CYCLIC ALKYL(AMINO)CARBENE LIGAND FOR RUTHENIUM OLEFIN METATHESIS CATALYSTS

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SYNTHESIS AND CHARACTERIZATION OF A NEW RUTHENIUM CATALYST AND APPLICATION IN ETHENOLYSIS OF METHYL OLEATE

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Abstract: We report here the synthesis of new ruthenium carbene complex, containing a cyclic alkyl(amino)carbene CAAC [$RuCl_2$(CAAC)(=CH-O^{i}Pr-C_6H_4)] **C81**. The structure and bonding parameters of complex **C81** have been determined by X-ray diffraction and are compared with catalysts **C65** and **C67** reported previously by Grubbs.

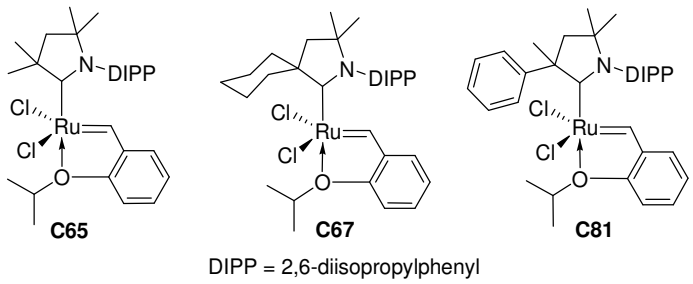


Figure 1. *Catalysts bearing cyclic (alkyl)(amino)carbenes synthesized*

These ruthenium-based complexes are efficient catalysts in the ethenolysis of methyl oleate where high selectivity is required. Our new catalyst **C81** displays higher activity than **C65** and **C67**. Indeed, noticeable differences in catalytic activity were observed when the substituents on the carbene ligand were changed. The activity increased with the electron donor ability of the substituents.

I Introduction

Olefin metathesis is a carbon-carbon bond forming reaction that is widely used in petrochemical, polymer, and specialty chemical industries[1,2]. Since the development of Grubbs catalysts which possess high functional group tolerance, significant current effort is focused on the modification of the ligand environment of ruthenium catalysts in order to produce new metathesis catalysts with improved stability, activity and selectivity.

The replacement of tricyclohexylphosphine of **C5** with N-heterocyclic carbene (NHC) gives rise to the more active and thermal stable complex **C9**[3], known as second-generation Grubbs

catalyst. The exchange of the remaining PCy_3 with a styrenyl ether ligand enhances the catalyst stability[4] and broadens the range of applications[5,6].

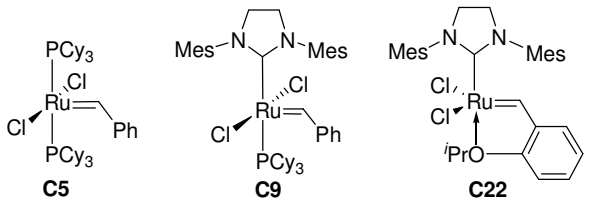


Figure 2. *Commonly used ruthenium olefin metathesis catalysts*

As demonstrated in Chapter one, NHC ligands are generally considered as more σ-donor ligand than PCy_3 (page 50). Indeed, the evaluation of **C5** and **C9** in the ethenolysis of methyl oleate (Chapter II, page 143) have shown that NHC-complex **C9** offers significantly enhanced activity relative to **C5** in optimised conditions. Whereas the first-generation PCy_3 based catalyst **C5** was very selective toward ethenolysis products (1-decene and methyl-9-decenoate), NHC complexes **C9** and **C22** also catalyzed secondary metathesis as self-metathesis and isomerization process, which results in moderate overall reaction selectivity.
We postulate that ligands which may have at once close steric environment to tricylcohexylphosphine to inhibit the self metathesis reaction, together with excellent σ-donor ability to provide a more stable ruthenacyclobutane during the catalytic cycle should afford tremendous precatalysts for the ethenolysis of methyl oleate.

We thus decided to investigate the use of cyclic alkyl(amino)carbenes (CAACs) owing to their excellent steric and electronic properties[7], as we have seen page 56. The steric environment of CAACs differs significantly from that of tertiary phosphines or NHCs. The exchange of an electronegative amine substituent in NHCs by the strong σ-donor carbon makes CAACs particularly electron-rich[8]. In addition, the presence of a quaternary carbon atom in α-position to the carbene center offers the possibility of constructing ligands featuring different types of steric environments. Bertand and co-workers have shown that CAACs can compete with NHC as ligands for transition metal-based catalysts[8]. There was only one report on their use as ligands for ruthenium olefin metathesis when we began this study[9].
In the first part, we report the different synthetic approaches for CAACs ligands. Then, we describe their introduction on ruthenium metal center and our first results in the ethenolysis of methyl oleate.

I.1 Cyclic alkyl(amino)carbene (CAAC)

I.1.1 Bertrand's synthetic approach

The first cyclic alkyl(amino)carbene was introduced by Bertrand in 2005[7] (Chapter I, page 56). The method used to prepare the precursor of acyclic alkyl(amino)carbenes, the alkylation of the corresponding enamines being limited[10], Bertrand thus proposed a new synthetic approach to prepare CAAC[11]. The choice of R^1 and R^2 substituents is virtually unlimited (except that R^1 and R^2 cannot be H).

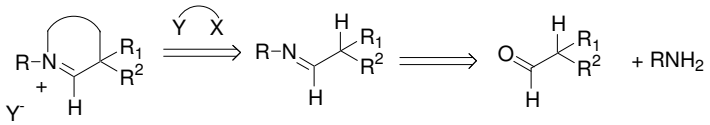
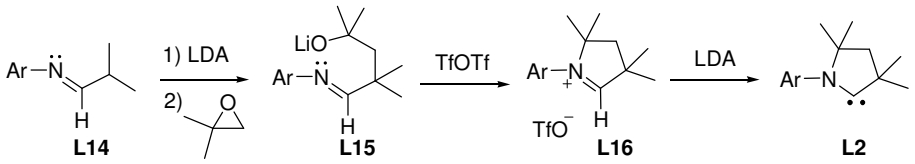


Figure 3. *Retrosynthetic analysis for the preparation of CAACs*

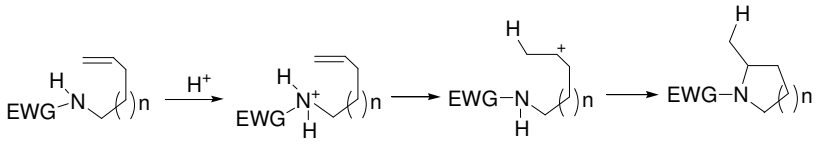
The first CAAC **L2** was obtained from imine **L14** which can be synthesized from 2,6-diisopropylaniline and 2-methylpropanal. Deprotonation of **L14** with lithium diisopropylamide (LDA) afforded the aza-allyle anion, which readily induces the ring opening of 1,2-epoxy-2-methylpropane leading to **L15**. The cyclic aldiminium salt **L16** was obtained from **L15** by reaction with trifluoromethanesulfonic anhydride (TfOTf) at -78°C.



Scheme 1. *Synthesis of the cyclic alkyl(amino)carbene **L2***

Finally, deprotonation of **L16** with LDA gives rise to the carbene **L2** as a white solid which is stable at ambient temperature.

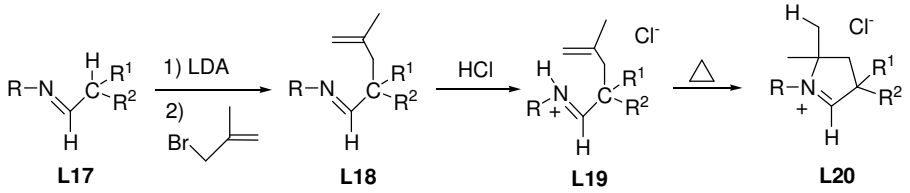
In this synthesis, the preparation of the nitrogen-containing heterocycles is tedious and time consuming, moreover 1,2-epoxy-2-methylpropane is difficult to obtain. Nitrogen-containing heterocycles are often obtained by intramolecular hydroamination of alkenes[12], in which the nitrogen-carbon bond is formed by addition of an amine to an olefin. Hartwig and Schlummer developed an acid-catalyzed intramolecular hydroamination for aminoalkenes bearing electron-withdrawing group (EWG) on the nitrogen atom[13].



Scheme 2. *Acid-catalyzed intramolecular hydroamination*

Mechanistic studies on this reaction (Scheme 2) indicate that the amine function is initially protonated, followed by intramolecular transfer of the proton to the double bond in the rate determining step. Then, the resulting carbocation reacts with the amine in ring-closing reaction. Accordingly, in the absence of an electron-withdrawing substituent at the nitrogen atom, the cyclization does not occur because the enhanced basicity of the amine prevents the transfer of the proton to the olefin.

Bertrand and co-workers adapted this acid-catalyzed cyclization to the less basic imines and developed the « hydroiminiumation » reaction[14] for the preparation of direct precursors **L20** of CAACs (Scheme 3). First, an aldimine **L17** was prepared in analogy to **L14** in Scheme 1. Deprotonation of **L17** with LDA leads to the corresponding 1-aza-allyl-anion, which was treated at room temperature with 3-bromo-2-methylpropene to give the alkenyl aldimine **L18**. Compound **L18** reacts with HCl/Et_2O to afford **L19** which has been characterized crystallographically. Heating of various derivatives of **L19** results in cyclization to give the cyclic iminium salts **L20**.



Scheme 3. *Hydroiminiumation*

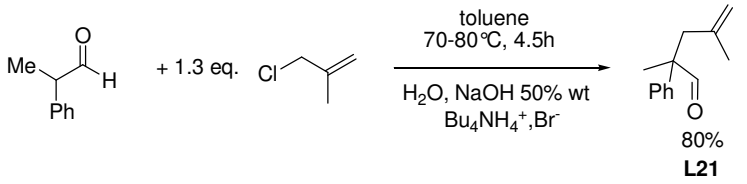
This reaction sequence allows the synthesis of iminium salts in which the quaternary carbon atom C(3) is part of a cyclohexyl ring. In addition, six membered heterocyclic aldiminium are accessible. An asymmetric version of the reaction[15] is also possible generating a stereocenter at atom C(5). Moreover, the new route uses the same precursor **L17**, but avoids the use of costly reagents 1,2-epoxy-2-methylpropane and trifluoromethanesulfonic anhydride (Scheme 1).

I.1.2 Rhodia's synthetic approach

Recently, Rhodia described a performant way to obtain a large variety of CAAC[16]. Contrary to Bertrand's route, this process is universal and does apply when the aryl group is replaced by a menthenyl group. The general method used to prepare the precursor of CAAC consists in 3 steps.

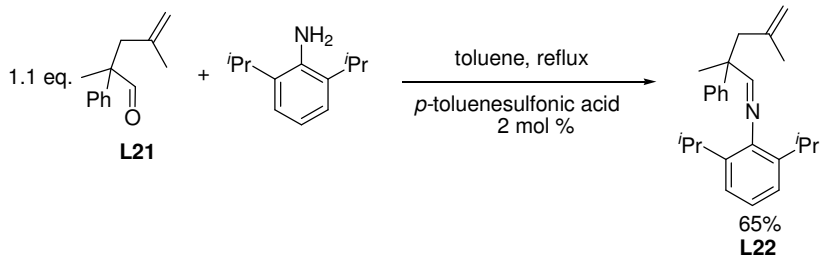
For example, **L23** was obtained as described below:

- allylation of α-disubstituted aldehyde with phase transfer agent.



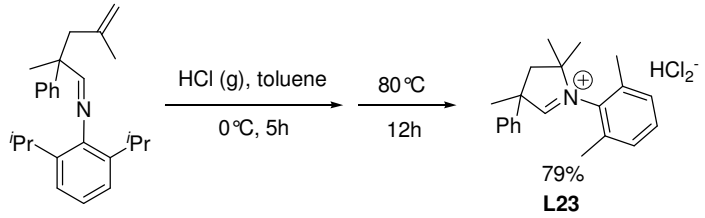
Scheme 4. *Nucleophilic substitution on allyle chloride by alcoolate*

- synthesis of imine **L22** from insaturated aldehyde **L21** and 2,6-diisopropylaniline.



Scheme 5. *Nucleophilic addition of primary amine to carbonyl under acidic conditions*

- cyclization of **L22** with strong acid HCl.



Scheme 6. *Ring closing*

The use of costly reactive TfOTf and epoxide is avoided by this method and, contrary to the iminium salt developed by Bertrand, these iminium salts possess HCl_2^- counter ion. This anion has the advantage to be cheaper than triflate, it also could be scaled up to the industrial scale.

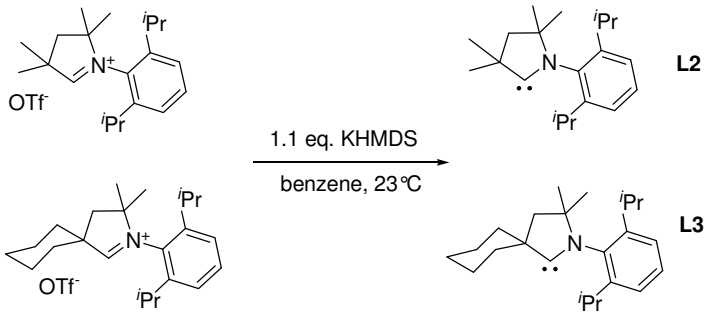
HCl_2^- is not often employed but there are some articles describing its use as anion in ionic liquids[17].

II Synthesis of ruthenium complexes containing CAAC

II.1 The work of Grubbs

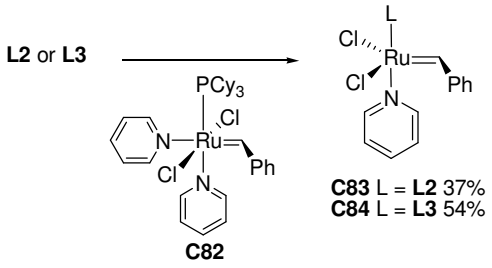
Grubbs reported the synthesis of ruthenium catalysts containing CAAC[9] for ring closing metathesis (page 58) while we were already working on these ligands.

They first choose to investigate carbenes which contain an N-DIPP (DIPP = 2.6-diisopropylphenyl) group and either two methyl groups (**L2**) or a spiro-fused cyclohexyl group (**L3**). These carbenes (Scheme 7) were provided by Bertrand's group.



Scheme 7. *Synthesis of carbenes **L2** and **L3***

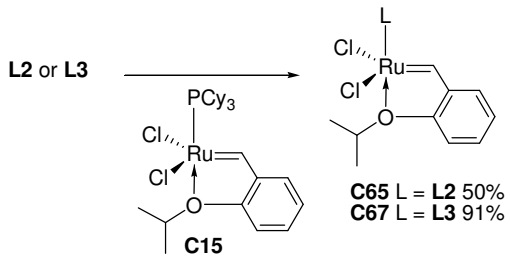
Upon treatment of pyridine complex **C82** with CAAC carbenes (generated in situ), **C83**, **C84** were isolated in modest yields.



Scheme 8. *Complexes Ru-pyridine-CAAC*

These catalysts give conversion less than 50% in RCM of diethyl diallylmalonate, which is attributed to catalyst decomposition.

To obtain more stable complexes, they targeted complexes **C65** and **C67**. After addition of **L2**, **L3** to first generation Hoveyda catalyst, **C65** and **C67** were isolated and purified in good yields by column chromatography.



Scheme 9. *Synthesis of Ru-CAAC chelating ether complexes*

The efficiency of catalysts **C65** and **C67** was examined in RCM of various substrates. They are less reactive than second generation NHC-based catalysts due to the steric bulk of the N-aryl ring[9]. A dramatic increase in activity for the synthesis of di- and trisubstituted olefins was observed after slightly decreasing the steric bulk of the N-aryl group, by replacement of N-DIPP with N-DEP.

However, CAACs employed by Grubbs were prepared by the first synthetic method developed by Bertrand (Scheme 1). This route involves non commercial and expensive reagent as epoxide. Besides, the strong base (LDA) cannot be used in industrial scale. The main disadvantage of this synthetic way is its non feasibility on a large scale.

II.2 Our work

We studied mainly three CAACs precursors synthesized by Rhodia[16] (Figure 4). As we previously shown, these iminium salts were prepared with a procedure avoiding the use of expensive reagents.

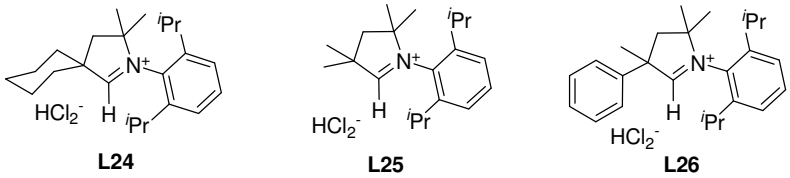
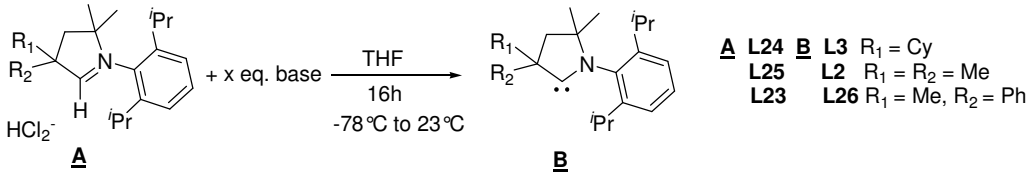


Figure 4. *Iminium salts studied*

The preparation of new complexes requires two steps. The first one consists in deprotonation of iminium salts to obtain the carbene ligand.

II.2.1 Deprotonation of iminium salts

The more acidic proton at the C(2) carbon atom of iminium salt **A** (relative to the imidazolinium salt) must be removed by a stronger base than potassium tert-butoxide (pKa ~ 18). Sterically more hindered and less nucleophilic bases, such as LDA (pKa ~ 36) or potassium bis(trimethylsilyl)amide (KHMDS, pKa ~ 26) have been employed successfully in THF for this reaction.



Scheme 10. *Synthesis of cyclic alkyl(amino) carbenes*

Our first attempts to prepare CAACs (**B**) with 1.1 equivalent of such bases failed. Evidence for the formation of an adduct CAAC-H_2O came from NMR spectroscopy (^{1}H NMR: 4.5 ppm and ^{13}C NMR: 96 ppm). This undesirable adduct may be generated by the reaction of free carbene and residual water contained in salts. In order to trap this water (1 wt%), we had to adjust the amount of base in order to avoid the decomposition of iminium salts and/or carbenes.

Moreover, these iminium salts contain mainly the anion HCl_2^-. Consequently, three equivalents of KHMDS were needed to obtain CAACs in good yield with high purity. Formation of carbene is easily remarkable by disappearance of the proton at the C(2) carbon atom between 10 and 12 ppm. In the ^{13}C NMR spectrum, the resonance signal for the C(2) carbene carbon atom is shifted downfield (δ = 280-350 ppm) compared to the carbon atom of the salt (δ = 160-200 ppm).

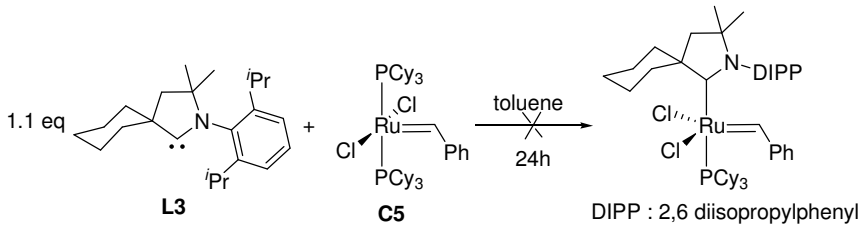
The use of non stoechiometric amount of base led us to isolate carbenes **B** before their complexation on the metal center.

II.2.2 Complexation of cyclic alkyl(amino)carbene

In an effort to broaden the utility of cyclic alkyl(amino)carbenes, we tried to coordinate these ligands on various ruthenium based systems.

II.2.2.1 $[RuCl_2(PCy_3)_2(=CHPh)]$

At first, we studied the first generation Grubbs catalyst **C5** to prepare the second generation analogous[3].



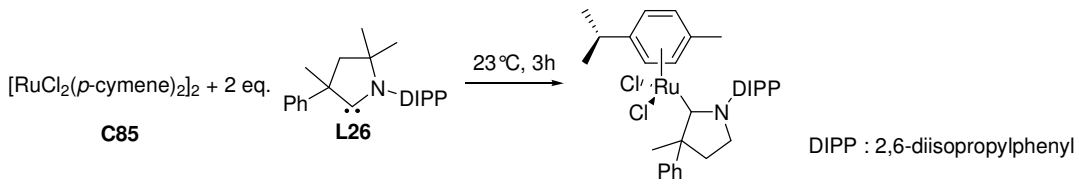
Scheme 11. *Attempted synthesis of $[RuCl_2(PCy_3)(CAAC)(=CHPh)]$ from **C5***

Treatment of **C5** with 1.1 equivalent of CAAC at room temperature affords no new signal in the downfield region of the ^1H NMR spectrum. Only benzylidene proton (Ru=C<u>H</u>) at 20 ppm attributed to **C5** was observed, even when heated at 60°C or in the presence of a phosphine scavenger (CuCl). ^{31}P NMR spectrum showed weak release of tricyclohexylphosphine and formation of its oxide, due to the slow decomposition of **C5** in solution.

We assume that **L3** does not coordinate on ruthenium for mainly steric reasons. Indeed, the bulky tricyclohexylphosphine may prevent the complexation of the CAAC which is more hindered.

II.2.2.2 $[RuCl_2(p\text{-cymene})]_2$

The ruthenium dimer $[RuCl_2(p\text{-cymene})]_2$ **C85** is air and moisture stable. This is an ideal starting material for the synthesis of allenylidene or vinylidene catalysts. Regardless of the solvent applied (toluene, THF); a mixture of products was observed (Scheme 12).

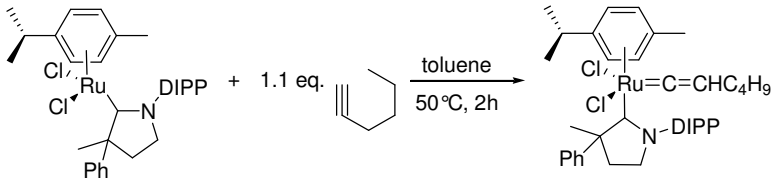


Scheme 12. *Attempted synthesis of [RuCl$_2$(p-cymene)CAAC] from **C85***

^{1}H NMR spectroscopic analysis revealed an undefined ruthenium hydride species at -3.8 ppm as already observed by Verpoort for the synthesis of [RuCl$_2$(*p*-cymene)(SIMes)][18]. Whereas the coordination of IMes to **C85**[19,20,21] proceeds readily, analogous binding of SIMes was found to be more problematic.

Furthermore, mass spectroscopy[§] of our brown red isolated product showed that desired product (m/z 653) was formed as a minor product together with an ion corresponding to the CAAC associated with arene ligand (m/z 480). Detailed analysis of the mixture should help us to clarify the possible intervention of CH-insertion reaction.

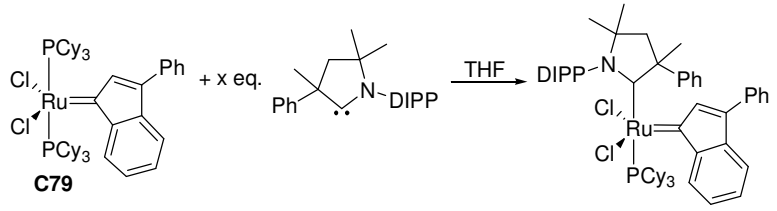
Besides, to the crude product obtained above is added hexyne to generate *in situ* the vinylidene complexe. However, this mixture is totally inactive in self-metathesis of methyl oleate and 1-octene at 50°C.



Scheme 13. *Formation in situ of vinylidene complex*

II.2.2.3 [RuCl$_2$(PCy$_3$)$_2$(3-phenyl-indenylidene)] : Neolyst M1

Another system **C79**[22] was also exploited under a variety of conditions. It has been necessary to heat at reflux the reaction mixture to release free phosphine in solution (Table 1, Entry **1** and **2**).



Scheme 14. *Attempted synthesis [RuCl$_2$(PCy$_3$)(CAAC)(3-phenylindenylidene)] from **C79***

While the coordination of the better σ-donor CAAC ligand (relative to the tricyclohexylphosphine), should lead to the upfield shift of the ^{31}P signal, one new singulet appears at 36 ppm.

Table 1. *Reaction conditions tested (δ ppm)*

Entry	Reagents	Reactions conditions	Characterization
1	**C79** + 1.1 eq. **L26**	23°C, 3h	**^{1}H NMR:** no change **^{31}P NMR:** 32.3 (PCy_3 **C79**)
2	**C79** + 1.1 eq. **L26**	65°C, 9.5h	**^{1}H NMR:** no change **^{31}P NMR:** 45.8 ($OPCy_3$, 22%), 36.1 (?, 5%), 32.3 (**C79, 55%**), 10 (free PCy_3, 18%)
3	**C79 +** 1.5 eq. **L23** + 3 eq. KHMDS	23°C, 99h	**^{31}P NMR:** 45.8 ($OPCy_3$, 20%), 36.6 (?, 4%), 32.3 (**C79, 2%**), 17.3 (?, 3%), 10 (free PCy_3, 71%)

Unfortunately, after 4 days of heating (Entry **2,** Table 1), the phosphine oxide is formed as the major product and the singulet at 36 ppm almost disappeared. **C79** probably decomposes at 65°C.

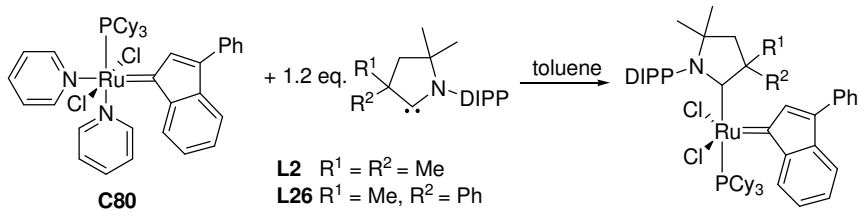
The last attempt consisted in the *in situ* generation of the carbene at room temperature (Entry **3**). NMR spectroscopy confirmed the deprotonation of the iminium salt because neither the signal corresponding to the precursor, nor that of the CAAC-H_2O adduct were observed after 75 hours of stirring in the presence of **C79**. As previously detected, the free phosphine and its oxide were produced in a majority fashion. A singulet at 17.3 ppm which could be assigned to the desired complex was obtained but it is only present as a minor product.

II.2.3 [$RuCl_2(PCy_3)(NC_5H_5)_2$(3-phenyl-indenylidene)]

As we have seen during the bibliographic study (page 73), pyridine is a labile ligand. Indeed, the exchange of ligand proceeds easily with stronger donor such as phosphines or NHCs[23]. In order to examine electronic effect on substitution reaction, we concentrated our efforts on the system bearing a pyridine ligand **C80**[24].

Moreover, if the ruthenium complex contains both CAAC and tricylohexylphosphine ligand, the strong electro donation of the two neutral ligands could destabilized ruthenium metal center leading to decomposition products. Furthermore, the geometry of the bisphosphine precursor may prevent the coordination of the sterically demanding CAAC ligand. Besides, the presence of the bulky alkylidene phenyl-indenylidene, could prevent the complexation.

We thus prepared **C80** (page 136) to attenuate steric hindrance around the ruthenium and facilitate CAAC complexation.



Scheme 15. *Attempted synthesis of [$RuCl_2(PCy_3)$(CAAC)(Ph-indenylidene)] from* ***C80***

Table 2. *Reaction conditions tested with* ***L27*** *and* ***L2*** *(δ ppm)*

Entry	Reagents	Conditions	Characterization
1	**C79** + 100 eq. NC_5H_5 + 1.2 eq. **L26**	23°C, 15h,	**^{31}P NMR:** 46 ($OPCy_3$, 7%), 32.3 (**C79**, 2%) 28 ([Ru-NC_5H_5]), 10%) 15 (**C80,** 10%), 10.1 (PCy_3, 71%)
2	**C80 +** 1.2 eq. **L26**	70°C, 3h,	**^{31}P NMR:** 46 ($OPCy_3$, 38%), 32.3 (**C79**, 55%) 28 ([Ru-NC_5H_5]), 7%)
3	**C80 +** 1.2 eq. **L2**	70°C, 9h,	**^{31}P NMR:** 46 ($OPCy_3$, 91%), 32.3 (**C79**, 5%), 28 ([Ru-NC_5H_5]), 4%)

For the first experiment, **C80** was prepared in situ (Entry **1,** Table 2). The reaction of **C79** with a large excess of pyridine (~100 eq) and CAAC ligand results in a rapid displacement of the phosphine ligand at room temperature. After 15h of stirring, the intensity of the signal corresponding to the obtained complex **C80** strongly decreased (10%). The absence of pyridine peaks on ^{1}H NMR spectrum suggested the replacement of pyridine ligand. In a surprising way, the bisphosphine phenylindenylidene complex **C79** was formed in good yield (55%), as revealed by ^{31}P NMR. We hypothesized that the pyridine might be displaced quickly by the free tricyclohexylphosphine instead of the CAAC ligand because of steric reasons.

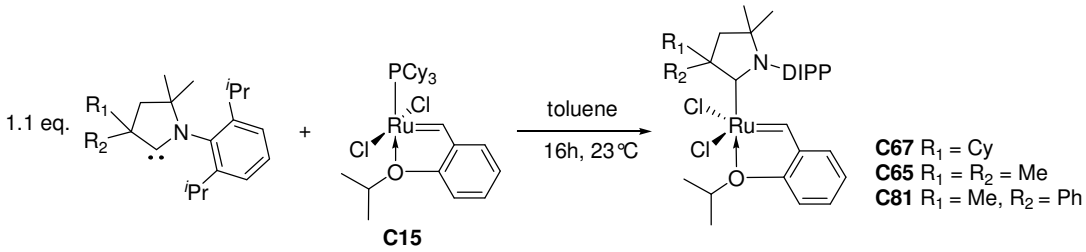
With the starting material **C80** (Entry **2,** Table 2), the reaction mixture was heated at 70°C. Similar to Entry **1**, **C79** was obtained as a major product in spite of the absence of free phosphine in the initial reaction mixture. The reaction **L2** with **C80** for 9 hours yielded a major formation of phosphine oxide. No evidence of the synthesis of Ru-CAAC complex was found in mass spectroscopy and by evaluation of the isolated product in ethenolysis of methyl oleate.

Complex **C80** does not react with CAAC to produce a stable product, presumably due to the prohibitive size of the incoming ligand. We thus postulate that CAAC complexation on ruthenium requires the use of less bulky ruthenium precursors.
Up to this point, all attempts to introduce CAAC ligand on ruthenium complexes failed. More efforts to obtain the desired complexes following alternative procedures such as carbene transfer reactions[25,26] could be envisaged.

In fact, silver NHC and thiazolylidene[27] complexes have been shown to be excellent agents for the transfer of a carbene ligand to another metal center[28,29]. This method often gives access to NHC complexes[30] where alternative syntheses are tedious or unsuccessful; it could be adapted to CAAC ligands.

Alternatively, the CAAC transfer from chloroform[31] or alkoxide adduct[32] could allow the synthesis of new complexes. However, this procedure has not reached the general applicability of the previous method.

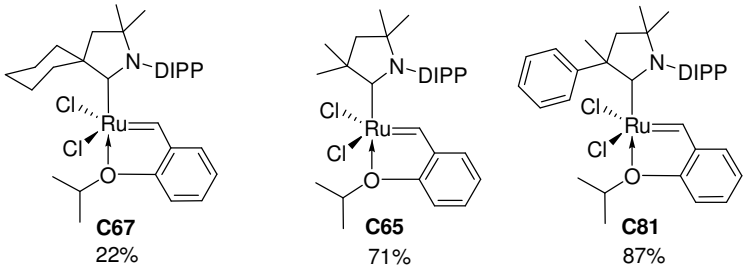
II.2.3.1 $[RuCl_2(PCy_3)(=CH\text{-}O^iPr\text{-}C_6H_4)]$



Scheme 16. *Synthesis of [$RuCl_2$(CAAC)(=CH-O^iPr-C_6H_4)] from* ***C15***

When first generation Hoveyda precursor **C15** was treated with **L26** carbene, ^{1}H NMR spectroscopy in C_6D_6 revealed an upfield shift of the alkylidene proton (H_α) peak at 16.6 ppm, versus 17.4 ppm for the starting complex **C15**[33,34] and for the *iso*-Pr methine proton (4.51 ppm instead of 5.36 ppm).
These findings are consistent with substitution of a tricylohexylphosphine ligand by the more σ-donor ligand cyclic alkyl(amino)carbene, leading to higher electron density at the metal center. ^{13}C NMR spectrum showed two characteristics peaks in downfield region, one corresponding to the alkylidene moiety (Ru=CH) at 293.7 ppm instead of 280.6 ppm in **C15** and the second was attributed to NCC at 266.2 ppm.

Complexes were obtained in good yields by washing crude products with hexane, without further chromatographic purification. The isolated Ru-alkylidene complexes are air and moisture stable compared to **C9**.



Scheme 17. *Catalysts synthesized*

Crystals of **C81** were prepared by slow diffusion of hexane into a concentrated solution of **C81** in dichloromethane. X-ray crystallographic analysis[§] was conducted to compare with those previously described by Grubbs[9] for **C65** and **C67**.

The X-ray analysis[§] of **C81** indicated a distorted square-pyramidal geometry with the benzylidene moiety in the apical position (Figure 5). As already noticed[9], the N-aryl ring is located above the benzylidene moiety. Similar to the other CAAC complexes, the Ru-carbene distance is shorter and Ru-O distance is longer than in second-generation Hoveyda **C22** (Table 5[§]). These observations are in agreement with the increase of the donor properties of cyclic (alkyl)(amino) carbenes over NHC[8]. Interestingly, the Ru-O bond distance (2.378 (3) Å) is significantly longer compared to the related complexes **C65** (2.325 (2) Å) and **C67** (2.354 (8) Å).

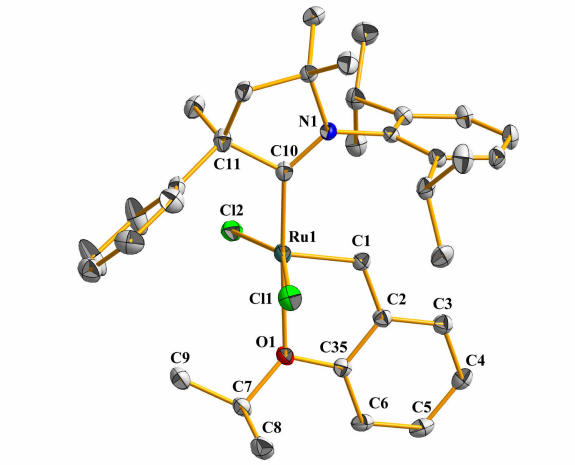


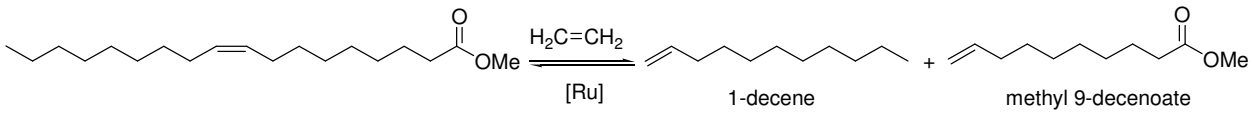
Figure 5. *X-ray crystal structure of **C81**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity*

In accordance with the structure determined by X-Ray diffraction, Hα appeared as a singlet in ^{1}H NMR spectra versus a doublet in **C15**. Thus, we success in isolating a new ruthenium complex bearing for the first time a CAAC carbene with an aromatic group on its C(3) position. We also noticed that the carbon atom C(11) is a stereogenic center.

The reactivity of these new complexes will further be studied in the metathesis of methyl oleate.

III Reactivity of ruthenium catalysts bearing CAAC

The catalytic properties of complexes **C65**, **C67** and **C81** were investigated in ethenolysis of methyl oleate to establish relationship between the carbenes's substituents and the pre-catalyst activity.



Scheme 18. *Ethenolysis of methyl oleate*

Experiments were carried out in toluene at 50°C under 10 bar ethylene pressure, with 0.1 mol% ruthenium loading, as described in experimental section. Results obtained are summarized in Table 3.

Table 3: *Comparison of ruthenium catalysts in the ethenolysis of methyl oleate* [a]

Entry	Catalysts	Conversion (%)[b]	Selectivity (%)[c]
1	**C67**	84	98
2	**C65**	83	97
3	**C81**	99	98
4	**C15**	61	91
5	**C22**	18	66
6	**C9**	92	72

a) 0.1 mol% Ru relative to methyl oleate, 50°C, 10 bar ethylene pressure, 1.5h

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}]

At a catalyst loading of 0.1 mol %, chelating ether catalysts **C67, C65, C81** achieved 84%, 83%, and 99% conversion of methyl oleate respectively, after 1.5h at 50°C.

Commonly used metathesis catalysts, first generation PCy_3-based Hoveyda catalyst **C15**, second generation NHC-based Grubbs **C9** and Hoveyda **C22** catalysts were evaluated for the ethenolysis of methyl oleate under the same conditions (10 bar ethylene, 50°C,).
The first generation Hoveyda complex **C15** yet known for its high selectivity for the production of terminal olefin over self-metathesis products, shows here moderate conversion and lower selectivity (Table 3, Entry **4**). The new systems **C65**, **C67**, **C81** exhibited better activity and provided higher selectivity than **C15** (Entry **1-3**).

NHC-containing systems **C9** and **C22** which are very active in the self-metathesis of methyl oleate demonstrated lower selectivity for terminal olefins than **C15** and than complexes bearing CAAC ligands. Nevertherless, second-generation Grubbs catalyst **C9** achieves 92% conversion with 72 % selectivity (Entry **6**).

As expected, these three CAAC complexes are efficient catalysts (Entry **1-3**). Only small quantities of self-metathesis products (9-octadecene and diester D18:1) were observed in gas chromatography. According to the nature of the CAAC ligand, the activity is superior or lower than that of complex **C9**. This observation suggested that the nature of substituents on the carbene has a direct influence on the reactivity.

The reactivity of **C81** which bears the CAAC with substituents methyl phenyl (Entry **3**) is greater than that of second generation catalyst **C9** as depicted in Table 3. In all cases, **C81** is the most active catalyst. Although selectivity is close to others CAAC complexes **C65** and **C7**, the activity towards ethenolysis is better.

We, thus, concentrated our efforts on this new efficient precatalyst **C81**. The optimum reactions conditions for **C81** were determined from varying the temperature and the ethylene pressure with 0.02 % mol Ru.

From varying the reaction temperature (Figure 6), the activity of **C81** is significantly improved over the temperature range 23-50°C. However, a decrease of the performances was observed at 70°C with the formation of secondary metathesis products resulting from double bond isomerisation in small amount.

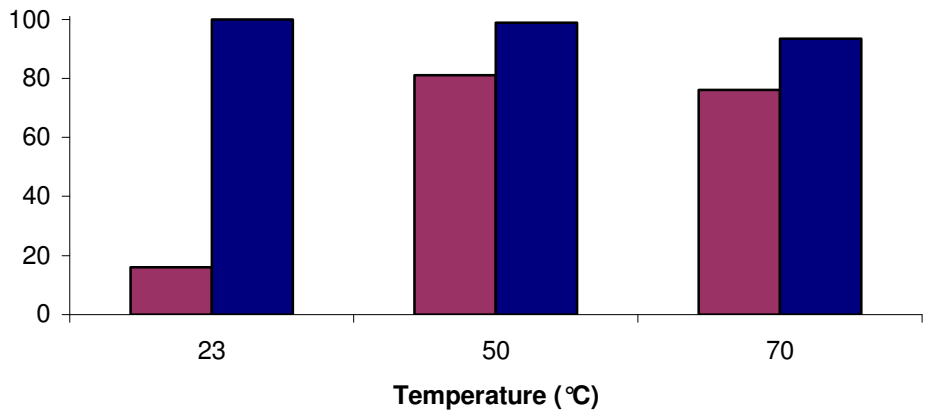


Figure 6. *Influence of reaction temperature on methyl oleate conversion ■ and ethenolysis selectivity ■ with 0.02 mol% Ru complex **C81**, toluene, 10 bar ethylene, 2h*

The efficiency of **C81** was then evaluated at 50°C to study the impact of ethylene pressure (Figure 7). The selectivity is nearly the same when the pressure changed from 1.5 bar to 30 bar. The conversion increased until 81% for P = 10 bar then decreased to 54% when the ethylene pressure is up to 30 bar.

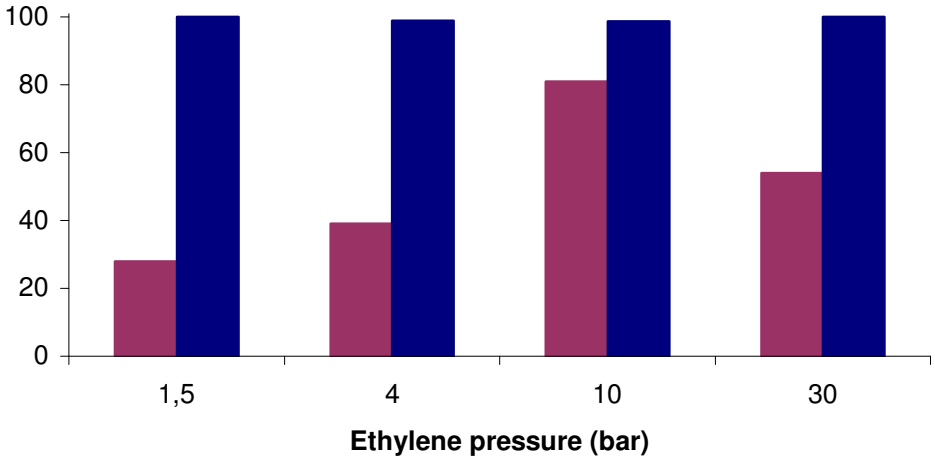


Figure 7. *Influence of ethylene pressure on methyl oleate conversion ■ and ethenolysis selectivity ■ with 0.02 mol% Ru, toluene, 50°C, 1h30*

Figure 8 illustrates the influence of ethylene content (function of the pressure) in the solvent reaction (toluene) at 50°C on the activity of the precatalyst **C81**. The maximum conversion is obtained when ethylene content reaches 4 wt% in toluene (50°C, 10 bar ethylene). This ethylene content corresponds to ~7 equivalents relative to the ruthenium catalyst. Contrary to second generation Grubbs catalyst **C9** (page 147), at ethylene/ruthenium ratio superior to one, there is no reduction of the activity.

Thus, CAAC ligands must slow down decomposition of the propagating methylidene species and/or methylidene CAAC complexes are more robust than NHC analogous.

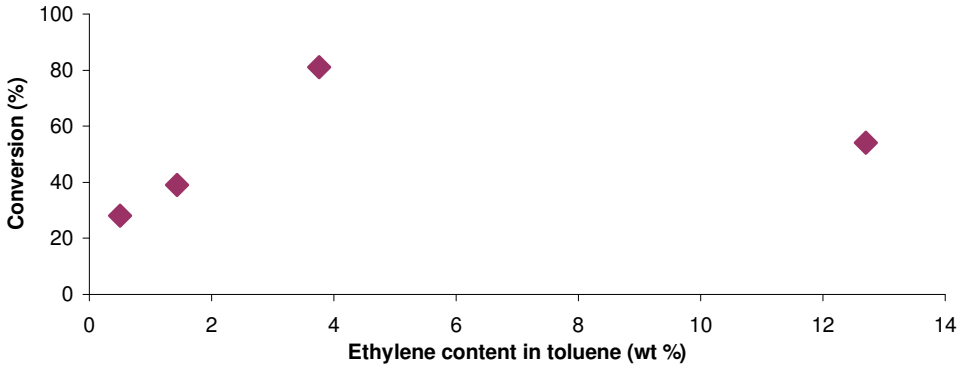


Figure 8. *Influence of ethylene content in toluene with 0.02 mol% Ru, 1h30*

With a large excess of ethylene in the reaction mixture (~13 wt%), we observed a significant decrease in conversion (from 81% to 54%).
CAAC systems are dramatically less sensitive to ethylene by comparison with Grubbs and Hoveyda catalysts.

We tried to understand the reasons of the increase of the selectivity with these systems in relation to second generation based catalysts. We have previously observed in presence of CAAC complexes that the selectivity for ethenolysis products is almost not affected by the temperature and ethylene pressure.
Thus, CAAC may have a dramatic impact on the ruthenium ligand sphere.

If X-ray crystal structures of second-generation Hoveyda precatalyst **C22** and **C81** are compared (Figure 9), we clearly observe that SIMes ligand has less volume than CAAC ligand around the ruthenium metal center. The N-mesityl ring of SIMes and the N-diisopropylphenyl ring of **L26** are both perpendiculars to the benzylidene group but the two larger isopropyl substituents accentuate the steric bulk in the last case.

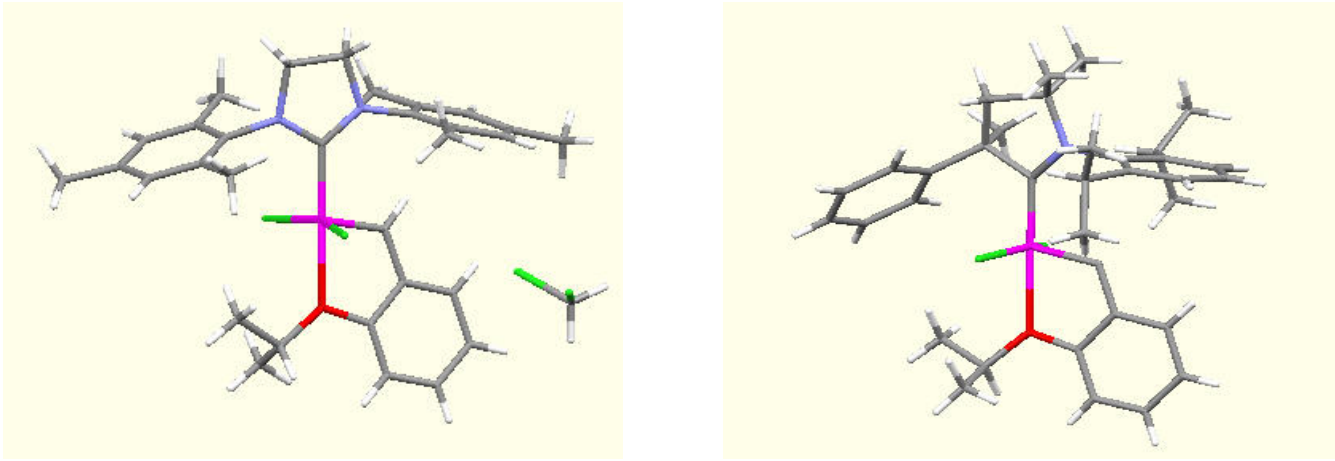


Figure 9. *X-ray crystal structures of **C22** (left) and **C81** (right)*

The Ru-C_{CAAC}-N_{CAAC} angle (134.4 (3)°) is larger than the corresponding angle in **C22** (131.65 (3)°), perhaps reflecting the more severe steric repulsion due to the presence of the bulkier isopropyl substituents.

In order to check the evolution of steric parameters from PCy_3 to SIMes and CAAC ligands, we measured the buried volume (% V_{Bur}), as previously calculated by Nolan and Cavallo for phosphine and NHC complexes[35]. % V_{Bur} gives a measure of the space occupied by the considered neutral ligand in the first coordination sphere of the metal centre (page 49).

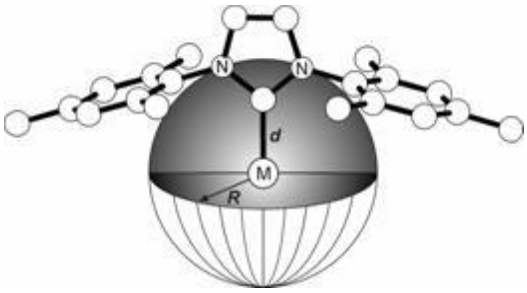


Figure 10. *Graphical representation of the sphere used to calculate the % V_{Bur}*

From the CIF format of the studied complex, the SamVca web application[36] provides a file with the coordinates of the ligand to be examined. Only the coordinates of the ligand must be supplied. We removed the coordinates of the metal and of all the others ligands. Then, we examined the DFT optimized geometry of the free ligand and positioned the putative metal atom at 2.1 Å from the coordinating C or P atom. This value is close to the average M-(NHC) distance in the DFT optimized geometry of a series of [Ir(NHC)$(CO)_2$Cl] complexes. 3.5 Å is the optimized radius, R, of the sphere built around the metal atom. This value is based on the DFT binding energy of 33 NHC ligands to the Ru atom in [RuCp*(NHC)Cl] complexes.

Different values for the radius of this sphere and the minimization of the ligand alone instead of the ligand in the transition metal complex result in different values of % V_{Bur}. A compilation of %V_{Bur} obtained values is presented in Table 4.

Table 4. *Steric parameters associated to PCy_3, SIMes and CAAC ligands Correlation with methyl oleate conversion and selectivity.*

Entry	Ligand (complex)	% V_{Bur}	Conversion (%)	Selectivity (%)
1	PCy_3 (**C15**)	34.9	61	91
2	SIMes (**C22**)	31.9	18	66
3	**L2** (**C65**)	36.2	83	97
4	**L3** (**C67**)	35.9	84	98
5	**L26** (**C81**)	38.1	99	98

0.1 mol % Ru relative to methyl oleate, toluene, 50°C, 10 bar ethylene, 1.5 h

As expected, PCy_3 is more sterically demanding than SIMes ligand in Hoveyda catalysts (Entry **1** and **2**). We assume that the bulky tricylohexylphosphine ligand prevents the competitive self-metathesis reaction of methyl oleate. In addition, CAAC ligands (Entry **3**-**5**) occupy larger amount of the sphere than SIMes and than PCy_3, providing greater % V_{Bur}. The data show a linear correlation between % V_{Bur} and reactivity profile. This model suggests that the activity and the selectivity are controlled by the steric requirements of the ligand. The more sterically hindered CAAC ligand (**L26**) providing the best reactivity.

We therefore postulate that the enhanced steric hindrance of the CAAC ligand allow for more effective protection of the metal center thus decreasing the rate of self-metathesis reaction[37]. CAACs appear as good ligand for ethenolysis of methyl oleate.

The characterization of the complex **C81** also provided some information to better understand its catalytic profile.
As we previously noticed, the Ru-O distance in **C81** is longer than in **C22**. Besides, X-ray diffraction studies of **C81** show a weaker Ru-O bond compared to that of CAAC complexes **C65** and **C67** already described by Grubbs, suggesting that initiation step could be faster.

In addition, we established a correlation between the chemical shift of the alkylidene moiety in ^{13}C NMR and the reactivity profiles of CAAC systems (Figure 11).

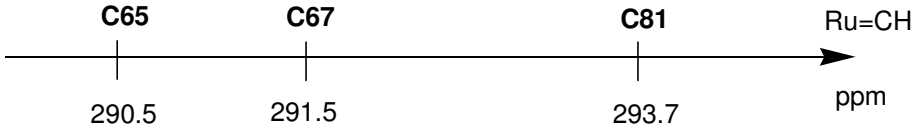


Figure 11. *Correlation between activity and ^{13}C NMR analysis*

The greater σ-donor ability of CAAC versus NHC results in higher electron density at the transition metal center and to the increased electrophilic character of the alkylidene carbon. Furthermore, according to the nature of the substituents of the CAAC ligand, we observed variation of the chemical shift of the alkylidene unit (Ru=CH). The carbene carbon atom in **C81** resonates downfield in comparison to that of **C65** and **C67**. We assumed that the phenyl substituent accentuates the electron density on the ruthenium atom by electronic delocalization. The best efficiency of **C81** may be attributed to the stabilization of propagating species and metallacyclobutane formed during the catalytic cycle owing to the enrichment of the metal. On the other hand, the weaker electron donation by the oxygen ligand to the ruthenium increases the rate of initiation step. These findings confirm previous X-ray analysis. Moreover, the chemical shift of alkylidene carbon in **C65** and **C67** are close together as it is the case with their performances.

Previous detailed studies of **C65** and **C67** in the ethenolysis of methyl oleate[37] revealed their high efficiency (Table 5). Under different conditions than in our studies (100 ppm, under 10 bar ethylene, neat and 40°C), catalysts **C65** and C67 achieve only 61% and 46% conversion with 92% and 94 % selectivity, resulting in 5600 and 4200 TONs, respectively. Another CAAC complex bearing N-DEP instead of N-DIPP **C66** was evaluated (page 58). **C66** exhibits the best performances as indicated in Table 5. At loading of 200 ppm, our new complex **C81** achieved 4058 TON at 50°C, in dilute conditions.

Table 5. *Comparison of ruthenium catalysts in the ethenolysis of methyl oleate*

Entry	Catalysts	Time (min)	Conversion (%)[d]	Selectivity (%)[e]	TON[f]
1[37]	**C65**[a]	1,320	61	92	5600
2[37]	**C67**[a]	360	46	94	4200
3[37]	**C66**[a]	<30	73	73	5300
		60	75	75	35000[b]
4	**C81**[c]	90	81	99	4058

a) 100 ppm, neat; b) 10 ppm, neat; c) 200 ppm, dilute conditions

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

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

f) TON = [(moles 1-decene + moles methyl-9-decenoate)/2 moles / moles of catalyst]

Thus, the substituents on CAAC ligand influence the reactivity. It is reasonable to accept that the performances of complexes are improved with electron donor mesomeric substituents. A dramatic increase in activity can be observed after slightly decreasing the steric bulk of the N-aryl group.

IV Conclusion

In this study, a new robust Ru-CAAC **C81** has been isolated and fully characterized. This catalyst was screened in ethenolysis of methyl oleate and compared with previously reported Ru-CAAC complexes and second generation of Grubbs and Hoveyda catalysts. The increased steric congestion in CAAC systems prevent undesirable side reactions (self-metathesis), they show excellent selectivity. We noticed that **C81** offers significantly enhanced activity at 50°C under 10 bar ethylene. The substituents on the carbene ligand were shown to also play a role in the activity of catalysts. Based on crystallographic data and ^{13}C NMR spectroscopy, the cyclic alkyl(amino) carbene which bearing methylphenyl substitutents on C^3 atom associated to the ruthenium affords higher activity. The mesomeric donor effect of the phenyl group has a significant influence on the catalytic performances. The synthesis and catalytic performances of **C81** have been patented in collaboration with Rhodia (French Patent N° FR08/06935 filed 10th December 2008). Modifications of this system are under investigation.

V Experimental section

General remarks:

All manipulations were performed under an argon atmosphere using standard Schlenk techniques.

Methyl oleate was purchased from Aldrich and dodecane was purchased from VWR, they were degassed by freeze pumping thaw prior to use.

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 coulometry using a Methrom 756 KF apparatus.

^{1}H NMR (300 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[38]and the refinement was by full-matrix least squares on F^2. No absorption correction was used.

Synthesis of 1-(2,6 diisopropylphenyl)-2,2,4-trimethyl-4-phenyl-pyrrolidinylidene (L26)

A 1/3 mixture of iminium salt **L23** (208 mg, 0.49 mmol) and KHMDS was cooled to -78°C and THF was added (10 mL). The suspension was warmed to room temperature and stirred for 16h. After evaporation of the solvent under vacuum, the solid residue was extracted with cyclohexane (2 x 8 mL). **L26** was obtained as a white solid after removal of solvent and was conserved in a glovebox (95% yield).

^{1}H NMR (300 MHz, C_6D_6): 7.84-7.26 (m, 8H, CH Ar), 3.18 (sept., 1H, C<u>H</u>$(CH_3)_2$), 2.04 (m, 1H, C<u>H</u>$(CH_3)_2$), 1.8 (s, 2H, C<u>H</u>$_2$-C), 1.51-1.02 (m, 21H, C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 310.5 (N<u>C</u>C), 150.6 (d), 146 (d), 139.95, 127.16, 126.44, 124.21, 124.02, 82.08 (<u>C</u>H$(CH_3)_2$), 64.85, 51.47 (<u>C</u>H$_2$-C), 29.79, 29.44, 28.37, 28.12, 27.23, 26.63, 26.42, 21.94 (<u>C</u>H$_3$).

1-(2,6-diisopropylphenyl)-2,2,4,4-tetramethyl-pyrrolidinylidene **(L2)** and
1-(2,6-diisopropylphenyl)-2,2,-dimethyl-4-cyclohexyl-pyrrolidinylidene **(L3)** were prepared from **L25** and **L24**, respectively in the same way as **L26**.

Synthesis of dichloride-{1-(2,6-diisopropylphenyl)-2,2-dimethyl- 4-cyclohexyl pyrrolidinylidene)} (o-isopropoxyphenylmethylene) ruthenium (C67)

L24 (0.22 g, 0.55 mmol) and 3 eq. of KHMDS (0.33 g, 1.67 mmol) were dissolved at -78°C in THF (10 mL). The reaction mixture was stirring for 16h, and then the solvent was evaporated. The solid residue was extracted with toluene (8 mL) and added to a vial containing Hoveyda 1st generation catalyst (49.5 mmol). The brown solution was stirring overnight at room temperature. After removal of solvent, the crude product was purified by flash column chromatography under argon (eluent: toluene/cyclohexane 9:1). The desired product eluted as a green band. Evaporation of the appropriate fractions afforded a green solid (73 mg, 22% yield).

^{1}H NMR (300 MHz, C_6D_6): 16.44 (s, 1H, Ru=C<u>H</u>), 7.25-7.22 (m, 1H, CH Ar), 7.16-7.13 (m, 2H, CH Ar), 7.01-6.88 (m, 1H, CH Ar), 6.53 (t, 1H, *p*-CH Ar), 6.31 (d, 1H, CH Ar), 4.54 (sept., 1H, (OC<u>H</u>$(CH_3)_2$), 3.65 (m, 2H, Cy), 3.09 (sept. 2H, C<u>H</u>$(CH_3)_2$), 2.38 (d, 2H, Cy), 1.8 (s, 2H, C<u>H</u>$_2$-C), 1.61 (d, 6H, OCH(C<u>H</u>$_3)_2$), 1.04 (d, 6H, CH(C<u>H</u>$_3)_2$), 0.88 (s, 6H, N-CC<u>H</u>$_3$), 0.81 (d, 6H, CH(C<u>H</u>$_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 291.51 (Ru=<u>C</u>H), 268.47 (N<u>C</u>C), 153.48, 148.98, 143.5, 137.2, 130.36, 129.58, 125.93, 123.75, 121.95, 113.53, 77.49, 75.02, 62.67, 44.43, 35.05, 30.14, 28.74, 27.01, 25.91, 24.43, 23.42, 22.24.
HRMS (FT-ICR) EI+ m/z: 645.2075 [M+].

Synthesis of dichloride-{1-(2,6-diisopropylphenyl)-2,2,4-trimethyl-4-phenyl-pyrrolidene} (o-isopropoxyphenylmethylene) ruthenium (C81)

L23 (417 mg, 0.99 mmol) and 3 eq. of KHMDS (597 mg, 2.99 mmol) were dissolved in THF (20 mL) at -78°C. The reaction mixture was stirring for 16h and then the solvent was evaporated. The solid residue was extracted with cyclohexane (20 mL) and dried under vacuum. A solution of Hoveyda 1st generation catalyst (0.83 mmol) in toluene (15 mL) was added to the vial containing the carbene. The brown solution was stirring overnight at room temperature. After removal of solvent, the crude product was washed with hexane (2 x 20 mL). The green solid thus obtained was filtered using a cannula filter and dried under vacuum (487 mg, 87% yield).

^{1}H NMR (300 MHz, C_6D_6): 16.59 (s, 1H, Ru=C<u>H</u>), 8.38 (d, *m*-CH Ar), 7.5 (m, 2H, *p*-CH Ar), 7.34-7.23 (m, 4H, CH Ar), 7.08-6.93 (m, 2H, CH Ar), 6.61 (t, 1H, *p*-CH), 6.37 (d, 1H, CH

Ar), 4.51 (sept., 1H, OC<u>H</u>$(CH_3)_2$), 3.25 (sept., 2H, C<u>H</u>$(CH_3)_2$), 2.87 (d, 1H, CC<u>H</u>$_2$), 2.49 (s, 3H, C<u>H</u>$_3$), 1.93 (d, 1H, CC<u>H</u>$_2$), 1.52 (d, 3H, C<u>H</u>$_3$), 1.35 (d, 3H, C<u>H</u>$_3$), 1.21 (d, 3H, CH_3), 1.13 (d, 3H, CH_3), 1.05 (m, 9H, CH(C<u>H</u>$_3)_3$), 0.78 (d, 3H, C<u>H</u>$_3$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 293.71 (Ru=<u>C</u>H), 266.23 (N<u>C</u>C), 153.53, 149.17, 148.85, 143.54, 143.03, 137.48, 130.53, 130.38, 129.66, 129.09, 126.19, 125.91, 123.9, 121.77, 113.58, 77.13, 74.77, 63.39, 48.96, 29.18, 28.53, 28.44, 27.76, 26.73, 24.49, 24.38, 22.42, 22.28.
HRMS (FT-ICR) EI+ m/z: 667.1921 [M+]. Anal. Calcd for $C_{35}H_{48}Cl_2NORu$: C, 62.958; H, 6.79; N, 2.098. Found: C, 62.59; H, 6.85; N, 1.99.

Synthesis of dichloride-{1-(2,6-diisopropylphenyl)-2,2,4,4-tetramethyl-pyrrolidinylidene} (o-isopropoxyphenylmethylene) ruthenium (C65)

C65 was obtained with the procedure used to prepare **C81** (71% yield).

^{1}H NMR (300 MHz, C_6D_6): 16.44 (d, 1H, Ru=CH), 7.38-7.32 (m, 1H, *p*-CH DIPP), 7.25-7.23 (m, 2H, *m*-CH DIPP), 7.1-7.08 (m, 1H, *p*-CH Ar), 7.01-6.98 (dd, 1H, *o*-CH Ar), 6.63 (t, 1H, m-CH Ar), 6.42 (d, 1H, m-CH Ar), 4.65 (sept., 1H, OC<u>H</u>$(CH_3)_2$), 3.17 (sept., 2H, C<u>H</u>$(CH_3)_2$), 2.25 (s, 6H, C(C<u>H</u>$_3)_2$), 1.77 (s, 2H, CCH2), 1.71 (d, 6H, OCH(C<u>H</u>$_3)_2$), 1.14 (d, 6H, CH(C<u>H</u>$_3)_2$), 0.93 (s, 6H, N-CC<u>H</u>$_3$), 0.91 (d, 6H,CH(C<u>H</u>$_3)_2$). ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): 290.49 (Ru=<u>C</u>H), 268.6 (N<u>C</u>C), 153.5, 149.01, 143.35, 137.23, 130.3, 129.61, 125.94, 123.61, 121.96, 113.47, 77.47, 75.14, 56.49, 51.5, 29.6, 29.28, 28.75, 27, 24.4, 22.18.
HRMS (FT-ICR) EI+ m/z: 605.1767 [M+].

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 desire pressure during 1 min and heated via computerized temperature controller to the desire 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 catalytic solution 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.

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VIISupporting information (§)

Table 6 : *Selected bond distances (Å) and angles (deg) for* ***C67, C65, C81*** *and* ***C22***

	Selected bond distances (Å):			
	C67	**C65**	**C81**	**C22**
Ru-$C_{carbene}$	1.9457 (10)	1.930 (3)	1.934 (4)	1.981 (5)
Ru-$C_{benzylidene}$	1.8318 (12)	1.822 (3)	1.835 (4)	1.828 (5)
Ru-Cl (1)	2.3326 (3)	2.3320 (8)	2.3497 (13)	2.328 (12)
Ru-Cl (2)	2.3319 (3)	2.3370 (7)	2.3157 (15)	2.340 (12)
Ru-O	2.3539 (8)	2.325 (2)	2.378 (3)	2.261 (3)
	Selected bond angles (deg) :			
$C_{carbene}$-Ru-O	175.84 (3)	177.51 (8)	177.06 (14)	176.2 (14)
$C_{benzylidene}$-Ru-O	77.74 (4)	78.09 (10)	77.20 (15)	79.3 (17)
Cl (1)-Ru- Cl (2)	151.627 (11)	152.78 (3)	153.54 (5)	156.5 (6)

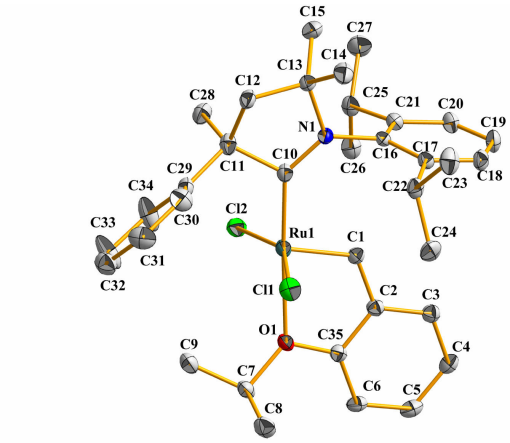

Figure 12. *X-ray crystal structure of* ***C81****. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity*

For crystallographic data and structure refinement of **C81**, see the experimental section page 272.

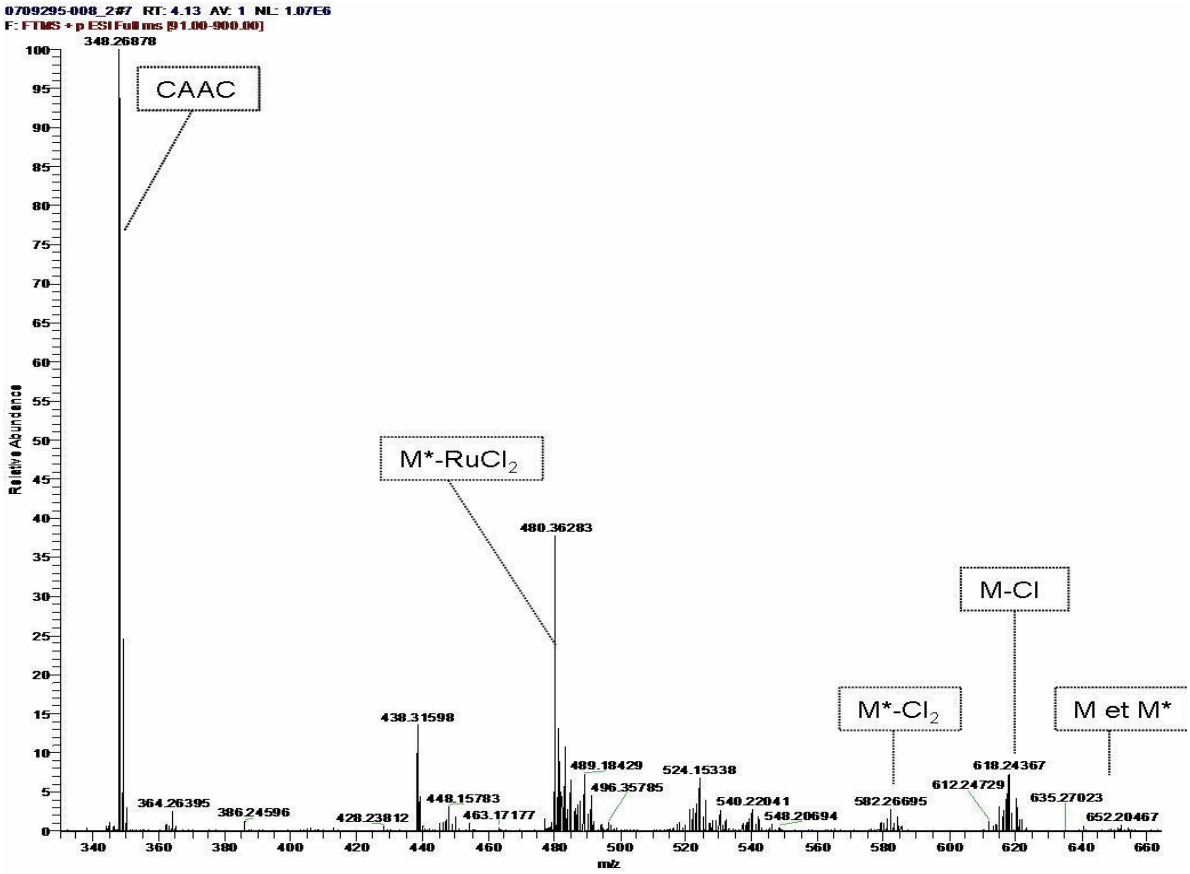

Figure 13. *Mass spectroscopy analysis of isolated product from [$RuCl_2$(p-cymene)CAAC]synthesis in CH_2Cl_2/CH_3CN*

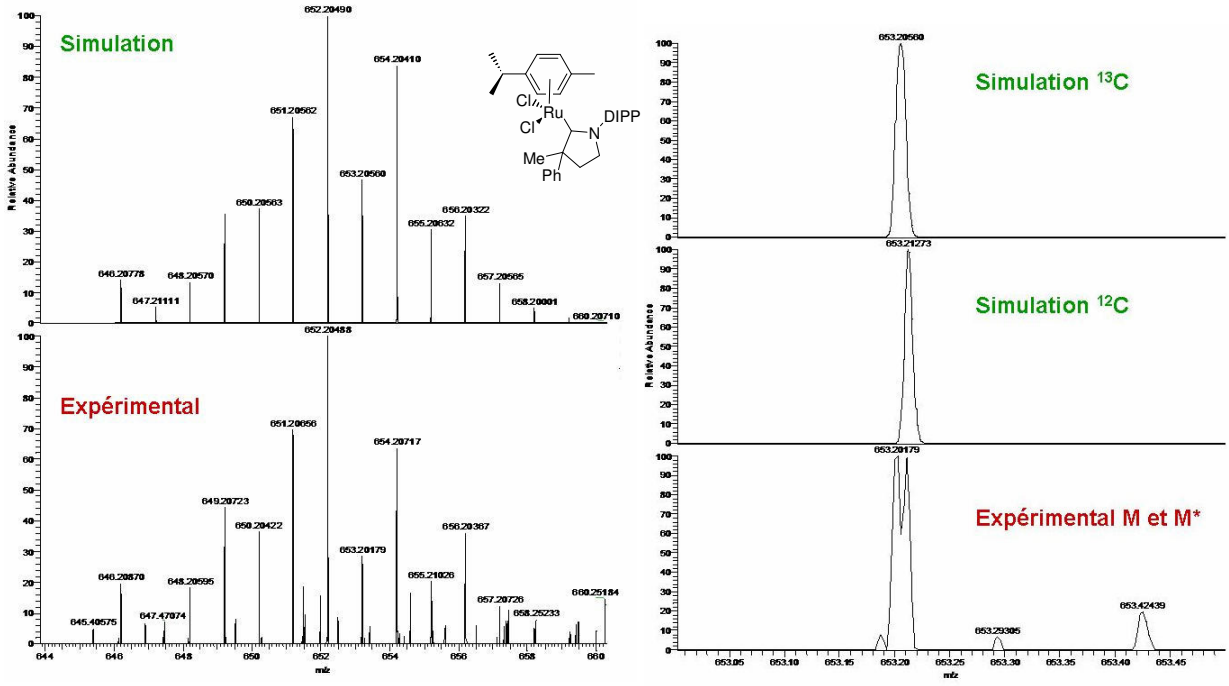

Figure 14. *Simulations of expected isotopic motifs*

VIII References

1. Grubbs, R. H., Handbook of metathesis, Ed Wiley-VCH: Weinheim Germany, **2003**

2. Ivin, K. and Mol, J. C., Olefin Metathesis and Metathesis Polymerisation, Ed San Diego: Academic Press, **1997**

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

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

5. Hoveyda, A. H., Gillingham, D. G., Van Veldhuizer, J. J. et al. *Org. Biomol. Chem.* **2004,** *2*, 8

6. Van Veldhuizer, J. J., Garber, S. B., Kingsbury, J. S., Hoveyda, A. H. *J. Am. Chem. Soc.* **2002,** *124*, 4954

7. Lavallo, V., Canac, Y., Präsang, C., Donnadieu, B., Bertrand, G. *Angew. Chem. Int. Ed. Engl.* **2005,** *44*, 5705

8. Lavallo, V., Canac, Y., DeHope, A., Donnadieu, B., Bertrand, G. *Angew. Chem. Int. Ed.* **2005,** *44*, 7236

9. Anderson, D. R., Lavallo, V., O'Leary, D. J., Bertrand, G., Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **2007,** *46*, 7262

10. Lavallo, V., Mafhouz, J., Canac, Y. et al. *J. Am. Chem. Soc.* **2004,** *126*, 8670

11. Bertrand, G., Lavallo, V., Canac, Y. **2007,** US 0004917 A1

12. Roesky, P. W. and Müller, T. E. *Angew. Chem. Int. Ed.* **2003,** *42*, 2708

13. Schlummer, B. and Hartwig, J. F. *Org. Lett.* **2002,** *4*, 1471

14. Jazzar, R., Dewhurst, R. D., Bourg, J-P., Donnadieu, B., Bertrand, G. *Angew. Chem. Int. Ed. Engl.* **2007,** *46*, 2899

15. Jazzar, R., Bourg, J-P., Dewhurst, R. D., Donnadieu, B., Bertrand, G. *J. Org. Chem.* **2007,** *72*, 3492

16. Mignani, G. (Rhodia operations), **2008,** WO 125568 A1

17. Dyson, P. J., Grossel, M. C., Srinivasan, N. et al. *J. Chem. Soc. , Dalton Trans.* **1997,** 3465

18. Ledoux, N., Allaret, B., Verpoort, F. *Eur. J. Inorg. Chem.* **2007,** 5578

19. Louie, J. and Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **2001,** *40*, 247

20. Delaude, L., Szypa, M., Demonceau, A., Noels, A. F. *Adv. Synth. Catal.* **2002,** *344*, 749

21. Jafarpour, L., Huang, J., Stevens, E. D., Nolan, S. P. *Organometallics* **1999,** *18*, 3760

22. Fürstner, A., Guth, O., Düffels, A. et al. *Chem. Eur. J.* **2001,** *7*, 4811

23. Sanford, M. S., Love, J. A., Grubbs, R. H. *Organometallics* **2001,** *20*, 5314

24. Clavier, H., Petersen, J. L., Nolan, S. P. *J. Organomet. Chem.* **2006,** *691*, 5444

25. Lin, I. J. B. and Vasam, C. S. *Coord. Chem. Rev.* **2007,** *251*, 642

26. Magill, A. M., McGuinness, D. S., Cavell, K. J. et al. *J. Organomet. Chem.* **2001,** *617-618*, 546

27. Vougioukalakis, G. C. and Grubbs, R. H. (California Institute of Technology), **2008,** WO 064223

28. Wang, H. M. J. and Lin, I. J. B. *Organometallics* **1998,** *17*, 972

29. Chen, C., Qiu, H. Y., Chen, W. Z., Wang, D. Q. *J. Organomet. Chem.* **2008,** *693*, 3273

30. Weskamp, T., Böhm, V. P. W., Herrmann, W. A. *J. Organomet. Chem.* **2000,** *600*, 12

31. Mosaert, S., Drozdzak, R., Dragutan, V., Dragutan, I., Verpoort, F. *Eur. J. Inorg. Chem.* **2008,** 432

32. Trnka, T. H., Morgan, J. P., Sanford, M. S. et al. *J. Am. Chem. Soc.* **2003,** *125*, 2546

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

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

35. Hillier, A. C., Sommer, W. J., Yong, B. S. et al. *Organometallics* **2003,** *22*, 4322

36. Poater, A., Cosenza, B., Correa, A. et al. *Eur. J. Inorg. Chem.* **2009,** 1759

37. Anderson, D. R., Ung, T., Mkrtumyam, G. et al. *Organometallics* **2008,** *27*, 563

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