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Novel [Ruthenium(substituted-tetramethylcyclopentadiene)(2-quinolinecarboxylato)(allyl)] Hexafluorophosphate Complexes as Efficient Catalysts for Highly Regioselective Nucleophilic Substitution of Aliphatic Allylic Substrates

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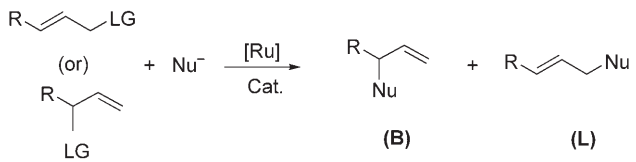
Abstract: Stable [ruthenium(R-substituted-tetramethylcyclopentadiene)(2-quinolinecarboxylato)(1-R′-substituted-allyl) hexafluorophosphate (R = Me, R′ = H, Me, *n*-Pr, Ph; R = *t*-Bu, R′ = Me) and [ruthenium(pentamethylcyclopentadiene)(2-quinolinecarboxylato)(1-*n*-propylallyl)] tetrafluoroborate (**4′a**), as allylruthenium(IV) complexes, have been synthesized in one step, starting from [ruthenium(R-substituted-tetramethylcyclopentadiene)tris(acetonitrile) hexafluorophosphate or tetrafluoroborate complexes, quinaldic acid, and allylic alcohols. Single stereoisomers are obtained and the X-ray single crystal structure determinations of **3b** (R = *t*-Bu, R′ = Me) and **4′a** allow one to specify the preferred arrangement. Complexes **3a** (R = R′ = Me) and **3b** are involved as precatalysts favoring the formation of branched products in regioselective nucleophilic allylic substitution reactions, starting from ethyl 2-*(E)*-hexen-1-yl carbonate and chlorohexene as unsymmetrical aliphatic allylic substrates. Phenols, dimethyl malonate, and primary (aniline) and secondary (pyrrolidine, piperidine) amines have been used as nucleophiles under mild basic conditions. For the first time, the regioselectivity in favor of the branched product obtained from purely aliphatic allylic substrates is close to the high regioselectivity previously reached starting from cinnamyl-type substrates in the presence of ruthenium catalysts.

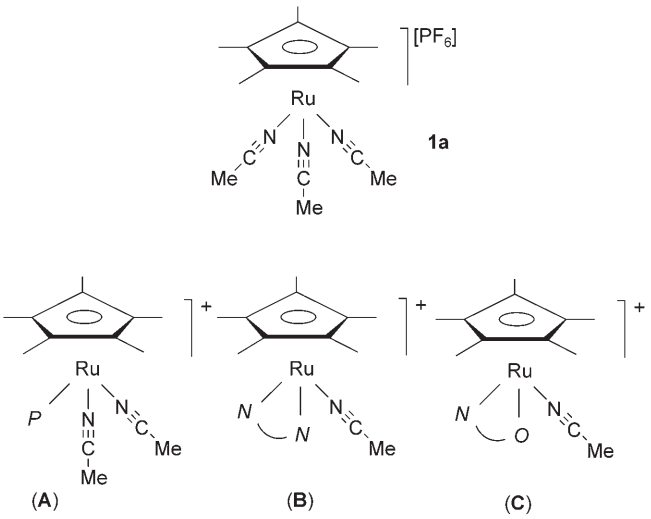
Keywords: allyl ligands; allylation; homogeneous catalysis; regioselectivity; ruthenium

Introduction

Since the discovery of the catalytic activity of the [Ru(C_5Me_5)(1,5-cyclooctadiene)Cl] complex in nucleophilic allylic substitution,[1] the precatalyst [Ru(C_5Me_5)($MeCN)_3$][PF_6], **1a**, has attracted the most interest as it provided higher regioselectivities in favor of the chiral branched products.[2]

Furthermore, the substitution of one or two acetonitrile ligands in the cationic complex **1a** by various nitrogen[3] or phosphorus[4] ligands (Scheme 1) has led to a family of precatalysts allowing one to extend the scope of the catalytic process and to enhance reactivity.[5] Thus, the regioselective formation of branched derivatives from aromatic cinnamyl-type linear substrates is almost perfect in several reactions involving carbon-carbon, oxygen-carbon, and nitrogen-carbon bond formation. However, the regioselectivity remained unsatisfactory starting from unsymmetrical aliphatic allylic substrates.[4]





Scheme 1. Ruthenium(II) precatalysts related to complex **1a**: (**A**) P=P(OMe)Ph_2, P(*o*-tolyl)Ph_2; (**B**) N,N=2,2′-bipyridine or α-diimine type ligands; (**C**) N,O=2-quinolinecarboxylic acid.

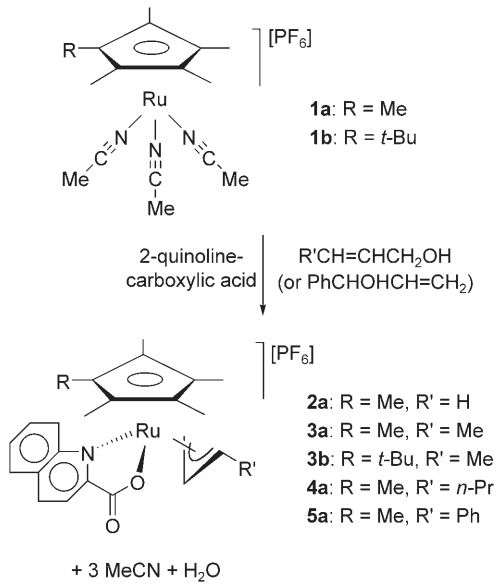
Very recently, it has been shown that the formation of phenyl 1-vinylbutyl ether from 1-chloro-2-butene and phenol in the presence of a ruthenium complex related to type (**A**) gave a high 20:1 branched to linear ratio, but with a moderate yield of 36%.[6] Various transition metal complexes have recently been invoked to tackle the challenge of regioselectivity with aliphatic substrates. Remarkably, iridium,[7] palladium,[8] and platinum,[9] complexes bearing appropriate ligands have been successfully used as catalyst precursors to reach good regioselectivies in favor of branched derivatives. Alternately, the formation of branched products has also been achieved starting from branched allylic substrates, but according to a distinct regiospecific process, using rhodium,[10] or ruthenium,[11] complexes as catalyst precursors.

On the other hand, 2-quinolinecarboxylic acid in a transient cationic [Ru(Cp)(*N,O*-chelate)(MeCN)]$^+$ species analogous to (**C**) in Scheme 1, has recently proved to cooperate with the metal center to achieve the activation of allyl alcohol.[12] From the hydroxy group of allyl alcohol and the acidic proton of 2-quinolinecarboxylic acid, water was produced in this reaction besides the stable [Ru(Cp)(2-quinolinecarboxylato)(η^3-C_3H_5)] [PF_6] as an allylruthenium(IV) complex which is a key intermediate for the ruthenium-catalyzed protection of alcohols as their allyl ethers, as well as their subsequent deprotection.[13] These remarkable results also suggested that a general route leading to [Ru(η^5-C_5R_5)(2-quinolinecarboxylato)(η^3-allyl)]$^+$ as allylruthenium(IV) cations might be possible.

We report herein the synthesis of new [Ru(C_5Me_4R)(2-quinolinecarboxylato)(η^3-CH_2CHCHR')][PF_6] derivatives as allylruthenium(IV) complexes from the reaction of allylic alcohols with *in situ* generated intermediates of type (**C**) (Scheme 1). We show that these complexes are very active and efficient catalysts for the regioselective nucleophilic allylic substitution reactions. Starting from aliphatic allylic chlorides or carbonates, the regioselectivity in favor of the branched products reaches the high level of regioselectivity previously obtained starting from aromatic substrates in the presence of a ruthenium precatalyst.

Results and Discussion

The addition of 2-quinolinecarboxylic acid to an orange solution of [Ru(C_5Me_5)($MeCN)_3$][PF_6] **1a** in dichloromethane resulted within a few minutes in a deep violet color accounting for the formation of the expected intermediate (**C**). The subsequent addition of allyl alcohol and further stirring for several hours, led to a yellow precipitate of [Ru(C_5Me_5)(2-quinolinecarboxylato)(η^3-CH_2CHCH_2)][PF_6], **2a** (Scheme 2).



Scheme 2. Synthesis of [Ru(C_5Me_4R)(2-quinolinecarboxylato)(η^3-allyl)] [PF_6] complexes.

The more soluble complexes [Ru(C_5Me_5)(2-quinolinecarboxylato)(η^3-CH_2CHCHR')][PF_6], **3a** (R'=Me), **4a** (R'=*n*-Pr), and **5a** (R'=Ph) were similarly prepared using crotyl alcohol, 2-*(E)*-hexen-1-ol, and isomeric cinnamyl and α-vinylbenzyl alcohols, respectively. The tetrafluoroborate salt [Ru(C_5Me_5)(2-quinolinecarboxylato)(η^3-CH_2CHCH*n*-Pr)][BF_4], **4′a** exhibiting the same cation as **4a** but arising from [Ru(C_5Me_5)($MeCN)_3$][BF_4] **1′a** instead of **1a**, was also prepared and, more peculiarly, allowed an X-ray single crystal structural study. Carrying a distinct cyclopentadienyl

ligand, the analogous complex [Ru(C_5Me_4t-Bu)(2-quinolinecarboxylato)(η^3-$CH_2CHCHMe$)][PF_6] **3b**, was synthesized starting from [Ru(C_5Me_4t-Bu)($MeCN)_3$][PF_6] **1b** and crotyl alcohol, to test the influence in catalysis of a bulky C_5Me_4t-Bu ligand.[14]

The new allylruthenium(IV) complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. The ^{1}H NMR spectra gave a straightforward evidence for the presence of the allyl and cyclopentadienyl ligands besides a quinoline fragment. Only complex **2a** involves a symmetrical allyl ligand whereas two stereoisomers (both as enantiomeric pairs) might be considered for the other complexes, depending on the position of the R′ group relative to the *N,O*-chelate. ^{1}H and ^{13}C NMR spectroscopy gave evidence for the selective formation of only one of them. Complex **5a** was obtained as very thin needles that retained both acetonitrile and dichloromethane as disclosed by ^{1}H NMR spectroscopy. Remarkably, the same stereoisomer **5a** was obtained starting from cinnamyl alcohol or α-vinylbenzyl alcohol, as linear and branched allylic isomers.

X-Ray single crystal analysis studies of **3b** and **4′a** allowed us to specify the preferred arrangement. Ortep drawings of **3b** and **4′a** are shown in Figure 1 and Figure 2, respectively, and selected bond distances are given in the captions. Cations of **3b** and **4a** displayed a similar square-pyramidal structure with the oxygen and nitrogen atom from the 2-quinolinecarboxylate anion at basal positions acting as a chelate to form a nearly planar metallacycle, and the terminal carbon atoms of an *endo* η^3-allyl ligand, the usual configuration for comparable allylruthenium(IV) complexes.[5] No more surprising was the observation of only slightly longer CH–CH_2 bond length [1.418(3) Å in **3b** and 1.408(3) Å in **4′a**] relative to the CH–CHR′ one [1.404(3) Å in **3b** and 1.400(3) Å in **4′a**], which accounts for a true allylic coordination. Complexes **3b** and **4′a** differ in the presence of a *tert*-butyl group at the cyclopentadienyl ring in **3b**, and in the presence of a *n*-propyl group at the substituted allylic terminal carbon atom in **4′a**. The ruthenium-oxygen and ruthenium-nitrogen bonds in **3b** [2.056(1) and 2.173(2) Å, respectively] are slightly shorter and longer, respectively, relative to **4′a** [2.065(1) and 2.165(2) Å, respectively].

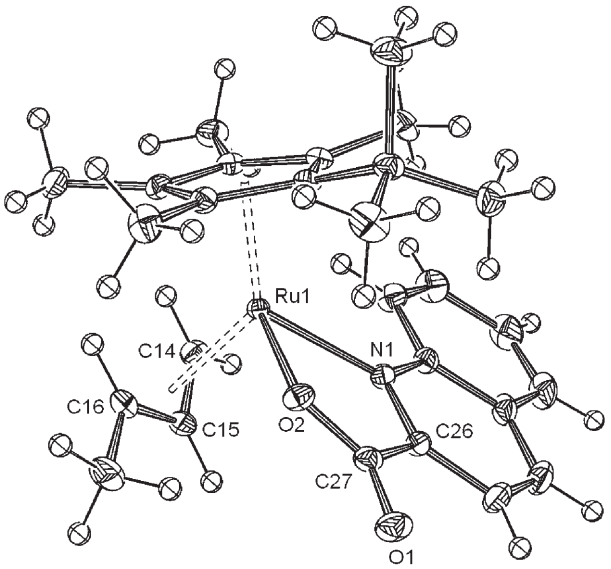


Figure 1. ORTEP drawing of **3b** showing 50% probability thermal ellipsoids. The PF_6 anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1-O2 2.056(1), Ru1-N1 2.173(2), Ru1–C14 2.196(2), Ru1–C15 2.176(2), Ru1–C16 2.327(2), C14–C15 1.418(3), C15–C16 1.404(3); O2–Ru1–N1 76.87(5), O2–Ru1–C16 78.45(6), N1–Ru1–C14 85.96(6), O2–Ru1–C14 126.04(6), N1–Ru1–C16 116.39(6), C14–Ru1–C16 64.33(7).

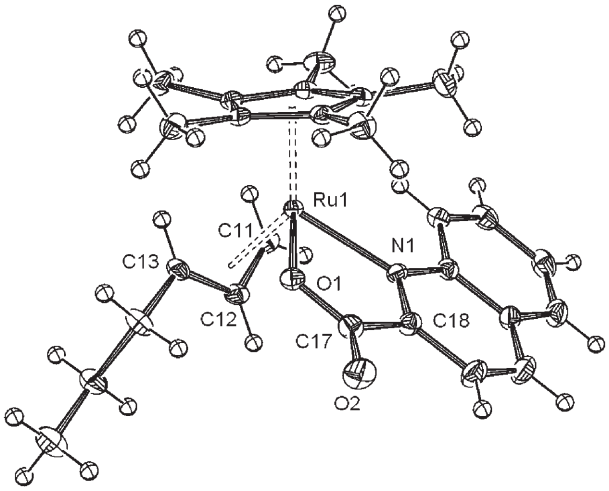


Figure 2. ORTEP drawing of **4′a** showing 50% probability thermal ellipsoids. The BF_4 anion and the CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–O1 2.065(1), Ru1–N1 2.165(2), Ru1–C11 2.195(2), Ru1–C12 2.168(2), Ru1–C13 2.315(2), C11–C12 1.408(3), C12–C13 1.400(3); O1–Ru1–N1 77.40(6), O1–Ru1–C13 80.34(7), N1–Ru1–C11 87.07(7), O1–Ru1–C11 127.17(7), N1–Ru1–C13 118.98(7), C11–Ru1–C13 63.88(8).

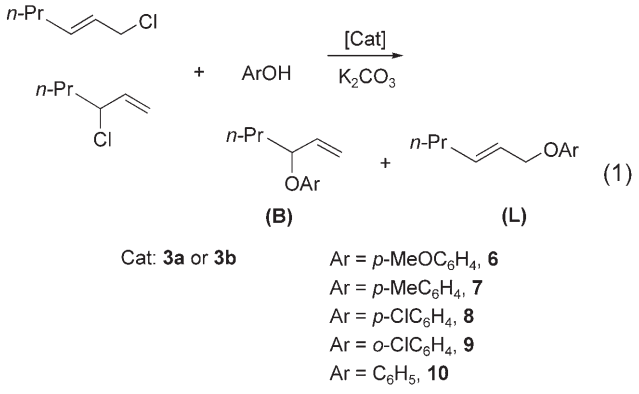
The comparison of the ruthenium-carbon bond lengths involving the unsubstituted terminal allylic carbon atom [2.196(2) Å in **3b** *vs.* 2.195(2) Å in **4′a**] as well as those involving the medium allylic carbon atom [2.176(2) Å in **3b** *vs.* 2.168(2) Å in **4′a**] and the substituted allylic terminal carbon [2.327(2) Å in **3b** *vs.* 2.315(2) Å in **4′a**], revealed even weaker differences between **3b** and **4′a**. Of interest also is the comparison of these structural features to those of the allylruthenium(IV) complex [Ru(C_5Me_5)Cl(Ph_2POMe)(η^3-CH_2CHCHn-Pr)][PF_6], which had indeed, already disclosed a very similar ruthenium-allyl tetrahedral arrangement [Ru–CH_2: 2.191(4) Å, Ru–CH: 2.198(4) Å, Ru–CH-*n*-Pr: 2.339(4) Å, CH–CH_2: 1.406(6) Å, CH–CH-*n*-Pr: 1.395(6) Å].[4] As the

preferred stereoisomer in this case, the substituted allylic terminal carbon is located in a *cis* position relative to a chlorine atom whereas the unsubstituted terminal allylic carbon atom is located in a *cis* position relative to the bulkier phosphorus ligand. Remarkably, **3b** and **4′a** similarly showed the substituted allylic terminal carbon located in a *cis* position relative to the oxygen atom from 2-quinolinecarboxylate anion whereas the unsubstituted terminal allylic carbon atom is located in a *cis* position relative to the nitrogen atom from the bulkier quinoline moiety.

Starting from cinnamyl-type allylic substrates, nucleophilic allylic substitution reactions catalyzed by **1a** and related complexes as precatalysts, most often occurred according to a highly regioselective formation of branched products.[5,15] By contrast, the moderate regioselectivities as yet reached starting from unsymmetrical aliphatic allylic substrates emphasized the interest to evaluate the potential of new species of type (**C**) (Scheme 1). In the light of the putative mechanism for these ruthenium-catalyzed reactions,[5] the new $[Ru(C_5Me_4R)(2\text{-quinolinecarboxylato})(\eta^3\text{-}CH_2CHCHR')][PF_6]$ derivatives as allylruthenium(IV) complexes might be considered as alternative precatalysts, as compared to previously reported $[Ru(C_5R_5)(\eta^2\text{-}O_2CO\text{-}t\text{-}Bu)(\eta^3\text{-}CH_2CHCHPh)][PF_6]$ (R = H or Me) cinnamylruthenium(IV) complexes.[16]

Allylation Reactions Catalyzed by Complexes 3a,b

The low solubility of **2a** in usual solvents while the crystals of **4a** retain dichloromethane, led us to select **3a** and **3b** as precatalysts for nucleophilic allylic substitution catalytic experiments. Chlorohexene as a 4:1 mixture of linear *n*-PrCH=CHCH$_2$Cl and branched *n*-PrCH(Cl)CH=CH$_2$ isomers resulting from the reaction between PCl_3 and 2-*(E)*-hexen-1-ol,[17] was selected as a typical aliphatic allylic substrate for the synthesis of allyl aryl ethers, according to a previously reported protocol involving ruthenium-catalyzed nucleophilic substitution with phenols under basic conditions [Eq. (1)].[18] Thus, the addition of various phenols (1 equiv.) to chlorohexene (0.5 mmol) in the presence of the ruthenium precatalyst **3a** or **3b** (3 mol%) and K_2CO_3 (1 equiv.), in 4.0 mL of solvent for 18 h at ambient temperature, resulted in the complete consumption of chlorohexene and quantitatively led to the formation of the allyl aryl ethers **6–10**, as mixtures of branched *n*-PrCH(OAr)CH=CH$_2$ and linear *n*-PrCH=CHCH$_2$OAr isomers [Eq. (1)]. Under similar conditions, the involvement of **1a** as precatalyst for these reactions, had already been studied. The formation of the allyl aryl ether **6** from the reaction with *p*-methoxyphenol, gave a moderate 61:39 B/L regioselectivity.[18]



The results given in Table 1, obtained using **3a** and **3b** as precatalyst, disclose a spectacular increase of the regioselectivity in favor of the branched products, and also reveal the beneficial effect of a *tert*-butyl group at the cyclopentadienyl ring in **3b**. Using acetonitrile as solvent, **6** was obtained in a 94:6 B/L ratio with **3a** and an enhanced 97:3 B/L regioselectivity with **3b** (entries 1 and 2). Furthermore, increased 95:5 B/L and 99:1 B/L selectivities, respectively, were reached when dichloromethane was used as solvent (entries 3 and 4). Similarly, excellent regioselectivities were obtained starting from *para*-cresol (entries 5 and 6) and *para*-chlorophenol (entries 7 and 8). Precatalyst **3a** was less efficient for the allylation of *ortho*-chlorophenol (entry 9) and phenol (entry 11) leading to 75:25 B/L and 88:12 B/L selectivities, respectively. However, the use of the precatalyst **3b** resulted in an excellent regioselectivity in favor of the branched products, as shown by the achievement of a 94:6 B/L

Table 1. Allylation of ArOH with chlorohexene in the presence of **3a** and **3b**.[a]

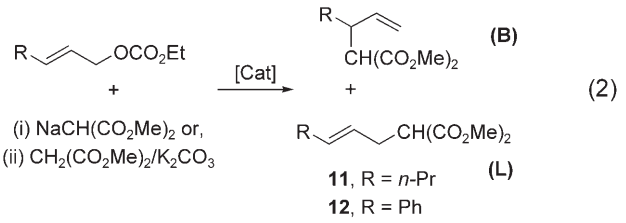
Entry	Ar	Catalyst	Solvent	Product	B/L[b]
1	*p*-MeOC$_6$H$_4$	**3a**	MeCN	**6**	94:6
2	*p*-MeOC$_6$H$_4$	**3b**	MeCN	**6**	97:3
3	*p*-MeOC$_6$H$_4$	**3a**	CH_2Cl_2	**6**	95:5
4	*p*-MeOC$_6$H$_4$	**3b**	CH_2Cl_2	**6**	99:1
5	*p*-MeC$_6$H$_4$	**3a**	MeCN	**7**	94:6
6	*p*-MeC$_6$H$_4$	**3b**	MeCN	**7**	95:5
7	*p*-ClC$_6$H$_4$	**3a**	MeCN	**8**	93:7
8	*p*-ClC$_6$H$_4$	**3b**	MeCN	**8**	97:3
9	*o*-ClC$_6$H$_4$	**3a**	MeCN	**9**	75:25
10	*o*-ClC$_6$H$_4$	**3b**	MeCN	**9**	94:6
11	C$_6$H$_5$	**3a**	CH_2Cl_2	**10**	88:12
12	C$_6$H$_5$	**3b**	CH_2Cl_2	**10**	97:3

[a] *Experimental conditions:* chlorohexene 0.5 mmol, ArOH 0.5 mmol, K_2CO_3 0.5 mmol, precatalyst **3a** or **3b** 3 mol%, room temperature, 18 h.

[b] Conversion and B/L ratio as determined by ^{1}H NMR spectroscopy and GC analysis.

ratio for *ortho*-chlorophenol (entry 10) and a 97:3 B/L ratio for phenol (entry 12).

This level of regioselectivity for the formation of allyl aryl ethers *via* nucleophilic substitution starting from aliphatic substrates, represents the best result ever obtained with ruthenium catalysts and competes with the results obtained with other metal catalysts. The efficiency of precatalysts **3a** and **3b** for the allylation of phenols with chlorohexene led us to evaluate their activity for other ruthenium-catalyzed nucleophilic allylic substitution reactions. The allylation of sodio dimethyl malonate with ethyl cinnamyl and ethyl 2-*(E)*-hexen-1-yl carbonates [Eq. (2)] was thus investigated.



(2)

Preliminary experiments were conducted at room temperature in THF as solvent according to path (i) [Eq. (2)] using a solution of sodio dimethyl malonate in THF prepared by reacting dimethyl malonate with NaH (Table 2). Thus, using **3a** as precatalyst, ethyl 2-*(E)*-hexen-1-yl carbonate led to the monosubstituted dimethyl malonates **11** [Eq. (2)]. A reaction time of 18 h ensured a complete consumption of the allylic carbonate and the linear allylic derivative was produced as the major compound as indicated by a 26:74 B/L ratio (entry 1). To compare the reactivities of **3a** and **3b** to those of the precatalysts **1a** or **1′a**, ethyl cinnamyl carbonate was then used as allylic substrate. The results given in Table 2 show a B/L ratio located in the range 94:6 with **1′a** as precatalyst (entry 2) and 96:4 with **3b** as precatalyst (entry 4). Thus, the precatalysts **1′a**, **3a**, and **3b** maintained the excellent regioselectivity in favor of the branched isomer of **12** [Eq. (2)] arising from ethyl cinnamyl carbonate, as already reached using **1a** as precatalyst.[2]

Table 2. Formation of monosubstituted dimethyl malonates **11** and **12**.[a]

Entry	R	Path	Catalyst	Solvent	Product	B/L[b]
1	*n*-Pr	(i)	**3a**	THF	**11**	26:74
2	Ph	(i)	**1′a**	THF	**12**	94:6
3	Ph	(i)	**3a**	THF	**12**	95:5
4	Ph	(i)	**3b**	THF	**12**	96:4
5	*n*-Pr	(ii)	**3a**	MeCN	**11**	89:11
6[c]	*n*-Pr	(ii)	**3b**	MeCN	**11**	86:14
7	*n*-Pr	(ii)	**1a**	MeCN	**11**	23:77
8[d]	Ph	(ii)	**1a**	MeCN	**12**	81:19
9[d]	Ph	(ii)	**3a**	MeCN	**12**	58:42
10	Ph	(ii)	**1a**	THF	**12**	80:20
11	Ph	(ii)	**3a**	THF	**12**	50:50

[a] *Experimental conditions:* substrate 0.5 mmol, precatalyst 3 mol%, room temperature, 18 h, (i) sodio dimethylmalonate 0.6 mmol or (ii), dimethyl malonate 0.5 mmol, K_2CO_3 0.5 mmol.

[b] Conversion and B/L ratio as determined by ^{1}H NMR spectroscopy and GC analysis.

[c] Conversion: 93%.

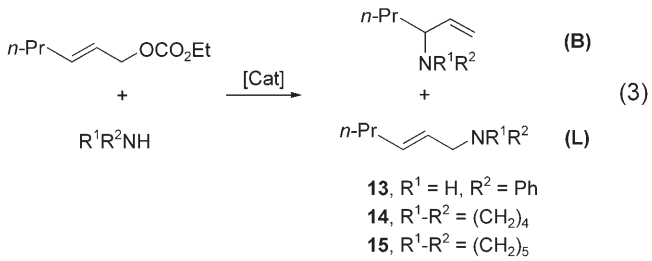
[d] 40 h.

Attempts to achieve the direct allylation of dimethyl malonate without prior deprotonation confirmed a lack of reactivity, which could be overcome by addition of K_2CO_3 as a base according to path (ii) [Eq. (2)]. Acetonitrile can be used as solvent and these conditions promoted the formation of the branched isomer of **11** starting from ethyl 2-*(E)*-hexen-1-yl carbonate. The best regioselectivity was obtained in the presence of the precatalyst **3a** allowing us to reach a 89:11 B/L ratio (entry 5). Under these conditions, the precatalyst **3b** featuring the *tert*-butyl-substituted cyclopentadienyl ligand failed to enhance this remarkable regioselectivity starting from an unsymmetrical aliphatic allylic substrate (entry 6).

For comparison, the involvement of **1a** as precatalyst under these mild conditions led to the favored formation of the linear product as indicated by a 23:77 B/L ratio (entry 7). The involvement of K_2CO_3 as a base to generate the dimethyl malonate anion as a soft carbonucleophile, might be reasonably assumed to ensure a large presence of dimethyl malonate relative to dimethyl malonate anion. The preserved dimethyl malonate might act as a source of protons for the regeneration of the type (**C**) intermediate allowing the release of the ethoxide anion as EtOH and making easier the activation of ethyl 2-*(E)*-hexen-1-yl carbonate. Accordingly, the addition of ethyl 2-*(E)*-hexen-1-yl carbonate to a solution of **1a** and quinaldic acid in dichloromethane as solvent, led to the quantitative formation of **4a**, thus providing an alternate synthesis of **4a** (experiment details in Supporting Information).

Under the conditions (ii), a longer reaction time was clearly required when starting from ethyl cinnamyl carbonate as the allylic substrate. More unexpectedly, the cinnamyl substrate led to a 81:19 B/L regioselectivity with **1a** as precatalyst (entry 8) and to a still lower 58:42 B/L ratio with **3a** as precatalyst (entry 9), which represent markedly reduced regioselectivities as compared to the experiments performed under conditions (i) (entries 3 and 4). The regioselectivity was even worse in THF as solvent (entries 10 and 11).

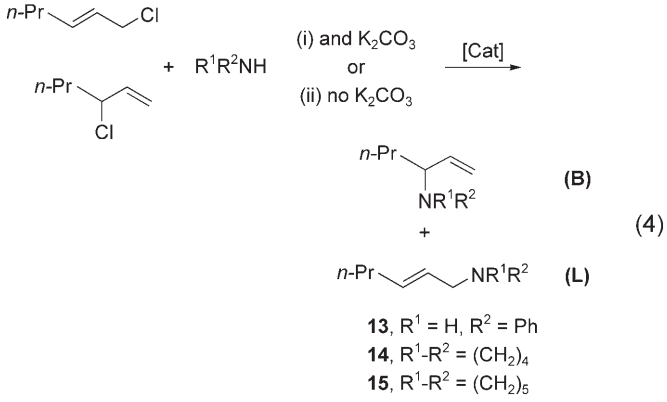
Finally, complexes **3a** and **3b** were evaluated as precatalysts for allylic substitution reactions leading to the formation of a carbon-nitrogen bond. Aniline was selected as a primary amine and pyrrolidine and piperidine were selected as secondary amines. Starting from ethyl 2-*(E)*-hexen-1-yl carbonate as the allylic substrate [Eq. (3)], the results are given in Table 3.



(3)

In acetonitrile as solvent, the reaction with aniline in the presence of **3a** (3 mol%) as precatalyst, resulted in a modest consumption of 49% of the allylic carbonate after a 16 h reaction time, and revealed a favored formation of the linear isomer of the allylic amines **13** (entry 1). No conversion at all had been previously observed using $[Ru(C_5Me_5)(\eta^2\text{-}O_2CO\text{-}t\text{-}Bu)(\eta^3\text{-}CH_2CHCHPh)][PF_6]$ as precatalyst and the analogous *tert*-butyl 2-*(E)*-hexen-1-yl carbonate as the allylic substrate.[16a] Under similar conditions, the consumption of ethyl 2-*(E)*-hexen-1-yl carbonate with pyrrolidine was complete and led to a favored formation of the branched isomer of the allylic amines **14**. The 85:15 B/L ratio (entry 2) was increased to an excellent 93:7 B/L regioselectivity by using dichloromethane instead of acetonitrile as solvent (entry 3). Surprisingly, the precatalyst **3b** achieved a markedly reduced regioselectivity (entry 4) whereas the involvement of **1a** as precatalyst showed the linear product to be formed selectively (entry 5). Pointing out the importance of the choice of the solvent, conversion and regioselectivity were both disfavored when the use of THF as solvent was attempted (entry 6). Under the most favorable conditions for the formation of the branched allylamine from pyrrolidine (entry 3), piperidine afforded the allylic amines **15** with a lower regioselectivity as determined by a 73:27 B/L ratio (entry 7).

The formation of allylruthenium(IV) intermediates is expected to be easier starting from chlorohexene relative to ethyl 2-*(E)*-hexen-1-yl carbonate. For this reason, the synthesis of the allylic amines **13–15** was also investigated starting from chlorohexene as the allylic substrate [Eq. (4)].



(4)

Two distinct procedures were introduced. In path (i) [Eq. (4)], the initial presence of one equivalent of K_2CO_3 with respect to the amine provided the formation of the free allylic amines **13–15**. In path (ii), no K_2CO_3 was added so that the allylic amines remained protected as their hydrochloride form. Whatever the conditions used, the results given in Table 4 show the favored formation of the branched isomers of the allylic amines **13–15**. As compared to the results obtained using ethyl 2-*(E)*-hexen-1-yl carbonate as the

Table 3. Formation of allylic amines **13–15** starting from ethyl 2-*(E)*-hexen-1-yl carbonate.[a]

Entry	R^1R^2NH	Catalyst	Solvent	Conversion[b]	Product	B/L[b]
1	Aniline	**3a**	MeCN	49	**13**	33:67
2	Pyrrolidine	**3a**	MeCN	100	**14**	85:15[c]
3	Pyrrolidine	**3a**	CH_2Cl_2	100	**14**	93:7
4	Pyrrolidine	**3b**	CH_2Cl_2	100	**14**	60:40
5	Pyrrolidine	**1a**	CH_2Cl_2	100	**14**	2:98
6	Pyrrolidine	**3a**	THF	68	**14**	44:56
7	Piperidine	**3a**	CH_2Cl_2	100	**15**	73:27[c]

[a] *Experimental conditions:* allylic carbonate 0.5 mmol, amine 0.75 mmol, catalyst 3 mol%, room temperature, 16 h.
[b] Conversion (%) and B/L ratio as determined by ^1H NMR spectroscopy and GC analysis.
[c] An unidentified additional minor product was detected by ^1H NMR spectroscopy.

Table 4. Formation of allylic amines **13–15** starting from chlorohexene.[a]

Entry	R^1R^2NH	Catalyst	Solvent	Path	Conversion[b]	Product	B/L[b]
1	Aniline	**3a**	Acetone	(i)	100	**13**	85:15
2	Aniline	**3b**	Acetone	(i)	100	**13**	88:12
3	Aniline	**3b**	Acetone	(ii)	77	**13**	87:13
4	Pyrrolidine	**3a**	CH_2Cl_2	(i)	100	**14**	71:29
5	Pyrrolidine	**3a**	CH_2Cl_2	(ii)	100	**14**	82:18
6	Pyrrolidine	**3b**	CH_2Cl_2	(ii)	100	**14**	83:17
7	Piperidine	**3b**	Acetone	(ii)	100	**15**	69:31
8	Piperidine	**3b**	CH_2Cl_2	(ii)	100	**15**	64:36

[a] *Experimental conditions:* chlorohexene 0.5 mmol, amine 0.75 mmol, catalyst 3 mol%, K_2CO_3 0.75 mmol for path (i) and none for path (ii), room temperature, 16 h.
[b] Conversion (%) and B/L ratio as determined by ^{1}H NMR spectroscopy and GC analysis.

allylic substrate, the reaction with aniline now led to the formation of the branched isomer of the allylic amines **13** as the major product. The 85:15 B/L regioselectivity reached when **3a** was used as precatalyst (entry 1) was enhanced to a 88:12 B/L regioselectivity with **3b** as precatalyst (entry 2). The reaction required the presence of K_2CO_3 to reach completion as compared to path (ii), which gave a moderate 77% consumption of chlorohexene (entry 3).

On the other hand, the 71:29 B/L regioselectivity provided by the more basic pyrrolidine and **3a** as precatalyst in the presence of K_2CO_3 (entry 4) could be increased to a 82:18 B/L selectivity according to path (ii) using **3a** or **3b** as precatalyst (entries 5, 6). As was observed from ethyl 2-*(E)*-hexen-1-yl carbonate as allylic substrate, piperidine afforded a lowered regioselectivity as compared to pyrrolidine, in acetone (entry 7) or in dichloromethane (entry 8) as solvent.

Conclusions

New stable allylruthenium(IV) complexes [Ru(C_5Me_4R)(2-quinolinecarboxylato)(η^3-CH_2CHCHR')] [PF_6] were synthesized as single stereoisomers, in one step starting from [Ru(C_5Me_4R)($MeCN)_3$] [PF_6], quinaldic acid, and allylic alcohols. They were demonstrated to be efficient precatalysts in nucleophilic allylic substitution and provided highly regioselective formation of branched products from allylic substrates such as ethyl 2-*(E)*-hexen-1-yl carbonate and chlorohexene. The selective formation of carbon-oxygen, carbon-carbon, and carbon-nitrogen bonds, was thus achieved under mild basic conditions using phenols, dimethyl malonate and primary and secondary amines as nucleophiles, respectively. With amines, the regioselectivity strongly depends on the nature of the amine. Variations of regioselectivity were also observed arising as well from a structural modification of the C_5Me_4R cyclopentadienyl ligand, from the nature of the allylic substrate, the nature of the solvent and the basic conditions. Therefore, a large choice is offered for variation to reach the optimal conditions with respect to regioselectivity.

The novel and most attractive property of this family of catalysts is their efficiency to provide, especially from phenols and soft carbonucleophiles, high regioselectivities in favor of branched products *starting from linear aliphatic allylic substrates.*

Experimental Section

Typical Synthesis of Complexes; [Ru(C_5Me_5)(2-quinolinecarboxylato)(η^3-$CH_2CHCHMe$)][PF_6] (3a)

As a typical procedure, dichloromethane (35 mL) was added to a stirred mixture of **1a** (2.01 g, 3.98 mmol) and quinaldic acid (0.69 g, 3.98 mmol),), to rapidly afford a dark violet-purple solution to which crotyl alcohol (0.60 mL, an excess) was added. The mixture was further stirred overnight and was then evaporated to dryness under vacuum. The remaining solid was dissolved in dichloromethane (20 mL) and the orange-red solution was then covered with diethyl ether (100 mL) to afford thin orange needles that were collected by filtration; yield: 1.97 g (81%).

Complete experimental details concerning the synthesis of complexes, ^{1}H and ^{13}C NMR data and elemental analysis are given as Supporting Information.

X-Ray Crystallography

The samples were studied with an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromator. Crystallographic data are given in Table 5. Data reduction was carried out with CrysAlis RED.[19] The structures were solved with SIR-97 which revealed the non-hydrogen atoms.[20] After anisotropic refinement, many hydrogen atoms may be 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).[21] ORTEP views were prepared with PLATON98.[22] CCDC 668006 (**3b**) and CCDC 666465 (**4′a**) contain the supplementary crystallographic data for this paper. These data can be

Table 5. Crystallographic data for complexes **3b** and **4′a**.[a]

Complex	**3b**	**4′a**
Empirical formula	$C_{27}H_{34}F_6NO_2PRu$	$C_{27}H_{34}BCl_2F_4NO_2Ru$
Molecular weight [g mol^{-1}]	650.59	663.33
Crystal size [mm]	0.22×0.20×0.20	0.25×0.12×0.10
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	8.7309(6)	13.7437(5)
b [Å]	14.4825(7)	8.2230(2)
c [Å]	21.2213(9)	25.6883(8)
β [°]	96.097(8)	104.320(3)
Volume [Å^3]	2668.2(3)	2813.0(2)
Z	4	4
Density [g cm^{-3}]	1.620	1.566
Temperature [K]	110(2)	110(2)
F(000)	1328	1352
Mo-K$_\alpha$ radiation, λ [Å]	0.71073	0.71073
Absorption coefficient [mm^{-1}]	0.716	0.800
θ range [°]	2.74 to 33.52	2.61 to 32.10
Index ranges	$-13<h<12$, $-21<k<22$, $-31<l<31$	$-20<h<19$, $-6<k<12$, $-38<l<37$
Reflections collected	47802	26113
Independent reflections	9359 ($R_{int}=0.0234$)	8933 ($R_{int}=0.0211$)
Reflections $I>2\sigma(I)$	8075	6961
Data/restraints/parameters	9359/0/344	8933/0/344
Goodness-of-fit on F^2	0.854	1.062
Final R indices [$I>2\sigma(I)$]	$R_1=0.0309$, $wR_2=0.0864$	$R_1=0.0353$, $wR_2=0.1041$
R indices (all data)	$R_1=0.0386$, $wR_2=0.0917$	$R_1=0.0481$, $wR_2=0.1078$
Largest diff. peak/hole [e·Å^{-3}]	0.802 and −0.846	1.295 and −0.982

[a] $w=1/[\sigma^2(F_0^2)+(0.0636P)^2+4.9341P]$ (**3b**), $1/[\sigma^2(F_0^2)+(0.0695P)^2+0.7219P]$ (**4′a**), where $P=(F_0^2+2F_c^2)/3$.

obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Typical Catalytic Experiment; Synthesis of Allyl Aryl Ether 6

As a typical experiment, a sample of *p*-methoxyphenol (0.5 mmol, 1 equiv.) was added to a stirred mixture consisting of hexenyl chloride (0.5 mmol, 1 equiv.), precatalyst **3b** (0.015 mmol, 3 mol%), K_2CO_3 (0.5 mmol, 1 equiv.), and dichloromethane (4.0 mL). The mixture was stirred at room temperature for 18 h and the resulting slurry was filtered for GC analysis. The filtrate was then concentrated under vacuum and ^{1}H NMR spectroscopy analysis solely disclosed 3-(4-methoxyphenoxy)-1-hexene as the branched isomer of allyl aryl ether **6** (B/L ratio = 99:1).

Complete experimental details concerning catalytic experiments and ^{1}H NMR spectra and data for compounds **6**–**15** are given as Supporting Information.

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