving these coordination modes have also been observed [4j,5c,6].

Within the group 8 metals, both ketenimine–iron [3a,4d,4i,7] and osmium [8] complexes have been described. However, no ruthenium representatives are actually known [9], in spite of the chemistry of ruthenium–carbene complexes have been extensively developed due to their utility in both stoichiometric and catalytic C–C and C–heteroatom bond forming processes [10]. In this context, we have recently reported the preparation of the first iminophosphorane-based ruthenium–carbene complexes [Ru(η^6-p-cymene)(κ^2-C,N-C[P{=NP(=X)-(OR)$_2$}Ph$_2$]$_2$)] (X = O, S; R = Et, Ph) (**D**; see Chart 2) [11] and their usefulness to form novel C–C bonds. Thus, unusual *ortho*-metallated derivatives **E**, containing an all-carbon bonded ligand, have been easily prepared under mild conditions (room temperature) by

* Corresponding authors. Tel.: +34 985 103 461; fax: +34 985 103 446.
E-mail addresses: vcm@uniovi.es (V. Cadierno), jgh@uniovi.es (J. Gimeno).
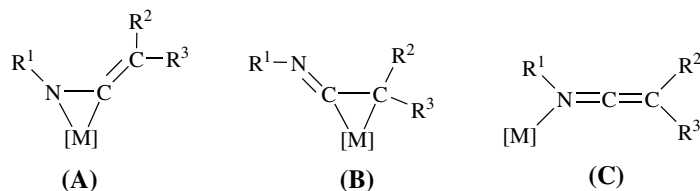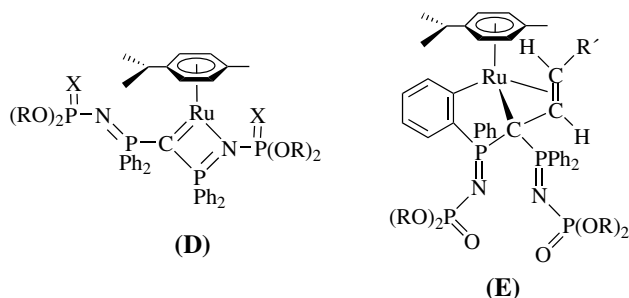
Chart 1. Coordination modes of ketenimine ligands.

Chart 2. Structure of ruthenium(II) complexes **D** and **E**.

reacting complexes **D** with terminal alkynes HC≡CR′, via coupling of the Ru=C and C≡C bonds and concomitant aryl C–H activation [12].

Continuing with these studies aimed at exploiting the utility of iminophosphorane-based carbenes **D** for the preparation of elaborated ruthenium compounds herein we describe the synthesis of the first examples of ketenimine–ruthenium complexes [Ru(η^6-p-cymene)(κ^3-C,C,N-C(C=NR′)[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (**F**; see Chart 3), via C–C coupling reactions of the carbene derivatives [Ru(η^6-p-cymene)(κ^2-C,N-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) with isocyanides R′NC. The selective protonation of these complexes to afford the cationic species **G** is also reported.

2. Results and discussion

The carbene–ruthenium(II) complexes [Ru(η^6-p-cymene)(κ^2-C,N-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) react with an stoichiometric amount of benzyl

isocyanide, 2,6-dimethylphenyl isocyanide or cyclohexyl isocyanide, in THF at room temperature, to generate the ketenimine–ruthenium derivatives [Ru(η^6-p-cymene)(κ^3-C,C,N-C(C=NR′)[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et, R′ = Bz (**3a**), 2,6-C$_6$H$_3$Me$_2$ (**3b**), Cy (**3c**); R = Ph, R′ = Bz (**4a**), 2,6-C$_6$H$_3$Me$_2$ (**4b**), Cy (**4c**)) (see Scheme 1). The reaction is instantaneous as it is evidenced by the color change of the solution from deep violet to bright yellow. After appropriate workup (see Section 3) complexes **3**–**4a**–**c** have been isolated as air-stable yellow solids in 67–81% yield.

Complexes **3**–**4a**–**c** have been characterized by elemental analyses, and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy [13], all data being fully consistent with the structural proposal (details are given in Section 3). The NMR spectra also indicate that the formation of these complexes proceeds in a diastereoselective manner (note that two stereogenic centers are generated, i.e., the ruthenium atom and the PCP carbon). ^{31}P{^{1}H} NMR spectra are consistent with the expected presence of four chemically inequivalent phosphorus nuclei i.e., (i) the downfield resonance at δ_P 45.94–51.02 ppm of the four-membered ruthenacycle Ph$_2$P=N moiety along with that of the uncoordinated Ph$_2$P=N unit at δ_P 13.55–20.22 ppm, and (ii) the two high-field signals of the phosphoryl (RO)$_2$P=O groups at δ_P from −10.89 to 10.20 ppm. The ^{13}C{^{1}H} NMR spectra display characteristic signals for the ketenimine carbon atoms P$_2$C= and =C=N which appear in the ranges from −9.35 to −6.72 (dddd, $^1J_{CP}$ = 101.3–118.6 and 81.9–95.7 Hz, $^3J_{CP}$ = 12.9–23.4 and 8.1–11.3 Hz) and 193.78–201.91 (s) ppm, respectively. These data can be compared with those reported in the literature for other C,C-bound ketenimine metal derivatives

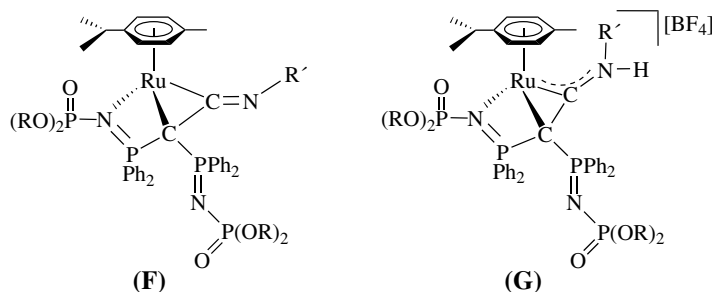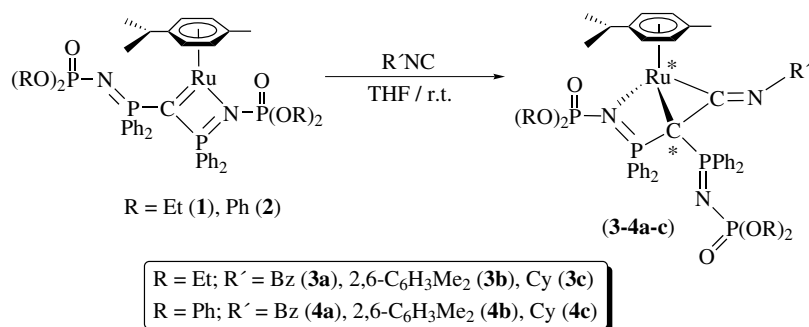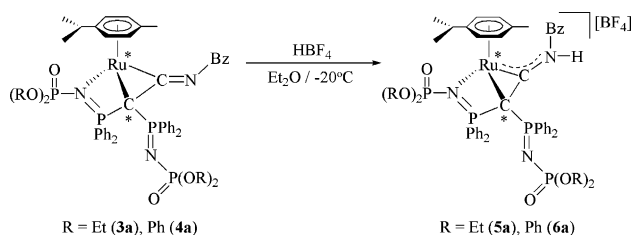Chart 3. Structure of the novel ruthenium complexes reported in this paper.

Scheme 1. Synthesis of ketenimine–ruthenium complexes **3**–**4a**–**c**.

(Mn, Co and Rh species) [3d,5b,5c,6]. Furthermore, the coordination of the $P_2C=C=NR'$ moieties to ruthenium via both carbon atoms of the cumulene chain is also supported by the appearance in the IR spectra of a characteristic $\nu(C=C=N)$ absorption band at 1636–1670 cm^{-1} [2b].

In order to find out the basicity of the coordinated ketenimine moiety $P_2C=C=NR'$, as compared to that of the iminophosphorane units $Ph_2P=N$, and the stability of the three-membered Ru–C–C metallacycle, the reactivity of compounds **3** and **4** towards acids has been explored. Thus, we have found that the treatment of complexes **3**–**4a** with $HBF_4 \cdot Et_2O$, in diethyl ether at −20 °C, yields the cationic derivatives [Ru(η^6-*p*-cymene)(κ^3-*C,C,N*-C(CNHBz)[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] [BF$_4$] (R = Et (**5a**), Ph (**6a**)) as the result of the selective protonation of the iminic C=N nitrogen atom (see Scheme 2).

Complexes **5**–**6a** have been isolated as air-sensitive brown solids in 75–79% yield. They have been characterized by elemental analyses, conductance measurements (1:1 electrolytes; $\Lambda_M = 134$–145 Ω^{-1} cm^2 mol^{-1}), and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy (see Section 3 for details) [13]. In particular, the ^{31}P{^{1}H} NMR spectra, which remain almost unchanged compared to those of their neutral precursors **3**–**4a** (shifts of ca. $\Delta\delta < \pm 9$ ppm of the four well-separated phosphorus signals are only observed), indicate that the bis(iminophosphorano)methanide skeleton is not altered through the protonation process. ^{13}C{^{1}H} NMR spectra are also consistent with the proposed formulation displaying resonances of the Ru–C–C framework in the

ranges 3.01–5.08 (ddd, $^1J_{CP} = 80.3$–82.5 and 69.4–70.4 Hz, $^3J_{CP} = 10.9$–12.1 Hz, PCP) and 226.70–228.12 (s, Ru–C=NH) ppm. The latter resonances are comparable to those described for iminium–ruthenium(II) complexes of the type [RuCp{C(CH=CPh$_2$)=NHR}(CO)(P^{i}Pr$_3$)][BF$_4$] (R = aryl or alkyl group) [14]. In their ^{1}H NMR spectra, the most noticeable facts are the splitting of the methylenic protons of the Bz group by the new NH proton, and the appearance of this last nucleus as a broad singlet at ca. 15 ppm, both confirming that protonation takes place at the nitrogen atom of the C=N unit.

At first glance, resonance structures of the type aminocarbene **H** and iminium salt **I** should be considered for the description of the keteniminium bonding in complexes **5**–**6a** (see Fig. 1). ^{1}H and ^{13}C{^{1}H} NMR data (see above), in addition to the IR spectra which show $\nu(NH)$ absorptions at 3229 (**5a**) and 3186 (**6a**) cm^{-1} and $\nu(C=N)$ absorptions at ca. 1590 cm^{-1}, suggest that the iminium resonance form **I** is the major contribution.

In summary, unprecedented ketenimine–ruthenium complexes, namely [Ru(η^6-*p*-cymene)(κ^3-*C,C,N*-C(C=NR')[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (**3**–**4a**–**c**), have been prepared by reacting the carbene derivatives [Ru(η^6-*p*-cymene)(κ^2-*C,N*-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) with isocyanides. To the best of our knowledge, compounds **3**–**4a**–**c**, which are stable in solution and do not undergo isomerization into their *C,N*-bound isomers (**A** in Chart 1), represent the first examples of ketenimine–ruthenium complexes reported to date. We also note that, in contrast to the reactivity pattern previously observed with terminal alkynes (**E** in Chart 2) [12],

Scheme 2. Protonation of ketenimine–ruthenium complexes **3**–**4a**.
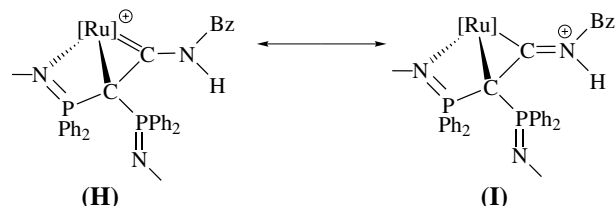
Fig. 1. Canonical forms of the cationic complexes **5**–**6a**.

the C–C coupling process of carbenes **1–2** with isocyanides is not accompanied by the *ortho*-metallation of one of the phenyl rings of the pendant iminophosphorane groups $Ph_2P=NP(=O)(OR)_2$. The results reported herein confirm the versatility and utility of these iminophosphorane-based ruthenium carbenes for the preparation of elaborated ruthenium organometallics via C–C coupling processes. Further studies in this direction are currently in progress.

3. Experimental

3.1. 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 and used without further purification with the exception of compounds $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}C,N\text{-}C[P\{=NP(=O)\text{-}(OR)_2\}Ph_2]_2)]$ (R = Et (**1**), Ph (**2**)) which were prepared by following the methods reported in the literature [11a]. 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. 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.

3.2. Synthesis of ketenimine–ruthenium complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}C,C,N\text{-}C(C=NR')[P\{=NP(=O)(OR)_2\}Ph_2]_2)]$ (R = Et, R' = Bz (**3a**), 2,6-C$_6$H$_3$-Me$_2$(**3b**), Cy (**3c**); R = Ph, R' = Bz (**4a**), 2,6-C$_6$H$_3$Me$_2$-(**4b**), Cy (**4c**))

A solution of the corresponding carbene complex $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}C,N\text{-}C[P\{=NP(=O)(OR)_2\}Ph_2]_2)]$ (R = Et (**1**), Ph (**2**)) (0.1 mmol) in 10 ml of THF was treated, at room temperature, with the appropriate isocyanide R'NC (0.1 mmol) for 10 min. The solvent was then removed in vacuo and the resulting oily residue dissolved in CH$_2$Cl$_2$ (ca. 2 ml). Addition of hexanes (ca. 50 ml) precipitated a yellow solid, which was washed with hexanes (3 × 10 ml) and dried in vacuo. (**3a**): Yield: 75% (0.078 g); Anal. Calc. for RuC$_{51}$H$_{61}$O$_6$P$_4$N$_3$ (1037.01 g mol^{-1}): C, 59.07; H, 5.93; N, 4.05. Found: C, 58.89; H, 5.86; N, 4.12%; IR (KBr) v = 1638 (C=C=N) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ = 0.28 (d, $^2J_{PP}$ = 34.8 Hz, (EtO)$_2$P=O), 8.39 (dd, $^2J_{PP}$ = 13.4 Hz, $^4J_{PP}$ = 8.0 Hz, Ru–NP(=O)(OEt)$_2$), 13.73 (ddd, $^2J_{PP}$ =

46.9 and 34.8 Hz, $^4J_{PP}$ = 8.0 Hz, Ph$_2$P=N), 47.28 (dd, $^2J_{PP}$ = 46.9 and 13.4 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (C$_6$D$_6$) δ = 0.67 and 1.12 (t, 3H each, $^3J_{HH}$ = 7.1 Hz, OCH$_2$CH$_3$), 0.74 and 1.10 (t, 3H each, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH$_3$), 1.11 (d, 3H, $^3J_{HH}$ = 7.1 Hz, CH(CH$_3$)$_2$), 1.37 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.87 (s, 3H, CH$_3$), 3.36 (m, 1H, CH(CH$_3$)$_2$), 3.66 and 3.92 (m, 4H each, OCH$_2$CH$_3$), 4.69 and 5.62 (d, 1H each, $^3J_{HH}$ = 5.5 Hz, CH of *p*-cymene), 4.97 and 5.43 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.05 and 5.33 (d, 1H each, $^2J_{HH}$ = 15.4 Hz, NCH$_2$Ph), 6.88–8.48 (m, 25H, Ph) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = −6.72 (dddd, $^1J_{CP}$ = 111.1 and 82.8 Hz, $^3J_{CP}$ = 12.9 and 8.1 Hz, PCP), 16.70 (d, 2C, $^3J_{CP}$ = 8.1 Hz, OCH$_2$CH$_3$), 17.42 (d, 2C, $^3J_{CP}$ = 7.1 Hz, OCH$_2$CH$_3$), 20.79 (s, CH$_3$), 22.69 and 25.58 (s, CH(CH$_3$)$_2$), 32.19 (s, CH(CH$_3$)$_2$), 61.57, 61.67 and 62.24 (d, $^2J_{CP}$ = 7.1 Hz, OCH$_2$CH$_3$), 61.99 (d, $^2J_{CP}$ = 6.1 Hz, OCH$_2$CH$_3$), 62.65 (s, NCH$_2$Ph), 80.46, 80.62, 80.93 and 84.63 (s, CH of *p*-cymene), 99.81 and 116.46 (s, C of *p*-cymene), 127.18–137.00 (m, Ph), 143.47 (s, C$_{ipso}$ of NCH$_2$*Ph*), 201.91 (s, Ru–C=N) ppm. (**3b**): Yield: 72% (0.076 g); Anal. Calcd for RuC$_{52}$H$_{63}$O$_6$P$_4$N$_3$ (1051.04 g mol^{-1}): C, 59.42; H, 6.04; N, 4.00. Found: C, 59.09; H, 6.25; N, 4.28%; IR (KBr) v = 1670 (C=C=N) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ = 1.80 (dd, $^2J_{PP}$ = 33.1 Hz, $^4J_{PP}$ = 5.1 Hz, (EtO)$_2$P=O), 10.20 (dd, $^2J_{PP}$ = 19.6 Hz, $^4J_{PP}$ = 8.3 Hz, Ru–NP(=O)(OEt)$_2$), 18.30 (ddd, $^2J_{PP}$ = 61.8 and 33.1 Hz, $^4J_{PP}$ = 8.3 Hz, Ph$_2$P=N), 50.75 (ddd, $^2J_{PP}$ = 61.8 and 19.6 Hz, $^4J_{PP}$ = 5.1 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (C$_6$D$_6$) δ = 0.85 (d, 3H, $^3J_{HH}$ = 7.1 Hz, CH(CH$_3$)$_2$), 0.89 (d, 3H, $^3J_{HH}$ = 7.1 Hz, CH(CH$_3$)$_2$), 0.95 (t, 6H, $^3J_{HH}$ = 7.1 Hz, OCH$_2$CH$_3$), 1.40 (t, 6H, $^3J_{HH}$ = 7.4 Hz, OCH$_2$CH$_3$), 2.12 and 2.50 (s, 3H each, C$_6$H$_3$Me$_2$), 2.25 (s, 3H, CH$_3$), 3.36 (m, 1H, CH(CH$_3$)$_2$), 3.65 (m, 8H, OCH$_2$CH$_3$), 4.90 and 5.31 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 5.07 and 5.09 (d, 1H each, $^3J_{HH}$ = 4.7 Hz, CH of *p*-cymene), 6.69–8.42 (m, 23H, Ph) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = −9.15 (dddd, $^1J_{CP}$ = 118.6 and 95.7 Hz, $^3J_{CP}$ = 23.4 and 11.3 Hz, PCP), 16.31 and 16.35 (d, $^3J_{CP}$ = 7.0 Hz, OCH$_2$CH$_3$), 16.66 (d, 2C, $^3J_{CP}$ = 7.1 Hz, OCH$_2$CH$_3$) 19.79 (s, CH$_3$), 21.45 and 23.09 (s, C$_6$H$_3$Me$_2$), 22.62 and 24.77 (s, CH(CH$_3$)$_2$), 31.12 (s, CH(CH$_3$)$_2$), 60.59 and 60.67 (d, $^2J_{CP}$ = 6.4 Hz, OCH$_2$CH$_3$), 61.44 and 61.50 (d, $^2J_{CP}$ = 5.1 Hz, OCH$_2$CH$_3$), 75.66, 77.05, 81.59 and 88.89 (s, CH of *p*-cymene), 107.22 and 114.71 (s, C of *p*-cymene), 122.26–135.02 (m, Ph), 152.14 (s, C$_{ipso}$ of C$_6$H$_3$Me$_2$), 197.56 (s, Ru–C=N) ppm. (**3c**): Yield: 70% (0.072 g); Anal. Calc. for RuC$_{50}$H$_{65}$O$_6$P$_4$N$_3$ (1029.03 g mol^{-1}): C, 58.36; H, 6.37; N, 4.08. Found: C, 58.15; H, 6.22; N, 4.16%; IR (KBr) v = 1636 (C=C=N) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ = 0.05 (d, $^2J_{PP}$ = 35.7 Hz, (EtO)$_2$P=O), 8.13 (dd, $^2J_{PP}$ = 16.1 Hz, $^4J_{PP}$ = 7.7 Hz, Ru–NP(=O)(OEt)$_2$), 13.55 (ddd, $^2J_{PP}$ = 48.2 and 35.7 Hz, $^4J_{PP}$ = 7.7 Hz, Ph$_2$P=N), 45.94 (dd,

$^2J_{PP}$ = 48.2 and 16.1 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (C$_6$D$_6$) δ = 0.86 (t, 3H, $^3J_{HH}$ = 6.7 Hz, OCH$_2$CH_3), 1.00 (t, 6H, $^3J_{HH}$ = 6.8 Hz, OCH$_2$CH_3), 1.15 (t, 3H, $^3J_{HH}$ = 6.8 Hz, OCH$_2$CH_3), 1.26 and 1.50 (d, 3H each, $^3J_{HH}$ = 5.9 Hz, CH(CH_3)$_2$), 1.44 and 1.70 (m, 4H each, CH$_2$), 2.12 (m, 2H, CH$_2$), 2.29 (s, 3H, CH$_3$), 3.42 (m, 1H, CH(CH$_3$)$_2$), 3.76 (m, 4H, OCH_2CH$_3$), 4.03 (m, 5H, OCH_2CH$_3$ and NCH), 4.86 and 5.02 (d, 1H each, $^3J_{HH}$ = 5.1 Hz, CH of *p*-cymene), 5.36 and 5.69 (d, 1H each, $^3J_{HH}$ = 4.4 Hz, CH of *p*-cymene), 6.99–8.56 (m, 20H, Ph) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = −7.86 (dddd, $^1J_{CP}$ = 112.7 and 82.8 Hz, $^3J_{CP}$ = 15.3 and 8.3 Hz, PCP), 15.89 and 16.43 (d, $^3J_{CP}$ = 7.4 Hz, OCH$_2$CH_3), 16.04 and 16.71 (d, $^3J_{CP}$ = 8.1 Hz, OCH$_2$CH_3), 20.23 (s, CH$_3$), 22.15 and 24.99 (s, CH(CH_3)$_2$), 25.21, 25.44, 29.94, 34.17 and 34.90 (s, CH$_2$), 31.71 (s, CH(CH$_3$)$_2$), 60.69, 60.73, 61.05 and 61.36 (d, $^2J_{CP}$ = 5.3 Hz, OCH_2CH$_3$), 67.55 (s, NCH), 77.25, 79.28, 80.69 and 84.86 (s, CH of *p*-cymene), 102.09 and 113.95 (s, C of *p*-cymene), 126.82–136.31 (m, Ph), 195.23 (s, Ru–C=N) ppm. (**4a**): Yield: 81% (0.099 g); Anal. Calc. for RuC$_{67}$H$_{61}$O$_6$P$_4$N$_3$ · 3/4CH$_2$Cl$_2$ (1292.88 g mol^{-1}): C, 62.94; H, 4.87; N, 3.25. Found: C, 62.90; H, 4.76; N, 3.53%; IR (KBr) v = 1640 (C=C=N) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ = −10.56 (d, $^2J_{PP}$ = 36.8 Hz, (PhO)$_2$P=O), −1.05 (dd, $^2J_{PP}$ = 12.7 Hz, $^4J_{PP}$ = 8.7 Hz, Ru–NP(=O)(OPh)$_2$), 16.46 (ddd, $^2J_{PP}$ = 47.5 and 36.8 Hz, $^4J_{PP}$ = 8.7 Hz, Ph$_2$P=N), 49.11 (dd, $^2J_{PP}$ = 47.5 and 12.7 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (C$_6$D$_6$) δ = 1.11 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.31 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.73 (s, 3H, CH$_3$), 3.24 (m, 1H, CH(CH$_3$)$_2$), 4.59 and 5.11 (d, 1H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 5.06 and 5.35 (d, 1H each, $^2J_{HH}$ = 15.4 Hz, NCH_2Ph), 5.48 and 5.71 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 6.65–8.42 (m, 45H, Ph) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = −8.09 (dddd, $^1J_{CP}$ = 101.3 and 91.2 Hz, $^3J_{CP}$ = 14.1 and 8.1 Hz, PCP), 19.88 (s, CH$_3$), 21.99 and 24.67 (s, CH(CH_3)$_2$), 31.50 (s, CH(CH$_3$)$_2$), 62.10 (s, NCH$_2$Ph), 80.53 and 84.72 (s, 2C each, CH of *p*-cymene), 98.37 and 116.30 (s, C of *p*-cymene), 120.57–134.85 (m, Ph), 142.52 (s, C$_{ipso}$ of NCH$_2$$Ph$), 152.12, 152.50, 153.71 and 153.74 (d, $^2J_{CP}$ = 7.1 Hz, C$_{ipso}$ of OPh), 199.18 (s, Ru–C=N) ppm. (**4b**): Yield: 79% (0.098 g); Anal. Calc. for RuC$_{68}$H$_{63}$O$_6$P$_4$N$_3$ (1243.21 g mol^{-1}): C, 65.70; H, 5.11; N, 3.38. Found: C, 65.55; H, 5.03; N, 3.49%; IR (KBr) v = 1669 (C=C=N) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ = −9.11 (dd, $^2J_{PP}$ = 33.3 Hz, $^4J_{PP}$ = 5.5 Hz, (PhO)$_2$P=O), −4.23 (dd, $^2J_{PP}$ = 17.6 Hz, $^4J_{PP}$ = 8.4 Hz, Ru–NP(=O)(OPh)$_2$), 20.22 (ddd, $^2J_{PP}$ = 64.3 and 33.3 Hz, $^4J_{PP}$ = 8.4 Hz, Ph$_2$P=N), 51.02 (ddd, $^2J_{PP}$ = 64.3 and 17.6 Hz, $^4J_{PP}$ = 5.5 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (C$_6$D$_6$) δ = 1.08 and 1.18 (d, 3H each, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 2.06 (s, 3H, CH$_3$), 2.28 (m, 1H, CH(CH$_3$)$_2$), 2.32 and 2.53 (s, 3H each, C$_6$H$_3$$Me_2$), 5.01 and 5.16 (d, 1H each, $^3J_{HH}$ = 5.3 Hz, CH of *p*-cym-

ene), 5.31 and 5.34 (d, 1H each, $^3J_{HH}$ = 6.4 Hz, CH of *p*-cymene), 6.67–8.57 (m, 43H, Ph) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = −9.35 (dddd, $^1J_{CP}$ = 104.8 and 89.7 Hz, $^3J_{CP}$ = 14.9 and 9.9 Hz, PCP), 19.63 (s, CH$_3$), 19.80 and 22.62 (s, C$_6$H$_3$$Me_2$), 21.66 and 24.87 (s, CH(CH_3)$_2$), 31.16 (s, CH(CH$_3$)$_2$), 75.07, 77.85, 81.45 and 89.42 (s, CH of *p*-cymene), 108.22 and 114.52 (s, C of *p*-cymene), 120.36–135.40 (m, Ph), 151.96 (s, C$_{ipso}$ of $C_6H_3Me_2$), 152.33 (d, 2C, $^2J_{CP}$ = 7.0 Hz, C$_{ipso}$ of OPh), 153.55 and 153.60 (d, $^2J_{CP}$ = 7.0 Hz, C$_{ipso}$ of OPh), 196.80 (s, Ru–C=N) ppm. (**4c**): Yield: 67% (0.082 g); Anal. Calc. for RuC$_{66}$H$_{65}$O$_6$P$_4$N$_3$ · $\frac{1}{2}$CH$_2$Cl$_2$ (1263.67 g mol^{-1}): C, 63.21; H, 5.26; N, 3.32. Found: C, 63.15; H, 5.00; N, 3.59%; IR (KBr) v = 1644 (C=C=N) cm^{-1}; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ = −10.89 (d, $^2J_{PP}$ = 37.6 Hz, (PhO)$_2$-P=O), −1.22 (dd, $^2J_{PP}$ = 14.6 Hz, $^4J_{PP}$ = 8.9 Hz, Ru–NP(=O)(OPh)$_2$), 16.64 (ddd, $^2J_{PP}$ = 47.7 and 37.6 Hz, $^4J_{PP}$ = 8.9 Hz, Ph$_2$P=N), 48.25 (dd, $^2J_{PP}$ = 47.7 and 14.6 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (C$_6$D$_6$) δ = 1.21 and 1.49 (d, 3H each, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.55 and 1.75 (m, 4H each, CH$_2$), 2.02 (s, 3H, CH$_3$), 2.25 (m, 2H, CH$_2$), 3.37 (m, 1H, CH(CH$_3$)$_2$), 4.21 (m, 1H, NCH), 4.72 and 5.06 (d, 1H each, $^3J_{HH}$ = 5.1 Hz, CH of *p*-cymene), 5.46 and 5.82 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 6.76–8.49 (m, 40H, Ph) ppm; ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = −8.91 (dddd, $^1J_{CP}$ = 108.2 and 81.9 Hz, $^3J_{CP}$ = 13.8 and 8.7 Hz, PCP), 20.10 (s, CH$_3$), 22.10 and 25.30 (s, CH(CH_3)$_2$), 25.50, 25.78, 30.16, 34.39 and 35.09 (s, CH$_2$), 31.91 (s, CH(CH$_3$)$_2$), 67.79 (s, NCH), 78.95 and 83.39 (s, CH of *p*-cymene), 80.29 (br, 2C, CH of *p*-cymene), 99.86 and 115.33 (s, C of *p*-cymene), 120.51–135.17 (m, Ph), 152.22, 152.57, 153.16 and 153.76 (d, $^2J_{CP}$ = 7.4 Hz, C$_{ipso}$ of OPh), 193.78 (s, Ru–C=N) ppm.

3.3. Synthesis of cationic complexes [Ru(η^6-p-cymene)-(κ^3-C,C,N-C(CNHBz)[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$]-[BF$_4$] (R = Et (**5a**), Ph (**6a**))

A diluted solution of HBF$_4$ · Et$_2$O in diethyl ether was added dropwise, at −20 °C, to a solution of the corresponding ketenimine complex [Ru(η^6-*p*-cymene)(κ^3-C,C,N-C(C=NBz)[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (**3**–**4a**) (0.1 mmol) in 50 ml of diethyl ether. Immediately, an insoluble solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted and the brown solid washed with diethyl ether (3 × 15 ml) and vacuum-dried. (**5a**): Yield: 75% (0.084 g); Conductivity (acetone, 20 °C) 145 Ω^{-1} cm^2 mol^{-1}; IR (Nujol) v = 1068 (BF$_4^-$), 1588 (C=N), 3229 (N–H) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ = 5.50 (d, $^2J_{PP}$ = 27.6 Hz, (EtO)$_2$P=O), 8.58 (dd, $^2J_{PP}$ = 7.3 Hz, $^4J_{PP}$ = 7.3 Hz, Ru–NP(=O)(OEt)$_2$), 13.41 (ddd, $^2J_{PP}$ = 44.2 and 27.6 Hz, $^4J_{PP}$ = 7.3 Hz, Ph$_2$P=N), 57.64 (dd, $^2J_{PP}$ = 44.2 and 7.3 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (CD$_2$Cl$_2$) δ = 0.84 (t, 9H, $^3J_{HH}$ = 8.8 Hz, OCH$_2$CH_3),

(1.08 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CH(CH_3)$_2$), (1.21 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(CH_3)$_2$), 2.09 (s, 3H, CH$_3$), 2.96 (m, 1H, CH(CH$_3$)$_2$), 3.49 and 3.84 (m, 4H each, OCH_2CH$_3$) 4.76 and 5.37 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 5.00 (dd, 1H, $^2J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 2.3 Hz, NHCH_2Ph), 5.22 (dd, 1H, $^2J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.8 Hz, NHCH_2Ph), 5.63 and 5.78 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 7.13–8.68 (m, 25H, Ph), 14.95 (br, 1H, NH) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 3.01 (ddd, $^1J_{CP}$ = 82.5 and 70.4 Hz, $^3J_{CP}$ = 10.9 Hz, PCP), 15.95 (d, $^3J_{CP}$ = 8.6 Hz, OCH$_2$$CH_3$), 16.05 (d, $^3J_{CP}$ = 5.5 Hz, OCH$_2$$CH_3$), 16.27 (d, $^3J_{CP}$ = 7.8 Hz, OCH$_2$$CH_3$), 16.39 (d, $^3J_{CP}$ = 9.4 Hz, OCH$_2$$CH_3$), 19.52 (s, CH$_3$), 22.68 and 23.42 (s, CH(CH_3)$_2$), 31.73 (s, CH(CH$_3$)$_2$), 57.18 (s, NCH$_2$Ph), 62.32 (d, $^2J_{CP}$ = 6.2 Hz, OCH$_2$CH$_3$), 62.53 (d, $^2J_{CP}$ = 7.0 Hz, OCH$_2$-CH$_3$), 62.72 (d, 2C, $^2J_{CP}$ = 6.3 Hz, OCH$_2$CH$_3$), 83.13, 86.40, 87.26 and 88.45 (s, CH of *p*-cymene), 106.18 and 118.25 (s, C of *p*-cymene), 123.02–135.08 (m, Ph), 138.91 (s, C$_{ipso}$ of NCH$_2$$Ph$), 226.70 (s, RuCNH) ppm. This complex was too sensitive to moisture to give satisfactory elemental analyses. **(6a):** Yield: 79% (0.104 g); Anal. Calc. for RuC$_{67}$H$_{62}$O$_6$F$_4$P$_4$N$_3$B (1316.99 g mol^{-1}): C, 61.10; H, 4.75; N, 3.19. Found: C, 60.97; H, 4.70; N, 3.35%; Conductivity (acetone, 20 °C) 134 Ω^{-1} cm^2 mol^{-1}; IR (Nujol) v = 1069 (BF$_4^-$), 1590 (C=N), 3186 (N–H) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ = −3.73 (d, $^2J_{PP}$ = 31.0 Hz, (PhO)$_2$P=O), −0.77 (dd, $^4J_{PP}$ = 7.2 Hz, $^2J_{PP}$ = 5.2 Hz, Ru–NP(=O)(OPh)$_2$), 15.36 (ddd, $^2J_{PP}$ = 45.3 and 31.0 Hz, $^4J_{PP}$ = 7.2 Hz, Ph$_2$P=N), 58.58 (dd, $^2J_{PP}$ = 45.3 and 5.2 Hz, Ru–N=PPh$_2$) ppm; ^{1}H NMR (CD$_2$Cl$_2$) δ = 1.21 and 1.36 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.90 (s, 3H, CH$_3$), 2.98 (m, 1H, CH(CH$_3$)$_2$), 4.97 and 5.16 (d, 1H each, $^3J_{HH}$ = 6.1 Hz, CH of *p*-cymene), 5.09 (dd, 1H, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 2.1 Hz, NHCH_2Ph), 5.46 (dd, 1H, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.7 Hz, NHCH_2Ph), 5.82 and 5.85 (d, 1H each, $^3J_{HH}$ = 6.4 Hz, CH of *p*-cymene), 6.35–7.95 (m, 45H, Ph), 14.34 (br, 1H, NH) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ = 5.08 (ddd, $^1J_{CP}$ = 80.3 and 69.4 Hz, $^3J_{CP}$ = 12.1 Hz, PCP), 19.43 (s, CH$_3$), 22.09 and 23.59 (s, CH(CH_3)$_2$), 31.55 (s, CH(CH$_3$)$_2$), 57.64 (s, NCH$_2$Ph), 86.29, 86.74, 90.40 and 90.84 (s, CH of *p*-cymene), 106.02 and 123.49 (s, C of *p*-cymene), 121.71–136.97 (m, Ph), 139.52 (s, C$_{ipso}$ of NCH$_2$$Ph$), 152.63 (d, $^2J_{CP}$ = 6.4 Hz, C$_{ipso}$ of OPh), 152,71 and 153.45 (d, $^2J_{CP}$ = 7.3 Hz, C$_{ipso}$ of OPh), 153.77 (d, $^2J_{CP}$ = 8.1 Hz, C$_{ipso}$ of OPh), 228.12 (s, RuCNH) ppm.

Acknowledgments

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