Imination reactions of free and coordinated 2-diphenylphosphino-1-phenyl-phospholane: Access to regioisomeric ruthenium(II) complexes containing novel iminophosphorane–phosphine ligands

Alba E. Díaz-Álvarez,[a] Pascale Crochet,*[a] Maria Zablocka,*[b] Victorio Cadierno,[a] Carine Duhayon,[c] José Gimeno[a] and Jean-Pierre Majoral*[c]

Received (in Montpellier, France) 12th May 2006, Accepted 23rd June 2006
First published as an Advance Article on the web 26th July 2006
DOI: 10.1039/b606781f

In this work, selective monoimination reactions of free and Ru-coordinated 2-diphenylphosphino-1-phenyl-phospholane with diphenylphosphoryl azide or 4-azido-2,3,5,6-tetrafluorobenzonitrile are described. Following this approach, a large variety of neutral and cationic mono- and dinuclear (η^6-arene)–ruthenium(II) complexes containing regioisomeric iminophosphorane–phosphine ligands could be prepared and, in some cases, structurally characterized by means of X-ray diffraction methods. The catalytic activity of these ruthenium complexes, both in racemic or enantiomerically pure form, in Diels–Alder cycloaddition reactions is also presented.

Introduction

The coordination chemistry of heterodifunctional chelating ligands has received considerable attention during recent decades, the continuous efforts in the design of new ligands being justified by their potential application in homogeneous catalysis. In particular, heterobidentate phosphines are widely used in catalysis as hemilabile ligands capable of generating open coordination sites on the metal for substrate binding.[1] Moreover, they can also control the reactivity of the metal sites owing to the different steric and electronic properties of the donor groups. Mixed bidentate P,N-donor ligands, such as phosphine–imines or phosphine–oxazolines, are probably the most attractive and widely used heterodifunctional ligands in catalysis, leading to impressive results in terms of both stereo/enantio-selectivity and reactivity.[2]

Iminophosphoranes, $R_3P{=}NR'$ (nitrogen analogues of phosphorus ylides), have found widespread application in organic synthesis[3] and proved to be versatile nitrogen-donor ligands for transition metals.[4] The combination of a phosphine function with an iminophosphorane unit within the same molecule leads to an almost unexploited family of bidentate P,N-donor ligands, *i.e.* the iminophosphorane–phosphines R_2P–X–P($=$NR$'$)R_2,[5] structurally related to the well-known diphosphine–monoxides.[1c] As far as we are aware, the only catalytic applications reported to date for these types of ligands, which are mainly derived from the symmetrical diphosphines Ph_2P–X–PPh_2 (X = CH_2, $(CH_2)_2$, 1,2-C_6H_4, NR) *via* selective monoimination,[5] are: olefin hydrogenation (Rh and Ir complexes)[6] and oligomerization (Ni complexes),[7] methanol carbonylation (Rh, Ni and Co complexes),[8] Sonogashira-type coupling (Pd complexes),[9] allylic alkylation (Pd and Rh complexes)[10] and transfer hydrogenation of ketones (Ru complexes).[11]

Some years ago, some of us reported a straightforward synthetic route to non-symmetrical α-diphosphines **2** through the hydrozirconation of readily available dihydrophosphole **1**,[12] and subsequent transmetallation of the resulting zirconated species with chlorophosphines (see Chart 1).[13] Following the same approach, enantiopure derivatives (S_PS_C)-**2** can be easily prepared starting from the optically active dihydrophosphole (R_P)-**1**.[13b]

Taking into account that the ruthenium chemistry of iminophosphorane–phosphines has been scarcely investigated,[11] and the growing interest in the design of ruthenium catalysts for organic synthesis,[14] we decided to explore the potential of our α-diphosphines **2** as precursors of these types of ligand and complex. Thus, in this paper, we report the selective synthesis of novel iminophosphorane–phosphines **A** (see Chart 2), derived from the α-diphosphine 2-diphenylphosphino-1-phenyl-phospholane, and their coordination to an (η^6-arene)–ruthenium(II) fragment (complexes **B**). Remarkably, the regioisomeric species **D** could also be readily prepared upon

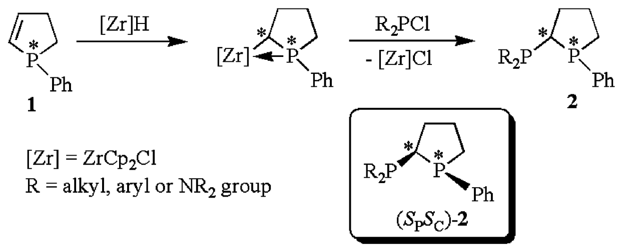


Chart 1 Zirconium-mediated synthesis of α-diphosphines **2**.

[a] *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. E-mail: pascale@fq.uniovi.es Fax: +34 985 103 446; Tel: +34 985 102 985*
[b] *Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Sienkiewicza 112, 90363 Łódź, Poland. E-mail: zabloc@bilbo.cbmm.lodz.pl; Fax: +48 426 847 126 Tel: +48 426 803 217*
[c] *Laboratoire de Chimie de Coordination CNRS, UPR8241, 205 route de Narbonne, 31077 Toulouse Cedex 4, France. E-mail: majoral@lcc-toulouse.fr; Fax: +33 561 553 003 Tel: +33 561 333 123*

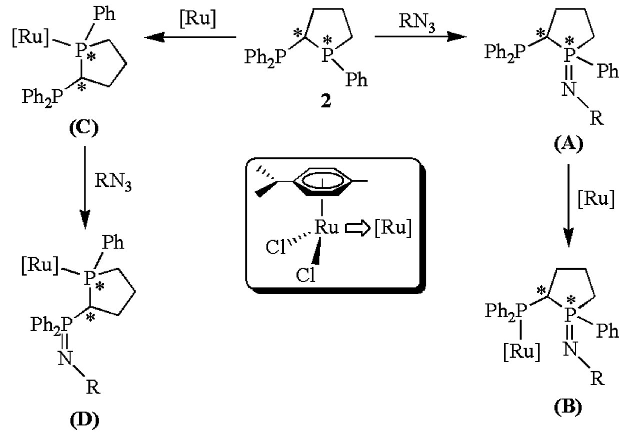


Chart 2 Access to the regioisomeric Ru(II) complexes **B** and **D**.

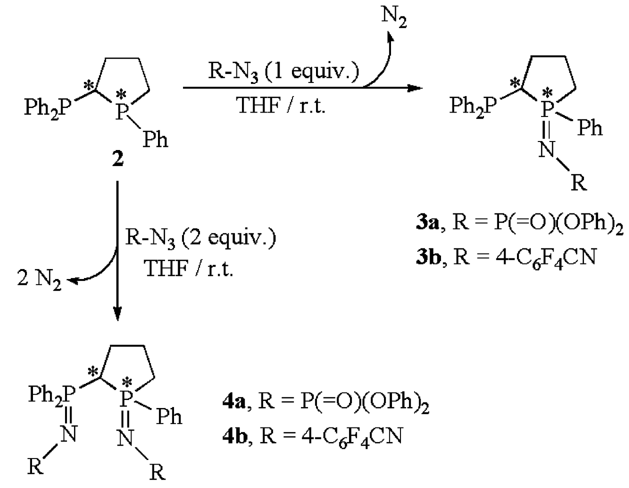
initial coordination of **2** to the metal (species **C**). Reactivity studies directed to the chelation of the novel iminophosphorane–phosphine ligands on these Ru(II) complexes, as well as their catalytic activity in Diels–Alder cycloadditions, are also reported.

Results and discussion

Synthesis of the iminophosphorane–phosphine ligands 3a–b

In general, iminophosphoranes are best prepared through one of two major routes, namely: (*i*) the reaction of azides with phosphines (the Staudinger reaction)[15,16] and (*ii*) the reaction of phosphine dibromides (R_3PBr_2) with primary amines, followed by treatment with a base (the Kirsanov reaction).[16,17] As illustrated in Scheme 1, we employed the former method to prepare the novel iminophosphorane–phosphine ligands **3a–b**, which have been isolated as air-stable solids in 90% and 75% yield, respectively, after stoichiometric reaction of racemic 2-diphenylphosphino-1-phenyl-phospholane (**2**) with diphenylphosphoryl azide or 4-azido-2,3,5,6-tetrafluorobenzonitrile, in THF at room temperature. Under these conditions, monoimination of **2** takes place exclusively at the more basic dialkyl-*P*-phospholane phosphorus atom, the oxidation of the Ph_2P unit being observed only when both an excess of azide and longer reactions times (1–6 d *vs.* 0.5–2 h) are employed. In this manner, the bis(iminophosphorane) derivatives **4a–b** could also be cleanly prepared and isolated in good yields (77–82%; Scheme 1).

The characterization of iminophosphorane–phosphines **3a–b** was straightforward following their analytical and spectroscopic data (details are given in the Experimental section). In particular, the $^{31}P\{^1H\}$ NMR spectra are very informative, showing a strong downfield of the phospholane PhP signal (δ_P = 44.0 (**3a**) and 52.0 (**3b**) ppm) with respect to that shown by the diphosphine precursor **2** (δ_P = −4.5 ppm) and the Ph_2P resonance remaining almost unchanged (δ_P = −13.9 (**3a**) and −10.9 (**3b**) *vs.* −13.5 (**2**) ppm). ^1H and $^{13}C\{^1H\}$ NMR spectra also exhibit signals in accordance with the proposed formulations, the most significant features being those concerning the methynic PCHP group of the ligands: (*i*) in the ^1H NMR, an unresolved multiplet at 3.42–4.15 ppm, and (*ii*) in the $^{13}C\{^1H\}$ NMR, a doublet of doublets resonance at 36.6–39.0 ppm (J_{CP} = 54.7 and 24.3 Hz (**3a**), 75.7 and 24.4 Hz (**3b**)).

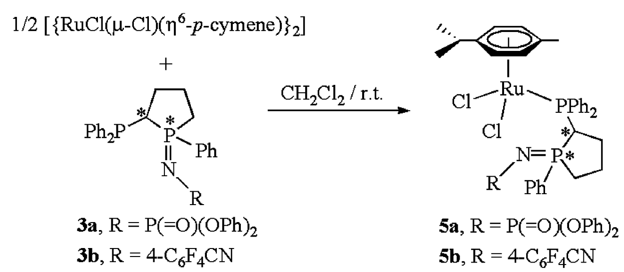


Scheme 1 Mono- and diimination reactions of 2-diphenylphosphino-1-phenyl-phospholane (**2**).

Coordination of the iminophosphorane–phosphine ligands 3a–b to an (η^6-arene)–ruthenium(II) fragment

The ability of the novel iminophosphorane–phosphines **3a–b** to act as mono- and bidentate ligands has been explored using the readily available ruthenium(II) chloro-bridged dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] as the starting material.[18] This dimeric compound was chosen as the precursor due to its versatile reactivity towards polyfunctional ligands.[19] Thus, we have found that the treatment of [{RuCl(μ–Cl)(η^6-*p*-cymene)}$_2$] with *ca.* 2.5 equivalents of **3a–b**, in dichloromethane at room temperature, results in the selective formation of the monomeric derivatives **5a–b** (see Scheme 2), which have been isolated as air-stable orange solids in good yields (80–82%).

The characterization of complexes **5a–b** was achieved by means of standard spectroscopic techniques (IR and multinuclear NMR) as well as elemental analyses, all data being fully consistent with the proposed formulations (see the Experimental section for details). In particular, the monohapto coordination of **3a–b** through the diphenylphosphino group is strongly supported by the $^{31}P\{^1H\}$ NMR spectra, which shows a remarkable downfield shift of the Ph_2P signals (*ca.* δ_P = 23 ppm, $\Delta\delta$ = 35 ppm) with respect to those of the free ligands. In contrast, a slight shielding is observed in the resonances corresponding to the iminophosphorane PhP=N units (**5a**,



Scheme 2 The monodentate coordination of iminophosphorane–phosphines **3a–b**.

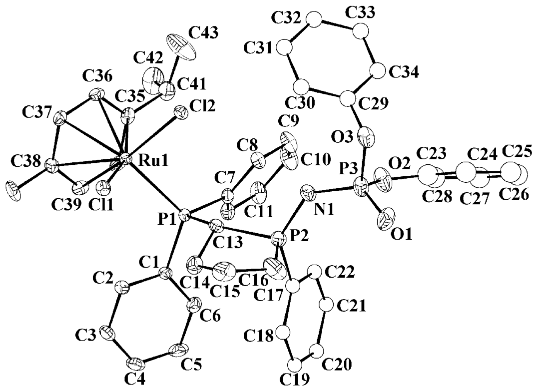
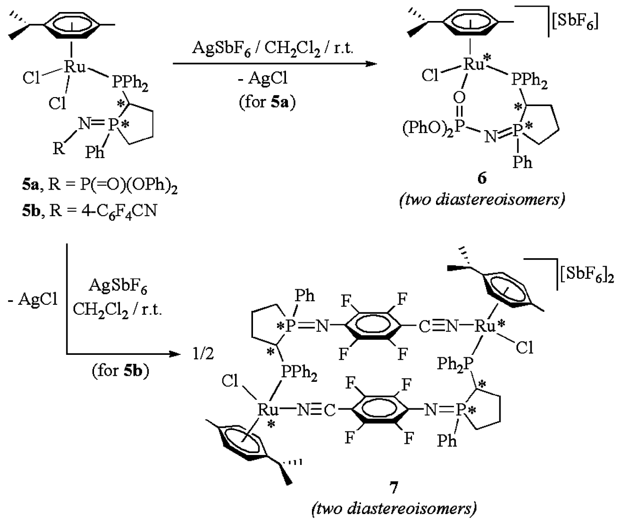


Fig. 1 CAMERON-type view of the structure of complex **5a**, showing the crystallographic labelling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Ru–C* = 1.71; Ru–Cl(1) = 2.4142(15); Ru–Cl(2) = 2.4083(14); Ru–P(1) = 2.3556(14); P(1)–C(13) = 1.875(6); C(13)–C(14) = 1.541(9); C(14)–C(15) = 1.497(10); C(15)–C(16) = 1.509(14); C(13)–P(2) = 1.830(6); C(16)–P(2) = 1.808(9); P(2)–N(1) = 1.577(6); N(1)–P(3) = 1.573(5); P(3)–O(1) = 1.452(6); P(3)–O(2) = 1.589(5); P(3)–O(3) = 1.582(5); C*–Ru–Cl(1) = 126; C*–Ru–Cl(2) = 128; C*–Ru–P(1) = 128; Cl(1)–Ru–Cl(2) = 85.20(5); Cl(1)–Ru–P(1) = 89.81(5); Cl(2)–Ru–P(1) = 85.91(5); Ru–P(1)–C(13) = 115.2(2); P(1)–C(13)–P(2) = 124.2(4); P(1)–C(13)–C(14) = 113.2(4); C(13)–C(14)–C(15) = 107.8(6); C(14)–C(15)–C(16) = 110.4(7); C(15)–C(16)–P(2) = 107.0(5); C(13)–P(2)–C(16) = 95.4(4); C(13)–P(2)–N(1) = 111.1(3); C(16)–P(2)–N(1) = 114.8(4); P(2)–N(1)–P(3) = 128.8(4); N(1)–P(3)–O(1) = 122.3(3); N(1)–P(3)–O(2) = 101.7(3); N(1)–P(3)–O(3) = 106.5(3); O(1)–P(3)–O(2) = 114.3(3); O(1)–P(3)–O(3) = 106.9(3); O(2)–P(3)–O(3) = 103.6(3). C* = centroid of the *p*-cymene ring (C(35), C(36), C(37), C(38), C(39), C(40)).

δ_P = 41.6 ppm, $\Delta\delta$ = −2 ppm; **5b**, δ_P = 44.1 ppm, $\Delta\delta$ = −8 ppm) and the phosphoryl $(PhO)_2P{=}O$ group (**5a**, δ_P = −7.8 ppm, $\Delta\delta$ = −3 ppm). X-Ray diffraction studies on **5a** unequivocally confirmed the structure of these complexes. A view of the molecule is shown in Fig. 1 and reveals the classic pseudooctahedral three-legged piano-stool geometry around the metal, the values of the interligand angles Cl(1)–Ru–Cl(2), Cl(1)–Ru–P(1) and Cl(2)–Ru–P(1), and those between the centroid of the *p*-cymene ring C* and the legs, being typical of a pseudo-octahedron. We also note that, as previously observed in other species containing the N-phosphorylated iminophophorane unit $–P{=}N–P({=}O)(OPh)_2$,[11b,20] the lengths of the formal single and double PN bonds were found to be almost identical (P(2)–N(1) = 1.577(6) Å *vs.* N(1)–P(3) = 1.573(5) Å). This fact clearly reflects the extensive electronic delocalization of the nitrogen lone pair across the P=N–P=O framework in this molecule.

In order to achieve the chelation of iminophosphorane–phosphines **3a–b**, the reactivity of neutral complexes **5a–b** towards silver hexafluoroantimonate has been studied. Thus, we have found that the treatment of **5a** with a stoichiometric amount of $AgSbF_6$ in dichloromethane at room temperature generates the cationic derivative **6**, which is readily formed *via* selective intramolecular *O*-coordination of the phosphoryl group (Scheme 3). Examination of the NMR data of **6** reveals that the chelate ring formation does not proceed in a diastereoselective manner (the Ru atom becomes a stereogenic center), a non-separable mixture of two diastereoisomers being obtained in *ca.* 60 : 40 ratio. The κ²-*P,O*-coordination of the N-phosphorylated ligand **3a** in complex **6** is fully supported by the $^{31}P\{^1H\}$ NMR data. Thus, as a common trend for both diastereoisomers, a remarkable downfield shift in the $(PhO)_2P({=}O)$ group resonance (*ca.* $\Delta\delta$ = 15 ppm), with respect to that of the parent compound **5a** (*i.e.* δ_P = 8.7 (major) and 6.2 (minor) *vs.* −7.8 ppm), is observed. The chemical shifts of the Ph_2P and PhP=N units are almost unaffected by the ring closure ($\Delta\delta$ = 3 ppm), ruling out the formation of a five-membered κ²-*P,N*-chelate complex. It should be noted that the preference shown by the iminophosphorane–phosphine **3a** for the κ²-*P,O*- *vs.* κ²-*P,N*-coordination is in complete accord with the behaviour recently described by some of us for the closely related ligands $Ph_2PCH_2P\{{=}NP({=}O)(OR)_2\}Ph_2$ (R = Et, Ph), from which the κ²-*P,O*-complexes **E** (Chart 3) are also selectively formed.[11b]

Surprisingly, the chelate κ²-*P,N*-coordination of the iminophosphorane–phosphine **3b** has been not observed after treatment of the neutral derivative **5b** with $AgSbF_6$. Instead, the dicationic dinuclear species **7**, in which **3b** is acting as a bridging ligand between two [RuCl(η⁶-*p*-cymene)] metallic fragments, is exclusively formed (Scheme 3). Complex **7**, which has been isolated as an air-stable orange solid in 90% yield,



Scheme 3 Reactivity of complexes **5a–b** towards $AgSbF_6$.

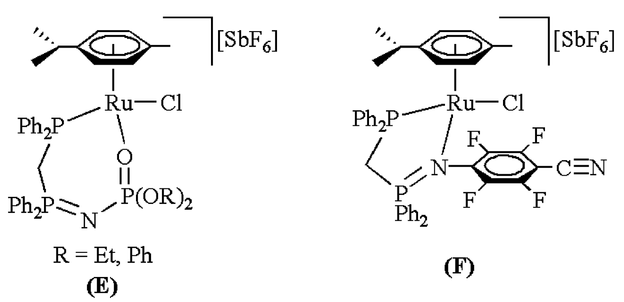


Chart 3 Structure of complexes **E** and **F**.

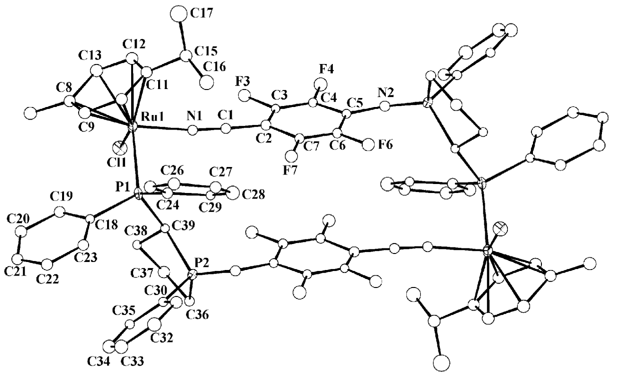


Fig. 2 CAMERON-type view of the structure of complex **7** showing the crystallographic labelling scheme. Unlabelled atoms are generated by a crystallographic center of symmetry. Hydrogen atoms and SbF_6^- anions are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Ru–C* = 1.72; Ru–Cl(1) = 2.390(5); Ru–P(1) = 2.376(5); Ru–N(1) = 2.043(14); N(1)–C(1) = 1.16(2); C(1)–C(2) = 1.41(2); C(5)–N(2) = 1.39(2); P(2)–N(2) = 1.570(15); P(2)–C(36) = 1.838(17); P(2)–C(39) = 1.867(16); C(36)–C(37) = 1.58(2); C(37)–C(38) = 1.55(2); C(38)–C(39) = 1.53(2); C(39)–P(1) = 1.872(16); C*–Ru–Cl(1) = 123; C*–Ru–P(1) = 129; C*–Ru–N(1) = 126; Cl(1)–Ru–N(1) = 86.8(4); Cl(1)–Ru–P(1) = 92.11(15); P(1)–Ru–N(1) = 86.1(4); Ru–N(1)–C(1) = 171.5(14); N(1)–C(1)–C(2) = 178.0(19); P(2)–N(2)–C(5) = 134.2(12); N(2)–P(2)–C(36) = 116.8(8); N(2)–P(2)–C(39) = 119.8(7); C(36)–P(2)–C(39) = 95.8(7); C(36)–C(37)–C(38) = 109.1(14); C(37)–C(38)–C(39) = 105.4(13); C(38)–C(39)–+P(2) = 102.5(10); C(38)–C(39)–P(1) = 112.4(11); P(1)–C(39)–P(2) = 123.0(8); Ru–P(1)–C(39) = 114.2(5). C* = centroid of the *p*-cymene ring (C(8), C(9), C(10), C(11), C(12), C(13)). Symmetry code related to moiety: $2 - x, 1 - y, 2 - z$.

results from the competitive dimerization *vs.* chelate ring formation of the cationic 16e$^-$ intermediate [RuCl(κ^1-*P*-**3b**)(η^6-*p*-cymene)][SbF_6]. Formation of **7** contrasts with the high-yield synthesis of the mononuclear species [RuCl(κ^2-*P*,*N*-Ph_2PCH_2P{=N-4-C_6F_4CN}Ph_2)(η^6-*p*-cymene)][SbF_6] (**F**; Chart 3), starting from the closely related ligand Ph_2PCH_2P{=N-4-C_6F_4CN}Ph_2, recently reported by us.[21] We also note that, although some ruthenium complexes containing *N*-coordinated RC_6F_4CN (R = F, CN) ligands are known,[22] the coordination of the nitrile unit of **3b** in the dinuclear complex **7** can be considered as rather unusual.[23]

The ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectroscopic data obtained for complex **7** suggest that, in solution, it exists as a mixture of two diastereoisomers in *ca.* 75 : 25 ratio. The nature of the major isomer has been unambiguously confirmed by means of X-ray diffraction. The molecular structure is depicted in Fig. 2; selected bond distances and angles are listed in the caption. The two metallic moieties exhibit the expected pseudooctahedral three-legged piano-stool geometry, the coordination sphere around each ruthenium atom consisting of the *p*-cymene ring, one chloride, the PPh_2 group of one of the ligands, and the nitrile unit of a second ligand. The latter is attached to the metal in a nearly linear fashion (Ru–N(1)–C(1) = 171.5(14)°; N(1)–C(1)–C(2) = 178.0(19)°) with bond lengths of Ru–N(1) = 2.043(14) Å and N(1)–C(1) = 1.16(2) Å. These values compare well to those reported in the literature for other nitrile–ruthenium(II) complexes.[24] The iminophosphorane P–N bond distance (P(2)–N(2) = 1.570(15) Å) is also in accord with those observed for related uncoordinated R_3P=N-4-C_6F_4CN moieties.[21,23b]

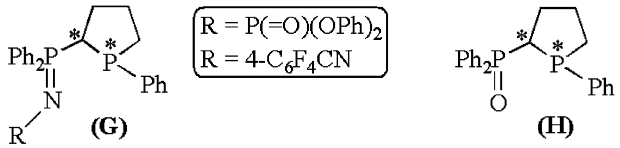


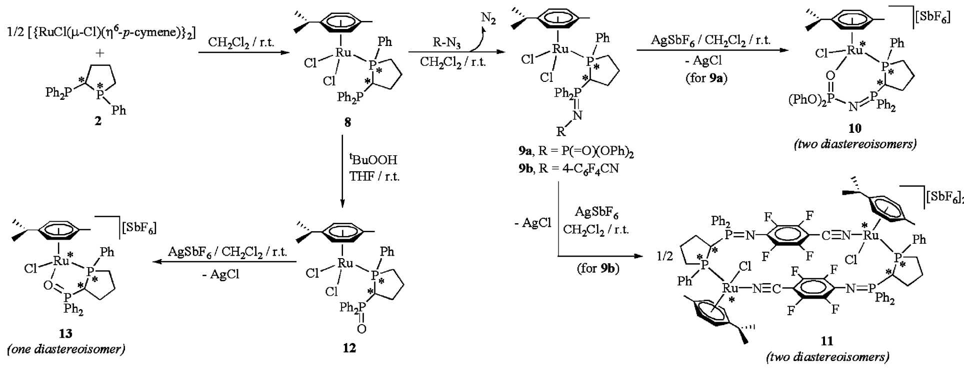
Chart 4 Structure of the iminophosphorane–phosphine ligands **G** and the diphosphine-monoxide **H**.

Finally, it is also interesting to note that the diastereoisomer shown in Fig. 2, the major form present in solution, is a centrosymmetric dimer that shows inverted configurations for the labelled and unlabelled metallic fragments, *i.e.* $S_{Ru(1)}R_{C(39)}S_{P(2)}$ and $R_{Ru}S_CR_P$, respectively.[25] This seems to indicate that the dimerization process of the 16e$^-$ intermediate [RuCl(κ^1-*P*-**3b**)(η^6-*p*-cymene)][SbF_6] takes place with chiral self-recognition.[26] Taking into account that the racemic α-diphosphine precursor **2** is exclusively composed of the S_PS_C and R_PR_C enantiomers,[13] and assuming that formation of **3b** occurs with retention of configuration,[27] we propose an $R_{Ru}R_CS_PS_{Ru}S_CR_P$ configuration for the minor diastereoisomer present in solution.

Imination reactions of coordinated 2-diphenylphosphino-1-phenyl-phospholane: Access to the (η^6-arene)–ruthenium(II) complexes 9–11

As discussed above, the Staudinger reaction of 2-diphenylphosphino-1-phenyl-phospholane (**2**) with one equivalent of azide takes place selectively on the endocyclic *P*-phospholane phosphorus atom, allowing the high-yield synthesis of the iminophosphorane–phosphines **3a,b** (Scheme 1). Remarkably, the regioisomeric ligands **G**, resulting from the selective imination of the diphenylphosphino group (Chart 4), can also be generated upon initial coordination of **2** to ruthenium.

Construction of the ligands **G** involves the imination of the free Ph_2P unit in the neutral (η^6-arene)–ruthenium(II) complex **8** (Scheme 4). This compound can be obtained in high-yield (92%) by treatment of a dichloromethane solution of the dimeric precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with *ca.* 2.5 equivalents of **2**. We note that neither the formation of the cationic species [RuCl(κ^2-*P*,*P*-**2**)(η^6-*p*-cymene)][Cl] nor the monodentate coordination of **2** through the Ph_2P group were observed in the crude reaction mixture by NMR spectroscopy. Complex **8** has been characterized by elemental analyses and multinuclear (^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}) NMR spectroscopy (details are given in the Experimental section). Key spectroscopic features are: (*i*) (^{31}P{^{1}H} NMR) the presence of two doublet signals (J_{PP} = 43.6 Hz) at δ_P −9.3 and 41.9 ppm, corresponding to the diphenylphosphino Ph_2P and phospholane PhP moieties, respectively (the chemical shift of the latter strongly supports its direct coordination to ruthenium), and (*ii*) (^{1}H and ^{13}C{^{1}H} NMR) the presence of characteristic resonances for the methynic PCHP unit, whose proton appears as an unresolved multiplet at δ_H 3.82 ppm, and its



Scheme 4 Synthesis, imination reactions and oxidation of the mononuclear complex **8**.

carbon as a doublet of doublets (J_{CP} = 33.7 and 23.5 Hz) at δ_C 34.5 ppm.

Reaction of complex **8** with a stoichiometric amount of diphenylphosphoryl azide or 4-azido-2,3,5,6-tetrafluorobenzonitrile in dichloromethane at room temperature leads to the clean formation of complexes **9a–b**, containing the novel iminophosphorane–phosphine ligands **G** κ^1-*P*-coordinated to ruthenium (Scheme 4). These compounds have been isolated as air-stable orange solids in 70–74% yield after appropriate work-up, being their analytical and spectroscopic data fully consistent with the proposed structures (see the Experimental section).[28] In particular, the $^{31}P\{^1H\}$ NMR spectra show the expected downfield shift of the Ph_2P signal (δ_P = 17.5 (**9a**) and 21.5 (**9b**) ppm) with respect to that shown by the parent complex **8** (δ_P = −9.3 ppm), confirming its transformation into an iminophosphorane $Ph_2P{=}N$ unit (a slight downfield shift (*ca.* $\Delta\delta$ = 8 ppm) is also observed for the phospholane Ru–PPh resonance in the course of these imination processes).

The reactivity of neutral complexes **9a–b** towards $AgSbF_6$ has also been explored. The results obtained, which are comparable to those previously observed starting from the regioisomeric species **5a–b** (Scheme 3), are summarized in Scheme 4. Thus, we have found that, while the treatment of **9a** with 1 equivalent of $AgSbF_6$ leads to the selective formation of the seven-membered chelate complex **10** (69% yield), *via* preferred κ^2-*P,O vs.* κ^2-*P,N* coordination of the phosphorylated iminophosphorane–phosphine ligand, the dinuclear species **11** is exclusively formed (79% yield) starting from the fluorinated complex **9b**. We also note that, as observed for their regioisomers **6–7**, compounds **10–11** were obtained as non-separable mixtures of two diastereoisomers (the Ru atoms are chiral centers in both complexes) in *ca.* 95 : 5 (**10**) and 60 : 40 (**11**) ratio. Characterization of **10–11** was achieved by means of elemental analyses, IR and multinuclear NMR spectroscopy (since their most characteristic spectroscopic features are comparable to those observed for **6–7** they will not be discussed further; details can be found in the Experimental section). In addition, the structure of the major diastereoisomer of the dinuclear derivative **11** has been determined by X-ray diffraction. The molecular structure is shown in Fig. 3; selected bond distances and angles are listed in the caption, all of them falling within the expected range. Once again, the molecule is a centrosymmetric dimer. The inverted configurations found for the two individual metallic subunits ($R_{Ru(1)}S_{C(4)}S_{P(1)}$ and $S_{Ru}R_CR_P$ configuration, respectively)[25] seems to indicate that a chiral self-recognition dimerization process has also taken place.[26]

The reluctance shown by the iminophosphorane–phosphine ligands **3a–b** and **G** to form five-membered chelate rings, *via* κ^2-*P,N* coordination, contrasts with the behaviour shown by the closely related diphosphine-monoxide **H** (Chart 4), from which the cationic κ^2-*P,O*-chelate complex **13** could be easily prepared (Scheme 4). Formation of **13** involves the initial oxidation of the pendant Ph_2P group of complex **8** and subsequent chloride abstraction in the resulting oxidized species **12**. Oxidation of **8** was readily achieved under mild

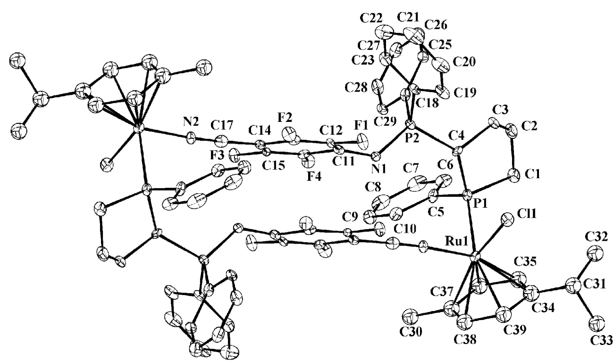
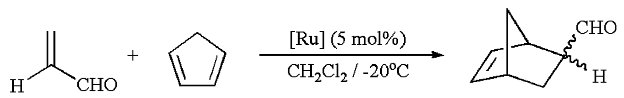


Fig. 3 CAMERON-type view of the structure of complex **11** showing the crystallographic labelling scheme. Unlabelled atoms are generated by a crystallographic center of symmetry. Hydrogen atoms and SbF_6^- anions are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Ru–C* = 1.71; Ru–Cl(1) = 2.396(2); Ru–P(1) = 2.342(2); Ru–N(2) = 2.022(7); N(2)–C(17) = 1.157(11); C(17)–C(14) = 1.416(12); C(11)–N(1) = 1.366(11); P(2)–N(1) = 1.579(7); P(2)–C(4) = 1.805(8); P(1)–C(1) = 1.804(9); P(1)–C(4) = 1.876(9); C(1)–C(2) = 1.505(14); C(2)–C(3) = 1.551(15); C(3)–C(4) = 1.547(12); C*–Ru–Cl(1) = 127; C*–Ru–P(1) = 128; C*–Ru–N(2) = 127; Cl(1)–Ru–N(2) = 87.0(2); Cl(1)–Ru–P(1) = 85.77(8); P(1)–Ru–N(2) = 88.5(2); Ru–N(2)–C(17) = 175.5(7); N(2)–C(17)–C(14) = 175.4(9); Ru–P(1)–C(1) = 112.2(3); Ru–P(1)–C(4) = 116.3(2); Ru–P(1)–C(5) = 114.7(3); C(1)–P(1)–C(4) = 94.2(4); C(1)–P(1)–C(5) = 106.0(4); C(4)–P(1)–C(5) = 111.2(4); P(1)–C(1)–C(2) = 106.2(7); C(1)–C(2)–C(3) = 105.9(8); C(2)–C(3)–C(4) = 107.9(8); C(3)–C(4)–P(1) = 105.5(6); C(3)–C(4)–P(2) = 112.6(6); C(4)–P(2)–N(1) = 107.8(4); P(2)–N(1)–C(11) = 126.1(6). C* = centroid of the *p*-cymene ring (C(34), C(35), C(36), C(37), C(38), C(39)). Symmetry code related to moiety: 1 − *x*, 1 − *y*, 1 − *z*.

Table 1 Diels–Alder reaction of acrolein with cyclopentadiene catalyzed by ruthenium[a]



Catalyst	Time/h	Yield (%)[b]	*Endo* : *exo*[b]	ee (%)[c]
5a	65	>99	68 : 32	48
5b	42	>99	62 : 38	5
9a	46	86	83 : 17	9
9b	91	>99	82 : 18	7
12	12	>99	75 : 25	13

[a] All reactions were conducted in CH_2Cl_2 at −20 °C using 1.5 mmol of acrolein, 9 mmol of CpH and the *in situ* Lewis acid generated from the appropriate Ru–dichloride complex (5 mol%) and $AgSbF_6$ (10 mol%). [b] GC determined using *cis*-decaline as an internal standard. [c] Enantiomeric excess of the major *endo* cycloadduct (GC determined).

conditions (THF, r.t.) by using an excess (*ca.* 2 : 1) of *tert*-butyl hydroperoxide.[29] In this manner, complex **12** could be isolated as an air-stable orange solid in excellent yield (94%), being characterized by means of elemental analysis and NMR spectroscopy. In particular, its $^{31}P\{^1H\}$ NMR spectrum clearly confirms the presence of a $Ph_2P{=}O$ unit showing a characteristic doublet signal (J_{PP} = 19.6 Hz) at δ_P = 31.0 ppm (to be compared with δ_P = −9.3 ppm (J_{PP} = 43.6 Hz) for the non-oxidized Ph_2P unit in the parent complex **8**). Remarkably, the formation of the five-membered chelate ring of the cationic complex **13** proceeds, as indicated by $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, in a diastereoselective manner, a single set of signals being observed in the NMR spectra. We also note that, as previously described in related (η^6-arene)–ruthenium(II) complexes,[30] the chelate coordination of the diphosphine–monoxide ligand results in a downfield shift of both PhP and $Ph_2P{=}O$ phosphorus resonances (*ca.* $\Delta\delta$ = 8 and 3 ppm, respectively).

Catalytic Diels–Alder reactions

During recent years, organometallic ruthenium cations have seen increased use as Lewis-acid catalysts for a variety of C–C bond forming reactions.[31] In particular, dicationic (η^6-arene)–ruthenium(II) complexes containing optically active ligands have recently found promising applications in asymmetric Diels–Alder cycloaddition processes, offering an appealing alternative to the classic Al-, B- or lanthanide-based Lewis-acids, due to their increased stability and resistance to hydrolysis.[32,33] With these precedents in mind, and taking into account that enantiomerically pure iminophosphorane–phosphine ligands can be readily accessible starting from the enantiopure α-diphosphine (S_PS_C)-**2** (Chart 1), we decided to explore the catalytic activity of our ruthenium complexes in this type of cycloaddition reaction. The Diels–Alder-type coupling between acrolein and cyclopentadiene (5 mol% of catalyst, CH_2Cl_2, −20 °C) was used as a model reaction. The catalytically active species, *i.e.* the dications $[Ru(L)(\eta^6\text{-}p\text{-cymene})]^{2+}$ (L = **3a–b** or ligands of type **G–H**), were prepared *in situ* by reacting the appropriate neutral dichloride precursor **5a–b**, **9a–b** or **12** with 2 equivalents of $AgSbF_6$.[34] Selected results are summarized in Table 1.

All the complexes studied have proven to be active catalysts for this particular transformation, leading to the nearly quantitative formation of the bicyclic adduct in 12–90 h, with the diphosphine–monoxide complex **12** showing the highest activity (>99% yield after 12 h). Unfortunately, only a moderate diastereoselectivity was observed, the *endo* cycloadduct being predominant in all cases (*endo* : *exo* ratio from 62 : 38 to 83 : 17). The enantioselectivity of this process could also be determined by using the corresponding enantiomerically pure dichloride–Ru(II) precatalysts (obtained from (S_PS_C)-**2**). As shown in Table 1, only an appreciable enantioselectivity (ee = 48%) was achieved starting from the N-phosphorylated precursor **5a**. Unfortunately, when compared to other arene–ruthenium(II) catalysts already reported in the literature,[32,33] the catalytic performances of **5a–b**, **9a–b** and **12** are in general lower both in term of activity and selectivity.

Conclusions

In summary, novel iminophosphorane–phosphines have been synthesized by selective Staudinger reactions on the α-diphosphine 2-diphenylphosphino-1-phenyl-phospholane (**2**). Remarkably, while selective imination of the more basic dialkyl-*P*-phospholane phosphorus atom takes place starting from the free diphosphine ligand, the diphenylphosphino group can also be selectively transformed into an iminophosphorane unit upon initial coordination of **2** to an (η^6-arene)–ruthenium(II) fragment. To the best of our knowledge, no examples of such a metal-template effect has been previously reported in the chemistry of iminophosphoranes. The novel regioisomeric iminophosphorane–phosphine ligands thus formed have shown a rich coordination chemistry, allowing the preparation of a variety of unusual mono- and dinuclear arene–ruthenium complexes. In addition, all the complexes synthesized were found to be active Lewis acid catalysts in Diels–Alder reactions, albeit with moderate diastereo- and enantioselectivities.

Experimental

General comments

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 with the exception of compounds [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$],[18] 2-diphenylphosphino-1-phenyl-phospholane (**2**),[13] and 4-azido-2,3,5,6-tetrafluorobenzonitrile,[35] which were prepared by following the methods reported in the literature. Diphenylphosphoryl azide was purchased from Aldrich and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. GC measurements were made on a Hewlett-Packard HP6890 equipment using a Supelco Gama-Dex™ 225 (30 m, 250 μm) column. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), 282.4 MHz (^{19}F), or 75.4 MHz (^{13}C) using $SiMe_4$, $CFCl_3$ or 85% H_3PO_4 as standards. Distortionless Enhancement by Polarisation Transfer (DEPT) experiments have been carried out for all compounds reported in this paper.

Syntheses

Iminophosphorane–phosphine ligand 3a. A solution of **2** (0.198 g, 0.570 mmol) in THF (10 mL) was treated, at room temperature, with diphenylphosphoryl azide (0.123 mL, 0.570 mmol) for 2 h. The solvent was then removed under vacuum and the resulting oily residue washed with pentane (2 × 3 mL) and dried *in vacuo* to give **3a** as a white solid. Yield: 0.305 g, 90%. ^{31}P{^{1}H} NMR (C_6D_6): δ −13.9 (d, J_{PP} = 47.3 Hz, PPh_2), −5.1 (d, J_{PP} = 31.9 Hz, P═O), 44.0 (dd, J_{PP} = 47.3 and 31.9 Hz, N═PPh) ppm. ^{1}H NMR (C_6D_6): δ 1.52–2.35 (m, 6H, CH_2), 4.15 (m, 1H, PCHP), 7.09–8.30 (m, 25H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 28.8 (dd, J_{CP} = 8.0 and 8.0 Hz, CH_2), 30.8 (d, J_{CP} = 62.5 Hz, CH_2P), 32.6 (dd, J_{CP} = 19.9 and 8.3 Hz, CH_2), 36.6 (dd, J_{CP} = 54.7 and 24.3 Hz, PCHP), 121.1–153.3 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $C_{34}H_{32}O_3P_3N$ (595.54): C, 68.57; H, 5.42; N, 2.35; found: C, 68.36; H, 5.30; N, 2.45.

Iminophosphorane–phosphine ligand 3b. A solution of **2** (0.100 g, 0.287 mmol) in THF (5 mL) was treated, at room temperature, with 4-azido-2,3,5,6-tetrafluorobenzonitrile (0.062 g, 0.287 mmol) for 30 min. The solvent was then removed under vacuum and the resulting oily residue washed with pentane (2 × 2 mL) and dried *in vacuo* to give **3b** as a yellow solid. Yield: 0.115 g, 75%. IR (KBr): 2226 cm^{-1} (ν_{CN}). ^{31}P{^{1}H} NMR (C_6D_6): δ −10.9 (d, J_{PP} = 59.5 Hz, PPh_2), 52.0 (d, J_{PP} = 59.5 Hz, N═PPh) ppm. ^{1}H NMR (C_6D_6): δ 1.78–2.63 (m, 6H, CH_2), 3.42 (m, 1H, PCHP), 7.13–7.75 (m, 15H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 24.7 (dd, J_{CP} = 7.8 and 7.8 Hz, CH_2), 29.6 (dd, J_{CP} = 54.8 and 1.7 Hz, CH_2P), 31.2 (dd, J_{CP} = 18.1 and 9.9 Hz, CH_2), 39.0 (dd, J_{CP} = 75.7 and 24.4 Hz, PCHP), 71.2 (t, J_{CF} = 15.0 Hz, C≡N), 109.9 (t, J_{CF} = 3.5 Hz, *C*C≡N), 125.8–149.6 (m, C_{arom} and CH_{arom}) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −155.27 and −139.45 (m, 2F each, 4-C_6F_4CN) ppm. Anal. calc. for $C_{29}H_{22}F_4N_2P_2$ (536.44): C, 64.93; H, 4.13; N, 5.22; found: C, 65.10; H, 4.08; N, 5.15.

Bis(iminophosphorane) derivative 4a. A solution of **2** (0.100 g, 0.287 mmol) in THF (5 mL) was treated, at room temperature, with diphenylphosphoryl azide (0.129 mL, 0.600 mmol) for 6 d. The solvent was then removed under vacuum and the resulting oily residue washed with pentane (2 × 3 mL) and dried *in vacuo* to give **4a** as a white solid. Yield: 0.198 g, 82%. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −9.5 (d, J_{PP} = 42.3 Hz, P═O), −5.3 (d, J_{PP} = 29.6 Hz, P═O), 12.1 (d, J_{PP} = 42.3 Hz, N═PPh_2), 41.4 (d, J_{PP} = 29.6 Hz, N═PPh) ppm. ^{1}H NMR ($CDCl_3$): δ 1.90–2.73 (m, 6H, CH_2), 4.77 (m, 1H, PCHP), 7.03–7.84 (m, 35H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.3 (dd, J_{CP} = 12.1 and 4.5 Hz, CH_2), 27.6 (dd, J_{CP} = 9.1 and 1.5 Hz, CH_2), 30.6 (d, J_{CP} = 68.0 Hz, CH_2P), 38.4 (ddd, J_{CP} = 68.8, 45.3 and 1.5 Hz, PCHP), 120.1–152.4 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $C_{46}H_{42}O_6P_4N_2$ (842.73): C, 65.56; H, 5.02; N, 3.32; found: C, 65.40; H, 5.19; N, 3.39.

Bis(iminophosphorane) derivative 4b. A solution of **2** (0.100 g, 0.287 mmol) in THF (5 mL) was treated, at room temperature, with 4-azido-2,3,5,6-tetrafluorobenzonitrile (0.130 g, 0.600 mmol) for 24 h. The solvent was then removed under vacuum and the resulting oily residue washed with pentane (2 × 3 mL) and dried *in vacuo* to give **4b** as a yellow solid. Yield: 0.160 g, 77%. IR (KBr): 2229 cm^{-1} (ν_{CN}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 14.3 (br, N═PPh_2), 43.6 (br, N═PPh) ppm. ^{1}H NMR ($CDCl_3$): δ 1.57–2.09 (m, 6H, CH_2), 3.82 (m, 1H, PCHP), 7.02–7.88 (m, 15H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.9 (d, J_{CP} = 12.6 Hz, CH_2), 28.4 (dd, J_{CP} = 11.4 and 2.4 Hz, CH_2), 29.3 (dd, J_{CP} = 53.5 and 3.0 Hz, CH_2P), 40.0 (dd, J_{CP} = 74.3 and 23.8 Hz, PCHP), 107.2 and 109.5 (t, J_{CF} = 3.8 Hz, *C*C≡N), 128.1–149.1 (m, C_{arom} and CH_{arom}) ppm; (C≡N signals not observed). ^{19}F{^{1}H} NMR (C_6D_6): δ −153.80, −151.79, −139.59 and −139.01 (m, 2F each, 4-C_6F_4CN) ppm. Anal. calc. for $C_{36}H_{22}F_8N_4P_2$ (724.52): C, 59.68; H, 3.06; N, 7.73; found: C, 59.56; H, 3.13; N, 7.59.

Complex 5a. A solution of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.145 g, 0.237 mmol) in dichloromethane (20 mL) was treated, at room temperature, with the iminophosphorane–phosphine ligand **3a** (0.340 g, 0.570 mmol) for 1 h. The solvent was then removed under vacuum and the resulting orange solid residue washed with a 1 : 1 mixture of hexane : diethyl ether (2 × 10 mL). Yield: 0.341 g, 80%. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −7.8 (d, J_{PP} = 25.9 Hz, P═O), 21.7 (d, J_{PP} = 38.8 Hz, Ru–PPh_2), 41.6 (dd, J_{PP} = 38.8 and 25.9 Hz, N═PPh) ppm. ^{1}H NMR ($CDCl_3$): δ 0.69, 1.93 and 3.05 (m, 1H each, CH_2), 0.89 and 1.08 (d, 3H each, J_{HH} = 6.9 Hz, CH(CH_3)$_2$), 1.68 (br, 4H, CH_3 and CH_2), 2.30 (m, 2H, CH_2), 2.46 (m, 1H, *CH*(CH_3)$_2$), 4.43 (m, 1H, PCHP), 4.64 and 4.92 (d, 1H each, J_{HH} = 6.0 Hz, CH of cymene), 5.13 and 5.18 (d, 1H each, J_{HH} = 6.3 Hz, CH of cymene), 6.88–7.98 (m, 25H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 17.1 (s, CH_3), 21.5 and 22.1 (s, CH(CH_3)$_2$), 22.5 (d, J_{CP} = 9.7 Hz, CH_2), 27.2 (d, J_{CP} = 62.8 Hz, CH_2P), 30.0 (s, *CH*(CH_3)$_2$), 31.5 (d, J_{CP} = 13.2 Hz, CH_2), 38.9 (ddd, J_{CP} = 63.7, 13.3 and 7.1 Hz, PCHP), 84.4 and 92.2 (d, J_{CP} = 5.3 Hz, CH of cymene), 85.6 (d, J_{CP} = 7.1 Hz, CH of cymene), 89.1 (d, J_{CP} = 2.6 Hz, CH of cymene), 94.8 and

109.5 (s, C of cymene), 120.7–152.2 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $RuC_{44}H_{46}O_3P_3Cl_2N$ (901.74): C, 58.61; H, 5.14; N, 1.55; found: C, 58.47; H, 5.26; N, 1.40.

Complex 5b. Complex **5b**, isolated as an orange solid, was prepared as described for **5a** starting from [{RuCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] (0.145 g, 0.237 mmol) and **3b** (0.306 g, 0.570 mmol). Yield: 0.327 g, 82%. IR (KBr): 2227 cm^{-1} (ν_{CN}). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.4 (d, J_{PP} = 37.8 Hz, Ru–PPh$_2$), 44.1 (d, J_{PP} = 37.8 Hz, N=PPh) ppm. ^1H NMR (C_6D_6): δ 0.59–1.65 (m, 5H, CH$_2$), 0.80 and 0.97 (d, 3H each, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.36 (s, 3H, CH$_3$), 2.47 (m, 1H, C*H*(CH$_3$)$_2$), 3.30 (m, 1H, CH$_2$), 4.28 and 4.98 (d, 1H each, J_{HH} = 6.0 Hz, CH of cymene), 4.49 and 4.56 (d, 1H each, J_{HH} = 5.7 Hz, CH of cymene), 4.97 (m, 1H, PCHP), 6.62–8.06 (m, 15H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.1 (s, CH$_3$), 20.0 and 23.1 (s, CH(*C*H$_3$)$_2$), 22.0 (d, J_{CP} = 10.8 Hz, CH$_2$), 27.6 (d, J_{CP} = 52.9 Hz, CH$_2$P), 30.1 (s, *C*H(CH$_3$)$_2$), 30.4 (d, J_{CP} = 7.5 Hz, CH$_2$), 37.5 (dd, J_{CP} = 59.3 and 13.1 Hz, PCHP), 78.5 (t, J_{CF} = 13.0 Hz, C≡N), 85.3, 85.5, 88.9 and 91.7 (s, CH of cymene), 94.8 and 109.2 (s, C of cymene), 109.7 (br, *C*C≡N), 121.9–153.5 (m, C_{arom} and CH_{arom}) ppm. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −154.78 and −139.60 (m, 2F each, 4-C$_6$F$_4$CN) ppm. Anal. calc. for $RuC_{39}H_{36}F_4Cl_2N_2P_2$ (842.63): C, 55.59; H, 4.31; N, 3.32; found: C, 55.79; H, 4.53; N, 3.13.

Complex 6. A solution of complex **5a** (0.154 g, 0.171 mmol) in dichloromethane (20 mL) was treated, at room temperature and in the absence of light, with AgSbF$_6$ (0.059 g, 0.171 mmol) for 2 h. After the AgCl thus formed was filtered off (Kieselguhr), the solution was evaporated to dryness, and the resulting solid orange residue washed with diethyl ether (3 × 10 mL) and dried *in vacuo*. Complex **6** was isolated as a non-separable mixture of two diastereoisomers in *ca*. 60 : 40 ratio. Yield: 0.139 g, 74%. Anal. calc. for $RuC_{44}H_{46}F_6O_3P_3ClNSb$ (1102.04): C, 47.96; H, 4.21; N, 1.27; found: C, 47.80; H, 4.33; N, 1.33. *Spectroscopic data for the major diastereoisomer are as follows*: $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 8.7 (dd, J_{PP} = 27.0 and 2.8 Hz, P=O–Ru), 25.3 (dd, J_{PP} = 6.9 and 2.8 Hz, Ru–PPh$_2$), 44.3 (dd, J_{PP} = 27.0 and 6.9 Hz, N=PPh) ppm. ^1H NMR (CDCl$_3$): δ 0.90 and 1.03 (d, 3H each, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.78 (s, 3H, CH$_3$), 1.84–2.80 (m, 7H, CH$_2$ and C*H*(CH$_3$)$_2$), 4.61 (m, 1H, PCHP), 4.72 and 4.83 (d, 1H each, J_{HH} = 6.0 Hz, CH of cymene), 5.35 and 5.62 (d, 1H each, J_{HH} = 5.2 Hz, CH of cymene), 6.89–7.69 (m, 25H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 17.3 (s, CH$_3$), 20.9 and 21.4 (s, CH(*C*H$_3$)$_2$), 22.3 (d, J_{CP} = 8.8 Hz, CH$_2$), 25.1 (dd, J_{CP} = 18.0 and 6.0 Hz, CH$_2$), 29.6 (s, *C*H(CH$_3$)$_2$), 32.6 (d, J_{CP} = 75.6 Hz, CH$_2$P), 39.7 (dd, J_{CP} = 43.9 and 8.8 Hz, PCHP), 83.3 and 87.9 (s, CH of cymene), 85.5 (d, J_{CP} = 7.7 Hz, CH of cymene), 89.8 (d, J_{CP} = 2.7 Hz, CH of cymene), 92.9 and 106.4 (s, C of cymene), 119.4–151.0 (m, C_{arom} and CH_{arom}) ppm. *Spectroscopic data for the minor diastereoisomer are as follows*: $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 6.2 (dd, J_{PP} = 22.8 and 5.3 Hz, P=O–Ru), 25.6 (dd, J_{PP} = 6.4 and 5.3 Hz, Ru–PPh$_2$), 44.0 (dd, J_{PP} = 22.8 and 6.4 Hz, N=PPh) ppm. ^1H NMR (CDCl$_3$): δ 0.82 and 1.10 (d, 3H each, J_{HH} = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.29 (s, 3H, CH$_3$), 1.84–2.80 (m, 7H, CH$_2$ and C*H*(CH$_3$)$_2$), 4.19 and 4.86 (d, 1H each, J_{HH} = 5.8 Hz, CH of cymene), 4.44 (m, 1H, PCHP), 5.44 and 5.51 (d, 1H each, J_{HH} = 6.0 Hz, CH of cymene), 6.89–7.69 (m, 25H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 15.9 (s, CH$_3$), 19.7 (d, J_{CP} = 6.0 Hz, CH$_2$), 21.2 and 21.5 (s, CH(*C*H$_3$)$_2$), 26.3 (d, J_{CP} = 13.0 Hz, CH$_2$), 29.7 (s, *C*H(CH$_3$)$_2$), 32.6 (d, J_{CP} = 75.6 Hz, CH$_2$P), 35.9 (dd, J_{CP} = 47.5 and 15.1 Hz, PCHP), 84.0 (d, J_{CP} = 5.5 Hz, CH of cymene), 86.0 (d, J_{CP} = 4.4 Hz, CH of cymene), 87.4 (d, J_{CP} = 2.7 Hz, CH of cymene), 94.1 and 106.7 (s, C of cymene), 95.6 (d, J_{CP} = 5.0 Hz, CH of cymene), 119.4–151.0 (m, C_{arom} and CH_{arom}) ppm.

Complex 7. The orange complex **7**, isolated as a unseparable mixture of two diastereoisomers in *ca*. 75 : 25 ratio, was prepared as described for **6** starting from **5b** (0.200 g, 0.237 mmol) and AgSbF$_6$ (0.086 g, 0.250 mmol). Yield: 0.222 g, 90%. Anal. calc. for $Ru_2C_{78}H_{72}F_{20}N_4P_4Cl_2Sb_2$ (2085.86): C, 44.91; H, 3.48; N, 2.69; found: C, 44.87; H, 3.65; N, 2.48. *Spectroscopic data for the major diastereoisomer are as follows*: IR (KBr): 2234 cm^{-1} (ν_{CN}). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 30.3 (d, J_{PP} = 34.3 Hz, Ru–PPh$_2$), 44.6 (d, J_{PP} = 34.3 Hz, N=PPh) ppm. ^1H NMR (CD$_2$Cl$_2$): δ 0.95 and 1.13 (d, 6H each, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.41–1.75 (m, 4H, CH$_2$), 1.82 (s, 6H, CH$_3$), 1.86–2.52 (m, 8H, CH$_2$ and C*H*(CH$_3$)$_2$), 2.79 (m, 2H, CH$_2$), 3.40 (m, 2H, PCHP), 5.00, 5.16, 5.42 and 5.75 (d, 2H each, J_{HH} = 6.3 Hz, CH of cymene), 6.39–7.99 (m, 30H, CH_{arom}) ppm. $^{19}F\{^1H\}$ NMR (CD$_2$Cl$_2$): δ −154.41 and −135.59 (m, 4F each, 4-C$_6$F$_4$CN) ppm. *Spectroscopic data for the minor diastereoisomer are as follows*: IR (KBr): 2234 cm^{-1} (ν_{CN}). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 30.9 (d, J_{PP} = 31.0 Hz, Ru–PPh$_2$), 40.6} (d, J_{PP} = 31.0 Hz, N=PPh) ppm. ^1H NMR (CD$_2$Cl$_2$): δ 0.98 and 1.19 (d, 6H each, J_{HH} = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.41–1.75 (m, 4H, CH$_2$), 1.54 (s, 6H, CH$_3$), 1.86–2.52 (m, 8H, CH$_2$ and C*H*(CH$_3$)$_2$), 2.79 (m, 2H, CH$_2$), 3.40 (m, 2H, PCHP), 5.00, 5.16, 5.49 and 5.80 (d, 2H each, J_{HH} = 6.3 Hz, CH of cymene), 6.39–7.99 (m, 30H, CH_{arom}) ppm. $^{19}F\{^1H\}$ NMR (CD$_2$Cl$_2$): δ −152.85 and −136.91 (m, 4F each, 4-C$_6$F$_4$CN) ppm. This compound was not soluble enough to be characterized by $^{13}C\{^1H\}$ NMR spectroscopy.

Complex 8. A solution of [{RuCl(μ-Cl)(η⁶-*p*-cymene)}$_2$] (0.234 g, 0.382 mmol) in dichloromethane (25 mL) was treated, at room temperature, with 2-diphenylphosphino-1-phenyl-phospholane (**2**) (0.320 g, 0.917 mmol) for 1 h. The solvent was then removed *in vacuo* and the resulting solid orange residue washed with a 1 : 1 mixture of hexane : diethyl ether (3 × 10 mL). Yield: 0.460 g, 92%. $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ −9.3 (d, J_{PP} = 43.6 Hz, PPh$_2$), 41.9 (d, J_{PP} = 43.6 Hz, Ru–PPh) ppm. ^1H NMR (CDCl$_3$): δ 1.19 (d, 3H, J_{HH} = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 3H, J_{HH} = 7.1 Hz, CH(C*H*$_3$)$_2$), 1.69 and 2.60 (m, 2H each, CH$_2$), 1.90 (s, 3H, CH$_3$), 1.98 and 2.18 (m, 1H each, CH$_2$), 2.78 (m, 1H, C*H*(CH$_3$)$_2$), 3.82 (m, 1H, PCHP), 5.01 and 5.38 (d, 1H each, J_{HH} = 5.7 Hz, CH of cymene), 5.17 and 5.21 (d, 1H each, J_{HH} = 6.1 Hz, CH of cymene), 6.86–7.98 (m, 15H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 18.0 (s, CH$_3$), 21.7 and 22.4 (s, CH(*C*H$_3$)$_2$), 26.6 and 32.8 (s, CH$_2$), 27.7 (d, J_{CP} = 29.2 Hz, CH$_2$P), 30.4 (s, *C*H(CH$_3$)$_2$), 34.5 (dd, J_{CP} = 33.7 and 23.5 Hz, PCHP), 85.2 (d, J_{CP} = 5.7 Hz, CH of cymene), 86.1 (br, 2C, CH of cymene), 88.4 (d, J_{CP} = 5.1 Hz, CH of cymene), 96.6 (s, C of cymene), 109.1 (d, J_{CP} = 2.5 Hz, C of cymene), 127.6–137.3 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $RuC_{32}H_{36}Cl_2P_2$ (654.55): C, 58.72; H, 5.54; found: C, 58.62; H, 5.37.

Complex 9a. A solution of **8** (0.200 g, 0.305 mmol) in dichloromethane (20 mL) was treated, at room temperature, with diphenylphosphoryl azide (0.066 mL, 0.305 mmol) for 7 days. The solvent was then removed under vacuum and the resulting orange solid residue washed with a 1 : 1 mixture of hexane : diethyl ether (3 × 10 mL) and dried *in vacuo*. Yield: 0.193 g, 70%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −11.0 (d, J_{PP} = 40.2 Hz, P=O), 17.5 (dd, J_{PP} = 40.2 and 27.2 Hz, Ph_2P=N), 48.6 (d, J_{PP} = 27.2 Hz, Ru–PPh) ppm. ^1H NMR ($CDCl_3$): δ 1.24 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.79 (s, 3H, CH_3), 2.17–3.73 (m, 7H, CH_2 and $CH(CH_3)_2$), 4.09 (m, 1H, PCHP), 4.83 and 5.37 (d, 1H each, J_{HH} = 4.8 Hz, CH of cymene), 4.96 and 5.26 (d, 1H each, J_{HH} = 5.2 Hz, CH of cymene), 6.34–7.69 (m, 25H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.2 (s, CH_3), 21.9 and 22.3 (s, $CH(CH_3)_2$), 26.3 and 32.5 (s, CH_2), 30.6 (s, $CH(CH_3)_2$), 30.9 (d, J_{CP} = 31.7 Hz, CH_2P), 33.5 (ddd, J_{CP} = 71.0, 15.0 and 3.6 Hz, PCHP), 85.7 (s, CH of cymene), 86.4 (d, J_{CP} = 8.2 Hz, CH of cymene), 87.2 and 88.0 (d, J_{CP} = 7.2 Hz, CH of cymene), 97.0 (s, C of cymene), 110.1 (d, J_{CP} = 7.2 Hz, C of cymene), 120.1–152.4 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $RuC_{44}H_{46}O_3P_3Cl_2N$ (901.74): C, 58.61; H, 5.14; N, 1.55; found: C, 58.40; H, 5.32; N, 1.48.

Complex 9b. Complex **9b**, isolated as an orange solid, was prepared as described for **9a** starting from **8** (0.100 g, 0.153 mmol) and 4-azido-2,3,5,6-tetrafluorobenzonitrile (0.033 g, 0.153 mmol). Reaction time: 8 h. Yield: 0.095 g, 74%. IR (KBr): 2226 cm^{-1} (ν_{CN}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.5 (d, J_{PP} = 28.5 Hz, Ph_2P=N), 49.6 (d, J_{PP} = 28.5 Hz, Ru–PPh) ppm. ^1H NMR ($CDCl_3$): δ 1.27 (d, 6H, J_{HH} = 4.3 Hz, $CH(CH_3)_2$), 1.84 (s, 3H, CH_3), 2.40 (m, 3H, CH_2), 2.71 (m, 2H, CH_2), 2.92 (m, 1H, $CH(CH_3)_2$), 3.21 (m, 1H, CH_2), 3.83 (m, 1H, PCHP), 4.82 and 4.90 (d, 1H each, J_{HH} = 4.8 Hz, CH of cymene), 5.19 and 5.41 (d, 1H each, J_{HH} = 5.1 Hz, CH of cymene), 7.02–7.61 (m, 15H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.2 (s, CH_3), 21.9 and 22.3 (s, $CH(CH_3)_2$), 26.9 and 37.8 (s, CH_2), 30.6 (s, $CH(CH_3)_2$), 31.3 (d, J_{CP} = 30.6 Hz, CH_2P), 36.1 (dd, J_{CP} = 81.1 and 12.6 Hz, PCHP), 79.3 (t, J_{CF} = 11.0 Hz, C≡N), 85.7, 86.8 and 87.0 (s, CH of cymene), 87.7 (d, J_{CP} = 3.5 Hz, CH of cymene), 97.1 (s, C of cymene), 107.1 (t, J_{CF} = 4.0 Hz, CC≡N), 110.5 (d, J_{CP} = 5.3 Hz, C of cymene), 128.6–152.8 (m, C_{arom} and CH_{arom}) ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −151.65, −149.11, −138.79 and −132.50 (m, 1F each, 4-C_6F_4CN) ppm. Anal. calc. for $RuC_{39}H_{36}F_4Cl_2N_2P_2$ (842.63): C, 55.59; H, 4.31; N, 3.32; found: C, 55.36; H, 4.23; N, 3.42.

Complex 10. A solution of complex **9a** (0.154 g, 0.171 mmol) in dichloromethane (10 mL) was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.059 g, 0.171 mmol) for 2 h. After the AgCl formed was filtered off (Kieselguhr), the solution was evaporated to dryness, and the resulting orange solid residue washed with diethyl ether (3 × 10 mL) and dried *in vacuo*. Complex **10** was isolated as a non-separable mixture of two diastereoisomers in *ca.* 95 : 5 ratio. Yield: 0.130 g, 69%. Anal. calc. for $RuC_{44}H_{46}F_6O_3P_3ClNSb$ (1102.04): C, 47.96; H, 4.21; N, 1.27; found: C, 47.85; H, 3.99; N, 1.08. *Spectroscopic data for the major diastereoisomer are as follows*: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.9 (d, J_{PP} = 34.9 Hz, P=O–Ru), 17.0 (d, J_{PP} = 34.9 Hz, Ph_2P=N), 49.2 (s, Ru–PPh) ppm. ^1H NMR ($CDCl_3$): δ 0.92–2.72 (m, 6H, CH_2), 1.21 and 1.28 (d, 3H each, J_{HH} = 7.0 Hz, $CH(CH_3)_2$), 1.82 (s, 3H, CH_3), 2.95 (m, 1H, $CH(CH_3)_2$), 4.58 (m, 1H, PCHP), 5.18 and 5.87 (d, 1H each, J_{HH} = 5.7 Hz, CH of cymene), 5.39 and 5.67 (d, 1H each, J_{HH} = 6.3 Hz, CH of cymene), 6.84–7.74 (m, 25H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.8 (s, CH_3), 21.3 and 23.0 (s, $CH(CH_3)_2$), 28.4 (dd, J_{CP} = 15.6 and 5.1 Hz, CH_2), 29.6 (dd, J_{CP} = 31.2 and 15.4 Hz, CH_2P), 30.6 (s, CH_2), 31.4 (s, $CH(CH_3)_2$), 39.9 (dd, J_{CP} = 61.0 and 14.6 Hz, PCHP), 81.7 (s, CH of cymene), 87.4 (d, J_{CP} = 1.9 Hz, CH of cymene), 87.5 (d, J_{CP} = 3.2 Hz, CH of cymene), 89.2 (d, J_{CP} = 6.0 Hz, CH of cymene), 97.4 (s, C of cymene), 112.5 (d, J_{CP} = 5.7 Hz, C of cymene), 120.5–152.0 (m, C_{arom} and CH_{arom}) ppm. *Spectroscopic data for the minor diastereoisomer are as follows:* $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.6 (d, J_{PP} = 33.2 Hz, P=O–Ru), 15.9 (d, J_{PP} = 33.2 Hz, Ph_2P=N), 49.2 (s, Ru–PPh) ppm. ^1H NMR ($CDCl_3$): δ 0.92–2.72 (m, 6H, CH_2), 1.09 and 1.33 (d, 3H each, J_{HH} = 6.9 Hz, $CH(CH_3)_2$), 1.99 (s, 3H, CH_3), 2.95 (m, 1H, $CH(CH_3)_2$), 4.58 (m, 1H, PCHP), 5.28 (br, 2H, CH of cymene), 5.46 and 5.73 (d, 1H each, J_{HH} = 6.0 Hz, CH of cymene), 6.84–7.74 (m, 25H, CH_{arom}) ppm.

Complex 11. The orange complex **11**, isolated as a non-separable mixture of two diastereoisomers in *ca.* 60 : 40 ratio, was prepared as described for **10** starting from **9b** (0.185 g, 0.219 mmol) and $AgSbF_6$ (0.075 g, 0.219 mmol). Yield: 0.180 g, 79%. Anal. calc. for $Ru_2C_{78}H_{72}F_{20}N_4P_4Cl_2Sb_2$ (2085.86): C, 44.91; H, 3.48; N, 2.69; found: C, 45.26; H, 3.56; N, 2.57. *Spectroscopic data for the major diastereoisomer are as follows*: IR (KBr): 2259 cm^{-1} (ν_{CN}). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 25.6 (d, J_{PP} = 20.2 Hz, Ph_2P=N), 52.2 (d, J_{PP} = 20.2 Hz, Ru–PPh) ppm. ^1H NMR (acetone-d_6): δ 0.85–3.45 (m, 14H, CH_2 and $CH(CH_3)_2$), 1.12–1.35 (m, 12H, $CH(CH_3)_2$), 2.03 (s, 6H, CH_3), 4.55 (m, 2H, PCHP), 5.60 (br, 2H, CH of cymene), 5.92–6.12 (m, 6H, CH of cymene), 7.13–7.80 (m, 30H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 23.4 (s, CH_3), 27.4 and 27.6 (s, $CH(CH_3)_2$), 34.4 and 40.0 (s, CH_2), 37.0 (s, $CH(CH_3)_2$), 38.6 (d, J_{CP} = 33.6 Hz, CH_2P), 41.8 (dd, J_{CP} = 53.4 and 13.8 Hz, PCHP), 94.1, 97.0, 97.9 and 98.6 (s, CH of cymene), 107.9 and 119.1 (s, C of cymene), 124.1 (br, CC≡N), 134.5–156.1 (m, C_{arom} and CH_{arom}) ppm; C≡N signal not observed. $^{19}F\{^1H\}$ NMR (acetone-d_6): δ −148.34 and −137.04 (m, 4F each, 4-C_6F_4CN) ppm. *Spectroscopic data for the minor diastereoisomer are as follows:* IR (KBr): 2259 cm^{-1} (ν_{CN}). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 25.2 (d, J_{PP} = 20.2 Hz, Ph_2P=N), 57.9 (d, J_{PP} = 20.2 Hz, Ru–PPh) ppm. ^1H NMR (acetone-d_6): δ 0.85–3.45 (m, 14H, CH_2 and $CH(CH_3)_2$), 1.12–1.35 (m, 12H, $CH(CH_3)_2$), 1.86 (s, 6H, CH_3), 4.63 (m, 2H, PCHP), 5.60 (br, 2H, CH of cymene), 5.92–6.12 (m, 6H, CH of cymene), 7.13–7.80 (m, 30H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 23.2 (s, CH_3), 27.2 and 27.6 (s, $CH(CH_3)_2$), 34.1 and 39.9 (s, CH_2), 36.9 (s, $CH(CH_3)_2$), 38.6 (d, J_{CP} = 33.6 Hz, CH_2P), 42.9 (dd, J_{CP} = 53.4 and 13.8 Hz,

Table 2 Selected crystallographic data for complexes **5a**, **7** and **11**

	Complex **5a**	Complex **7**	Complex **11**
Empirical formula	$RuC_{44}H_{46}O_3P_3Cl_2N \cdot CHCl_3$	$Ru_2C_{78}H_{72}F_{20}N_4P_4Cl_2Sb_2$	$Ru_2C_{78}H_{72}F_{20}N_4P_4Cl_2Sb_2 \cdot 2Et_2O$
Formula weight	1021.07	2085.86	2234.10
Temperature/K	180(2)	180(2)	180(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	*P*-1	$P2_1/c$
a/Å	22.247(4)	9.2949(18)	15.4570(10)
b/Å	10.040(2)	12.576(3)	14.6930(8)
c/Å	20.632(4)	18.412(3)	20.1840(11)
α/°	90	101.298(17)	90
β/°	95.89(3)	90.983(15)	99.750(5)
γ/°	90	95.652(17)	90
Volume/Å^3	4584.0(16)	2098.8(7)	4517.8(5)
Z	4	1	2
μ/mm^{-1}	0.779	1.218	1.139
Reflns/unique	34425/9554	12150/6010	39404/12075
Refinement	on F	on F	on F
Weighting scheme	Chebychev polynomial	Chebychev polynomial	Chebychev polynomial
Final R_1	0.0417 [$I > 2.5\sigma(I)$]	0.0831 [$I > 2\sigma(I)$]	0.0637 [$I > 2\sigma(I)$]
Final wR_2	0.0493 [$I > 2.5\sigma(I)$]	0.0848 [$I > 2\sigma(I)$]	0.0675 [$I > 2\sigma(I)$]

PCHP), 93.6, 96.8 and 97.0 (s, CH of cymene), 97.6 (d, J_{CP} = 6.0 Hz, CH of cymene), 108.5 and 120.1 (s, C of cymene), 124.1 (br, $CC{\equiv}N$), 134.5–156.1 (m, C_{arom} and CH_{arom}) ppm; $C{\equiv}N$ signal not observed. $^{19}F\{^1H\}$ NMR (acetone-d_6): δ −147.04 and −135.70 (m, 4F each, 4-C_6F_4CN) ppm.

Complex 12. A solution of **8** (0.160 g, 0.244 mmol) in THF (20 mL) was treated, at room temperature, with ^tBuOOH (0.100 mL, 0.500 mmol) for 3 h. The solvent was then removed under vacuum and the resulting orange solid residue washed with a 1 : 1 mixture of hexane : diethyl ether (3 × 10 mL) and dried *in vacuo*. Yield: 0.154 g, 94%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.0 (d, J_{PP} = 19.6 Hz, $Ph_2P{=}O$), 46.2 (d, J_{PP} = 19.6 Hz, Ru–PPh) ppm. ^1H NMR ($CDCl_3$): δ 1.15 (d, 6H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.80 (s, 3H, CH_3), 1.99–2.86 (m, 7H, CH_2 and $CH(CH_3)_2$), 3.86 (m, 1H, PCHP), 5.03 and 5.40 (d, 1H each, J_{HH} = 5.7 Hz, CH of cymene), 5.15 (br, 2H, CH of cymene), 6.82–7.95 (m, 15H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.1 (s, CH_3), 21.8 and 22.3 (s, $CH(CH_3)_2$), 27.0 and 32.9 (s, CH_2), 30.1 (s, $CH(CH_3)_2$), 30.5 (d, J_{CP} = 31.4 Hz, CH_2P), 36.6 (dd, J_{CP} = 62.5 and 15.6 Hz, PCHP), 86.0 (s, 2C, CH of cymene), 86.9 (d, J_{CP} = 4.8 Hz, CH of cymene), 87.3 (d, J_{CP} = 3.6 Hz, CH of cymene), 96.8 (s, C of cymene), 110.2 (d, J_{CP} = 4.4 Hz, C of cymene), 127.2–130.3 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $RuC_{32}H_{36}Cl_2P_2O$ (670.55): C, 57.32; H, 5.41; found: C, 57.14; H, 5.38.

Complex 13. A solution of complex **12** (0.097 g, 0.145 mmol) in dichloromethane (10 mL) was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.050 g, 0.145 mmol) for 2 h. After the AgCl formed was filtered off (Kieselguhr), the solution was evaporated to dryness, and the resulting orange solid residue washed with diethyl ether (3 × 10 mL) and dried *in vacuo*. Yield: 0.076 g, 60%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.5 (d, J_{PP} = 3.5 Hz, $Ph_2P{=}O$–Ru), 49.1 (d, J_{PP} = 3.5 Hz, Ru–PPh) ppm. ^1H NMR ($CDCl_3$): δ 1.42–3.44 (m, 7H, CH_2 and $CH(CH_3)_2$), 1.47 and 1.49 (d, 3H each, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 2.13 (s, 3H, CH_3), 4.41 (m, 1H, PCHP), 5.78 and 6.06 (d, 1H each, J_{HH} = 6.5 Hz, CH of cymene), 5.94 and 6.09 (d, 1H each, J_{HH} = 6.0 Hz, CH of cymene), 7.23–8.04 (m, 15H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.4 (s, CH_3), 22.1 and 22.4 (s, $CH(CH_3)_2$), 27.3 (dd, J_{CP} = 14.6 and 5.1 Hz, CH_2), 29.2 (d, J_{CP} = 31.2 and 5.7 Hz, CH_2P), 29.4 (s, CH_2), 31.6 (s, $CH(CH_3)_2$), 39.9 (dd, J_{CP} = 67.4 and 14.0 Hz, PCHP), 85.6 (d, J_{CP} = 5.1 Hz, CH of cymene), 87.3 and 88.2 (d, J_{CP} = 3.8 Hz, CH of cymene), 88.6 (d, J_{CP} = 3.2 Hz, CH of cymene), 97.4 and 109.1 (s, C of cymene), 124.6–134.1 (m, C_{arom} and CH_{arom}) ppm. Anal. calc. for $RuC_{32}H_{36}F_6P_2ClOSb$ (870.85): C, 44.14; H, 4.17; found: C, 43.83; H, 4.34.

General procedure for the catalytic Diels–Alder reaction

A Schlenk tube was charged, under N_2 atmosphere, with the corresponding neutral dichloride–ruthenium(II) pre-catalyst (0.075 mmol) and $AgSbF_6$ (0.051 g, 0.15 mmol). CH_2Cl_2 (5 mL) was added and the mixture stirred at room temperature for 30 min, followed by filtration (over Kieselguhr) to remove the precipitated AgCl. The filtrate was evaporated to dryness, dissolved in 2 mL of CH_2Cl_2 and transferred, under N_2 atmosphere, into a jacketed Schlenk tube refrigerated by a closed ^{i}PrOH circuit kept at −20 °C with a cryostat. Freshly distilled acrolein (0.1 mL, 1.5 mmol), 2,6-lutidine (4 μL, 0.0375 mmol) and *cis*-decaline (0.231 mL, 1.5 mmol) were added. The resulting yellow solution was equilibrated at −20 °C for 30 min before addition of freshly distilled cyclopentadiene (0.6 mL, 9 mmol). The course of the reaction, *i.e.* conversion, *endo* : *exo* ratio and ee excess, was monitored by GC [Supelco Gama-Dex™ 225 (30 m, 250 μm) column; helium 4 mL min^{-1}, 60 °C, 10 °C min^{-1} to 200 °C: 5.53 min (*cis*-decaline), 5.88 and 6.00 min (*exo* cycloadducts), 6.60 and 6.66 min (*endo* cycloadducts)].

X-Ray crystal structure determination of complexes 5a, 7 and 11

Single crystals suitable for X-ray diffraction analysis were obtained, in all cases, by slow diffusion of diethyl ether into a saturated solution of the complex in dichloromethane. The most relevant crystallographic data are given in Table 2. Data were collected at low temperature on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-Kα radiation and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods using SIR92,[36] and refined by means of least-squares procedures on *F* using the programs of the PC version of CRYSTALS.[37] The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography.[38] Complex **5a** contains two disordered phenyl rings refined isotropically. All other non-H atoms were refined anisotropically. The poor quality of the data for complex **7** did not allow the refinement with anisotropic thermal parameters, except for ruthenium, phosphorus, antimony and chlorine atoms. The structure of compound **11** was refined with anisotropic thermal parameters for all non-hydrogen atoms and ether molecules.

CCDC reference numbers 612113–612115.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606781f

Acknowledgements

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. P. C. and V. C. thank the MCyT and the European Social Fund for "Ramón y Cajal" contracts. M. Z. thanks the Ministry of Science and Information Society Technologies Poland for financial support (Grant No 3T09A 158 29). A. E. D. A., M. Z. and J. P. M. thank the LEA (Laboratoire Européen Associé, Toulouse-Łódź) for financial support.

References

1 See for example: (*a*) A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27; (*b*) C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233; (*c*) V. V. Grushin, *Chem. Rev.*, 2004, **104**, 1629.

2 For reviews see: (*a*) G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067; (*b*) P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193–195**, 499; (*c*) P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680; (*d*) G. Chelucci, G. Orrù and G. A. Pinna, *Tetrahedron*, 2003, **59**, 9471; (*e*) P. J. Guiry and C. P. Saunders, *Adv. Synth. Catal.*, 2004, **346**, 497; (*f*) P. Braunstein, *J. Organomet. Chem.*, 2004, **689**, 3953.

3 For reviews see: (*a*) Y. G. Gololobov, I. N. Zhamurova and L. F. Kasukhin, *Tetrahedron*, 1981, **37**, 437; (*b*) Y. G. Gololobov and L. F. Kasukhin, *Tetrahedron*, 1992, **48**, 1353; (*c*) A. W. Johnson, in *Ylides and Imines of Phosphorus*, Wiley, New York, 1993, p. 403; (*d*) P. Molina and M. J. Vilaplana, *Synthesis*, 1994, 1197; (*e*) H. Wammhoff, G. Richardt and S. Stölben, *Adv. Heterocycl. Chem.*, 1999, **64**, 159; (*f*) P. M. Fresneda and P. Molina, *Synlett*, 2004, 1; (*g*) A. Arques and P. Molina, *Curr. Org. Chem.*, 2004, **8**, 827.

4 For recent references see: (*a*) H.-R. Wu, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Eur. J. Inorg. Chem.*, 2003, 3152; (*b*) L. P. Spencer, R. Altwer, P. Wei, L. Gelmini, J. Gauld and D. W. Stephan, *Organometallics*, 2003, **22**, 3841; (*c*) J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2003, 3500; (*d*) J. Vicente, J.-A. Abad, R. Clemente, J. López-Serrano, M. C. Ramírez de Arellano, P. G. Jones and D. Bautista, *Organometallics*, 2003, **22**, 4248; (*e*) K. Bernardo-Gusmão, L. F. T. Queiroz, R. F. de Souza, F. Leca, C. Loup and R. Réau, *J. Catal.*, 2003, **219**, 59; (*f*) K. T. K. Chan, L. P. Spencer, J. D. Masuda, J. S. J. McCahill, P. Wei and D. W. Stephan, *Organometallics*, 2004, **23**, 381; (*g*) G. C. Welch, W. E. Piers, M. Parvez and R. McDonald, *Organometallics*, 2004, **23**, 1811; (*h*) M. J. Sarsfield, I. May, S. M. Cornet and M. Helliwell, *Inorg. Chem.*, 2005, **44**, 7310; (*i*) C.-H. Qi, S.-B. Zhang and J.-H. Sun, *J. Organomet. Chem.*, 2005, **690**, 3946; (*j*) N. D. Jones and R. G. Cavell, *J. Organomet. Chem.*, 2005, **690**, 5485, and references cited therein; (*k*) V. Cadierno, M. Zablocka, B. Donnadieu, A. Igau, J.-P. Majoral and A. Skowronska, *Chem.–Eur. J.*, 2000, **6**, 346; (*l*) J. P. Majoral and M. Zablocka, *New J. Chem.*, 2005, **29**, 32.

5 For overviews on the coordination chemistry of iminophosphorane–phosphine ligands see: (*a*) K. V. Katti and R. G. Cavell, *Comments Inorg. Chem.*, 1990, **10**, 53; (*b*) R. G. Cavell, *Curr. Sci.*, 2000, **78**, 440.

6 (*a*) D. J. Law and R. G. Cavell, *J. Mol. Catal.*, 1994, **91**, 175; (*b*) R. G. Cavell, D. J. Law and R. W. Reed, *US. Pat. Appl.*, US 887014, 1994; (*c*) T. T. Co, S. C. Shim, C. S. Cho, T.-J. Kim, S. O. Kang, W.-S. Han, J. Ko and C.-K. Kim, *Organometallics*, 2005, **24**, 4824.

7 (*a*) R. G. Cavell, B. Creed, L. Gelmini, D. J. Law, R. McDonald, A. R. Sanger and A. Somogyvary, *Inorg. Chem.*, 1998, **37**, 757; (*b*) R. G. Cavell, B. Creed, D. J. Law, A. P. Nicola, A. R. Sanger and A. Somogyvary, *US. Pat. Appl.*, US 447887, 1996.

8 R. G. Cavell and K. V. Katti, *US. Pat. Appl.*, US 752348, 1994.

9 (*a*) A. Arques, D. Auñon and P. Molina, *Tetrahedron Lett.*, 2004, **45**, 4337; (*b*) We note that the application of iminophosphorane–phosphine ligands in the palladium catalyzed cross coupling of secondary amines with aryl halides has also been briefly commented on: P. Molina, A. Arques, A. García and M. C. Ramírez de Arellano, *Tetrahedron Lett.*, 1997, **38**, 7613.

10 T. T. Co, S. C. Shim, C. S. Cho, D.-U. Kim and T.-J. Kim, *Bull. Korean Chem. Soc.*, 2005, **26**, 1359.

11 (*a*) V. Cadierno, P. Crochet, J. García-Álvarez, S. E. García-Garrido and J. Gimeno, *J. Organomet. Chem.*, 2002, **663**, 32; (*b*) V. Cadierno, P. Crochet, J. Díez, J. García-Álvarez, S. E. García-Garrido, J. Gimeno, S. García-Granda and M. A. Rodríguez, *Inorg. Chem.*, 2003, **42**, 3293; (*c*) V. Cadierno, P. Crochet, J. Díez, J. García-Álvarez, S. E. García-Garrido, S. García-Granda, J. Gimeno and M. A. Rodríguez, *Dalton Trans.*, 2003, 3240; (*d*) L. Boubekeur, S. Ulmer, L. Ricard, N. Mézailles and P. Le Floch, *Organometallics*, 2006, **25**, 315.

12 (*a*) M. Zablocka, A. Igau, J.-P. Majoral and K. M. Pietrusiewicz, *Organometallics*, 1993, **12**, 603; (*b*) M. Zablocka, B. Delest, A. Igau, A. Skowronska and J. P. Majoral, *Tetrahedron Lett.*, 1997, **38**, 5997.

13 (*a*) M. Zablocka, F. Boutonnet, A. Igau, F. Dahan, J. P. Majoral and K. M. Pietrusiewicz, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1735; (*b*) M. Zablocka, A. Igau, N. Cenac, B. Donnadieu, F. Dahan, J. P. Majoral and M. K. Pietrusiewicz, *J. Am. Chem. Soc.*, 1995, **117**, 8083.

14 For reviews and books covering this field see: (*a*) C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1997, 507; (*b*) T. Naota, H. Takaya and S.-I. Murahashi, *Chem. Rev.*, 1998, **98**, 2599; (*c*) B. M. Trost, F. D. Toste and A. B. Pinkerton, *Chem. Rev.*, 2001, **101**, 2067; (*d*) T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; (*e*) V. Ritleng, C. Sirlin and M. Pfeffer, *Chem. Rev.*, 2002, **102**, 1731; (*f*) *Ruthenium in Organic Synthesis*, ed. S.-I. Murahashi, Wiley-VCH, Weinheim, 2004; (*g*) *Ruthenium Catalysts and Fine Chemistry*, ed. C. Bruneau and P. H. Dixneuf, Springer, Berlin, 2004; (*h*) B. M. Trost, M. U. Fredericksen and M. T. Rudd, *Angew. Chem., Int. Ed.*, 2005, **44**, 6630; (*i*) C. Bruneau and P. H. Dixneuf, *Angew. Chem., Int. Ed.*, 2006, **45**, 2176; (*j*) *Curr. Org. Chem.*, 2006, **10**, 113–225 (a thematic issue devoted to ruthenium-catalyzed processes).

15 H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

16 For reviews see: (*a*) Y. G. Gololobov, I. N. Zhamurova and L. F. Kasukhin, *Tetrahedron*, 1981, **37**, 437; (*b*) Y. G. Gololobov and L. F. Kasukhin, *Tetrahedron*, 1992, **48**, 1353; (*c*) A. W. Johnson, in *Ylides and Imines of Phosphorus*, Wiley, New York, 1993, p. 403.

17 A. V. Kirsanov, *Izv. Akad. Nauk. SSSR*, 1950, **426**.

18 M. A. Bennett, T.-N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 74.

19 For reviews on the chemistry of dimers $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ see: (*a*) H. Le Bozec, D. Touchard and P. H. Dixneuf, *Adv. Organomet. Chem.*, 1989, **29**, 163; (*b*) M. A. Bennett, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, Vol. 7, p. 549; (*c*) M. A. Bennett, *Coord. Chem. Rev.*, 1997, **166**, 225; (*d*) F. C. Pigge and J. J. Coniglio, *Curr. Org. Chem.*, 2001, **5**, 757.

20 See for example: (*a*) C. Larré, B. Donnadieu, A.-M. Caminade and J.-P. Majoral, *Eur. J. Inorg. Chem.*, 1999, 601; (*b*) M. S. Balakrishna, R. M. Abhyankar and M. G. Walawalker, *Tetrahedron Lett.*, 2001, **42**, 2733; (*c*) V. Maraval, R. Laurent, B.

Donnadieu, A.-M. Caminade and J.-P. Majoral, *Synthesis*, 2003, 389; (*d*) V. Cadierno, J. Díez, J. García-Álvarez, J. Gimeno, M. J. Calhorda and L. F. Veiros, *Organometallics*, 2004, **23**, 2421; (*e*) V. Cadierno, J. Díez, J. García-Álvarez and J. Gimeno, *Organometallics*, 2004, **23**, 3425; (*f*) V. Cadierno, J. Díez, J. García-Álvarez and J. Gimeno, *Organometallics*, 2005, **25**, 2801.

21 V. Cadierno, J. Díez, S. E. García-Garrido, S. García-Granda and J. Gimeno, *J. Chem. Soc., Dalton Trans.*, 2002, 1465.

22 See for example: (*a*) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 1970, **9**, 227; (*b*) C. P. Guengerich and K. Schug, *J. Am. Chem. Soc.*, 1977, **99**, 3298; (*c*) G. S. Ashby, M. I. Bruce, I. B. Tomkins and R. C. Wallis, *Aust. J. Chem.*, 1979, **32**, 1003; (*d*) M. I. Bruce, T. W. Hambley, M. J. Liddell, A. G. Swincer and E. R. T. Tiekink, *Organometallics*, 1990, **9**, 2886; (*e*) L. Shao, K. Takeuchi, M. Ikemoto, T. Kawai, M. Ogasawara, H. Takeuchi, H. Kawano and M. Saburi, *J. Organomet. Chem.*, 1992, **435**, 133; (*f*) M. Hanack, K. Dürr, A. Lange, J. O. Barcina, J. Pohmer and E. Witke, *Synth. Met.*, 1995, **71**, 2275.

23 (*a*) The coordination chemistry of $Ph_2PCH_2P\{{=}N\text{-}4\text{-}C_6F_4CN\}Ph_2$ and related bidentate ligands, such as $Ph_2PCH_2P\{{=}N\text{-}3,4\text{-}C_6F_4(CN)_2\}Ph_2$, $Ph_2PCH_2P\{{=}N\text{-}3,6\text{-}C_6F_4(CN)_2\}Ph_2$ or *o*-$Ph_2PC_6H_4P\{{=}N\text{-}4\text{-}C_6F_4CN\}Ph_2$, has been extensively studied by R. G. Cavell and co-workers, the coordination of the nitrile function never being observed. See for example: (*a*) K. V. Katti and R. G. Cavell, *Organometallics*, 1989, **8**, 2147; (*b*) K. V. Katti, B. D. Santarsiero, A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 1993, **32**, 5919; (*c*) D. J. Law, G. Bigam and R. G. Cavell, *Can. J. Chem.*, 1995, **73**, 635; (*d*) R. W. Reed, B. Santarsiero and R. G. Cavell, *Inorg. Chem.*, 1996, **35**, 4292; (*e*) J. Li, R. McDonald and R. G. Cavell, *Organometallics*, 1996, **15**, 1033.

24 See for example: R. L. Cordiner, D. Albesa-Jové, R. L. Roberts, J. D. Farmer, H. Puschmann, D. Corcoran, A. E. Goeta, J. A. K. Howard and P. J. Low, *J. Organomet. Chem.*, 2005, **690**, 4908, and references cited therein.

25 Note that the priority order to determine the ruthenium configuration is: η^6-*p*-cymene > Cl > P > N.

26 A possible driving force for the formation of this particular isomer may be the π-stacking interaction between the two C_6F_4 units.

27 Note that, although the spatial disposition of the substituents remains unchanged, the preference orders for the phosphorus atom change after imination inverting the *R*/*S* assignment.

28 We note that, as previously observed in the synthesis of the bis(iminophosphorane) derivatives **4a–b** (see Scheme 1), the imination of the Ph_2P unit by $(PhO)_2P({=}O)N_3$ requires a considerably longer reaction time (7 days) when compared to the highly activated 4-azido-2,3,5,6-tetrafluorobenzonitrile (8 h). Attempts to accelerate this reaction working under refluxing conditions resulted in the formation of a non-separable mixture containing **9a** and the oxidized complex **12** (see Scheme 4).

29 We note that attempts to promote the selective monooxidation of the PhP or Ph_2P units in the free α-diphosphine **2** by using 1 equivalent of ^{t}BuOOH or H_2O_2 failed. Thus, under different reaction conditions, unseparable mixtures containing the corresponding dioxide (δ_P ($CDCl_3$) = 25.0 (s, $Ph_2P{=}O$), 53.6 (s, $PhP{=}O$)), phospholane–monooxide (δ_P ($CDCl_3$) = −12.9 (d, J_{PP} = 46.1 Hz, Ph_2P), 56.3 (d, J_{PP} = 46.1 Hz, $PhP{=}O$)) and unreacted **2** (δ_P ($CDCl_3$) = −13.5 (d, J_{PP} = 31.5 Hz, Ph_2P), −4.5 (d, J_{PP} = 31.5 Hz, PhP)) were obtained in all cases.

30 For example: J. W. Faller, B. P. Patel, M. A. Albrizzio and M. Curtis, *Organometallics*, 1999, **18**, 3096, and references cited therein.

31 For a recent review on this topic see: J. W. Faller and J. Parr, *Curr. Org. Chem.*, 2006, **10**, 151.

32 Recent advances in enantioselective Diels–Alder reactions catalyzed by chiral transition-metal complexes are summarized in: D. Carmona, M. P. Lamata and L. A. Oro, *Coord. Chem. Rev.*, 2000, **200–202**, 717.

33 For recent references involving (η^6-arene)–Ru(II) complexes see: (*a*) D. Carmona, C. Vega, N. García, F. J. Lahoz, S. Elipe, L. A. Oro, M. P. Lamata, F. Viguri and R. Borao, *Organometallics*, 2006, **25**, 1592; (*b*) J. W. Faller and P. P. Fontaine, *Organometallics*, 2005, **24**, 4132; (*c*) A. J. Davenport, D. L. Davies, J. Fawcett and D. R. Russell, *Dalton Trans.*, 2004, 1481; (*d*) J. W. Faller and D. G. D'Alliessi, *Organometallics*, 2003, **22**, 2749; (*e*) H. Brunner, F. Henning, M. Weber, M. Zabel, D. Carmona and F. J. Lahoz, *Synthesis*, 2003, 1091; (*f*) J. W. Faller, A. R. Lavoie and B. J. Grimmond, *Organometallics*, 2002, **21**, 1662; (*g*) J. W. Faller and B. J. Grimmond, *Organometallics*, 2001, **20**, 2454; (*h*) J. W. Faller and A. R. Lavoie, *J. Organomet. Chem.*, 2001, **630**, 17; (*i*) A. J. Davenport, D. L. Davies, J. Fawcett and D. R. Russell, *J. Chem. Soc., Perkin Trans. 1*, 2001, 1500; (*j*) J. W. Faller, B. J. Grimmond and D. G. D'Alliessi, *J. Am. Chem. Soc.*, 2001, **123**, 2525; (*k*) J. W. Faller and J. Parr, *Organometallics*, 2000, **19**, 1829; (*l*) J. W. Faller, X. Liu and J. Parr, *Chirality*, 2000, **12**, 325.

34 (*a*) All the catalytic reactions were performed in the presence of 2,6-lutidine (2.5 mol%) acting as a scavenger of acid impurities. (*b*) Similar results were obtained in all cases starting from the cationic species **6**, **7**, **10**, **11** and **13** after treatment with $AgSbF_6$ (1 equivalent per ruthenium).

35 J. M. Birchall, R. N. Haszeldine and M. E. Jones, *J. Chem. Soc. C*, 1971, 1343.

36 SIR92—A program for crystal structure solution, A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

37 CRYSTALS, P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.

38 *International Tables for X-Ray Crystallography*, Kynoch press, Birmingham, UK, 1974, vol. IV.

