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Ruthenium(II) and Ruthenium(IV) Complexes Containing κ^1-*P*-, κ^2-*P,O*-, and κ^3-*P,N,O*-Iminophosphorane-Phosphine Ligands $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et, Ph): Synthesis, Reactivity, Theoretical Studies, and Catalytic Activity in Transfer Hydrogenation of Cyclohexanone

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[{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] and [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] react with $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et (**1a**), Ph (**1b**)) affording complexes [Ru(η^6-*p*-cymene)Cl_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)] (R = Et (**2a**), Ph (**2b**)) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)] (R = Et (**6a**), Ph (**6b**)). While treatment of **2a** with 1 equiv of $AgSbF_6$ yields a mixture of [Ru(η^6-*p*-cymene)Cl(κ^2-*P,O*-$Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2$)][$SbF_6$] (**3a**) and [Ru($\eta^6$-*p*-cymene)Cl($\kappa^2$-*P,N*-$Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2$)][$SbF_6$] (**4a**), [Ru($\eta^6$-*p*-cymene)Cl($\kappa^2$-*P,O*-$Ph_2PCH_2P\{=NP(=O)(OPh)_2\}Ph_2$)][$SbF_6$] (**3b**) and [Ru($\eta^3$:$\eta^3$-$C_{10}H_{16}$)Cl($\kappa^2$-*P,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}$-$Ph_2$)][$SbF_6$] (R = Et (**7a**), Ph (**7b**)) are selectively formed from **2b** and **6a**,**b**. Complexes [Ru(η^6-*p*-cymene)(κ^3-*P,N,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (R = Et (**5a**), Ph (**5b**)) and [Ru(η^3:η^3-$C_{10}H_{16}$)(κ^3-*P,N,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (R = Et (**8a**), Ph (**8b**)) have been prepared using 2 equiv of $AgSbF_6$. The reactivity of **3**–**5a**,**b** has been explored allowing the synthesis of [Ru(η^6-*p*-cymene)X_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)] (R = Et, Ph; X = Br, I, N_3, NCO (**9**–**12a**,**b**)). The catalytic activity of **2**–**8a**,**b** in transfer hydrogenation of cyclohexanone, as well as theoretical calculations on the models [Ru(η^6-C_6H_6)Cl(κ^2-*P,N*-$H_2PCH_2P\{=NP(=O)(OH)_2\}H_2$)]$^+$ and [Ru(η^6-C_6H_6)Cl(κ^2-*P,O*-$H_2PCH_2P\{=NP(=O)(OH)_2\}H_2$)]$^+$, has been also studied.

Introduction

There is a considerable interest in the coordination chemistry of phosphine ligands with hemilabile properties because they combine strong binding via the phosphorus atom and a hemilabile donor group (i.e. N- or O-donor) capable of reversibly dissociating from the metal liberating a coordination site.[1] Such behavior has been exploited in homogeneous catalysis since the formation of unsaturated intermediate species is often favored.[1] Iminophosphorane-phosphines $R_2P-X-P(=NR')R_2$ (readily accessible by selective monoimination of bis-phosphines with azides via the

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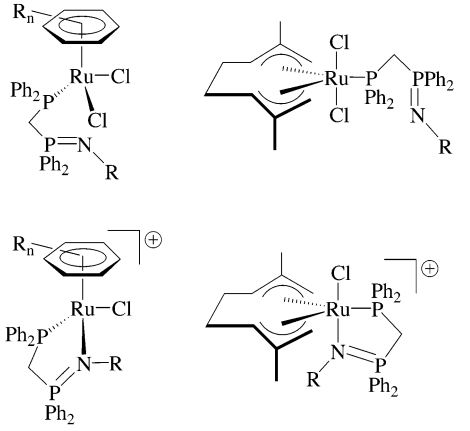
Chart 1

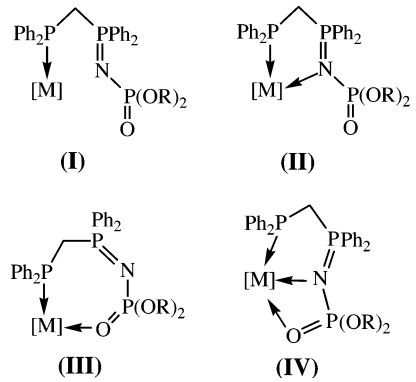


R = H, $SiMe_3$, *p*-C_5F_4N or *p*-C_6F_4CN
η^6-arene = C_6H_6, 1-^{i}Pr-4-C_6H_4Me, 1,3,5-$C_6H_3Me_3$ or C_6Me_6

Staudinger reaction)[2,3] are an important class of hemilabile ligands belonging to the wide series of those containing phosphorus−nitrogen donor atoms.[4] In this context, we have recently reported the preparation of the first ruthenium complexes bearing iminophosphorane-phosphine ligands (see Chart 1) which show excellent hemilabile properties.[5]

Following these studies, and because the chemistry of the closely related bis-phosphine monoxides (BPMOs) of general formula $R_2P-X-P(=O)R_2$ (*X* = divalent bridging group) has revealed successful applications in a large number of catalytic transformations,[6] in this paper we report the synthesis of the novel iminophosphorane-phosphines $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et (**1a**), Ph (**1b**)) containing a coordinating phosphoryl substituent. Our interest stems from the expected hemilabile properties and its potential coordination versatility since bidentate chelating modes κ^2-*P,N*- (**II**) and κ^2-*P,O*- (**III**) as well as tridentate κ^3-*P,N,O*- behavior (**IV**) can be envisaged (see Chart 2).[7] Starting from the ruthenium(II) and ruthenium(IV) dimers $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ and $[\{Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl), respectively, here we describe that the tridentate ligands **1a**,**b** can be coordinated selectively in κ^1-*P*-, κ^2-*P,O*-, and κ^3-*P,N,O*-manners (**I**, **III**, and **IV** in Chart 2). The hemilabile properties of the chelate complexes and their catalytic activity in transfer hydrogenation of cyclohexanone by propan-2-ol have been also explored.[8] In addition, a theoretical study devoted to rationalize the competitive ability of the ligands for the formation of a five- versus seven-membered chelate ring (κ^2-*P,N*- (**II**) vs κ^2-*P,O*- (**III**)) is described using the models $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}\text{-}H_2)]^+$ and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=O)\text{-}(OH)_2\}H_2)]^+$.

Chart 2



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

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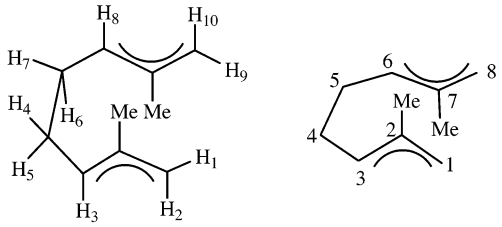
(7) The related ligands $Ph_2PN(R)P\{=NP(=O)(OPh)_2\}Ph_2$ (R = Me, Et) and 2-$Ph_2PC_6H_4P\{=NP(=O)(OPh)_2\}Ph_2$ have been described by R. G. Cavell and co-workers. Remarkably, its complexation to Rh(I), Pd(II), and Pt(II) fragments leads exclusively to the bidentate κ^2-*P,N*-coordination. See ref 3e,f.

(8) Although several transition-metal complexes containing iminophosphorane-phosphine ligands are known (see refs 3 and 4), their involvement in homogeneous catalysis has been almost neglected when compared to their BPMO counterparts. 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. Patent Application US 887014, 1994. Methanol carbonylation (Rh, Ni, and Co complexes): (c) Cavell, R. G.; Katti, K. V. U.S. Patent Application 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. Patent Application US 447887, 1996. Cross coupling of secondary amines with aryl halides (Pd complexes): ref 3h.

nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$],[9] [{Ru(η^3:η^3-$C_{10}H_{16}$)-(μ-Cl)Cl}$_2$],[10] and $(EtO)_2P(=O)N_3$,[11] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. All melting points were determined on a Büchi CH-9230 oil-based apparatus and are uncorrected. Mass spectra (MALDI-TOF) were recorded using a VOYAGER-DE STR spectrometer; α-cyano-4-hydroxycinnamic acid was used as the matrix. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported. $^{31}P\{^1H\}$ NMR spectroscopic data for all the compounds reported are collected in Table 2.

The numbering for protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton is as follows:



Synthesis of $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et (1a), Ph (1b)). The corresponding azide $(RO)_2P(=O)N_3$ (5.2 mmol) was added at −78 °C to a solution of bis(diphenylphosphino)methane (2 g, 5.2 mmol) in 80 mL of THF. The reaction mixture was slowly warmed to room temperature and then evaporated to dryness to give a colorless oil. A microcrystalline white solid was obtained by slow diffusion of pentane into a saturated dichloromethane solution of the product at room temperature. Characterization data for **1a** follow: yield 93% (2.589 g), mp 148−150 °C. Anal. Calcd for $C_{29}H_{32}O_3P_3N$: C, 65.04; H, 6.02; N, 2.61. Found: C, 65.12; H, 5.89; N, 2.76. ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 6H, J_{HH} = 7.1 Hz, OCH_2CH_3), 3.46 (d, 2H, $^2J_{HP}$ = 13.9 Hz, PCH_2P), 3.95 (m, 4H, OCH_2), 7.21−7.77 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.29 (d, $^3J_{CP}$ = 7.9 Hz, OCH_2CH_3), 29.81 (dd, J_{CP} = 64.4 and 33.9 Hz, PCH_2P), 61.42 (d, $^2J_{CP}$ = 6.8 Hz, OCH_2), 128.26−132.90 (m, Ph), 137.62 (dd, J_{CP} = 22.6 Hz, $^3J_{CP}$ = 7.9 Hz, C_{ipso} of Ph) ppm. MS (MALDI-TOF): *m*/*z* 536 $[M + 1]^+$. For **1b**: yield 86% (2.824 g), mp 107−109 °C. Anal. Calcd for $C_{37}H_{32}O_3P_3N$: C, 70.36; H, 5.11; N, 2.22. Found: C, 70.20; H, 5.01; N, 2.30. ^{1}H NMR ($CDCl_3$) δ 3.36 (d, 2H, $^2J_{HP}$ = 13.7 Hz, PCH_2P), 7.06−7.62 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 29.76 (dd, J_{CP} = 65.3 and 34.1 Hz, PCH_2P), 120.20−134.23 (m, Ph), 138.99 (dd, J_{CP} = 14.9 Hz, $^3J_{CP}$ = 7.8 Hz, C_{ipso} of Ph), 152.22 (d, $^2J_{CP}$ = 7.8 Hz, C_{ipso} of OPh) ppm. MS (MALDI-TOF): *m*/*z* 632 $[M + 1]^+$.

Synthesis of [Ru(η^6-*p*-cymene)Cl_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)] (R = Et (2a), Ph (2b)). A solution of [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] (0.245 g, 0.4 mmol) and the corresponding iminophosphorane-phosphine $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (**1a**,**b**) (0.85 mmol) in 30 mL of dichloromethane was stirred at room temperature for 1 h. The resulting solution was then concentrated to ca. 2 mL, and 50 mL of diethyl ether was added yielding a microcrystalline orange solid which was washed with diethyl ether (3 × 10 mL) and vacuum-dried. For **2a**: yield 81% (0.545 g), mp 194−196 °C. Anal. Calcd for $RuC_{39}H_{46}O_3P_3Cl_2N\cdot 1/4CH_2Cl_2$: C, 54.63; H, 5.43; N, 1.62. Found: C, 54.50; H, 5.39; N, 1.67. ^{1}H NMR ($CDCl_3$) δ 0.79 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 0.99 (t, 6H, J_{HH} = 6.6 Hz, OCH_2CH_3), 1.74 (s, 3H, CH_3), 2.34 (sept, 1H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 3.45 (m, 4H, OCH_2), 3.87 (dd, 2H, $^2J_{HP}$ = 9.1 and 9.1 Hz, PCH_2P), 5.05 and 5.20 (d, 2H each, J_{HH} = 5.0 Hz, CH of *p*-cymene), 7.30−8.01 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.46 (d, $^3J_{CP}$ = 9.0 Hz, OCH_2CH_3), 17.41 (s, CH_3), 21.40 (ddd, J_{CP} = 78.6 and 19.2 Hz, $^3J_{CP}$ = 8.4 Hz, PCH_2P), 21.46 (s, $CH(CH_3)_2$), 30.38 (s, $CH(CH_3)_2$), 61.03 (d, $^2J_{CP}$ = 6.8 Hz, OCH_2), 86.06 (d, $^2J_{CP}$ = 6.8 Hz, CH of *p*-cymene), 90.58 (d, $^2J_{CP}$ = 4.1 Hz, CH of *p*-cymene), 94.73 and 108.28 (s, C of *p*-cymene), 128.17−134.49 (m, Ph) ppm. For **2b**: yield 73% (0.547 g), mp 222−224 °C. Anal. Calcd for $RuC_{47}H_{46}O_3P_3Cl_2N$: C, 60.19; H, 4.94; N, 1.49. Found: C, 60.26; H, 4.81; N, 1.52. ^{1}H NMR ($CDCl_3$) δ 0.78 (d, 6H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 1.77 (s, 3H, CH_3), 2.38 (sept, 1H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 3.98 (dd, 2H, $^2J_{HP}$ = 9.9 and 9.9 Hz, PCH_2P), 5.06 and 5.21 (d, 2H each, J_{HH} = 6.0 Hz, CH of *p*-cymene), 7.04−7.91 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.49 (s, CH_3), 20.43 (ddd, J_{CP} = 79.4 and 18.1 Hz, $^3J_{CP}$ = 6.4 Hz, PCH_2P), 21.39 (s, $CH(CH_3)_2$), 30.43 (s, $CH(CH_3)_2$), 86.20 (d, $^2J_{CP}$ = 6.4 Hz, CH of *p*-cymene), 90.70 (d, $^2J_{CP}$ = 4.7 Hz, CH of *p*-cymene), 96.40 and 108.28 (s, C of *p*-cymene), 120.63−134.44 (m, Ph), 152.69 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru(η^6-*p*-cymene)Cl(κ^2-*P*,*O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$] (R = Et (3a), Ph (3b)) and [Ru(η^6-*p*-cymene)Cl(κ^2-*P*,*N*-$Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2$)][$SbF_6$] (4a). Method A. A solution of the corresponding neutral complex [Ru(η^6-*p*-cymene)Cl_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)] (**2a**,**b**) (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. Starting from **2a**, an inseparable mixture containing compounds **3a** and **4a** (ca. 3:1 ratio) was obtained in 85% yield (0.443 g). Mp: 178−180 °C (dec). Anal. Calcd for $RuC_{39}H_{46}F_6O_3P_3ClNSb\cdot 1/4CH_2Cl_2$: C, 44.34; H, 4.41; N, 1.32. Found: C, 44.18; H, 4.21; N, 1.30. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 115. For **3a**: ^{1}H NMR (CD_2Cl_2) δ 0.96 and 1.17 (d, 3H each, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.13 and 1.35 (t, 3H each, J_{HH} = 7.0 Hz, OCH_2CH_3), 1.73 (s, 3H, CH_3), 2.23 (m, 1H, $CH(CH_3)_2$), 3.09 and 5.17 (m, 1H each, PCH_2P), 3.63−4.15 (m, 4H, OCH_2), 4.92 and 5.40 (d, 1H each, J_{HH} = 5.4 Hz, CH of *p*-cymene), 5.79 and 5.98 (d, 1H each, J_{HH} = 6.0 Hz, CH of *p*-cymene), 7.05−8.00 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 16.10 and 16.50 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 17.73 (s, CH_3), 21.70 and 22.24 (s, $CH(CH_3)_2$), 28.97 (dd, J_{CP} = 56.5 and 15.7 Hz, PCH_2P), 30.76 (s, $CH(CH_3)_2$), 63.43 and 63.54 (d, $^2J_{CP}$ = 7.0 Hz, OCH_2), 84.06 (d, $^2J_{CP}$ = 4.1 Hz, CH of *p*-cymene), 88.06 (d, $^2J_{CP}$ = 5.7 Hz, CH of *p*-cymene), 88.50 (d, $^2J_{CP}$ = 2.3 Hz, CH of *p*-cymene), 90.36 (d, $^2J_{CP}$ = 5.3 Hz, CH of *p*-cymene), 97.53 and 107.96 (s, C of *p*-cymene), 124.31−137.12 (m, Ph) ppm. For **4a:** ^{1}H NMR (CD_2Cl_2) δ 0.80 and 1.01 (d, 3H each, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 0.93 and 1.25 (t, 3H each, J_{HH} = 7.0 Hz, OCH_2CH_3), 1.93 (s, 3H, CH_3), 3.46 (m,

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1H, C*H*(CH_3)$_2$), 3.63−4.15 (m, 6H, PCH_2P and OCH_2), 5.69 and 5.96 (d, 1H each, J_{HH} = 5.4 Hz, CH of *p*-cymene), 5.86 (br, 2H, CH of *p*-cymene), 7.05−8.00 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 16.01 (d, $^3J_{CP}$ = 6.4 Hz, OCH_2CH_3), 16.30 (d, $^3J_{CP}$ = 8.1 Hz, OCH_2CH_3), 18.06 (s, CH_3), 20.65 and 23.35 (s, CH(CH_3)$_2$), 29.69 (s, *C*H(CH_3)$_2$), 36.74 (ddd, J_{CP} = 75.4 and 16.7 Hz, $^3J_{CP}$ = 8.2 Hz, PCH_2P), 63.73 (d, $^2J_{CP}$ = 7.0 Hz, OCH_2), 63.82 (d, $^2J_{CP}$ = 6.4 Hz, OCH_2), 82.45 (s, CH of *p*-cymene), 87.02 (d, $^2J_{CP}$ = 4.1 Hz, CH of *p*-cymene), 87.15 (d, $^2J_{CP}$ = 5.3 Hz, CH of *p*-cymene), 91.31 (d, $^2J_{CP}$ = 5.1 Hz, CH of *p*-cymene), 106.72 and 113.68 (s, C of *p*-cymene), 124.31−137.12 (m, Ph) ppm. For **3b**: yield 86% (0.489 g), mp 188−190 °C (dec). Anal. Calcd for $RuC_{47}H_{46}F_6O_3P_3ClNSb$: C, 49.60; H, 4.07; N, 1.23. Found: C, 50.05; H, 3.93; N, 1.31. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 102. ^1H NMR (CD_2Cl_2) δ 0.85 (d, 3H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.10 (d, 3H, J_{HH} = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.64 (s, 3H, CH_3), 2.17 (m, 1H, C*H*(CH_3)$_2$), 3.15 and 5.16 (m, 1H each, PCH_2P), 4.60 and 5.29 (d, 1H each, J_{HH} = 5.7 Hz, CH of *p*-cymene), 5.07 and 5.75 (d, 1H each, J_{HH} = 6.2 Hz, CH of *p*-cymene), 6.85−7.64 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 17.76 (s, CH_3), 21.45 and 22.22 (s, CH(*C*H$_3$)$_2$), 28.27 (dd, J_{CP} = 57.1 and 15.8 Hz, PCH_2P), 30.66 (s, *C*H(CH_3)$_2$), 83.43 and 87.96 (s, CH of *p*-cymene), 88.84 (d, $^2J_{CP}$ = 6.4 Hz, CH of *p*-cymene), 90.83 (d, $^2J_{CP}$ = 5.3 Hz, CH of *p*-cymene), 97.91 and 108.10 (s, C of *p*-cymene), 120.93−135.64 (m, Ph), 151.74 (d, $^2J_{CP}$ = 8.7 Hz, C_{ipso} of OPh), 151.85 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh) ppm.

Method B. A suspension of [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] (0.122 g, 0.2 mmol), the corresponding iminophosphorane-phosphine **1a**,**b** (0.43 mmol), and $AgSbF_6$ (0.137 g, 0.4 mmol) in 30 mL of dichloromethane was stirred, at room temperature and in the absence of light, for 1.5 h. After the AgCl formed was filtered off (Kieselguhr), the solution was concentrated to ca. 2 mL, and 30 mL of diethyl ether was then added yielding an orange microcrystalline solid which was washed with diethyl ether (3 × 10 mL) and vacuum-dried. For **3a**/**4a**: yield 82% (0.342 g). For **3b**: yield 83% (0.378 g).

Synthesis of [Ru(η^6-*p*-cymene)(κ^3-*P*,*N*,*O*-Ph_2PCH_2P{=NP(=O)(OR)$_2$}Ph_2)][SbF_6]$_2$ (R = Et (5a), Ph (5b)). Method A. A solution of the corresponding neutral complex [Ru(η^6-*p*-cymene)Cl_2(κ^1-*P*-Ph_2PCH_2P{=NP(=O)(OR)$_2$}Ph_2)] (**2a,b**) (0.5 mmol) in 50 mL of dichloromethane was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.378 g, 1.1 mmol) for 1 h. After the excess of $AgSbF_6$ used and the AgCl formed were 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. For **5a**: yield 93% (0.577 g), mp 139−141 °C (dec). Anal. Calcd for $RuC_{39}H_{46}F_{12}O_3P_3Sb_2N$: C, 37.71; H, 3.73; N, 1.13. Found: C, 37.59; H, 3.82; N, 1.09. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 198. ^1H NMR (CD_2Cl_2) δ 0.68 and 1.15 (t, 3H each, J_{HH} = 6.8 Hz, OCH_2CH_3), 0.95 and 1.22 (d, 3H each, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.40 (s, 3H, CH_3), 2.45 (m, 1H, C*H*(CH_3)$_2$), 3.45 and 3.88 (m, 2H each, OCH_2), 4.78 and 5.02 (m, 1H each, PCH_2P), 5.78 and 6.55 (d, 1H each, J_{HH} = 5.0 Hz, CH of *p*-cymene), 5.91 and 6.30 (d, 1H each, J_{HH} = 5.5 Hz, CH of *p*-cymene), 7.03−8.33 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 14.33 and 15.87 (br, OCH_2CH_3), 16.21 (s, CH_3), 20.58 and 22.40 (s, CH(*C*H$_3$)$_2$), 26.69 (dd, J_{CP} = 66.4 and 17.9 Hz, PCH_2P), 31.95 (s, *C*H(CH_3)$_2$), 67.03 (d, $^2J_{CP}$ = 9.0 Hz, OCH_2), 68.03 (d, $^2J_{CP}$ = 4.9 Hz, OCH_2), 76.09 and 91.60 (s, CH of *p*-cymene), 88.27 (d, $^2J_{CP}$ = 9.1 Hz, CH of *p*-cymene), 94.30 (d, $^2J_{CP}$ = 10.8 Hz, CH of *p*-cymene), 99.93 and 113.33 (s, C of *p*-cymene), 120.86−136.28 (m, Ph) ppm. For **5b**: yield 77% (0.515 g), mp 141−143 °C (dec). Anal. Calcd for $RuC_{47}H_{46}F_{12}O_3P_3Sb_2N$: C, 42.18; H, 3.16; N, 1.05. Found: C, 41.87; H, 3.02; N, 1.12. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 184. ^1H NMR (CD_2Cl_2) δ 1.04 (d, 3H, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.29 (d, 3H, J_{HH} = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.43 (s, 3H, CH_3), 2.25 (m, 1H, C*H*(CH_3)$_2$), 2.78 and 4.00 (m, 1H each, PCH_2P), 5.32 (br, 2H, CH of *p*-cymene), 6.29 and 6.45 (br, 1H each, CH of *p*-cymene), 6.95−7.99 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 15.77 (s, CH_3), 21.37 and 23.33 (s, CH(*C*H$_3$)$_2$), 27.23 (ddd, J_{CP} = 63.1 and 13.0 Hz, $^3J_{CP}$ = 7.2 Hz, PCH_2P), 32.05 (s, *C*H(CH_3)$_2$), 81.10 and 85.46 (s, CH of *p*-cymene), 87.11 and 89.50 (d, $^2J_{CP}$ = 5.5 Hz, CH of *p*-cymene), 98.59 and 113.52 (s, C of *p*-cymene), 120.15−135.70 (m, Ph), 151.06 (d, $^2J_{CP}$ = 9.0 Hz, C_{ipso} of OPh), 151.63 (d, $^2J_{CP}$ = 9.0 Hz, C_{ipso} of OPh) ppm.

Method B. A solution containing [Ru(η^6-*p*-cymene)Cl(κ^2-*P*,*O*-Ph_2PCH_2P{=NP(=O)(OPh)$_2$}Ph_2)][SbF_6] (**3b**), or a mixture of [Ru(η^6-*p*-cymene)Cl(κ^2-*P*,*O*-Ph_2PCH_2P{=NP(=O)(OEt)$_2$}Ph_2)]-[SbF_6] (**3a**) and [Ru(η^6-*p*-cymene)Cl(κ^2-*P*,*N*-Ph_2PCH_2P{=NP(=O)(OEt)$_2$}Ph_2)][SbF_6] (**4a**), (0.2 mmol) in 20 mL of dichloromethane was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.072 g, 0.21 mmol) for 1 h. After the excess of $AgSbF_6$ used and the AgCl formed were filtered off (Kieselguhr), the solution was concentrated to ca. 2 mL, and 30 mL of diethyl ether was then added yielding an orange microcrystalline solid which was washed with diethyl ether (3 × 10 mL) and vacuum-dried. For **5a**: yield: 87% (0.216 g). For **5b**: yield: 80% (0.214 g).

Synthesis of [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-Ph_2PCH_2P{=NP(=O)(OR)$_2$}Ph_2)] (R = Et (6a), Ph (6b)). Complexes **6a**,**b**, isolated as orange microcrystalline solids, were prepared as described for **2a**,**b** starting from [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (0.246 g, 0.4 mmol) and the corresponding iminophosphorane-phosphine **1a**,**b** (0.85 mmol). For **6a**: yield: 97% (0.655 g), mp 96−98 °C. Anal. Calcd for $RuC_{39}H_{48}O_3P_3Cl_2N$: C, 55.52; H, 5.73; N, 1.66. Found: C, 55.67; H, 5.59; N, 1.78. ^1H NMR ($CDCl_3$) δ 1.05 (t, 6H, J_{HH} = 7.0 Hz, OCH_2CH_3), 2.12 (s, 6H, CH_3), 2.64 (m, 2H, H_4 and H_6), 3.22 (d, 2H, $^3J_{HP}$ = 3.1 Hz, H_2 and H_{10}), 3.48 (m, 6H, OCH_2, H_5 and H_7), 3.94 and 4.23 (m, 1H each, PCH_2P), 4.20 (d, 2H, $^3J_{HP}$ = 9.8 Hz, H_1 and H_9), 5.16 (m, 2H, H_3 and H_8), 7.00−7.90 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.47 (d, $^3J_{CP}$ = 7.8 Hz, OCH_2CH_3), 20.87 (s, CH_3), 24.98 (ddd, J_{CP} = 74.7 and 16.2 Hz, $^3J_{CP}$ = 7.0 Hz, PCH_2P), 36.88 (s, C_4 and C_5), 61.24 (d, $^2J_{CP}$ = 6.2 Hz, OCH_2), 68.51 (d, $^2J_{CP}$ = 4.9 Hz, C_1 and C_8), 107.87 (d, $^2J_{CP}$ = 10.3 Hz, C_3 and C_6), 125.92 (s, C_2 and C_7), 127.00−135.00 (m, Ph) ppm. For **6b**: yield 86% (0.646 g), mp 160−162 °C. Anal. Calcd for $RuC_{47}H_{48}O_3P_3Cl_2N$: C, 60.07; H, 5.15; N, 1.49. Found: C, 60.21; H, 4.70; N, 1.34. ^1H NMR ($CDCl_3$) δ 2.13 (s, 6H, CH_3), 2.63 (m, 2H, H_4 and H_6), 3.24 (d, 2H, $^3J_{HP}$ = 3.4 Hz, H_2 and H_{10}), 3.45 (m, 2H, H_5 and H_7), 3.95 and 4.23 (m, 1H each, PCH_2P), 4.22 (d, 2H, $^3J_{HP}$ = 9.4 Hz, H_1 and H_9), 5.18 (m, 2H, H_3 and H_8), 6.85−7.70 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 20.86 (s, CH_3), 24.75 (ddd, J_{CP} = 74.9 and 15.2 Hz, $^3J_{CP}$ = 6.6 Hz, PCH_2P), 36.89 (s, C_4 and C_5), 68.40 (d, $^2J_{CP}$ = 5.4 Hz, C_1 and C_8), 108.01 (d, $^2J_{CP}$ = 9.9 Hz, C_3 and C_6), 120.56−134.82 (m, Ph), 125.96 (s, C_2 and C_7), 152.71 (d, $^2J_{CP}$ = 7.2 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*O*-Ph_2PCH_2P{=NP(=O)(OR)$_2$}Ph_2)][SbF_6] (R = Et (7a), Ph (7b)). Complexes **7a**,**b**, isolated as orange microcrystalline solids, were prepared as described for **3a**,**b** starting either from [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-Ph_2PCH_2P{=NP(=O)(OR)$_2$}Ph_2)] (**6a**,**b**) (0.5 mmol) (method A) or [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (0.123 g, 0.2 mmol) (method B). For **7a**: yield (method A) 91% (0.475 g), yield (method B) 88% (0.367 g); mp 130−132 °C (dec). Anal. Calcd for $RuC_{39}H_{48}F_6O_3P_3ClNSb\cdot1/4CH_2Cl_2$: C, 44.26; H, 4.59; N, 1.31. Found: C, 44.40;

H, 4.44; N, 1.40. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 122. ^{1}H NMR (CD_2Cl_2) δ 1.14 and 1.23 (t, 3H each, J_{HH} = 6.8 Hz, OCH_2CH_3), 2.14 and 2.18 (s, 3H each, CH_3), 2.83 (m, 2H, H_4 and H_6), 2.90 (d, 1H, $^3J_{HP}$ = 3.4 Hz, H_2 or H_{10}), 3.64 (m, 2H, H_5 and H_7), 3.79 (m, 5H, OCH_2 and H_2 or H_{10}), 4.02 and 4.46 (m, 1H each, PCH_2P), 4.93 (d, 1H, $^3J_{HP}$ = 8.6 Hz, H_1 or H_9), 5.03 (d, 1H, $^3J_{HP}$ = 10.5 Hz, H_1 or H_9), 5.23 (m, 2H, H_3 and H_8), 7.10−7.70 (m, 20H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 16.20 (d, $^3J_{CP}$ = 5.7 Hz, OCH_2CH_3), 16.22 (d, $^3J_{CP}$ = 8.9 Hz, OCH_2CH_3), 19.70 and 21.01 (s, CH_3), 32.31 (dd, J_{CP} = 54.0 and 8.9 Hz, PCH_2P), 37.29 and 37.44 (s, C_4 and C_5), 62.41 (d, $^2J_{CP}$ = 4.4 Hz, C_1 or C_8), 63.53 (d, $^2J_{CP}$ = 6.4 Hz, OCH_2), 64.32 (d, $^2J_{CP}$ = 7.0 Hz, OCH_2), 72.39 (d, $^2J_{CP}$ = 5.7 Hz, C_1 or C_8), 110.50 and 114.53 (d, $^2J_{CP}$ = 9.5 Hz, C_3 and C_6), 127.25 (s, C_2 and C_7), 128.00−134.50 (m, Ph) ppm. For **7b**: yield (method A) 85% (0.484 g), yield (method B) 84% (0.383 g); mp 141−143 °C (dec). Anal. Calcd for $RuC_{47}H_{48}F_6O_3P_3ClNSb\cdot 1/4CH_2Cl_2$: C, 48.87; H, 4.21; N, 1.21. Found: C, 48.80; H, 4.07; N, 1.28. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 118. ^{1}H NMR (CD_2Cl_2) δ 1.88 and 2.07 (s, 3H each, CH_3), 2.64 and 2.74 (m, 1H each, H_4 and H_6), 3.09 (d, 1H, $^3J_{HP}$ = 3.1 Hz, H_2 or H_{10}), 3.47 (m, 2H, H_5 and H_7), 3.65 (d, 1H, $^3J_{HP}$ = 4.8 Hz, H_2 or H_{10}), 4.16 and 4.57 (m, 1H each, PCH_2P), 4.75 (d, 1H, $^3J_{HP}$ = 8.8 Hz, H_1 or H_9), 4.95 and 5.20 (m, 1H each, H_3 and H_8), 5.24 (d, 1H, $^3J_{HP}$ = 10.8 Hz, H_1 or H_9), 6.90−7.60 (m, 30H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 18.75 and 21.19 (s, CH_3), 33.68 (dd, J_{CP} = 56.9 and 10.8 Hz, PCH_2P), 37.13 and 37.54 (s, C_4 and C_5), 61.76 (d, $^2J_{CP}$ = 5.0 Hz, C_1 or C_8), 73.25 (d, $^2J_{CP}$ = 6.4 Hz, C_1 or C_8), 111.26 and 113.86 (d, $^2J_{CP}$ = 9.5 Hz, C_3 and C_6), 119.93−132.73 (m, Ph), 127.61 (s, C_2 and C_7), 151.81 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh), 152.00 (d, $^2J_{CP}$ = 8.4 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru(η^3:η^3-$C_{10}H_{16}$)(κ^3-*P,N,O*-Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2)][SbF_6]$_2$ (R = Et (8a), Ph (8b)). Complexes **8a**,**b**, isolated as yellow solids, were prepared as described for **5a**,**b** starting either from neutral complexes [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2(κ^1-*P*-Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2)] (**6a**,**b**) (0.5 mmol) (method A) or cationic derivatives [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2)][SbF_6] (**7a,b**) (0.5 mmol) (method B). For **8a**: yield (method A) 83% (0.516 g), yield (method B) 85% (0.529 g); mp 136−138 °C (dec). Anal. Calcd for $RuC_{39}H_{48}F_{12}O_3P_3Sb_2N$: C, 37.65; H, 3.89; N, 1.12. Found: C, 37.47; H, 3.96; N, 1.22. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 193. ^{1}H NMR (CD_2Cl_2) δ 1.09 and 1.35 (td, 3H each, J_{HH} = 7.0 Hz, $^4J_{HP}$ = 1.1 Hz, OCH_2CH_3), 1.74 and 2.46 (s, 3H each, CH_3), 2.83 (m, 1H, H_4 or H_6), 2.96 (m, 2H, H_4, H_5, H_6 or H_7), 3.22 (m, 1H, H_5 or H_7), 3.55 (s, 1H, H_1 or H_9), 3.92 (m, 4H, OCH_2), 3.96 (d, 1H, $^3J_{HP}$ = 2.8 Hz, H_2 or H_{10}), 4.12 and 4.40 (m, 1H each, PCH_2P), 4.51 and 4.80 (m, 1H each, H_3 and H_8), 4.56 (s, 1H, H_1 or H_9), 5.19 (d, 1H, $^3J_{HP}$ = 1.8 Hz, H_2 or H_{10}), 7.15−8.15 (m, 20H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 15.28 and 15.51 (d, $^3J_{CP}$ = 7.4 Hz, OCH_2CH_3), 17.61 and 18.70 (s, CH_3), 32.32 and 36.13 (s, C_4 and C_5), 39.72 (ddd, J_{CP} = 81.0 and 23.6 Hz, $^3J_{CP}$ = 7.7 Hz, PCH_2P), 66.76 (d, $^2J_{CP}$ = 7.9 Hz, OCH_2), 67.11 (d, $^2J_{CP}$ = 7.4 Hz, OCH_2), 77.25 and 80.48 (s, C_1 and C_8), 98.63 and 108.13 (s, C_3 and C_6), 123.99 and 125.61 (s, C_2 and C_7), 121.30−135.65 (m, Ph) ppm. For **8b**: yield (method A) 84% (0.563 g), yield (method B) 80% (0.535 g); mp 153−155 °C (dec). Anal. Calcd for $RuC_{47}H_{48}F_{12}O_3P_3Sb_2N$: C, 42.12; H, 3.61; N, 1.04. Found: C, 42.30; H, 3.55; N, 1.10. Conductivity (acetone, 20 °C, Ω^{-1} cm^2 mol^{-1}): 177. ^{1}H NMR (CD_2Cl_2) δ 1.73 and 2.25 (s, 3H each, CH_3), 2.92 (m, 3H, H_4, H_5, H_6 or H_7), 3.22 (m, 1H, H_5 or H_7), 3.67 (s, 1H, H_1 or H_9), 3.74 (d, 1H, $^3J_{HP}$ = 1.9 Hz, H_2 or H_{10}), 4.20 and 4.60 (m, 1H each, PCH_2P), 4.50 (s, 1H, H_1 or H_9), 4.71 and 4.91 (m, 1H each, H_3 and H_8), 5.25 (s, 1H, H_2 or H_{10}), 6.50−8.30 (m, 30H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 18.27 (d, $^3J_{CP}$ = 1.2 Hz, CH_3), 19.79 (s, CH_3), 33.51 and 36.79 (s, C_4 and C_5), 39.55 (ddd, J_{CP} = 90.8 and 23.4 Hz, $^3J_{CP}$ = 8.1 Hz, PCH_2P), 78.51 and 81.17 (s, C_1 and C_8), 100.23 and 109.16 (s, C_3 and C_6), 125.72 and 128.20 (s, C_2 and C_7), 119.50−137.00 (m, Ph), 149.39 (d, $^2J_{CP}$ = 9.6 Hz, C_{ipso} of OPh), 149.69 (d, $^2J_{CP}$ = 10.2 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru(η^6-*p*-cymene)X_2(κ^1-*P*-Ph_2PCH_2P{=NP(=O)-$(OR)_2$}Ph_2)] (R = Et, X = Br (9a), I (10a), N_3 (11a), NCO (12a); R = Ph, X = Br (9b), I (10b), N_3 (11b), NCO (12b)). Method A. A solution containing [Ru(η^6-*p*-cymene)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OPh)_2$}Ph_2)][SbF_6] (**3b**), or a mixture of [Ru(η^6-*p*-cymene)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)][SbF_6] (**3a**) and [Ru(η^6-*p*-cymene)Cl(κ^2-*P,N*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}-Ph_2)][SbF_6] (**4a**), (0.5 mmol) in 40 mL of methanol was treated, at room temperature, with the appropriate sodium salt NaX (5 mmol) for 4 h. The solution was then evaporated to dryness and the solid residue extracted with dichloromethane and filtered off (Kieselguhr). The resulting solution was concentrated to ca. 2 mL, and 50 mL of diethyl ether was then added yielding a yellow-orange microcrystalline solid which was washed with diethyl ether (2 × 10 mL) and vacuum-dried. For **9a**: yield 85% (0.395 g). Anal. Calcd for $RuC_{39}H_{46}O_3P_3Br_2N\cdot 1/2CH_2Cl_2$: C, 48.75; H, 4.87; N, 1.44. Found: C, 48.99; H, 4.83; N, 1.39. ^{1}H NMR ($CDCl_3$) δ 0.78 (d, 6H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 0.97 (t, 6H, J_{HH} = 7.0 Hz, OCH_2CH_3), 1.86 (s, 3H, CH_3), 2.66 (sept, 1H, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 3.43 (m, 4H, OCH_2), 4.14 (dd, 2H, $^2J_{HP}$ = 9.9 and 9.9 Hz, PCH_2P), 5.04 and 5.23 (d, 2H each, J_{HH} = 6.0 Hz, CH of *p*-cymene), 7.19−8.07 (m, 20H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.07 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 17.55 (s, CH_3), 21.23 (s, CH-$(CH_3)_2$), 23.32 (ddd, J_{CP} = 69.5 and 18.8 Hz, $^3J_{CP}$ = 9.5 Hz, PCH_2P), 30.40 (s, $CH(CH_3)_2$), 60.63 (d, $^2J_{CP}$ = 6.0 Hz, OCH_2), 85.43 (d, $^2J_{CP}$ = 6.3 Hz, CH of *p*-cymene), 90.47 (d, $^2J_{CP}$ = 4.1 Hz, CH of *p*-cymene), 94.18 and 109.49 (s, C of *p*-cymene), 127.55−134.12 (m, Ph) ppm. For **9b**: yield 83% (0.426 g). Anal. Calcd for $RuC_{47}H_{46}O_3P_3Br_2N\cdot 1/4CH_2Cl_2$: C, 54.16; H, 4.47; N, 1.34. Found: C, 54.14; H, 4.34; N, 1.40. ^{1}H NMR ($CDCl_3$) δ 0.73 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.87 (s, 3H, CH_3), 2.61 (sept, 1H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 4.19 (dd, 2H, $^2J_{HP}$ = 9.8 and 9.8 Hz, PCH_2P), 5.03 and 5.23 (d, 2H each, J_{HH} = 6.1 Hz, CH of *p*-cymene), 6.79−7.91 (m, 30H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.98 (s, CH_3), 21.43 (s, $CH(CH_3)_2$), 23.99 (ddd, J_{CP} = 74.3 and 20.1 Hz, $^3J_{CP}$ = 6.4 Hz, PCH_2P), 30.97 (s, $CH(CH_3)_2$), 86.11 (d, $^2J_{CP}$ = 5.8 Hz, CH of *p*-cymene), 91.07 (d, $^2J_{CP}$ = 4.7 Hz, CH of *p*-cymene), 94.67 and 109.64 (s, C of *p*-cymene), 120.60−135.84 (m, Ph), 152.66 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh) ppm. For **10a**: yield 82% (0.420 g). Anal. Calcd for $RuC_{39}H_{46}O_3P_3I_2N\cdot CH_2Cl_2$: C, 43.30; H, 4.36; N, 1.26. Found: C, 43.63; H, 4.11; N, 1.28. ^{1}H NMR ($CDCl_3$) δ 0.64 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 0.88 (t, 6H, J_{HH} = 7.0 Hz, OCH_2CH_3), 1.94 (s, 3H, CH_3), 2.91 (sept, 1H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 3.32 (m, 4H, OCH_2), 4.33 (dd, 2H, $^2J_{HP}$ = 9.6 and 9.6 Hz, PCH_2P), 4.89 and 5.15 (d, 2H each, J_{HH} = 6.0 Hz, CH of *p*-cymene), 7.08−7.96 (m, 20H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.14 (d, $^3J_{CP}$ = 7.8 Hz, OCH_2CH_3), 18.66 (s, CH_3), 21.63 (s, $CH(CH_3)_2$), 30.08 (ddd, J_{CP} = 76.3 and 23.0 Hz, $^3J_{CP}$ = 7.7 Hz, PCH_2P), 31.74 (s, $CH(CH_3)_2$), 60.74 (d, $^2J_{CP}$ = 6.0 Hz, OCH_2), 85.79 (d, $^2J_{CP}$ = 6.0 Hz, CH of *p*-cymene), 90.89 (d, $^2J_{CP}$ = 4.2 Hz, CH of *p*-cymene), 95.68 and 111.91 (s, C of *p*-cymene), 127.51−134.39 (m, Ph) ppm. For **10b**: yield 83% (0.465 g). Anal. Calcd for $RuC_{47}H_{46}O_3P_3I_2N$: C, 50.37; H, 4.14; N, 1.25. Found: C, 49.98; H, 3.72; N, 1.22. ^{1}H NMR ($CDCl_3$) δ 0.73 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.59 (s, 3H, CH_3), 3.04 (sept, 1H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 4.51 (dd, 2H, $^2J_{HP}$ = 8.8 and 8.8 Hz, PCH_2P), 5.00 and 5.25 (d, 2H each, J_{HH} = 5.5 Hz, CH of *p*-cymene), 6.80−

Table 1. Crystallographic Data for Complexes **2b**, **3b**, **7a**, and **12b**

	2b	**3b**	**7a**	**12b**
chemical formula	$C_{47}H_{46}O_3P_3Cl_2NRu$	$C_{47}H_{46}F_6P_4O_3ClNRu$	$C_{39}H_{48}F_4O_3P_3BClNRu$	$C_{49}H_{46}O_5N_3P_3{\cdot}CH_2Cl_2$
fw	937.73	1047.25	895.02	1035.79
T (°C)	−153(2)	20(2)	20(2)	−73(2)
wavelength (Å)	1.54184	0.71073	0.71073	1.54184
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$Pca2_1$ (No. 29)
a, Å	10.518(1)	10.2905(9)	13.959(5)	23.3059(3)
b, Å	13.869(2)	21.584(2)	15.042(6)	9.1822(1)
c, Å	15.856(2)	22.0612(2)	19.966(8)	22.6599(4)
α, deg	80.267(6)	90	90	90
β, deg	85.289(6)	95.640(2)	100.253(9)	90
γ, deg	70.543(6)	90	90	90
Z	2	4	4	4
V, Å^3	2148.7(4)	4876.3(7)	4125(3)	4849.2(1)
ρ_{calcd}, g cm^{-3}	1.449	1.426	1.441	1.419
μ, cm^{-1}	5.488	5.70	6.16	4.965
weight function (a, b)	(0.0492, 0)	(0.0963, 0)	(0.0573, 0)	(0.0755, 2.5453)
R1[a] [$I > 2\sigma(I)$]	0.0480	0.0688	0.0586	0.0385
wR2[a] [$I > 2\sigma(I)$]	0.0978	0.1517	0.1156	0.1070
R1 (all data)	0.0933	0.2272	0.1684	0.0424
wR2 (all data)	0.1241	0.2073	0.1464	0.1354

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

8.00 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 19.05 (s, CH_3), 21.77 (s, $CH(CH_3)_2$), 30.36 (ddd, J_{CP} = 72.3 and 22.3 Hz, $^3J_{CP}$ = 5.9 Hz, PCH_2P), 32.23 (s, $CH(CH_3)_2$), 86.46 (d, $^2J_{CP}$ = 5.7 Hz, CH of *p*-cymene), 91.35 (d, $^2J_{CP}$ = 4.5 Hz, CH of *p*-cymene), 96.26 and 112.06 (s, C of *p*-cymene), 120.80−133.81 (m, Ph), 152.63 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh) ppm. For **11a**: yield: 79% (0.338 g). Anal. Calcd for $RuC_{39}H_{46}N_7O_3P_3$: C, 54.80; H, 5.42; N, 11.47. Found: C, 54.81; H, 5.10; N, 11.99. IR (KBr, cm^{-1}) ν 2036 (N═N═N). ^1H NMR (CD_2Cl_2) δ 0.92 (d, 6H, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 1.00 (t, 6H, J_{HH} = 6.9 Hz, OCH_2CH_3), 1.75 (s, 3H, CH_3), 2.33 (sept, 1H, J_{HH} = 6.6 Hz, $CH(CH_3)_2$), 3.41 (m, 4H, OCH_2), 4.03 (dd, 2H, $^2J_{HP}$ = 9.7 and 9.7 Hz, PCH_2P), 5.09 and 5.14 (d, 2H each, J_{HH} = 5.1 Hz, CH of *p*-cymene), 7.07−7.85 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 16.12 (d, $^3J_{CP}$ = 8.0 Hz, OCH_2CH_3), 16.63 (s, CH_3), 20.72 (ddd, J_{CP} = 77.4 and 14.5 Hz, $^3J_{CP}$ = 7.6 Hz, PCH_2P), 21.62 (s, $CH(CH_3)_2$), 30.19 (s, $CH(CH_3)_2$), 60.95 (d, $^2J_{CP}$ = 6.5 Hz, OCH_2), 86.26 (d, $^2J_{CP}$ = 5.1 Hz, CH of *p*-cymene), 89.63 (s, CH of *p*-cymene), 95.86 and 109.05 (s, C of *p*-cymene), 125.50−135.44 (m, Ph) ppm. For **11b**: yield 78% (0.371 g). Anal. Calcd for $RuC_{47}H_{46}N_7O_3P_3$: C, 59.36; H, 4.87; N, 10.31. Found: C, 59.47; H, 4.37; N, 10.20. IR (KBr, cm^{-1}) ν 2035 (N═N═N). ^1H NMR ($CDCl_3$) δ 0.89 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.78 (s, 3H, CH_3), 2.35 (sept, 1H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 3.48 (dd, 2H, $^2J_{HP}$ = 9.8 and 9.8 Hz, PCH_2P), 5.08 and 5.15 (d, 2H each, J_{HH} = 5.8 Hz, CH of *p*-cymene), 6.76−7.75 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.94 (s, CH_3), 20.35 (ddd, J_{CP} = 73.4 and 14.0 Hz, $^3J_{CP}$ = 6.6 Hz, PCH_2P), 21.81 (s, $CH(CH_3)_2$), 30.43 (s, $CH(CH_3)_2$), 86.53 (d, $^2J_{CP}$ = 5.3 Hz, CH of *p*-cymene), 90.02 (d, $^2J_{CP}$ = 3.5 Hz, CH of *p*-cymene), 95.75 and 109.18 (s, C of *p*-cymene), 120.61−133.96 (m, Ph), 152.61 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh) ppm. For **12a**: yield 77% (0.329 g). Anal. Calcd for $RuC_{41}H_{46}O_5N_3P_3{\cdot}CH_2Cl_2$: C, 53.67; H, 5.14; N, 4.47. Found: C, 53.26; H, 4.77; N, 4.57. IR (KBr, cm^{-1}) ν 2227 (N═C═O). ^1H NMR ($CDCl_3$) δ 0.93 (m, 12H, $CH(CH_3)_2$ and OCH_2CH_3), 1.77 (s, 3H, CH_3), 2.19 (sept, 1H, J_{HH} = 5.6 Hz, $CH(CH_3)_2$), 3.46 (m, 4H, OCH_2), 3.58 (dd, 2H, $^2J_{HP}$ = 10.0 and 10.0 Hz, PCH_2P), 5.12 and 5.16 (br, 2H each, CH of *p*-cymene), 7.26−7.94 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.10 (d, $^3J_{CP}$ = 8.2 Hz, OCH_2CH_3), 17.54 (s, CH_3), 21.50 (s, $CH(CH_3)_2$), 22.52 (ddd, J_{CP} = 75.7 and 19.5 Hz, $^3J_{CP}$ = 10.8 Hz, PCH_2P), 30.37 (s, $CH(CH_3)_2$), 60.78 (d, $^2J_{CP}$ = 5.8 Hz, OCH_2), 86.47 (d, $^2J_{CP}$ = 4.7 Hz, CH of *p*-cymene), 89.97 (s, CH of *p*-cymene), 96.00 and 108.52 (s, C of *p*-cymene), 127.82−133.54 (m, Ph and NCO) ppm. For **12b**: yield 75% (0.356 g). Anal. Calcd for $RuC_{49}H_{46}O_5N_3P_3$: C, 61.89; H, 4.87; N, 4.42. Found: C, 61.68; H, 4.82; N, 4.03. IR (KBr, cm^{-1}) ν 2225 (N═C═O). ^1H NMR ($CDCl_3$) δ 0.83 (d, 6H, J_{HH} = 6.7 Hz, $CH(CH_3)_2$), 1.74 (s, 3H, CH_3), 2.18 (sept, 1H, J_{HH} = 6.7 Hz, $CH(CH_3)_2$), 3.59 (dd, 2H, $^2J_{HP}$ = 9.6 and 9.6 Hz, PCH_2P), 5.06 and 5.14 (br, 2H each, CH of *p*-cymene), 6.77−7.79 (m, 30H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.62 (s, CH_3), 21.43 (s, $CH(CH_3)_2$), 21.68 (ddd, J_{CP} = 71.2 and 17.5 Hz, $^3J_{CP}$ = 7.2 Hz, PCH_2P), 30.39 (s, $CH(CH_3)_2$), 86.56 (d, $^2J_{CP}$ = 5.6 Hz, CH of *p*-cymene), 90.10 (d, $^2J_{CP}$ = 4.5 Hz, CH of *p*-cymene), 95.79 and 108.04 (s, C of *p*-cymene), 120.31−133.53 (m, Ph and NCO), 152.00 (d, $^2J_{CP}$ = 6.8 Hz, C_{ipso} of OPh) ppm.

Method B. A solution of the corresponding complex [Ru(η^6-*p*-cymene)(κ^3-*P*,*N*,*O*-$Ph_2PCH_2P\{{=}NP({=}O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (**5a**,**b**) (0.2 mmol) in 20 mL of methanol was treated, at room temperature, with the appropriate sodium salt NaX (2 mmol) for 2 h. The solution was then evaporated to dryness and the solid residue extracted with dichloromethane and filtered off (Kieselguhr). The resulting solution was concentrated to ca. 2 mL, and 30 mL of diethyl ether was added yielding a yellow-orange microcrystalline solid which was washed with diethyl ether (2 × 5 mL) and vacuum-dried. For **9a**: yield 80% (0.149 g). For **9b**: yield 87% (0.178 g). For **10a**: yield 84% (0.172 g). For **10b**: yield 80% (0.179 g). For **11a**: yield 82% (0.140 g). For **11b**: yield 72% (0.137 g). For **12a**: yield 79% (0.135 g). For **12b**: yield 77% (0.146 g).

General Procedure for Catalytic Transfer Hydrogenation of Cyclohexanone. Under inert atmosphere, cyclohexanone (0.49 g, 5 mmol), the ruthenium catalyst precursor (0.02 mmol, 0.4 mol %), and 20 mL of propan-2-ol are introduced into a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min. Then NaOH is added (5 mL of a 0.096 M solution in propan-2-ol, 9.6 mol %), and the reaction is monitored by gas chromatography. Cyclohexanol and acetone are the only products detected in all cases.

X-ray Crystal Structure Determination of Complexes 2b, 3b, 7a, and 12b. Crystals suitable for X-ray diffraction analysis were obtained, in all the cases, by slow diffusion of pentane in a saturated solution of the complex in dichloromethane.[12] The most relevant crystal and refinement data are collected in Table 1. Diffraction data for **3b** and **7a** were recorded on a Bruker Smart CCD diffractometer using Mo Kα radiation with a nominal crystal−detector distance of 40 mm, using 1371 frames at 0.3° intervals with 15 s exposure time per frame and 1271 frames at 0.3° intervals

Table 2. $^{31}P\{^1H\}$ NMR Data for the Iminophosphorane-Phosphine Ligands and Their Metal Complexes[a]

compd	Ph_2P	$Ph_2P{=}N$	$(RO)_2P{=}O$
	$Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2$		
R = Et (**1a**)[b]	−27.39 (d, $^2J_{PP}$ = 61.0)	15.29 (dd, $^2J_{PP}$ = 61.0, 28.5)	4.59 (d, $^2J_{PP}$ = 28.5)
R = Ph (**1b**)[b]	−27.65 (d, $^2J_{PP}$ = 63.1)	16.87 (dd, $^2J_{PP}$ = 63.1, 31.3)	−6.04 (d, $^2J_{PP}$ = 31.3)
	$[Ru(\eta^6\text{-}p\text{-cymene})X_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)]$		
R = Et; X = Cl (**2a**)[b]	22.97 (d, $^2J_{PP}$ = 38.5)	11.00 (dd, $^2J_{PP}$ = 38.5, 30.0)	1.83 (d, $^2J_{PP}$ = 30.0)
R = Et; X = Br (**9a**)[b]	16.00 (d, $^2J_{PP}$ = 36.6)	8.82 (dd, $^2J_{PP}$ = 36.6, 31.7)	1.05 (d, $^2J_{PP}$ = 31.7)
R = Et; X = I (**10a**)[b]	16.20 (d, $^2J_{PP}$ = 35.6)	13.08 (dd, $^2J_{PP}$ = 35.6, 31.1)	1.52 (d, $^2J_{PP}$ = 31.1)
R = Et; X = N_3 (**11a**)[c]	27.62 (d, $^2J_{PP}$ = 37.9)	9.00 (dd, $^2J_{PP}$ = 37.9, 32.5)	1.57 (d, $^2J_{PP}$ = 32.5)
R = Et; X = NCO (**12a**)[b]	26.62 (d, $^2J_{PP}$ = 39.1)	9.69 (dd, $^2J_{PP}$ = 39.1, 31.7)	1.40 (d, $^2J_{PP}$ = 31.7)
R = Ph; X = Cl (**2b**)[b]	23.29 (d, $^2J_{PP}$ = 38.9)	13.06 (dd, $^2J_{PP}$ = 38.9, 31.3)	−8.57 (d, $^2J_{PP}$ = 31.3)
R = Ph; X = Br (**9b**)[b]	19.29 (d, $^2J_{PP}$ = 37.8)	13.77 (dd, $^2J_{PP}$ = 37.8, 31.7)	−8.57 (d, $^2J_{PP}$ = 31.7)
R = Ph; X = I (**10b**)[b]	16.74 (d, $^2J_{PP}$ = 36.6)	15.17 (dd, $^2J_{PP}$ = 36.6, 32.6)	−8.90 (d, $^2J_{PP}$ = 32.6)
R = Ph; X = N_3 (**11b**)[b]	28.00 (d, $^2J_{PP}$ = 38.9)	12.64 (dd, $^2J_{PP}$ = 38.9, 32.5)	−8.44 (d, $^2J_{PP}$ = 32.5)
R = Ph; X = NCO (**12b**)[b]	26.95 (d, $^2J_{PP}$ = 36.6)	12.30 (dd, $^2J_{PP}$ = 36.6, 32.5)	−9.12 (d, $^2J_{PP}$ = 32.5)
	$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)]$		
R = Et (**6a**)[b]	19.81 (d, $^2J_{PP}$ = 36.6)	9.91 (dd, $^2J_{PP}$ = 36.6, 31.7)	1.64 (d, $^2J_{PP}$ = 31.7)
R = Ph (**6b**)[b]	20.23 (d, $^2J_{PP}$ = 36.6)	12.02 (dd, $^2J_{PP}$ = 36.6, 34.0)	−8.89 (d, $^2J_{PP}$ = 34.0)
	$[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]$		
R = Et (**3a**)[c]	22.97 (s)	11.82 (d, $^2J_{PP}$ = 38.5)	8.21 (d, $^2J_{PP}$ = 38.5)
R = Ph (**3b**)[c]	23.94 (s)	9.20 (d, $^2J_{PP}$ = 48.1)	−0.79 (d, $^2J_{PP}$ = 48.1)
	$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]$		
R = Et (**7a**)[c]	22.22 (s)	10.56 (d, $^2J_{PP}$ = 37.0)	9.49 (d, $^2J_{PP}$ = 37.0)
R = Ph (**7b**)[c]	24.86 (s)	10.37 (d, $^2J_{PP}$ = 49.5)	−1.88 (d, $^2J_{PP}$ = 49.5)
	$[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]$		
R = Et (**4a**)[c]	47.22 (dd, $^2J_{PP}$ = 20.2, $^3J_{PP}$ = 6.1)	58.68 (dd, $^2J_{PP}$ = 20.2, 6.1)	10.24 (dd, $^2J_{PP}$ = 6.1, $^3J_{PP}$ = 6.1)
	$[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]_2$		
R = Et (**5a**)[c]	41.90 (d, $^2J_{PP}$ = 36.3)	54.45 (dd, $^2J_{PP}$ = 36.3, 3.8)	18.28 (d, $^2J_{PP}$ = 3.8)
R = Ph (**5b**)[c]	41.68 (d, $^2J_{PP}$ = 35.7)	55.62 (d, $^2J_{PP}$ = 35.7)	6.33 (s)
	$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\kappa^3\text{-}P,N,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]_2$		
R = Et (**8a**)[c]	46.64 (d, $^2J_{PP}$ = 11.5)	50.88 (dd, $^2J_{PP}$ = 11.5, 6.5)	4.45 (d, $^2J_{PP}$ = 6.5)
R = Ph (**8b**)[c]	45.76 (d, $^2J_{PP}$ = 9.0)	51.09 (dd, $^2J_{PP}$ = 9.0, 8.1)	−6.47 (d, $^2J_{PP}$ = 8.1)

[a] δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets. [b] Spectra recorded in $CDCl_3$. [c] Spectra recorded in CD_2Cl_2.

with 20 s exposure time per frame, respectively. The diffraction frames were integrated using the SAINT package[13] and corrected for absorption with SADABS.[14] Sets for compounds **2b** and **12b** were collected on a Nonius Kappa CCD single crystal diffractometer using Cu Kα radiation with a crystal−detector distance fixed at 29 mm; a total of 1238 (20 s exposure time per frame) and 1125 frames (60 s exposure time per frame), respectively, were recorded using the oscillation method (with 2° oscillation). Data collection strategy was calculated with the program Collect.[15] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[16] Absorption correction was applied by means of XABS2.[17]

All the structures were solved by Patterson interpretation and phase expansion using DIRDIF.[18] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[19] During the final stages of the refinements, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined (the F atoms of the disordered PF_6^- anion in **3b** were isotropically refined). The H atoms for all the structures were geometrically located and refined riding on their parent atoms with common isotropic thermal parameters. 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 $\sigma(F_o^2)$ from counting statistics and $P = (\max(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[20] Geometrical calculations were made with PARST.[21] The crystallographic plots were made with PLATON.[22]

Computational Details. All calculations were carried out with the Gaussian98 program package.[23] The molecular geometries were optimized, without any molecular symmetry constraint, using Schlegel's analytical gradient procedure[24] at the B3-LYP variant of density functional theory[25] with the standard split-valence 6-31G-(d) basis set for C, N, O, and H,[26] and the pseudorelativistic effective core potential (ECP) by Hay and Wadt for Ru, P, and Cl.[27] This basis set was referred to as DZV(d). The optimized structures were characterized as minima (representing equilibrium structures) by analytic frequency calculations which also yielded zero-point vibrational energy and thermochemical analysis. Single-point

(12) Only the hexafluorophosphate salt of **3b** (Anal. Calcd for $RuC_{47}H_{46}F_6P_4O_3ClN$: C, 53.90; H, 4.43; N, 1.34. Found: C, 53.72; H, 4.51; N, 1.27.) and the tetrafluoroborate salt of **7a** (Anal. Calcd for $RuC_{39}H_{48}F_4O_3P_3BClN$: C, 52.33; H, 5.40; N, 1.56. Found: C, 52.21; H, 5.31; N, 1.68.) gave crystals suitable for X-ray diffraction. These compounds were obtained using $AgPF_6$ and $AgBF_4$, respectively, instead of $AgSbF_6$.

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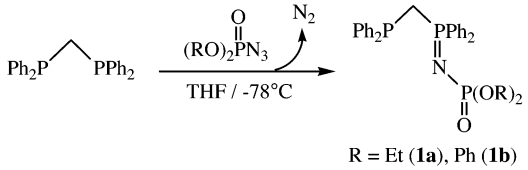
Scheme 1



calculations on the DFT geometries were performed with the incorporation of correlation energy using Møller−Plesset perturbation theory with second-order corrections (MP2).[28]

Results and Discussion

Synthesis and Characterization of $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et (1a), Ph (1b)). Monoimination of bis(diphenylphosphino)methane (dppm) with azides has been successfully applied to the preparation of several iminophosphorane-phosphine ligands $Ph_2PCH_2P(=NR)Ph_2$.[3] The high selectivity of these reactions seems to be sterically controlled since the proximity of the two diphenylphosphino groups hinders the imination at the second phosphorus atom.[29] As expected, we have found that dppm reacts with an equimolar amount of the phosphoryl azides $(RO)_2P(=O)N_3$ (R = Et, Ph), in THF at −78°C, to afford the new (*N*-phosphoryl-iminophosphoranyl)(phosphino)methane derivatives $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et (**1a**), Ph (**1b**)) in good yields (93% and 86%, respectively) (Scheme 1).

Compounds **1a**,**b** have been isolated as air-stable white solids. They are soluble in chlorinated solvents, THF, acetonitrile, and diethyl ether, and are insoluble in apolar solvents such as pentane or hexane. Their NMR spectroscopic data (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$) and elemental analyses are in agreement with the proposed structures (see the Experimental Section and Table 2),[30] the former corresponding well with those reported in the literature for related compounds.[3] Relevant spectroscopic features are the following: (i) Regarding $^{31}P\{^1H\}$ NMR, three well separated signals with equal relative intensities are present (**1a**, δ −27.39 (d, $^2J_{PP}$ = 61.0 Hz, Ph_2P), 4.59 (d, $^2J_{PP}$ = 28.5 Hz, $(EtO)_2P=O$), and 15.29 (dd, $^2J_{PP}$ = 61.0 and 28.5 Hz, $Ph_2P=N$); **1b**, δ −27.65 (d, $^2J_{PP}$ = 63.1 Hz, Ph_2P), −6.04 (d, $^2J_{PP}$ = 31.3 Hz, $(PhO)_2P=O$), and 16.87 (dd, $^2J_{PP}$ = 63.1 and 31.3 Hz, $Ph_2P=N$)). (ii) Regarding ^1H NMR, there is a doublet resonance (ca. 3.4 ppm) for the methylenic hydrogens due to the coupling with the phosphorus atom of the $Ph_2P=N$ unit (ca. $^2J_{HP}$ = 14 Hz; coupling with the Ph_2P phosphorus atom, usually in the range $^2J_{HP}$ = 1−3 Hz for related $Ph_2PCH_2P(=NR)Ph_2$ ligands,[3] has been not observed). And, (iii) regarding $^{13}C\{^1H\}$ NMR, there is a doublet of doublets signal (ca. J_{CP} = 65 (coupling with $Ph_2P=N$) and 34 Hz (coupling with Ph_2P)) for the PCH_2P carbon which appears at ca. 30 ppm.

Coordination of $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et (1a), Ph (1b)) to Ruthenium(II) and Ruthenium(IV) Fragments. The ability of the novel iminophosphorane-phosphines $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (**1a**,**b**) to act as mono-, bi-, or tridentate ligands has been explored. The readily available ruthenium(II) and ruthenium(IV) chloro-bridged dimers $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$[9] and $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$,[10] respectively, were chosen as starting materials due to their versatile reactivity toward polyfunctional ligands.[31,32] Results are summarized in Schemes 2 and 3.

(a) κ^1-*P*-Complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)]$ (R = Et (2a), Ph (2b)) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)]$ (R = Et (6a), Ph (6b)). As expected from our previous results,[5] the treatment of dimers $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ and $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$ with a 2-fold excess of **1a**,**b**, in dichloromethane at room temperature, results in the cleavage of the chloride bridges and the clean formation of monomeric compounds $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)]$ (R = Et (**2a**), Ph (**2b**); Scheme 2) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)]$ (R = Et (**6a**), Ph (**6b**); Scheme 3), respectively (73−97% yield).

The characterization of complexes **2a**,**b** and **6a**,**b** was achieved by means of standard spectroscopic techniques (^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR) as well as elemental analyses

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(30) IR absorption bands which appear in the range 900−1300 cm^{-1} can be tentatively assigned to ν(P=N) and ν(P=O) of the *N*-phosphoryl-iminophosphoranyl units, but they are in general overlapped by those of the rest of the groups, and consequently, the correct assignment is uncertain.

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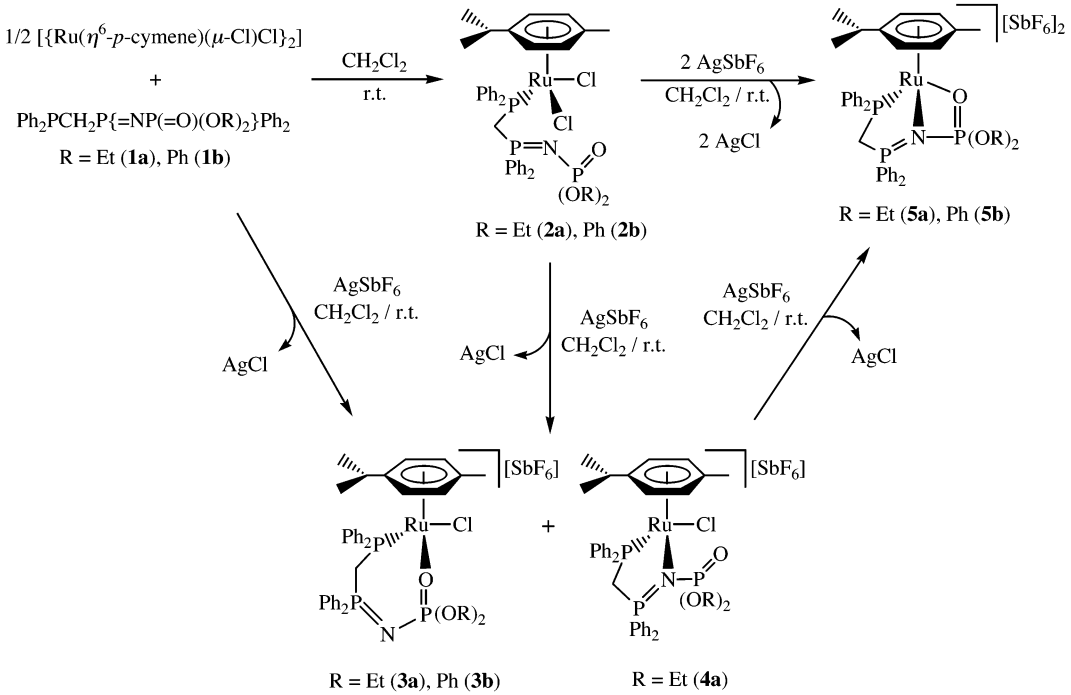
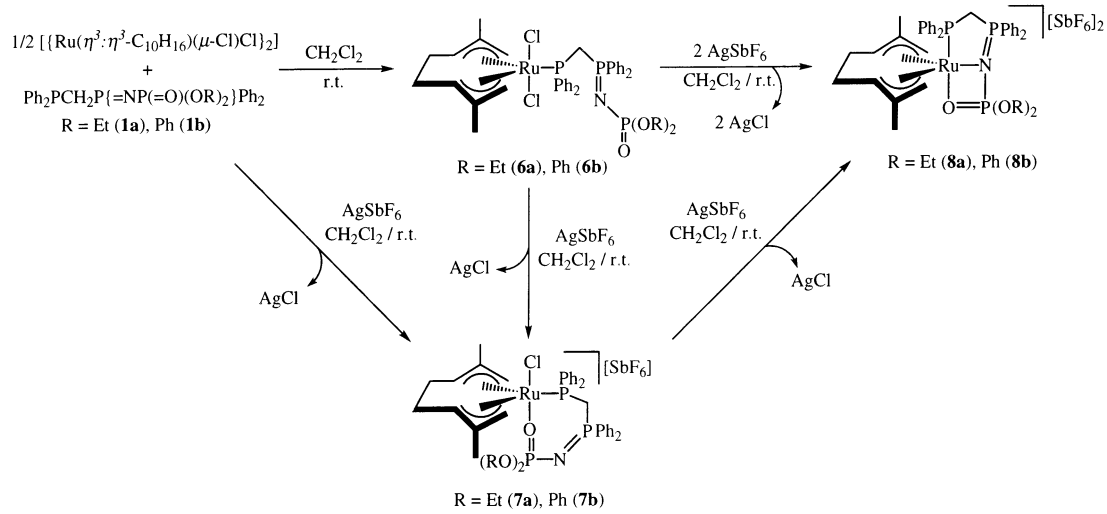
Scheme 2



Scheme 3



(details are given in the Experimental Section and Table 2).[30] In particular, the $^{31}P\{^1H\}$ NMR spectra are very informative showing a strong downfield shift of the diphenylphosphino group signals (ca. $\Delta\delta$ 48 ppm) with respect to those shown by the free ligands **1a**,**b** (see Table 2). In contrast, the $(RO)_2P{=}O$ and $Ph_2P{=}N$ resonances appear only slightly shielded ($\Delta\delta$ −2 to −5 ppm; Table 2). ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit signals in accordance with the proposed formulations, the most significant features being those concerning the methylenic PCH_2P group of the ligands: (i) in the ^1H NMR, a doublet of doublet resonance ($^2J_{HP(III)} = {}^2J_{HP(V)} = 9.1-9.9$ Hz) for **2a**,**b** and two unresolved multiplets for **6a**,**b** (δ 3.87−4.23), and (ii) in the $^{13}C\{^1H\}$ NMR, a characteristic doublet of doublet of doublets signal in the range 20.43−24.98 ppm ($J_{CP(V)} = 74.7-79.4$ Hz, $J_{CP(III)} = 15.2-19.2$ Hz, $^3J_{CP(V)} = 6.4-8.4$ Hz). We note also that the presence of a single set of signals for the two allylic moieties of the 2,7-dimethyl-2,6-diene-1,8-diyl ligand in the spectra of compounds **6a**,**b** (only five resonances are observed in the $^{13}C\{^1H\}$ NMR spectra) supports the formation of a simple equatorial adduct $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2L]$ with a local C_2-symmetry for the octadienediyl chain.[32]

The structure of complex **2b** has been unequivocally confirmed by a single-crystal X-ray diffraction study. An ORTEP view is shown in Figure 1; selected bond distances and angles are listed in the caption and in Table 3. The molecule exhibits a usual pseudooctahedral three-legged piano-stool geometry around the metal with values of the interligand angles P(1)−Ru−Cl(1), P(1)−Ru−Cl(2), and Cl(1)−Ru−Cl(2), and those between the centroid of the arene ring C* and the legs, typical of a pseudo-octahedron. The most remarkable feature is that the P(2)−N(1) (1.578(4) Å)

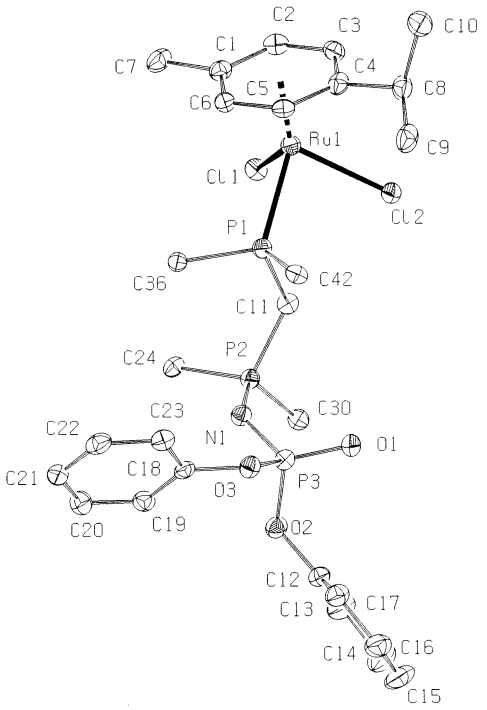


Figure 1. ORTEP-type view of the structure of [Ru(η^6-*p*-cymene)Cl_2-(κ^1-*P*-Ph_2PCH_2P{=NP(=O)$(OPh)_2$}Ph_2)] (**2b**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg) involving the Ru atom: Ru−C* = 1.6969(48); Ru−Cl(1) = 2.4249(12); Ru−Cl(2) = 2.4140(12); Ru−P(1) = 2.3467(13); C*−Ru−Cl(1) = 125.38(18); C*−Ru−Cl(2) = 125.96(17); C*−Ru−P(1) = 131.76(17); P(1)−Ru-Cl(1) = 86.69(4); P(1)−Ru−Cl(2) = 83.07(4); Cl(1)−Ru−Cl(2) = 89.87(4); Ru−P(1)−C(11) = 111.04(17); Ru−P(1)−C(36) = 115.36(16); Ru−P(1)−C(42) = 112.88(16). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), C(6)).

Table 3. Selected Bond Lengths and Angles for the Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2 Unit in Complexes **2b**, **3b**, **7a**, and **12b**

	2b	**3b**	**7a**	**12b**
Bond Lengths (Å)				
P(1)−C(11)	1.846(5)	1.836(5)	1.858(4)	1.846(5)
C(11)−P(2)	1.802(5)	1.799(5)	1.821(4)	1.792(5)
P(2)−N(1)	1.578(4)	1.550(5)	1.560(3)	1.577(5)
N(1)−P(3)	1.569(4)	1.552(5)	1.585(4)	1.588(4)
P(3)−O(1)	1.467(3)	1.474(4)	1.488(3)	1.466(3)
P(3)−O(2)	1.611(4)	1.587(4)	1.557(3)	1.606(4)
P(3)−O(3)	1.601(3)	1.588(4)	1.574(3)	1.598(4)
Bond Angles (deg)				
P(1)−C(11)−P(2)	120.9(3)	119.7(3)	123.7(2)	123.3(3)
C(11)−P(2)−N(1)	114.2(2)	117.2(2)	115.89(18)	110.0(2)
C(11)−P(2)−C(24)	108.1(2)	108.1(3)	109.63(19)	102.3(2)
C(11)−P(2)−C(30)	104.2(2)	104.4(3)	106.12(18)	105.5(2)
P(2)−N(1)−P(3)	133.7(3)	147.7(3)	134.5(2)	128.6(3)
N(1)−P(3)−O(1)	122.9(2)	120.9(2)	116.07(18)	119.7(2)
N(1)−P(3)−O(2)	103.95(19)	105.7(3)	107.55(18)	102.8(2)
N(1)−P(3)−O(3)	104.97(19)	109.7(3)	112.51(19)	107.8(2)
O(1)−P(3)−O(2)	111.55(19)	112.4(2)	109.12(16)	113.0(2)
O(1)−P(3)−O(3)	107.51(19)	102.6(2)	108.63(17)	113.0(2)
O(2)−P(3)−O(3)	104.43(19)	104.6(2)	101.98(17)	97.7(2)

and P(3)−N(1) (1.569(4) Å) bond lengths are quite similar although the former is a double P=N bond.[33] This fact can be explained on the basis of the strong π-acceptor nature of the phosphoryl group which imposes delocalization of the lone pair of electrons on nitrogen through the $-Ph_2P{=}N-P(=O)(OPh)_2$ framework. These bond distances, as well as the value for the P(2)−N(1)−P(3) angle (133.7(3)°), compare well with data previously reported for iminophosphorane derivatives of general formula $R_3P{=}N-P(=O)(OR')_2$.[3e,34,35]

(b) κ^2-*P,O*-Complexes [Ru(η^6-*p*-cymene)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2)][SbF_6] (R = Et (3a), Ph (3b)) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2)][SbF_6] (R = Et (7a), Ph (7b)). Neutral complexes **2b** and **6a**,**b** react with a stoichiometric amount of silver hexafluoroantimonate, in dichloromethane at room temperature, to give the cationic derivatives [Ru(η^6-*p*-cymene)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OPh)_2$}Ph_2)]-[SbF_6] (**3b**; Scheme 2) and [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2)][SbF_6] (R = Et (**7a**), Ph (**7b**); Scheme 3), respectively, which are readily formed (84−91% yield) via selective intramolecular O-coordination of the phosphoryl group. In contrast, an inseparable mixture containing complexes [Ru(η^6-*p*-cymene)Cl(κ^2-*P,O*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)][SbF_6] (**3a**) and [Ru(η^6-*p*-cymene)-Cl(κ^2-*P,N*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)][SbF_6] (**4a**) (ca. 3:1 ratio) was obtained, under the same reaction conditions, starting from **2a** (Scheme 2).[36] Alternatively, **3a**/**4a**, **3b**, and **7a**,**b** can be prepared in similar yields directly from dimers [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$] and [{Ru(η^3:η^3-$C_{10}H_{16}$)(μ-Cl)-Cl}$_2$], respectively, by treatment with 2 equiv of **1a**,**b** and $AgSbF_6$ in dichloromethane (see Schemes 2 and 3).

Conductance measurements in acetone confirm that compounds **3a**,**b** and **7a**,**b** are 1:1 electrolytes (Λ_M = 102−122 Ω^{-1} cm^2 mol^{-1}). Their NMR spectroscopic data (see the Experimental Section and Table 2 for details) provide significant structural information.[30] Thus, in the $^{31}P\{^1H\}$ NMR spectra the κ^2-*P,O*-chelating coordination of **1a**,**b** is marked by a slight downfield shift (ca. $\Delta\delta$ 7 ppm) in the $(RO)_2P{=}O$ group resonances (δ −1.88−9.49; d, $^2J_{PP}$ = 37.0−49.5 Hz) with respect to the parent compounds **2a**,**b**

(33) Although P−N single bonds frequently display distances (1.64−1.77 Å) bordering on the range for double bonds (1.45−1.62 Å), the P(3)−N(1) bond length found in the structure of complex **2b** is remarkably very low. See for example: (a) Abel, E. W.; Mucklejohn, S. A. *Phosphorus Sulfur Relat. Elem.* **1981**, *9*, 235. (b) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217. (c) Witt, M.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 1163. (d) Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *14*, 3367. (e) Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 2893. (f) Ly, T. Q.; Woollins, J. D. *Coord. Chem. Rev.* **1998**, *176*, 451. (g) Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19.

(34) 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.

(35) Similar P=N bond lengths and $P{=}N-C_{arom}$ angles have been reported for iminophosphorane-phosphine ligands $Ph_2PCH_2P(=NR)Ph_2$ containing π-acceptor fluoroaromatic substituents. See for example: (a) Katti, K. V.; Santarsiero, B. D.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5919. (b) Li, J.; McDonald, R.; Cavell, R. G. *Organometallics* **1996**, *15*, 1033.

(36) Variable-temperature $^{31}P\{^1H\}$ NMR experiments were carried out with CD_2Cl_2 (from 20 to −80 °C), CD_3NO_2 (from 20 to 80 °C), and CD_3CN (from −40 to 80 °C) solutions of this mixture. While no changes in the **3a**/**4a** ratio (ca. 3:1) could be detected in the case of CD_2Cl_2 and CD_3NO_2, this ratio was found to be temperature dependent when acetonitrile was used as solvent (ca. 1:1 and 7:1 at −40 and 80 °C, respectively). This fact, which is in accord with the theoretical calculations, seems to indicate the existence of a dynamic equilibrium between both species in solution. Isomerizations between the κ^2-*P,N*- and κ^2-*P,O*-isomers evidence the hemilabile properties of iminophosphorane-phosphine ligands **1a**,**b**.

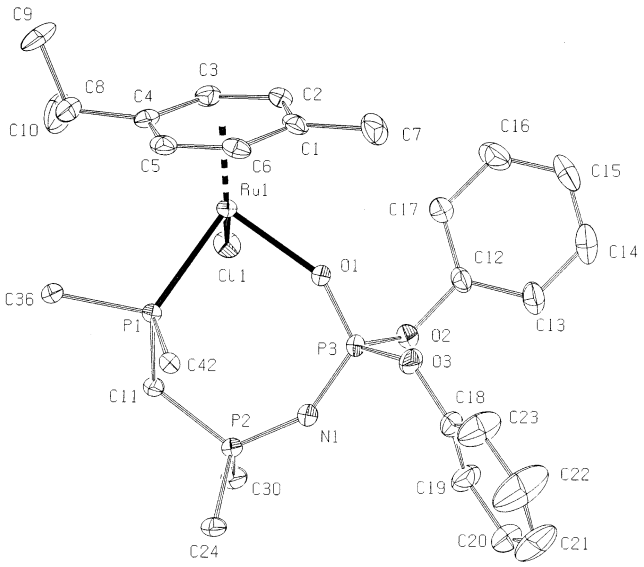


Figure 2. ORTEP-type view of the structure of the cation [Ru(η^6-*p*-cymene)Cl(κ^2-*P*,*O*-$Ph_2PCH_2P\{=NP(=O)(OPh)_2\}Ph_2$)]$^+$ (**3b**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at 20% probability level. Selected bond lengths (Å) and angles (deg) involving the Ru atom: Ru−C* = 1.697(6); Ru−O(1) = 2.116(3); Ru−Cl(1) = 2.3982(16); Ru−P(1) = 2.3775(14); C*−Ru−O(1) = 123.5(2); C*−Ru−Cl(1) = 126.8(2); C*−Ru−P(1) = 130.1(2); O(1)−Ru−P(1) = 88.77(10); O(1)−Ru−Cl(1) = 86.22(12); P(1)−Ru−Cl(1) = 87.93(5); Ru−P(1)−C(11) = 116.10(19); Ru−P(1)−C(36) = 113.97(18); Ru−P(1)−C(42) = 117.25(18); P(3)−O(1)−Ru = 144.7(2). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), C(6)).

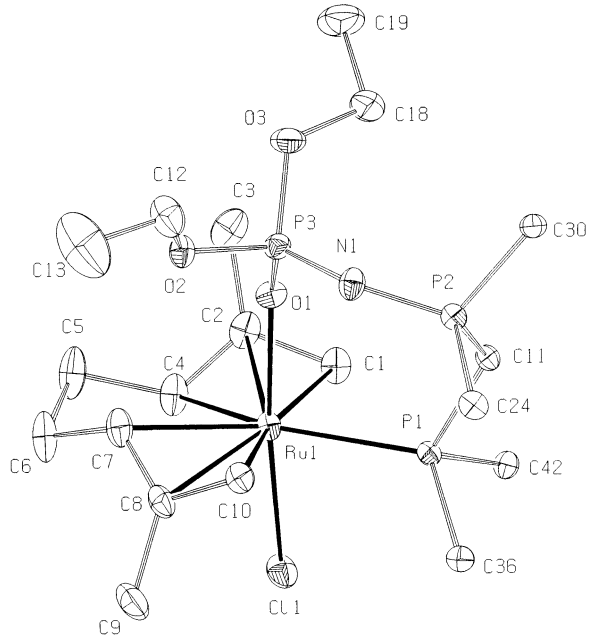


Figure 3. ORTEP-type view of the structure of the cation [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*O*-$Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2$)]$^+$ (**7a**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at 20% probability level. Selected bond lengths (Å) and angles (deg) involving the Ru atom: Ru−C(1) = 2.227(4); Ru−C(2) = 2.304(4); Ru−C(4) = 2.309(4); Ru−C(7) = 2.265(4); Ru−C(8) = 2.297(4); Ru−C(10) = 2.232(4); Ru−C* = 2.0317(44); Ru−C** = 2.0178(42); Ru−P(1) = 2.4288(12); Ru−O(1) = 2.128(3); Ru−Cl(1) = 2.3960(13); C*−Ru−C** = 129.68(17); C*−Ru−O(1) = 88.93(16); C**−Ru−O(1) = 89.91(15); C*−Ru−Cl(1) = 88.89(14); C**−Ru−Cl(1) = 95.94(14); C*−Ru−P(1) = 114.01(14); C**−Ru−P(1) = 116.31(13); O(1)−Ru−P(1) = 91.91(8); O(1)−Ru−Cl(1) = 173.80(8); P(1)−Ru−Cl(1) = 83.69(5); Ru−P(1)−C(11) = 115.21(13); Ru−P(1)−C(36) = 119.73(14); Ru−P(1)−C(42) = 114.35(14); P(3)−O(1)−Ru = 143.89(18). C* and C** = centroids of the allyl units (C(1), C(2), C(4) and C(7), C(8), C(10), respectively).

and **6a**,**b**, respectively (see Table 2). The chemical shifts of the Ph_2P=N and Ph_2P groups are almost unaffected by the ring closure (δ 9.20−11.82 (d, $^2J_{PP}$ = 37.0−49.5 Hz) and 22.22−24.86 (s), respectively; Table 2).[37] In contrast to **2a**,**b** and **6a**,**b**, the PCH_2P carbon resonates in the $^{13}C\{^1H\}$ NMR spectra as a doublet of doublets (δ 28.27−33.68) due to the exclusive coupling with the phosphorus atoms of the Ph_2P=N (J_{CP} = 54.0−57.1 Hz) and Ph_2P (J_{CP} = 8.9−15.8 Hz) units. We note also that, as a consequence of the stereogenicity of the ruthenium atom, the methylenic PCH_2P protons are, in all the cases, chemically inequivalent appearing as two unresolved multiplets in the range 3.09−5.17 ppm.

The molecular structures of **3b** and **7a** have been confirmed by X-ray diffraction.[12] ORTEP plots are shown in Figures 2 and 3, respectively; selected bonding parameters appear in the captions and in Table 3. While **3b** exhibits the expected pseudooctahedral three-legged piano-stool geometry around the metal, the structure of **7a** can be described as a distorted trigonal bipyramid (TBPY) by considering the allyl groups as monodentate ligands bound to ruthenium through their centers of mass (C* and C**; see caption for Figure 3), in which C*, C**, and P(1) occupy the equatorial sites and Cl(1) and O(1) the axial sites.[38] Remarkably, no appreciable changes are observed in the bond distances along the P=N−P=O unit in **3b** as compared to its precursor **2b** (i.e., P(2)−N(1) = 1.550(5) Å vs 1.578(4) Å; N(1)−P(3) = 1.552(5) Å vs 1.569(4) Å; P(3)−O(1) = 1.474(3) Å vs 1.467(3) Å; similar bond distances have been found in the structure of **7a**; see Table 3), the elongation of the P=N−P angle (147.7(3)° vs 133.7(3)°) being the most significant difference between both structures. It seems to indicate that the electronic delocalization of the nitrogen lone pair is

(37) These chemical shifts contrast with those found for κ^2-*P*,*N*-isomer **4a** (δ 10.24 (dd, $^2J_{PP}$ = 6.1 Hz, $^3J_{PP}$ = 6.1 Hz, $(EtO)_2P$=O), 47.22 (dd, $^2J_{PP}$ = 20.2 Hz, $^3J_{PP}$ = 6.1 Hz, Ph_2P), and 58.68 (dd, $^2J_{PP}$ = 20.2 and 6.1 Hz, Ph_2P=N)). The highly deshielded chemical shifts observed for the Ph_2P=N and Ph_2P groups in **4a** compare well with those recently reported for related [Ru(η^6-arene)Cl{κ^2-*P*,*N*-$Ph_2PCH_2P(=NR)Ph_2$}]$^+$ complexes (see ref 5). Deshielding due to phosphorus incorporation into five-membered ring systems is a common trend in transition-metal complexes containing chelating P-donor ligands: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(38) The allyl groups of the 2,7-dimethyl-2,6-diene-1,8-diyl ligand are both η^3-bound to the ruthenium atom with Ru−C distances in the range 2.227(4)−2.309(4) Å (see caption for Figure 3). These values, together with the C−C distances (1.392(7)−1.417(6) Å) and the internal C−C−C angles (114.9(4)° and 116.2(5)°) within the allyl groups (details are given in the Supporting Information), are similar to those found in related complexes containing the [Ru(η^3:η^3-$C_{10}H_{16}$)] fragment. See for example: (a) Hitchcock, P. B.; Nixon, J. F.; Sinclair, J. *J. Organomet. Chem.* **1975**, *86*, C34. (b) Toerien, J. G.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1991**, 1563. (c) Cox, D. N.; Small, R. W. H.; Roulet, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2013. (d) Toerien, J. G.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2693. (e) Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 459. (f) Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2765. (g) Kavanagh, B.; Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1993**, 327. (h) Belchem, G.; Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1994**, 1949.

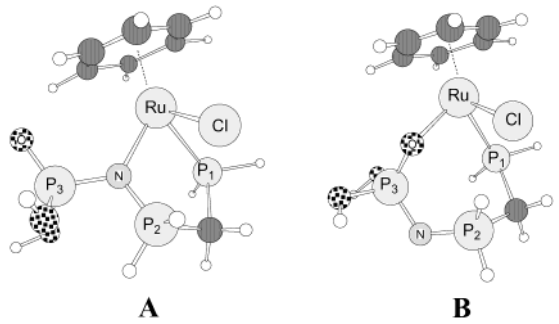


Figure 4. Computer plot of the B3LYP/DZV(d) optimized structutes for the model complexes $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ (**A**) and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ (**B**). Selected bond lengths (Å) and angles (deg) for model **A**: Ru−P_1 = 2.444; P_1−C = 1.905; C−P_2 = 1.872; P_2−N = 1.702; N−Ru = 2.173; Ru−Cl = 2.496; average Ru−C_{arene} = 2.272; Ru−P_1−C = 107.6; P_1−C−P_2 = 107.6; C−P_2−N = 107.4; P_2−N−Ru = 117.3; P_1−Ru−N = 80.2; P_1−Ru−Cl = 80.0; N−Ru−Cl = 84.7. For model **B**: Ru−P_1 = 2.464; P_1−C = 1.900; C−P_2 = 1.877; P_2−N = 1.678; N−P_3 = 1.658; P_3−O = 1.567; O−Ru = 2.154; Ru−Cl = 2.484; average Ru−C_{arene} = 2.260; Ru−P_1−C = 118.5; P_1−C−P_2 = 112.4; C−P_2−N = 115.6; P_2−N−P_3 = 118.3; N−P_3−O = 115.7; P_3−O−Ru = 128.0; P_1−Ru−O = 91.8; P_1−Ru−Cl = 82.5; O−Ru−Cl = 86.3.

maintained upon coordination of the phosphoryl unit to the metal.[3e] The Ru−O(1) bond length (**3b**, 2.116(3) Å; **7a**, 2.128(3) Å) compares well to that shown by ruthenium complexes containing O-coordinated phosphine-oxides.[39]

Theoretical Studies. It is interesting to note the observed preference for the κ^2-*P*,*O*- vs κ^2-*P*,*N*-coordination (i.e., seven-membered vs five-membered rings) of **1a**,**b**. This is in sharp contrast with the well-known fact of coordination chemistry establishing that an increase in the size of a chelate ring usually leads to a drop in complex stability.[40] In fact, analogous ((iminophosphoranyl)amino)phosphine ligands $Ph_2PN(R)P\{=NP(=O)(OPh)_2\}Ph_2$ (R = Me, Et) are able to form typical κ^2-*P*,*N*-five-membered chelate rings.[3e] In order to evaluate to what extent electronic effects are responsible for this unexpected behavior, we thought it to be of interest to study theoretically their relative stability. To the best of our knowledge, no ab initio calculations on transition-metal complexes bearing iminophosphorane-phosphine ligands have been reported to date.

The size of the complexes to be studied required the use of models for the calculations. Thus, $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ (**A**) was used for the five-membered ring and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ (**B**) for the seven-membered (Figure 4). The relevant geometrical parameters of the optimized structures with the B3LYP/DZV(d) wave function are given in the caption. The **A** and **B** structures were characterized as minima on the potential energy surface. The optimized bond distances for **B** are in good agreement with those experimentally obtained for **3b** by X-ray diffraction, deviating only ca. 0.1 Å (see captions for Figures 2 and 4, and Table 3). The calculated bond angle values within the seven-membered ring in **B** are also in accordance with those found in **3b** with the exception of the angles P_2—N—P_3 (118.3° vs 147.7(3)°) and P_3—O—Ru (128.0° vs 144.7(2)°). These differences are probably due to the replacement of the phenyl groups (**3b**) in the phosphoryl unit by hydrogens (**B**).[41]

Table 4. Calculated Total (hartree) and Relative (kcal/mol) Energies for the Model Complexes $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ (**A**) and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ (**B**)[a]

	B3LYP/DZV(d)	MP2/DZV(d)
A	−683.690437 (0.0)	−680.855667 (0.0)
B	−683.680498 (6.2)	−680.837274 (11.5)

[a] B3LYP/DZV(d)-optimized geometries.

The absolute and relative energies of **A** and **B** are given in Table 4. According to our calculations, **A** should be 6.2 kcal/mol more stable than **B** at the B3LYP/DZV(d)//B3LYP/DZV(d) level. Moreover, inclusion of correlation increases this energy gap to 11.5 kcal/mol [MP2/DZV(d)//B3LYP/DZV(d) level]. These values deserve noting. There is a general opinion that decreases in complex stability associated with increases in the size of the chelate ring are due to steric strain effects on the metal.[40] Steric strain exists in a molecule when bonds are forced to make abnormal angles, which results in higher energy than would be the case in the absence of angle distortions. The interligand angles P_1−Ru−Cl (82.5°), P_1−Ru−O (91.8°), and O−Ru−Cl (86.3°) in model **B** and P_1−Ru−Cl (80.0°), P_1−Ru−N (80.2°), and N−Ru−Cl (84.7°) in model **A** present typical values for pseudo-octahedral three-legged piano-stool geometries. This seems to indicate a very similar strain energy for both complexes. On the other hand, looking at the geometrical parameters, it can be observed that Ru−L distances are larger for donor ligands in **A** than in **B** (Ru−Cl, from 2.496 to 2.484 Å; average Ru−C_{arene}, from 2.272 to 2.260 Å) and shorter for the σ-donor−π-acceptor phosphine ligand (Ru−P_1, from 2.444 to 2.464 Å). These values may be explained by taking into account the larger electron-donor ability of nitrogen compared to oxygen, which is probably the reason for the greater stability of **A**.

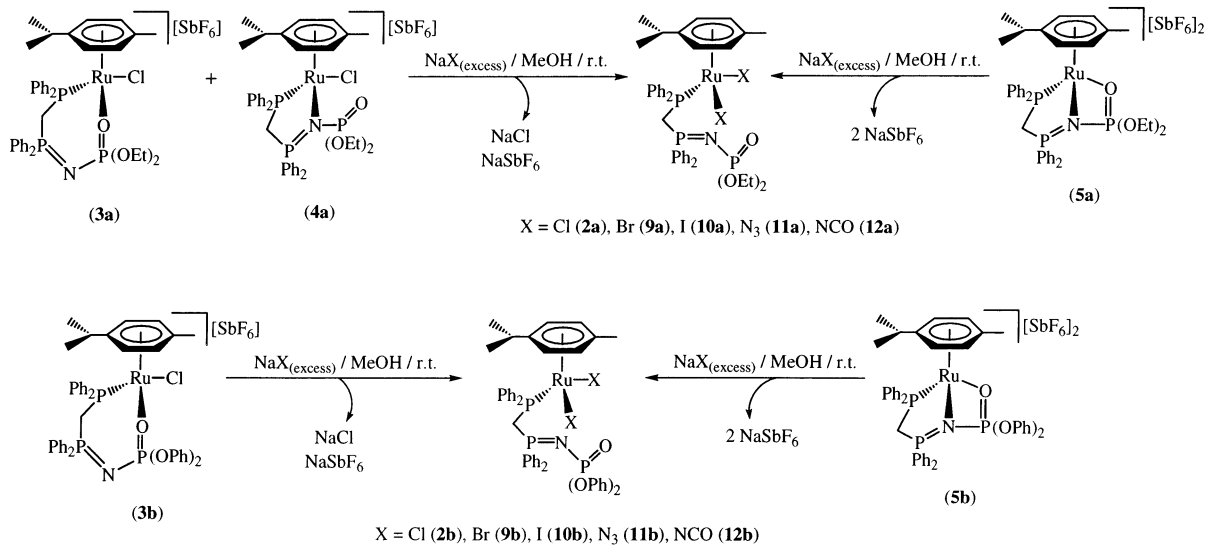
The experimental preference observed for the κ^2-*P*,*O*- versus the κ^2-*P*,*N*-coordination of **1a**,**b** in these ruthenium fragments must, therefore, be explained on the basis of steric effects. As can be appreciated in Figure 4, the formation of a five-membered metallacycle (**A**) results in a higher steric hindrance between the phosphoryl group substituents and the substituents of the η^6-coordinated arene ring when compared to model **B**. This fact is in accord with the formation of the κ^2-*P*,*N*-isomer **4a** which is only observed when the bulky phenyl groups are replaced by ethyls (see Scheme 2). This steric hindrance, which seems to increase in the case of the (η^3:η^3-octadienediyl)−ruthenium(IV) fragment since no κ^2-

(39) See for example: (a) Faller, J. W.; Patel, B. P.; Albrizzio, A.; Curtis, M. *Organometallics* **1999**, *18*, 3096. (b) Faller, J. W.; Parr, J. *Organometallics* **2000**, *19*, 1829. (c) Faller, J. W.; Grimmond, B. J.; Curtis, M. *Organometallics* **2000**, *19*, 5174.

(40) See for example: (a) Hancock, R. D.; Martell, A. E. *Comments Inorg. Chem.* **1988**, *6*, 237. (b) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875. (c) Hancock, R. D.; Martell, A. E. In *Coordination Chemistry: A Century of Progress*; Kauffman, G. B., Ed.; ACS Symposium Series 565; American Chemical Society: Washington, DC, 1994; p 251.

(41) In **3b**, the steric hindrance between the Ph groups, which participate in the electronic delocalization along the P=N−P=O−Ru fragment, and the η^6-arene substituents seems to be reflected in the elongation of these angles.

Scheme 4



P,N-coordination of **1a** is observed (Scheme 3), is probably the reason for the experimental preference of the κ^2-*P,O*-bidentate coordination of **1a**,**b**.

(c) κ^3-*P,N,O*-Complexes [Ru(η^6-*p*-cymene)(κ^3-*P,N,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (R = Et (5a), Ph (5b)) and [Ru(η^3:η^3-$C_{10}H_{16}$)(κ^3-*P,N,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (R = Et (8a), Ph (8b)). Treatment of neutral complexes **2a**,**b** and **6a**,**b** with a 2-fold excess of $AgSbF_6$, in dichloromethane at room temperature, leads to the formation of the dicationic derivatives [Ru(η^6-*p*-cymene)(κ^3-*P,N,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (R = Et (**5a**), Ph (**5b**)) and [Ru(η^3:η^3-$C_{10}H_{16}$)(κ^3-*P,N,O*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)][$SbF_6$]$_2$ (R = Et (**8a**), Ph (**8b**)), respectively, via coordination of both the iminophosphorane and phosphoryl groups (77−93% yield; see Schemes 2 and 3). These complexes can be also prepared in similar yields from **3a/4a**, **3b**, and **7a**,**b** by reaction with 1 equiv of $AgSbF_6$ in dichloromethane at room temperature. In contrast to their neutral or cationic precursors, **5a**,**b** and **8a**,**b** are moisture sensitive both in solution and in the solid state, slowly generating complicated mixtures of uncharacterized products.[42]

Conductance values for **5a**,**b** and **8a**,**b** in acetone reflect that these complexes are 2:1 electrolytes (Λ_M = 177−198 Ω^{-1} cm^2 mol^{-1}). The coordination of the iminophosphorane group to ruthenium is confirmed in the $^{31}P\{^1H\}$ NMR spectra by the presence of characteristic downfield resonances of the Ph_2P═N (δ 50.88−55.62; dd or d (for **5b**), $^2J_{PP}$ = 9.0−36.3 and 3.8−8.1 Hz) and Ph_2P (δ 41.68−46.64; d, $^2J_{PP}$ = 9.0−36.3 Hz) groups (see Table 2).[37] The phosphorus nucleus of the $(RO)_2P$═O unit in **5a**,**b** resonates at 18.28 (d, $^2J_{PP}$ = 3.8 Hz) and 6.33 (s) ppm, respectively, also in agreement with its coordination to the metal. In contrast, the chemical shifts found for the $(RO)_2P$═O fragments in **8a**,**b** (**8a**, 4.45 ppm (d, $^2J_{PP}$ = 6.5 Hz); **8b**, −6.47 ppm (d, $^2J_{PP}$ = 8.1 Hz)) are closer to those observed for **6a**,**b** (in which these groups are not bound to ruthenium) than those for **7a**,**b** (see Table 2). This fact can be explained on the basis of the different *trans* influence of the diphenylphosphino and chloride ligands. ^1H and $^{13}C\{^1H\}$ NMR spectra are also in accordance with the proposed formulations (see the Experimental Section).[30] In particular, the methylenic PCH_2P proton and carbon resonances appear at 2.78−5.02 ppm (two unresolved multiplets) and 26.69−39.72 ppm (ddd or dd (for **5a**); $J_{CP(V)}$ = 63.1−90.8 Hz, $J_{CP(III)}$ = 13.0−23.4 Hz, $^3J_{CP(V)}$ = 7.2−8.1 Hz), respectively.

Reactivity Studies: Synthesis of [Ru(η^6-*p*-cymene)X_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$)] (R = Et, X = Br (9a), I (10a), N_3 (11a), NCO (12a); R = Ph, X = Br (9b), I (10b), N_3 (11b), NCO (12b)). Taking advantage of the hemilabile properties of iminophosphorane-phosphine ligands **1a**,**b** both in their κ^2-*P,O*-, κ^2-*P,N*-, and κ^3-*P,N,O*-coordination modes,[36,43] we decided to explore the reactivity of complexes **3a/4a**, **3b**, and **5a,b** toward a series of anionic ligands. Thus, we have found that by treating complex **3b**, or a mixture containing compounds **3a/4a**, with an excess (ca. 10 equiv) of sodium salts NaX (X^- = Cl^-, Br^-, I^-, N_3^-, NCO^-), in methanol at room temperature, the neutral derivatives [Ru(η^6-*p*-cymene)X_2(κ^1-*P*-$Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2$)] (**2a**,**b**, **9**−**12a**,**b**) are formed (77−85% yield) via chelate ring opening and, in the case of **9**−**12a**,**b**, concomitant chloride metathesis (Scheme 4). As expected,

(42) The instability of these complexes in solution prevented their crystallization. A reviewer has brought to our attention that probably water coordinates to the metal upon decoordination of the P═N unit in complexes **5a**,**b** and **8a**,**b**. Coordination of water on oxophilic ruthenium complexes containing P,N-donor ligands has been recently reported. See, for instance: Stoop, R. M.; Bachmann, S.; Valentini, M.; Mezzetti, A. *Organometallics* **2000**, *19*, 4117. Bachmann, S.; Furler, M.; Mezzetti, A. *Organometallics* **2001**, *20*, 2102. All attempts to obtain stable complexes by treatment of dichloromethane solutions of **5a**,**b** and **8a**,**b** with water failed.

(43) We note that complex [Ru(η^6-*p*-cymene)(κ^1-*O*-Me_2C═O)(κ^2-*P,O*-$Ph_2PCH_2P\{=NP(=O)(OEt)_2\}Ph_2$)][$SbF_6$]$_2$ is readily formed when **5a** is dissolved in acetone as inferred by $^{31}P\{^1H\}$ NMR spectroscopy which shows signals at 11.43 (d, $^2J_{PP}$ = 37.0 Hz, $(EtO)_2P$═O), 12.24 (d, $^2J_{PP}$ = 37.0 Hz, Ph_2P═N), and 24.13 (s, Ph_2P) ppm. All attempts to isolate this complex failed, leading instead to its precursor **5a** quantitatively after evaporation of the solvent. The reversibility of this process evidences clearly the hemilability of the P═N unit in complexes containing iminophosphorane-phosphine ligands **1a**,**b** coordinated in κ^3-*P,N,O*-manner.

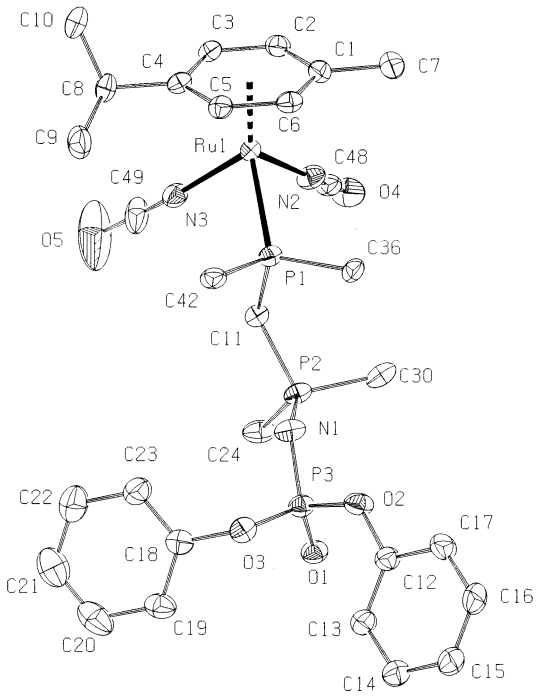


Figure 5. ORTEP-type view of the structure of [Ru(η^6-*p*-cymene)(κ^1-*N*-NCO)$_2$(κ^1-*P*-Ph_2PCH_2P{=NP(=O)(OPh)$_2$}Ph_2)] (**12b**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg) involving the Ru atom: Ru−C* = 1.6925(49); Ru−N(2) = 2.083(4); Ru−N(3) = 2.062(4); Ru−P(1) = 2.358(1); C*−Ru−N(2) = 126.25(21); C*−Ru−N(3) = 128.24(21); C*−Ru−P(1) = 131.04(17); Ru−N(2)−C(48) = 159.4(5); Ru−N(3)−C(49) = 173.7(6); N(2)−Ru−N(3) = 86.46(19); P(1)−Ru−N(2) = 85.32(12); P(1)−Ru−N(3) = 84.20(12); Ru−P(1)−C(11) = 108.82(15); Ru−P(1)−C(36) = 115.97(17); Ru−P(1)−C(42) = 111.93(15). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), C(6)).

complexes **9**−**12a**,**b** are also formed starting from the dicationic complexes **5a**,**b** (Scheme 4).

Analytical and spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) for **9**−**12a**,**b** strongly support the proposed formulations being comparable to those observed in monodentate complexes **2a**,**b** (see the Experimental Section and Table 2).[30] Moreover, the structure of complex **12b** has been confirmed by single-crystal X-ray diffraction studies (see Figure 5 and Table 3). Since the structural parameters at the [Ru(η^6-*p*-cymene)(κ^1-*P*-Ph_2PCH_2P{=NP(=O)(OPh)$_2$}Ph_2)] fragment are quite similar to those observed for **2b** (see Figure 1 and Table 3), they are not worth further discussion. The two cyanate ligands are N-bound to ruthenium in a nearly linear fashion (Ru−N(2)−C(48) = 159.4(5)°, N(2)−C(48)−O(4) = 178.6(6)°, Ru−N(3)−C(49) = 173.7(6)°, N(3)−C(49)−O(5) = 177.7(12)°) showing bond lengths of Ru−N(2) = 2.083(4) Å, N(2)−C(48) = 1.150(7) Å, C(48)−O(4) = 1.213(6) Å, Ru−N(3) = 2.062(4) Å, N(3)−C(49) = 1.088(8) Å, and C(49)−O(5) = 1.190(9) Å.[44]

Catalytic Transfer Hydrogenation of Cyclohexanone. The well-known ability of ruthenium(II) species to act as efficient catalysts in hydrogen transfer reactions between alcohols and ketones[45] prompted us to study the catalytic activity of complexes **2a**,**b**, **3a**/**4a**, **3b**, and **5a**,**b** in transfer hydrogenation of cyclohexanone by propan-2-ol (Scheme 5). For comparative purposes, the activity of ruthenium(IV) complexes **6a**,**b**, **7a**,**b**, and **8a**,**b** has also been examined. In a typical experiment, the ruthenium catalyst precursor (0.4 mol %) and NaOH (9.6 mol %) were added to a 0.2 M solution of cyclohexanone in ^{i}PrOH at 82 °C, the reaction being monitored by gas chromatography. Selected results are shown in Table 5.

Scheme 5

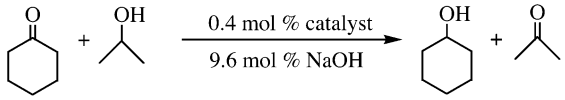


Table 5. Catalytic Transfer Hydrogenation of Cyclohexanone[a]

entry	catalyst	yield (%)[b]	TOF_{50} (h^{-1})[c]
	Ruthenium(II) Complexes		
1	**2a**	40 (>99)[d]	50
2	**2b**	25 (98)[d]	26
3	**3a**/**4a**	24 (>99)[d]	33
4	**3b**	15 (78)[d]	12
5	**5a**	25 (>99)[d]	37
6	**5b**	14 (76)[d]	10
	Ruthenium(IV) Complexes		
7	**6a**	>99	367
8	**6b**	64 (>99)[e]	93
9	**7a**	>99	426
10	**7b**	78 (>99)[e]	165
11	**8a**	61 (>99)[d]	86
12	**8b**	14 (83)[d]	12

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of cyclohexanone (0.2 M in ^{i}PrOH). Ketone/catalyst/NaOH ratio: 250/1/24. [b] Yield of cyclohexanol after 2 h. GC determined. [c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at 50% conversion. [d] Yield after 24 h in parentheses. GC determined. [e] Yield after 9 h in parentheses. GC determined.

All the complexes studied have proven to be active and efficient catalysts leading to nearly quantitative conversions of cyclohexanone into cyclohexanol, with the cationic derivative [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(κ^2-*P*,*O*-Ph_2PCH_2P{=NP(=O)(OEt)$_2$}Ph_2)][SbF_6] (**7a**) showing the highest activity (TOF_{50} of 426 h^{-1}; entry 9). The following features are worth noting: (a) The catalytic performances shown by the bis(allyl)−ruthenium(IV) complexes are in all the cases higher than those of their corresponding (η^6-*p*-cymene)−ruthenium(II) counterparts (see entries 1−6 vs 7−12).[46] These results are promising since, as far as we know, this is the first time that ruthenium(IV) complexes have been used in this type

(44) Although the cyanate ion can potentially act as an ambidentate ligand, it tends to exhibit only the N-bonding when coordinated as a monodentate ligand to a transition-metal. For reviews see: (a) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231. (b) Burmeister, J. L. *Coord. Chem. Rev.* **1990**, *105*, 77. In our case, since N and O have very similar sizes and scattering factors, both the N- and O-bonded models were refined to convergence, and the former gave significantly lower residuals (R = 0.0385 and R_w = 0.1070 as against R = 0.0400 and R_w = 0.1121). This fact, along with the linearity of the Ru−N−C−O chains, confirms the N-coordination of the cyanato ligands in **12b**.

(45) For reviews on transition-metal catalyzed transfer hydrogenation of ketones see: (a) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (c) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045. (d) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (e) Bäckvall, J. E. *J. Organomet. Chem.* **2002**, *652*, 105. (f) Carmona, D.; Lamata, M. P.; Oro, L. A. *Eur. J. Inorg. Chem.* **2002**, 2239.

of catalytic transformation.[45] (b) Both in the Ru(II) and Ru(IV) series those catalysts containing the ligand **1a** (R = Et) are more effective than those containing **1b** (R = Ph) (see odds vs evens entries). Since coordination of the substrate to the metal is generally proposed during the catalytic cycle,[47] this difference is most probably due to steric effects, the approach of cyclohexanone to ruthenium being facilitated when the phenyl substituents on the phosphoryl unit are replaced by the smaller ethyl groups. Also, (c) there is no direct relationship between the catalytic activity and the coordination mode of the ligands. Thus, while for the ruthenium(II) series the neutral κ^1-*P*-complexes are the most active (entries 1 vs 3 and 5, and 2 vs 4 and 6), the cationic κ^2-*P,O*-derivatives show the highest rate in the ruthenium(IV) series (entries 9 vs 7 and 11, and 10 vs 8 and 12). Finally, with regard to comparative catalytic performance with respect to other ruthenium complexes containing P,N,O-donor ligands, the efficiencies found are unfortunately lower than those of neutral octahedral ruthenium(II) complexes $[RuCl_2(PPh_3)(\kappa^3\text{-}P,N,O\text{-L})]$ (L = $Ph_2PCH(2\text{-Py})CH_2OR$ (R = ethyl, menthyl; Py = pyridyl)) reported by Mathieu and co-workers.[48]

Conclusions

Novel heterotrifunctional ligands $Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2$ (**1a**,**b**) showing a P,N,O-donor framework have been easily prepared via single-stage oxidation of bis(diphenylphosphino)methane with phosphoryl azides $(RO)_2P(=O)N_3$ (R = Et, Ph). These ligands show a versatile coordination ability in ruthenium fragments derived from the readily available ruthenium(II) and ruthenium(IV) chloro-bridged dimers $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ and $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$, respectively. Thus, the following coordination modes have been observed: (a) κ^1-*P*-, i.e., $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)]$ (**2a**,**b**) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)]$ (**6a**,**b**); (b) κ^2-*P,O*-, i.e., $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]$ (**3a**,**b**) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]$ (**7a**,**b**); (c) κ^2-*P,N*-, i.e., $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P\{{=}NP(=O)(OEt_2)\}Ph_2)][SbF_6]$ (**4a**); (d) κ^3-*P,N,O*-, i.e., $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]_2$ (**5a**,**b**) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\kappa^3\text{-}P,N,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)][SbF_6]_2$ (**8a**,**b**). Theoretical calculations (DFT level) on the models $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{{=}NP(=O)(OH)_2\}H_2)]^+$ (**A**) and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{{=}NP(=O)(OH)_2\}H_2)]^+$ (**B**) show that the κ^2-*P,N*-isomer **A** is ca. 11.5 kcal/mol more stable than **B**. This contrasts with the experimental results since seven-membered chelate rings (κ^2-*P,O*-complexes) are obtained preferentially. The apparent discrepancy arises probably from the steric hindrance between the phosphoryl group substituents and the η^6-*p*-cymene or $\eta^3{:}\eta^3$-octadiene-diyl ligands in the five-membered chelates (κ^2-*P,N*-complexes). The preference observed for the κ^2-*P,N*-coordination in the theoretical calculations is mostly a consequence of the greater bond energy of the Ru−N bond versus the corresponding Ru−O.

The potential hemilabile properties of iminophosphorane-phosphines **1a**,**b** have been proven in the reactivity of the chelate κ^2-*P,O*-, κ^2-*P,N*-, and κ^3-*P,N,O*-complexes. This has allowed the synthesis of κ^1-*P*-derivatives $[Ru(\eta^6\text{-}p\text{-cymene})X_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)]$ (R = Et, Ph; X = Br, I, N_3, NCO; **9**−**12a**,**b**), in excellent yields and under very mild reaction conditions, by treatment of **3a**/**4a** and **3b** with the appropriate anionic ligand X^- via chelate ring opening and concomitant chloride metathesis. By monitoring the course of these reactions by $^{31}P\{^1H\}$ NMR spectroscopy, we observed that the latter process is slightly slower than the former since, besides the signals of **3a**/**4a**−**3b** and **9**−**12a**,**b**, resonances attributable to neutral species $[Ru(\eta^6\text{-}p\text{-cymene})ClX(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{{=}NP(=O)(OR)_2\}Ph_2)]$ could be observed. In accord with this observation, we found that complexes **9**−**12a**,**b** are formed faster (2 h vs 4 h), under the same reaction conditions, starting from the dicationic complexes **5a**,**b** (see Scheme 4). In addition, compounds **2**−**8a**,**b** have proven to be suitable catalyst precursors for the transfer hydrogenation of cyclohexanone by propan-2-ol (see Scheme 5). Further studies devoted to the application of these P,N,O-ligands in other catalytic transformations are now in progress.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **2b**, **3b**, **7a**, and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) We note that TOF_{50} values for complexes **2**−**5a**,**b** (10−50 h^{-1}) are comparable to those found in the related complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2\{\kappa^1\text{-}P\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}]$ and $[Ru(\eta^6\text{-}p\text{-cymene})Cl\{\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P(=N\text{-}p\text{-}C_5F_4N)Ph_2\}][SbF_6]$ (23 and 20 h^{-1}, respectively, under the same reaction conditions). See ref 5b.

(47) Although no detailed mechanistic studies have been performed, we assume that the catalytic transformation follows the classical pathway in which cyclohexanone coordinates on hydride−ruthenium intermediates (see refs 5b and 45). In fact, $^{31}P\{^1H\}$ NMR spectra of the catalytic reaction mixture derived from **7a** showed, after 30 min, the clean formation of a novel species with resonances at 4.25 (d, $^2J_{PP}$ = 28.3 Hz, $(EtO)_2P{=}O$), 14.89 (d, $^2J_{PP}$ = 28.3 Hz, $Ph_2P{=}N$), and 20.51 (s, Ph_2P) ppm. These chemical shifts and coupling constants show the κ^2-*P,O*-coordination mode of the ligand arising probably from the hydride derivative $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})H(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{{=}NP(=O)(OEt)_2\}Ph_2)][SbF_6]$. Attempts to isolate this complex failed.

(48) These derivatives, which are among the most active for transfer hydrogenation of carbonyl compounds, are the only examples reported in the literature of ruthenium catalysts containing tridentate P,N,O-ligands: (a) Yang, H.; Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1721. (b) Yang, H.; Alvarez-Gressier, M.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 1401.