IMMOBILIZATION OF CAAC RUTHENIUM CATALYSTS

CONTENT OF CHAPTER IV

SYNTHESIS, CHARACTERIZATION, REACTIVITIES AND IMMOBILIZATION OF RUTHENIUM CATALYSTS CONTAINING CAAC LIGAND.

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Abstract

New complexes of ruthenium bearing cyclic alkyl(amino)carbene and 2-isopropoxybenzylidene ligand modified by an additional 4-diethylamino group were synthesized with a novel and elegant synthesis strategy. These catalysts were characterized by NMR and single-crystal X-ray diffraction studies. The catalytic performances of these systems were investigated for ethenolysis of methyl oleate. The results show a decrease of the activity which can be improved by chemical activation of the precatalyst with an acidic treatment. The reactivity profile of the ammonium complex was evaluated and compared to those of diethylamino precursor and non-substituted CAAC system for our benchmark reaction. The electron withdrawing quaternary ammonium group not only activates the catalyst, but will allow its efficient separation after reaction in an ionic liquid/organic solvent biphasic medium.

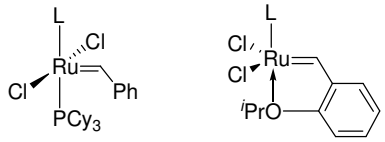
I Introduction

Over the last decade olefin metathesis[1] become a useful tool for carbon-carbon bond forming method[2,3]. The increased interest for this reaction was attributed to the discovering of ruthenium catalysts[4] which combines excellent tolerance to a variety of functional groups and high catalytic activity.

In the mid 1990's, Grubbs introduced bisphosphane catalyst **C5**[5] which presents good activity in ROMP, RCM[6]. Nevertheless, it shows low efficiency towards substituted olefins and suffers from its thermal instability[7]. Further studies on improving catalytic activity of the 1st generation precursor lead to the synthesis of alkylidene complexe **C9** bearing N-heterocyclic

carbene (NHC)[8]. This catalyst extend the potential of ruthenium catalysts[9,10] and provide good yield.

Later, Hoveyda synthesized catalysts **C15**[11,12] and **C22**[13] containing chelating isopropoxybenzylidene ligands. These systems are remarkably robust; they can be purified by column chromatography. The second generation based Hoveyda catalyst **C22** was found to perform well in reaction involving challenging substrates (electron-deficient, substituted olefins) reaction.



C5 L = PCy_3 **C15** L = PCy_3
C9 L = SIMes **C22** L = SIMes

Figure 1. *Grubbs (**C5** and **C9**) and Hoveyda (**C15** and **C22**) catalysts*

One major drawback which limited the industrial application of these catalysts is the formation of deeply colored ruthenium by-products, which are difficult to remove from the reaction products. The presence of catalyst or compounds of catalyst decomposition in the reaction can promote undesired reactions such as carbon double bond isomerization during workup. Removal of metal impurities is crucial in pharmaceutical and fine chemical production. Several methods have been proposed to reduce ruthenium content in final products by purification on silica gel and by using different scavengers (PPh_3=O, DMSO[14], lead tetraacetate[15]). Chromatographic purification procedures[16,17] are generally required to bring the ruthenium content below the 100 ppm level. However, this method is difficult and expensive to implement on an industrial scale.

To reduce ruthenium waste levels, the use of tagged catalysts has received a dramatic increased of interest. Numerous studies have been carried out to develop supported or tagged versions of homogeneous catalysts[18] on various supports such as solid and soluble polymers[19], fluorous phases[20], ionic liquids[21], and also supercritical carbon dioxide media[22]. Hoveyda catalysts[23] have been specifically modified due to their good stability, as we shown in the bibliographic part (page 29). Some catalytic systems developed by Mauduit, Yao and Grela using ionic liquids were found to lead to low levels of metal leaching (10 ppm) and to be efficient in terms of reusability (10 consecutives runs). However, large amounts of

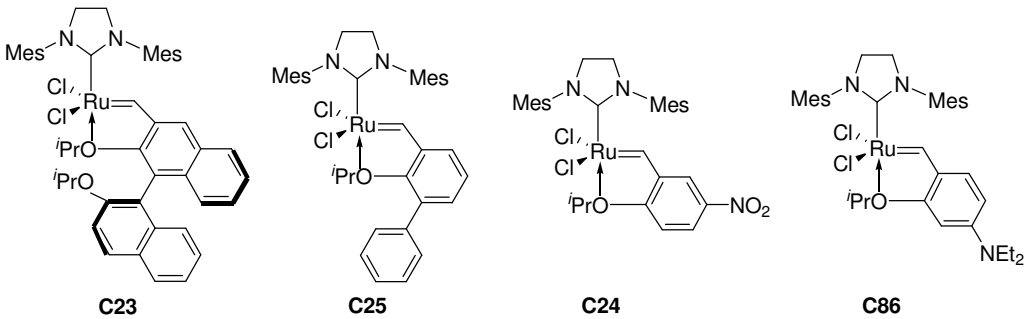
immobilized catalyst are required (2.5 to 6 mol % Ru) to keep the efficiency of homogeneous analogues.

One of the aims of the thesis is to design effective recoverable catalysts for a better use of the catalyst due to its synthetic cost. We choose to modify efficient ruthenium containing cyclic alkyl(amino)carbene complexes with the goal to immobilize them in ionic liquids. Indeed, the department of molecular catalysis in IFP possesses a recognized skill in this field[24,25,26,27]. They developed the Difasol process[28] which oligomerize short chain alkenes into alkenes of higher molecular weight in ionic liquids. A simple biphasic separation based on the good affinity of the catalyst for the ionic phase allows isolating the final organic products.

Thus, we examined the potential structural changing of the CAAC complexes to improve the affinity of the catalyst for the ionic liquid phase.

We focused on tuning the benzylidene moiety. Several groups have reported the modification on the chelating ligand. Blechert has shown that catalysts **C23**[29] and **C25**[30] which contain *ortho* substituents to the isopropoxy group, show increased initiation rate. These studies suggested that steric parameter is the main factor securing the higher activity of these complexes.

On the other hand, Grela has shown that second generation based Hoveyda catalyst can be significantly improved by changing the electron density on the isopropoxy fragment[31]. The introduction of the strongly electron-withdrawing (EWG) NO_2 group to the isopropoxybenzylidene ring of **C22** leads to complex **C24**[31] which is as stable as **C22** but more reactive. Then, they observed that the increase of electron density in the benzylidene part of **C22** results in an increased stability. Nevertheless, the activity of **C86** does not reach the level outlined by **C24** and **C25**.



C23 **C25** **C24** **C86**

Figure 2. *Olefin metathesis catalysts*

Blechert group prepared a series of catalysts with modified isopropoxybenzylidene ligands[32]. They confirmed that increasing steric hindrance adjacent to the isopropoxy group enhanced reaction rates. Decreasing electron density at both the chelating oxygen atom and the Ru=C bond accelerated reaction rate in NHC complexes, while higher electron density at oxygen enhanced reaction rates of first generation catalysts.

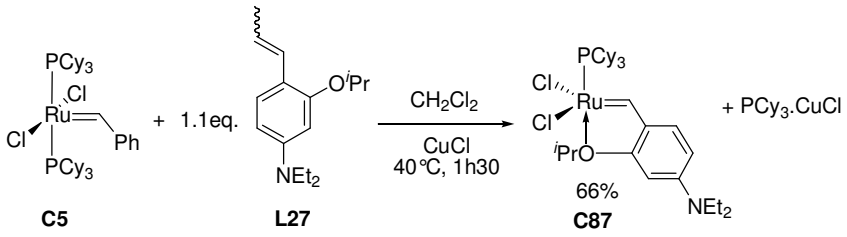
With the aim of decreasing the level of ruthenium by products in pharmaceutical processes, Grela has described a new strategy for the non covalent immobilisation of Ru catalysts that relies on electrostatic binding[33]. A complex bearing the electron-donating diethylamino group **C86** was synthesized and it showed, as expected little or no activity. This catalyst was then immobilized on sulfonated Dowex support and affords good reactivity and recyclability. In fact, the diethylamino group reacts with sulfonic acid leading to the formation of ammonium (EWG).

We chose to use the last concept of "electron-donating to electron-withdrawing activity switch" developed by Grela[34] to prepare CAAC catalysts which bear a quaternary ammonium group.

II Synthesis and characterization of diethylamino-CAAC complexes

II.1 Initial synthesis

We synthesized the desired catalysts from the first-generation Grubbs precursor **C5** in two steps.



Scheme 1. *Preparation of **C87** from first-generation complex **C5***

First, **C5** reacts with 4-diethylamino-2-isopropoxy-propenylbenzene[33] in dichloromethane to provide the first-generation Hoveyda modified **C87** (Scheme 1), as shown by the peak

observed in ^{31}P NMR spectrum at 62.9 ppm (instead of 36.6 ppm **C5**[5]). After purification by silica gel column chromatography and several washing with hexane, **C87** was obtained with 66 wt% yield. Crystals suitable for X-ray analysis[§] were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution at room temperature.

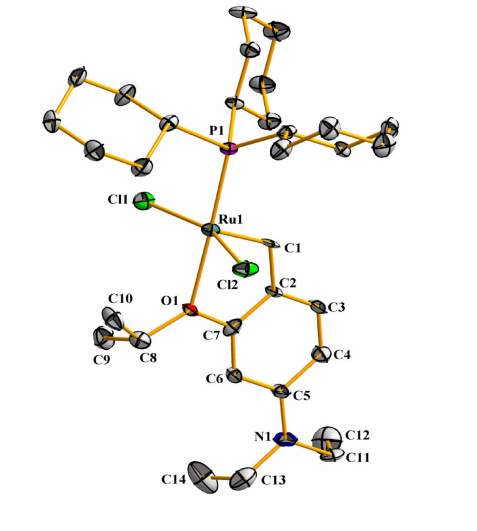
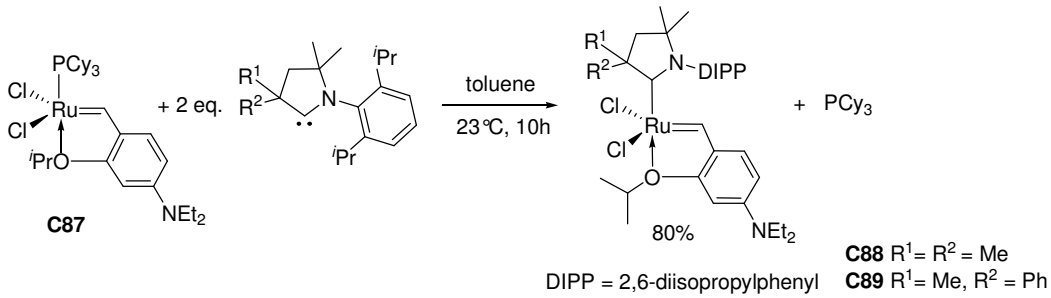


Figure 3. *X-Ray crystal structure of **C87**. Thermal ellipsoids are drawn at 30% probability level.*

By analogy to the first-generation Hoveyda catalyst[12], **C87** is a distorded trigonal bipyramid with the two chlorides and the carbene carbon atom in the equatorial plane. The Cl(1)-Ru-Cl(2) and P-Ru-O angle are larger than the corresponding angle in **C15**. The Ru-O bond in **C87** (2.278 (5)) is shorter and therefore likely stronger than that in **C15** (2.309 (2)). Thus the diethylamino group reinforces O→Ru chelation. In addition, the Ru-P bond length in **C87** (2.2589 (18)) is longer, probably due to the *trans* effect.



Scheme 2. *Preparation of diethylamino-CAAC complexes from **C87***

In the second step, a solution of **C87** in toluene was added to the free CAAC carbene (Scheme 2). The formation of CAAC complexes can be monitored by ^1H NMR with the appearance of a new carbene proton (Ru=C<u>H</u>) signal near 15.8 ppm. The complete disappearance of the

sharp singlet at 62.9 ppm corresponding to the coordinated tricyclohexylphosphine in the ^{31}P NMR spectrum corroborates the replacement of this neutral ligand. Moreover, two characteristic peaks attributed to the new alkylidene (Ru=CH) and to the carbene ligand (NCC) were observed near 285 and 270 ppm, respectively in the ^{13}C NMR. However, numerous washing were required to remove impurities observed in the aliphatic region. The final pure complexes **C88** and **C89** were obtained with yield around 80 wt%. Besides, X-ray analysis confirmed the formation of these new complexes **C88** and **C89**.

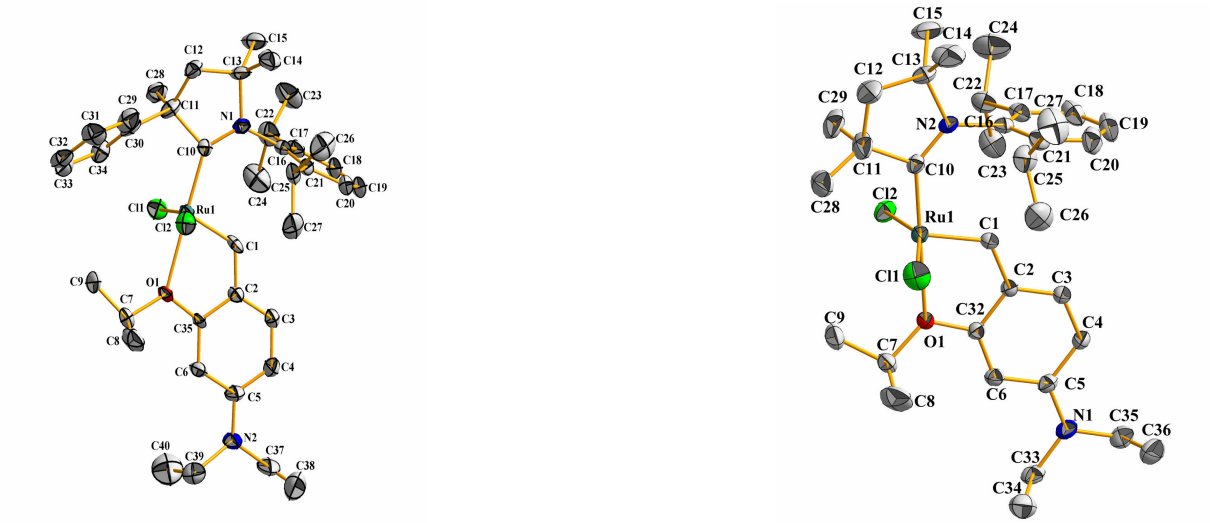
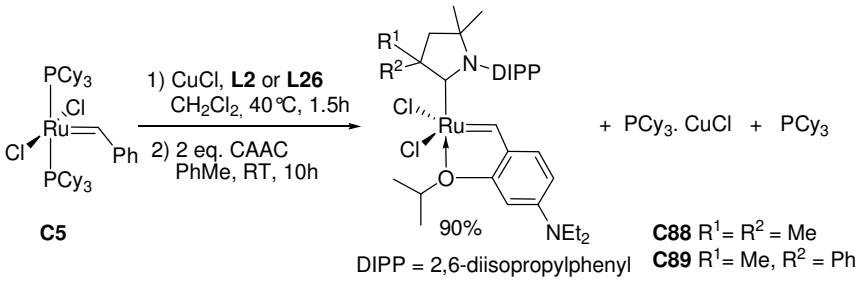


Figure 4. *X-ray crystal structures of **C88** (right) and **C89** (left). Thermal ellipsoids are drawn at 30% probability level.*

It deserves mention that the intermediate monophosphine **C87** does not need to be isolated prior to the neutral ligand exchange (Scheme 3). In this procedure, **C5** is stirred with **L27** in the presence of copper chloride in dichloromethane. The *in situ* generated **C87** was filtered and added to the CAAC, providing, after several washings, the desired complex in good yield (90 wt%).



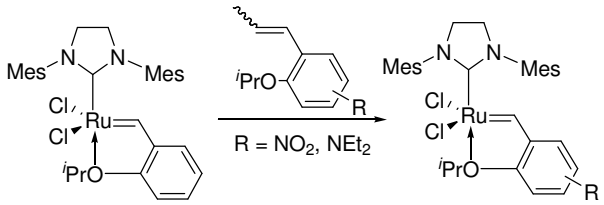
Scheme 3. *One pot synthesis of diethelyamino-CAAC complexes from **C5***

Despite of a slightly decreased of purity of these complexes obtained in one pot reaction, they have been used in ethenolysis of methyl oleate without a loss of reactivity.

However, in attempts to develop a new easily scalable synthetic way leading to modified CAAC systems, we envisaged exchange reaction between the more stable CAAC complexes and the ligand precursor **L27**.

II.2 Alternative synthesis

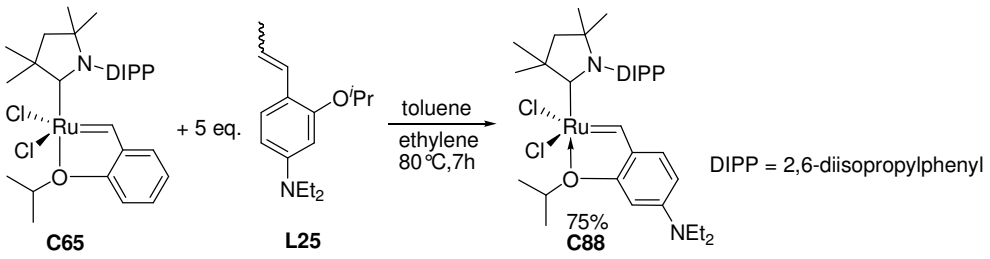
The group of Grela has recently reported method to prepare different catalysts starting from **C22** via the replacement of the 2-isopropoxybenzylidene ligand present in **C22** by differently substituted 2-isopropoxybenzylidene ligands[35].



Scheme 4. *Preparation of catalysts by ligand exchange*

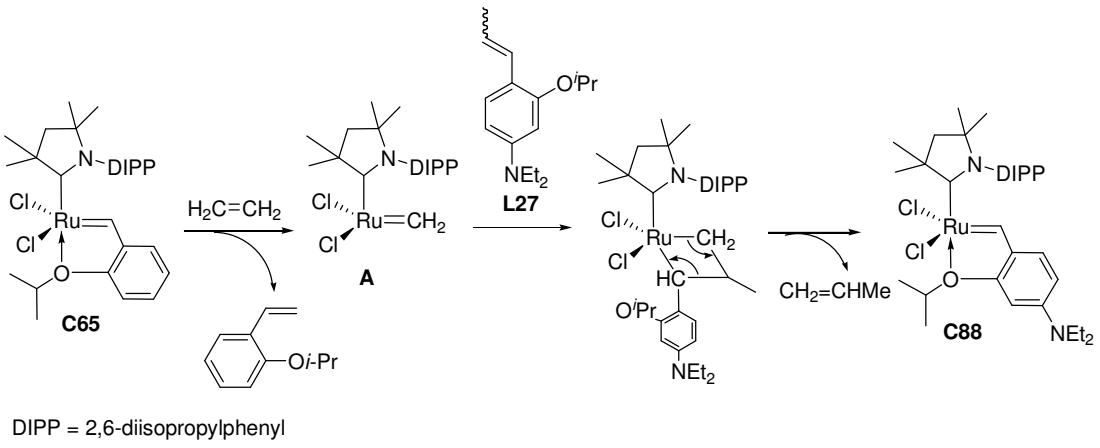
Whereas 10-fold excess of 1-isopropoxy-4-nitro-2-propenylbenzene gives best results allowing conversion of the 80-90 wt% of the Hoveyda-Grubbs catalysts, although only a 3-fold excess of the electron-donating diethylamino-susbtituted benzylidene ligand **L27** was required to afford a good yield (70 wt%) of the corresponding complexes[36].

We assumed that this procedure could be adapted to CAAC complexes. Unfortunately, ligand exchange reaction with **C65** proved to be inefficient. Indeed, treatment of **C65** with 10 equivalents of **L27** in toluene for seven hours affords a mixture of initial reagents.This synthesis probably doesn't work because of the sterically hindered ligands (CAAC and styrenyl ether). In order to reduce steric congestion and allow the synthesis to work, we postulate that the methylidene species of **C65** could react more easily with **L27**. In order to avoid the isolation of the non stable methylidene, we then proceeded to the ligand-exchange-cross-metathesis sequence in the presence of ethylene and with only a 5-fold excess of **L27**.



Scheme 5. *Preparation of **C88** by ligand exchange in the presence of ethylene*

We assumed that due to its small size and excess, ethylene reacted first with the styrenyl ether complex **C65,** releasing the methylidene species (**A**) and the isopropoxystyrene (Scheme 6). Then, **L27** was subjected to cross olefin metathesis with **A,** affording **C88** and propylene. Moreover, the ligand bearing an electron-donating diethylamino group should exhibit a much higher affinity to the ruthenium as compared with the non functionalized styrenyl ether fragment.



Scheme 6. *Mechanism of ligand exchange reaction*

This elegant method affords the desired catalyst with an excellent purity and good yield (75%) without drastic purification. The remaining unreacted **L27** can be separated by simple washing with hexane.

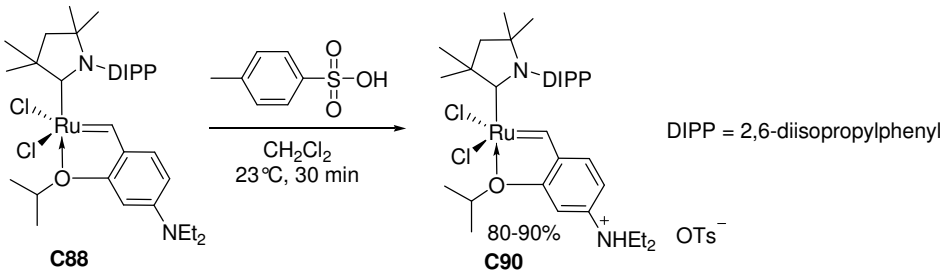
III Synthesis of CAAC catalysts bearing a quaternary ammonium group

Catalysts bearing an electron-donating group are known to show little or no activity in olefin metathesis[34]. However, the in situ formed ammonium salts obtained by treatment of these complexes with various Brönsted acids are of high activity.

In a first attempts, we tested different acids to validate this concept of activity switch with our CAAC systems. This study will be detailed in the fourth part.

Afterward, we envisaged the isolation of the ammonium salt for a better understanding of parameters which govern the reactivity. We were also interested to check the *in situ* conversion of the Et_2N group into polar quaternary ammonium.

Addition of *p*-toluenesulfonic acid (PTSA) to complex **C88** in dichloromethane caused a rapid color change of the solution from red brown to green (Scheme 7).



Scheme 7. *Preparation of **C88** from **C65** by addition of PTSA*

Protonation of diethylamino group was observed in ^{1}H NMR by the formation of a new singulet at 12 ppm attributed to $N^{+}\underline{H}Et_2$. The signal corresponding to the alkylidene proton resonates downfield (Ru=C<u>H</u> (**C90**) 16.3 ppm) in comparison to that of **C88** (15.88 ppm). Thus, ^{1}H NMR analysis confirmed the generation of ammonium cation with electron-withdrawing properties.

Electron spray ionization positive mass spectroscopy of **C90** in C_6D_6 showed the precursor **C88** losing a hydrogen atom (m/z 676.24). On the other hand, the negative ion ESI-MS spectrum revealed the anionic part of the complex **C90** (m/z 171.01). These observations suggested also the formation of the ammonium catalyst **C90**.

Besides, suitable crystals for X-ray analysis (Figure 5) were obtained by slow diffusion of hexane into a concentrated solution of **C90** in dichloromethane.

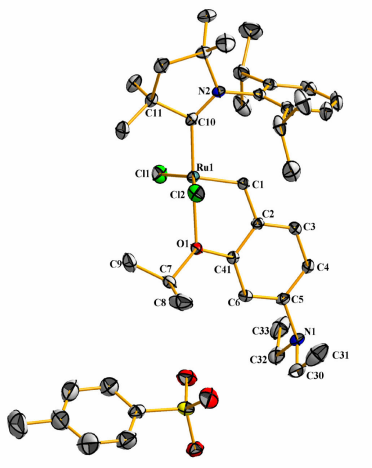
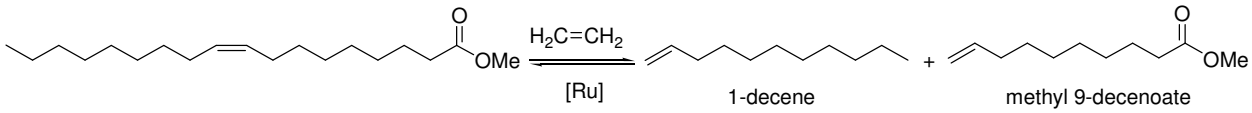


Figure 5. *X-ray crystal structure of **C90**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity*

The bond lengths were found in the same range as those obtained for complex **C88**, except for the C(5)-N(1) bond (1.474 (3) Å), which is significantly longer than in **C88** (1.365 (3) Å) indicating the electron-withdrawing ability of the ammonium group.

IV Catalytic performance

To compare the relative activities of catalysts **C81**, **C89**, **C88** and **C65**, the ethenolysis of methyl oleate was investigated under the same conditions.



Scheme 8. *Ethenolysis of methyl oleate*

As expected, the results summarized in Table 1, show that the activity was markedly decreased in the case of electron-donating substituted **C88** and **C89**. The introduction of diethylamino group clearly affects the activity of ruthenium CAAC catalysts **C65** and **C81**. However, the selectivity for ethenolysis products (1-decene and methyl 9-decenoate) remained high.

Table 1. *Comparison of ruthenium catalysts in the ethenolysis of methyl oleate* [a]

Entry	Catalysts	Conversion (%)[b]	Selectivity (%)[c]
1	**C89**	29	99
2	**C81**	99	97
3	**C88**	35	99
4	**C65**	83	97

a) 0.1 mol% Ru, toluene, 50°C, 10 bar ethylene pressure, 2h

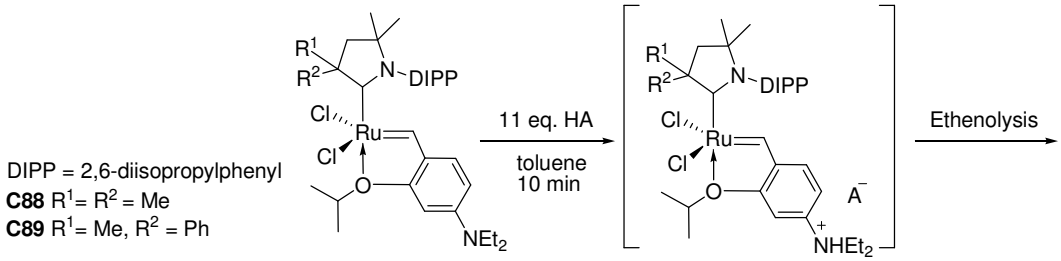
b) Conversion = 100 x [moles $MO_{initial}$ – moles MO_{final} / moles $MO_{initial}$] with MO: methyl oleate

c) Selectivity =100 x [(moles 1-decene + moles methyl-9-decenoate)/2 / moles $MO_{initial}$-moles MO_{final}]

The effect of donor group is generally applicable to Hoveyda-based catalysts whatever the neutral carbene ligand associated to the metal center is (CAAC, NHC). During the catalytic cycle, the initiation step requires dissociation of the aryl ether ligand before the metathesis propagation. We proposed that the diethylamino group in the benzylidene fragment increases the electron density on the chelating oxygen atom and reinforces the O→Ru coordination, decreasing the rate of the initiation step.

We envisaged that addition of acid can activate diethylamino-CAAC systems and accelerate the initiation step of the target reaction.

As displayed on Scheme 9, we treated complexes by acid before to proceed to the ethenolysis of methyl oleate. The effect of various acids on complex **C88** and **C89** activity was screened.



Scheme 9. *Activation of precatalyst **C88** and **C89** before ethenolysis of methyl oleate*

Table 2. *Comparison of reactivity of differently chemical activated **C88** and **C89***

Entry	Catalysts	Additives (11 eq./Ru)	Conversion (%)[b]	Selectivity (%)[c]
1	**C89**	**-**	29	99
2	**C89**	HCl_{aq}	91	>99
3	**C89**	$Me_3O^+BF_4^-$ [d]	11	>99
4	**C89**	HCl in Et_2O	32	>99
5	**C88**	-	35	99
6	**C88**	(-)-camphor-10-sulfonic acid	67	>99
7	**C88**	ethane sulfonic acid	50	>99

a) 0.1 mol% Ru, toluene, 50°C, 10 bar ethylene pressure, 2h

b) Conversion = 100 x [moles $MO_{initial}$ – moles MO_{final} / moles $MO_{initial}$] with MO: methyl oleate

c) Selectivity =100 x [(moles 1-decene + moles methyl-9-decenoate)/2 / moles $MO_{initial}$-moles MO_{final}]

d) $Me_3O^+BF_4^-$ formed a suspension in dichloromethane before adding to a solution of **C89** in toluene.

In line with this expectation, the in situ formed ammonium salt obtained by treatment of **C89** with hydrochloride acid is of high activity (Entry **2**). Nevertheless, the performances remain slightly lower than those of non-substituted **C81** (Entry **2,** Table 1).

The analysis of the solution of **C81** and HCl confirmed the in situ formation of the ammonium salts by the appearance of the more downfield signal at 16.44 ppm (instead of 15.88 for **C81**). This information is consistent with characterization of isolated ammonium catalyst **C88**.

Trimethyloxonium tetrafluoroborate was used as an alkylating agent. Addition of $Me_3O^+BF_4^-$ to complex **C89** produces a system with lowest activity, probably due to its low solubility in

the solvent. As already observed for NHC catalysts[34], hydrochloric acid (used as a 1M solution in ether) provides lower activity than aqueous HCl (37% wt).
The use of (-)-camphor-10-sulfonic acid (CSA) and ethane sulfonic acid did not allow the effective activation of **C88** contrary to previous results obtained by Grela.
In the presence of a strong Brönsted acid, the amino electron-donor group is converted into the corresponding ammonium electron-withdrawing group leading to a catalytic species comparable to CAAC non-substituted catalyst in term of activity.

For practical reasons, we use 11-fold excess of additive but the activation of catalyst requires only one equivalent of acid. This large amount can accelerate catalyst's decomposition (e.g. protonation of CAAC ligand). In order to check this assumption we also made a blank test with the non substituted complex **C81** in harsher reaction conditions (0.01 mol% Ru, 50°C, 10 bar ethylene pressure). Whereas **C81** usually leads to 71% of conversion, when HCl was added to **C81,** only 50 % of conversion was reached. Interestingly, selectivity remains high (99%). Thus, the role of the acid is to protonate the electron-donating diethylamino group of **C88** and **C89,** to give rise to the electron-withdrawing group. If the increased of the performances would have been the result of the formation of another species, we should observe an improved activity when HCl is added to **C81**.

We also evaluated the isolated ammonium catalyst **C90** in ethenolysis of methyl oleate in homogeneous phase and in ionic liquid/organic solvent biphasic media. This complex is slightly soluble in aromatic solvent such as toluene and C_6D_6. Dichloromethane was used as solvent and allowed to obtain better conversion (Table 3, Entry **1** and **2**). As expected, the ammonium complex **C90** is more efficient than the diethylamino-catalyst **C88**. However, **C90** is less active than non substituted catalyst **C65**. Unfortunately, in these cases, no correlation between X-ray analysis and reactivity profile was found[§].

Table 3. *Ethenolysis of methyl oleate with 0.1 % mol **C90**, at 50°C, under 10 bar ethylene pressure, 2 hours*

Entry	Conditions	Conversion (%)[a]	Selectivity (%)[b]
1	**C90** in toluene	49	98
2	**C90** in CH_2Cl_2	88	93
3	**C90** in BMP.NTf_2	70	98
4	**C90** in BMP.NTf_2/ 10 eq. PTSA	77	99

a) Conversion = 100 x [moles $MO_{initial}$ – moles MO_{final} / moles $MO_{initial}$] with MO: methyl oleate

b) Selectivity =100 x [(moles 1-decene + moles methyl-9-decenoate)/2 / moles $MO_{initial}$-moles MO_{final}]

When **C90** was dissolved in 1-butyl-3-methylpyrrolidinium bis(trifluoromethanesulfonyle)imide (BMP.NTf_2) ionic liquid[§], a reduction of the reactivity was observed (Entry **3**). However, this decrease is not as significant as that noticed with the second-generation Grubbs catalyst **C9** in this solvent (Chapter II, page 154). Furthermore, no additional treatment to remove impurities in the ionic liquid was realized. **C90** is probably more stable than **C9** owing to the styrenyl ether ligand and the more hindered and better σ-donor CAAC (relative to SIMes).

We have already shown that the presence of residual base in BMP.NTf_2 can contribute to the fast decomposition of the catalyst. To improve the catalytic performances, we added 10 equivalents of free acid in the BMP.NTf_2 before the ethenolysis reaction with **C90** (Entry **5**). 77% of conversion was reached in the presence of excess of PTSA instead of 70%. We assume that the free acid must neutralize the residual base in the ionic liquid and stabilize the ammonium precatalyst **C90**.

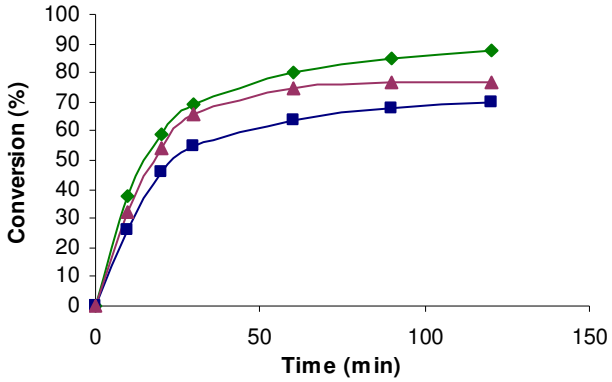


Figure 6. *Ethenolysis of methyl oleate with 0.1 mol% Ru, 50°C, 10 bar ethylene pressure, 2h*
◆*: **C90**,* ■*: **C90** in BMP.NTf_2,* ▲*: **C90** in BMP.NTf_2 + 10 eq. PTSA*

Our first attempts of recycling the catalyst **C90** failed. Only 5% of conversion was achieved at the second run. We hypothesized that the decomposition of the precatalyst occurs during the first catalytic run or that the excess of acid slowly destroys the active species. Because of the short duration of the first run (30 minutes), it is reasonable to postulate that **C90** may loose its activity due in the work up procedure (See Experimental section).

However, quite surprisingly, the coloration of the organic and ionic phases after catalysis (See Figure 7) indicated that the ruthenium complex is immobilized in the ionic liquid. Indeed,

after the first run, the organic phase is slightly coloured. After three hours of decantation, the ionic phase is red purple and the organic phase appears colorless.

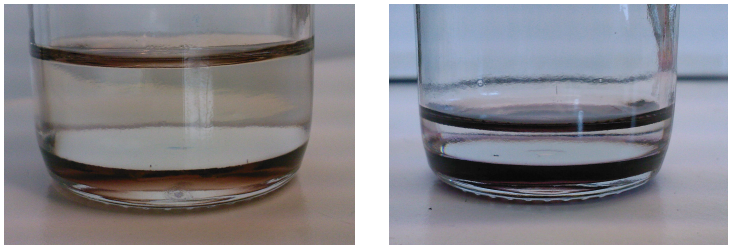


Figure 7. *Photography of the reaction mixture after the ethenolysis (left) and three hours after the run*

More efforts are under investigation to determine the ruthenium content in the organic phase by ICP-MS analysis.

Up to this point, we don't know the exact nature of the species in ionic liquid. Analysis of the reaction mixture by NMR spectroscopy should lead to the best understanding of the desactivation process.

V Conclusion

We have reported herein a new synthesis method for CAAC catalyst containing 2-isopropoxy-4-diethylamino-benzylidene ligand. The newly synthesized precatalysts have been fully characterized and their reactivity has been studied for ethenolysis of methyl oleate. These systems are less active than non-modified CAAC precursor.

Treatment of diethylamino-CAAC catalysts with acids result in improvement of the catalytic profiles. The results show the importance of the choice of the acid. Strong Brönsted acids must be employed to completely transform the diethylamino group.

The introduction of a polar electron-withdrawing ammonium can be used not only to increase the catalyst activity, but also to alter its physical-chemical properties, such as affinity to ionic liquid. We believe that the adjustment of the amount of acid to neutralize residual base in ionic liquid will allow the recycling of ammonium-CAAC catalysts.

From an economical point of view on the whole chemical process the catalyst's cost is an important attribute. Immobilization of CAAC catalysts in ionic liquid will offer economic and practical advantages over the parent soluble catalysts.

VI Experimental section

General remarks:

All manipulations were performed under an argon atmosphere using standard Schlenk techniques.
Starting materials were purchased from Aldrich or VWR, and BMP.NTf_2 ionic liquid from Solvionic. Methyl oleate and BMP.NTf_2 were degassed by freeze pumping thaw prior to use.

The water content of BMP.NTf_2 was determined by Karl Fisher coulometry using a Methrom 756 KF apparatus. Mesasurements were performed in duplicate, and agreed within 5%. Content of halides (mainly chloride) were determined by Volhard titration. 17g of silver (I) nitrate was dissolved in deionized water (100 mL). 5 mL of nitric acid (70% wt) were added to the solution. 1 mL of the mixture was added to the ionic liquid (1 mL) in order to precipitate the halide. No precipitate was observed. The low limit detection for halide is 100 ppm, corresponding to ~ 0.9 equivalent of halide relative to ruthenium.

Solvents were purchased from SDS and dried by a solvent purification system (SPS-M-Braun). The water contents of these solvents were periodically controlled by Karl-Fischer titration.

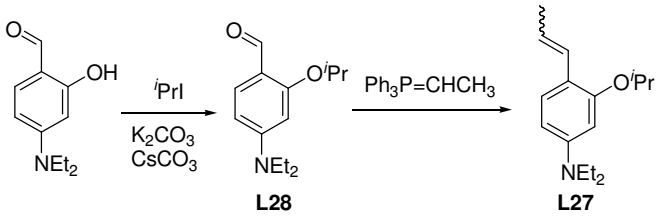
^{1}H NMR (300 MHz), ^{31}P $\{^{1}H\}$ NMR (122 MHz) and ^{13}C $\{^{1}H\}$ NMR (75 MHz) spectra were recorded on a Bruker AC 300 MHz instrument at room temperature. Deuterated solvent (C_6D_6) was purchased from Eurisotop. Chemical shifts are reported in ppm *vs* $SiMe_4$ and were determined by reference to the residual solvent peaks. All coupling constant are given in Hertz.

Mass spectra were collected with an Agilent 6890 N apparatus with Agilent 5975B inert XL EI/CI MSD mass spectrometer.

C, H, N elemental analyses were performed by the Service Central d'Analyses of CNRS (Vernaison, France).

Diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data were collected using Ψ scans; the structure was solved by direct methods using the SIR97 software[37]and the refinement was by full-matrix least squares on F^2. No absorption correction was used.

Preparation of a ligand precursor L27



Synthesis of 4-diethylamino-2-isopropoxybenzaldehyde (L28)

Solid powdered K_2CO_3 (15.42 g, 111.5 mmol) and $CsCO_3$ (4.04 g, 12.4 mmol) were placed in a round bottom flask. A solution of 4-diethylamino-2-hydroxybenzaldehyde (12 g, 62.1 mmol) in dry DMF (145.1 mL) was added. After stirring for 30 minutes 2-iodopropane (9.38 mL, 93.9 mmol) was added to the red solution. The reaction mixture was heated overnight at 50°C. After pouring onto a saturated aqueous solution of K_2CO_3 the reaction mixture was extracted with MTBE. The combined organic layers were washed with 1M solution of NaOH, water and then with brine. The dark red solution was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. **L28** was obtained as a dark red oil (12.45 g, 85.3% yield).

^{1}H NMR (300 MHz, C_6D_6): 10.78 (s, 1H, C$\underline{H}$O), 8.17 (d, J = 8.5 Hz, 1H, C$\underline{H}$ Ar), 6.02 (dd, J = 8.91, 2.37 Hz, 1H, C$\underline{H}$ Ar), 5.91 (d, J = 2.32 Hz, 1H, C$\underline{H}$ Ar), 4.26 (sept, J = 6.1 Hz, 1H, OC$\underline{H}$(CH$_3$)$_2$), 2.81 (q, J = 7.1 Hz, 4H, N(C$\underline{H}_2$CH$_3$)$_2$), 1.07 (d, J = 6 Hz, 6H, OCH(C$\underline{H}_3$)$_2$), 0.78 (t, J = 7.1 Hz, 6H, N(CH$_2$C$\underline{H}_3$)$_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 186.43 (C$\underline{H}$O), 162.93 (C$\underline{C}$N(CH$_2$CH$_3$)$_2$), 153.4 (C$\underline{C}$OCH(CH$_3$)$_2$), 130.64 (C$\underline{C}$HO), 120.26 (C$\underline{H}$ Ar), 116.75 (C$\underline{C}$ Ar), 105.1, 95.73 (C$\underline{H}$ Ar); 70.75 (OC$\underline{H}$(CH$_3$)$_2$), 44.55 (N(C$\underline{H}_2$CH$_3$)$_2$), 21.91 (OCH(C$\underline{H}_3$)$_2$), 12.58 (N(CH$_2$C$\underline{H}_3$)$_2$).

Synthesis of N, N diethyl-N-{3-isopropoxy-4-[(E,Z)-1-propenyl]phenyl}amine (L27)

To a cold solution (0°C) of dry THF (300 mL) and ethyl(triphenyl)phosphonium bromide (27.39 g, 73.8 mmol) was added NaH (4.22 g, 105.4 mmol) under argon. The reaction mixture was heated at 70°C for two hours. After this period, the solution was cooled to -50°C and a solution of 4-diethylamino-2-isopropoxy-benzaldehyde (12.4 g, 52.7 mmol) in THF (40 mL) was dropwise added to the orange mixture. The reaction mixture was stirred overnight at room temperature. The product was extracted with ethyl acetate then washed with brine and dried over $MgSO_4$. The solution was filtered then concentrated under reduced pressure. The crude product was purified by flash column chromatography with pentane/ethyl acetate (90:10) as eluent to afford **L27** as a yellow oil (13 g, 99.8% yield).

^{1}H NMR (300 MHz, C_6D_6): isomer (E) 7.19 (d, *J* = 8.61 Hz, 1H, C<u>H</u> Ar), 6.55 (dq, *J* = 15.77, 1.8 Hz, 1H, C<u>H</u>=CH(CH_3)), 6.23 (m, 1H, C<u>H</u> Ar), 5.95 (m, 1H, CH=C<u>H</u>(CH_3)), 4.4 (sept, *J* = 6Hz, 1H, OC<u>H</u>(CH_3)$_2$), 3.27 (q, *J* = 7.1 Hz, 4H, N(C<u>H</u>$_2$CH$_3$)$_2$), 1.8 (dd, *J* = 7, 1.8 Hz, 3H, CH=CH(C<u>H</u>$_3$)), 1.28 (d, *J* = 6Hz, 6H, OCH(C<u>H</u>$_3$)$_2$), 1.1 (t, *J* = 7.11 Hz, 6H, N(CH$_2$C<u>H</u>$_3$)$_2$); isomer (Z) 7.12 (d, *J* = 8.61 Hz, 1H, C<u>H</u> Ar), 6.43 (dq, *J* = 11.7, 1.8 Hz, 1H, C<u>H</u>=CH(CH_3)), 6.23 (m, 1H, C<u>H</u> Ar), 5.55 (m, 1H, CH=C<u>H</u>(CH_3)), 4.4 (sept, *J* = 6Hz, 1H, OC<u>H</u>(CH_3)$_2$), 3.27 (q, *J* = 7.11 Hz, 4H, N(C<u>H</u>$_2$CH$_3$)$_2$), 1.8 (dd, *J* = 7, 1.8 Hz, 3H, CH=CH(C<u>H</u>$_3$)), 1.28 (d, *J* = 6Hz, 6H, OCH(C<u>H</u>$_3$)$_2$), 1.1 (t, *J* = 7.11 Hz, 6H, N(CH$_2$C<u>H</u>$_3$)$_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 157.49, 148.23, 131.43, 126.63, 120.24, 122.86 (<u>C</u>H Ar), 116.82 (<u>C</u> Ar), 105.02, 100 (<u>C</u>H Ar); 70.8 (O<u>C</u>H(CH_3)$_2$), 44.65 (N(<u>C</u>H$_2$CH$_3$)$_2$), 22.37 (OCH(<u>C</u>H$_3$)$_2$), 15.13, 12.87 (N(CH$_2$<u>C</u>H$_3$)$_2$).

Synthesis of dichloride (*o*-isopropoxy-*p*-diethylamino-phenylmethylene) tricyclohexylphosphine ruthenium (C87)

A solution of 496 mg (2 mmol) of **L27** in 40 mL of CH_2Cl_2 was added to a solution of 1.5 g (1.82 mmol) of benzylidene dichloride bis(tricyclohexylphosphine) ruthenium **C5** and 180 mg of CuCl in 5.75 mL of CH_2Cl_2. The resulting solution was stirred at 40°C for two hours. The reaction mixture was concentrated in vacuo and the residue was purified by column chromatography on silica. Elution with cyclohexane/ethyl acetate/triethyl amine (4:1:0.1) removed **C87** as a brown band. Removal of the solvent, three washing of cold hexane (20 mL) and drying under vacuum afforded **C87** as a brown solid (807 mg, 66% yield).

^{1}H NMR (300 MHz, C_6D_6): 17 (d, *J* = 4.3 Hz, 1H, Ru=C<u>H</u>), 7.38 (d, *J* = 8.7 Hz, 1H, C<u>H</u> Ar), 6.04 (m, 2H, C<u>H</u> Ar), 4.89 (sept, *J* = 6.2 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 2.81 (q, *J* = 7.1 Hz, 4H, N($C\underline{H}_2CH_3)_2$), 2.49-1.07 (m, 39H, PCy_3, OCH($C\underline{H}_3)_2$), 0.82 (t, *J* = 7.1 Hz, 6H, N($CH_2C\underline{H}_3)_2$). ^{31}P {^{1}H} NMR (122 MHz, C_6D_6): 62.88. ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 274 (Ru=CH), 156.4, 149.7, 136.96, 124.85, 104.34, 96.91, 74.91 (O<u>C</u>H$(CH_3)_2$), 44.97 (N($\underline{C}H_2CH_3)_2$), 36.45, 36.12, 31.97, 30.65, 30.22, 28.24, 28.1, 26.78, 22.3 (OCH($\underline{C}H_3)_2$), 12.58 (N($CH_2\underline{C}H_3)_2$).
HRMS (FT-ICR) EI+ (CH_2Cl_2) m/z: 636.26 [M-Cl].

Synthesis of dichloride-{1-(2,6-diisopropylphenyl)-2,2, 4-trimethyl- 4-phenyl-pyrrolidinylidene)} (*o*-isopropoxy-*p*-diethylamino-phenylmethylene) ruthenium (C89)

Iminium salt **L23** (374 mg 0.89 mmol) and three equivalents of KHMDS (536 mg, 2.68 mmol) in THF (15 mL) were stirred at room temperature for 16h. After evaporation of the solvent, the solid residue was extracted with cyclohexane (20 mL), and then the CAAC **L26** was obtained after removal of volatiles in vacuum. A solution of **C87** (0.5 g, 0.744 mmol) in toluene (15 mL) was added to **L26**. The reaction mixture was stirred at room temperature until complete disappearance of the initial complex in ^{1}H and ^{31}P NMR (10h). Removal of volatiles in vacuum afforded a brown powder that was dissolved in CH_2Cl_2 (40 mL) before filtration and concentration until 1-2 mL. The complex was obtained as a red brown powder by washing with cold hexane (3*20 mL) and dried under vacuum (435 mg, 79% yield).

^{1}H NMR (300 MHz, C_6D_6): 15.89 (s, 1H, Ru=C<u>H</u>), 8.45 (d, 2H, *m*-C<u>H</u> Ar), 7.55-7.42 (m, 2H, *p*-C<u>H</u> Ar), 7.34 (m, 6H, C<u>H</u> Ar), 6.77 (d, 1H, *o*-C<u>H</u> Ar), 4.64 (sept, 1H, OC<u>H</u>$(CH_3)_2$), 3.4 (sept, 2H, C<u>H</u>$(CH_3)_2$), 2.93 (d, 1H, NCC<u>H</u>$_2$), 2.69 (q, 4H, N($C\underline{H}_2CH_3)_2$), 2.56 (s, 3H, $C\underline{H}_3$), 2 (d, 1H, NCC<u>H</u>$_2$), 1.65 (d, 3H, CH($C\underline{H}_3)_2$), 1.47 (d, 3H, CH($C\underline{H}_3)_2$), 1.4 (s, 3H, $C\underline{H}_3$), 1.27 (d, 3H, CH($C\underline{H}_3)_2$), 1.21 (d, 3H, CH($C\underline{H}_3)_2$), 1.18 (d, 3H, CH($C\underline{H}_3)_2$), 1.15 (s, 3H, $C\underline{H}_3$), 1.1 (d, 3H, CH($C\underline{H}_3)_2$), 0.72 (t, 6H, N($CH_2C\underline{H}_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 289.61 (Ru=<u>C</u>H), 268.66 (N<u>C</u>C), 156.63, 150.82, 149.6, 149.26, 143.58, 138.05, 136.16, 130.38, 129.29, 129.21, 103.55, 96.28, 76.43, 73.91, 63.16, 49.25, 44.83, 36.24, 35.43, 32.28, 30.25, 29.2, 28.6, 28.08, 27.75, 27.34, 27.19, 27, 26.85, 24.6, 24.51, 22.6.
HRMS (FT-ICR) EI+ (C_6D_6) m/z: 777.23 [M+K], 738.26 [M], 703.29 [M-Cl], 667.32 [M-HCl_2], 348.26 [**L26**].

One pot synthesis of C89

203 mg of iminium salt **L23** (0.48 mmol) and 3 equivalents of KHMDS (290 mg, 1.45 mmol) in THF (15 mL) were stirred overnight at room temperature. The reaction solution was concentrated under vacuum. The carbene was extracted with cyclohexane (20 mL) and the solvent was removed under vacuum. Then, 67.8 mg of **L27** (0.27 mmol) in dichloromethane (10 mL) was added to 200 mg of **C5** (0.24 mmol) and 24 mg of copper chloride (0.24 mmol). After stirring at 40°C for two hours, the reaction solution was filtered and the solvent was removed under vacuum. The brown residue was dissolved in toluene (10 mL). The resulting solution was added via cannula to the schlenk containing the free carbene. The mixture was stirred for 10 hours and filtered. The volatiles were removed under vacuum and the residue was washed with cold hexane (3*5 mL). 162 mg of **C89** were obtained (90% yield).

Alternative synthesis

Synthesis of dichloride-{1-(2,6-diisopropylphenyl)-2,2, 4,4-tetramethyl-pyrrolidinylidene)} (*o*-isopropoxy-*p*-diethylamino-phenylmethylene) ruthenium (C88)

C65 (501 mg, 0.83 mmol) and 5 equivalents of **L27** were placed in a tricol flask and dissolved in toluene (20 mL). The flask was then connected to a condenser and an ethylene line. The reaction mixture was heated at 80°C with ethylene bubbling until complete disappearance of the initial complex is observed by ^{1}H NMR. The solvent was evaporated under vacuum, the residue was washed with hexane (3*20 mL). The resulting green precipitate was filtered and dried under vacuum to afford the catalyst as a green solid (420 mg, 75%).

^{1}H NMR (300 MHz, C_6D_6): 15.84 (s, 1H, Ru=C<u>H</u>), 7.43 (m, 1H, *p*-C<u>H</u> Ar), 7.33 (m, 2H, *m*-C<u>H</u> Ar), 6.84 (d, *J* = 8.5Hz, 1H, *o*-C<u>H</u> Ar), 5.89-5.83 (dd, *J* = 11, 2.6 Hz, 2H, *m*-C<u>H</u> Ar), 4.8 (sept, *J* =6.1 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 3.33 (sept, *J* = 6.7 Hz, 2H, C<u>H</u>$(CH_3)_2$), 2.7 (q, *J* = 7Hz, 4H, N($C\underline{H}_2CH_3)_2$), 2.74 (s, 6H, NC($C\underline{H}_3)_2$), 1.87 (s, NCC$\underline{H}_2$, 2H), 1.86 (d, *J* = 6.1 Hz, 6H, OCH($C\underline{H}_3)_2$), 1.21 (d, *J* = 6.6 Hz, 6H, CH($C\underline{H}_3)_2$), 1.07 (d, *J* = 6.4 Hz, 6H, CH($C\underline{H}_3)_2$), 1.04 (s, 6H, NCC($C\underline{H}_3)_2$), 0.75 (t, 6H, N($CH_2C\underline{H}_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 287.06 (Ru=<u>C</u>H), 271.02 (N<u>C</u>C), 156.5, 154.9, 152.2, 150.6, 150.3, 149.4, 148.3, 137.8, 135.89, 129.3, 126.1, 125.8, 103.7, 96.3, 76.8 (O<u>C</u>H$(CH_3)_2$), 74.3 (<u>C</u>H$(CH_3)_2$), 56.2, 51.7 (NC<u>C</u>H_2), 44.9 (N($\underline{C}H_2CH_3)_2$), 29.8, 29.3, 28.8, 27.3, 24.5, 22.3, 12.5 (N($CH_2\underline{C}H_3)_2$).

Synthesis of dichloride-{1-(2,6-diisopropylphenyl)-2,2, 4,4-tetramethyl-pyrrolidinylidene)} (*o*-isopropoxy-*p*-diethylammonium-phenylmethylene) ruthenium tosylate (C90)

42.8 mg of PTSA.H_2O (0.22 mmol) was added to a solution of complex **CX** (150 mg, 0.22 mmol) in dichloromethane (12 mL). The initially red brown reaction mixture becomes rapidly green. This mixture was stirred for 30 min then evaporated under vacuum. The green residue was washed with hexane and dried under vacuum to afford **C90** as a green solid (169 mg, 90%).

^{1}H NMR (300 MHz, CD_2Cl_2): 16.27 (s, 1H Ru=C<u>H</u>), 12.20 (br s, 1H N<u>H</u>($CH_2CH_3)_2$), 7.72 (d, *J* = 8.1 Hz, 2H, C<u>H</u> Ar), 7.64 (t, *J* = 7.7 Hz, 1H, *p*-C<u>H</u> Ar), 7.47 (d, *J* = 7.7 Hz, 2H, C<u>H</u> Ar), 7.43 (s, 1H, C<u>H</u> Ar), 7.20 (d, *J* = 7.9 Hz, 2H, C<u>H</u> Ar), 6.97 (s, 2H, C<u>H</u> Ar), 5.15 (sept, *J* = 6.1 Hz, 1H, OC<u>H</u>($CH_3)_2$), 3.63 (br s, 2H, NC<u>H</u>$_2CH_3$), 3.36 (br s, 2H, NC<u>H</u>$_2CH_3$), 2.95 (sept, *J* = 6.5 Hz, 2H, C<u>H</u>($CH_3)_2$), 2.37 (s, 3H, Ar-C<u>H</u>$_3$), 2.19 (s, 2H, NCC<u>H</u>$_2$), 2.08 (s, 6H, NCC(C<u>H</u>$_3)_2$), 1.70 (d, *J* = 6.1 Hz, 6H, OCH(C<u>H</u>$_3)_2$), 1.35 (s, 6H, NC(C<u>H</u>$_3)_2$), 1.26 (d, *J* = 6.7 Hz, 6H, CH($CH_3)_2$), 1.17 (t, *J* = 7.2 Hz, 6H, NH(CH_2C<u>H</u>$_3)_2$), 0.64 (d, *J* = 6.4 Hz, 6H, CH(C<u>H</u>$_3)_2$).^{13}C {^{1}H} NMR (75 MHz, CD_2Cl_2): 288.3 (Ru=<u>C</u>H), 265.5 (N<u>C</u>C), 153.7, 148.6, 142.8, 140.7, 136.8, 130.0, 129.2, 126.2, 124.6, 78.7 (O<u>C</u>H($CH_3)_2$), 77.4 (<u>C</u>H($CH_3)_2$), 56.5, 51.7 (NC<u>C</u>H_2), 30.0 (NH(<u>C</u>$H_2CH_3)_2$), 29.3, 28.7, 26.6, 24.4, 22.1, 21.4, 10.5 (NH(CH_2<u>C</u>$H_3)_2$). HRMS (FT-ICR) EI+ (C_6D_6) m/z: 676.249 [M-(HOTs+H)] EI- (C_6D_6) m/z: 171.01 [OTs].

In situ activation of diethylamino-CAAC catalysts

11 equivalents of acid were added to a solution of catalyst (~0.02 mmol) in toluene (10 mL). The resulting solution was stirred at room temperature for 10 minutes before its using in ethenolysis of methyl oleate.

Ethenolysis of methyl oleate (batch reaction procedure)

All catalytic reactions were carried out in a magnetically stirred (~ 1600 rpm) 50 mL stainless steel autoclave. The evacuated reactor was heated to 23°C.
Methyl oleate and dodecane were degassed by freeze pumping thaw prior to use. 19. 25 mL of a solution containing methyl oleate (1.15 mL, 3.3 mmol), dodecane (0.25 mL, 1.1 mmol, internal standard) and docosane (80 mg, 0.25 mmol, internal standard) in toluene (20 mL) was

charged in the autoclave. The ruthenium catalyst was then dissolved in toluene (10 mL). 2 mL of the catalyst solution (0.1 mol% Ru) was introduced in one portion to the reactor.
The reactor was pressurized to the desired pressure during 1 min and heated via computerized temperature controller to the desired temperature. The reaction was monitored by sampling via a shutoff valve through a tube inserted into the reaction mixture. The sample was quenched with excess butyl vinyl ether.
After 1.5 h, the autoclave was cooled down at room temperature. At t = 2h, the reaction mixture was collected in a recipient containing butyl vinyl ether.
Conversions and selectivity were determined on an Agilent Technologies 6890 Plus instrument using a BPX70 column (50 m x 0.32 x 0.25 µm film thickness) and a flame ionization detector (FID). The following conditions were used: inlet temperature of 280°C and detector temperature of 300°C were used with the following temperature ramp (39 min):
Starting temperature, 80°C; ramp rate 1, 3°C/min to 100°C ; ramp rate 2, 5°C/min to 150°C ; ramp 3, 10°C/min to 220 °C ; hold time 1, 15 min.

Biphasic ethenolysis of methyl oleate was performed by L. Chahen
(batch reaction procedure)

All catalytic reactions were carried out in a magnetically stirred (~ 1100 rpm) 35 mL stainless steel autoclave. The evacuated reactor was heated to 23°C.
Methyl oleate was degassed by freeze pumping thaw prior to use. 19. 00 mL of a solution containing methyl oleate (1.2 mL, 3.3 mmol), and docosane (100 mg internal standard) in toluene (20 mL) was charged in the autoclave. The ruthenium catalyst was then dissolved in dichloromethane (10 mL). 2 mL of the catalyst solution (0.1 mol% Ru) was introduced in a Schlenk tube. The dichloromethane was evaporated and the “dry” catalyst was stirred for 10 minutes in 1 mL of ionic liquid BMP NTf_2. The ionic liquid was added in one portion to the reactor.
The reactor was pressurized to 12 bars during 1 min and heated via computerized temperature controller to 50°C. The reaction was monitored by sampling via a shutoff valve through a tube inserted into the reaction mixture. The sample was quenched with excess butyl vinyl ether.
After 2 h, the autoclave was cooled down to room temperature and the reaction mixture was collected in a recipient containing butyl vinyl ether. After decantation, the organic phase was analyzed by gas chromatography with the conditions described above.

Acidified biphasic ethenolysis of methyl oleate was performed by L. Chahen (batch reaction procedure)

All catalytic reactions were carried out in a magnetically stirred (~ 1100 rpm) 35 mL stainless steel autoclave. The evacuated reactor was heated to 23°C.

Methyl oleate was degassed by freeze pumping thaw prior to use. 19. 00 mL of a solution containing methyl oleate (1.2 mL, 3.3 mmol), and docosane (100 mg internal standard) in toluene (20 mL) was charged in the autoclave. The ruthenium catalyst was then dissolved in dichloromethane (10 mL). 2 mL of the catalyst solution (0.1 mol% Ru) was introduced in a Schlenk tube. The dichloromethane was evaporated and the dry catalyst was stirred for 5 minutes in 1 mL of ionic liquid BMP NTf_2. An excess of the corresponding acid was added and the mixture was stirred for 5 more minutes. Then, the ionic liquid was added in one portion to the reactor.

The reactor was pressurized to 12 bars during 1 min and heated via computerized temperature controller to 50°C. The reaction was monitored by sampling via a shutoff valve through a tube inserted into the reaction mixture. The sample was quenched with excess butyl vinyl ether.

After 2 h, the autoclave was cooled down to room temperature and the reaction mixture was collected in a recipient containing butyl vinyl ether. After decantation, the organic phase was analyzed by gas chromatography.

VII Acknowledgements

We thank ANRT and the IFP-Lyon for financial support. Rhodia is acknowledged for a generous gift of iminium salts. We are thankful to E. Jeanneau of Claude Bernard Lyon I University for the crystal structure determination.

VIII Supporting information (§)

Table 4. *Selected bond distances (Å) and angles (deg) for* ***C81****,* ***C89****,* ***C65, C88*** *and* ***C90***

Selected bond distances (Å):					
	C81	**C89**	**C65**	**C88**	**C90**
Ru-$C_{carbene}$	1.934 (4)	1.933 (10)	1.930 (3)	1.925 (2)	1.936 (2)
Ru-$C_{benzylidene}$	1.835 (4)	1.826 (11)	1.822 (3)	1.842 (2)	1.82 (2)
Ru-Cl (1)	2.3497 (13)	2.353 (3)	2.3320 (8)	2.3382 (8)	2.3257 (7)
Ru-Cl (2)	2.3157 (15)	2.336 (3)	2.3370 (7)	2.337 (7)	2.3131 (7)
Ru-O	2.378 (3)	2.379 (6)	2.325 (2)	2.3893 (16)	2.3732 (15)
Selected bond angles (deg) :					
$C_{carbene}$-Ru-O	177.06 (14)	177.6 (3)	177.51 (8)	178.49 (9)	176.25 (8)
$C_{benzylidene}$-Ru-O	77.20 (15)	76.4 (4)	78.09 (10)	76.79 (8)	77.65 (8)
Cl (1)-Ru- Cl (2)	153.54 (5)	155.63 (12)	152.78 (3)	153.25 (3)	151.03 (3)

For crystallographic data and structure refinement, see the experimental section page 272.

IX References

1. Chauvin, Y. *Angew. Chem. Int. Ed.* **2006,** *45*, 3740

2. Rouhi, A. M. *Chemical & Engineering News* **2002,** 29

3. Borman, S. A. *Chemical & Engineering News* **2008,** *86*, 37

4. Grubbs, R. H. *Tetrahedron* **2004,** *60*, 7117

5. Schwab, P., France, M. B., Ziller, J. W., Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **1995,** *34*, 2039

6. Schwab, P., Grubbs, R. H., Ziller, J. W. *J. Am. Chem. Soc.* **1996,** *118*, 100

7. Sanford, M. S., Love, J. A., Grubbs, R. H. *J. Am. Chem. Soc* **2001,** *123*, 6543

8. Scholl, M., Ding, S., Lee, C. W., Grubbs, R. H. *Org. Lett.* **1999,** *1*, 953

9. Huang, J., Stevens, E. D., Nolan, S. P., Petersen, J. L. *J. Am. Chem. Soc.* **1999**, 121, 2674

10. Scholl, M., Trnka, T. M., Morgan, J. P., Grubbs, R. H. *Tetrahedron Lett.* **1999,** *40*, 2247

11. Harrity, J. P. A., La, D. S., Cefalo, D. R., Visser, M. S., Hoveyda, A. H. *J. Am. Chem. Soc.* **1998,** *120*, 2343

12. Kingsbury, J. S., Harrity, J. P. A., Bonitatebus, P. J., Hoveyda, A. H. *J. Am. Chem. Soc.* **1999,** *121*, 791

13. Garber, S. B., Kinsgbury, J. S., Gray, B. L., Hoveyda, A. H. *J. Am. Chem. Soc.* **2000,** *122*, 8168

14. Ahn, Y. M., Yang, K., Georg, J. I. *Org. Lett.* **2001,** *3*, 1411

15. Paquette, L. A., Schloss, J. D., Efremov, I. et al. *Org. Lett.* **2000,** *2*, 1259

16. Cho, J. H. and Kim, B. M. *Org. Lett.* **2003,** *5*, 531

17. Sutton, A. E., Seigal, B. A., Finnegan, D. F., Snapper, M. L. *J. Am. Chem. Soc.* **2002,** *124*, 13390

18. Clavier, H., Grela, K., Kirschning, A., Mauduit, M., Nolan, S. P. *Angew. Chem. Int. Ed. Engl.* **2007,** *46*, 6786

19. Buchmeiser, M. R. *Chem. Rev.* **2009,**

20. Matsugi, M. and Curran, D. P. *J. Org. Chem.* **2005,** *70*, 1636

21. Sledz, P., Mauduit, M., Grela, K. *Chem. Soc. Rev.* **2008**, 37, 2433

22. Gallou, F., Saim, S., Yee, N. K. **2005,** WO 056182 A1

23. Borre, E., Caijo, F., Rix, D., Crévisy, C., Mauduit, M. *Chimica Oggi-Chemistry Today* **2008**, 26, 89

24. Favre, F., Olivier-Bourbigou, H., Commereuc, D., Saussine, L. *Chem. Commun.* **2001,** 1360

25. Olivier-Bourbigou, H. and Magna, L. *J. Mol. Cat. A. : Chem.* **2002,** *182-183*, 419

26. Séméril, D., Olivier-Bourbigou, H., Bruneau, C., Dixneuf, P. H. *Chem. Commun.* **2002,** 146

27. Chauvin, Y. and Olivier-Bourbigou, H. *Chemtech* **1995,** *26*, 25

28. Favre, F., Forestiere, A., Olivier-Bourbigou, H., Chodorge, J-A. *Oil Gas-Eur. Mag.* **2005,** *31*, 83

29. Wakamatsu, H. and Blechert, S. *Angew. Chem. Int. Ed. Engl.* **2002,** *41*, 794

30. Wakamatsu, H. and Blechert, S. *Angew. Chem. Int. Ed. Engl.* **2002,** *41*, 2403

31. Grela, K., Harutyunyan, S., Michrowska, A. *Angew. Chem. Int.* **2002,** *41*, 4038

32. Zaja, M., Connon, S. J., Dunne, A. M. et al. *Tetrahedron* **2003,** *59*, 6545

33. Michrowska, A., Mennecke, K., Kunz, U., Kirschning, A., Grela, K. *J. Am. Chem. Soc.* **2006,** *128*, 13261

34. Gulajski, L., Michrowska, A., Bujok, R., Grela, K. *J. Mol. Cat. A. : Chem.* **2006,** *254*, 118

35. Grela, K. L., Michrowska, A. A., Bienek, M. (Boehringer Ingelheim Pharma GMBH & CO.KG), **2007,** WO 054483 A1

36. Bienek, M., Michrowska, A., Gulajski, L., Grela, K. *Organometallics* **2007,** *26*, 1096

37. Altomare, A., Burla, M. C., Camalli, M. et al. *J. Appl. Crystallogr.* **1999,** *32*, 115