

Ruthenium catalysts for selective nucleophilic allylic substitution*

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Abstract: Recent developments in the chemistry of η^3 -allylruthenium(IV) complexes are due to their straightforward synthesis resulting from oxidative addition of allylic substrates to a ruthenium(II) center. Subsequent reaction with a nucleophile is the basis of their involvement in the catalytic allylic substitution reaction. We focus here on ruthenium-catalyzed substitution of allylic substrates by C-, N-, and O-nucleophiles and show that selected ligands make regio- and enantioselective reactions possible.

Keywords: ruthenium catalysis; allylic substitution; regioselectivity.

INTRODUCTION

Ruthenium-catalyzed reactions have recently provided a great contribution to the development of new efficient organic syntheses [1–3]. Ruthenium derivatives usually tolerate functionalized substrates, and as they can accommodate a wide range of oxidation states, they present a very good ability to promote catalytic cycles with easy oxidation state modulation. This is probably one of the reasons why ruthenium catalysts are now used for almost all types of chemical transformations, from hydrogenation to oxidation, and involving C–C, C–H, and C-heteroatom bond activation and bond formation. Among these transformations, ruthenium derivatives are able to activate allylic substrates via oxidative addition to produce reactive η^3 -allylruthenium catalyst precursors. The ambiphilic reactivity of η^3 -allylruthenium species, where the allylic ligand can react either as an electrophile or a nucleophile depending on the nature of the other ancillary ligands, as well as other catalytic transformations involving allylic intermediates, have recently been reported [4,5].

We focus on recent studies on the development of ruthenium catalysts for nucleophilic substitution of allylic carbonates and halides via η^3 -allyl intermediates to produce allylic diketone and diester derivatives, aryl and alkyl allylic ethers, amines, and alcohols.

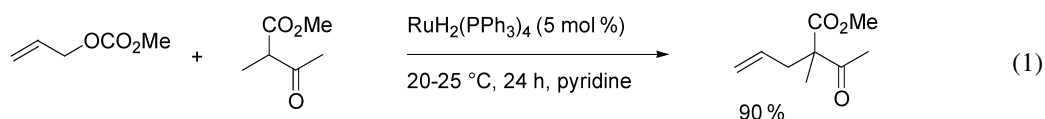
Ruthenium complexes in catalytic allylation of nucleophiles

To the best of our knowledge, the first utilization of ruthenium complexes to promote the nucleophilic substitution of allylic carbonates by stabilized carbonucleophiles was reported by J. Tsuji [6]. The ruthenium dihydride $\text{RuH}_2(\text{PPh}_3)_4$ catalyzed the allylation of methyl 2-methyl-3-oxobutanoate by allyl

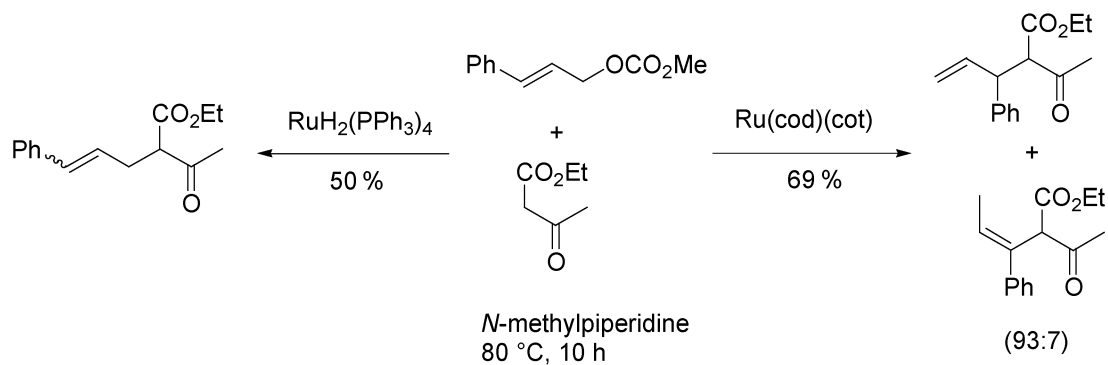
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methyl carbonate at room temperature in pyridine without previous deprotonation of the pronucleophile, to give the corresponding allylic ketoester in 90 % yield (eq. 1).



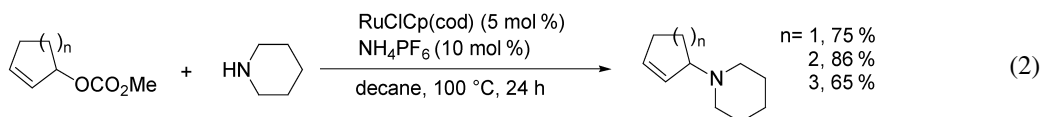
Starting from cinnamyl methyl carbonate, the allylation of ethyl acetoacetate in the presence of the same ruthenium(II) precatalyst, in *N*-methylpiperidine at 80 °C provided the (*E*)- and (*Z*)-isomers of 3-phenylprop-2-enyl acetoacetate in 50 % yield, whereas under similar conditions, the ruthenium(0) precursor Ru(cod)(cot) led to the major formation of 1-phenylprop-2-enyl acetoacetate in 69 % isolated yield (Scheme 1) [7].



Scheme 1

The formation of these two compounds via selective addition of the nucleophile at one of the two different termini of the activated unsymmetrical allylic fragment illustrates the versatility of the reaction and the influence of the nature of the ruthenium precursor.

Neutral ruthenium(II) complexes containing a cyclopentadienyl ligand have shown activity at high temperature. The amination of cyclic carbonates bearing an endocyclic allylic double bond has been reported with RuClCp(cod)/NH₄PF₆ as catalyst precursor in decane at 100 °C (eq. 2) [8]. The allylation of stabilized *C*-nucleophiles in the presence of RuClCp(cod) was also effective as dimethyl sodiomalonate reacted with the six-membered allylic carbonate to give the corresponding allylated product in 92 % yield.

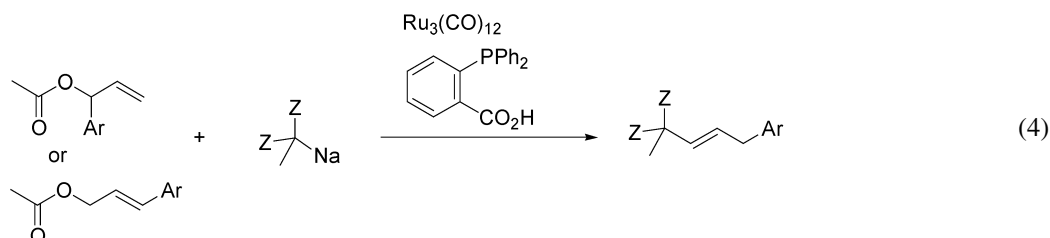


Cationic cyclopentadienyl ruthenium complexes are also able to generate π -allylruthenium(IV) species, which promote the catalytic cleavage of allyl esters and ethers to form acids and alcohols, respectively. Thus, [RuCp(PPh₃)(CH₃CN)₂]PF₆ efficiently catalyzes the ester deprotection via nucleophilic substitution by simple aliphatic alcohols, with concomitant formation of allyl ether (eq. 3) [9].



This system is completely inert to deprotect allyl ethers. However, the addition of one catalytic equivalent of 2-quinolinecarboxylic acid to $[\text{RuCp}(\text{CH}_3\text{CN})_3]\text{PF}_6$ provides a very efficient catalytic system, which makes possible the deprotection of various allyl ethers at 30 °C in methanol [10].

From these catalytic reactions with simple allyl derivatives, which generate unsubstituted allyl metal intermediate, it is not possible to conclude about their regioselectivity during the transformation of unsymmetrical substrates. It is noteworthy that very recently, a catalytic system generated from $\text{Ru}_3(\text{CO})_{12}$ and 2-diphenylphosphinobenzoic acid has led to the regioselective formation of linear compounds upon substitution of α - and γ -substituted allylic acetates by carbon nucleophiles (eq. 4) [11], whereas a catalytic system based on $[\text{RuCl}_2(p\text{-cymene})]_2/\text{PPh}_3$ gave a regiospecific allylation of various types of nucleophiles from allylic acetates [12].



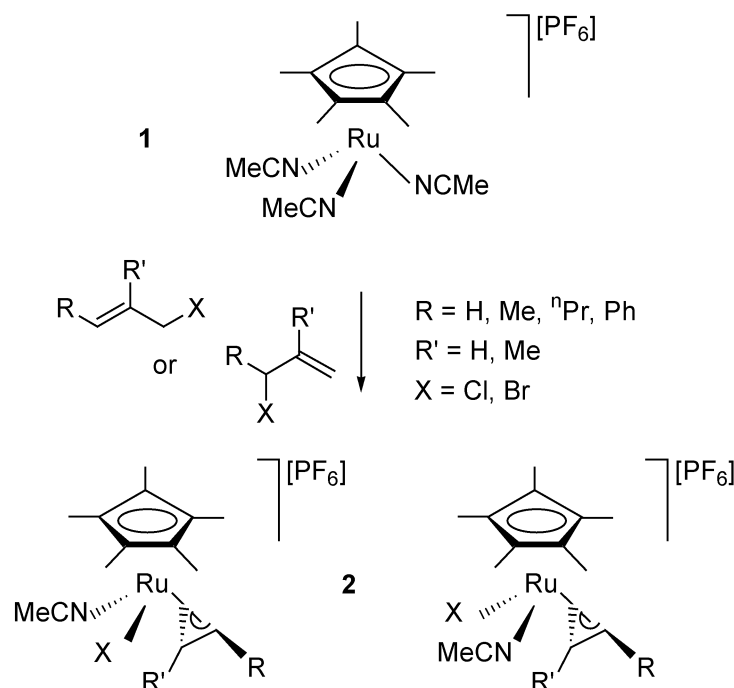
[Cp*Ru] catalysts for regioselective formation of branched compounds

Ruthenium complexes containing the bulky and electron-rich pentamethylcyclopentadienyl ligand have revealed remarkable activities for the preparation of branched products resulting from nucleophilic substitution of unsymmetrical allylic carbonates at low temperature. This regioselectivity is enhanced when the allylic fragment is substituted by an aromatic group as compared to an alkyl group. The reaction of piperidine with cinnamyl methyl carbonate thus provides a branched:linear (B:L) ratio of 84:16, whereas the reaction with *trans*-2-butenyl methyl carbonate leads to a 56:44 ratio [13].

With $\text{RuClCp}^*(\text{cod})$ as catalyst precursor, the allylation of stabilized carbon nucleophiles such as dimethyl malonate is also possible, and leads to monoallylation and diallylation products depending on the solvent and the nature of the pronucleophile [14,15]. $\text{RuClCp}^*(\text{cod})$ is also a very efficient pre-catalyst for the preparation of allyl thioethers from aliphatic and aromatic thiols under very mild conditions [15]. Other cationic $[\text{RuCp}^*]$ catalyst precursors bearing nitrogen-containing ligands were investigated. Trost et al. [16] reported that the branched product resulting from alkylation of allylic carbonates with malonate anion was obtained in good yield and with a high 19:1 ratio of B:L compound in the presence of only 1 mol % of $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ as catalyst. In the same reaction, it was noticed that the ancillary ligand plays a crucial role in the regioselectivity as the analog $[\text{CpRu}(\text{CH}_3\text{CN})_3][\text{PF}_6]$ precursor mainly led to the linear product. Recently, Pregosin and colleagues have also shown that $[\text{RuCp}^*]$ complexes containing either acetonitrile or carbonate ligands were very effective and selective catalysts for the formation of branched allylic compounds [17–20].

FORMATION OF η^3 -ALLYLRUTHENIUM(IV) COMPLEXES FROM $\text{Cp}^*\text{Ru(II)}$ PRECURSORS

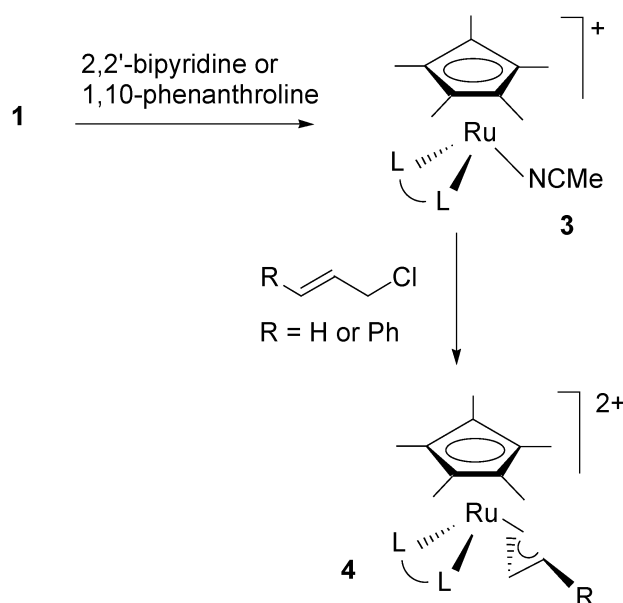
Oxidative addition of allylic halides to the highly reactive ruthenium(II) precursor $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{MeCN})_3][\text{PF}_6]$ (**1**) quantitatively yields the cationic η^3 -allylruthenium(IV) derivatives $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuX}(\eta^3\text{-C}_3\text{H}_5)(\text{MeCN})][\text{PF}_6]$ (**2**) (Scheme 2) [21].



Scheme 2

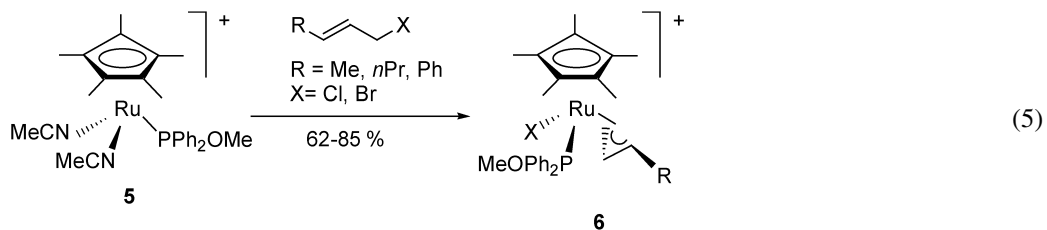
Complexes (**2**) are chiral at the metal center, and are obtained as single enantiomeric pairs when $\text{R} = \text{H}$, but the introduction of an unsymmetrical η^3 -allyl ligand results in the observation of two stereoisomers that disclose a dynamic equilibrium in solution. The expected *endo* configuration of the η^3 -allyl ligand is confirmed by the X-ray structure determination of one stereoisomer of complex (**2**) wherein $\text{R} = \text{Me}$, $\text{R}' = \text{H}$, $\text{X} = \text{Br}$.

2,2'-Bipyridyls as strong four-electron donor chelates react with complex (**1**) to generate complexes $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-N,N-bipyridine})\text{Ru}(\text{MeCN})][\text{PF}_6]$ (**3**) in very good yields. The stoichiometric reaction with allylic halides leads to the dicationic η^3 -allylruthenium(IV) derivatives (**4**) (Scheme 3) [22]. X-ray crystal structure determination of complex (**4**) arising from cinnamyl chloride ($\text{R} = \text{Ph}$), and containing the 1,10-phenanthroline ligand also reveals η^3 -cinnamyl ligand with an *endo* configuration.

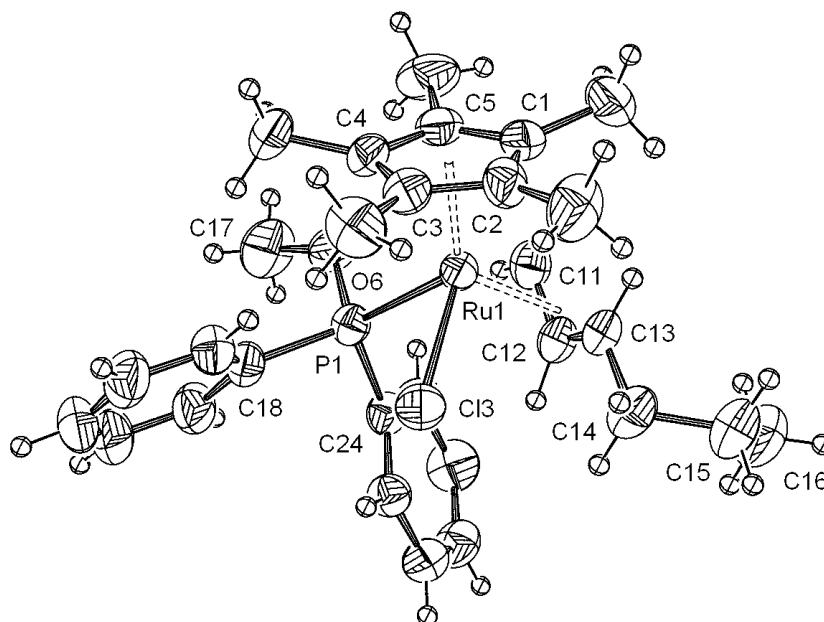


Scheme 3

Starting from the phosphinite-containing complex **5**, it was also possible to prepare the allylic complexes **6** in dichloromethane at room temperature in good yields (eq. 5) [23].



In the solid state, all these η^3 -allyl pentamethylcyclopentadienyl ruthenium(IV) complexes disclosed an *endo-trans*- CH_2CHCHR η^3 -allyl ligand (see Scheme 4 for a typical structure). The selected data collected in Table 1 allow a comparison between the (η^3 -allyl)Ru fragments of these complexes. The examination of bond lengths emphasizes for each complex a longer Ru-CHR bond relative to the Ru-CH₂ one ($0.072 \text{ \AA} < \Delta < 0.270$). The comparison of Ru-CH₂, and Ru-CH bond lengths in all the complexes reveals slight differences. The main variation concerns the Ru-CHR bond length. The Ru-CHAr bond lengths decreased from 2.452(4) Å in **6a** to 2.351(5) Å in **2a**, thus remarkably following the order of decreasing steric requirement from Ph₂POMe, Cl (**6a**) > N-N chelate (**4**) > MeCN, Cl (**2a**). However, the Ru-CHR bond is significantly shorter when R is an alkyl instead of an aryl group [2.280(5) Å in **2b** vs. 2.351(2) Å in **2a**; 2.339(4) Å in **6b** vs. 2.452(4) Å in **6a**], and thus becomes less distinct relative to the Ru-CH₂ bond distance. The CH-CH₂ and CH-CHR bond lengths are close as might be assumed for a true η^3 -allyl ligand. Results from density functional theory (DFT) calculations showed that the less negative carbon atom of the allylic moiety, thus more favorable to nucleophilic attack, was located at the substituted CHR terminus [17]. The structural analyses and calculations reveal that geometrically and electronically distorted η^3 -allylic ligands are present in these complexes.



Scheme 4 ORTEP drawing of complex **6b** showing 50 % probability thermal ellipsoids. The PF_6 anion is omitted for clarity.

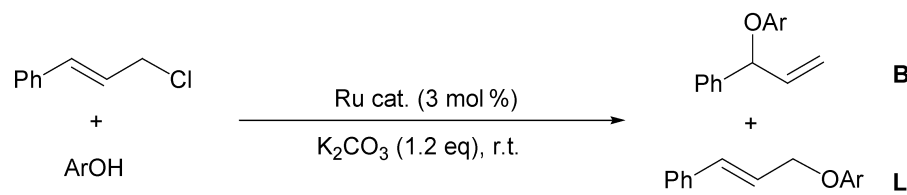
Table 1 Selected bond lengths (Å) in $\text{RuCp}^*(\eta^3\text{-allyl})$ complexes.

Complex	Ru–CH ₂	Ru–CHR	Ru–CH	Δ^a
2a (R' = H, R = Ph, X = Cl)	2.192(3)	2.351(2)	2.162(3)	0.159(5)
4 (R = Ph, L-L = phenanthroline)	2.196(3)	2.398(3)	2.197(3)	0.202(6)
6a (R = Ph, X = Cl)	2.182(5)	2.452(4)	2.210(4)	0.270(9)
2b (R' = H, R = Me, X = Br)	2.208(4)	2.280(5)	2.165(5)	0.072(9)
6b (R = nPr, X = Cl)	2.191(4)	2.339(4)	2.198(4)	0.148(8)

$$^a\Delta = (\text{Ru-CHR}) - (\text{Ru-CH}_2).$$

CATALYTIC ALLYLATION WITH CATALYSTS 1, 3, 5

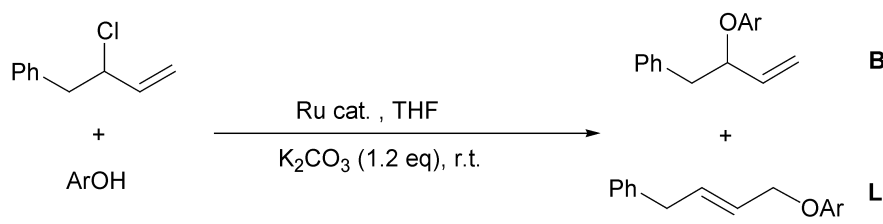
We have investigated the use of cinnamyl chloride to perform the regioselective etherification by phenol derivatives, in the presence of K_2CO_3 as a base and various ruthenium catalysts (Table 2). Very highly regioselective substitutions took place when $[\text{RuCp}^*(\text{CH}_3\text{CN})_3]\text{PF}_6$ (**1**) was used in CH_3CN at room temperature [24,25]. The regioselectivity was slightly lower in acetonitrile with (**3**) as catalyst precursor, and by contrast, the best efficiencies with $[\text{RuCp}^*(\text{CH}_3\text{CN})_2(\text{PPh}_2\text{OMe})]\text{PF}_6$ (**5**) were obtained in dichloromethane. Various aryl 1-phenylprop-2-enyl ethers were obtained with good regioselectivities from *o*, *m*, *p*-cresols, *p*-methoxy- and *o*-chlorophenol (Table 2), and $[\text{RuCp}^*(\text{CH}_3\text{CN})(\text{bipy})]\text{PF}_6$ led to modest regioselectivities.

Table 2 Catalytic formation of allylic phenyl ethers with catalysts **1**, **3**, **5**.


Catalyst precursor	Ar	Solvent	Reaction time (h)	Conv. (%)	B:L ratio
[RuCp*(CH ₃ CN) ₃]PF ₆ (1)	C ₆ H ₅	CH ₃ CN	40	100	98:2
"	4-MeOC ₆ H ₄	CH ₃ CN	40	100	98:2
"	4-MeC ₆ H ₄	CH ₃ CN	40	100	97:3
"	4-ClC ₆ H ₄	CH ₃ CN	40	100	98:2
[RuCp*(CH ₃ CN)(bipy)]PF ₆ (3)	C ₆ H ₅	CH ₃ CN	16	97	92:8
[RuCp*(CH ₃ CN) ₂ (PPh ₂ OMe)]PF ₆ (5)	C ₆ H ₅	CH ₂ Cl ₂	16	100	85:15
"	4-MeOC ₆ H ₄	CH ₂ Cl ₂	16	76	92:8
"	4-MeC ₆ H ₄	CH ₂ Cl ₂	16	61	88:12

The efficiency of ruthenium catalysts for the preparation of phenyl ethers derived from other allylic substrates and phenol was also investigated. From 3-chloro-4-phenylbut-1-ene, [RuCp*(CH₃CN)₃]PF₆ (**1**) showed low reactivity and regioselectivity. On the other hand, [RuCp*(MeCN)₂(PPh₂OMe)]PF₆ was more active and led to very good regioselectivities (Table 3).

From a purely aliphatic allylic substrate such as 3-chlorohex-1-ene or 1-chlorohex-2-ene, the regioselective allylation of phenol was more challenging. Our best results were obtained with catalyst **5** in tetrahydrofuran at room temperature, where complete conversion was reached within 16 h with a B:L ratio of 75:25 [23].

Table 3 Ruthenium-catalyzed allylation of 3-chloro-4-phenylbut-1-ene.


Catalyst precursor	Ar	Reaction time (h)	Conv. (%)	B:L ratio
[RuCp*(CH ₃ CN) ₂ (PPh ₂ OMe)]PF ₆ (5)	C ₆ H ₅	16	87	92:8
"	4-MeOC ₆ H ₄	"	88	96:4
"	4-MeC ₆ H ₄	"	93	91:9
[RuCp*(CH ₃ CN) ₃]PF ₆ (1)	C ₆ H ₅	40	100	60:40

Complexes (**3**) with bipyridine, 4,4'-substituted-2,2'-bipyridine or phenanthroline as bidentate ligand were especially active for the allylation by allylic carbonates of carbonucleophiles without previous deprotonation of the pronucleophile (Table 4). Thus, dimethylmalonate and pentan-2,4-dione were monoallylated by cinnamyl carbonate in acetonitrile at room temperature in 20:1 and 55:1 B:L ratio, respectively [22]. This is assumed to result from the high electrophilicity of the dicationic allylic intermediate of type **4**.

Table 4 Ruthenium-catalyzed allylation of carbonucleophiles.

Catalyst (bipyridine)	Nucleophile (NuH)	B:L ratio
3 (4,4'-diMe-bipy)	CH ₂ (CO ₂ Me) ₂	25:1
3 (phenanthroline)	CH ₂ (CO ₂ Me) ₂	20:1
3 (4,4'-di ^t Bu-bipy)	CH ₂ (COMe) ₂	57:1
3 (phenanthroline)	CH ₂ (COMe) ₂	55:1

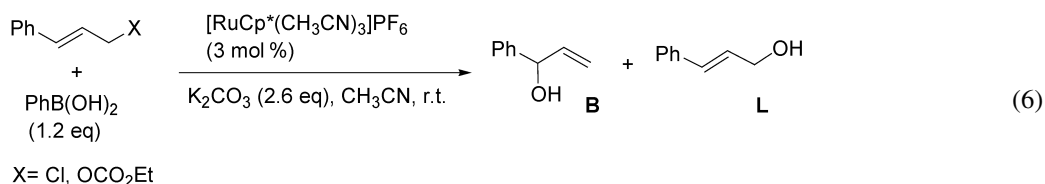
The regioselective allylation of aliphatic alcohols such as methanol and ethanol was also carried out with catalysts (**3**) in acetonitrile or directly in the alcohol as solvent, and regioselectivities in the range 10:1 to 30:1 were obtained with the different bipyridyl ligands [22]. In the case of amines, the branched product was initially formed as the major compound but after prolonged reaction time, isomerization into the linear allylic product was observed (Table 5). The mechanism of this transformation is unclear, but probably related to the presence of the protic methanol solvent [26].

Table 5 Allylation of secondary amines.

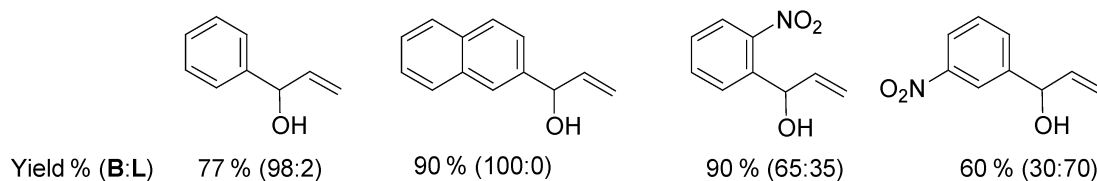
Reaction time	Conversion	B:L ratio
3 min	100 %	100:0
30 min	100 %	100:0
2 h	100 %	85:15
5 h	100 %	65:35

FORMATION OF ALLYLIC ALCOHOLS FROM BORONIC ACID

With the objective of transferring a phenyl group via a classical transmetalation from boron to a transition metal, the reaction of cinnamyl chloride with boronic acid was attempted. No expected diphenylpropene derivative was formed, but the branched and linear allylic alcohols were formed according to eq. 6. [27]. This reaction, which corresponds to the delivery of a nucleophile via a boron intermediate, has very few precedents in the literature, and mainly concerns the alkoxy group [28–30].



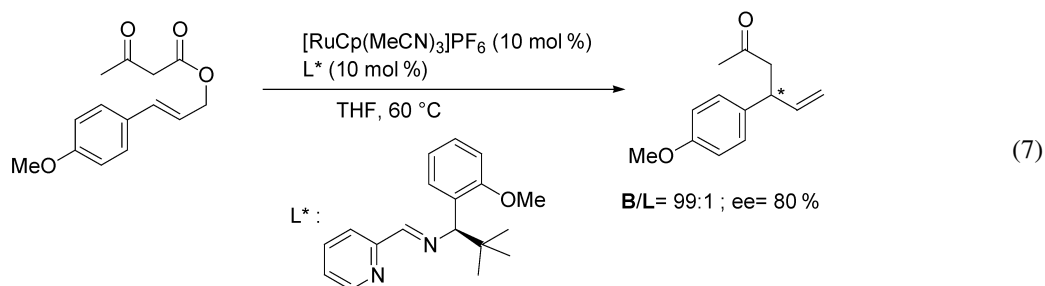
Under the above conditions (eq. 6), a variety of allylic chlorides were transformed into allylic alcohols with regioselectivities strongly depending on the substitution pattern of the aromatic group as can be seen below.



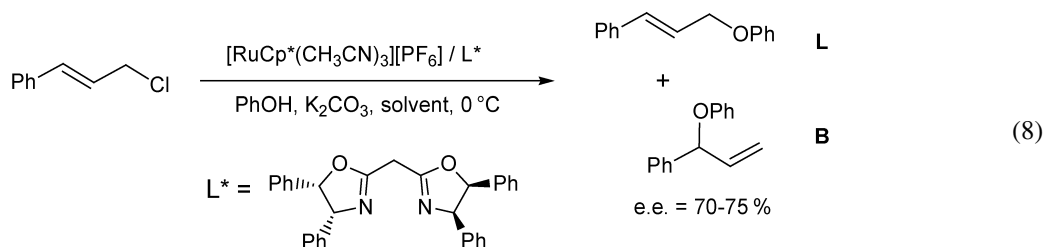
RUTHENIUM-CATALYZED ALLYLIC SUBSTITUTION: THE ASYMMETRIC VERSION

B. Trost has shown that in the presence of catalyst (1), the allylation of phenol from optically pure branched cinnamyl carbonate was stereospecific and led to the branched ether with retention of configuration and a high enantiomeric excess [16]. The use of ruthenium complexes containing a tethered cyclopentadienyl-phosphine ligand with planar chirality provided excellent enantioselectivities during the allylation of carbonucleophiles and amines with racemic 1,3-diphenylpropen-1-yl carbonate generating a symmetrical allylic ligand [31].

It has also been shown that the Carroll rearrangement of allylic β -ketoesters, which corresponds to the allylation of an in situ generated enolate, was also stereospecific in the presence of $[\text{RuCp}^*\text{Cl}]_4/\text{bipyridine}$ as catalyst [32]. The regio- and enantioselective version of the Carroll rearrangement has recently been achieved by J. Lacour and colleagues by using a catalytic system based on $[\text{RuCp}(\text{MeCN})_3]\text{PF}_6/\text{optically pure pyridine-imine}$ (eq. 7) [33]. This represents the second example of enantioselective allylation involving an unsymmetrical allylic moiety with ruthenium catalysts.



After testing diimines as optically active ligands without success [34,35], we disclosed the first example of enantioselective allylic substitution involving an unsymmetrical η^3 -allylruthenium intermediate in 2004, when we showed that $[\text{RuCp}^*(\text{MeCN})_3]\text{PF}_6$ associated to an optically pure bisoxazoline led to very good enantioselectivities during the allylation of phenol by cinnamyl chloride according to eq. 8 [36].



Among the chiral bisoxazolines, (4*R*, 5*S*, 4'*R*, 5'*S*)-2,2'-methylenebis-(4,5-diphenyl-2-oxazoline) led to the best enantioselectivities. Both regio- and enantioselectivity of the *O*-allylation of phenol by cinnamyl chloride were found to be dependent on the nature of the solvent. In our best reaction conditions, satisfactory regioselectivities (up to 4/1) and quite good enantioselectivities (70–75 %) were obtained. Further studies with *para*-substituted phenols also provided good results and demonstrated that this catalyst tolerates different substituents on the aromatic ring, and that the electronic properties of the substituted phenols have little influence on the enantioselectivity (Table 6). Moreover, we have recently observed that this allylic etherification can be run at room temperature in acetone without any loss of enantioselectivity.

Table 6 Allylic etherification of phenols.

ArOH	Conversion (%)	Selectivity (B:L)	ee (%)
C ₆ H ₅ OH	88	2.5:1	80 (<i>R</i>)
4-MeO-C ₆ H ₄ OH	75	2.2:1	81 (<i>R</i>)
4-Cl-C ₆ H ₄ OH	96	1.6:1	82 (<i>R</i>)
4-Me-C ₆ H ₄ OH	96	3:1	52 (<i>R</i>)

CONCLUSION

The oxidative addition of allylic halides and carbonates to ruthenium centers is relatively easy and provides reactive organometallic allylic species. Pentamethylcyclopentadienyl ruthenium(II) complexes containing nitrogen ligands are efficient precursors of η^3 -allylruthenium(IV) intermediates with distorted unsymmetrical allylic ligands. They show high catalytic activities for substitution of allylic halides and carbonates by a variety of nucleophiles such as stabilized carbonucleophiles, amines, alcohols, and masked hydroxyl groups. They provide regioselective substitution of unsymmetrical allylic derivatives in favor of the branched isomers. The coordination of optically pure bisoxazoline ligands gives an access to chiral catalysts, which allow the regio- and enantioselective formation of allylic ethers from phenols.

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