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

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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 ( $\eta^6$ -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.<sup>1</sup> 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.<sup>2</sup>

Iminophosphoranes,  $R_3P=NR'$  (nitrogen analogues of phosphorus ylides), have found widespread application in organic synthesis<sup>3</sup> and proved to be versatile nitrogen-donor ligands for transition metals.<sup>4</sup> 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  $R_2P-X-P(=NR')R_2$ ,<sup>5</sup> structurally related to the well-known diphosphine–monoxides.<sup>1c</sup> 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<sub>2</sub>P–X–PPh<sub>2</sub> (X = CH<sub>2</sub>, (CH<sub>2</sub>)<sub>2</sub>, 1,2-C<sub>6</sub>H<sub>4</sub>, NR) *via* selective monoimination,<sup>5</sup> are: olefin hydrogenation (Rh and Ir complexes)<sup>6</sup> and oligomerization (Ni complexes),<sup>7</sup> methanol carbonylation (Rh, Ni and Co complexes),<sup>8</sup> Sonogashira-type coupling (Pd complexes),<sup>9</sup> allylic alkylation (Pd and Rh complexes)<sup>10</sup> and transfer hydrogenation of ketones (Ru complexes).<sup>11</sup>

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

Taking into account that the ruthenium chemistry of iminophosphorane–phosphines has been scarcely investigated,<sup>11</sup> and the growing interest in the design of ruthenium catalysts for organic synthesis,<sup>14</sup> we decided to explore the potential of our  $\alpha$ -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  $\alpha$ -diphosphine 2-diphenylphosphino-1-phenyl-phospholane, and their coordination to an ( $\eta^6$ -arene)– ruthenium( $\pi$ ) fragment (complexes **B**). Remarkably, the regioisomeric species **D** could also be readily prepared upon



Chart 1 Zirconium-mediated synthesis of  $\alpha$ -diphosphines 2.

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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)<sup>15,16</sup> and (ii) the reaction of phosphine dibromides (R<sub>3</sub>PBr<sub>2</sub>) with primary amines, followed by treatment with a base (the Kirsanov reaction).<sup>16,17</sup> 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 2diphenylphosphino-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 vields (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 <sup>31</sup>P{<sup>1</sup>H} NMR spectra are very informative, showing a strong downfield of the phospholane PhP signal ( $\delta_P = 44.0$  (**3a**) and 52.0 (**3b**) ppm) with respect to that shown by the diphosphine precursor **2** ( $\delta_P = -4.5$  ppm) and the Ph<sub>2</sub>P resonance remaining almost unchanged ( $\delta_P = -13.9$  (**3a**) and -10.9 (**3b**) *vs.* -13.5 (**2**) ppm). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} 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 <sup>1</sup>H NMR, an unresolved multiplet at 3.42–4.15 ppm, and (*ii*) in the <sup>13</sup>C{<sup>1</sup>H}



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

NMR, a doublet of doublets resonance at 36.6–39.0 ppm  $(J_{CP} = 54.7 \text{ and } 24.3 \text{ Hz} (3a), 75.7 \text{ and } 24.4 \text{ Hz} (3b)).$ 

## Coordination of the iminophosphorane-phosphine ligands 3a-b to an $(\eta^6$ -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( $\mu$ -Cl)( $\eta^6$ -*p*-cymene)}<sub>2</sub>] as the starting material.<sup>18</sup> This dimeric compound was chosen as the precursor due to its versatile reactivity towards polyfunctional ligands.<sup>19</sup> Thus, we have found that the treatment of [{RuCl( $\mu$ -Cl)( $\eta^6$ -*p*-cymene)}<sub>2</sub>] 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 <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which shows a remarkable downfield shift of the Ph<sub>2</sub>P signals (*ca.*  $\delta_P = 23$ 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) = 128; Cl(1)-Ru-Cl(2); Cl(1)-Ru-Cl(2) = 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);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);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)).

 $\delta_{\rm P} = 41.6$  ppm,  $\Delta \delta = -2$  ppm; **5b**,  $\delta_{\rm P} = 44.1$  ppm,  $\Delta \delta = -8$ ppm) and the phosphoryl (PhO)<sub>2</sub>P=O group (5a,  $\delta_{\rm P} = -7.8$ 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  $-P = N - P (=O)(OPh)_2$ , <sup>11b,20</sup> 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-btowards silver hexafluoroantimonate has been studied. Thus, we have found that the treatment of 5a with a stoichiometric amount of AgSbF<sub>6</sub> 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 diaster-



Scheme 3 Reactivity of complexes 5a-b towards AgSbF<sub>6</sub>.

eoselective manner (the Ru atom becomes a stereogenic center), a non-separable mixture of two diastereoisomers being obtained in *ca*. 60 : 40 ratio. The  $\kappa^2$ -*P*,*O*-coordination of the N-phosphorylated ligand **3a** in complex **6** is fully supported by the  ${}^{31}P{}^{1}H$  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.*  $\delta_{\rm P} = 8.7$ (major) and 6.2 (minor) vs. -7.8 ppm), is observed. The chemical shifts of the Ph2P and PhP=N units are almost unaffected by the ring closure ( $\Delta \delta = 3$  ppm), ruling out the formation of a five-membered  $\kappa^2$ -P,N-chelate complex. It should be noted that the preference shown by the iminophosphorane-phosphine **3a** for the  $\kappa^2$ -P,O- vs.  $\kappa^2$ -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  $\kappa^2$ -P,O-complexes E (Chart 3) are also selectively formed.11b

Surprisingly, the chelate  $\kappa^2$ -*P*,*N*-coordination of the iminophosphorane–phosphine **3b** has been not observed after treatment of the neutral derivative **5b** with AgSbF<sub>6</sub>. Instead, the dicationic dinuclear species **7**, in which **3b** is acting as a bridging ligand between two [RuCl( $\eta^6$ -*p*-cymene)] metallic fragments, is exclusively formed (Scheme 3). Complex **7**, which has been isolated as an air-stable orange solid in 90% yield,



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<sub>6</sub> 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)-C(2) = 1.39(2); P(3)-C(3) = 1.39(3); P(3)-C(3), P(3), P(3), P(3)-C(3), P(3), P(3), P(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); $C(39)-P(1) = 1.872(16); C^*-Ru-Cl(1) = 123; C^*-Ru-P(1) = 129; C^*-R$ 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(37)-C(39) = 95.8(7); C(36)-C(37)-C(39) = 95.8(7); C(36)-C(37)-C(37)-C(39) = 95.8(7); C(36)-C(37)-C(39) = 95.8(7); C(36)-C(37)-C(3C(38) = 109.1(14); C(37)-C(38)-C(39) = 105.4(13); C(38)-C(39)-C(+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 pcymene 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<sup>-</sup> intermediate [RuCl( $\kappa^1$ -P-**3b**)( $\eta^6$ -p-cymene)][SbF<sub>6</sub>]. Formation of 7 contrasts with the high-yield synthesis of the mononuclear species [RuCl( $\kappa^2$ -P,N-Ph<sub>2</sub>PCH<sub>2</sub>P{=N-4-C<sub>6</sub>F<sub>4</sub>CN}Ph<sub>2</sub>)( $\eta^6$ -p-cymene)][SbF<sub>6</sub>] (F; Chart 3), starting from the closely related ligand Ph<sub>2</sub>PCH<sub>2</sub>P {=N-4-C<sub>6</sub>F<sub>4</sub>CN}Ph<sub>2</sub>, recently reported by us.<sup>21</sup> We also note that, although some ruthenium complexes containing *N*-coordinated RC<sub>6</sub>F<sub>4</sub>CN (R = F, CN) ligands are known,<sup>22</sup> the coordination of the nitrile unit of **3b** in the dinuclear complex 7 can be considered as rather unusual.<sup>23</sup>

The <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>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<sub>2</sub> 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



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

the literature for other nitrile–ruthenium(II) complexes.<sup>24</sup> 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.<sup>21,23b</sup>

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.*  $S_{\text{Ru}(1)}R_{\text{C}(39)}S_{\text{P}(2)}$  and  $R_{\text{Ru}}S_{\text{C}}R_{\text{P}}$ , respectively.<sup>25</sup> This seems to indicate that the dimerization process of the 16e<sup>-</sup> intermediate [RuCl( $\kappa^{1}$ -*P*-**3b**)( $\eta^{6}$ -*p*-cymene)][SbF<sub>6</sub>] takes place with chiral self-recognition.<sup>26</sup> Taking into account that the racemic  $\alpha$ diphosphine precursor **2** is exclusively composed of the  $S_{\text{P}}S_{\text{C}}$ and  $R_{\text{P}}R_{\text{C}}$  enantiomers,<sup>13</sup> and assuming that formation of **3b** occurs with retention of configuration,<sup>27</sup> we propose an  $R_{\text{Ru}}R_{\text{C}}S_{\text{P}}S_{\text{Ru}}S_{\text{C}}R_{\text{P}}$  configuration for the minor diastereoisomer present in solution.

# Imination reactions of coordinated 2-diphenylphosphino-1-phenyl-phospholane: Access to the $(\eta^6$ -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<sub>2</sub>P unit in the neutral ( $\eta^6$ -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( $\mu$ -Cl)( $\eta^6$ -*p*-cymene)}<sub>2</sub>] with *ca.* 2.5 equivalents of 2. We note that neither the formation of the cationic species [RuCl( $\kappa^2$ -P,P-2)( $\eta^6$ -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 (<sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>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 ( $J_{\rm PP}$  = 43.6 Hz) at  $\delta_{\rm P}$  -9.3 and 41.9 ppm, corresponding to the diphenylphosphino Ph<sub>2</sub>P and phospholane PhP moieties, respectively (the chemical shift of the latter strongly supports its direct coordination to ruthenium), and (*ii*) (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR) the presence of characteristic resonances for the methynic PCHP unit, whose proton appears as an unresolved multiplet at  $\delta_{\rm H}$  3.82 ppm, and its



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

carbon as a doublet of doublets ( $J_{\rm CP}$  = 33.7 and 23.5 Hz) at  $\delta_{\rm C}$  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**  $\kappa^{1}$ -*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).<sup>28</sup> In particular, the  ${}^{31}P{}^{1}H$  NMR spectra show the expected downfield shift of the Ph<sub>2</sub>P signal ( $\delta_{\rm P} = 17.5$  (9a) and 21.5 (9b) ppm) with respect to that shown by the parent complex 8 ( $\delta_{\rm P}$  = -9.3 ppm), confirming its transformation into an iminophosphorane Ph<sub>2</sub>P=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<sub>6</sub> 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  $\kappa^2$ -P,O vs.  $\kappa^2$ -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)<sup>25</sup> seems to indicate that a chiral self-recognition dimerization process has also taken place.<sup>26</sup>

The reluctance shown by the iminophosphorane–phosphine ligands **3a–b** and **G** to form five-membered chelate rings, *via*  $\kappa^2$ -*P*,*N* coordination, contrasts with the behaviour shown by the closely related diphosphine-monoxide **H** (Chart 4), from which the cationic  $\kappa^2$ -*P*,*O*-chelate complex **13** could be easily prepared (Scheme 4). Formation of **13** involves the initial oxidation of the pendant Ph<sub>2</sub>P 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<sub>6</sub><sup>-</sup> 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);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 pcymene 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<sup>a</sup>

$H \xrightarrow{(HO)} + (HO) \xrightarrow{(Ru] (5 \text{ mol}\%)} (HO) \xrightarrow{(HO)} H$					
Catalyst	Time/h	Yield (%) <sup>b</sup>	$Endo: exo^b$	ee (%) <sup>c</sup>	
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	

<sup>*a*</sup> All reactions were conducted in CH<sub>2</sub>Cl<sub>2</sub> 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<sub>6</sub> (10 mol%). <sup>*b*</sup> GC determined using *cis*-decaline as an internal standard. <sup>*c*</sup> Enantiomeric excess of the major *endo* cycloadduct (GC determined).

conditions (THF, r.t.) by using an excess (ca. 2 : 1) of tertbutyl hydroperoxide.<sup>29</sup> 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  ${}^{31}P{}^{1}H$  NMR spectrum clearly confirms the presence of a Ph2P=O unit showing a characteristic doublet signal ( $J_{\rm PP}$  = 19.6 Hz) at  $\delta_{\rm P}$  = 31.0 ppm (to be compared with  $\delta_{\rm P} = -9.3$  ppm ( $J_{\rm PP} = 43.6$  Hz) for the nonoxidized Ph<sub>2</sub>P unit in the parent complex 8). Remarkably, the formation of the five-membered chelate ring of the cationic complex 13 proceeds, as indicated by  ${}^{31}P{}^{1}H$ ,  ${}^{1}H$  and  $^{13}C{^{1}H}$  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 ( $\eta^6$ -arene)– ruthenium(II) complexes,<sup>30</sup> the chelate coordination of the diphosphine-monoxide ligand results in a downfield shift of both PhP and Ph<sub>2</sub>P=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.<sup>31</sup> In particular, dicationic (n<sup>6</sup>-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 Lewisacids, due to their increased stability and resistance to hydrolysis.<sup>32,33</sup> With these precedents in mind, and taking into account that enantiomerically pure iminophosphoranephosphine ligands can be readily accessible starting from the enantiopure  $\alpha$ -diphosphine (S<sub>P</sub>S<sub>C</sub>)-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<sub>2</sub>Cl<sub>2</sub>, -20 °C) was used as a model reaction. The catalytically active species, *i.e.* the dications  $[Ru(L)(\eta^6-p-cym$ ene)]<sup>2+</sup> (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  $AgSbF_6$ <sup>34</sup> 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 areneruthenium(II) catalysts already reported in the literature,<sup>32,33</sup> 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  $\alpha$ -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 ( $\eta^{6}$ -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.

#### 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  $[{RuCl(\mu-Cl)(\eta^6-p-cymene)}_2]$ ,<sup>18</sup> 2-diphenylphosphino-1-phe-nyl-phospholane (2),<sup>13</sup> and 4-azido-2,3,5,6-tetrafluorobenzonitrile,<sup>35</sup> 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<sup>™</sup> 225 (30 m, 250 µm) column. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (<sup>1</sup>H), 121.5 MHz (<sup>31</sup>P), 282.4 MHz (<sup>19</sup>F), or 75.4 MHz (<sup>13</sup>C) using SiMe<sub>4</sub>, CFCl<sub>3</sub> or 85% H<sub>3</sub>PO<sub>4</sub> 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  $(2 \times 3 \text{ mL})$ and dried in vacuo to give 3a as a white solid. Yield: 0.305 g, 90%. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -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. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.52–2.35 (m, 6H, CH<sub>2</sub>), 4.15 (m, 1H, PCHP), 7.09-8.30 (m, 25H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  28.8 (dd,  $J_{CP}$  = 8.0 and 8.0 Hz, CH<sub>2</sub>), 30.8 (d,  $J_{CP} = 62.5$  Hz, CH<sub>2</sub>P), 32.6 (dd,  $J_{CP} = 19.9$ and 8.3 Hz, CH<sub>2</sub>), 36.6 (dd,  $J_{CP} = 54.7$  and 24.3 Hz, PCHP), 121.1-153.3 (m, Carom and CHarom) ppm. Anal. calc. for C34H32O3P3N (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  $(2 \times 2 \text{ mL})$  and dried *in vacuo* to give **3b** as a yellow solid. Yield: 0.115 g, 75%. IR (KBr): 2226 cm<sup>-1</sup> ( $\nu_{CN}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –10.9 (d,  $J_{PP}$  = 59.5 Hz, PPh<sub>2</sub>), 52.0 (d,  $J_{\rm PP}$  = 59.5 Hz, N=PPh) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 1.78-2.63 (m, 6H, CH2), 3.42 (m, 1H, PCHP), 7.13-7.75 (m, 15H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  24.7 (dd,  $J_{CP}$  = 7.8 and 7.8 Hz, CH<sub>2</sub>), 29.6 (dd,  $J_{CP} = 54.8$  and 1.7 Hz, CH<sub>2</sub>P), 31.2 (dd,  $J_{CP} = 18.1$  and 9.9 Hz, CH<sub>2</sub>), 39.0 (dd,  $J_{CP} = 75.7$ and 24.4 Hz, PCHP), 71.2 (t,  $J_{CF} = 15.0$  Hz,  $C \equiv N$ ), 109.9 (t,  $J_{\rm CF}$  = 3.5 Hz, CC  $\equiv$  N), 125.8–149.6 (m, C<sub>arom</sub> and CH<sub>arom</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -155.27 and -139.45 (m, 2F each, 4-C<sub>6</sub>F<sub>4</sub>CN) ppm. Anal. calc. for C<sub>29</sub>H<sub>22</sub>F<sub>4</sub>N<sub>2</sub>P<sub>2</sub> (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  $\times$  3 mL) and dried in vacuo to give 4a as a white solid. Yield: 0.198 g, 82%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -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<sub>2</sub>), 41.4 (d,  $J_{PP} = 29.6$  Hz, N=PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.90–2.73 (m, 6H, CH<sub>2</sub>), 4.77 (m, 1H, PCHP), 7.03–7.84 (m, 35H, CH<sub>arom</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$ 23.3 (dd,  $J_{CP} = 12.1$  and 4.5 Hz, CH<sub>2</sub>), 27.6 (dd,  $J_{CP} = 9.1$ and 1.5 Hz, CH<sub>2</sub>), 30.6 (d,  $J_{CP} = 68.0$  Hz, CH<sub>2</sub>P), 38.4 (ddd,  $J_{\rm CP} = 68.8, 45.3$  and 1.5 Hz, PCHP), 120.1–152.4 (m, C<sub>arom</sub> and CH<sub>arom</sub>) ppm. Anal. calc. for C<sub>46</sub>H<sub>42</sub>O<sub>6</sub>P<sub>4</sub>N<sub>2</sub> (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  $\times$  3 mL) and dried *in vacuo* to give **4b** as a yellow solid. Yield: 0.160 g, 77%. IR (KBr): 2229 cm<sup>-1</sup> ( $\nu_{CN}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  14.3 (br, N=PPh<sub>2</sub>), 43.6 (br, N=PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.57-2.09 (m, 6H, CH<sub>2</sub>), 3.82 (m, 1H, PCHP), 7.02–7.88 (m, 15H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR  $(CD_2Cl_2)$ :  $\delta$  23.9 (d,  $J_{CP}$  = 12.6 Hz, CH<sub>2</sub>), 28.4 (dd,  $J_{CP}$  = 11.4 and 2.4 Hz, CH<sub>2</sub>), 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,  $CC \equiv N$ ), 128.1–149.1 (m,  $C_{arom}$  and CH<sub>arom</sub>) ppm; (C $\equiv$ N signals not observed). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -153.80, -151.79, -139.59 and -139.01 (m, 2F each, 4-C<sub>6</sub>F<sub>4</sub>CN) ppm. Anal. calc. for C<sub>36</sub>H<sub>22</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub> (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  $[{RuCl(\mu-Cl)(\eta^6-p-cymene)}_2]$ (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  $(CDCl_3): \delta - 7.8 (d, J_{PP} = 25.9 \text{ Hz}, P = 0), 21.7 (d, J_{PP} = 38.8)$ Hz, Ru-PPh<sub>2</sub>), 41.6 (dd, J<sub>PP</sub> = 38.8 and 25.9 Hz, N=PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.69, 1.93 and 3.05 (m, 1H each, CH<sub>2</sub>), 0.89 and 1.08 (d, 3H each,  $J_{\rm HH} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (br, 4H, CH<sub>3</sub> and CH<sub>2</sub>), 2.30 (m, 2H, CH<sub>2</sub>), 2.46 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.43 (m, 1H, PCHP), 4.64 and 4.92 (d, 1H each,  $J_{\rm HH} = 6.0$  Hz, CH of cymene), 5.13 and 5.18 (d, 1H each,  $J_{\rm HH}$ = 6.3 Hz, CH of cymene), 6.88–7.98 (m, 25H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  17.1 (s, CH<sub>3</sub>), 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<sub>2</sub>P), 30.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 31.5 (d,  $J_{CP} = 13.2$  Hz, CH<sub>2</sub>), 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( $\mu$ -Cl)( $\eta^6$ -pcymene)}<sub>2</sub>] (0.145 g, 0.237 mmol) and **3b** (0.306 g, 0.570 mmol). Yield: 0.327 g, 82%. IR (KBr): 2227 cm<sup>-1</sup> ( $\nu_{CN}$ ).  ${}^{31}P{}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  23.4 (d,  $J_{PP}$  = 37.8 Hz, Ru–PPh<sub>2</sub>), 44.1 (d,  $J_{PP} = 37.8$  Hz, N=PPh) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 0.59–1.65 (m, 5H, CH<sub>2</sub>), 0.80 and 0.97 (d, 3H each,  $J_{\rm HH} = 6.8$ Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (s, 3H, CH<sub>3</sub>), 2.47 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.30 (m, 1H, CH<sub>2</sub>), 4.28 and 4.98 (d, 1H each,  $J_{\rm HH} = 6.0$  Hz, CH of cymene), 4.49 and 4.56 (d, 1H each,  $J_{\rm HH} = 5.7$  Hz, CH of cymene), 4.97 (m, 1H, PCHP), 6.62-8.06 (m, 15H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  17.1 (s, CH<sub>3</sub>), 20.0 and 23.1 (s,  $CH(CH_3)_2$ ), 22.0 (d,  $J_{CP} = 10.8$  Hz,  $CH_2$ ), 27.6 (d,  $J_{CP} = 52.9$ Hz, CH<sub>2</sub>P), 30.1 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 30.4 (d,  $J_{CP} = 7.5$  Hz, CH<sub>2</sub>), 37.5 (dd,  $J_{CP} = 59.3$  and 13.1 Hz, PCHP), 78.5 (t,  $J_{CF} = 13.0$ Hz,  $C \equiv N$ ), 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, CC=N), 121.9-153.5 (m,  $C_{arom}$  and  $CH_{arom}$ ) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ -154.78 and -139.60 (m, 2F each,  $4-C_6F_4CN$ ) ppm. Anal. calc. for RuC<sub>39</sub>H<sub>36</sub>F<sub>4</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub> (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  $(3 \times 10 \text{ mL})$ 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<sub>44</sub>H<sub>46</sub>F<sub>6</sub>O<sub>3</sub>P<sub>3</sub>ClNSb (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:  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$  8.7 (dd,  $J_{PP} = 27.0$ and 2.8 Hz, P=O-Ru), 25.3 (dd, J<sub>PP</sub> = 6.9 and 2.8 Hz, Ru–PPh<sub>2</sub>), 44.3 (dd,  $J_{PP} = 27.0$  and 6.9 Hz, N=PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.90 and 1.03 (d, 3H each,  $J_{\rm HH}$  = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.78 (s, 3H, CH<sub>3</sub>), 1.84–2.80 (m, 7H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 4.61 (m, 1H, PCHP), 4.72 and 4.83 (d, 1H each,  $J_{\rm HH} = 6.0$  Hz, CH of cymene), 5.35 and 5.62 (d, 1H each,  $J_{\rm HH}$ = 5.2 Hz, CH of cymene), 6.89–7.69 (m, 25H, CH<sub>arom</sub>) ppm.  $^{13}C{^{1}H}$  NMR (CDCl<sub>3</sub>):  $\delta$  17.3 (s, CH<sub>3</sub>), 20.9 and 21.4 (s,  $CH(CH_3)_2$ ), 22.3 (d,  $J_{CP} = 8.8$  Hz,  $CH_2$ ), 25.1 (dd,  $J_{CP} = 18.0$ and 6.0 Hz, CH<sub>2</sub>), 29.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 32.6 (d,  $J_{CP} = 75.6$  Hz, CH<sub>2</sub>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, Carom and CHarom) ppm. Spectroscopic data for the minor diastereoisomer are as follows: <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  6.2 (dd,  $J_{PP}$  = 22.8 and 5.3 Hz, P=O-Ru), 25.6 (dd, J<sub>PP</sub> = 6.4 and 5.3 Hz, Ru-PPh<sub>2</sub>), 44.0 (dd,  $J_{PP} = 22.8$  and 6.4 Hz, N=PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.82 and 1.10 (d, 3H each,  $J_{\rm HH}$  = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (s, 3H, CH<sub>3</sub>), 1.84-2.80 (m, 7H, CH<sub>2</sub> and  $CH(CH_3)_2$ ), 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,  $J_{\rm HH}$ = 6.0 Hz, CH of cymene), 6.89–7.69 (m, 25H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  15.9 (s, CH<sub>3</sub>), 19.7 (d,  $J_{\rm CP}$  = 6.0 Hz, CH<sub>2</sub>), 21.2 and 21.5 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 26.3 (d,  $J_{\rm CP}$  = 13.0 Hz, CH<sub>2</sub>), 29.7 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 32.6 (d,  $J_{\rm CP}$  = 75.6 Hz, CH<sub>2</sub>P), 35.9 (dd,  $J_{\rm CP}$  = 47.5 and 15.1 Hz, PCHP), 84.0 (d,  $J_{\rm CP}$  = 5.5 Hz, CH of cymene), 86.0 (d,  $J_{\rm CP}$  = 4.4 Hz, CH of cymene), 87.4 (d,  $J_{\rm CP}$  = 2.7 Hz, CH of cymene), 94.1 and 106.7 (s, C of cymene), 95.6 (d,  $J_{\rm CP}$  = 5.0 Hz, CH of cymene), 119.4–151.0 (m, C<sub>arom</sub> and CH<sub>arom</sub>) 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<sub>6</sub> (0.086 g, 0.250 mmol). Yield: 0.222 g, 90%. Anal. calc. for Ru<sub>2</sub>C<sub>78</sub>H<sub>72</sub>F<sub>20</sub>N<sub>4</sub>P<sub>4</sub>Cl<sub>2</sub>Sb<sub>2</sub> (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<sup>-1</sup> ( $\nu_{CN}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  30.3 (d,  $J_{PP} = 34.3$  Hz, Ru–PPh<sub>2</sub>), 44.6 (d,  $J_{PP} = 34.3$  Hz, N=PPh) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.95 and 1.13 (d, 6H each,  $J_{\rm HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41–1.75 (m, 4H, CH<sub>2</sub>), 1.82 (s, 6H, CH<sub>3</sub>), 1.86–2.52 (m, 8H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 2.79 (m, 2H, CH<sub>2</sub>), 3.40 (m, 2H, PCHP), 5.00, 5.16, 5.42 and 5.75 (d, 2H each,  $J_{\rm HH} = 6.3$  Hz, CH of cymene), 6.39–7.99 (m, 30H, CH<sub>arom</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –154.41 and -135.59 (m, 4F each, 4-C<sub>6</sub>F<sub>4</sub>CN) ppm. Spectroscopic data for the minor diastereoisomer are as follows: IR (KBr): 2234 cm<sup>-1</sup> ( $\nu_{CN}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  30.9 (d,  $J_{PP}$  = 31.0 Hz, Ru–PPh<sub>2</sub>), 40.6} (d,  $J_{PP} = 31.0$  Hz, N=PPh) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.98 and 1.19 (d, 6H each,  $J_{\rm HH} = 6.5$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41–1.75 (m, 4H, CH<sub>2</sub>), 1.54 (s, 6H, CH<sub>3</sub>), 1.86-2.52 (m, 8H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 2.79 (m, 2H, CH<sub>2</sub>), 3.40 (m, 2H, PCHP), 5.00, 5.16, 5.49 and 5.80 (d, 2H each, J<sub>HH</sub> = 6.3 Hz, CH of cymene), 6.39–7.99 (m, 30H, CH<sub>arom</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –152.85 and –136.91 (m, 4F each,  $4-C_6F_4CN$ ) ppm. This compound was not soluble enough to be characterized by  ${}^{13}C{}^{1}H$  NMR spectroscopy.

**Complex 8.** A solution of  $[{RuCl(\mu-Cl)(\eta^6-p-cymene)}_2]$ (0.234 g, 0.382 mmol) in dichloromethane (25 mL) was treated, at room temperature, with 2-diphenylphosphino-1phenyl-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  $\times$  10 mL). Yield: 0.460 g, 92%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -9.3 (d,  $J_{PP}$  = 43.6 Hz, PPh<sub>2</sub>), 41.9 (d,  $J_{PP}$  = 43.6 Hz, Ru–PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.19 (d, 3H, J<sub>HH</sub> = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d, 3H,  $J_{HH} = 7.1$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.69 and 2.60 (m, 2H each, CH<sub>2</sub>), 1.90 (s, 3H, CH<sub>3</sub>), 1.98 and 2.18 (m, 1H each, CH<sub>2</sub>), 2.78 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.82 (m, 1H, PCHP), 5.01 and 5.38 (d, 1H each,  $J_{\rm HH} = 5.7$  Hz, CH of cymene), 5.17 and 5.21 (d, 1H each,  $J_{\rm HH}$ = 6.1 Hz, CH of cymene), 6.86–7.98 (m, 15H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  18.0 (s, CH<sub>3</sub>), 21.7 and 22.4 (s,  $CH(CH_3)_2$ ), 26.6 and 32.8 (s,  $CH_2$ ), 27.7 (d,  $J_{CP} = 29.2$  Hz, CH<sub>2</sub>P), 30.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 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  $(3 \times 10 \text{ mL})$  and dried *in vacuo*. Yield: 0.193 g, 70%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -11.0 (d,  $J_{PP}$  = 40.2 Hz, P=O), 17.5 (dd,  $J_{PP} = 40.2$  and 27.2 Hz, Ph<sub>2</sub>P=N), 48.6 (d,  $J_{PP} = 27.2$  Hz, Ru–PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.24 (d, 6H,  $J_{\rm HH}$  = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.79 (s, 3H, CH<sub>3</sub>), 2.17-3.73 (m, 7H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 4.09 (m, 1H, PCHP), 4.83 and 5.37 (d, 1H each,  $J_{\rm HH}$  = 4.8 Hz, CH of cymene), 4.96 and 5.26 (d, 1H each,  $J_{\rm HH}$  = 5.2 Hz, CH of cymene), 6.34–7.69 (m, 25H, CH<sub>arom</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$ 15.2 (s, CH<sub>3</sub>), 21.9 and 22.3 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 26.3 and 32.5 (s, CH<sub>2</sub>), 30.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 30.9 (d,  $J_{CP} = 31.7$  Hz, CH<sub>2</sub>P), 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<sub>arom</sub> and CH<sub>arom</sub>) ppm. Anal. calc. for RuC<sub>44</sub>H<sub>46</sub>O<sub>3</sub>P<sub>3</sub>Cl<sub>2</sub>N (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<sup>-1</sup> ( $\nu_{CN}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  21.5 (d,  $J_{PP} = 28.5 \text{ Hz}, Ph_2P=N$ ), 49.6 (d,  $J_{PP} = 28.5 \text{ Hz}, Ru-PPh$ ) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.27 (d, 6H,  $J_{HH}$  = 4.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.84 (s, 3H, CH<sub>3</sub>), 2.40 (m, 3H, CH<sub>2</sub>), 2.71 (m, 2H, CH<sub>2</sub>), 2.92 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.21 (m, 1H, CH<sub>2</sub>), 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,  $J_{\rm HH} = 5.1$  Hz, CH of cymene), 7.02–7.61 (m, 15H, CH\_arom) ppm.  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta$  18.2 (s, CH<sub>3</sub>), 21.9 and 22.3 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 26.9 and 37.8 (s, CH<sub>2</sub>), 30.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 31.3 (d,  $J_{CP} = 30.6$  Hz, CH<sub>2</sub>P), 36.1 (dd, J<sub>CP</sub> = 81.1 and 12.6 Hz, PCHP), 79.3 (t, J<sub>CF</sub>  $= 11.0 \text{ Hz}, C \equiv N$ ), 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,  $CC \equiv N$ ), 110.5 (d,  $J_{CP} = 5.3$  Hz, C of cymene), 128.6–152.8 (m,  $C_{arom}$  and  $CH_{arom}$ ) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -151.65, -149.11, -138.79 and -132.50 (m, 1F each, 4-C<sub>6</sub>F<sub>4</sub>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, 55.36; 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<sub>6</sub> (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 ( $3 \times 10$  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 RuC44H46F6O3P3CINSb (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:  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  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. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.92–2.72 (m, 6H, CH<sub>2</sub>), 1.21 and 1.28 (d, 3H each,  $J_{\text{HH}} = 7.0$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.82 (s, 3H, CH<sub>3</sub>), 2.95 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.58 (m, 1H, PCHP), 5.18 and 5.87 (d, 1H each,  $J_{\rm HH} = 5.7$  Hz, CH of cymene), 5.39 and 5.67 (d, 1H each,  $J_{\rm HH}$  = 6.3 Hz, CH of cymene), 6.84-7.74 (m, 25H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 18.8 (s, CH<sub>3</sub>), 21.3 and 23.0 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 28.4 (dd,  $J_{CP} = 15.6$  and 5.1 Hz, CH<sub>2</sub>), 29.6 (dd,  $J_{CP} = 31.2$  and 15.4 Hz, CH<sub>2</sub>P), 30.6 (s, CH<sub>2</sub>), 31.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 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, Carom and CHarom) ppm. Spectroscopic data for the minor diastereoisomer are as follows:  ${}^{31}P{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta - 0.6$ (d, J<sub>PP</sub> = 33.2 Hz, P=O-Ru), 15.9 (d, J<sub>PP</sub> = 33.2 Hz, Ph<sub>2</sub>P=N), 49.2 (s, Ru-PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 0.92–2.72 (m, 6H, CH<sub>2</sub>), 1.09 and 1.33 (d, 3H each,  $J_{\rm HH}$  = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.99 (s, 3H, CH<sub>3</sub>), 2.95 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.58 (m, 1H, PCHP), 5.28 (br, 2H, CH of cymene), 5.46 and 5.73 (d, 1H each,  $J_{\rm HH}$  = 6.0 Hz, CH of cymene), 6.84-7.74 (m, 25H, CH<sub>arom</sub>) ppm.

Complex 11. The orange complex 11, isolated as a nonseparable 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<sub>6</sub> (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<sup>-1</sup> ( $\nu_{CN}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone- $d_6$ ):  $\delta$  25.6 (d,  $J_{PP} = 20.2$  Hz,  $Ph_2P=N$ ), 52.2 (d,  $J_{PP} = 20.2$  Hz, Ru–PPh) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta$  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<sub>3</sub>), 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<sub>arom</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (acetone- $d_6$ ):  $\delta$  23.4 (s, CH<sub>3</sub>), 27.4 and 27.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 34.4 and 40.0 (s, CH<sub>2</sub>), 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,  $CC \equiv N$ ), 134.5–156.1 (m, C<sub>arom</sub> and CH<sub>arom</sub>) ppm; C $\equiv N$ signal not observed. <sup>19</sup>F{<sup>1</sup>H} NMR (acetone- $d_6$ ):  $\delta$  -148.34 and -137.04 (m, 4F each, 4-C<sub>6</sub>F<sub>4</sub>CN) ppm. Spectroscopic data for the minor diastereoisomer are as follows: IR (KBr): 2259  $\text{cm}^{-1}(\nu_{\text{CN}})$ . <sup>31</sup>P{<sup>1</sup>H} NMR (acetone- $d_6$ ):  $\delta$  25.2 (d,  $J_{\text{PP}} = 20.2$ Hz, Ph<sub>2</sub>P=N), 57.9 (d,  $J_{PP} = 20.2$  Hz, Ru–PPh) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta 0.85-3.45$  (m, 14H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 1.12-1.35 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.86 (s, 6H, CH<sub>3</sub>), 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. <sup>13</sup>C{<sup>1</sup>H} NMR (acetone- $d_6$ ):  $\delta$  23.2 (s, CH<sub>3</sub>), 27.2 and 27.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 34.1 and 39.9 (s, CH<sub>2</sub>), 36.9 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 38.6  $(d, J_{CP} = 33.6 \text{ Hz}, CH_2P), 42.9 (dd, J_{CP} = 53.4 \text{ and } 13.8 \text{ Hz},$ 

	Complex 5a	Complex 7	Complex 11
Empirical formula	RuC44H46O3P3Cl2N·CHCl3	Ru <sub>2</sub> C <sub>78</sub> H <sub>72</sub> F <sub>20</sub> N <sub>4</sub> P <sub>4</sub> Cl <sub>2</sub> Sb <sub>2</sub>	$Ru_2C_{78}H_{72}F_{20}N_4P_4Cl_2Sb_2 \cdot 2Et_2O$
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	$P2_1/c$	<i>P</i> -1	$P2_1/c$
a/Å	22.247(4)	9.2949(18)	15.4570(10)
$\dot{b}/\dot{A}$	10.040(2)	12.576(3)	14.6930(8)
c/Å	20.632(4)	18.412(3)	20.1840(11)
a/°	90	101.298(17)	90
$\beta/^{\circ}$	95.89(3)	90.983(15)	99.750(5)
v/°	90	95.652(17)	90
Volume/Å <sup>3</sup>	4584.0(16)	2098.8(7)	4517.8(5)
Z	4	1	2
$\mu/\text{mm}^{-1}$	0.779	1.218	1.139
Reflns/unique	34425/9554	12150/6010	39404/12075
Refinement	on F	on F	on F
Weighting scheme	Chebychey polynomial	Chebychey polynomial	Chebychey polynomial
Final $R_1$	$0.0417 [I > 2.5\sigma(I)]$	$0.0831 [I > 2\sigma(I)]$	$0.0637 [I > 2\sigma(I)]$
Final $wR_2$	$0.0493 [I > 2.5\sigma(I)]$	$0.0848 [I > 2\sigma(I)]$	$0.0675 [I > 2\sigma(I)]$

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

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<sub>arom</sub> and CH<sub>arom</sub>) ppm; C $\equiv N$  signal not observed. <sup>19</sup>F{<sup>1</sup>H} NMR (acetone- $d_6$ ):  $\delta$  –147.04 and –135.70 (m, 4F each, 4-C<sub>6</sub>F<sub>4</sub>CN) ppm.

Complex 12. A solution of 8 (0.160 g, 0.244 mmol) in THF (20 mL) was treated, at room temperature, with <sup>t</sup>BuOOH (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  $(3 \times 10 \text{ mL})$  and dried in vacuo. Yield: 0.154 g, 94%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ 31.0 (d,  $J_{PP} = 19.6$  Hz,  $Ph_2P=O$ ), 46.2 (d,  $J_{PP} = 19.6$  Hz, Ru–PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.15 (d, 6H,  $J_{HH} = 6.8$ Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.80 (s, 3H, CH<sub>3</sub>), 1.99–2.86 (m, 7H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 3.86 (m, 1H, PCHP), 5.03 and 5.40 (d, 1H each,  $J_{\rm HH} = 5.7$  Hz, CH of cymene), 5.15 (br, 2H, CH of cymene), 6.82–7.95 (m, 15H, CH<sub>arom</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta$ 18.1 (s, CH<sub>3</sub>), 21.8 and 22.3 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 27.0 and 32.9 (s, CH<sub>2</sub>), 30.1 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 30.5 (d,  $J_{CP} = 31.4$  Hz, CH<sub>2</sub>P), 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<sub>32</sub>H<sub>36</sub>Cl<sub>2</sub>P<sub>2</sub>O (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<sub>6</sub> (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%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  39.5 (d,  $J_{PP} = 3.5$  Hz, Ph<sub>2</sub>P=O-Ru), 49.1 (d,  $J_{PP} = 3.5$  Hz, Ru–PPh) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.42–3.44 (m, 7H, CH<sub>2</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 and 1.49 (d, 3H each,  $J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.13 (s, 3H, CH<sub>3</sub>), 4.41 (m, 1H, PCHP),

5.78 and 6.06 (d, 1H each,  $J_{\rm HH} = 6.5$  Hz, CH of cymene), 5.94 and 6.09 (d, 1H each,  $J_{\rm HH} = 6.0$  Hz, CH of cymene), 7.23–8.04 (m, 15H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ 18.4 (s, CH<sub>3</sub>), 22.1 and 22.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 27.3 (dd,  $J_{\rm CP} =$ 14.6 and 5.1 Hz, CH<sub>2</sub>), 29.2 (d,  $J_{\rm CP} = 31.2$  and 5.7 Hz, CH<sub>2</sub>P), 29.4 (s, CH<sub>2</sub>), 31.6 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 39.9 (dd,  $J_{\rm CP} = 67.4$  and 14.0 Hz, PCHP), 85.6 (d,  $J_{\rm CP} = 5.1$  Hz, CH of cymene), 87.3 and 88.2 (d,  $J_{\rm CP} = 3.8$  Hz, CH of cymene), 88.6 (d,  $J_{\rm CP} = 3.2$ Hz, CH of cymene), 97.4 and 109.1 (s, C of cymene), 124.6–134.1 (m, C<sub>arom</sub> and CH<sub>arom</sub>) ppm. Anal. calc. for RuC<sub>32</sub>H<sub>36</sub>F<sub>6</sub>P<sub>2</sub>ClOSb (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<sub>6</sub> (0.051 g, 0.15 mmol). CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub> and transferred, under N<sub>2</sub> atmosphere, into a jacketed Schlenk tube refrigerated by a closed <sup>*i*</sup>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<sup>™</sup> 225 (30 m, 250  $\mu$ m) column; helium 4 mL min<sup>-1</sup>, 60 °C, 10 °C min<sup>-1</sup> 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-K $\alpha$  radiation and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods using SIR92,<sup>36</sup> and refined by means of least-squares procedures on *F* using the programs of the PC version of CRYSTALS.<sup>37</sup> The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography.<sup>38</sup> 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

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- 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<sub>2</sub>P unit by (PhO)<sub>2</sub>P(=O)N<sub>3</sub> 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<sub>2</sub>P units in the free  $\alpha$ -diphosphine **2** by using 1 equivalent of <sup>*i*</sup>BuOOH or H<sub>2</sub>O<sub>2</sub> failed. Thus, under different reaction conditions, unseparable mixtures containing the corresponding dioxide ( $\delta_P$  (CDCl<sub>3</sub>) = 25.0 (s, Ph<sub>2</sub>P=O), 53.6 (s, PhP=O)), phospholane-monooxide ( $\delta_P$  (CDCl<sub>3</sub>) = -12.9 (d, J<sub>PP</sub> = 46.1 Hz, Ph<sub>2</sub>P), 56.3 (d, J<sub>PP</sub> = 46.1 Hz, PhP=O)) and unreacted **2** ( $\delta_P$  (CDCl<sub>3</sub>) = -13.5 (d, J<sub>PP</sub> = 31.5 Hz, Ph<sub>2</sub>P), -4.5 (d, J<sub>PP</sub> = 31.5 Hz, PhP)) were obtained in all cases.
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