Ruthenium-Catalyzed *O*-Allylation of Phenols from Allylic Chlorides *via* Cationic [Cp*(η³-allyl)(MeCN)RuX][PF$_6$] Complexes

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Dedicated to Dr. Joe P. Richmond on the occasion of his 60th birthday in appreciation of his expertise and tremendous activity in the field of scientific publishing.

Abstract: The [Cp*(MeCN)$_3$Ru(II)][PF$_6$] complex is an efficient catalyst precursor for the *O*-allylation of phenols with allylic chlorides in the presence of K_2CO_3 under mild conditions. This ruthenium precursor affords branched allyl aryl ethers according to a regioselective reaction, which contrasts with the uncatalyzed nucleophilic substitution from the same substrates. Stable (η³-allyl)Ru(IV) cationic complexes resulting from the reaction of [Cp*(MeCN)$_3$Ru][PF$_6$] with allylic halides were identified as intermediate catalytic species. An X-ray structure determination of the complex [Cp*(MeCHCHCH$_2$)(MeCN)RuBr][PF$_6$] disclosed an (*endo-trans*-MeCHCHCH$_2$) allylic ligand. The structural information obtained from the study of Cp*(allyl)Ru(IV) complexes indicated that electronic effects at the coordinated allylic ligand likely account for the better regioselectivity obtained from cinnamyl chloride as compared to aliphatic allylic chlorides.

Keywords: allylation; allylic ligands; homogeneous catalysis; regioselectivity; ruthenium

Introduction

The oxidative addition of allylic halides to neutral Cp*Ru(II) centers generating Cp*(η³-allyl)XRu(IV) complexes undoubtedly provides a crucial key for the understanding of ruthenium-catalyzed allylic substitution reactions.[1–4] Thus, the neutral complex Cp*(η³-PhCHCHCH$_2$)RuCl$_2$ was isolated and structurally characterized when the complex Cp*(cod)RuCl was involved as a catalyst precursor.[5] Of primordial interest, nucleophilic additions at unsymmetrical allylic ligands were shown to favor the formation of branched organic compounds, and a remarkably high regioselectivity was reached using [Cp*(MeCN)$_3$Ru][PF$_6$] as a cationic catalyst precursor.[6,7] We have recently reported that new dicationic Cp*(η³-allyl)Ru(IV) complexes containing a bipyridine ligand are also efficient catalysts for the allylic substitution reaction.[8] By contrast, a monocationic Cp*(η³-allyl)Ru(IV) complex containing nitrogen donor ligands has revealed a sluggish catalytic activity.[9]

Allyl aryl ethers are valuable intermediates in organic chemistry. Through a regioselective addition to unsymmetrical allylic ligands from allylic carbonates, enantioselective syntheses of branched allyl aryl ethers have been achieved by using chiral iridium or rhodium catalysts.[10,11] On the other hand, palladium catalysts most often favored the formation of linear allyl aryl ethers.[12–14] An alternative copper-catalyzed etherification of allylic alcohols with aryltrifluoroborate salts has been reported recently.[15] By contrast, the involvement of aryloxide anions as nucleophiles in ruthenium-catalyzed allylation is rare.[7]

In our ongoing work on ruthenium allylic species, we report herein that the readily available [Cp*(MeCN)$_3$Ru][PF$_6$] complex reacts with allylic halides to afford the new [Cp*(η³-allyl)(MeCN)RuX][PF$_6$] complexes, and behaves as an efficient catalyst precursor for the ruthenium-catalyzed synthesis of allyl aryl ethers from allylic chlorides and phenols. Electrophilic Cp*(η³-allyl)ClRu(IV) intermediates are likely the key for the se-

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lective formation of branched ethers when the allylic ligand is unsymmetrical.

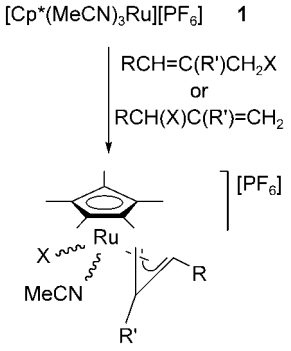
Results and Discussion

Synthesis of Complexes 2a–f

A slight change in color was immediately observed when an allylic halide was added at room temperature to a solution of $[Cp^*(MeCN)_3Ru][PF_6]$ (**1**) in acetonitrile under argon. Indicating also that a fast reaction had occurred, the solution was now stable in air and the addition of diethyl ether subsequently allowed the isolation of orange to red crystals of **2a–f** in 68–92% yield (Scheme 1). Complex **2a** was thus easily prepared from allyl chloride, **2b** from 3-chloro-2-methylpropene, **2c** from crotyl chloride or alternatively from 3-chloro-1-butene, **2d** from crotyl bromide, **2e** from a mixture of 1-chloro-2-hexene and 3-chloro-1-hexene (4:1), and **2f** from cinnamyl chloride.

The new complexes are weakly soluble in halogenated hydrocarbons (**2c–f**) such as $CDCl_3$ or CD_2Cl_2 but are very soluble in acetonitrile, and were found to be stable in air at least in the solid state. Complexes **2a–f** were characterized from a combination of ^1H, $^{13}C\{^1H\}$, and ^{13}C DEPT NMR spectroscopy, elemental analysis, and an X-ray structure determination of **2d**. The ^1H NMR spectra of **2a–f** were consistent with the presence of an η^3-coordinated allylic fragment and showed **2a** and **2b** (which both involve a symmetrical allylic ligand) as single species in solution. By contrast, the ^1H NMR spectra of **2c–f** (which contain an unsymmetrical allylic ligand) showed the presence of two species, suggesting a non-stereoselective coordination of the unsymmetrical allylic fragment relative to the two distinct halide and acetonitrile ligands (Scheme 2). The ratio between the two isomers, as determined by ^1H NMR spectroscopy, was unaffected after attempts at fractional crystallization but was affected by the nature of the solvent. These observations suggest a dynamic equilibrium between the two species. Of interest, the ^1H NMR spectra recorded from a CD_3CN solution showed only uncoordinated CH_3CN, thus revealing that a fast substitution of the acetonitrile ligand by CD_3CN rapidly occurred in solution. Such a behavior might account for a fast equilibrium between the two stereoisomers of **2c–f**. For both stereoisomers, the ^1H NMR resonance of the RCH allylic proton disclosed, when available, a high ^3J coupling constant values (close to 11 Hz) indicating an *anti* configuration. The synthesis of the bromo derivative **2d** afforded crystals of high quality. An X-ray structure determination revealed **2d** to form a monohydrate adduct and showed the ruthenium atom to be coordinated to a π-bonded C_5Me_5 ring, an η^3-$CH_2CHCHMe$ allylic fragment displaying an *endo* orientation, and to an acetonitrile and a bromide ligand. An ORTEP view of **2d** is shown in Figure 1 and selected bond distances and angles are reported in the caption.

It is worth to mention that an *endo* orientation of the allylic ligand in **2c–f** and an *anti* position of the RCH proton avoid steric hindrance between the R group and the C_5Me_5 ring. The observation of close Br–Ru–CH_2 and N–Ru–CHMe angles [81.7(2) and 82.7(2)°, respectively] provides evidence for a lack of steric constraints in **2d**, that agrees with the presence of the two stereoisomers in solution, both as enantio-



2a: R = R' = H, X = Cl
2b: R = H, R' = Me, X = Cl
2c: R = Me, R' = H, X = Cl
2d: R = Me, R' = H, X = Br
2e: R = *n*-Pr, R' = H, X = Cl
2f: R = Ph, R' = H, X = Cl

Scheme 1. Synthesis of the new complexes **2a–f**.

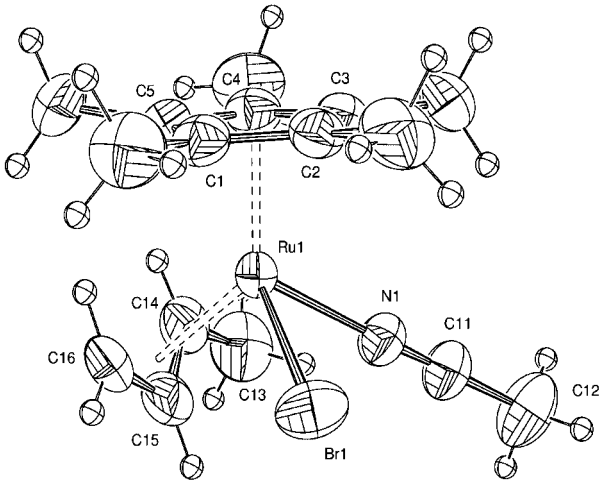
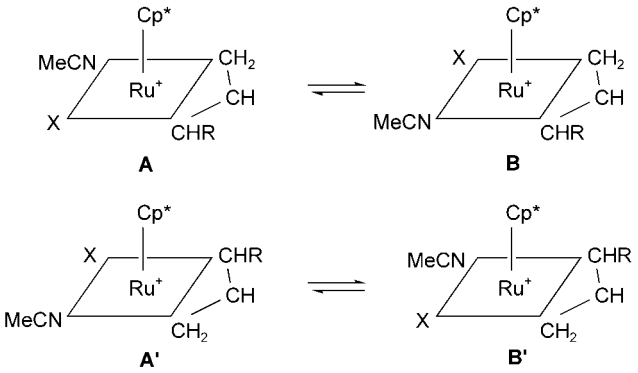


Figure 1. ORTEP drawing of **2d** showing 50% thermal ellipsoids; selected bond distances (Å) and angles (°): Ru(1)–Br(1) 2.552(6), Ru(1)–N(1) 2.077(4), Ru(1)–C(14) 2.280(5), Ru(1)–C(15) 2.165(5), Ru(1)–C(16) 2.208(4), C(13)–C(14) 1.495(8), C(14)–C(15) 1.403(8), C(15)–C(16) 1.394(7), Br(1)–Ru(1)–N(1) 82.2(1), Br(1)–Ru(1)–C(16) 81.7(2), N(1)–Ru(1)–C(14) 82.7(2), C(13)–C(14)–C(15) 123.5(5), C(14)–C(15)–C(16) 115.8(5); the PF_6 anion and the water molecule are omitted for clarity.



Scheme 2. Simple representation of the two stereoisomers of **2c–f** as their enantiomeric pairs **AA'** and **BB'** (the formation of **2c–f** is diastereoselective with respect to the chiral CHR and CH carbon atoms).

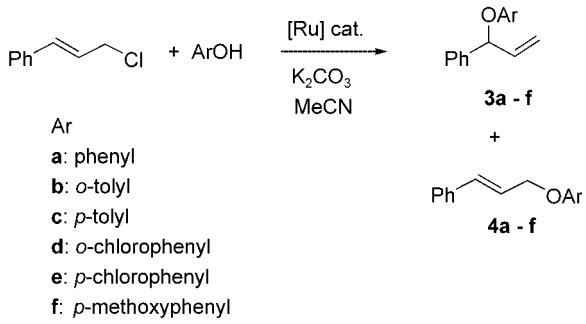
meric pairs arising from a chiral metal center (Scheme 2).

The coordination of a $CH_2CHCHPh$ allylic ligand in other Cp*Ru(IV) complexes has been depicted as involving a minor contribution of an olefinic coordination of a formal $CH_2{=}CH{-}C^{(+)}HPh$ moiety, on the basis of the observation of close Ru–CH_2 and Ru–CH bond lengths [2.196(3) Å and 2.197(3) Å, respectively] besides a longer Ru–CHPh bond [2.398(3) Å].[8] Emphasizing that an analogous contribution of a $CH_2{=}CH{-}C^{(+)}HMe$ HMe olefinic coordination is at least markedly reduced in **2d**, the Ru–CHMe bond [2.280(5) Å] is slightly longer [0.072 *vs.* 0.202 Å] than the Ru–CH_2 bond [2.208(4) Å] and a short Ru–CH bond [2.165(5) Å] is observed.

Ruthenium-Catalyzed Formation of Allyl Aryl Ethers from Cinnamyl Chloride and Phenols

The cationic Ru(IV) complexes **2a–f** are expected to be highly electrophilic, but further catalytic involvement will obviously require a nucleophilic reactant, which will be inert towards the free allylic chloride. Although a slow reaction may occur at room temperature, it is worthy of note that the reaction of allylic chlorides with phenols in the presence of K_2CO_3 requires a thermal activation. After prolonged heating, cinnamyl chloride is thus selectively converted to the corresponding linear ether $PhCH{=}CHCH_2OPh$.[16,17] The opposite regioselectivity was observed at room temperature when complex **1** was added as a catalyst to a mixture of cinnamyl chloride and K_2CO_3 in acetonitrile prior to the addition of phenol. Under typical conditions, the addition of phenol (1.0 to 1.6 equivalents) to a mixture of cinnamyl chloride (0.5 mmol), K_2CO_3 (excess), in 4 mL of acetonitrile in the presence of **1** (0.015 mmol, 3 mol %) led to the formation of the branched allyl phenyl ether **3a** as the major compound (Scheme 3). The consumption of cinnamyl chloride (60%) was not complete when an equimolar amount of phenol was used (Table 1). Total conversion was reached by using an excess of phenol but with a concomitant decrease in regioselectivity (Table 1). The reaction was also achieved on a preparative scale (3.50 g) to give the allylic ethers **3a** and **4a** in 78% overall yield and a 19:1 ratio (**3a**: 95%, **4a**: 5%).

The reaction could be extended to various substituted phenols such as *meta*- and *para*-cresol, 2-chlorophenol, 4-chlorophenol, or 4-methoxyphenol as functionalized phenols, and afforded the corresponding branched ethers **3b–f** with good regioselectivities (Table 1). It is worth noting that potassium carbonate generated the aryloxide anion *in situ*, and thus avoided a preliminary preparation of the nucleophile.



Scheme 3. Ruthenium-catalyzed synthesis of allyl aryl ethers from cinnamyl chloride.

Ruthenium-Catalyzed Synthesis of Allyl Phenyl Ethers from Aliphatic Allylic Chlorides

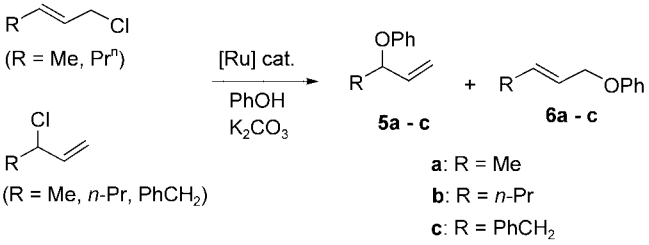
To take advantage of the regioselectivity induced by ruthenium catalysis offering an opportunity to develop a simple access to branched allyl aryl ethers starting from allylic chlorides, the involvement of aliphatic allylic chlorides in the catalytic process was then investigated. The isomeric 3-chloro-1-butene $MeCH(Cl)CH{=}CH_2$, and crotyl chloride $MeCH{=}CHCH_2Cl$ both react with phenol and K_2CO_3 in acetone at reflux to afford the corresponding branched and linear phenyl ethers $MeCH(OPh)CH{=}CH_2$, **5a**, and $MeCH{=}CHCH_2OPh$, **6a**, respectively.[18] We have verified that the reaction is sluggish at room temperature, especially with respect to 3-chloro-1-butene. Under our catalytic conditions (*vide supra*), the reaction of crotyl chloride led to a mixture of **5a** and **6a** in a 5:1 molar ratio as determined by ^1H NMR spectroscopy (Scheme 4). The regioselectivity was enhanced by using acetone instead of acetonitrile as a solvent, thus allowing us to reach an 8:1 ratio in favor of the branched ether **5a**. Crotyl chloride is too volatile to allow a significant determination of the conversion. On a preparative scale (4–5 g) the 8:1 mixture of **5a** and **6a** was obtained in an overall yield of 68% after distillation under vacuum and it should be mentioned that the linear ether **6a** consisted of a mixture of the *trans*

Table 1.

ArOH	Equivalent[a]	Conversion (%)[b]	Products	Ratio (**3**:**4**)[c]
Phenol	1	60	**3a, 4a**	50:1
Phenol	1.2	90	**3a, 4a**	53:1
Phenol	1.6	100	**3a, 4a**	42:1
Phenol	2	100	**3a, 4a**	29:1
m-Cresol	1	100	**3b, 4b**	36:1
p-Cresol	1.6	100	**3c, 4c**	38:1
2-Chlorophenol	1	100	**3d, 4d**	4:1
4-Chlorophenol	1.6	100	**3e, 4e**	40:1
4-Methoxyphenol	1	65	**3f, 4f**	36:1
4-Methoxyphenol	1.6	100	**3f, 4f**	40:1

Experimental conditions: catalyst 3 mol %, solvent: MeCN, room temperature, 40 h.
[a] Equivalent = ArOH/cinnamyl chloride molar ratio.
[b] Relative to cinnamyl chloride.
[c] As determined by ^{1}H NMR spectroscopy.

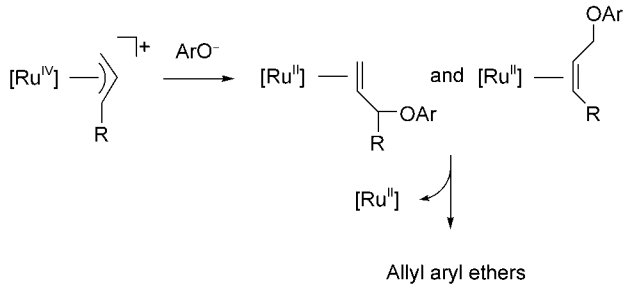
(very major) and *cis* (minor) isomers. The involvement of 3-chloro-1-butene instead of crotyl chloride in such a procedure resulted in a gain of regioselectivity (12:1). The isomeric chlorohexenes *n*-PrCH=CHCH$_2$Cl and *n*-PrCH(Cl)CH=CH$_2$ (as a 4:1 mixture) were also converted under our catalytic conditions into the phenyl ethers *n*-PrCH(OPh)CH=CH$_2$ **5b**, and *n*-PrCH=CHCH$_2$OPh **6b**, but the regioselectivity was lower (1.7:1 in acetonitrile, 2.4:1 in acetone). 3-Chloro-4-phenyl-1-butene, PhCH$_2$CH(Cl)CH=CH$_2$, is readily available from benzyl bromide and allyl chloride and was tested under our conditions.[19] Emphasizing that bulky groups such as *n*-Pr and PhCH$_2$ disfavor the regioselectivity, the phenyl ethers **5c** and **6c** were formed in a 1.5:1 ratio (in acetonitrile or acetone) but the conversion was found to be complete by ^{1}H NMR spectroscopy.



Scheme 4. Ruthenium-catalyzed synthesis of allyl phenyl ethers from aliphatic allylic chlorides.

Mechanistic Considerations

From a mechanistic point of view, the addition of an aryloxide anion to a cationic ruthenium(IV) allylic intermediate is likely involved in the catalytic process (Scheme 5). Such a reductive addition will generate a labile olefinic ruthenium(II) intermediate, allowing again oxidative addition of allylic chloride to occur at the ruthenium center. The molecular structure of **2d** suggested a less pronounced cationic charge at the RCH allylic center when R = alkyl than when R = Ph, in the intermediate (η^3-allyl)Ru(IV) species. This is in agreement with the observation of a better regioselectivity in favor of the branched isomers when cinnamyl chloride is compared to crotyl chloride.



Scheme 5. A plausible mechanism for the ruthenium-catalyzed formation of allyl aryl ethers.

Conclusion

The readily available tris-acetonitrile ruthenium(II) complex [Cp*(MeCN)$_3$Ru][PF$_6$] **1** is an active catalyst precursor for the synthesis of allyl aryl ethers starting from allylic chlorides and phenols and using K$_2$CO$_3$ as a base. The reaction takes place under mild conditions at room temperature and provides a regioselective formation of branched products, especially when an arylallylic chloride such as cinnamyl chloride is involved. As a key-step of the catalytic process and accounting for a favored formation of branched products, fast oxidative addition of allylic halides to the Ru(II) center will generate reactive electrophilic (η^3-allyl)Ru(IV) intermediates related to the stable [Cp*(allyl)(MeCN)RuX][PF$_6$] complexes.

Experimental Section

General Remarks

The reactions were performed under an argon atmosphere using Schlenk-type techniques. Diethyl ether and dichloromethane were distilled after drying according to conventional methods, whereas HPLC grade acetonitrile, acetone and methanol were used as obtained. Elemental analyses were performed by the Service de Microanalyse du CNRS, Vernaison, France. NMR spectra were recorded at 297 K on an AC 200 FT Bruker instrument (^{1}H: 200.13, ^{13}C: 50.32 MHz) and referenced internally to the solvent peak. 3-Chloro-4-phenyl-1-butene was prepared as reported previously.[19] The mixture of 1-chloro-2-hexene and 3-chloro-1-hexene (4:1) was obtained by reacting *trans*-3-hexen-1-ol with PCl_3.[20] The other allylic chlorides were commercially available compounds and were used without further purification. The synthesis of $[Cp^*(MeCN)_3Ru][PF_6]$ (**1**) was adapted from previous work as detailed below.[4,21]

$[Cp^*(MeCN)_3Ru][PF_6]$ (1)

A mixture consisting of $[Cp^*RuCl]_4$ (12.4 g, 11.4 mmol), KPF_6 (8.50 g, 46.2 mmol), and acetonitrile (100 mL) was stirred overnight and then heated to reflux to be filtered. The hot dark-orange filtrate deposited orange crystals of **1** upon cooling to 0 °C. The crystals were collected, then washed with methanol (20 mL) and diethyl ether (30 mL), and finally dried under vacuum. Yield: 16.1 g (70%).

Alternatively, a mixture consisting of $[Cp^*RuCl_2]_2$, granular zinc (in excess) and acetonitrile, was stirred overnight to afford a dark-orange solution. KPF_6 was then added and the mixture was treated as described above.

$[Cp^*(\eta^3\text{-}CH_2CHCH_2)(MeCN)RuCl][PF_6]\cdot 1/4CH_2Cl_2\cdot H_2O$ (2a)

To a solution of **1** (2.44 g, 4.84 mmol) in acetonitrile (40 mL), allyl chloride (1.00 mL, 12.3 mmol) was added. After being stirred for 10 min, the solution was evaporated under vacuum. The remaining solid was dissolved in dichloromethane (30 mL) and the solution was then covered with diethyl ether (100 mL) to afford orange crystals. Yield: 2.40 g (92%); ^{1}H NMR (CD_2Cl_2): $\delta = 1.70$ (s, 15H, C_5Me_5), 2.49 (s, 3H, MeCN), 2.61 (d, $^3J = 10.4$ Hz, 1H, CH*H*, *anti*), 2.71 (d, $^3J = 10.4$ Hz, 1H, CH*H*, *anti*), 4.17 (dd, $^3J = 6.1$, $^4J = 3.1$ Hz, 1H, CH*H*, *syn*), 4.33 (dd, $^3J = 6.2$, $^4J = 3.1$ Hz, 1H, CH*H*, *syn*), 5.28 (m, 1H, CH); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 4.65$ (*Me*CN), 9.83 (C_5Me_5), 65.50 (CH_2), 73.96 (CH_2), 98.85 (CH), 107.64 (C_5Me_5), 129.98 (Me*C*N); anal. calcd. for $C_{15}H_{23}ClF_6NPRu\cdot 1/4CH_2Cl_2\cdot H_2O$ (538.09): C 34.04, H 4.78, Cl 9.88, N 2.60, P 5.76; found C 33.80, H 4.56, Cl 10.56, N 2.69, P 5.96.

$[Cp^*(\eta^3\text{-}CH_2CMeCH_2)(MeCN)RuCl][PF_6]$ (2b)

Complex **2b** was similarly obtained starting from **1** (1.52 g, 3.01 mmol) and 3-chloro-2-methylpropene (0.60 mL, 6.14 mmol). Yield: 1.26 g (82%); ^{1}H NMR (CD_2Cl_2): $\delta = 1.71$ (s, 15H, C_5Me_5), 2.25 (s, 3H, Me), 2.51 (s, 1H, CH*H*, *anti*), 2.56 (s, 3H, MeCN), 2.71 (s, 1H, CH*H*, *anti*), 3.83 (d, $^4J =$ 3.3 Hz, 1H, CH*H*, *syn*), 4.05 (d, $^4J = 3.4$ Hz, 1H, CH*H*, *syn*); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 4.47$ (*Me*CN), 9.65 (C_5Me_5), 18.90 (Me), 61.90 (CH_2), 71.28 (CH_2), 107.41 (C_5Me_5), 113.98 (*C*Me), 129.93 (Me*C*N); anal. calcd. for $C_{16}H_{25}ClF_6NPRu$ (512.87): C 37.47, H 4.91, Cl 6.91, N 2.73; found C 37.68, H 5.00, Cl 6.65, N 2.84.

$[Cp^*(\eta^3\text{-}CH_2CHCHMe)(MeCN)RuCl][PF_6]$ (2c)

From crotyl chloride: To a solution of **1** (2.00 g, 3.96 mmol) in acetonitrile (30 mL), crotyl chloride (1-chloro-2-butene) (0.60 mL, 6.16 mmol) was added. After being stirred for 10 min, the solution was evaporated under vacuum. The residue was dissolved in dichloromethane (30 mL) and this solution was covered with diethyl ether (100 mL) to afford orange crystals. Yield: 1.70 g (84%).

From 3-chloro-1-butene: To a solution of **1** (2.05 g, 4.06 mmol) in acetonitrile (20 mL), 3-chloro-1-butene (0.60 mL, 5.86 mmol) was added. After being stirred for 10 min, the solution was diluted with dichloromethane (20 mL) then covered with diethyl ether (120 mL) to afford large dark-orange crystals. Yield: 1.80 g (86%).

Solutions in CD_2Cl_2 and CD_3CN were consistent with a mixture of two isomers in a 1:1 and 1.5:1 ratio, respectively, as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): $\delta =$ 1.53 and 1.61 (2 d, $^3J = 6.4$ and 6.4 Hz, 3H, *Me*CH), 1.70 and 1.71 (2 s, 15H, C_5Me_5), 2.53 and 2.58 (2 s, 3H, MeCN), 2.54 and 2.62 (broad d and d, $^3J = 9.0$ and 11.5 Hz, 1H, CH*H*, *anti*), 3.33–3.54 (m, 1 H, MeC*H*), 4.15 and 4.32 (dd and d, $^3J = 6.0$ and 6.2, $^4J = 0.6$ Hz, 1H, CH*H*, *syn*), 5.06–5.27 (m, 1 H, CH); ^{1}H NMR (CD_3CN, asterisk marks values for the minor isomer when distinct): $\delta = 1.47$* and 1.55 (2 d, $^3J = 6.2$* and 6.4 Hz, 3H, *Me*CH), 1.65* and 1.66 (2 s, 15H, C_5Me_5), 1.99 (s, 3H, MeCN), 2.59* and 2.66 (2 d, $^3J = 10.1$* and 10.1 Hz, 1H, CH*H*, *anti*), 3.43–3.61 (m, 1H, MeC*H*), 4.06* and 4.20 (2 d, $^3J = 6.2$* and 6.2 Hz, 1H, CH*H*, *syn*), 5.04–5.23 (m, 1H, CH); ^{13}C{^{1}H} NMR (CD_3CN, asterisk marks values for the minor isomer): $\delta = 9.01$ and 9.05* (C_5Me_5), 17.2* and 17.6 (*Me*CH), 62.0* and 69.9 (CH_2), 86.5 and 95.4* (Me*C*H), 99.0* and 99.3 (CH), 106.2* and 106.7 (C_5Me_5); anal. calcd. for $C_{16}H_{25}ClF_6NPRu$ (512.87): C 37.47, H 4.91; found C 37.54, H 4.95.

$[Cp^*(\eta^3\text{-}CH_2CHCHMe)(MeCN)RuBr][PF_6]\cdot H_2O$ (2d)

Complex **2d** was similarly obtained starting from **1** (2.00 g, 3.96 mmol) in acetonitrile (30 mL) and crotyl bromide (0.60 mL, 5.83 mmol). Yield: 1.61 g (71%). Solutions in CD_2Cl_2 or CD_3CN were consistent with a mixture of two isomers in a 4:1 ratio as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_2Cl_2, asterisk marks values for the minor isomer when distinct): $\delta = 1.59$* and 1.60 (2 d, $^3J = 6.2$* and 6.4 Hz, 3H, *Me*CH), 1.76* and 1.77 (2 s, 15H, C_5Me_5), 2.41 and 2.56* (2 d, $^3J = 10.1$ and 10.8* Hz, 1H, CH*H*, *anti*), 2.55* and 2.60 (2 s, 3H, MeCN), 3.41–3.27 (m, 1H, MeC*H*), 4.10* and 4.58 (2 d, $^3J = 6.2$* and 6.2 Hz, 1H, CH*H*, *syn*), 5.09–5.25 (m, 1H, CH); ^{1}H NMR (CD_3CN, asterisk marks values for the minor isomer when distinct): $\delta = 1.54$ (d, $^3J = 6.3$ Hz, 3H, *Me*CH), 1.72 (s,

15H, C_5Me_5), 1.99 (s, 3H, MeCN), 2.50 and 2.55* (2 d, $^3J=10.1$ and 10.5* Hz, 1H, CH*H*, *anti*), 3.33–3.51 (m, 1H, MeC*H*), 4.01* and 4.45 (2 d, $^3J=6.1$* and 6.3 Hz, 1H, CHH, *syn*), 5.07–5.21 (m, 1H, CH); $^{13}C\{^1H\}$ NMR (CD_3CN, asterisk marks values for the minor isomer): $\delta=9.35$ and 9.39* (C_5Me_5), 17.5 and 19.0* (*Me*CH), 62.0* and 66.9 (CH_2), 86.4 and 94.1* (MeCH), 98.3* and 98.6 (CH), 105.8* and 106.3 (C_5Me_5); anal. calcd. for $C_{16}H_{25}BrF_6NPRu$ (575.34): C 33.40, H 4.73, Br 13.89, N 2.43, P 5.38; found C 34.42, H 4.52, Br 13.87, N 2.76, P 5.10. The high carbon value suggests the loss of the molecule of water as calcd. for the anhydrous compound C 34.48.

[Cp*(η³-CH₂CHCHPr-*n*)(MeCN)RuCl][PF₆] (2e)

Complex **2e** was obtained as above in 68% yield starting from **1** and 1-chloro-2-hexene and 3-chloro-1-hexene as a (4:1) mixture. Solutions in CD_2Cl_2 and CD_3CN are consistent with a mixture of two isomers in a 1:1 and 1.5:1 ratio, respectively, as determined by ^1H NMR spectroscopy. ^1H NMR (CD_2Cl_2): $\delta=$ 1.05 and 1.10 (2 t, $^3J=7.1$ and 7.0 Hz, 3H, *Me*CH_2), 1.57–1.82 (m, very broad, 4H, C*H*$_2$C*H*$_2$), 1.70 and 1.71 (2 s, 15H, C_5Me_5), 2.53 and 2.57 (2 s, 3H, MeCN), 2.53 and 2.58 (2 d, $^3J=$ 10.2 and 9.9 Hz, 1H, CH*H*, *anti*), 3.15–3.38 (m, 1H, *n*-PrC*H*), 4.19 and 4.35 (dd and d, $^3J=6.1$ and 6.2 Hz, 1H, CH*H*, *syn*), 5.08–5.25 (m, 1H, CH); ^1H NMR (CD_3CN, asterisk marks values for the minor isomer when distinct) $\delta=1.01$* and 1.06 (2 t, $^3J=7.2$* and 7.2 Hz, 3H, *Me*CH_2), 1.52–1.79 (m, very broad, 4H, C*H*$_2$C*H*$_2$), 1.65* and 1.66 (2 s, 15H, C_5Me_5), 1.99 (s, 3H, MeCN), 2.59* and 2.67 (2 d, $^3J=9.9$* and 10.1 Hz, 1H, CH*H*, *anti*), 3.24–3.46 (m, 1H, *n*-PrC*H*), 4.09* and 4.23 (2 d, $^3J=$ 6.0* and 6.2, 1H, CH*H*, *syn*), 5.06 – 5.22 (m, 1H, CH); $^{13}C\{^1H\}$ NMR (CD_3CN, asterisk marks values for the minor isomer): $\delta=9.04$ and 9.11* (C_5Me_5), 13.3 and 13.5* (Me), 23.1* and 23.9 (Me*C*H$_2$), 34.3* and 34.6 (MeCH$_2$*C*H$_2$), 62.4* and 70.5 (CH_2, allyl), 90.3 and 98.4* (*n*-Pr*C*H), 98.9 and 99.3 (CH), 106.3* and 106.7 (C_5Me_5); anal. calcd. for $C_{18}H_{29}ClF_6$ NPRu (540.92): C 39.97, H 5.40, Cl 6.55, N 2.59, P 5.73; found C 40.10, H 5.50, Cl 6.23, N 2.65, P 5.60.

[Cp*(η³-CH₂CHCHPh)(MeCN)RuCl][PF₆] (2f)

Complex **2f** was also obtained in 68% yield as red crystals, starting from **1** and cinnamyl chloride. Solutions in CD_2Cl_2 or CD_3CN are consistent with a mixture of two isomers in a 3:1 ratio as determined by ^1H NMR spectroscopy. ^1H NMR (CD_2Cl_2, asterisk marks values for the minor isomer when distinct): $\delta=1.70$* and 1.71 (2 s, 15H, C_5Me_5), 2.11 and 2.55* (2 s, 3H, MeCN), 2.78 (d, $^3J=10.1$ Hz, 1H, CH*H*, *anti*), 4.30* and 4.46 (dd and d, $^3J=6.5$* and 6.4, $^4J=0.5$* Hz, 1H, CH*H*, *syn*), 4.55* and 4.60 (dd and d, $^3J=11.0$* and 11.2, $^4J=0.5$* Hz, 1H, PhC*H*), 5.64–5.78* and 5.87–6.01 (2 m, 1H, CH), 7.40–7.68 (m, 5H, Ph); ^1H NMR (CD_3CN, asterisk marks values for the minor isomer when distinct): $\delta=1.66$ (s, 15H, C_5Me_5), 1.99 (s, 3H, MeCN), 2.85* and 2.86 (2 d, $^3J=9.7$* and 9.6 Hz, 1H, CH*H*, *anti*), 4.19* and 4.35 (2 d, $^3J=6.2$* and 6.4, 1H, CH*H*, *syn*), 4.62* and 4.64 (2 d, $^3J=12.2$* and 11.2, 1H, PhC*H*), 5.79* and 5.92 (2 ddd, $^3J=11.8$*, 9.9*, 6.4* and 11.1, 9.7, 6.4 Hz, 1H, CH), 7.34–7.64 (m, 5H, Ph); $^{13}C\{^1H\}$ NMR (CD_3CN, asterisk marks values for the minor isomer when distinct): $\delta=9.20$ (C_5Me_5), 59.8* and 67.7 (CH_2), 91.4 and 101.2* (Ph*C*H), 93.2* and 94.0 (CH), 105.9* and 106.9 (C_5Me_5), 128.4–131.8 (Ph, CH carbon atoms), 134.1* and 134.9 (Ph, *ipso*); anal. calcd. for $C_{21}H_{27}ClF_6NPRu$ (574.94): C 43.87, H 4.73, Cl 6.17, N 2.44, P 5.39; found C 43.04, H 4.80, Cl 6.98, N 2.73, P 5.40.

X-ray Crystallographic Study

$C_{16}H_{25}BrF_6NPRu\cdot H_2O$, $M_r=575.34$, crystal size $0.40\times0.32\times$ 0.28 mm, monoclinic, space group $P2_1/c$, $Z=4$, $a=8.4097(1)$ Å, $b=15.1228(3)$ Å, $c=17.6318(4)$ Å, $\beta=93.595(1)^\circ$, $V=$ 2237.97(7) Å^3, $\delta_{calcd.}=1.708$ g cm^{-3}, T = 293(2) K, F(000) = 1144, Mo-K_α radiation ($\lambda=0.71069$ Å), $\mu=2.612$ mm^{-1}, 9810 reflections measured in the range $3.07^\circ=\theta=27.47^\circ$, 5098 unique ($R_{int}=0.02\%$) which were used in all calculations. The sample was studied with a Nonius Kappa CCD diffractometer with graphite monochromator. The cell parameters were obtained with Denzo and Scalepack.[22] The data collection ($2\theta_{max}=54^\circ$, 199 frames *via* 2.0° ω rotation and 20 s per frame, index ranges 0 = h = 10, 0 = k = 19, −22 = l = 22) gave 33539 reflections.[23] The data reduction led to 9810 independent reflections from which 4230 with $I>2\sigma(I)$ and 248 parameters, R_1(all data) = 0.0569, wR_2(all data) = 0.1355, goodness-of-fit on $F_2=$ 1.076. The structure was solved with SIR-97 which revealed the non-hydrogen atoms.[24] After anisotropic refinement, many hydrogen atoms may be found with Fourier difference calculations. The whole structure was refined with SHELXL97 by full-matrix least-squares on F^2 [x, y, z, β_{ij} for Ru, Br, P, F, C, O and N atoms; x, y, z in riding mode for H atoms; $w=1/[\sigma^2(F_0^2)+(0.075P)^2+2.94P]$ where $P=(F_0^2+2F_c^2)/3$ with the resulting $R_1=0.045$, $wR_2=0.127$ and $S=1.076$, $\Delta\rho<0.9$ eÅ^{-3}; minimum and maximum final electron density: −0.619 and 0.998 eÅ^{-3}.[25] ORTEP views were prepared with PLATON98.[26]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-225761. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

Catalytic Experiments

In a typical experiment, a 0.5 mmol sample of allylic chloride was added to a mixture consisting of K_2CO_3 (K_2CO_3/phenol molar ratio = 1.2, or 1 for aliphatic allylic chlorides), **1** (0.015 mmol) and acetonitrile or acetone (4.0 mL). Then, the phenol derivative was added and the mixture was stirred at room temperature for 40 h. The resulting slurry was evaporated under vacuum and the residue was extracted with dichloromethane (20 mL). The collected solution was filtered and the filtrate was evaporated to leave the crude product that was analyzed by ^1H NMR spectroscopy ($CDCl_3$).

1-Phenyl-1-phenoxy-2-propene (3a)

A 3.00 mL (21.5 mmol) sample of cinnamyl chloride was added to a mixture consisting of 4.16 g (30.1 mmol, 1.4 equivs.) of K_2CO_3, 0.33 g (0.65 mmol) of **1**, and acetonitrile (120 mL). Then, phenol (2.84 g, 30.2 mmol, 1.4 equivs.) was added and the mix-

ture was stirred at room temperature for 40 h. The resulting slurry was evaporated under vacuum and the residue was extracted with dichloromethane (100 mL) in several parts. The collected solution was filtered. Small amounts of NaH were added to the filtrate (to trap residual phenol) until evolution of gas ceased and the solution was filtered again. The filtrate was evaporated under vacuum to leave a pale brown oil consisting of a 19:1 mixture of the expected branched 1-phenyl-1-phenoxy-2-propene and linear aryl ethers, as determined by ^{1}H NMR spectroscopy.[10] Yield: 3.50 g (78%).

1-Methyl-1-phenoxy-2-propene (5a)

From crotyl chloride: A 4.85 mL (49.7 mmol) sample of crotyl chloride was added to a mixture consisting of 8.23 g (59.5 mmol) of K_2CO_3, 0.38 g (0.75 mmol) of **1**, and acetone (100 mL). Phenol (4.68 g, 49.7 mmol) was added and the mixture was stirred at room temperature for 20 h. Then, 0.38 g (0.75 mmol) of **1** was added again and the mixture was stirred for another 20 h. The resulting slurry was evaporated under vacuum and the residue was extracted with dichloromethane (100 mL) in several parts. After subsequent work-up as above, the crude oil was distilled under vacuum (bp: 38 °C/torr)[27] to obtain a pale-yellow oil. Yield : 5.00 g (68%).

From 3-chloro-1-butene: A 5.00 mL (49.7 mmol) sample of 3-chloro-1-butene was involved instead of crotyl chloride according to the same procedure. Yield: 4.60 g, 62%. The ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data are given elsewhere.[15]

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