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Bis(iminophosphorano)methane Derivatives as Precursors of Unusual Ruthenium Carbene Complexes: A Synthetic and DFT Study

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The symmetric bis(iminophosphorano)methanes $CH_2[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2$ (R = Ph (**2a**), Et (**2b**)) have been obtained by treatment of bis(diphenylphosphino)methane with a 2-fold excess of phosphorylated azides $(RO)_2P({=}O)N_3$. The asymmetric ligand $CH_2[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2]$ (**2c**) has been prepared by oxidation of $Ph_2PCH_2P\{{=}NP({=}O)(OEt)_2\}Ph_2$ (**1b**) with $(PhO)_2P({=}O)N_3$. Compounds **2a**−**c** can be deprotonated with sodium hydride, affording the corresponding methanide anions $NaCH[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2$ (R = Ph (**3a**), Et (**3b**)) and $NaCH[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2]$ (**3c**). Treatment of $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ with **3a**−**c** results in the formation of the neutral complexes $[RuCl(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}CH[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2)]$ (R = Ph (**4a**), Et (**4b**)) and $[RuCl(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}CH[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2])]$ (**4c**), via selective κ^2(C,N) coordination of the bis(iminophosphorano)methanide anions to ruthenium. The cationic species $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3(C,N,O)\text{-}CH[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2)][SbF_6]$ (R = Ph (**5a**), Et (**5b**)) and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3(C,N,O)\text{-}CH[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2])][SbF_6]$ (**5c**/**5c′**) have been also prepared by reaction of **4a**−**c** with $AgSbF_6$. Deprotonation of complexes **4a**−**c** or **5a**−**c′** with NaH generates the unprecedented ruthenium carbenes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2)]$ (R = Ph (**6a**), Et (**6b**)) and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2])]$ (**6c**). The structures of compounds **2a**, **5a**, and **6a** have been confirmed by X-ray crystallography. DFT calculations on a model for complexes **6a**−**c**, $[Ru(\eta^6\text{-}C_6H_6)(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]$, suggest a nucleophilic character for the carbon atom in Ru=C. In agreement with this theoretical prediction, protonation of complexes **6a**−**c** with HCl or HBF_4 takes place selectively on the carbenic carbon, regenerating **4a**−**c** or **5a**−**c′**, respectively.

Introduction

The search for novel transition-metal carbene derivatives is one of the most important goals in organometallic chemistry today, due to their widespread applications in both stoichiometric and catalytic organic transformations.[1] In this respect, Cavell and co-workers have recently demonstrated that "pincer" (**A**) or bridged (**B**) carbene complexes (see Chart 1) can be readily obtained from bis(iminophosphorano)methane ligands, $CH_2\{P({=}NSiMe_3)R_2\}_2$ (R = Ph, Me, Cy), by deprotonation of the methylenic backbone.[2] Until now, structures of type **A** have been found in some complexes of group 4 metals,[3] samarium,[4] and molybdenum,[5] while the bridged species **B** are known for chromium,[6] aluminum,[7] and group 14 metals.[8]

As part of our current work dealing with the synthesis and catalytic activity of ruthenium complexes containing iminophosphorane ligands,[9] we have recently reported

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(1) See for example: (a) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (b) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187. (c) Zaragoza Dörwald, F. In *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999. (d) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (e) A special issue on transition-metal carbene complexes: *J. Organomet. Chem.* **2001**, *617*−*618*, 1−754. (f) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (g) Barluenga, J.; Flórez, J.; Fañanas, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (h) Guerchais, V. *Eur. J. Inorg. Chem.* **2002**, 783.

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10.1021/om030658w CCC: $27.50
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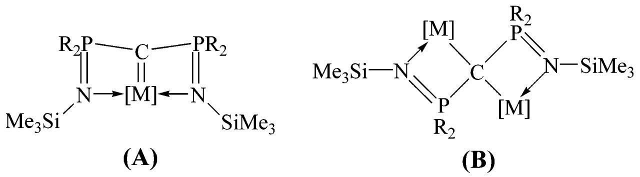
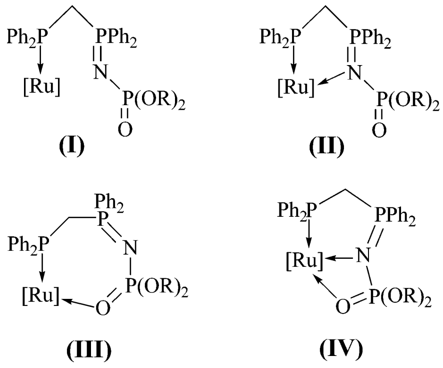
Chart 1



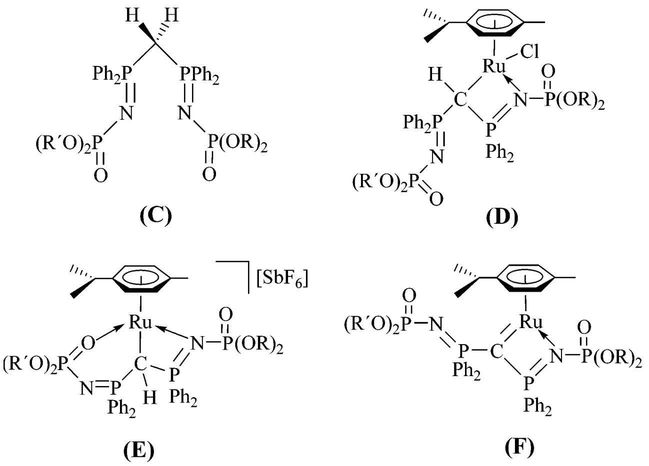
(A) **(B)**

Chart 2



(I) **(II)** **(III)** **(IV)**

Chart 3[a]



(C) **(D)** **(E)** **(F)**

[a] R = R′ = Ph, Et; R = Et, R′ = Ph.

the preparation of the heterotrifunctional iminophosphorane−phosphines Ph$_2$PCH$_2$P{=NP(=O)(OR)$_2$}Ph$_2$ (R = Ph, Et), via single-stage oxidation of bis(diphenylphosphino)methane (dppm) with the phosphorylated azides (RO)$_2$P(=O)N$_3$ (R = Ph, Et).[9c] As a consequence of the presence of coordinating phosphoryl substituents, these ligands have shown a versatile coordination ability in ruthenium fragments adopting κ^1(P) (**I**), κ^2(P,N) (**II**), κ^2(P,O) (**III**), and κ^3(P,N,O) coordination modes (**IV**) (see Chart 2).[9c]

Continuing with our interest in exploiting the coordination ability and the reactivity of these polydentate heterofunctional ligands, we report in this paper (see Chart 3) (i) the synthesis of the novel bis(iminophosphorano)methane derivatives CH$_2$[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$ (R = Ph, Et) and CH$_2$[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$] (**C**), (ii) deprotonation reactions of these ligands to afford the corresponding bis(iminophosphorano)methanide monoanionic species and their coordination to (η^6-*p*-cymene)ruthenium(II) fragments (**D** and **E**), and (iii) the synthesis of the unprecedented ruthenium(II) carbene complexes [Ru(η^6-*p*-cymene)(κ^2-(*C*,*N*)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Ph, Et) and [Ru(η^6-*p*-cymene)(κ^2(*C*,*N*)-C[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$])] (**F**). In addition, a theoretical study (DFT level) devoted to rationalizing the electronic nature of the carbene moiety in complexes **F** is described.

Results and Discussion

Synthesis of the Bis(iminophosphorano)methane Compounds CH$_2$[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$ (R = Ph (2a), Et (2b)) and CH$_2$[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$] (2c). Since the discovery in 1919 of the imination reaction of phosphines with azides (Staudinger reaction),[10] a large number of mono- and bis(phosphines) have been effectively converted into the corresponding iminophosphoranes or bis(iminophosphoranes), respectively.[11] We have found that bis(diphenylphosphino)methane (dppm) reacts with a 2-fold excess of the readily available phosphoryl azides (RO)$_2$P(=O)N$_3$ (R = Ph, Et), in THF at room temperature, to afford the novel symmetrical *N*-phosphoryl bis(iminophosphorano)methanes CH$_2$[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$ (R = Ph (**2a**), Et (**2b**); 86 and 81% yields, respectively) (Scheme 1).[12] Compounds **2a**,**b** can be also prepared in similar yields by treatment of the previously reported iminophosphorane−phosphines Ph$_2$PCH$_2$P{=NP(=O)(OR)$_2$}Ph$_2$ (R = Ph (**1a**), Et (**1b**))[9c] with 1 equiv of the appropriate phosphoryl azide (Scheme 1). In addition, the unsymmetrical bis(iminophosphorano)methane CH$_2$-

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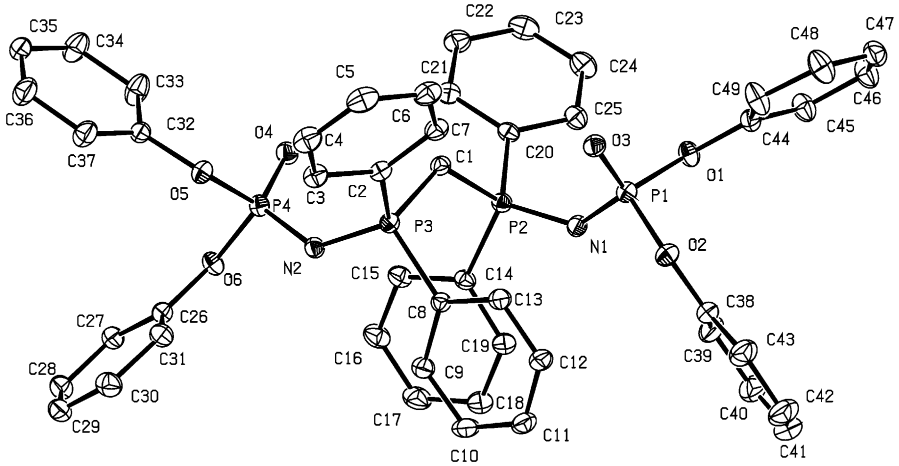
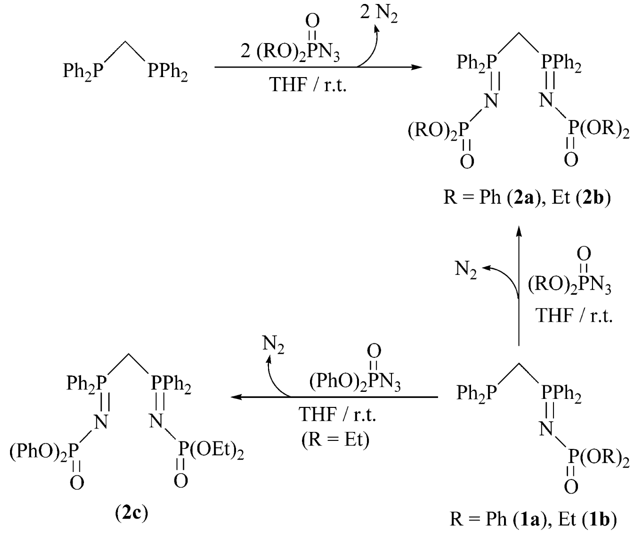


Figure 1. ORTEP-type view of the structure of $CH_2[P\{=NP(=O)(OPh)_2\}Ph_2]_2$ (**2a**), showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): C(1)−P(2) = 1.810(3); P(2)−N(1) = 1.571(2); N(1)−P(1) = 1.576(2); P(1)−O(1) = 1.593(2); P(1)−O(2) = 1.588(2); P(1)−O(3) = 1.458(2); C(1)−P(3) = 1.814(3); P(3)−N(2) = 1.573(2); N(2)−P(4) = 1.586(2); P(4)−O(4) = 1.469(2); P(4)−O(5) = 1.597(2); P(4)−O(6) = 1.588(2); C(1)−P(2)−N(1) = 113.87(12); P(2)−N(1)−P(1) = 131.98(15); N(1)−P(1)−O(1) = 102.84(11); N(1)−P(1)−O(2) = 109.27(12); N(1)−P(1)−O(3) = 119.66(12); P(2)−C(1)−P(3) = 121.94(14); C(1)−P(3)−N(2) = 113.34(12); P(3)−N(2)−P(4) = 130.10(15); N(2)−P(4)−O(4) = 119.34(12); N(2)−P(4)−O(5) = 103.82(11); N(2)−P(4)−O(6) = 108.13(12).

Scheme 1



$[P\{=NP(=O)(OPh)_2\}Ph_2][P\{=NP(=O)(OEt)_2\}Ph_2]$ (**2c**) has been synthesized (75% yield) by oxidation of **1b** with $(PhO)_2P(=O)N_3$ in THF at room temperature (Scheme 1).[13]

Bis(iminophosphorano)methanes **2a**−**c** have been isolated as air-stable microcrystalline white solids and characterized by standard spectroscopic techniques (IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR) as well as elemental analyses (details are given in the Experimental Section). Relevant spectroscopic features are as follows. (i) In the $^{31}P\{^1H\}$ NMR spectra are found two multiplets for **2a**,**b** (**2a**, δ −6.79 ($(PhO)_2P{=}O$) and 11.48 ($Ph_2P{=}N$); **2b**, δ 4.09 ($(EtO)_2P{=}O$) and 9.72 ($Ph_2P{=}N$); AA'XX' spin system) and four well-separated signals with equal relative intensities for **2c** (δ −6.42 (d, $^2J_{PP}$ = 32.9 Hz, $(PhO)_2P{=}O$), 4.03 (d, $^2J_{PP}$ = 29.8 Hz, $(EtO)_2P{=}O$), 9.32 (dd, $^2J_{PP}$ = 29.8 and 16.2 Hz, $Ph_2\mathit{P}{=}NP(=O)(OEt)_2$), and 11.86 (dd, $^2J_{PP}$ = 32.9 and 16.2 Hz, $Ph_2\mathit{P}{=}NP(=O)(OPh)_2$)). The chemical shifts as well as the coupling constants found can be compared to those described in the literature for the related iminophosphorane compounds $CH_2\{P(=NR)Ph_2\}\{P(=NR')Ph_2\}$ (R = R' or R $\neq$ R')[12,13] and $R_3P{=}NP(=O)(OR')_2$.[14] (ii) In the ^1H and $^{13}C\{^1H\}$ NMR spectra are found triplet (**2a**,**b**) or doublet of doublets (**2c**) signals at ca. 4.6 and 28 ppm for both proton and carbon resonances, respectively, of the methylenic PCH_2P group, due to the coupling with the phosphorus atom of the $Ph_2P{=}N$ units (ca. $^2J_{HP}$ = 15 Hz and $^1J_{CP}$ = 54 Hz). Moreover, the molecular structure of **2a** has been confirmed by X-ray diffraction. An ORTEP plot is shown in Figure 1; selected bonding parameters appear in the caption. As previously observed in other species containing $-R_2P{=}NP(=O)(OR')_2$ units,[9c,14c,d,h] the lengths of the formal single and double PN bonds were found to be very similar (N(1)−P(1) = 1.576(2) Å and N(2)−P(4) = 1.586(2) Å vs P(2)−N(1) = 1.571(2) Å and P(3)−N(2) = 1.573(2) Å). This fact is probably determined by the strong π-acceptor natures of the phosphoryl groups, which enhance the delocalization of the electronic lone pair on the nitrogen atom within the P−N−P unit. The P=O (P(1)−O(3) = 1.458(2) Å; P(4)−O(4) = 1.469(2) Å) and P−O (ca. 1.59 Å) bond lengths are also typical for these types of compounds.[9c,14c,d,h]

Synthesis of the Anionic Bis(iminophosphorano)methanide Species NaCH[P{=NP(=O)(OR)$_2$}-

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[13] An exhaustive literature search revealed that the compound $CH_2\{P(=NPh)Ph_2\}\{P(=NMes)Ph_2\}$ (Mes = 2,4,6-trimethylphenyl) is the only reported example of a bis(iminophosphorano)methane bearing dissimilar nitrogen-bound substituents: Hill, M. S.; Hitchcock, P. B. *Dalton* **2002**, 4694.

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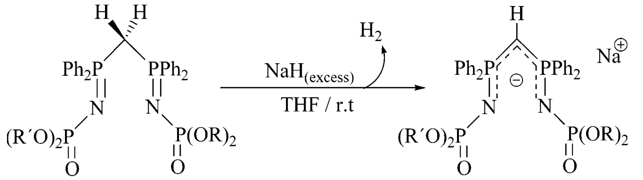
Scheme 2



R = R′ = Ph (**2a**), Et (**2b**)
R = Et, R′ = Ph (**2c**)

R = R′ = Ph (**3a**), Et (**3b**)
R = Et, R′ = Ph (**3c**)

Ph$_2$]$_2$ (R = Ph (3a), Et (3b)) and NaCH[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$] (3c). In accord with the well-known acidic character of the methylenic backbone in bis(iminophosphorano)methane derivatives,[12e,f,15] compounds **2a**−**c** can be easily deprotonated by NaH, in THF at room temperature, to generate the corresponding bis(iminophosphorano)methanide species NaCH[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$ (R = Ph (**3a**), Et (**3b**)) and NaCH[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$] (**3c**) in almost quantitative yields (Scheme 2). All attempts to promote the double deprotonation of **2a**−**c** with NaH, KH, LDA, MeLi, or ^{n}BuLi failed.[16]

Compounds **3a**−**c** have been isolated as moisture-sensitive colorless oils and characterized by means of ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy (details are given in the Experimental Section). As a common trend, when the ^{31}P{^{1}H} NMR spectra of **3a**−**c** are compared to those of their parent bis(iminophosphorano)methane precursors **2a**−**c**, slight shifts of the corresponding resonances are observed: i.e. to low field for the Ph$_2$P=N groups ($\Delta\delta$ ca. 5 ppm) and to high field for the (RO)$_2$P=O units ($\Delta\delta$ ca. −3 ppm). The methine PCHP proton appears in the ^{1}H NMR spectra as a broad signal ($\nu_{1/2} = 6-8$ Hz) at ca. 2.1 ppm. In contrast, the ^{13}C{^{1}H} NMR spectra show the expected well-defined triplet (**3a**,**b**) or doublet of doublets (**3c**) PCHP resonance (δ 16.10−19.95) with $^1J_{CP}$ values in the range of 25.8−34.5 Hz.

Reactions of the Bis(iminophosphorano)methanide Anions 3a−c with [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$]. Treatment of the ruthenium(II) dimer [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] with **3a**−**c** in refluxing toluene results in the stereoselective formation of the neutral four-membered metallacycles [RuCl(η^6-*p*-cymene)(κ^2-(*C*,*N*)-CH[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Ph (**4a**), Et (**4b**)) and [RuCl(η^6-*p*-cymene)(κ^2(*C*,*N*)-CH[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$])] (**4c**) (68−70% yield), via selective κ^2(C,N) coordination of the bis(iminophosphorano)methanide anions to ruthenium (Scheme 3).

The coordination chemistry of bis(iminophosphorano)methanide species [CH{P(=NR′)R$_2$}$_2$]$^-$ has been extensively studied over the last few years. Thus, these anionic ligands can adopt two coordination modes, either κ^2(N,N) or κ^2(C,N), forming a six-[7a,c,12f,13,17] or four-membered chelate ring,[18] respectively. The assignment of the κ^2(C,N) coordination mode of the bis(iminophosphorano)methanide ligands in **4a**−**c** is based on the NMR spectra, which also clearly show that the formation of **4a**−**c** proceeds in a diastereoselective manner (two stereogenic centers are formed, i.e. the ruthenium atom and the PCHP carbon). Significantly, the ^{31}P{^{1}H} NMR spectra of **4a**,**b** are very informative, showing in both cases the presence of four well-separated signals, in accordance with the coordination of only one of the two iminophosphorane groups. This fact discards the symmetric κ^2(N,N) coordination of **3a**,**b**, for which only two signals should be expected. Moreover, a strong downfield shift is observed ($\Delta\delta$ ca. 47 ppm) for one of the two Ph$_2$P=N resonances (δ 61.40−64.26 ppm) in comparison to those shown by the free ligands **3a**,**b**. The ^{31}P{^{1}H} NMR spectrum of complex **4c**, containing the unsymmetrical bis(iminophosphorano)methanide ligand **3c**, indicates the selective κ^2(C,N) coordination through the iminophosphorane group attached to the more basic phosphoryl substituent, i.e. P(=O)(OEt)$_2$ vs P(=O)(OPh)$_2$, for which the expected resonance shifting is also observed (see the Experimental Section). ^{1}H and ^{13}C{^{1}H} NMR spectra for **4a**−**c** exhibit signals consistent with the proposed formulation, the most significant features being those concerning the methine PCHP group of the ligands: (i) in the ^{1}H NMR, an unresolved multiplet at 2.96−3.38 ppm and (ii) in the ^{13}C{^{1}H} NMR, a well-resolved dddd signal in the range 2.10−4.02 ppm ($^1J_{CP}$ = 93.2−95.8 and 60.0−63.5 Hz; $^3J_{CP}$ = 17.6−19.2 and 10.6−12.3 Hz).

The reaction of the neutral complexes [RuCl(η^6-*p*-cymene)(κ^2(*C*,*N*)-CH[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Ph (**4a**), Et (**4b**)) with 1 equiv of AgSbF$_6$ generates, via diastereoselective intramolecular O-coordination of the free *N*-phosphoryl iminophosphoranyl fragment, the cationic derivatives [Ru(η^6-*p*-cymene)(κ^3(*C*,*N*,*O*)-CH[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)][SbF$_6$] (R = Ph (**5a**), Et (**5b**)), isolated as air-stable microcrystalline solids in 82 and 79% yields, respectively (Scheme 3). In contrast, with [RuCl(η^6-*p*-cymene)(κ^2(*C*,*N*)-CH[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$])] (**4c**) as the starting material, a nonseparable mixture of the isomers **5c** and **5c′** (ca. 2:3 ratio) was obtained (see Scheme 3). The competitive coordination ability of both arms of the ligand evidences the hemilabile properties of the *N*-phosphoryl iminophosphoranyl fragments −Ph$_2$P=NP(=O)(OR)$_2$, in accordance with the behavior described in related ruthenium(II) complexes.[9c,19]

Compounds **5a**−**c′** have been characterized by elemental analyses, conductance measurements (1:1 elec-

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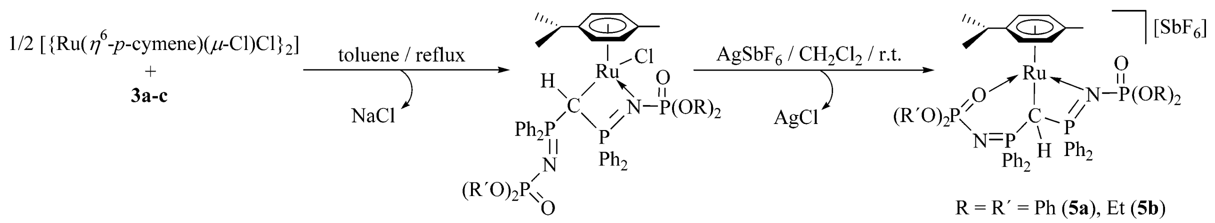
(15) (a) Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2000**, *39*, 4981. (b) Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G. *Organometallics* **2001**, *20*, 1451. (c) Gamer, M. T.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2001**, *627*, 877.

(16) The bis(iminophosphorano)methanediide species Li$_2$C{P(=N-SiMe$_3$)Ph$_2$}$_2$ is known: (a) Kasani, A.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1483. (b) Ong, C. M.; Stephan, D. W. *J. Am. Chem. Soc.* **1999**, *121*, 2939.

(17) (a) Kasani, A.; McDonald, R.; Cavell, R. G. *Organometallics* **1999**, *18*, 3775. (b) Ong, C. M.; McKarns, P.; Stephan, D. W. *Organometallics* **1999**, *18*, 4197. (c) Gamer, M. T.; Dehnen, S.; Roesky, P. W. *Organometallics* **2001**, *20*, 4230. (d) Aharonian, G.; Feghali, K.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2616. (e) Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2002**, *647*, 123. (f) Wei, P.; Stephan, D. W. *Organometallics* **2002**, *21*, 1308. (g) Sarsfield, M. J.; Helliwell, M.; Collison, D. *Chem. Commun.* **2002**, 2264. (h) Wei, P.; Stephan, D. W. *Organometallics* **2003**, *22*, 601. (i) Evans, D. J.; Hill, M. S.; Hitchcock, P. B. *Dalton* **2003**, 570. (j) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2003**, 1758.

(18) (a) Imhoff, P.; Van Asselt, R.; Ernsting, J. M.; Vrieze, K.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Kentgens, A. P. M. *Organometallics* **1993**, *12*, 1523. (b) Imhoff, P.; Gülpen, J. H.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Elsevier, C. J. *Inorg. Chim. Acta* **1995**, *235*, 77. (c) Avis, M. W.; Vrieze, K.; Kooijman, H.; Veldman, N.; Spek, A. L.; Elsevier, C. J. *Inorg. Chem.* **1995**, *34*, 4092. (d) Avis, M. W.; Vrieze, K.; Ernsting, J. M.; Elsevier, C. J.; Veldman, N.; Spek, A. L.; Katti, K. V.; Barnes, C. L. *Organometallics* **1996**, *15*, 2376. (e) Aharonian, G.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 5008.

Scheme 3



R = R′ = Ph (**4a**), Et (**4b**)
R = Et, R′ = Ph (**4c**)

R = R′ = Ph (**5a**), Et (**5b**)
R = Et, R′ = Ph (**5c**)
R = Ph, R′ = Et (**5c′**)

trolytes), and IR and NMR spectroscopy (see the Experimental Section for details). In particular, the NMR spectra support (i) the diastereoselective formation of **5a**−**c′** and (ii) the κ^3(*C,N,O*) coordination of the ligands, showing the expected resonance shiftings with respect to those of their neutral precursors **4a**−**c**. Thus, a downfield shift ($\Delta\delta$ 8−12 ppm) in the coordinated $(RO)_2P{=}O$ group phosphorus resonances (the rest of the signals being almost unaffected), a slight deshielding of the methine protons (ca. $\Delta\delta$ 1 ppm), and a shielding of the PCHP carbon resonances (ca. $\Delta\delta$ −9 ppm) are observed. Moreover, the formation of a metallabicyclic structure and the absolute configurations at the metal as well as the metalated carbon atom have been unambiguously determined by a X-ray diffraction study on complex **5a**. As expected, the two enantiomers are present in the unit cell displaying $R_{Ru}S_C$ and $S_{Ru}R_C$ configurations. A drawing of the molecular structure of the $R_{Ru}S_C$ enantiomer is depicted in Figure 2; selected bond distances and angles are listed in the caption. The molecule exhibits the usual pseudooctahedral three-legged piano-stool geometry around the metal with values of the interligand angles C(11)−Ru−N(1), C(11)−Ru−O(4), and N(1)−Ru−O(4) and those between the centroid of the *p*-cymene ring C* and the legs typical of a pseudo-octahedron. Remarkably, despite the unsymmetrical κ^3(*C,N,O*) coordination of the bis(iminophosphorane)methanide ligand, the bond distances within the two $-Ph_2P{=}NP({=}O)(OPh)_2$ frameworks are almost identical (ca. ±0.04 Å) and comparable to those found in the structure of the free ligand $CH_2[P\{{=}NP({=}O)(OPh)_2\}Ph_2]_2$ (**2a**) (see Figure 1 and caption). This fact seems to indicate that electronic delocalization of the nitrogen lone pair is maintained upon N or O coordination of the $-Ph_2P{=}NP({=}O)(OPh)_2$ units to ruthenium.[9c] The Ru−C(11) bond length (2.228(5) Å) shows the expected value for a ruthenium−carbon single bond.[20]

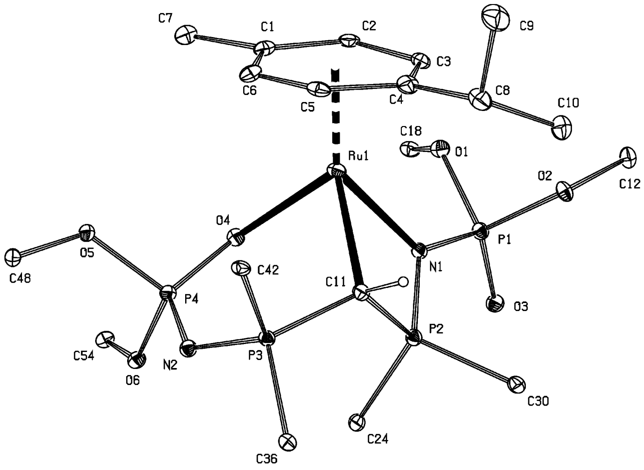


Figure 2. ORTEP-type view of the structure of the cation $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3(C,N,O)\text{-}CH[P\{{=}NP({=}O)(OPh)_2\}Ph_2]_2)]^+$ (**5a**), showing the crystallographic labeling scheme. Phenyl groups and hydrogen atoms (except that on the C(11) carbon) have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru−N(1) = 2.164(4); Ru−C(11) = 2.228(5); Ru−O(4) = 2.154(3); Ru−C* = 1.679(1); C(11)−P(2) = 1.786(5); P(2)−N(1) = 1.623(4); N(1)−P(1) = 1.610(4); P(1)−O(1) = 1.593(4); P(1)−O(2) = 1.584(4); P(1)−O(3) = 1.458(4); C(11)−P(3) = 1.779(5); P(3)−N(2) = 1.593(4); N(2)−P(4) = 1.569(4); P(4)−O(4) = 1.485(3); P(4)−O(5) = 1.596(3); P(4)−O(6) = 1.575(4); C*−Ru−N(1) = 134.84(1); C*−Ru−C(11) = 134.86(1); C*−Ru−O(4) = 125.30(1); C(11)−Ru−N(1) = 71.59(17); C(11)−Ru−O(4) = 87.44(16); N(1)−Ru−O(4) = 83.20(14); Ru−C(11)−P(2) = 91.1(2); C(11)−P(2)−N(1) = 97.7(2); P(2)−N(1)−Ru = 98.13(19); P(2)−N(1)−P(1) = 128.4(3); Ru−N(1)−P(1) = 138.8(2); N(1)−P(1)−O(1) = 105.5(2); N(1)−P(1)−O(2) = 104.2(2); N(1)−P(1)−O(3) = 115.3(2); Ru−C(11)−P(3) = 113.5(3); P(2)−C(11)−P(3) = 122.4(3); C(11)−P(3)−N(2) = 115.0(2); P(3)−N(2)−P(4) = 127.7(3); N(2)−P(4)−O(4) = 119.8(2); N(2)−P(4)−O(5) = 111.2(2); N(2)−P(4)−O(6) = 104.6(2); P(4)−O(4)−Ru = 127.6(2). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

Synthesis of Ruthenium(II) Carbene Complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2)]$ (R = Ph (6a), Et (6b)) and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2])]$ (6c). Although the double deprotonation of the methylenic PCH_2P groups in bis(iminophosphorano)methane derivatives **2a**−**c** failed, the attachment of the bis(iminophosphorano)methanide anions **3a**−**c** at the (η^6-arene)ruthenium(II) center enhances the acidity of the methynic PCHP hydrogen, promoting its deprotonation. Thus, the treatment of complexes **4a**−**c** with NaH, in THF at room temperature, generates the carbene derivatives $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2)]$ (R = Ph (**6a**), Et (**6b**)) and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2])]$ (**6c**), isolated as air-stable violet solids in 78−82% yield (Scheme 4). Compounds **6a**−**c** can be also prepared in similar yields from cationic species **5a**−**c′** by reaction with NaH in THF at room temperature (Scheme 4). We note that **6c** is selectively formed, starting from a mixture of the isomers **5c** and **5c′**. It is apparent that the formation of the carbenic metallacycle

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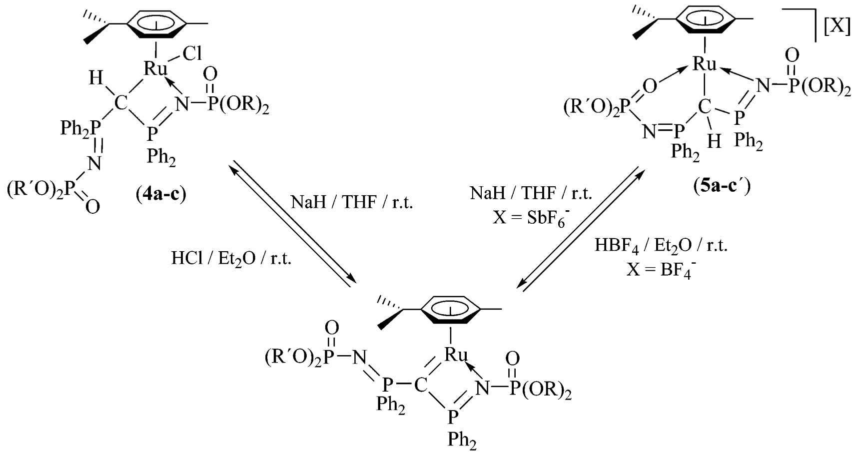
[19] Variable-temperature $^{31}P\{^1H\}$ NMR spectra of the mixture **5c**/**5c′** (from −30 to 80 °C) in CD_3CN show that the ratio is temperature dependent (ca. 1:2 and 1:1 at −30 and 80 °C, respectively). This is also in accord with the hemilabile properties of the iminophosphorane $-Ph_2P{=}NP({=}O)(OR)_2$ fragments.

[20] See for example: Seddon, E. A.; Seddon, K. R. In *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984 and references therein.

Scheme 4



R = R′ = Ph (**6a**), Et (**6b**)
R = Et, R′ = Ph (**6c**)

in which the iminophosphorane group bearing the more basic phosphoryl substituent $-P(=O)(OEt)_2$ is coordinated to ruthenium is preferred.

Compounds **6a**−**c** have been characterized by elemental analyses and IR and NMR (^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}) spectroscopy (see the Experimental Section). Thus, the deprotonation of the bis(iminophosphorano)methanide ligands is clearly confirmed by the absence of methinic PCHP signals in the ^{1}H NMR spectra. Moreover, an unambiguous characterization of the complex [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OPh)$_2$}Ph$_2$]$_2$)] (**6a**) by single-crystal X-ray analysis was undertaken (see Figure 3 and caption).[21] The molecular structure shows a formally pentacoordinated ruthenium atom, which is bonded to the *p*-cymene unit acting as a η^6 ligand, the nitrogen atom of one of the iminophosphorane groups, and a carbenic PCP carbon. The Ru−C(11) bond length (1.976(6) Å), which is ca. 0.25 Å shorter than that found in **5a**, is in accord with the multiple-bond character expected for a metal carbene.[22,23] Remarkably, in contrast to the classical “pincer” (**A**) or bridging (**B**) coordination modes (see Chart 1), the bis(iminophosphorano)methanediide units in **6a**−**c** coordinate via a single four-membered C,N-chelate ring.[24] We also note that, with the exception of the Ru−C(11) bond length, distances within the four-membered metallacycle in **6a** are only slightly altered in comparison with the related values in **5a** (ca. ±0.06 Å), suggesting weak contribution of its ylidic resonance form (see Chart 4).[25]

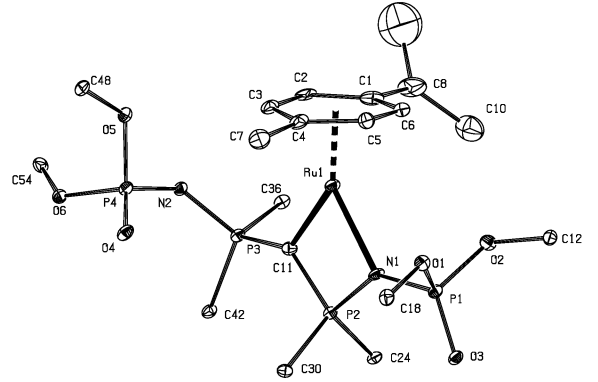


Figure 3. ORTEP-type view of the structure of [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OPh)$_2$}Ph$_2$]$_2$)] (**6a**), showing the crystallographic labeling scheme. Phenyl groups and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru−N(1) = 2.140(5); Ru−C(11) = 1.976(6); Ru−C* = 1.679(1); C(11)−P(2) = 1.717(6); P(2)−N(1) = 1.628(5); N(1)−P(1) = 1.597(5); P(1)−O(1) = 1.596(4); P(1)−O(2) = 1.597(4); P(1)−O(3) = 1.464(4); C(11)−P(3) = 1.738(6); P(3)−N(2) = 1.587(5); N(2)−P(4) = 1.567(5); P(4)−O(4) = 1.468(4); P(4)−O(5) = 1.617(5); P(4)−O(6) = 1.600(4); C*−Ru−N(1) = 140.75(1); C*−Ru−C(11) = 144.66(1); C(11)−Ru−N(1) = 74.6(2); Ru−C(11)−P(2) = 96.0(3); C(11)−P(2)−N(1) = 96.6(3); P(2)−N(1)−Ru = 92.7(2); Ru−N(1)−P(1) = 131.5(3); P(2)−N(1)−P(1) = 135.7(3); N(1)−P(1)−O(1) = 108.0(3); N(1)−P(1)−O(2) = 102.4(3); N(1)−P(1)−O(3) = 117.4(3); Ru−C(11)−P(3) = 128.6(4); P(2)−C(11)−P(3) = 134.6(4); C(11)−P(3)−N(2) = 116.6(3); P(3)−N(2)−P(4) = 132.8(3); N(2)−P(4)−O(4) = 121.7(3); N(2)−P(4)−O(5) = 101.7(3); N(2)−P(4)−O(6) = 109.1(3). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

DFT Calculations. To interpret the nature of the Ru=C bond in the carbene complexes **6a**−**c**, the electronic structures of the complexes described in this work have been investigated by means of B3LYP/DFT calculations.[26,27] The compounds [RuCl(η^6-C$_6$H$_6$)(κ^2(*C,N*)-CH-

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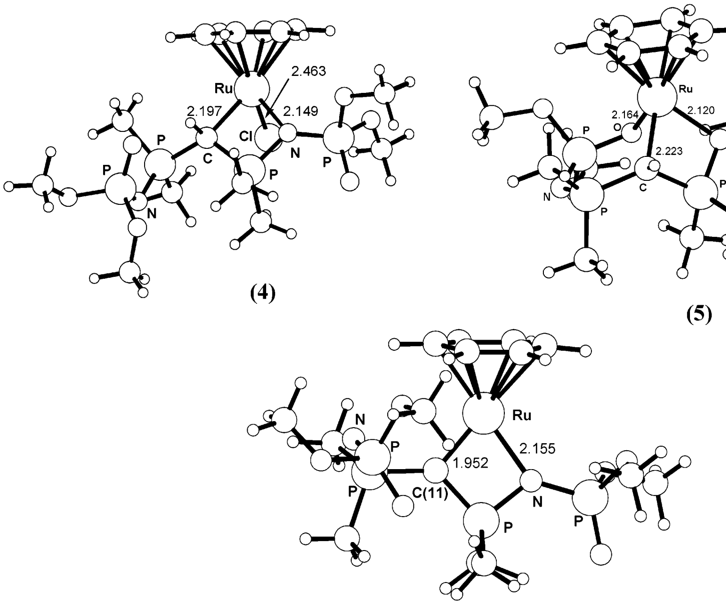
[21] The crystals measured contain two molecules in the asymmetric unit with very similar structural parameters. For brevity, only one conformer is represented in Figure 3 and only its bond distances and angles are presented.

[22] Typical Ru=C double-bond distances fall in the range 1.8−2.0 Å. For instance, bond distances in the well-known Grubbs carbenes [Ru(=CHR)Cl$_2$(PCy$_3$)$_2$] are 1.851(21) Å (R = CH=CPh$_2$) and 1.839(3) Å (R = *p*-C$_6$H$_4$Cl): (a) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

[23] No ^{13}C{^{1}H} NMR signal was observed for the Ru=C carbon atoms, despite trials with long acquisition periods.

[24] The related carbene species [Pt(κ^2(*C,N*)-C{P(=NSiMe$_3$)Ph$_2$}$_2$)(COD)] has been recently reported: (a) Jones, N. D.; Lin, G.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Organometallics* **2003**, *22*, 2832. (b) Lin, G.; Jones, N. D.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4054. The bis(iminophosphorano)methaniide fragment [C{P(=NSiMe$_3$)Ph$_2$}$_2$]$^{2-}$ also presents a κ^2(C,N) coordination mode in the bis(germavinylidene) [(Me$_3$SiN=PPh$_2$)$_2$C=Ge→Ge=C(Ph$_2$P=NSiMe$_3$)$_2$] and the chalcogen-bridged dimers [(Me$_3$SiN=PPh$_2$)$_2$C=Ge(μ-X)]$_2$ (X = S, Se, Te). See ref 8 and: (c) Leung, W.-P.; So, C.-W.; Wang, Z.-X.; Wang, J.-Z.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4305.

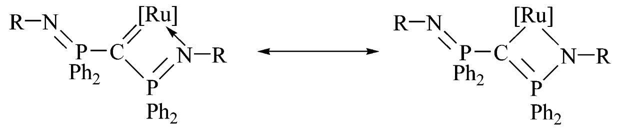
[25] An important ylidic contribution has been proposed for “pincer” carbene complexes [MCl$_2$(κ^2(*C,N*)-C{P(=NSiMe$_3$)R$_2$}$_2$)] (M = Ti, Zr, Hf, Sm; R = Ph, Cy).[3,4]



(6)

Figure 4. Optimized geometries (B3LYP) for the complexes $[RuCl(\eta^6\text{-}C_6H_6)(\kappa^2(C,N)\text{-}CH[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]$ (**4**), $[Ru(\eta^6\text{-}C_6H_6)(\kappa^3(C,N,O)\text{-}CH[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]^+$ (**5**), and $[Ru(\eta^6\text{-}C_6H_6)(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]$ (**6**), with the more relevant bond distances (Å) around the metal.

Chart 4



$[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]$ (**4**), $[Ru(\eta^6\text{-}C_6H_6)(\kappa^3(C,N,O)\text{-}CH[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]^+$ (**5**), and $[Ru(\eta^6\text{-}C_6H_6)\text{-}(\kappa^2(C,N)\text{-}C[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2)]$ (**6**) were used as models for complexes **4a**−**c**, **5a**−**c**′, and **6a**−**c**, respectively, the *p*-cymene ligand being replaced by benzene and the phenyl substituents by methyl groups (see Computational Details). Figure 4 shows the calculated structures and the more relevant distances (Tables S1−S3, giving atomic coordinates, are provided in the Supporting Information).

The fully optimized geometries obtained for complexes **5** and **6** compare very well with the experimental X-ray structures of compounds **5a** and **6a**. In complex **5**, the $\kappa^3(C,N,O)$ coordination of the bis(iminophosphorane)methanide ligand results in a three-legged piano-stool geometry, forming a metallabicyclic structure. In complex **6**, the $C[P\{{=}NP({=}O)(OMe)_2\}Me_2]_2$ ligand acts as a bidentate ligand, leading to a four-membered metallacyclic carbene coordinated by C and N, and the overall geometry corresponds to a two-legged piano stool. The agreement between the calculated and experimental structures is also reflected by mean and maximum absolute deviations of the relevant bond distances around the metal coordination sphere of 0.03 and 0.06 Å for **5** and 0.04 and 0.07 Å for **6**, respectively.

The optimized structure for complex **4** (Figure 4), for which no X-ray structure could be obtained, corresponds to a three-legged piano-stool geometry in which the ruthenium atom is bonded to a η^6-benzene unit, a chloride anion, and a $\kappa^2(C,N)$-coordinated bis(iminophosphorane)methanide ligand. The resulting four-membered metallacycle, at first sight similar to that found in the carbene complex **6**, is consistent with the structure proposed above for complexes **4a**−**c** on the basis of NMR data.

Although both complexes **4** and **5** bear a four-membered Ru−C−P−N metallacycle, it is interesting to note that the corresponding Ru−C and Ru−N bond lengths are different (see Chart 5). Thus, the Ru−C bond is shorter in complex **4** than that in **5** (2.197 vs 2.223 Å) while the opposite occurs with the Ru−N distance (2.149 Å vs 2.120 Å). This behavior is supported on electronic grounds, since the Wiberg indices (WI), well-known as bond strength indicators,[28] decrease from 0.567 (**4**) to 0.529 (**5**) for the Ru−C bond, while the corresponding Ru−N values rise from 0.407 (**4**) to 0.430 (**5**). Therefore, in complex **5**, the longer and weaker Ru−C bond is balanced by the shorter and stronger Ru−N bond. The opposite occurs in complex **4**. This probably arises from the constrained $\kappa^3(C,N,O)$ coordination of the bis(iminophosphorane)methanide ligand in **5**, where the pivotal Ru−C central bond adapts to the stereochemical requirements of the metallabicycle upon forming the Ru−O and Ru−N bonds. In compound **4**, there is no Ru−O bond, and the open metallacycle originates a less constrained structure.

The (η^6-benzene)Ru fragments are essentially equivalent in the three complexes **4**−**6**, as shown by the same mean distance between the metal and the six coordinating carbon atoms for all species (2.25 Å). The electronic delocalization along the P−N−P frame of each iminophosphorano arm of the ligand, discussed above on the basis of experimental data, is also a common feature of the ligands in the three model complexes. In all the

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(27) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.

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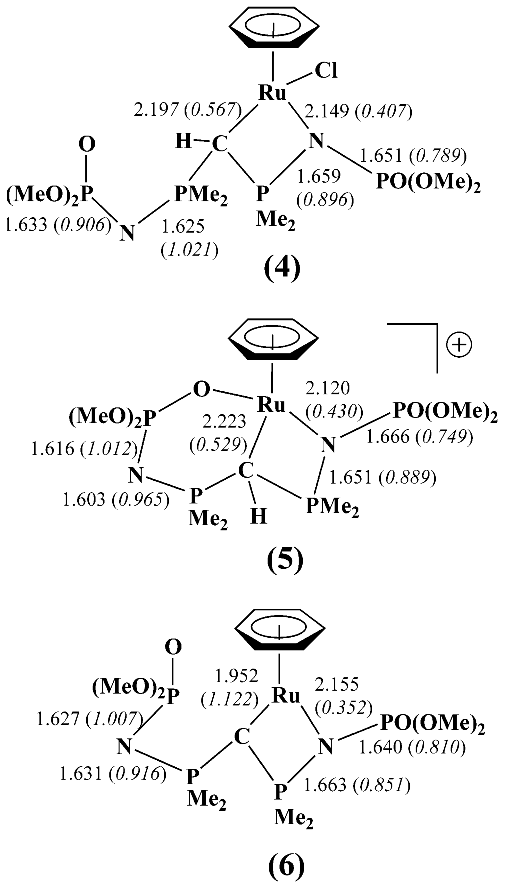
Chart 5. More Relevant Distances and Wiberg Indices (in Italics) for 4−6



optimized structures, the maximum difference between the lengths of the two adjacent N−P bond distances is 0.02 Å, showing from a structural point of view that the two N−P bonds are similar and suggesting a high degree of electronic delocalization. This view is further confirmed, from an electronic point of view, by the corresponding Wiberg indices, which only deviate up to 0.14 for the same two adjacent N−P bonds, in the three species **4**−**6**. This discussion is related with the two resonance forms for complexes **6a**−**c** depicted in Chart 4. The experimental C(11)−P distances obtained in the X-ray structure of complex **6a** suggest a minimum contribution of the ylidic form (see above), as do the calculations. In fact, the two C(11)−P bond lengths in the optimized structure of **6** differ by only 0.02 Å, and the corresponding Wiberg indices are within 0.08, indicating that the C−P bonds are essentially equivalent. These data also show that the ylidic PC=P form is negligible in the description of the bonding around the carbon.

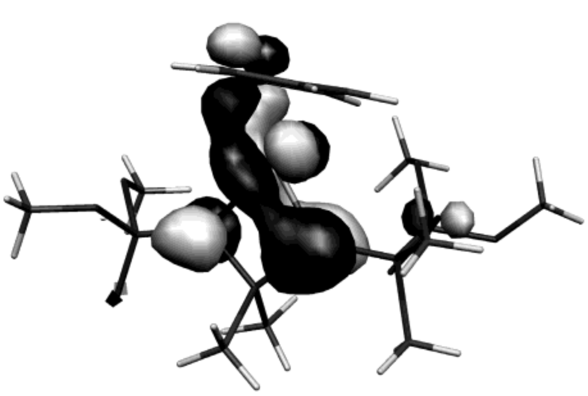


Figure 5. 3D representation of the HOMO of the complex $[Ru(\eta^6\text{-}C_6H_6)(\kappa^2(C,N)\text{-}C[P\{=NP(=O)(OMe)_2\}Me_2]_2)]$ (**6**).

In contrast to **4** and **5**, complex **6** appears to be coordinatively unsaturated. As a matter of fact, the Ru−C bond distance in complex **6** is much shorter (1.952 Å) than in **4** and **5** (2.197 and 2.223 Å, respectively). This bond is also stronger, according to the Wiberg indexes, which range from 1.122 in **6** to 0.567 in **4** and 0.529 in **5**, thus confirming the carbenic character of the Ru=C(11) bond in complex **6**. These parameters (bond lengths and WI values) can be compared to those calculated, at the same theory level, for the Ru=C bond in complexes $[Ru(\eta^5\text{-}C_5H_5)(C_4H_4)X]^{n+}$ ($n = 0$, X = Cl; $n = 1$, X = PH$_3$, CO, NCH), where the two Ru−C bonds within the RuC$_4$ metallacyclopentatriene fragment have a carbenic nature ($d_{C-C} = 1.94-1.97$ Å and WI = 0.95−1.07).[29] The carbenic character of the Ru=C(11) bond in **6** is further confirmed by the nature of the HOMO (highest occupied molecular orbital), represented in Figure 5. This orbital is mainly localized on the metal and the C and N donor atoms of the ligand, and it describes the π bonding component of the Ru=C double bond, with a smaller π^* antibonding (N−Ru) contribution of the nitrogen.

Charges in the carbon atom of the carbenic bond of model **6** can be calculated from a Natural Population Analysis (NPA),[30] and can also shed light on the electronic nature of the carbene group in complexes **6a**−**c**. In order for them to be meaningful, the model carbene complexes $[Ru\{=C(OH)_2\}(PMe_3)_2(CO)_2]$ (**7**) and $[RuCl_2(=CH_2)(PMe_3)_2]$ (**8**) have been studied for comparison. The former can be taken as a typical electrophilic carbene (Fischer type), while the latter (belonging to the well-known family of Grubbs catalysts)[22] represents a nucleophilic carbene. Some important bond lengths from their optimized geometries are given in Figure 6. The Ru=C bond is much longer in the heteroatomic carbene **7** ($d_{Ru=C} = 2.026$ Å) than in **8** ($d_{Ru=C} = 1.807$ Å). More interestingly, the charges on the carbenic carbon atoms reveal a clearly positive carbon in the electrophilic carbene complex **7** ($C_C = 0.386$) and an electron-rich carbon in the nucleophilic carbene **8** ($C_C = -0.015$). Although the calculated and experimental Ru=C bond distances in the model **6** (1.952 Å) and complex **6a** (1.976(6) Å; see Figure 3) are intermediate between the two previous calculated values, the charge at the carbon

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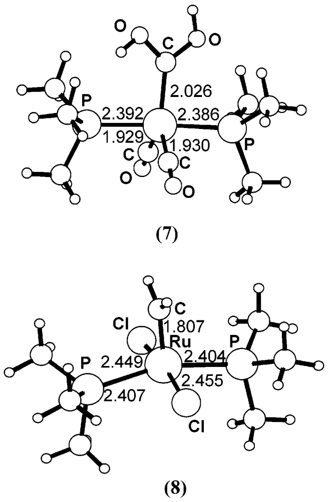

Figure 6. Optimized structures (B3LYP) of [Ru{$=$C(OH)$_2$}(PMe$_3$)$_2$(CO)$_2$] (**7**) and [RuCl$_2$($=$CH$_2$)(PMe$_3$)$_2$] (**8**), with the more relevant bond distances around the metal.

in **6** is clearly negative ($C_C = -1.191$), emphasizing the nucleophilic character of the carbene in complexes **6a**−**c**. In agreement with this theoretical prediction, we have experimentally found that protonation of complexes **6a**−**c** with HCl or HBF$_4$ takes place selectively on the carbenic carbon, regenerating compounds **4a**−**c** and **5a**−**c′**, respectively (see Scheme 4).

Since ^{13}C NMR spectroscopy can also be used to identify carbenic carbon atoms, the carbon chemical shifts of **6** have been calculated using the gauge-independent atomic orbital method (GIAO).[31,32] The most significant features concern the calculated values of C(11) and the benzene carbon nuclei, which are located at δ 119 and 90 (mean value) ppm, respectively. While the latter value falls in the experimental range measured for the coordinated carbon atoms of the *p*-cymene ring in complexes **6a**−**c** (δ 80−99 ppm), the former value is located close to the chemical shifts observed experimentally for the resonances arising from the aromatic carbons (δ 120−137 ppm). This is in agreement with the fact that no signal could be experimentally observed for the Ru$=$C carbon nuclei in **6a**−**c**,[23] which probably is overlapped. Although carbenic Ru$=$C carbon nuclei typically resonate at 250−350 ppm, the unusual upfield chemical shift calculated for the Ru$=$C carbon in **6** may be explained on the basis of either the electronic influence of the phosphorus substituents or the constrained geometry of the four-membered carbene metallacycle.[3a,c]

In summary, in this work novel ruthenium(II) carbene complexes have been prepared via the sequential double deprotonation of bis(iminophosphorano)methane derivatives. These unusual carbenes belong to a scarce series of transition-metal complexes in which the carbene moiety is part of a four-membered chelate ligand in a κ^2(C,N) coordination mode (Chart 1; **A**).[3−5,24] DFT studies shed light on the electronic nature of the carbene group. Both calculated negative charges and the HOMO distribution on the carbenic carbon atom reveal its nucleophilic character. In accord with this, protonation reactions take place at the carbene moiety. Reactivity studies aimed at understanding the role of analogous bis(iminophosphorano)methanes in stabilizing these atypical carbene moieties are currently in progress.

Experimental Section

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 the compounds Ph$_2$PCH$_2$P{$=$NP($=$O)(OR)$_2$}Ph$_2$ (R = Ph (**1a**), R = Et (**1b**)),[9c] [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$],[33] and (EtO)$_2$P($=$O)N$_3$,[34] which were prepared by following the methods described 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. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 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 in this paper.

Synthesis of CH$_2$[P{$=$NP($=$O)(OR)$_2$}Ph$_2$]$_2$ (R = Ph (2a), Et (2b)). Method A. A solution of bis(diphenylphosphino)methane (2 g, 5.2 mmol) in 80 mL of THF was treated, at room temperature, with the corresponding azide (RO)$_2$P($=$O)N$_3$ (10.6 mmol) for 6 h. The solvent was then removed under reduced pressure to give a colorless oil. A microcrystalline white solid was obtained by slow diffusion of *n*-pentane into a saturated solution of the crude reaction mixture in CH$_2$Cl$_2$ at room temperature. **2a**: yield 86% (3.93 g). Anal. Calcd for C$_{49}$H$_{42}$O$_6$P$_4$N$_2$: C, 66.97; H, 4.82; N, 3.19. Found: C, 66.72; H, 4.90; N, 3.10. IR (KBr, cm^{-1}): ν 503 (s), 576 (s), 616 (m), 689 (s), 764 (m), 802 (m), 936 (s), 1000 (m), 1027 (m), 1072 (m), 1111 (s), 1181 (vs), 1297 (vs), 1439 (s), 1455 (m), 1481 (s), 1598 (s), 2983 (m), 3057 (m). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −6.79 (m, (PhO)$_2$P$=$O), 11.48 (m, Ph$_2$P$=$N) ppm; AA'XX' spin system. ^{1}H NMR (CDCl$_3$): δ 4.60 (t, 2H, $^2J_{HP}$ = 14.9 Hz, PCH$_2$P), 7.04−7.46 (m, 28H, Ph), 7.71−7.81 (m, 12H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 28.39 (t, $^1J_{CP}$ = 54.6 Hz, PCH$_2$P), 120.18−132.22 (m, Ph), 151.97 (d, $^2J_{CP}$ = 7.1 Hz, C$_{ipso}$ of OPh) ppm. **2b**: yield 81% (2.89 g). Anal. Calcd for C$_{33}$H$_{42}$O$_6$P$_4$N$_2$: C, 57.73; H, 6.16; N, 4.08. Found: C, 57.66; H, 5.99; N, 4.00. IR (KBr, cm^{-1}): ν 497 (s), 540 (s), 617 (w), 643 (w), 696 (s), 734 (s), 759 (s), 798 (s), 843 (m), 962 (vs), 1038 (vs), 1109 (s), 1200 (vs), 1311 (vs), 1367 (m), 1391 (m), 1444 (s), 1484 (m), 1590 (w), 1627 (w), 2899 (m), 2944 (m), 2983 (s), 3059 (m). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 4.09 (m, (EtO)$_2$P$=$O), 9.72 (m, Ph$_2$P$=$N) ppm; AA'XX' spin system. ^{1}H NMR (CDCl$_3$): δ 1.19 (t, 12H, $^3J_{HH}$ = 7.1 Hz, OCH$_2$C*H*$_3$), 3.87 (m, 8H, OC*H*$_2$CH$_3$), 4.63 (t, 2H, $^2J_{HP}$ = 15.1 Hz, PCH$_2$P), 7.29−7.86 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 16.17 (d, $^3J_{CP}$ = 7.6 Hz, OCH$_2$*C*H$_3$), 27.78 (t, $^1J_{CP}$ = 53.3 Hz, PCH$_2$P), 61.41 (d, $^2J_{CP}$ = 6.4 Hz, O*C*H$_2$CH$_3$), 128.17−131.89 (m, Ph) ppm.

Method B. A solution of the corresponding iminophosphorane−phosphine Ph$_2$PCH$_2$P{$=$NP($=$O)(OR)$_2$}Ph$_2$ (**1a**,**b**; 5 mmol) in 80 mL of THF was treated, at room temperature, with the

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(32) This method has proved to be successful in determining the coordination modes of pyrrolyl ligands in Zr and W organometallic complexes, by comparison with experimental data: (a) Dias, A. R.; Ferreira, A. P.; Veiros, L. F. *Organometallics* **2003**, *22*, 5114. (b) Ascenso, J. R.; Dias, A. R.; Ferreira, A. P.; Galvão, A. C.; Salema, M. S.; Veiros, L. F. *Inorg. Chim. Acta* **2003**, *356*, 249.

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appropriate azide $\mathrm{(RO)_2P({=}O)N_3}$ (5.2 mmol) for 4 h. Workup as described in method A allows the isolation of compounds **2a**,**b** in 84 and 78% yields, respectively.

Synthesis of $\mathbf{CH_2[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2]}$ (2c). A solution of the iminophosphorane−phosphine $\mathrm{Ph_2PCH_2P\{{=}NP({=}O)(OEt)_2\}Ph_2}$ (**1b**; 1 g, 1.87 mmol) in 60 mL of THF was treated, at room temperature, with $\mathrm{(PhO)_2P({=}O)N_3}$ (0.55 g, 2 mmol) for 4 h. The solvent was then removed under reduced pressure to give a colorless oil. A microcrystalline white solid was obtained by slow diffusion of *n*-pentane into a saturated solution of the crude reaction mixture in $\mathrm{CH_2Cl_2}$ at room temperature. Yield: 75% (1.10 g). Anal. Calcd for $\mathrm{C_{41}H_{42}O_6P_4N_2}$: C, 62.92; H, 5.41; N, 3.58. Found: C, 62.90; H, 5.71; N, 3.59. IR (KBr, $\mathrm{cm^{-1}}$): ν 505 (s), 616 (w), 690 (s), 772 (m), 797 (s), 920 (s), 1035 (s), 1057 (s), 1108 (s), 1189 (vs), 1271 (vs), 1439 (s), 1481 (s), 1483 (s), 1590 (s), 2897 (m), 2926 (m), 2976 (m), 3057 (m). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ −6.42 (d, $^2J_{PP} = 32.9$ Hz, $\mathrm{(PhO)_2P{=}O}$), 4.03 (d, $^2J_{PP} = 29.8$ Hz, $\mathrm{(EtO)_2P{=}O}$), 9.32 (dd, $^2J_{PP} = 29.8$ and 16.2 Hz, $\mathrm{Ph_2}P\mathrm{{=}NP({=}O)(OEt)_2}$), 11.86 (dd, $^2J_{PP} = 32.9$ and 16.2 Hz, $\mathrm{Ph_2}P\mathrm{{=}NP({=}O)(OPh)_2}$) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.20 (t, 6H, $^3J_{HH} = 7.1$ Hz, $\mathrm{OCH_2C}H_3$), 3.87 (m, 4H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.61 (dd, 2H, $^2J_{HP} = 15.2$ and 15.2 Hz, $\mathrm{PCH_2P}$), 7.06−7.81 (m, 30H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 16.53 (d, $^3J_{CP} = 7.6$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 28.38 (dd, $^1J_{CP} = 54.2$ and 54.2 Hz, $\mathrm{PCH_2P}$), 61.83 (d, $^2J_{CP} = 6.4$ Hz, $\mathrm{O}C\mathrm{H_2CH_3}$), 120.76−132.68 (m, Ph), 152.64 (d, $^2J_{CP} = 7.6$ Hz, $\mathrm{C_{ipso}}$ of OPh) ppm.

Synthesis of $\mathbf{NaCH[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2}$ (R = Ph (3a), Et (3b)) and $\mathbf{NaCH[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2]}$ (3c). A solution of the corresponding bis(iminophosphorano)methane **2a**−**c** (1 mmol) in 30 mL of THF was treated, at room temperature, with NaH (0.24 g, 10 mmol) for 30 min. The solvent was then evaporated to dryness and the residue dissolved in diethyl ether (ca. 30 mL). The resulting suspension was filtered through Kieselguhr and the filtrate evaporated to dryness, giving **3a**−**c** as colorless oils in almost quantitative yield. **3a**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −8.99 (m, $\mathrm{(PhO)_2P{=}O}$), 16.29 (m, $\mathrm{Ph_2P{=}N}$) ppm; AA'XX' spin system. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.29 (broad, 1H, PCHP), 6.81−7.81 (m, 40H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ 19.41 (t, $^1J_{CP} = 25.8$ Hz, PCHP), 121.75−132.55 (m, Ph), 153.46 (d, $^2J_{CP} = 11.7$ Hz, $\mathrm{C_{ipso}}$ of OPh) ppm. **3b**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ 1.33 (m, $\mathrm{(EtO)_2P{=}O}$), 14.47 (m, $\mathrm{Ph_2P{=}N}$) ppm; AA'XX' spin system. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.11 (t, 12H, $^3J_{HH} = 6.9$ Hz, $\mathrm{OCH_2C}H_3$), 2.02 (broad, 1H, PCHP), 3.87 (m, 8H, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.15−8.36 (m, 20H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ 17.27 (d, $^3J_{CP} = 8.0$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 19.95 (t, $^1J_{CP} = 34.5$ Hz, PCHP), 61.68 (d, $^2J_{CP} = 4.8$ Hz, $\mathrm{O}C\mathrm{H_2CH_3}$), 128.38−141.39 (m, Ph) ppm. **3c**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −9.24 (d, $^2J_{PP} = 22.0$ Hz, $\mathrm{(PhO)_2P{=}O}$), 2.07 (d, $^2J_{PP} = 14.7$ Hz, $\mathrm{(EtO)_2P{=}O}$), 14.76 (dd, $^2J_{PP} = 24.4$ and 14.7 Hz, $\mathrm{Ph_2}P\mathrm{{=}NP({=}O)(OEt)_2}$), 16.25 (dd, $^2J_{PP} = 24.4$ and 22.0 Hz, $\mathrm{Ph_2}P\mathrm{{=}NP({=}O)(OPh)_2}$) ppm. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.97 (t, 6H, $^3J_{HH} = 6.9$ Hz, $\mathrm{OCH_2C}H_3$), 2.16 (broad, 1H, PCHP), 3.89 (m, 4H, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.78−8.02 (m, 30H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ 14.85 (d, $^3J_{CP} = 8.0$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.10 (dd, $^1J_{CP} = 34.4$ and 34.4 Hz, PCHP), 60.04 (d, $^2J_{CP} = 6.3$ Hz, $\mathrm{O}C\mathrm{H_2CH_3}$), 119.71−137.37 (m, Ph), 152.03 (d, $^2J_{CP} = 8.0$ Hz, $\mathrm{C_{ipso}}$ of OPh) ppm. Compounds **3a**−**c** were too sensitive to moisture to give satisfactory elemental analyses.

Synthesis of [RuCl(η^6-*p*-cymene)(κ^2(*C,N*)-$\mathbf{CH[P\{{=}NP({=}O)(OR)_2\}Ph_2]_2}$)] (R = Ph (4a), Et (4b)) and [RuCl(η^6-*p*-cymene)(κ^2(*C,N*)-$\mathbf{CH[P\{{=}NP({=}O)(OPh)_2\}Ph_2][P\{{=}NP({=}O)(OEt)_2\}Ph_2]}$)] (4c). To a solution of [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] (0.150 g, 0.245 mmol) in 30 mL of toluene was added, at room temperature, the corresponding bis(iminophosphorano)methanide compound **3a**−**c** (0.6 mmol), and the reaction mixture was refluxed for 1 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. 5 mL) followed by the addition of hexanes (ca. 50 mL) precipitated an orange solid, which was filtered, washed with hexanes (3 × 10 mL), and dried in vacuo. **4a**: yield 70% (0.394 g). Anal. Calcd for $\mathrm{RuC_{59}H_{55}O_6P_4N_2Cl}$: C, 61.70; H, 4.83; N, 2.44. Found: C, 61.42; H, 4.78; N, 2.24. IR (KBr, $\mathrm{cm^{-1}}$): ν 525 (m), 577 (m), 616 (m), 748 (s), 797 (s), 916 (vs), 1025 (s), 1071 (s), 1102 (vs), 1144 (vs), 1195 (vs), 1260 (s), 1436 (s), 1489 (s), 1591 (s), 2961 (w), 3055 (w). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): δ −8.59 (d, $^2J_{PP} = 40.6$ Hz, $\mathrm{(PhO)_2P{=}O}$), −2.15 (dd, $^2J_{PP} = 12.6$ Hz, $^4J_{PP} = 7.2$ Hz, $\mathrm{Ru{-}NP({=}O)(OPh)_2}$), 21.90 (ddd, $^2J_{PP} = 40.6$ and 4.7 Hz, $^4J_{PP} = 7.2$ Hz, $\mathrm{Ph_2P{=}N}$), 64.26 (dd, $^2J_{PP} = 12.6$ and 4.7 Hz, $\mathrm{Ru{-}N{=}PPh_2}$) ppm. ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): δ 1.12 (d, 3H, $^3J_{HH} = 6.8$ Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.38 (d, 3H, $^3J_{HH} = 7.1$ Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 2.40 (s, 3H, $\mathrm{CH_3}$), 2.85 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.22 (m, 1H, PCHP), 4.77 and 6.41 (d, 1H each, $^3J_{HH} = 5.7$ Hz, CH of *p*-cymene), 5.79 and 6.04 (d, 1H each, $^3J_{HH} = 6.2$ Hz, CH of *p*-cymene), 6.98−8.58 (m, 40H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): δ 4.02 (dddd, $^1J_{CP} = 93.2$ and 62.5 Hz, $^3J_{CP} = 19.2$ and 11.4 Hz, PCHP), 18.78 (s, $\mathrm{CH_3}$), 22.52 and 22.75 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 31.42 (s, $C\mathrm{H(CH_3)_2}$), 74.38, 82.00, 83.22 and 87.59 (s, CH of *p*-cymene), 92.17 and 107.76 (s, C of *p*-cymene), 120.02−136.53 (m, Ph), 152.24 (d, $^2J_{CP} = 7.8$ Hz, $\mathrm{C_{ipso}}$ of OPh), 153.07 and 153.70 (d, $^2J_{CP} = 7.2$ Hz, $\mathrm{C_{ipso}}$ of OPh), 153.79 (d, $^2J_{CP} = 6.6$ Hz, $\mathrm{C_{ipso}}$ of OPh) ppm. **4b**: yield 69% (0.322 g). Anal. Calcd for $\mathrm{RuC_{43}H_{55}O_6P_4N_2Cl}$: C, 54.00; H, 5.80; N, 2.93. Found: C, 54.12; H, 5.89; N, 3.07. IR (KBr, $\mathrm{cm^{-1}}$): ν 509 (s), 536 (s), 588 (m), 694 (s), 732 (s), 799 (s), 980 (s), 1050 (vs), 1109 (s), 1141 (s), 1202 (s), 1238 (s), 1389 (m), 1437 (s), 1482 (m), 1588 (m), 1591 (s), 1639 (m), 2901 (w), 2976 (w), 3053 (w). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −1.75 (d, $^2J_{PP} = 37.2$ Hz, $\mathrm{(EtO)_2P{=}O}$), 7.47 (dd, $^2J_{PP} = 12.6$ Hz, $^4J_{PP} = 6.3$ Hz, $\mathrm{Ru{-}NP({=}O)(OEt)_2}$), 17.80 (ddd, $^2J_{PP} = 37.2$ and 2.7 Hz, $^4J_{PP} = 6.3$ Hz, $\mathrm{Ph_2P{=}N}$), 61.40 (dd, $^2J_{PP} = 12.6$ and 2.7 Hz, $\mathrm{Ru{-}N{=}PPh_2}$) ppm. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.87 and 1.19 (t, 3H each, $^3J_{HH} = 6.8$ Hz, $\mathrm{OCH_2C}H_3$), 1.03 (d, 3H, $^3J_{HH} = 6.9$ Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.12 (t, 3H, $^3J_{HH} = 7.3$ Hz, $\mathrm{OCH_2C}H_3$), 1.15 (d, 3H, $^3J_{HH} = 6.8$ Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.20 (t, 3H, $^3J_{HH} = 6.0$ Hz, $\mathrm{OCH_2C}H_3$), 2.34 (s, 3H, $\mathrm{CH_3}$), 3.02 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.38 (m, 1H, PCHP), 4.05 (m, 8H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.62 and 6.59 (d, 1H each, $^3J_{HH} = 5.3$ Hz, CH of *p*-cymene), 5.66 and 6.09 (d, 1H each, $^3J_{HH} = 5.9$ Hz, CH of *p*-cymene), 6.74−8.77 (m, 20H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ 2.10 (dddd, $^1J_{CP} = 95.8$ and 60.0 Hz, $^3J_{CP} = 18.6$ and 10.6 Hz, PCHP), 16.17 and 16.67 (d, $^3J_{CP} = 7.8$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.57 (d, $^3J_{CP} = 6.6$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.91 (d, $^3J_{CP} = 8.0$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 18.59 (s, $\mathrm{CH_3}$), 22.06 and 22.85 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 31.02 (s, $C\mathrm{H(CH_3)_2}$), 61.18, 61.39, 61.82, and 62.48 (d, $^2J_{CP} = 5.4$ Hz, $\mathrm{O}C\mathrm{H_2CH_3}$), 73.56, 80.16, 83.68, and 87.77 (s, CH of *p*-cymene), 90.28 and 108.66 (s, C of *p*-cymene), 127.56−137.90 (m, Ph) ppm. **4c**: yield 68% (0.351 g). Anal. Calcd for $\mathrm{RuC_{51}H_{55}O_6P_4N_2Cl}$: C, 58.21; H, 5.27; N, 2.66. Found: C, 58.02; H, 5.18; N, 2.39. IR (KBr, $\mathrm{cm^{-1}}$): ν 500 (s), 577 (s), 652 (s), 689 (s), 745 (vs), 799 (s), 914 (vs), 1026 (vs), 1108 (s), 1160 (vs), 1198 (vs), 1239 (s), 1285 (s), 1388 (m), 1436 (s), 1488 (s), 1590 (s), 2960 (w), 3054 (w). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): δ −8.38 (d, $^2J_{PP} = 39.9$ Hz, $\mathrm{(PhO)_2P{=}O}$), 8.02 (dd, $^2J_{PP} = 12.7$ Hz, $^4J_{PP} = 5.9$ Hz, $\mathrm{Ru{-}NP({=}O)(OEt)_2}$), 22.47 (ddd, $^2J_{PP} = 39.9$ and 4.2 Hz, $^4J_{PP} = 5.9$ Hz, $\mathrm{Ph_2P{=}N}$), 63.71 (dd, $^2J_{PP} = 12.7$ and 4.2 Hz, $\mathrm{Ru{-}N{=}PPh_2}$) ppm. ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): δ 0.98 (t, 3H, $^3J_{HH} = 6.9$ Hz, $\mathrm{OCH_2C}H_3$), 1.03 (d, 3H, $^3J_{HH} = 6.7$ Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.17 (t, 3H, $^3J_{HH} = 7.0$ Hz, $\mathrm{OCH_2C}H_3$), 1.24 (d, 3H, $^3J_{HH} = 6.8$ Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 2.34 (s, 3H, $\mathrm{CH_3}$), 2.80 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.96 (m, 1H, PCHP), 3.91 (m, 4H, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.36 and 6.28 (d, 1H each, $^3J_{HH} = 5.3$ Hz, CH of *p*-cymene), 5.60 and 5.95 (d, 1H each, $^3J_{HH} = 5.9$ Hz, CH of *p*-cymene), 7.10−8.44 (m, 30H, Ph) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): δ 2.93 (dddd, $^1J_{CP} = 93.5$ and 63.5 Hz, $^3J_{CP} = 17.6$ and 12.3 Hz, PCHP), 16.68 and 16.98 (d, $^3J_{CP} = 8.0$ Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 18.90 (s, $\mathrm{CH_3}$), 22.44 and 23.38 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 31.86 (s, $C\mathrm{H(CH_3)_2}$), 62.50 and 63.00 (d, $^2J_{CP} = 5.6$ Hz, $\mathrm{O}C\mathrm{H_2CH_3}$), 73.70, 81.09, 83.76, and 90.00 (s, CH of *p*-cymene), 91.05 and 109.71 (s, C of *p*-cymene), 121.60−135.26 (m, Ph), 154.05 and 154.12 (d, $^2J_{CP} = 7.2$ Hz, $\mathrm{C_{ipso}}$ of OPh) ppm.

Synthesis of [Ru(η^6-*p*-cymene)(κ^3(*C,N,O*)-CH[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)][SbF$_6$] (R = Ph (5a), Et (5b)) and [Ru(η^6-*p*-cymene)(κ^3(*C,N,O*)-CH[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$])][SbF$_6$] (5c/5c′). A solution of the corresponding neutral complex **4a**−**c** (0.25 mmol) in 30 mL of CH_2Cl_2 was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.086 g, 0.25 mmol) for 1 h. The AgCl that formed was then filtered off (Kieselguhr) and the resulting solution concentrated to ca. 2 mL. Addition of diethyl ether (ca. 50 mL) gave an orange microcrystalline solid which was filtered, washed with diethyl ether (3 × 20 mL), and vacuum-dried. Starting from **4c** a nonseparable mixture of complexes **5c** and **5c′** was obtained in ca. 2:3 ratio. **5a**: yield 82% (0.276 g). Anal. Calcd for $RuC_{59}H_{55}F_6O_6P_4N_2Sb\cdot{}^2/_3CH_2Cl_2$: C, 50.99; H, 4.04; N, 1.99. Found: C, 50.66; H, 3.76; N, 2.04. Conductivity (acetone, 20 °C): 110 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν 502 (m), 541 (m), 560 (m), 657 (s), 689 (s), 749 (s), 799 (s), 896 (s), 928 (vs), 1006 (m), 1024 (s), 1133 (vs), 1201 (vs), 1265 (s), 1390 (w), 1435 (s), 1455 (m), 1489 (s), 1590 (s), 2966 (w), 3061 (w). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −2.70 (dd, $^2J_{PP}$ = 20.3 Hz, $^4J_{PP}$ = 4.2 Hz, Ru−NP(=O)(OPh)$_2$), −0.23 (d, $^2J_{PP}$ = 21.2 Hz, (PhO)$_2$P=O−Ru), 23.51 (ddd, $^2J_{PP}$ = 21.2 and 4.0 Hz, $^4J_{PP}$ = 4.2 Hz, Ph$_2$P=N), 63.74 (dd, $^2J_{PP}$ = 20.3 and 4.0 Hz, Ru−N=PPh$_2$) ppm. ^1H NMR (CD_2Cl_2): δ 0.97 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.87 (s, 3H, CH$_3$), 2.52 (m, 1H, C*H*(CH$_3$)$_2$), 4.00 (m, 1H, PCHP), 4.86 and 5.07 (d, 1H each, $^3J_{HH}$ = 5.3 Hz, CH of *p*-cymene), 4.94 and 5.39 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 6.88−8.15 (m, 40H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −5.58 (dddd, $^1J_{CP}$ = 60.5 and 60.5 Hz, $^3J_{CP}$ = 18.4 and 8.6 Hz, PCHP), 18.77 (s, CH$_3$), 21.99 and 22.78 (s, CH(*C*H$_3$)$_2$), 31.23 (s, *C*H(CH$_3$)$_2$), 77.61, 79.18, 83.42, and 84.19 (s, CH of *p*-cymene), 93.97 and 107.97 (s, C of *p*-cymene), 119.89−135.16 (m, Ph), 151.82 and 151.86 (broad, C$_{ipso}$ of OPh), 152.17 (d, $^2J_{CP}$ = 6.0 Hz, C$_{ipso}$ of OPh), 152.27 (d, $^2J_{CP}$ = 7.8 Hz, C$_{ipso}$ of OPh) ppm. **5b**: yield 79% (0.228 g). Anal. Calcd for $RuC_{43}H_{55}F_6O_6P_4N_2Sb\cdot{}^3/_2CH_2Cl_2$: C, 41.63; H, 4.55; N, 2.18. Found: C, 41.35; H, 4.37; N, 2.42. Conductivity (acetone, 20 °C) 113 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν 500 (m), 531 (s), 553 (s), 586 (s), 657 (vs), 692 (s), 731 (s), 746 (s), 800 (s), 908 (m), 965 (s), 1049 (vs), 1111 (s), 1160 (s), 1240 (s), 1391 (m), 1438 (s), 1489 (m), 1589 (m), 2871 (w), 2906 (m), 2931 (m), 2981 (m), 3060 (w). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 7.47 (dd, $^2J_{PP}$ = 18.9 Hz, $^4J_{PP}$ = 4.5 Hz, Ru−NP(=O)(OEt)$_2$), 10.29 (d, $^2J_{PP}$ = 20.2 Hz, (EtO)$_2$P=O−Ru), 21.10 (ddd, $^2J_{PP}$ = 20.2 and 3.0 Hz, $^4J_{PP}$ = 4.5 Hz, Ph$_2$P=N), 60.87 (dd, $^2J_{PP}$ = 18.9 and 3.0 Hz, Ru−N=PPh$_2$) ppm. ^1H NMR (CD_2Cl_2): δ 1.01 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.08 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$C*H*$_3$), 1.16 (t, 3H, $^3J_{HH}$ = 6.8 Hz, OCH$_2$C*H*$_3$), 1.20 (t, 3H, $^3J_{HH}$ = 6.5 Hz, OCH$_2$C*H*$_3$), 1.41 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.48 (t, 3H, $^3J_{HH}$ = 7.2 Hz, OCH$_2$C*H*$_3$), 1.81 (s, 3H, CH$_3$), 2.64 (m, 1H, C*H*(CH$_3$)$_2$), 4.05 (m, 8H, OC*H*$_2$CH$_3$), 4.25 (m, 1H, PCHP), 4.86 and 5.05 (d, 1H each, $^3J_{HH}$ = 5.3 Hz, CH of *p*-cymene), 4.94 and 4.98 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 6.85−8.15 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −6.56 (dddd, $^1J_{CP}$ = 61.3 and 61.3 Hz, $^3J_{CP}$ = 16.3 and 7.6 Hz, PCHP), 16.25 (d, $^3J_{CP}$ = 8.2 Hz, OCH$_2$*C*H$_3$), 16.41 (d, $^3J_{CP}$ = 7.6 Hz, OCH$_2$*C*H$_3$), 16.46 (d, $^3J_{CP}$ = 7.0 Hz, OCH$_2$*C*H$_3$), 16.54 (d, $^3J_{CP}$ = 6.5 Hz, OCH$_2$*C*H$_3$), 18.10 (s, CH$_3$), 21.89 and 22.00 (s, CH(*C*H$_3$)$_2$), 30.83 (s, *C*H(CH$_3$)$_2$), 62.65 and 63.58 (d, $^2J_{CP}$ = 5.8 Hz, O*C*H$_2$CH$_3$), 62.90 (d, $^2J_{CP}$ = 5.2 Hz, O*C*H$_2$CH$_3$), 63.43 (d, $^2J_{CP}$ = 6.4 Hz, O*C*H$_2$CH$_3$), 77.40, 78.96, 82.35, and 83.93 (s, CH of *p*-cymene), 94.37 and 105.04 (s, C of *p*-cymene), 126.79−135.07 (m, Ph) ppm. **5c/5c′**: yield 76% (0.238 g). Anal. Calcd for $RuC_{51}H_{55}F_6O_6P_4N_2Sb\cdot{}^3/_2CH_2Cl_2$: C, 45.69; H, 4.23; N, 2.03. Found: C, 45.50; H, 3.93; N, 2.29. Conductivity (acetone, 20 °C): 106 Ω^{-1} cm^2 mol^{-1}. IR (KBr, cm^{-1}): ν 501 (m), 587 (w), 658 (vs), 690 (s), 730 (s), 750 (s), 799 (m), 904 (m), 933 (s), 956 (s), 1026 (vs), 1047 (vs), 1110 (vs), 1141 (vs), 1194 (s), 1260 (s), 1390 (w), 1438 (s), 1489 (s), 1590 (m), 2978 (m), 3061 (w). NMR spectroscopic data for **5c**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.93 (d, $^2J_{PP}$ = 22.6 Hz, (PhO)$_2$P=O−Ru), 8.30 (dd, $^2J_{PP}$ = 20.2 Hz, $^4J_{PP}$ = 3.9 Hz, Ru−NP(=O)(OEt)$_2$), 24.90 (dd, $^2J_{PP}$ = 22.6 Hz, $^4J_{PP}$ = 3.9 Hz, Ph$_2$P=N), 61.90 (d, $^2J_{PP}$ = 20.2 Hz, Ru−N=PPh$_2$) ppm. ^1H NMR (CD_2Cl_2): δ 1.09 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.20 (t, 3H, $^3J_{HH}$ = 7.4 Hz, OCH$_2$C*H*$_3$), 1.27 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.55 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$C*H*$_3$), 1.92 (s, 3H, CH$_3$), 2.94 (m, 1H, C*H*(CH$_3$)$_2$), 4.10 (m, 4H, OC*H*$_2$CH$_3$), 4.44 (m, 1H, PCHP), 5.13 and 5.38 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.16 and 5.27 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 7.06−8.50 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −6.66 (m, PCHP), 16.45 (d, $^3J_{CP}$ = 7.8 Hz, OCH$_2$*C*H$_3$), 16.62 (d, $^3J_{CP}$ = 7.2 Hz, OCH$_2$*C*H$_3$), 18.37 (s, CH$_3$), 21.82 and 22.36 (s, CH(*C*H$_3$)$_2$), 31.13 (s, *C*H(CH$_3$)$_2$), 62.76 and 62.98 (d, $^2J_{CP}$ = 5.4 Hz, O*C*H$_2$CH$_3$), 77.82, 79.08, 82.88, and 84.84 (s, CH of *p*-cymene), 93.78 and 106.74 (s, C of *p*-cymene), 126.79−135.07 (m, Ph), 152.35 (d, $^2J_{CP}$ = 6.6 Hz, C$_{ipso}$ of OPh), 152.45 (d, $^2J_{CP}$ = 7.8 Hz, C$_{ipso}$ of OPh) ppm. NMR spectroscopic data for **5c’**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −1.21 (dd, $^2J_{PP}$ = 23.3 Hz, $^4J_{PP}$ = 5.9 Hz, Ru−NP(=O)(OPh)$_2$), 11.15 (d, $^2J_{PP}$ = 20.7 Hz, (EtO)$_2$P=O−Ru), 21.68 (ddd, $^2J_{PP}$ = 20.7 and 5.2 Hz, $^4J_{PP}$ = 5.9 Hz, Ph$_2$P=N), 65.65 (dd, $^2J_{PP}$ = 23.3 and 5.2 Hz, Ru−N=PPh$_2$) ppm. ^1H NMR (CD_2Cl_2): δ 1.01 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.23 (t, 3H, $^3J_{HH}$ = 7.5 Hz, OCH$_2$C*H*$_3$), 1.27 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.38 (t, 3H, $^3J_{HH}$ = 6.9 Hz, OCH$_2$C*H*$_3$), 1.90 (s, 3H, CH$_3$), 2.63 (m, 1H, C*H*(CH$_3$)$_2$), 4.05 (m, 4H, OC*H*$_2$CH$_3$), 4.62 (m, 1H, PCHP), 5.07 and 5.29 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 5.15 and 5.24 (d, 1H each, $^3J_{HH}$ = 5.2 Hz, CH of *p*-cymene), 7.06−8.50 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −5.77 (m, PCHP), 16.45 (d, $^3J_{CP}$ = 7.8 Hz, OCH$_2$*C*H$_3$), 16.62 (d, $^3J_{CP}$ = 7.2 Hz, OCH$_2$*C*H$_3$), 18.27 (s, CH$_3$), 21.56 and 22.76 (s, CH(*C*H$_3$)$_2$), 31.09 (s, *C*H(CH$_3$)$_2$), 63.07 and 64.76 (d, $^2J_{CP}$ = 6.6 Hz, O*C*H$_2$CH$_3$), 78.13, 79.58, 83.33, and 84.50 (s, CH of *p*-cymene), 97.16 and 104.18 (s, C of *p*-cymene), 126.79−135.07 (m, Ph), 152.13 (d, $^2J_{CP}$ = 6.6 Hz, C$_{ipso}$ of OPh), 152.78 (d, $^2J_{CP}$ = 7.8 Hz, C$_{ipso}$ of OPh) ppm.

Synthesis of [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Ph (6a), Et (6b)) and [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OPh)$_2$}Ph$_2$][P{=NP(=O)(OEt)$_2$}Ph$_2$])] (6c). Method A. A solution of the corresponding neutral complex **4a**−**c** (0.2 mmol) in 30 mL of THF was treated, at room temperature, with NaH (0.048 g, 2 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 × 10 mL), and dried in vacuo. **6a**: yield 82% (0.182 g). Anal. Calcd for $RuC_{59}H_{54}O_6P_4N_2$: C, 63.72; H, 4.89; N, 2.52. Found: C, 63.66; H, 4.77; N, 2.76. IR (KBr, cm^{-1}): ν 475 (s), 520 (s), 540 (s), 574 (m), 622 (m), 691 (s), 754 (s), 803 (s), 847 (m), 917 (vs), 1025 (s), 1106 (vs), 1184 (vs), 1262 (s), 1343 (m), 1488 (s), 1594 (s), 2853 (w), 2922 (w), 2958 (w), 3055 (w). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −8.55 (d, $^2J_{PP}$ = 35.7 Hz, (PhO)$_2$P=O), 0.49 (dd, $^2J_{PP}$ = 14.9 Hz, $^4J_{PP}$ = 9.9 Hz, Ru−NP(=O)(OPh)$_2$), 13.46 (ddd, $^2J_{PP}$ = 93.3 and 35.7 Hz, $^4J_{PP}$ = 9.9 Hz, Ph$_2$P=N), 67.49 (dd, $^2J_{PP}$ = 93.9 and 14.9 Hz, Ru−N=PPh$_2$) ppm. ^1H NMR (C_6D_6): δ 1.15 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.90 (s, 3H, CH$_3$), 2.39 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 5.43 and 5.48 (d, 2H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 6.77−7.86 (m, 40H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.70 (s, CH$_3$), 23.96 (s, CH(*C*H$_3$)$_2$), 30.85 (s, *C*H(CH$_3$)$_2$), 80.41 and 82.24 (s, CH of *p*-cymene), 87.33 and 98.78 (s, C of *p*-cymene), 120.16−136.97 (m, Ph), 153.36 (d, $^2J_{CP}$ = 7.2 Hz, C$_{ipso}$ of OPh), 154.85 (d, $^2J_{CP}$ = 8.2 Hz, C$_{ipso}$ of OPh) ppm; PCP signal not observed. **6b**: yield 79% (0.145 g). Anal. Calcd for $RuC_{43}H_{54}O_6P_4N_2$: C, 56.15; H, 5.92; N, 3.04. Found: C, 55.85; H, 5.87; N, 3.19. IR (KBr, cm^{-1}): ν 554 (m), 668 (s), 693 (s), 801 (vs), 959 (m), 1028 (vs), 1099 (vs), 1182 (m), 1260 (s), 1435 (s), 1622 (s), 2854 (w), 2924 (w), 2981 (w). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.10 (d, $^2J_{PP}$ = 31.1 Hz, (EtO)$_2$P=O), 9.38 (dd, $^2J_{PP}$ = 13.3 Hz, $^4J_{PP}$ = 8.9 Hz, Ru−

Table 1. Crystallographic Data for Compounds 2a, 5a, and 6a

	2a	**5a**	**6a**
chem formula	$C_{49}H_{42}O_6P_4N_2$	$C_{59}H_{55}F_6O_6P_4$-N_2RuSb	$C_{59}H_{54}O_6P_4$-N_2Ru
fw	878.73	1348.75	1111.99
T (°C)	20(2)	−153(2)	−123(2)
wavelength (Å)	1.54180	1.54180	1.54180
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.277(1)	11.9545(3)	11.1659(6)
b, Å	11.643(1)	12.7210(3)	18.8234(9)
c, Å	21.744(1)	18.6112(4)	25.721(2)
α, deg	86.738(10)	81.534(2)	95.451(3)
β, deg	84.131(10)	84.437(2)	94.862(5)
γ, deg	76.204(10)	86.828(2)	102.152(4)
Z	2	2	4
V, Å^3	2267.6(3)	2783.8(1)	5230.4(6)
ρ_{calcd}, g cm^{-3}	1.287	1.609	1.412
μ, mm^{-1}	1.951	7.760	4.017
wt function (a)	0.0740	0.0278	0.1007
R1[a] ($I > 2\sigma(I)$)	0.0476	0.0538	0.0642
wR2[a] ($I > 2\sigma(I)$)	0.1184	0.1372	0.1772
R1 (all data)	0.0893	0.0715	0.1207
wR2 (all data)	0.1443	0.1466	0.2003

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

NP(═O)(OEt)$_2$), 13.63 (ddd, $^2J_{PP}$ = 87.8 and 31.1 Hz, $^4J_{PP}$ = 8.9 Hz, Ph$_2$P═N), 66.34 (dd, $^2J_{PP}$ = 87.8 and 13.3 Hz, Ru−N═PPh$_2$) ppm. ^{1}H NMR (C$_6$D$_6$): δ 1.23 (t, 6H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$C*H*$_3$), 1.46 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.53 (t, 6H, $^3J_{HH}$ = 7.2 Hz, OCH$_2$C*H*$_3$), 1.94 (s, 3H, CH$_3$), 2.68 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 4.06 (m, 8H, OC*H*$_2$CH$_3$), 5.68 and 5.71 (d, 2H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 6.88−8.92 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 16.38 (d, $^3J_{CP}$ = 7.2 Hz, OCH$_2$*C*H$_3$), 16.71 (d, $^3J_{CP}$ = 7.8 Hz, OCH$_2$*C*H$_3$), 17.27 (s, CH$_3$), 24.04 (s, CH(*C*H$_3$)$_2$), 33.22 (s, *C*H(CH$_3$)$_2$), 61.01 (d, $^2J_{CP}$ = 4.8 Hz, O*C*H$_2$CH$_3$), 61.36 (d, $^2J_{CP}$ = 6.0 Hz, O*C*H$_2$CH$_3$), 79.53 and 81.38 (s, CH of *p*-cymene), 86.29 and 97.60 (s, C of *p*-cymene), 129.67−136.89 (m, Ph) ppm; PCP signal not observed. **6c**: yield 78% (0.158 g). Anal. Calcd for RuC$_{51}$H$_{54}$O$_6$P$_4$N$_2$: C, 60.29; H, 5.35; N, 2.76. Found: C, 60.15; H, 5.12; N, 2.98. IR (KBr, cm^{-1}): ν 488 (m), 685 (s), 702 (m), 743 (s), 796 (s), 912 (vs), 955 (m), 1027 (vs), 1109 (vs), 1200 (s), 1258 (s), 1383 (m), 1436 (s), 1484 (s), 1585 (s), 1628 (m), 2854 (w), 2951 (w), 2986 (w), 3057 (w). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −8.56 (d, $^2J_{PP}$ = 35.6 Hz, (PhO)$_2$P═O), 9.44 (dd, $^2J_{PP}$ = 15.1 Hz, $^4J_{PP}$ = 9.5 Hz, Ru−NP(═O)(OEt)$_2$), 13.65 (ddd, $^2J_{PP}$ = 91.1 and 35.6 Hz, $^4J_{PP}$ = 9.5 Hz, Ph$_2$P═N), 66.20 (dd, $^2J_{PP}$ = 91.1 and 15.1 Hz, Ru−N═PPh$_2$) ppm. ^{1}H NMR (C$_6$D$_6$): δ 1.29 (t, 6H, $^3J_{HH}$ = 6.9 Hz, OCH$_2$C*H*$_3$), 1.56 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 2.31 (s, 3H, CH$_3$), 2.81 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.09 (m, 4H, OC*H*$_2$CH$_3$), 5.78 and 5.81 (broad, 2H each, CH of *p*-cymene), 7.18−8.59 (m, 30H, Ph) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 16.42 (d, $^3J_{CP}$ = 7.2 Hz, OCH$_2$*C*H$_3$), 19.83 (s, CH$_3$), 24.04 (s, CH(*C*H$_3$)$_2$), 31.72 (s, *C*H(CH$_3$)$_2$), 61.38 (d, $^2J_{CP}$ = 6.0 Hz, O*C*H$_2$CH$_3$), 79.63 and 81.58 (s, CH of *p*-cymene), 86.24 and 97.61 (s, C of *p*-cymene), 121.32−136.49 (m, Ph), 154.20 (d, $^2J_{CP}$ = 7.2 Hz, C$_{ipso}$ of OPh) ppm; PCP signal not observed.

Method B. A solution of the corresponding cationic complex **5a**−**c′** (0.2 mmol) in 30 mL of THF was treated, at room temperature, with NaH (0.048 g, 2 mmol) for 2 h. Workup as described in method A allows the isolation of compounds **6a**−**c** in 77−85% yield.

X-ray Crystal Structure Determination of Compounds 2a, 5a, and 6a. Crystals suitable for X-ray diffraction analysis were obtained, in all of the cases, by slow diffusion of *n*-pentane in a saturated solution of the compound in dichloromethane. The most relevant crystal and refinement data are collected in Table 1. Data collections were performed on a Nonius Kappa CCD single-crystal diffractometer using Cu Kα radiation with the crystal to detector distance fixed at 29 mm, using the oscillation method, with 2° oscillation and 200 s (**2a**), 40 s (**5a**), or 25 s (**6a**) exposure time per frame. The data collection strategy was calculated with the program Collect.[35] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[36] Absorption correction was applied by means of XABS2[37] (**2a** and **5a**) or SORTAV[38] (**6a**).

All the structures were solved by Patterson interpretation and phase expansion using DIRDIF.[39] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[40] During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined, with the exception of F atoms of the SbF$_6{}^-$ anion in **5a** (this highly disordered group was found and isotropically refined) and C(5), C(5'), C(9), and C(9') atoms in **6a** (these atoms were refined isotropically because they were persistently nonpositive definite). The H atoms were geometrically located, and their coordinates were refined riding on their parent atoms. The function minimized was $[\sum w(F_o{}^2 - F_c{}^2)/\sum w(F_o{}^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2) + (aP)^2]$ (a values are shown in Table 1) with $\sigma^2(F_o{}^2)$ from counting statistics and $P = (\max(F_o{}^2, 0) + 2F_c{}^2)/3$. Atomic scattering factors were taken from ref 41. Geometrical calculations were made with PARST.[42] The crystallographic plots were made with PLATON.[43]

Computational Details. All calculations were performed using the Gaussian 98 software package.[44] The B3LYP hybrid functional was used for the geometry optimizations. That functional includes a mixture of Hartree−Fock[45] exchange with DFT[26] exchange correlation, given by Becke's three-parameter functional[27a] with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms.[27b,c] The LanL2DZ basis set[46] augmented with an f-polarization function[47] was used for Ru, and the same basis set augmented with a d-polarization function[48] was employed for P and Cl. A

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standard 6-31G(d,p) set[49] was used for the remaining elements. All geometries were optimized without symmetry constraints. In the models used for complexes **4**−**6**, the *p*-cymene ligand was replaced by benzene and the phenyl substituents by methyl groups. A natural population analysis (NPA)[30] and the resulting Wiberg indices[28] were used for a detailed study of the electronic structure and bonding of the optimized species. NMR shielding tensors were calculated using the gauge-independent atomic orbital method (GIAO)[31] at the Hartree−Fock level using a 3-21G basis set[50] augmented with a f-polarization function[47] for Ru and a 6-311+G(2d,p) set[51] for the remaining elements. The orbital representation was obtained with the MOLEKEL 4.0 program.[52]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **2a**, **5a**, and **6a** and tables of atomic coordinates (Tables S1−S5) and figures (Figures S1−S5), with the structures and relevant electronic and geometrical parameters, for all of the optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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