Regio- and enantioselectivity in the alkylation and etherification reactions of cinnamyl allylic derivatives catalyzed by [(η5-C5R5)Ru(N–N*)(NCCH3)]PF6 (R = H, Me) complexes containing N–N* bulky chiral ligands of different rigidity and flexibility

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A B S T R A C T

$[(\eta^5$-C5R5)Ru(N–N*)(NCMe)]PF6 (R = H, N–N* = (Sa)-**1**, **5**; (Sa)-**2**, **6**; (R,R)-**3**, **7**; (R,R)-**4**; **8**; R = Me, N–N* = (Sa)-**1**, **9**) complexes containing N–N* bulky chiral ligands of different rigidity and flexibility were synthesized by reacting the precursor $[(\eta^5$-C5R5)Ru(NCMe)3]PF6 (R = H, Me) with the N–N* ligand in a 1:1 molar *ratio*. The more bulky $(\eta^5$-C5Me5) ligand gave low stability to the complexes $[(\eta^5$-C5Me5)Ru(N–N*)(NCMe)]PF6, when N–N* = (Sa)-**2**, (R,R)-**3**, (R,R)-**4**, in comparison to $(\eta^5$-C5H5) ligand and prevented their characterization. The catalytic activity of complexes **5**–**9** in allylic alkylation and etherifications reactions, using malonate and phenoxide anions as nucleophiles respectively, were investigated and compared to the results obtained with corresponding precursors $[(\eta^5$-C5H5)Ru(NCMe)3]PF6 and $[(\eta^5$-C5Me5)Ru(NCMe)3]PF6. The effect of bulkiness and of rigidity and flexibility ligand features is discussed.

1. Introduction

Transition metal-catalyzed allylic substitution reaction provides an effective process for carbon–carbon and carbon–heteroatom bond formation, under mild conditions [1]. The possibility of having a stereogenic centre with high enantiomeric excess in the product increased the interest for this research area. Several studies showed important results achieved by the use of appropriate chiral ligands able to lead to good asymmetric induction [2]. While palladium-catalyzed allylic substitution reactions on a symmetric allylic moiety, like the 1,3-diphenylallyl, have been extensively studied and the main factors determining the enantioselectivity of the process were largely identified [3], the control of the regio- and enantioselectivity in nucleophilic substitution of unsymmetrical allylic substrates is still a challenging area. In fact, in the latter case the regioselectivity is strongly dependent on the transition metal involved in the catalytic species. Palladium-catalysts normally direct the nucleophile attack towards the less substituted allyl terminus of the unsymmetrical allylic moiety, giving the linear product; while molybdenum [4], tungsten [5], iridium [6], rhodium [7] and ruthenium [8] catalysts induce high regioselectivity in

favour of the branched isomer, containing a stereogenic centre. Recently, Bruneau and co-workers [9] and Pregosin and co-workers [10] research groups highlighted that $(\eta^5$-C5Me5)Ru complexes are effective catalysts in these reactions affording the branched isomer with high regioselectivity and, in some cases, enantioselectivity [11]. These works, carried out combining NMR spectroscopy, X-ray diffractometry and DFT calculations, demonstrated that the origin of regioselectivity is due to the ruthenium–allyl bond character. In fact, in the square pyramidal intermediate, the coordination mode of the asymmetric allyl group may be depicted considering also a minor contribution of a formal η^2-olefinic species, where the more substituted carbon bears a positive charge [9,10]. The oxidative addition of the asymmetric allylic halides, acetates or carbonates to $(\eta^5$-C5Me5)Ru^{II} centre, generating the $[(\eta^5$-C5Me5)Ru$^{IV}(\eta^3$-allyl)] species, and the presence of labile ligands, such as acetonitrile, coordinated to the metal centre seems to be required for the occurrence of the catalytic process [9,10].

Nearly all of the ruthenium catalysts studied in the allylic substitution reactions contain the η^5-C5Me5 ligand, whereas not so much is known about the influence of the electronic and steric hindrance features of the cyclopentadienyl ring on the catalytic process [12].

Trost et al. [8b] found that by increasing the steric demand of the catalyst by substitution of hydrogen atoms with methyl groups in the cyclopentadienyl ring of the catalyst, the branched product is obtained in a higher yield.

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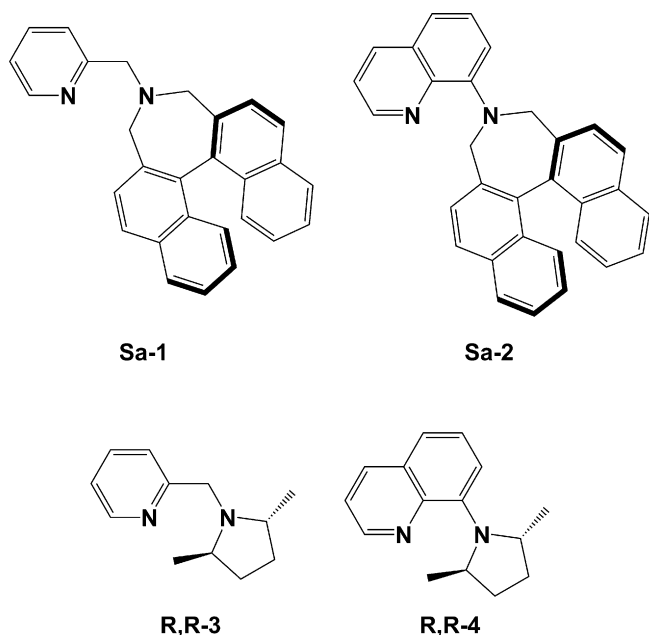 *E-mail address:* ffaraone@unime.it (F. Faraone).

Fig. 1. Scheme of the N–N* chiral ligands.

Recently, Bruneau and co-workers [13] reported the use of the $[(\eta^5\text{-}C_5Me_4R)Ru(NCMe)_3]PF_6$ (in which R is a bulky substituent CH_2tBu, *i*Pr, *t*Bu, and CF_3) as catalysts in allylic alkylation and etherification reactions.

Herein, we focus on the results obtained by using the complexes $[(\eta^5\text{-}C_5R_5)Ru(N–N^*)(NCMe)]PF_6$ (R = H, N–N* = (Sa)-**1**, (Sa)-**2**, (R,R)-**3**, (R,R)-**4**; R = Me, N–N* = (Sa)-**1**) as precatalysts and the cinnamyl derivatives as substrates. The N–N* bidentate chiral ligands, containing the rigid 2-pyridinyl or 8-quinolinyl building block skeleton and the C_2-symmetric chiral framework (S)-(+)-2,2'-(2-azapropane-1,3-diyl)-1,1'-binaphthalene or *trans*-2,5-dimethyl-pyrrolidinyl, have been previously reported by our research group [3d,14]. Each ligand shows different basicity at the N-donor atoms; the ligand pairs having the same C_2-symmetric chiral framework but different building block skeleton differ in rigidity and flexibility features (Fig. 1).

Besides considering the efficiency of catalytic ruthenium systems containing the N–N* chiral ligands, this work emphasizes the effect of different steric and electronic features of $\eta^5\text{-}C_5R_5$ ligands in determining the regio- and enantioselectivity of the process. In fact, owing to the presence of the N–N* donor ligand bulkiness, (the $\eta^5\text{-}C_5H_5$ ring may facilitate the process because it leads to a less congested precatalyst, whereas the $\eta^5\text{-}C_5Me_5$ ring) which induces high electron density at the ruthenium centre, may assist the oxidative addition, that involves a change in the oxidation state from Ru(II) to Ru(IV).

The work was also supported by theoretical DFT calculations on the relative stability of the precatalysts $[(\eta^5\text{-}C_5Me_5)Ru(N–N^*)(NCMe)]^+$. (N–N* = (Sa)-**1**, (Sa)-**2**). The study was carried out with the aim of gaining insight into the origin of the regio- and enantioselectivity in the $(\eta^5\text{-}C_5R_5)Ru^{II}$ catalyzed (R = H, Me) allylic substitution process.

2. Experimental

2.1. General methods

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Freshly distilled solvents were used throughout and dried by standard procedures. Published methods were used to prepare compounds (Sa)-(+)-2,2'-[2-(methyl-2-pyridyl)-2-azapropane-1,3-diyl]1,1'-binaphthalene [15] (Sa)-**1** and (Sa)-(−)-2,2'-[(7-quinolinyl)-2-azapropane-1,3-diyl] 1,1'-binaphthalene (Sa)-**2** [3d]. (R,R)-(+)-2-(2,5-dimethyl-pyrrodin-1-ylmethyl)-pyridine (R,R)-**3** and (R,R)-(+)-8-(2,5-dimethyl-pyrro-din-1-yl)-quinoline (R,R)-**4** were prepared starting from (2S,5S)-2,5-hexandiol cyclic sulphate as reported in literature [3d]. Cinnamyl methyl carbonate was prepared according to a published procedure [16]. All other reagents were purchased from Sigma–Aldrich and Strem and were used as supplied. For column chromatography, silica gel 60 (220 ± 440 mesh) purchased from Fluka was used. ^{1}H NMR experiments were carried out using a Bruker AMX R300 spectrometer and referenced to internal tetramethylsilane. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

All calculations were carried out using the Gaussian G03W program package [17]. The structures and bonding parameters were computed at the density functional (DFT) PBE1PBE level of theory, using Becke's exchange functional, which includes the Slater exchange along with corrections involving the gradient of the density [18] and Perdew and Wang's gradient-corrected correlation functional [19,20].

2.2. General procedure for the synthesis of $[(\eta^5\text{-}C_5R_5)Ru(N–N^*)(NCMe)]PF_6$ (5–9) (R = H or Me)

The $[(\eta^5\text{-}C_5R_5)Ru(N–N^*)(NCMe)]PF_6$ complexes with N–N* = (Sa)-**1** (R = H, **5**, R = Me, **9**), (Sa)-**2** (R = H, **6**), (R,R)-**3** (R = H, **7**), (R,R)-**4** (R = H, **8**), were synthesized in the same way with the following procedure.

A solution of the N–N* ligand (0.1 mmol) in toluene (2 mL) was added to a solution of $[C_5H_5(MeCN)_3Ru]PF_6$ (45 mg, 0.1 mmol) or $[C_5Me_5(MeCN)_3Ru]PF_6$ (50.4 mg, 0.1 mmol) in acetonitrile (1 mL). The mixture was stirred for about 1 h while the colour became from dark orange to brown depending on the ligand. After this time the solvent was removed under inert atmosphere and the residue was washed with diethyl ether still in inert atmosphere. The complexes were obtained as brownish powders.

2.2.1. $[(\eta^5\text{-}C_5H_5)Ru(Sa\text{-}1)(NCMe)]PF_6$ (5)
Yield: 78.5% (58 mg, 0.078 mmol). ^{1}H NMR (CDCl$_3$): δ 9.2 (d, 1H, ^3J 5 Hz, H *a*-pyridine), 8.1–7.8 (m, 6H), 7.54–7.14 (m, 9H), 4.22 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 4.14 (d, 1H, ^3J 14 Hz, CH$_2$ ligand), 3.83 (d, 1H, ^3J 16 Hz, CH$_2$ ligand), 3.76 (s, 5H, cyclopentadienyl), 3.73 (d, 1H, ^3J 14 Hz, CH$_2$ ligand), 3.57 (d, 1H, ^3J 16 Hz, CH$_2$ ligand), 3.34 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 2.39 (s, 3H, CH$_3$CN). Anal. calcd. for C$_{35}$H$_{30}$F$_6$N$_3$PRu (738,7): C, 56.91; H, 4.09; N, 5.69. Found: C, 57.01; H, 4.21; N, 5.59.

2.2.2. $[(\eta^5\text{-}C_5H_5)Ru(Sa\text{-}2)(NCMe)]PF_6$ (6)
Yield: 85% (66 mg, 0.085 mmol). ^{1}H NMR (CDCl$_3$): δ 9.65 (d, 1H, ^3J 5 Hz, H *a*-quinoline), 8.31 (d, 1H, ^3J 8 Hz), 8.21 (d, 1H, ^3J 8 Hz) 8.1–7.9 (m, 4H), 7.85 (d, 1H, ^3J 8 Hz), 7.65–7.15 (m, 8H), 6.96 (d, 1H, ^3J 8 Hz), 6.91 (d, 1H, ^3J 8 Hz), 5.02 (d, 1H, ^3J 14 Hz, CH$_2$ ligand), 4.40 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 4.23 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 4.20 (d, 1H, ^3J 14 Hz, CH$_2$ ligand), 3.80 (s, 5H, cyclopentadienyl), 2.25 (s, 3H, CH$_3$CN). Anal. calcd. for C$_{38}$H$_{30}$F$_6$N$_3$PRu (774,70): C, 58.91; H, 3.90; N, 5.42. Found: C, 59.20; H, 4.08; N, 5.22.

2.2.3. $[(\eta^5\text{-}C_5H_5)Ru(R,R\text{-}3)(NCMe)]PF_6$ (7)
Yield: 70% (38 mg, 0.07 mmol). ^{1}H NMR (CDCl$_3$): δ 9.07 (d, 1H, ^3J 5 Hz, H *a*-pyridine), 7.70 (t, 1H, ^3J 9 Hz), 7.33 (d, 1H, ^3J 8 Hz), 7.18 (m, 1H), 4.10 (5, 5H, cyclopentadienyl), 4.07 (d, 1H, ^3J 17 Hz, CH$_2$ ligand), 3.91 (mb, 1H, CH pyrrolidinyl), 3.61 (d, 1H, ^3J 17 Hz, CH$_2$ ligand), 3.39 (mb, 1H, CH pyrrolidinyl), 2.35 (s, 3H, CH$_3$CN), 2.12 (mb, 2H, CH$_2$ pyrrolidinyl), 1.72 (mb, 2H, CH$_2$ pyrrolidinyl), 1.56 (b,

3H, CH$_3$ pyrrolidinyl), 1.04 (b, 3H, CH$_3$ pyrrolidinyl). Anal. calcd. for C$_{19}$H$_{26}$F$_6$N$_3$PRu (542,43): C, 42.07; H, 4.83; N, 7.75. Found: C, 42.75; H, 5.09; N, 7.58.

2.2.4. *[(η^5-C$_5$H$_5$)Ru(R,R-**4**)(NCMe)]PF$_6$ (**8**)*

Yield: 75% (44 mg, 0.075 mmol). ^{1}H NMR (CDCl$_3$): δ 9.56 (d, 1H, ^3J 5 Hz, H *a*-quinoline), 8.24 (d, 1H, ^3J 8 Hz), 7.72 (d, 1H, ^3J 8 Hz), 7.58–7.47 (m, 2H), 7.42 (d, 1H, ^3J 8 Hz), 4.39 (m, 1H, CH pyrrolidinyl), 4.25 (s, 5H, cyclopentadienyl), 3.97 (m, 1H, CH pyrrolidinyl), 2.64 (m, 1H, CH$_2$ pyrrolidinyl), 2.01–1.82 (mb, 2H, CH$_2$ pyrrolidinyl), 1.99 (s, 3H, CH$_3$CN), 1.81 (d, 3H, ^3J 6 Hz CH$_3$ pyrrolidinyl), 0.94 (m, 1H, CH$_2$ pyrrolidinyl), 0.64 (d, 3H, ^3J 6 Hz CH$_3$ pyrrolidinyl). Anal. calcd. for C$_{22}$H$_{26}$F$_6$N$_3$PRu (578,50): C, 45.68; H, 4.53; N, 7.26. Found: C, 45.43; H, 4.70; N, 7.75.

2.2.5. *[(η^5-C$_5$Me$_5$)Ru(Sa-**1**)(NCMe)]PF$_6$ (**9**)*

Yield: 78% (63 mg, 0.078 mmol). ^{1}H NMR (CDCl$_3$): δ 8.56 (d, 1H, ^3J 9 Hz, H *a*-pyridine), 8.37 (d, 1H, ^3J 5 Hz), 8.17 (d, 1H, ^3J 9 Hz), 8.05–7.85 (m, 5H), 7.53–7.38 (m, 6H), 7.27 (m, 2H), 4.63 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 4.47 (d, 1H, ^3J 16 Hz, CH$_2$ ligand), 4.10 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 3.96 (d, 1H, ^3J 12 Hz, CH$_2$ ligand), 3.94 (d, 1H, ^3J 16 Hz, CH$_2$ ligand), 2.74 (d, 1H, ^3J 12 Hz, CH$_2$ ligand, 1.65 (s, 3H, CH$_3$CN), 1.54 (s, 15H, pentamethylcyclopentadienyl). Anal. calcd. for C$_{40}$H$_{40}$F$_6$N$_3$PRu (808,80): C, 59.40; H, 4.98; N, 5.20. Found: C, 60.01; H, 4.21; N, 5.59.

2.3. Catalytic allylic substitution reaction

2.3.1. Allylic alkylation reaction

In a 30 mL Schlenk tube equipped with magnetic stirring bar, under argon, [(η^5-C$_5$R$_5$)Ru(MeCN)$_3$]PF$_6$ (0.015 mmol) in 1 mL of acetonitrile was treated with the N–N* ligand (0.015 mmol) in 2 mL of toluene. The solution was stirred for 1 h. After this period, the solvent was evaporated under inert atmosphere. The precatalyst so prepared *in situ* was solubilized in anhydrous THF (3 mL) and, to this solution, the substrate (cinnamyl acetate or cinnamyl methyl carbonate, 0.5 mmol) and sodium dimethyl malonate (0.6 mmol) were sequentially added. The sodium dimethylmalonate was freshly prepared by reaction of NaH (0.6 mmol, 15.2 mg) in 1 mL of THF and dimethyl malonate (0.6 mmol, 0.069 mL) under argon atmosphere. The solution was then degassed by three freeze–thaw cycles and left stirring at room temperature for 24 h. The reaction was monitored by TLC (hexane/EtOAc 4:1). The solution was diluted with 50 mL of Et$_2$O and washed with water (2× 10 mL). The aqueous phases were extracted with diethyl ether; all the organic phases were collected and dried over MgSO$_4$, filtered and evaporated *in vacuo*. The regioselectivity was determined by integration of ^{1}H NMR peaks relative to the linear and the branched substituted products. The optical purity was determined by NMR using paramagnetic shift reagent [Eu(hfc)$_3$]. Assignment of the absolute configuration was made by the sign of the optical rotation.

2.3.2. Allylic etherification reaction

After stirring 0.015 mmol of [(η^5-C$_5$R$_5$)Ru(MeCN)$_3$]PF$_6$ and 0.015 mmol of N–N* ligand in the solvent (dichloromethane or acetonitrile) at room temperature for 1 h, 0.75 mmol of potassium carbonate and 0.5 mmol of cinnamyl chloride were added and after 15 min. 0.75 mmol of phenol was added and the mixture was stirred for 40 h and monitored by TLC (hexane/1% Et$_2$OAc). After this time the solution was filtered on silica and concentrated under *vacuo*.

The resulting oil was analyzed by ^{1}H NMR spectroscopy and the enantiomeric excess was determined by HPLC.

3. Results and discussion

3.1. Synthesis of the precatalysts [(η^5-C$_5$R$_5$)Ru(N–N*)(NCMe)]PF$_6$ (R = H, N–N* = (Sa)-**1**, (Sa)-**2**, (R,R)-**3**, (R,R)-**4**; R = Me, N–N* = (Sa)-**1**)

Preliminarily to the catalytic study, the complexes [(η^5-C$_5$R$_5$)Ru(N–N*)(NCMe)]PF$_6$ (R = H, N–N* = (Sa)-**1**, **5**; (Sa)-**2**, **6**; (R,R)-**3**, **7**; (R,R)-**4**, **8**; R = Me, N–N* = (Sa)-**1**, **9**) were synthesized by reacting the cationic complex [(η^5-C$_5$H$_5$)Ru(NCMe)$_3$]PF$_6$, in acetonitrile, with an equimolar amount of the N–N* ligand, in toluene. Starting from the [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]PF$_6$ complex, only the compound [(η^5-C$_5$Me$_5$)Ru((Sa)-**1**)(NCMe)]PF$_6$, **9**, was isolated, as the reaction with (Sa)-**2**, (R,R)-**3** and (R,R)-**4** ligands afforded unstable complexes in solution. The compounds **5**–**9** are brownish solids and their stability to oxygen and moisture is limited in time; they were characterized by ^{1}H NMR spectroscopy and elemental analysis. ^{1}H NMR spectra showed only one singlet relative to the C$_5$R$_5$ resonance, allowing us to establish that compounds **5**–**9** were formed with 100% of diastereomeric excess. Particularly, ^{1}H NMR spectra in CDCl$_3$ of complexes **5**–**8** showed a singlet in the 3.76–4.25 ppm range for the five equivalent hydrogen atoms from the cyclopentadienyl ring, while, in ^{1}H NMR spectra in the same solvent of complex **9**, one singlet at 1.54 ppm consistent with the presence of the five equivalent methyl groups from the pentamethylcyclopentadienyl ring was present. Methyl signal of acetonitrile ligand was in the 1.65–2.39 ppm range for complexes **5**–**9**. Signal from the α-pyridinyl or α-quinolinyl hydrogen atom of the ligand shifted downfield after coordination to the metal centre. The coordination mode of each ligand with both nitrogen atoms to the ruthenium centre was indicated by the splitting of some representative signals of the ligand.

We could not have information about the absolute configuration at the ruthenium centre of the single diastereomer observed because no crystals suitable for X-ray diffraction of **5**–**9** were obtained. However, the acquaintance of this data does not seem to be indispensable for the use of these compounds as precatalysts and the interpretation of the related results. The missing of change in ^{1}H NMR spectra in CDCl$_3$ of samples containing the precatalysts **5**–**9** in 24 h, let us to exclude the possibility of epimerization processes in solution that could lead to both diastereomers. DFT calculations indicated a significant major stability of the diastereomer with the absolute configuration R at the ruthenium centre (see later). In a previous work we proved the ability of these N–N* chiral ligands to induce a 100% diastereomeric excess and configurational stability at the metal centre in the synthesized half-sandwich [(η^6-*p*-cymene)Ru(N–N*)Cl]PF$_6$ and [(η^5-C$_5$Me$_5$)Rh(N–N*)Cl]SbF$_6$ complexes [14b].

3.2. Catalytic experiments

The catalytic activities of the cationic precatalysts **5**–**9**, in the allylic alkylation of cinnamyl acetate or methyl carbonate and the etherification of cinnamyl chloride were investigated and compared, using malonate and phenoxide anions as nucleophiles. The alkylation reaction (1) afforded the linear and branched cinnamyl malonate, forming a C–C bond; the etherification reaction (2) led to the linear and branched allyl phenyl ethers (Scheme 1).

In the allylic alkylation reactions, cinnamyl methyl carbonate or acetate (0.5 mmol) and sodium dimethyl malonate (0.6 mmol) were added to a solution in THF of **5**–**9** (0.015 mol). The mixture was left to react for 24 h at room temperature to ensure the highest yield of the substituted product. After this period, no further conversion was observed. Results of the catalytic experiments are present in Table 1.
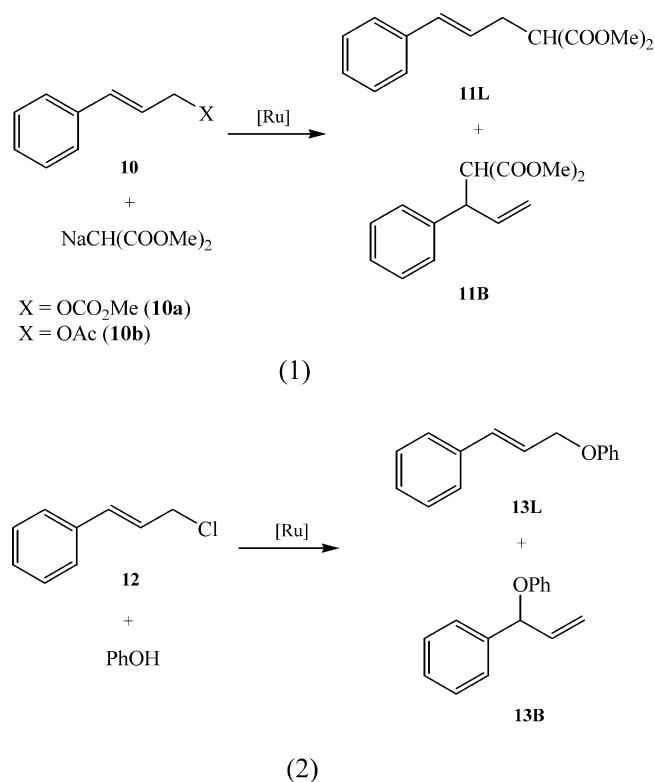
Scheme 1. Allylic substitution reactions: alkylation (1), etherification (2).

In the reported conditions, the reactions of complexes **5**–**8** with both cinnamyl methyl carbonate and acetate, using dimethyl malonate anion as nucleophile (reaction (1)) gave a poor regioselectivity being the linear (**11L**) and branched (**11B**) allylic derivatives almost in equimolar *ratio* with a modest conversion. The linear allyl isomer (**11L**) was even obtained as the major product when the catalysts **8** containing the rigid (R,R)-**4** ligand was used (Table 1, entry 11). We observed, using the (Sa)-**1** ligand, that lowering the temperature, the regioselectivity was improved in favour of the linear isomer whereas conversion and enantioselectivity decreased. The precatalysts **5**–**8** gave enantioselectivity values of the branched product very low or similar to those of the racemic mixture, either using cinnamyl methyl carbonate or acetate as source of the allylic moiety. The best e.e. values were obtained using the precatalysts **5**

Table 1
Ruthenium-catalyzed allylic alkylation of cinnamyl derivatives with sodium dimethylmalonate[a].

Entry	Catalyst	Substrate	Conversion [%][b]	11B/11L[b]	e.e. (%)[c]
1[d]	5	10a	7	30/70	10 (S)
2[e]	5	10a	27	43/57	20 (S)
3	5	10a	60	51/49	36 (S)
4	6	10a	65	56/44	4 (S)
5	7	10a	75	52/48	36 (R)
6	8	10a	86	41/59	2 (S)
7	9	10a	90	85/15	4 (S)
8	5	10b	20	49/51	20 (S)
9	6	10b	100	47/53	4 (S)
10	7	10b	90	44/56	20 (R)
11	8	10b	90	30/70	rac
12	9	10b	66	74/26	rac

[a] Experimental conditions: catalyst (3 mol%), THF as solvent, room temperature (if not stated otherwise), 24 h.
[b] Conversion and B/L were determined by ^{1}H NMR.
[c] Determined by NMR with chiral shift reagent [Eu(hfc)$_3$].
[d] The reaction was carried out at 0 °C.
[e] The reaction was carried out at 10 °C.

Table 2
Ruthenium-catalysed allylic etherification of cinnamyl chloride (12) with phenol[a].

Entry	Catalyst	Conversion [%][b]	13B/13L[b]	e.e. [%][c]
1	5	99	94/6	54 (R)
2	6	100	83/17	44 (R)
3[d]	7	100	84/16	rac
4	8	100	83/17	3 (S)
5	9	90	86/14	2 (S)
6	[(C$_5$H$_5$)Ru(NCMe)$_3$]PF$_6$	100	75/25	–

[a] Experimental conditions: catalyst (3 mol%), K$_2$CO$_3$ (1 equiv.), CH$_2$Cl$_2$ as solvent, room temperature, 40 h.
[b] Determined by ^{1}H NMR.
[c] Determined by chiral HPLC (OJ-CHIRACEL column). Assignment of the absolute configuration was made by comparison with literature data[15].
[d] CH$_3$CN was used as solvent.

and **7** containing the more flexible ligands (Sa)-**1** and (R,R)-**3**, up to 36% (Table 1, entries 3 and 5).

In the alkylation of cinnamyl ethyl carbonate with dimethylmalonate anion, by the use of [(η^5-C$_5$Me$_5$)Ru(N–N)(NCMe)]PF$_6$ precatalysts (N–N = 4,4′-alkyl-2,2′-bipyridine or 1,10-phenantroline) Bruneau and co-workers [9] obtained the branched isomer with high yield and regioselectivity of 100% (when N–N is 4,4′-dimethyl-2,2′-bipyridine) or close to this value. Under analogous experimental conditions the [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]PF$_6$ precatalyst gave the branched product in a lower regioselectivity (B/L = 90/10). When N–N ligands are α-diimines RN=CH–CH=NR (R = *i*-Pr or mesityl), a lower regioselectivity in favour of the branched isomer, compared to the result obtained with the [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]PF$_6$ precursor, was observed (80–85%) [21].

The different behaviour of 4,4′-alkyl-2,2′-bipyridine and 1,10-phenanthroline ligands in comparison with the ligands **1**–**4** could be attributed to a planar structure where the substituents are out of the metal coordination sphere, in the former ones.

The results reported in the present work indicate that the coordination of the N–N* ligands to the precatalyst [(η^5-C$_5$H$_5$)Ru)(NCMe)$_3$]PF$_6$ does not improve the regioselectivity in favour of the branched isomer in the allylic alkylation reaction.

The comparison of the corresponding (η^5-C$_5$H$_5$)Ru and (η^5-C$_5$Me$_5$)Ru as precatalysts in allylic substitution reactions has been limited to complexes **5** and **9**, because of the failure in the formation of the (η^5-C$_5$Me$_5$)Ru complexes with (Sa)-**2**, (R,R)-**3** and (R,R)-**4** ligands. In the same experimental conditions used for precatalysts **5**–**8**, complex **9** gave the branched cinnamyl malonate (**11B**) with regioselectivity of 85:15 (Table 1, entry 7). This value is lower than that obtained with the [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$] and [(η^5-C$_5$Me$_5$)Ru(N–N)(NCMe)]PF$_6$ (N–N = 4,4′-alkyl-2,2′-bipyridine, α-diimines or 1,10-phenantroline) precatalysts, but higher than the one obtained with precatalyst **5**.

More interesting results were observed in the catalytic etherification reactions (2) of cinnamyl chloride. The results are given in Table 2. The process affording allyl phenyl ethers was carried out in CH$_2$Cl$_2$, or acetonitrile, at room temperature, using cinnamyl chloride and phenol in the presence of K$_2$CO$_3$ and the precatalysts **5**–**9**. Using the (η^5-C$_5$H$_5$)Ru precatalysts **5**–**8**, after 40 h a complete conversion of the substrate was observed in almost all cases, and the cinnamyl phenyl ether was produced with excellent or good regioselectivity in favour of the branched isomer with values in the range from 94/6 to 83/17. The regioselectivity 13B/13L of 94:6, obtained using the precatalyst **5**, containing the more flexible (Sa)-**1** ligand, is very close to the highest values reported for the catalytic classic test of allylic etherification with PhOH/K$_2$CO$_3$ [8j,22,11]. Differently, when the more congested precatalyst **9** was used a lower B/L *ratio* of 86/14 (Table 2, entry 5) was observed compared to complex **5**.

Changing the solvent from dichloromethane (Table 2, entry 5), to acetonitrile, only a slight increase in the conversion of the cinnamyl chloride but not in regioselectivity, was observed.

However, the branched cinnamyl phenyl ether was obtained with modest e.e. values of 54 and 44% (Table 2, entries 1 and 2).

It is noteworthy that, in the same experimental conditions, $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]PF_6$ precatalyst (Table 2, entry 6) gave the allyl phenyl ether product with a B/L ratio of 75/25, lower than the values obtained using the precatalysts **5**–**8**. This result supports that both electronic and steric effects from $(\eta^5\text{-}C_5R_5)$ ring and ligand features have to be considered in order to explain the results of the catalytic process.

The reported results emphasizes that the regioselectivity of the catalytic allylic alkylation and etherification reactions, in which bidentate nitrogen ligands are coordinated to the precatalyst, is strongly influenced by the steric features of the coordinated ligand.

As concerns the N–N* ligands, the more flexible (Sa)-**1** ligand confers an improved efficiency to the precatalyst. In a previous work [14], we showed by X-ray diffractometry study, that the *trans*-2,5-dimethylpyrrolidinyl chiral fragment congests the metal centre more than the binaphthylazepine moiety ((R,R)-**3** compared to (Sa)-**1** ligand). It should be also considered that, besides the nucleophilic attack to the allylic substrate coordinated to ruthenium(IV), the occurrence of the elimination product as an olefinic species involves a rotation step, which is affected by the rigidity and flexibility features, besides the bulkiness, of the coordinated N–N* ligand.

We previously highlighted that the knowledge of the origin of the enantioselectivity in a palladium-catalyzed allylic substitution process requires, in principle, information about the conformational isomers of the catalytic species in solution, their relative concentration, possible exchange processes and equilibria, occurring under Curtin–Hammett conditions [3d].

In fact, the observed enantioselectivity value is the result of the nucleophilic attack to the allylic carbon in a well-determined conformer; actually, the product may present opposite absolute configuration depending on the considered isomer. Consequently, beyond the electronic and steric features of the ligands coordinated to the metal centre, the acquaintance of the conformational isomers in solution is required in order to discuss the origin of the enantioselectivity. The possibility of having height possible conformational isomers from the catalyst $[(\eta^5\text{-}C_5R_5)Ru(N\text{-}N^*)(PhHCCHCH_2)]^{2+}$ prevented a study that could reveal dynamic processes associated with chelated rings. This could be necessary to rationalize the enantioselectivity values obtained in these processes [3d].

Catalytic allylic dicationic intermediate species of Ru(IV) containing N,N chelating bidentate ligands have been reported [9,11,16].

The X-ray diffraction structural determinations of $(\eta^5\text{-}C_5R_5)Ru(IV)(\eta^3\text{-}PhHCCHCH_2)$ (R = H, Me) complexes reported in literature [23,8d,9] support, for the catalytic intermediate species $[(\eta^5\text{-}C_5R_5)Ru(N\text{-}N^*)(PhHCCHCH_2)]^{2+}$ considered in this study, an almost square pyramidal geometry in which the ruthenium atom is surrounded by the $(\eta^5\text{-}C_5R_5)$, in apical position, the η^3-allyl moiety and the N–N* bidentate ligand in the square plane.

All these factors make difficult a ^1H NMR study for ruthenium-catalyzed allylic substitution of unsymmetrical substrates, that allow to preview the origin of the enantioselectivity, as in palladium-catalyzed allylic substitution of diphenyl allyl substrates, in which the number of possible conformers is reduced [3d]. The results in terms of e.e. are modest both in allylic alkylation, with a maximum value of 36%, and etherification reactions, where 55% is the best e.e. value found. These results are not surprising considering the data reported in literature to date; in fact, with analogous ruthenium catalysts, only a few examples referring to good enantioselectivity can be found.

3.3. DFT calculations

Density functional calculations were performed on models of the diastereoisomers $[Ru(\eta^5\text{-}C_5R_5)(N\text{-}N^*)(NCMe)]^+$ (R = H, Me; N–N* = (Sa)-**1**, (Sa)-**2**). These models reproduce the features of the complete structures of the species, namely the coordination environment of the ruthenium atom, the chelate ring and the core of the complex, in a reliable way. The complexity and number of atoms in the considered structures prevents the use of *ab initio* methods for all the models of interest, therefore we performed density calculations on molecules containing the (Sa)-**1** or (Sa)-**2** ligand but with a biphenyl moiety instead of a binaphthyl one. We have verified in a previous work [3d] that the difference between the real binaphthyl moiety and the biphenyl-optimised model in density functional calculations is not significant.

We performed DFT calculations on complexes containing the C_5H_5 ligand, since in literature [8d,9,16,17] there are only calculations about complexes with the C_5Me_5 ligand. Our study showed that the $[(\eta^5\text{-}C_5H_5)Ru((Sa)\text{-}\mathbf{2})(NCMe)]^+$ complex in the diastereomeric form (Sa, R_{Ru}) is more stable than in the (Sa, S_{Ru}) configuration, being the difference in energy of 3.51 kcal, a value high enough to justify the presence in solution of only one diastereomer. Starting from these data, the structures of the complexes $[(\eta^5\text{-}C_5R_5)Ru(N\text{-}N^*)(NCMe)]^+$ (R = H, CH_3; N–N* = (Sa)-**1**, (Sa)-**2**) were optimised assigning the R configuration at the ruthenium centre. The models of the complexes $[(\eta^5\text{-}C_5R_5)Ru((Sa)\text{-}\mathbf{1})(NCMe)]^+$ (R = H, Me) show an identical coordination geometry and very similar Ru–N1 distances for both $(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5Me_5)$ species (2.250(3) Å and 2.252(3) Å respectively); the same was found for the Ru–N2 bond distances (2.081(6) Å and 2.071(6) Å respectively). This supports the fact that the flexibility features of the ligand (Sa)-**1** allow a spatial arrangement which does not affect the complex stability. Significant differences, particularly in the Ru–N1 bond distances, were found in the $[(\eta^5\text{-}C_5R_5)Ru(Sa\text{-}\mathbf{2})(NCMe)]^+$ complexes changing from the $(\eta^5\text{-}C_5H_5)$ to the $(\eta^5\text{-}C_5Me_5)$ species (Ru–N1 2.213(7) Å with $(\eta^5\text{-}C_5H_5)$ and 2.276(0) Å with $(\eta^5\text{-}C_5Me_5)$; Ru–N2 2.060(2) Å and 2.066(5) Å respectively). The weakening of the Ru–N1 bond in the $[(\eta^5\text{-}C_5R_5)Ru(Sa\text{-}\mathbf{2})(NCMe)]^+$, changing from the $\eta^5\text{-}C_5H_5$ to the $\eta^5\text{-}C_5Me_5$ species, could be responsible for the very low stability of the $[(\eta^5\text{-}C_5Me_5)Ru((Sa)\text{-}\mathbf{2})(NCMe)]^+$ complex (and of those containing the (R,R)-**3** and (R,R)-**4** ligands) in solution; changing from the $\eta^5\text{-}C_5H_5$ to the $\eta^5\text{-}C_5Me_5$ species, the rigidity of the ligand (Sa)-**2** does not allow the hindered binaphthyl moiety to rearrange in a form at lower energy, reducing the repulsive interactions.

Then, DFT calculations on the precatalyst monocationic species $[(\eta^5\text{-}C_5R_5)Ru(N\text{-}N^*)(NCMe)]^+$ (R = H, CH_3) show that the bulkiness of the cyclopentadienyl ligand has a strong influence on the complex stability, when bulky ligands are coordinated to the ruthenium centre.

DFT calculations on the models of all eight possible conformers of $[(\eta^5\text{-}C_5R_5)Ru((Sa)\text{-}\mathbf{2})(PhHCCHCH_2)]^{2+}$ complex revealed the isomer whose allylic carbon atom C2 is present in a *endo* configuration (C–H bond points away from the cyclopentadienyl ring) and the substituent on C3 carbon atom have a syn configuration (aryl moiety is directed as the C–H bond), while C1 carbon atom assumes a facial position respect to the sp^2 nitrogen atom N2, as the isomer at lowest energy (see Chart 1). For this reason, the calculations were carried out only on this conformer isomer for all the complexes. Thus, missing data related to ligands different from Sa-**2**, a comparison between the stability of all conformers would not be significant.

As concerns the Ru-allyl bond, the calculations on the $[(\eta^5\text{-}C_5H_5)Ru((Sa)\text{-}\mathbf{2})(NCMe)]^+$ complex allowed to notice that the distances Ru–C1 (C1 = CH_2) are in the range of 2.12–2.16 Å and Ru–C3 (C3 = CHPh) in the range of 2.57–3.24 Å (the latter value
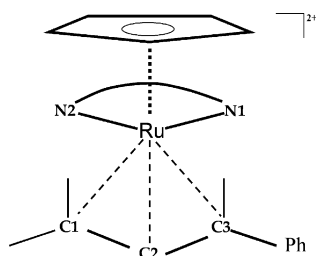
Chart 1.

referred to (R,R)-**4** ligand supports a non-coordinated N-sp^3 atom). These differences in the allylic carbon atoms Ru–C1 and Ru–C3 are indicative of a strong electrophilic contribution at C3 allyl carbon atom and support also for (η^5-C$_5$H$_5$)Ru(PhHCCHCH$_2$) complexes the allyl coordination mode depicted by Pregosin and Bruneau [8d,9,16,17].

These data let to preview that, unless steric repulsive interactions are effective, the nucleophilic attack occurs at C3 allylic carbon atom.

Actually, in the etherification reaction we observe a pronounced regioselectivity in favour of the branched isomer as predicted by the theoretical calculation. It is likely that the lack of a significant B/L regioselectivity in the allylic alkylation reaction is due to steric effects, which influence the rotation step, that follows the nucleophilic attack by malonate anion, leading to an olefinic ruthenium(II) complex before the elimination step.

4. Conclusions

Complexes **5**–**9**, obtained as stable compounds from the (η^5-C$_5$R$_5$)Ru (R = H, Me) precursors, acted as precatalysts, under mild conditions, in the allylic substitution reactions.

The coordination of the N–N* ligand to the Ru(II) metal centre decreased the B/L *ratio* in the allylic alkylation reaction, compared to the related precursor [(η^5-C$_5$H$_5$)Ru(NCMe)$_3$]PF$_6$; nevertheless, the highest B/L value, 85:15, was observed by using the precatalyst **9**. On the other hand, the branched isomer cinnamyl phenyl ether was obtained with excellent regioselectivity, comparable to the best data present in literature for the allylic etherification reaction, higher than the precursor [(η^5-C$_5$H$_5$)Ru(NCMe)$_3$]PF$_6$. These last results are indicative of an improving effect due to the ligand coordination.

As concerns the enantioselectivity in the cinnamyl malonate and cinnamyl phenyl ether branched isomers formation, the best values are moderate. The origin of the enantioselectivity in these catalytic processes still remains an unresolved question, even when high values of e.e. are obtained [11].

However, in our study we cannot exclude that the nitrile loss and the subsequent oxidative addition of the allylic fragment could give the catalytic species as a pair of geometrical isomers differing each other from the position of phenyl group on the allyl carbon atom respect to N1 and N2 donor atoms. Then, the nucleophilic attack to the CHPh carbon atom could give the product of substitution in the R or S absolute configuration.

Nevertheless, this work emphasizes the importance of the flexibility features of the N–N* coordinated ligand in order to determine the regio- and enantioselectivity of the process. In fact, the best catalytic efficiency in the regio- and enantioselectivity of the process was observed when the more flexible (Sa)-**1** ligand was coordinated in the precatalyst.

Furthermore, it should be considered that the rotation step, which leads to the olefin intermediate, and the following product elimination could be influenced by the nucleophile steric demand.

Moreover, the work shows, for the first time, the possibility of obtaining good regioselectivity and modest enantioselectivity values with (η^5-C$_5$H$_5$)Ru complexes.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.05.011.

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