Iminophosphorane-Based Nucleophilic Ruthenium(II) Carbene Complexes: Unusual C−C Coupling and C−H Activation Promoted by the Addition of Alkynes to the Ru═C 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

Received February 18, 2005

Treatment of the nucleophilic carbene complexes [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{═NP(═O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) with an excess of terminal alkynes HC≡CR′ (R′ = Ph, *p*-Tol, CPh$_2$(OH), CHPh(OH), C_6H_9, C(Me)═CH$_2$), in THF at room temperature, results in the chemo- and stereoselective formation of complexes **3a**−**f** and **4a**−**f**, via coupling of the carbenic Ru═C carbon with the C≡C triple bond of the alkyne and concomitant phenyl ortho metalation. Under the same reaction conditions the carbene derivative [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{═NP(═O)(OEt)$_2$}Ph$_2$][P{═NP(═O)(OPh)$_2$}Ph$_2$])] (**5**) reacts with phenylacetylene to afford a nonseparable mixture of the complexes **6** and **7** resulting from the ortho metalation of both *N*-phosphoryl iminophosphoranyl fragments −Ph$_2$P═NP(═O)(OR)$_2$ (R = Et, Ph). The structure of complex **3c** has been unambiguously confirmed by a single-crystal X-ray diffraction study. The reaction of complex **1** with deuterated phenylacetylene suggests that these C−C coupling processes involve transient (η^2-alkyne)−Ru(II) species rather than their η^1-vinylidene tautomers [Ru]═C═CHR′. Protonation of complexes **3a** and **4a** with HBF$_4$ generates the cationic derivatives [Ru(η^6-*p*-cymene)(κ^4(*C,C,C,N*)-C[P{═NP(═O)(OR)$_2$}Ph$_2$]$_2$-{(*E*)-C(H)═C(H)Ph})][BF$_4$] (R = Et (**8**), Ph (**9**)) via selective cleavage of the Ru−C$_{aryl}$ bond in **3a** and **4a**.

Introduction

Since the discovery by Fischer and Maasböl of the first transition-metal carbene complexes in 1964,[1] the chemistry of this class of compounds has spectacularly blossomed over the past few decades. In fact, nowadays, novel transition-metal carbene derivatives and their reactivity patterns are among the most important goals in organometallic chemistry, mainly due to the wealth of their applications in both stoichiometric and catalytic organic synthesis.[2] In this context, Cavell and coworkers have demonstrated the usefulness of bis(iminophosphorano)methane ligands CH$_2${P(═NSiMe$_3$)R$_2$}$_2$ (R = Ph, Me, Cy) as precursors of a large variety of unique "pincer" (**A**; known for Ti, Zr, Hf, Sm, and Mo)[3] or bridged (**B**; known for Cr, Al, Pb, and Sn)[4] carbene complexes (see Chart 1), via double deprotonation of the methylenic backbone.[5] Recently, Cavell's group and our group have extended this synthetic methodology to electron-rich metals, giving rise to the isolation of the first iminophosphorane-based platinum (**C**)[6] and ruthenium (**D**)[7] carbene complexes (see Chart 1). In contrast to the "pincer" (**A**) and bridged (**B**) species, the carbene moiety in complexes **C** and **D** is included into a single four-membered metallacycle as the result of the selec-

---

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

[1] Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

[2] See for example: (a) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (b) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187. (c) Zaragoza Dörwald, F. In *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999. (d) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (e) *J. Organomet. Chem.* **2001**, *617–618*, 1−754 (special issue on transition-metal carbene complexes). (f) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (g) Barluenga, J.; Flórez, J.; Fañanas, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (h) Guerchais, V. *Eur. J. Inorg. Chem.* **2002**, 783. (i) *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*; Bertrand, G., Ed.; Marcel Dekker: New York, 2002. (j) Echavarren, A. M.; Nevado, C. *Chem. Soc. Rev.* **2004**, *33*, 431. (k) *Metal Carbenes in Organic Synthesis*; Dötz, K. H., Ed.; Topics in Organometallic Chemistry 13; Springer-Verlag: Berlin, 2004. (l) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539.

[3] (a) Cavell, R. G.; Kamalesh Babu, R. P.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805. (b) Kamalesh Babu, R. P.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226. (c) Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **2000**, 481. (d) Aparna, K.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 726. (e) Aparna, K.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Angew. Chem.*, *Int. Ed.* **2001**, *40*, 4400. (f) Leung, W.-P.; So, C.-W.; Wang, J.-Z.; Mak, T. C. W. *Chem. Commun.* **2003**, 248.

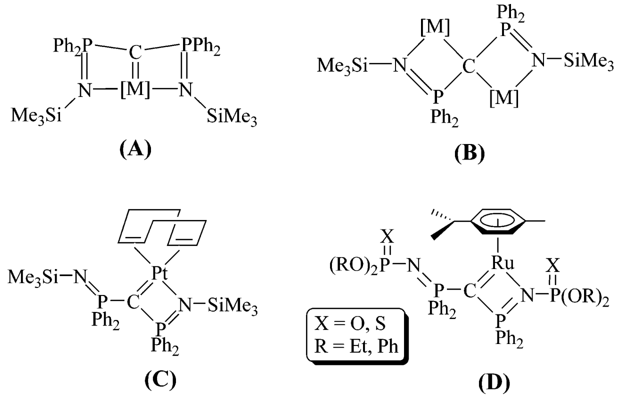
[4] (a) Aparna, K.; McDonald, R.; Ferguson, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4241. (b) Aparna, K.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **1999**, 1993. (c) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem.*, *Int. Ed.* **2001**, *40*, 2501. (d) Cavell, R. G.; Aparna, K.; Kamalesh Babu, R. P.; Wang, Q. *J. Mol. Catal. A: Chem.* **2002**, *189*, 137.

[5] The "pincer" palladium carbene derivative [Pd(κ^3(*C,S,S*)-C{P(═S)Ph$_2$}$_2$)(PPh$_3$)], closely related to complexes of type **A**, has been recently prepared by reacting [PdCl$_2$(PPh$_3$)$_2$] with the bis(diphenylthiophosphinoyl)methanediide dianion, [C{P(═S)Ph$_2$}$_2$]$^{2-}$: Cantat, T.; Mézailles, N.; Ricard, L.; Jean, Y.; Le Floch, P. *Angew. Chem.*, *Int. Ed.* **2004**, *43*, 6382.

[6] (a) Jones, N. D.; Lin, G.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Organometallics* **2003**, *22*, 2832. (b) Lin, G.; Jones, N. D.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Angew. Chem.*, *Int. Ed.* **2003**, *42*, 4054.

10.1021/om050121d CCC: $30.25

Chart 1



tive κ^2(C,N) coordination of the bis(iminophosphorano)methanediide anions to the metal.[8] We have also described that the carbenic carbon atom in ruthenium complexes **D** undergoes protonation reactions, pointing out a marked nucleophilic character.[7a] This has been confirmed by DFT calculations on the model complex $[Ru(\eta^6\text{-}C_6H_6)(\kappa^2(C,N)\text{-}C[P\{=NP(=O)(OMe)_2\}Me_2]_2)]$, which show a negative charge at the carbenic carbon atom (C_C = −1.191).[7a]

It is well-known that transition-metal carbene complexes are prone to undergo C−C coupling processes with a large variety of unsaturated organic substrates.[2] This reactivity is indeed one of the most desired goals in metal−carbene chemistry because of the potential applications in catalytic organic synthesis, particularly in the field of olefin and enyne metathesis.[9] Preliminary studies by Cavell and co-workers have confirmed the usefulness of iminophosphorane-based carbenes of the type **A** and **B** to form novel C−C bonds. In particular, they have found that (see Scheme 1) (i) the group 4 "pincer" carbenes $[MCl_2\{\kappa^3(C,N,N)\text{-}C(Ph_2P{=}NSiMe_3)_2\}]$ (M = Zr, Hf) undergo [2 + 2] cycloadditions of heterocumulenes across the M=C bond to afford the metallatricyclic compounds **E**[10] and (ii) the bimetallic carbene $[(AlMe_2)_2\{\mu_2{:}\kappa^4(C,C,N,N)\text{-}C(Ph_2P{=}NSiMe_3)_2\}]$ inserts heterocumulenes into the Al−C bonds to give the bicyclic aluminum complexes **F**, in which a novel C=C bond is formed.[11]

Since the ability of the late-transition-metal carbenes **C** and **D** to form novel C−C bonds is still unexplored,

Scheme 1

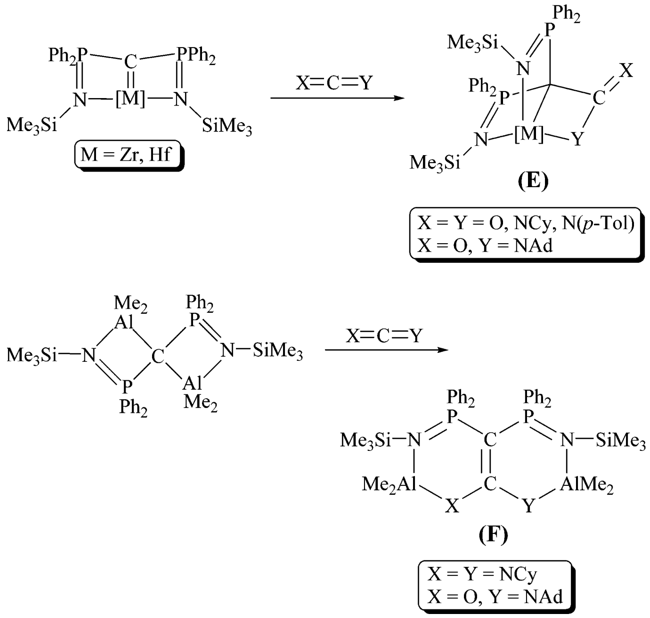
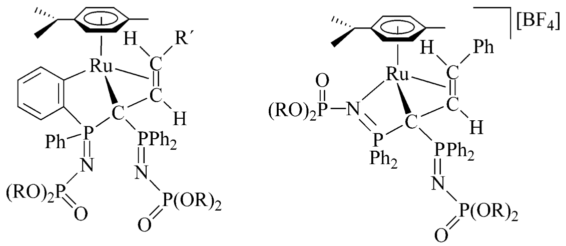


Chart 2



we have investigated the reactivity of the ruthenium(II) complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}C[P\{=NP(=O)(OR)_2\}Ph_2]_2)]$ (R = Et (**1**), Ph (**2**); type **D**) toward terminal alkynes HC≡CR′. Herein we report an interesting reaction outcome since, in addition to the anticipated coupling of the Ru=C and C≡C bonds, a concomitant ortho metalation of one of the phenyl rings of the pendant iminophosphorane groups occurs, leading to compounds **G** (see Chart 2). The preparation of complexes **H**, via selective cleavage of the Ru−C_{aryl} bond in complexes **G** by treatment with HBF_4, is also described.

Results and Discussion

Activation of Terminal Alkynes by the Ruthenium(II) Carbene Complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}(C,N)\text{-}C[P\{=NP(=O)(OR)_2\}Ph_2]_2)]$ (R = Et (1), Ph (2)). We have found that the treatment of carbenes **1** and **2** with an excess of phenylacetylene or *p*-tolylacetylene (ca. 20 equiv), in THF at room temperature, results in the chemo- and stereoselective formation of the ortho-metalated complexes **3a**,**b** and **4a**,**b** (see Scheme 2), which have been isolated as air-stable yellow solids in 70−77% yield. The generality of this process was assessed by using functionalized alkynes such as propargylic alcohols (1,1-diphenyl-2-propyn-1-ol (**3c** and **4c**) and 1-phenyl-2-propyn-1ol (**3d** and **4d**); 61−66% yield) and 1,3-enynes (1-ethynylcyclohexene (**3e** and **4e**)

---

(7) (a) Cadierno, V.; Díez, J.; García-Álvarez, J.; Gimeno, J.; Calhorda, M. J.; Veiros, L. F. *Organometallics* **2004**, *23*, 2421. (b) Cadierno, V.; Díez, J.; García-Álvarez, J.; Gimeno, J. *J. Organomet. Chem.* **2005**, *690*, 2087.

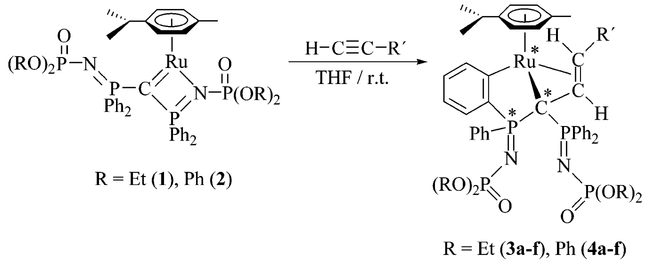
(8) The synthesis and reactivity of the bis(germavinylidene) derivative $[\{(Me_3SiN{=})PPh_2\}_2C{=}Ge{\rightarrow}Ge{=}C\{P({=}NSiMe_3)Ph_2\}_2]$, in which the bis(iminophosphorano)methanediide units $C\{P({=}NSiMe_3)Ph_2\}_2$ are κ^2-(C,N)-coordinated to germanium, have been also reported: Leung, W.-P.; So, C.-W.; Wang, Z.-X.; Wang, J.-Z.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4305. See also refs 3f and 4c.

(9) See for example: (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446. (b) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036. (c) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (d) Armstrong, S. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 371. (e) *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Springer: Berlin, 1998. (f) Schrock, R. R. *Tetrahedron* **1999**, *55*, 8141. (g) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (h) Hoveyda, A. H.; Schrock, R. R. *Chem. Eur. J.* **2001**, *7*, 945. (i) Poulsen, C. S.; Madsen, R. *Synthesis* **2003**, 1. (j) Mol, J. C. *J. Mol. Catal. A: Chem.* **2004**, *213*, 39. (k) Mori, M. *J. Mol. Catal. A: Chem.* **2004**, *213*, 73.

(10) Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Organometallics* **2000**, *19*, 3462.

(11) Aparna, K.; McDonald, R.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 9314.

Scheme 2



R′ = Ph (**a**), *p*-Tol (**b**), $CPh_2(OH)$ (**c**), CHPh(OH) (**d**), C_6H_9 (**e**), $C(Me)=CH_2$ (**f**)

and 2-methyl-1-buten-3-yne (**3f** and **4f**); 61–70% yield) (see Scheme 2).[12]

Ortho-metalated complexes **3a**–**f** and **4a**–**f** have been characterized by standard spectroscopic techniques (IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR), FAB mass spectra (complexes **3a** and **3c**), and elemental analyses, all data being fully consistent with the structural proposal (details are given in the Experimental Section). The NMR spectra also show that the formation of these complexes proceeds in a diastereoselective manner (note that three stereogenic centers are generated: i.e., the ruthenium atom, the PCP carbon, and the phosphorus atom of the metalated iminophosphorane unit). Moreover, the structure of complex **3c** has been unambiguously confirmed by a single-crystal X-ray diffraction study (a $R_{Ru}R_CR_P/S_{Ru}S_CS_P$ racemic mixture is present). An ORTEP-type drawing of the molecular structure of the $R_{Ru}R_CR_P$ enantiomer showing the classical piano-stool geometry is depicted in Figure 1; selected bond distances and angles are listed in the caption. The coordination sphere around ruthenium consists of the η^6-*p*-cymene ring, one C_{aryl} carbon, and the three carbon atoms of the allylic $P_2CCH{=}CHR'$ unit (C(11), C(12), and C(13)) in a $\kappa^3(C,C,C)$ bonding mode. The Ru–C(28) (2.095(3) Å) and Ru–C(13) (2.223(3) Å) bond lengths show the expected values for Ru–C_{aryl} and Ru–C_{alkyl} single bonds, respectively.[13] The bond distance C(11)–C(12) (1.404(4) Å) and those between these carbons and ruthenium (Ru–C(11) = 2.222(3) Å; Ru–C(12) = 2.127(3) Å) are also comparable with those found in related (arene)ruthenium(II) π-olefin complexes such as $[RuH(\eta^6\text{-}C_6Me_6)(CH_2{=}CH_2)(PPh_3)][PF_6]$ (C=C = 1.410(3) Å; Ru–C = 2.168(10) and 2.194(9) Å),[14] $[RuH(\eta^6\text{-}p\text{-cymene})(CH_2{=}CHPh)(PPh_3)][SbF_6]$ (C=C = 1.397(8) Å; Ru–C = 2.195(6) and 2.216(6) Å)[15] and $[RuH(\eta^6{:}\eta^1\text{-}C_6H_5CH_2CH_2PPh_2)(CH_2{=}CH_2)(PPh_3)][PF_6]$ (C=C = 1.367(6) Å; Ru–C = 2.199(4) and 2.195(4) Å).[16] As we can clearly observe in Figure 1, the metal-coordinated olefinic unit $-CH{=}CHCPh_2(OH)$ adopts an *E* configuration.

The NMR spectra obtained for complexes **3a**–**f** and **4a**–**f** show that the structures in solution are consistent with that of **3c** in the solid state. Thus, the most relevant spectroscopic features are the presence of (i) ($^{31}P\{^1H\}$ NMR) four well-separated signals with equal relative intensities (see Table 1), the chemical shifts as well as the coupling constants observed being in accord with the presence of uncoordinated $Ph_2P{=}NP({=}O)(OR)_2$ (R = Et, Ph) moieties,[7a,17] and (ii) ($^{13}C\{^1H\}$ NMR) characteristic resonances for the Ru–C_{aryl} and $P_2CCH{=}CHR'$ carbons at ca. δ 173 (d, $^2J_{CP}$ = 31–33 Hz; Ru–C_{aryl}), 52 (dddd, $^1J_{CP}$ = 83–101 and 75–85 Hz, $^3J_{CP}$ = 8–16 and 0–7 Hz; PCP), 83 (broad singlet; *C*H=CHR′), and 78 (d, $^3J_{CP}$ = 10–13 Hz; CH=*C*HR′) ppm (see Table 2).

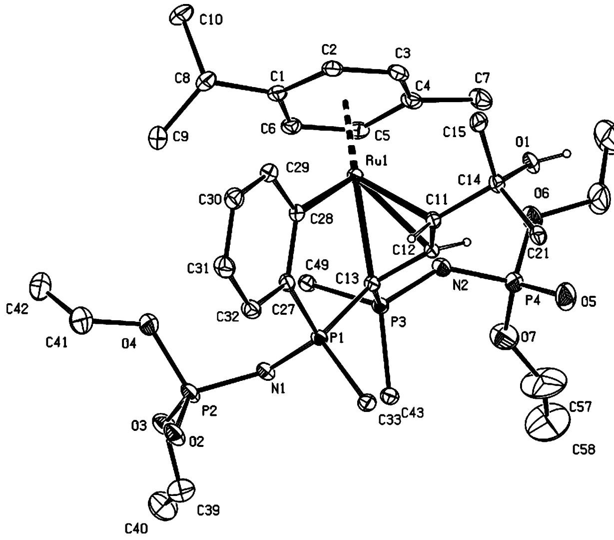


Figure 1. ORTEP-type view of the structure of complex **3c** showing the crystallographic labeling scheme. The diethyl ether molecule, phenyl groups (except the ortho metalated one), and hydrogen atoms (except those on O(1), C(11), and C(12)) have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru–C* = 1.7838(4); Ru–C(11) = 2.222(3); Ru–C(12) = 2.127(3); Ru–C(13) = 2.223(3); Ru–C(28) = 2.095(3); C(11)–C(12) = 1.404(4); C(11)–C(14) = 1.541(4); C(12)–C(13) = 1.461(4); C(13)–P(1) = 1.809(3); P(1)–N(1) = 1.574(2); N(1)–P(2) = 1.583(3); P(2)–O(2) = 1.478(3); P(2)–O(3) = 1.556(3); P(2)–O(4) = 1.598(3); C(13)–P(3) = 1.828(3); P(3)–N(2) = 1.572(3); N(2)–P(4) = 1.558(3); P(4)–O(5) = 1.442(3); P(4)–O(6) = 1.574(3); P(4)–O(7) = 1.596(4); P(1)–C(27) = 1.773(3); C(27)–C(28) = 1.410(4); C*–Ru–C(11) = 135.82(8); C*–Ru–C(12) = 134.31(8); C*–Ru–C(13) = 137.95(7); C*–Ru–C(28) = 127.49(7); C(11)–Ru–C(12) = 37.60(11); C(11)–Ru–C(13) = 68.99(10); C(11)–Ru–C(28) = 78.64(11); C(12)–Ru–C(13) = 39.17(10); C(12)–Ru–C(28) = 97.69(11); C(13)–Ru–C(28) = 84.64(10); Ru–C(11)–C(12) = 67.51(15); Ru–C(11)–C(14) = 124.8(2); Ru–C(12)–C(11) = 74.89(16); Ru–C(12)–C(13) = 73.97(15); Ru–C(13)–P(1) = 111.37(13); Ru–C(28)–C(27) = 121.5(2); C(13)–P(1)–N(1) = 108.48(13); C(13)–P(1)–C(27) = 103.45(13); P(1)–C(27)–C(28) = 117.7(2); P(1)–C(13)–P(3) = 116.47(14); C(13)–P(3)–N(2) = 110.07(14); P(1)–C(13)–C(12) = 122.6(2); C(13)–C(12)–C(11) = 122.9(3); C(12)–C(11)–C(14) = 120.1(3). C* = centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

---

[12] No dehydration products derived from complexes **3c**,**d** and **4c**,**d** have been observed in the course of these reactions. Moreover, attempts to dehydrate selectively **3c**,**d** and **4c**,**d** by treatment with HCl or CF_3SO_3H failed, giving instead complicated reaction mixtures of uncharacterized products.

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

[14] (a) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed.* **1983**, *22*, 46. (b) Werner, H.; Keltzin, H.; Höhn, A.; Paul, W.; Knaup, W.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1986**, *306*, 227.

[15] Faller, J. W.; Chase, K. J. *Organometallics* **1995**, *14*, 1592.

[16] Umezawa-Vizzini, K.; Lee, T. R. *Organometallics* **2004**, *23*, 1448.

[17] (a) Cadierno, V.; Crochet, P.; Díez, J.; García-Álvarez, J.; García-Garrido, S. E.; Gimeno, J.; García-Granda, S.; Rodríguez, M. A. *Inorg. Chem.* **2003**, *42*, 3293. (b) Cadierno, V.; Díez, J.; García-Álvarez, J.; Gimeno, J. *Organometallics* **2004**, *23*, 3425.

Table 1. ^{31}P{^{1}H} NMR Data for the Ortho-Metalated Complexes 3a–f, 4a–f, 6, and 7[a]

	Ph$_2$P=N		(RO)$_2$P=O	
complex	metalated arm	nonmetalated arm	metalated arm	nonmetalated arm
R = Et; R′ = Ph (**3a**)[b]	34.37 (ddd; $^2J_{PP}$ = 39.1, 28.1; $^4J_{PP}$ = 3.0)	27.31 (dd; $^2J_{PP}$ = 39.1, 28.1)	0.51 (d; $^2J_{PP}$ = 28.1)	1.57 (dd; $^2J_{PP}$ = 28.1; $^4J_{PP}$ = 3.0)
R = Et; R′ = *p*-Tol (**3b**)[b]	34.40 (ddd; $^2J_{PP}$ = 32.5, 28.7; $^4J_{PP}$ = 3.2)	27.16 (dd; $^2J_{PP}$ = 32.5, 28.7)	0.50 (d; $^2J_{PP}$ = 28.7)	1.54 (dd; $^2J_{PP}$ = 28.7; $^4J_{PP}$ = 3.2)
R = Et; R′ = CPh$_2$(OH) (**3c**)[b]	35.08 (ddd; $^2J_{PP}$ = 36.0, 26.9 $^4J_{PP}$ = 6.1)	28.22 (dd; $^2J_{PP}$ = 36.0, 26.9)	0.36 (d; $^2J_{PP}$ = 26.9)	1.87 (dd; $^2J_{PP}$ = 26.9; $^4J_{PP}$ = 6.1)
R = Et; R′ = CHPh(OH) (**3d**)[b]	33.87 (dd; $^2J_{PP}$ = 31.9, 29.6)	27.56 (dd; $^2J_{PP}$ = 31.9, 29.6)	0.56 (d; $^2J_{PP}$ = 29.6)	1.49 (d; $^2J_{PP}$ = 29.6)
R = Et; R′ = C$_6$H$_9$ (**3e**)[c]	35.16 (ddd; $^2J_{PP}$ = 32.6, 28.8; $^4J_{PP}$ = 3.6)	26.82 (dd; $^2J_{PP}$ = 32.6, 32.2)	1.80 (d; $^2J_{PP}$ = 28.8)	2.44 (dd; $^2J_{PP}$ = 32.2; $^4J_{PP}$ = 3.6)
R = Et; R′ = C(Me)=CH$_2$ (**3f**)[b]	34.10 (ddd; $^2J_{PP}$ = 32.2, 29.6; $^4J_{PP}$ = 3.1)	28.58 (dd; $^2J_{PP}$ = 32.2, 29.6)	0.52 (d; $^2J_{PP}$ = 29.6)	1.58 (dd; $^2J_{PP}$ = 29.6; $^4J_{PP}$ = 3.1)
R = Ph; R′ = Ph (**4a**)[b]	36.12 (ddd; $^2J_{PP}$ = 33.4, 28.0; $^4J_{PP}$ = 4.1)	28.97 (dd; $^2J_{PP}$ = 33.4, 28.0)	−9.76 (d; $^2J_{PP}$ = 28.0)	−9.08 (dd; $^2J_{PP}$ = 28.0; $^4J_{PP}$ = 4.1)
R = Ph; R′ = *p*-Tol (**4b**)[b]	36.11 (ddd; $^2J_{PP}$ = 33.4, 28.2; $^4J_{PP}$ = 4.2)	28.86 (dd; $^2J_{PP}$ = 33.4, 28.2)	−9.80 (d; $^2J_{PP}$ = 28.2)	−9.10 (dd; $^2J_{PP}$ = 28.2; $^4J_{PP}$ = 4.2)
R = Ph; R′ = CPh$_2$(OH) (**4c**)[b]	35.65 (ddd; $^2J_{PP}$ = 34.8, 28.9; $^4J_{PP}$ = 4.5)	29.87 (dd; $^2J_{PP}$ = 34.8, 28.9)	−9.81 (d; $^2J_{PP}$ = 28.9)	−8.70 (dd; $^2J_{PP}$ = 28.9; $^4J_{PP}$ = 4.5)
R = Ph; R′ = CHPh(OH) (**4d**)[b]	35.78 (ddd; $^2J_{PP}$ = 34.2, 30.1; $^4J_{PP}$ = 4.3)	28.71 (dd; $^2J_{PP}$ = 34.2, 28.3)	−9.71 (d; $^2J_{PP}$ = 30.1)	−9.17 (dd; $^2J_{PP}$ = 28.3; $^4J_{PP}$ = 4.3)
R = Ph; R′ = C$_6$H$_9$ (**4e**)[b]	35.81 (ddd; $^2J_{PP}$ = 34.1, 28.3; $^4J_{PP}$ = 4.5)	28.73 (dd; $^2J_{PP}$ = 34.1, 28.3)	−9.78 (d; $^2J_{PP}$ = 28.3)	−9.13 (dd; $^2J_{PP}$ = 28.3; $^4J_{PP}$ = 4.5)
R = Ph; R′ = C(Me)=CH$_2$ (**4f**)[b]	35.90 (ddd; $^2J_{PP}$ = 33.8, 29.3; $^4J_{PP}$ = 4.5)	28.81 (dd; $^2J_{PP}$ = 33.8, 28.0)	−9.84 (d; $^2J_{PP}$ = 29.3)	−8.94 (dd; $^2J_{PP}$ = 28.0; $^4J_{PP}$ = 4.5)
complex **6**[b]	34.79 (ddd; $^2J_{PP}$ = 32.4, 28.9; $^4J_{PP}$ = 3.7)	29.14 (dd; $^2J_{PP}$ = 32.4, 30.3)	0.97 (d; $^2J_{PP}$ = 28.9)	−8.45 (dd; $^2J_{PP}$ = 30.3; $^4J_{PP}$ = 3.7)
complex **7**[b]	36.34 (ddd; $^2J_{PP}$ = 32.1, 28.7; $^4J_{PP}$ = 3.0)	26.24 (dd; $^2J_{PP}$ = 32.1, 31.4)	−8.98 (d; $^2J_{PP}$ = 28.7)	−1.85 (dd; $^2J_{PP}$ = 31.4; $^4J_{PP}$ = 3.0)

[a] Units: δ in ppm and J in Hz. Abbreviations: d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets. [b] Spectra recorded in CDCl$_3$. [c] Spectra recorded in acetone-d_6.

Table 2. Selected ^{1}H and ^{13}C{^{1}H} NMR Data for the Ortho-Metalated Complexes 3a–f, 4a–f, 6, and 7[a]

	^{1}H	^{13}C{^{1}H}			
complex	CH=C*H*R′	PCP	CH=*C*HR′	*C*H=CHR′	Ru−C$_{aryl}$
R = Et; R′ = Ph (**3a**)[b]	3.74 (m)[d]	52.91 (dddd; $^1J_{CP}$ = 95.2, 80.8; $^3J_{CP}$ = 15.0, 3.6)	74.84 (d; $^3J_{CP}$ = 12.3)	83.96 (br)	173.09 (d; $^2J_{CP}$ = 32.4)
R = Et; R′ = *p*-Tol (**3b**)[b]	3.78 (d; $^3J_{HH}$ = 12.0)	52.67 (dddd; $^1J_{CP}$ = 99.0, 80.7; $^3J_{CP}$ = 14.7, 4.2)	75.36 (d; $^3J_{CP}$ = 12.8)	83.89 (br)	173.31 (d; $^2J_{CP}$ = 32.5)
R = Et; R′ = CPh$_2$(OH) (**3c**)[b]	3.16 (d; $^3J_{HH}$ = 10.6)	51.29 (ddd; $^1J_{CP}$ = 95.5, 77.0; $^3J_{CP}$ = 14.9)	86.20 (d; $^3J_{CP}$ = 11.3)	83.03 (br)	172.99 (d; $^2J_{CP}$ = 31.8)
R = Et; R′ = CHPh(OH) (**3d**)[b]	2.96 (m)[e]	53.13 (dddd; $^1J_{CP}$ = 95.2, 78.4; $^3J_{CP}$ = 14.4, 3.6)	78.67 (d; $^3J_{CP}$ = 11.4)	87.22 (br)	172.52 (d; $^2J_{CP}$ = 31.8)
R = Et; R′ = C$_6$H$_9$ (**3e**)[c]	2.87 (d; $^3J_{HH}$ = 11.2)	53.04 (dddd; $^1J_{CP}$ = 101.3, 78.5; $^3J_{CP}$ = 15.4, 6.0)	78.42 (d; $^3J_{CP}$ = 12.8)	82.77 (br)	174.73 (d; $^2J_{CP}$ = 32.6)
R = Et; R′ = C(Me)=CH$_2$ (**3f**)[b]	2.89 (d; $^3J_{HH}$ = 11.2)	52.56 (dddd; $^1J_{CP}$ = 95.8, 80.2; $^3J_{CP}$ = 10.6, 5.4)	76.23 (d; $^3J_{CP}$ = 12.7)	83.10 (br)	172.75 (d; $^2J_{CP}$ = 32.6)
R = Ph; R′ = Ph (**4a**)[b]	3.86 (d; $^3J_{HH}$ = 11.2)	51.16 (dddd; $^1J_{CP}$ = 96.1, 80.9; $^3J_{CP}$ = 14.2, 5.7)	75.04 (d; $^3J_{CP}$ = 12.2)	82.91 (br)	173.38 (d; $^2J_{CP}$ = 32.6)
R = Ph; R′ = *p*-Tol (**4b**)[b]	3.84 (d; $^3J_{HH}$ = 11.2)	50.71 (dddd; $^1J_{CP}$ = 96.7, 84.7; $^3J_{CP}$ = 12.8, 4.7)	75.47 (d; $^3J_{CP}$ = 12.2)	82.71 (br)	173.60 (d; $^2J_{CP}$ = 32.6)
R = Ph; R′ = CPh$_2$(OH) (**4c**)[b]	3.12 (d; $^3J_{HH}$ = 10.5)	48.94 (dddd; $^1J_{CP}$ = 96.1, 82.3; $^3J_{CP}$ = 13.9, 6.1)	83.70 (d; $^3J_{CP}$ = 11.1)	81.65 (br)	172.51 (d; $^2J_{CP}$ = 32.0)
R = Ph; R′ = CHPh(OH) (**4d**)[b]	2.92 (m)	51.18 (dddd; $^1J_{CP}$ = 95.2, 81.2; $^3J_{CP}$ = 16.3, 7.1)	78.54 (d; $^3J_{CP}$ = 10.5)	85.82 (br)	172.99 (d; $^2J_{CP}$ = 32.0)
R = Ph; R′ = C$_6$H$_9$ (**4e**)[b]	2.94 (m)[e]	49.72 (ddd; $^1J_{CP}$ = 82.9, 75.7; $^3J_{CP}$ = 7.8)	78.40 (d; $^3J_{CP}$ = 12.0)	80.66 (br)	173.30 (d; $^2J_{CP}$ = 32.3)
R = Ph; R′ = C(Me)=CH$_2$ (**4f**)[b]	2.91 (d; $^3J_{HH}$ = 11.1)	50.92 (dddd; $^1J_{CP}$ = 101.3, 81.7; $^3J_{CP}$ = 14.7, 6.5)	76.36 (d; $^3J_{CP}$ = 12.8)	82.13 (br)	173.09 (d; $^2J_{CP}$ = 32.1)
mixture of complexes **6** and **7**[b]	3.86 (m)[d]	52.09 (m; two carbons)	74.82 (d; $^3J_{CP}$ = 12.8)	83.30 (br)	172.52 (d; $^2J_{CP}$ = 31.8)
			75.06 (d; $^3J_{CP}$ = 12.2)	83.55 (br)	173.81 (d; $^2J_{CP}$ = 33.2)

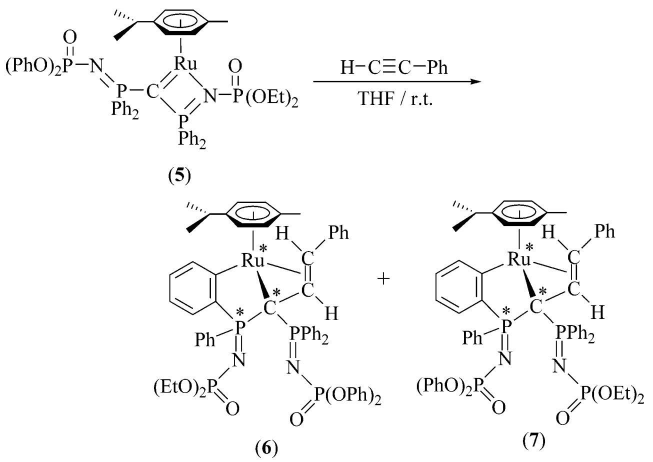
[a] Units: δ in ppm and J in Hz. Abbreviations: br, broad singlet; d, doublet; ddd, doublet of doublets of doublets; dddd, doublet of doublets of doublets of doublets; m, multiplet. [b] Spectra recorded in CDCl$_3$. [c] Spectra recorded in acetone-d_6. [d] Overlapped by the OCH_2CH$_3$ signals. [e] Overlapped by the CH(CH$_3$)$_2$ signals.

The reactivity of the carbene complex [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OEt)$_2$}Ph$_2$][P{=NP(=O)(OPh)$_2$}Ph$_2$])] (**5**),[7a] containing an unsymmetrical bis(iminophosphorano)methanediide ligand, toward phenylacetylene has been also explored. In this case, a nonseparable mixture of the ortho-metalated isomers **6** and **7** was obtained in a ca. 1:1 ratio (see Scheme 3).[18]

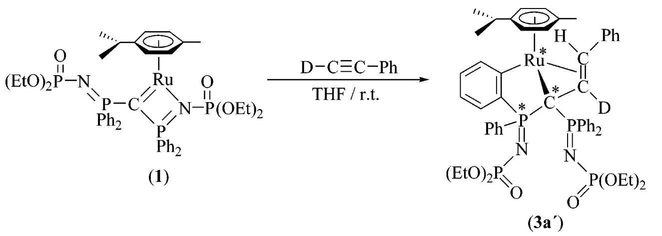
---

[18] Analytical and spectroscopic data for this mixture are included in the Experimental Section and Tables 1 and 2.

Scheme 3



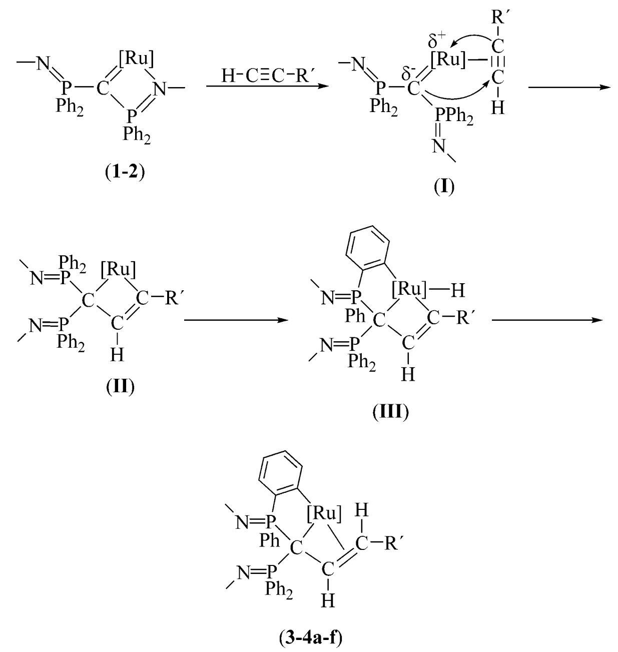
Scheme 4



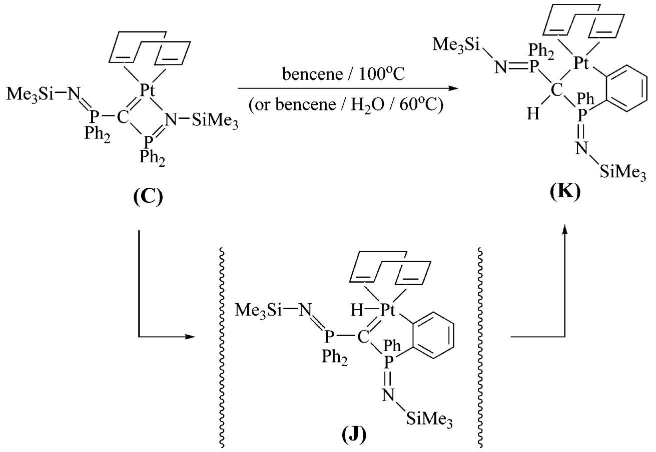
This means that phenyl rings in both Ph_2P groups of the ligand are able to undergo ortho metalation, proving that decoordination of the $Ph_2P{=}N$ unit occurs in the course of these unusual coupling processes. The known hemilability of the *N*-phosphoryl iminophosphoranyl fragments $-Ph_2P{=}NP({=}O)(OR)_2$ probably promotes the ready coordination of the alkyne to ruthenium.[7a,17]

To shed light on the mechanism and the fate of the terminal hydrogen of the alkynes, the reaction of the complex [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OEt)$_2$}-Ph$_2$]$_2$)] (**1**) with deuterated phenylacetylene was performed. The reaction affords **3a′**, which selectively incorporates deuterium at the central allylic carbon (see Scheme 4).[19] This fact clearly indicates that a transient η^2-alkyne complex is initially formed and that no tautomerization into the corresponding η^1-vinylidene isomer [Ru]=C=CDPh occurs. This is in accord with the nucleophilic nature of the Ru=C bond and therefore with the electron deficiency of the metal in carbene complexes **1** and **2**. Otherwise, as is well-known, electron-rich ruthenium fragments would have favored the tautomerization of η^2-alkyne complexes into their η^1-vinylidene isomers.[20] All attempts to detect intermediate species by NMR spectroscopy have been unsuccessful, the spectra showing only the signals of the carbenic precursors and the final products.

Scheme 5



Scheme 6



On the basis of all these observations a mechanistic proposal for the formation of ortho-metalated complexes **3a**−**f** and **4a**−**f** is illustrated in Scheme 5. We assume that the first step is the π-coordination of the alkyne to ruthenium, via decoordination of the iminophosphorane fragment, to afford **I**. The subsequent regioselective C−C coupling between the carbenic Ru=C carbon and the less sterically hindered carbon of the coordinated alkyne gives the 16e metallacyclobutene intermediate **II**. An intramolecular aryl ortho metalation within **II** generates the 18e ruthenium(IV) hydride complex **III**, which evolves into the final product **3a**−**f** and **4a**−**f** by reductive elimination. The diastereoselectivity observed in the formation of **3a**−**f** and **4a**−**f** seems to indicate that the C−H activation step (**II** → **III**) proceeds in a concerted manner.

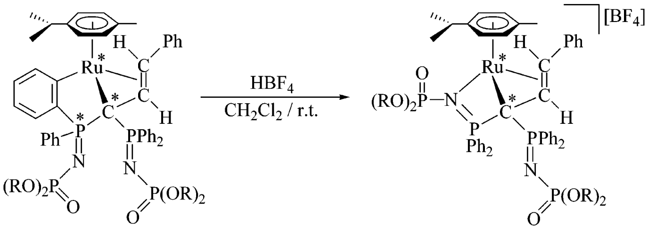
It should be noted that the related platinum carbene derivative [Pt(κ^2(*C,N*)-C{P(=NSiMe$_3$)Ph$_2$}$_2$)(COD)] (**C**) undergoes, under thermal conditions, a related aryl ortho metalation to afford complex **K** (see Scheme 6).[6a] The proposed mechanism for this transformation involves also the formation of a metallic hydride intermediate **J**, via oxidative addition of one of the C_{aryl}−H

---

[19] This was confirmed by $^{13}C\{^1H\}$ NMR spectroscopy (in ^1H NMR, all the olefinic signals are overlapped). Thus, the olefinic CD=CHPh carbons of **3a′** resonate at $\delta_C(C_6D_6)$ 84.61 (broad triplet, $^1J_{CD}$ = 12.1 Hz) and 75.73 (d, $^3J_{CP}$ = 12.6 Hz) ppm, respectively (to be compared with $\delta_C(CDCl_3)$ 83.96 (broad singlet) and 74.84 (d, $^3J_{CP}$ = 12.3 Hz) ppm, respectively, in **3a**).

[20] For reviews on the chemistry of transition-metal vinylidene complexes see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (d) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977. (e) Selegue, J. P. *Coord. Chem. Rev.* **2004**, *248*, 1543. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627. (g) Werner, H. *Coord. Chem. Rev.* **2004**, *248*, 1692. (h) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703.

Scheme 7



R = Et (**3a**), Ph (**4a**)

R = Et (**8**), Ph (**9**)

bonds, which evolves through the transfer of the hydride ligand from the metal to the carbenic carbon atom. In our case, no ortho-metalation processes were observed in the absence of the terminal alkynes, supporting the involvement of the η^2-alkyne intermediate **I** in the formation of complexes **3a**–**f** and **4a**–**f** (see Scheme 5).

Synthesis of the Ruthenium(II) Complexes [Ru(η^6-*p*-cymene)(κ^4(*C,C,C,N*)-C[P{=NP(=O)(OR)$_2$}-Ph$_2$]$_2${(*E*)-C(H)=C(H)Ph})][BF$_4$] (R = Et (8), Ph (9)). To evaluate the strength of the Ru–C bonds in the ortho-metalated complexes **3a**–**f** and **4a**–**f**, their behavior toward acids has been explored. Thus, we have found that the treatment of complexes **3a** and **4a** with 1 equiv of HBF$_4$, in dichloromethane at room temperature, generates the cationic derivatives [Ru(η^6-*p*-cymene)(κ^4(*C,C,C,N*)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2${(*E*)-C(H)=C(H)Ph})][BF$_4$] (R = Et (**8**), Ph (**9**)), which have been isolated as air-stable yellow solids in 78 and 79% yields, respectively (see Scheme 7). Complexes **8** and **9** result from the selective cleavage of the Ru–C$_{\text{aryl}}$ bond in **3a** and **4a** and subsequent N-coordination to ruthenium of one of the iminophosphorane fragments Ph$_2$P=NP(=O)-(OR)$_2$.

Compounds **8** and **9** have been characterized by elemental analyses, conductance measurements (1:1 electrolytes), and IR and NMR spectroscopy (see the Experimental Section for details), the last measurements supporting their diastereoselective formation (the ruthenium atom and the PCP carbon are again stereogenic centers). In particular, the ^{31}P{^{1}H} NMR spectra show the expected presence of four chemically inequivalent phosphorus nuclei (see Table 3). The downfield chemical shift observed for one of the two Ph$_2$P=N phosphorus resonances, 57.41 (**8**) and 58.31 ppm (**9**), confirms its coordination to the metal, forming part of a four-membered ruthenacarbocycle (the uncoordinated Ph$_2$P=N units resonate at ca. 25 ppm). These data can be compared to those observed in the carbenic precursors [Ru(η^6-*p*-cymene)(κ^3(*C,N*)-C[P{=NP(=O)(OR)$_2$}-Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) also containing a four-membered metallacycle.[7] The cleavage of the Ru–aryl bond in ortho-metalated complexes **3a** and **4a** is clearly confirmed in the ^{13}C{^{1}H} NMR spectra of compounds **8** and **9** by the disappearance of the characteristic Ru–C$_{\text{aryl}}$ signals. The ^{13}C{^{1}H} NMR spectra are also consistent with the presence of a coordinated allylic P$_2$-CCH=CHPh unit, showing characteristic resonances at ca. δ 33 (PCP), 81 (CH=*C*HPh) and 89 ppm (*C*H=CHPh) (see Table 4). As previously observed for **3a** and **4a**, the olefinic CH=C*H*Ph proton in complexes **8** and **9** resonates, in ^{1}H NMR, as a doublet (ca. $^3J_{\text{HH}}$ = 13 Hz) at 5.3 ppm, while that of the C*H*=CHPh proton appears within the aromatic signal region (see Table 4 and the Experimental Section).

Conclusions

Although C–C coupling reactions of carbene complexes[2] and aryl ring ortho metalations[21] are well-known, in this paper we show for the first time the ability of a ruthenium carbene to undergo both processes simultaneously. Thus, new types of (η^6-arene)ruthenium(II) complexes (**3a**–**f** and **4a**–**f**) containing an all-carbon-bonded ligand, consisting of one C$_{\text{aryl}}$ and an allylic P$_2$CCH=CHR unit in a κ^3(*C,C,C*) bonding mode, have been easily prepared in high yields by reacting the nucleophilic carbenes [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) with terminal alkynes. Remarkably, the C–C coupling and C–H activation processes involved in the formation of these unusual hydrocarbon ligands take place under mild conditions (room temperature) in a totally chemo- and stereoselective manner. To the best of our knowledge, these are the first examples proving the ability of an iminophosphorane-based carbene complex of an electron-rich metal to undergo C–C coupling reactions. This is a significant step to match the reactivity of these unusual carbenes with that shown by the well-known Grubbs type ruthenium carbenes. In summary, the results reported in this paper suggest useful applications of the ruthenium(II) carbenes [Ru(η^6-*p*-cymene)-(κ^2(*C,N*)-C{P(=NR)Ph$_2$}$_2$)] to the preparation of elaborated ruthenium organometallics. Further studies in this direction are currently under active investigation.

Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of the compounds [Ru(η^6-*p*-cymene)-(κ^2(*C,N*)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2$)] (R = Et (**1**), Ph (**2**)) and [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OEt)$_2$}Ph$_2$][P{=NP-(=O)(OPh)$_2$}Ph$_2$])] (**5**), which were prepared by following the method reported in the literature.[7a] 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. Mass spectra (FAB) were recorded using a VG Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol 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$_3$PO$_4$ as standards. DEPT experiments have

---

(21) Ortho metalations of aromatic rings in (η^6-arene)ruthenium(II) complexes are well documented. See for example: (a) Ceccanti, A.; Diversi, P.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Magagna, S.; Zanello, P. *J. Organomet. Chem.* **1996**, *526*, 251. (b) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber./Recl.* **1997**, *130*, 1253. (c) Steenwinkel, P.; James, S. L.; Gossage, R. A.; Grove, D. M.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 4680. (d) Brunner, H.; Zwack, T. *Organometallics* **2000**, *19*, 2423. (e) Ritleng, V.; Bertani, P.; Pfeffer, M.; Sirlin, C.; Hirschinger, J. *Inorg. Chem.* **2001**, *40*, 5117. (f) Pérez, J.; Riera, V.; Rodríguez, A.; Miguel, D. *Organometallics* **2002**, *21*, 5437. (g) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Giardiello, M.; Milton, S. T.; Russell, D. R. *Dalton* **2003**, 4132. (h) Le Lagadec, R.; Rubio, L.; Alexandrova, L.; Toscano, R. A.; Ivanova, E. V.; Meškys, R.; Laurinavičius, V.; Pfeffer, M.; Ryabov, A. D. *J. Organomet. Chem.* **2004**, *689*, 4820.

Table 3. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR Data for the Complexes $[\mathrm{Ru}(\eta^6\text{-}p\text{-cymene})(\kappa^4(C,C,C,N)\text{-}\mathrm{C}[\mathrm{P}\{{=}\mathrm{NP}({=}\mathrm{O})(\mathrm{OR})_2\}\mathrm{Ph}_2]_2\{(E)\text{-}\mathrm{C(H){=}C(H)Ph}\})][\mathrm{BF}_4]$ (8 and 9)[a]

complex	Ru−N=PPh$_2$	Ph$_2$P=N	Ru−NP(=O)(OR)$_2$	(RO)$_2$P=O
R = Et (**8**)	57.41 ppm (ddd; $^2J_\mathrm{PP}$ = 61.4, 14.5; $^4J_\mathrm{PP}$ = 9.3)	24.86 ppm (ddd; $^2J_\mathrm{PP}$ = 61.4, 40.4; $^4J_\mathrm{PP}$ = 7.5)	6.80 ppm (ddd; $^2J_\mathrm{PP}$ = 14.5; $^4J_\mathrm{PP}$ = 7.5; $^6J_\mathrm{PP}$ = 6.8)	−5.57 ppm (ddd; $^2J_\mathrm{PP}$ = 40.4; $^4J_\mathrm{PP}$ = 9.3; $^6J_\mathrm{PP}$ = 6.8)
R = Ph (**9**)	58.31 ppm (ddd; $^2J_\mathrm{PP}$ = 65.4, 13.4; $^4J_\mathrm{PP}$ = 10.6)	26.71 ppm (ddd; $^2J_\mathrm{PP}$ = 65.4, 36.0; $^4J_\mathrm{PP}$ = 8.5)	−3.78 ppm (ddd; $^2J_\mathrm{PP}$ = 13.4; $^4J_\mathrm{PP}$ = 8.5; $^6J_\mathrm{PP}$ = 9.9)	−16.12 ppm (ddd; $^2J_\mathrm{PP}$ = 36.0; $^4J_\mathrm{PP}$ = 10.6; $^6J_\mathrm{PP}$ = 9.9)

[a] Spectra recorded in $\mathrm{CD_2Cl_2}$. *J* values are given in Hz. Abbreviations: ddd, doublet of doublets of doublets.

Table 4. Selected ^{1}H and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR Data for Cationic Complexes 8 and 9[a]

	^{1}H	$^{13}\mathrm{C}\{^1\mathrm{H}\}$		
complex	CH=C*H*Ph	PCP	CH=*C*HPh	*C*H=CHPh
R = Et (**8**)	5.28 (d; $^3J_\mathrm{HH}$ = 12.5)	33.90 (dddd, $^1J_\mathrm{CP}$ = 113.6, 81.7; $^3J_\mathrm{CP}$ = 17.8, 10.7)	81.21 (dd; $^3J_\mathrm{CP}$ = 10.2, 4.4)	89.18 (d; $^2J_\mathrm{CP}$ = 2.9)
R = Ph (**9**)	5.30 (d; $^3J_\mathrm{HH}$ = 13.4)	32.77 (ddd; $^1J_\mathrm{CP}$ = 103.9, 85.5; $^3J_\mathrm{CP}$ = 12.7)	81.86 (dd; $^3J_\mathrm{CP}$ = 10.1, 3.7)	89.18 (br)

[a] Spectra recorded in $\mathrm{CD_2Cl_2}$. Units: δ in ppm and *J* in Hz. Abbreviations: br, broad singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; dddd, doublet of doublets of doublets of doublets.

been carried out for all the compounds reported. ^{1}H and ^{13}C assignments were confirmed by ^{1}H−^{1}H COSY45, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC NMR experiments. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopic data for all the compounds reported in this paper are collected in Tables 1 and 3.

Synthesis of the Ortho-Metalated Complexes 3a−f and 4a−f. A solution of the corresponding carbene complex $[\mathrm{Ru}(\eta^6\text{-}p\text{-cymene})(\kappa^2(C,N)\text{-}\mathrm{C}[\mathrm{P}\{{=}\mathrm{NP}({=}\mathrm{O})(\mathrm{OR})_2\}\mathrm{Ph}_2]_2)]$ (R = Et (**1**), Ph (**2**)) (0.2 mmol) and the appropriate terminal alkyne (4 mmol) in 30 mL of THF was stirred at room temperature for 36 h (complexes **3a**,**c**,**d** and **4c**,**d**) or 48 h (complexes **3b**,**e**,**f** and **4a**,**b**,**e**,**f**). The solvent was then removed in vacuo and the resulting solid residue transferred to a silica gel chromatography column. Elution with a dichloromethane/methanol (4/1) mixture gave a yellow band, from which complexes **3a**−**f** and **4a**−**f** were isolated after solvent removal.

3a. Yield: 70% (0.143 g). Anal. Calcd for $\mathrm{RuC_{51}H_{60}O_6P_4N_2}$: C, 59.94; H, 5.92; N, 2.74. Found: C, 59.61; H, 5.59; N, 2.64. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.92 and 1.24 (t, 3H each, $^3J_\mathrm{HH}$ = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 0.98 (d, 3H, $^3J_\mathrm{HH}$ = 6.5 Hz, $\mathrm{CH(C}H_3)_2$), 1.02 and 1.16 (t, 3H each, $^3J_\mathrm{HH}$ = 6.9 Hz, $\mathrm{OCH_2C}H_3$), 1.19 (d, 3H, $^3J_\mathrm{HH}$ = 6.7 Hz, $\mathrm{CH(C}H_3)_2$), 1.91 (s, 3H, $\mathrm{CH_3}$), 2.86 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.56 (m, 4H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.74 (m, 5H, $\mathrm{OC}H_2\mathrm{CH_3}$ and CH=C*H*Ph), 4.26 and 5.29 (d, 1H each, $^3J_\mathrm{HH}$ = 5.8 Hz, CH of *p*-cymene), 5.10 and 5.56 (d, 1H each, $^3J_\mathrm{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.72−8.84 (m, 25H, $\mathrm{CH_{arom}}$ and C*H*=CHPh) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 16.15 (d, 2C, $^3J_\mathrm{CP}$ = 4.2 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.26 (d, 2C, $^3J_\mathrm{CP}$ = 3.6 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 17.34 (s, $\mathrm{CH_3}$), 19.88 and 24.90 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 30.10 (s, $C\mathrm{H(CH_3)_2}$), 52.91 (dddd, $^1J_\mathrm{CP}$ = 95.2 and 80.8 Hz, $^3J_\mathrm{CP}$ = 15.0 and 3.6 Hz, PCP), 60.30 (d, $^2J_\mathrm{CP}$ = 5.4 Hz, $\mathrm{OCH_2}$), 60.47 (d, $^2J_\mathrm{CP}$ = 6.0 Hz, $\mathrm{OCH_2}$), 61.16 (d, 2C, $^2J_\mathrm{CP}$ = 6.0 Hz, $\mathrm{OCH_2}$), 74.84 (d, $^3J_\mathrm{CP}$ = 12.3 Hz, CH=*C*HPh), 83.96 (br, *C*H=CHPh), 89.24, 90.99, 92.93, and 97.57 (s, CH of *p*-cymene), 105.66 and 117.84 (s, C of *p*-cymene), 122.07−145.85 (m, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 173.09 (d, $^2J_\mathrm{CP}$ = 32.4 Hz, Ru−$\mathrm{C_{aryl}}$) ppm. MS (FAB) *m*/*z* 1023.9 [M$^+$ + 1], 888.5 [M$^+$ − *p*-cymene].

3b. Yield: 77% (0.159 g). Anal. Calcd for $\mathrm{RuC_{52}H_{62}O_6P_4N_2}$: C, 60.28; H, 6.03; N, 2.70. Found: C, 60.54; H, 6.11; N, 2.83. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.93 (t, 3H, $^3J_\mathrm{HH}$ = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 0.99 (d, 3H, $^3J_\mathrm{HH}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 1.03 (t, 3H, $^3J_\mathrm{HH}$ = 6.7 Hz, $\mathrm{OCH_2C}H_3$), 1.16 (t, 3H, $^3J_\mathrm{HH}$ = 7.1 Hz, $\mathrm{OCH_2C}H_3$), 1.20 (d, 3H, $^3J_\mathrm{HH}$ = 7.1 Hz, $\mathrm{CH(C}H_3)_2$), 1.25 (t, 3H, $^3J_\mathrm{HH}$ = 6.6 Hz, $\mathrm{OCH_2C}H_3$), 1.93 (s, 3H, $\mathrm{CH_3}$), 2.30 (s, 3H, $\mathrm{C_6H_4C}H_3$), 2.88 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.57 and 3.87 (m, 4H each, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.78 (d, 1H, $^3J_\mathrm{HH}$ = 12.0 Hz, $\mathrm{CH{=}C}H\mathrm{C_6H_4Me}$), 4.27, 5.09, 5.29 and 5.56 (d, 1H each, $^3J_\mathrm{HH}$ = 6.0 Hz, CH of *p*-cymene), 6.74−8.85 (m, 24H, $\mathrm{CH_{arom}}$ and $\mathrm{C}H\mathrm{{=}CHC_6H_4Me}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 14.65 (d, 2C, $^3J_\mathrm{CP}$ = 3.0 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.26 (d, 2C, $^3J_\mathrm{CP}$ = 3.8 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 17.40 (s, $\mathrm{CH_3}$), 19.88 and 24.93 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 21.32 (s, $\mathrm{C_6H_4}C\mathrm{H_3}$), 30.10 (s, $C\mathrm{H(CH_3)_2}$), 52.67 (dddd, $^1J_\mathrm{CP}$ = 99.0 and 80.7 Hz, $^3J_\mathrm{CP}$ = 14.7 and 4.2 Hz, PCP), 60.50 (d, $^2J_\mathrm{CP}$ = 6.0 Hz, $\mathrm{OCH_2}$), 60.78 (d, $^2J_\mathrm{CP}$ = 5.3 Hz, $\mathrm{OCH_2}$), 61.09 (d, $^2J_\mathrm{CP}$ = 6.8 Hz, $\mathrm{OCH_2}$), 61.18 (d, $^2J_\mathrm{CP}$ = 6.1 Hz, $\mathrm{OCH_2}$), 75.36 (d, $^3J_\mathrm{CP}$ = 12.8 Hz, $\mathrm{CH{=}}C\mathrm{HC_6H_4Me}$), 83.89 (br, $C\mathrm{H{=}CHC_6H_4Me}$), 89.10, 90.85, 92.84, and 97.58 (s, CH of *p*-cymene), 105.54 and 117.64 (s, C of *p*-cymene), 122.00−145.87 (m, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 173.31 (d, $^2J_\mathrm{CP}$ = 32.5 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

3c. Yield: 61% (0.138 g). Anal. Calcd for $\mathrm{RuC_{58}H_{66}O_7P_4N_2}$: C, 61.75; H, 5.90; N, 2.48. Found: C, 61.61; H, 5.57; N, 2.28. IR (KBr, cm^{-1}): 3205 (ν(OH)). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.85 and 1.94 (t, 3H each, $^3J_\mathrm{HH}$ = 6.8 Hz, $\mathrm{OCH_2C}H_3$), 0.94 (d, 3H, $^3J_\mathrm{HH}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 0.97 (t, 3H, $^3J_\mathrm{HH}$ = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 1.17 (d, 3H, $^3J_\mathrm{HH}$ = 7.0 Hz, $\mathrm{CH(C}H_3)_2$), 1.26 (t, 3H, $^3J_\mathrm{HH}$ = 6.7 Hz, $\mathrm{OCH_2C}H_3$), 2.22 (s, 3H, $\mathrm{CH_3}$), 2.90 (m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.16 (d, 1H, $^3J_\mathrm{HH}$ = 10.6 Hz, $\mathrm{CH{=}C}H\mathrm{CPh_2OH}$), 3.58 and 3.99 (m, 4H each, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.71 and 4.93 (d, 1H each, $^3J_\mathrm{HH}$ = 5.5 Hz, CH of *p*-cymene), 4.84 and 5.17 (d, 1H each, $^3J_\mathrm{HH}$ = 5.9 Hz, CH of *p*-cymene), 6.60−8.90 (m, 30H, $\mathrm{CH_{arom}}$ and $\mathrm{C}H\mathrm{{=}CHCPh_2OH}$) ppm; OH signal not observed. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 15.71 (d, 2C, $^3J_\mathrm{CP}$ = 8.2 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.24 (d, 2C, $^3J_\mathrm{CP}$ = 7.7 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 17.93 (s, $\mathrm{CH_3}$), 19.02 and 25.32 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 29.96 (s, $C\mathrm{H(CH_3)_2}$), 51.29 (ddd, $^1J_\mathrm{CP}$ = 95.5 and 77.0 Hz, $^3J_\mathrm{CP}$ = 14.9 Hz, PCP), 60.32 (d, $^2J_\mathrm{CP}$ = 4.3 Hz, $\mathrm{OCH_2}$), 60.52 and 61.16 (d, $^2J_\mathrm{CP}$ = 5.6 Hz, $\mathrm{OCH_2}$), 61.25 (d, $^2J_\mathrm{CP}$ = 7.8 Hz, $\mathrm{OCH_2}$), 80.86 (s, $C\mathrm{Ph_2OH}$), 83.03 (br, $C\mathrm{H{=}CHCPh_2OH}$), 86.20 (d, $^3J_\mathrm{CP}$ = 11.3 Hz, $\mathrm{CH{=}}C\mathrm{HCPh_2OH}$), 86.93, 88.55, 92.46, and 93.73 (s, CH of *p*-cymene), 107.74 and 125.86 (s, C of *p*-cymene), 126.22−148.35 (m, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 172.99 (d, $^2J_\mathrm{CP}$ = 31.8 Hz, Ru−$\mathrm{C_{aryl}}$) ppm. MS (FAB) *m*/*z* 1129.9 [M$^+$ + 1], 994.8 [M$^+$ − *p*-cymene], 977.7 [M$^+$ − NP(=O)(OEt)$_2$].

3d. Yield: 61% (0.128 g). Anal. Calcd for $\mathrm{RuC_{52}H_{62}O_7P_4N_2\cdot{}^1/_2CH_2Cl_2}$: C, 57.61; H, 5.80; N, 2.56. Found: C, 57.86; H, 5.63; N, 2.49. IR (KBr, cm^{-1}): 3215 (ν(OH)). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.82 and 1.25 (t, 3H each, $^3J_\mathrm{HH}$ = 7.0 Hz, $\mathrm{OCH_2C}H_3$), 0.94 and 1.04 (t, 3H each, $^3J_\mathrm{HH}$ = 6.8 Hz, $\mathrm{OCH_2C}H_3$), 1.02 (d, 3H, $^3J_\mathrm{HH}$ = 6.8 Hz, $\mathrm{CH(C}H_3)_2$), 1.20 (d, 3H, $^3J_\mathrm{HH}$ = 6.6 Hz, $\mathrm{CH(C}H_3)_2$), 2.24 (s, 3H, $\mathrm{CH_3}$), 2.96 (m, 2H, $\mathrm{C}H\mathrm{(CH_3)_2}$ and $\mathrm{CH{=}C}H\mathrm{CHPhOH}$), 3.54 and 3.90 (m, 4H each, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.92 and 5.09 (d, 1H each, $^3J_\mathrm{HH}$ = 6.0 Hz, CH of *p*-cymene), 4.98 (d, 1H, $^3J_\mathrm{HH}$ = 8.0 Hz, CH of *p*-cymene), 5.19 (br, 2H, CH of *p*-cymene and C*H*PhOH), 6.21−8.83 (m, 25H, $\mathrm{CH_{arom}}$ and C*H*=CHCHPhOH) ppm; OH signal not observed. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 15.80 (d, 2C, $^3J_\mathrm{CP}$ = 7.8 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 16.20 (d, 2C, $^3J_\mathrm{CP}$ = 8.4 Hz, $\mathrm{OCH_2}C\mathrm{H_3}$), 18.06 (s, $\mathrm{CH_3}$), 19.31 and 25.29 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 30.01 (s, $C\mathrm{H(CH_3)_2}$), 53.13 (dddd, $^1J_\mathrm{CP}$ = 95.2 and 78.4 Hz, $^3J_\mathrm{CP}$ = 14.4 and 3.6 Hz, PCP), 60.29 (d, $^2J_\mathrm{CP}$ = 5.4 Hz, $\mathrm{OCH_2}$), 60.55, 61.16 and 61.36 (d, $^2J_\mathrm{CP}$ = 6.0 Hz, $\mathrm{OCH_2}$), 78.20 (s, *C*HPhOH), 78.67 (d, $^3J_\mathrm{CP}$ = 11.4 Hz, CH=*C*HCHPhOH), 87.22 (br, *C*H=CHCHPhOH), 89.46, 89.68, 93.46, and 93.73 (s, CH of *p*-cymene), 104.84 and 120.91 (s, C of *p*-cymene), 122.28−145.38 (m, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 172.52 (d, $^2J_\mathrm{CP}$ = 31.8 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

3e. Yield: 66% (0.135 g). Anal. Calcd for $\mathrm{RuC_{51}H_{64}O_6P_4N_2}$: C, 59.70; H, 6.29; N, 2.73. Found: C, 59.47; H, 6.12; N, 2.55. IR (KBr, cm^{-1}): 1567 (ν(C=C)). ^{1}H NMR (acetone-d_6): δ 0.91 (t, 3H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 0.98 and 1.25 (d, 3H each, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.04 (t, 3H, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 1.13 (t, 3H, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 1.22 (t, 3H, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 1.25 and 1.63 (m, 4H each, $\mathrm{CH_2}$), 2.15 (s, 3H, $\mathrm{CH_3}$), 2.87 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 11.2 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{C_6H_9}$), 3.00 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.54 (m, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 4.01 (m, 6H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 5.20 and 5.31 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, CH of *p*-cymene), 5.47 and 6.13 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.2 Hz, CH of *p*-cymene), 6.19 (br, 1H, $\mathrm{{=}C}\mathit{H}\mathrm{CH_2}$), 6.70−8.90 (m, 20H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHC_6H_9}$) ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 16.59 (d, $^{3}J_{\mathrm{CP}}$ = 7.8 Hz, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 16.62, 16.70 and 16.75 (d, $^{3}J_{\mathrm{CP}}$ = 8.2 Hz, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 17.66 (s, $\mathrm{CH_3}$), 20.50 and 25.21 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 23.30, 23.60, 26.03, and 30.21 (s, $\mathrm{CH_2}$), 30.93 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 53.04 (dddd, $^{1}J_{\mathrm{CP}}$ = 101.3 and 78.5 Hz, $^{3}J_{\mathrm{CP}}$ = 15.4 and 6.0 Hz, PCP), 60.71, 60.81, and 61.84 (d, $^{2}J_{\mathrm{CP}}$ = 5.8 Hz, $\mathrm{OCH_2}$), 61.42 (d, $^{2}J_{\mathrm{CP}}$ = 5.2 Hz, $\mathrm{OCH_2}$), 78.42 (d, $^{3}J_{\mathrm{CP}}$ = 12.8 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HC_6H_9}$), 82.77 (br, $\mathit{C}\mathrm{H{=}CHC_6H_9}$), 90.19, 92.22, 93.98, and 96.42 (s, CH of *p*-cymene), 106.51 and 118.74 (s, C of *p*-cymene), 120.26−145.43 (m, $\mathit{C}\mathrm{{=}CHCH_2}$, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 138.52 (s, $\mathrm{C{=}}\mathit{C}\mathrm{HCH_2}$), 174.73 (d, $^{2}J_{\mathrm{CP}}$ = 32.6 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

3f. Yield: 68% (0.134 g). Anal. Calcd for $\mathrm{RuC_{48}H_{60}O_6P_4N_2}$: C, 58.47; H, 6.13; N, 2.84. Found: C, 58.50; H, 6.18; N, 2.74. IR (KBr, cm^{-1}): 1589 (ν(C=C)). ^{1}H NMR (CDCl$_3$): δ 0.95 and 1.15 (t, 6H each, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 1.02 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.27 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.84 (s, 3H, $\mathrm{C(C}\mathit{H}_3\mathrm{){=}CH_2}$), 2.20 (s, 3H, $\mathrm{CH_3}$), 2.89 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 11.2 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{C(Me){=}CH_2}$), 2.96 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.58 and 3.89 (m, 4H each, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 4.88 and 5.49 (br, 1H each, $\mathrm{C(Me){=}C}\mathit{H}_2$), 5.04 and 5.22 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.0 Hz, CH of *p*-cymene), 5.38 and 5.68 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.4 Hz, CH of *p*-cymene), 6.74−8.87 (m, 20H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHC(Me){=}CH_2}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 16.12 (br, 4C, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 16.98 (s, $\mathrm{CH_3}$), 19.68, 23.32, and 25.04 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$ and $\mathrm{C(}\mathit{C}\mathrm{H_3){=}CH_2}$), 30.14 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 52.56 (dddd, $^{1}J_{\mathrm{CP}}$ = 95.8 and 80.2 Hz, $^{3}J_{\mathrm{CP}}$ = 10.6 and 5.4 Hz, PCP), 61.09 (m, 4C, $\mathrm{OCH_2}$), 76.23 (d, $^{3}J_{\mathrm{CP}}$ = 12.7 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HC(Me){=}CH_2}$), 83.10 (br, $\mathit{C}\mathrm{H{=}CHC(Me){=}CH_2}$), 89.61, 89.93, 93.23, and 96.15 (s, CH of *p*-cymene), 105.72 and 118.72 (s, C of *p*-cymene), 108.72 (s, $\mathrm{C(Me){=}}\mathit{C}\mathrm{H_2}$), 120.14−145.69 (m, $\mathit{C}\mathrm{(Me){=}CH_2}$, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 172.75 (d, $^{2}J_{\mathrm{CP}}$ = 32.6 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

4a. Yield: 76% (0.184 g). Anal. Calcd for $\mathrm{RuC_{67}H_{60}O_6P_4N_2}$: C, 66.28; H, 4.98; N, 2.31. Found: C, 65.93; H, 4.79; N, 2.24. ^{1}H NMR (CDCl$_3$): δ 0.93 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.4 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.20 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 2.01 (s, 3H, $\mathrm{CH_3}$), 2.88 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.86 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 11.2 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{Ph}$), 4.38 and 5.66 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, CH of *p*-cymene), 5.28 and 5.42 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, CH of *p*-cymene), 6.73−8.66 (m, 45H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHPh}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.60 (s, $\mathrm{CH_3}$), 20.16 and 24.76 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 30.25 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 51.16 (dddd, $^{1}J_{\mathrm{CP}}$ = 96.1 and 80.9 Hz, $^{3}J_{\mathrm{CP}}$ = 14.2 and 5.7 Hz, PCP), 75.04 (d, $^{3}J_{\mathrm{CP}}$ = 12.2 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HPh}$), 82.91 (br, $\mathit{C}\mathrm{H{=}CHPh}$), 90.19, 91.73, 92.86, and 97.73 (s, CH of *p*-cymene), 106.00 and 118.39 (s, C of *p*-cymene), 120.08−144.69 (m, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 152.22, 152.40, and 152.43 (d, $^{2}J_{\mathrm{CP}}$ = 8.1 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.51 (d, $^{2}J_{\mathrm{CP}}$ = 7.1 Hz, $\mathrm{C_{ipso}}$ of OPh), 173.38 (d, $^{2}J_{\mathrm{CP}}$ = 32.6 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

4b. Yield: 71% (0.174 g). Anal. Calcd for $\mathrm{RuC_{68}H_{62}O_6P_4N_2}$: C, 66.50; H, 5.09; N, 2.28. Found: C, 66.73; H, 5.07; N, 2.17. ^{1}H NMR (CDCl$_3$): δ 0.92 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.18 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 2.02 (s, 3H, $\mathrm{CH_3}$), 2.33 (s, 3H, $\mathrm{C_6H_4C}\mathit{H}_3$), 2.88 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.84 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 11.2 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{C_6H_4Me}$), 4.36 and 5.63 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, CH of *p*-cymene), 5.26 and 5.40 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, CH of *p*-cymene), 6.71−8.64 (m, 44H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHC_6H_4Me}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.59 (s, $\mathrm{CH_3}$), 20.03 and 24.75 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 21.26 (s, $\mathrm{C_6H_4}\mathit{C}\mathrm{H_3}$), 30.11 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 50.71 (dddd, $^{1}J_{\mathrm{CP}}$ = 96.7 and 84.7 Hz, $^{3}J_{\mathrm{CP}}$ = 12.8 and 4.7 Hz, PCP), 75.47 (d, $^{3}J_{\mathrm{CP}}$ = 12.2 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HC_6H_4Me}$), 82.71 (br, $\mathit{C}\mathrm{H{=}CHC_6H_4Me}$), 89.98, 91.46, 92.65, and 97.76 (s, CH of *p*-cymene), 105.74 and 118.18 (s, C of *p*-cymene), 120.00−140.53 (m, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 152.04 (d, $^{2}J_{\mathrm{CP}}$ = 11.7 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.19 (d, $^{2}J_{\mathrm{CP}}$ = 10.5 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.33 (d, $^{2}J_{\mathrm{CP}}$ = 6.6 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.42 (d, $^{2}J_{\mathrm{CP}}$ = 7.0 Hz, $\mathrm{C_{ipso}}$ of OPh), 173.60 (d, $^{2}J_{\mathrm{CP}}$ = 32.6 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

4c. Yield: 66% (0.174 g). Anal. Calcd for $\mathrm{RuC_{74}H_{66}O_7P_4N_2}$: C, 67.32; H, 5.04; N, 2.12. Found: C, 67.52; H, 5.12; N, 2.07. IR (KBr, cm^{-1}): 3220 (ν(OH)). ^{1}H NMR (CDCl$_3$): δ 0.88 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.4 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.18 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 2.41 (s, 3H, $\mathrm{CH_3}$), 2.92 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 3.12 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 10.5 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{CPh_2OH}$), 4.68 and 5.09 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, CH of *p*-cymene), 5.31 and 5.47 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.6 Hz, CH of *p*-cymene), 6.49−8.66 (m, 50H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHCPh_2OH}$) ppm; OH signal not observed. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.64 (s, $\mathrm{CH_3}$), 18.47 and 24.80 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 29.70 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 48.94 (dddd, $^{1}J_{\mathrm{CP}}$ = 96.1 and 82.3 Hz, $^{3}J_{\mathrm{CP}}$ = 13.9 and 6.1 Hz, PCP), 80.16 (s, $\mathit{C}\mathrm{Ph_2OH}$), 81.65 (br, $\mathit{C}\mathrm{H{=}CHCPh_2OH}$), 83.70 (d, $^{3}J_{\mathrm{CP}}$ = 11.1 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HCPh_2OH}$), 87.83, 88.18, 92.57, and 94.07 (s, CH of *p*-cymene), 107.61 (s, C of *p*-cymene), 119.55−147.34 (m, C of *p*-cymene, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 151.59, 151.79, and 151.93 (d, $^{2}J_{\mathrm{CP}}$ = 7.6 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.02 (d, $^{2}J_{\mathrm{CP}}$ = 6.4 Hz, $\mathrm{C_{ipso}}$ of OPh), 172.51 (d, $^{2}J_{\mathrm{CP}}$ = 32.0 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

4d. Yield: 62% (0.154 g). Anal. Calcd for $\mathrm{RuC_{68}H_{62}O_7P_4N_2}$: C, 65.64; H, 5.02; N, 2.25. Found: C, 65.30; H, 5.21; N, 2.36. IR (KBr, cm^{-1}): 3215 (ν(OH)). ^{1}H NMR (CDCl$_3$): δ 0.93 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.18 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 2.29 (s, 3H, $\mathrm{CH_3}$), 2.67 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 2.92 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{CHPhOH}$), 4.96 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, CH of *p*-cymene), 5.02 and 5.12 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.4 Hz, CH of *p*-cymene), 5.35 (br, 2H, CH of *p*-cymene and $\mathrm{C}\mathit{H}\mathrm{PhOH}$), 6.69−8.67 (m, 45H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHCHPhOH}$) ppm; OH signal not observed. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.23 (s, $\mathrm{CH_3}$), 19.24 and 25.19 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 30.12 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 51.18 (dddd, $^{1}J_{\mathrm{CP}}$ = 95.2 and 81.2 Hz, $^{3}J_{\mathrm{CP}}$ = 16.3 and 7.1 Hz, PCP), 77.89 (s, $\mathit{C}\mathrm{HPhOH}$), 78.54 (d, $^{3}J_{\mathrm{CP}}$ = 10.5 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HCHPhOH}$), 85.82 (br, $\mathit{C}\mathrm{H{=}CHCHPhOH}$), 89.68, 90.62, 93.76, and 93.82 (s, CH of *p*-cymene), 105.44 (s, C of *p*-cymene), 120.09−144.47 (m, C of *p*-cymene, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 152.07 and 152.33 (d, $^{2}J_{\mathrm{CP}}$ = 7.6 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.26 and 152.45 (d, $^{2}J_{\mathrm{CP}}$ = 6.4 Hz, $\mathrm{C_{ipso}}$ of OPh), 172.99 (d, $^{2}J_{\mathrm{CP}}$ = 32.0 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

4e. Yield: 70% (0.170 g). Anal. Calcd for $\mathrm{RuC_{67}H_{64}O_6P_4N_2}$: C, 66.06; H, 5.30; N, 2.30. Found: C, 66.17; H, 5.29; N, 2.24. IR (KBr, cm^{-1}): 1594 (ν(C=C)). ^{1}H NMR (CDCl$_3$): δ 0.94 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.22 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.66 and 2.05 (m, 4H each, $\mathrm{CH_2}$), 2.24 (s, 3H, $\mathrm{CH_3}$), 2.94 (m, 2H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$ and $\mathrm{CH{=}C}\mathit{H}\mathrm{C_6H_9}$), 5.07 and 5.71 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.8 Hz, CH of *p*-cymene), 5.39 and 5.45 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.6 Hz, CH of *p*-cymene), 6.11 (br, 1H, $\mathrm{{=}C}\mathit{H}\mathrm{CH_2}$), 6.68−8.63 (m, 40H, $\mathrm{CH_{arom}}$ and $\mathrm{C}\mathit{H}\mathrm{{=}CHC_6H_9}$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.02 (s, $\mathrm{CH_3}$), 19.40 and 24.43 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 22.12, 22.40, 24.99, and 29.01 (s, $\mathrm{CH_2}$), 29.73 (s, $\mathit{C}\mathrm{H(CH_3)_2}$), 49.72 (ddd, $^{1}J_{\mathrm{CP}}$ = 82.9 and 75.7 Hz, $^{3}J_{\mathrm{CP}}$ = 7.8 Hz, PCP), 78.40 (d, $^{3}J_{\mathrm{CP}}$ = 12.0 Hz, $\mathrm{CH{=}}\mathit{C}\mathrm{HC_6H_9}$), 80.66 (br, $\mathit{C}\mathrm{H{=}CHC_6H_9}$), 89.64, 90.18, 92.47, and 95.10 (s, CH of *p*-cymene), 104.94 and 117.97 (s, C of *p*-cymene), 119.56−144.29 (m, $\mathit{C}\mathrm{{=}CHCH_2}$, $\mathrm{CH_{arom}}$ and $\mathrm{C_{arom}}$), 136.59 (s, $\mathrm{C{=}}\mathit{C}\mathrm{HCH_2}$), 151.78 and 151.90 (d, $^{2}J_{\mathrm{CP}}$ = 8.4 Hz, $\mathrm{C_{ipso}}$ of OPh), 151.93 (d, $^{2}J_{\mathrm{CP}}$ = 7.2 Hz, $\mathrm{C_{ipso}}$ of OPh), 152.02 (d, $^{2}J_{\mathrm{CP}}$ = 6.6 Hz, $\mathrm{C_{ipso}}$ of OPh), 173.30 (d, $^{2}J_{\mathrm{CP}}$ = 32.3 Hz, Ru−$\mathrm{C_{aryl}}$) ppm.

4f. Yield: 61% (0.144 g). Anal. Calcd for $\mathrm{RuC_{64}H_{60}O_6P_4N_2}$: C, 65.25; H, 5.13; N, 2.38. Found: C, 65.71; H, 5.20; N, 2.45. IR (KBr, cm^{-1}): 1593 (ν(C=C)). ^{1}H NMR (CDCl$_3$): δ 0.93 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.22 (d, 3H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.83 (s, 3H, $\mathrm{C(C}\mathit{H}_3\mathrm{){=}CH_2}$), 2.29 (s, 3H, $\mathrm{CH_3}$), 2.91 (d, 1H, $^{3}J_{\mathrm{HH}}$ = 11.1 Hz, $\mathrm{CH{=}C}\mathit{H}\mathrm{C(Me){=}CH_2}$), 2.97 (m, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$), 4.88 and 5.29 (br, 1H each, $\mathrm{C(Me){=}C}\mathit{H}_2$), 5.08 and 5.72 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, CH of *p*-cymene), 5.34 and 5.44 (d, 1H each, $^{3}J_{\mathrm{HH}}$ = 5.6 Hz, CH of *p*-cymene), 6.59−8.64

(m, 40H, CH$_{arom}$ and C*H*=CHC(Me)=CH$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.21 (s, CH$_3$), 19.78 (s, C(*C*H$_3$)=CH$_2$), 23.36 and 24.92 (s, CH(*C*H$_3$)$_2$), 30.21 (s, *C*H(CH$_3$)$_2$), 50.92 (dddd, $^1J_{CP}$ = 101.3 and 81.7 Hz, $^3J_{CP}$ = 14.7 and 6.5 Hz, PCP), 76.36 (d, $^3J_{CP}$ = 12.8 Hz, CH=*C*HC(Me)=CH$_2$), 82.13 (br, *C*H=CHC(Me)=CH$_2$), 90.44 (s, 2C, CH of *p*-cymene), 92.99 and 96.40 (s, CH of *p*-cymene), 105.85 and 115.82 (s, C of *p*-cymene), 109.02 (s, C(Me)=*C*H$_2$), 118.38−144.74 (m, *C*(Me)=CH$_2$, CH$_{arom}$ and C$_{arom}$), 152.16 (d, $^2J_{CP}$ = 7.8 Hz, C$_{ipso}$ of OPh), 152.26 and 152.43 (d, $^2J_{CP}$ = 6.3 Hz, C$_{ipso}$ of OPh), 152.34 (d, $^2J_{CP}$ = 7.0 Hz, C$_{ipso}$ of OPh), 173.09 (d, $^2J_{CP}$ = 32.1 Hz, Ru−C$_{aryl}$) ppm.

Reactivity of the Carbene Complex [Ru(η^6-*p*-cymene)(κ^2(*C,N*)-C[P{=NP(=O)(OEt)$_2$}Ph$_2$][P{=NP(=O)(OPh)$_2$}Ph$_2$])] (5) toward Phenylacetylene. A solution of complex **5** (0.203 g, 0.2 mmol) and phenylacetylene (0.440 mL, 4 mmol) in 30 mL of THF was stirred at room temperature for 48 h. The solvent was then removed in vacuo and the resulting solid residue transferred to a silica gel chromatography column. Elution with a dichloromethane/methanol (4/1) mixture gave a yellow band, from which a nonseparable mixture of complexes **6** and **7** was obtained after solvent removal. Yield: 80% (0.179 g). Analytical and spectroscopic data for this mixture are as follows. Anal. Calcd for RuC$_{59}$H$_{60}$O$_6$P$_4$N$_2$: C, 63.38; H, 5.41; N, 2.51. Found: C, 63.25; H, 5.33; N, 2.46. ^{1}H NMR (CDCl$_3$): δ 0.89−1.28 (m, 24H, CH(C*H*$_3$)$_2$ and OCH$_2$C*H*$_3$), 1.95 (s, 6H, CH$_3$), 2.85 (m, 2H, C*H*(CH$_3$)$_2$), 3.59 (m, 4H, OC*H*$_2$CH$_3$), 3.86 (m, 6H, OC*H*$_2$CH$_3$ and CH=C*H*Ph), 4.30, 4.35, 5.14, and 5.23 (d, 1H each, $^3J_{HH}$ = 6.0 Hz, CH of *p*-cymene), 5.36 and 5.59 (br, 2H each, CH of *p*-cymene), 6.74−8.23 (m, 70H, CH$_{arom}$ and C*H*=CHPh) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 15.95 (d, $^3J_{CP}$ = 7.6 Hz, OCH$_2$*C*H$_3$), 16.19 (d, 2C, $^3J_{CP}$ = 8.2 Hz, OCH$_2$*C*H$_3$), 16.23 (d, $^3J_{CP}$ = 8.2 Hz, OCH$_2$*C*H$_3$), 17.40 and 17.49 (s, CH$_3$), 19.91, 20.19, 24.68, and 24.85 (s, CH(*C*H$_3$)$_2$), 30.13 and 30.16 (s, *C*H(CH$_3$)$_2$), 52.09 (m, 2C, PCP), 60.31 (d, $^2J_{CP}$ = 5.2 Hz, OCH$_2$), 60.53 (d, $^2J_{CP}$ = 5.8 Hz, OCH$_2$), 61.19 (d, 2C, $^2J_{CP}$ = 6.4 Hz, OCH$_2$), 74.82 (d, $^3J_{CP}$ = 12.8 Hz, CH=*C*HPh), 75.06 (d, $^3J_{CP}$ = 12.2 Hz, CH=*C*HPh), 83.30 and 83.55 (br, *C*H=CHPh), 89.63, 89.79, 91.08, 91.75, 92.67, 93.09, 97.33, and 97.77 (s, CH of *p*-cymene), 105.81, 105.88, 117.69, and 118.39 (s, C of *p*-cymene), 120.02−145.77 (m, CH$_{arom}$ and C$_{arom}$), 152.26 and 152.37 (d, $^2J_{CP}$ = 8.2 Hz, C$_{ipso}$ of OPh), 152.45 and 152.52 (d, $^2J_{CP}$ = 7.0 Hz, C$_{ipso}$ of OPh), 172.52 (d, $^2J_{CP}$ = 31.8 Hz, Ru−C$_{arom}$), 173.81 (d, $^2J_{CP}$ = 33.2 Hz, Ru−C$_{aryl}$) ppm.

Synthesis of the Complexes [Ru(η^6-*p*-cymene)(κ^4-(*C,C,C,N*)-C[P{=NP(=O)(OR)$_2$}Ph$_2$]$_2${(*E*)-C(H)=C(H)Ph})][BF$_4$] (R = Et (8), Ph (9)). A solution of the corresponding ortho-metalated complex **3a** or **4a** (0.2 mmol) in 30 mL of dichloromethane was treated, at room temperature, with a solution of HBF$_4$ in diethyl ether (0.14 mL of a 1.6 M solution, 0.22 mmol) for 30 min. Concentration of the resulting solution (ca. 2 mL) followed by the addition of hexanes (ca. 30 mL) gave a yellow precipitate, which was washed with hexanes (3 × 20 mL) and vacuum-dried.

8. Yield: 78% (0.173 g). Anal. Calcd for RuC$_{51}$H$_{61}$O$_6$F$_4$P$_4$N$_2$B: C, 55.19; H, 5.54; N, 2.52. Found: C, 54.91; H, 5.42; N, 2.42. Conductivity (acetone, 20 °C): 103 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.88 (t, 6H, $^3J_{HH}$ = 6.1 Hz, OCH$_2$C*H*$_3$), 0.94 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.00 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH(C*H*$_3$)$_2$), 1.02 (t, 6H, $^3J_{HH}$ = 6.0 Hz, OCH$_2$C*H*$_3$), 1.93 (s, 3H, CH$_3$), 2.08 (m, 1H, C*H*(CH$_3$)$_2$), 3.76 (m, 8H, OC*H*$_2$CH$_3$), 5.15 and 5.40 (d, 1H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 5.28 (d, 1H, $^3J_{HH}$ = 12.5 Hz, CH=C*H*Ph), 5.81 and 6.10 (d, 1H each, $^3J_{HH}$ = 4.2 Hz, CH of *p*-cymene), 6.96−7.95 (m, 26H, CH$_{arom}$ and C*H*=CHPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 15.86 (d, 2C, $^3J_{CP}$ = 7.6 Hz, OCH$_2$*C*H$_3$), 16.10 (d, $^3J_{CP}$ = 6.4 Hz, OCH$_2$*C*H$_3$), 16.16 (d, $^3J_{CP}$ = 7.0 Hz, OCH$_2$*C*H$_3$), 18.57 (s, CH$_3$), 21.67 and 22.81 (s, CH(*C*H$_3$)$_2$), 28.24 (s, *C*H(CH$_3$)$_2$), 33.90 (dddd, $^1J_{CP}$ = 113.6 and 81.7 Hz, $^3J_{CP}$ = 17.8 and 10.7 Hz, PCP), 63.96 (d, $^2J_{CP}$ = 5.8 Hz, OCH$_2$), 64.97 (d, 2C, $^2J_{CP}$ = 6.4 Hz, OCH$_2$), 65.47 (d, $^2J_{CP}$ = 7.6 Hz, OCH$_2$), 81.21 (dd, $^3J_{CP}$ = 10.2 and 4.4 Hz, CH=*C*HPh), 83.40, 86.80, 88.33, and 89.19 (s, CH of *p*-cymene), 89.18 (d, $^2J_{CP}$ = 2.9 Hz, *C*H=CHPh), 109.23 and 116.82 (s, C of *p*-cymene), 122.56−137.14 (m, CH$_{arom}$ and C$_{arom}$) ppm.

Table 5. Crystal Data and Structure Refinement Details for 3c

chem formula	RuC$_{58}$H$_{66}$O$_7$P$_4$N$_2$·Et$_2$O
fw	1202.20
T, K	293(2)
wavelength, Å	1.54184
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cryst size, mm	0.35 × 0.26 × 0.08
a, Å	16.057(3)
b, Å	18.188(4)
c, Å	22.403(5)
α, deg	90
β, deg	109.04(3)
γ, deg	90
Z	4
V, Å^3	6185(2)
ρ_{calcd}, g cm^{-3}	1.291
μ, mm^{-1}	3.455
F(000)	2520
θ range, deg	2.98−63.88
index ranges	$-17 \le h \le 18$ $-19 \le k \le 21$ $-23 \le l \le 24$
completeness to θ = 63.88°, %	94.4
no. of data collected	45 157
no. of unique data	9664 (R_{int} = 0.0645)
no. of params/restraints	817/2
refinement method	full-matrix least squares on F^2
goodness of fit on F^2	1.031
R1^a ($I > 2\sigma(I)$)	0.0394
wR2^a ($I > 2\sigma(I)$)	0.1081
R1 (all data)	0.0453
wR2 (all data)	0.1132
largest diff peak and hole, e Å^{-3}	0.811 and −0.297

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

9. Yield: 79% (0.206 g). Anal. Calcd for RuC$_{67}$H$_{61}$O$_6$F$_4$P$_4$N$_2$B: C, 61.81; H, 4.72; N, 2.15. Found: C, 61.59; H, 4.63; N, 2.10. Conductivity (acetone, 20 °C): 109 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.90 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.00 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.57 (s, 3H, CH$_3$), 1.81 (m, 1H, C*H*(CH$_3$)$_2$), 5.23 and 5.44 (d, 1H each, $^3J_{HH}$ = 5.9 Hz, CH of *p*-cymene), 5.30 (d, 1H, $^3J_{HH}$ = 13.4 Hz, CH=C*H*Ph), 6.09 and 6.17 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of *p*-cymene), 6.27−7.78 (m, 46H, CH$_{arom}$ and C*H*=CHPh) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 17.98 (s, CH$_3$), 21.27 and 23.23 (s, CH(*C*H$_3$)$_2$), 28.11 (s, *C*H(CH$_3$)$_2$), 32.72 (ddd, $^1J_{CP}$ = 103.9 and 85.5 Hz, $^3J_{CP}$ = 12.7 Hz, PCP), 81.86 (dd, $^3J_{CP}$ = 10.1 and 3.7 Hz, CH=*C*HPh), 83.44, 84.71, 86.37, and 90.08 (s, CH of *p*-cymene), 89.18 (br, *C*H=CHPh), 110.60 and 119.37 (s, C of *p*-cymene), 119.82−137.09 (m, CH$_{arom}$ and C$_{arom}$), 150.23 and 150.72 (d, $^2J_{CP}$ = 8.5 Hz, C$_{ipso}$ of OPh), 150.61 (d, 2C, $^2J_{CP}$ = 7.4 Hz, C$_{ipso}$ of OPh) ppm.

X-ray Crystal Structure Determination of Complex 3c. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexanes into a saturated solution of the complex in diethyl ether. The most relevant crystal and refinement data are collected in Table 5. A yellow single crystal with prismatic shape was mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer (Cu Kα radiation, λ = 1.5418 Å).[22] X-ray data were collected at 293(2) K, with a combination of three runs at different φ and 2θ angles. The data were collected using 0.3° wide ω scans with a crystal-to-detector distance of 4.0 cm. The substantial redundancy in data allows empirical

---

[22] SMART version 5.625, Area-Detector Software Package; Bruker AXS, Madison, WI, 1997−2001.

absorption corrections (SADABS)[23] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission 0.389 534). A total number of 45 157 reflections were collected, with 9664 independent reflections ($R_{\text{int}} = 0.0645$). The raw intensity data frames were integrated with the SAINT program,[24] which also applied corrections for Lorentz and polarization effects.

The software package WINGX was used for space group determination, structure solution, and refinement.[25] The space group determination was based on a check of the Laue symmetry and systematic absences and ascertained from the structure solution. The structure was solved by Patterson interpretation and phase expansion using DIRDIF,[26] completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97.[27] Weighted R factors (R_w) and all goodness of fit values S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference maps and refined isotropically (with the exception of the H atoms of both the ethyl substituents and Et_2O molecule, which were geometrically located; their coordinates were refined riding on their parent atoms). The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 2.3401P]$ with $\sigma^2(F_o^2)$ being obtained from counting statistics and $P = (\max(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from ref 28. Geometrical calculations were made with PARST.[29] Plots were made with PLATON.[30]

Acknowledgment. We are indebted to the Ministerio de Ciencia y Tecnología (MCyT) of Spain (Project BQU2003-00255) and the Gobierno del Principado de Asturias (Project PR-01-GE-6) for financial support. V.C. thanks the MCyT for a “Ramón y Cajal” contract.

Supporting Information Available: Tables and a CIF file giving crystallographic data for complex **3c**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been also deposited with the Cambridge Crystallographic Data Centre, CCDC No. 256978. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (internat.) (+44)1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

OM050121D

---

[23] Sheldrick, G. M. SADABS version 2.03: Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 1997−2001.

[24] SAINT+ NT version 6.04, SAX Area-Detector Integration Program; Bruker AXS, Madison, WI, 1997−2001.

[25] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

[26] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallographic Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1999.

[27] Sheldrick, G. M. SHELXL97: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

[28] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (present distributor: Kluwer Academic Publishers: Dordrecht, The Netherlands).

[29] Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

[30] Spek, A. L. PLATON: A Multipurpose Crystallographic Tool; University of Utrecht, Utrecht, The Netherlands, 2005.