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(Cyclopentadienyl)ruthenium-Catalyzed Regio- and Enantioselective Decarboxylative Allylic Etherification of Allyl Aryl and Alkyl Carbonates

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Abstract: (Cyclopentadienyl)tris(acetonitrile)ruthenium hexafluorophosphate {[CpRu(NCMe)$_3$][PF$_6$]} or (cyclopentadienyl)(η^6-naphthalene)ruthenium hexafluorophosphate {[CpRu(η^6-naphthalene)][PF$_6$]} in combination with a pyridine oxazoline ligand efficiently catalyze the decarboxylative allylic rearrangement of allyl aryl carbonates. Good levels of regio- and enantioselectivity are obtained. Starting from enantioenriched secondary carbonates, the reaction is stereospecific and the corresponding allylic ethers are obtained with net retention of configuration. An intermolecular version of this transformation was also developed using allyl alkyl carbonates as substrates. Conditions were found to obtain the corresponding products with similar selectivity as in the *intramolecular* process. Through the use of a hemilabile hexacoordinated phosphate counterion, a zwitterionic air- and moisture-stable chiral ruthenium complex was synthesized and used in the enantioselective etherification reactions. This highly lipophilic metal complex can be recovered and efficiently reused in subsequent catalysis runs.

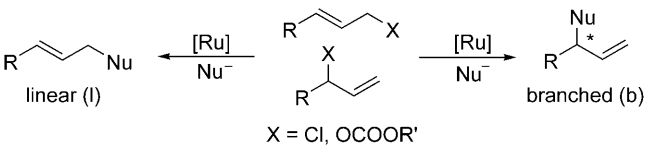
Keywords: allylic compounds; catalyst recyclability; enantioselective catalysis; etherification; ruthenium catalysts

Introduction

Among the large variety of synthetic methods available to obtain a chiral allylic molecule, the nucleophilic attack onto an electrophilic allyl-metal moiety is one of the most studied.[1] In the case of unsymmetrical allyl-metal intermediates, the nature of the metal at play is of crucial importance to control the regio- and enantioselectivity of the nucleophilic attack.[2] Many different metal catalysts have been studied in the last decades, and successful enantioselective allylic substitutions have been reported using Pd,[3] Ir,[2a,4] Ru,[5] Mo,[6] or Rh[2c] catalysts among others. For instance, effective protocols have been developed to introduce O-nucleophiles.[7] The products, i.e., enantioenriched allylic ethers, are important building blocks in the synthesis of natural products and biologically active molecules, such as brevetoxine[8] or fluoxetine.[9]

In this field, as just mentioned, ruthenium is able to promote allylation reactions. Several Ru(II) complexes have been shown to catalyze the attack of nucleophiles onto π-allyl fragments. High regioselectivity is observed usually in favor of the chiral branched (b) product rather than the achiral linear (l) moiety [Eq. (1)]; the reaction occurring on the more substituted allyl terminus of the intermediate.[10] Generally Cp*Ru[11] (Cp* = C_5Me_5) or Cp′Ru[5,12] (planar chiral complexes with a tethered phosphane ligand) derivatives are preferred over CpRu (Cp = C_5H_5) catalysts; the more electron-rich complexes being more reactive. The most common substrates are primary or secondary allyl chlorides and carbonates for which successful alkylation, etherification or amination reactions have been reported. In the topic of enantioselective allylic etherification, the group of Bruneau reported first the use of a Cp*Ru complex in

Eq. (1)



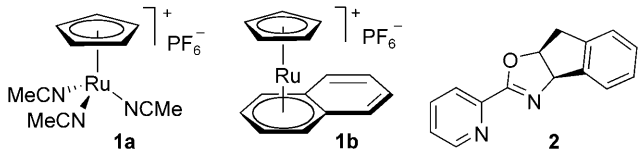


Figure 1. Ruthenium complexes and pymox ligand.

combination with bisoxazoline box-type ligands. The corresponding allyl ethers were obtained with good enantioselectivity (up to 82% *ee*) and but modest regioselectivity (b:l ratio, up to 6.5:1).[13] Recently excellent enantio- and regioselectivities (up to 95% *ee* and b:l ratio >20:1) were obtained for this reaction by Onitsuka and co-workers using a planar-chiral Cp′Ru complex.[14] In that particular case the use of allylic chlorides and bromides as substrates is mandatory.[15] Finally, with secondary enantioenriched allylic alkyl carbonates as substrates and phenols as nucleophiles, conditions were found to enable the reaction to proceed with very high stereospecificity.[16]

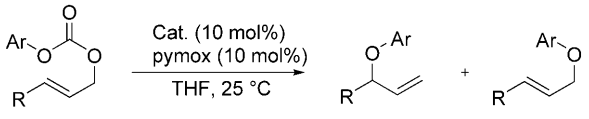
Recently, our group has reported that CpRu complexes can also be efficient catalysts for this type of transformations. More specifically, the first example of an effective enantioselective decarboxylative allylic etherification was detailed.[17] Our group showed that allyl aryl carbonates are suitable substrates. In the presence of a combination of $[CpRu(NCMe)_3][PF_6]$ **1a**,[18] and readily prepared pyridine monooxazoline (pymox) ligand **2** (Figure 1),[19] the substrates provided, after carbon dioxide extrusion, the corresponding allyl phenyl ethers with high enantiomeric purity and regioselectivity (up to 87% *ee* and b:l >20:1). We also demonstrated that, over time, the branched product can isomerize to the more thermodynamically stable linear product, leading to a net loss of regio- and enantioselectivity. Since this communication, these substrates were used by the group of Tunge in the presence of an iron catalyst to yield, in this case, the linear product as the exclusive adduct.[20]

Herein we provide a full report on the CpRu-catalyzed regio- and enantioselective etherification reactions of cinnamyl aryl carbonates and extend the chemistry further. The results of the "intramolecular" reactions are now compared to those of intermolecular processes using combinations of allyl alkyl carbonates and phenols as starting materials. Rather different results are obtained and discussed. We also report on the synthesis and application of a recyclable chiral CpRu catalyst – something that has not been previously detailed.

Results and Discussion

As mentioned, our group has recently shown that a combination of $[CpRu(NCMe)_3][PF_6]$ **1a** (10 mol%) and pymox **2** (10 mol%) catalyzes the decarboxylative allylic rearrangement of cinnamyl aryl carbonates giving the corresponding allylic ethers with high regio- and enantioselectivity.[17] These previous results and new information are summarized in Table 1. For instance, starting from the unsubstituted cinnamyl phenyl carbonate (**3a**), full conversion was achieved in 2 h and good selectivity levels were measured for the corresponding phenyl ether **4a** (b:l ratio >95:05, *ee* 84%, entry 1). Care was then taken to substitute the periphery of the aryl rings. The effect of substituents at the *para* position of the phenyl group of the

Table 1. Decarboxylative rearrangement of primary cinnamyl aryl carbonates.[a]

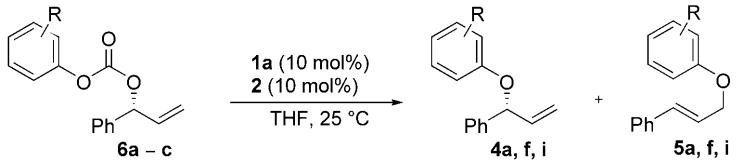


3a – h **4a – h** **5a – h**

Entry	Allyl	R	Ar	Time	Conversion	Ether	*ee*[c]	Configuration	b:l[b]
1	**3a**[d]	Ph	Ph	2.0 h	> 97%	**4a**	84%	(+)	>95:05
2	**3b**[d]	*p*-ClC_6H_4	Ph	2.5 h	92%	**4b**	87%	(+)	>95:05
3	**3c**[d]	*p*-$NO_2C_6H_4$	Ph	7.0 h	87%	**4c**	85%	(−)	75:25
4	**3d**[d]	Ph	*p*-MeC_6H_4	2.5 h	90%	**4d**	84%	(−)	90:10
5	**3e**[d]	*p*-ClC_6H_4	*p*-MeC_6H_4	3.5 h	90%	**4e**	85%	(−)	90:10
6	**3f**	Ph	*p*-$CF_3C_6H_4$	1.5 h	>97%	**4f**	68%	(+)-(*S*)	95:05
7	**3g**[d]	Ph	*p*-$NO_2C_6H_4$	0.5 h	94%	**4g**	34%	(−)	87:13
8	**3h**	Pr	Ph	6.0 h	>97%	**4h**	60%	nd	75:25

[a] **1a** (10 mol%), ligand **2** (10 mol%), THF, 25 °C, $c[\mathbf{3}] = 0.5$ M; the results are the average of at least two runs.
[b] Determined by ^{1}H NMR (400 MHz).
[c] Determined by CSP-HPLC. Absolute configuration assigned by comparison with literature reports.
[d] Results reported in a preliminary form in ref.[17]

Table 2. Decarboxylative rearrangement of secondary cinnamyl aryl carbonates.[a]



6a: R = H *ee* = 94% (*R*)-(+)
6b: R = *p*-CF_3 *ee* > 99% (*R*)-(+)
6c: R = *o*-Me *ee* > 99% (*R*)-(+)

Entry	Allyl	R	Ligand	Time	Conversion[b]	Ethers	*ee*[c]	b:l[b]
1	**6a**	H	bpy	7.0 h	>95%	**4a**	(−)-88%	>97:03
2	**6a**	H	**2**	2.0 h	>95%	**4a**	(−)-86%	94:06
3	**6a**	H	*ent*-**2**	2.0 h	>95%	**4a**	(−)-87%	94:06
4	**6b**	*p*-CF_3	bpy	7.0 h	95%	**4f**	(−)-(*R*)-96%	96:04
5	**6c**	*o*-Me	bpy	7.0 h	>95%	**4i**	(−)-(*R*)-97%	92:08

[a] **1a** (10 mol%), ligand (10 mol%), THF, 25 °C, c[**6**] = 0.5 M; the results are the average of at least two runs.
[b] Determined by ^{1}H NMR (400 MHz).
[c] Determined by CSP-HPLC. Absolute configuration assigned by comparison with literature reports.

cinnamyl moiety was first evaluated. A slight increase of the reaction time was noticed with a *para*-chlorine atom (2.5 h, 92% conv., entry 2) while a stronger effect was induced by a nitro substituent (7 h, 87% conv., entry 3). In terms of regioselectivity, while no difference was noticed with the *para*-chlorine atom (b:l >95:05), a negative effect was observed in the case of the *para*-nitro substituent (b:l = 75:25). Interestingly, the enantioselectivity was not affected by the substitution and constantly high values were measured (*ee* 87%, 85% entries 2 and 3 respectively).

On the other hand, modifying the aryloxy moiety by introducing a *para*-methyl group resulted in a decrease of reactivity (entries 4 and 5). While no influence of the electron-donating methyl group was observed on the enantioselectivity (*ee* 84%, 85% entries 4 and 5 respectively), a slight decrease of the branched to linear ratio was observed (b:l = 90:10).

The introduction of electron-withdrawing groups (allyl **3f** and **3g** Ar = *p*-$CF_3C_6H_4$ and Ar = *p*-$NO_2C_6H_4$, respectively) clearly caused a remarkable acceleration of the reaction, in line with an increased aryloxide "leaving group ability". Unfortunately, the enantioselectivity was also strongly influenced by these substituents on the phenoxides and the branched products were recovered only with modest enantiopurities in these cases (*ee* 68% and 34%, entries 6 and 7 respectively). The primary hexenyl substrate (allyl **3h**) was prepared and, interestingly, it reacted in the catalytic conditions giving the corresponding product with moderate regio- and enantioselectivity (b:l 75:25, *ee* 60%, entry 8). This drop in selectivity is in line with previously reported results.[10a]

Mechanistic Studies

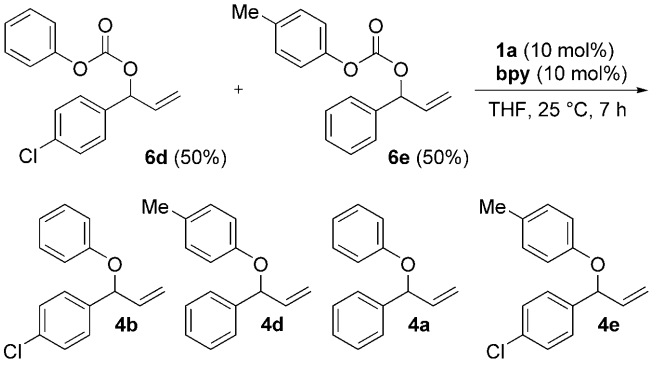
To gain some insight on the mechanism of this decarboxylative allylic etherification, enantioenriched secondary allylic carbonate **6a** was synthesized. Starting from the commercially available enantiopure (*S*)-styrene oxide, the corresponding enantiopure (*ee* >99%) allylic alcohol was obtained following the Mioskowski protocol.[21] Subsequent condensation with phenyl chloroformate yielded the corresponding enantioenriched carbonate **6a** (*ee* 94%).[22] Carbonate **6a** was submitted to the classical catalytic conditions in the presence of the achiral bpy (2,2′-biyridine) as ligand. After 7 h, the levorotatory enantiomer of the allylic ether **4a** was recovered with excellent regioselectivity (b:l >97:03, entry 1, Table 2) and high conservation of enantiopurity (*ee* 88%, *cee* 94%).[23,16] It was hypothesized that the loss of stereochemical information could derive from a rearrangement from the branched to the linear carbonate prior to the oxidative addition.[11r] In an attempt to test this assumption and enhance the enantioselectivity altogether, both enantiomers of the chiral pymox **2** (entries 2 and 3)[24] were thus used as ligand instead of bpy. In both cases, very similar reactivity was observed and the levorotatory allylic ethers were recovered as major products with virtually identical enantiomeric excesses (entries 2 and 3 *ee* 86% and 87%). A matched/mismatched situation was not detected and it tends to exclude the possibility of an isomerization process of the branched to the linear carbonate.

Moreover, to determine precisely the sense of stereoinduction within the reaction (global retention or inversion), we turned our attention to the making of ethers **4f** and **4i**; their absolute configuration being

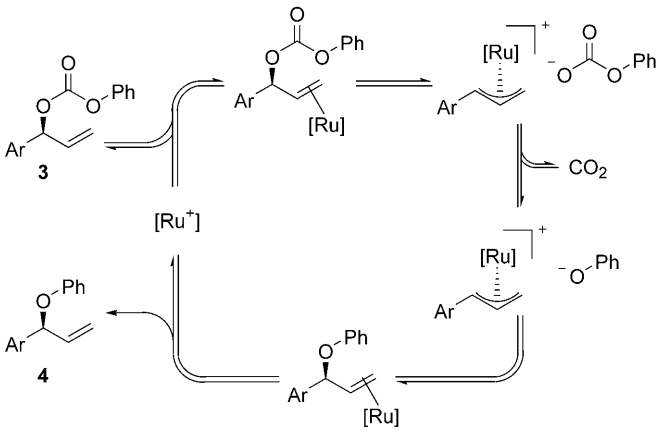
clearly established previously.[16] The corresponding enantiopure secondary allylic carbonate precursors were synthesized (allyl **6b** and **6c**, Table 2).[25] Under our set of conditions with achiral bpy as ligand, the two carbonates reacted giving, in both cases, the corresponding products with a net retention of configuration and an excellent enantiopurity. In the case of the *p*-CF_3-phenyl allyl ether, a better regioselectivity was obtained (b:l = 96:04, entry 4).

At this stage, a cross-over experiment was also performed to assess if the etherification of these secondary carbonates was occurring through a dissociative pathway – as previously established for linear substrates.[17] A 1:1 mixture of two differently substituted secondary allylic carbonates (**6d**, **6e**) was treated under our standard catalytic conditions (Scheme 1). At the end of the reaction, ^{1}H NMR (400 MHz, C_6D_6) analysis showed a statistical mixture of products (**4b** and **4d**) and of cross-over products (**4a** and **4e**). In addition, a small amount of all the four possible linear products was detected. These results show that, at one moment during the etherification reaction, the electrophilic and the nucleophilic partners are completely separated in solution yielding all possible cross-over products.

All these results are consistent with the mechanistic rational proposed in Scheme 2. In detail, following the formation of the ruthenium olefin complex, the oxidative addition occurs *anti* to the leaving group, giving rise to the formation of a chiral π-allyl species. Considering the high level of conservation of the stereochemical information during the reaction, the π-allyl intermediate is isomerizing only very slowly. Its formation is thus the enantiodetermining step. In the case of secondary allylic substrates, the stereochemical information derives only from the chiral starting material, whereas, with linear carbonates, it is the chiral ligand that dictates the outcome. Subsequent decarboxylation generates the nucleophilic phenoxide as part of a dissociated ion pair. The nucleophilic attack occurs from the opposite side of the metal,



Scheme 1. Cross-over experiment. Ratio 0.9:1.3:1.0:1.0 for **4b**:**4d**:**4a**:**4e**.



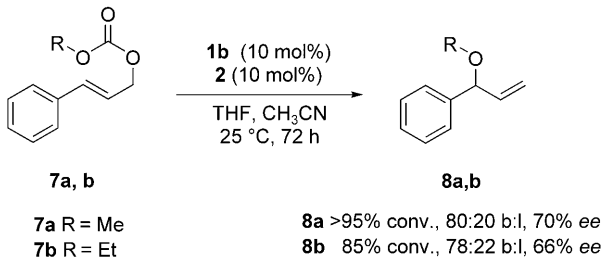
Scheme 2. Mechanistic rationale.

yielding, after decomplexation, the corresponding product with a net retention of configuration, through a double inversion pathway.

Allyl Alkyl Carbonates

It has been shown many times before that allyl alkyl carbonates can be used as substrates in metal-catalyzed allylic substitutions. The alkoxides, generated *in situ* by decarboxylation, act furthermore as effective bases with acidic moieties. The resulting anionic species behave as nucleophiles and attack π-allyl intermediates giving rise to products of intermolecular coupling. In this context and that of Ru catalysis, Pregosin has shown that phenols react in the presence of allylic alkyl carbonates and Cp*Ru catalysts to yield the corresponding allyl aryl ethers;[11i] phenoxides being formed cleanly with no need for an additional base and reacting effectively.

The advantage of this approach is the simplicity of the protocol and the opportunity to generate many different products from – possibly – a single starting carbonate. In view of these benefits, it was decided to study this process exactly, and this using our previously developed conditions. However, rather than use $[CpRu(NCMe)_3][PF_6]$ **1a** as catalyst, we used for this study the air- and moisture-stable [CpRu(η^6-naphthalene)][PF_6] **1b** as direct metal source.[18b,26] In the context of allylation reactions, this complex has been shown to be an effective catalyst for the related enantioselective Carroll rearrangement.[27] However, in this case, we quickly found out that it was necessary to add 30 mol% of acetonitrile to the reaction mixture prior to the addition of the substrates. This provided a homogeneous solution for the whole duration of the catalysis and assured high reproducibility, something that was difficult to achieve without the Lewis basic additive.



Scheme 3. Decarboxylative allylic etherification of allyl alkyl carbonates.

First, allyl alkyl carbonates **7a** and **7b** were prepared and a couple of experiments were performed under standard reaction conditions to estimate the global reactivity of these substrates in the absence of external nucleophiles. While long reaction times were necessary, the expected products were formed together with moderate enantioselectivity but good branched to linear ratios (Scheme 3). With these results in hand demonstrating the reactivity of compounds **7**, phenol (1 equiv.) was added to the reaction mixture and provided the products of aryloxide incorporation. Unfortunately, only low regioselectivity was measured for the corresponding adducts (b:l < 75:25). Considering that the long reaction time was detrimental, by favoring the isomerization of the branched aryl ethers to the linear adducts,[17] an excess of the starting carbonate was used to favor the first coupling reaction. Experiments were then conducted using 2 equivalents of allyl alkyl carbonates and 1 equivalent of phenols. This time, selectivity ratios comparable to those obtained with pre-made allyl aryl carbonates were observed (Table 3).

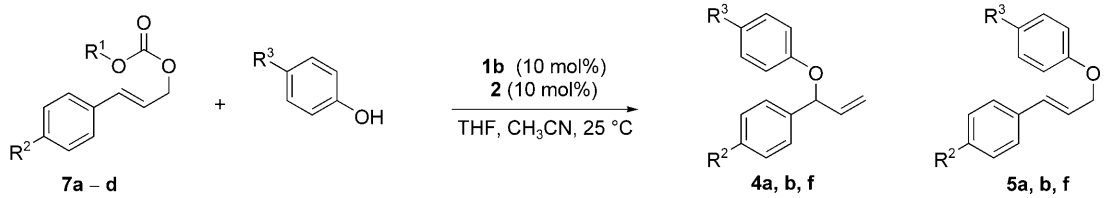
Different alkyl carbonates were then tested (Me, Et and *t*-Bu as substituents). Clearly, the bulk of the leaving group had a detrimental effect on the reactivity (Table 3, entries 1–3). Going from methyl to ethyl, and then to *tert*-butyl, the reaction time increased. In the latter case, 72 h were necessary to reach a 62% conversion of the phenol (entry 3). Yet, the same level of enantiomeric excess was measured for the three reactions (*ee* 80%, 80%, 79% respectively). Only in terms of regioselectivity was a difference observed; the ethyl carbonate **7b** giving a lower b:l ratio (84:16, entry 2) in respect to the other two substrates (95:05, entries 1 and 3).

Substitutions both on the carbonate and on the phenol partners were also carried out and results followed our expectations. While an electron-withdrawing group on the aryl part of the cinnamyl moiety allowed better selectivities (entry 4), the use of *p*-CF_3-phenol as nucleophile led to the expected ethers with lower selectivity (*ee* 73%, b:l = 84:16, entry 5). In addition, the reaction of cinnamyl methyl carbonate **7a** and unsubstituted phenol was tested at 0 °C. Only a 60% conversion in respect to the phenol was reached after 24 h. The branched ether was obtained with better enantioselectivity though (*ee* 88%).

Trisphat-N Complex

Finally, our group previously reported the synthesis and resolution of the hexacoordinated phosphorus anion TRISPHAT-N (TTN, Figure 2).[28] This anion, thanks to presence of the pyridine moiety, efficiently coordinates to metal centers and the resulting zwitterionic species are usually air and moisture stable. In

Table 3. Intermolecular decarboxylative etherification of cinnamyl alkyl carbonates.[a]



Entry	Allyl	R^1	R^2	R^3	Time (h)	Conversion[b]	Ether	*ee*[c]	b:l[b]
1	**7a**	Me	H	H	24	>95%	**4a**	(+)-80%	95:05
2	**7b**	Et	H	H	42	94%	**4a**	(+)-80%	84:16
3	**7c**	*t*-Bu	H	H	72	62%	**4a**	(+)-79%	>95:05
4	**7d**	Me	Cl	H	24	85%	**4b**	(+)-84%	90:10
5	**7a**	Me	H	CF_3	24	>97%	**4f**	(+)-(*S*)-73%	84:16
6[d]	**7a**	Me	H	H	24	60%	**4a**	(+)-88%	95:05

[a] **1b** (10 mol%), ligand **2** (10 mol%), THF, 25 °C, *c*[**7**] = 0.5 M; the results are the average of at least two runs.
[b] Determined by ^{1}H NMR (400 MHz).
[c] Determined by CSP-HPLC. See the Supporting Information. Absolute configuration assigned by comparison with literature reports.
[d] Reaction performed at 0 °C.

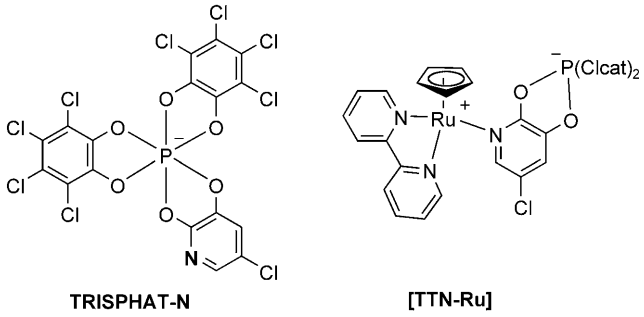


Figure 2. Hexacoordinated phosphorus anion TRISPHAT-N and ruthenium complex.

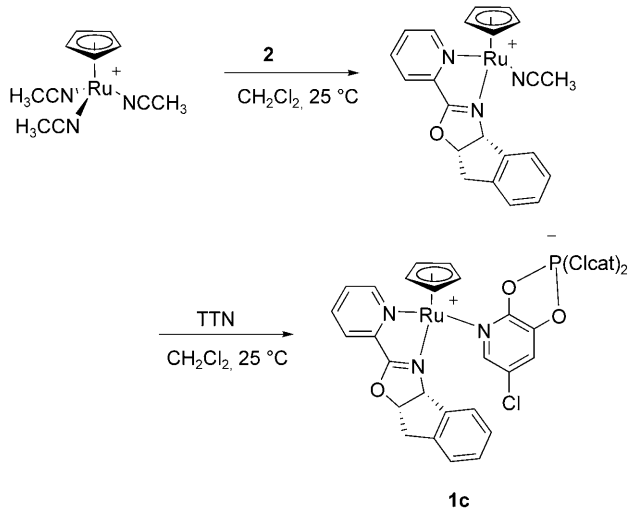
the context of the Carroll rearrangement, it was shown that mixing equimolar amounts of [CpRu-$(NCMe)_3$][PF_6] **1a**, bpy and [Bu_3NH][TRISPHAT-N] salt results in the [CpRu(bpy)(TTN)] complex which catalyzes efficiently the reaction of β-keto esters. The corresponding unsaturated ketones are produced with excellent regioselectivity at high temperature under microwave irradiation.[29] In addition, thanks to its high chemical stability and lipophilicity, this complex could be easily recovered after the catalysis by silica gel chromatography and then reused in subsequent catalytic runs. After five runs, the pre-catalyst was still showing the same level of reactivity and regioselectivity.

For this study, the possibility to synthesize an analogous metal complex was considered – with enantiopure pymox **2** instead of bpy. As planned, the zwitterionic metal complex was synthesized from the reaction of equimolar amounts of **1a**, ligand **2** and [Bu_3NH][*rac*-TTN] in CH_2Cl_2 at 25 °C. This metal complex, obtained as a mixture of four diastereomers,[30] was tested as pre-catalyst in the decarboxylative etherification of the cinnamyl phenyl carbonates. Linear carbonate **3a** was reacted in THF at 25 °C in the presence of 10 mol% of **1c**. Although long reaction times were needed to reach full conversion (3 days, Table 4), the branched product **4a** was obtained with same b:l ratio and *ee* value as under standard conditions (**1a** 10 mol%, **2** 10 mol%). Moreover, metal complex **1c** could be recovered (Scheme 4), purified from the reaction mixture by chromatography, and reused in subsequent catalysis runs. After 3 cycles, no loss of efficiency or selectivity was detected (Table 4).

Table 4. Use of [CpRu(**2**)(TTN)] as recyclable catalyst.[a]

Run	Conversion[b]	*ee*[c]	b:l[b]	Catalyst recovery
1	>97%	(+)-81%	95:05	80%
2	>97%	(+)-84%	95:05	80%
3	>97%	(+)-84%	95:05	78%

[a] **1c** (10 mol%), THF, 25 °C, *c*[**3a**] = 0.5 M.
[b] Determined by ^{1}H NMR (400 MHz) and GC-MS.
[c] Determined by CSP-HPLC.



Scheme 4. Synthesis of the recyclable catalyst. Clcat = tetrachlorocatecholate.

Conclusions

In conclusion, we have just described that CpRu moieties in combination with a pymox ligand efficiently catalyze the decarboxylative allylic rearrangement of allyl aryl carbonates. Good levels of regio- and enantioselectivity are obtained. Starting from enantioenriched secondary carbonate, the reaction is stereospecific and the corresponding allylic ethers are obtained with net retention of configuration. In addition, an intermolecular version of this type of transformation was developed using allyl alkyl carbonates. Conditions were found to obtain the corresponding adducts with similar selectivity as in the *intramolecular* process. Finally, through the use of a hemi-labile hexacoordinated phosphate counterion, a zwitterionic air and moisture stable chiral ruthenium complex was synthesized and used in the enantioselective etherification. This highly lipophilic metal complex could be recovered and efficiently reused in subsequent catalysis runs.

Experimental Section

General Remarks

Unless otherwise stated, solvents and chemicals were purchased and used as received. Chloroform-*d* was filtered through a plug of basic alumina prior to use. NMR spectra were recorded on a Bruker ARX-400 or AMX-500 spectrometer. ^{1}H NMR: chemical shifts are given in ppm relative to Me_4Si with solvent resonances used as internal standards. Data are reported as follows: chemical shift (δ) in ppm,

multiplicity (s = singlet, d = doublet, t = triplet, h = septet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet), coupling constant (Hz). Electrospray ionization mass spectra were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy of the University of Geneva. Optical rotations were measured on a JASCO P-1030 polarimeter in a thermostatted (20 °C) 10.0 cm long microcell with high pressure lamps of sodium. Determination of the enantiomeric purity of compounds was achieved by CSP-HPLC on an Agilent LC-1100 HPLC equipped with a binary pump, an auto-sampler, a column thermostat, a diode array detector or by CSP-GC on a Hewlett Packard 6890 GC equipped with an autosampler and an FID detector. Determination of the branched to linear ratios was achieved by GC-MS on a Agilent 6890 GC-MS using a capillary column HP-5. IR spectra were recorded with a Perkin–Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling.

General Procedure for the Preparation of Chloroformates[31]

In a 2-necked round-bottom flask, $COCl_2$ (1.35 equiv., 20% solution in toluene) was added to a solution of the corresponding phenol (1 equiv., 5 mmol) under a N_2 atmosphere. The solution was cooled at 0 °C with an ice-bath and *N*,*N*-dimethyl aniline (1 equiv.) was added dropwise. The temperature was allowed to slowly increase to 25 °C while the suspension was stirred for 2 h. The conversion was followed by GC-MS. When no more phenol was present in the reaction mixture, the excess of $COCl_2$ was hydrolyzed with slow addition of water. The organic layers were extracted with Et_2O (3×) and dried on $MgSO_4$. The residue was purified by bulb-to-bulb distillation.

General Procedure for Preparation of Allylic Carbonates[32]

The desired chloroformate (12 mmol) was added dropwise to a solution of the allylic alcohol (10 mmol) dissolved in dichloromethane (10 mL) and pyridine (2 mL) at 0 °C. The reaction mixture was allowed to warm at room temperature and it was stirred until all allylic alcohol was consumed (TLC monitoring). Typically, 12 h were necessary to reach completion. The crude reaction mixtures were then treated with an aqueous ammonium chloride solution (saturated, 10 mL). The organic layer was separated, and the aqueous layer extracted with Et_2O (2×10 mL). The combined organic layers were washed with water, separated, and dried over Na_2SO_4. Concentration under reduced pressure followed by purification by flash column chromatography (SiO_2) gave the desired carbonates.

General Procedure for Catalytic Etherification of the Allyl Aryl Carbonates

In a 1.0-mL vial under a dinitrogen atmosphere, [CpRu(NCMe)$_3$][PF$_6$] **1a** (6.3 mg, 14.4 μmol, 10 mol%) and pymox ligand **2** (3.4 mg, 10 mol%) were dissolved in 300 μL of distilled anhydrous THF. The resulting deep red solution was stirred for 5 min at room temperature before the addition of the allyl aryl carbonate **3** (0.144 mmol). The reaction was stirred under N_2 at 25 °C until no trace of the starting material could be seen on TLC (SiO_2, Et_2O:pentane, 8:2). The reaction mixture was diluted with 1.5 mL of an 8:2 mixture of ether and pentane. The precipitated metal salts were filtered on a short SiO_2 column (0.5 cm×4 cm, elution Et_2O:pentane, 8:2): The solvents were evaporated under reduced pressure to afford the crude reaction mixture as a pale yellow oil which was analyzed by ^{1}H NMR and CSP-HPLC.

General Procedure for Intermolecular Catalysis

In a 2-mL screw-cap vial equipped with a magnetic stirring bar, [CpRu(η^6-naphthalene)][PF$_6$] **1b** (6.3 mg, 14.4 μmol, 10 mol%) and **2** (3.4 mg, 14.4 μmol, 10 mol%) were dissolved in 0.3 mL of distilled anhydrous THF. The vial was flushed with argon and capped. After 1 h of heating at 60 °C, the vial was cooled at 25 °C and a solution (0.3 mL of THF and 3 μL of CH_3CN) of allyl alkyl carbonate **7** (0.288 mmol, 2 equiv.) and phenol (1 equiv.) was added in one portion. After 24 h, the reaction mixture was diluted with 1.5 mL of a mixture of ether and pentane (60:40). After precipitation, the metal salts were filtered off on a short SiO_2 column (0.5 cm×4 cm, elution Et_2O:pentane, 60:40); the solvents then being evaporated under reduced pressure to afford the crude reaction mixture as a pale yellow oil.

Synthesis of Complex 1c [CpRu(3a*R*,8a*S*)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole][*rac*-TTN]

In a Schlenk tube under a dinitrogen flow [CpRu(NCMe)$_3$][PF$_6$] (1 equiv., 0.34 mmol, 150 mg) was dissolved in dried and degassed CH_2Cl_2 (10 mL). The dark red solution was stirred at 25 °C for 10 min. [(*n*-Bu)$_3$NH] [*rac*-TTN] (1 equiv, 0.34 mmol)) and pyridine-oxazoline **2** (1 equiv., 0.34 mmol) were added to the solution in one portion. The solution was stirred for other 10 min. The solvent was evaporated under vacuum and the residue was purified by silica gel column chromatography (eluent CH_2Cl_2). A dark red powder was isolated; yield: 290 mg (78%).

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