Base-Assisted Cyclometalation and Phosphorus−Carbon Bond Cleavage in (Arene)ruthenium(II) Complexes Containing Functionalized Iminophosphorane-Phosphine Ligands $Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$ (X = O, S; R = Et, Ph)

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Complexes $[RuCl(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)][SbF_6]$ (X = O, R = Et (**1a**), Ph (**1b**); X = S, R = Et (**2a**), Ph (**2b**)) react with a stoichiometric amount of NaH, in THF at rt, to generate the neutral cyclometalated compounds $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (X = O, R = Et (**3a**), Ph (**3b**); X = S, R = Et (**4a**), Ph (**4b**)), via selective deprotonation of the methylenic backbone of the coordinated iminophosphorane-phosphine ligands. Treatment of **3**−**4a**,**b** with $AgSbF_6$, in CH_2Cl_2 at rt, affords the corresponding cationic species $[Ru(\kappa^3\text{-}P,C,X\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})][SbF_6]$ (X = O, R = Et (**7a**), Ph (**7b**); X = S, R = Et (**8a**), Ph (**8b**)) through the intramolecular *O*- or *S*-coordination of the free $-Ph_2P{=}NP(=X)(OR)_2$ fragment. Complexes **7**−**8a**,**b** can also be prepared by reaction of the dicationic derivatives $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)][SbF_6]_2$ (**5**−**6a**,**b**) with 1 equiv of NaH. Formation of complexes **3**−**4a**,**b** and **7**−**8a**,**b** proceeds, in all cases, in a diastereoselective manner. Phosphorus−carbon bond splitting has been observed upon treatment of complexes **1**−**2a**,**b**, **3**−**4a**,**b**, or **7**−**8a**,**b** with an excess of NaH, in wet THF at rt, affording the novel phosphinito derivatives $[Ru(\kappa^2\text{-}C,X\text{-}CH_2P\{=NP(=X)(OR)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P(=O)Ph_2\}(\eta^6\text{-}p\text{-cymene})]$ (X = O, R = Et (**10a**); X = S, R = Et (**11a**), Ph (**11b**)). Protonation and methylation of **10**−**11a**,**b** generates the cationic species $[Ru(\kappa^2\text{-}C,X\text{-}CH_2P\{=NP(=X)(OR)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P(OH)Ph_2\}(\eta^6\text{-}p\text{-cymene})][BF_4]$ (X = O, R = Et (**12a**); X = S, R = Et (**13a**), Ph (**13b**)) and $[Ru(\kappa^2\text{-}C,X\text{-}CH_2P\{=NP(=X)(OR)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P(OMe)Ph_2\}(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]$ (X = O, R = Et (**14a**); X = S, R = Et (**15a**), Ph (**15b**)), respectively, via selective electrophilic addition at the $Ph_2P{=}O$ group. The structure of compounds $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=O)(OPh)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (**3b**) and $[Ru(\kappa^2\text{-}C,S\text{-}CH_2P\{=NP(=S)(OEt)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P(=O)Ph_2\}(\eta^6\text{-}C_6H_6)]$ (**11a′**) has been determined by X-ray crystallography.

Introduction

The selective monoimination of bis-phosphines with azides, via the Staudinger reaction,[1,2] has been successfully applied to the preparation of several bidentate iminophosphorane-phosphine ligands $R_2P-X-P(=NR')R_2$ (X = divalent bridging group).[3] Nevertheless, despite its great potential as hemilabile ligands[4] and anticipated diversity, the coordination chemistry[5] and catalytic applications[6] of these heterodifunctional ligands still remain scarcely explored when compared to their bis-phosphine-monoxide counterparts $R_2P-X-P(=O)R_2$.[7]

As part of our ongoing work dealing with the synthesis and catalytic activity of ruthenium complexes containing iminophosphorane-phosphine ligands,[4a,6f] we have recently reported the preparation of the heterotrifunctional systems $Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$ (X = O, S; R = Et, Ph), via single-stage oxidation of bis-

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(1) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.
(2) For reviews on the Staudinger reaction see: (a) Gololobov, Y. G.; Zhamurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437. (b) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353. (c) Johnson, A. W. In *Ylides and Imines of Phosphorus*; Wiley: New York, 1993; p 403.
(3) See for example: (a) Gilyarov, V. A.; Kovtum, V. Y.; Kabachmich, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *5*, 1159. (b) Katti K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413. (c) Katti, K. V.; Batchelor, R. J.; Einstein F. W. B.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 808. (d) Cavell, R. G.; Reed, R. W.; Katti, K. V.; Balakrishna, M. S.; Collins, P. W.; Mozol V.; Bartz, I. *Phosphorus, Sulfur, Silicon* **1993**, *76*, 9. (e) Saravanamuthu, A.; Ho, D. M.; Kerr, M. E.; Fitzgerald, C.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1993**, *32*, 2202. (f) Balakrishna, M. S.; Santarsiero B. D.; Cavell, R. G. *Inorg. Chem.* **1994**, *33*, 3079. (g) Reed, R. W.; Santarsiero, B.; Cavell, R. G. *Inorg. Chem.* **1996**, *35*, 4292. (h) Avis, M. W.; Goosen, M.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **1997**, *264*, 43. (i) Molina, P.; Arques, A.; García, A.; Ramírez de Arellano, M. C. *Tetrahedron Lett.* **1997**, *38*, 7613. (j) Molina, P.; Arques, A.; García, A.; Ramírez de Arellano, M. C. *Eur. J. Inorg. Chem.* **1998**, 1359. (k) Pandurangi, R. S.; Katti, K. V.; Stillwell, L.; Barnes, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 11364. (l) Alajarín, M.; López-Leonardo, C.; Llamas-Lorente, P.; Bautista, D. *Synthesis* **2000**, 2085. (m) Arques, A.; Molina, P.; Auñon, D.; Vilaplana, M. J.; Desamparados Velasco, M.; Martínez, F.; Bautista, D.; Lahoz, F. J. *J. Organomet. Chem.* **2000**, *598*, 329. (n) Balakrishna, M. S.; Teipel, S.; Pinkerton A. A.; Cavell, R. G. *Inorg. Chem.* **2001**, *40*, 1802.

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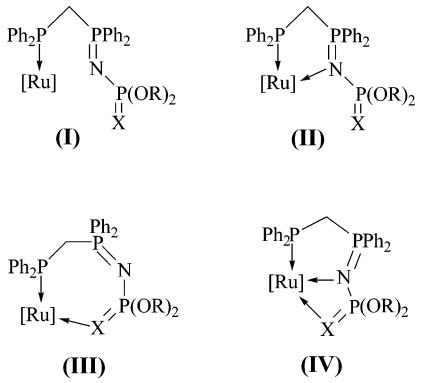
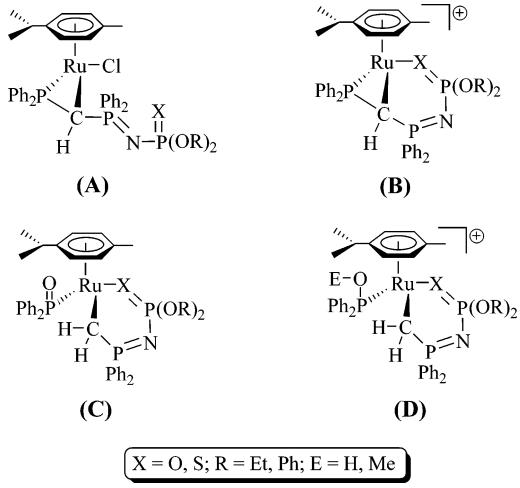
Chart 1



(diphenylphosphino)methane (dppm) with the corresponding phosphorylated or thiophosphorylated azide $(RO)_2P(=X)N_3$ (X = O, S; R = Et, Ph).[8] The attachment of these functionalities at one of the phosphorus atoms of dppm generates a new class of versatile polydentate ligands with ability to adopt κ^1-*P*- (**I**), κ^2-*P*,*N*- (**II**), κ^2-*P*,*X*- (**III**), and κ^3-*P*,*N*,*X*-coordination modes (**IV**) (see Chart 1).[8,9] In a series of reactivity studies we have also proved the utility of these ligands to design valuable precursors for the preparation of a host of novel ruthenium(II) derivatives.[8]

We now report further examples of the synthetic utility of these complexes. In particular, we describe the role of the coordinated iminophosphorane-phosphines $Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$ (X = O, S; R = Et, Ph) in the generation of novel ruthenium(II) complexes bearing metal−carbon bonds, including (see Chart 2) (i) cyclometalated complexes $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (**A**) and $[Ru(\kappa^3\text{-}P,C,X\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]^+$ (**B**), (ii) neutral phosphinito derivatives $[Ru(\kappa^2\text{-}C,X\text{-}CH_2P\{=NP(=X)(OR)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P(=O)Ph_2\}(\eta^6\text{-}p\text{-cymene})]$ (**C**),

Chart 2



obtained via base-induced phosphorus−carbon bond splitting in complexes **A** and **B**, and (iii) cationic complexes $[Ru(\kappa^2\text{-}C,X\text{-}CH_2P\{=NP(=X)(OR)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P(OE)Ph_2\}(\eta^6\text{-}p\text{-cymene})]^+$ (**D**), generated by selective protonation or methylation at the phosphinito $Ph_2P=O$ group of complexes **C**.

Results and Discussion

Synthesis and Characterization of Cyclometalated Compounds $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (X = O, R = Et (3a), Ph (3b); X = S, R = Et (4a), Ph (4b)) and $[Ru(\kappa^3\text{-}P,C,X\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})][SbF_6]$ (X = O, R = Et (7a), Ph (7b); X = S, R = Et (8a), Ph (8b)). Complexes $[RuCl(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)][SbF_6]$ (**1**−**2a**,**b**)[8,10] react with a stoichiometric amount of NaH, in THF at room temperature, to generate cyclometalated compounds $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (X = O, R = Et (**3a**), Ph (**3b**); X = S, R = Et (**4a**), Ph (**4b**); 67−99% yield), via selective deprotonation of the methylenic backbone and concomitant decoordination of the $(RO)_2P=X$ group of the iminophosphorane-phosphine ligands (Scheme 1). $^{31}P\{^1H\}$ and ^1H NMR spectra of the crude reaction mixtures show no formation of a ruthenium−hydride bond.

Complexes **3**−**4a**,**b** have been characterized by means of standard spectroscopic techniques (IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR) as well as elemental analyses (details are given in the Experimental Section and the Supporting Information). In particular, the NMR spectra clearly indicate the diastereoselective formation of a three-membered Ru−P−C metallacycle (two stereogenic centers are present, i.e., the ruthenium atom and the PCHP carbon). The most significant features are the following: (i) (^1H NMR) a doublet of doublets signal at 2.07−2.22 ppm ($^2J_{HP(III)} = {}^2J_{HP(V)} = 6.7$−$7.8$ Hz) for the methine PCHP proton, (ii) ($^{13}C\{^1H\}$ NMR) a characteristic high-field doublet of doublets of doublets resonance in the range 7.06−10.04 ppm ($^1J_{CP(V)} = 102.8$−104.5 Hz;

(4) Hemilabile behavior of iminophosphorane-phosphine ligands has been reported in: (a) Cadierno, V.; Díez, J.; García-Garrido, S. E.; García-Granda, S.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2002**, 1465. For a general review on hemilabile functionalized phosphine ligands see: (b) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

(5) For overviews on the coordination chemistry of $R_2P-X-P(=NR')-R_2$ ligands see: (a) Katti, K. V.; Cavell, R. G. *Comments Inorg. Chem.* **1990**, *10*, 53. (b) Cavell, R. G. *Curr. Sci.* **2000**, *78*, 440.

(6) Hydrogenation of olefins (Rh and Ir complexes): (a) Law, D. J.; Cavell, R. G. *J. Mol. Catal.* **1994**, *91*, 175. (b) Cavell, R. G.; Law, D. J.; Reed, R. W. U.S. Pat. Appl. US 887014, 1994. Methanol carbonylation (Rh, Ni, and Co complexes): (c) Cavell, R. G.; Katti, K. V. U.S. Pat. Appl. US 752348, 1994. Olefin oligomerization (Ni complexes): (d) Cavell, R. G.; Creed, B.; Gelmini, L.; Law, D. J.; McDonald, R.; Sanger, A. R.; Somogyvary, A. *Inorg. Chem.* **1998**, *37*, 757. (e) Cavell, R. G.; Creed, B.; Law, D. J.; Nicola, A. P.; Sanger, A. R.; Somogyvary, A. U.S. Pat. Appl. US 447887, 1996. Transfer hydrogenation of ketones (Ru complexes): (f) Cadierno, V.; Crochet, P.; García-Álvarez, J.; García-Garrido, S. E.; Gimeno, J. *J. Organomet. Chem.* **2002**, *663*, 32. Cross-coupling of secondary amines with aryl halides (Pd complexes): see ref 3i.

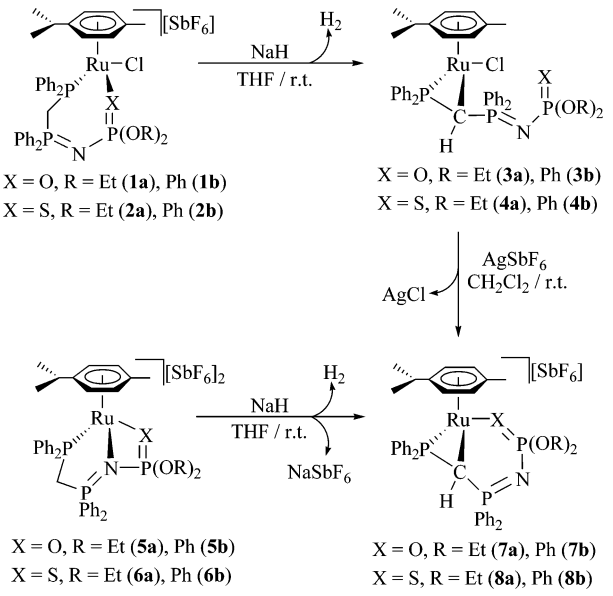
(7) (a) Grushin, V. V. *Organometallics* **2001**, *20*, 3950, and references therein. (b) Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629, and references therein.

(8) X = O: (a) Cadierno, V.; Crochet, P.; Díez, J.; García-Álvarez, J.; García-Garrido, S. E.; Gimeno, J.; García-Granda, S.; Rodríguez, M. A. *Inorg. Chem.* **2003**, *42*, 3293. X = S: (b) Cadierno, V.; Crochet, P.; Díez, J.; García-Álvarez, J.; García-Garrido, S. E.; García-Granda, S.; Gimeno, J.; Rodríguez, M. A. *Dalton Trans.* **2003**, 3240.

(9) Although theoretical calculations (DFT level) on the model complexes $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=X)(OH)_2\}H_2)]^+$ (X = O, S) and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,X\text{-}H_2PCH_2P\{=NP(=X)(OH)_2\}H_2)]^+$ (X = O, S) predicted that the κ^2-*P*,*N*-isomers **II** are more stable than their κ^2-*P*,*X*-counterparts **III**, a marked preference for the bidentate κ^2-*P*,*X*-coordination, probably due to steric reasons, was experimentally observed.

(10) We note that complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2)][SbF_6]$ (**1a**) is always obtained as an equilibrium mixture along with its κ^2-*P*,*N*-isomer $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2)][SbF_6]$. See ref 8a. For clarity, and in order to save space, in this paper we will refer to this mixture as complex **1a** exclusively.

Scheme 1



$^1J_{CP(III)}$ = 19.0−21.6 Hz; $^3J_{CP(V)}$ = 8.5−12.2 Hz) assigned to the metal-bonded carbon of the PCHP unit, and (iii) ($^{31}P\{^1H\}$ NMR) the presence of three well-separated signals with equal relative intensities (δ 6.26−7.18 (d, $^2J_{PP}$ = 24.4−25.3 Hz; Ph_2P), 18.61−24.00 (dd, $^2J_{PP}$ = 24.4−25.3 and 11.3−34.4 Hz; $Ph_2P{=}N$), and −9.93−1.53 (d, $^2J_{PP}$ = 29.3−34.4 Hz; $(RO)_2P{=}O$) or 48.73−58.13 (d, $^2J_{PP}$ = 11.3−12.6 Hz; $(RO)_2P{=}S$) ppm), the chemical shifts observed being in accord with the presence of uncoordinated $Ph_2P{=}N{-}P(=X)(OR)_2$ moieties[8] and the incorporation of the diphenylphosphino group into a strained three-membered chelate ring.[11,12]

The X-ray crystal structure of [RuCl(κ^2-*P,C*-Ph_2PCHP{=NP(=O)$(OPh)_2$}Ph_2)(η^6-*p*-cymene)] (**3b**) unambiguously confirmed the proposed structure. As the ORTEP-type drawing (Figure 1) reveals,[13] the ruthenium atom is coordinated by the *p*-cymene ring, one chloride, and the P,C-bonded phosphinomethanide ligand. As expected, the P(1)−Ru−C(11) bond angle (46.57(10)°) is significantly smaller than the Cl(1)−Ru−P(1) and Cl(1)−Ru−C(11) angles (91.43(4)° and 83.12(11)°, respectively). In addition, the bond distances within the three-membered Ru−P−C metallacycle (Ru−P(1) = 2.244(1) Å, Ru−C(11) = 2.204(4) Å, and P(1)−C(11) = 1.759(4) Å) compare well with those found in the related (η^6-arene)-ruthenium(II) complexes [RuCl{κ^2-*P,C*-^{i}Pr$_2$PCH(CO$_2$Me)}(η^6-1,3,5-$C_6H_3Me_3$)] (**E**) (Ru−P = 2.2694(8) Å, Ru−C = 2.201(2) Å, P−C = 1.761(2) Å),[14a] [Ru(κ^3-*P,C,O*-^{i}PrP{CH(CO$_2$Me)}C(H)=CO$_2$Me)(η^6-1,3,5-$C_6H_3Me_3$)] (**F**) (Ru−P = 2.301(2) Å, Ru−C = 2.217(4) Å, P−C = 1.727(4) Å),[14b] and [Ru(κ^3-*P,C,O*-Ph_2PCH{C(Ph)=C(H)C(=O)^{t}Bu})(η^6-1,3,5-$C_6H_3Me_3$)][BF_4] (**G**) (Ru−P = 2.243(2) Å, Ru−C = 2.211(8) Å, P−C = 1.761(4) Å)[12a] (see Chart 3). P−N and P−O bond lengths are also similar to those found in other species containing $-R_2P{=}NP(=X)(OR')_2$ units (X = O, S).[3f,8,15] Cyclometalations leading to the formation of a strained three-membered M−P−C ring are well documented,[12,14,16] but

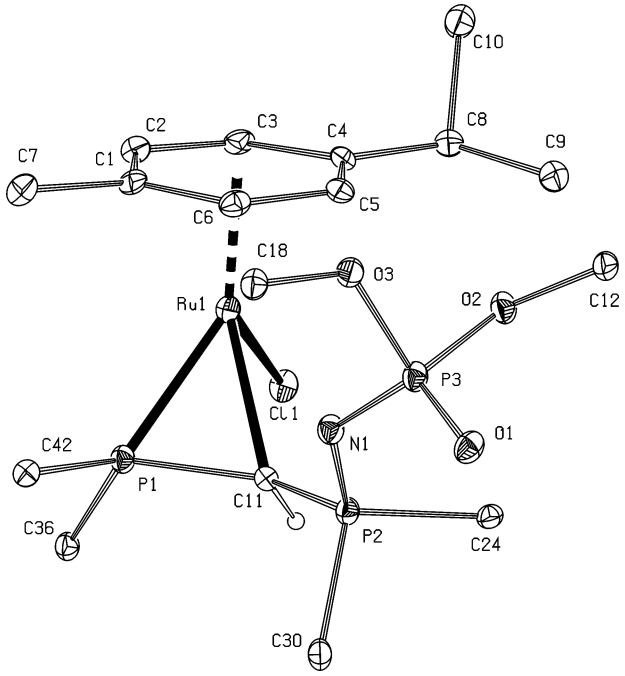
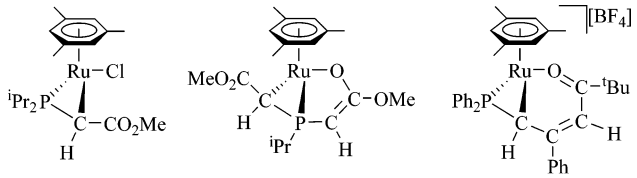


Figure 1. ORTEP-type view of the structure of [RuCl(κ^2-*P,C*-Ph_2PCHP{=NP(=O)$(OPh)_2$}Ph_2)(η^6-*p*-cymene)] (**3b**) showing the crystallographic labeling scheme. Phenyl groups and hydrogen atoms (except that on C(11)) have been omitted for clarity. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (deg): Ru−Cl(1) = 2.417(1); Ru−P(1) = 2.244(1); Ru−C(11) = 2.204(4); Ru−C* = 1.717(2); P(1)−C(11) = 1.759(4); C(11)−P(2) = 1.758(4); P(2)−N(1) = 1.581(4); N(1)−P(3) = 1.582(4); P(3)−O(1) = 1.469(3); P(3)−O(2) = 1.605(3); P(3)−O(3) = 1.611(3); C*−Ru−Cl(1) = 124.81(1); C*−Ru−P(1) = 139.63(1); C*−Ru−C(11) = 142.64(1); Cl(1)−Ru−P(1) = 91.43(4); Cl(1)−Ru−C(11) = 83.12(11); P(1)−Ru−C(11) = 46.57(10); Ru−C(11)−P(1) = 67.93(14); Ru−P(1)−C(11) = 65.50(13); Ru−C(11)−P(2) = 125.6(2); P(1)−C(11)−P(2) = 134.3(3); C(11)−P(2)−N(1) = 114.3(2); P(2)−N(1)−P(3) = 132.4(2); N(1)−P(3)−O(1) = 120.14(19); N(1)−P(3)−O(2) = 105.74(18); N(1)−P(3)−O(3) = 105.17(17); O(1)−P(3)−O(2) = 112.52(17); O(1)−P(3)−O(3) = 112.67(17); O(2)−P(3)−O(3) = 98.06(16). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

Chart 3



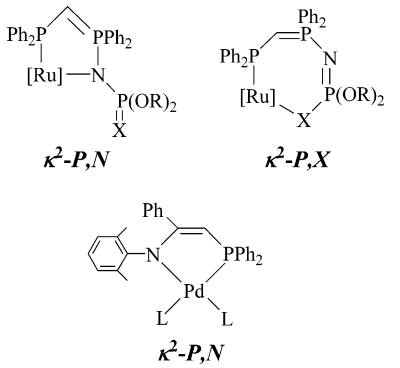
(11) An important shielding is observed in the Ph_2P phosphorus resonances when moving from **1**−**2a**,**b** (22.97−26.36 ppm) to **3**−**4a**,**b** (6.26−7.18 ppm). This fact is in agreement with the formation of a smaller chelate ring: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(12) The diphenylphosphino group in ruthenium(II) complexes containing Ru(κ^2-*P,C*-Ph_2PCHR) units usually resonate, in ^{31}P NMR, at δ 4−9 ppm. See for example: (a) Demerseman, B.; Guilbert, B.; Renouard, C.; Gonzalez, M.; Dixneuf, P. H.; Masi, D.; Mealli, C. *Organometallics* **1993**, *12*, 3906. (b) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048, and references therein.

(13) As expected, the two enantiomers are present in the unit cell displaying $S_{Ru}S_C$ and $R_{Ru}R_C$ configurations. For brevity, only the molecular structure of the $S_{Ru}S_C$ enantiomer is depicted in Figure 1 (selected bond distances and angles listed in the caption refer to this enantiomer).

(14) (a) Henig, G.; Schulz, M.; Windmüller, B.; Werner, H. *Dalton Trans.* **2003**, 441. (b) Werner, H.; Bank, J.; Windmüller, B.; Gevert, O.; Wolfsberger, W. *Helv. Chim. Acta* **2001**, *84*, 3162.

Chart 4

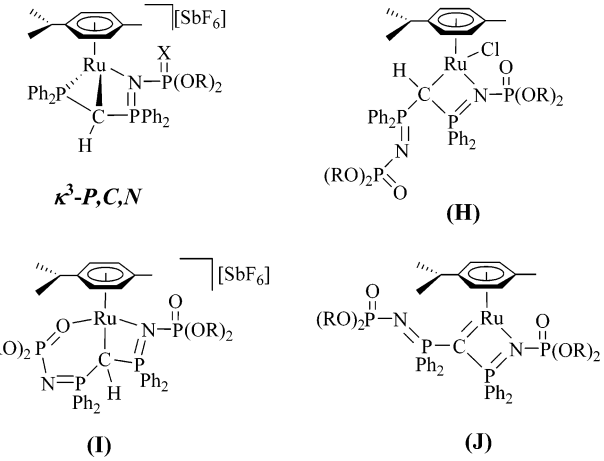


no example is known in the chemistry of iminophosphorane-phosphine ligands $R_2PCH_2P(=NR')R_2$.[5]

It is apparent that the bidentate κ^2-*P,C*-coordination mode of the anions $[Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2]^-$ (**A** in Chart 2) is preferred versus the κ^2-*P,N*- or κ^2-*P,X*-coordination isomers (see Chart 4). It is worth noting the favorable formation of a relatively strained Ru−P−C ring versus the more relaxed five- (κ^2-*P,N*) or seven-membered (κ^2-*P,X*) chelates. In fact, it has been recently reported the selective formation of five-membered κ^2-*P,N*-rings, i.e., complexes $[PdL_2\{\kappa^2\text{-}P,N\text{-}Ph_2PCH{=}C(Ph)\text{-}N(2,6\text{-}C_6H_3Me_2)\}]$ (see Chart 4), by deprotonation of the methylenic unit in compounds $[PdL_2\{\kappa^2\text{-}P,N\text{-}Ph_2PCH_2C(Ph){=}N(2,6\text{-}C_6H_3Me_2)\}]$ containing a related iminophosphine ligand.[17]

Analogous deprotonations also occur starting from the dicationic complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)][SbF_6]_2$ (X = O, R = Et (**5a**), Ph (**5b**); X = S, R = Et (**6a**), Ph (**6b**)).[8] Thus, the treatment of complexes **5**−**6a**,**b** with a stoichiometric amount of NaH, in THF at room temperature, affords the cyclometalated complexes $[Ru(\kappa^3\text{-}P,C,X\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})][SbF_6]$ (X = O, R = Et (**7a**), Ph (**7b**); X = S, R = Et (**8a**), Ph (**8b**)) via PCH_2P deprotonation and selective decoordination of the labile iminophosphorane $Ph_2P{=}N$ unit (Scheme 1). Compounds **7**−**8a**,**b** have been isolated as air-stable microcrystalline solids in 79−93% yield. As expected, **7**−**8a**,**b** can also be prepared in similar yields by reaction of the neutral complexes $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (X = O, R = Et (**3a**), Ph (**3b**); X = S, R = Et (**4a**), Ph (**4b**)) with 1 equiv of $AgSbF_6$, in dichloromethane at room temperature, via diastereoselective intramolecular *O*- or *S*-coordination of the free $-Ph_2P{=}NP(=X)(OR)_2$ fragment (see Scheme 1).

Chart 5



Complexes **7**−**8a**,**b** have been characterized by elemental analyses, conductance measurements (1:1 electrolytes; Λ_M = 111−120 Ω^{-1} cm^2 mol^{-1}), and IR and NMR spectroscopy (see the Experimental Section and the Supporting Information for details), the latter supporting its diastereoselective formation. Characteristic spectroscopic features are (i) (^{1}H NMR) the methinic PCHP proton resonance at 1.89−2.07 ppm which, in contrast to **3**−**4a**,**b**, appears as doublet due to the exclusive coupling with the phosphorus atom of the $Ph_2P{=}N$ unit ($^2J_{HP}$ = 6.1−6.4 Hz), (ii) ($^{13}C\{^1H\}$ NMR) the ddd signal for the PCHP carbon (δ from −8.69 to −6.22 ppm; $^1J_{CP(V)}$ = 67.6−69.2 Hz; $^1J_{CP(III)}$ = 11.5−15.5 Hz; $^3J_{CP(V)}$ = 7.8−11.5 Hz) which is ca. 16 ppm high-field shifted when compared to that of their neutral precursors **3**−**4a**,**b**, and (iii) ($^{31}P\{^1H\}$ NMR) the typical signals for the Ph_2P (δ 4.34−9.87 (d or dd, $^2J_{PP}$ = 15.9−22.6 Hz, $^3J_{PP}$ = 0−4.5 Hz)) and $(RO)_2P{=}O$ (δ −0.28−8.85 (d, $^2J_{PP}$ = 16.2−17.1 Hz)) or $(RO)_2P{=}S$ (δ 40.94−47.75 (d or dd, $^2J_{PP}$ = 7.2−9.0 Hz, $^3J_{PP}$ = 0−4.5 Hz)) units. The chemical shifts found for the $Ph_2P{=}N$ phosphorus nuclei (δ 23.32−31.29 (dd, $^2J_{PP}$ = 15.9−22.6 and 7.2−17.1 Hz)) strongly support the κ^3-*P,C,X*-coordination of the ligands versus the potential κ^3-*P,C,N*-coordination isomers (Chart 5). We note that $Ph_2P{=}N$ phosphorus resonances in the related species **H**, **I**, and **J** (see Chart 5) are observed at 60−70 ppm.[18] The preference for the κ^3-*P,C,X*- versus κ^3-*P,C,N*-coordination mode observed in complexes **7**−**8a**,**b** could probably be due to the higher steric strain associated with the presence of an unfavorable three- and four-membered fused metalla-bicycle in the latter.

Protonation of complexes $[RuCl(\kappa^2\text{-}P,C\text{-}Ph_2PCHP\{=NP(=O)(OPh)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})]$ (**3b**) and $[Ru(\kappa^3$-

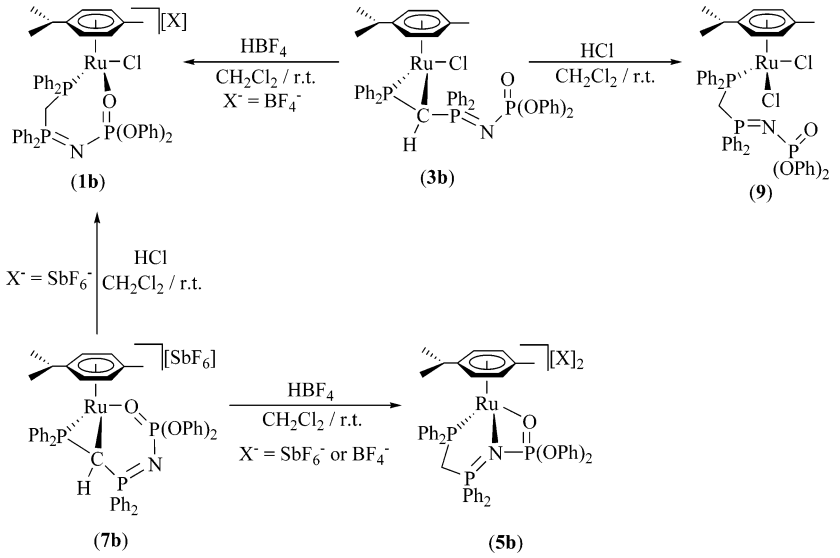
(15) See for example: (a) Larré, C.; Donnadieu, B.; Caminade, A. M.; Majoral, J. P. *Eur. J. Inorg. Chem.* **1999**, 601. (b) Balakrishna, M. S.; Abhyankar, R. M.; Walawalker, M. G. *Tetrahedron Lett.* **2001**, *42*, 2733. (c) Longlet, J. J.; Bodige, S. G.; Watson, W. H.; Nielson, R. H. *Inorg. Chem.* **2002**, *41*, 6507. (d) Maraval, V.; Laurent, R.; Donnadieu, B.; Caminade, A. M.; Majoral, J. P. *Synthesis* **2003**, 389.

(16) Cyclometalation of coordinated tertiary alkyl-phosphines is a widely occurring phenomenon. See for example: (a) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (b) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem.* **1975**, *87*, 630. (c) Al-Jibori, S.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1572. (d) Karsch, H. H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 312. (e) Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 921. (f) Karsch, H. H. *Chem. Ber.* **1984**, *117*, 783. (g) Karsch, H. H. *Chem. Ber.* **1984**, *117*, 3123. (h) Mainz, V. V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675. (i) Gotzig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99. (j) Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821. (k) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (l) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (m) Dahlenburg, L.; Kerstan, S.; Werner, D. *J. Organomet. Chem.* **1991**, *411*, 457. (n) Werner, H.; Henig, G.; Wecker, U.; Mahr, N.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1995**, *128*, 1175. (o) Holland, A. W.; Bergman, R. G. *Organometallics* **2002**, *21*, 2149. (p) Janak, K. E.; Tanski, J. M.; Churchill, D. G.; Parkin, G. *J. Am. Chem. Soc.* **2002**, *124*, 4182. (q) Liu, S. H.; Lo. S. T.; Wen, T. B.; Williams, I. D.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Inorg. Chim. Acta* **2002**, *334*, 122.

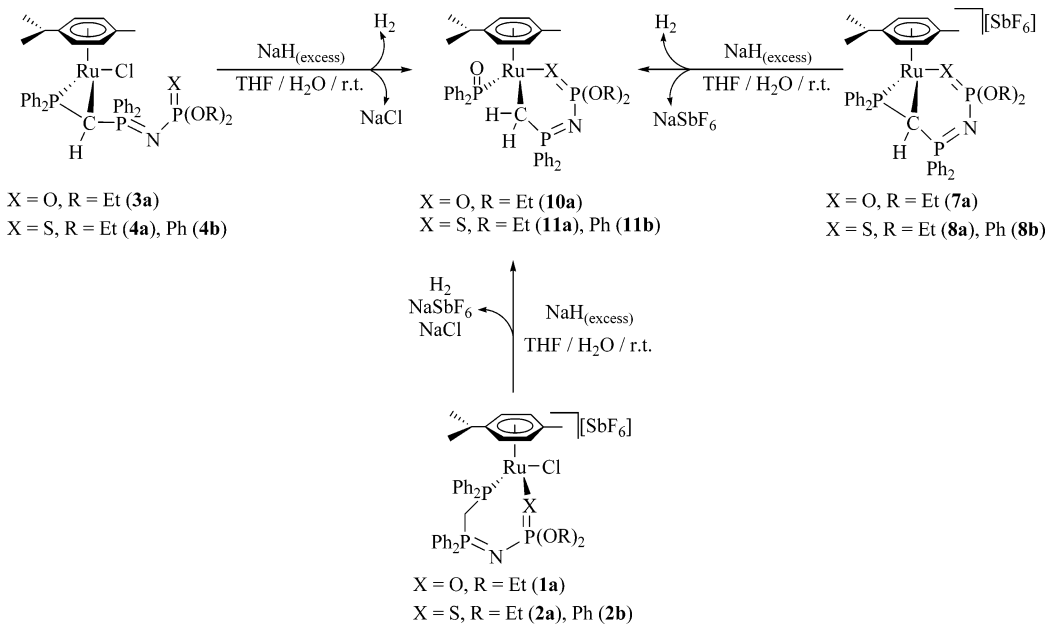
(17) (a) Coleman, K. S.; Green, M. L. H.; Pascu, S. I.; Rees, N. H.; Cowley, A. R.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2001**, 3384. Imine-enamine tautomerism has been also observed for this type of P,N-ligands in solution: (b) Liu, X.; Mok, K. F.; Leung, P.-H. *Organometallics* **2001**, *20*, 3918. (c) Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton Trans.* **2003**, 3500.

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

Scheme 2



Scheme 3



P,C,X-$Ph_2PCHP\{=NP(=O)(OPh)_2\}Ph_2$)($\eta^6$-*p*-cymene)][$SbF_6$] (**7b**) shows the reversibility of the processes depicted in Scheme 1 (see Scheme 2). Thus, we have found that, while the treatment of **3b** with an equimolar amount of HBF_4 regenerates complex **1b** (as the tetrafluoroborate salt) quantitatively, the use of HCl (1 equiv) results in the selective formation of the previously reported neutral complex [$RuCl_2$(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OPh)_2\}Ph_2$)($\eta^6$-*p*-cymene)] (**9**) via competitive chloride coordination.[8a] Similar results were obtained starting from **7b**, which can be selectively transformed into **5b** or **1b** depending on the protic acid used.

Synthesis and Characterization of Phosphinito Derivatives [Ru(κ^2-*C,X*-$CH_2P\{=NP(=X)(OR)_2\}Ph_2$)-{$\kappa^1$-*P*-$P(=O)Ph_2$}($\eta^6$-*p*-cymene)] (X = O, R = Et (10a); X = S, R = Et (11a), Ph (11b)) and [Ru(κ^2-*C,S*-$CH_2P\{=NP(=S)(OEt)_2\}Ph_2$){$\kappa^1$-*P*-$P(=O)Ph_2$}($\eta^6$-$C_6H_6$)] (11a′). Providing that the methylenic carbon−hydrogen bonds are activated in the iminophosphorane complexes **1**−**2a**,**b** and **5**−**6a**,**b** promoting the formation of a ruthenium−carbon bond, we speculated the possibility to generate ruthenium-carbene complexes via subsequent deprotonation of the remaining C−H bond. We have recently reported the synthesis of unusual ruthenium-carbene derivatives [Ru(κ^2-*C,N*-C[$P\{=NP(=O)(OR)_2\}Ph_2$]$_2$)(η^6-*p*-cymene)] (R = Ph, Et) (**J** in Chart 5) from complexes containing bis(iminophosphorano)methanide groups of the type **H** and **I** (Chart 5).[18] However, the treatment of complexes **3a** and **4a**,**b** with a 10-fold excess of NaH in THF at room temperature leads instead to the formation of diphenylphosphinitoruthenium(II) derivatives [Ru(κ^2-*C,X*-$CH_2P\{=NP(=X)(OR)_2\}Ph_2$){$\kappa^1$-*P*-$P(=O)Ph_2$}($\eta^6$-*p*-cymene)] (X = O, R = Et (**10a**); X = S, R = Et (**11a**), Ph (**11b**)) (Scheme 3). It is interesting to note that the reaction proceeds faster (ca. 6 h) when undistilled THF (wet) was used as solvent (versus ca. 48 h with predistilled THF). Complexes **10a** and **11a**,**b** can also be obtained (74−91% yield), under the same reaction conditions, starting from the cationic species [Ru(κ^3-*P,C,X*-$Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2$)($\eta^6$-

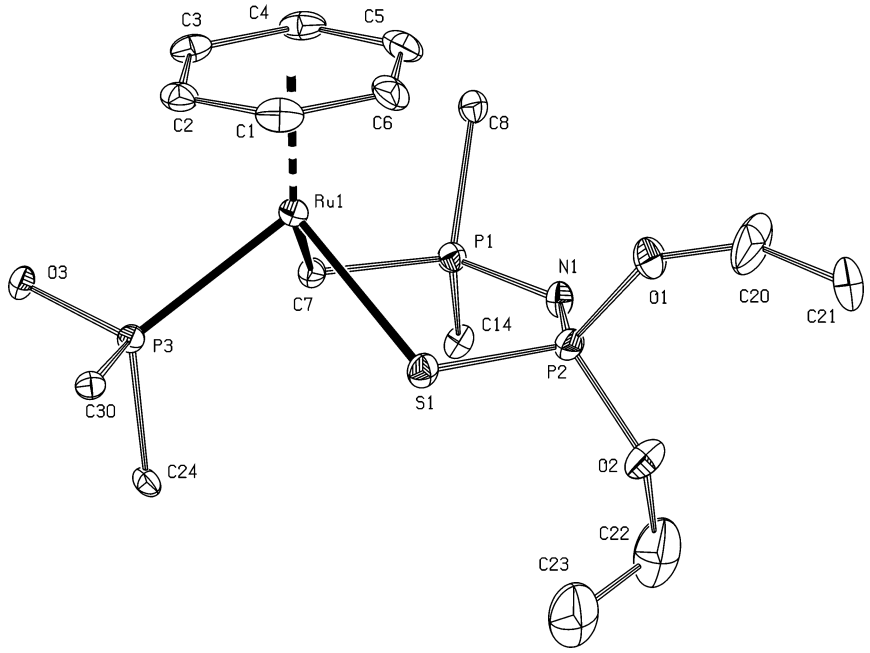


Figure 2. ORTEP-type view of the structure of [Ru(κ^2-*C,S*-$CH_2P\{=NP(=S)(OEt)_2\}Ph_2$)($\kappa^1$-*P*-$P(=O)Ph_2$}($\eta^6$-$C_6H_6$)] (**11a′**) showing the crystallographic labeling scheme. Phenyl groups and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond distances (Å) and angles (deg): Ru−C(7) = 2.158(7); Ru−P(3) = 2.338(2); Ru−S(1) = 2.405(2); Ru−C* = 1.7384(9); C(7)−P(1) = 1.756(7); P(1)−N(1) = 1.590(6); N(1)−P(2) = 1.556(6); P(2)−S(1) = 1.982(3); P(2)−O(1) = 1.577(6); P(2)−O(2) = 1.563(6); P(3)−O(3) = 1.519(5); C*−Ru−C(7) = 130.8(2); C*−Ru−P(3) = 123.85(6); C*−Ru−S(1) = 127.00(7); C(7)−Ru−P(3) = 82.7(2); C(7)−Ru−S(1) = 87.3(2); P(3)−Ru−S(1) = 91.50(8); Ru−P(3)−O(3) = 113.1(2); Ru−P(3)−C(24) = 118.2(2); Ru−P(3)−C(30) = 111.7(3); O(3)−P(3)−C(24) = 106.1(3); O(3)−P(3)−C(30) = 106.4(3); C(24)−P(3)−C(30) = 100.2(3); Ru−C(7)−P(1) = 116.4(4); C(7)−P(1)−N(1) = 115.8(4); P(1)−N(1)−P(2) = 133.1(4); N(1)−P(2)−O(1) = 109.7(4); N(1)−P(2)−O(2) = 111.0(4); N(1)−P(2)−S(1) = 118.8(3); O(1)−P(2)−O(2) = 100.2(4); O(1)−P(2)−S(1) = 107.4(3); O(2)−P(2)−S(1) = 108.1(3); P(2)−S(1)−Ru = 105.25(11). C* = centroid of the benzene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

p-cymene)][SbF_6] (X = O, R = Et (**7a**); X = S, R = Et (**8a**), Ph (**8b**)) or [RuCl(η^6-*p*-cymene)(κ^2-*P,X*-$Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$)][$SbF_6$] (X = O, R = Et (**1a**); X = S, R = Et (**2a**), Ph (**2b**)) (Scheme 3).[19,20] Compounds **10a** and **11a**,**b** formally arise from an OH^--promoted phosphorus−carbon bond splitting with concomitant formation of P=O and C−H bonds.[21] All attempts to avoid the P−C cleavage have failed.

Complexes **10a** and **11a**,**b** have been isolated as air-stable yellow solids. They have been characterized by elemental analyses and IR and NMR spectroscopy (details are given in the Experimental Section and the Supporting Information), which are fully consistent with the structural proposal. In particular, (i) the presence of a coordinated $Ph_2P(=O)$ ligand is strongly supported by the $^{31}P\{^1H\}$ NMR spectra, which show a downfield doublet (**10a**) or doublet of doublets signal (**11a**,**b**) at δ 70.92−73.75 ppm ($^3J_{PP}$ = 14.8−19.0 Hz). These chemical shifts fit well with those reported in the literature for related diphenylphosphinito-ruthenium(II) complexes.[20c] (ii) Typical Ru−CH_2 carbon resonances appear in the $^{13}C\{^1H\}$ NMR spectra as a high-field doublet of doublet of doublets signal in the range from −2.74 to 0.30 ppm ($^1J_{CP}$ = 38.1−41.1 Hz; $^2J_{CP}$ = 13.7−16.1 Hz; $^3J_{CP}$ = 8.3−11.7 Hz).

X-ray diffraction studies on the related η^6-benzene derivative [Ru(κ^2-*C,S*-$CH_2P\{=NP(=S)(OEt)_2\}Ph_2$)($\kappa^1$-*P*-$P(=O)Ph_2$}($\eta^6$-$C_6H_6$)] (**11a′**) unequivocally confirmed the molecular structure proposed for complexes **10**−**11a**,**b**.[22] An ORTEP plot is shown in Figure 2; selected bond distances and angles are listed in the caption. The coordination sphere around ruthenium consists of the η^6-benzene fragment, the phosphorus atom of the diphenylphosphinito unit, and the carbon and sulfur atoms of the novel anionic ligand $[CH_2P\{=NP(=S)(OEt)_2\}Ph_2]^-$, which forms along with the metal a six-membered ring with chair conformation. The P(1)−N(1) and N(1)−P(2) distances within this six-membered ring are quite similar (1.590(6) and 1.556(6) Å, respectively), indicating, as observed in **3b**, that electronic delocalization of the nitrogen lone pair is also present.[3f,8,15] The P(3)−O(3) bond length (1.519(5) Å) is in good agreement with

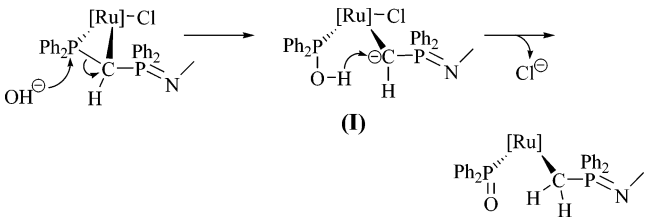
(19) Treatment of complex **1b**, **3b**, or **7b** with 10 equiv of NaH in wet THF generates also the corresponding phosphinito derivative [Ru(κ^2-*C,O*-$CH_2P\{=NP(=O)(OPh)_2\}Ph_2$)($\kappa^1$-*P*-$P(=O)Ph_2$}($\eta^6$-*p*-cymene)] (**10b**), as clearly assessed by $^{31}P\{^1H\}$ NMR spectroscopy (δ_P 7.72 (d, $^2J_{PP}$ = 17.1 Hz, $(PhO)_2P(=O)$), 27.77 (dd, $^2J_{PP}$ = 17.1 Hz, $^3J_{PP}$ = 12.2 Hz, $Ph_2P(=N)$), 80.89 (d, $^3J_{PP}$ = 12.2 Hz, $Ph_2P(=O)$)), along with several unidentified species, which prevented its isolation in pure form.

(20) Mononuclear phosphinito-ruthenium(II) and osmium(II) complexes [M]-{$PR_2(=O)$} are known. For recent references see: (a) Esteruelas, M. A.; López, A. M.; Tolosa, J. I.; Vela, N. *Organometallics* **2000**, 19, 4650. (b) Geldbach, T. J.; Pregosin, P. S.; Bassetti, M. *Organometallics* **2001**, *20*, 2990. (c) Geldbach, T. J.; den Reijer, C. J.; Wörle, M.; Pregosin, P. S. *Inorg. Chim. Acta* **2002**, *330*, 155.

(21) Scission of phosphorus−cabon bonds in ruthenium-coordinated phosphine ligands is known to occur in both basic and acidic media. See for example ref 12b and: Geldbach, T. J.; Pregosin, P. S. *Eur. J. Inorg. Chem*. **2002**, 1907, and references therein.

(22) All attempts to obtain crystals of compounds **10**−**11a**,**b** suitable for X-ray diffraction studies failed. Complex **11a′** was prepared in 77% yield, as described for **10**−**11a**,**b**, starting from [RuCl(η^6-C_6H_6)(κ^2-*P,S*-$Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2$)][$SbF_6$] (**2a′**). Synthetic details and characterization data for **2a′**, **11a′**, and the precursor species [$RuCl_2$-(η^6-C_6H_6)(κ^1-*P*-$Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2$)] are given in the Experimental Section.

Scheme 4



literature P−O distances for phosphine oxides,[23] and the Ru−C(7) and Ru−P(3) lengths (2.158(7) and 2.338(2) Å, respectively) show also the expected values for ruthenium−carbon and ruthenium−phosphorus single bonds.[24]

A mechanistic proposal for the formation of complexes **10**−**11a**,**b** is depicted in Scheme 4. We assume that a nuclephilic attack of OH^- (generated in situ from NaH and the water present in the undistilled solvent) at the phosphorus atom of the three-membered metallacycle takes place in the first step, giving rise to the cleavage of the P−C bond to form intermediate species **I**. A subsequent H-migration from oxygen to the resulting nucleophilic carbon atom gives the final product. In the case of **3**−**4a**,**b** the concomitant chloride abstraction leaves a free coordination site, allowing the attachment of the phosphoryl or thiophosphoryl unit. We note that such P−C bond cleavage has no precedent in the chemistry of the three-membered metallacyclic compounds of the type [M]-(κ^2-*P*,*C*-R_2PCHR).[12,14,16]

Synthesis and Characterization of [Ru(κ^2-*C*,*X*-$CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2$)($\kappa^1$-*P*-$P(OH)Ph_2$)($\eta^6$-*p*-cymene)][$BF_4$] (X = O, R = Et (12a); X = S, R = Et (13a), Ph (13b)) and [Ru(κ^2-*C*,*X*-$CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2$)($\kappa^1$-*P*-$P(OMe)Ph_2$)($\eta^6$-*p*-cymene)][$CF_3SO_3$] (X = O, R = Et (14a); X = S, R = Et (15a), Ph (15b)). In agreement with the presence of the phosphinito $Ph_2P{=}O$ group, complexes **10**−**11a**,**b** are prone to add electrophiles at the oxygen atom. Thus, the treatment of dichloromethane solutions of **10**−**11a**,**b** with 1 equiv of HBF_4 generates the novel hydroxydiphenylphosphine-ruthenium(II) derivatives [Ru(κ^2-*C*,*X*-$CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2$)($\kappa^1$-*P*-$P(OH)Ph_2$)($\eta^6$-*p*-cymene)][$BF_4$] (X = O, R = Et (**12a**); X = S, R = Et (**13a**), Ph (**13b**)) (60−75% yield) (Scheme 5). Similarly, complexes [Ru(κ^2-*C*,*X*-$CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2$)($\kappa^1$-*P*-$P(OMe)Ph_2$)($\eta^6$-*p*-cymene)][$CF_3SO_3$] (X = O, R = Et (**14a**); X = S, R = Et (**15a**), Ph (**15b**)) have been prepared (70−78% yield) via methylation reactions with $MeOSO_2CF_3$ (Scheme 5). Analogous transformations of coordinated phosphinito ligands into hydroxy- or alkoxyphosphines have been described.[20a]

Complexes **12**−**13a**,**b** and **14**−**15a**,**b** have been isolated as yellow air-stable tetrafluoroborate or triflouromethanesulfonate salts, respectively, and characterized by elemental analysis, conductance masurements (1:1 electrolytes; $\Lambda_M = 116-132\ \Omega^{-1}\ cm^2\ mol^{-1}$), and IR and NMR spectroscopy. The presence of the hydroxy- and methoxy-phosphine ligands Ph_2POR (R = H, Me) is fully suported by IR and NMR spectroscopy. Particular features are (i) (IR) a characteristic ν(OH) absorption band at 3230−3280 cm^{-1} for **12**−**13a**,**b**, (ii) (^{1}H NMR) a low-field broad singlet (**12**−**13a**,**b**) or a high-field doublet (**14**−**15a**,**b**) signal corresponding to the OH (δ 8.91−11.60 ppm) and OMe (δ 3.40−3.51 ppm; ca. $^3J_{HP} = 11$ Hz) protons, respectively, and (iii) (^{31}P-{^{1}H} NMR) a doublet of doublets signal (δ 112.34−117.61 ppm; $^3J_{PP} = 4.4-24.4$ Hz) for the Ph_2POH phosphorus nucleus, the low-field chemical shifts observed being in accord with those observed in other hydroxydiphenylphosphine-ruthenium(II) complexes (for **14**−**15a**,**b** the signal of the Ph_2POMe ligand appears at δ 130.31−135.81 ppm).[25] NMR spectra also show the resonances arising from the presence of the bidentate ligands κ^2-*C*,*X*-$CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2$. Since they show no significant differences with respect to those of the precursor complexes **10**−**11a**,**b**, no further comment is deserved.

Conclusion

In this paper we have shown that the functionalized iminophosphorane-phosphines $Ph_2PCH_2P\{{=}NP({=}X)(OR)_2\}Ph_2$ (X = O, S; R = Et, Ph) act as versatile ligands upon coordination to a (η^6-arene)-ruthenium(II) fragment, generating through selective transformations unusual systems containing ruthenium−carbon bonds. These are generated by the formation of two novel anionic ligands of the type (i) $[Ph_2PCHP\{{=}NP({=}X)(OR)_2\}Ph_2]^-$ (**I**) obtained by deprotonation of the methylenic backbone of the iminophosphorane-phosphine ligands in complexes **1**−**2a**,**b** and **5**−**6a**,**b**, and (ii) $[CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2]^-$ (**II**) via base-assisted P−C bond splitting in the latter complexes in which ligands **I** show κ^2-*P*,*C* (complexes **3**−**4a**,**b**) and κ^3-*P*,*C*,*X* (complexes **7**−**8a**,**b**) coordination modes. The coordination ability of the anionic polydentate ligands of the type **I** in complexes **7**−**8a**,**b** is remarkable, adopting selectively the rare case of a κ^3-*P*,*C*,*X*-coordination mode in which two fused three- and six-membered metallacycles are stabilized.

It is also worth noting that the closely related ligands bis(diphenylphosphino)methanide monochalcogenides $[Ph_2PCHP({=}X)Ph_2]^-$ (X = O, S, Se) show in contrast a marked preference for the κ^2-*P*,*X*- versus κ^2-*P*,*C*-coordination mode, leading to less strained five-membered chelates.[26,27] In summary, the results reported here, which have no precedents in the chemistry of iminophosphorane-phosphine ligands $Ph_2PCH_2P({=}NR)Ph_2$,[5] represent a clear example of the usefulness of these ligands as templates for the construction and stabilization of unusual organometallic ruthenium(II) complexes.

(23) See for example: Allen, F. H.; Kennard, O.; Watson, D. G.; Orpen, A. G.; Brammer, L.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

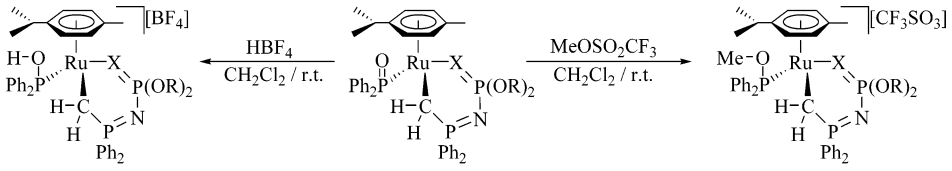
(24) See for example: Seddon, E. A.; Seddon, K. R. In *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984, and references therein.

(25) See for example: (a) den Reijer, C. J.; Wörle, M.; Pregosin, P. S. *Organometallics* **2000**, *19*, 309. (b) Geldbach, T. J.; Drago, D.; Pregosin, P. S. *J. Organomet. Chem.* **2002**, *643*−*644*, 214. (c) Geldbach, T. J.; Pregosin, P. S.; Albinati, A. *Organometallics* **2003**, *22*, 1443.

(26) See for example: (a) Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W. *Can. J. Chem.* **1988**, *66*, 1272. (b) Browning, J.; Dixon, K. R.; Hilts, R. W. *Organometallics* **1989**, *8*, 552. (c) Usón, R.; Laguna, A.; Laguna, M.; Nieves Fraile, M.; Jones, P. G.; Freire Erdbrügger, C. *J. Chem. Soc., Dalton Trans.* **1989**, 73. (d) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1993**, *452*, 205.

(27) The dinuclear complex [$Pd_2\{\mu{:}\kappa^2$-*P*,*C*-$Ph_2PCHP({=}O)Ph_2\}(CN$-2,6-$C_6H_3Me_2)_2(\mu$-dppm)$_2$], in which the Pd−Pd unit is bridged by a κ^2-*P*,*C*-$[Ph_2PCHP({=}O)Ph_2]^-$ ligand, is known: Rashidi, M.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1283.

Scheme 5



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 compounds [RuCl(η^6-*p*-cymene)(κ^2-*P,X*-$Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$)][$SbF_6$] (X = O, R = Et (**1a**), Ph (**1b**); X = S, R = Et (**2a**), Ph (**2b**)),[8] [Ru(η^6-*p*-cymene)-(κ^3-*P,N,X*-$Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (X = O, R = Et (**5a**), Ph (**5b**); X = S, R = Et (**6a**), Ph (**6b**)),[8] $Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2$,[8b] and [{Ru($\eta^6$-$C_6H_6$)($\mu$-Cl)Cl}$_2$],[28] 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_3PO_4 as standard. DEPT experiments have been carried out for all the compounds reported in this paper.

Synthesis of [RuCl(κ^2-*P,C*-$Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2$)($\eta^6$-*p*-cymene)] (X = O, R = Et (3a), Ph (3b); X = S, R = Et (4a), Ph (4b)). A solution of the corresponding complex [RuCl(η^6-*p*-cymene)(κ^2-*P,X*-$Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$)]-[$SbF_6$] (**1**−**2a**,**b**) (0.2 mmol) in 30 mL of THF was treated, at room temperature, with NaH (0.005 g, 0.21 mmol) for 30 min. After removing the solvent under reduced presure, the solid residue was extracted with dichloromethane and filtered over Kieselguhr. The resulting solution was then concentrated to ca. 2 mL, and 50 mL of hexanes was added, yielding a microcrystalline yellow solid, which was washed with hexanes (3 × 10 mL) and vaccum-dried. **3a**: Yield 99% (0.159 g). Anal. Calcd for $RuC_{39}H_{45}O_3P_3ClN$: C, 58.17; H, 5.63; N, 1.74. Found: C, 57.90; H, 5.46; N, 1.63. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.53 (d, $^2J_{PP}$ = 34.4 Hz, $(EtO)_2P$=O), 7.18 (d, $^2J_{PP}$ = 25.1 Hz, Ph_2P), 19.53 (dd, $^2J_{PP}$ = 34.4 and 25.1 Hz, Ph_2P=N) ppm. ^{1}H NMR (C_6D_6): δ 1.17 and 1.26 (d, 3H each, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.22 (t, 3H, $^3J_{HH}$ = 7.3 Hz, OCH_2CH_3), 1.31 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 2.08 (s, 3H, CH_3), 2.22 (dd, 1H, $^2J_{HP}$ = 7.0 and 7.0 Hz, PCHP), 2.38 (m, 1H, $CH(CH_3)_2$), 4.26 (m, 4H, OCH_2CH_3), 5.02 and 6.37 (d, 1H each, $^3J_{HH}$ = 5.3 Hz, CH of *p*-cymene), 5.33 and 5.99 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 7.02−8.71 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.23 (ddd, $^1J_{CP}$ = 104.4 and 19.8 Hz, $^3J_{CP}$ = 11.1 Hz, PCHP), 16.84 and 16.94 (d, $^3J_{CP}$ = 7.6 Hz, OCH_2CH_3), 18.99 (s, CH_3), 22.95 and 24.44 (s, $CH(CH_3)_2$), 31.38 (s, $CH(CH_3)_2$), 61.24 (d, $^2J_{CP}$ = 5.2 Hz, OCH_2CH_3), 61.31 (d, $^2J_{CP}$ = 5.8 Hz, OCH_2CH_3), 80.16, 84.82, 85.34, and 91.13 (s, CH of *p*-cymene), 99.80 (d, $^2J_{CP}$ = 7.6 Hz, C of *p*-cymene), 110.12 (d, $^2J_{CP}$ = 4.1 Hz, C of *p*-cymene), 126.45−135.84 (m, Ph) ppm. **3b**: Yield 92% (0.166 g). Anal. Calcd for $RuC_{47}H_{45}O_3P_3ClN$: C, 62.63; H, 5.03; N, 1.55. Found: C, 62.92; H, 5.01; N, 1.43. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −9.93 (d, $^2J_{PP}$ = 29.3 Hz, $(PhO)_2P$=O), 6.26 (d, $^2J_{PP}$ = 24.4 Hz, Ph_2P), 24.00 (dd, $^2J_{PP}$ = 29.3 and 24.4 Hz, Ph_2P=N) ppm. ^{1}H NMR (C_6D_6): δ 1.04 and 1.06 (d, 3H each, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.94 (s, 3H, CH_3), 2.07 (dd, 1H, $^2J_{HP}$ = 6.7 and 6.7 Hz, PCHP), 2.20 (m, 1H, $CH(CH_3)_2$), 4.86 and 6.05 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.17 and 5.75 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.79−8.54 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 8.71 (ddd, $^1J_{CP}$ = 102.8 and 21.0 Hz, $^3J_{CP}$ = 11.7 Hz, PCHP), 18.93 (s, CH_3), 22.91 and 24.43 (s, $CH(CH_3)_2$), 31.35 (s, $CH(CH_3)_2$), 79.83, 84.87, 85.11 and 91.50 (s, CH of *p*-cymene), 99.59 (d, $^2J_{CP}$ = 7.6 Hz, C of *p*-cymene), 109.87 (d, $^2J_{CP}$ = 4.1 Hz, C of *p*-cymene), 120.47−147.68 (m, Ph), 153.56 (d, $^2J_{CP}$ = 6.4 Hz, C_{ipso} of OPh), 153.66 (d, $^2J_{CP}$ = 7.0 Hz, C_{ipso} of OPh) ppm. **4a**: Yield 67% (0.110 g). Anal. Calcd for $RuC_{39}H_{45}P_3O_2ClNS\cdot 1/4CH_2Cl_2$: C, 55.95; H, 5.44; N, 1.66. Found: C, 56.09; H, 5.29; N, 1.56. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 7.04 (d, $^2J_{PP}$ = 24.4 Hz, Ph_2P), 18.61 (dd, $^2J_{PP}$ = 24.4 and 12.6 Hz, Ph_2P=N), 58.13 (d, $^2J_{PP}$ = 12.6 Hz, $(EtO)_2P$=S) ppm. ^{1}H NMR (C_6D_6): δ 1.15 (t, 3H, $^3J_{HH}$ = 7.2 Hz, OCH_2CH_3), 1.18 and 1.20 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.25 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 2.13 (s, 3H, CH_3), 2.14 (dd, 1H, $^2J_{HP}$ = 7.0 and 7.0 Hz, PCHP), 2.40 (m, 1H, $CH(CH_3)_2$), 4.28 (m, 4H, OCH_2CH_3), 5.09 and 6.43 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.34 and 6.01 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.98−8.67 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 7.06 (ddd, $^1J_{CP}$ = 104.3 and 19.0 Hz, $^3J_{CP}$ = 8.5 Hz, PCHP), 16.96 (d, $^3J_{CP}$ = 8.6 Hz, OCH_2CH_3), 17.11 (d, $^3J_{CP}$ = 7.1 Hz, OCH_2CH_3), 19.68 (s, CH_3), 23.63 and 25.05 (s, $CH(CH_3)_2$), 31.98 (s, $CH(CH_3)_2$), 62.80 (d, $^2J_{CP}$ = 4.2 Hz, OCH_2CH_3), 63.54 (d, $^2J_{CP}$ = 4.8 Hz, OCH_2CH_3), 80.95, 85.66, and 85.94 (s, CH of *p*-cymene), 91.13 (d, $^2J_{CP}$ = 3.0 Hz, CH of *p*-cymene), 100.61 (d, $^2J_{CP}$ = 7.5 Hz, C of *p*-cymene), 110.52 (d, $^2J_{CP}$ = 4.1 Hz, C of *p*-cymene), 120.05−136.58 (m, Ph) ppm. **4b**: Yield 91% (0.167 g). Anal. Calcd for $RuC_{47}H_{45}P_3O_2ClNS$: C, 61.53; H, 4.94; N, 1.53. Found: C, 61.60; H, 4.97; N, 1.48. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 6.70 (d, $^2J_{PP}$ = 25.3 Hz, Ph_2P), 22.80 (dd, $^2J_{PP}$ = 25.3 and 11.3 Hz, Ph_2P=N), 48.73 (d, $^2J_{PP}$ = 11.3 Hz, $(PhO)_2P$=S) ppm. ^{1}H NMR (C_6D_6): δ 1.16 (br, 6H, $CH(CH_3)_2$), 2.10 (s, 3H, CH_3), 2.16 (dd, 1H, $^2J_{HP}$ = 7.8 and 7.8 Hz, PCHP), 2.36 (m, 1H, $CH(CH_3)_2$), 5.06 and 6.25 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 5.29 and 5.95 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.97−8.72 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 10.04 (ddd, $^1J_{CP}$ = 104.5 and 21.6 Hz, $^3J_{CP}$ = 12.2 Hz, PCHP), 18.93 (s, CH_3), 22.84 and 24.35 (s, $CH(CH_3)_2$), 31.26 (s, $CH(CH_3)_2$), 80.11, 84.55, 85.61, and 91.56 (s, CH of *p*-cymene), 99.38 (d, $^2J_{CP}$ = 7.6 Hz, C of *p*-cymene), 109.97 (d, $^2J_{CP}$ = 4.1 Hz, C of *p*-cymene), 120.33−136.73 (m, Ph), 153.20 and 153.31 (br, C_{ipso} of OPh) ppm.

Synthesis of [Ru(κ^3-*P,C,X*-$Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2$)($\eta^6$-*p*-cymene)][$SbF_6$] (X = O, R = Et (7a), Ph (7b); X = S, R = Et (8a), Ph (8b)). Method A. A solution of the corresponding neutral complex [RuCl(κ^2-*P,C*-$Ph_2PCHP\{=NP(=X)(OR)_2\}Ph_2$)($\eta^6$-*p*-cymene)] (**3**−**4a**,**b**) (0.2 mmol) in 40 mL of CH_2Cl_2 was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.072 g, 0.21 mmol) for 1 h. The AgCl formed was then filtered off (Kieselghur) and the resulting solution concentrated to ca. 2 mL. Addition of hexanes (ca. 30 mL) gave a yellow microcrystalline solid, which was filtered, washed with hexanes (3 × 20 mL), and vacuum-dried. **7a**: Yield 93% (0.187 g). Anal. Calcd for $RuC_{39}H_{45}F_6O_3P_3NSb$: C, 46.59; H, 4.51; N, 1.39. Found: C, 46.88; H, 4.39; N, 1.37. Conductivity (acetone, 20 °C): 117 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$

(28) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

NMR ($(CD_3)_2CO$): δ 8.85 (d, $^2J_{PP}$ = 16.2 Hz, $(EtO)_2P{=}O$), 9.87 (d, $^2J_{PP}$ = 15.9 Hz, Ph_2P), 23.32 (dd, $^2J_{PP}$ = 16.2 and 15.9 Hz, $Ph_2P{=}N$) ppm. ^{1}H NMR ($(CD_3)_2CO$): δ 1.00 (t, 3H, $^3J_{HH}$ = 6.7 Hz, OCH_2CH_3), 1.23 (d, 6H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 1.27 (t, 3H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 1.69 (s, 3H, CH_3), 1.89 (d, 1H, $^2J_{HP}$ = 6.1 Hz, PCHP), 2.51 (m, 1H, $CH(CH_3)_2$), 3.96 (m, 4H, OCH_2CH_3), 4.73 and 5.69 (d, 1H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 5.21 and 5.62 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 7.05−8.38 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ −7.34 (ddd, $^1J_{CP}$ = 68.5 and 14.0 Hz, $^3J_{CP}$ = 8.0 Hz, PCHP), 16.30 (d, $^3J_{CP}$ = 7.6 Hz, OCH_2CH_3), 16.51 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 18.67 (s, CH_3), 23.32 and 23.90 (s, $CH(CH_3)_2$), 32.11 (s, $CH(CH_3)_2$), 63.09 (d, $^2J_{CP}$ = 2.9 Hz, OCH_2CH_3), 63.17 (d, $^2J_{CP}$ = 4.0 Hz, OCH_2CH_3), 79.20 and 80.57 (s, CH of *p*-cymene), 89.69 (d, $^2J_{CP}$ = 1.7 Hz, CH of *p*-cymene), 89.99 (d, $^2J_{CP}$ = 5.2 Hz, CH of *p*-cymene), 98.67 (d, $^2J_{CP}$ = 3.5 Hz, C of *p*-cymene), 113.18 (s, C of *p*-cymene), 122.16−137.48 (m, Ph) ppm. **7b**: Yield 82% (0.181 g). Anal. Calcd for $RuC_{47}H_{45}F_6O_3P_3NSb{\cdot}1/4CH_2Cl_2$: C, 50.54; H, 4.08; N, 1.25. Found: C, 50.62; H, 4.14; N, 1.17. Conductivity (acetone, 20 °C): 111 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ −0.28 (d, $^2J_{PP}$ = 17.1 Hz, $(PhO)_2P{=}O$), 8.37 (d, $^2J_{PP}$ = 17.1 Hz, Ph_2P), 26.08 (dd, $^2J_{PP}$ = 17.1 and 17.1 Hz, $Ph_2P{=}N$) ppm. ^{1}H NMR ($(CD_3)_2CO$): δ 0.89 (d, 3H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$), 1.22 (d, 3H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.63 (s, 3H, CH_3), 1.91 (d, 1H, $^2J_{HP}$ = 6.4 Hz, PCHP), 2.46 (m, 1H, $CH(CH_3)_2$), 4.27 and 5.21 (d, 1H each, $^3J_{HH}$ = 6.5 Hz, CH of *p*-cymene), 5.57 (br, 2H, CH of *p*-cymene), 7.12−8.35 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ −6.22 (ddd, $^1J_{CP}$ = 67.6 and 15.5 Hz, $^3J_{CP}$ = 7.8 Hz, PCHP), 18.66 (s, CH_3), 23.30 and 24.10 (s, $CH(CH_3)_2$), 32.30 (s, $CH(CH_3)_2$), 76.73 and 81.64 (s, CH of *p*-cymene), 89.93 (d, $^2J_{CP}$ = 5.8 Hz, CH of *p*-cymene), 92.07 (d, $^2J_{CP}$ = 3.2 Hz, CH of *p*-cymene), 97.63 and 113.71 (s, C of *p*-cymene), 120.34−137.31 (m, Ph), 151.85 and 152.54 (d, $^2J_{CP}$ = 7.8 Hz, C_{ipso} of OPh) ppm. **8a**: Yield 92% (0.188 g). Anal. Calcd for $RuC_{39}H_{45}F_6P_3O_2NSSb$: C, 45.85; H, 4.44; N, 1.37. Found: C, 46.11; H, 4.58; N, 1.51. Conductivity (acetone, 20 °C): 118 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 4.34 (d, $^2J_{PP}$ = 22.3 Hz, Ph_2P), 30.76 (dd, $^2J_{PP}$ = 22.3 and 7.2 Hz, $Ph_2P{=}N$), 47.75 (d, $^2J_{PP}$ = 7.2 Hz, $(EtO)_2P{=}S$) ppm. ^{1}H NMR ($(CD_3)_2CO$): δ 0.94 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.18 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.31 (t, 3H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 1.69 (s, 3H, CH_3), 2.07 (d, 1H, $^2J_{HP}$ = 6.4 Hz, PCHP), 2.44 (m, 1H, $CH(CH_3)_2$), 4.04 (m, 4H, OCH_2CH_3), 5.19 and 5.53 (d, 1H each, $^3J_{HH}$ = 5.5 Hz, CH of *p*-cymene), 5.32 and 5.73 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 7.18−8.40 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ −7.42 (ddd, $^1J_{CP}$ = 68.2 and 13.7 Hz, $^3J_{CP}$ = 9.1 Hz, PCHP), 15.56 (d, $^3J_{CP}$ = 8.0 Hz, OCH_2CH_3), 15.69 (d, $^3J_{CP}$ = 10.6 Hz, OCH_2CH_3), 18.07 (s, CH_3), 23.01 (s, 2C, $CH(CH_3)_2$), 31.18 (s, $CH(CH_3)_2$), 62.52 (d, $^2J_{CP}$ = 6.9 Hz, OCH_2CH_3), 63.84 (d, $^2J_{CP}$ = 7.4 Hz, OCH_2CH_3), 85.04 and 85.16 (s, CH of *p*-cymene), 90.31 (d, $^2J_{CP}$ = 2.7 Hz, CH of *p*-cymene), 90.95 (d, $^2J_{CP}$ = 4.8 Hz, CH of *p*-cymene), 102.09 (d, $^2J_{CP}$ = 4.2 Hz, C of *p*-cymene), 113.28 (d, $^2J_{CP}$ = 2.6 Hz, C of *p*-cymene), 121.40−135.99 (m, Ph) ppm. **8b**: Yield 90% (0.201 g). Anal. Calcd for $RuC_{47}H_{45}F_6P_3O_2NSSb{\cdot}1/2CH_2Cl_2$: C, 49.17; H, 3.99; N, 1.21. Found: C, 49.22; H, 3.94; N, 1.23. Conductivity (acetone, 20 °C): 120 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 5.44 (dd, $^2J_{PP}$ = 22.6 Hz, $^3J_{PP}$ = 4.5 Hz, Ph_2P), 31.29 (dd, $^2J_{PP}$ = 22.6 and 9.0 Hz, $Ph_2P{=}N$), 40.94 (dd, $^2J_{PP}$ = 9.0 Hz, $^3J_{PP}$ = 4.5 Hz, $(PhO)_2P{=}S$) ppm. ^{1}H NMR ($(CD_3)_2CO$): δ 1.06 (d, 3H, $^3J_{HH}$ = 6.0 Hz, $CH(CH_3)_2$), 1.15 (d, 3H, $^3J_{HH}$ = 5.8 Hz, $CH(CH_3)_2$), 1.58 (s, 3H, CH_3), 1.98 (br, 1H, PCHP), 2.27 (m, 1H, $CH(CH_3)_2$), 4.73 (br, 1H, CH of *p*-cymene), 5.16 (d, 1H, $^3J_{HH}$ = 4.7 Hz, CH of *p*-cymene), 5.63 (m, 2H, CH of *p*-cymene), 6.71−8.34 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ −8.69 (ddd, $^1J_{CP}$ = 69.2 and 11.5 Hz, $^3J_{CP}$ = 11.5 Hz, PCHP), 18.57 (s, CH_3), 22.62 and 24.00 (s, $CH(CH_3)_2$), 31.39 (s, $CH(CH_3)_2$), 84.76 and 85.16 (s, CH of *p*-cymene), 90.82 (d, $^2J_{CP}$ = 5.2 Hz, CH of *p*-cymene), 93.00 (d, $^2J_{CP}$ = 3.5 Hz, CH of *p*-cymene), 101.88 and 113.54 (s, C of *p*-cymene), 121.05−136.08 (m, Ph), 151.77 (d, $^2J_{CP}$ = 10.4 Hz, C_{ipso} of OPh), 152.49 (d, $^2J_{CP}$ = 8.7 Hz, C_{ipso} of OPh) ppm.

Method B. A solution of the corresponding complex $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,X\text{-}Ph_2PCH_2P\{{=}NP({=}X)(OR)_2\}Ph_2)][SbF_6]_2$ (**5**−**6a**,**b**) (0.2 mmol) in 30 mL of THF was treated, at room temperature, with NaH (0.005 g, 0.21 mmol) for 30 min. The reaction mixture was then evaporated to dryness and the solid residue extracted with dichloromethane and filtered off (Kieselguhr). Concentration of the resulting solution (ca. 2 mL) followed by the addition of hexanes (ca. 30 mL) gave a yellow microcrystalline solid, which was washed with hexanes (3 × 20 mL) and vacuum-dried. **7a**: Yield 80% (0.176 g). **7b**: Yield 88% (0.177 g). **8a**: Yield 93% (0.208 g). **8b**: Yield 79% (0.161 g).

Synthesis of $[Ru(\kappa^2\text{-}C,X\text{-}CH_2P\{{=}NP({=}X)(OR)_2\}Ph_2)\{\kappa^1\text{-}P\text{-}P({=}O)Ph_2\}(\eta^6\text{-}p\text{-cymene})]$ (X = O, R = Et (10a); X = S, R = Et (11a), Ph (11b)). Method A. A solution of the corresponding cationic complex $[RuCl(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{{=}NP({=}X)(OR)_2\}Ph_2)][SbF_6]$ (**1**−**2a**,**b**) (0.2 mmol) in 30 mL of undistilled THF was treated, at room temperature, with NaH (0.05 g, 2.1 mmol) for 6 h. After removing the solvent under reduced presure, the solid residue was extracted with dichloromethane and filtered over Kieselguhr. The resulting solution was then concentrated to ca. 2 mL, and 50 mL of hexanes was added, yielding a microcrystalline yellow solid, which was washed with hexanes (3 × 10 mL) and vaccum-dried. **10a**: Yield 83% (0.130 g). Anal. Calcd for $RuC_{39}H_{46}O_4P_3N$: C, 59.54; H, 5.89; N, 1.78. Found: C, 59.56; H, 5.91; N, 1.58. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 12.50 (d, $^2J_{PP}$ = 17.8 Hz, $(EtO)_2P{=}O$), 36.63 (dd, $^2J_{PP}$ = 17.8 Hz, $^3J_{PP}$ = 14.8 Hz, $Ph_2P{=}N$), 70.92 (d, $^3J_{PP}$ = 14.8 Hz, $Ph_2P{=}O$) ppm. ^{1}H NMR (C_6D_6): δ 0.82 (t, 3H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 0.96 (d, 3H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 1.15 (d, 3H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.17 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.71 (s, 3H, CH_3), 2.42 (m, 1H, $CH(CH_3)_2$), 3.40 and 3.94 (m, 1H each, $RuCH_2P$), 4.06 (m, 4H, OCH_2CH_3), 4.63 and 4.69 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 5.07 and 5.10 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.92−8.62 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.30 (ddd, $^1J_{CP}$ = 38.1 Hz, $^2J_{CP}$ = 16.1 Hz, $^3J_{CP}$ = 8.3 Hz, $RuCH_2P$), 15.97 and 16.48 (d, $^3J_{CP}$ = 8.4 Hz, OCH_2CH_3), 17.41 (s, CH_3), 21.96 and 22.87 (s, $CH(CH_3)_2$), 30.38 (s, $CH(CH_3)_2$), 62.06 (d, $^2J_{CP}$ = 6.0 Hz, OCH_2CH_3), 62.26 (d, $^2J_{CP}$ = 7.2 Hz, OCH_2CH_3), 83.67 (d, $^2J_{CP}$ = 7.7 Hz, CH of *p*-cymene), 86.24 and 89.24 (s, CH of *p*-cymene), 89.20 and 104.48 (s, C of *p*-cymene), 93.23 (d, $^2J_{CP}$ = 4.8 Hz, CH of *p*-cymene), 127.70−145.63 (m, Ph) ppm. **11a**: Yield 91% (0.146 g). Anal. Calcd for $RuC_{39}H_{46}O_3P_3NS$: C, 58.34; H, 5.78; N, 1.74. Found: C, 58.26; H, 5.66; N, 1.52. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 39.85 (dd, $^2J_{PP}$ = 26.6 Hz, $^3J_{PP}$ = 18.8 Hz, $Ph_2P{=}N$), 55.73 (dd, $^2J_{PP}$ = 26.6 Hz, $^3J_{PP}$ = 16.8 Hz, $(EtO)_2P{=}S$), 73.75 (dd, $^3J_{PP}$ = 18.8 and 16.8 Hz, $Ph_2P{=}O$) ppm. ^{1}H NMR (C_6D_6): δ 0.73 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.06 (d, 3H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$), 1.15 (d, 3H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.20 (t, 3H, $^3J_{HH}$ = 7.3 Hz, OCH_2CH_3), 1.92 (s, 3H, CH_3), 2.13 (m, 1H, $CH(CH_3)_2$), 3.07 and 3.28 (m, 1H each, $RuCH_2P$), 4.12 (m, 4H, OCH_2CH_3), 4.47 and 5.23 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 4.70 and 5.36 (d, 1H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 6.88−8.53 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ −2.74 (ddd, $^1J_{CP}$ = 41.1 Hz, $^2J_{CP}$ = 14.9 Hz, $^3J_{CP}$ = 11.7 Hz, $RuCH_2P$), 15.64 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 16.26 (d, $^3J_{CP}$ = 8.7 Hz, OCH_2CH_3), 17.90 (s, CH_3), 20.69 and 24.21 (s, $CH(CH_3)_2$), 30.34 (s, $CH(CH_3)_2$), 62.17 (d, $^2J_{CP}$ = 5.2 Hz, OCH_2CH_3), 62.47 (d, $^2J_{CP}$ = 7.0 Hz, OCH_2CH_3), 86.88 (d, $^2J_{CP}$ = 7.6 Hz, CH of *p*-cymene), 87.27 (s, CH of *p*-cymene), 90.46 (d, $^2J_{CP}$ = 3.5 Hz, CH of *p*-cymene), 92.83 (d, $^2J_{CP}$ = 2.9 Hz, CH of *p*-cymene), 94.00 and 110.48 (s, C of *p*-cymene), 126.54−151.31 (m, Ph) ppm. **11b**: Yield 78% (0.140 g). Anal. Calcd for $RuC_{47}H_{46}O_3P_3NS$: C, 62.80; H, 5.16; N, 1.56. Found: C, 62.60; H, 5.26; N, 1.52. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 42.46 (dd, $^2J_{PP}$ = 20.8 Hz, $^3J_{PP}$ = 19.0 Hz, $Ph_2P{=}N$), 47.79 (dd, $^2J_{PP}$ = 20.8 Hz, $^3J_{PP}$ = 19.0 Hz, $(PhO)_2P{=}S$), 71.44 (dd, $^3J_{PP}$ = 19.0 and 19.0 Hz, $Ph_2P{=}O$)

ppm. ^{1}H NMR (C_6D_6): δ 1.12 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.24 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.99 (s, 3H, CH_3), 2.32 (m, 2H, CH(CH$_3$)$_2$ and RuCH_2P), 2.75 (m, 1H, RuCH_2P), 4.52 and 5.44 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 4.81 and 5.53 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 6.71−8.51 (m, 30H, Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ −2.17 (ddd, $^1J_{CP}$ = 40.5 Hz, $^2J_{CP}$ = 13.7 Hz, $^3J_{CP}$ = 11.2 Hz, RuCH_2P), 17.85 (s, CH_3), 20.47 and 24.60 (s, CH(CH_3)$_2$), 30.39 (s, CH(CH$_3$)$_2$), 86.95 (d, $^2J_{CP}$ = 7.6 Hz, CH of *p*-cymene), 87.79, 91.22, and 93.58 (s, CH of *p*-cymene), 92.70 and 111.90 (s, C of *p*-cymene), 120.85−144.51 (m, Ph), 151.78 (d, $^2J_{CP}$ = 8.5 Hz, C_{ipso} of OPh), 153.27 (d, $^2J_{CP}$ = 12.3 Hz, C_{ipso} of OPh) ppm.

Method B. A solution of the corresponding neutral complex [RuCl(κ^2-*P,C*-Ph_2PCHP{=NP(=X)(OR)$_2$}Ph_2)(η^6-*p*-cymene)] (**3**−**4a**,**b**) (0.2 mmol) in 30 mL of undistilled THF was treated, at room temperature, with NaH (0.05 g, 2.1 mmol) for 6 h. Workup as described in method A allows the isolation of complexes **10a** and **11a**,**b** in 80% (0.126 g), 85% (0.136 g), and 79% (0.142 g) yield, respectively.

Method C. A solution of the corresponding cationic complex [Ru(κ^3-*P,C,X*-Ph_2PCHP{=NP(=X)(OR)$_2$}Ph_2)(η^6-*p*-cymene)][SbF$_6$] (**7**−**8a**,**b**) (0.2 mmol) in 30 mL of undistilled THF was treated, at room temperature, with NaH (0.05 g, 2.1 mmol) for 6 h. Workup as described in method A allows the isolation of complexes **10a** and **11a**,**b** in 82% (0.129 g), 87% (0.140 g), and 74% (0.133 g) yield, respectively.

Synthesis of [RuCl$_2$(η^6-C$_6$H$_6$)(κ^1-*P*-Ph$_2$PCH$_2$P{=NP(=S)(OEt)$_2$}Ph$_2$)]. A solution of [{Ru(η^6-C_6H_6)(μ-Cl)Cl}$_2$] (0.250 g, 0.5 mmol) and the iminophosphorane-phosphine ligand Ph_2PCH_2P{=NP(=S)(OEt)$_2$}Ph_2 (0.552 g, 1 mmol) in 50 mL of CH_2Cl_2 was stirred at room temperature for 1 h. The solution was then concentrated (ca. 5 mL) and diethyl ether (ca. 30 mL) was added, yielding an orange solid, which was washed with diethyl ether (3 × 10 mL) and vacuum-dried. Yield: 65% (0.521 g). Anal. Calcd for $RuC_{35}H_{38}P_3Cl_2O_2NS$: C, 52.44; H, 4.78; N, 1.75. Found: C, 52.62; H, 4.45; N, 1.59. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 11.09 (dd, $^2J_{PP}$ = 39.1 and 24.4 Hz, Ph_2P=N), 23.53 (d, $^2J_{PP}$ = 39.1 Hz, Ph_2P), 59.18 (d, $^2J_{PP}$ = 24.4 Hz, (EtO)$_2$P=S) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.05 (t, 6H, $^3J_{HH}$ = 6.9 Hz, OCH$_2$CH_3), 3.50 (m, 4H, OCH_2CH$_3$), 3.91 (dd, 2H, $^2J_{HP}$ = 10.1 and 10.1 Hz, PCH_2P), 5.29 (s, 6H, C_6H_6), 7.25−8.08 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 16.23 (d, $^3J_{CP}$ = 8.9 Hz, OCH$_2$CH_3), 22.61 (ddd, $^1J_{CP}$ = 76.9 and 19.2 Hz, $^3J_{CP}$ = 6.7 Hz, PCH_2P), 61.63 (d, $^2J_{CP}$ = 6.3 Hz, OCH_2CH$_3$), 88.68 (d, $^2J_{CP}$ = 3.4 Hz, C_6H_6), 128.35−134.38 (m, Ph) ppm.

Synthesis of [RuCl(η^6-C$_6$H$_6$)(κ^2-*P,S*-Ph$_2$PCH$_2$P{=NP(=S)(OEt)$_2$}Ph$_2$)][SbF$_6$] (2a′). A solution of the neutral complex [RuCl$_2$(η^6-C_6H_6)(κ^1-*P*-Ph_2PCH_2P{=NP(=S)(OEt)$_2$}-Ph_2)] (0.400 g, 0.5 mmol) in 50 mL of dichloromethane was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.172 g, 0.5 mmol) for 1 h. After the AgCl formed was filtered off (Kieselguhr), the solution was concentrated to ca. 2 mL, and 50 mL of diethyl ether was then added, yielding an orange microcrystalline solid, which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield: 88% (0.441 g). Anal. Calcd for $RuC_{35}H_{38}F_6P_3O_2ClNSSb$: C, 41.96; H, 3.82; N, 1.40. Found: C, 41.63; H, 3.54; N, 1.66. Conductivity (acetone, 20 °C): 111 Ω^{-1} cm^2 mol^{-1}. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 17.16 (dd, $^2J_{PP}$ = 28.7 and 3.8 Hz, Ph_2P=N), 26.85 (dd, $^3J_{PP}$ = 12.1 Hz, $^2J_{PP}$ = 3.8 Hz, Ph_2P), 54.30 (dd, $^2J_{PP}$ = 28.7 Hz, $^3J_{PP}$ = 12.1 Hz, (EtO)$_2$P=S) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.09 (t, 3H, $^3J_{HH}$ = 6.9 Hz, OCH$_2$CH_3), 1.59 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH_3), 3.29 and 4.62 (m, 1H each, PCH_2P), 4.10 (m, 4H, OCH_2CH$_3$), 5.74 (s, 6H, C_6H_6), 7.10−7.62 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 15.95 (d, $^3J_{CP}$ = 7.7 Hz, OCH$_2$CH_3), 16.48 (d, $^3J_{CP}$ = 8.3 Hz, OCH$_2$CH_3), 25.52 (dd, $^1J_{CP}$ = 59.2 and 17.7 Hz, PCH_2P), 64.88 (d, $^2J_{CP}$ = 10.2 Hz, OCH_2CH$_3$), 65.01 (d, $^2J_{CP}$ = 7.2 Hz, OCH_2CH$_3$), 91.36 (d, $^2J_{CP}$ = 2.8 Hz, C_6H_6), 124.84−138.31 (m, Ph) ppm.

Synthesis of [Ru(κ^2-*C,S*-CH$_2$P{=NP(=S)(OEt)$_2$}Ph$_2$){κ^1-*P*-P(=O)Ph$_2$}(η^6-C$_6$H$_6$)] (11a′). Complex **11a′**, isolated as a yellow solid, was prepared as described for complexes **10**−**11a**,**b** (method A) starting from [RuCl(η^6-C_6H_6)(κ^2-*P,S*-Ph_2-PCH_2P{=NP(=S)(OEt)$_2$}Ph_2)][SbF$_6$] (**2a′**) (0.200 g, 0.2 mmol) and NaH (0.048 g, 2 mmol). Yield: 77% (0.115 g). Anal. Calcd for $RuC_{35}H_{38}O_3P_3NS$: C, 56.29; H, 5.13; N, 1.88. Found: C, 56.54; H, 5.15; N, 1.95. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.40 (dd, $^2J_{PP}$ = 26.3 Hz, $^3J_{PP}$ = 19.1 Hz, Ph_2P=N), 54.42 (dd, $^2J_{PP}$ = 26.3 Hz, $^3J_{PP}$ = 16.0 Hz, (EtO)$_2$P=S), 74.70 (dd, $^3J_{PP}$ = 19.1 and 16.0 Hz, Ph_2P=O) ppm. ^{1}H NMR (C_6D_6): δ 0.80 and 1.18 (t, 3H each, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH_3), 3.30 and 3.49 (m, 1H each, RuCH_2P), 4.07 (m, 4H, OCH_2CH$_3$), 5.13 (s, 6H, C_6H_6), 6.91−8.54 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ −4.37 (ddd, $^1J_{CP}$ = 41.1 Hz, $^2J_{CP}$ = 14.6 Hz, $^3J_{CP}$ = 11.5 Hz, RuCH_2P), 15.70 (d, $^3J_{CP}$ = 7.5 Hz, OCH$_2$CH_3), 16.23 (d, $^3J_{CP}$ = 8.4 Hz, OCH$_2$CH_3), 62.41 (d, $^2J_{CP}$ = 5.8 Hz, OCH_2CH$_3$), 62.68 (d, $^2J_{CP}$ = 6.6 Hz, OCH_2CH$_3$), 89.32 (d, $^2J_{CP}$ = 2.7 Hz, C_6H_6), 126.55−151.30 (m, Ph) ppm.

Synthesis of [Ru(κ^2-*C,X*-CH$_2$P{=NP(=X)(OR)$_2$}Ph$_2$){κ^1-*P*-P(OH)Ph$_2$}(η^6-*p*-cymene)][BF$_4$] (X = O, R = Et (12a); X = S, R = Et (13a), Ph (13b)). A solution of the corresponding neutral complex [Ru(κ^2-*C,X*-CH$_2$P{=NP(=X)(OR)$_2$}Ph_2){κ^1-*P*-P(=O)Ph_2}(η^6-*p*-cymene)] (**10**−**11a**,**b**) (0.2 mmol) in 30 mL of dichloromethane was treated, at room temperature, with a solution of HBF_4 in diethyl ether (0.14 mL of a 1.6 M solution, 0.22 mmol) for 30 min. Concentration of the resulting solution (ca. 2 mL) followed by the addition of hexanes (ca. 30 mL) gave a yellow microcrystalline solid, which was washed with hexanes (3 × 20 mL) and vacuum-dried. **12a**: Yield 75% (0.131 g). Anal. Calcd for $RuC_{39}H_{47}F_4O_4P_3BN$: C, 53.56; H, 5.42; N, 1.60. Found: C, 53.51; H, 5.45; N, 1.85. Conductivity (acetone, 20 °C): 121 Ω^{-1} cm^2 mol^{-1}. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO): δ 9.90 (dd, $^2J_{PP}$ = 6.6 Hz, $^3J_{PP}$ = 4.4 Hz, (EtO)$_2$P=O), 57.41 (dd, $^3J_{PP}$ = 10.8 Hz, $^2J_{PP}$ = 6.6 Hz, Ph_2P=N), 112.34 (dd, $^3J_{PP}$ = 10.8 and 4.4 Hz, Ph_2POH) ppm. ^{1}H NMR ((CD$_3$)$_2$CO): δ 0.73 and 1.51 (t, 3H each, $^3J_{HH}$ = 6.8 Hz, OCH$_2$CH_3), 0.99 and 1.51 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.95 (s, 3H, CH_3), 2.68 (m, 2H, CH(CH$_3$)$_2$ and RuCH_2P), 3.70 (m, 1H, RuCH_2P), 4.21 (m, 4H, OCH_2CH$_3$), 4.79 and 5.37 (d, 1H each, $^3J_{HH}$ = 5.1 Hz, CH of *p*-cymene), 5.06 and 5.58 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 6.75−8.21 (m, 20H, Ph), 11.60 (br, 1H, POH) ppm. ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ −12.86 (ddd, $^1J_{CP}$ = 64.1 Hz, $^2J_{CP}$ = 12.8 Hz, $^3J_{CP}$ = 12.8 Hz, RuCH_2P), 17.46 (d, $^3J_{CP}$ = 6.4 Hz, OCH$_2$CH_3), 18.09 (d, $^3J_{CP}$ = 7.6 Hz, OCH$_2$CH_3), 20.33 (s, CH_3), 23.41 and 25.47 (s, CH(CH_3)$_2$), 31.20 (s, CH(CH$_3$)$_2$), 65.47 and 66.25 (d, $^2J_{CP}$ = 5.8 Hz, OCH_2CH$_3$), 84.71 and 88.92 (s, CH of *p*-cymene), 91.58 (d, $^2J_{CP}$ = 3.5 Hz, CH of *p*-cymene), 95.07 (d, $^2J_{CP}$ = 8.7 Hz, CH of *p*-cymene), 110.64 (d, $^2J_{CP}$ = 3.5 Hz, C of *p*-cymene), 118.47 (s, C of *p*-cymene), 129.94−144.56 (m, Ph) ppm. **13a**: Yield 60% (0.107 g). Anal. Calcd for $RuC_{39}H_{47}F_4P_3O_3BNS\cdot 1/4CH_2Cl_2$: C, 51.70; H, 5.25; N, 1.53. Found: C, 51.72; H, 5.17; N, 1.23. Conductivity (acetone, 20 °C): 114 Ω^{-1} cm^2 mol^{-1}. ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO): δ 40.00 (dd, $^2J_{PP}$ = 26.4 Hz, $^3J_{PP}$ = 19.3 Hz, Ph_2P=N), 53.48 (dd, $^2J_{PP}$ = 26.4 Hz, $^3J_{PP}$ = 22.7 Hz, (EtO)$_2$P=S), 117.61 (dd, $^3J_{PP}$ = 22.7 and 19.3 Hz, Ph_2POH) ppm. ^{1}H NMR ((CD$_3$)$_2$CO): δ 0.91 (t, 3H, $^3J_{HH}$ = 6.8 Hz, OCH$_2$CH_3), 1.02 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.12 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.49 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH_3), 2.00 (s, 3H, CH_3), 2.06 and 2.55 (m, 1H each, RuCH_2P), 2.45 (m, 1H, CH(CH$_3$)$_2$), 4.37 (m, 4H, OCH_2CH$_3$), 5.10 (d, 2H, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 5.42 and 5.47 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 7.10−8.35 (m, 20H, Ph), 8.91 (br, 1H, POH) ppm. ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ −2.45 (ddd, $^1J_{CP}$ = 42.9 Hz, $^2J_{CP}$ = 14.7 Hz, $^3J_{CP}$ = 11.3 Hz, RuCH_2P), 16.46 and 17.13 (d, $^3J_{CP}$ = 8.3 Hz, OCH$_2$CH_3), 18.58 (s, CH_3), 21.73 and 23.94 (s, CH(CH_3)$_2$), 30.93 (s, CH(CH$_3$)$_2$), 63.97 (d, $^2J_{CP}$ = 5.8 Hz, OCH_2CH$_3$), 64.75 (d, $^2J_{CP}$ = 8.3 Hz, OCH_2CH$_3$), 90.04 (d, $^2J_{CP}$ = 6.2 Hz, CH of *p*-cymene), 91.53 (d, $^2J_{CP}$ = 5.0 Hz, CH of *p*-cymene), 91.78 (d, $^2J_{CP}$ = 2.5 Hz, CH of *p*-cymene), 95.70 (d, $^2J_{CP}$ = 3.7 Hz, CH of *p*-cymene), 102.16 and 114.23 (s, C of *p*-cymene), 129.30−141.40 (m, Ph) ppm. **13b**: Yield 64% (0.126 g). Anal. Calcd

for $RuC_{47}H_{46}F_4O_3P_3BNS\cdot 1/4CH_2Cl_2$: C, 56.36; H, 4.65; N, 1.39. Found: C, 56.40; H, 4.94; N, 1.39. Conductivity (acetone, 20 °C): 116 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 43.34 (dd, $^2J_{PP}$ = 22.6 Hz, $^3J_{PP}$ = 19.9 Hz, Ph_2P═N), 47.00 (dd, $^3J_{PP}$ = 24.4 Hz, $^2J_{PP}$ = 22.6 Hz, $(PhO)_2P$═S), 115.70 (dd, $^3J_{PP}$ = 24.4 and 19.9 Hz, Ph_2POH) ppm. ^1H NMR ($(CD_3)_2CO$): δ 0.99 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.09 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH(CH_3)$_2$), 1.95 (s, 3H, CH_3), 2.06 and 2.44 (m, 1H each, $RuCH_2P$), 2.37 (m, 1H, CH(CH$_3$)$_2$), 5.01 and 5.55 (d, 1H each, $^3J_{HH}$ = 5.9 Hz, CH of *p*-cymene), 5.14 and 5.42 (d, 1H each, $^3J_{HH}$ = 4.8 Hz, CH of *p*-cymene), 6.76−8.04 (m, 30H, Ph), 9.00 (br, 1H, POH) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ −3.07 (ddd, $^1J_{CP}$ = 41.3 Hz, $^2J_{CP}$ = 15.5 Hz, $^3J_{CP}$ = 12.2 Hz, $RuCH_2P$), 18.44 (s, CH_3), 20.81 and 24.19 (s, CH(CH_3)$_2$), 30.82 (s, CH(CH$_3$)$_2$), 88.58 (d, $^2J_{CP}$ = 7.6 Hz, CH of *p*-cymene), 90.28 (d, $^2J_{CP}$ = 2.3 Hz, CH of *p*-cymene), 91.15 (s, CH of *p*-cymene), 96.05 (d, $^2J_{CP}$ = 4.1 Hz, CH of *p*-cymene), 98.80 and 116.21 (s, C of *p*-cymene), 121.11−142.88 (m, Ph), 151.72 (d, $^2J_{CP}$ = 8.7 Hz, C_{ipso} of OPh), 152.98 (d, $^2J_{CP}$ = 12.2 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru(κ^2-*C,X*-CH_2P{═NP(═X)(OR)$_2$}Ph_2)(κ^1-*P*-P(OMe)Ph_2}(η^6-*p*-cymene)][CF_3SO_3] (X = O, R = Et (14a); X = S, R = Et (15a), Ph (15b)). A solution of the corresponding neutral complex [Ru(κ^2-*C,X*-CH_2P{═NP(═X)-(OR)$_2$}Ph_2}(κ^1-*P*-P(═O)Ph_2}(η^6-*p*-cymene)] (**10**−**11a**,**b**) (0.2 mmol) in 30 mL of dichloromethane was treated, at room temperature, with $MeOSO_2CF_3$ (0.025 mL, 0.22 mmol) for 30 min. Concentration of the resulting solution (ca. 2 mL) followed by the addition of hexanes (ca. 30 mL) gave a yellow microcrystalline solid, which was washed with hexanes (3 × 20 mL) and vacuum-dried. **14a**: Yield 70% (0.133 g). Anal. Calcd for $RuC_{41}H_{49}O_7F_3P_3NS$: C, 51.79; H, 5.19; N, 1.47. Found: C, 51.57; H, 4.96; N, 1.36. Conductivity (acetone, 20 °C): 132 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 10.24 (d, $^2J_{PP}$ = 20.3 Hz, $(EtO)_2P$═O), 35.13 (dd, $^2J_{PP}$ = 20.3 Hz, $^3J_{PP}$ = 12.2 Hz, Ph_2P═N), 130.31 (d, $^3J_{PP}$ = 12.2 Hz, Ph_2POMe) ppm. ^1H NMR ($(CD_3)_2CO$): δ 0.87 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.06 and 1.48 (t, 3H each, $^3J_{HH}$ = 6.6 Hz, OCH_2CH_3), 1.73 (s, 3H, CH_3), 2.38 (m, 1H, CH(CH$_3$)$_2$), 2.81 and 4.20 (m, 1H each, $RuCH_2P$), 3.40 (d, 3H, $^3J_{HP}$ = 11.0 Hz, $POCH_3$), 3.76 (m, 4H, OCH_2CH_3), 5.02 (br, 1H, CH of *p*-cymene), 5.13 (d, 1H, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.21 (m, 2H, CH of *p*-cymene), 7.10−8.32 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ −1.62 (ddd, $^1J_{CP}$ = 40.6 Hz, $^2J_{CP}$ = 17.1 Hz, $^3J_{CP}$ = 8.6 Hz, $RuCH_2P$), 16.13 (d, $^3J_{CP}$ = 7.8 Hz, OCH_2CH_3), 16.52 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 17.18 (s, CH_3), 21.07 and 22.23 (s, CH(CH_3)$_2$), 30.70 (s, CH-(CH$_3$)$_2$), 55.00 (d, $^2J_{CP}$ = 12.3 Hz, $POCH_3$), 62.63 (d, $^2J_{CP}$ = 6.0 Hz, OCH_2CH_3), 63.53 (d, $^2J_{CP}$ = 6.7 Hz, OCH_2CH_3), 85.73 (d, $^2J_{CP}$ = 7.5 Hz, CH of *p*-cymene), 86.17 and 91.79 (s, CH of *p*-cymene), 94.12 and 110.66 (s, C of *p*-cymene), 95.11 (d, $^2J_{CP}$ = 5.6 Hz, CH of *p*-cymene), 128.68−136.01 (m, Ph) ppm. **15a**: Yield 73% (0.141 g). Anal. Calcd for $RuC_{41}H_{49}O_6F_3P_3S_2N$: C, 50.93; H, 5.11; N, 1.45. Found: C, 50.54; H, 5.47; N, 1.35. Conductivity (acetone, 20 °C): 128 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 39.24 (dd, $^2J_{PP}$ = 26.2 Hz, $^3J_{PP}$ = 18.1 Hz, Ph_2P═N), 52.64 (dd, $^2J_{PP}$ = 26.2 Hz, $^3J_{PP}$ = 23.5 Hz, $(EtO)_2$-P═S), 135.81 (d, $^3J_{PP}$ = 23.5 and 18.1 Hz, Ph_2POMe) ppm. ^1H NMR ($(CD_3)_2CO$): δ 0.91 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.01 (t, 3H, $^3J_{HH}$ = 6.9 Hz, OCH_2CH_3), 1.07 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.50 (t, 3H, $^3J_{HH}$ = 6.8 Hz, OCH_2CH_3), 2.02 (s, 3H, CH_3), 2.45 (m, 1H, CH(CH$_3$)$_2$), 2.94 and 3.63 (m, 1H each, $RuCH_2P$), 3.51 (d, 3H, $^3J_{HP}$ = 11.2 Hz, $POCH_3$), 4.36 (m, 4H, OCH_2CH_3), 5.23 (d, 1H, $^3J_{HH}$ = 5.5 Hz, CH of *p*-cymene), 5.43 (br, 2H, CH of *p*-cymene), 5.53 (d, 1H, $^3J_{HH}$ = 5.3 Hz, CH of *p*-cymene), 7.10−8.18 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2$-CO): δ −2.21 (ddd, $^1J_{CP}$ = 34.7 Hz, $^2J_{CP}$ = 10.8 Hz, $^3J_{CP}$ = 6.4 Hz, $RuCH_2P$), 15.97 (d, $^3J_{CP}$ = 7.8 Hz, OCH_2CH_3), 16.61 (d, $^3J_{CP}$ = 8.4 Hz, OCH_2CH_3), 18.03 (s, CH_3), 21.49 and 23.01 (s, CH(CH_3)$_2$), 30.81 (s, CH(CH$_3$)$_2$), 56.37 (d, $^2J_{CP}$ = 13.8 Hz, $POCH_3$), 63.53 (d, $^2J_{CP}$ = 6.0 Hz, OCH_2CH_3), 64.21 (d, $^2J_{CP}$ = 8.4 Hz, OCH_2CH_3), 89.98 (d, $^2J_{CP}$ = 6.0 Hz, CH of *p*-cymene), 91.71 (d, $^2J_{CP}$ = 3.6 Hz, CH of *p*-cymene), 91.82 and 94.29 (s, CH of *p*-cymene), 102.57 and 112.63 (s, C of *p*-cymene), 129.41−137.33 (m, Ph) ppm. **15b**: Yield 78% (0.166 g). Anal. Calcd for $RuC_{49}H_{49}O_6F_3P_3S_2N$: C, 55.36; H, 4.65; N, 1.32. Found: C, 55.44; H, 4.93; N, 1.18. Conductivity (acetone, 20 °C): 119 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 42.36 (dd, $^2J_{PP}$ = 22.6 Hz, $^3J_{PP}$ = 17.7 Hz, Ph_2P═N), 45.67 (dd, $^3J_{PP}$ = 24.4 Hz, $^2J_{PP}$ = 22.6 Hz, $(EtO)_2P$═S), 134.24 (d, $^3J_{PP}$ = 24.4 and 17.7 Hz, Ph_2POMe) ppm. ^1H NMR ($(CD_3)_2CO$): δ 0.80 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 0.99 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH-(CH_3)$_2$), 1.93 (s, 3H, CH_3), 2.25 (m, 1H, CH(CH$_3$)$_2$), 2.37 and 3.50 (m, 1H each, $RuCH_2P$), 3.46 (d, 3H, $^3J_{HP}$ = 11.4 Hz, $POCH_3$), 5.19 and 5.36 (d, 1H each, $^3J_{HH}$ = 5.9 Hz, CH of *p*-cymene), 5.27 and 5.49 (d, 1H each, $^3J_{HH}$ = 6.5 Hz, CH of *p*-cymene), 6.93−8.09 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($(CD_3)_2$-CO): δ −2.76 (ddd, $^1J_{CP}$ = 42.4 Hz, $^2J_{CP}$ = 15.1 Hz, $^3J_{CP}$ = 11.4 Hz, $RuCH_2P$), 18.46 (s, CH_3), 21.30 and 23.86 (s, CH-(CH_3)$_2$), 31.23 (s, CH(CH$_3$)$_2$), 56.91 (d, $^2J_{CP}$ = 13.2 Hz, $POCH_3$), 90.60 (d, $^2J_{CP}$ = 7.2 Hz, CH of *p*-cymene), 92.18 and 92.27 (s, CH of *p*-cymene), 95.36 (d, $^2J_{CP}$ = 4.2 Hz, CH of *p*-cymene), 101.89 and 114.34 (s, C of *p*-cymene), 122.00−134.42 (m, Ph), 152.06 (d, $^2J_{CP}$ = 9.0 Hz, C_{ipso} of OPh), 153.18 (d, $^2J_{CP}$ = 10.9 Hz, C_{ipso} of OPh) ppm.

Table 1. Crystal Data and Structure Refinement for 3b and 11a′

	3b	**11a′**
chemical formula	$RuC_{47}H_{45}O_3P_3NCl$	$RuC_{35}H_{38}O_3P_3NS\cdot H_2O$
fw	901.27	764.72
T (K)	120(2)	293(2)
wavelength (Å)	1.54180	1.71073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst size, mm	0.10 × 0.05 × 0.025	0.26 × 0.16 × 0.13
a, Å	10.3434(5)	10.859(4)
b, Å	12.6084(7)	12.174(2)
c, Å	16.4528(9)	15.189(4)
α, deg	84.595(3)	69.71(3)
β, deg	76.211(3)	87.735(19)
γ, deg	82.999(3)	69.09(2)
Z	2	2
V, Å^3	2063.6(2)	1751.2(8)
ρ_{calcd}, g cm^{-3}	1.450	1.450
μ, mm^{-1}	5.110	0.683
F(000)	928	788
θ range, deg	2.77 to 69.53	1.44 to 25.98
index ranges	$-11 \le h \le 12$ $-14 \le k \le 14$ $0 \le l \le 19$	$-13 \le h \le 13$ $-14 \le k \le 14$ $-18 \le l \le 18$
completeness to θ_{max}	95.2%	100.0%
no. of data coll	33 680	14 408
no. of unique data	7370 (R_{int} = 0.029)	6860 (R_{int} = 0.1202)
no. of params/ restraints	505/0	414/2
goodness of fit on F^2	1.038	1.005
weight function (a, b)	0.0270, 0.0000	0.0597, 0.9784
R1[a] [$I > 2\sigma(I)$]	0.0428	0.0587
wR2[a] [$I > 2\sigma(I)$]	0.1041	0.1171
R1 (all data)	0.0628	0.2021
wR2 (all data)	0.1120	0.1632
largest diff peak and hole, e Å^{-3}	0.600 and −0.716	0.697 and −0.988

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

X-ray Crystal Structure Determination of Complexes 3b and 11a′. Crystals suitable for X-ray diffraction analysis were obtained by cooling a saturated toluene solution of **3b** at 0 °C or by slow diffusion of hexane into a saturated solution of **11a′** in toluene. **11a′** was obtained as solvated crystals that contained one water molecule per molecular unit. The most relevant crystal and refinement data are collected in Table 1.

For 3b: diffraction data were recorded at 120(2) K on a Nonius KappaCCD single-crystal diffractometer using Cu Kα radiation. The crystal−detector distance was fixed at 29 mm, and a total of 1120 frames were collected using the oscillation

method, with 2° oscillations and 40 s exposure time per frame. Data collection strategy was calculated with the program Collect.[29] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[30] Unit cell dimensions were determined from 6275 reflections. Absorption correction was applied by means of SORTAV.[31]

For 11a′: diffraction data were recorded at 293(2) K on a Nonius CAD4 single-crystal diffractometer using Mo Kα radiation. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 5° and 13°). Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. On all reflections, profile analysis was performed.[32,33] Some double measured reflections were averaged, and Lorentz and polarization corrections were applied. Absorption correction was applied by means of XABS2.[34]

The software package WINGX was used for space group determination, structure solution, and refinement.[35] All the structures were solved by Patterson interpretation and phase expansion using DIRDIF.[36] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[37] During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. Hydrogen atoms were geometrically placed and isotropically refined with a common thermal parameter, riding on their parent atoms (except the H atoms of the H_2O molecule in **11a′**, which were located by difference Fourier maps and refined isotropically). The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b 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 International Tables for X-ray Crystallography.[38] Geometrical calculations were made with PARST.[39] The crystallographic plots were made with PLATON.[40]

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Supporting Information Available: IR data for all the complexes reported in this paper. X-ray crystallographic files, in CIF format, for the structure determinations of complexes **3b** and **11a′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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