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α-Diimines as nitrogen ligands for ruthenium-catalyzed allylation reactions and related (pentamethylcyclopentadienyl) ruthenium complexes

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Abstract

The new Cp*Ru(II) (Cp*: pentamethylcyclopentadienyl) complexes Cp*(dab-R)RuCl, [Cp*(dab-R)(MeCN)Ru][PF_6] (dab-R: RN=CH–CH=NR; R: *iso*-propyl, mesityl), and [Cp*(cod)(MeCN)Ru][PF_6], are synthesized in high yields by reacting the corresponding α-diimine or 1,5-cyclooctadiene with [Cp*RuCl]$_4$ and [Cp*$(MeCN)_3$Ru][PF_6], respectively. The α-diimine ligands are strongly bonded to the ruthenium centre as shown by the subsequent formation of the alkynyl derivatives Cp*(dab-R)RuC≡CR′ (R′ = *tert*-butyl or phenyl) and of the cationic derivatives [Cp*(dab-R)(L)Ru][PF_6] (L = CO, PMe_3). The neutral and cationic α-diimine or 1,5-cyclooctadiene ruthenium complexes are compared as catalyst precursors for the ruthenium-catalyzed allylation of diethyl-sodiomalonate and diethylamine with cinnamyl acetate or ethyl cinnamyl carbonate.

Keywords: Allylation; Regioselective; Homochelate NN ligand; Ligand effect; Ruthenium

1. Introduction

Transition metal-catalyzed allylic substitution reactions represent an important tool for organic synthesis [1]. Since the pioneering work using Cp*(cod)RuCl (Cp*: pentamethylcyclopentadienyl, cod: 1,5-cyclooctadiene) as catalyst for highly regioselective allylic substitution reactions favouring the formation of branched products [2], Cp*Ru-complexes have received an increasing interest. Thus, the cationic [Cp*$(MeCN)_3$Ru][PF_6] precursor was recently observed to conveniently allow the synthesis of drugs and allylic ethers [3,4]. Recently also, very high reactivities and remarkable catalytic activies were reached when involving [Cp*(2,2′-bipyridine)(MeCN)Ru][PF_6] analogous complexes still displaying a ruthenium centre coordinated to a Cp* ring and to three nitrogen atoms [5]. Furthermore, the combination of the [Cp*$(MeCN)_3$Ru][PF_6] complex which contains very labile acetonitrile ligands, with a chiral bisoxazoline led to effficient enantioselective processes [6]. The catalytic activity in such allylation reactions is commonly believed to occur through formation of a reactive (η^3-allyl)-metal species, and the following (η^3-allyl)-Ru(IV) complexes have been successfully characterized, including X-ray structure determination: Cp*(PhCHCHCH$_2$)RuCl$_2$ [2], [Cp*(MeCHCHCH$_2$)(MeCN)RuBr][PF_6] [4], [Cp*(PhCHCHCH$_2$)(*o*-phenanthroline) Ru][PF_6]$_2$ [5]. The combination of a Cp*Ru fragment with an α-diimine has been reported to generate efficient catalyst precursors for allylic substitution reactions [7]. However no special attention was devoted to the determination of the active species. Furthermore, little is known concerning Cp*(α-diimine)Ru complexes although

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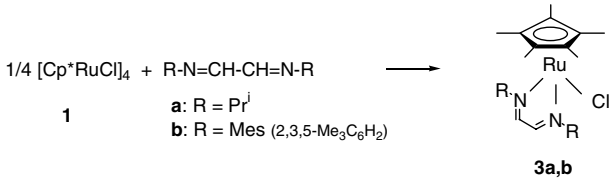
Cp(α-diimine)Ru derivatives have been studied [8,9] as well as structurally close (η^6-arene)(α-diimine) Ru complexes [10,11]. We report herein the synthesis of both neutral and cationic Cp(α-diimine) ruthenium complexes and the study of their catalytic properties toward allylic substitution reactions. To further compare neutral to cationic complexes, the cationic complex [Cp*(cod)-(MeCN)Ru][PF_6] was synthesized also.

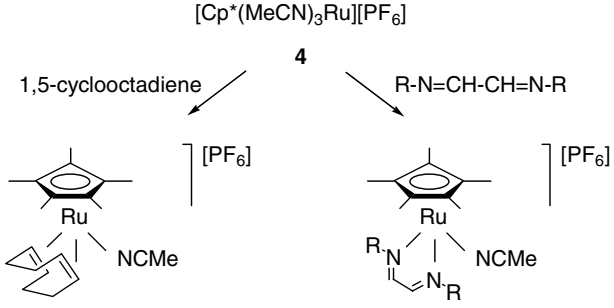
2. Results and discussion

The readily available complex [Cp*RuCl]$_4$ (**1**), is a convenient source of the 14-electron Cp*RuCl fragment as previously emphasized by the formation of the derivative Cp*(cod)RuCl (**2**), merely according to addition of 1,5-cyclooctadiene [12]. Similarly nicely, the α-diimines RN=CH–CH=NR [or 1,4-diaza-1,3-butadienes, dab-R; **a**, R = iPr; **b**, R = 2,4,6-$Me_3C_6H_2$ (mesityl)] reacted with **1** in dichloromethane solution at room temperature to afford Cp*(dab-R)RuCl, (**3a**,**b**) (Eq. (1)).



(1)

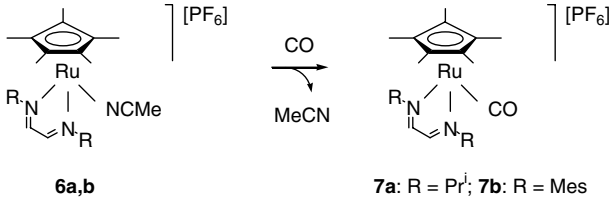
The acetonitrile ligands in the cationic complex [Cp*(MeCN)$_3$Ru][PF_6] (**4**) which is conveniently prepared from **1** and KPF_6 in acetonitrile [4], are labile enough to allow the synthesis of the cationic complexes [Cp*(cod)(MeCN)Ru][PF_6] (**5**) and [Cp*(dab-R)-(MeCN)Ru][PF_6] (**6a**,**b**) by reacting at room temperature 1,5-cyclooctadiene and α-diimines, respectively, with a solution of **4** in a dichloromethane–acetonitrile mixture (Eq. (2)).



(2)

The orange complex **5** and the deeply coloured (purple to violet) α-diimine complexes **3a**,**b** and **6a**,**b** are stable in air and were characterized from a combination of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and elemental analysis. Peculiarly characteristic of the α-diimine complexes **3a**,**b** and **6a**,**b** is the low field value (δ range: 8.44–8.71 ppm) of the ^{1}H NMR resonance corresponding to the two equivalent N=CH protons. The low field value (δ range: 152.7–163.9 ppm) observed for the ^{13}C{^{1}H} resonance corresponding to the two equivalent N=CH carbon nuclei support an η^2-(*N*,*N*)-coordination of the α-diimine ligand [13].

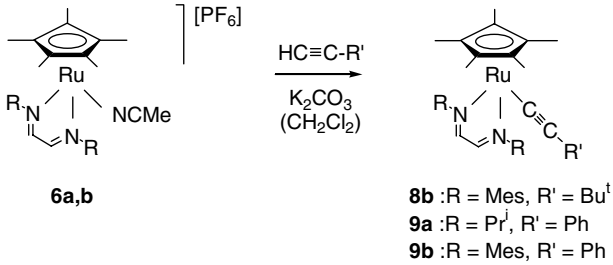
To check the lability of the α-diimine ligand in the new complexes, the reactivity of complexes **6a**,**b** toward carbon monoxide was first investigated. The reaction was achieved by stirring a dichloromethane solution of **6a**,**b** under a carbon monoxide atmosphere at room temperature and afforded the carbonyl derivatives **7a**,**b** (Eq. (3)).



(3)

Thus, we observed that only the acetonitrile ligand in **6a**,**b** was easily substituted by carbon monoxide. The IR spectra of **7a**,**b** showed the characteristic carbonyl absorption located at ν = 1959 and 1963 cm^{-1}, respectively. The carbonyl IR absorptions were located at ν = 1928 and 1963 cm^{-1} for the bipyridine complexes [Cp*(2,2′-bipyridine)(CO)Ru][PF_6] and [Cp(2,2′-bipyridine)(CO)Ru][PF_6], respectively [14]. These observations clearly indicate a markedly lower electron-donating ability of the α-diimines **a**,**b** as compared to 2,2′-bipyridine, since the effect is coarsely similar to an exchange between a Cp* ring and an unsubstituted Cp one.

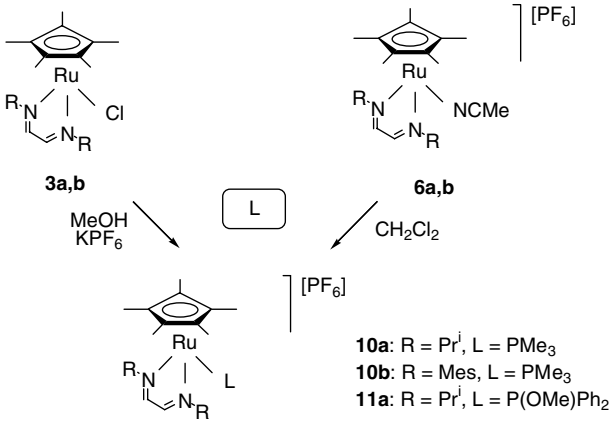
The acetonitrile ligand in complexes **6a**,**b** is not labile enough to allow substitution by terminal alkynes as no reaction was detected when *tert*-butylacetylene or phenylacetylene was added to a solution of **6a**,**b** in dichloromethane. However, under forcing conditions in the presence of K_2CO_3 acting as a base, the formation of the alkynyl derivatives **8b** and **9a**,**b** was observed (Eq. (4)).



(4)

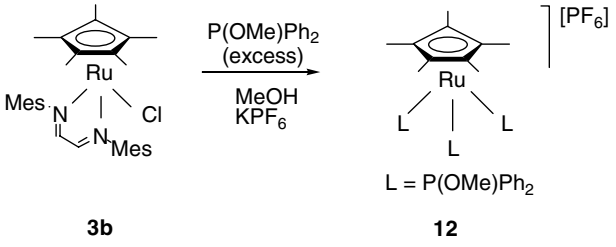
The stability of the Cp*(dab-R)Ru fragment was then investigated by reacting complexes **3a**,**b** and **6a**,**b** with monophosphorus compounds. Selective substitution of

the chloride ligand from complexes **3a**,**b** or of acetonitrile from **6a**,**b** by trimethylphosphine was achieved as summarized in Eq. (5).



(5)

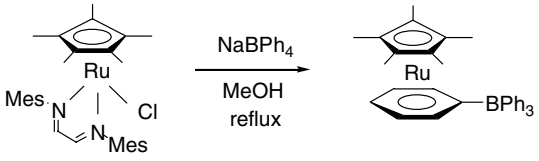
A similar selective substitution reaction occurred when **3a** and **6a** were treated with the bulkier methyldiphenylphosphinite (Eq. (5)). By contrast, **6b** appeared to be unreactive toward $P(OMe)Ph_2$. On the other hand, the reaction of **3b** with $P(OMe)Ph_2$ in methanol resulted in the substitution of both the chloride and α-diimine ligands without detection of any intermediate (Eq. (6)). Indeed, the reaction of **3b** with only one equivalent of methyldiphenylphosphinite resulted in a mixture of **12** and free α-diimine besides unreacted **3b** as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.



(6)

Thus, removal of the α-diimine ligand was detected only in this case. The inefficiency of the more basic trimethylphosphine to substitute α-diimine ligands indicated that the release of the α-diimine ligand only resulted from steric constraints.

The easy substitution of the chloride ligand from complexes **3a**,**b** indicated that an easy cleavage of the Ru–Cl bond might occur in methanol as polar solvent. Complex **3b** was found inert when a mixture of **3b** and $NaBPh_4$ was stirred at room temperature for two days in methanol. However, the formation of a white precipitate of $Cp^*Ru(\eta^6\text{-}C_6H_5BPh_3)$ was gradually observed when the mixture was heated at reflux for a prolonged time (20 h) together with the complete disappearance of the violet colour of **3b** (Eq. (7)) indicating the loss of both the chloride and α-diimine ligands from **3b**.



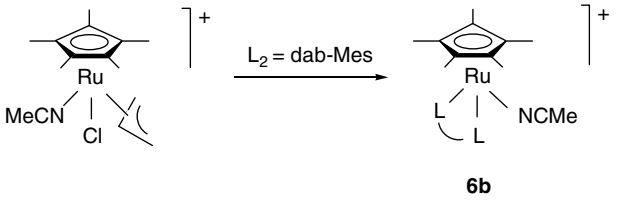
(7)

The zwitterionic derivative $Cp^*Ru(\eta^6\text{-}C_6H_5BPh_3)$ was isolated in 77% yield and had been merely prepared by reacting the labile Cp*(tmeda)RuCl complex with $NaBPh_4$ in dichloromethane at room temperature [15].

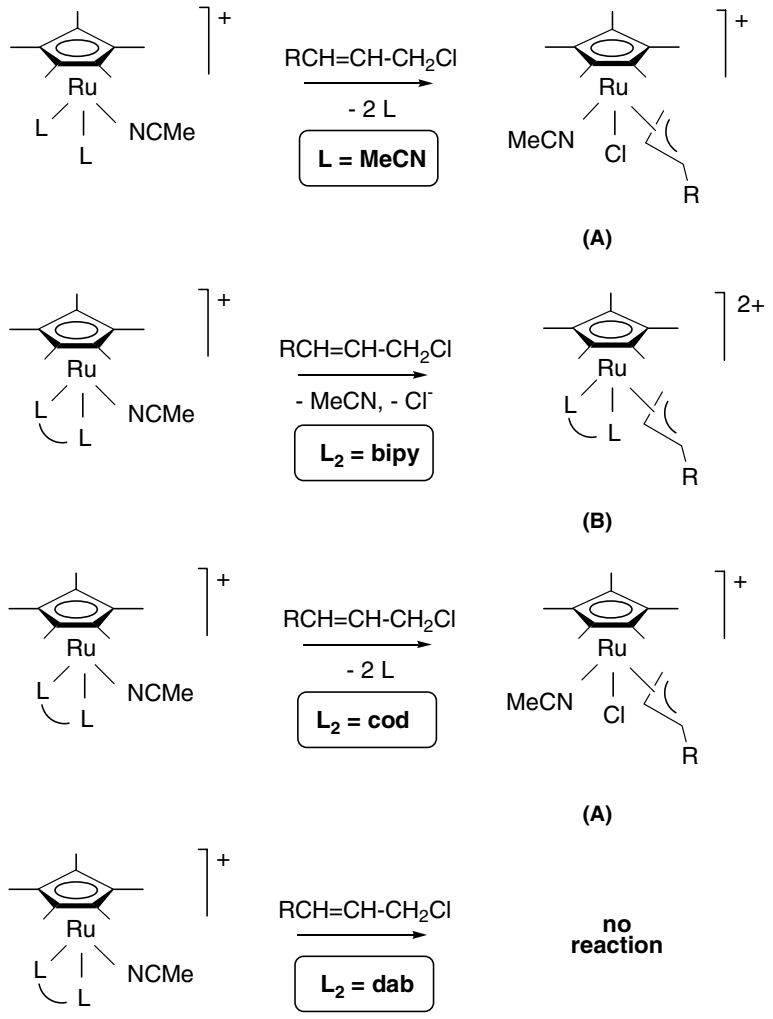
We have previously reported some ruthenium-catalyzed allylic substitution reactions starting from an unsymmetrical allylic carbonate and using a combination of an α-diimine and Cp*(cod)RuCl (**2**), or $[Cp^*(MeCN)_3\text{-}Ru][PF_6]$ (**4**) [7]. Complexes **3a**,**b** and **6a**,**b** are obviously the complexes resulting from such combinations and might be expected to behave as catalyst precursors via a subsequent formation of an (η^3-allyl)ruthenium(IV) intermediate. Indeed, the formation of neutral $Cp^*(\eta^3\text{-allyl})RuCl_2$ complexes [2], monocationic $[Cp^*(\eta^3\text{-allyl})(MeCN)RuX]^+$ (**A**) [4] and dicationic $[Cp^*(\eta^3\text{-allyl})(2,2'\text{-bipy})Ru]^{2+}$ (**B**) [5] derivatives is well documented.

The formation of the cationic structures (**A**) and (**B**) (See Scheme 1) corresponded to the oxidative addition of an allylic halide at a ruthenium(II) centre from a $[Cp^*(L_2)(MeCN)Ru][PF_6]$ complex. The formation of (**A**) involved the loss of the two labile L=MeCN ligands and the coordination of chloride whereas the retention of the strongly coordinated chelate L_2 = 2,2′-bipyridine led to (**B**). The cationic complex $[Cp^*(cod)(MeCN)Ru][PF_6]$ (**5**), was found to react with 3-chloro-2-methylpropene at ambient temperature to afford the allylic derivative $[Cp^*(\eta^3\text{-}CH_2CMeCH_2)(MeCN)RuCl][PF_6]$ [4]. Thus, complex **5** reacted with allylic halides according to the first pathway leading to derivatives (**A**) (Scheme 1). Not surprisingly, the reaction was slowed down as compared to the similar formation of (**A**) starting from the more labile $[Cp^*(MeCN)_3Ru][PF_6]$ **4**, and required several hours instead of minutes to reach completion.

Less expectedly, no reaction was observed when α-diimine complexes **6a**,**b** were treated with allylic halides. The neutral chloro complexes **3a**,**b** were also found to be inert toward allylic halides. The α-diimine ligands seemed thus neither labile enough to allow a formation of compounds of type (**A**) nor able to stabilize a speculative dicationic $[Cp^*(\eta^3\text{-allyl})(dab\text{-}R)Ru]^{2+}$ species of type (**B**).



(8)



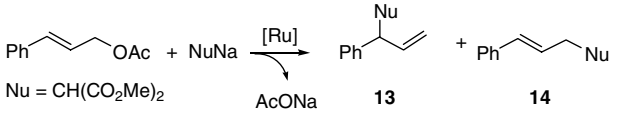
Scheme 1. Reactivity of [Cp*(L_2)(MeCN)Ru][PF_6] complexes toward allylic halides; L = MeCN or L_2 = 2,2′-bipyridine, 1,5-cyclooctadiene or α-diimine (dab).

Furthermore, we observed that α-diimines reacted with complexes of type (**A**) to trigger a reductive elimination of the allylic halide as shown by the reaction with the allylic derivative [Cp*(η^3-CH_2CHCH_2)(MeCN)-RuCl][PF_6] [4] leading to **6b** (Eq. (8)).

Such a reductive elimination of allylic halide induced by the coordination of an ancillary ligand is not a novel process and has been previously reported using carbon monoxide or even an arene ring under thermal activation [16]. This behaviour of α-diimines likely resulted from their markedly reduced electron-donating properties as compared to 2,2′-bipyridines. When the formation of Cp*(η^3-allyl)Ru(IV) intermediates is assumed to be the crucial step for catalytic activity, the incapability of Cp*(α-diimine)Ru complexes to generate Cp*(η^3-allyl)Ru(IV) derivatives unavoidably suggested that α-diimines should prevent catalytic activity. Therefore, a new investigation of the catalytic properties of **3a**,**b** and **6a**,**b** was undertaken.

3. Catalytic experiments

The catalytic activities of the neutral **2**, **3a**,**b** and cationic **5**, **6a**,**b** complexes were compared during the reaction of cinnamyl acetate with methyl sodiomalonate in tetrahydrofuran at room temperature (Eq. (9)).



(9)

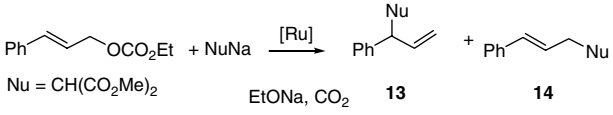
The results are given in Table 1 and clearly show that complexes **2** and **5** gave higher conversions than the α-diimine derivatives. The greater activity of **2** and **5** is likely induced by the lability of the 1,5-cyclooctadiene ligand. Better regioselectivities in favour of the branched isomer were also observed when the catalyst precursor contained the labile 1,5-cyclooctadiene ligand.

Table 1
Ruthenium-catalyzed allylation reactions with cinnamyl acetate

Entry	Catalyst	Conversion (%)[a]	**13**:**14**[a]
1	**2**	95	85:15
2	**3a**	20	80:20
3	**3b**	0	
4	**5**	85	90:10
5	**6a**	35	75:25
6	**6b**	30	74:26

Conditions: catalyst 3 mol%, THF, 17 h, room temperature.
[a] As determined by ^{1}H NMR spectroscopy.

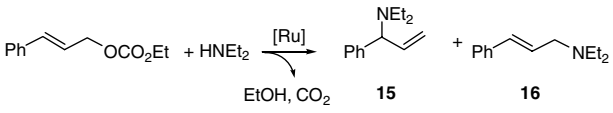
The complexes were then tested as catalysts for the nucleophilic substitution of ethyl cinnamyl carbonate with methyl sodiomalonate (Eq. (10)).



(10)

The cationic precursors **5**, **6a**,**b** and even the carbon monoxide derivative **7b** showed very comparable catalytic activities (see Table 2). A complete conversion was reached within 17 h and the major formation of the branched product **13** was observed (80–90%). With the neutral precursors **2**, **3a**,**b**, a high regioselectivity in favour of branched isomer is also obtained but the conversions strongly depend on the ancillary ligands. In this case, the ruthenium precursors bearing an α-diimine bidentate ligand appear more efficient than Cp*(cod)RuCl. Of peculiar interest, the alkynyl derivative **9b** was found completely inert thus suggesting the requirement of the labile Ru–Cl bond in **2** and **3a**,**b** for catalytic activity.

The catalytic activity of complexes was finally studied from the reaction of the unsymmetrical ethyl cinnamyl carbonate with diethylamine (Eq. (11), Table 3).



(11)

Table 2
Ruthenium-catalyzed allylation reactions with ethyl cinnamyl carbonate

Entry	Catalyst	Conversion (%)[a]	**13**:**14**[a]
1	**2**	45	95:5
2	**3a**	100	80:20
3	**3b**	85	65:35
4	**9b**	0	
5	**5**	100	85:15
6	**6a**	100	80:20
7	**6b**	100	85:15
8	**7b**	97	90:10

Conditions: catalyst 3 mol%, THF, 17 h, room temperature.
[a] As determined by ^{1}H NMR spectroscopy.

Table 3
Ruthenium-catalyzed allylation of diethylamine with ethyl cinnamyl carbonate

Entry	Catalyst	Conversion (%)[a]	**15**:**16**[a]
1	**2**	0	
2[b]	**2**	97	29:71
3	**3a**	0	
4[c]	**3a**	100	0:100
5[b,c]	**3a**	32	40:100
6	**3b**	0	
7[b]	**3b**	0	
8	**9b**	0	
9	**5**	100	0:100
10[b]	**5**	100	9:91
11	**6a**	100	5:95
12	**6b**	100	2:98
13[b]	**6b**	0	
14[d]	**6b**	95	84:16
15[e]	**6b**	40	19:81
16	**7a**	0	
17	**7b**	0	

Conditions: catalyst 3 mol%, THF, 17 h, room temperature.
[a] As determined by ^{1}H NMR spectroscopy.
[b] 0 °C instead of room temperature.
[c] In methanol instead of THF as solvent.
[d] In the presence of 2 moles of 4,4′-dimethyl-2,2′-bipyridine per mole of Ru.
[e] In the presence of 3 moles of α-diimine **b** per mole of Ru.

Conducting the experiments at room temperature and using THF as solvent, the neutral chloro complexes **2**, **3a**,**b** and the alkynyl derivative **9b** were all observed to be inert as catalyst for the reaction (Table 3, entries 1, 3, 6, 8). Using the 1,5-cyclooctadiene precursor **2**, the catalytic process worked at 0 °C (entry 2) indicating that a low stability of catalytically active species was responsible of the observed lack of reactivity at room temperature. By contrast, the α-diimine complex **3b** remained inert at 0 °C (entry 7) suggesting that the reactivity of **2** at 0 °C is also related to the lability of its 1,5-cyclooctadiene ligand. However, using methanol instead of THF as solvent to facilitate a cleavage of their Ru–Cl bond, the α-diimine complexes **3a**,**b** became active catalysts. Thus, the conversion of cinnamyl carbonate was complete at room temperature and the linear amine **16** was selectively obtained (entry 4). At a lowered temperature of 0 °C, a moderate conversion of 32% was reached but a substantial amount of the branched amine **15** was detected (entry 5). The ruthenium-catalyzed isomerization of branched allylic amines into their linear isomers has been previously reported [2] and a similar process may account for the observed selective formation of the linear amine **16** at room temperature (entry 4). Using THF as solvent, the cationic 1,5-cyclooctadiene complex **5** exhibited a high catalytic efficiency. At room temperature, the conversion of cinnamyl carbonate was complete and the linear allylic amine **16** was selectively obtained (entry 9). A complete conversion was still observed when the reaction was carried out at

0 °C but a minor formation of the branched allylic amine **15** was detected (entry 10). Very similar results were obtained when the cationic α-diimine complexes **6a**,**b** were involved at room temperature (entries 11 and 12) but these complexes were inert at 0 °C (entry 13). Remarkably, a nearly complete conversion was retained in the presence of additional free 4,4′-dimethyl-2,2′-bipyridine but resulted in a major formation of the branched amine (84:16) (entry 14). A very close result has been reported using the corresponding [Cp*(4,4′-dimethyl-2,2′-bipyridine)(MeCN)Ru][PF_6] complex as catalyst [5]. By contrast and as expected from our stoichiometric studies (vide supra), the additional presence of free α-diimine resulted in a markedly reduced conversion of 40% (entry 15). Finally, the carbon monoxide derivatives **7a**,**b** were inert even at room temperature (entries 16 and 17). This lack of reactivity likely indicated the requirement of the labile acetonitrile ligand in **6a**,**b** for the catalytic process.

4. Conclusion

The coordination of α-diimines on a Cp*Ru fragment provides a route to a new family of stable organometallic complexes. Furthermore, the catalytic experiments reported in this study emphazise the complexity of the involved catalytic processes. Distinct intermediates are probably involved depending on both the nature of reactants and the nature of the catalyst precursor. Thus, in the case of the amination reaction the activity of **2** only at 0 °C whereas the parent cationic complex **5** is active at room temperature provides evidence for distinct catalytically active intermediates. The comparison between α-diimine and 1,5-cyclooctadiene ruthenium complexes shows the α-diimine complexes to be less reactive catalysts as expected if the activity is assumed to be related to the lability of the α-diimine and 1,5-cyclooctadiene ligands. In agreement, no significant distinction was disclosed concerning the observed regioselectivities. A supplementary addition of a 2,2′-bipyridine is enough to reach distinct regioselectivies as obtained from 2,2′-bipyridine ruthenium precursors. This result also suggests a removal of the α-diimine ligand that may consist of a more complex process than a simple dissociation or substitution one, and remains to be elucidated.

5. Experimental

5.1. General comments

The reactions were performed under an inert argon atmosphere according to Schlenk type techniques. Diethyl ether and dichloromethane were distilled after drying according to conventional methods, whereas HPLC grade acetonitrile, acetone and methanol were straightforwardly used. Elemental analyses were performed by the ''Service de Microanalyse du CNRS'' Vernaison, France. NMR spectra were recorded at 297 K on AC 200 FT Bruker instrument (^{1}H: 200.13, ^{13}C: 50.32, ^{31}P: 81.01 MHz) and referenced internally to the solvent peak. The ruthenium complexes [Cp*RuCl]$_4$ (**1**), Cp*(cod)RuCl (**2**), and [Cp*(MeCN)$_3$Ru][PF_6] (**4**), were synthesized as described in the literature [4,12].

5.2. Synthesis of (C_5Me_5)(Pr^i–N=CH–CH=N–Pr^i)-RuCl, (**3a**)

A mixture consisting of a sample of **1** (3.21 g, 2.95 mmol), dab-iPr (1.66 g, 11.8 mmol) and dichloromethane (40 mL) was stirred overnight. Hexane (40 mL) was then added and the solution was filtered. The filtrate was slowly evaporated under vacuum to afford a brown–purple crystalline solid. Yield: 4.51 g, 93%. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.50 (d, ^3J = 5.6 Hz, 6H, 2CH*Me*), 1.53 (d, ^3J = 6.2 Hz, 6H, 2CH*Me*), 1.71 (s, 15H, C_5Me_5), 4.67 (broad, 2H, C*H*Me), 8.52 (s, 2H, CH=N); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 10.2 (C_5*Me*$_5$), 23.5 (CH*Me*), 23.7 (CH*Me*), 62.4 (*C*HMe$_2$), 87.9 (*C*$_5$Me$_5$), 152.7 (CH=N). Anal. Found: C, 52.63; H, 7.85; Cl, 8.26; N, 6.90%. Calc. for $C_{18}H_{31}ClN_2Ru$ (411.98): C, 52.48; H, 7.58; Cl, 8.61; N, 6.80.

5.3. Synthesis of (C_5Me_5)(Mes-N=CH–CH=N-Mes)-RuCl, (**3b**)

A mixture consisting of a sample of **1** (3.01 g, 2.77 mmol), dab-Mes (3.24 g, 11.1 mmol) and dichloromethane (35 mL) was stirred overnight. Hexane (40 mL) was then added and the solution was filtered. The filtrate was slowly evaporated under vacuum to afford a dark violet crystalline solid. Yield: 5.93 g, 95%. ^{1}H NMR ($CDCl_3$, δ, ppm): (s, 15H, C_5Me_5), 1.87 (s, 6H, 2Me), 2.30 (s, 6H, 2Me), 2.38 (s, 6H, 2Me), 6.82 (s, 2H, C_6H_2), 6.92 (s, 2H, C_6H_2), 8.68 (s, 2H, CH=N); ^{1}H NMR (CD_3OD, δ, ppm): 1.08 (s, 15H, C_5Me_5), 1.95 (s, 6H, 2Me), 2.32 (s, 6H, 2Me), 2.33 (s, 6H, 2Me), 6.90 (s, 2H, C_6H_2), 6.94 (s, 2H, C_6H_2), 8.71 (s, 2H, CH=N); ^{1}H NMR (C_6D_6, δ, ppm): 1.10 (s, 15H, C_5Me_5), 1.74 (s, 6H, 2Me), 2.17 (s, 6H, 2Me), 2.71 (s, 6H, 2Me), 6.70 (s, 2H, C_6H_2), 6.81 (s, 2H, C_6H_2), 8.07 (s, 2H, CH=N); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 8.9 (C_5*Me*$_5$), 18.9 (Me), 20.6 (Me), 20.9 (Me), 92.9 (*C*$_5$Me$_5$), 128.1 (CH), 129.4 (*C*Me), 129.8 (CH), 131.6 (*C*Me), 135.3 (*C*Me), 150.6 (CN), 160.6 (CH=N). Anal. Found: C, 64.19; H, 7.04; N, 5.03%. Calc. for $C_{30}H_{39}ClN_2Ru$ (564.18): C, 63.87; H, 6.97; N, 4.97.

5.4. Synthesis of [Cp*(cod)(MeCN)Ru][PF_6] (**5**)

To a solution of **4** (2.50 g, 4.96 mmol) in acetonitrile (30 mL), 1,5-cyclooctadiene (0.80 mL, 6.51 mmol) was

added. After to be stirred for 2 h, the mixture was evaporated under vacuum. The residue was dissolved in dichloromethane (30 mL) and the solution was covered with diethyl ether (120 mL) to allow the formation of dark-orange crystals according to the solvent diffusion technique. Yield: 2.29 g, 87%. Alternatively, a mixture consisting of a sample of Cp*(cod)RuCl (2.02 g, 5.32 mmol), KPF_6 (1.00 g, 5.43 mmol) and acetonitrile (35 mL) was stirred overnight and then evaporated under vacuum. The residue was extracted with dichloromethane (30 mL) and the solution was filtered to remove the potassium salts, then covered with diethyl ether as above. Yield: 2.20 g, 78%. ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.61 (s, 15H, C_5Me_5), 2.01–2.36 (m, 8H, CH_2), 2.62 (s, 3H, MeCN), 3.82–3.90 (m, 2H, CH=), 4.24–4.30 (m, 2H, CH=); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 4.87 (*Me*CN), 9.50 (C_5Me_5), 28.26 (CH_2), 30.68 (CH_2), 86.32 (CH=), 90.67 (CH=), 95.62 (C_5Me_5), 130.39 (Me*C*N). Anal. Found: C, 45.22; H, 5.60; N, 2.66; P, 5.77%. Calc. for $C_{20}H_{30}F_6NPRu$ (530.50): C, 45.28; H, 5.70; N, 2.64; P, 5.84.

5.5. Synthesis of [(C_5Me_5)(Pr^i–N=CH–CH=N–Pr^i)(MeCN)Ru](PF_6) (**6a**)

A mixture consisting of a sample of **4** (5.20 g, 10.3 mmol), dab-iPr (1.45 g, 10.3 mmol) and dichloromethane (40 mL) was stirred overnight. The resulting solution was concentrated (20 mL) and then covered with diethyl ether (90 mL) to afford dark-purple crystals. Yield: 5.64 g, 97%. ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.41 (d, ^3J = 6.6 Hz, 6 H, 2CH*Me*), 1.61 (d, ^3J = 6.8 Hz, 6H, 2CH*Me*), 1.69 (s, 15H, C_5Me_5), 2.25 (s, 3H, MeCN), 4.68 (m, 2H, C*H*Me), 8.44 (s, 2H, CH=N); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 3.8 (*Me*CN), 9.7 (C_5Me_5), 22.4 (CH*Me*), 24.3 (CH*Me*), 62.7 (*C*HMe$_2$), 87.5 (C_5Me_5), 126.5 (Me*C*N), 156.9 (CH=N). Anal. Found: C, 42.42; H, 6.11; N, 7.51; P, 5.50%. Calc. for $C_{20}H_{34}F_6N_3PRu$ (562.54): C, 42.70; H, 6.09; N, 7.47; P, 5.51.

5.6. Synthesis of [(C_5Me_5)(Mes-N=CH–CH=N-Mes)(MeCN)Ru](PF_6).1/2toluene (**6b**)

To a solution of **4** (2.70 g, 5.35 mmol) in dichloromethane (40 mL) and acetonitrile (10 mL), dab-Mes (1.57 g, 5.37 mmol) was added. The mixture was stirred overnight and toluene (20 mL) was added to the resulting violet solution. The solution was slowly concentrated under vacuum to afford a violet crystalline solid that was collected and washed with diethyl ether. Yield: 3.97 g, 98%. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.12 (s, 15H, C_5Me_5), 1.91 (s, 6H, 2Me), 2.12 (s, 6H, 2Me), 2.32 (s, 6H, 2Me), 2.50 (s, 3H, MeCN), 6.92 (s, 2H, C_6H_2), 6.96 (s, 2H, C_6H_2), 8.58 (s, 2H, CH=N); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 4.6 (*Me*CN), 8.8 (C_5Me_5), 18.6 (Me), 19.2 (Me), 20.9 (Me), 93.0 (C_5Me_5), 129.1 (*C*Me), 129.2 (*C*Me), 129.2 (CH), 130.1 (CH), 131.0 (Me*C*N), 137.0 (*C*Me), 148.7 (CN), 163.9 (CH=N). Anal. Found: C, 55.85; H, 6.02; N, 5.51; P, 4.08%. Calc. for $C_{32}H_{42}F_6N_3PRu.1/2C_7H_8$ (760.81): C, 56.04; H, 6.09; N, 5.52; P, 4.07.

5.7. Synthesis of [(C_5Me_5)(Pr^i–N=CH–CH=N–Pr^i)(CO)Ru](PF_6) (**7a**)

A solution of **6a** (1.00 g, 1.78 mmol) in dichloromethane (30 mL) was stirred overnight under a carbon monoxide atmosphere and was then evaporated under vacuum. The crude product was dissolved in chloroform (25 mL) and the purple solution was covered with diethyl ether (90 mL) to afford red–brown crystals. Yield: 0.82 g, 84%. IR (Nujol, ν, cm^{-1}): 1959 (C≡O); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.40 (d, ^3J = 6.6 Hz, 6 H, 2CH*Me*), 1.56 (d, ^3J = 6.6 Hz, 6 H, 2CH*Me*), 1.78 (s, 15H, C_5Me_5), 4.19 (m, 2H, 2C*H*Me), 8.34 (s, 2H, CH=N); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 9.7 (C_5Me_5), 21.7 (CH*Me*), 25.1 (CH*Me*), 64.1 (*C*HMe$_2$), 95.7 (C_5Me_5), 160.5 (CH=N), 197.5 (CO). Anal. Found: C, 41.37; H, 5.72; N, 5.17; P, 5.70%. Calc. for $C_{19}H_{31}F_6N_2OPRu$ (549.50): C, 41.53; H, 5.69; N, 5.10; P, 5.64.

5.8. Synthesis of [(C_5Me_5)(Mes-N=CH–CH=N-Mes)(CO)Ru](PF_6) (**7b**)

A solution of **6b** (2.00 g, 2.63 mmol) in dichloromethane (50 mL) was similarly stirred overnight under a carbon monoxide atmosphere and was then evaporated under vacuum. The crude product was recrystallized from chloroform (25 mL) and diethyl ether (120 mL) to afford dark-violet crystals. Yield: 1.60 g, 87%. IR (Nujol, ν, cm^{-1}): 1963 (C≡O); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.30 (s, 15 H, C_5Me_5), 1.97 (s, 6H, 2Me), 2.29 (s, 6H, 2Me), 2.33 (s, 6H, 2Me), 6.99 (s, 4H, C_6H_2), 8.47 (s, 2H, CH=N); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 8.9 (C_5Me_5), 18.7 (Me), 19.4 (Me), 21.0 (Me), 97.9 (C_5Me_5), 129.0 (*C*Me), 129.0 (*C*Me), 129.8 (CH), 130.6 (CH), 138.4 (*C*Me), 147.0 (CN), 165.7 (CH=N), 200.2 (CO). Anal. Found: C, 52.34; H, 5.62; N, 4.08; P, 4.02%. Calc. for $C_{31}H_{39}F_6N_2OPRu$ (701.70): C, 53.06; H, 5.60; N, 3.99; P, 4.41.

5.9. Synthesis of (C_5Me_5)(Mes-N=CH–CH=N-Mes)Ru–CC–Bu^t (**8b**)

A detailed procedure is given for **9b**. Starting from **6b** and *tert*-butylacetylene, a dark violet crystalline powder was obtained in quantitative yield after a slow evaporation of the solution of the crude product in a mixture of dichloromethane and hexane. The very high solubility of **8b** in usual solvents preclude for further

recrystallization. ^{1}H NMR (C_6D_6, δ, ppm): 1.30 (s, 15H, C_5Me_5), 1.44 (s, 9H, Bu^t), 1.71 (s, 6H, 2Me), 2.24 (s, 6H, 2Me), 2.84 (s, 6H, 2Me), 6.76 (s, 2H, C_6H_2), 6.97 (s, 2H, C_6H_2), 7.70 (s, 2H, CH=N); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 9.0 (C_5Me_5), 18.0 (Me), 20.8 (Me), 20.9 (Me), 29.2 (*C* Me_3), 33.3 (C*Me*$_3$), 94.3 (C_5Me_5), 102.2 (RuC≡C), 121.4 (RuC≡C), 127.6 (CH), 129.3 (CH), 130.2 (*C* Me), 132.7 (*C*Me), 134.4 (*C* Me), 150.6 (CH=N), 151.6 (CN). Anal. Found: C, 70.84; H, 8.00; N, 4.48%. Calc. for $C_{36}H_{48}N_2Ru$ (609.86): C, 70.90; H, 7.93; N, 4.59.

5.10. Synthesis of (*C*$_5$*Me*$_5$)(*Pr*^{i}–*N*=*CH*–*CH*=*N*–*Pr*^{i})-*Ru*–*CC*–*Ph* (**9a**)

Complex **9a** was similarly prepared starting from **6a** and phenylacetylene and was obtained as a dark orange–brown crystalline solid after a slow evaporation of the solution of the crude product in a mixture of dichloromethane and hexane. Complex **9a** was too soluble to allow further recrystallization. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.50 (d, ^3J = 7.0 Hz, 6H, 2CH*Me*), 1.54 (d, ^3J = 6.6 Hz, 6H, 2CH*Me*), 1.82 (s, 15H, C_5Me_5), 4.51 (m, 2H, C*H*Me), 6.86–7.08 (m, 5H, Ph), 8.10 (s, 2H, CH=N); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 10.5 (C_5Me_5), 23.5 (CH*Me*), 24.9 (CH*Me*), 63.0 (*C*HMe$_2$), 92.0 (C_5Me_5), 111.2 (RuC≡C–C), 123.6 (Ph, para), 127.1 (RuC≡C–C), 128.0 (Ph, CH), 130.5 (RuC≡C–C), 130.8 (Ph, CH), 145.8 (CH=N). Anal. Found: C, 65.15; H, 7.52; N, 5.58%. Calc. for $C_{26}H_{36}N_2Ru$ (477.66): C, 65.38; H, 7.60; N, 5.86.

5.11. Synthesis of (*C*$_5$*Me*$_5$)(*Mes*-*N*=*CH*–*CH*=*N*-*Mes*)-*Ru*–*CC*–*Ph* (**9b**)

A mixture of **6b** (0.76 g, 1.00 mmol), phenylacetylene (1.00 mL, an excess), K_2CO_3 (1.00 g, an excess) and dichloromethane (30 mL) was stirred for 2 days and the resulting mixture was filtered. The dark-orange filtrate was evaporated under vacuum to leave the product as a violet solid that was found pure by ^{1}H NMR spectroscopy. Dark-violet crystals were obtained in a moderate yield (29%) by cooling the solution of the product in a dichloromethane (20 mL)/hexane (120 mL) mixture. Note that solutions of the product in acetone or halogenated solvents are orange whereas the solid is violet. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.26 (s, 15H, C_5Me_5), 1.75 (s, 6H, 2Me), 2.33 (s, 6H, 2Me), 2.62 (s, 6H, 2Me), 6.85 (s, 2H, C_6H_2), 6.95 (s, 2H, C_6H_2), 7.00–7.20 (m, 5H, Ph), 8.04 (s, 2H, CH=N); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 9.0 (C_5Me_5), 18.1 (Me), 20.1 (Me), 20.9 (Me), 95.0 (C_5Me_5), 114.8 (RuC≡C–C), 124.2 (Ph, para), 127.1 (RuC≡C–C), 127.9 (Ph, CH), 128.1 (Ph, CH), 129.5 (CH), 130.1 (*C*Me), 130.4 (RuC≡C–C), 130.8 (CH), 132.1 (*C*Me), 134.8 (*C*Me), 151.3 (CN), 151.9 (CH=N). Anal. Found: C, 72.04; H, 7.00; N, 4.38%. Calc. for $C_{38}H_{44}N_2Ru$ (629.85): C, 72.46; H, 7.04; N 4.45.

5.12. Synthesis of [(*C*$_5$*Me*$_5$)(*Pr*^{i}–*N*=*CH*–*CH*=*N*–*Pr*^{i})-(*PMe*$_3$)*Ru*](*PF*$_6$) (**10a**)

A 1.0 M solution of PMe_3 in THF (3.50 mL, 3.50 mmol) was added to a solution of **6a** (1.27 g, 2.26 mmol) in methanol (30 mL), and the mixture was stirred for 2 h. The solution was then evaporated under vacuum and the residue was recrystallized from a dichloromethane (20 mL)/diethyl ether (100 mL) mixture to obtain green–black crystals. Yield: 1.28 g, 95%. ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.18 (d, $^2J_{PH}$ = 8.8 Hz, 9H, PMe_3), 1.40 (d, ^3J = 6.6 Hz, 6H, 2CH*Me*), 1.55 (d, ^3J = 6.8 Hz, 6H, 2CH*Me*), 1.79 (d, $^4J_{PH}$ = 0.9 Hz, 15H, C_5Me_5), 4.46 (m, 2H, C*H*Me), 8.34 (d, $^4J_{PH}$ = 3.3Hz, CH=N); ^{31}P{^{1}H} NMR (CD_2Cl_2, δ, ppm): −3.2 (s), −143.2 (sept, PF_6); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 10.5 (C_5Me_5), 15.2 (d, $^1J_{PC}$ = 29.7 Hz, PMe_3), 24.5 (CH*Me*), 24.9 (CH*Me*), 63.9 (*C* HMe$_2$), 92.3 (C_5Me_5), 153.9 (d, $^3J_{PC}$ = 2.1 Hz, CH=N). Anal. Found: C, 41.94; H, 6.68; N, 4.68; P, 10.39%. Calc. for $C_{21}H_{40}F_6N_2P_2Ru$ (597.57): C, 42.21; H, 6.75; N, 4.69; P, 10.37.

5.13. Synthesis of [(*C*$_5$*Me*$_5$)(*Mes*-*N*=*CH*–*CH*=*N*-*Mes*)-(*PMe*$_3$)*Ru*](*PF*$_6$) (**10b**)

A 1.0 M solution of PMe_3 in THF (2.70 mL, 2.70 mmol) was added to a cold mixture of **3b** (1.00 g, 1.77 mmol), KPF_6 (0.35 g, 1.90 mmol), and methanol (30 mL). The mixture was stirred for 2 h at room temperature and the resulting purple mixture was evaporated under vacuum. The residue was extracted with dichloromethane (20 mL) and mineral salts were removed by filtration. The filtrate was then covered with diethyl ether (120 mL) to afford green–black crystals. Yield: 0.97 g, 73%. ^{1}H NMR (CD_2Cl_2, δ, ppm): 1.28 (d, $^4J_{PH}$ = 1.3 Hz, 15H, C_5Me_5), 1.46 (d, $^2J_{PH}$ = 8.9 Hz, 9H, PMe_3), 1.93 (s, 6H, Me), 2.24 (s, 6H, Me), 2.36 (s, 6H, Me), 7.02 (m, 4H, CH), 8.35 (d, $^4J_{PH}$ = 4.0 Hz, 2H, CH=N); ^{31}P{^{1}H} NMR (CD_2Cl_2, δ, ppm): −9.2 (s), −143.3 (sept, PF_6); ^{13}C{^{1}H} NMR (CD_2Cl_2, δ, ppm): 9.7 (C_5Me_5), 15.4 (d, $^1J_{PC}$ = 30.5 Hz, PMe_3), 20.0 (Me), 20.8 (2Me), 95.5 (C_5Me_5), 128.1 (*C* Me), 129.8 (CH), 130.0 (CH), 130.7 (*C*Me), 137.4 (*C*Me), 149.7 (CN), 160.5 (d, $^3J_{PC}$ = 3.2 Hz, CH=N). Anal. Found: C, 52.61; H, 6.49; N, 3.79; P, 8.30%. Calc. for $C_{33}H_{48}F_6N_2P_2Ru$ (749.77): C, 52.86; H, 6.45; N, 3.74; P, 8.26.

5.14. Synthesis of [(*C*$_5$*Me*$_5$)(*Pr*^{i}–*N*=*CH*–*CH*=*N*–*Pr*^{i})-(*Ph*$_2$*POMe*)*Ru*](*PF*$_6$) (**11a**)

A mixture consisting of a sample of **3a** (1.00 g, 2.43 mmol), Ph_2POMe (0.50 mL, 2.49 mmol), KPF_6

(0.50 g, 2.76 mmol) and methanol (40 mL) was stirred overnight. The mixture was evaporated under vacuum and the residue was washed with diethyl ether and was then extracted with dichloromethane (20 mL). The solution was filtered and the filtrate was covered with diethyl ether (100 mL) to afford very dark yellow–brown crystals. Yield: 1.51 g, 92%. ^{1}H NMR (CD_2Cl_2, δ, ppm): 0.97 (d, $^3J_{HH}$ = 6.6 Hz, 6H, 2CH*Me*), 1.42 (d, $^3J_{HH}$ = 6.6 Hz, 6H, 2CH*Me*), 1.73 (d, $^4J_{PH}$ = 1.5 Hz, 15H, C_5Me_5), 3.48 (d, $^3J_{PH}$ = 11.4 Hz, 3H, OMe), 4.40 (m, 2H, 2 C*H* Me), 7.06–7.16 (m, 4H, Ph), 7.45–7.53 (m, 6H, Ph), 8.00 (d, $^4J_{PH}$ = 3.7 Hz, 2H, CH=N); ^{31}P{^{1}H} NMR (CD_2Cl_2, δ, ppm): 140.2 (s), −143.2 (sept, PF_6). Anal. Found: C, 50.41; H, 6.21; N, 3.66; P, 8.54%. Calc. for $C_{31}H_{44}F_6N_2OP_2Ru$ (737.71): C, 50.47; H, 6.01; N, 3.80; P, 8.40.

5.15. Synthesis of [(C_5Me_5)(Ph_2POMe)$_3$Ru](PF_6). 1/2H_2O (**12**)

A mixture consisting of a sample of **3b** (1.41 g, 2.50 mmol), Ph_2POMe (1.80 mL, 8.97 mmol), KPF_6 (0.50 g, 2.72 mmol) and methanol (40 mL) was stirred at ambient temperature for 20 h. The resulting mixture was evaporated under vacuum and the solid was extracted with dichloromethane. The solution was filtered and then evaporated again. The residue was extracted with hot ethanol (40 mL) and the yellow solution was separated from crude **12** by filtration. The filtrate deposited yellow crystals of dab-Mes upon cooling (0.54 g, 74%). The crude complex **12** was recrystallized from dichloromethane and ethanol to afford yellow crystals. Yield: 1.71 g, 66%. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.44 (s, 15H, C_5Me_5), 3.01 (very broad resonance, 9 H, OMe), 6.95–7.41 (broad m, 30H, Ph); ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): 146.4 (s, POMe), −143.0 (sept, PF_6). Anal. Found: C, 56.44; H, 5.28; P, 12.00%. Calc. for $C_{49}H_{54}F_6O_3P_4Ru.1/2H_2O$ (1038.93): C, 56.65; H, 5.34; P, 11.93.

5.16. Reaction of **3b** with $NaBPh_4$ in methanol

A deep violet solution of **3b** (0.50 g, 0.89 mmol) and $NaBPh_4$ (0.35 g, 1.02 mmol) in methanol (20 mL) was stirred at room temperature for 2 days without any change was observed. The mixture was then heated at reflux for 20 h to gradually afford a white precipitate and a red–brown solution. The precipitate was collected by filtration, washed with methanol (10 mL) then dried under vacuum. Yield: 0.38 g, 77%. The product was identified to Cp*Ru(η^6-$C_6H_5BPh_3$) by ^{1}H NMR spectroscopy [15].

5.17. Synthesis of [Cp*(η^3-CH_2CMeCH_2)(MeCN)RuCl][PF_6] from **5**

To a solution of **5** (1.00 g, 1.89 mmol) in acetonitrile (20 mL), 3-chloro-2-methylpropene (0.60 mL, 6.14 mmol) was added. After to be stirred overnight, the solution was evaporated under vacuum. The residue was dissolved in dichloromethane (20 mL) and this solution was covered with diethyl ether (100 mL) to afford orange crystals. Yield: 0.48 g, 50%. The product was identified by ^{1}H NMR spectroscopy [4].

5.18. Reaction of [Cp*(η^3-CH_2CHCH_2)(MeCN)RuCl][PF_6] with dab-Mes

To an orange solution of [Cp*(η^3-CH_2CHCH_2)(MeCN)RuCl][PF_6] [4] in dichloromethane, dab-Mes (1.5 eq) was added and the mixture was stirred at ambient temperature for 20 h. The resulting violet solution was evaporated under vacuum and the residue was analyzed by ^{1}H NMR spectroscopy that unambiguously indicated a main presence of **6b**.

5.19. General procedure for catalytic experiments

The catalyst precursor (3 mol%) was dissolved in the appropriate solvent (4.0 mL), and the allylic reactant (0.5 mmol) then the nucleophile (0.6 mmol) were added to the solution. After to be stirred while the reaction occurred, the mixture was evaporated under vacuum and the residue was extracted with dichloromethane (20 mL). The collected solution was filtered and the filtrate was evaporated to leave the crude product that was analyzed by ^{1}H NMR spectroscopy ($CDCl_3$).

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