(η^6-Arene)−Ruthenium(II) Complexes Containing Methanide and Methandiide Anions of $Ph_2P(=S)CH_2P(=NR)Ph_2$: Unprecedented Insertion of Isocyanide into a Ruthenium−Carbene Bond

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

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

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The novel (iminophosphoranyl)(thiophosphoranyl)methane ligands $Ph_2P(=S)CH_2P(=NR)Ph_2$ (R = 2,4,6-$C_6H_2Me_3$ (**2a**), 4-C_6F_4CHO (**2b**), 4-C_6F_4CN (**2c**), 4-C_5F_4N (**2d**), $P(=O)(OEt)_2$ (**2e**), $P(=O)(OPh)_2$ (**2f**), $P(=S)(OEt)_2$ (**2g**), $P(=S)(OPh)_2$ (**2h**)) have been synthesized by oxidation of the phosphine unit in $Ph_2PCH_2P(=NR)Ph_2$ with elemental sulfur. Treatment of **2a**−**f** with Li^{n}Bu generates the corresponding methanide anions which react in situ with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] to afford the mononuclear derivatives [Ru{κ^3(*C*,*N*,*S*)-$Ph_2P(=S)CHP(=NR)Ph_2$}(η^6-*p*-cymene)][Cl] (R = 2,4,6-$C_6H_2Me_3$ (**3a**), 4-C_6F_4CHO (**3b**), 4-C_6F_4CN (**3c**), 4-C_5F_4N (**3d**), $P(=O)(OEt)_2$ (**3e**), $P(=O)(OPh)_2$ (**3f**)), via tridentate κ^3(*C*,*N*,*S*) coordination of the anions to ruthenium. In contrast, complexes [Ru(κ^3(*C*,*S*,*S*)-$Ph_2P(=S)CHP\{=NP(=S)(OR)_2\}Ph_2$)($\eta^6$-*p*-cymene)][Cl] (R = Et (**4g**), Ph (**4h**)) are selectively formed in the reactions of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with the methanide anions derived from **2g**−**h**. Deprotonation of **3a** with NaH generates the carbenic derivative [Ru{κ^2(*C*,*N*)-$Ph_2P(=S)CP(=N$-2,4,6-$C_6H_2Me_3)Ph_2$}(η^6-*p*-cymene)] (**5**), which readily reacts with an excess of 2,6-dimethylphenyl isocyanide to afford the octahedral complex [Ru{κ^2(*C*,*N*)-$Ph_2P(S)C(C=N$-2,6-$C_6H_3Me_2)P(N$-2,4,6-$C_6H_2Me_3)Ph_2$}(CN-2,6-$C_6H_3Me_2)_4$] (**7**), via release of the arene ring and insertion of one isocyanide molecule into the Ru=C bond of **5**. The intermediate ketenimine complex [Ru{κ^3(*C*,*C*,*N*)-$Ph_2P(=S)C(C=N$-2,6-$C_6H_3Me_2)P(=N$-2,4,6-$C_6H_2Me_3)Ph_2$}(η^6-*p*-cymene)] (**6**) could be isolated working under stoichiometric conditions. The structure of compounds **2f**, **2h**, **3f**, **4g**, and **7** has been determined by X-ray crystallography.

Introduction

The chemistry of metal−carbenes continues to be the focus of intense research due to their widespread applications in organic synthesis and catalysis. An unusual series, involving both transition and main-group metals, is formed by complexes containing carbene groups derived from bis(iminophosphoranyl)methane ligands. Thus, since the discovery in 1999 by R. G. Cavell and co-workers that the bis(iminophosphoranyl)methane derivative $CH_2\{P(=NSiMe_3)Ph_2\}_2$ is a suitable precursor for the preparation of metal−carbenes,[1] via double deprotonation of the PCH_2P backbone,[2] a large number of unusual "pincer" (**A**) and bridged (**B**) carbenic species have been described in the literature (Figure 1).[3] Thus, pincer-type structures **A** have been found in some complexes of group II (Ca, Ba)[4] and IV (Ti, Zr, Hf)[1,5] metals, samarium,[6] and molybdenum,[7] while both homobimetallic (M = M′= Cr,[8] Al,[9] Sn,[10] Pb[10]) and heterobimetallic (M = Ge, M′ = Rh;[11] M = Li, M′ = Rh[12]) species of type **B** are presently known. In addition, the synthesis and reactivity of the platinum carbene **C**, containing only one four-membered metallacarbene ring,[13] and the bis(germavinylidene) complex **D**,[7,10,11,14] which comprises two germavinylidene

* To whom correspondence should be addressed. E-mail: jgh@uniovi.es (J.G.); vcm@uniovi.es (V.C.).

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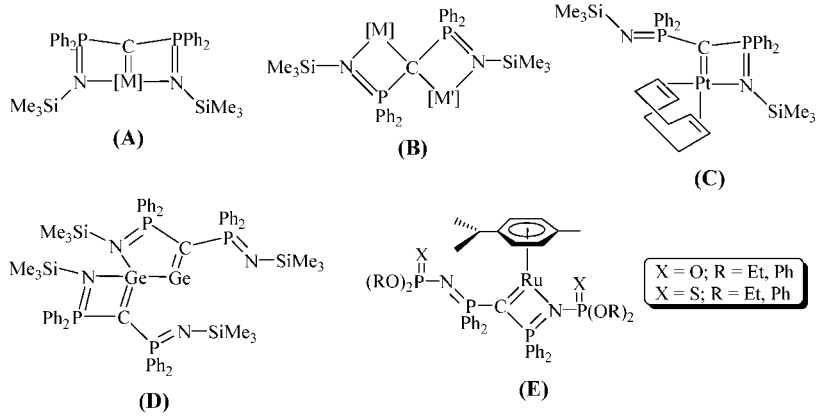

Figure 1. Structure of the carbenic species **A**−**E**.

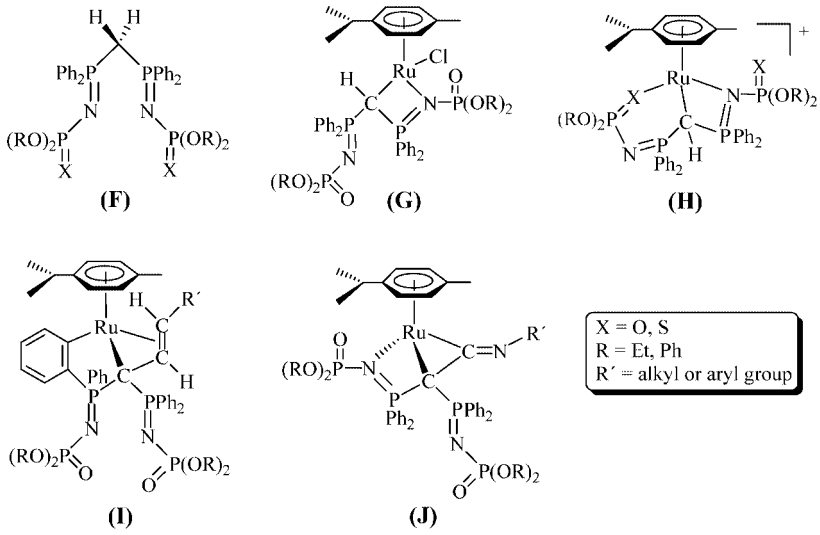

Figure 2. Structure of the ligands **F** and the ruthenium complexes **G**−**J**.

moieties [:Ge═C{P(═NSiMe$_3$)Ph$_2$}$_2$] bonded together in a head-to-head manner, has also been described.

The contribution of our group to this field has been the preparation of the half-sandwich ruthenium−carbene complexes **E** (see Figure 1), closely related to the platinum derivative **C**, starting from the *N*-phosphorylated or thiophosphorylated bis(iminophosphoranyl)methane ligands CH$_2$[P{═NP(═X)(OR)$_2$}Ph$_2$]$_2$ (X = O, S; R = Ph, Et; **F** in Figure 2).[15] The synthesis of these compounds, which represent rare examples of ruthenium complexes in which the carbene moiety is part of a four-membered chelate ring,[16] involved the following steps: (i) initial monodeprotonation of CH$_2$[P{═NP(═X)(OR)$_2$}Ph$_2$]$_2$ by means of NaH (X = O) or KH (X = S), (ii) subsequent $\kappa^2(C,N)$ (X = O) or $\kappa^3(C,N,X)$ (X = O, S) coordination of the resulting bis(iminophosphoranyl)methanide anions to ruthenium to afford intermediates **G** and **H** (Figure 2),[17] and (iii) final deprotonation of the acidic methynic PCHP hydrogen in **G**−**H** with NaH. DFT calculations on the model complex [Ru(κ^2(*C*,*N*)-C[P{═NP(═O)(OMe)$_2$}Me$_2$]$_2$)(η^6-C$_6$H$_6$)] revealed a marked nucleophilic character of these carbenes, which was in complete accord with experimental results showing that protonations of **E** take place selectively on the carbenic carbon atom.[15a] The versatility and utility of these iminophosphorane-based ruthenium carbenes for the preparation of elaborated ruthenium organometallics, via C−C coupling processes, could also be demonstrated. Thus, unusual ortho-metalated derivatives **I**, containing an unusual η^4-coordinated all-carbon ligand, were easily prepared under mild conditions (room temperature) by reacting complexes **E** (X = O) with terminal alkynes HC≡CR′, via coupling of the Ru═C and C≡C bonds and concomitant aryl C−H activation.[18a] In addition, unprecedented ketenimine−ruthenium complexes **J**

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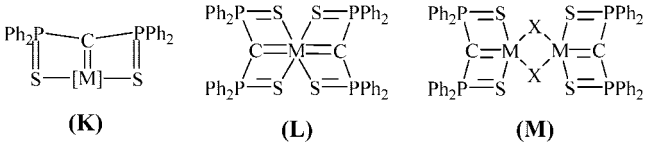

Figure 3. Structure of the pincer-type carbenes **K**−**M**.

were synthesized by reacting carbenes **E** (X = O) with isocyanides.[18b] In contrast to the reactivity pattern observed with terminal alkynes, in this case the C−C coupling process is not accompanied by the ortho-metalation of one of the phenyl rings of the pendant iminophosphorane groups $Ph_2P{=}NP(=O)(OR)_2$.

Simultaneous to our work, Le Floch and co-workers have studied the ability of the readily available bis(diphenylthiophosphoranyl)methane ligand $CH_2\{P(=S)Ph_2\}_2$ to act also as a precursor of transition-metal carbenes.[19] To this end, they synthesized the dilithium salt $[Li_2C\{P(=S)Ph_2\}_2]_2$, whose dimeric solid state structure bears some resemblance with that of its bis(iminophosphoranyl) analogue $[Li_2C\{P(=NSiMe_3)Ph_2\}_2]_2$,[2,20] by reacting $CH_2\{P(=S)Ph_2\}_2$ with 2 equiv of MeLi. In a first series of experiments they have nicely illustrated the utility of this methandiide dianion to access novel pincer-type carbenic structures of type **K** (Pd,[21] Ru,[22] and Zr[23] complexes), **L** (Sm[24] and Tm[25] complexes), and **M** (Zr,[23] Sm,[24] and Tm[25] complexes; X = halide ligand) (see Figure 3). We note that, as previously observed for the bis(iminophosphoranyl)methandiide species **A** and **C** (Figure 1), extensive π-electron delocalization takes place within the four-membered chelate rings in this type of compounds elongating the M=C bond distances and reducing therefore their carbenic character.

With all these precedents in mind, and following with our interest in the iminophosphorane−ruthenium chemistry,[15,18,26] our attention was turned to the mixed (iminophosphoranyl)(thiophosphoranyl)methane species $Ph_2P(=S)CH_2P(=NR)Ph_2$ as potential candidates for the preparation of novel ruthenium carbenes since, to the best of our knowledge, no precedent on its use as a carbene source has been described. There is only one related work dealing with the synthesis of platinum compounds containing the neutral and monodeprotonated forms of the ligands $Ph_2P(=S)CH_2P(=NR)Ph_2$ (R = 4-C_6H_4Me, 4-C_6H_4OMe).[27] Such heteroditopic species might be interesting not only for the study of the interrelations between the various possible coordination modes of their mono- and dianionic forms, but also to gain more insight into the reactivity of the resulting nucleophilic carbene complexes. Thus, herein we report (see Figure 4) (i) the synthesis and characterization of a family of novel (iminophosphoranyl)(thiophosphoranyl)methane $Ph_2P(=S)CH_2P(=NR)Ph_2$ ligands, (ii) the reactions of their methanide anions with the ruthenium dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ giving rise to the ruthenacarbobicycles **N** and **O**, and (iii) the preparation of the novel carbene derivative **P** as well as its reactivity toward 2,6-dimethylphenyl isocyanide. In the course of this study an unusual insertion of one isocyanide molecule into the Ru=C bond of **P**, leading to the octahedral derivative **Q**, was encountered upon treatment of **P** with a large excess of 2,6-dimethylphenyl isocyanide.

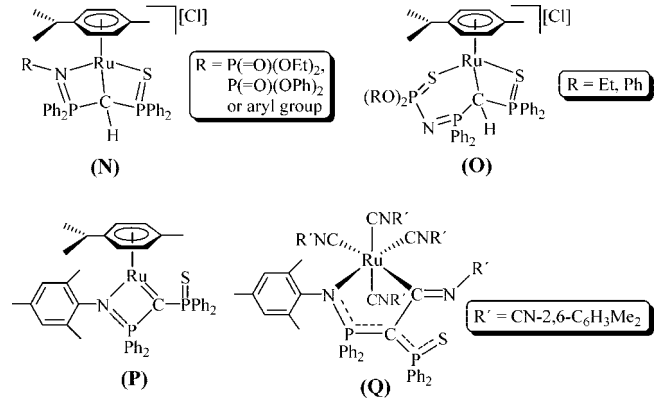

Figure 4. Structure of some ruthenium complexes reported in this paper.

Results and Discussion

Synthesis and Characterization of the Mixed (Iminophosphoranyl)(thiophosphoranyl)methane Ligands $Ph_2P(=S)CH_2P(=NR)Ph_2$ (R = 2,4,6-$C_6H_2Me_3$ (2a), 4-C_6F_4CHO (2b), 4-C_6F_4CN (2c), 4-C_5F_4N (2d), $P(=O)(OEt)_2$ (2e), $P(=O)(OPh)_2$ (2f), $P(=S)(OEt)_2$ (2g), $P(=S)(OPh)_2$ (2h)). Following the experimental procedure used previously by Elsevier and coworkers for the synthesis of $Ph_2P(=S)CH_2P(=NR)Ph_2$ (R = 4-C_6H_4Me, 4-C_6H_4OMe)[27] we have now prepared the novel (iminophosphoranyl)(thiophosphoranyl)methane compounds $Ph_2P(=S)CH_2P(=NR)Ph_2$ (R = 2,4,6-$C_6H_2Me_3$ (**2a**), 4-C_6F_4CHO (**2b**), 4-C_6F_4CN (**2c**), 4-C_5F_4N (**2d**), $P(=O)(OEt)_2$ (**2e**), $P(=O)(OPh)_2$ (**2f**), $P(=S)(OEt)_2$ (**2g**), $P(=S)(OPh)_2$ (**2h**)). The synthetic procedure involves a two-step sequence starting from commercially available bis(diphenylphosphino)methane (dppm): (i) the initial selective monoimination of one of its PPh_2 units with the appropriate azide RN_3, by means of the classical Staudinger reaction,[28,29] to afford the known iminophosphoranyl-phosphines $Ph_2PCH_2P(=NR)Ph_2$ (**1a**−**h**) and (ii) subsequent oxidation of

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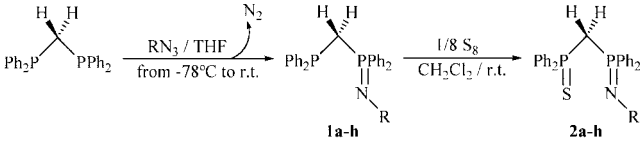
Scheme 1. Synthesis of the (Iminophosphoranyl)(thiophosphoranyl)methanes 2a−h



R = 2,4,6-$C_6H_2Me_3$ (**a**), 4-C_6F_4CHO (**b**), 4-C_6F_4CN (**c**), 4-C_5F_4N (**d**), P(=O)$(OEt)_2$ (**e**), P(=O)$(OPh)_2$ (**f**), P(=S)$(OEt)_2$ (**g**), P(=S)$(OPh)_2$ (**h**)

1a−h with elemental sulfur in dichloromethane at room temperature for 4 h (Scheme 1). Compounds **2a−h** have been isolated as air-stable microcrystalline white solids in 79–91% yield after a simple workup consisting of the filtration and evaporation of the solution, and subsequent washings of the solid residue with *n*-pentane.

The characterization of **2a−h** was straightforward by following their analytical and spectroscopic data (details are given in the Experimental Section). In particular, sulfuration of the diphenylphosphino group is clearly reflected in the $^{31}P\{^1H\}$ NMR spectra by a strong downfield shift of its signal (δ_P from 32 to 35 ppm; see Table 1) with respect to that shown by the corresponding iminophosphoranyl-phosphine precursor **1a−h** (δ_P from −30 to −27 ppm), the $Ph_2P{=}NR$ resonance remaining almost unchanged ($\Delta\delta \leq 7$ ppm). We note that the ^{31}P chemical shifts and coupling constants observed for **2a−h** fit well with those described previously for their counterparts $Ph_2P(=S)CH_2P(=NR)Ph_2$ (R = 4-C_6H_4Me, 4-C_6H_4OMe).[27] ^1H and $^{13}C\{^1H\}$ NMR spectra of **2a−h** also exhibit signals in accordance with the proposed formulations, the most significant features being those concerning the methylenic PCH_2P group of the ligands whose protons and carbon resonate as doublet of doublets at ca. δ_H 4 ppm and δ_C 33 ppm, respectively, due to the coupling with the vicinal phosphorus atoms of the $Ph_2P{=}S$ and $Ph_2P{=}N$ units ($^2J_{HP}$ = 13.1–15.4 Hz and $^1J_{CP}$ = 43.1–53.0 Hz).

Moreover, the molecular structures of $Ph_2P(=S)CH_2P\{=NP(=X)(OPh)_2\}Ph_2$ (X = O (**2f**), S (**2h**)) have been determined by X-ray diffraction methods. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of compounds **2f** and **2h** in dichloromethane. ORTEP plots of the structures are shown in Figure 5; selected bonding parameters are listed in Table 2.

The most noticeable features of these structures are the following: (i) The P=S bond distances of the diphenylthiophosphoryl groups (P(3)−S(1) = 1.9471(8) (**2f**) and 1.9479(8) Å (**2h**)), which fall within the expected range for a phosphorus−sulfur double bond,[30] and are in good agreement with that previously reported for the related (iminophosphoranyl)(thiophosphoranyl)methane derivative $Ph_2P(=S)CH_2P(=N\text{-}4\text{-}C_6H_4Me)Ph_2$ (1.9515(19) Å)[27] and (ii) the similarity between the lengths of the formal single (P(1)−N(1) = 1.582(2) (**2f**) and 1.5774(19) Å (**2h**)) and double (P(2)−N(1) = 1.575(2) (**2f**) and 1.572(2) Å (**2h**)) phosphorus−nitrogen bonds in the *N*-phosphorylated or thiophosphorylated units $-Ph_2P{=}NP(=X)(OPh)_2$ (X = O, S). This fact is probably determined by the strong π-acceptor nature of the phosphoryl and thiophosphoryl groups, which enhance the delocalization of the electronic lone pair of the nitrogen atom along the P=N−*P*=X framework.[31]

Synthesis and characterization of complexes [Ru{κ^3(*C*,*N*,*S*)-$Ph_2P(=S)CHP(=NR)Ph_2$}(η^6-*p*-cymene)][Cl] (R = 2,4,6-$C_6H_2Me_3$ (3a), 4-C_6F_4CHO (3b), 4-C_6F_4CN (3c), 4-C_5F_4N (3d), P(=O)$(OEt)_2$ (3e), P(=O)$(OPh)_2$ (3f)) and [Ru(κ^3(*C*,*S*,*S*)-$Ph_2P(=S)CHP\{=NP(=S)(OR)_2\}Ph_2$)($\eta^6$-*p*-cymene)][Cl] (R = Et (4g), Ph (4h)). In accord with the well-known acidic character of the methylenic backbone in the dioxidized forms of dppm, i.e, $Ph_2P(=X)CH_2P(=X)Ph_2$ (X = O,[32] S,[19,33] NR[2,15,34]), the mixed compounds $Ph_2P(=S)CH_2P(=NR)Ph_2$ (**2a−h**) can be easily deprotonated, upon treatment with a stoichiometric amount of Li^{n}Bu in tetrahydrofuran at –20 °C, to generate the corresponding lithium−methanide species $Li[Ph_2P(=S)CHP(=NR)Ph_2]$. Nevertheless, as previously observed by Elsevier and co-workers for the closely related anion $[Ph_2P(=S)CHP(=N\text{-}p\text{-Tolyl})Ph_2]^-$,[27] they are extremely moisture sensitive avoiding their isolation in pure form.[35] Fortunately, this was not a serious impediment to study their coordination chemistry. Thus, as shown in Scheme 2, we have found that these in situ generated methanide anions readily react with the ruthenium(II) dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$], in THF at room temperature, to afford cationic metallabicyclic mononuclear compounds via tridentate coordination of the ligands to ruthenium. Thus, starting from **2a−f**, complexes [Ru{κ^3(*C*,*N*,*S*)-$Ph_2P(=S)CHP(=NR)Ph_2$}(η^6-*p*-cymene)][Cl] (R = 2,4,6-$C_6H_2Me_3$ (**3a**), 4-C_6F_4CHO (**3b**), 4-C_6F_4CN (**3c**), 4-C_5F_4N (**3d**), P(=O)$(OEt)_2$ (**3e**), P(=O)$(OPh)_2$ (**3f**)) are formed as the result of the selective κ^3(*C*,*N*,*S*)-coordination of the anions to ruthenium, i.e., they are bonded through the methynic carbon and the $Ph_2P{=}S$ and $Ph_2P{=}N$ groups. In contrast, when the reactions are performed with their *N*-thiophosphorylated counterparts **2g**,**h**, preference for the *S*- vs *N*-coordination of the iminophosphoranyl units $-Ph_2P{=}N-P(=S)(OR)_2$ (R = Et, Ph) is observed, obtaining selectively the complexes [Ru(κ^3(*C*,*S*,*S*)-$Ph_2P(=S)CHP\{=NP(=S)(OR)_2\}Ph_2$)($\eta^6$-*p*-cymene)][Cl] (R = Et (**4g**), Ph (**4 h**)). Formation of complexes **4g**,**h**, which leads to a less strained structure when compared to that of **2g**,**h**, is in complete accord with published literature showing that the coordination chemistry of *N*-

(30) See for example: (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1. (b) Allen, F. H.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. In *International Tables for X-Ray Crystallography*; Prince, E., Ed.; Kluwer Academic Publishers; Dordrecht, The Netherlands, 2004; Vol. C, p 790.

(31) Extensive electronic delocalization is a classical feature of *N*-phosphorylated or thiophosphorylated iminophophorane units $-Ph_2P{=}N-P(=X)(OR)_2$ (X = O, S). See for example: (a) Larré, C.; Donnadieu, B.; Caminade, A. M.; Majoral, J. P. *Eur. J. Inorg. Chem.* **1999**, 601. (b) Maraval, V.; Laurent, R.; Donnadieu, B.; Mauzac, M.; Caminade, A.-M.; Majoral, J.-P. *J. Am. Chem. Soc.* **2000**, *122*, 2499. (c) Balakrishna, M. S.; Abhyankar, R. M.; Walawalker, M. G. *Tetrahedron Lett.* **2001**, *42*, 2733. (d) Longlet, J. J.; Bodige, S. G.; Watson, W. H.; Nielson, R. H. *Inorg. Chem.* **2002**, *41*, 6507. (e) Maraval, V.; Laurent, R.; Donnadieu, B.; Caminade, A. M.; Majoral, J. P. *Synthesis* **2003**, 389. (f) Magro, G.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. *Chem. Eur. J.* **2003**, *9*, 2151 See also refs 15 and 26.

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(34) (a) Imhoff, P.; Van Asselt, R.; Elsevier, C. J.; Vrieze, K.; Goubitz, K.; Van Malssen, K. F.; Stam, C. H. *Phosphorus, Sulfur and Silicon* **1990**, *47*, 401. (b) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Brès, P.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4247. (c) Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2000**, *39*, 4891. (d) Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G. *Organometallics* **2001**, *20*, 1451. (e) Gamer, M. T.; Roesky, P. W. *Z. Anorg. Allg. Chem.* **2001**, *627*, 877.

(35) (a) Attempts to isolate in pure form the corresponding sodium or potassium salts $M[Ph_2P(=S)CHP(=NR)Ph_2]$ ($M^+ = Na^+$, K^+), generated by treatment of **2a−h** with NaH or KH in THF at room temperature, also failed. (b) The moisture sensitivity of the related lithium salt $Li[C(Ph_2P{=}S)_2\{Ph_2P{=}N(p\text{-Tolyl})\}]$ has also been reported: Grim, S. O.; Kettler, P. B. *J. Chem. Soc., Chem. Commun.* **1991**, 979.

Table 1. $^{31}P\{^1H\}$ NMR Data for All Compounds Described in This Article [a]

compd	$Ph_2P_A{=}S$	$Ph_2P_B{=}NR$	$^2J_{PAPB}$	$(R'O)_2P_C{=}X$	$^2J_{PBPC}$
		$Ph_2P(=S)CH_2P(=NR)Ph_2$			
R = 2,4,6-$C_6H_2Me_3$ (**2a**)[b]	34.13 (d)	−11.19 (d)	15.3		
R = 4-C_6F_4CHO (**2b**)[b]	33.13 (d)	6.30 (dt)[e]	10.8		
R = 4-C_6F_4CN (**2c**)[b]	32.88 (d)	5.99 (dt)[f]	9.8		
R = 4-C_5F_4N (**2d**)[b]	33.06 (d)	6.64 (dt)[g]	10.6		
R = $P(=O)(OEt)_2$ (**2e**)[b]	34.89 (d)	11.14 (dd)	13.5	4.36 (d)	28.9
R = $P(=O)(OPh)_2$ (**2f**)[b]	34.49 (d)	12.71 (dd)	12.2	−6.01 (d)	31.7
R = $P(=S)(OEt)_2$ (**2g**)[b]	34.69 (d)	9.98 (dd)	12.1	58.46 (d)	32.1
R = $P(=S)(OPh)_2$ (**2h**)[b]	34.29 (d)	12.20 (dd)	10.8	51.43 (d)	32.5
		$[Ru\{\kappa^3(C,N,S)\text{-}Ph_2P(=S)CHP(=NR)Ph_2\}(\eta^6\text{-}p\text{-cymene})][Cl]$			
R = 2,4,6-$C_6H_2Me_3$ (**3a**)[c]	45.20 (d)	46.61 (d)	8.1		
R = 4-C_6F_4CHO (**3b**)[c]	45.44 (s)	55.40 (t)[h]			
R = 4-C_6F_4CN (**3c**)[c]	45.13 (s)	55.62 (t)[i]			
R = 4-C_5F_4N (**3d**)[c]	44.87 (s)	55.55 (t)[j]			
R = $P(=O)(OEt)_2$ (**3e**)[c]	44.17 (s)	51.63 (d)		7.21 (d)	18.9
R = $P(=O)(OPh)_2$ (**3f**)[c]	44.74 (s)	54.93 (d)		−2.32 (d)	18.1
		$[Ru(\kappa^3(C,S,S)\text{-}Ph_2P(=S)CHP\{=NP(=S)(OR)_2\}Ph_2)(\eta^6\text{-}p\text{-cymene})][Cl]$			
R = $P(=S)(OEt)_2$ (**4g**)[c]	62.85 (s)	26.05 (d)		54.71 (d)	20.8
R = $P(=S)(OPh)_2$ (**4h**)[b]	62.38 (d)	29.71 (d)	2.3	49.08 (d)	16.2
		$[Ru\{\kappa^2(C,N)\text{-}Ph_2P(=S)CP(=NR)Ph_2\}(\eta^6\text{-}p\text{-cymene})]$			
R = 2,4,6-$C_6H_2Me_3$ (**5**)[d]	42.75 (d)	63.15 (d)	75.1		
		$[Ru\{\kappa^3(C,C,N)\text{-}Ph_2P(=S)C(C{=}N\text{-}2,6\text{-}C_6H_3Me_2)P(=NR)Ph_2\}(\eta^6\text{-}p\text{-cymene})]$			
R = 2,4,6-$C_6H_2Me_3$ (**6**)[d]	45.72 (d)	52.90 (d)	64.1		
		$[Ru\{\kappa^2(C,N)\text{-}Ph_2P(=S)C(C{=}N\text{-}2,6\text{-}C_6H_3Me_2)P(NR)Ph_2\}(CN\text{-}2,6\text{-}C_6H_3Me_2)_4]$			
R = 2,4,6-$C_6H_2Me_3$ (**7**)[d]	35.26 (d)	53.49 (d)	97.5		

[a] δ in ppm and J in Hz. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt, doublet of triplets. [b] Spectra recorded in $CDCl_3$. [c] Spectra recorded in CD_2Cl_2. [d] Spectra recorded in C_6D_6. [e] $^4J_{PF}$ = 5.4 Hz. [f] $^4J_{PF}$ = 5.7 Hz. [g] $^4J_{PF}$ = 4.5 Hz. [h] $^4J_{PF}$ = 2.1 Hz. [i] $^4J_{PF}$ = 4.1 Hz. [j] $^4J_{PF}$ = 2.7 Hz.

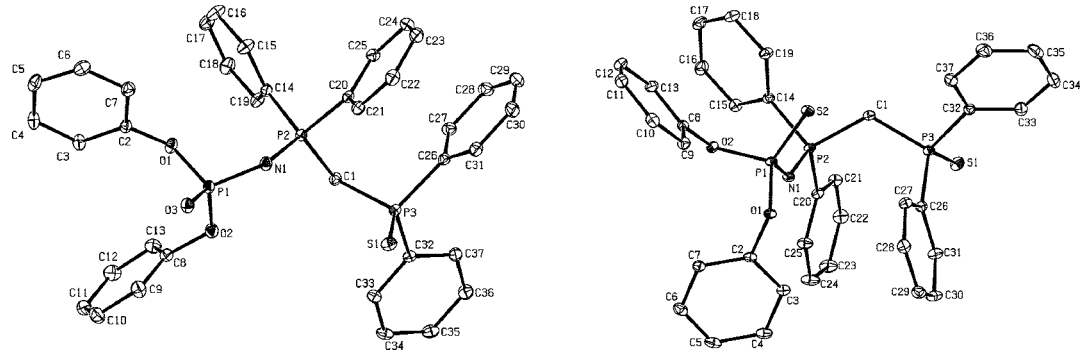


Figure 5. ORTEP-type views of the structures of compounds **2f** (left) and **2h** (right) showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 2f and 2h

	compd			compd	
distances	**2f**	**2h**	angles	**2f**	**2h**
P(1)−O(3)	1.4603(17)		O(3)−P(1)−N(1)	116.51(11)	
P(1)−S(2)		1.9430(8)	S(2)−P(1)−N(1)		121.75(8)
P(1)−N(1)	1.582(2)	1.5774(19)	P(1)−N(1)−P(2)	133.43(14)	135.83(13)
P(2)−N(1)	1.575(2)	1.572(2)	N(1)−P(2)−C(1)	114.07(11)	119.99(10)
P(2)−C(1)	1.825(2)	1.822(2)	P(2)−C(1)−P(3)	117.78(13)	120.99(12)
C(1)−P(3)	1.831(2)	1.827(2)	C(1)−P(3)−S(1)	114.96(8)	112.57(8)
P(3)−S(1)	1.9471(8)	1.9479(8)			

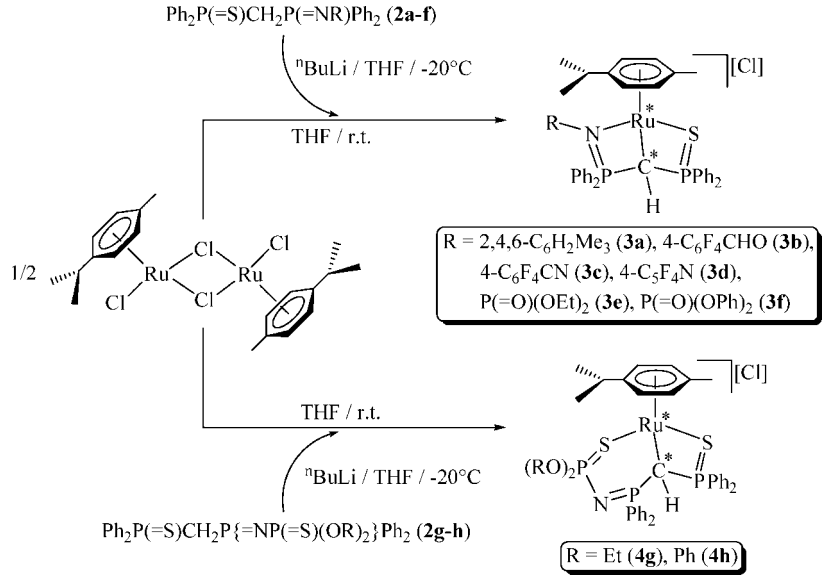
thiophosphorylated iminophosphoranes $R_3P{=}N{-}P(=S)(OR')_2$ is almost entirely dominated by the coordination of the sulfur atom.[36,37]

Complexes **3a−f** and **4g,h**, isolated as air-stable orange solids in 70–81% yield, have been characterized by means of standard spectroscopic techniques (IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR), conductance measurements (1:1 electrolytes; Λ_M =

(36) (a) Larré, C.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. *Chem. Eur. J.* **1998**, *4*, 2031. (b) Rossell, O.; Seco, M.; Caminade, A.-M.; Majoral, J.-P. *Gold Bull.* **2001**, *34*, 88. (c) Turrin, C.-O.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2881. (d) Maraval, A.; Magro, G.; Maraval, V.; Vendier, L.; Caminade, A.-M.; Majoral, J.-P. *J. Organomet. Chem.* **2006**, *691*, 1333. See also ref 26i.

(37) As shown in Figures 1 and 2 (structures **E** and **H**), while studying the coordination to ruthenium of the methanide and methandiide anions derived from $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$ (R = Et, Ph), some complexes showing the *N*-coordination of the $P{=}N{-}P{=}S$ framework could be isolated: see ref 15b.

Scheme 2. Synthesis of the Ruthenium(II) Complexes 3a−f and 4g,h



111–123 Ω^{-1} cm^2 mol^{-1}), as well as elemental analyses, all data being fully consistent with the structural proposals (details are given in the Experimental Section and Table 1). Moreover, the NMR spectra also indicate that the formation of all these species proceeds in a diastereoselective manner (note that two stereogenic centers are generated, i.e., the ruthenium atom and the methynic PCHP carbon), the diastereoselectivity of the process being controlled by the steric hindrance between the *p*-cymene ring and the Ph_2P units of the ligands. Close examination of the $^{31}P\{^1H\}$ NMR spectra allows the coordination mode adopted by the (iminophosphoranyl)(thiophosphoranyl)methanide anions in **3a**−**f** and **4g**,**h** (see Table 1) to be distinguished. Thus, for complexes **3a**−**f** the $\kappa^3(C,N,S)$ coordination is reflected in a appreciable downfield shift of both the Ph_2P═N (ca. $\Delta\delta$ 50 ppm) and Ph_2P═S (ca. $\Delta\delta$ 11 ppm) resonances in comparison with those shown by the free ligands **2a**−**f**, confirming the direct involvement of these groups in the bonding (for the *N*-phosphorylated species **3e**−**f**, the signal corresponding to the $(RO)_2P$═O unit remains almost unaffected; ca. $\Delta\delta$ 3 ppm). Concerning complexes **4g**,**h**, although downfield shifts are also observed for the Ph_2P═N and Ph_2P═S signals with respect to **2g**,**h**, the $\Delta\delta$ values differ considerably from those shown by **3a**−**f**, i.e., 17 vs 48 and 28 vs 11 ppm, respectively, suggesting a different coordination of the anions. This fact along with the slight high-field shifting of the $(RO)_2P$═S resonances (ca. $\Delta\delta$ –3 ppm when compared to **2g**,**h**), previously observed in the *S*-coordination of related −Ph_2P═N−P(═S)$(OR)_2$ units to Au(I), Ag(I), and Cu(I) fragments,[36] allows us to propose that in this case ruthenium complexation takes place selectively on the $(RO)_2P$═S vs Ph_2P═N groups.

The most remarkable features in the ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes are those associated with the methynic PCHP group of the ligands. Thus, while for **3a**−**f** its PCHP proton resonates at 3.87–4.28 ppm, as a broad signal (**3a**,**e**,**f**) or a well-resolved doublet of doublets (**3b**,**c**,**d**; ca. $^2J_{HP}$ = 12 Hz), the different coordination mode adopted by the methanide anions in **4g**,**h** is reflected in a deshielding of the signal appearing now at 5.58–5.58 ppm (dd; $^2J_{HP}$ = 4.3–7.4 Hz). A similar trend is also observed in $^{13}C\{^1H\}$ NMR, the PCHP carbon resonance appearing at ca. –20 ppm for **3a**−**f** and –12 ppm for **4g**,**h**. Concerning the multiplicity of the signals, well-resolved doublet of doublets (**3a**−**d**) or doublet of doublets of doublets (**3e**,**f** and **4g**,**h**) are observed due to the coupling with the vicinal phosphorus atoms ($^1J_{CP}$ = 27.6–87.0 Hz; $^3J_{CP}$ = 2.1–2.7 Hz). The high-field chemical shifts observed for the PCHP carbon compare well with those previously described by us for the related metallacyclic species **G** and **H** (see Figure 2),[15] supporting the direct bonding of the methynic PCHP unit to ruthenium.

X-ray diffraction studies on complexes [Ru(κ^3(*C*,*N*,*S*)-Ph_2P(═S)CHP{═NP(═O)$(OPh)_2$}Ph_2)(η^6-*p*-cymene)][SbF_6] (**3f**) and [Ru(κ^3(*C*,*S*,*S*)-Ph_2P(═S)CHP{═NP(═S)$(OEt)_2$}Ph_2)(η^6-*p*-cymene)][SbF_6] (**4g**) unequivocally confirmed the molecular structures proposed for the metallabicyclic species **3a**−**f** and **4g**,**h**, respectively.[38] As expected, two enantiomers are present in the unit cell of each compound displaying $R_{Ru}R_C/S_{Ru}S_C$ (**3f**) and $R_{Ru}S_C/S_{Ru}R_C$ (**4g**) configurations. Drawings of the molecular structures of the $R_{Ru}R_C$ (**3f**) and $R_{Ru}S_C$ (**4g**) enantiomers are depicted in Figure 6; selected bond distances and angles are collected in Table 3.

The coordination spheres around ruthenium consist of the η^6-*p*-cymene ring, the methynic PCHP carbon, the sulfur atom of the Ph_2P═S group, and the nitrogen (**3f**) or sulfur (**4g**) atom of the *N*-phosphorylated or thiophosphorylated iminophosphorane arms −Ph_2P═NP(═X)$(OR)_2$ (X = O, S), all disposed in a classical pseudooctahedral three-legged piano-stool geometry as clearly indicated by the values of the interligand angles C(1)−Ru−S(1), C(1)−Ru−N(1)/S(2), S(1)−Ru−N(1)/S(2), and those between the centroid of the *p*-cymene ring C* and the legs. The Ru−C(1) bond lengths (2.205(6) (**3f**) and 2.214(3) Å (**4g**)) show the expected value for a ruthenium−carbon single bond,[39] comparing well with those previously observed by us in the ruthenabicyclic bis(iminophosphoranyl)methanide species [Ru(κ^3(*C*,*N*,*O*)-CH[P{═NP(═O)$(OPh)_2$}Ph_2]$_2$)(η^6-*p*-cymene)][SbF_6] (Ru−C = 2.228(5) Å)[15a] and [Ru(κ^3(*C*,*N*,*S*)-CH[P{═NP(═S)$(OEt)_2$}Ph_2]$_2$)(η^6-*p*-cymene)][PF_6] (Ru−C = 2.160(3) Å)[15b] (**H** in Figure 2). The Ru−N(1) (**3f**) and Ru−S(2) (**4g**) lengths are also similar to those observed in these compounds.

(38) All attempts to obtain crystals suitable for X-ray diffraction analysis of the chloride salts of complexes **3f** and **4g** failed. The corresponding hexafluoroantimonate salts, which readily crystallize by slow diffusion of *n*-pentane into a saturated dichloromethane solution, were obtained by chloride metathesis, using 1 equiv of $AgSbF_6$ in methanol at room temperature.

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

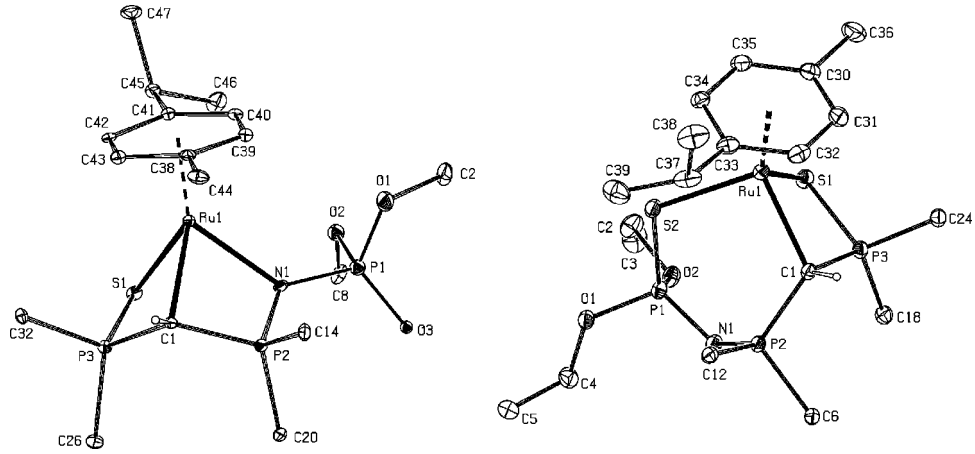


Figure 6. ORTEP-type views of the structures of compounds **3f** (left) and **4g** (right) showing the crystallographic labeling scheme. Phenyl groups, SbF_6^- anions, and hydrogen atoms (except that on C(1)) have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level.

Table 3. Selected Bond Distances (Å) and Bond angles (deg) for Complexes 3f and 4g [a]

	complex			complex	
distances	**3f**	**4g**	angles	**3f**	**4g**
Ru−C(1)	2.205(6)	2.214(3)	C*−Ru−C(1)	134.14(17)	129.43(10)
Ru−S(1)	2.4689(16)	2.4608(10)	C*−Ru−S(1)	131.63(5)	128.75(3)
Ru−C*	1.6894(5)	1.7144(3)	C*−Ru−N(1)	133.58(17)	
Ru−N(1)	2.159(5)		C*−Ru−S(2)		122.11(3)
Ru−S(2)		2.4282(10)	C(1)−Ru−S(1)	77.51(15)	77.71(9)
P(1)−O(3)	1.446(8)		C(1)−Ru−N(1)	72.5(2)	
P(1)−S(2)		1.9948(14)	C(1)−Ru−S(2)		96.26(9)
P(1)−N(1)	1.623(5)	1.582(3)	S(1)−Ru−N(1)	84.69(16)	
N(1)−P(2)	1.609(5)	1.585(3)	S(1)−Ru−S(2)		89.34(4)
P(2)−C(1)	1.781(6)	1.785(4)	P(1)−N(1)−P(2)	130.1(3)	126.2(2)
C(1)−P(3)	1.760(6)	1.797(3)	N(1)−P(2)−C(1)	98.9(3)	114.44(17)
P(3)−S(1)	2.005(2)	2.0040(13)	P(2)−C(1)−P(3)	121.5(3)	115.4(2)

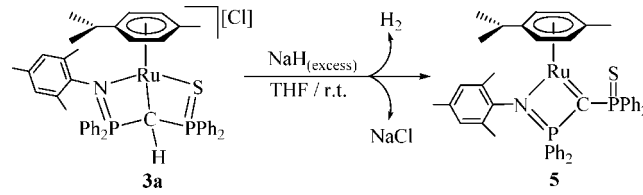
[a] C* = centroid of the *p*-cymene ring.

Remarkably, despite their different coordination to ruthenium, the P−N bond distances within the $Ph_2P{=}NP(=X)(OR)_2$ frameworks are quite similar in both structures (see Table 3) and comparable to those found in the X-ray structures of the free ligands **2f**,**h** (ca. ±0.04 Å; see Figure 5 and Table 2), indicating that the π-electronic delocalization is maintained upon *N*- or *S*-coordination. Concerning the Ru−S(1) bond distances (2.4689(16) (**3f**) and 2.4608(10) Å (**4g**)), they fit well with those reported by Le Floch and co-workers for the pincer-type ruthenium carbene [Ru(κ^3(*C*,*S*,*S*)-C{$Ph_2P(=S)$}$_2$)] (Ru−S = 2.4739(5) and 2.4843(5) Å), which also incorporates four-membered metallacyclic RuCPS units.[22]

Finally, it is also interesting to note that the preference shown by the methanide anions derived from **2a**−**h** to selectively adopt a tridentate coordination mode (complexes **3a**−**f** or **4g**,**h**) contrasts with the bidentate coordination adopted by the closely related anionic ligand $[Ph_2P(=S)CHP(=N\text{-}4\text{-}C_6H_4Me)Ph_2]^-$ in the square-planar Pt(II) derivative [PtCl{κ^2(*C*,*N*)-$Ph_2P(=S)CHP(=N\text{-}4\text{-}C_6H_4Me)Ph_2$}($PEt_3$)], the only example previously described of a metallic complex incorporating a coordinated (iminophosphoranyl)(thiophosphoranyl)methanide ligand.[27]

Synthesis and Reactivity toward 2,6-Dimethylphenyl Isocyanide of the Ruthenium−Carbene Complex [Ru{κ^2(*C*,*N*)-$Ph_2P(=S)CP(=N\text{-}2,4,6\text{-}C_6H_2Me_3)Ph_2$}($\eta^6$-*p*-cymene)] (5). As previously observed in the bis(iminophosphoranyl)methanide species **G** and **H** (see Figure 2),[15] the attachment of the related (iminophosphoranyl)(thiophosphoranyl)methanide anions to the ruthenium(II) fragment [Ru(η^6-*p*-cymene)]$^{2+}$ (complexes **3a**−**f** and **4g**,**h**) enhances the acidity of the methynic PCHP hydrogen

Scheme 3. Synthesis of the Ruthenium−Carbene Complex 5



allowing its deprotonation under mild conditions. Thus, we have found that treatment of **3a**−**f** and **4g**,**h** with an excess of NaH (10 equiv), in THF at room temperature, leads to an immediate change of the solution color from orange to deep violet. Monitoring the course of the reactions by $^{31}P\{^1H\}$ NMR showed after ca. 4–5 h the total consumption of the starting materials and the clean appearance of a novel set of signals attributed to the corresponding neutral carbenic species [Ru{κ^2(*C*,*N*)-$Ph_2P(=S)CP(=NR)Ph_2$}(η^6-*p*-cymene)]. Unfortunately, only complex [Ru{κ^2(*C*,*N*)-$Ph_2P{=}S)CP(=N\text{-}2,4,6\text{-}C_6H_2Me_3)Ph_2$}($\eta^6$-*p*-cymene)] (**5**), containing the bulky and electron-rich mesityl group attached to the iminophosphoranyl unit, could be isolated in pure form from these solutions (Scheme 3). In the rest of the cases, extensive reprotonation of the carbenes occurs during workup, due probably to the moisture traces present in the solvents used, leading to mixtures containing the starting materials **3b**−**f** and **4g**,**h** as the major components. It is worth noting the complete regioselectivity observed in the formation of carbene **5**, the generation of the Ru=C bond leading to the exclusive decoordination of the $Ph_2P{=}S$ vs $Ph_2P{=}N{-}R$ unit. In addition, despite the known hemilabile character of imino-

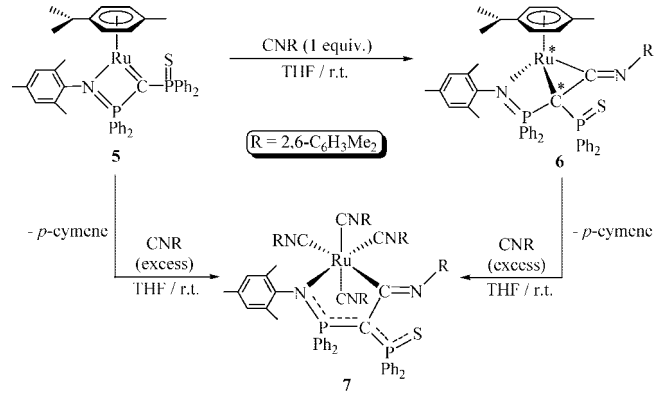
phosphoranes,[26] no fluxional $\kappa^2(C,N)/\kappa^2(C,S)$ behavior was detected in solution for complex **5**.

Carbene **5**, isolated as a moisture-sensitive violet solid in 82% yield, has been characterized by elemental analyses and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy (see the Experimental Section for details). Although all attempts to obtain crystals of **5** suitable for X-ray diffraction studies have been unsuccessful, the proposed structure could be readily deduced from its NMR data. Thus, the absence of the characteristic methynic PCHP signal in the ^{1}H NMR spectrum of **5** unambiguously confirms that deprotonation of this unit has taken place. The ^{31}P{^{1}H} NMR spectrum is also very informative, showing the presence of two doublets ($^2J_{PP}$ = 75.1 Hz) at 42.75 and 63.15 ppm assigned to the Ph_2P═S and Ph_2P═N groups, respectively. The downfield chemical shift of the iminophosphoranyl unit also confirms its direct coordination to ruthenium, being comparable with that previously reported by us for the coordinated Ph_2P═N unit in the closely related four-membered ruthenacarbocyclic carbene complexes [Ru($\kappa^2(C,N)$-C[P{═NP(═X)(OR)$_2$}Ph$_2$]$_2$)(η^6-*p*-cymene)] (X = O, S; R = Et, Ph; δ_P = 60.39–67.49 ppm; **E** in Figure 1).[15] Concerning the ^{13}C{^{1}H} NMR data, the most significant feature is the signal corresponding to the carbenic Ru═C carbon, which appears as a doublet of doublets at 124.98 ppm ($^1J_{CP}$ = 73.4 and 69.4 Hz), this chemical shift being also coherent with data published for the metallacarbenes **E** (ca. 128 ppm).[15]

The ability of the Ru═C bond of metallacarbene complex **5** to participate in C−C coupling processes has also been explored. As commented in the introduction of this paper, we recently described the high-yield preparation of the first examples of ketenimine−ruthenium complexes **J** by treatment of metallacarbenes **E** with isocyanides (see Figure 2).[18b,40] With this precedent in mind, we decided to explore the behavior of [Ru{$\kappa^2(C,N)$-Ph_2P(═S)CP(═N-2,4,6-$C_6H_2Me_3$)Ph_2}(η^6-*p*-cymene)] (**5**) toward 2,6-dimethylphenyl isocyanide (CN-2,6-$C_6H_3Me_2$) to extent the family of available ketenimine−ruthenium complexes.

As shown in Scheme 4, we found that the reaction outcome was strongly dependent on the stoichiometry employed. Thus, the reaction of **5** with an equimolar amount of 2,6-dimethylphenyl isocyanide, in THF at room temperature, generates the expected ketenimine−ruthenium derivative [Ru{$\kappa^3(C,C,N)$-Ph_2P(═S)C(C═N-2,6-$C_6H_3Me_2$)P(═N-2,4,6-$C_6H_2Me_3$)Ph_2}(η^6-*p*-cymene)] (**6**) isolated as an air-stable yellow solid in 77% yield. It has been characterized by elemental analyses, and IR and NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) spectroscopy, the latter indicating clearly its diastereoselective formation (note that two stereogenic centers are generated, i.e., the ruthenium atom and the PCP carbon). The most significant spectroscopic features of **6** are the following: (i) (^{31}P{^{1}H} NMR) the presence of two doublet resonances ($^2J_{PP}$ = 64.1 Hz) at 45.72 and 52.90 ppm assigned to the Ph_2P═S and Ph_2P═N moieties, respectively, the downfield chemical shift of the latter confirming its direct attachment to ruthenium and (ii) (^{13}C{^{1}H} NMR) characteristic signals for the PCP and C═N carbon atoms which appear at −7.22 (dd, $^1J_{CP}$ = 93.1 and 59.5 Hz) and 189.84 (d, $^2J_{CP}$ = 3.9 Hz) ppm, respectively. These data compare well with those previously reported for the closely related ketenimine−ruthenium compounds **J** (Figure 2),[18b] as well as for other *C*,*C*-bound ketenimine metal derivatives (Mn, Co, and Rh species) known.[41]

Scheme 4. Reactivity of Carbene Complex 5 toward 2,6-Dimethylphenyl Isocyanide



The reaction of **5** with a 10-fold excess of the isocyanide proceeds, however, in a different way since the octahedral compound [Ru{$\kappa^2(C,N)$-Ph_2P(S)C(C═N-2,6-$C_6H_3Me_2$)P(N-2,4,6-$C_6H_2Me_3$)Ph_2}(CN-2,6-$C_6H_3Me_2$)$_4$] (**7**) is selectively obtained. Formation of **7** involves the insertion of one 2,6-dimethylphenyl isocyanide molecule into the Ru═C unit and concomitant coordination of four molecules of the isocyanide to ruthenium via displacement of the arene ligand. We have confirmed that the ketenimine−ruthenium derivative **6** is an intermediate in the formation of complex **7**, the latter being cleanly formed by reacting **6** with an excess of CN-2,6-$C_6H_3Me_2$.

Complex **7** was unambiguously characterized by means of a single-crystal X-ray diffraction study. An ORTEP-type drawing of the molecular structure is depicted in Figure 7; selected bond distances and angles are listed in the caption. The ruthenium atom is in a slightly distorted octahedral environment, being bonded to four 2,6-dimethylphenyl isocyanide molecules, the nitrogen atom of the iminophosphoranyl group, and the carbon atom of the iminic C═N-2,6-$C_6H_3Me_2$ unit. As expected, all the isocyanide ligands are bound to ruthenium in a nearly linear fashion (Ru−C−N angles within the range 168.8(3)–174.5(3)°) with metal–carbon bond distances of 1.932(4)–2.042(3) Å. These bonding parameters fit well with those reported in the literature for other isocyanide−ruthenium(II) complexes.[42]

Bond distances within the N(6)−P(2)−C(1)−P(1)−S(1) framework seem to indicate that electronic delocalization is present in this part of the molecule. In particular, the observed

(40) C−C coupling processes between metal−carbenes [M]═CR^{1}R^2 and isocyanides (CNR^3) is one of the most popular methods to generate ketenimine complexes. (a) See for example: Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954. (b) Kreiter, C. G.; Aumann, R. *Chem. Ber.* **1978**, *111*, 1223. (c) Fisher, E. O.; Schambeck, W.; Kreissl, F. R. *J. Organomet. Chem.* **1979**, *169*, C27. (d) Mitsudo, T.-A.; Watanabe, H.; Komiya, Y.; Watanebe, Y.; Takaegami, Y.; Nakutso, K.; Kinoshita, K.; Miyagawa, Y. *J. Organomet. Chem.* **1980**, *190*, C39. (e) Fisher, E. O.; Schambeck, W. *J. Organomet. Chem.* **1980**, *201*, 311. (f) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *Angew. Chem., Int. Ed.* **1984**, *23*, 912. (g) Aumann, R.; Heinen, H.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1986**, *119*, 3141. (h) Aumann, R.; Heinen, H. *Chem. Ber.* **1988**, *121*, 1085. (i) Aumann, R.; Heinen, H. *Chem. Ber.* **1988**, *121*, 1739. (j) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. O. H.; Rettig, S. J.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 1707. (k) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewsky, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886.

(41) Both the C═C and C═N π-bonds of ketenimines R^{1}R^{2}C═C═NR^3 can complexate transition-metal fragments (see ref 40). For examples involving the C═C bond, see: (a) Strecker, B.; Hörlin, G.; Schulz, M.; Werner, H. *Chem. Ber.* **1991**, *124*, 285. (b) Treichel, P. M.; Firsich, D. W.; Lemmen, T. H. *J. Organomet. Chem.* **1991**, *202*, C77. (c) Fandos, R.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A.; Ruiz, M. J.; Teuben, J. H *Organometallics* **1997**, *16*, 5283. (d) Werner, H.; Strecker, B.; Hörlin, G.; Jones, W. D. *J. Organomet. Chem.* **1998**, *562*, 45.

(42) See for example: Cadierno, V.; Crochet, P.; Díez, J.; García-Garrido, S. E.; Gimeno, J. *Organometallics* **2004**, *23*, 4836 and references cited therein.

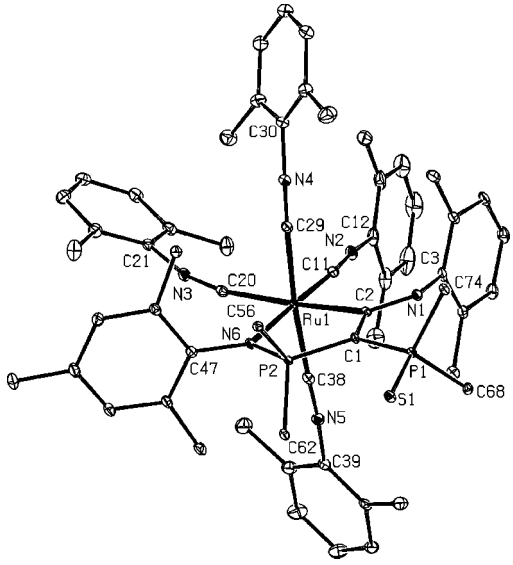
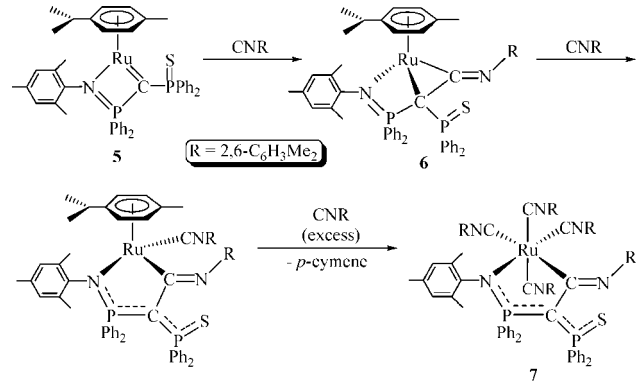


Figure 7. ORTEP-type view of the structure of complex **7** showing the crystallographic labeling scheme. Phenyl groups and hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Selected bond distances (Å) and angles (deg): Ru−N(6) = 2.174(3); Ru−C(2) = 2.148(3); Ru−C(11) = 1.932(4); Ru−C(20) = 2.042(3); Ru−C(29) = 1.991(4); Ru−C(38) = 2.004(4); C(2)−N(1) = 1.297(4); C(11)−N(2) = 1.168(5); C(20)−N(3) = 1.165(4); C(29)−N(4) = 1.158(5); C(38)−N(5) = 1.164(5); C(1)−C(2) = 1.458(4); C(1)−P(1) = 1.761(3); P(1)−S(1) = 1.9865(11); C(1)−P(2) = 1.734(3); P(2)−N(6) = 1.630(3); N(6)−Ru-C(2) = 84.38(11); N(6)−Ru−C(11) = 177.33(12); N(6)−Ru−C(20) = 92.50(11); N(6)−Ru−C(29) = 95.50(12); N(6)−Ru−C(38) = 90.22(12); C(2)−Ru−C(11) = 96.25(13); C(2)−Ru−C(20) = 173.49(13); C(2)−Ru−C(29) = 86.67(13); C(2)−Ru−C(38) = 91.67(13); C(11)−Ru−C(20) = 87.13(13); C(11)−Ru−C(29) = 87.13(14); C(11)−Ru−C(38) = 87.16(14); C(29)−Ru−C(38) = 173.85(14); Ru−C(11)−N(2) = 172.8(3); Ru−C(20)−N(3) = 168.8(3); Ru−C(29)−N(4) = 171.5(3); Ru−C(38)−N(5) = 174.5(3); Ru−C(2)−N(1) = 130.3(2); C(2)−N(1)−C(3) = 128.9(3); Ru−C(2)−C(1) = 114.4(2); N(1)−C(2)−C(1) = 115.2(3); C(2)−C(1)−P(1) = 118.6(2); C(2)−C(1)−P(2) = 119.9(2); P(1)−C(1)−P(2) = 121.22(18); C(1)−P(1)−S(1) = 112.95(11); C(1)−P(2)−N(6) = 105.11(14); P(2)−N(6)−Ru = 162.4(4).

P−C−P distances, i.e., C(1)−P(1) (1.761(3) Å) and C(1)−P(2) (1.734(3) Å), are shorter than those observed in the solid-state structures of the uncoordinated ligands **2f,h** (up to 0.9 Å) and complexes **3f** and **4g** (up to 0.6 Å) (see Figures 5 and 6 and Tables 2 and 3). Electronic delocalization is also reflected in the P(1)−S(1) (1.9865(11) Å) bond length which is ca. 0.3 Å longer than those found in **2f**,**h**. The Ru(1)−C(2) bond length (2.148(3) Å), although longer than that found in related iminoacyl−ruthenium complexes (as an example the Ru−C distance in complex [RuCp{C(CH=CPh$_2$)=NCH=CHMe}(CO)(P^{i}Pr$_3$)] is 2.071 Å),[43] is coherent with the presence of a Ru−C single bond.[39] The observed C(2)−N(1) distance (1.297(4) Å) is typical for a C(sp^2)=N double bond.[30]

NMR data obtained for complex **7** in solution are in complete accord with the structure found in the solid state (details are given in the Experimental Section and Table 1). In particular, no signals for the *p*-cymene ligand are observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **7**, the appearance of characteristic resonances for the coordinated 2,6-dimethylphenyl isocyanides being instead observed, i.e., three singlet resonances are observed at 160.64, 161.18, and 167.01 ppm in the ^{13}C{^{1}H} NMR spectrum, typical of ruthenium-coordinated isocyanide ligands.[42] The ^{13}C{^{1}H} NMR spectrum also displays characteristic doublet of doublets signals for PCP and iminic C=N carbons at 65.52 (dd, $^1J_{CP}$ = 167.4 and 82.4 Hz) and 188.64 (dd, $^2J_{CP}$ = 32.2 and 7.7 Hz) ppm, respectively. The chemical shift observed for the former, strongly downfield shifted when compared to that of the ketenimine intermediate complex **6** (−7.22 ppm), confirms that cleavage of the Ru−CP$_2$ bond has taken place. The remarkably large $^1J_{CP}$ coupling constants observed for this carbon resonance are also in complete accord with the electronic delocalization observed in the solid-state structure of **7**.

Scheme 5. Proposed Pathway for the Transformation of 5 into 7



Although insertion reactions of isocyanides into metal−carbene bonds are well documented,[40] to the best of our knowledge, such reactivity has no precedent in the chemistry of ruthenium. After the initial formation of the ketenimine intermediate **6**, when an excess of isocyanide is present in the reaction medium, a subsequent coordination of a second isocyanide molecule to ruthenium with concomitant cleavage of the Ru−CP$_2$ bond probably takes place. The displacement of the *p*-cymene ligand by the excess of isocyanide gives finally the six-coordinate complex **7** (see Scheme 5).

Conclusions

In summary, in this work novel ruthenium(II) complexes containing mixed (iminophosphoranyl)(thiophosphoranyl)methanide anions, i.e., [Ru{κ^3(*C*,*N*,*S*)-Ph$_2$P(=S)CHP(=NR)Ph$_2$}(η^6-*p*-cymene)][Cl] (**3a**−**f**) and [Ru(κ^3(*C*,*S*,*S*)-Ph$_2$P(=S)CHP{=NP(=S)(OR)$_2$}Ph$_2$)(η^6-*p*-cymene)][Cl] (**4g**,**h**), have been synthesized. They have been prepared through the in situ deprotonation of neutral ligands Ph$_2$P(=S)CH$_2$P(=NR)Ph$_2$ (**2a**−**h**) and subsequent treatment with the dimeric precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$]. Although all these species readily undergo deprotonation of the methynic PCHP unit, only in the case of **3a** could a stable ruthenium carbene, namely [Ru{κ^2(*C*,*N*)-Ph$_2$P(=S)CP(=N-2,4,6-C$_6$H$_2$Me$_3$)Ph$_2$}(η^6-*p*-cymene)] (**5**), be isolated. Apparently, the enhanced nucleophilic nature of the carbenic carbon atom in the rest of the derivatives, which are very prone to undergo a reversible protonation, precludes their isolation. The synthetic utility of the ruthenium−carbene complex **5** could also be demonstrated. Thus, the octahedral complex [Ru{κ^2(*C*,*N*)-Ph$_2$P(S)C(C=N-2,6-C$_6$H$_3$Me$_2$)P(N-2,4,6-C$_6$H$_2$Me$_3$)Ph$_2$}(CN-2,6-C$_6$H$_3$Me$_2$)$_4$] (**7**) bearing an unprecedented Ru−N−P−C−C ruthenacycle has been synthesized in high yield and crystallographically characterized. Its formation

(43) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 5274.

involves the insertion of one isocyanide molecule into the Ru=C bond of **5** and concomitant coordination of four molecules of 2,6-dimethylphenyl isocyanide to the metal via release of the arene ring. This result, in addition to those obtained previously in our laboratory starting from the related derivatives [Ru(κ^2(*C*,*N*)-C[P{=NP(=X)(OR)$_2$}Ph$_2$]$_2$)(η^6-*p*-cymene)] (X = O, S; R = Et, Ph; **E** in Figure 1),[15,18] confirms the utility of these unusual nucleophilic ruthenium carbenes for the construction of complex molecular architectures.

Experimental Section

Synthetic procedures were performed under an atmosphere of dry nitrogen with vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds $Ph_2PCH_2P(=NR)Ph_2$ (R = 2,4,6-$C_6H_2Me_3$ (**1a**),[44] 4-C_6F_4CHO (**1b**),[26f] 4-C_6F_4CN (**1c**),[45] 4-C_5F_4N (**1d**),[45] P(=O)(OEt)$_2$ (**1e**),[26c] P(=O)(OPh)$_2$ (**1f**),[26c] P(=S)(OEt)$_2$ (**1g**),[26d] P(=S)(OPh)$_2$ (**1h**),[26d] and [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$],[46] which were prepared by following the method 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. NMR spectra were recorded on a Bruker DPX300 instrument at 300 (^{1}H), 121.5 (^{31}P), 282.4 (^{19}F), or 75.4 MHz (^{13}C), using $SiMe_4$, $CFCl_3$, or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper.

Synthesis of Ph$_2$P(=S)CH$_2$P(=NR)Ph$_2$ (R = 2,4,6-C$_6$H$_2$Me$_3$ (2a), 4-C$_6$F$_4$CHO (2b), 4-C$_6$F$_4$CN (2c), 4-C$_5$F$_4$N (2d), P(=O)(OEt)$_2$ (2e), P(=O)(OPh)$_2$ (2f), P(=S)(OEt)$_2$ (2g), P(=S)(OPh)$_2$ (2h)). A solution of the corresponding iminophosphorane−phosphine $Ph_2PCH_2P(=NR)Ph_2$ (**1a**−**h**; 2 mmol) in 40 mL of dichloromethane was treated, at room temperature, with S_8 (0.066 g, 0.26 mmol) for 4 h. The solution was then filtered over silica gel and evaporated to dryness. The resulting solid residue was washed with *n*-pentane (3 × 20 mL) and dried in vacuo. **2a:** Yield 89% (0.978 g). Anal. Calcd for $C_{34}H_{33}P_2NS$: C, 74.30; H, 6.05; N, 2.55. Found: C, 74.22; H, 6.11; N, 2.45. IR (KBr, cm^{-1}): ν 476 (w), 507 (m), 525 (w), 598 (w), 691 (s), 735 (vs), 773 (s), 794 (m), 856 (w), 1047 (w), 1102 (m), 1154 (w), 1291 (w), 1352 (s), 1435 (vs), 1478 (vs), 2915 (w), 2931 (w), 2954 (w). ^{1}H NMR ($CDCl_3$): δ 2.04 (s, 6H, CH_3), 2.22 (s, 3H, CH_3), 3.89 (dd, 2H, $^2J_{HP}$ = 13.9 and 13.9 Hz, PCH_2P), 6.75 (br, 2H, CH_{arom}), 7.27–7.44 (m, 12H, CH_{arom}), 7.63–7.87 (m, 8H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.53 and 21.38 (s, CH_3), 34.31 (dd, $^1J_{CP}$ = 48.9 and 43.1 Hz, PCH_2P), 127.69–143.37 (m, C_{arom} and CH_{arom}) ppm. **2b:** Yield 82% (0.996 g). Anal. Calcd for $C_{32}H_{23}F_4P_2NOS$: C, 63.26; H, 3.82; N, 2.31. Found: C, 63.12; H, 3.70; N, 2.40. IR (KBr, cm^{-1}): ν 498 (m), 512 (w), 535 (w), 628 (w), 691 (m), 739 (m), 785 (m), 881 (s), 974 (s), 1038 (w), 1107 (m), 1166 (w), 1225 (vs), 1310 (w), 1397 (s), 1437 (s), 1488 (vs), 1516 (vs), 1637 (s), 1690 (m), 2878 (w), 2936 (w), 3056 (w). ^{1}H NMR ($CDCl_3$): δ 4.06 (dd, 2H, $^2J_{HP}$ = 13.2 and 13.2 Hz, PCH_2P), 7.34–7.57 (m, 12H, CH_{arom}), 7.75–7.86 (m, 8H, CH_{arom}), 10.07 (s, 1H, CHO) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 35.05 (dd, $^1J_{CP}$ = 51.5 and 49.7 Hz, PCH_2P), 103.78 (t, $^2J_{CF}$ = 9.6 Hz, *C*CHO), 128.67–149.95 (m, C_{arom}, CH_{arom}, and CF), 182.98 (s, CHO) ppm. ^{19}F NMR ($CDCl_3$): δ –155.32 and –150.64 (m, 2F each, C_6F_4CHO) ppm. **2c:** Yield 90% (1.088 g). Anal. Calcd for $C_{32}H_{22}F_4N_2P_2S$: C, 63.58; H, 3.67; N, 4.63. Found: C, 63.50; H, 3.55; N, 4.81. IR (KBr, cm^{-1}): ν 479 (w), 509 (m), 535 (w), 611 (w), 620 (w), 688 (s), 739 (m), 781 (s), 792 (m), 873 (m), 980 (s), 999 (m), 1014 (s), 1105 (s), 1153 (m), 1227 (vs), 1310 (w), 1327 (w), 1437 (m), 1513 (vs), 1647 (s), 2218 (m), 2888 (w), 2953 (w), 3054 (w). ^{1}H NMR ($CDCl_3$): δ 4.02 (dd, 2H, $^2J_{HP}$ = 13.3 and 13.3 Hz, PCH_2P), 7.28–7.53 (m, 12H, CH_{arom}), 7.69–7.85 (m, 8H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 34.48 (dd, $^1J_{CP}$ = 47.5 and 47.5 Hz, PCH_2P), 78.10 (t, $^3J_{CF}$ = 15.0, CN), 110.08 (t, $^2J_{CF}$ = 4.5 Hz, *C*CN), 128.22–149.42 (m, C_{arom}, CH_{arom} and CF) ppm; ^{19}F NMR ($CDCl_3$): δ –152.78 and –139.20 (m, 2F each, C_6F_4CN) ppm. **2d:** Yield 87% (1.010 g). Anal. Calcd for $C_{30}H_{22}F_4N_2P_2S$: C, 62.07; H, 3.82; N, 4.83. Found: C, 62.13; H, 3.90; N, 4.94. IR (KBr, cm^{-1}): ν 479 (w), 497 (m), 513 (w), 536 (w), 569 (w), 610 (m), 688 (s), 728 (s), 742 (m), 789 (m), 914 (w), 956 (s), 998 (w), 1026 (w), 1104 (m), 1178 (vs), 1308 (m), 1367 (w), 1436 (s), 1471 (s), 1521 (s), 1581 (w), 1640 (m), 2867 (w), 2951 (w), 3058 (w). ^{1}H NMR ($CDCl_3$): δ 3.98 (dd, 2H, $^2J_{HP}$ = 13.4 and 13.4 Hz, PCH_2P), 7.26–7.52 (m, 12H, CH_{arom}), 7.70–7.83 (m, 8H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 34.32 (dd, $^1J_{CP}$ = 47.5 and 47.5 Hz, PCH_2P), 128.23–145.71 (m, C_{arom}, CH_{arom}, and CF) ppm. ^{19}F NMR ($CDCl_3$): δ –157.28 and –97.78 (m, 2F each, C_5F_4N) ppm. **2e:** Yield 91% (1.033 g). Anal. Calcd for $C_{29}H_{32}O_3P_3NS$: C, 61.37; H, 5.68; N, 2.47. Found: C, 61.29; H, 5.66; N, 2.53. IR (KBr, cm^{-1}): ν 492 (m), 543 (w), 606 (w), 687 (m), 738 (vs), 761 (s), 800 (m), 852 (w), 954 (m), 1000 (w), 1048 (s), 1106 (m), 1167 (w), 1202 (s), 1227 (m), 1265 (m), 1387 (w), 1437 (m), 2901 (w), 2926 (w), 2978 (w), 3053 (w). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 6H, $^3J_{HH}$ = 7.1 Hz, CH_3), 3.95 (m, 4H, OCH_2), 4.43 (dd, 2H, $^2J_{HP}$ = 14.9 and 14.9 Hz, PCH_2P), 7.25–7.40 (m, 12H, CH_{arom}), 7.75–7.86 (m, 8H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.75 (d, $^3J_{CP}$ = 7.8 Hz, CH_3), 33.60 (dd, $^1J_{CP}$ = 51.4 and 46.1 Hz, PCH_2P), 61.94 (d, $^2J_{CP}$ = 6.4 Hz, OCH_2), 128.42–132.84 (m, C_{arom} and CH_{arom}) ppm. **2f:** Yield 88% (1.168 g). Anal. Calcd for $C_{37}H_{32}O_3P_3NS$: C, 66.96; H, 4.86; N, 2.11. Found: C, 66.79; H, 4.99; N, 2.29. IR (KBr, cm^{-1}): ν 497 (w), 510 (m), 526 (w), 581 (m), 606 (m), 688 (m), 732 (m), 774 (s), 797 (m), 820 (w), 921 (m), 927 (m), 1007 (w), 1024 (w), 1071 (m), 1109 (m), 1203 (vs), 1303 (s), 1437 (m), 1453 (w), 1486 (m), 1588 (m), 2877 (w), 2936 (w), 3055 (w). ^{1}H NMR ($CDCl_3$): δ 4.32 (dd, 2H, $^2J_{HP}$ = 14.6 and 14.6 Hz, PCH_2P), 7.07–7.43 (m, 18H, CH_{arom}), 7.66–7.83 (m, 12H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 33.39 (dd, $^1J_{CP}$ = 51.1 and 46.1 Hz, PCH_2P), 120.64–132.39 (m, C_{arom} and CH_{arom}), 152.02 (d, $^2J_{CP}$ = 7.1 Hz, C_{ipso} of OPh) ppm. **2g:** Yield 79% (0.922 g). Anal. Calcd for $C_{29}H_{32}P_3O_2S_2N$: C, 59.68; H, 5.53; N, 2.40. Found: C, 59.62; H, 5.60; N, 2.51. IR (KBr, cm^{-1}): ν 477 (w), 492 (m), 510 (w), 537 (w), 619 (m), 670 (w), 688 (m), 737 (s), 763 (m), 801 (m), 835 (m), 948 (m), 1031 (s), 1044 (s), 1109 (m), 1179 (w), 1284 (vs), 1361 (w), 1387 (w), 1439 (m), 1481 (w), 2820 (w), 2916 (w), 2971 (w), 3055 (w). ^{1}H NMR ($CDCl_3$): δ 1.22 (t, 6H, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.01 (m, 4H, OCH_2), 4.78 (dd, 2H, $^2J_{HP}$ = 15.4 and 15.4 Hz, PCH_2P), 7.24–7.43 (m, 12H, CH_{arom}), 7.77–7.89 (m, 8H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.04 (d, $^3J_{CP}$ = 8.7 Hz, CH_3), 30.55 (dd, $^1J_{CP}$ = 53.0 and 46.0 Hz, PCH_2P), 61.98 (d, $^2J_{CP}$ = 6.4 Hz, OCH_2), 127.91–132.56 (m, C_{arom} and CH_{arom}) ppm. **2h:** Yield 85% (1.155 g). Anal. Calcd for $C_{37}H_{32}P_3O_2S_2N$: C, 65.38; H, 4.75; N, 2.06. Found: C, 65.24; H, 4.69; N, 2.14. IR (KBr, cm^{-1}): ν 479 (w), 500 (m), 537 (w), 610 (w), 691 (m), 769 (s), 778 (s), 837 (m), 891 (s), 916 (m), 1026 (w), 1118 (w), 1159 (m), 1200 (vs), 1290 (w), 1299 (m), 1437 (m), 1487 (m), 1592 (m), 2862 (w), 2910 (w), 3053 (w). ^{1}H NMR ($CDCl_3$): δ 4.55 (dd, 2H, $^2J_{HP}$ = 14.7 and 14.7 Hz, PCH_2P), 7.15–7.46 (m, 18H, CH_{arom}), 7.72–7.83 (m, 12H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.31 (dd, $^1J_{CP}$ = 53.0 and 45.6 Hz, PCH_2P), 122.24–133.19 (m, C_{arom} and CH_{arom}), 152.33 (d, $^2J_{CP}$ = 9.0 Hz, C_{ipso} of OPh) ppm.

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Synthesis of [Ru{κ^3(*C*,*N*,*S*)-$Ph_2P(=S)CHP(=NR)Ph_2$}(η^6-*p*-cymene)][Cl] (R = 2,4,6-$C_6H_2Me_3$ (3a), 4-C_6F_4CHO (3b), 4-C_6F_4CN (3c), 4-C_5F_4N (3d), $P(=O)(OEt)_2$ (3e), $P(=O)(OPh)_2$ (3f)). A solution of the corresponding (iminophosphoranyl)(thiophosphoranyl)methane ligand **2a−f** (1 mmol) in 30 mL of THF was treated, at −20 °C, with Li^{n}Bu (0.625 mL of a 1.6 M solution in hexanes, 1 mmol) for 30 min. A solution of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.306 g, 0.5 mmol) in 10 mL of THF was then added and the reaction mixture was stirred at room temperature for 1 h. The solvent was then removed under vacuum, the crude product extracted with dichloromethane (ca. 30 mL), and the extract filtered over Kieselguhr. Concentration of the resulting solution (ca. 5 mL) followed by the addition of hexanes (ca. 50 mL) precipitated an orange solid, which was filtered, washed with diethyl ether (3 × 10 mL), and dried in vacuo. **3a:** Yield 79% (0.647 g). Anal. Calcd for $RuC_{44}H_{46}P_2ClNS$: C, 64.50; H, 5.66; N, 1.71. Found: C, 64.39; H, 5.70; N 1.82. Conductivity (acetone, 20 °C): 119 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 488 (w), 503 (m), 525 (s), 544 (m), 590 (m), 606 (w), 669 (w), 705 (s), 747 (s), 803 (w), 858 (w), 999 (w), 1107 (s), 1158 (w), 1256 (m), 1306 (w), 1387 (w), 1436 (vs), 1473 (m), 2927 (w), 2958 (w), 3051 (w). ^{1}H NMR (CD_2Cl_2): δ 1.04 and 1.25 (d, 3H each, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.42, 2.23, 2.29, and 2.86 (s, 3H each, CH_3), 2.37 (m, 1H, CH(CH$_3$)$_2$), 3.95 (br, 1H, PCHP), 4.22 and 5.13 (d, 1H each, $^3J_{HH}$ = 5.9 Hz, CH of *p*-cymene), 4.58 and 4.92 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 6.69–8.65 (m, 22H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –23.51 (dd, $^1J_{CP}$ = 87.0 and 50.1 Hz, PCHP), 20.06, 20.42, 20.69, 22.79, 23.56, and 23.74 (s, CH_3), 31.33 (s, *C*H(CH$_3$)$_2$), 79.66, 80.59, 81.65, and 86.43 (s, CH of *p*-cymene), 97.72 and 107.07 (s, C of *p*-cymene), 127.70–141.82 (m, C_{arom} and CH_{arom}) ppm. **3b:** Yield 73% (0.640 g). Anal. Calcd for $RuC_{42}H_{36}F_4P_2ClNOS$: C, 57.50; H, 4.14; N, 1.60. Found: C, 57.32; H, 4.21; N 1.72. Conductivity (acetone, 20 °C): 111 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 497 (w), 508 (m), 538 (w), 603 (w), 692 (m), 740 (m), 804 (w), 877 (w), 973 (m), 1030 (m), 1106 (s), 1197 (s), 1223 (m), 1397 (s), 1438 (s), 1488 (vs), 1517 (m), 1637 (s), 1690 (m), 2929 (w), 2964 (w), 3055 (w). ^{1}H NMR (CD_2Cl_2): δ 1.01 and 1.22 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.51 (s, 3H, CH_3), 2.35 (m, 1H, CH(CH$_3$)$_2$), 4.16 (dd, 1H, $^2J_{HP}$ = 13.1 and 13.1 Hz, PCHP), 4.59 and 5.37 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 4.95 (br, 2H, CH of *p*-cymene), 6.86–8.64 (m, 20H, CH_{arom}), 10.04 (s, 1H, CHO) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –18.86 (dd, $^1J_{CP}$ = 81.4 and 50.9 Hz, PCHP), 18.40 (s, CH_3), 22.72 and 23.86 (s, CH(*C*H$_3$)$_2$), 31.78 (s, *C*H(CH$_3$)$_2$), 80.66, 81.82, 82.91, and 83.99 (s, CH of *p*-cymene), 99.92 and 110.87 (s, C of *p*-cymene), 106.12 (t, $^2J_{CF}$ = 5.5 Hz, *C*CHO), 127.63–149.98 (m, C_{arom}, CH_{arom} and CF), 182.18 (s, CHO) ppm. ^{19}F NMR (CD_2Cl_2): δ –155.48, −151.24, −148.03 and −147.60 (m, 1F each, C_6F_4CHO) ppm. **3c:** Yield 75% (0.656 g). Anal. Calcd for $RuC_{42}H_{35}F_4N_2P_2ClS$: C, 57.70; H, 4.04; N, 3.20. Found: C, 57.61; H, 4.12; N 3.11. Conductivity (acetone, 20 °C): 122 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 498 (w), 509 (m), 533 (w), 603 (w), 691 (m), 740 (m), 792 (w), 874 (w), 981 (m), 990 (m), 1105 (s), 1189 (s), 1225 (m), 1387 (w), 1437 (s), 1498 (vs), 1645 (m), 2234 (m), 2879 (w), 2961 (w), 3051 (w). ^{1}H NMR (CD_2Cl_2): δ 1.05 and 1.23 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.47 (s, 3H, CH_3), 2.39 (m, 1H, CH(CH$_3$)$_2$), 4.09 (dd, 1H, $^2J_{HP}$ = 13.4 and 13.4 Hz, PCHP), 4.53 and 4.96 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 5.13 and 5.37 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 6.84–8.55 (m, 20H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –18.84 (dd, $^1J_{CP}$ = 81.8 and 51.3 Hz, PCHP), 18.36 (s, CH_3), 22.49 and 23.94 (s, CH(*C*H$_3$)$_2$), 31.81 (s, *C*H(CH$_3$)$_2$), 80.31 (t, $^3J_{CF}$ = 12.9, CN), 80.62, 81.63, 82.93, and 84.12 (s, CH of *p*-cymene), 100.00 and 110.95 (s, C of *p*-cymene), 109.04 (t, $^2J_{CF}$ = 2.6 Hz, *C*CN), 127.49–143.48 (m, C_{arom}, CH_{arom}, and CF) ppm. ^{19}F NMR (CD_2Cl_2): δ –152.98, –145.51, –139.97, and –136.28 (m, 1F each, C_6F_4CN) ppm. **3d:** Yield 70% (0.595 g). Anal. Calcd for $RuC_{40}H_{35}F_4N_2P_2ClS$: C, 56.50; H, 4.15; N, 3.29. Found: C, 56.36; H, 4.23; N 3.35. Conductivity (acetone, 20 °C): 117 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 503 (w), 517 (m), 539 (w), 620 (w), 709 (m), 740 (m), 779 (w), 916 (w), 956 (m), 977 (m), 1105 (s), 1153 (vs), 1178 (s), 1310 (w), 1438 (s), 1471 (s), 1495 (s), 1522 (m), 1637 (s), 2929 (w), 2963 (w), 3054 (w). ^{1}H NMR (CD_2Cl_2): δ 1.10 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.34 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(CH_3)$_2$), 1.52 (s, 3H, CH_3), 2.43 (m, 1H, CH(CH$_3$)$_2$), 4.28 (dd, 1H, $^2J_{HP}$ = 13.2 and 13.2 Hz, PCHP), 4.56 and 5.18 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.02 and 5.41 (d, 1H each, $^3J_{HH}$ = 5.1 Hz, CH of *p*-cymene), 6.91–8.65 (m, 20H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –19.04 (dd, $^1J_{CP}$ = 81.2 and 50.9 Hz, PCHP), 18.37 (s, CH_3), 22.65 and 24.01 (s, CH(*C*H$_3$)$_2$), 31.81 (s, *C*H(CH$_3$)$_2$), 80.45, 81.74, 82.98, and 84.21 (s, CH of *p*-cymene), 100.09 and 111.09 (s, C of *p*-cymene), 127.51–146.70 (m, C_{arom}, CH_{arom}, and CF) ppm. ^{19}F NMR (CD_2Cl_2): δ −157.21, −150.00, −98.51, and −94.71 (m, 1F each, C_6F_4CN) ppm. **3e:** Yield 81% (0.678 g). Anal. Calcd for $RuC_{39}H_{45}O_3P_3ClNS$: C, 55.94; H, 5.42; N, 1.67. Found: C, 55.75; H, 5.51; N 1.83. Conductivity (acetone, 20 °C): 120 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 481 (w), 505 (m), 522 (m), 539 (w), 601 (m), 619 (w), 706 (m), 740 (s), 800 (m), 961 (w), 1047 (vs), 1104 (s), 1158 (m), 1236 (w), 1320 (w), 1387 (w), 1436 (m), 1472 (w), 2865 (w), 2924 (w), 2962 (w), 3050 (w). ^{1}H NMR (CD_2Cl_2): δ 1.15 (t, 3H, $^3J_{HH}$ = 6.9 Hz, OCH_2CH_3), 1.19 (t, 3H, $^3J_{HH}$ = 7.2 Hz, OCH_2CH_3), 1.29 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH(CH_3)$_2$), 1.36 (d, 3H, $^3J_{HH}$ = 7.1 Hz, CH(CH_3)$_2$), 1.68 (s, 3H, CH_3), 2.76 (m, 1H, CH(CH$_3$)$_2$), 3.87–4.21 (m, 5H, OCH_2 and PCHP), 4.62 and 5.44 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 4.97 and 5.62 (d, 1H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene),6.93–8.60 (m, 20H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –23.68 (ddd, $^1J_{CP}$ = 83.8 and 57.9 Hz, $^3J_{CP}$ = 15.5 Hz, PCHP), 16.32 (d, $^3J_{CP}$ = 8.1 Hz, OCH_2CH_3), 16.60 (d, $^3J_{CP}$ = 7.4 Hz, OCH_2CH_3), 18.90 (s, CH_3), 22.52 and 23.49 (s, CH(*C*H$_3$)$_2$), 31.89 (s, *C*H(CH$_3$)$_2$), 62.78 (d, $^2J_{CP}$ = 5.1 Hz, OCH_2), 63.19 (d, $^2J_{CP}$ = 5.9 Hz, OCH_2), 80.63, 82.03, 83.77, and 83.98 (s, CH of *p*-cymene), 97.87 and 110.54 (s, C of *p*-cymene), 127.58–136.24 (m, C_{arom} and CH_{arom}) ppm. **3f:** Yield 74% (0.690 g). Anal. Calcd for $RuC_{47}H_{45}O_3P_3ClNS$: C, 60.48; H, 4.86; N, 1.50. Found: C, 60.23; H, 4.75; N 1.66. Conductivity (acetone, 20 °C): 113 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 490 (w), 541 (m), 687 (m), 623 (w), 691 (m), 728 (w), 743 (m), 773 (w), 853 (w), 899 (s), 918 (s), 933 (m), 1026 (w), 1105 (m), 1160 (m), 1199 (vs), 1242 (m), 1284 (w), 1436 (m), 1487 (m), 1590 (m), 2855 (w), 2926 (w), 2960 (w), 3050 (w). ^{1}H NMR (CD_2Cl_2): δ 1.08 and 1.20 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.73 (s, 3H, CH_3), 2.71 (m, 1H, CH(CH$_3$)$_2$), 3.94 (br, 1H, PCHP), 4.59 (d, 1H, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 4.95 (br, 2H, CH of *p*-cymene), 5.68 (d, 1H, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.89–8.91 (m, 30H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –24.11 (ddd, $^1J_{CP}$ = 82.5 and 57.1 Hz, $^3J_{CP}$ = 16.1 Hz, PCHP), 18.99 (s, CH_3), 22.39 and 23.42 (s, CH(*C*H$_3$)$_2$), 31.83 (s, *C*H(CH$_3$)$_2$), 80.29, 82.35, 83.61, and 84.11 (s, CH of *p*-cymene), 98.46 and 110.63 (s, C of *p*-cymene), 120.67–136.52 (m, C_{arom} and CH_{arom}), 151.42 and 151.99 (d, $^2J_{CP}$ = 7.6 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru(κ^3(*C*,*S*,*S*)-$Ph_2P(=S)CHP\{=NP(=S)(OR)_2\}$-$Ph_2$)($\eta^6$-*p*-cymene)][Cl] (R = Et (4g), Ph (4h)). Complexes **4g**,**h**, isolated as orange solids, were prepared as described for **3a−f** starting from the appropriate (iminophosphoranyl)(thiophosphoranyl)methane ligand **2g**,**h** (1 mmol) and [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.306 g, 0.5 mmol). **4g:** Yield 77% (0.657 g). Anal. Calcd for $RuC_{39}H_{45}P_3O_2S_2ClN$: C, 54.89; H, 5.32; N, 1.64. Found: C, 54.68; H, 5.43; N 1.80. Conductivity (acetone, 20 °C): 123 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 476 (w), 494 (w), 543 (s), 556 (m), 603 (s), 619 (w), 699 (s), 725 (m), 749 (s), 798 (w), 833 (m), 880 (m), 955 (s), 1037 (vs), 1099 (m), 1156 (w), 1243 (s), 1388 (w), 1436 (m), 2899 (w), 2972 (w), 3049 (w). ^{1}H NMR (CD_2Cl_2): δ 0.81 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 0.86 (d, 3H,

$^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.23 (s, 3H, CH_3), 1.43 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH_3), 1.52 (t, 3H, $^3J_{HH}$ = 6.8 Hz, OCH$_2$CH_3), 1.67 (m, 1H, CH(CH$_3$)$_2$), 4.04–4.35 (m, 4H, OCH$_2$), 5.18 and 5.74 (br, 2H each, CH of *p*-cymene), 5.58 (dd, 1H, $^2J_{HP}$ = 5.6 and 5.6 Hz, PCHP), 6.85–8.80 (m, 20H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –12.59 (ddd, $^1J_{CP}$ = 54.3 and 27.6 Hz, $^3J_{CP}$ = 2.1 Hz, PCHP), 15.95 (d, $^3J_{CP}$ = 9.7 Hz, OCH$_2$CH_3), 16.57 (d, $^3J_{CP}$ = 7.6 Hz, OCH$_2$CH_3), 17.27 (s, CH_3), 21.34 and 23.73 (s, CH(CH_3)$_2$), 30.49 (s, CH(CH$_3$)$_2$), 62.83 (d, $^2J_{CP}$ = 7.6 Hz, OCH$_2$), 63.50 (d, $^2J_{CP}$ = 5.6 Hz, OCH$_2$), 83.01, 84.16, 86.46 and 87.92 (s, CH of *p*-cymene), 98.17 and 108.50 (s, C of *p*-cymene), 127.63–135.14 (m, C_{arom} and CH_{arom}) ppm. **4h:** Yield 75% (0.712 g). Anal. Calcd for $RuC_{47}H_{45}P_3O_2S_2ClN$: C, 59.46; H, 4.78; N, 1.48. Found: C, 59.77; H, 4.69; N 1.57. Conductivity (acetone, 20 °C): 118 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. IR (KBr, cm^{-1}): ν 499 (w), 544 (m), 603 (m), 669 (w), 689 (s), 733 (m), 758 (m), 825 (w), 884 (m), 920 (m), 1026 (w), 1110 (m), 1161 (s), 1190 (vs), 1260 (w), 1437 (m), 1489 (s), 1590 (w), 2936 (w), 2959 (w), 3049 (w). ^{1}H NMR ($CDCl_3$): δ 0.77 and 0.86 (d, 3H each, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.23 (s, 3H, CH_3), 1.62 (m, 1H, CH(CH$_3$)$_2$), 5.22 and 5.91 (d, 2H each, $^3J_{HH}$ = 5.7 Hz, CH of *p*-cymene), 5.82 (dd, 1H, $^2J_{HP}$ = 7.4 and 4.3 Hz, PCHP), 6.49–8.88 (m, 30H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ –12.90 (ddd, $^1J_{CP}$ = 54.8 and 27.7 Hz, $^3J_{CP}$ = 2.7 Hz, PCHP), 16.91 (s, CH_3), 20.97 and 23.45 (s, CH(CH_3)$_2$), 30.08 (s, CH(CH$_3$)$_2$), 82.71, 83.66, 86.63, and 87.57 (s, CH of *p*-cymene), 97.82 and 108.32 (s, C of *p*-cymene), 120.43–134.53 (m, C_{arom} and CH_{arom}), 150.94 (d, $^2J_{CP}$ = 9.7 Hz, C_{ipso} of OPh), 151.82 (d, $^2J_{CP}$ = 10.4 Hz, C_{ipso} of OPh) ppm.

Synthesis of [Ru{κ^2(*C*,*N*)-Ph$_2$P(=S)CP(=N-2,4,6-C$_6$H$_2$Me$_3$)-Ph$_2$}(η^6-*p*-cymene)] (5). A solution of complex **3a** (0.410 g, 0.5 mmol) in 25 mL of THF was treated, at room temperature, with NaH (0.120 g, 5 mmol) for 4 h. The solvent was then removed under vacuum, the crude product extracted with diethyl ether (ca. 60 mL), and the extract filtered over Kieselguhr. Concentration of the resulting solution (ca. 5 mL) followed by the addition of hexanes (ca. 30 mL) precipitated a violet solid, which was filtered, washed with hexanes (2 × 5 mL), and dried in vacuo. Yield 82% (0.320 g). Anal. Calcd for $RuC_{44}H_{45}P_2NS$: C, 67.50; H, 5.79; N, 1.79. Found: C, 67.33; H, 5.87; N 1.93. IR (KBr, cm^{-1}): ν 498 (m), 527 (m), 551 (w), 613 (w), 637 (w), 692 (s), 738 (s), 786 (m), 852 (w), 997 (w), 1027 (w), 1098 (s), 1185 (w), 1262 (m), 1308 (w), 1435 (s), 1474 (m), 2872 (w), 2906 (w), 2958 (w), 3050 (w). ^{1}H NMR (C_6D_6): δ 1.24 (d, 6H, $^3J_{HH}$ = 7.1 Hz, CH(CH_3)$_2$), 1.98 (s, 6H, CH_3), 2.19 and 2.21 (s, 3H each, CH_3), 2.59 (sept, 1H, $^3J_{HH}$ = 7.1 Hz, CH(CH$_3$)$_2$), 4.59 and 4.73 (d, 2H each, $^3J_{HH}$ = 5.8 Hz, CH of *p*-cymene), 6.82–8.25 (m, 22H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 19.99, 20.62, 20.93, and 24.12 (s, CH_3), 32.30 (s, CH(CH$_3$)$_2$), 78.62 and 79.44 (s, CH of *p*-cymene), 85.92 and 97.73 (s, C of *p*-cymene), 124.98 (dd, $^1J_{CP}$ = 73.4 and 69.4 Hz, PCP), 127.36–145.11 (m, C_{arom} and CH_{arom}) ppm.

Synthesis of [Ru{κ^3(*C*,*C*,*N*)-Ph$_2$P(=S)C(C=N-2,6-C$_6$H$_3$Me$_2$)P(=N-2,4,6-C$_6$H$_2$Me$_3$)Ph$_2$}(η^6-*p*-cymene)] (6). A solution of carbene complex **5** (0.235 g, 0.3 mmol) in 15 mL of THF was treated, at room temperature, with 2,6-dimethylphenyl isocyanide (0.040 g, 0.3 mmol) for 10 min. The solvent was then removed in vacuo and the resulting oily residue dissolved in dichloromethane (ca. 3 mL). Addition of hexanes (ca. 50 mL) precipitated a yellow solid, which was washed with hexanes (2 × 10 mL) and dried in vacuo. Yield 77% (0.211 g). Anal. Calcd for $RuC_{53}H_{54}N_2P_2S$: C, 69.64; H, 5.95; N, 3.06. Found: C, 69.48; H, 6.09; N 3.21. IR (KBr, cm^{-1}): ν 488 (w), 521 (m), 547 (w), 669 (w), 694 (s), 723 (s), 742 (m), 774 (m), 864 (m), 969 (w), 1010 (m), 1033 (w), 1105 (s), 1205 (w), 1254 (m), 1308 (w), 1354 (w), 1436 (s), 1474 (m), 1600 (m), 1647 (m), 2915 (w), 2959 (w), 3052 (w). ^{1}H NMR (C_6D_6): δ 0.96 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.15 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH(CH_3)$_2$), 1.78, 2.12, 2.19, 2.33, 2.42, and 2.51 (s, 3H each, CH_3), 3.01 (m, 1H, CH(CH$_3$)$_2$), 4.21 and 5.60 (d, 1H each, $^3J_{HH}$ = 5.3 Hz, CH of *p*-cymene), 4.91 and 5.20 (d, 1H each, $^3J_{HH}$ = 5.5 Hz, CH of *p*-cymene), 6.87–8.45 (m, 25H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ –7.22 (dd, $^1J_{CP}$ = 93.1 and 59.5 Hz, PCP), 18.50, 20.28, 20.86, 22.17, 22.38, 23.18, 23.44, and 24.62 (s, CH_3), 30.35 (s, CH(CH$_3$)$_2$), 77.75, 82.57, 83.13, and 87.09 (s, CH of *p*-cymene), 100.53 and 109.66 (s, C of *p*-cymene), 126.99–152.01 (m, C_{arom} and CH_{arom}), 189.84 (d, $^2J_{CP}$ = 3.9 Hz, Ru-CN) ppm.

Synthesis of [Ru{κ^2(*C*,*N*)-Ph$_2$P(=S)C(C=N-2,6-C$_6$H$_3$Me$_2$)P(N-2,4,6-C$_6$H$_2$Me$_3$)Ph$_2$}(CN-2,6-C$_6$H$_3$Me$_2$)$_4$] (7). Method A. A solution of carbene complex **5** (0.235 g, 0.3 mmol) in 15 mL of THF was treated, at room temperature, with 2,6-dimethylphenyl isocyanide (0.400 g, 3 mmol) for 1 h. The solvent was then removed in vacuo and the resulting oily residue dissolved in dichloromethane (ca. 3 mL). Addition of hexanes (ca. 50 mL) precipitated a yellow solid, which was washed with hexanes (5 × 10 mL) and dried in vacuo. Yield 75% (0.293 g). Anal. Calcd for $RuC_{79}H_{76}N_6P_2S$: C, 72.73; H, 5.87; N, 6.44. Found: C, 72.49; H, 6.01; N 6.32. IR (KBr, cm^{-1}): ν 485 (w), 529 (w), 555 (w), 601 (m), 668 (w), 692 (m), 732 (m), 769 (w), 805 (w), 976 (w), 1031 (m), 1061 (s), 1087 (s), 1113 (s), 1156 (w), 1216 (m), 1263 (w), 1436 (m), 1472 (m), 1521 (s), 2088 (vs), 2151 (m), 2918 (w), 3008 (w), 3048 (w). ^{1}H NMR (C_6D_6): δ 1.55, 1.76, 1.94, and 2.27 (s, 6H each, CH_3), 2.06 (s, 3H, CH_3), 2.43 (s, 12H, CH_3), 6.49–8.53 (m, 37H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 18.08, 18.61, 19.51, 20.69, 20.74, and 20.94 (s, CH_3), 65.52 (dd, $^1J_{CP}$ = 167.4 and 82.4 Hz, PCP), 126.28–155.56 (m, C_{arom} and CH_{arom}), 160.64, 161.18, and 167.01 (s, Ru−CN), 188.64 (dd, $^2J_{CP}$ = 32.2 and 7.7 Hz, Ru−CN) ppm.

Method B. A solution of the ketenimine complex **6** (0.183 g, 0.2 mmol) in 5 mL of THF was treated, at room temperature, with 2,6-dimethylphenyl isocyanide (0.262 g, 2 mmol) for 1 h. Workup as described in method A allows the isolation of complex **7** in 79% (0.206 g) yield.

X-ray Crystal Structure Determination of Complexes 2f, 2h, 3f, 4g, and 7. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into saturated solutions of appropriate compound in dichloromethane. The most relevant crystal and refinement data are collected in Table 4. For **2f** and **2h** diffraction data were recorded on a Nonius KappaCCD single-crystal diffractometer, using Cu Kα radiation with the crystal-to-detector distance fixed at 29 mm, using the oscillation method, with 2° oscillation and 120 s exposure time per frame. The data collection strategy was calculated with the program Collect.[47] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[48] Absorption correction was applied by means of SORTAV.[49] For **3f**, **4g**, and **7** data collection was performed on a Bruker SMART 6K CCD area-detector three-circle diffractometer (Cu Kα radiation) with a combination of three runs at different φ and 2θ angles. The data were collected with use of 0.3° wide ω scans with a crystal-to-detector distance of 40 mm. The diffraction frames were integrated with use of the SAINT package,[50] and corrected for absorption with SADABS.[51]

In all cases, the software package WINGX was used for space group determination, structure solution, and refinement.[52] The structures were solved by Patterson interpretation and phase expansion by using DIRDIF.[53] Isotropic least-squares refinement on F^2 with SHELXL97 was performed.[54] During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined, with the exception of several atoms of the phosphoryl P(=O)(OPh)$_2$ group in **3f** (they were found to be disordered over two different positions

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Table 4. Crystal Data and Structure Refinement Details for Compounds 2f, 2h, 3f, 4g, and 7

	2f	2h	3f	4g	7
chemical formula	$C_{37}H_{32}O_3P_3NS$	$C_{37}H_{32}P_3O_2S_2N$	$RuC_{47}H_{45}F_6O_3P_3NSSb$	$RuC_{39}H_{45}F_6P_3O_2S_2NSb$	$RuC_{79}H_{76}N_6P_2S \cdot 2CH_2Cl_2$
fw	663.61	679.67	1133.63	1053.61	1474.38
T (K)	293(2)	200(2)	293(2)	297(2)	100(2)
wavelength (Å)	1.5418	1.5418	1.5418	1.5418	1.5418
cryst syst	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
space group	$Pca2_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
cryst size, mm^3	0.35 × 0.27 × 0.15	0.45 × 0.275 × 0.05	0.25 × 0.20 × 0.08	0.09 × 0.08 × 0.05	0.22 × 0.19 × 0.05
a, Å	16.15480(10)	9.7483(10)	20.0192(2)	11.3019(2)	13.2605(2)
b, Å	9.25410(10)	13.3566(10)	12.3803(2)	12.3320(2)	31.3082(3)
c, Å	22.0546(2)	13.8758(12)	20.9031(2)	16.0514(3)	17.3833(2)
α, deg	90	87.933(6)	90	97.0420(10)	90
β, deg	90	82.946(6)	115.9120(10)	95.0580(10)	91.2410(10)
γ, deg	90	72.760(5)	90	90.7310(10)	90
Z	4	2	4	2	4
V, $Å^3$	3297.12(5)	1712.5(3)	4695.86(10)	2211.01(7)	7215.20(15)
ρ_{calcd}, g cm^{-3}	1.337	1.318	1.616	1.583	1.357
μ, mm^{-1}	2.553	3.003	9.179	10.030	4.189
F(000)	1384	708	2272	1056	3064
θ range, deg	5.48 to 70.07	6.07 to 65.09	2.55 to 70.61	2.79 to 70.63	2.82 to 68.26
index ranges	$-19 \le h \le 19$, $-11 \le k \le 11$, $-26 \le l \le 26$	$-11 \le h \le 11$, $-14 \le k \le 15$, $-16 \le l \le 16$	$-24 \le h \le 24$, $-14 \le k \le 14$, $-20 \le l \le 25$	$-13 \le h \le 11$, $-14 \le k \le 14$, $-19 \le l \le 19$	$-15 \le h \le 15$, $-37 \le k \le 37$, $-20 \le l \le 20$
completeness to θ_{max}	99.0%	96.9%	95.4%	92.4%	97.7%
no. of data collected	23196	34979	28909	20114	52956
no. of unique data	5795 (R_{int} = 0.0410)	5665 (R_{int} = 0.0700)	8540 (R_{int} = 0.0548)	7828 (R_{int} = 0.0353)	12905 (R_{int} = 0.0820)
no. of params/restraints	406/1	406/0	562/38	501/0	889/0
refinement method	full-matrix least squares on F^2				
goodness of fit on F^2	1.033	1.035	1.015	1.048	0.999
weight function (a, b)	0.467, 0.6101	0.1187, 0.2655	0.821, 25.8365	0.0745, 0.8229	0.0663, 0.000
R1[a] [$I > 2\sigma(I)$]	0.0322	0.0608	0.0609	0.0415	0.0440
wR2[a] [$I > 2\sigma(I)$]	0.0842	0.1615	0.1586	0.1164	0.1048
R1 (all data)	0.0334	0.0669	0.0704	0.0461	0.0686
wR2 (all data)	0.0852	0.1744	0.1684	0.1216	0.1181
largest diff peak and hole, e $Å^{-3}$	0.173 and −0.255	0.660 and −0.657	2.433 and −2.364	1.035 and −0.745	0.897 and −0.727

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

and isotropically refined). The H atoms were geometrically located and their coordinates were refined riding on their parent atoms. For **3f** the maximum residual electron density is located near the disordered atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are shown in Table 4) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}\ (F_o^2,0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[55] Geometrical calculations were made with PARST.[56] The crystallographic plots were made with PLATON.[57]

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Supporting Information Available: CIF file giving crystallographic data for compounds **2f**, **2h**, **3f**, **4g**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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