ORGANOMETALLICS

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pubs.acs.org/Organometallics

Synthesis, Characterization, and Reactivity of Ruthenium Bis-Allyl Complexes with Chiral Phosphine-Phosphite Ligands

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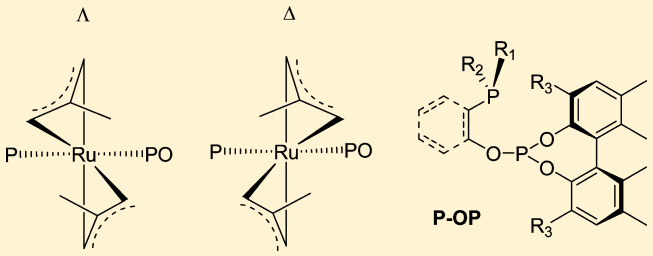
Supporting Information

ABSTRACT: A series of ruthenium bis-allyl complexes of formula Ru(η^3-2-MeC$_3$H$_4$)$_2$(P-OP) (**1**) which incorporate chiral phosphine-phosphite ligands (P-OP) have been prepared and characterized. Compounds **1** exist in solution as a mixture of two diastereomers (maj and min) differing in the configuration at the metal. Both isomers are in equilibrium in solution, and their ratio varies with the nature of the P-OP ligand. Along the series, higher values of the maj/min ratio were observed with complexes bearing less sterically encumbered phosphite groups. In reactions of compounds **1** with protic reagents removal of one or two allyl ligands has been observed. Thus, reaction of **1h** with pentachlorophenol produces the mixed allyl-phenoxide **3h**, whereas reaction of **1a** or **1h** with tiglic acid produces the corresponding tiglates **4a**,**h**, respectively. In addition, compounds **1** generate active catalysts for the hydrogenation of tiglic and 2-methyl-2-pentenoic acids. By appropriate optimization of the structure of the P-OP ligand, enantioselectivities up to 89% ee were obtained in these reactions. In addition, complexes **1** also catalyze the ROMP reaction of norbornene, although low initiation rates have been observed for this process.



INTRODUCTION

Ruthenium allyl complexes bearing phosphine ligands constitute an important class of compounds in homogeneous catalysis. They have shown a rich reactivity and have been applied in diverse catalytic processes such as enantioselective hydrogenations,[1] ROMP reactions,[2] and carboxylic acid additions to alkynes,[3] among other transformations.[4] Moreover, regarding activation of these complexes for the attainment of reactive species, stoichiometric reactions involving removal of allyl ligands have also been a subject of considerable interest. For instance, several studies about the hydrogenation of some allyl complexes to give interesting polyhydrides have been described.[5] In addition, protonation reactions have also been studied thoroughly, and a diverse range of reagents such as hydracids, phenols, and 1,3-dicarbonyl compounds have shown allyl elimination from the complex.[6] In this regard, protonation of bis-allyl diphosphine complexes provides a very convenient procedure for the nontrivial preparation of ruthenium dihalide derivatives, which are excellent catalyst precursors for the hydrogenation of several types of olefins and ketones.[7]

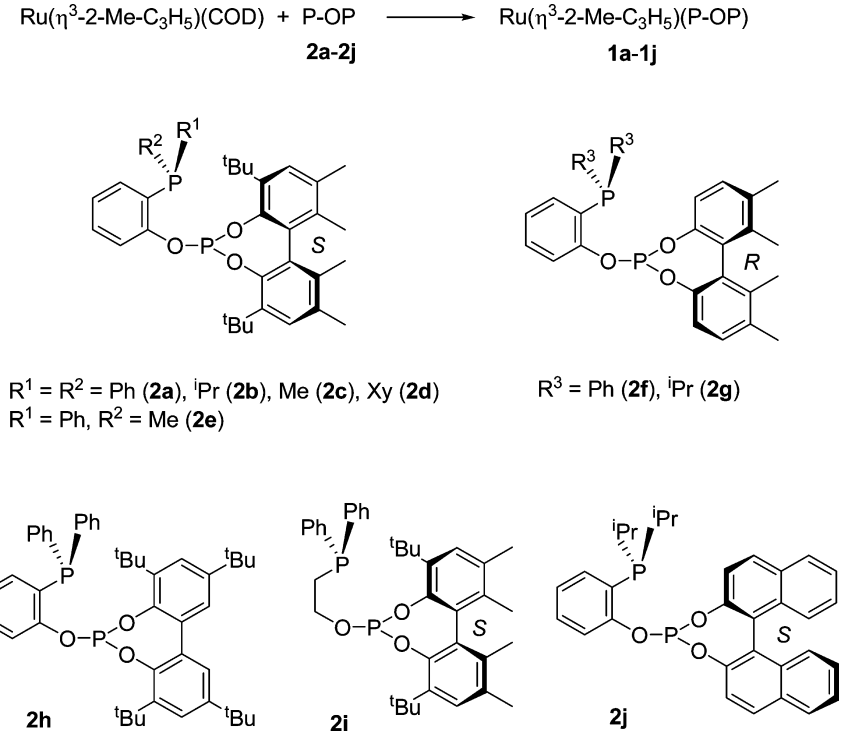
Concerning the application of ruthenium allyl complexes in asymmetric catalysis, it should be noted that, with few exceptions,[8] the examples reported in the literature are based on C_2-symmetric diphosphines. Moreover, the range of ligands based on phosphorus fragments grows continuously and ligands incorporating a range of functionalities such as phosphite, phosphinite, phosphoramidite, and aminophosphine have gained prominence.[9] Notably, these phosphorus fragments possess electronic properties different from those of phosphines;[10] therefore, the synthesis of Ru allyl complexes based on the latter ligands and a comparison of their reactivity and catalytic performance with those of pertinent diphosphine examples constitute a topic of interest.

Chiral phosphine-phosphite ligands are becoming an important class of ligands for asymmetric catalysis. A wide range of transformations such as hydroformylation, hydrogenation, and conjugate addition, among others, have been achieved very efficiently with catalysts based on these ligands.[11] In this respect, we have studied the synthesis and application in enantioselective hydrogenation of a family of highly modular phosphine-phosphites based on simple ethane or benzene backbones (P-OP). Thus, following an extensive catalyst screening, highly enantioselective rhodium catalysts for several

Received: January 10, 2012
Published: April 19, 2012

   dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

Scheme 1. Preparation of Allyl Complexes 1



types of olefins have been obtained.[12] In this contribution we present the preparation of a series of ruthenium allyl complexes based on P-OP ligands which, to the best of our knowledge, are the first Ru examples incorporating chiral phosphine-phosphite ligands. These complexes have been structurally studied in detail, and several aspects of their reactivity involving allyl elimination have been examined. Finally, their behavior in the enantioselective hydrogenation of α,β-unsaturated acids as well as in the ROMP reaction of norbornene has also been investigated.

RESULTS AND DISCUSSION

Preparation of Phosphine-Phosphite Ruthenium Allyl Complexes. A series of complexes of formulation [Ru(η^3-2-MeC_3H_4)$_2$(P-OP)] (**1a**–**j**) have been prepared by reactions between [Ru(η^3-2-MeC_3H_4)$_2$(COD)][13] and a stoichiometric amount of the desired phosphine-phosphite (P-OP = **2a**–**j**) in hexanes (Scheme 1). The reaction is quite general and allows the synthesis of a wide variety of complexes **1**. Only the reaction with ligand **2b** led to a complex reaction mixture, and we were unable to isolate the desired compound **1b**.

Solid-State Structure of Compounds 1. One of the most interesting features of compounds **1** is the presence of a stereogenic center on the metal with either Λ or Δ configuration. Therefore, for complexes with P-OP ligands possessing a stereogenic element (all but **2h**, due to rapid atropisomerization of the phosphite biphenyl moiety) two diastereomers are possible. The two diastereomeric structures can be distinguished readily with a typical quadrant diagram (Figure 1). Then, the diastereomer with configuration Λ places allyl ligands in quadrants II and IV, while the diastereomer with Δ configuration at the metal distributes the allyl ligands in quadrants I and III.

Upon these considerations, we were interested in determining the metal configuration in some selected examples. Thus,

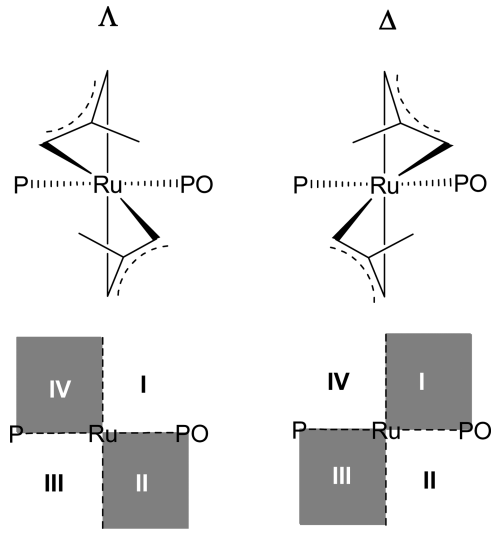


Figure 1. Quadrant diagrams for Λ and Δ diastereomeric bis-allyl complexes.

complexes **1a**,**g** have been studied by X-ray diffraction. ORTEP views, along with selected bond distances and angles, are depicted in Figures 2 and 3, respectively. Both complexes show a distorted-octahedral structure, with the phosphorus atoms and two of the terminal allyl carbon atoms in the equatorial plane, while the other two terminal carbons occupy the axial positions. The phosphine-phosphite bite angle (89°) is similar to values previously found in Rh, Ir, and Pd complexes,[12,14] whereas P–Ru–C angles range between 86 and 96°. As observed before in complexes with P-OP ligands, the Ru–P bond of the phosphite is shorter than that of the phosphine (ca. 0.1 Å). Moreover, no significant differences in the structure of the Ru(η^3-2-Me-C_3H_4)$_2$ fragment of **1a**,**g** are observed, despite the different sizes of the phosphite groups. Also remarkably,

dx.doi.org/10.1021/om300018s | Organometallics 2012, 31, 3551–3564

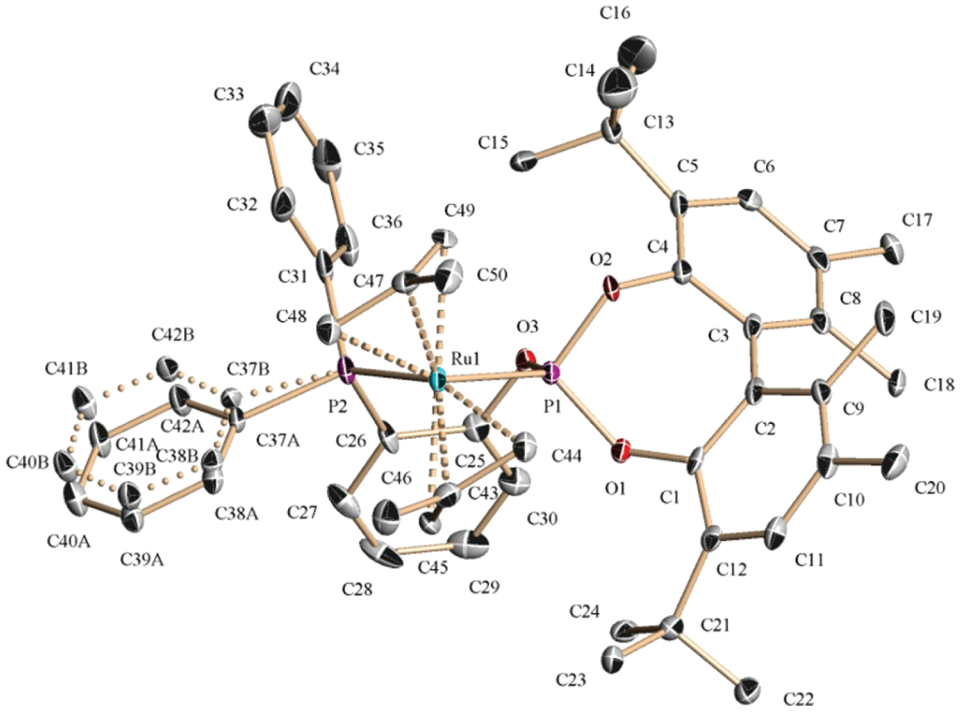


Figure 2. ORTEP view of complex **1a**. Selected bond lengths (Å) and angles (deg): Ru(1)−C(47) = 2.179(3), Ru(1)−C(48) = 2.261(3), Ru(1)−C(49) = 2.213(4), Ru(1)−P(1) = 2.2227(11), Ru(1)−P(2) = 2.3095(10); P(1)−Ru(1)−P(2) = 89.45(4), C(49)−Ru(1)−P(1) = 90.67(10), C(45)−Ru(1)−P(1) = 93.50(9), P(1)−Ru(1)−C(44) = 87.13(10), C(45)−Ru(1)−P(2) = 89.79(10), C(48)−Ru(1)−P(2) = 88.55(10).

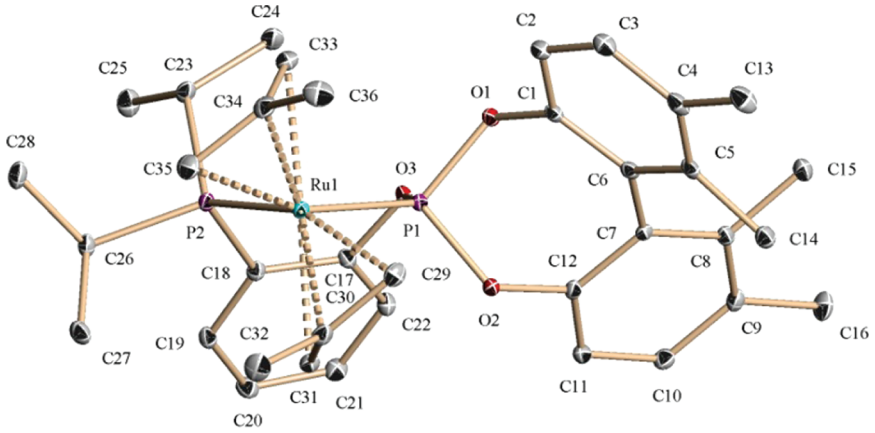


Figure 3. ORTEP view of complex **1g**. Selected bond lengths (Å) and angles (deg): Ru(1)−C(33) = 2.220(2), Ru(1)−C(34) = 2.1891(18), Ru(1)−C(35) = 2.2712(19), Ru(1)−P(1) = 2.1999(5), Ru(1)−P(2) = 2.3337(5); P(1)−Ru(1)−P(2) = 89.071(17), P(1)−Ru(1)−C(29) = 86.05(6), P(1)−Ru(1)−C(31) = 87.67(5), C(33)−Ru(1)−P(2) = 90.48(5), C(35)−Ru(1)−P(2) = 93.29(5).

both compounds show a Λ configuration at the metal irrespective of their phosphite biaryl configuration.

Solution Behavior of Complexes 1. Most studies considering ruthenium configurations in bis-allyl diphosphine complexes are restricted to the structure in the solid state, whereas the behavior in solution has not been investigated in great detail. It is therefore of interest to investigate the existence of isomers of compounds **1** in solution and the Ru configuration of the preferred isomer in each case. This goal is facilitated by the existence of two different phosphorus functionalities, which allow us to analyze in detail the structures of the isomers by NMR techniques.

As expected, most of complexes **1** showed the presence of two isomers (which will be denoted from now on as maj and min) in solution. The ratio between the two species has been determined by $^{31}P\{^{1}H\}$ NMR and range between 1.3 in the case of **1c** and higher than 20 in the case of **1g** (Table 1). Thus, larger values are observed in the case of smaller phosphite fragments. Both sets of signals show resonances in the ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra corresponding to P-OP and two η^3-2-Me-C_3H_4 ligands. In contrast, compound **1h** provides more simple spectra which contain only one set of signals. Atropisomerization of the biphenyl fragment rapidly exchanges isomers with *R* and *S* phosphite biaryl configurations at room temperature; therefore, the spectra for **1h** correspond to a mixture of two enantiomers differing in Ru configuration.

In order to analyze the structural features of the two isomers of complexes **1**, the resonances of the allyl ligands have been studied in detail. Both ligands are nonequivalent, as a result of the C_1 symmetry of the P-OP ligand, and give two

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

Table 1. $^{31}P\{^1H\}$ NMR Data of Isomers of Complexes 1[a]

complex	maj/min	isomer	δ_{PO}	δ_{PC}	$^2J_{PP}$
1a	6.0	maj-**1a**	168.4	42.3	40
		min-**1a**	154.3	40.2	47
1c	1.3	maj-**1c**	161.7	2.5	50
		min-**1c**	158.8	1.4	52
1d	4.0	maj-**1d**	168.5	41.3	40
		min-**1d**	154.3	39.4	47
1e	9.0	maj-**1e**	162.1	21.6	46
		min-**1e**	152.7	15.7	51
1f	14.0	maj-**1f**	177.8	45.6	44
		min-**1f**	173.4	44.6	58
1g	>20	maj-**1g**[b,c]	175.0	36.5	47
1h		**1h**	157.5	42.4	46
1i	2.0	maj-**1i**	157.2	40.1	35
		min-**1i**	156.1	32.3	40
1j	13.1	maj-**1j**	180.2	37.7	47
		min-**1j**[d]		42.9	

[a]Chemical shifts in ppm and $^2J_{PP}$ values in Hz. Spectra were obtained in CD_2Cl_2 unless stated otherwise. [b]min isomer not observed. [c]Obtained in $CDCl_3$. [d]Phosphite signal overlapped with that of the maj isomer. $^2J_{PP}$ could not be determined, due to the broad phosphine signal.

differentiated groups of resonances. Thus, in the $^{13}C\{^1H\}$ NMR one signal is observed for each terminal carbon (C^a–C^d, Figure 4), between 35 and 49 ppm, while each central carbon atom gives a resonance around 100 ppm. Most interestingly, resonances of the terminal carbons show a different coupling pattern with ^{31}P nuclei, which is repeated along the series. Then, two of them appear as singlets, whereas the other two appear as doublets of doublets. Typically, one of the latter is characterized by J_{CP} constants around 45 and 5 Hz, whereas the coupling constants in the other doublet of doublets have values around 20 and 5 Hz. From these observations, the singlets can reasonably be assigned to terminal carbons in axial positions (C^a and C^c) and the doublets of doublets attributed to terminal allyl carbons in equatorial positions (C^b and C^d).

Further analysis requires the assignment of equatorial terminal carbons trans to each phosphorus atom. For that purpose, compound **1e**, characterized by a P-stereogenic phosphine fragment, has been studied. This compound shows a maj/min ratio around 9, which facilitates the study of the preferred isomer. An analysis by a 2D-NOESY experiment allows us to assign the allyl protons in positions syn (H^a–H^d) and anti ($H^{a\prime}$–$H^{\prime}$) to the 2-Me groups. In addition, meaningful NOE contacts between anti protons of an allyl group and the ortho protons of the P-Ph fragment (Figure 5), indicate the existence of an allyl group in quadrant III and hence a Δ configuration for the maj isomer. Other contacts between allyl protons and phosphite ^{t}Bu groups are in good accord with this structure. From these observations and with the help of a ^{13}C–^1H HMQC experiment it is possible to assign the doublet of doublets with the higher J_{CP} value, that corresponding to C^b, to the terminal allyl carbon in a position trans to the phosphorus of the phosphite. Consequently, C^d can finally be assigned to the equatorial carbon trans to the phosphine. From this analysis the resonances for terminal allyl carbons in the $^{13}C\{^1H\}$ NMR spectra have been assigned to the rest of complexes **1**.

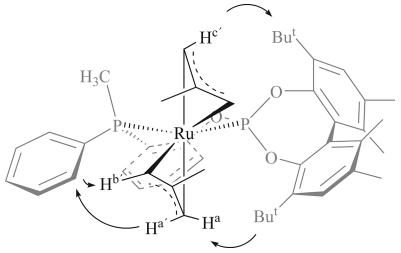


Figure 5. Selected NOE contacts observed in compound maj-**1e**.

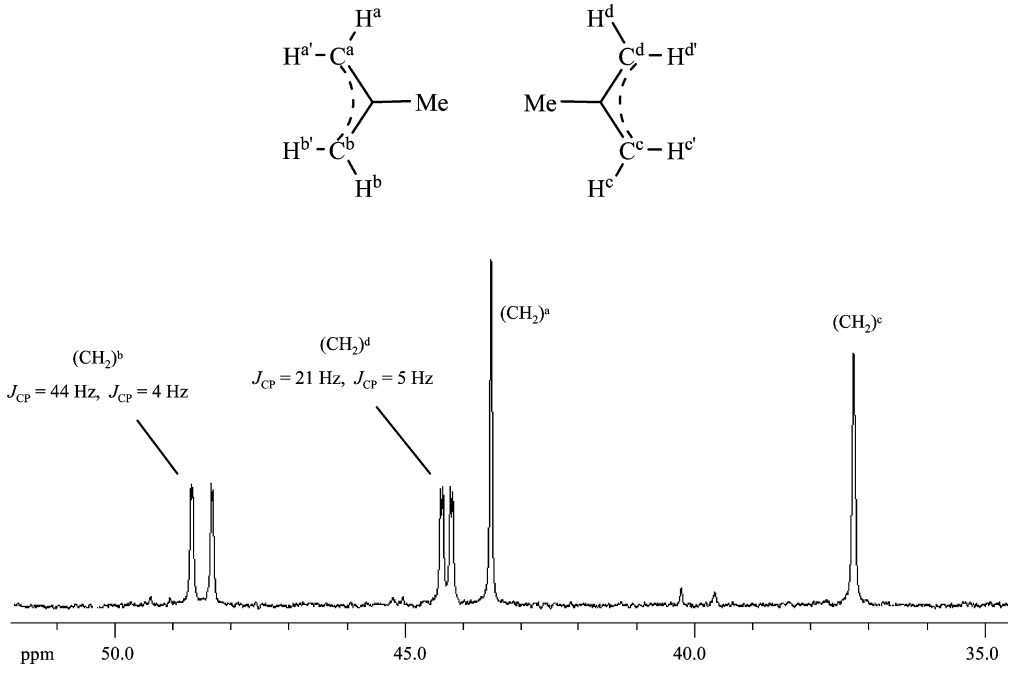


Figure 4. Notation of terminal allyl nuclei and corresponding region in the $^{13}C\{^1H\}$ NMR spectrum of **1f** in CD_2Cl_2.

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551–3564

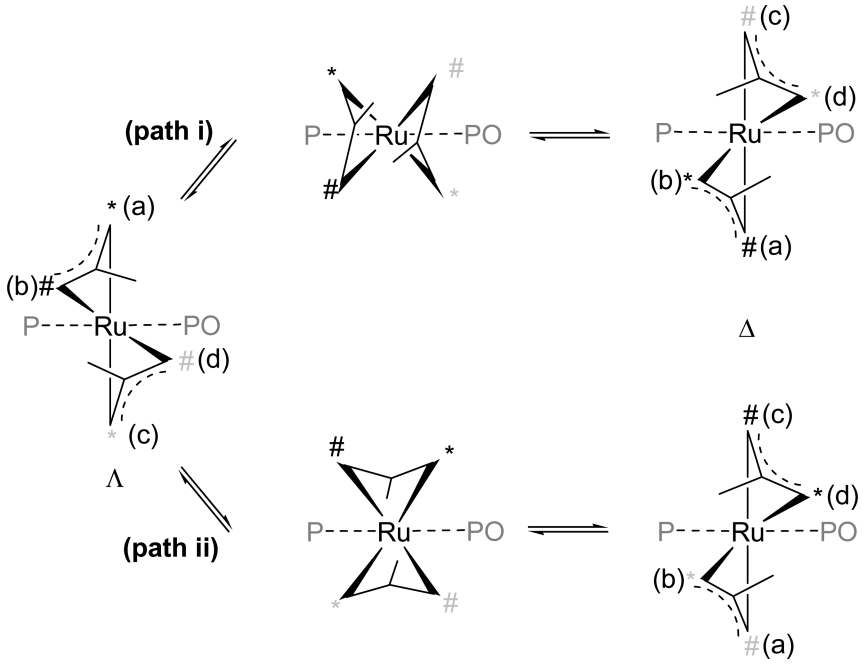


Figure 6. Intramolecular interconversion between maj and min isomers of **1**.

As a further step we were committed to assign the configuration of the maj and min isomers in other complexes. As mentioned above, compound **1g** has shown a Λ configuration in the solid state. In addition, only the maj isomer is observed in solution. An analysis of the 2D-NOESY experiment is in good accord with a Λ configuration for the maj isomer. Moreover, compound **1f**, which contains the same phosphite fragment as **1g**, displays analogous behavior. The maj isomer is very predominantly observed (maj/min = 14), and the NMR data are in good accord with a Λ configuration for the maj isomer.

To determine the configuration of the maj isomer of **1a**, a crystalline sample of this compound was dissolved at −80 °C in CD_2Cl_2, and a $^{31}P\{^1H\}$ NMR spectrum was registered at this temperature. This spectrum showed only one isomer. When the temperature was raised, a second species appeared. At room temperature a 6/1 ratio was observed favoring the isomer exclusively observed at −80 °C. The maj/min ratio did not change significantly when the temperature was lowered again. These observations, in connection with the Λ configuration observed for **1a** in solid state (see above), allow us to conclude that the maj isomer in solution also corresponds to a Λ configuration.

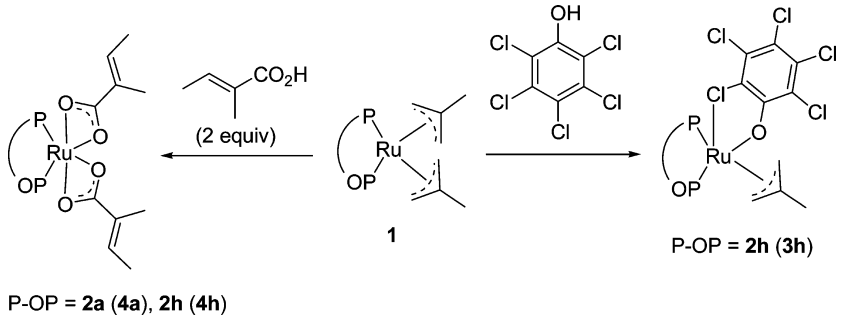
Regarding the preferred configuration, it should be mentioned that for both **1f** and **1g** a Λ configuration is highly favored. However, in the case of compound **1a**, which has the opposite configuration in the biaryl phosphite, the configuration is also Λ. Moreover, **1e** also has an *S* phosphite fragment, while the configuration of maj-**1e** is Δ. Then, the preferred metal configuration does not correlate with the phosphite biaryl configuration. It should be noted, however, that a common feature of solid-state structures of **1a**,**g** is the existence of an axial phosphine substituent in quadrant IV which finds an adjacent allyl group with the 2-Me group oriented anti with respect to this phosphine substituent. This structural feature looks more general and is also present in other bis-allyl complexes with chiral diphosphines,[7b,15] although we cannot find a clear explanation for this arrangement.

The results mentioned above also indicate the existence of an equilibrium between the maj and min isomers of **1a**. Moreover, the ratio between diastereomers depends on the solvent. As stated, the value of the maj/min ratio is 6 in CD_2Cl_2 at room temperature, while it increases to 8 in hexanes and to 16 in C_6D_6. In order to investigate the exchange mechanism between maj and min isomers, we have examined in more detail the behavior in solution of **1c**. This compound gives a 1/1.3 ratio of the two isomers; therefore, the NMR signals of both species have enough intensity to be studied. Initially, the exchange between the two isomers of **1c** has been evidenced in a $^{31}P-^{31}P$ EXSY experiment by the appearance of cross-peaks between the two isomers in the phosphine and the phosphite regions. On the other hand, an analysis of the $^1H-^1H$ EXSY spectrum does not show exchanges between the syn and anti protons of allyl methylene groups. This observation excludes the existence of $\eta^3-\eta^1$-rotation$-\eta^3$ mechanisms.[16] Moreover, no intramolecular exchanges have been observed. All the exchanges detected involve signals of the maj and min isomers. This feature rules out the existence of mechanisms produced by phosphorus decoordination, rotation, and coordination.[14a] Upon these observations it can be concluded that the mechanism should be nondissociative, which is a dynamic process frequently found in octahedral compounds.[17] In particular, exchanges between H^a, H^b, H^c, and $H^{c'}$ protons of the maj isomer with H^d, H^c, H^b, and $H^{b'}$ protons of the min isomer, respectively, can be assigned. This pattern allows us to explain the interconversion between diastereomers of **1c** by simple allyl migration through axial positions (path ii, Figure 6).[18] Conversely, allyl migration through the more hindered equatorial plane (path i) does not match the results, as this mechanism would exchange H^a and H^b protons with H^d and H^c, respectively.

Stoichiometric Reactions of Compounds 1. Due to the interesting reactivity reported for bis-allyl ruthenium diphosphine complexes, we were interested in examining the behavior of compounds **1** in several representative reactions. Initially, some allyl protonation reactions were examined. Then, reaction

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

Scheme 2. Protonation Reactions of Allyls 1



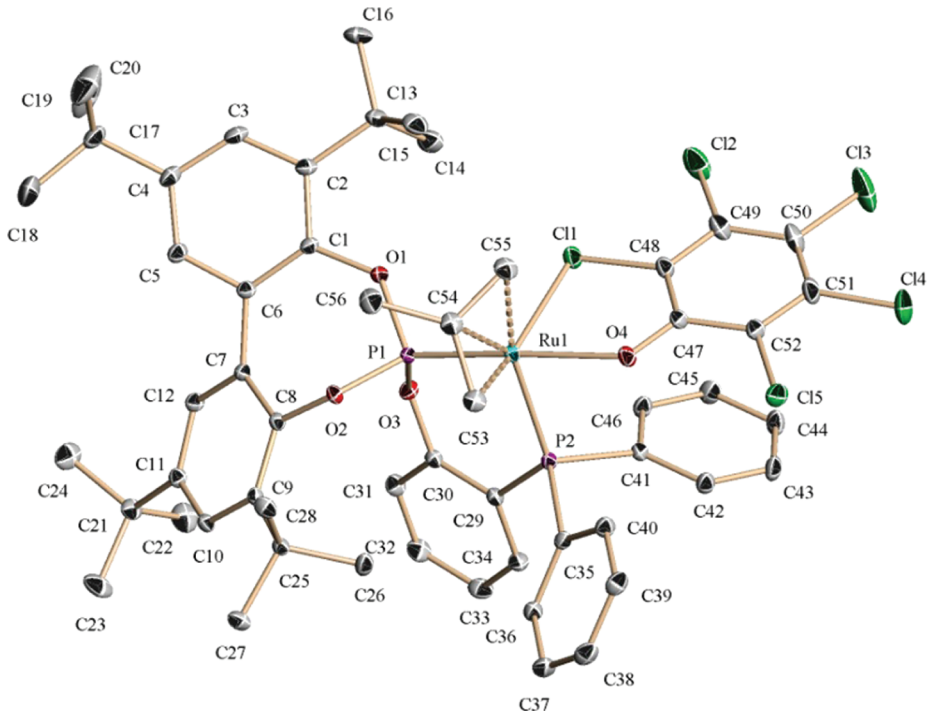


Figure 7. ORTEP view of complex **3h**. Selected bond lengths (Å) and angles (deg): Ru(1)−C(53) = 2.134(2), Ru(1)−C(54) = 2.254(2), Ru(1)−C(55) = 2.302(2), Ru(1)−O(4) = 2.1731(15), Ru(1)−Cl(1) = 2.4924(6), Ru(1)−P(1) = 2.1607(5), Ru(1)−P(2) = 2.3061(6); C(53)−Ru(1)−P(1) = 98.75(7), C(53)−Ru(1)−O(4) = 90.53(8), P(1)−Ru(1)−O(4) = 168.69(5), P(1)−Ru(1)−C(55) = 109.95(7), C(53)−Ru(1)−P(2) = 99.28(7), P(1)−Ru(1)−P(2) = 89.91(2).

between **1h** and 2 equiv of pentachlorophenol at room temperature yielded the monoallyl monophenoxide compound **3h** (Scheme 2). Interestingly, no bis-phenoxide complex was observed, despite heating the reaction mixture to 50 °C for 16 h. This behavior contrasts with the easy displacement of two allyl ligands in diphosphine analogues described by Werner.[6a,b] Compound **3h** is characterized by one group of resonances in the $^{31}P\{^{1}H\}$ NMR spectrum, composed by doublets at 16.9 and 133.6 ppm with J_{PP} = 71 Hz. This coupling constant is higher than values observed for complexes **1**, which range between 35 and 58 Hz. In addition, the presence of an allyl ligand is evidenced by resonances for the terminal CH_2 groups. Thus, in the ^{1}H NMR spectrum signals at 2.00, 2.30, 2.70, and 3.98 ppm are observed, while the corresponding carbons appear in the $^{13}C\{^{1}H\}$ NMR experiment as a broad singlet at 42.1 ppm and a broad doublet centered at 74.1 ppm (J_{CP} = 22 Hz). The assignment of these resonances has been further confirmed by a $^{13}C-^{1}H$ HMQC experiment. Considering the $^{2}J_{CP}$ value for the doublet, this signal can tentatively be assigned to a terminal carbon in a position trans to a phosphine group. Confirmation of this structural proposal has been provided by a X-ray diffraction study (Figure 7). Complex **3h** displays a distorted-octahedral structure with the two phosphorus atoms, the oxygen of the phenoxide, and an allyl terminal carbon in the equatorial plane. Accordingly, the remaining terminal carbon of the allyl group and the coordinated Cl atom are placed in axial positions. As observed before, the Ru−P bond distance of the phosphite is shorter than that of the phosphine (2.161 and 2.306 Å, respectively). Moreover, the value of the Ru−Cl bond distance (2.492 Å) is in the typical range for Ru complexes with this halo-phenoxy ligand. A notable feature of this structure is the asymmetric bonding of the allyl ligand, evidenced by a substantial difference in distances between the Ru and the terminal allyl carbon atoms. Thus, a bond length of 2.134 Å is observed for Ru(1)−C(53), while the Ru(1)−C(55) bond distance is 2.302 Å. As reference values, it can be mentioned that the differences between the Ru−CH_2 bond distances in **1a** are much smaller (0.03−0.05 Å). In addition, the C(54)−C(55) bond is shorter than C(53)−C(54) (1.397 and 1.445 Å, respectively). These bonds are shorter and longer, respectively,

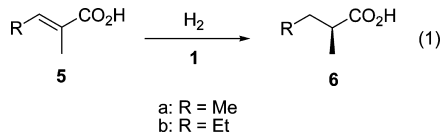
dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

than C(terminal)−C(central) bonds in **1a**. Overall, these data can be interpreted in terms of a more pronounced σ component for the Ru(1)−C(53) bond, while the ruthenium interaction with C(54) and C(55) atoms resembles an olefin−metal interaction. Moreover, these considerations are in good agreement with the low-field shift of the resonance of the terminal carbon trans to the phosphine from the typical range observed in compounds **1** (ca. 35−45 ppm).

In addition, protonation reactions with tiglic acid (**5a**) have also been examined, as the removal of allyl ligands is expected in the hydrogenation of unsaturated acids (see below). For instance, complex **1h** reacted slowly with **5a** at room temperature, while at 50 °C the reaction proceeded at a appreciable rate. After a 12 h heating period complete conversion into the corresponding bis-tiglate **4h** was observed (Scheme 2).[19] The complex is characterized by two doublets in the $^{31}P\{^1H\}$ NMR spectrum centered at ca. 144 and 51 ppm (J_{PP} = 79 Hz). On the other hand, one singlet for each ^{t}Bu and one group of signals for each tiglate were observed in the ^1H NMR spectrum. Moreover, **4h** displays fluxional behavior in solution. Then, cross-peaks in the $^1H-^1H$ EXSY experiment between the olefin proton signals of the tiglates, between ^{t}Bu group singlets at positions 3 and 3′, as well as between those at positions 5 and 5′, were detected. These observations can be explained by the existence of an atropisomerization of the phosphite group, already mentioned for **1h**, although tiglate migration with a concomitant switch in metal configuration, as discussed for **1c**, may also take place. On the other hand, the protonation of allyl **1a** with **5a** at 50 °C has been monitored by $^{31}P\{^1H\}$ NMR. These spectra show the disappearance of both isomers of **1a** while two new species appeared. The predominant one is characterized by two doublets centered at 141.6 and 48.4 ppm (J_{PP} = 81 Hz). The minor species shows a similar pattern with two doublets at 144.2 and 50.0 ppm (J_{PP} = 80 Hz). At the final stage of the reaction the minor species disappeared and only the major compound was observed. This compound (**4a**) has been fully characterized, and the data obtained are in accord with a bis-tiglate formulation. Upon comparison with the formation of **4h**, a reasonable proposal for the less thermodynamically stable, minor species observed during the generation of **4a** is a diastereomer differing in metal configuration.

In relation with the application of allyl complexes **1** in catalytic hydrogenation, we have also explored their reactivity under hydrogen pressure. Thus, when a solution of **1h** in C_6D_{12} is heated at 60 °C under 2 atm of hydrogen, no reaction was observed after 12 h. In contrast, addition of **5a** starts the allyl activation and the hydrogenation reaction (see below). Moreover, when compound **1a** was dissolved in CD_2Cl_2 and heated at 60 °C under hydrogen, reaction of the allyl complex was observed, leading to a mixture in which several hydride species were observed. No further characterization of these species has been achieved, due to the complexity of this system. We do note, however, the presence of a quintet at 3.0 ppm with a coupling constant of 1.7 Hz in the ^1H NMR spectra. This signal is attributable to CD_2HCl and points to the participation of ruthenium chlorides in this reaction.[20]

Asymmetric Hydrogenation of Unsaturated Acids. We next studied the performance of bis-allyl complexes **1** in the catalytic hydrogenation of **5a** and (*E*)-2-methyl-2-pentenoic acid (**5b**) as representative examples of prochiral α,β-unsaturated acids (eq 1).[21] Initially, a set of hydrogenations of **5a** with **1h** was prepared to find appropriate reaction



(1)

conditions. Attempts at room temperature under hydrogen pressures between 4 and 20 atm, in MeOH or ^{i}PrOH (entries 1−3, Table 2), did not show conversion. Alternatively, when the reaction was performed at 40 °C, complete conversion was observed in MeOH (entry 4). As the solubility of **1h** in MeOH is low, a MeOH/CH_2Cl_2 (1/1) mixture was also tested at 40 °C. Complete conversion was observed again (entry 5). This solvent mixture provides a rather active catalyst able to complete reactions at *S*/*C* values of 500 and 1000 in 24 h (entries 6 and 7). In contrast, no conversion was observed in pure CH_2Cl_2 at 50 °C (entry 8). The performance of **1a** in the hydrogenation of **5a** was next examined. The data obtained showed a dramatic influence of the solvent on enantioselectivity (Table 3). Thus, complete conversions in MeOH and ^{i}PrOH were observed, although the enantioselectivities were low (20 and 39% ee, respectively, entries 1 and 3). Complete conversion and low ee values were likewise observed in a THF/MeOH mixture (entry 2). On the other hand, enantioselectivity increased up to 77% ee in *n*-hexane (entry 4). However, the reaction in this solvent is slower under these

Table 2. Hydrogenation of 5a using Complex 1h[a]

entry	*S*/*C*	temp (°C)	$P(H_2)$ (atm)	solvent	conversn (%)
1	100	room temp	4	MeOH	0
2		room temp	20	MeOH	0
3		room temp	20	^{i}PrOH	0
4		40	4	MeOH	100
5		40	4	MeOH/CH_2Cl_2 (1/1)	100
6	500	40	4	MeOH/CH_2Cl_2 (1/1)	100
7	1000	40	4	MeOH/CH_2Cl_2 (1/1)	100
8	100	50	4	CH_2Cl_2	0

[a]All hydrogenations were completed under the conditions specified. Reactions were carried out at room temperature with an initial hydrogen pressure of 4 bar. Reaction time 24 h. The conversion was determined by ^1H NMR.

Table 3. Hydrogenation of 5a using Complex 1a[a]

entry	temp (°C)	solvent	conversn (%)	ee (%) (confign)
1	40	MeOH	100	20 (*R*)
2	40	THF/MeOH (1/3)	100	23 (*R*)
3	40	^{i}PrOH	100	39 (*R*)
4	40	*n*-hexane	53	77 (*R*)
5	60	*n*-hexane	100	77 (*R*)
6[b]	60	*n*-hexane	75	82 (*R*)

[a]Reactions were carried with an initial hydrogen pressure of 4 bar at *S*/*C* = 100, unless otherwise stated. Reaction time 24 h. The conversion was determined by ^1H NMR and enantiomeric excess (ee) by chiral GC. The configuration was determined by comparison of optical rotations with literature values.[21a] [b]Reaction at *S*/*C* = 1000.

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

conditions and conversion was only moderate. An increase in temperature to 60 °C produced a complete conversion without erosion of enantioselectivity (entry 5). The use of a lower catalyst loading (S/C = 1000) also produced a good value of conversion and a small increase in enantioselectivity (entry 6). Interestingly, **1a** showed poor performance in alcoholic solvents, which are usually the solvents of choice for the Ru-catalyzed hydrogenation of unsaturated acids.[21] This observation can be attributed to the detrimental role of an alcohol in the catalytic cycle, as well as to a reduced stability of the chiral phosphite group under the reaction conditions.

The influence of the P-OP ligand in the hydrogenation of **5a** was next investigated by comparing the performance of complexes **1** (Table 4). The results obtained indicate that all

Table 4. Hydrogenation of Acids 5 using Complexes 1[a]

entry	substrate	cat. precursor	conversn (%)	ee (%) (confign)
1	**5a**	**1a**	100	77 (*R*)
2	**5a**	**1c**	37	55 (*R*)
3	**5a**	**1d**	100	65 (*R*)
4	**5a**	**1f**	20	41 (*S*)
5	**5a**	**1g**	100	87 (*S*)
6	**5a**	**1i**	100	67 (*R*)
7	**5a**	**1j**	66	77 (*R*)
8	**5b**	**1g**	100	89 (*S*)

[a]Reactions were carried with an initial hydrogen pressure of 4 bar at S/C = 100 in *n*-hexane at 60 °C. Reaction time 24 h. The conversion was determined by ^{1}H NMR and enantiomeric excess (ee) by chiral GC. The configuration was determined by comparison of optical rotations with literature values.[21a]

catalyst precursors based on diarylphosphino groups, except **1f**, gave full conversion. On the other hand, for dialkylphosphino derivatives, only **1g** gave full conversion. In addition, this catalyst precursor gave the best enantioselectivity of the series (87% ee, entry 5). Likewise, this catalyst precursor hydrogenates **5b** with a good value of enantioselectivity (89% ee, entry 8). From a practical point of view we were interested to examine catalyst precursor **1j**, which due to a straightforward preparation of the BINOL phosphine-phosphite **2j** is easier to obtain than **1g**. Unfortunately, **1j** was less active and enantioselective than **1g** (entries 7 and 5).

Considering the slow release of allyl ligands in the reaction between complexes **1** and **5a**, we were interested in comparing the performance of **1a** and **4a** in **5a** hydrogenation. A series of reactions in different solvents were prepared (Table 5). As observed before with **1a**, complete conversion but low

Table 5. Hydrogenation of 5a using Tiglate 4a[a]

entry	temp (°C)	solvent	conversn (%)	ee (%) (confign)
1	40	MeOH	100	19 (*R*)
2	40	CH_2Cl_2	3	nd
3	40	^{i}PrOH	100	30 (*R*)
4	40	benzene	3	nd
5	room temp	*n*-hexane	0	nd
6	40	*n*-hexane	69	77 (*R*)

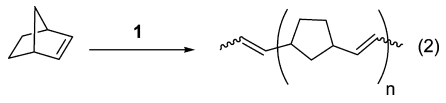
[a]Reactions were carried with an initial hydrogen pressure of 4 bar at S/C = 100 in *n*-hexane at 60 °C. Reaction time 24 h. The conversion was determined by ^{1}H NMR and enantiomeric excess (ee) by chiral GC. The configuration was determined by comparison of optical rotations with literature values.[21a]

selectivity values were observed in MeOH and ^{i}PrOH (entries 1 and 3), while almost no reaction was observed in CH_2Cl_2 (entry 2). Moreover, an important increase in enantioselectivity up to 77% ee was observed in *n*-hexane (entry 6). The results with **4a** reproduce well the solvent effect observed with **1a** in terms of both conversion and enantioselectivity. Therefore, as expected, both precatalysts should lead to the same catalyst. However, despite allyl activation not being needed in the case of **4a**, any differences in reaction rate do not lead to enhanced conversion after 24 h when comparing **1a** and **4a** (entry 4, Table 3, and entry 6, Table 5).

In a complementary experiment, the hydrogenation of **5a** (4 equiv) with **1h** under 2 atm of hydrogen in C_6D_{12} at 60 °C was monitored. After 14 h, the reaction mixture displayed signals of tiglate **4h** and unreacted **1h** in a 1/1 approximate ratio. As the reaction proceeded, disappearance of the signals of **5a** was observed in the ^{1}H NMR spectra. Moreover, no signals were detected in the hydride region. In addition, the ^{31}P{^{1}H} NMR spectra showed several overlapped signals around 148.0 and 58.5 ppm. These chemical shift values are similar to those of the bis-tiglate **4h** and can be assigned to carboxylate species of formula $Ru(O_2CC{=}CH\text{-}Me)_n(O_2CCHCH_2Me)_{2-n}$ (**2h**; n = 0, 1).[22]

The broadly accepted mechanism for the hydrogenation of acrylic acids with Ru diphosphine catalysts proposes that the hydrogen atom delivered at position 2 comes from the gas phase (through a Ru hydride), whereas the atom at position 3 results from a protonation step produced by the solvent or the carboxylic acid at low hydrogen pressures. Moreover, at higher pressures competitive hydrogenolysis also takes place.[23] In addition, exchange between hydrogen gas and acid protons has been observed.[22,23a] The present system also shows this exchange. Then, in a deuteration experiment of **5a** catalyzed by **1a** (4 atm D_2, S/C = 100, 60 °C, C_6D_{12}), extensive labeling of the carboxylic position (MeCH═C(Me)COOH/MeCH═C(Me)COOD ratio 0.1/1.0) was observed after 6 h. After this reaction time no reduced product was detected. In a parallel reaction run, a 60% conversion was observed after 24 h, the product obtained being fully deuterated at positions 2 and 3, as well as at the carboxylic group. Deuteration at position 3 can reasonably be ascribed to protonation by MeCH═C(Me)-COOD, as proposed before in the hydrogenation of **5a** in supercritical CO_2.[24]

ROMP Reaction of Norbornene. Another interesting application of Ru bis-allyl complexes is with regard to their use as catalyst precursors for the ROMP reaction (eq 2).[2] More



(2)

specifically, the Leitner group described the behavior of bis-allyl complexes bearing highly basic chelating trialkylphosphine in the ROMP reaction of norbornene.[2a] Interestingly, this reaction proceeds without an additional activator and the formation of the requisite metallacyclobutane species from the Ru(η^3-2-MeC_3H_4)$_2$ moiety is proposed. Inspired by this study, we were interested on examining the performance of allyl complexes **1** in the ROMP reaction of norbornene.

A series of ROMP reactions of norbornene indicated that compounds **1** led to active catalysts in this reaction (Table 6). However, conversions were generally low and only **1g** gave a good value (74%, entry 4). Polymeric materials obtained from

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

Table 6. ROMP Reaction of Norbornene with Complexes 1[a]

entry	precursor	yield (%)	trans (%)	M_n	PDI
1	**1a**	6	79	36 900	2.3
2	**1c**	24	70	8 300	3.3
3	**1f**	18	67	16 200	3.6
4[b,c]	**1g**	74	78	4 800	2.8
5	**1h**	4	79	41 600	1.4
6	**1i**	10	70	6 400	4.2

[a]Reactions were carried out at 40 °C in CH_2Cl_2 ([norbornene] = 0.35 M), at S/C = 100. The reaction time was 24 h, unless otherwise stated. % trans: percentage of trans olefinic bonds as determined by ^1H NMR. PDI: polydispersity index (M_w/M_n). M_n and PDI values were determined by GPC ($CHCl_3$). The obtained polymers are completely soluble in $CHCl_3$, unless otherwise noted. [b]The reaction time was 7 h. [c]The product was not fully soluble in $CHCl_3$; % trans, M_n, and PDI values refer to the soluble part in $CHCl_3$.

these reactions were characterized by IR and NMR spectroscopy as polynorbornene.[25] Depending on the P-OP ligand the cis/trans ratio ranges from 67% produced by **1f** (entry 3) to 79% obtained in the reactions performed with **1a** and **1h** (entries 1 and 5). Moreover, molecular weights of the obtained polymers also depend on the P-OP ligand, although they are significantly lower than those obtained by Leitner (M_n = 210 000−381 000). In addition, broad molecular weight distributions, indicated by the high polidispersity index (PDI) values,[26] were obtained. Along the series, higher molecular weight and lower PDI were obtained with precatalysts **1a**,**h**. An interesting aspect is the ratio of ruthenium complex acting as polymer initiator. Considering the yield and the molecular weight of the polymers obtained, it is apparent that only small parts of the Ru species act as polymerization initiators.[27] This amount is as low as 1% in the case of **1a**,**h**. Moreover, ^1H NMR monitoring of a reaction performed at S/C = 10 with **1g** only showed signals for starting allyl, unreacted norbornene, and polymer. Therefore, only a small part of the starting allyl should be responsible for the catalysis and the rate of chain propagation is therefore higher than that of initiation.

CONCLUSIONS

A series of Ru allyl complexes of formulation [Ru(η^3-2-MeC_3H_5)$_2$(P-OP)] has been prepared and characterized. These compounds exist as mixtures of two diastereomers which differ in the configuration at the metal, the preferred configuration and the ratio between maj and min isomers being dependent on the P-OP ligand. Allyl ligand protonation with **5a** and pentachlorophenol has been studied, and these reactions lead to the corresponding bis-tiglate and monoallyl phenoxy derivatives.

Complexes **1** are effective catalysts for the hydrogenation of α,β-unsaturated acids. This reaction has shown the important influence of the solvent, and the best results are obtained in *n*-hexane. Optimization of the catalytic system by tuning the reaction conditions and selecting the appropriate P-OP ligand has allowed the reduction of these substrates with enantioselectivities up to 89% ee. Moreover, deuteration studies and hydrogenation monitoring by NMR indicate a behavior similar to that exhibited by diphosphine derivatives.

Finally, compounds **1** are also active in the ROMP reaction of norbornene, although they are less active than their bis-allyl diphosphine counterparts. In this reaction, the initiation step is slow and only a small part of the Ru allyl precursor acts as a catalyst.

EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen with the following desiccants: sodium benzophenone ketyl for diethyl ether and tetrahydrofuran (THF), sodium for hexanes and toluene, CaH_2 for dichloromethane, and NaOMe for methanol. Phosphine-phosphite ligands **2** were prepared as described previously.[12] [Ru(η^3-2-MeC_3H_4)$_2$(COD)] was synthesized according to a literature procedure.[13] All other reagents were purchased from commercial suppliers and used as received. NMR spectra were obtained on Bruker DPX-300, DRX-400, and DRX-500 spectrometers. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si. All NMR measurements were carried out at 25 °C, unless otherwise stated. maj and min denote major and minor diastereomers, respectively. GC analyses were performed by using a Hewlett-Packard Model HP 6890 chromatograph. HRMS data were obtained on a JEOL JMS-SX 102A mass spectrometer, and ESI-MS experiments were carried out in a Bruker 6000 apparatus by the Mass Spectrometry Services of the Universidad de Sevilla (CITIUS) and Instituto de Investigaciones Químicas (IIQ), respectively. Elemental analyses were run by the Analytical Service of the IIQ in a Leco CHNS-932 elemental analyzer. Optical rotations were measured on a Perkin-Elmer Model 341 polarimeter. IR spectra were acquired on a Bruker Vector 22 instrument. Gel permeation chromatography (GPC) analyses were performed using a Waters apparatus equipped with a Waters 2414 refractive index detector and two Styragel HR columns (7.8 × 300 mm) linked in series, thermostated at 60 °C, and using $CHCl_3$ as the mobile phase at a flow rate of 0.5 mL/min. Molecular weights were estimated against polystyrene standards.

[Ru(η^3-2-MeC_3H_4)$_2$(2a)] (1a). A solution of [Ru(η^3-2-MeC_3H_4)$_2$(COD)] (0.096 g, 0.30 mmol) and **2a** (0.200 g, 0.30 mmol) in *n*-hexane (5 mL) was refluxed for 9 h, and the solvent was removed under vacuum. The resulting residue was washed with MeOH (3 × 5 mL), yielding the desired product as a 6/1 mixture of two diastereomers (CD_2Cl_2): white solid (0.175 g, 66%). ^1H NMR (CD_2Cl_2, 500 MHz): δ 0.86 (br s, 1H, MeC(CH*H*)$_2$ (maj)), 0.89 (m, 1H, MeC(CH*H*)$_2$ (min)), 0.98 (s, 9H, CMe_3 (maj)), 1.10 (m, 2H, MeC(CH*H*)$_2$ (maj) + MeC(CH*H*)$_2$ (min)), 1.15 (s, 9H, CMe_3 (min)), 1.17 (s, 9H, CMe_3 (min)), 1.24 (m, 1H, MeC(CH*H*)$_2$ (maj)), 1.26 (s, 9H, CMe_3 (maj)), 1.34 (m, 2H, MeC(CH*H*)$_2$ (maj) + MeC(CH*H*)$_2$ (min)), 1.43 (br s, 1H, MeC(CH*H*)$_2$ (maj)), 1.44 (m, 1H, MeC(CH*H*)$_2$ (min)), 1.55 (s, 3H, Ar-*Me* (maj)), 1.58 (s, 3H, Ar-*Me* (min)), 1.61 (s, 3H, Ar-*Me* (min)), 1.62 (d, $^3J_{HP}$ = 15.5 Hz, 1H, MeC(CH*H*)$_2$ (maj)), 1.67 (m, 1H, MeC(CH*H*)$_2$ (min)), 1.76 (s, 3H, *Me*C(CH$_2$)$_2$ (min)), 1.81 (s, 3H, Ar-*Me* (maj)), 1.86 (s, 3H, *Me*C(CH$_2$)$_2$ (maj)), 1.98 (m, 1H, MeC(CH*H*)$_2$ (min)), 2.03 (s, 3H, *Me*C(CH$_2$)$_2$ (min)), 2.04 (s, 3H, *Me*C(CH$_2$)$_2$ (maj)), 2.21 (s, 3H, Ar-*Me* (maj)), 2.23 (s, 3H, Ar-*Me* (min)), 2.25 (s, 3H, Ar-*Me* (min)), 2.27 (s, 3H, Ar-*Me* (maj)), 2.37 (br s, 1H, MeC(CH*H*)$_2$ (min)), 2.45 (br s, 1H, MeC(CH*H*)$_2$ (maj)), 2.79 (br s, 1H, MeC(CH*H*)$_2$ (min)), 2.88 (br, 1H, MeC(CH*H*)$_2$ (maj)), 6.67 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, H arom (min)), 6.74 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, 2 H arom (maj)), 6.79 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, H arom (maj)), 6.90 (m, 1H, H arom (maj)), 6.95 (s, 1H, H arom (maj)), 7.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H arom (maj)), 7.06 (s, 1H, H arom (min)), 7.10 (s, 1H, H arom (min)), 7.17−7.30 (m, 5H, 5 H arom (maj)), 7.43 (m, 3H, 3 H arom (maj)), 7.54 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, 2 H arom (min)), 7.58 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, 2 H arom (maj)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): major δ 42.3 (d, P−C), 168.4 (d, P−O, J_{PP} = 40 Hz); minor δ 40.2 (d, P−C), 154.3 (d, P−O, J_{PP} = 47 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): major δ 16.0 (Ar-*Me*), 16.4 (Ar-*Me*), 19.8 (Ar-*Me*), 20.5 (Ar-*Me*), 25.4 (*Me*C-(CH$_2$)$_2$), 26.6 (*Me*C(CH$_2$)$_2$), 31.7 (*C*Me$_3$), 32.1 (C*Me*$_3$), 35.0

dx.doi.org/10.1021/om300018s | Organometallics 2012, 31, 3551−3564

(CMe_3), 35.9 (CMe_3), 36.7 ($MeC(CH_2)_2$), 39.2 (dd, J_{CP} = 21 Hz, J_{CP} = 5 Hz, $MeC(CH_2)_2$), 44.2 ($MeC(CH_2)_2$), 45.8 (dd, J_{CP} = 46 Hz, J_{CP} = 4 Hz, $MeC(CH_2)_2$), 98.6 ($MeC(CH_2)_2$), 100.9 ($MeC(CH_2)_2$), 124.5 (d, J_{CP} = 5 Hz, CH arom), 124.5 (CH arom), 128.0 (d, J_{CP} = 9 Hz, CH arom), 128.1 (CH arom), 128.2 (CH arom), 128.2 (CH arom), 128.3 (CH arom), 130.1 (CH arom), 130.1 (d, J_{CP} = 5 Hz, CH arom), 130.2 (CH arom), 130.8 (CH arom), 131.0 (C_q arom), 132.0 (C_q arom), 132.5 (CH arom), 132.5 (d, J_{CP} = 8 Hz, 2 CH arom), 133.8 (dd, J_{CP} = 44 Hz, J_{CP} = 3 Hz, C_q arom), 134.3 (C_q arom), 135.0 (C_q arom), 135.1 (C_q arom), 135.2 (C_q arom), 135.5 (C_q arom), 137.5 (C_q arom), 137.9 (d, J_{CP} = 13 Hz, 2 CH arom), 147.2 (d, J_{CP} = 9 Hz, C_q arom), 147.3 (d, J_{CP} = 9 Hz, C_q arom), 155.2 (d, J_{CP} = 10 Hz, C_q arom). Due to spectrum complexity and low signal intensities, 2 C_q atoms could not be assigned. MS (ESI, 2-propanol): m/z 872 ($[M]^+$, 100), 817 ($[M - C_4H_7]^+$, 16). Fragmentation of ion m/z 872: 762 ($[M - 2C_4H_7]^+$, 100). Anal. Calcd for $C_{50}H_{60}O_3P_2Ru$: C, 68.9; H, 6.9. Found: C, 68.8; H, 7.2.

[Ru(η^3-2-MeC_3H_4)$_2$(2c)] (1c). A solution of [Ru(η^3-2-MeC_3H_4)$_2$(COD)] (0.063 g, 0.20 mmol) and **2c** (0.100 g, 0.20 mmol) in *n*-hexane (5 mL) was refluxed for 9 h. The resulting mixture was cooled to −10 °C, and the precipitated solid was filtered off and washed with cold *n*-hexane (2 × 2 mL). Compound **1c** was isolated as a 1.3/1 mixture of two diastereomers (CD_2Cl_2): white solid (0.070 g, 50%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.78 (dd, $^3J_{HP}$ = 18.0 Hz, $^3J_{HP}$ = 9.0 Hz, 1H, $MeC(CHH)_2$ (maj)), 0.80 (s, 1H, $MeC(CHH)_2$ (min)), 0.84 (s, 1H, $MeC(CHH)_2$ (maj)), 0.91 (d, $^3J_{HP}$ = 15.5 Hz, 1H, $MeC(CHH)_2$ (min)), 0.95 (dd, $^3J_{HP}$ = 18.0 Hz, $^3J_{HP}$ = 9.0 Hz, 1H, $MeC(CHH)_2$ (maj)), 1.00 (s, 9H, CMe_3 (maj)), 1.02 (d, $^2J_{HP}$ = 7.0 Hz, 3H, PMe (maj)), 1.12 (dd, $^3J_{HP}$ = 21.0 Hz, $^3J_{HP}$ = 4.0 Hz, 1H, $MeC(CHH)_2$ (maj)), 1.14 (d, $^2J_{HP}$ = 7.0 Hz, 3H, PMe (min)), 1.18 (s, 9H, CMe_3 (min)), 1.30 (br s, 1H, $MeC(CHH)_2$ (maj)), 1.37 (m, 1H, $MeC(CHH)_2$ (min)), 1.37 (s, 9H, CMe_3 (min)), 1.47 (d, $^3J_{HP}$ = 14.0 Hz, 1H, $MeC(CHH)_2$ (min)), 1.48 (d, $^3J_{HP}$ = 14.0 Hz, 1H, $MeC(CHH)_2$ (maj)), 1.54 (s, 3H, Ar-*Me* (maj)), 1.59 (s, 9H, CMe_3 (maj)), 1.69 (s, 3H, Ar-*Me* (min)), 1.72 (s, 3H, Ar-*Me* (min)), 1.75 (s, 3H, $MeC(CH_2)_2$ (min)), 1.80 (s, 3H, $MeC(CH_2)_2$ (maj)), 1.83 (s, 3H, Ar-*Me* (maj)), 1.84 (d, $^2J_{HP}$ = 7.0 Hz, 6H, PMe (maj) + PMe (min)), 1.88 (s, 3H, $MeC(CH_2)_2$ (min)), 1.90 (s, 3H, $MeC(CH_2)_2$ (maj)), 1.90 (m, 1H, $MeC(CHH)_2$ (min)), 2.03 (br s, 1H, $MeC(CHH)_2$ (maj)), 2.05 (d, $^3J_{HP}$ = 12.0 Hz, 1H, $MeC(CHH)_2$ (min)), 2.20 (s, 3H, Ar-*Me* (maj)), 2.21 (s, 3H, Ar-*Me* (min)), 2.26 (s, 3H, Ar-*Me* (maj)), 2.29 (s, 3H, Ar-*Me* (min)), 2.39 (br s, 1H, $MeC(CHH)_2$ (min)), 2.75 (br s, 1H, $MeC(CHH)_2$ (min)), 3.00 (br s, 1H, $MeC(CHH)_2$ (maj)), 6.30 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 4.0 Hz, 1H, H arom (min)), 6.71 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 4.5 Hz, 1H, H arom (maj)), 6.94 (s, 1H, H arom (maj)), 7.03 (s, 1H, H arom (min)), 7.10 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H arom (min)), 7.11 (s, 1H, H arom (min)), 7.17 (m, 2H, H arom (maj) + H arom (min)), 7.22 (s, 1H, H arom (maj)), 7.27 (m, 2H, H arom (maj) + H arom (min)), 7.50 (dd, $^3J_{HP}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H arom (maj)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz): major δ 2.5 (d, P−C), 161.7 (d, P−O, J_{PP} = 50 Hz); minor δ 1.4 (d, P−C), 158.8 (d, P−O, J_{PP} = 52 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 13.6 (d, J_{CP} = 27 Hz, PMe (min)), 13.9 (d, J_{CP} = 21 Hz, PMe (maj)), 16.2 (Ar-*Me* (maj)), 16.5 (2 Ar-*Me* (min) + Ar-*Me* (maj)), 19.9 (Ar-*Me* (maj)), 20.0 (Ar-*Me* (min)), 20.3 (Ar-*Me* (min)), 20.6 (Ar-*Me* (maj)), 20.7 (d, J_{CP} = 31 Hz, PMe (maj)), 22.9 (d, J_{CP} = 32 Hz, PMe (min)), 24.8 ($MeC(CH_2)_2$ (min)), 26.0 ($MeC(CH_2)_2$ (maj)), 26.4 ($MeC(CH_2)_2$ (maj)), 27.0 ($MeC(CH_2)_2$ (min)), 30.8 (CMe_3 (min)), 31.4 (CMe_3 (maj)), 32.1 (CMe_3 (maj)), 32.2 (CMe_3 (min)), 34.7 (CMe_3 (min)), 35.0 ($MeC(CH_2)_2$ (maj)), 35.1 (CMe_3 (maj)), 35.6 ($MeC(CH_2)_2$ (min)), 35.9 (CMe_3 (maj)), 36.0 (CMe_3 (min)), 36.9 ($MeC(CH_2)_2$ (min)), 39.8 ($MeC(CH_2)_2$ (maj)), 39.9 (dd, J_{CP} = 19 Hz, J_{CP} = 5 Hz, $MeC(CH_2)_2$ (maj)), 42.8 (dd, J_{CP} = 21 Hz, J_{CP} = 4 Hz, $MeC(CH_2)_2$ (min)), 45.2 (dd, J_{CP} = 46 Hz, J_{CP} = 4 Hz, $MeC(CH_2)_2$ (maj)), 48.2 (dd, J_{CP} = 45 Hz, J_{CP} = 4 Hz, $MeC(CH_2)_2$ (min)), 97.9 ($MeC(CH_2)_2$ (maj)), 98.9 ($MeC(CH_2)_2$ (min)), 100.9 ($MeC(CH_2)_2$ (maj)), 101.5 ($MeC(CH_2)_2$ (min)), 123.4 (d, J_{CP} = 47 Hz, CH arom (min)), 123.8 (d, J_{CP} = 49 Hz, CH arom (maj)), 127.3 (dd, J_{CP} = 37 Hz, J_{CP} = 8 Hz, C_q arom), 128.0 (CH arom), 128.2 (CH arom), 128.3 (2 CH arom), 128.3 (CH arom), 128.6 (CH arom), 129.5 (2 CH arom), 129.6 (m, 3 C_q arom), 130.6 (CH arom), 130.8 (CH arom), 131.2 (2 C_q arom), 131.5 (C_q arom), 131.6 (C_q arom), 134.5 (C_q arom), 134.9 (C_q arom), 135.4 (2 C_q arom), 135.5 (2 C_q arom), 136.4 (2 C_q arom), 136.7 (C_q arom), 137.3 (C_q arom), 146.8 (d, J_{CP} = 6 Hz, C_q arom (maj)), 147.0 (d, J_{CP} = 10 Hz, C_q arom (min)), 147.6 (d, J_{CP} = 16 Hz, C_q arom (maj)), 149.1 (d, J_{CP} = 15 Hz, C_q arom (min)), 156.0 (m, C_q arom (maj) + C_q arom (min)). MS (ESI, THF): m/z 748.2 ($[M]^+$, 100). Fragmentation of ion m/z 748.2: 638.1 ($[M - 2C_4H_7]^+$, 100). Anal. Calcd for $C_{40}H_{56}O_3P_2Ru$: C, 64.2; H, 7.6. Found: C, 64.2; H, 8.0.

[Ru(η^3-2-MeC_3H_4)$_2$(2d)] (1d). A solution of [Ru(η^3-2-MeC_3H_4)$_2$(COD)] (0.046 g, 0.13 mmol) and **2d** (0.094 g, 0.13 mmol) in *n*-hexane (3 mL) was refluxed for 5 h, and the solvent was removed under vacuum. The resulting mixture was cooled to 0 °C, and the precipitated solid was filtered off and washed with cold *n*-hexane (2 × 2 mL). Compound **1d** was isolated as a 4/1 mixture of two diastereomers (CD_2Cl_2): white solid (0.069 g, 57%). Due to the low proportion of the minor diastereomer, only signals assignable to the major isomer are reported. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.26 (m, 2H, 2 $MeC(CHH)_2$), 1.27 (s, 9H, CMe_3), 1.55 (s, 3H, Ar-*Me*), 1.59 (s, 9H, CMe_3), 1.63 (s, 3H, Ar-*Me*), 1.74 (m, 2H, 2 $MeC(CHH)_2$), 1.89 (m, 4H, $MeC(CHH)_2$ + $MeC(CH_2)_2$), 1.93 (s, 6H, 2 PAr-*Me*), 2.05 (s, 3H, Ar-*Me*), 2.09 (s, 3H, Ar-*Me*), 2.11 (s, 6H, 2 PAr-*Me*), 2.14 (m, 1H, $MeC(CHH)_2$), 2.22 (s, 3H, $MeC(CH_2)_2$), 2.91 (br s, 1H, $MeC(CHH)_2$), 3.44 (br s, 1H, $MeC(CHH)_2$), 6.67 (s, 1H, H arom), 6.75 (m, 3H, 3 H arom), 6.81 (s, 1H, H arom), 6.88 (m, 1H, H arom), 6.97 (m, 1H, H arom), 7.11 (s, 1H, H arom), 7.17 (m, 1H, H arom), 7.37 (s, 1H, H arom), 7.60 (d, $^3J_{HP}$ = 9.3 Hz, 2H, 2 H arom). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz): major δ 41.3 (d, P−C), 168.5 (d, P−O, J_{PP} = 40 Hz); minor δ 39.4 (d, P−C), 154.3 (d, P−O, J_{PP} = 47 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 202 MHz): δ 15.9 (Ar-*Me*), 16.3 (Ar-*Me*), 19.5 (Ar-*Me*), 20.2 (Ar-*Me*), 21.0 (2 PAr-*Me*), 21.2 (2 PAr-*Me*), 25.3 ($MeC(CH_2)_2$), 26.2 ($MeC(CH_2)_2$), 31.6 (CMe_3), 32.3 (CMe_3), 34.9 (CMe_3), 35.9 (CMe_3), 36.9 ($MeC(CH_2)_2$), 38.9 (dd, J_{CP} = 21 Hz, J_{CP} = 6 Hz, $MeC(CH_2)_2$), 44.5 ($MeC(CH_2)_2$), 46.0 (dd, J_{CP} = 46 Hz, J_{CP} = 4 Hz, $MeC(CH_2)_2$), 98.0 ($MeC(CH_2)_2$), 101.0 ($MeC(CH_2)_2$), 124.1 (d, J_{CP} = 5 Hz, CH arom), 124.6 (d, J_{CP} = 3 Hz, CH arom), 128.3 (CH arom), 128.4 (CH arom), 128.9 (C_q arom), 129.8 (CH arom), 130.0 (CH arom), 130.1 (2 CH arom), 130.2 (CH arom), 130.3 (CH arom), 130.7 (C_q arom), 131.3 (dd, J_{CP} = 43 Hz, J_{CP} = 9 Hz, C_q arom), 131.7 (C_q arom), 131.8 (d, J_{CP} = 46 Hz, C_q arom), 133.6 (d, J_{CP} = 41 Hz, C_q arom), 134.4 (C_q arom), 134.6 (C_q arom), 134.8 (m, 2 C_q arom), 135.7 (CH arom), 135.8 (CH arom), 136.9 (C_q arom), 137.0 (C_q arom), 137.0 (C_q arom), 137.1 (C_q arom), 137.7 (C_q arom), 147.3 (d, J_{CP} = 8 Hz, C_q arom), 147.4 (d, J_{CP} = 15 Hz, C_q arom), 155.4 (d, J_{CP} = 12 Hz, C_q arom). MS (ESI, THF): m/z 928 ($[M]^+$, 100). Fragmentation of ion m/z 928: 818 ($[M - 2C_4H_7]^+$, 100). Anal. Calcd for $C_{54}H_{68}O_3P_2Ru$: C, 69.9; H, 7.4. Found: C 69.7; H, 7.7.

[Ru(η^3-2-MeC_3H_4)$_2$(2e)] (1e). This compound was prepared from phosphine-phosphite **2e** by the procedure described for **1a**: white solid (0.038 g, 28%). Complex **1e** exists in solution (CD_2Cl_2) as a mixture of two isomers in a 9/1 ratio. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.51 (dd, $^3J_{HP}$ = 19.0 Hz, $^3J_{HP}$ = 8.5 Hz, 1H, $MeC(CHH)_2$), 0.72 (d, $^3J_{HP}$ = 14.5 Hz, 1H, $MeC(CHH)_2$), 0.94 (s, 9H, CMe_3), 1.15 (br s, 1H, $MeC(CHH)_2$), 1.44 (br s, 1H, $MeC(CHH)_2$), 1.52 (s, 9H, CMe_3), 1.55 (s, 3H, Ar-*Me*), 1.57 (m, 1H, $MeC(CHH)_2$), 1.82 (s, 3H, $MeC(CH_2)_2$), 1.92 (s, 3H, Ar-*Me*), 1.96 (s, 3H, $MeC(CH_2)_2$), 2.17 (d, $^2J_{HP}$ = 7.5 Hz, 3H, PMe), 2.19 (m, 1H, $MeC(CHH)_2$), 2.21 (s, 3H, Ar-*Me*), 2.34 (s, 3H, Ar-*Me*), 2.50 (br s, 1H, $MeC(CHH)_2$), 2.78 (br s, 1H, $MeC(CHH)_2$), 6.30 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 5.0 Hz, 1H, H arom), 6.88 (s, 1H, H arom), 6.92 (m, 1H, H arom), 6.96 (dd, $^3J_{HP}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, 2 H arom), 7.04 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H arom), 7.10−7.28 (m, 5H, 5 H arom). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz): major δ 15.7 (d, P−C), 152.7 (d, P−O, J_{PP} = 51 Hz); minor δ 21.6 (d, P−C), 162.1 (d, P−O, J_{PP} = 46 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 101 MHz): δ 16.5 (2 Ar-*Me*), 19.8 (Ar-*Me*), 20.2 (Ar-*Me*), 22.5 (d, J_{CP} = 32 Hz, PMe), 23.8 ($MeC(CH_2)_2$), 26.1 ($MeC(CH_2)_2$), 30.2 (CMe_3), 31.6 (CMe_3), 34.4 (CMe_3), 35.2 (CMe_3), 38.7 ($MeC(CH_2)_2$), 39.8 ($MeC(CH_2)_2$), 40.9 (dd, J_{CP} = 19 Hz, J_{CP} = 5 Hz, $MeC(CH_2)_2$), 48.6 (dd, J_{CP} = 42 Hz, J_{CP} = 4 Hz,

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

MeC(CH_2)$_2$), 101.1 (MeC(CH_2)$_2$), 102.1 (MeC(CH_2)$_2$), 123.2 (CH arom), 123.8 (CH arom), 127.7 (CH arom), 127.8 (CH arom), 127.9 (CH arom), 128.0 (CH arom), 128.2 (CH arom), 130.9 (2 CH arom), 132.0 (d, J_{CP} = 7 Hz, 2 CH arom), 133.2 (C_q arom), 134.6 (C_q arom), 135.2 (C_q arom), 135.7 (C_q arom), 136.3 (2 C_q arom), 137.1 (C_q arom), 137.4 (C_q arom), 141.9 (m, 2 C_q arom), 157.6 (d, J_{CP} = 15 Hz, C_q arom). Because of spectrum complexity and low signal intensities, three quaternary aromatic carbons of the minor diastereomer could not be assigned. MS (ESI, THF): m/z 810.3 ([M]$^+$, 100). Fragmentation of ion m/z 810.3: 700.1 ([M − 2C_4H_7]$^+$, 100). Satisfactory elemental analysis could not be obtained for this compound, due to its high solubility and tendency to retain solvent.

[Ru(η^3-2-MeC_3H_4)$_2$(2f)] (1f). This compound was obtained by following the procedure described for **1e**, as a mixture of two diastereomers in a 14/1 ratio (CD_2Cl_2): white solid (0.030 g, 43%). Due to the low proportion of the minor diastereomer, only signals assignable to the major one are reported. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.79 (d, $^3J_{HP}$ = 14.0 Hz, 1H, MeC(CHH)$_2$), 0.90 (br s, 1H, MeC(CHH)$_2$), 1.14 (dd, $^3J_{HP}$ = 15.5 Hz, $^3J_{HP}$ = 4.5 Hz, 1H, MeC(CHH)$_2$), 1.19 (dd, $^3J_{HP}$ = 14.5 Hz, $^3J_{HP}$ = 9.0 Hz, 1H, MeC(CHH)$_2$), 1.34 (d, $^3J_{HP}$ = 12.3 Hz, 1H, MeC(CHH)$_2$), 1.49 (br s, 1H, MeC(CHH)$_2$), 1.94 (s, 3H, MeC(CH_2)$_2$), 1.96 (s, 3H, Ar-Me), 2.04 (s, 3H, Ar-Me), 2.08 (s, 3H, MeC(CH_2)$_2$), 2.30 (s, 3H, Ar-Me), 2.36 (s, 3H, Ar-Me), 2.57 (br s, 1H, MeC(CHH)$_2$), 2.84 (br s, 1H, MeC(CHH)$_2$), 6.63 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H arom), 6.86 (m, 3H, 3 H arom), 7.02−7.30 (m, 8H, 8 H arom), 7.47 (m, 4H, 4 H arom), 7.69 (dd, $^3J_{HP}$ = 8.7 Hz, $^3J_{HH}$ = 8.7 Hz, 2H, 2 H arom). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz): major δ 45.6 (d, P−C), 177.8 (d, P−O, J_{PP} = 44 Hz); minor δ 44.6 (d, P−C), 173.4 (d, P−O, J_{PP} = 58 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 17.5 (Ar-Me), 17.6 (Ar-Me), 20.3 (Ar-Me), 20.4 (Ar-Me), 26.0 (MeC(CH_2)$_2$), 26.2 (MeC(CH_2)$_2$), 37.2 (MeC(CH_2)$_2$), 43.5 (MeC(CH_2)$_2$), 44.3 (dd, J_{CP} = 21 Hz, J_{CP} = 5 Hz, MeC(CH_2)$_2$), 48.5 (dd, J_{CP} = 44 Hz, J_{CP} = 4 Hz, MeC(CH_2)$_2$), 99.2 (MeC(CH_2)$_2$), 101.7 (MeC(CH_2)$_2$), 119.7 (CH arom), 119.9 (d, J_{CP} = 3 Hz, CH arom), 124.3 (d, J_{CP} = 5 Hz, CH arom), 124.5 (CH arom), 128.0 (CH arom), 128.1 (2 CH arom), 128.3 (CH arom), 128.5 (CH arom), 129.2 (C_q arom), 129.3 (CH arom), 129.4 (CH arom), 129.5 (C_q arom), 130.5 (CH arom), 130.6 (CH arom), 131.0 (CH arom), 131.8 (CH arom), 131.9 (CH arom), 132.4 (dd, J_{CP} = 40 Hz, J_{CP} = 4 Hz, C_q arom), 133.7 (C_q arom), 134.0 (C_q arom), 135.3 (C_q arom), 135.6 (C_q arom), 137.4 (C_q arom), 137.6 (C_q arom), 138.1 (CH arom), 138.2 (CH arom), 147.4 (d, J_{CP} = 5 Hz, C_q arom), 148.7 (d, J_{CP} = 13 Hz, C_q arom), 155.5 (d, J_{CP} = 11 Hz, C_q arom). MS (ESI, THF): m/z 760.2 ([M]$^+$, 100). Anal. Calcd for $C_{42}H_{44}O_3P_2Ru$: C, 66.4; H, 5.8. Found: C, 66.1; H, 5.8.

[Ru(η^3-2-MeC_3H_4)$_2$(2g)] (1g). This compound was obtained by following the procedure described for **1a**, as a single isomer: white solid (0.040 g, 70%). ^{1}H NMR (C_6D_6, 500 MHz): δ 0.78 (dd, $^3J_{HP}$ = 11.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, CHMe_2), 1.03 (dd, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, CHMe_2), 1.13 (dd, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, CHMe_2), 1.15 (br s, 1H, MeC(CHH)$_2$), 1.21 (dd, $^3J_{HP}$ = 14.5 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, CHMe_2), 1.38 (br s, 1H, MeC(CHH)$_2$), 1.43 (br d, $^3J_{HP}$ = 12.5 Hz, 1H, MeC(CHH)$_2$), 1.55 (dd, $^3J_{HP}$ = 15.5 Hz, $^3J_{HP}$ = 4.0 Hz, 1H, MeC(CHH)$_2$), 1.70 (dd, $^3J_{HP}$ = 13.0 Hz, $^3J_{HP}$ = 9.5 Hz, 1H, MeC(CHH)$_2$), 1.78 (s, 3H, Ar-Me), 1.79 (m, 4H, Ar-Me + CHMe$_2$), 1.85 (d, $^3J_{HP}$ = 11.5 Hz, 1H, MeC(CHH)$_2$), 1.98 (s, 3H, MeC(CH_2)$_2$), 2.00 (s, 3H, Ar-Me), 2.03 (s, 3H, Ar-Me), 2.21 (s, 3H, MeC(CH_2)$_2$), 2.71 (m, 1H, CHMe$_2$), 2.92 (br s, 1H, MeC(CHH)$_2$), 3.10 (br s, 1H, MeC(CHH)$_2$), 6.83 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H arom), 6.90 (t, $^3J_{HH}$ = 7.5 Hz, 1H, H arom), 6.96 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H arom), 7.00−7.08 (m, 4H, 4 H arom), 7.34 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H arom). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz): δ 36.5 (d, P−C), 175.0 (d, P−O, J_{PP} = 47 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz, 308 K): δ 17.0 (d, J_{CP} = 5 Hz, CHMe_2), 17.4 (2 Ar-Me), 19.1 (CHMe_2), 20.1 (d, J_{CP} = 4 Hz, CHMe_2), 20.2 (Ar-Me), 20.4 (Ar-Me), 20.8 (d, J_{CP} = 4 Hz, CHMe_2), 22.2 (d, J_{CP} = 15 Hz, CHMe$_2$), 25.5 (MeC(CH_2)$_2$), 26.2 (MeC-(CH_2)$_2$), 27.8 (d, J_{CP} = 19 Hz, CHMe$_2$), 35.4 (MeC(CH_2)$_2$), 38.2 (d, J_{CP} = 4 Hz, MeC(CH_2)$_2$), 42.5 (dd, J_{CP} = 45 Hz, J_{CP} = 5 Hz, MeC(CH_2)$_2$), 43.7 (dd, J_{CP} = 20 Hz, J_{CP} = 5 Hz, MeC(CH_2)$_2$), 98.5 (MeC(CH_2)$_2$), 98.6 (MeC(CH_2)$_2$), 119.6 (CH arom), 120.0 (CH arom), 123.0 (CH arom), 123.9 (CH arom), 129.2 (2 CH arom), 129.3 (C_q arom), 129.5 (C_q arom), 129.5 (m, C_q arom), 130.2 (CH arom), 130.3 (CH arom), 133.3 (C_q arom), 133.5 (C_q arom), 137.1 (C_q arom), 137.5 (C_q arom), 148.0 (d, J_{CP} = 5 Hz, C_q arom), 149.1 (d, J_{CP} = 14 Hz, C_q arom), 157.1 (d, J_{CP} = 10 Hz, C_q arom). MS (ESI, THF): m/z 692.2 ([M]$^+$, 100). Anal. Calcd for $C_{36}H_{48}O_3P_2Ru\cdot{}^1/_2C_6H_{14}$: C, 63.7; H, 7.5. Found: C, 63.6; H, 7.4.

[Ru(η^3-2-MeC_3H_4)$_2$(2h)] (1h). This complex was synthesized by following the procedure described for **1a**: white solid (0.118 g, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.82 (d, $^3J_{HP}$ = 13.2 Hz, 1H, MeC(CHH)$_2$), 0.98 (s, 9H, CMe_3), 1.08 (dd, $^3J_{HP}$ = 15.7 Hz, $^3J_{HP}$ = 9.2 Hz, 1H, MeC(CHH)$_2$), 1.19 (br s, 1H, MeC(CHH)$_2$), 1.33 (s, 9H, CMe_3), 1.34 (s, 9H, CMe_3), 1.39 (s, 9H, CMe_3), 1.50 (br s, 3H, MeC(CHH)$_2$), 1.66 (dd, $^3J_{HP}$ = 17.1 Hz, $^3J_{HP}$ = 4.2 Hz, 1H, MeC(CHH)$_2$), 1.78 (s, 3H, MeC(CH_2)$_2$), 1.81 (m, 1H, MeC-(CHH)$_2$), 2.05 (s, 3H, MeC(CH_2)$_2$), 2.32 (br s, 1H, MeC(CHH)$_2$), 2.73 (br s, 1H, MeC(CHH)$_2$), 6.10 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HP}$ = 4.8 Hz, 1H, H arom), 6.81 (m, 5H, 5 H arom), 7.02 (td, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H arom), 7.13 (m, 3H, 3 H arom), 7.20 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H arom), 7.30 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H arom), 7.35 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H arom), 7.40 (m, 3H, 3 H arom), 7.62 (m, 2H, 2 H arom). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 42.4 (d, P−C), 157.5 (d, P−O, J_{PP} = 46 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 25.5 (MeC(CH_2)$_2$), 25.7 (MeC(CH_2)$_2$), 30.8 (CMe_3), 30.9 (CMe_3), 31.8 (CMe_3), 31.8 (CMe_3), 34.7 (CMe_3), 34.8 (CMe_3), 35.5 (CMe_3), 36.0 (CMe_3), 39.4 (MeC(CH_2)$_2$), 42.1 (MeC(CH_2)$_2$), 42.8 (dd, $^2J_{CP}$ = 27 Hz, $^2J_{CP}$ = 7 Hz, MeC(CH_2)$_2$), 48.7 (dd, $^2J_{CP}$ = 44 Hz, $^2J_{CP}$ = 2 Hz, MeC(CH_2)$_2$), 99.9 (MeC(CH_2)$_2$), 102.3 (MeC(CH_2)$_2$), 123.5 (CH arom), 123.8 (d, J_{CP} = 8 Hz, CH arom), 124.2 (CH arom), 124.5 (CH arom), 127.3 (CH arom), 127.7 (CH arom), 127.8 (CH arom), 127.9 (CH arom), 128.0 (CH arom), 128.2 (CH arom), 128.7 (CH arom), 129.9 (CH arom), 130.0 (d, J_{CP} = 4 Hz, C_q arom), 130.7 (CH arom), 131.4 (CH arom), 131.8 (C_q arom), 132.1 (CH arom), 132.2 (CH arom), 134.4 (dd, J_{CP} = 41 Hz, J_{CP} = 1 Hz, C_q arom), 135.1 (C_q arom), 135.5 (C_q arom), 137.1 (CH arom), 137.2 (CH arom), 138.6 (d, J_{CP} = 1 Hz, C_q arom), 139.3 (d, J_{CP} = 6 Hz, C_q arom), 145.1 (C_q arom), 145.4 (C_q arom), 148.3 (d, J_{CP} = 14 Hz, C_q arom), 149.2 (d, J_{CP} = 15 Hz, C_q arom), 155.9 (d, J_{CP} = 12 Hz, C_q arom). MS (ESI, THF): m/z 928.3 ([M]$^+$, 100). Fragmentation of ion m/z 928.3: 818.2 ([M − 2C_4H_7]$^+$, 100). Anal. Calcd for $C_{54}H_{68}O_3P_2Ru$: C, 69.9; H, 7.4. Found: C, 69.9; H, 7.6.

Ru(η^3-2-MeC_3H_4)$_2$(2i)] (1i). This complex was obtained by following the procedure described for **1a** as a mixture of two diastereomers in a 2/1 ratio (CD_2Cl_2): white solid (0.057 g, 43%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.21 (d, $^3J_{HP}$ = 14.0 Hz, 1H, MeC(CHH)$_2$ (maj)), 0.55 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HP}$ = 9.0 Hz, 1H, MeC(CHH)$_2$ (min)), 0.73 (dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HP}$ = 8.5 Hz, 1H, MeC(CHH)$_2$ (maj)), 0.76 (d, $^3J_{HP}$ = 14.0 Hz, 1H, MeC(CHH)$_2$ (min)), 0.87 (br s, 1H, MeC(CHH)$_2$ (min)), 0.89 (br s, 1H, MeC(CHH)$_2$ (maj)), 1.19 (m, 1H, MeC(CHH)$_2$ (min)), 1.22 (s, 9H, CMe_3 (min)), 1.26 (br s, 2H, MeC(CHH)$_2$ (maj) + MeC(CHH)$_2$ (min)), 1.32 (s, 9H, CMe_3 (maj)), 1.46 (s, 3H, Ar-Me (maj)), 1.47 (s, 3H, MeC(CH_2)$_2$ (maj)), 1.48 (s, 9H, CMe_3 (maj)), 1.51 (s, 3H, Ar-Me (min)), 1.58 (s, 9H, CMe_3 (min)), 1.76 (dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HP}$ = 5.5 Hz, 1H, MeC(CHH)$_2$ (maj)), 1.77 (s, 3H, Ar-Me (min)), 1.81 (s, 3H, MeC(CH_2)$_2$ (min)), 1.85 (s, 3H, Ar-Me (maj)), 1.97 (s, 3H, MeC(CH_2)$_2$ (min)), 1.98 (br s, 1H, MeC(CHH)$_2$ (min)), 2.06 (s, 3H, MeC(CH_2)$_2$ (maj)), 2.07 (br s, 1H, MeC(CHH)$_2$ (maj)), 2.15 (d, $^3J_{HP}$ = 13.0 Hz, 1H, MeC(CHH)$_2$ (maj)), 2.19 (s, 3H, Ar-Me (maj)), 2.20 (s, 3H, Ar-Me (min)), 2.22 (s, 6H, Ar-Me (maj) + Ar-Me (min)), 2.24 (m, 1H, MeC(CHH)$_2$ (min)), 2.83 (m, 5H, CH_2P (maj) + CHHP (min) + MeC(CHH)$_2$ (maj) + MeC(CHH)$_2$ (min)), 3.03 (m, 1H, CHHP (min)), 4.50−4.80 (m, 4H, OCH_2 (maj) + OCH_2 (min)), 6.88 (ddd, $^3J_{HP}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.0 Hz, 2H, 2 H arom (maj)), 6.96 (s, 1H, H arom (min)), 7.01 (dd, $^3J_{HP}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, 2 H arom (min)), 7.07 (s, 1H, H arom (maj)), 7.12 (s, 1H, H arom (maj)), 7.18 (s, 1H, H arom (min)), 7.20 (m, 6H, 3 H arom (maj) + 3 H arom (min)), 7.43 (m, 6H, 3 H arom (maj) + 3 H arom (min)), 7.67 (ddd, $^3J_{HP}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, 2 H arom (maj)), 7.75 (dd, $^3J_{HP}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, 2 H

dx.doi.org/10.1021/om300018s | Organometallics 2012, 31, 3551−3564

arom (min)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): major: δ 40.1 (d, P−C), 157.2 (d, P−O, J_{PP} = 35 Hz); min: δ 32.3 (d, P−C), 156.1 (d, P−O, J_{PP} = 40 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 15.9 (Ar-*Me* (min)), 16.0 (Ar-*Me* (maj)), 16.2 (Ar-*Me* (maj)), 16.3 (Ar-*Me* (min)), 19.6 (Ar-*Me* (maj)), 19.9 (Ar-*Me* (min)), 20.4 (Ar-*Me* (min)), 20.4 (Ar-*Me* (maj)), 25.9 (*Me*C(CH_2)$_2$ (min)), 26.3 (*Me*C(CH_2)$_2$ (maj)), 26.4 (*Me*C(CH_2)$_2$ (maj)), 26.5 (*Me*C(CH_2)$_2$ (min)), 30.3 (dd, J_{CP} = 26 Hz, J_{CP} = 11 Hz, CH_2P (min)), 31.2 (C*Me*$_3$ (maj)), 31.3 (C*Me*$_3$ (min)), 31.8 (dd, J_{CP} = 26 Hz, J_{CP} = 4 Hz, CH_2P (maj)), 32.6 (C*Me*$_3$ (min)), 32.8 (C*Me*$_3$ (maj)), 34.2 (C*Me*$_3$ (maj)), 34.8 (C*Me*$_3$ (min)), 36.1 (C*Me*$_3$ (min)), 36.3 (MeC(CH_2)$_2$ (maj)), 36.7 (C*Me*$_3$ (maj)), 38.2 (MeC(CH_2)$_2$ (min)), 38.9 (MeC(CH_2)$_2$ (maj)), 40.2 (MeC(CH_2)$_2$ (min)), 40.5 (dd, J_{CP} = 21 Hz, J_{CP} = 5 Hz, MeC(CH_2)$_2$ (min)), 46.8 (dd, J_{CP} = 42 Hz, J_{CP} = 4 Hz, MeC(CH_2)$_2$ (maj)), 47.3 (d, J_{CP} = 49 Hz, MeC(CH_2)$_2$ (min)), 47.8 (d, J_{CP} = 22 Hz, MeC(CH_2)$_2$ (maj)), 63.6 (m, OCH_2 (min) + OCH_2 (maj)), 99.2 (MeC(CH_2)$_2$ (maj)), 99.3 (MeC(CH_2)$_2$ (min)), 99.7 (MeC(CH_2)$_2$ (maj)), 99.9 (MeC(CH_2)$_2$ (min)), 127.7 (CH arom (min) + CH arom (maj)), 127.8 (CH arom (min) + CH arom (maj)), 127.9 (CH arom (min) + CH arom (maj)), 128.0 (CH arom (min)), 128.1 (2 CH arom (min) + 2 CH arom (maj)), 128.2 (CH arom (maj)), 128.4 (CH arom (maj)), 129.5 (CH arom (min)), 129.6 (CH arom (min)), 129.6 (CH arom (maj)), 130.7 (d, J_{CP} = 10 Hz, C_q arom (maj)), 131.1 (C_q arom (maj) + C_q arom (min)), 131.3 (C_q arom (maj) + C_q arom (min)), 131.7 (C_q arom (min)), 132.1 (CH arom (min) + CH arom (maj)), 132.2 (CH arom (min) + CH arom (maj)), 132.7 (C_q arom (min)), 133.8 (CH arom (min)), 133.9 (CH arom (min)), 134.2 (CH arom (maj)), 134.3 (CH arom (maj)), 134.5 (C_q arom (maj)), 135.0 (d, J_{CP} = 6 Hz, C_q arom (maj)), 135.3 (C_q arom (maj)), 136.7 (C_q arom (maj) + 2 C_q arom (min)), 137.3 (C_q arom (maj)), 137.4 (C_q arom (min)), 137.5 (C_q arom (maj)), 137.6 (C_q arom (min)), 138.0 (C_q arom (maj)), 138.1 (C_q arom (min)), 146.6 (m, C_q arom (min) + C_q arom (may)), 147.4 (d, J_{CP} = 6 Hz, C_q arom (min)), 148.5 (d, J_{CP} = 16 Hz, C_q arom (maj)). One signal corresponding to a quaternary aromatic carbon of the minor isomer could not be assigned. MS (ESI, 2-propanol): *m*/*z* 824.3 ([M]$^+$, 100), 769.2 ([M − C_4H_7]$^+$, 33). Fragmentation of ion *m*/*z* 824.3: 714.1 ([M − 2C_4H_7]$^+$, 100). Satisfactory elemental analysis could not be obtained for this compound due to its high solubility and tendency to retain solvent.

[Ru(η^3-2-MeC_3H_4)$_2$(2j)] (1j). A solution of [Ru(COD)(η^3-2-MeC_3H_4)$_2$] (0.065 g, 0.18 mmol) and **2j** (0.101 g, 0.18 mmol) in hexane (3 mL) was refluxed for 5 h. The resulting mixture was cooled to 0 °C, and the precipitated solid was filtered off and washed with cold hexane (2 × 2 mL). Compound **1j** was isolated as a 16/1 mixture of two diastereomers (CD_2Cl_2): white solid (0.070 g, 50%). Due to the low proportion of the minor diastereomer, only signals assignable to the major derivative are reported. ^1H NMR (CD_2Cl_2, 500 MHz): δ 0.75 (br s, 1H, MeC(CH*H*)$_2$), 0.98 (m, 4H, CH*Me*$_2$ + MeC(CH*H*)$_2$), 1.12 (dd, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, CH*Me*$_2$), 1.17 (dd, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, CH*Me*$_2$), 1.19 (m, 1H, MeC(CH*H*)$_2$), 1.34 (m, 5H, CH*Me*$_2$ + 2 MeC(CH*H*)$_2$), 1.61 (dd, $^3J_{HP}$ = 13.5 Hz, $^3J_{HP}$ = 9.7 Hz, 1H, MeC(CH*H*)$_2$), 1.85 (s, 3H, *Me*C(CH_2)$_2$), 2.04 (s, 3H, *Me*C(CH_2)$_2$), 2.05 (m, 1H, C*H*Me$_2$), 2.72 (s, 1H, MeC(CH*H*)$_2$), 2.89 (s, 1H, MeC(CH*H*)$_2$), 2.98 (m, 1H, C*H*Me$_2$), 6.85 (m, 1H, H arom), 7.14 (d, $^3J_{HH}$ = 9.0 Hz, 1H, H arom), 7.26 (m, 5H, 5 H arom), 7.43 (m, 4H, 4 H arom), 7.65 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H arom), 7.98 (m, 4H, 4 H arom). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): major δ 37.7 (br s, P−C), 180.2 (br d, P−O, J_{PP} = 47 Hz); minor 42.9 (br s, P−C), 180.2 (overlapped signal, P−O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): δ 17.2 (d, J_{CP} = 4 Hz, CH*Me*$_2$), 19.1 (CH*Me*$_2$), 20.2 (d, J_{CP} = 3 Hz, CH*Me*$_2$), 20.7 (d, J_{CP} = 3 Hz, CH*Me*$_2$), 22.3 (d, J_{CP} = 15 Hz, CHMe$_2$), 25.7 (*Me*C(CH_2)$_2$), 26.1 (*Me*C(CH_2)$_2$), 28.3 (d, J_{CP} = 22 Hz, CHMe$_2$), 35.6 (MeC(CH_2)$_2$), 38.5 (d, J_{CP} = 3 Hz, MeC(CH_2)$_2$), 43.2 (m, 2 MeC(CH_2)$_2$), 98.9 (MeC(CH_2)$_2$), 99.1 (MeC(CH_2)$_2$), 122.6 (br s, C_q arom), 122.9 (CH arom), 123.3 (2 CH arom), 123.7 (CH arom), 125.1 (CH arom), 125.2 (CH arom), 126.2 (CH arom), 126.4 (CH arom), 127.1 (CH arom), 127.2 (CH arom), 128.5 (CH arom), 128.6 (CH arom), 129.6 (CH arom), 129.7 (CH arom), 130.4 (CH arom), 130.6 (CH arom), 131.4 (C_q arom), 131.5 (2 C_q arom), 133.0 (2 C_q arom), 133.2 (C_q arom), 149.0 (d, J_{CP} = 5 Hz, C_q arom), 150.1 (d, J_{CP} = 14 Hz, C_q arom), 157.0 (d, J_{CP} = 10 Hz, C_q arom). MS (ESI, 2-propanol): *m*/*z* 692.2 ([M]$^+$, 100). Anal. Calcd for $C_{40}H_{44}O_3P_2Ru$: C, 65.3; H, 6.0. Found: C, 65.2; H, 6.0.

[Ru(η^2-OC_6Cl_5)(η^3-2-MeC_3H_4)$_2$(2h)] (3h). A solution of **1h** (0.078 g, 0.08 mmol) and pentachlorophenol (0.044 g, 0.17 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 5 h. The resulting mixture was evaporated and recrystallized at −20 °C in *n*-hexane. The solid obtained was filtered and washed with *n*-hexane, giving **3h** as a yellow solid (0.039 g, 41%). ^1H NMR (CD_2Cl_2, 500 MHz): δ 0.92 (s, 9H, CMe_3), 1.36 (s, 9H, CMe_3), 1.38 (s, 9H, CMe_3), 1.56 (s, 9H, CMe_3), 2.00 (br s, 1H, MeC(CH*H*)$_2$), 2.11 (br s, 3H, *Me*C(CH_2)$_2$), 2.30 (s, 1H, MeC(CH*H*)$_2$), 2.70 (br s, 1H, MeC(CH*H*)$_2$), 3.98 (s, 1H, MeC(CH*H*)$_2$), 5.93 (br s, 1H, H arom), 6.90 (s, 3H, 3H arom), 7.01 (s, 3H, 3H arom), 7.15 (m, 4H, 4H arom), 7.28 (d, J_{HH} = 2.2 Hz, 1H, 1H arom), 7.48 (d, J_{HH} = 2.2 Hz, 1H, 1H arom), 7.52 (s, 3H, 3H arom), 8.15 (br s, 1H, H arom). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.5 MHz): δ 16.9 (d, P−C), 133.6 (d, P−O, J_{PP} = 71 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 202.5 MHz): δ 25.4 (CH_3CH═), 31.3 (C*Me*$_3$), 31.6 (br s, C*Me*$_3$), 31.7 (C*Me*$_3$), 31.8 (C*Me*$_3$), 35.0 (2 C*Me*$_3$), 35.6 (C*Me*$_3$), 36.1 (C*Me*$_3$), 42.5 (br, MeC(CH*H*)$_2$), 74.0 (d, J_{CP} = 22 Hz, MeC(CH*H*)$_2$), 114.1 MeC(CH*H*)$_2$), 120.1 (C_q arom), 121.8 (CH arom), 122.6 (d, J_{CP} = 4 Hz, C_q arom), 124.1 (CH arom), 124.7 (C_q arom), 125.1 (CH arom), 125.2 (CH arom), 127.3 (d, J_{CP} = 9 Hz, 2 CH arom), 127.9 (CH arom), 128.1 (d, J_{CP} = 9 Hz, 2 CH arom), 128.3 (C_q arom), 128.6 (CH arom), 129.4 (br, C_q arom), 129.5 (CH arom), 130.3 (CH arom), 131.0 (C_q arom), 131.9 (C_q arom), 132.2 (C_q arom), 132.6 (d, J_{CP} = 9 Hz, 2 CH arom), 133.0 (CH arom), 134.3 (C_q arom), 134.6 (C_q arom), 134.8 (d, J_{CP} = 10 Hz, 2 CH arom), 136.1 (CH arom), 138.8 (C_q arom), 139.4 (d, J_{CP} = 5 Hz, C_q arom), 146.3 (C_q arom), 147.1 (C_q arom), 147.5 (d, J_{CP} = 18 Hz, C_q arom), 148.1 (d, J_{CP} = 16 Hz, C_q arom), 157.9 (br, C_q arom), 159.9 (br, C_q arom). Anal. Calcd for $C_{56}H_{61}P_2O_4Cl_5Ru$: C, 59.1, H, 5.40. Found: C, 59.0; H, 5.7.

[Ru(η^2-O_2CC(Me)═CHMe)$_2$(2a)] (4a). A solution of **1a** (0.056 g, 0.067 mmol) and **5a** (0.013 g, 0.13 mmol) in CH_2Cl_2 (3 mL) was stirred at 50 °C for 70 h. The resulting mixture was evaporated and recrystallized in *n*-hexane. The precipitated solid was filtered and washed with *n*-hexane to give **4a** as a yellow solid (0.054 g, 84%). ^1H NMR (300 MHz, CD_2Cl_2): δ 0.81 (s, 9 H, C*Me*$_3$), 1.28 (s, 9 H, C*Me*$_3$), 1.39 (s, 3 H, Ar-*Me*), 1.49 (s, 3 H, CH_3C(CO_2H)═), 1.61 (s, 6H, CH_3CH═), 1.69 (s, 3H, CH_3C(CO_2H)═), 1.79 (s, 3H, Ar-*Me*), 2.24 (s, 6H, Ar-*Me*), 6.34 (bm, 2H, CH_3CH═), 6.91 (m, 1H, 1H arom), 7.04 (m, 3H, 3H arom), 7.16 (m, 3H, 3H arom), 7.28 (m, 3H, 3H arom), 7.43 (m, 4H, 4H arom), 7.59 (m, 2H, 2H arom). ^{31}P NMR (CD_2Cl_2, 121 MHz): 49.9 (P−C, J_{PP} = 79 Hz), 143.0 (P−O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): δ 10.7 (CH_3C(CO_2H)═), 10.9 (CH_3C(CO_2H)═), 14.1 (CH_3CH═), 14.2 (CH_3CH═), 16.6 (Ar-*Me*), 16.8 (Ar-*Me*), 20.4 (Ar-*Me*), 20.6 (Ar-*Me*), 30.8 (br, C*Me*$_3$), 32.5 (br, C*Me*$_3$), 34.6 (br, C*Me*$_3$), 36.2 (br, C*Me*$_3$), 122.4 (br, CH arom), 123.7 (br, CH arom), 128.1 (CH arom), 128.3 (d, J_{CP} = 9 Hz, 2 CH arom), 128.7 (d, J_{CP} = 10 Hz, 2 CH arom), 129.9 (br, CH arom), 130.4 (br, CH arom), 130.9 (br, CH arom), 132.0 (C_q), 132.4 (2 C_q), 132.7 (2 C_q), 133.5 (CH_3CH═), 133.7 (br, 3 CH arom), 134.4 (CH_3CH═), 135.0 (m, 3 CH arom), 135.2 (C_q), 137.9 (C_q), 138.9 (br C_q), 139.7 (br, C_q), 145.3 (C_q), 147.7 (d, J_{CP} = 16 Hz, C_q), 157.3 (br, C_q), 185.7 (br, CO_2), 186.1 (br, CO_2). Two signals for C_q atoms could not be located due to spectrum crowding. HRMS (FAB): *m*/*z* 960.2858, [M]$^+$ (exact mass calculated for $C_{52}H_{60}O_7P_2Ru$ 960.2395).

[Ru(η^2-O_2CC(Me)═CHMe)$_2$(2h)] (4h). A solution of **1h** (0.085 g, 0.09 mmol) and **5a** (0.018 g, 0.18 mmol) in CH_2Cl_2 (2 mL) was stirred at 50 °C for 24 h. The resulting mixture was evaporated and recrystallized in *n*-hexane. The solid obtained was filtered and washed with *n*-hexane, giving **4h** as a yellow solid (0.046 g, 49%). ^1H NMR (500 MHz, CD_2Cl_2): δ 0.85 (s, 9 H, C*Me*$_3$), 1.30 (s, 9 H, C*Me*$_3$), 1.36 (s, 9 H, C*Me*$_3$), 1.43 (s, 9 H, C*Me*$_3$), 1.52 (br s, 3H, CH_3C(CO_2H)═), 1.68 (s, 3H, CH_3C(CO_2H)═), 1.69 (s, 6H, 2 CH_3CH═), 6.11 (dd, 1H, J_{HP} = 4.9, 7.9 Hz, 1H arom), 6.56 (brm, 1H, CH_3CH═), 6.73 (br m, 1H, CH_3CH═), 6.99 (m, 4H, 4H arom), 7.15 (m, 3H, 3H arom), 7.27 (m, 3H, 3H arom), 7.45 (m, 4H, 4H arom), 7.52 (m, 1H, 1H arom), 7.65 (m, 2H, 2H arom). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ 51.1 (P−C, J_{PP} = 79 Hz), 143.9 (P−O).

dx.doi.org/10.1021/om300018s | *Organometallics* 2012, 31, 3551−3564

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): δ 11.1 (s, CH_3CH═), 11.3 (s, CH_3CH═), 14.1 (s, $CH_3C(CO_2H)$═), 14.2 (s, $CH_3C(CO_2H)$═), 30.3 (CMe_3), 30.9 (CMe_3), 31.8 (2 CMe_3), 35.0 (CMe_3), 35.2 (CMe_3), 35.5 (CMe_3), 36.4 (CMe_3), 120.8 (CH arom), 121.4 (CH arom), 122.4 (CH arom), 124.5 (d, J_{CP} = 7 Hz, CH arom), 124.8 (CH arom), 125.5 (CH arom), 127.0 (CH arom), 128.4 (d, J_{CP} = 11 Hz, CH arom), 128.8 (d, J_{CP} = 11 Hz, CH arom), 128.9 (CH arom), 129.7 (d, J_{CP} = 5 Hz, C_q), 130.0 (2 C_q), 130.4 (C_q), 130.9 (C_q), 131.2 (CH arom), 132.0 (C_q), 132.6 (CH arom), 133.0 (C_q), 133.1 (CH arom), 133.4 (d, J_{CP} = 10 Hz, CH arom), 135.1 (d, J_{CP} = 12 Hz, CH arom), 135.2 (CH_3CH═), 135.2 (C_q), 136.1 (CH_3CH═), 140.3 (C_q), 140.8 (C_q), 146.5 (C_q), 147.6 (C_q), 148.3 (C_q), 156.4 (C_q), 186.0 (CO_2), 186.7 (CO_2). Anal. Calcd for $C_{56}H_{70}O_7P_2Ru\cdot{}^1/_2C_6H_{14}$: C, 66.8; H, 7.3. Found: C, 67.0; H, 7.2.

General Procedure for ROMP Reactions of Norbornene. A solution of 2-norbornene (0.050 g, 0.53 mmol) in CH_2Cl_2 (0.75 mL) was added to an agitated solution of [Ru(η^3-2-MeC_3H_4)$_2$(P-OP)] complex (5.3 μmol) in CH_2Cl_2 (0.75 mL). The flask was immediately immersed in an oil bath preheated to 40 °C and stirred for the desired time. The reaction mixture was quenched by addition of 2−3 mL of a 10% v/v solution of ethyl vinyl ether in $CHCl_3$ and stirred for 2 h. MeOH (20 mL) was gradually added to produce polymer precipitation. After complete precipitation the resulting polymer was isolated by filtration, washed with small amounts of MeOH, and dried under vacuum. Polymer cis/trans double-bond content was analyzed by ^{1}H NMR. Average molecular weights were determined by GPC in $CHCl_3$ calibrated with polystyrene standards.

General Procedure for Catalytic Hydrogenation of Unsaturated Carboxylic Acids. In a glovebox, a Fischer−Porter vessel (80 mL) was charged with a solution of the [Ru(η^3-2-MeC_3H_4)$_2$(P-OP)] complex (2.5 μmol) and **5a** (0.025 g, 0.25 mmol) in hexane (2.0 mL). The reactor was purged three times with H_2 and finally pressurized to 4 bar and heated to 60 °C. After 24 h, the reactor was slowly cooled to room temperature and depressurized. The reaction solution was evaporated, and conversions were determined by ^{1}H NMR. The enantiomeric excess was analyzed from an aliquot of the reaction mixture by GC using a Chrompack CP-Cyclodex-β-236 M column. 2-Methylbutanoic acid: 95 °C (isotherm); 20.0 psi of He; $t_1(S)$ = 4.41 min, $t_2(R)$ = 4.56 min. 2-Methylpentanoic acid: 95 °C (isotherm), 2 mL/min of He; $t_1(S)$ = 8.38 min, $t_2(R)$ = 9.32 min.

X-ray Structure Determinations. Crystallographic data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer using graphite-monochromated Mo Kα_1 radiation (λ = 0.710 73 Å). The data were reduced (SAINT)[28] and corrected for Lorentz−polarization and absorption effects by a multiscan method (SADABS).[29] Structures were solved by direct methods (SIR-2002)[30] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12).[31] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. A summary of cell parameters, data collection, structure solution, and refinement is given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing the superposition of Ru(P)$_2$(η^3-2-MeC_3H_4)$_2$ fragments of Λ-**1a** and Λ-**1d**, M^+ isotope patterns, selected NMR spectra, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge Dr. P. M. Nieto (IIQ) for assistance in $^{31}P-^{31}P$ EXSY experiments. the MICINN (CTQ2009-11867, CTQ2009-08746 and the CONSOLIDER-INGENIO, CSD2007-00006, FEDER support), the EU (PITN 2008-215193), and the Junta de Andalucía (2008/FQM-3830). We also thank Dr. Reddy's group for a generous gift of enantiomers of 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-bisphenol. M.V. and S.E.G.-G. thank the MICINN for a FPI fellowship and a Ramón y Cajal contract, respectively.

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