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Synthesis and Reactivity of $[Ru(Cp^*)(L)(MeCN)_2][PF_6]$ (L = Ph_2POMe or Ph_2P-*o*-tolyl) and $\{Ru(Cp^*)[Ph_2PCH_2C(tBu)=O](MeCN)\}[PF_6]$ Complexes, Their Involvement as Catalyst Precursors for Regioselective Allylic Substitution Reactions and Related $[Ru(Cp^*)Cl(Ph_2POMe)(RCHCHCH_2)][PF_6]$ η^3-Allyl Ruthenium(IV) Intermediates

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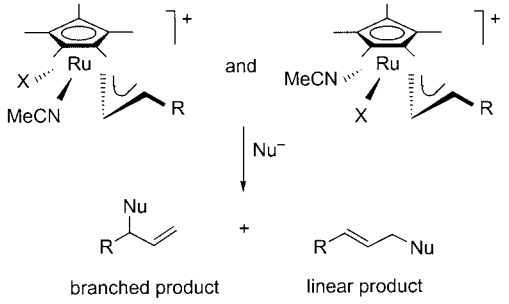
The synthesis of the new complexes $[Ru(Cp^*)(L)(MeCN)_2][PF_6]$ (L = Ph_2POMe or Ph_2P-*o*-tolyl) and $\{Ru(Cp^*)[Ph_2PCH_2C(tBu)=O](MeCN)\}[PF_6]$ (**2a–c**) is achieved starting from $[Ru(Cp^*)(MeCN)_3][PF_6]$. The acetonitrile ligands in complexes **2a–c** are labile, as emphasised by the easy formation of $\{Ru(Cp^*)(CO)_2[Ph_2PCH_2C(=O)tBu]\}[PF_6]$ (**3**). The keto-phosphane is used as a tool to convert **3** into $\{Ru(Cp^*)(CO)[Ph_2PCH_2C(tBu)=O]\}[PF_6]$ (**5**). Complex **5** reacts with 1,1-diphenyl-2-propyn-1-ol in methanol as solvent to afford the vinyl-carbene complex $\{Ru(Cp^*)(CO)[=C(OMe)CH=CPh_2][Ph_2PCH_2C(=O)tBu]\}[PF_6]$. The new η^3-allyl ruthenium(IV) derivatives $[Ru(Cp^*)Cl(Ph_2POMe)(CH_2CMeCH_2)][PF_6]$ and $[Ru(Cp^*)Cl(Ph_2POMe)(RCHCHCH_2)][PF_6]$ (R = Me; *n*Pr, **8d**; or Ph, **8e**) are obtained by reacting **2a** with the appropriate allylic halide. The X-ray crystal structure determination of the compounds **8d** and **8e** disclosed an *endo-trans*-$RCHCHCH_2$ η^3-allyl ligand. The formation of branched allyl aryl ethers is regioselectively favoured when complexes **2a–c** are involved as catalyst precursors for the etherification of cinnamyl chloride, chlorohexene and 3-chloro-4-phenylbut-1-ene with phenol, *p*-methoxyphenol, cresols and (*o* or *p*)-chlorophenols, in the presence of K_2CO_3.

Introduction

Recently, the labile ruthenium(II) complex $[Ru(Cp^*)(MeCN)_3][PF_6]$ (**1**) (Cp* = pentamethylcyclopentadienyl) was disclosed as an efficient catalyst precursor for the allylation of phenols with cinnamyl derivatives according to stereospecific and regioselective processes.[1,2] Furthermore, enantioselective synthesis was also achieved in the additional presence of a chiral bis-oxazoline ligand.[3] Enantioselective allylic amination and alkylation involving related catalysts based on tethered Cp′ rings resulting in planar chirality at the ruthenium centre have also been reported.[4] From a mechanistic point of view, these catalytic reactions occur through transient formation of electrophilic η^3-allyl ruthenium(IV) species.[5] Indeed, complexes $[Ru(Cp^*)X(MeCN)(\eta^3\text{-}RCHCHCH_2)][PF_6]$ resulted from the oxidative addition of allylic halides to **1**, but have been disclosed to be a mixture of stereoisomers in solution, as enantiomeric pairs (see Scheme 1).[2] The recently reported tethered complexes $[Ru(Cp'\text{-}PR_2)Cl(\eta^3\text{-}CH_2CRCH_2)][PF_6]$ involved a symmetrical η^3-allyl ligand precluding analogous stereoisomerism arising from the presence of four distinct coordinating centres besides the cyclopentadienyl ligand.[6]



Scheme 1. Stereoisomerism and isomerism from unsymmetrical η^3-CH_2CHCHR allyl ligand.

Therefore, no information was available concerning the relationship between the regioselectivity of the catalytic nucleophilic substitution and the stereoselective formation of the putative η^3-allyl ruthenium(IV) intermediate. Moreover, using such ruthenium catalysts, the regioselective formation of branched products by nucleophilic attack at an unsymmetrical η^3-$RCHCHCH_2$ allyl ligand, as depicted in Scheme 1, largely remained a challenge when R was an alkyl group instead of an aryl one arising from cinnamyl substrates. On the other hand, while the reactivity of

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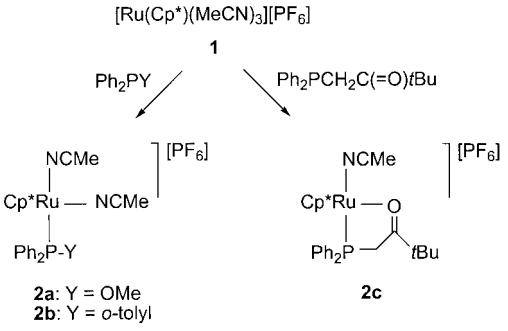
$[Ru(Cp)(PR_3)(MeCN)_2][PF_6]$ complexes towards alkynes continued to stimulate studies,[7] little was known concerning their reactivity towards allylic organic substrates, although $[Ru(Cp)Br(PR_3)(\eta^3\text{-}CH_2CHCH_2)][PF_6]$ complexes have been synthesised.[8]

We wish to report herein (i) the reaction between $[Ru(Cp^*)(MeCN)_3][PF_6]$ and methyl diphenylphosphinite, *o*-tolyldiphenylphosphane or a hemilabile β-keto-phosphane, which provides an efficient tool for the building of new organometallic derivatives, (ii) the synthesis of $[Ru(Cp^*)X(Ph_2POMe)(RCHCHCH_2)][PF_6]$ η^3-allyl ruthenium(IV) complexes bearing an unsymmetrical monosubstituted allyl ligand and (iii) the involvement of these complexes as catalyst precursors for regioselective allylic etherification.

Results and Discussion

Synthesis of Complexes

With a procedure very similar to the reported synthesis of $[Ru(Cp^*)(PEt_3)(MeCN)_2][PF_6]$,[9] the reaction of $[Ru(Cp^*)(MeCN)_3][PF_6]$ (**1**) with one equiv. of methyl diphenylphosphinite or of the bulkier *o*-tolyldiphenylphosphane selectively resulted in the substitution of one acetonitrile ligand to afford the expected complexes $[Ru(Cp^*)(L)(MeCN)_2][PF_6]$ (L = Ph_2POMe, **2a** and L = Ph_2P-*o*-tolyl, **2b**), in 78% and 99% yield, respectively (Scheme 2).



Scheme 2. Synthesis of the new complexes **2a**–**c**.

Distinctly, the reaction between **1** and the β-keto-phosphane $Ph_2PCH_2C(=O)tBu$ showed the substitution of two acetonitrile ligands to afford **2c** wherein the functional phosphane acted as a chelate, in 95% yield (Scheme 2). The new complexes **2a**–**c** were characterised by ^1H, $^{13}C\{^1H\}$, ^{13}C DEPT and $^{31}P\{^1H\}$ NMR, IR spectroscopy and elemental analysis. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **2a**–**c** unambiguously indicated the presence of coordinated acetonitrile and one phosphorus ligand besides the Cp* one. Additionally, IR spectroscopy provided evidence for the coordination of the keto function in **2c** ($\tilde{\nu}$ = 1611 cm^{-1}) as previously specified in the case of CpRu complexes.[10] Attempts of recrystallisation of **2b**,**c** invariably led to oils that transform to yellow solids under prolonged vacuum. By contrast, orange crystals of **2a** suitable for X-ray crystal structure determination easily formed according to diffusion of diethyl ether into a concentrated dichloromethane solution. An ORTEP drawing of **2a** is shown in Figure 1 and selected bond lengths and angles are given in the caption.

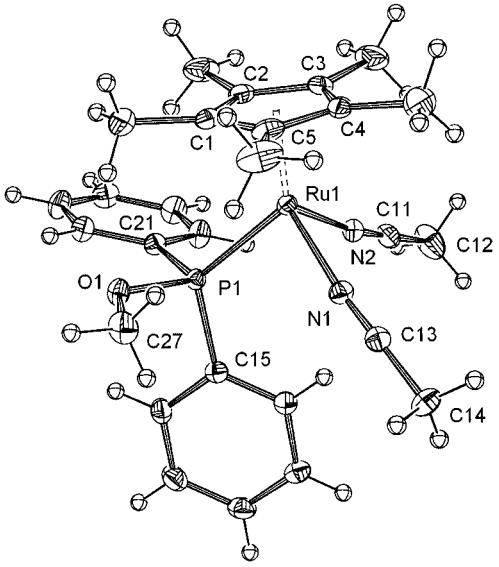
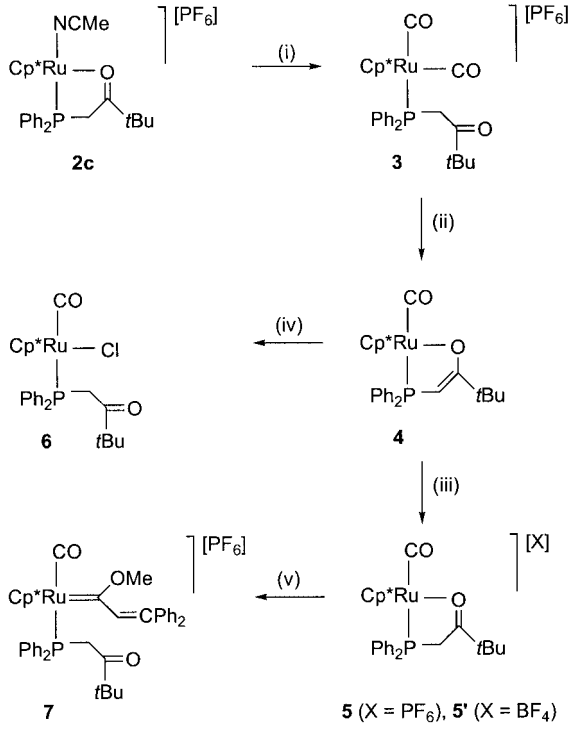


Figure 1. ORTEP drawing of **2a** showing 50% probability thermal ellipsoids. The PF_6 anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N1 2.076(2), Ru1–N2 2.067(2), Ru1–P1 2.2894(6); N1–Ru1–N2 87.74(8), N1–Ru1–P1 94.55(6), N2–Ru1–P1 90.77(6).

The cation of **2a** showed the expected piano-stool geometry. The N–Ru–N and N–Ru–P angles are close to 90° and the structure of **2a** thus consisted of a pseudo-octahedron with the Cp* ligand occupying three facial coordination sites.

Complex **2c** retained two labile coordinating atoms, as indicated by its reaction with carbon monoxide, which occurred under mild conditions (1 atm, ambient temperature) to straightforwardly afford the dicarbonyl complex **3** (Scheme 3).

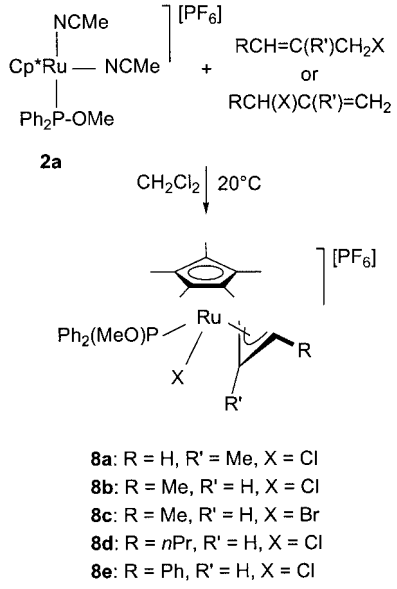
The formal selective substitution of the acetonitrile ligand in **2c** by carbon monoxide was indirectly achieved by reacting **3** with $Me_3NO{\cdot}2H_2O$ to form the enolato-phosphane derivative **4** (Scheme 3). The reaction consisted of the oxidation of one carbon monoxide ligand into carbon dioxide, thus also generating NMe_3, which subsequently deprotonated the keto-phosphane. The neutral complex **4** was then easily reprotonated with HPF_6 as its aqueous solution or with HBF_4 as its Me_2O adduct, to obtain **5** and **5′**, respectively, in yields up to 81%. The protonation of **4** was also achieved with hydrochloric acid, but the additional coordination of the chloride anion resulted in the neutral chloro complex **6** (Scheme 3). These reactions emphasised the usefulness of hemilabile keto-phosphanes as a tool for the building of coordination compounds. Furthermore, the coordinated keto-function in **5** is labile enough to allow the coordination of alkynols such as 1,1-diphenyl-2-propyn-1-ol. Using methanol as solvent, the reaction led at room temperature to a red precipitate of the vinyl-carbene derivative



Scheme 3. Reactivity of complex **2c**: (i) CO, 1 atm; (ii) $Me_3NO{\cdot}2H_2O$; (iii) HPF_6 or HBF_4; (iv) HCl; (v) $Ph_2C(OH)C{\equiv}CH$, MeOH.

7 (Scheme 3). The reaction might be conceived as an addition of methanol to a transient allenylidene species as previously investigated for $[Ru(Cp)(CO)(acetone)(P\textit{i}Pr_3)][BF_4]$.[11] Complexes **3**–**7** were characterised from a combination of ^1H, $^{13}C\{^1H\}$, ^{13}C DEPT and $^{31}P\{^1H\}$ NMR, IR spectroscopy and elemental analysis. Owing to the chiral ruthenium centre, the two PCH_2 protons of the keto-phosphane were found to be diastereotopic in complexes **2c**, **5**, **5′**, **6** and **7**. Characteristic of the vinyl-carbene ligand in **7** is the observation by $^{13}C\{^1H\}$ NMR spectroscopy of a very low field resonance at δ = 303.7 ppm (d, $^2J_{PC}$ = 2.5 Hz) corresponding to the Ru=C carbon nucleus.[11] Some steric congestion in **7** is likely responsible for the broadness of both the $^{31}P\{^1H\}$ NMR resonance at δ = 38.8 ppm and the ^1H NMR resonance assigned to the OMe protons at δ = 4.05 ppm. IR spectroscopic data accounted for the presence of carbon monoxide as a ligand and for the coordination mode of the functional phosphane ($\tilde{\nu} \approx 1700\ cm^{-1}$, uncoordinated C=O, in **3**, **6** and **7**; $\tilde{\nu} \approx 1600\ cm^{-1}$, coordinated C=O, in **5** and **5′**; $\tilde{\nu} = 1500\ cm^{-1}$, C=CO, in **4**).[10]

Complexes **2a**–**c** were observed to react with allylic halides but crystallisable products were obtained only starting from **2a**. Using dichloromethane as solvent, the η^3-allyl ruthenium(IV) derivatives **8a**–**e** resulted from the reaction at room temperature between **2a** and 3-chloro-2-methylpropene, crotyl chloride or bromide, chlorohexene as a mixture of isomeric nPrCH=CHCH$_2$Cl and nPrCH(Cl)CH=CH$_2$, and cinnamyl chloride (Scheme 4). Complexes **8a**–**e** were isolated in high yield (62–85%) as yellow to red crystals that were observed to be stable in air. Of interest, the formation of complexes **8** was observed to be sluggish in acetonitrile as solvent. Thus, the addition of cinnamyl chloride (an excess) to a solution of **2a** in acetonitrile showed only about 10% of **2a** to be converted into **8e** after standing for two days at room temperature, as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Indicating an irreversible formation, solutions of **8e** in acetonitrile were observed to be stable and unchanged after 8 days. Such an observation of a formation hindered by the presence of acetonitrile as coordinating solvent suggests a dissociative mechanism. The coordination of the olefinic bond of the allylic halide at a transient 16e-intermediate resulting from the loss of an acetonitrile ligand by **2a** would be a preliminary step allowing subsequent intramolecular oxidative addition.



Scheme 4. Synthesis of the new η^3-allyl ruthenium(IV) complexes, **8a**–**e**.

Complexes **8a**–**e** were characterised by NMR spectroscopic techniques including $^1H\{^{31}P\}$ for **8c**,**d**, and elemental analysis. Of main interest, CD_2Cl_2 solutions of **8a**–**e** disclosed single species by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The characterisation of complexes **8a**–**e** was finally completed by an X-ray crystal structure determination of **8d** and **8e**. ORTEP drawings of cations of **8d** and **8e** are shown on Figure 2 and Figure 3, respectively. Selected bond lengths and angles are given in the captions of the figures.

Cations of **8d** and **8e** displayed a square-pyramidal structure with a chlorine, a phosphorus and the terminal carbon atoms of an *endo*-η^3-allyl ligand, at basal positions. Likely resulting from an increased steric demand, the Ru–P bond length in **8d** or **8e** [Ru1–P1 = 2.368(1) and 2.360(1) Å, respectively] is longer than in **2a** [Ru1–P1 = 2.2894(6) Å]. Moreover, the phosphorus atom in **8d** and **8e** is located in a *trans* position relative to the substituted allylic carbon and such an arrangement would minimise steric constraints between the allyl and the phosphorus ligands. The Ru–Cl bond lengths [2.406(1) Å in **8d**, 2.396(1) Å in **8e**] revealed

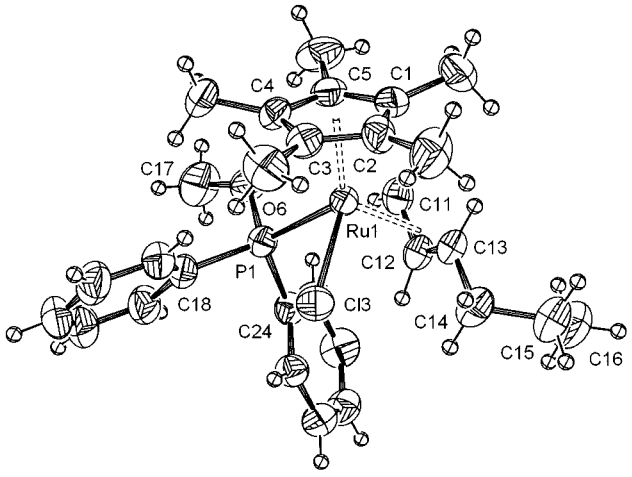


Figure 2. ORTEP drawing of **8d** showing 50% probability thermal ellipsoids. The PF_6 anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C11 2.191(4), Ru1–C12 2.198(4), Ru1–C13 2.339(4), Ru1–P1 2.368(1), C11–C12 1.406(6), C12–C13 1.395(6), C13–C14 1.497(6), Ru1–P1 2.368(1); C11–C12–C13 119.1(4), C12–C13–C14 123.7(4).

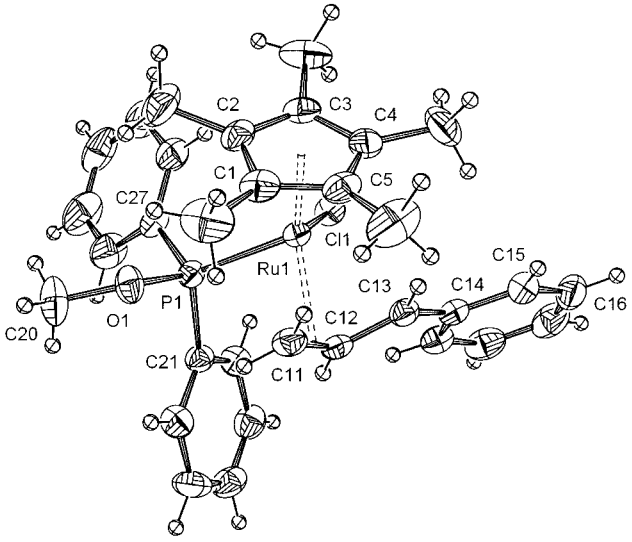


Figure 3. ORTEP drawing of **8e** showing 50% probability thermal ellipsoids. The PF_6 anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C11 2.182(5), Ru1–C12 2.210(4), Ru1–C13 2.452(4), C11–C12 1.398(6), C12–C13 1.396(6), C13–C14 1.457(6), Ru1–P1 2.360(1); C11–C12–C13 119.5(4), C12–C13–C14 125.7(4).

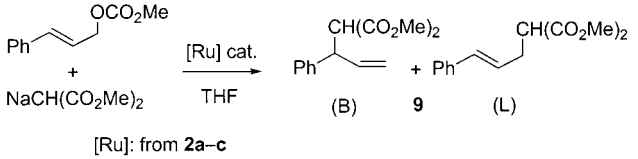
no special feature and are very close to the values previously reported in the case of the related complexes $[Ru(Cp^*)Cl(MeCN)(\eta^3\text{-}PhCHCHCH_2)][PF_6]$ and $[Ru(Cp^*)Cl_2(\eta^3\text{-}PhCHCHCH_2)]$ [2.3998(7) and 2.398(3) Å, respectively].[5,13]

The only difference between **8d** and **8e** was an alkyl *n*-propyl group instead of a phenyl group, respectively, as the substituent linked to one terminal carbon of the η^3-allyl ligand. The Ru–C bond lengths involving the unsubstituted terminal allylic C11 carbon atom [2.191(4) Å in **8d** and 2.182(5) Å in **8e**] and the medium C12 carbon atom [2.198(4) Å in **8d** and 2.210(4) Å in **8e**] were close. The Ru–C13 bond length involving the substituted terminal carbon of the η^3-allyl ligand was significantly longer, especially in the case of **8e** [2.452(4) vs. 2.339(4) Å in **8d**]. These observations are in agreement with those arising from the study of the complexes $[Ru(Cp^*)(phenanthroline)(\eta^3\text{-cinnamyl})][PF_6]_2$,[12] $[Ru(Cp^*)Br(MeCN)(\eta^3\text{-crotyl})][PF_6]$[2] and $[Ru(Cp^*)Cl(MeCN)(\eta^3\text{-cinnamyl})][PF_6]$.[13]

A minor contribution from a formal η^2-olefinic $CH_2{=}CH{-}C^{(+)}HR$ coordination of the allyl ligand might intuitively account for both observation of a longer Ru–CHR bond and enhanced electrophilic reactivity at the substituted allylic carbon.[2,12,13] The comparison between the Ru–CHR bond lengths in **8d** and **8e** [2.339(4) and 2.452(4) Å, respectively] obviously suggested a reduced contribution from the formal η^2-olefinic coordination of the allyl ligand in **8d**. Therefore, high regioselectivities in favour of branched products might be expected to be more difficult to reach when starting from unsymmetrical alkyl-allylic substrates compared to cinnamyl derivatives.[2] However, the location of a bulky phosphane ligand close to the unsubstituted terminal allylic carbon atom, as displayed in **8d** and **8e**, might distinctly contribute to favour nucleophilic addition at the substituted one. To test these assumptions, the study of the potential of complexes **2a**–**c** as catalyst precursors for ruthenium-catalysed allylic substitution reactions was undertaken.

Allylation Reactions Catalysed by Complexes 2a–c

The characterisation of an η^3-allyl ruthenium(IV) complex arising from an oxidative addition reaction between $[Ru(Cp^*)(MeCN)_3][PF_6]$ and *tert*-butyl cinnamyl carbonate recently provided further evidence for the key role of η^3-allyl ruthenium(IV) catalytic intermediates in ruthenium-catalysed nucleophilic allylic substitution reactions.[14] The activity of complexes **2a**–**c** as catalyst precursors for the allylation of dimethyl sodiomalonate with methyl cinnamyl carbonate was investigated. Thus, the addition of dimethyl sodiomalonate (1.2 equiv.) to a solution of methyl cinnamyl carbonate (0.5 mmol) in THF (3.0 mL) in the presence of **2a**–**c** (1.5 mol-%) at ambient temperature led to the monosubstituted dimethyl malonate **9** as a mixture of branched (B) and linear (L) isomers [Equation (1)], and disclosed a favoured formation of the branched isomer (Table 1).



(1)

The results given in Table 1 clearly indicate that the three catalyst precursors **2a**–**c** provided complete conversion after 16 h of reaction. The regioselectivities in favour of the branched isomer of **9**, B/L ranging between 86:14 with **2c** and 92:8 with **2a**, were fairly good in comparison with those

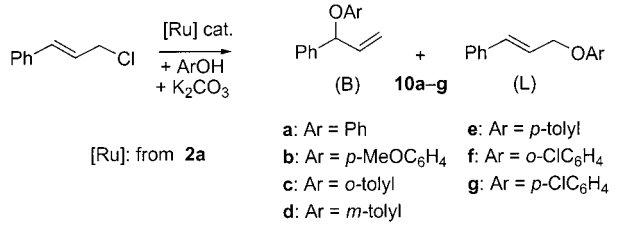
Table 1. Comparison of complexes **2a**–**c** as catalyst precursors for the allylation of dimethyl sodiomalonate with methyl cinnamyl carbonate.[a]

Entry	Catalyst	Conversion[b][c]	B/L ratio
1	**2a**	100	92:8
2	**2b**	100	90:10
3	**2c**	100	86:14

[a] Conditions: 0.6 mmol of dimethyl sodiomalonate, 0.5 mmol of methyl cinnamyl carbonate, 0.0075 mmol of **2a** in 3 mL of THF, room temperature, 16 h. [b] Relative to methyl cinnamyl carbonate (%). [c] As determined by ^{1}H NMR spectroscopy.

observed using **1** as the catalyst precursor.[1] However, complexes **2a**–**c**, as well as **1**,[2] were unable to catalyse this allylic alkylation without prior deprotonation of dimethyl malonate as achieved with [RuCp*(bipy)(CH_3CN)][PF_6] precursors.[12]

The reaction of phenol with cinnamyl chloride in the presence of **2a** and potassium carbonate in dichloromethane as solvent was investigated also [Equation (2)]. The results are given in Table 2. Under experimental conditions analogous to those used with **1** as catalyst,[2] the reaction led to the formation of the allyl phenyl ether **10a** in a 85:15 branched to linear ratio (entry 1).



(2)

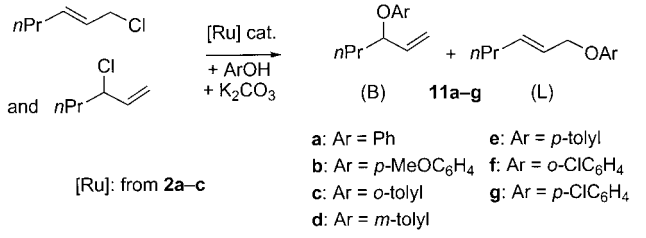
Table 2. Allylation of phenols ArOH with PhCH=$CHCH_2$Cl in the presence of **2a**.[a]

Entry	Ar	Conversion[b][c]	Products	B/L ratio
1	Ph	100	**10a**	85:15
2[d]	Ph	0		
3[e]	Ph	0		
4	*p*-$MeOC_6H_4$	76	**10b**	92:8
5	*o*-tolyl	43	**10c**	88:12
6	*m*-tolyl	75	**10d**	73:27
7	*p*-tolyl	61	**10e**	88:12
8	*o*-ClC_6H_4	52	**10f**	86:14
9	*p*-ClC_6H_4	100	**10g**	50:50

[a] Conditions: 1.2 mmol of ArOH, 1.2 mmol of K_2CO_3, 1.0 mmol of cinnamyl chloride, 0.015 mmol of **2a** in 6 mL of CH_2Cl_2, room temperature, 16 h. [b] Relative to cinnamyl chloride (%). [c] As determined by ^{1}H NMR spectroscopy. [d] THF as solvent. [e] Acetonitrile as solvent.

The regioselectivity was still fairly good although lower than that obtained with complex **1**.[2] Moreover, attempts to use THF or acetonitrile as solvent disclosed a lack of reactivity (entries 2, 3), whereas acetonitrile provided the best results in the case of catalyst **1**.[2] These observations suggested that the entrance of a phosphane ligand in complexes **2** would result in the strongest coordination of acetonitrile or THF, thus hindering the preliminary η^2-olefinic coordination of cinnamyl chloride as required for catalytic activity. The catalytic process proceeded smoothly for the allylation of various phenols in dichloromethane as solvent. Good regioselectivities were obtained starting from *p*-methoxyphenol (entry 4) and cresols (entries 5–7) as substituted phenols. Chlorophenols were also involved in the catalytic process (entries 8, 9) but only *o*-chlorophenol provided good regioselectivity.

Allyl aryl ethers arising from cinnamyl derivatives, valuable intermediates in organic chemistry, have drawn the main interest,[15] but another challenge is the development of efficient access to branched allyl aryl ethers starting from aliphatic allylic halides (vs. cinnamyl chloride-type substrates). The allylation of phenols with selected aliphatic or unconjugated allylic halides in the presence of **2a**–**c** as catalyst precursors was then investigated. Chlorohexene, synthesised as a 4:1 mixture of linear *n*PrCH=$CHCH_2$Cl and branched *n*PrCH(Cl)$CH=CH_2$ isomers starting from *trans*-2-hexen-1-ol and PCl_3,[16] reacted with various phenols to afford the allyl aryl ethers **11a**–**g**, as mixtures of branched *n*PrCH(OAr)$CH=CH_2$ and linear *n*PrCH=$CHCH_2$OAr isomers [Equation (3)]. The results are given in Table 3.



(3)

Table 3. Allylation of phenols ArOH with chlorohexene in the presence of **2a**–**c**.[a]

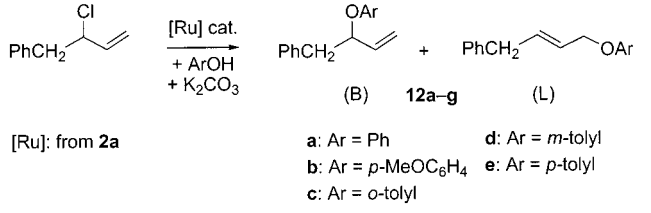
Entry	Catalyst	Ar	Conversion[b][c]	Products	B/L ratio
1	**2a**	Ph	100	**11a**	75:25
2[d]	**2a**	Ph	100	**11a**	75:25
3[e]	**2a**	Ph	100	**11a**	57:43
4	**2b**	Ph	94	**11a**	77:23
5	**2c**	Ph	100	**11a**	70:30
6	**2a**	*p*-$MeOC_6H_4$	100	**11b**	61:39
7	**2a**	*o*-tolyl	74	**11c**	81:19
8	**2a**	*m*-tolyl	62	**11d**	75:25
9	**2a**	*p*-tolyl	88	**11e**	75:25
10	**2a**	*o*-ClC_6H_4	62	**11f**	84:16
11	**2a**	*p*-ClC_6H_4	99	**11g**	49:51

[a] Conditions: 1.2 mmol of ArOH, 1.5 mmol of K_2CO_3, 1.0 mmol of chlorohexene, 0.015 mmol of **2a**–**c** in 6 mL of THF, room temperature, 16 h. [b] Relative to chlorohexene (%). [c] As determined by ^{1}H NMR spectroscopy. [d] Dichloromethane as solvent. [e] Acetonitrile as solvent.

In a typical run, the addition of phenol (1.2 equiv.) to chlorohexene (1.0 mmol) and K_2CO_3 (1.5 equiv.) in THF (6.0 mL) in the presence of **2a** (1.5 mol-%) for 16 h at ambient temperature resulted in the complete consumption of

chlorohexene and led to the formation of the allyl phenyl ether **11a** in a 75:25 B/L ratio (entry 1). Using complex **1** under similar catalytic conditions, chlorohexene was also converted into **11a**, but the regioselectivity was moderate, as emphasised by a B/L ratio of 60:40 in acetonitrile and 70:30 in acetone as solvent.[2] In the presence of complexes **2a**–**c**, the regioselectivity was slightly improved using THF or dichloromethane as solvent (entries 1, 2). As observed when starting from cinnamyl chloride, acetonitrile markedly disfavoured regioselectivity (entry 3). The involvement of **2b** and **2c** as catalysts (entries 4, 5) resulted in regioselectivities located in the same range as from **2a**. Complex **2a** was selected for the allylation of the substituted phenols. Using THF as solvent, satisfactory conversion and regioselectivity were reached with *p*-methoxyphenol and cresols (entries 6–9). The involvement of *p*-chlorophenol led to a 1:1 mixture of the branched and linear isomers of **11g** (entry 11), while *o*-chlorophenol was less reactive but provided a good B/L = 84:16 regioselectivity (entry 10). The low selectivity observed with *p*-chlorophenol might result from enhanced competition of the noncatalysed process, which contributed to the consumption of allylic halide but selectively led to the linear ether.

Readily available from benzyl bromide and allyl chloride,[17] 3-chloro-4-phenylbut-1-ene, $PhCH_2CH(Cl)CH=CH_2$, offered both the convenience of low volatility facilitating experimental work and an opportunity to test a pure branched allylic chloride under such catalytic conditions [Equation (4)]. The results are given in Table 4.



(4)

Table 4. Allylation of phenols ArOH with $PhCH_2CH(Cl)CH=CH_2$ catalysed by **2a**.[a]

Entry	Ar	Conversion[b][c]	Products	B/L ratio
1	Ph	87	**12a**	92:8
2[d]	Ph	60	**12a**	73: 7
3[e]	Ph	34	**12a**	50:50
4	*p*-$MeOC_6H_4$	88	**12b**	96:4
5	*o*-tolyl	89	**12c**	92:8
6	*m*-tolyl	100	**12d**	96:4
7	*p*-tolyl	93	**12e**	91:9
8	*o*-ClC_6H_4	0		
9	*p*-ClC_6H_4	0		

[a] Conditions: 1.2 mmol of ArOH, 1.2 mmol of K_2CO_3, 1.0 mmol of allylic chloride, 0.015 mmol of **2a**–**c** in 6 mL of THF, room temperature, 16 h. [b] Relative to allylic chloride (%). [c] As determined by ^1H NMR spectroscopy. [d] Dichloromethane as solvent. [e] Acetonitrile as solvent.

Whereas the allylation of phenoxide anion in the presence of 3 mol-% of **1** afforded the ether **12a** with a rather poor B/L = 1.5:1 regioselectivity,[2] significantly increased regioselectivities up to B/L = 92:8 (entries 1, 2) were reached when catalyst **2a** was used. THF was an appropriate solvent but much lower conversion and regioselectivity were obtained in dichloromethane or acetonitrile (entries 1–3). It is worth noting the lack of reactivity when (*o*- or *p*-) chlorophenols were involved as the nucleophile (entries 8, 9), whereas good regioselectivities up to B/L = 96:4 were reached when *p*-methoxyphenol or (*o*-, *m*- or *p*-)cresols were involved as the nucleophile (entries 4–7).

Conclusions

The reaction of one equiv. of phosphorus ligand with $[Ru(Cp^*)(MeCN)_3][PF_6]$ (**1**) allowed the selective substitution of one acetonitrile ligand, and the involvement of a hemilabile β-keto-phosphane provided a tool to selectively achieve the successive substitution of the three acetonitrile ligands by one phosphane, one carbon monoxide and one vinyl-carbene ligand. The products retaining acetonitrile as a ligand reacted with allylic halides to afford η^3-allyl ruthenium(IV) complexes and behave as catalyst precursors for allylic etherification of phenols with allylic chlorides in the presence of K_2CO_3, and alkylation of cinnamyl carbonate with dimethyl sodiomalonate under mild conditions. Although slightly less reactive than the unsubstituted parent complex **1**, the phosphane derivatives also favoured the formation of branched products when an unsymmetrical monosubstituted allylic substrate was involved, especially when starting from alkyl-substituted allylic substrates such as chlorohexene and 3-chloro-4-phenylbut-1-ene.

Experimental Section

General Comments: The reactions were performed under inert argon according to Schlenk-type techniques. THF, diethyl ether and dichloromethane were distilled after drying according to conventional methods, whereas HPLC grade acetonitrile was straightforwardly used. NMR spectra were recorded at 297 K with AC 200 FT and AC 300 Bruker instruments and referenced internally to the solvent peak. IR spectra were recorded as Nujol mulls with Bruker IFS28. Elemental analyses were performed by the "Service de Microanalyse du CNRS" Vernaison, France. Complex **1** was synthesised according to the reported procedure.[2] Commercially available allylic halides were used without further purification whereas chlorohexene and 3-chloro-4-phenylbut-1-ene were prepared according to procedures described in the literature.[16,17]

$[Ru(Cp^*)(Ph_2POMe)(MeCN)_2][PF_6]$ (2a): Methyl diphenylphosphinite (2.0 mL, 9.98 mmol) was added to a cold solution (–80 °C) of **1** (5.04 g, 10.0 mmol) in a mixture of dichloromethane (70 mL) and acetonitrile (20 mL). After being stirred overnight at room temperature, the mixture was evaporated under vacuum. The crude product was dissolved in dichloromethane (80 mL) and the orange solution was covered with diethyl ether (200 mL). The natural diffusion of solvents resulted in the formation of orange crystals of **2a**. Yield: 5.30 g, 78%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.57 (d, $^4J_{PH}$ = 2.0 Hz, 15 H, C_5Me_5), 2.27 (d, $^5J_{PH}$ = 1.3 Hz, 6 H, MeCN), 3.45 (d, $^3J_{PH}$ = 12.4 Hz, 3 H, OMe), 7.48–7.57 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 4.2 (s, *Me*CN),

9.5 (s, C_5Me_5), 53.5 (d, ^2J = 5.7 Hz, OMe), 89.0 (d, ^2J = 2.2 Hz, C_5Me_5), 126.4 (s, Me*C*N), 128.7 (d, ^2J = 9.3 Hz, Ph, *ortho*), 130.8 (d, ^4J = 2.4 Hz, Ph, *para*), 131.8 (d, ^3J = 12.4 Hz, Ph, *meta*), 137.1 (d, ^1J = 37.3 Hz, Ph, *ipso*) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 143.7 (s). $C_{27}H_{34}F_6N_2OP_2Ru$ (679.59): calcd. C 47.72, H 5.04, N 4.12, P 9.12; found C 47.56, H 5.12, N 4.06, P 9.17.

[Ru(Cp*)(Ph$_2$P-*o*-tolyl)(MeCN)$_2$][PF$_6$] (2b): Complex **2b** was similarly obtained by adding *o*-tolyldiphenylphosphane (1.68 g, 6.07 mmol) to a cold solution of **1** (3.06 g, 6.07 mmol) in a mixture of dichloromethane (70 mL) and acetonitrile (20 mL). After being stirred overnight at room temperature, the mixture was evaporated under vacuum to leave an oil that slowly crystallised. Diethyl ether (30 mL) was then added and the mixture was stirred to obtain a yellow powder that was collected by filtration and dried under vacuum. Yield: 4.45 g, 99%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.42 (d, $^4J_{PH}$ = 1.6 Hz, 15 H, C_5Me_5), 2.11 (s, 3 H, Me), 2.20 (d, $^5J_{PH}$ = 1.5 Hz, 6 H, MeCN), 7.05–7.51 (m, 14 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 4.2 (s, *Me*CN), 9.2 (s, C_5Me_5), 22.5 (d, ^3J = 7.0 Hz, Me), 87.1 (d, ^2J = 2.3 Hz, C_5Me_5), 126.4 (s, Me*C*N), 125.9–142.8 (m, C_6 rings) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 46.2 (s) ppm. $C_{33}H_{38}F_6N_2P_2Ru$ (739.69): calcd. C 53.59, H 5.18, N 3.79, P 8.37; found C 52.98, H 5.22, N 3.71, P 8.33.

{Ru(Cp*)[Ph$_2$PCH$_2$C(*t*Bu)=O](MeCN)}[PF$_6$] (2c): A solution of $Ph_2PCH_2C(=O)tBu$ (2.58 g, 9.07 mmol) in dichloromethane (20 mL) was added to a cold solution (–80 °C) of **1** (4.58 g, 9.08 mmol) in a mixture of dichloromethane (60 mL) and acetonitrile (10 mL). After being stirred overnight at room temperature, the mixture was evaporated under vacuum. Methanol (30 mL) and diethyl ether (40 mL) were added to the residue and the mixture was stirred while an orange precipitate formed. The mixture was evaporated, then methanol (8 mL) and diethyl ether (60 mL) were added. The resulting orange crystalline precipitate was collected by filtration, then washed with diethyl ether and dried under vacuum. Yield: 6.06 g, 95%. IR: $\tilde{\nu}$ = 2269 cm^{-1}, C≡N; 1611 cm^{-1}, C=O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.26 (s, 9 H, *t*Bu), 1.47 (d, $^4J_{PH}$ = 1.8 Hz, 15 H, C_5Me_5), 2.09 (d, $^5J_{PH}$ = 1.5 Hz, 3 H, MeCN), 2.94 (dd, $^2J_{HH}$ = 18.6, $^2J_{PH}$ = 7.5 Hz, 1 H, PCH_2, H_a), 4.24 (dd, $^2J_{HH}$ = 18.6, $^2J_{PH}$ = 10.1 Hz, 1 H, PCH_2, H_b), 6.85–7.65 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 4.1 (s, *Me*CN), 9.9 (s, C_5Me_5), 27.0 (s, CMe_3), 45.8 (d, ^3J = 1.8 Hz, *C*Me$_3$), 46.5 (d, ^1J = 21.5 Hz, PCH_2), 85.7 (d, ^2J = 2.2 Hz, C_5Me_5), 127.7 (s, Me*C*N), 129.2 (d, ^2J = 10.3 Hz, Ph, *ortho*), 129.4 (d, ^1J = 42.1 Hz, Ph, *ipso*), 129.6 (d, ^2J = 10.2 Hz, Ph, *ortho*), 130.7 (d, ^3J = 10.9 Hz, Ph, *meta*), 130.7 (d, ^4J = 2.5 Hz, Ph, *para*), 132.1 (d, ^4J = 1.3 Hz, Ph, *para*), 134.9 (d, ^3J = 14.0 Hz, Ph, *meta*), 137.0 (d, ^1J = 39.3 Hz, Ph, *ipso*), 228.9 (d, ^2J = 7.1 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 62.1 (s) ppm. $C_{30}H_{39}F_6NOP_2Ru$ (706.65): calcd. C 50.99, H 5.56, N 1.98, P 8.77; found C 50.37, H 5.64, N 1.89, P 8.79.

{Ru(Cp*)(CO)$_2$[Ph$_2$PCH$_2$C(=O)*t*Bu]}[PF$_6$]·CH$_2$Cl$_2$ (3): A solution of **2c** (6.06 g, 8.58 mmol) in a mixture of methanol (40 mL) and dichloromethane (40 mL) was stirred for 24 h under carbon monoxide and was then evaporated under vacuum. The residue was dissolved in dichloromethane (25 mL) and the solution was covered with methanol (5 mL) then diethyl ether (250 mL), to afford pale brown crystals. Yield: 6.03 g, 87%. Note that several recrystallisations are needed to obtain almost colourless crystals. ^1H NMR spectroscopy and elemental analysis provided evidence for the retention of one molecule of dichloromethane. However, a minor crystalline form free of dichloromethane was also detected. IR: $\tilde{\nu}$ = 2046, 2005 cm^{-1}, C≡O; 1701 cm^{-1}, C=O. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 0.97 (s, 9 H, *t*Bu), 1.72 (d, $^4J_{PH}$ = 2.0 Hz, 15 H, C_5Me_5), 3.83 (d, $^2J_{PH}$ = 9.6 Hz, 2 H, PCH_2), 7.33–7.56 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.8 (s, C_5Me_5), 26.2 (s, CMe_3), 40.0 (d, ^1J = 36.8 Hz, PCH_2), 45.8 (d, ^3J = 2.2 Hz, *C*Me$_3$), 103.6 (s, C_5Me_5), 130.0 (d, ^1J = 50.2 Hz, Ph, *ipso*), 130.0 (d, ^2J = 11.1 Hz, Ph, *ortho*), 132.5 (d, ^3J = 11.6 Hz, Ph, *meta*), 132.6 (d, ^4J = 3.0 Hz, Ph, *para*), 198.8 (d, ^2J = 15.6 Hz, C≡O), 209.7 (d, ^2J = 4.0 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 32.5 (s) ppm. $C_{30}H_{36}F_6O_3P_2Ru{\cdot}CH_2Cl_2$ (806.56): calcd. C 46.16, H 4.75, Cl 8.79, P 7.68; found C 46.47, H 4.68, Cl 7.35, P 7.67 (some presence of the minor form free of dichloromethane is likely responsible for the high carbon and low chlorine values).

Ru(Cp*)(CO)[Ph$_2$PCH=C(*t*Bu)O] (4): A mixture consisting of **3** (6.25 g, 7.75 mmol), $Me_3NO{\cdot}2H_2O$ (1.00 g, 9.00 mmol) and methanol (60 mL) was stirred overnight to afford a yellow slurry. Dissolution of the precipitate was subsequently obtained upon heating and completed by adding some dichloromethane (≈10 mL). The hot solution deposited yellow crystals of **4** upon cooling to –20 °C after partial removal of solvents (20 mL) under a stream of argon. Yield: 3.43 g, 81%. Note that further concentration of the solution led to a mixture of additional **4** and of ammonium salt. However, treatment of the mother liquor with an excess of NH_4Cl allowed conversion of residual **4** into **6**, which may be subsequently separated according to selective dissolution in diethyl ether. IR: $\tilde{\nu}$ = 1933 cm^{-1}, C≡O; 1500 cm^{-1}, C=CO. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = 1.19 (s, 9 H, *t*Bu), 1.53 (d, $^4J_{PH}$ = 1.5 Hz, 15 H, C_5Me_5), 4.59 (d, $^2J_{PH}$ = 2.9 Hz, 1 H, PCH=), 7.13–7.66 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.7 (s, C_5Me_5), 30.0 (s, CMe_3), 38.5 (d, ^3J = 12.2 Hz, *C*Me$_3$), 74.5 (d, ^1J = 59.8 Hz, PCH), 95.3 (s, C_5Me_5), 128.2 (d, ^2J = 10.3 Hz, Ph, *ortho*), 128.4 (d, ^2J = 11.0 Hz, Ph, *ortho*), 128.9 (d, ^4J = 2.4 Hz, Ph, *para*), 129.8 (s, *para*), 131.7 (d, ^3J = 9.8 Hz, Ph, *meta*), 133.3 (d, ^3J = 11.0 Hz, Ph, *meta*), 138.5 (d, ^1J = 59.8 Hz, Ph, *ipso*), 140.2 (d, ^1J = 40.3 Hz, Ph, *ipso*), 200.8 (d, ^2J = 17.1 Hz, =CO), 206.0 (d, ^2J = 19.5 Hz, C≡O) ppm. ^{13}C NMR (50.32 MHz, CD_2Cl_2, selected values): δ = 74.5 (dd, J_{HC} = 162.4, J_{PC} = 58.6 Hz, PCH=) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 55.3 (s) ppm. $C_{29}H_{35}O_2PRu$ (547.64): calcd. C 63.60, H 6.44, P 5.66; found C 63.65, H 6.39, P 5.98.

{Ru(Cp*)(CO)[Ph$_2$PCH$_2$C(*t*Bu)=O]}[PF$_6$] (5): A commercial 60% weight aqueous solution of HPF_6 (0.54 mL, 3.66 mmol) was added to a cold slurry (–80 °C) of **4** (2.00 g, 3.65 mmol) in methanol (40 mL). The mixture was warmed to room temperature and further stirred for 1 h. The resulting yellow solution was evaporated to dryness under vacuum and the residue was dissolved in dichloromethane (20 mL). The solution was covered with methanol (5 mL) then diethyl ether (140 mL) to afford orange needles. Yield: 2.05 g, 81%. IR: $\tilde{\nu}$ = 1975 cm^{-1}, C≡O; 1603 cm^{-1}, C=O. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.38 (s, 9 H, *t*Bu), 1.70 (d, $^4J_{PH}$ = 2.0 Hz, 15 H, C_5Me_5), 3.33 (dd, $^2J_{HH}$ = 18.5, $^2J_{PH}$ = 8.6 Hz, 1 H, PCH_2, H_a), 4.77 (dd, $^2J_{HH}$ = 18.4, $^2J_{PH}$ = 10.7 Hz, 1 H, PCH_2, H_b), 6.79–6.89 (m, 2 H, Ph), 7.48–7.72 (m, 8 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.9 (s, C_5Me_5), 27.1 (s, CMe_3), 46.8 (d, ^3J = 2.3 Hz, *C*Me$_3$), 48.8 (d, ^1J = 29.2 Hz, PCH_2), 97.6 (d, ^2J = 1.6 Hz, C_5Me_5), 128.9 (d, ^1J = 57.1 Hz, Ph, *ipso*), 129.9 (d, ^2J = 10.2 Hz, Ph, *ortho*), 130.1 (d, ^2J = 11.7 Hz, Ph, *ortho*), 130.4 (d, ^3J = 11.0 Hz, Ph, *meta*), 132.1 (d, ^4J = 2.5 Hz, Ph, *para*), 132.6 (part of d, Ph, *ipso*), 133.3 (d, ^4J = 2.5 Hz, Ph, *para* and hidden part of d, Ph, *ipso*), 134.5 (d, ^3J = 12.5 Hz, Ph, *meta*), 202.8 (d, ^2J = 16.5 Hz, C≡O), 233.1 (d, ^2J = 4.0 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 66.5 (s), –143.2 (sept, PF_6) ppm. $C_{29}H_{36}F_6O_2P_2Ru$ (693.61): calcd. C 50.22, H 5.23, P 8.93; found C 50.06, H 5.31, P 8.47.

{Ru(Cp*)(CO)[$Ph_2PCH_2C(tBu)$=O]}[BF_4] (5′): Large yellow-brown crystals of **5′** were similarly obtained in 80% yield after adding $HBF_4{\cdot}OMe_2$ (as a 0.7 M solution in methanol) to a cold slurry of **4** in methanol. IR: $\tilde{\nu}$ = 1957 cm^{-1}, C≡O; 1597 cm^{-1}, C=O. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.38 (s, 9 H, *t*Bu), 1.70 (d, $^4J_{PH}$ = 2.0 Hz, 15 H, C_5Me_5), 3.38 (dd, $^2J_{HH}$ = 18.7, $^2J_{PH}$ = 8.6 Hz, 1 H, PCH_2, H_a), 4.85 (dd, $^2J_{HH}$ = 18.6, $^2J_{PH}$ = 10.7 Hz, 1 H, PCH_2, H_b), 6.79–7.72 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.9 (s, C_5Me_5), 27.1 (s, CMe_3), 46.8 (d, ^3J = 2.4 Hz, CMe_3), 48.7 (d, ^1J = 29.0 Hz, PCH_2), 97.5 (d, ^2J = 1.5 Hz, C_5Me_5), 129.0 (d, ^1J = 57.2 Hz, Ph, *ipso*), 129.8 (d, ^2J = 10.0 Hz, Ph, *ortho*), 130.0 (d, ^2J = 10.4 Hz, Ph, *ortho*), 130.4 (d, ^3J = 10.9 Hz, Ph, *meta*), 132.0 (d, ^4J = 2.2 Hz, Ph, *para*), 133.0 (d, ^1J = 39.8 Hz, Ph, *ipso*), 133.2 (d, ^4J = 3.0 Hz, Ph, *para*), 134.6 (d, ^3J = 12.7 Hz, Ph, *meta*), 202.9 (d, ^2J = 17.3 Hz, C≡O), 233.4 (d, ^2J = 4.9 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 66.2 (s) ppm. $C_{29}H_{36}BF_4O_2PRu$ (635.45): calcd. C 54.81, H 5.71, P 4.87; found C 54.79, H 5.76, P 4.87.

Ru(Cp*)Cl(CO)[Ph_2PCH_2C(=O)*t*Bu] (6): 37% weight aqueous hydrochloric acid (0.30 mL, 3.65 mmol) was added to a cold slurry (–80 °C) of **4** (2.00 g, 3.65 mmol) in methanol (35 mL). The mixture was warmed to room temperature and further stirred for 1 h. The resulting solution was evaporated to dryness under vacuum and the residue was extracted with diethyl ether (30 mL). The solution was filtered and then slowly evaporated under vacuum to leave an orange-yellow solid. Yield: 2.04 g, 96%. IR: $\tilde{\nu}$ = 1916 cm^{-1}, C≡O; 1690 cm^{-1}, C=O. ^1H NMR (200.13 MHz, $CDCl_3$): δ = 0.82 (s, 9 H, *t*Bu), 1.48 (d, $^4J_{PH}$ = 1.9 Hz, 15 H, C_5Me_5), 3.90 (dd, $^2J_{HH}$ = 16.1, $^2J_{PH}$ = 6.6 Hz, 1 H, PCH_2, H_a), 4.08 (dd, $^2J_{HH}$ = 16.0, $^2J_{PH}$ = 8.5 Hz, 1 H, PCH_2, H_b), 7.39–7.43 (m, 6 H, Ph), 7.65–7.78 (m, 4 H, Ph) ppm. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 0.86 (s, 9 H, *t*Bu), 1.49 (d, $^4J_{PH}$ = 1.8 Hz, 15 H, C_5Me_5), 4.00 (d, $^2J_{PH}$ = 7.8 Hz, 2 H, PCH_2), 7.43–7.77 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.9 (s, C_5Me_5), 26.5 (s, CMe_3), 38.0 (d, ^1J = 23.4 Hz, PCH_2), 46.2 (d, ^3J = 1.5 Hz, CMe_3), 96.9 (d, ^2J = 2.5 Hz, C_5Me_5), 128.6 (d, ^2J = 10.2 Hz, Ph, *ortho*), 128.8 (d, ^2J = 9.3 Hz, Ph, *ortho*), 130.9 (d, ^4J = 1.6 Hz, 2 C, Ph, *para*), 133.3 (d, ^1J = 40.0 Hz, Ph, *ipso*), 134.2 (d, ^3J = 11.0 Hz, Ph, *meta*), 134.3 (d, ^3J = 10.2 Hz, Ph, *meta*), 134.3 (d, ^1J = 46.9 Hz, Ph, *ipso*), 207.2 (d, ^2J = 21.2 Hz, C≡O), 210.8 (d, ^2J = 7.9 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 41.9 (s) ppm. $C_{29}H_{36}ClO_2PRu$ (584.10): calcd. C 59.63, H 6.21, Cl 6.07, P 5.30; found C 60.09, H 6.38, Cl 6.30, P 5.20.

{Ru(Cp*)(CO)[=C(OMe)CH=CPh_2][Ph_2PCH_2C(=O)*t*Bu]}[PF_6] (7): A solution of **5** (1.00 g, 1.44 mmol) and of 1,1-diphenyl-2-propyn-1-ol (0.50 g, 2.40 mmol) in methanol (30 mL) was stirred at room temperature for 20 h. The resulting dark red precipitate was collected by filtration and washed with diethyl ether (20 mL), then dissolved in dichloromethane (25 mL). This solution was covered first with methanol (10 mL) then diethyl ether (120 mL) to afford orange-red crystals. Yield: 1.16 g, 88%. IR: $\tilde{\nu}$ = 1948 cm^{-1}, C≡O; 1709 cm^{-1}, C=O. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.06 (s, 9 H, *t*Bu), 1.56 (d, $^4J_{PH}$ = 1.7 Hz, 15 H, C_5Me_5), 3.76 (dd, $^2J_{HH}$ = 17.3, $^2J_{PH}$ = 7.2 Hz, 1 H, PCH_2, H_a), 3.86 (dd, $^2J_{HH}$ = 17.5, $^2J_{PH}$ = 8.1 Hz, 1 H, PCH_2, H_b), 4.05 (s, broad, 3 H, OMe), 6.15 (d, $^4J_{PH}$ = 1.8 Hz, 1 H, CH=), 6.99–7.59 (m, 20 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.8 (s, C_5Me_5), 26.3 (s, CMe_3), 38.9 (d, ^1J = 31.9 Hz, PCH_2), 46.0 (s, CMe_3), 65.6 (s, OCH_3), 103.0 (s, C_5Me_5), 129.0–144.6 (m, CH= and Ph), 205.0 (d, ^2J = 17.1 Hz, C≡O), 209.0 (d, ^2J = 6.3 Hz, C=O), 303.7 (d, ^2J = 2.5 Hz, Ru=C) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 38.8 (s, broad) ppm. $C_{45}H_{50}F_6O_3P_2Ru$ (915.90): calcd. C 59.01, H 5.50, P 6.76; found C 58.73, H 5.57, P 6.60.

[Ru(Cp*)Cl(Ph_2POMe)(CH_2CMeCH_2)][PF_6] (8a): An excess of 3-chloro-2-methylpropene (0.40 mL, 4.1 mmol) was added to a solution of **2a** (0.67 g, 0.99 mmol) in dichloromethane (25 mL). After being stirred overnight, the solution was covered with diethyl ether (100 mL) to afford orange-yellow crystals. Yield: 0.48 g, 70%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.01 (s, 3 H, Me), 1.71 (d, $^4J_{PH}$ = 2.2 Hz, 15 H, C_5Me_5), 2.01 (broad s, 1 H, CH_2, *anti*), 3.07 (d, $^3J_{PH}$ = 3.8 Hz, 1 H, CH_2, *anti*), 3.41 (dd, $^4J_{HH} \approx {}^3J_{PH} \approx$ 2.3 Hz, 1 H, CH_2, *syn*), 3.60 (broad d, $^3J_{PH}$ = 11.0 Hz, 1 H, CH_2, *syn*), 3.79 (d, $^3J_{PH}$ = 11.0 Hz, 3 H, OMe), 7.45–7.70 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.9 (s, C_5Me_5), 17.0 (s, Me, allyl), 53.4 (d, ^2J = 4.0 Hz, CH_2), 58.5 (d, ^2J = 14.8 Hz, OMe), 70.2 (d, ^2J = 6.2 Hz, CH_2), 107.2 (d, ^2J = 1.5 Hz, C_5Me_5), 116.1 (d, ^2J = 1.6 Hz, *C*Me, allyl), 128.5 (d, ^2J = 10.1 Hz, Ph, *ortho*), 128.6 (d, ^1J = 43.6 Hz, Ph, *ipso*), 129.4 (d, ^2J = 10.3 Hz, Ph, *ortho*), 131.9 (d, ^1J = 43.1 Hz, Ph, *ipso*), 133.2 (d, ^3J = 9.2 Hz, Ph, *meta*), 133.2 (d, ^4J = 3.8 Hz, Ph, *para*), 133.3 (d, ^4J = 2.5 Hz, Ph, *para*), 135.7 (d, ^3J = 11.0 Hz, Ph, *meta*) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 124.5 (s) ppm. $C_{27}H_{35}ClF_6OP_2Ru$ (688.04): calcd. C 47.13, H 5.13, Cl 5.15, P 9.00; found C 47.11, H 5.02, Cl 5.27, P 8.70.

[Ru(Cp*)Cl(Ph_2POMe)($MeCHCHCH_2$)][PF_6] (8b): An excess of 3-chloro-1-butene (0.50 mL, 5.0 mmol) was added to a solution of **2a** (0.84 g, 1.24 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the solution was covered with diethyl ether (110 mL) to afford orange-yellow crystals. Yield: 0.72 g, 84%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.27 (dd, $^3J_{HH}$ = 6.3, $^4J_{PH}$ = 1.4 Hz, 3 H, Me), 1.79 (d, $^4J_{PH}$ = 2.2 Hz, 15.5 H, C_5Me_5 and part of d, 0.5 H, CH_2, *anti*), 1.83 (part of d, 0.5 H, CH_2, *anti*), 3.29 (dddd, $^3J_{HHtrans} \approx$ 10.4, $^3J_{HHcis}$ = 6.0, $^3J_{PH}$ = 3.9 Hz, 1 H, CH), 3.67 (d, $^3J_{PH}$ = 11.0 Hz, 3 H, OMe), 3.72–3.83 (m, 2 H, C*H*Me and CH_2, *syn*), 7.41–7.71 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.4 (s, C_5Me_5), 16.9 (d, ^3J = 1.5 Hz, CH*Me*), 52.8 (d, ^2J = 3.9 Hz, CH_2), 58.1 (d, ^2J = 14.7 Hz, OMe), 96.4 (d, $^2J \approx$ 3 Hz, *C*HMe) 96.4 (s, CH), 106.0 (d, ^2J = 1.6 Hz, C_5Me_5), 125.8 (d, ^1J = 49.4 Hz, Ph, *ipso*), 127.9 (d, ^2J = 10.9 Hz, Ph, *ortho*), 128.7 (d, ^2J = 10.4 Hz, Ph, *ortho*), 130.2 (d, ^1J = 44.5 Hz, Ph, *ipso*), 131.2 (d, ^3J = 9.2 Hz, Ph, *meta*), 132.2 (d, ^4J = 3.0 Hz, Ph, *para*), 132.9 (d, ^4J = 2.5 Hz, Ph, *para*), 135.8 (d, ^3J = 10.3 Hz, Ph, *meta*) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 128.5 (s) ppm. $C_{27}H_{35}ClF_6OP_2Ru$ (688.04): calcd. C 47.13, H 5.13, Cl 5.15, P 9.00; found C 46.85, H 5.27, Cl 4.97, P 9.20.

[Ru(Cp*)Br(Ph_2POMe)($MeCHCHCH_2$)][PF_6] (8c): An excess of crotyl bromide (0.40 mL, 3.9 mmol) was added to a solution of **2a** (0.86 g, 1.27 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the solution was covered with diethyl ether (120 mL) to afford orange crystals. Yield: 0.72 g, 77%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.53 (dd, $^3J_{HH}$ = 6.1, $^4J_{PH}$ = 1.5 Hz, 3 H, Me), 1.76 (broad d, $^3J_{HHtrans}$ = 10.0 Hz, 1 H, CH_2, *anti*), 1.87 (d, $^4J_{PH}$ = 2.0 Hz, 15 H, C_5Me_5), 3.21 (dddd, $^3J_{HHtrans}$ = 11.1 and 9.9, $^3J_{HHcis}$ = 5.9, $^3J_{PH}$ = 3.6 Hz, 1 H, CH), 3.59 (d, $^3J_{PH}$ = 11.0 Hz, 3 H, OMe), 3.71 (ddq, $^3J_{HHtrans}$ = 11.0, $^3J_{HH}$ = 6.2, $^3J_{PH}$ = 3.2 Hz, 1 H, C*H*Me), 3.85 (ddd, $^3J_{HHcis}$ = 6.0, $^2J_{HH}$ = 2.2, $^3J_{PH}$ = 8.4 Hz, 1 H, CH_2, *syn*), 7.38–7.72 (m, 10 H, Ph) ppm. $^1H\{^{31}P\}$ NMR (200.13 MHz, CD_2Cl_2, selected values): δ = 1.79 (d, $^3J_{HHtrans}$ = 10.2 Hz, 1 H, CH_2, *anti*), 3.22 (dt, $^3J_{HHtrans} \approx$ 10.5, $^3J_{HHcis}$ = 6.4 Hz, 1 H, CH), 3.71 (dq, $^3J_{HHtrans}$ = 11.7, $^3J_{HH}$ = 6.1 Hz, 1 H, C*H*Me), 3.87 (broad d, $^3J_{HHcis}$ = 4.3 Hz, 1 H, CH_2, *syn*) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 10.5 (s, C_5Me_5), 15.1 (d, ^3J = 1.6 Hz, CH*Me*), 53.1 (d, ^2J = 4.4 Hz, CH_2), 58.8 (d, ^2J = 14.8 Hz, OMe), 96.3 (s, CH), 96.9 (d, ^2J = 4.8 Hz, *C*HMe), 106.5 (d, ^2J = 1.7 Hz, C_5Me_5), 127.5 (d, ^1J = 50.9 Hz, Ph, *ipso*), 128.6 (d, ^2J = 10.3 Hz, Ph, *ortho*), 129.5 (d, ^2J = 10.1 Hz, Ph, *ortho*),

130.8 (d, ^1J = 45.0 Hz, Ph, *ipso*), 132.1 (d, ^3J = 8.6 Hz, Ph, *meta*), 133.1 (d, ^4J = 2.1 Hz, Ph, *para*), 133.8 (d, ^4J = 2.2 Hz, Ph, *para*), 137.0 (d, ^3J = 11.1 Hz, Ph, *meta*) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 128.7 (s) ppm. $C_{27}H_{35}BrF_6OP_2Ru$ (732.49): calcd. C 44.27, H 4.82, Br 10.91, P 8.46; found C 44.18, H 4.80, Br 10.57, P 7.96.

[Ru(Cp*)Cl(Ph$_2$POMe)(*n*PrCHCHCH$_2$)][PF$_6$] (8d): An excess of chlorohexene (0.80 mL of a 4:1 mixture of linear 1-chloro-2-hexene and branched 3-chloro-1-hexene) was added to a solution of **2a** (1.84 g, 2.71 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the solution was covered with diethyl ether (150 mL) to afford orange-yellow crystals. Yield: 1.65 g, 85%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 0.92 (m, broad, 3 H, Me), 1.49 (m, broad, 4 H, 2 CH_2), 1.78 (d, $^4J_{PH}$ = 2.2 Hz, 15 H, C_5Me_5 and overlapped: m, 1 H, CH_2, *anti*), 3.32 (m, 1 H, CH), 3.67 (d, $^3J_{PH}$ = 10.8 Hz, 3 H, OMe and overlapped: m, 1 H, *n*PrC*H*), 3.86 (ddd, $^3J_{HHcis}$ = 5.9, $^2J_{HH}$ = 2.2, $^3J_{PH}$ = 8.2 Hz, 1 H, CH_2, *syn*), 7.42–7.68 (m, 10 H, Ph) ppm. $^1H\{^{31}P\}$ NMR (200.13 MHz, CD_2Cl_2): δ = 0.94 (m, broad, 3 H, Me), 1.51 (m, broad, 4 H, 2 CH_2), 1.80 (s, 15 H, C_5Me_5 and overlapped: m, 1 H, CH_2, *anti*), 3.34 (ddd, $^3J_{HHtrans} \approx {}^3J_{H'Htrans} \approx$ 10.5, $^3J_{HHcis}$ = 6.1 Hz,1 H, CH), 3.69 (s, 3 H, OMe and overlapped: m, 1 H, *n*PrC*H*), 3.88 (dd, $^3J_{HHcis}$ = 6.1, $^2J_{HH}$ = 2.1 Hz, 1 H, CH_2, *syn*), 7.47–7.70 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 9.9 (s, C_5Me_5), 14.0 (s, CH_3), 23.1 (s, CH_2), 33.9 (s, CH_2) 53.3 (s, =CH_2), 58.5 (d, ^2J = 15.0 Hz, OMe), 96.1 (s, CH), 100.4 (d, ^2J = 4.4 Hz, *n*Pr*C*H), 106.5 (d, ^2J = 1.8 Hz, C_5Me_5), 126.2 (d, ^1J = 49.1 Hz, Ph, *ipso*), 128.4 (d, ^2J = 10.7 Hz, Ph, *ortho*), 129.2 (d, ^2J = 9.9 Hz, Ph, *ortho*), 130.6 (d, ^1J = 45.1 Hz, Ph, *ipso*), 131.6 (d, ^3J = 8.5 Hz, Ph, *meta*), 132.7 (d, ^4J = 2.6 Hz, Ph, *para*), 133.3 (d, ^4J = 2.3 Hz, Ph, *para*), 136.2 (d, ^3J = 10.6 Hz, Ph, *meta*) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 128.2 (s) ppm. $C_{29}H_{39}ClF_6OP_2Ru$ (716.09): calcd. C 48.64, H 5.49, Cl 4.95, P 8.65; found C 48.39, H 5.55, Cl 5.16, P 8.72.

[Ru(Cp*)Cl(Ph$_2$POMe)(PhCHCHCH$_2$)][PF$_6$] (8e): An excess of cinnamyl chloride (0.60 mL, 4.3 mmol) was added to a solution of **2a** (1.00 g, 1.47 mmol) in dichloromethane (25 mL). After being stirred for 20 h, the solution was covered first with methanol (15 mL), then diethyl ether (130 mL) to afford dark red crystals. Yield: 0.68 g, 62%. ^1H NMR (200.13 MHz, CD_2Cl_2): δ = 1.79 (d, $^4J_{PH}$ = 1.9 Hz, 15 H, C_5Me_5), 2.12 (d, broad, $^3J_{HH}$ = 9.2 Hz, 1 H, CH_2, *anti*), 3.71 (d, $^3J_{PH}$ = 11.0 Hz, 3 H, OMe), 3.79–3.93 (m, broad, 1 H, CH), 3.94–4.03 (m, 1 H, CH_2, *syn*), 4.73 (dd, $^3J_{HH}$ = 12.0, $^3J_{PH}$ = 3.1 Hz, 1 H, C*H*Ph), 6.94–7.70 (m, 15 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ = 10.0 (s, C_5Me_5), 51.4 (d, ^2J = 5.0 Hz, CH_2), 58.5 (d, ^2J = 14.9 Hz, OMe), 91.0 (s, CH), 103.4 (d, ^2J = 4.7 Hz, *C*HPh), 106.3 (s, C_5Me_5), 127.0 (s, Ph, *ipso*), 128.4 (s, Ph, *ortho*), 128.4 (d, ^2J = 10.0 Hz, PhP, *ortho*), 129.3 (d, ^2J = 10.0 Hz, PhP, *ortho*), 131.2 (d, ^1J = 44.5 Hz, PhP, *ipso*), 131.5 (d, ^3J = 8.6 Hz, PhP, *meta*), 131.5 (s, Ph, *para*), 132.3 (s, Ph, *meta*), 132.5 (d, ^1J = 34.5 Hz, PhP, *ipso*), 133.0 (d, ^4J = 2.6 Hz, PhP, *para*), 133.4 (d, ^4J = 2.3 Hz, PhP, *para*), 136.0 (d, ^3J = 10.3 Hz, PhP, *meta*) ppm. $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2): δ = 129.0 (s) ppm. $C_{32}H_{37}ClF_6OP_2Ru$ (750.11): calcd. C 51.24, H 4.97, Cl 4.73, P 8.26; found C 51.05, H 5.08, Cl 4.65, P 8.49.

X-ray Crystallography: The samples were studied with a NONIUS Kappa CCD (**2a**, **8d**) or Oxford Diffraction Xcalibur Saphir 3 (**8e**) diffractometer with graphite monochromator. Crystallographic

Table 5. Crystallographic data for complexes **2a**, **8d** and **8e**.[a]

Complex	**2a**	**8d**	**8e**
Empirical formula	$C_{27}H_{34}F_6N_2OP_2Ru$	$C_{29}H_{39}ClF_6OP_2Ru$	$C_{32}H_{37}ClF_6OP_2Ru$
Molecular weight [g mol^{-1}]	679.57	716.06	750.08
Crystal size [mm]	0.30 × 0.30 × 0.28	0.22 × 0.22 × 0.22	0.24 × 0.22 × 0.20
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	*Pbca*	*Pbca*
a [Å]	14.8025(2)	14.6192(2)	14.8064(6)
b [Å]	11.5147(1)	20.5531(2)	21.0835(8)
c [Å]	17.0685(2)	20.7975(2)	20.6072(9)
β [°]	90.258(1)		
Volume [Å^3]	2909.23(6)	6248.0(1)	6433.0(5)
Z	4	8	8
Density [g cm^{-3}]	1.552	1.522	1.549
Temperature [K]	130(1)	293(2)	293(2)
F(000)	1384	2928	3056
Mo-K_α radiation, λ [Å]	0.71073	0.71073	0.71073
Absorption coefficient [mm^{-1}]	0.711	0.747	0.730
θ range [°]	2.39–27.48	2.21–27.00	3.08–27.00
Index ranges	$0 < h < 19$	$0 < h < 18$	$-12 < h < 12$
	$0 < k < 14$	$0 < k < 26$	$-26 < k < 26$
	$-22 < l < 22$	$0 < l < 26$	$-26 < l < 26$
Reflections collected	52105	105939	27593
Independent reflections	6652 (R_{int} = 0.030)	6811 (R_{int} = 0.050)	5899 (R_{int} = 0.0519)
Reflections $I > 2\sigma(I)$	6121	5637	4981
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	6652/0/371	6811/0/374	5899/0/389
Goodness-of-fit on F^2	1.065	1.003	1.086
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0374	R_1 = 0.0492	R_1 = 0.0545
	wR_2 = 0.0968	wR_2 = 0.1347	wR_2 = 0.1411
R indices (all data)	R_1 = 0.0408	R_1 = 0.0612	R_1 = 0.0642
	wR_2 = 0.1004	wR_2 = 0.1514	wR_2 = 0.1507
Largest diff. peak/hole [e Å^{-3}]	1.005 and –0.797	0.709 and –0.734	0.982 and –0.786

[a] $w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 6.0599P]$ (**2a**), $1/[\sigma^2(F_o^2) + (0.0843P)^2 + 11.8733P]$ (**8d**), $1/[\sigma^2(F_o^2) + (0.0754P)^2 + 15.1442P]$ (**8e**), where $P = (F_o^2 + 2F_c^2)/3$.

data are given in Table 5. The cell parameters were obtained with Denzo and Scalepack[18] (**2a**, **8d**) and data collection with NONIUS KappaCCD Software[19] (**2a**, **8d**) and CrysAlis RED[20] (**8e**). Data reduction was carried out with Denzo and Scalepack[18] (**2a**, **8d**) and CrysAlis RED[20] (**8e**). The structures were solved with SIR−97, which revealed the non-hydrogen atoms.[21] After anisotropic refinement, many hydrogen atoms were found with Fourier difference calculations. The whole structures were refined with SHELXL97 by full-matrix least-squares methods on F^2 (x, y, z, β_{ij} for Ru, P, N, Cl, F, C and O atoms; x, y, z in riding mode for H atoms).[22] ORTEP views were prepared with PLATON98.[23]

CCDC-261933 (for **2a**), -272359 (for **8d**) and -258428 (for **8e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic Experiments: Organic compounds were identified from the comparison of ^{1}H NMR spectra with available ^{1}H NMR spectroscopic data.[24–26] In a typical experiment, a sample of phenol (1.2 mmol, 1.2 equiv.) was added to a stirred mixture consisting of allylic halide (1.0 mmol, 1.0 equiv.), catalyst precursor (0.015 mmol, 1.5 mol-%), K_2CO_3 (1.2–1.5 equiv.) and solvent (6.0 mL). The slurry was stirred at room temperature for 16 h and then was evaporated under vacuum. The residue was extracted with dichloromethane (20 mL) and the solution was filtered. The filtrate was evaporated to leave the crude product that was analysed by ^{1}H NMR spectroscopy ($CDCl_3$) for conversion and regioselectivity determination.

[1] B. M. Trost, P. L. Fraisse, Z. T. Ball, *Angew. Chem. Int. Ed.* **2002**, *41*, 1059–1061.
[2] M. D. Mbaye, B. Demerseman, J.-L. Renaud, L. Toupet, C. Bruneau, *Adv. Synth. Catal.* **2004**, *346*, 835–841.
[3] M. D. Mbaye, J.-L. Renaud, B. Demerseman, C. Bruneau, *Chem. Commun.* **2004**, 1870–1871.
[4] Y. Matsushima, K. Onitsuka, T. Kondo, T. Mitsudo, S. Takahashi, *J. Am. Chem. Soc.* **2001**, *123*, 10405–10406.
[5] T. Kondo, H. Ono, N. Satabe, T. Mitsudo, Y. Watanabe, *Organometallics* **1995**, *14*, 1945–1953.
[6] Y. Matsushima, K. Onitsuka, S. Takahashi, *Organometallics* **2004**, *23*, 3763–3765.
[7] R. Schmid, K. Kirchner, *Eur. J. Inorg. Chem.* **2004**, 2609–2626.
[8] E. Rüba, W. Simanko, K. Mauthner, K. M. Soldouzi, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1999**, *18*, 3843–3850.
[9] E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, E. Bustelo, M. C. Puerta, P. Valerga, *Organometallics* **2002**, *21*, 2912–2920.
[10] P. Crochet, B. Demerseman, M. I. Vallejo, M. P. Gamasa, J. Gimeno, J. Borge, S. García-Granda, *Organometallics* **1997**, *16*, 5406–5415.
[11] M. A. Esteruelas, A. V. Gómez, F. J. Lahoz, A. M. López, E. Oñate, L. A. Oro, *Organometallics* **1996**, *15*, 3423–3435.
[12] M. D. Mbaye, B. Demerseman, J.-L. Renaud, L. Toupet, C. Bruneau, *Angew. Chem. Int. Ed.* **2003**, *42*, 5066–5068.
[13] R. Hermatschweiler, I. Fernández, P. S. Pregosin, E. J. Watson, A. Albinati, S. Rizzato, L. F. Veiros, M. J. Calhorda, *Organometallics* **2005**, *24*, 1809–1812.
[14] R. Hermatschweiler, I. Fernández, F. Breher, P. S. Pregosin, L. F. Veiros, M. J. Calhorda, *Angew. Chem. Int. Ed.* **2005**, *44*, 4397–4400.
[15] B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2944.
[16] C. D. Hurd, R. W. McNamee, *J. Am. Chem. Soc.* **1932**, *54*, 1648–1651.
[17] M. Julia, J.-N. Verpeaux, T. Zahneisen, *Bull. Soc. Chim. Fr.* **1994**, *131*, 539–554.
[18] Processing of X-ray diffraction data collected in oscillation mode: Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
[19] *NONIUS KappaCCD Software*, Nonius BV, Delft, The Netherlands, **1999**.
[20] Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, **2004**.
[21] *SIR-97* – a new tool for crystal structure determination and refinement: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74–77.
[22] G. M. Sheldrick, *SHELXL97 – Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
[23] A. L. Spek, *PLATON – A Multipurpose Crystallographic Tool*, University of Utrecht, The Netherlands, **1998**.
[24] F. Lopez, T. Ohmura, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 3426–3427.
[25] T. Satoh, M. Ikeda, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 4877–4879.
[26] C. Goux, M. Massacret, P. Lhoste, D. Sinou, *Organometallics* **1995**, *14*, 4585–4593.

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