

Lehrstuhl für Anorganische Chemie  
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# Application of Rhenium and Ruthenium Organometallic Complexes in Carbonyl Olefination

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## **Abbreviations**

4-nba	4-nitrobenzaldehyde
AO	aldehyde olefination
Brij-30	1,3-diacetoxy-1,1,3,3-tetrabutyltin oxide polyethylene glycol dodecyl ether
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
CTABr	hexadecyl-trimethyl ammonium bromide
Cy	cyclohexyl
$\delta$	chemical shift (ppm)
d	doublet
EDA	ethyldiazoacetate
EA	elemental analysis
GC-MS	gas chromatography coupled with mass spectroscopy
Fig.	figure
m	multiplet
Me	methyl
MTO	methyltrioxorhenium
NMR	nuclear magnetic resonance
RT	room temperature
RTIL	room temperature ionic liquid
s	singlet
t	triplet
TEM	transmission electron microscopy
TEOS	tetraethyl orthosilicate
TGA	thermogravimetric analysis
TG-MS	thermogravimetry coupled with mass spectroscopy
THF	tetrahydrofuran
TMAOH	tetramethyl ammonium hydroxide
TOF	turn over frequency
TON	turn over number
XRD	X-ray diffraction

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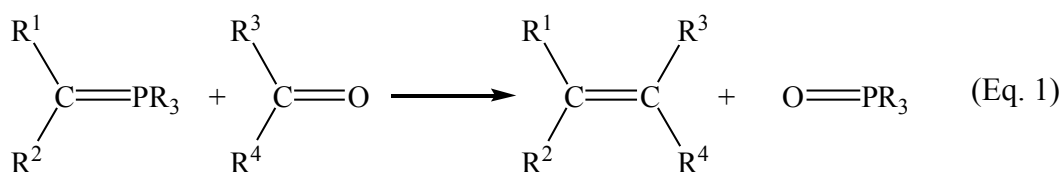
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## 1. Introduction

### 1.1 Wittig reaction: Overview

The formation of carbon-carbon bonds is a challenge permanently faced by the synthetic chemist. Since its discovery in 1953 by Wittig and Geissler,<sup>1</sup> the Wittig reaction (Eq. 1) has been successfully used for producing carbon-carbon double bonds due to its reliability, efficiency and stereoselectivity.



The extraordinary potential of this reaction was immediately acknowledged and soon afterwards the BASF company engaged in the development of a process for the synthesis of Vitamin A based on the Wittig reaction,<sup>2</sup> in a remarkable display of cooperation between academic research and industry.

The Wittig reaction basically comprises two steps: (a) the generation of a phosphorus ylide from its phosphonium salt with a base; (b) followed by reaction of the ylide with a carbonyl compound to produce an olefin and a phosphane oxide.

The nature of the group attached to the ylidic carbon atom determines the reactivity of the ylide. Strongly conjugating substituents (e.g. C(O)R, CN) stabilize the phosphonium ylide, making it less reactive and usually isolable. For this reason, such ylides are commonly designated as “stabilized” or “resonance-stabilized” ylides. “Semistabilized” or “moderated” ylides possess mildly conjugating substituents (e.g. Ph, allyl). Ylides that lack the functionalities described above are the most reactive ones and are termed “non-stabilized” ylides. The two latter types of ylides are too unstable for isolation and usually are generated in situ for immediate reaction with the aldehyde or ketone.

Currently, the Wittig reaction and its derivatives are widely used in research and industry for the synthesis of carotenoids, fragrance and aroma compounds, steroids, hormones, pheromones, fatty acid derivatives, terpenes, prostaglandins, and several other types of olefinic natural and synthetic compounds,<sup>3</sup> still proving to be an invaluable tool for today’s chemist.



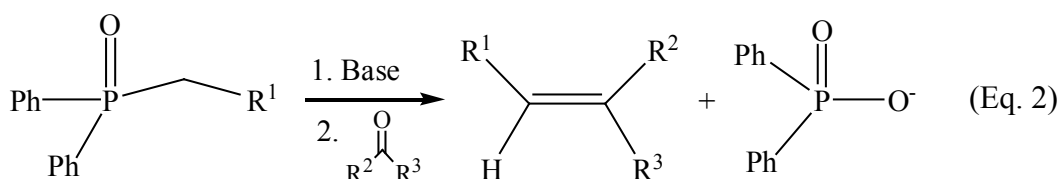
A second reason for the continuous research interest in the Wittig reaction is its mechanism and stereoselectivity patterns.<sup>4</sup>

Quite often the effective stereocontrol of a reaction determines its application (or not) in synthesis.

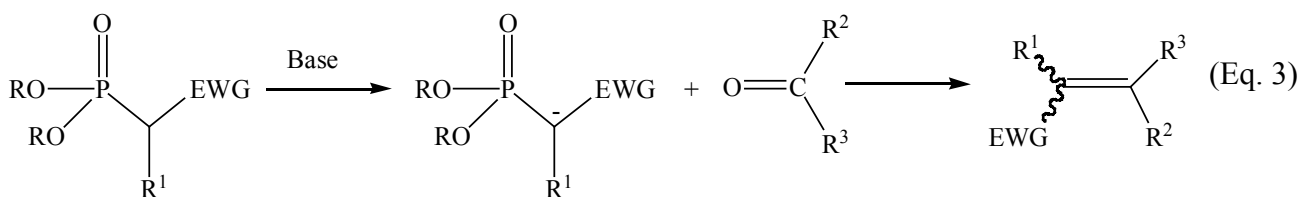
The stereoselectivity of the Wittig reaction is largely ruled by the type of ylide used: (a) stabilized ylides usually favour the production of the olefin's *E*-isomer; (b) semistabilized ylides normally produce mixtures of the *E* and *Z*-isomer; (c) non-stabilized ylides yield mainly the olefin's *Z*-isomer. There are of course notable exceptions to these general rules.

## 1.2 Variations to the Wittig reaction

Horner developed the first variants to the Wittig reaction,<sup>5</sup> reacting anions derived from a phosphane oxide (Eq. 2) or diethyl phosphonate with a carbonyl compound to generate alkenes.



Following the pioneering work of Horner, Wadsworth and Emmons published a detailed account on the general applicability of resonance-stabilized carbanions.<sup>6</sup> This work proved to be crucial to the acceptance of this methodology and therefore the reaction of a phosphonate carbanion with a carbonyl compound to produce an alkene (Eq. 3) is referred to as the Horner-Wadsworth-Emmons reaction (HWE).



Phosphonate carbanions are more nucleophilic than the corresponding phosphonium ylides, such that they react, often exothermically, with both aldehydes and ketones under milder conditions. The water-soluble phosphate anion formed as by-product allows much easier purification of the olefin, when compared to the phosphane oxide generated by the Wittig reaction.

The enhanced reactivity of the phosphonate carbanion allows the  $\alpha$ -carbon to be elaborated by alkylation, whereas generally phosphonium ylides do not undergo smooth alkylation.

The main drawback of using phosphonate carbanions is the need of an electron-withdrawing  $\alpha$ -substituent at the carbanion centre to promote the reaction intermediate decomposition into products, otherwise a two-step addition elimination strategy must be employed.<sup>7</sup>

### 1.3 Scope and limitations of the Wittig reaction and its variants

The stereoselectivity control of the Wittig reaction is still a major concern. The typical *Z*-geometry obtained with non-stabilized ylides or the *E*-geometry tendency observed with stabilized ylides and phosphonate carbanions is in several cases no longer a limitation. These preferences can often be tuned by judicious choosing of solvent, temperature, base, ylide (or phosphonate carbanion) structure and type of carbonyl compound.

The Schlosser modification<sup>8</sup> allows the formation of predominantly *E*-alkenes with non-stabilized ylides and the Still-Gennari modification<sup>9</sup> of the HWE reaction to synthesize *Z*-alkenes from a stabilized phosphonate carbanion are examples of the current versatility and stereocontrol available for this kind of reactions.

Despite its obvious attributes there are still important drawbacks such as the possible epimerisation of base-sensitive substrates, the low selectivities observed in the olefination using moderated ylides, as well as in the olefination of ketones and the fact that usually multi-step processes are required.

The application of the Wittig methodology to higher oxidation state carbonyls, such as ester and amides is complicated by the undesired cleavage of the ester or amide bond.

### 1.4 Organometallic alternatives to the Wittig reaction

To overcome the limitations of the Wittig reaction several systems employing organometallic reagents based on tantalum, titanium, zirconium, molybdenum, tungsten, zinc and other metals have been developed for the olefination of carbonyl compounds. The majority of these systems require stoichiometric amounts of organometallic reagents.

Schrock discovered a *t*-butylalkylidene Ta (tantalum) complex,<sup>10</sup> structurally analogous to the corresponding phosphonium ylide. Among the olefination reactions

tried most notable was the ability of the complex to react with esters and amides to form the corresponding t-butylalkenes in good yields.

The methylenation of carbonyl compounds by organometallic reagents such as the Tebbe reagent<sup>11,12</sup> or the Zn/Ti system developed by Oshima<sup>13</sup> is perhaps, from the synthetic point of view, the most relevant contribution to this field. These reagents surpass the scope of the Wittig methylenation since they extend it to esters, lactones and amides. Methylenation of enolizable aldehydes and ketones is also possible under these non-basic conditions.

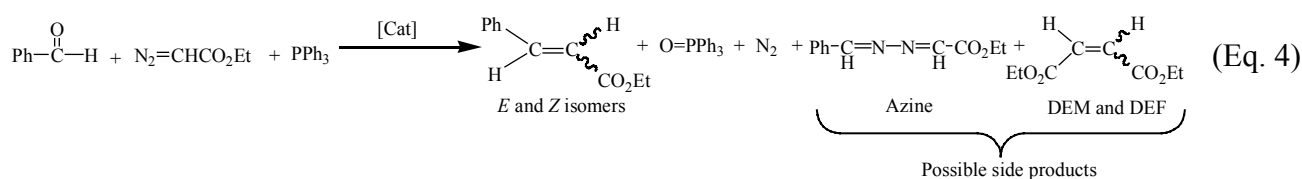
These organometallic systems still present several disadvantages: (a) the use of stoichiometric amounts of generally expensive and sometimes difficult to handle starting materials; (b) The reaction is (practically) limited to methylenation since higher alkyl analogs failed to produce the olefins.

Low valent titanium stoichiometric reagents have been successfully used for the reductive dimerization of aldehydes and ketones.<sup>14</sup> Unfortunately this method only applies to the dimerization reaction, as mixtures of aldehydes and ketones produce mixtures of the possible alkene coupling products.

### 1.5 Catalytic aldehyde olefination

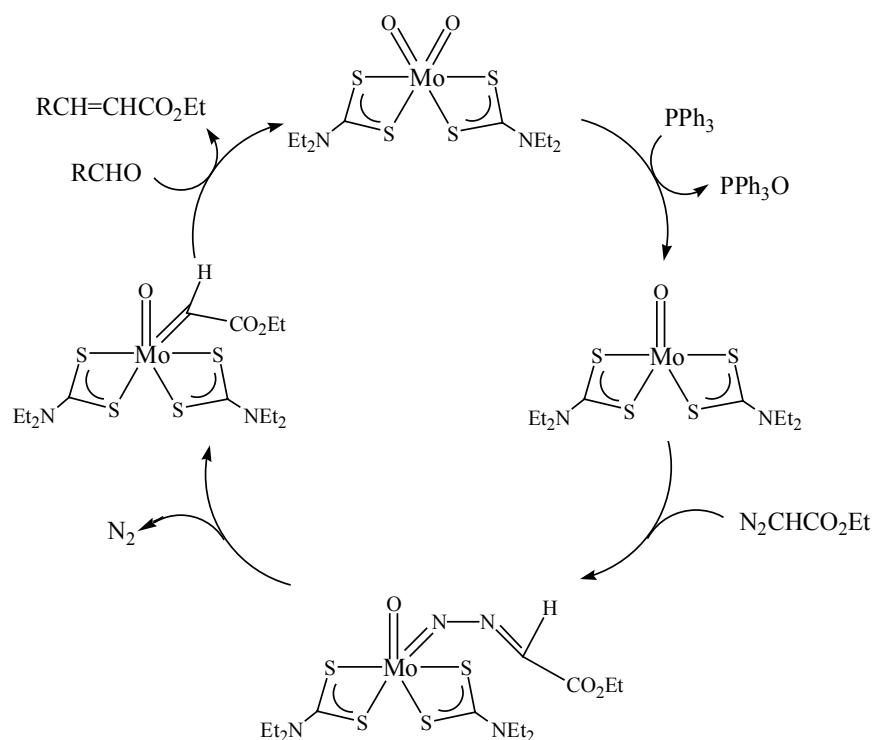
A particularly favourable way to utilize organometallic reagents to improve or enable aldehyde or ketone olefination reactions is to use them as catalysts.

Lu *et al.*<sup>15</sup> reported in 1989 the first work on Mo based aldehyde olefination, using  $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$  as catalyst in the presence of triphenylphosphine ( $\text{PPh}_3$ ) and ethyl diazoacetate (EDA) (Eq. 4). Several aldehydes were converted to olefins using 10 mol % of catalyst, being that aromatic aldehydes showed better yields than aliphatic, and within the aromatic aldehydes, the presence of electron donating groups on the phenyl ring had a positive effect on the yield, while electronwithdrawing groups produced azines in high yields and vestigial amounts of olefins, in sharp contrast to the reactivity pattern of the Wittig reaction.



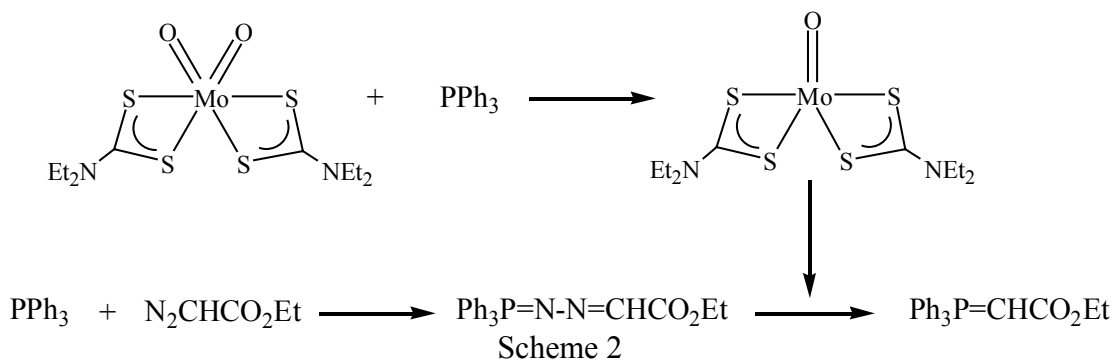
Olefin yields of up to 83 % were reached at 80 °C reaction temperature within 5 h, the *E*-isomer being by far the main product, in some cases (with varying aldehyde) the only product. Without catalyst, the corresponding azine was formed in high yields.

Mechanistically two viable pathways were suggested by the authors: (a) the phosphane abstracts an oxygen from the catalyst producing the tetravalent molybdenum species,  $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$ , which in turn reacts with ethyl diazoacetate to give a metalloazine as described by Schwarz.<sup>16</sup> The metalloazine releases one molecule of dinitrogen to form a molybdenum-carbene species, which then reacts with the aldehyde to yield the olefin regenerating the original molybdenum catalyst (scheme 1); (b)  $\text{PPh}_3$  reacts with the diazoacetate to produce a phosphazine that by action of the molybdenum catalyst loses dinitrogen to give the phosphorus ylide, which reacts in a Wittig way with the aldehyde to produce the olefin and triphenyl phosphane oxide ( $\text{O}=\text{PPh}_3$ ) (scheme 2).



Scheme 1

The formation of some phosphonium ylide was experimentally observed, thus providing evidence of the latter mechanism. However, independently synthesized  $\text{MoO}(\text{S}_2\text{CNEt}_2)_2$  reacted with ethyl diazoacetate and aldehyde to produce the olefin. Since none of the processes seems to account for the overall olefin yield the authors concluded that both pathways must run simultaneously.



The reactivity pattern observed with electron-rich and electron-poor aromatic aldehydes was explained in terms of the electronic effect influence on the relative rate of the nitrogen release (to produce a molybdenum carbene or the phosphorus ylide) vs. the nitrogen attack on the carbonyl by the phosphazine (to produce the unwanted azine). Aldehydes with electron-donating groups (lower reactivity) are less susceptible of nitrogen attack on the carbonyl, delaying the azine formation, thus allowing nitrogen release and consequent increase of the olefin yield. Reactive aldehydes (with electron-withdrawing groups) are promptly attacked by the phosphazine's nitrogen, thus forming azines as the main products.

### 1.5.1 Rhenium based catalytic aldehyde olefination

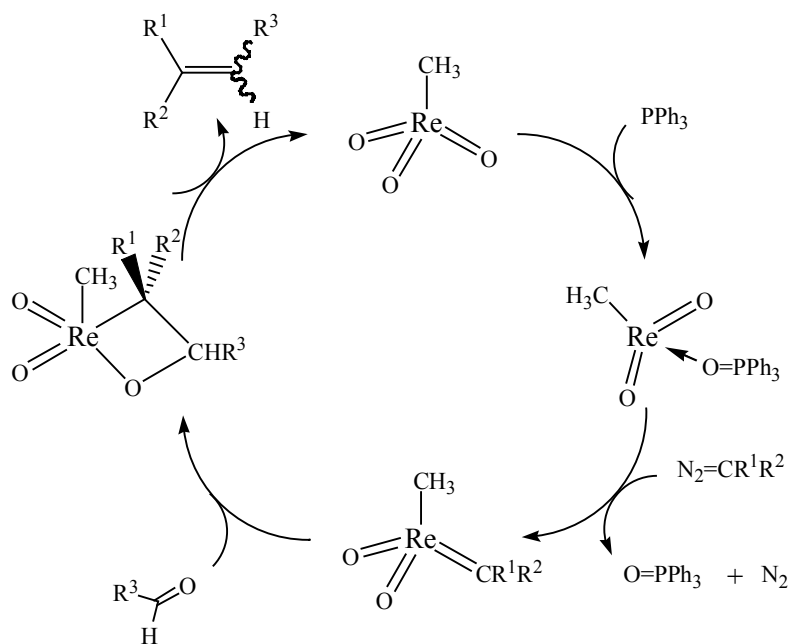
Since its accidental discovery<sup>17</sup>  $\text{CH}_3\text{ReO}_3$  (methyltrioxorhenium) was acknowledged as a unique and promising compound. However the lack of an efficient and reliable synthetic procedure for the production of methyltrioxorhenium (MTO) prevented its rich catalytic chemistry to be developed. In fact by this time most findings in high oxidation state organorhenium chemistry were obtained fortuitously and therefore did not push a fast growth of this field. The first reliable synthesis of  $\eta^5\text{-(C}_5\text{(CH}_3\text{))}_5\text{ReO}_3$ <sup>18</sup> and the following studies performed in W. A. Herrmann's group<sup>19</sup> disclosed a rich reaction chemistry that promptly stimulated further research in this field, but unfortunately the catalytic activity of this compound did not match its versatile chemistry as no catalytic applications could be found. Soon afterwards the same group established the first reliable synthesis of MTO<sup>20</sup> paving the way for a new era in the high oxidation state organometallic chemistry.

MTO is a remarkably stable compound, highly volatile and virtually soluble in any solvent from n-pentane to water. It easily forms adducts with  $\text{Cl}^-$ ,  $\text{Br}^-$  and a wide array of nitrogen ligands, which are usually more prone to hydrolysis in wet solvents and are thermally less stable than MTO itself. The most developed catalytic applications of

MTO are within oxidation catalysis, olefin epoxidation<sup>21</sup> and to a lesser extent organic sulfides sulfoxidation being the prime examples, but also olefin metathesis and aldehyde olefination have been thoroughly investigated, among other less studied reactions.<sup>22</sup>

In 1991 W. A. Herrmann *et al.* reported on an aldehyde olefination catalysed by MTO.<sup>23</sup> The aldehyde olefination reaction with MTO was carried out at room temperature by adding diazoalkane dissolved in benzene or tetrahydrofuran (THF) dropwise to a solution of stoichiometric amounts of aldehyde and triphenylphosphine and a catalytic amount of MTO (1-10 mol %) in the same solvent. The reaction temperature (-20 to +80 °C) had little effect on the product distribution. Ethyl diazoacetate and diethyl diazomalonate have been applied together with both saturated and  $\alpha,\beta$ -unsaturated aldehydes and triphenylphosphine or tri-*n*-butylphosphane. Dependent on the aldehyde used, yields up to 98 % and *E:Z* ratios of up to 97:3 could be reached within 20 min reaction time at 20 °C. The more catalyst is present, the worse is the selectivity towards *E*-product and the less azines, are produced. Electron withdrawing substituents on the aldehyde favour the olefination in contrast to the Mo-based catalytic system established by Lu *et al.*<sup>15</sup>. Another important difference is that olefins derived from diazomalonate are received with MTO as a catalyst but not with  $[\text{MoO}_2\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_2]$ . Instead a stable phosphorus ylide,  $(\text{C}_6\text{H}_5)_3\text{P}=\text{C}(\text{CO}_2\text{CH}_3)_2$ , is formed in the latter case, which does not react with aldehydes in a Wittig reaction. Therefore, a significant advantage of the MTO catalysed system is that the synthesis of olefins from otherwise unreactive precursor compounds is possible. The mechanistic implications of this observation are discussed below in some detail. Some cyclic ketones also undergo the olefination reaction with MTO as the catalyst. However, the yields and activities are in this case considerably lower. The predominant side reaction here is a metal catalysed formation of the symmetric olefin from the diazoalkane.

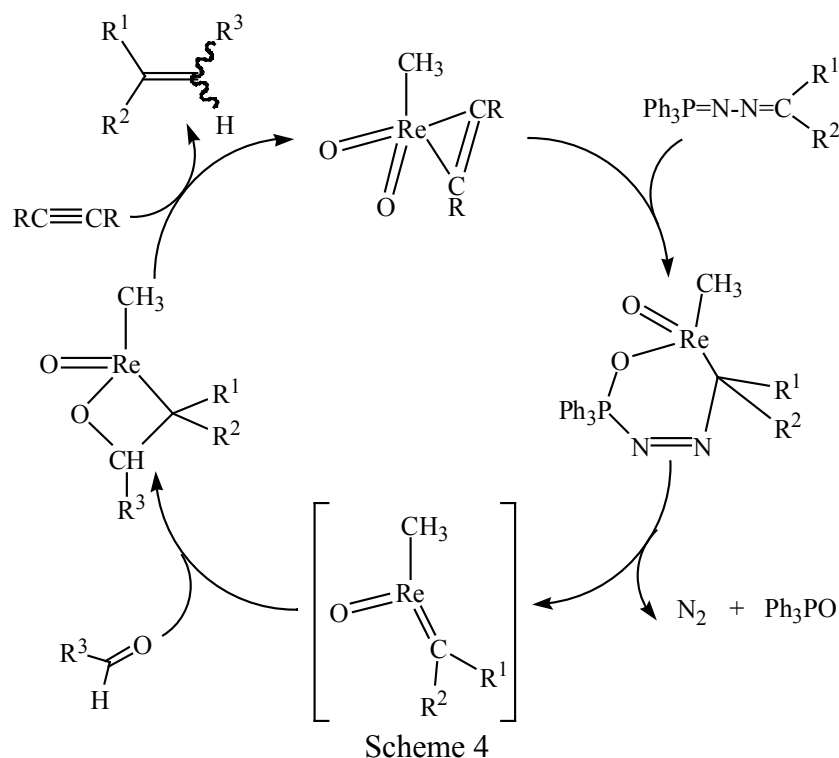
Since it was already known that MTO reacts readily with phosphanes, it was assumed that in a first step of the catalytic reaction one of the terminal oxo atoms originally bound the rhenium centre is abstracted by the phosphane, forming a compound of composition  $\text{CH}_3\text{ReO}_2\cdot\text{OPPh}_3$ , which then would react in a further step with the diazo acetate under liberation of both phosphane oxide and dinitrogen.<sup>23a</sup>



Scheme 3

A follow up work showed, that the catalytically active species really was a rhenium(V) complex based on methylidyne rhenium(V), nowadays known as “MDO” (MethylDiOxorhenium).<sup>23b</sup> This compound is formed, as it has been previously anticipated, *via* reduction of MTO with the phosphane under formation of phosphane oxide. It was assumed that in the catalytic cycle, after the formation of the Re(V) species, in a second step a rhenium carbene complex is formed by the reaction of MDO with the diazocomplex under extrusion of dinitrogen gas. The carbene would then react with the aldehyde and form a metallacycle, which finally reforms MTO (with oxygen from the aldehyde) and olefin.<sup>23</sup> The whole reaction cycle is shown in scheme 3. Neither the rhenium carbene nor the metallacycle could be directly observed, however, rhenium(VII) carbenes could be generated independently already before, but have never been applied as catalysts or carbene transfer reagents for the aldehyde olefination.<sup>24</sup>

Recently, two studies with other Re catalyst systems performed independently by Romão, Kühn *et al.*<sup>25</sup> and by Chen *et al.*<sup>26</sup> proved the presence of Re carbenes under the applied reaction conditions by NMR and MS techniques. The first group used several stable derivatives of MDO, such as  $\text{CH}_3\text{ReO}_2(\text{PhC}\equiv\text{CPh})$  as catalysts for the aldehyde olefination. It was found that the formation of a phosphazine prior to the reaction with the Re(V) catalyst is a decisive step of the reaction. Abstraction of an oxygen from the MDO moiety by the positively polarized phosphane (observed by  $^{17}\text{O}$ -NMR spectroscopy) leads to the formation of a labile Re(V) carbene complex (observed by  $^{13}\text{C}$ -NMR) and phosphane oxide (scheme 4).



Addition of excess alkyne lead to a significant slowing down of the reaction, probably due to a competition between phosphazine and alkyne for the coordination to the MDO moiety.<sup>25</sup> In the work of Chen *et al.* ionic catalyst systems based on Lewis-base adducts of dirheniumheptoxide ( $\text{Re}_2\text{O}_7$ ) were used.<sup>26</sup> In the gas phase evidence for Re carbene species has been found by ESI-MS spectroscopy. However, both groups did not find evidence for the formation of a “rhena-oxethane” intermediate. Chen *et al.* observed Re bound ylides in the gas phase and by NMR spectroscopy in solution and assumed the Re catalysed formation of ylides. Since the observed *E:Z*-relationships are dependent on the phosphane used, it is assumed that  $\text{PR}_3$  cannot only be a deoxygenation agent.<sup>26</sup>

An interesting detail in the context of the Re catalysed aldehyde olefination is the following observation: while the stable phosphorus ylide  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{CH}_3)_3$  does not even react with aldehydes in boiling benzene, the reaction takes place at room temperature in the presence of MTO. Under these conditions olefins of the formula  $\text{RCH}=\text{C}(\text{CO}_2\text{CH}_3)_2$  are formed. MTO in benzene does not catalyse olefin formation from ylides and phosphazines (without aldehyde being present) at room temperature.<sup>23a</sup> MTO therefore implements the Wittig olefination of aldehydes with otherwise unreactive phosphorus ylides. With respect to the mechanism, this latter observation may indicate that MTO either catalyses the aldehyde olefination according to scheme 3 or catalyses the formation of ylides in a similar way as suggested by Chen *et al.* for



ReO<sub>3</sub><sup>+</sup> derivatives<sup>26</sup> and afterwards, in a second step, catalyses the classical Wittig reaction with the previously formed ylide and the aldehyde. This question still remains unsettled.

The use of MTO as aldehyde olefination catalyst as described by Herrmann *et al.*<sup>23</sup> has – notwithstanding the mechanistic debate – some practical drawbacks, among them being the use of dry solvents, the formation of OPPh<sub>3</sub> as co-product, which can sometimes complicate product isolation and purification. Carreira *et al.*<sup>27</sup> therefore set out to develop a variation based on Cl<sub>3</sub>(O)Re(PPh<sub>3</sub>)<sub>2</sub> as catalyst (1 mol%), which could be performed in reagent grade solvents without purification of any reagent prior to use. Good yields (ca. 85 %) and diastereoselectivities of 20:1 have been reached by replacing PPh<sub>3</sub> by P(OEt)<sub>3</sub>. The by-product OP(OEt)<sub>3</sub> can be easily removed by aqueous work up. Since then the synthesis of MTO has also been significantly modified, so that it can be directly synthesized from Re powder.<sup>28</sup> This is a particularly easy and inexpensive way to get to this stable and easy to handle compound. From the cost, stability and preparative, point of view, no other Re(VII) compound is nowadays a match for MTO.

### 1.5.2 Catalytic generation of stabilized ylides

The field comprising the catalytic generation of phosphorus ylides by organometallic complexes as alternative to the Wittig base generated ylides is one of the most promising topics and has received considerable attention in the last years.

The advantages of this approach are the non-basic conditions under which the ylide is produced, allowing the olefination of sensitive substrates, and the potential reuse of the organometallic catalyst for further catalysis.

Fujimura *et al.* reported on the transformation of aldehydes and ethyl diazo acetate with PPh<sub>3</sub> in the presence of 0.5 – 2.5 mol % RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> as the catalyst at 50 °C to olefins within 4 – 24 h with yields between 82 and 92 % and *E:Z* ratios of up to 99:1.<sup>29</sup> Since it is known that ruthenium carbene species are generated from RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and diazo compounds by carbene transfer,<sup>30</sup> it was assumed that the carbene moiety could be further transferred from ruthenium to phosphorus, which is capable of olefinating aldehydes.<sup>31</sup> The olefination did not take place without triphenylphosphine. Therefore, a phosphorus ylide was considered being formed. In the case the reaction was performed in the absence of the ruthenium catalyst, azine was obtained as the only product.<sup>29</sup>

The application of an Iron(II) porphyrin complex Fe(TPP) as catalyst for the aldehyde olefination with ethyl diazoacetate has been described by Woo *et al.*<sup>32</sup> After reaction times of 3 – 23 h at room temperature with 1 – 2 mol % catalyst olefin yields between 85 and 99 % and *E:Z* ratios of 10:1 – 49:1 have been reached. Electron poor aldehydes were found to be more readily transformed than electron rich ones. Turnover numbers (TON) of 64 – 128 were observed. In the absence of catalyst azine was formed as main product when the reaction mixture was allowed to react for two days.

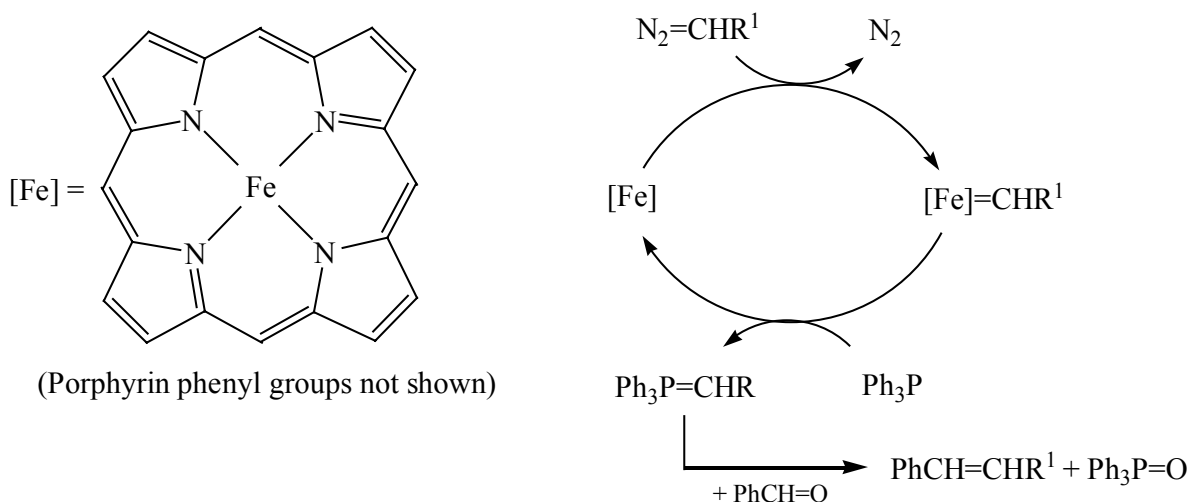
Lowering the catalyst loading with reactive substrates lead only to a slight slowdown of the reaction velocity, but to a higher *E:Z* selectivity, favouring even more the *E*- product. With less reactive substrates a lowering of the catalyst loading led to an increased formation of azine, finally becoming the main reaction product.<sup>32b</sup>

With respect to the solvent applied it was found that non coordinating solvents (such as toluene) lead to a higher product yield within a given time than coordinating solvents (such as THF).<sup>32b</sup>

The ketones reactions were substantially slower than the aldehyde reactions. Large excesses of ketone were necessary to yield acceptable amounts of olefination products. Typical reaction conditions were 10 equiv. of ketone, 1.1 equiv. of triphenylphosphine, one equiv. of ethyl diazoacetate and 1 mol % Fe(TPP) catalyst versus ethyl diazoacetate. After 2 – 4 days of reaction time 64 – 89 % of olefin (yield given versus ethyl diazoacetate) with a *Z:E* selectivity of maximum 2.8:1 could be isolated.<sup>32b</sup> Without using a significant ketone excess, EDA dimerization was the only reaction observed after 2 days of stirring at room temperature or higher temperatures (50 °C).

Woo *et al.* performed detailed experiments to elucidate the mechanism of the Fe(II) catalysed reaction.<sup>32b</sup> They came to the conclusion, that the catalytic cycle does not proceed in a way that would be analogous to that suggested by Herrmann *et al.*<sup>23</sup> with MTO as the catalyst (precursor) (see scheme 3). The existence of a carbene seems likely according to the authors, although (*meso*-tetratoluyloporphyrin) Fe=CHCO<sub>2</sub>Et is very reactive and has never been isolated or detected spectroscopically. Nevertheless, related compounds have been observed spectroscopically or have even been isolated.<sup>33</sup> The formation of an intermediate with a Fe=O bond, however, is considered as unlikely, as control experiments evidence indicates otherwise. Oxygen atom acceptors do not react as they should do with an oxoiron(IV) complex, for example, epoxidation reactions do not occur when cyclohexene is added instead of PPh<sub>3</sub>. Epoxidation, however, should readily proceed under the conditions applied if a oxoiron(IV) porphyrin would be

present.<sup>32</sup> Woo et al. concluded, that the catalytic cycle should not include a Fe=O intermediate but instead, as depicted in scheme 5, the phosphane reacts with the Fe=CHCO<sub>2</sub>Et carbene to produce a phosphorus ylide (the latter could be detected by <sup>1</sup>H- and <sup>31</sup>P-NMR spectroscopy).<sup>32b</sup> For ketones and electron rich aldehydes the selectivities, reaction rates and yields were in accordance with the model proposed in scheme 5.<sup>32b</sup>



Scheme 5

For more reactive, electron deficient aldehydes, however, the experimental results did not match the expectations solely based on scheme 5. More *Z*-olefin than to be expected was found, particularly with higher catalyst loadings,. Woo *et al.* therefore observed, based on UV-Vis studies, that a  $\pi$ -complex between Fe(TPP) and electron poor aldehydes, such as 4-nitrobenzaldehyde forms and changes the *cis/trans* selectivity in favour of the *cis* product. The reason for such a change is that the Lewis acidic iron(II) porphyrin will activate the carbonyl group toward nucleophilic attack by the phosphorane and the transition state for oxethane formation occurs earlier than without the metal complex. In the earlier transition state, steric factors are not as important as in the late transition state and consequently, a larger fraction of *cis*-oxethane is produced.<sup>32b</sup>

Based on the results of Woo *et al.*, Zhang *et al.* described the commercially available Fe(III),<sup>34</sup> Ru(II)<sup>34</sup> and Co<sup>35</sup> porphyrin complexes Fe(TPP)Cl, Ru(TPP)(CO) and Co(TPP) as efficient catalysts for the selective olefination of a variety of aldehydes with ethyl diazoacetate in the presence of triphenylphosphine. Yields of usually more than 90 % and *E:Z* selectivities of > 90:10 were obtained with a broad variety of aldehydes at a reaction temperature of 80 °C within one hour or less with a catalyst loading of 0.01 – 2.0 mol%. Air was tolerated as reaction atmosphere. A broad variety of first row

transition metal TPP catalysts have been investigated, including V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ru, but only the above mentioned Fe, Ru and Co complexes gave significant amounts of olefin.

The good results obtained with aldehydes by these catalysts extend to the olefination of trifluoro-ketones.<sup>36</sup> With a slight selectivity decrease, a wide variety of ketones could be olefinated by these systems, using both EDA and *t*-butyl diazoacetate.

Under similar reaction conditions it is not feasible to olefinate non-fluorinated ketones, probably due to the lack of electrophilicity of the ketone carbonyl. However, the addition of 0.5 eq of benzoic acid as co-catalyst enabled the olefination of aromatic, aliphatic and cyclic ketones to proceed, with low selectivity though (usually slight predominance of the *Z*-isomer), as it is observed in the Wittig reaction.<sup>37</sup> Protonation of the carbonyl oxygen and concomitant increase of the carbon electrophilicity was proposed as explanation for the activity increase promoted by benzoic acid.<sup>38</sup>

As a rule diazo compounds have inherent hazards to their use. The toxicity and explosion potential must be taken into account when working with them and these features have prevented the use of diazo compounds at industrial production level (with the exception of EDA, but again in very limited cases).

The synthetic utility of this class of compounds drives considerable attention to safer alternatives, such as the in situ generation of diazo compounds or alternative sources of carbene equivalents and precursors, to avoid the associated dangers.

The in situ generation of diazo compounds from tosylhydrazone salts developed by Aggarwal et al.<sup>39</sup> was successfully applied to aldehyde olefination using FeCl(TPP) as catalyst. The degradation of the tosylhydrazone salts in solution produces the diazo compounds in small amounts avoiding the high concentration risks of pure diazo solutions and hampering any unwanted side reactions. As phosphites (P(OMe)<sub>3</sub>) are used instead of phosphanes the ylide's reactivity changes considerably. Indeed a very high *E*-selectivity (typical *E:Z* ratios above 95:5) was observed with moderated ylides, unlike the usual lack of selectivity obtained with PPh<sub>3</sub> derived moderated ylides. The yields are within the 80-95 % range, which is much higher than the obtained with a pure solution of phenyl diazomethane (30 % yield). This untypical selectivity is explained in terms of the electronic effect obtained by the improved overlap of the negative charge on the ylide carbon with the P-O antibonding ( $\sigma^*$ ) orbitals, which results in an increased stabilization of the ylide. This ylide is therefore best regarded as a stabilized ylide that is known to give high *E*-selectivity.



stabilization of reactive intermediates. Moreover, ruthenium complexes demonstrate a variety of important features, which include low redox potential, high electron transfer ability, high coordination ability to heteroatoms, Lewis acid acidity, unique reactivity of metallic species and intermediates such as oxo-metals, metallacycles, and metal carbene complexes. For these reasons, in the last 20 years an unprecedented large number of novel, useful reactions have begun to be developed using ruthenium complexes as catalysts, among them hydrogenation and transfer hydrogenation, oxidation reactions, diverse carbon-carbon bond forming reactions, olefin metathesis and cyclopropanation, just to name a few.<sup>40</sup> Some ruthenium-catalysed reactions have also become industrial processes such as the asymmetric hydrogenation of 2-benzamidomethyl-3-oxobutanate via kinetic resolution<sup>41</sup> and the oxidation of (1R',3S)-3-[1'-(tert-butyl)dimethylsilyloxy]ethyl]azetidin-2-one.<sup>42</sup> The second generation Grubbs' ruthenium carbene complexes have been also applied for industrial metathesis reactions (ex. ROMP).<sup>43</sup>

Ruthenium compounds of the general formula  $\text{Cp}'\text{RuXL}^1\text{L}^2$  ( $\text{L}^1 = \text{PR}_3$  and  $\text{L}^2 = \text{PR}_3$ , CO or NHC) found widespread applications in catalysis.<sup>44</sup> The simplest derivative  $\text{CpRuCl}(\text{PPh}_3)_2$  was first synthesized by Wilkinson *et al.* in 1969, but no catalytic studies were performed.<sup>45</sup> The development of catalytic applications using this family of compounds was slowly disclosed during the 1980's and shared the exponential increase in catalytic applications found in the last decade with other ruthenium (II) complexes. Besides being generally a very stable class of compounds, they possess an inordinate amount of tuning possibilities due to the different type of ligands surrounding the ruthenium centre.

Baratta *et al.* used catalytic amounts (1 % mol) of these compounds in conjunction with ethyl diazoacetate to produce the diazo decomposition coupling products, diethyl maleate (DEM) and diethyl fumarate (DEF).<sup>44b</sup> The authors systematically studied the structure/activity relationships by changing the ligands around the ruthenium center. It was found that the temperature necessary for the reaction to start becomes lower with increasing bulkiness of the catalyst phosphanes, decreasing by more than 45 °C between  $\text{CpRuCl}(\text{PPh}_3)_2$  and  $\text{CpRuCl}(\text{PPh}_2(o\text{-tolyl}))$ . The steric requirements and electron donation properties of the  $\eta^5\text{-Cp}'$  ligand also affected the temperature at which the reaction starts: complexes bearing bulky, electron-releasing ligands required lower temperatures to trigger the catalytic cycle, as  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  ( $\text{Cp}^* = \text{Cp}(\text{CH}_3)_5$ )

already catalyses the reaction at 35 °C, in contrast to the 65 °C needed for  $\text{CpRuCl}(\text{PPh}_3)_2$  to work.

The presence of an  $\pi$ -donor ancillary ligand X also decreased the temperature required to decompose the EDA.

The structure/stereoselectivity relationships of the reaction could not be so easily rationalized; nevertheless every (active) catalyst displayed an excellent selectivity, having at least 95 % preference for DEM formation over DEF.

While the authors could not detect the existence of a  $\text{CpRuCl}(\text{=CHCO}_2\text{Et})(\text{PPh}_3)$  carbene during the catalytic cycle, they were able to observe it in solution (via a different synthetic route) and postulated its existence as other ruthenium compounds have the ability to produce ruthenium carbene species with diazo compounds.<sup>46</sup> Interestingly, vestigial amounts of phosphorus ylide were detected.<sup>44b</sup> This observation suggests that under the appropriate reaction conditions such ruthenium complexes might catalyse the formation of phosphorus ylides from diazo compounds and phosphanes, which in the presence of aldehydes or ketones should produce olefins in a Wittig fashion. The adjustment of the catalyst structure by ligand change can, in principle, optimise the catalyst reactivity and stability as well as the stereoselectivity of the overall reaction.

#### 1.5.4 Immobilization of Re and Ru catalysts

The industrial implementation of organometallic complexes as catalysts for organic synthesis requires efficient, selective, and low cost catalysts that can be easily separated from the product(s) and recyclable for subsequent reactions.

The traditional way of achieving easy catalyst separation from a reaction mixture is to heterogenize it, i. e., to apply it in a different phase than the remaining reaction components. The incorporation of metal catalysts in supporting matrices can be pursued in several ways, such as covalent bonding, ionic bonding, chemisorption, physisorption, entrapping and immobilization via supported liquids.<sup>47</sup> The matrices can be either organic (e.g. polymers) or inorganic (e.g. zeolites, silica, microporous or mesoporous molecular sieves).<sup>48</sup> The ideal support material should be inert and not interfere with the catalyst performance. However, as a general rule upon immobilization the catalyst activity changes and this constitutes the greatest challenge to heterogeneous catalysis: to combine simultaneously the high catalyst activity of homogeneous catalysis with the inherent easy recyclability of the heterogeneous catalysts. Leaching of the

catalyst and in some cases diffusion limitations are also drawbacks frequently encountered in immobilized catalysts, which are bound to decrease the efficiency of the heterogeneous catalyst.

The vast array of catalytic applications found for MTO prompted investigations on its immobilization on different carrier materials.

MTO has been successfully immobilized in NaY zeolite,<sup>49</sup> Niobia (Nb<sub>2</sub>O<sub>5</sub>),<sup>50</sup> silica with polyether tethers,<sup>51</sup> in modified mesoporous silica MCM-41,<sup>52</sup> and in polymers (poly(4-vinylpyridine) and polystyrene)<sup>53</sup> mainly for application in alkene epoxidation. Notwithstanding lower activities (than MTO in homogeneous phase) and some leaching were observed, in most cases higher selectivities were obtained and recycling was possible.

Recently Kühn et al. devised a new immobilization technique for MTO on surface modified mesoporous silica MCM-41 and applied in benzaldehyde olefination.<sup>54</sup> The MCM-41 surface was modified with iodomethyl(phenyl)trimethoxysilane, which was then reacted with MTO. The grafted material exhibits low catalytic activity in the olefination of benzaldehyde with PPh<sub>3</sub> and EDA, as the olefin yield is only 18 % (MTO itself produces 49 % yield under similar reaction conditions). Azine is the main product, a typical result of complexes that display low catalytic activity for aldehyde olefination. The selectivity is slightly better than in homogeneous catalysis with a final *E:Z* ratio of 96:4 similar to the obtained in the Wittig reaction. Noteworthy is the absence of significant leaching and the fact that activity level remains constant in subsequent runs proving that the immobilized catalyst is stable on the surface of the modified MCM-41.

The immobilization of Ru(II) catalysts has focused on Ru(II) porphyrin and amine derivatives.<sup>55</sup> These particularly effective immobilized catalysts were mainly applied in alkene epoxidation<sup>55b-g</sup> and in a few cases also in intermolecular cyclopropanation.<sup>55f</sup> As a rule, the performance of the immobilized catalysts surpassed in these cases that obtained with their homogeneous phase counterparts.

Currently, there is a lack of studies on immobilization of Ru(II) complexes, specially the Cp'RuXL<sup>1</sup>L<sup>2</sup> and application in aldehyde olefination has never been investigated.

Recently ionic liquids have been employed as reaction media for catalytic generation of phosphorus ylides by organometallic complexes. Ionic liquids are salts that have the special characteristic of being liquid at RT and present several advantages



over traditional solvents, such as extremely low volatility, ability to dissolve a wide range of organic and inorganic materials and their properties (ex. hydrophobicity/hydrophilicity character) can be easily tuned changing the anion/cation structures.<sup>56</sup>

They can be used solely, mixed with other solvents or in two-phase systems, using water or organic solvents according to the reaction needs. The operation principle is to conduct the reaction in ionic liquid media and to isolate the product by simple separation or extraction techniques, after which the catalyst remains “immobilized” in the ionic liquid phase and the ionic liquid/catalyst system can be reused, (ideally) without activity decrease.

Kühn *et al.* developed ionic liquid/organometallic catalyst systems for aldehyde olefination in [(Bmim)PF<sub>6</sub>]. The catalysts FeCl(TPP)<sup>57</sup> and Ru(II) salen<sup>58</sup> work efficiently in this ionic liquid with 2 mol % catalyst loadings, producing high yields of alkenes (usually above 90 %) and high *E*-selectivity. In the case of the Ru(II) salen catalyst the selectivity is higher in the ionic liquid:toluene medium used than in simple toluene.

Recycling of the ionic liquid/FeCl(TPP) phase is effective (simple extraction with diethyl ether to remove the olefin and by-products), such as the activity remains unchanged in the 2<sup>nd</sup> run. The recycling of the Ru(II) salen system suffers from catalyst loss upon extraction/separation due to the catalyst solubility in toluene.

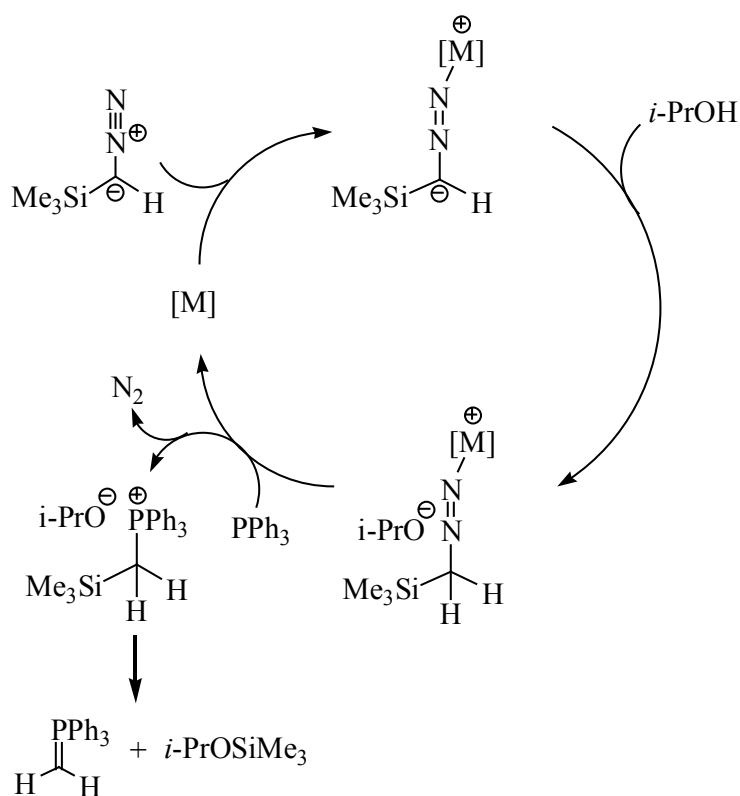
### 1.5.5 Methylenation of carbonyl compounds

Lebel *et al.* used several Ru and Rh catalysts with TMSCHN<sub>2</sub> (trimethylsilyl diazomethane), 2-propanol and PPh<sub>3</sub> for the methylenation of carbonyl compounds.<sup>59,60</sup> Among the investigated catalysts RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub> and particularly the Wilkinson's catalyst, RhCl(PPh<sub>3</sub>)<sub>3</sub> afforded high olefin yields (usually above 85%). The optimised reaction conditions allow the methylenation of sensitive compounds such as enolizable substrates, and are mild enough to keep intact sensitive groups such as epoxides, secondary amides, a variety of protecting groups and chiral centers. Moreover the system has higher chemoselectivity than the corresponding Wittig reaction with Ph<sub>3</sub>P=CH<sub>2</sub>.

No reaction is observed when cinnamaldehyde is reacted with the preformed metal carbene [CH<sub>2</sub>=RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub>] obtained from CH<sub>2</sub>=N<sub>2</sub> and RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub>. Furthermore no carbene is detected by spectroscopic methods when TMSCHN<sub>2</sub> and 2-propanol are added to RuCl(NO)(PPh<sub>3</sub>)<sub>2</sub>. Rhodium (II) acetate, known for producing

metal carbenes with diazo compounds is inefficient at catalysing the methylenation reaction at room temperature.<sup>59a,59c-d</sup> The authors thus concluded it to be unlikely that the reaction runs through a metal carbene intermediate.

It has been observed that diazo compounds react with Rh(I) through nitrogen complexation and the adduct does not produce carbene species. The authors proposed a catalytic cycle (scheme 6) involving the activation of TMSCHN<sub>2</sub> by RhCl(PPh<sub>3</sub>)<sub>3</sub> through nitrogen complexation. Protonation of the TMSCHN<sub>2</sub> Rh(I) complex by 2-propanol, followed by attack of triphenylphosphine with nitrogen exclusion forms a silylated salt and regenerates the catalyst. Desilylation by the alkoxide produces the methylenetriphenylphosphorane (detected by NMR).<sup>59c</sup>



Scheme 6

The alcohol plays an essential role, as the reaction is not observed in its absence. The alcohol participates in the desilylation as confirmed by the formation of *i*-PrOTMS and is responsible for the protonation of the TMSCHN<sub>2</sub> Rh(I) complex as it was observed the deuteration of the terminal bond when using deuterated 2-propanol.<sup>59d</sup>

Lebel *et al.* have further extended the method to the methylenation of functionalised ketones,<sup>60a</sup> fluorine-containing ketones,<sup>60b</sup> in both cases obtaining, as a rule, higher

yields and better chemoselectivity, than the corresponding Wittig reaction and other methylenation methods (ex. Tebbe reaction).

## 1.6 Objectives

Several rhenium complexes in the formal oxidation states VII and V display interesting features in the olefination of aldehydes: (a) high olefination rates and generally high *E*-selectivity; (b) the ability to produce olefins from substrates unreactive under Wittig conditions. In this work we aimed to investigate the performance of a series of known and new organorhenium oxides as catalysts for aldehyde olefination. The studied complexes helped to establish a better understanding of the catalyst structure/activity relationships in order to optimise the catalyst activity. Reaction parameters such as catalyst loading, type of phosphane, type of diazo compound, temperature and solvent were studied to ascertain their influence in the overall reaction outcome and to better elucidate the reaction mechanism.

The olefination of ketones with organorhenium oxides was not well established and therefore MTO will be applied for such purpose. The choice of MTO was linked not only to its high catalytic activity among the rhenium catalysts but also to its high stability that is crucial, since ketone olefination required harsher reaction conditions.

The ruthenium compounds of general formula  $\text{Cp}'\text{RuCl}^1\text{L}^2$  displayed good catalytic activity in carbene transfer reactions such as diazo compound decomposition and olefin cyclopropanation with diazo compounds. Interaction of catalytic amounts of  $\text{CpRuCl}(\text{PPh}_3)_2$  with EDA produced vestigial amounts of  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ , thus in the presence of stoichiometric amounts of  $\text{PPh}_3$  the formation of the phosphorus ylide might compete (or even be formed preferentially) with the formation of coupling products. In such case the reaction with aldehydes and ketones to produce alkenes should be possible.

Once confirmed the potential of these compounds to olefinate aromatic aldehydes, the reaction was optimised by adjustment of the catalyst structure and reaction conditions, such as temperature, solvent, phosphane and catalyst loading. Under the optimised reaction conditions the best ruthenium catalyst tested were applied in the olefination of a series of aldehydes and ketones.

The reaction mechanism was studied to correct the current lack of experimental work on this topic, since it is likely that these ruthenium catalysts follow common reaction pathway(s) to other known active olefination catalysts (ex: Fe, Ru and Co

porphyrins). The majority of the proposed olefination mechanisms are based on indirect evidence or are logical extrapolations from similar reaction systems, as only rarely reaction intermediates could be observed or isolated. The ongoing debate over the reaction mechanism(s) would be enriched by additional experimental evidence, and when possible the isolation of reactive intermediates. The same applies to the olefination of ketones.

There were no studies regarding the heterogenization of  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  complexes. The mesoporous silicates MCM-41, MCM-48 and SBA-15 were used as supporting materials due to their high thermal, chemical and physical stability with different pore widths and three-dimensional features. The complexes immobilization was made using different grafting methods and the stable heterogeneous catalysts were applied in aldehyde olefination and styrene cyclopropanation.

## 2. Oxorhenium Complexes as Aldehyde Olefination Catalysts

### 2.1 Background

The olefination of aldehydes and ketones is a very important transformation in organic synthesis. In spite of the existence of highly efficient and general stoichiometric methods like the Wittig reaction and its several variations<sup>1,2</sup> a selective catalytic system would be highly desirable in order to speed up reactions, shorten experimental multi-step procedures and avoid expensive reagents difficult to handle.<sup>3</sup>

The quest for effective catalysts has been developing slowly since the late 1980s.<sup>4</sup> Presently, several efficient catalytic aldehyde olefination reactions have been reported based on Re,<sup>5,6</sup> Ru,<sup>7,8</sup> Rh,<sup>8a</sup> Fe<sup>9a-e</sup> and Co<sup>9f</sup> complexes. In some cases they operate under very mild conditions (room temperature), short reaction times (even below one hour nearly quantitative yields are reached), and usually high *E*-selectivities. However, the mechanism of the reactions is still a matter of open debate. The key role of carbene complexes is meanwhile well accepted and has been recently established for certain Re- and Fe systems by independent groups.<sup>6,9</sup> However, the situation is still unclear with respect to the fate and mode of reaction of these carbene complexes. In some cases they are considered to react with coordinated aldehyde with formation of a metallaoxetane ring,<sup>10</sup> whereas in other cases evidence suggests that they originate free ylides that perform the Wittig reaction in a classical, un-catalyzed fashion. In other words, it is the formation of the ylides that is catalyzed, not their reaction with the aldehydes. Given the variety of metals and systems studied, it may indeed be the case that both possibilities are true, depending on the actual catalytic system.

Herrmann and co-workers as well as others<sup>5,11</sup> have shown that ReMeO<sub>3</sub> (MTO) and ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> are good catalysts for aldehyde olefination (AO) according to equation (1).



They also showed that Cp\*ReO<sub>3</sub>, CpReO<sub>3</sub> and (*t*-Bu<sub>2</sub>bipy)ReO<sub>3</sub> display a lower activity in AO. In the case of these trioxo complexes it was also shown that PPh<sub>3</sub> is necessary to reduce the Re(VII) trioxo species to an active Re(V) dioxo species, which in the case of MTO was isolated as ReMeO<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>•ReMeO<sub>3</sub> (R = Ph, Cy). Kühn and Romão were able to confirm the activity of these Re(V) dioxo complexes, by using MeReO<sub>2</sub>(η<sup>2</sup>-RC≡CR) as efficient catalysts for olefination of activated aldehydes.<sup>6a</sup> We also proposed that reaction (1) is initiated by the intermediate formation of a phosphazine, Ph<sub>3</sub>PN=NCH(CO<sub>2</sub>Et).

In the present study we explore the activity of other types of  $\text{Re(VII)O}_3$ ,  $\text{Re(V)O}_2$  and  $\text{Re(V)O}$  complexes in this reaction and present detailed investigations on the influence of changing the nature of the reaction components and conditions on catalytic activity, in order to attempt establishing a better understanding of the olefination reaction catalyzed by Re-oxo complexes.

## 2.2 Results and discussion

### 2.2.1 Survey of Re-oxo complexes for aldehyde olefination catalysis

The complexes in Chart 1 were preliminarily screened as catalysts in AO according to equation 1, with 4-nitrobenzaldehyde (4-nba), ethyl diazoacetate (EDA) and  $\text{PPh}_3$ . A selection of these complexes was further tested under controlled standardized conditions to allow meaningful comparisons. These latter results are summarized in Table 1 for the olefination of 4-nba with EDA and  $\text{PPh}_3$  at room temperature, and 2 h reaction time. TOF values were taken at 5 min reaction time. Details are given in the experimental section.

**Table 1.** Catalytic results for compounds **1-9** in the olefination of 4-nba at room temperature; 5 mol % catalyst. The yields obtained with compounds **10-19** are below 5 % and therefore considered as negligible, the TOFs are below 10 mol/ mol•h.

Catalyst	Yield(%) <sup>a</sup>	TOF <sup>b</sup> (mol/mol•h)
<b>1</b>	80	150
<b>2</b>	77	150
<b>3</b>	70	120
<b>4</b>	41	70
<b>5</b>	46	95
<b>6</b>	82	150
<b>7</b>	14	30
<b>8</b>	12	30
<b>9</b>	68	120

<sup>a</sup> yield calculated after 2h reaction time; <sup>b</sup> calculated after 5 minutes reaction time

The  $\text{Re}^{\text{VII}}$  trioxo complexes **4** and **5** show similar yields and TOF values. These are, however, only about half of those observed for MTO, a coordinatively unsaturated molecule. The influence of the electronegativity of the chlorine ligand is felt in slightly higher yield/activity counts for Cl over  $\text{CH}_3$ . More importantly, **6** shows values of yield/activity quite

similar to those of MTO. This can be assigned to the fact that the diazabutadiene ligand is both more labile and weaker donor than  $t\text{Bu}_2\text{-bipy}$ . In fact, it is likely that the diazabutadiene ligand is at least partially removed from the metal during the catalytic reaction.<sup>12</sup> Indeed, the reaction of **6** is slowed down by addition of  $\text{OPPh}_3$  whereby the yield decreases to 53%. Exploratory experiments carried out with other diazabutadiene complexes,  $(\text{DAB})\text{ReClO}_3$ , **11-12** have shown virtually no activity. DAB-derivatives with saturated organic ligands on the nitrogens are known to coordinate more strongly to metal atoms in high oxidation states.<sup>12</sup> A marginal activity was also observed for the neutral complex  $\text{ReO}_3\{\kappa^3\text{-B}(\text{pz})_4\}$  (**13**) analogue of  $\text{Cp}^*\text{ReO}_3$ . These results show that reduced Lewis acidity and coordinative saturation of the metal centre hamper the catalytic reaction. Unfortunately, the extreme reactivity of  $\text{ClReO}_3$ , the limiting reagent in this series, does not allow its use as catalyst.

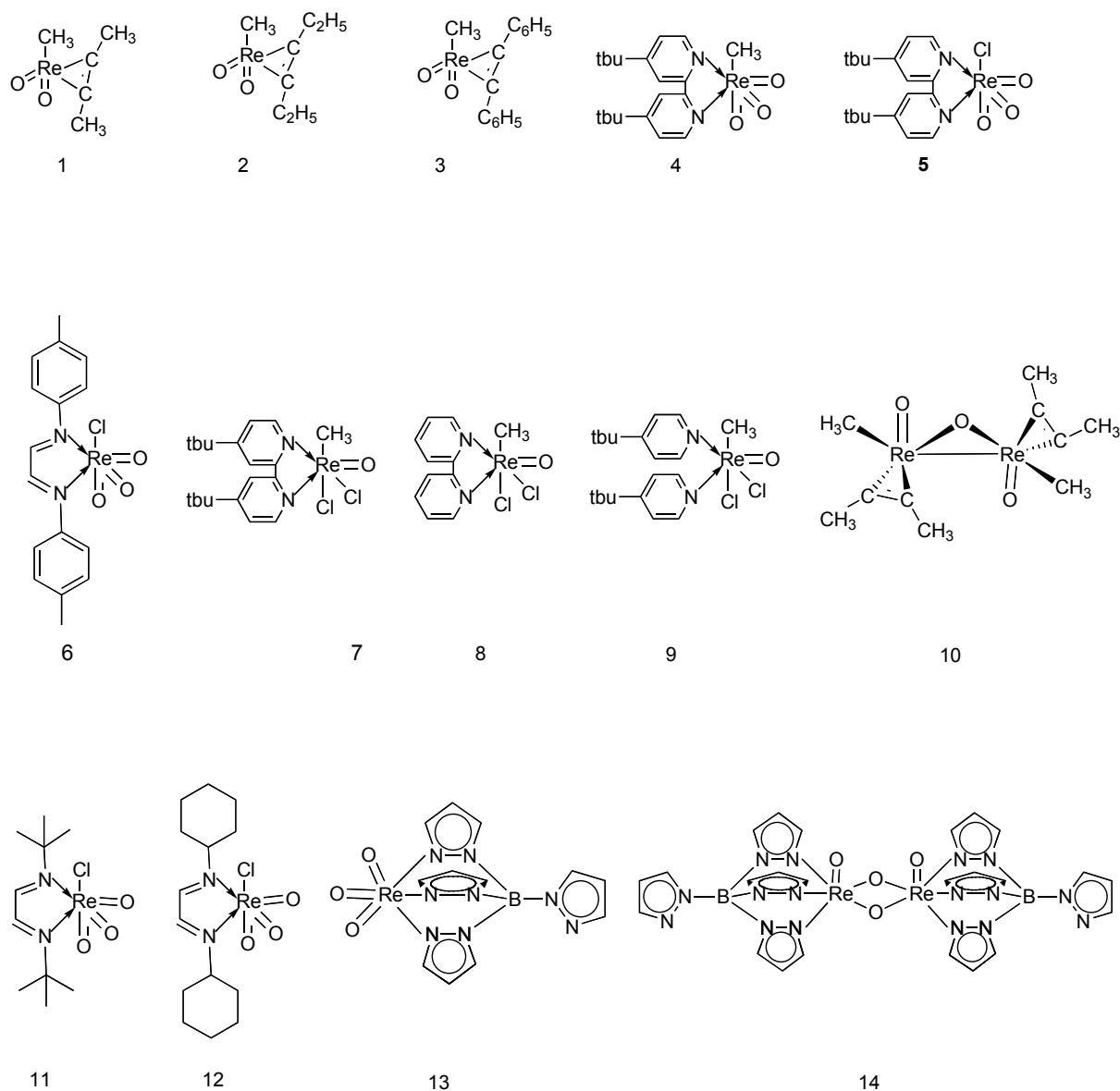


Chart 1

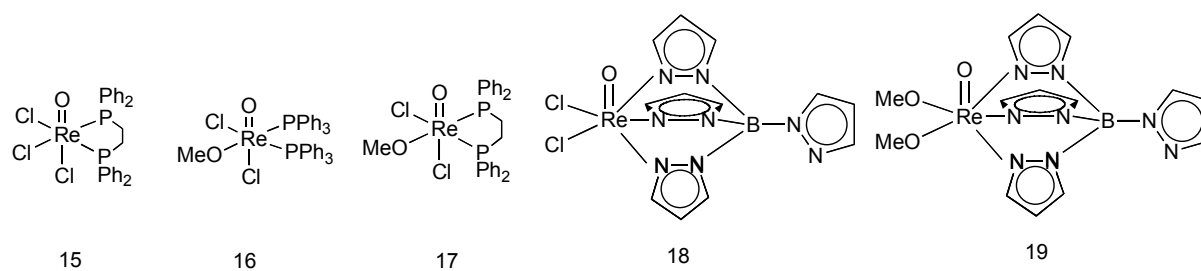


Chart 1 (continuation)

The Re(V) complexes are divided in two groups:  $\text{ReXO}_2$  and  $\text{ReX}_3\text{O}$  derivatives.

The  $\text{ReMeO}_2(\eta^2\text{-alkyne})$  complexes **1-3** perform at levels close to that of MTO. There is a slight dependence on the nature of the alkyne ligand in the decreasing order of activity  $\text{Me}_2\text{C}_2 > \text{Et}_2\text{C}_2 > \text{Ph}_2\text{C}_2$ . Excess alkyne slows down the reaction. In the case of **3** the yield goes down from 70 to 50% when excess  $\text{Ph}_2\text{C}_2$  is added. This suggests that the alkyne ligand has to be displaced during the reaction cycle, in which case the above reactivity order simply derives from the increasing stability of the complexes in the order  $\mathbf{1} < \mathbf{2} < \mathbf{3}$ . In fact, **3** can be stored at room temperature for several months, whereas **1** and **2** have to be stored below room temperature to avoid decomposition.<sup>13</sup>

Interestingly, both the dimeric Re(V) complex  $[\text{Re}\{\kappa^3\text{-B}(\text{pz})_4\}\text{O}(\mu\text{-O})]_2$ , (**14**) and the Re(IV) dimer **10** are totally inactive. The formation of a similar dimer in the reaction of  $\text{Cp}^*\text{ReO}_3$  with  $\text{PPh}_3$ , namely  $[\text{Cp}^*\text{ReO}(\mu\text{-O})]_2$  has been held responsible for the lack of aldehyde olefination reactivity of  $\text{Cp}^*\text{ReO}_3$ .<sup>14</sup> Dimerization is not favoured for the  $\text{MeReO}_2$  (MDO) complex.<sup>15</sup>

The prototypical catalyst in the  $\text{ReX}_3\text{O}$  family is  $\text{ReOCl}_3(\text{PPh}_3)_2$ , by far the most active Re catalyst for aldehyde olefination. Under appropriate circumstances (reaction temperature:  $50\text{ }^\circ\text{C}$ , cat:substrate = 1:1000) it can reach TOF values of 1200/h. Replacement of  $\text{PPh}_3$  by the bidentate dppe, as in complex (**15**), totally blocks catalysis suggesting the importance of  $\text{PPh}_3$  dissociation as a condition for forming an active species. Also devoid of any catalytic action in aldehyde olefination are the complexes  $\text{ReO}(\text{OMe})\text{Cl}_2(\text{PPh}_3)_2$ , (**16**)  $\text{ReO}(\text{OMe})\text{Cl}_2(\text{dppe})$ , (**17**)  $\text{Re}(\text{O})\text{Cl}_2\{\kappa^3\text{-B}(\text{pz})_4\}$ , (**18**)  $\text{Re}(\text{O})(\text{OMe})_2\{\kappa^3\text{-B}(\text{pz})_4\}$  (**19**). The organometallic complexes **7** and **8**, bearing bidentate nitrogen donor ligands, also show a rather limited catalytic activity. However, the analogue complex **9**, possessing two monodentate *t*Bupy ligands shows an activity already in the range of the values for MTO and the MDO derivatives **1-3**.



In summary, the crucial factor for an active AO catalyst on Re basis seems to be high Lewis acidity (usually Re in higher oxidation states) and either a sterical unsaturated compound such as MTO or a species, coordinated with easily removable “protecting ligands” such as the PPh<sub>3</sub> groups in ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, the R<sub>2</sub>C<sub>2</sub> ligands in compounds **1-3** or the weak N-donor ligands in compounds **6** and **9**. Sterically demanding and strong donor ligands such as Cp\* in Cp\*ReO<sub>3</sub> or the {κ<sup>3</sup>-B(pz)<sub>4</sub>} ligands in the compounds **13**, **14**, **18** and **19**, bidentate aliphatic diimines (as in **11** and **12**), bidentate phosphines (as in **15** and **17**) or OMe-ligands as in **16** reduce the activity considerably or totally and are therefore not useful for Re-based AO catalysts.

### 2.2.2 The influence of the substrates on the catalytic performance of ReMeO<sub>2</sub>(η<sup>2</sup>-alkyne) complexes

Equ. 1 represents a complex multi-component reaction involving, at its start, aldehyde, diazo compound, phosphine and catalyst precursor. It is, therefore, not easy to predict how the reaction starts and what is the influence of each reagent in its course. In the following we study the reaction using catalyst **3** varying the initial reagents in order to identify their action and influence in the outcome of the reaction.

#### A) The diazo compounds

In our previous study<sup>6a</sup> we used 4-nba as aldehyde, PPh<sub>3</sub> as oxygen abstractor and eda as standard diazo reagent. In this case it was shown that none of the initial reagents interacts directly with **3**. Instead, the formation of phosphazine Ph<sub>3</sub>P=NN=CH(CO<sub>2</sub>Et) from PPh<sub>3</sub> and eda precedes and triggers the catalytic reaction. The formation of phosphazine is fast, as can be observed conveniently with <sup>31</sup>P-NMR spectroscopy (see below, section B). Addition of **3** to a solution of phosphazine preformed from PPh<sub>3</sub> and eda, leads to a very exothermic reaction and liberation of N<sub>2</sub>. If 4-nba is present, catalysis is then observed (see section F for the characterization of this interaction).

In contrast, the use of trimethylsilyl diazomethane N<sub>2</sub>CH(TMS) instead of eda leads to no formation of olefination products, neither for aldehydes nor for ketones with selected Re complexes (**1,3**). <sup>31</sup>P NMR also shows that no phosphazine, Ph<sub>3</sub>P=NN=CH(TMS) is formed from N<sub>2</sub>CH(TMS) and PPh<sub>3</sub>: the only signal present in <sup>31</sup>P-NMR of a 1:1 mixture of these compounds, even after several hours, belongs to free PPh<sub>3</sub>. Other catalysts, however, e. g. Ru based systems<sup>4c,9</sup> generate AO products starting from phosphanes, N<sub>2</sub>CH(TMS) and aldehydes, under comparable conditions. We confirmed this by control experiments. These

observations indicate that phosphazine formation is a necessary prerequisite for a successful catalytic reaction, regardless of the known fact that phosphazines exist in equilibrium with free diazo compound and free phosphine.

Diazomalonate leads to a lower overall yield of olefin than eda. With catalyst **3** only 22% is obtained after 24h.  $^{31}\text{P}$ -NMR experiments have shown that in this case the corresponding phosphazine is formed but at a much slower rate than with eda, even after 2 days the reaction was not complete. The fast and quantitative formation of a phosphazine in the beginning of the catalytic cycle seems decisive for the catalytic performance with  $\text{ReMeO}_2(\eta^2\text{-alkyne})$  catalysts. Without formation of phosphazine complexes **1-3** are seemingly unable to catalyze AO.

These observations, however, do not rule out the possibility that concomitant formation of ylides under the reaction conditions, with or without metal catalysis, may be responsible for the catalytic activity since they would then react with the aldehyde either in a metal catalyzed process or in the classic un-catalyzed Wittig fashion. This possibility has been clearly observed in other metal catalyzed olefination reactions according to eq 1.<sup>6b,9b</sup>

There is, however, an important additional set of experiments, which demonstrates that in the case of the catalysts examined here, particularly in the cases of the MDO-derivatives **1-3** the catalytic formation of ylides is not the decisive step of the reaction. No olefin is formed upon reaction of 4-nitrobenzaldehyde (4-nba) with the ylide  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})_2$  in the absence of catalyst. Furthermore, when a catalytic amount of compound **3** is added to the mixture  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})_2/4\text{-nba}$ , no olefination products are obtained even after 4 days reaction time. As described already above, however, compound **3** catalyzes the reaction of 4-nba,  $\text{PPh}_3$  and diazomalonate. This reaction is slow, but reaches good yields after several days. Accordingly, compound **3** does not initiate or catalyze the reaction of  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})_2$  with 4-nba and an olefination mechanism operating *via* the catalytic formation of ylides and the further reaction of these ylides with aldehydes (both catalyzed or un-catalyzed) can be excluded at least for  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})_2$ . Therefore, it is important to point out that olefination of 4-nba with  $\text{N}_2\text{C}(\text{CO}_2\text{Et})_2/\text{PPh}_3$  according to equation (1) is feasible albeit slow, showing an intrinsic advantage of the catalytic reaction (1) over the classical Wittig reaction.

As already mentioned, in the case of some other aldehyde olefination catalysts the intermediate formation of ylides has been clearly observed.<sup>6b,9b</sup> We have selected some of those Ru(II) and Fe(II) based AO catalysts, namely  $\text{Cp}^*\text{RuCl}(\text{PR}_3)_2$ <sup>16</sup> and  $\text{Fe}(\text{TPP})\text{Cl}^{9c-e}$  (TPP = tetra(*p*-tolyl)porphyrin), and observed that they catalyze (very efficiently) the Wittig reaction of  $\text{PPh}_3=\text{CHCO}_2\text{Et}$  with various aldehydes, but do not catalyze either the reaction of

$\text{PPh}_3=\text{C}(\text{CO}_2\text{Et})_2$  with aldehydes or the four component reaction of  $\text{N}_2\text{C}(\text{CO}_2\text{Et})_2$  with aldehyde and  $\text{PPh}_3$ .

Taken together, these observations show that: i) Phosphazine formation from the diazo compound and phosphane prior to the reaction with the catalyst seems to be an important feature for a fast catalytic reaction; ii) The four component reaction catalyzed by  $\text{ReMeO}_2(\eta^2\text{-alkyne})$  is able to form olefins from  $\text{N}_2\text{C}(\text{CO}_2\text{Et})_2$  that are not available by the Wittig reaction of  $\text{Ph}_3\text{PC}(\text{CO}_2\text{Et})_2$  with aldehyde nor by the action of other, usually more active catalysts, such as  $\text{Fe}(\text{TPP})\text{Cl}$  that operate *via* an ylide intermediate.<sup>9c-e</sup> Therefore, the  $\text{ReMeO}_2$  catalysts have the important advantage of being able to catalyze AO reactions that are not feasible under classical or catalyzed Wittig conditions, i.e., from ylide and aldehyde.

In the four-component reaction of equation 1 *there must be a catalytic process involved, which allows olefin formation without intermediate ylide formation.* The original assumption of Herrmann and Wang that a rhenaxethane is involved as an intermediate for the reaction between aldehyde and metal carbene instead of a reaction between metal carbene and phosphine leading to a phosphorus ylide, which then would react in a Wittig type reaction seems to be the simplest explanation that accommodates our findings. Recently Chen *et al.* also reported experiments pointing to an intermediary presence of rhenacycles in closely related reactions.<sup>6c</sup> Although it has been convincingly shown to operate in other catalytic AO systems, a catalytic reaction yielding an ylide can be by no means the only way to get to AO products. Furthermore, for the  $\text{MeReO}_2$ -systems examined in this work we never observed the formation of significant amounts of ylides (by  $^{31}\text{P}$  NMR) during the course of the catalytic reactions.

### B) The phosphanes

The type of phosphines used for oxygen abstraction is also a factor of major influence on the catalytic performance of eq. (1). The reaction of the phosphine with the diazo compound is fast in the case of ethyldiazoacetate (eda) and  $\text{PPh}_3$ . In less than 5 min all starting materials are completely consumed. Phosphazine,  $\text{Ph}_3\text{P}=\text{NN}=\text{CH}(\text{CO}_2\text{Et})$  is the only product formed according to  $^{31}\text{P}$  NMR. The chemical shift observed in  $^{31}\text{P}$ -NMR,  $\delta_{\text{P}} = 23.3$  ppm is identical within the error range to the value found in the literature for this phosphazine.<sup>17</sup> The signal for the  $\alpha$  proton of eda at  $\delta_{\text{H}} = 4.69$  ppm is replaced by a new signal at  $\delta_{\text{H}} = 7.70$  ppm, in full accordance with the literature data for such reactions.<sup>18</sup> The presence of certain amounts of free phosphine and diazo compound due to equilibrium reactions does not influence the proposal that the phosphazine is the important species for the catalytic reaction. As we have

shown (see section A)  $\text{N}_2\text{CH}(\text{TMS})$ , which does not react with  $\text{PPh}_3$  to form a phosphazine under the conditions applied, also fails to start the catalytic cycle, although – of course - plenty of free  $\text{PPh}_3$  and  $\text{N}_2\text{CH}(\text{TMS})$  is available. When **3** is added to a solution containing the phosphazine in a 1:10 ratio, a rapid reaction ensues with liberation of  $\text{N}_2$  and increase in temperature. Already after 5 min the  $^{31}\text{P}$ -NMR of the mixture reveals a significant decrease of the peak corresponding to the phosphazine as well as the appearance of new peak at  $\delta_{\text{P}} = 29$  ppm (triphenylphosphine oxide). The peak corresponding to the  $\text{OPPh}_3$  increases with time, limited in growth by the amount of catalyst present. Small peaks at  $\delta_{\text{P}} = 18.68$  and  $17.10$  ppm indicate the formation of ylides  $\text{Ph}_3\text{P}=\text{CH}(\text{CO}_2\text{Et})$  (*cisoid* and *transoid* form). In this case, since the amount of catalyst present is higher than in the usual catalytic runs and in the previously described experiment, the peak of the phosphazine is significantly reduced in size and the ylides are formed in a 1:10 ratio to  $\text{OPPh}_3$ . Therefore, again, the catalytic ylide formation can not be the major reaction with the Re catalysts of type  $\text{ReMeO}_2(\eta^2\text{-alkyne})$  (see section A). It should be noted that all these reactions occur quickly and the  $^{31}\text{P}$ -NMR spectra do not change significantly from 10 minutes to 4 hours reaction time, which is in good accord with the catalysis results of the catalysts **1–3**, where after 30 min the yield is close to the final yield in most cases. After the reaction stops, the peaks obtained in the  $^{31}\text{P}$ -NMR spectrum, correspond to the following species: un-reacted phosphazine, triphenylphosphine oxide and the ylides,  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ , with signals of low intensity.<sup>9a</sup> The ylides are formed in small amounts either by decomposition of the phosphazine<sup>17</sup> or by reaction of  $\text{PPh}_3$  with some  $\text{Re}=\text{CH}(\text{CO}_2\text{Et})$  species formed during the course of the reaction, that cannot be consumed otherwise in the absence of aldehydes.

In order to confirm the latter point, the reaction was also monitored in the presence of an aldehyde by  $^{31}\text{P}$  and  $^1\text{H}$  - NMR spectroscopy. The reaction mixture consisted of  $\text{PPh}_3$ , eda, **3**, 4-nba, 1.1:1:0.07:1, which were added in this order. In the  $^{31}\text{P}$  NMR spectrum already after 5 minutes reaction time only one significant signal is present, corresponding to  $\text{OPPh}_3$ . The ylides are not observed even in trace amounts, and within 4 h measurement time no further changes are detected in the spectrum.

MTO and compounds **3** and **5** were tested using  $\text{P}(\text{OEt})_3$  as deoxygenating agent in catalytic aldehyde olefinations according to eq. (1) with 4-nba and eda under the same conditions as described above for  $\text{PPh}_3$ . The catalytic activity decreases significantly (Table 2). An analogous observation was made with  $\text{ReOCl}_3(\text{PPh}_3)_2$  as the catalyst. This is very likely due to the fact that phosphazine formation is much slower with triethylphosphite than with  $\text{PPh}_3$  as can be seen from  $^{31}\text{P}$ -NMR measurements.

**Table 2.** Comparison of the catalytic results for MTO and compounds **3** and **5** in the olefination of 4-nba using two different oxygen abstraction agents after 2 h reaction time.

Compound	PPh <sub>3</sub>	<i>cis/trans</i>	P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	<i>cis/trans</i>
MTO	77	10/90	17	22/78
<b>3</b>	70	5/95	7	29/71
<b>5</b>	46	10/90	15	10/90

In fact, reacting triethylphosphite with eda gives rise in the <sup>31</sup>P-NMR spectra to the appearance of a new signal at  $\delta_p = 20.2$  ppm, assigned to the corresponding phosphazine, the signal corresponding to the triethylphosphite being found at  $\delta_p = 139$  ppm. However, in this case the reaction is not complete, even after days.

To conclude it can be again said that formation of phosphazine is essential to start AO in the four-component system EDA, PR<sub>3</sub>, 4-nba, ReO<sub>x</sub>L<sub>n</sub> catalyst. Free ylides are only detected in small amounts at high catalyst concentration in the absence of aldehyde.

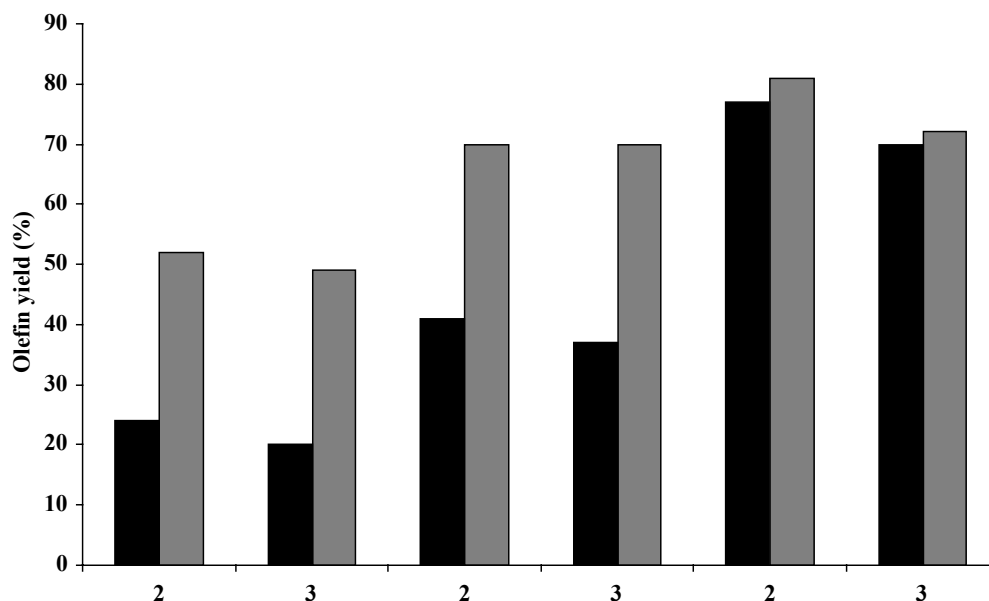
### C) The carbonyl compounds

Compounds **2** and **3** were tested as olefination catalysts for 4-nitrobenzaldehyde, 4-bromobenzaldehyde, and benzaldehyde using the following reagent ratios: aldehyde/PPh<sub>3</sub>/eda/catalyst = 1/1.1/1/0.05. In all three cases compound **2** as the catalyst leads to the best product yields after 24 h. With 4-bromobenzaldehyde it takes more time to reach the same yields as with 4-nitrobenzaldehyde as substrate under the same reaction conditions. After 24 h reaction time, however, in both cases high yields of 70–82 % are reached. In the case of benzaldehyde the yields after 24 h are ca. 50 % both with complex **2** and **3** as the catalysts. It is interesting to note that in the case of 4-nitrobenzaldehyde the product yield increase from 2 to 24 h is only marginal (5 % or less) while in case of 4-bromobenzaldehyde and benzaldehyde the yield approximately doubles in the same period of time (See Figure 1).

The reason for this observation in the case of 4-nitrobenzaldehyde may be related to the fast accumulation of the by-product OPPh<sub>3</sub> that significantly blocks the reaction at an early stage. In fact, if extra OPPh<sub>3</sub> is added in the beginning of the catalysis the yield is reduced significantly, as well as the reaction rate.

The use of the ketones acetophenone and benzophenone as substrates instead of the aldehydes does not lead to significant olefin yields within 24 h reaction time with both catalysts **2** and **3**. It should be noted that benzophenone does not react with the ylide Ph<sub>3</sub>P=CHCO<sub>2</sub>Et even after 8 days reaction time, whereas, this ylide reacts promptly with 4-

nitrobenzaldehyde with quantitative formation of the olefin. It is therefore clear that electron poor carbonyls react faster under the present catalytic olefination conditions.



**Fig. 1-** Catalytic activity of compounds **2** and **3** with benzaldehyde, 4-bromo benzaldehyde and 4-nba respectively. Black columns yield after 2h, grey after 24h.

The interaction of different aldehydes with catalyst **3** was also examined by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR in  $\text{CDCl}_3$ . When the components were reacted in a 2:1 and 1:1 ratio no change in the chemical shifts could be observed since the deviations from the signals of the isolated compounds always stayed significantly below 0.1 ppm. Addition of a ketone, such as acetophenone, however, leads to a shift of both the Re bound methyl group (from  $\delta_{\text{H}} = 2.61$  ppm in the free molecule to  $\delta_{\text{H}} = 2.49$  ppm in the mixture) and the  $\text{CH}_3$  protons of the ketone from  $\delta_{\text{H}} = 2.55$  ppm to  $\delta_{\text{H}} = 2.51$  ppm. In order to examine this behaviour in more detail, we reacted MTO and polymer bound triphenylphosphine, the usual method of preparation of the alkyne adducts of MDO **1-3**. However, instead of offering an alkyne as reaction partner we added – under the same conditions – acetophenone. The reaction mixture turned yellow and the NMR signals of both the ketone and the Re bound methyl group changed as observed in the way described above. Unfortunately, we were unable to isolate the reaction product due to its sensitivity to both temperature and moisture. Also, when acetophenone is added to a catalytic aldehyde olefination run (4-nba, eda,  $\text{PPh}_3$  as the substrates) with compound **3** as catalyst in a 1:1 (acetophenone:catalyst) ratio, the reaction rate and yield decrease somewhat (yield obtained after 2 h 65 %). However, after 24 h the same yield is achieved as in the absence of ketone. These results suggest that ketones are able to coordinate to the  $\text{Re}(\text{V})$

centre of  $\text{ReMeO}_2(\eta^2\text{-alkyne})$  in competition with the substrates of catalysis, namely the phosphazine, thus blocking the catalytic site.

#### *D) Substrate ratios*

In the blank runs performed in the absence of catalyst no olefination products were formed for all tested aldehydes. In all cases azine,  $\text{RC}_6\text{H}_4\text{CH}=\text{NN}=\text{CH}(\text{CO}_2\text{Et})$  was the main product. The formation of diethyl maleate or diethyl fumarate was not observed in a detectable amount (in the catalytic runs these products were also not detected). The formation of azine results from a competing reaction between the initially formed phosphazine and the aldehyde, which is not influenced by the presence of the catalyst.

Since this reaction is slower than the reaction between the catalyst and phosphazine, if the catalyst is present in sufficient amount, the reaction between the phosphazine and the aldehyde does not occur to a significant extent, and the azine is a minor side product. The order by which the catalysis components of eq. (1) are added, can be varied without negative effects on the catalytic performance, *provided the EDA and the aldehyde are not added in the absence of catalyst* (see above). This means, either all components can be mixed and eda added as the last reaction component, or both the catalyst and the aldehyde can be added after mixing all other reaction components. This latter procedure in the case of compound **3** even leads to slightly higher yields after two hours reaction time (78 % instead of 70 %). The ratios of the substrate were changed and runs with 4-nba/ $\text{PPh}_3$ /EDA/catalyst ratios of 1/2/1/0.05 and 1/1.1/2/0.05 were performed exemplary for compound **3**. The catalytic performance was not affected by the presence of excess of  $\text{PPh}_3$  or eda. In the presence of an excess of EDA the formation of diethyl maleate as by-product is observed.

#### *E) Influence of the solvent, catalyst amount and reaction temperature*

When the aldehyde olefination with catalyst **3** is conducted in toluene instead of THF the olefin yield decreases from 70% to 52% after 2h. The results in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$  were 26, 24 and 38% respectively after 2h. In this case the same amounts of azine and olefin are formed. The *cis/trans* selectivity also decreases to 10:90 in the case of  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$ . When the catalyst charge is decreased to 2 mol % (instead of 5 mol %) the olefin yield (*cis* and *trans*) obtained decreases to 55%, for 1 mol % to 40%, and for 0.5 mol % to 20 % yield. Azine is the main by-product. Catalytic runs were performed with catalyst **3** at 0, 20, 50, and 67°C in THF. At 0°C the yield reaches 65% after 2 hours only slightly below the yield achieved at room temperature. At 50°C the yield reaches after 30 min the same value obtained

after 2 h at room temperature. The TOF (determined after 5 min reaction time) increases from ca. 120/h at 20°C to ca. 170/h at 50 °C. A further raise in the reaction temperature, however, does not accelerate the reaction significantly, the TOF staying below 200 1/h.

#### F) Catalyst-phosphazine interaction

As shown above, the catalysts **1-3** interact strongly with phosphazine but seemingly not with the other components of the catalytic reaction mixture or with ylides. Upon reaction of **1-3** with phosphazine, N<sub>2</sub> and OPPh<sub>3</sub> are liberated and a Re-carbene complex is formed. A terminal oxygen atom of the catalyst is abstracted under formation of phosphine oxide as observed by <sup>17</sup>O-NMR spectroscopy from a reaction with <sup>17</sup>O labeled **3\*** and published already previously.<sup>6a</sup>

In the case of catalyst **3** at – 30°C, the carbene species was characterized by the signals at  $\delta_C = 323$  ppm and Re=C-H at  $\delta_H = 16.32$  ppm both in accordance with the values reported in the literature for related complexes, such as [RuClCp(=CHCO<sub>2</sub>Et)(PPh<sub>3</sub>)].<sup>19</sup> The corresponding signals of the carbene complexes formed from compounds **1** and **2** are, as expected, identical within the measurement error. This Re(V) carbene is observable *in situ* only at low temperatures (see Scheme 1 for its possible formula). At room temperature and above it decomposes quickly if no aldehyde is available for the continuation of the catalytic cycle. In fact, when the carbene species, formed from catalyst and phosphazine at low temperature, is allowed to react with aldehyde, fast formation of olefin and the re-formation of the catalyst can be observed by NMR spectroscopy.

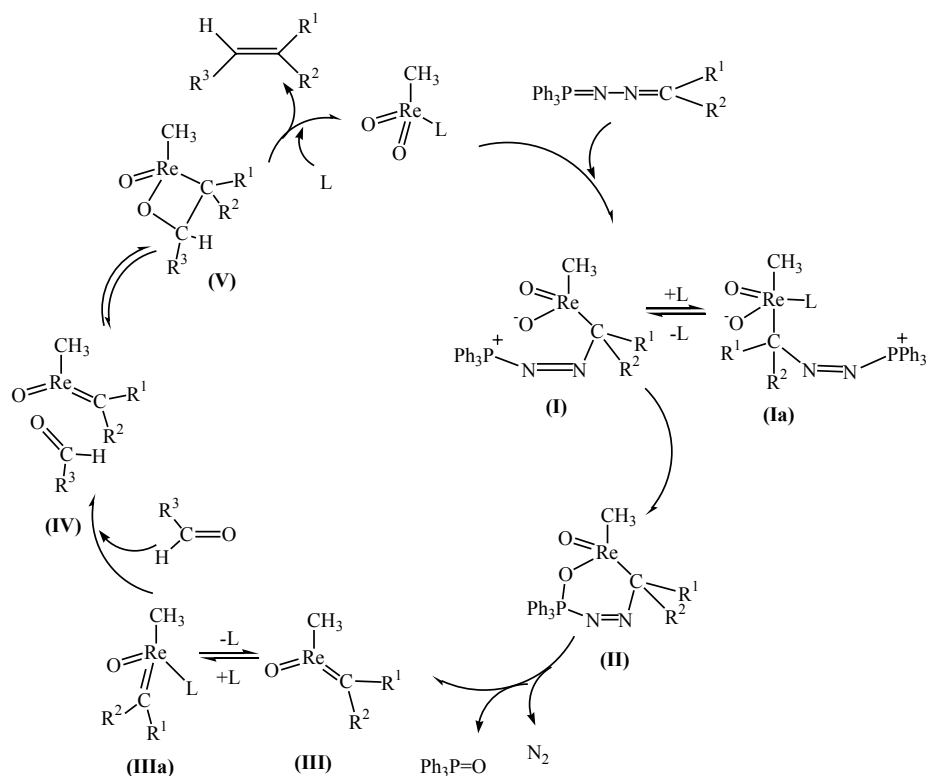
The involvement of Re carbenes in the catalytic aldehyde olefination has independently been confirmed by Chen *et al.* for Re<sub>2</sub>O<sub>7</sub> based, cationic catalysts in the gas phase by MS spectroscopy, although in his systems a catalytic ylide formation (following the carbene formation) seems to take place.<sup>6b</sup>

#### G) The catalytic cycle for aldehyde olefination with ReMeO<sub>2</sub>L<sub>2</sub> complexes.

Based upon the experimental results presented before a catalytic cycle describing the reaction of equation (1) can be postulated as depicted in Scheme 1 taking as examples, catalysts **1-3**, PPh<sub>3</sub>, eda and 4-nba as reaction partners.

A first and important point is the observation that we only obtained olefination of aldehydes in the cases where the phosphine reacts with the diazo compound to form a phosphazine. Besides, catalysts **1-3** do not interact directly with either aldehydes, diazo compounds, ylides or PPh<sub>3</sub> whereas a rapid reaction is observed between them and phosphazine.





**Scheme 1** Catalytic cycle for aldehyde olefination with  $ReMeO_2L$  complexes ( $L =$  alkyne,  $PPh_3$ ) with  $PPh_3$  and  $N_2CR^1R^2$ .

Therefore, the first step is the interaction of  $ReMeO_2(\eta^2\text{-alkyne})$  with the phosphazene  $Ph_3P=N-N=CR^1R^2$  leading to the species (I) or (Ia). This reaction is most probably accompanied by displacement of the alkyne ligand since this one retards the reaction rate when present in excess. Admitting total displacement of the alkyne, and formation of (I), the next step depicts the intramolecular arrangement (II) that precedes  $Ph_3PO$  elimination. A six-membered ring is formed where the positively charged P atom faces the negatively charged O ligand. The ensuing liberation of  $Ph_3PO$  will lead also to  $N_2$  liberation and formation of the carbene complex (III). Again, this coordinatively unsaturated species may be stabilized by any ligand present in the reaction mixture ( $PPh_3$ ,  $OPPh_3$ , alkyne) forming (IIIa).  $^{13}C$  NMR performed in a test reaction that was forced to stop at this stage due to absence of aldehyde, showed a signal for the carbene C atom in the range expected for this kind of species (see section F). In a catalytic reaction, however, aldehyde  $R^3CHO$  is present in large amounts and may replace any of the L ligands in (IIIa). This leads to complex (IV). Coordination will impart increased electrophilicity to the carbonyl carbon facilitating the formation of a metallaoxetane ring, (V). Splitting of this ring liberates the olefin while reforming the starting complex or simply a  $ReMeO_2$  species able to re-enter the catalytic cycle. It can not be

excluded that alternatively a reaction of a Re coordinated triphenyl phosphine in (IIIa) leads to the formation of an ylide, as has been suggested by Chen et al.<sup>6b,c</sup> and that the ylide then reacts with an aldehyde in a classical Wittig reaction. This possibility, however, is very unlikely to occur with diazo malonate derived compounds, since otherwise no products other than ylides would be obtained. Furthermore, we did not observe high amounts of ylides, even in the absence of aldehydes, which would be necessary, however, if the catalyzed reaction would be a ylide formation. Therefore, formation of the metallacycle (V) is, in our view, the simplest way to accommodate the fact that olefination of 4-nba is still possible with  $\text{N}_2\text{C}(\text{CO}_2\text{Et})_2$ . Since a phosphazine is formed from  $\text{PPh}_3$  and  $\text{N}_2\text{C}(\text{CO}_2\text{Et})_2$ , the reaction just follows the ordinary course albeit more slowly since this phosphazine is more difficult to form and other electronic or steric factors may also play a role. If the reaction were to proceed via ylide formation, it would not take place since  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})_2$  does not react with aldehydes, even 4-nba. Moreover, Ru(II) and Fe(II) catalysts known to operate via ylide formation are not active catalysts for olefination with  $\text{N}_2\text{C}(\text{CO}_2\text{Et})_2$ . Therefore, this catalytic system, although not being equally active as some other aldehyde olefination catalyst systems, is useful for the olefination of aldehydes that are incapable of reacting with ylides, thus circumventing the lack of reactivity of electron-poor ylides. In actual fact, this catalyst presents one of the key characteristics desirable in avoiding the drawbacks of the classical Wittig reaction: the total absence of basic, carbanionic intermediates, like ylides.

In spite of its interest, this system is, unfortunately, still un-capable of promoting ketone olefination and of activating electron-rich diazo compounds, e.g. the synthetically useful  $\text{N}_2\text{CH}(\text{TMS})$ . Ketones were found to compete for the catalytic intermediates, slowing down but not blocking aldehyde olefination. This suggests that they do not disrupt the catalytic cycle by deactivating its most reactive species, namely the carbene (III). Therefore, it seems likely that they do not have the electronic characteristics necessary to either form metallacycle (V) or lead to its productive (clockwise sense) disruption. Further studies are necessary in order to eventually tune the reactivity of the  $\text{Re}(\text{V})\text{O}_2$  derivatives for enlarging their scope of applications in olefination reactions.

### 2.3 Conclusions

Several oxorhenium compounds act as catalysts for the aldehyde olefination starting from diazo compounds, phosphines and aldehydes. Steric and electronic reasons allow the selection of “ideal” catalysts quite easily. Among the Re based catalysts  $\text{ReMeO}_2(\eta^2\text{-alkyne})$  complexes provide the simplest catalysts to study, although they are not the most active ones.

The first step of the catalytic cycle involves the formation of a carbene intermediate by the reaction of preformed phosphazine and catalyst under extrusion of phosphine oxide and dinitrogen. In a second step the carbene reacts with aldehyde under olefin formation and catalyst regeneration. Formation of significant amounts of ylides as intermediates cannot be observed. Furthermore, the olefination of diazomalonate can be catalyzed while the corresponding ylide does not react in a Wittig reaction in the presence of the same Re compound. It can therefore be assumed that the catalytic formation of ylides does not play a dominant role in the catalytic aldehyde olefination with the  $\text{ReMeO}_2$  type catalysts. This does, of course, not exclude that other catalysts lead to olefin formation by an entirely or partially different pathway where ylide intermediates play a prominent role.

### 3. Catalytic Ketone Olefination with Methyltrioxorhenium

#### 3.1 Background

The olefination of aldehydes and ketones is an important transformation in organic synthesis. The Wittig reaction and its variations provide a highly effective and general method, but still have several drawbacks.<sup>1</sup> The catalytic approach to aldehyde olefination has received considerable attention in recent years,<sup>2</sup> while the research on ketone olefination is far less developed and only a few examples of transition metal complex-mediated ketone olefination systems are known.<sup>3</sup>

Methyltrioxorhenium (MTO) is an easily accessible organometallic complex whose stability and high catalytic activity in several processes makes it an attractive target for new catalytic applications.<sup>4</sup> Recently we published a detailed study on the catalytic aldehyde olefination reaction with several organometallic rhenium complexes and we observed that some MTO derived complexes are able to catalyse the olefination of ketones.<sup>5</sup> Based on the good results obtained with MTO in the catalytic aldehyde olefination, where it was one of the first catalysts reported,<sup>2,6</sup> we tested its suitability for the catalytic ketone olefination.

Herein the results of our research on catalytic ketone olefination with MTO as catalyst are presented. The developed method proves to be general and straightforward to apply for a wide range of ketones.

#### 3.2 Results and discussion

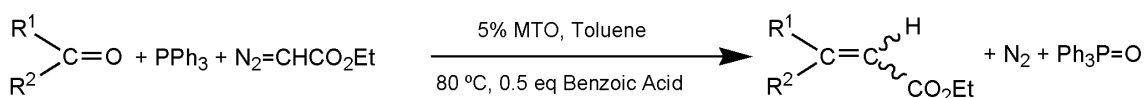
The olefination of cyclohexanone with triphenylphosphane (PPh<sub>3</sub>) and ethyldiazoacetate (EDA) at 80°C in toluene with 5% mol MTO as catalyst (see experimental part for details) proceeds comparatively slowly, affording less than 10% of olefin after 48h of reaction time. The slow progress, being in contrast to the reaction rate of the correspondent aldehyde olefination system<sup>6</sup> is expected since the ketone carbonyl group is generally much less electrophilic than the aldehyde carbonyl moiety. This difference is also known for the Wittig ketone olefination, which in the absence of other reactants usually requires harsh reaction conditions to obtain good results.<sup>7</sup>

To overcome this problem ways to enhance the electrophilicity of the carbonyl group and render it a higher reactivity were surveyed. It is reasonable to assume that Lewis or Brønsted acids can form complexes with or protonate the ketone's carbonyl

group increasing its electrophilic character and possibly its reactivity. Therefore the olefination of cyclohexanone using Lewis acids ( $\text{SbCl}_5$  and  $\text{Et}_3\text{OBF}_4$ ) as co-catalysts for the olefination of cyclohexanone under the same reaction conditions was attempted. Along with unreacted ketone, the main reaction products are the coupling products of EDA (*ca.* 35%), as well as the ring extension product 2-oxocycloheptanecarboxylic acid ethyl ester (*ca.* 25%). The olefin yield remains below 10% showing that strong Lewis acids do not activate the ketones towards the olefination reaction.

The Wittig reaction between aldehydes<sup>8</sup> or ketones<sup>8,9</sup> and  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$  can be strongly accelerated by sub-molar quantities of benzoic acid, and Zhang et al. have already successfully applied this Brønsted acid for catalytic ketone olefination<sup>3c,3d</sup> applying  $\text{Fe}(\text{TPP})\text{Cl}$  and  $\text{Co}(\text{TPP})$  as the catalysts.

The olefination of cyclohexanone with  $\text{PPh}_3$  and EDA at 80°C in toluene, using 5% mol MTO and 0.5 eq of benzoic acid as co-catalyst (scheme 1), affords 70% olefin after a reaction time of 48h. This remarkable improvement in activity led us to further explore the potential of this reaction system.



Scheme 1

The olefination of acetophenone under the same reaction conditions affords 65% of olefin with an E:Z ratio of 13:87 (table 1, entry 3) after 48h of reaction. If only 0.2 eq of benzoic acid are used in the same reaction the olefin yield remains below 15%. Therefore 0.5 eq of co-catalyst was applied throughout all further experiments.

A comparatively electron-deficient ketone such as 4-nitroacetophenone is more reactive than acetophenone and the olefination reaction is completed after 24h with 70% olefin yield. Performing the reaction at room temperature causes a significant decrease of the reaction rate, though it is beneficial for the reaction's selectivity (entries 5 and 6).

Reducing the MTO loading to half (2.5% mol) requires a longer time for the olefination of 4-nitroacetophenone to reach completeness, however the yield and selectivity remain quite similar (entries 5 and 7).

To test the effectiveness of MTO in the olefination of ketones we extended the study to a series of other substrates (entries 8-12), using the optimized reaction conditions, namely, toluene at 80 °C with a catalyst loading of 5 mol % and 0.5 eq of benzoic acid as co-catalyst.

**Table 1** Performance of MTO in ketone olefination with PPh<sub>3</sub> and EDA using 0.5 eq of benzoic acid as co-catalyst.

Entry	Ketone	%MTO	T /°C	Yield <sup>a</sup> /%	E:Z <sup>d</sup>	Reaction time
1	Cyclohexanone	5	80	<10 <sup>b</sup>	-	50
2	Cyclohexanone	5	80	71	-	50
3	Acetophenone	5	80	65	13:87	50
4	Acetophenone	5	80	15 <sup>c</sup>	42:58	68
5	4-nitro acetophenone	5	80	70	30:70	24
6	4-nitro acetophenone	5	RT	40	20:80	48
7	4-nitro acetophenone	2.5	80	70	31:69	44
8	4-methoxy acetophenone	5	80	30	32:68	132
9	Cycloheptanone	5	80	40	-	72
10	2-nonanone	5	80	54	48:52	120
11	( <i>E</i> )-4-phenyl-3- buten-2-one	5	80	45	26:74	42
12	Trifluoro acetophenone	5	80	93 <sup>b</sup>	11:89	48

a. Isolated yields, product authenticity was checked by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR.

b. No co-catalyst used.

c. 0.2 eq of benzoic acid used as co-catalyst.

d. *E:Z* ratios determined by GC.

This set of results allows drawing the following conclusions: activated ketones, i.e. electron-deficient ketones, react well and reach good to excellent yields within short reaction times (entries 5 and 12). In fact  $\alpha,\alpha,\alpha$ -trifluoro-acetophenone is active enough to be olefinated with quantitative yield in the absence of any co-catalyst with a high *Z*-isomer selectivity.<sup>3b</sup>

The olefination of inactivated ketones (entry 8) is also possible although – as expected - with lower yields and longer reaction times. This outcome is due to the low electrophilicity of the not activated carbonyl group.

The ability of MTO to catalyze a wide array of ketones is noteworthy: aromatic, cyclic,  $\alpha,\beta$ -unsaturated, aliphatic, and trifluoromethyl ketones can all be successfully olefinated by the MTO system, most importantly with the highest selectivities reported so far.

In conclusion a useful process for the olefination of ketones under non-basic conditions could be developed, confirming once more that MTO is one of the most versatile catalysts available.

## 4. Organometallic Ruthenium Complexes: Application in the Olefination of Carbonyl Compounds

### 4.1 Background

The olefination of carbonyl compounds, namely the transformation of a carbonyl group into a carbon-carbon double bond, is one of the most convenient and universal methods for the preparation of alkenes.<sup>1</sup> The catalytic alternative to the classic Wittig reaction has proven to be quite promising, avoiding the need for stepwise generation of phosphorous ylides under basic conditions. Furthermore, the use of transition metal complexes as catalysts also opens the possibility of efficient asymmetric olefination.<sup>2</sup> Accordingly, several catalytic aldehyde and ketone olefination systems have been reported based on Ru,<sup>3</sup> Re,<sup>4</sup> Rh,<sup>5</sup> Fe<sup>6</sup> and Co<sup>7</sup> complexes.

Compounds of the general formula  $Cp^*RuX(PR_3)_2$  found widespread applications in catalysis. The ease of synthesis, the wide array of ligands available to coordinate with the metal centre and their general high stabilities make them a versatile and promising class of catalysts. Baratta *et al.*<sup>8</sup> studied the decomposition of ethyl diazoacetate (EDA) with this type of catalysts presenting evidence for  $PPh_3=CHCO_2Et$  formation in the presence of triphenylphosphane ( $PPh_3$ ). This prompted us to study these compounds in the aldehyde olefination reaction as catalysts for phosphorous ylide generation. In a preliminary communication, we were able to confirm the activity of organometallic ruthenium complexes, by using  $Cp^*RuX(PR_2R')_2$  as efficient catalysts for the olefination of activated aldehydes.<sup>9</sup>

In the present study we explore the activity of these complexes more broadly, including the olefination reaction of non-activated aldehydes and ketones. Investigations on the influence of changing the nature of the reaction components and conditions on catalytic activity are performed, in order to attempt establishing a better understanding of the olefination reaction catalyzed by  $Cp^*RuX(PR_2R')_2$  complexes.



## 4.2 Results and discussion

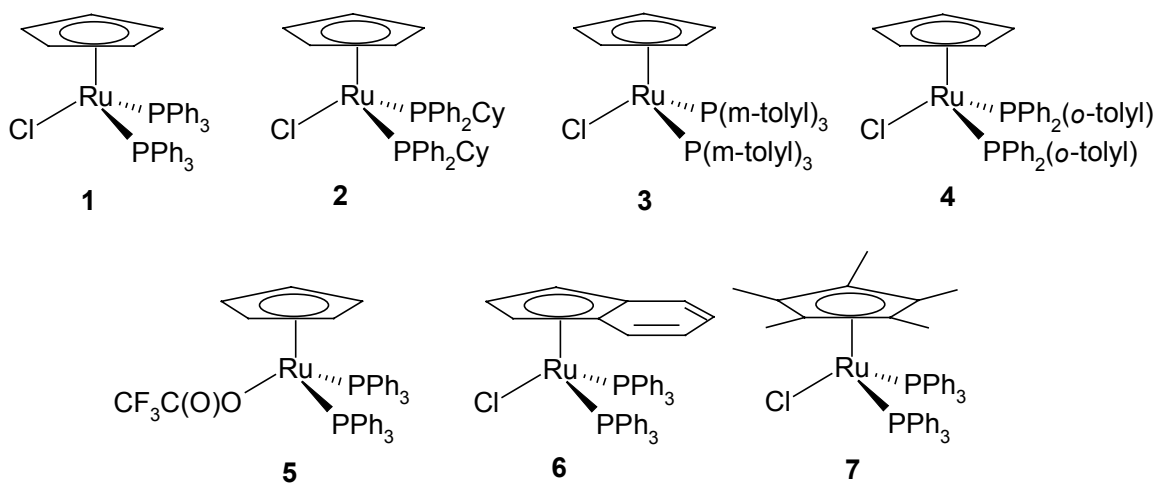
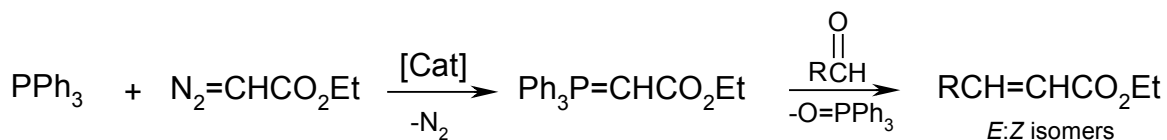


Chart 1

Compounds **1-7**, CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (**1**), CpRuCl(PPh<sub>2</sub>Cy)<sub>2</sub> (**2**), CpRuCl(P(*m*-tolyl)<sub>3</sub>)<sub>2</sub> (**3**), CpRuCl(PPh<sub>2</sub>(*o*-tolyl))<sub>2</sub> (**4**), CpRu(CF<sub>3</sub>C(O)O)(PPh<sub>3</sub>)<sub>2</sub> (**5**), IndRuCl(PPh<sub>3</sub>)<sub>2</sub> (**6**), and Cp<sup>\*</sup>RuCl(PPh<sub>3</sub>)<sub>2</sub> (**7**) (see chart 1) were tested for the aldehyde olefination reaction as catalysts for phosphorous ylide generation in non-basic conditions (scheme 1).

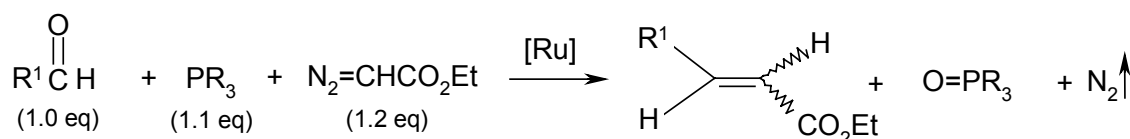


Scheme 1

In the aldehyde olefination leading to  $\alpha,\beta$ -unsaturated esters, both the reaction rate and *E:Z* selectivity have to be considered. Frequently, the most active catalysts present relatively low selectivities.<sup>10</sup> The aldehydes and ketones used as substrates are depicted in chart 2.

### 4.2.1 Catalyst optimization

Compound **1** shows a comparatively low activity in the olefination of 4-nitrobenzaldehyde (4-nba) reaching an olefin yield of 42 % (table 1, entry 1) after two hours reaction time. Simultaneously the selectivity is rather poor with a final *E:Z* ratio of 88:12.

**Table 1.** Catalytic aldehyde olefination with compounds **1-7** as catalysts.

Entry	Aldehyde	Catalyst / Phosphane	Catalyst loading /% mol	Yield <sup>a</sup> /%	Time /h	<i>E</i> : <i>Z</i> ratio <sup>b</sup>
1	I	<b>1</b> / PPh <sub>3</sub>	2	42	2	88:12
2	I	<b>2</b> / PPh <sub>2</sub> Cy	2	46	2	94:6
3	I	<b>3</b> / P( <i>m</i> -tolyl) <sub>3</sub>	2	63	2	98:2
4	I	<b>4</b> / PPh <sub>2</sub> ( <i>o</i> -tolyl)	2	92	2	96:4
5	I	<b>5</b> / PPh <sub>3</sub>	2	29	2	87:13
6	I	<b>6</b> / PPh <sub>3</sub>	1	96	1	92:8
7	I	<b>7</b> / PPh <sub>3</sub>	1	98	5 min	99:1
8	II	<b>7</b> / PPh <sub>3</sub>	1	97	0.5	94:6
9	I	Fe(TPP)Cl / PPh <sub>3</sub>	1	97	2	92:8
10	I	Cl <sub>3</sub> ORe(PPh <sub>3</sub> ) <sub>2</sub> / PPh <sub>3</sub>	1	95	2	98:2
11	II	<b>7</b> / PPh <sub>3</sub>	0.6	96	2	96:4
12	II	Fe(TPP)Cl / PPh <sub>3</sub>	0.6	96	2	91:9
13	II	Cl <sub>3</sub> ORe(PPh <sub>3</sub> ) <sub>2</sub> / PPh <sub>3</sub>	0.6	42	2	93:7

<sup>a</sup>Isolated yields. <sup>b</sup>*E*:*Z* ratios determined by GC-MS. Reaction temperature 50°C, except entry 8, reaction conducted at 80°C. Solvent THF, entry 8 toluene.

It has been observed for several other processes that the phosphane structure has a paramount effect on the catalysts performance,<sup>11</sup> since it allows the fine-tuning of the metal's reactivity and selectivity. According to previous studies, for example, complexes **2-4**, bearing bulky phosphanes decompose EDA at lower temperatures compared to compound **1** ligated by PPh<sub>3</sub>.<sup>8b</sup> Based on this observation compounds **1-4**

were tested in the aldehyde olefination reaction in this study. The use of phosphanes with high Tolman cone angles,<sup>11c</sup> has a positive influence on the reaction outcome, since these catalysts improve both the olefin yield and the *E*-isomer selectivity. The best yield among the compounds **1-4** is obtained with complex **4** (entry 4), affording 92% olefin yield after 2 hours reaction time, and the best selectivity with complex **3**, with a final *E:Z* ratio of 98:2 (entry 3). For all of these catalytic runs it is essential to use the same phosphane both as ligand and as oxygen abstractor during the reaction, since the use of PPh<sub>3</sub> as oxygen abstractor in combination with another phosphane as ligand rapidly ensues the replacement of (at least one of) the bulkier phosphanes, and would therefore change the activity of the catalyst, turning it increasingly similar to that of compound **1** (in a control experiment with compound **4** with 4-nba, using PPh<sub>3</sub> as oxygen abstractor only 63% of olefin yield were observed).

Changing the phosphane ligand of the studied complexes has a twofold influence on the catalytic reaction: (1) It changes the catalyst activity as a result of combined effects of the steric bulk of the phosphanes (main factor) and their electron donation abilities; (2) the generated phosphorous ylides show different reactivity towards the aldehyde, once again, depending on both electron donor ability and bulkiness.

Bulkier phosphanes than PPh<sub>3</sub> are less strongly bonded to the Ru centre due to their increased steric requirements<sup>12</sup> and thus removal of one phosphane ligand becomes easier in complexes **2-4**, a key factor for triggering the catalytic cycle (see scheme 3, below). Based on this rationalization complexes **2-4** should also show higher catalytic activity than PPh<sub>3</sub> - as they in fact do.

Ylides of the type (*p*-R-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P=CHCO<sub>2</sub>Et bearing electron donating groups R react faster with aldehydes than Ph<sub>3</sub>P=CHCO<sub>2</sub>Et does.<sup>13,14</sup> However, bulkier ylides than Ph<sub>3</sub>P=CHCO<sub>2</sub>Et like Ph<sub>2</sub>(*o*-tolyl)P=CHCO<sub>2</sub>Et react slower with aldehydes.<sup>14</sup> When the electron donation of the ligands is not significantly different (both PPh<sub>2</sub>(*o*-tolyl) and P(*m*-tolyl)<sub>3</sub> display only slightly higher electron donation abilities than PPh<sub>3</sub>),<sup>15</sup> bulkiness seems to exert a stronger effect over the ylide reactivity than the electron donation. Therefore, when it concerns the ylides reactivity, PPh<sub>2</sub>Cy should be the most effective ligand, followed by PPh<sub>2</sub>(*o*-tolyl) and P(*m*-tolyl)<sub>3</sub>.

Bulkier phosphanes enable an easier formation of the phosphorous ylide, by facilitating the release of a phosphane ligand, but also produce less reactive ylides, which slow down the second step. These observations emphasize the importance of the ease of phosphane release in the ylide generation, since it overcompensates, at least to a

certain degree, the more sluggish second step. The results presented here show that the optimal result is found in a compromise between the ease of phosphane release from the catalyst and the reactivity of the ylide, which is accomplished in this case with  $\text{PPh}_2(o\text{-tolyl})$  and complex **4**.

The increase of selectivity towards the *E*-isomer follows the trend also observed in the Wittig reaction,<sup>14</sup> where an increase of the ligand bulkiness leads to higher *E*:*Z* ratios. Although an eventual influence of the catalyst in the second step can not be entirely discarded, the *E*:*Z* ratios improve exactly with the bulkiness of the phosphane:<sup>12c</sup>  $\text{PPh}_3 < \text{PPh}_2\text{Cy} < \text{PPh}_2(o\text{-tolyl}) < \text{P}(m\text{-tolyl})_3$ .

The substitution of the -Cl ligand by a more electron withdrawing group, namely -OC(O)CF<sub>3</sub> (compound **5**) has a negative effect on the outcome of the catalytic reaction, producing only 29% yield. This is not surprising, since a more electron poor metal withdraws more electron density from the attached phosphanes and coordinates them more strongly. The *E*:*Z* ratio is within the measurement error equal to that received with compound **1**.

The most striking results were obtained when instead of the cyclopentadienyl ligand bulkier ligands like indenyl (Ind) **6**, or pentamethylcyclopentadienyl (Cp\*) **7** were applied. These catalysts show an enhanced activity that allows 100 % conversion of 4-nba into olefin after 60 min (entry 6) and 5 min (entry 7) of reaction time, for **6** and **7**, respectively. For these catalysts it was possible to decrease the catalyst loading to 1 mol% without any activity decrease or additional side product formation. The *E*:*Z* ratios, 92:8 for **6** and 99:1 for **7**, show a substantial selectivity improvement in comparison to **1**.

On going from Cp to Ind and Cp\* ligands the catalyst activities rise in accord to the increasing bulkiness and better electron donation abilities of the ligands.<sup>16</sup> The increased bulkiness weakens the P-Ru bond,<sup>12b</sup> enabling a faster dissociation of the phosphine<sup>17</sup> (see scheme 3 below). The increased electron donation is likely to stabilize the  $16e^-$  active species and thus favor the P-Ru bond cleavage as well.

The promising results obtained with compound **7** regarding both activity and selectivity tempted us to compare its performance to other known aldehyde olefination catalysts.  $\text{Fe}(\text{TPP})\text{Cl}^{6c}$  (TPP = tetra(*p*-tolyl)porphyrin), and  $\text{Cl}_3\text{ORe}(\text{PPh}_3)_2^{4h}$  have been tested successfully in the olefination of several aldehydes and presented the highest activities reported previously.

Three catalysts,  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ ,  $\text{Fe}(\text{TPP})\text{Cl}$  and  $\text{Cl}_3\text{ORe}(\text{PPh}_3)_2$  were tested in the olefination of 4-nba under the same reaction conditions, namely at 50 °C in THF, using 1 mol% catalyst loading. All three compounds reach quantitative yield within 2 hours of reaction time. The *E*:*Z* ratios are 99:1, 92:8 and 98:2, and the TOFs (determined after 5 min reaction time) 900, 890 and 1200  $\text{h}^{-1}$ , respectively. With a catalyst loading of 0.1 % mol none of the catalysts reaches quantitative yield. The TOFs are 1600, 3680 and 1230  $\text{h}^{-1}$ , respectively. The differences in initial activity between these catalysts at low concentrations are explained by the mechanism depicted in scheme 3 (see below). The huge excess of free  $\text{PPh}_3$  when low concentrations of catalyst **7** are applied (more than 1000 times excess for a 0.1 mol% loading) shifts the equilibrium strongly towards the inactive  $18e^-$  species, reducing greatly the catalytic activity. This effect very likely also occurs for  $\text{Cl}_3\text{ORe}(\text{PPh}_3)_2$ , while  $\text{Fe}(\text{TPP})\text{Cl}$  having no  $\text{PPh}_3$  ligands is devoid of any  $\text{PPh}_3$  inhibition, and so maintains high activity even at low concentrations. Also in the olefination of benzaldehyde  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  affords the highest *E*-isomer selectivity for this set of catalysts (entries 12 to 14).

None of the tested catalysts produces any olefin product when we attempted aldehyde olefination with diethyl diazomalonate in place of ethyl diazoacetate. By  $^{31}\text{P}$ -NMR spectroscopy the formation of the corresponding phosphorus ylide,  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})_2$ , can be observed, but this ylide is unable to react further with 4-nba. This strongly suggests that this class of complexes catalyzes phosphorus ylide formation from phosphanes and diazo compounds, but not the further reaction of ylide to the desired olefin.

Through careful tuning of the ligands coordinating to the metal, it was possible to turn a medium performance catalyst (compound **1**) into a good catalyst (compound **7**) combining fast reaction rates with high *E*-olefin selectivity. Based on these results, complex **7** was tested for the olefination of several other aldehydes and also ketones as described below.

#### 4.2.2 Aldehyde and ketone olefination with compound **7**

Before testing its activity towards different aldehydes and ketones, studies were carried out on the optimization of the reaction conditions. Taking the olefination of benzaldehyde as model reaction, it was shown that the best results are obtained at 80 °C in toluene (table 1, entry 8), the reaction is – not surprisingly - much faster under these conditions than at 50 °C in THF (table 1, entry 12).

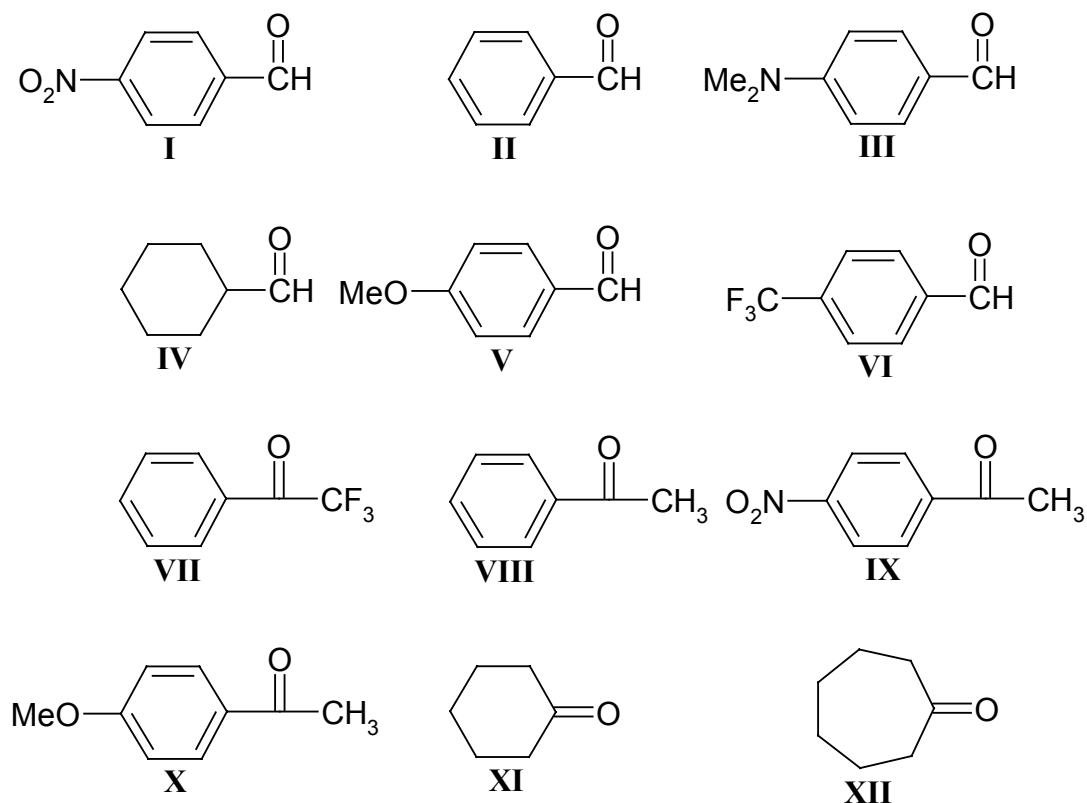


Chart 2

The same reaction in toluene at room temperature (table 2, entry 1) reaches quantitative yield after 3 h, also with an *E:Z* ratio of 95:5. Using ethanol as solvent (table 2, entry 2), the reaction is completed after 25 min, but the selectivity decreases notably to a final *E:Z* ratio of 84:16.

As it seems, the solvent influences both the reaction rate and selectivity. While in THF and toluene the selectivities are similar, the reaction time can be considerably shortened in toluene due to its higher boiling point. In ethanol the reaction is slightly faster than in toluene, but the loss in selectivity overcomes the gain in reaction speed. This decrease is also observed for the Wittig reaction in different solvents.<sup>18</sup> Therefore all further olefination reactions were performed in toluene at 80 °C. The obtained results are summarized in table 2.

Regarding the aldehyde olefination, the results present the expected trends: activated aldehydes, i.e., compounds containing electron withdrawing groups like aldehyde **I** and **VI** (entry 4) reach quantitative yields in short reaction times, typically in less than one hour. Deactivated aldehydes, containing electron-donating groups, react comparatively slow. By extending the reaction time to 24 h high yields (98%) in the olefination of **V** (entry 6) are obtained, while with substrate **III** even with prolonged reaction times, only

moderate yields are observed (entry 3). A non-aromatic aldehyde, **IV**, reacts fairly fast under the conditions applied reaching 92% yield after 5 h reaction time (entry 5).

**Table 2.** Catalytic aldehyde and ketone olefination with compound **7** as catalyst.

Entry	Aldehyde/Ketone	Catalyst	Yield <sup>a</sup> /%	Time/h	<i>E:Z</i> ratio <sup>b</sup>
1	II	<b>7</b>	95	3	95:5
2	II	<b>7</b>	96	0.25	84:16
3	III	<b>7</b>	61 <sup>c</sup>	24	96:4
4	VI	<b>7</b>	92	1	97:3
5	IV	<b>7</b>	92	5	97:3
6	V	<b>7</b>	98	24	94:6
7	III	<b>7</b> <sup>d</sup>	98 <sup>c</sup>	2	92:8
8	VII	<b>7</b>	85	4	88:12
9	VIII	<b>7</b> <sup>d</sup>	78	72	42:58
10	IX	<b>7</b> <sup>d</sup>	92	44	35:65
11	X	<b>7</b> <sup>d</sup>	57	7 days	41:59
12	XI	<b>7</b> <sup>d</sup>	84	24	-
13	XII	<b>7</b> <sup>d</sup>	58	48	-

<sup>a</sup>Isolated yields. <sup>b</sup>*E:Z* ratios determined by GC-MS. <sup>c</sup>Yield determined by GC-MS. <sup>d</sup>Benzoic acid (0.5 eq) as co-catalyst. Solvent: toluene, except entry 2, ethanol. Temperature: 80 °C, except entry 1, RT and entry 2, 78 °C. Catalyst loading: 1% mol of carbonyl compound.

A common feature found among all the results presented in this work is the high *E*-isomer selectivity displayed by catalyst **7**, being the highest selectivity reported so far.

The Wittig reaction between aldehydes<sup>13b</sup> or ketones<sup>6d,7,13b,19</sup> and Ph<sub>3</sub>P=CHCO<sub>2</sub>Et can be strongly accelerated by sub-molar quantities of benzoic acid. The acid activation is not limited to benzoic acid as several other acids display similar properties,<sup>19a</sup> but it seems to have a broader efficiency regarding the ketones and ylides. The influence of benzoic acid was therefore also investigated in this work. The olefination of **III** proceeds smoothly in the presence of 0.5 eq of benzoic acid as co-catalyst, reaching 100% yield after just 2 h of reaction time (entry 7). The selectivity decreases to an *E:Z* ratio of 92:8, though. When using just 0.1 eq of benzoic acid quantitative olefin formation is observed within 4 h, displaying the same *E:Z* ratio.

Ketone olefination with stabilized ylides, such as  $\text{PPh}_3=\text{CHCO}_2\text{Et}$  is usually a sluggish process and requires both harsh reaction conditions and/or long reaction times<sup>20</sup> to obtain reasonable yields. Exceptions to this rule are trifluoromethyl ketones, in which the carbonyl group is sufficiently electron deficient to undergo fast nucleophilic attack by the phosphorus ylide.<sup>21,4c</sup>

The olefination of  $\alpha,\alpha,\alpha$ -trifluoroacetophenone proceeds smoothly at 80 °C in toluene producing a 85 % olefin yield after a reaction time of 5 h (entry 8). With an *E:Z* ratio of 88:12, the selectivity of this reaction is not as high as that observed for aldehyde olefination, but considerably higher than that obtained applying non-activated ketones (see below).

The set of ketones tested included non-activated aromatic rings (**VIII**), activated aromatic rings (**IX**), deactivated aromatic rings (**X**) and cyclic ketones (**XI** and **XII**) (using the same terminology as applied for the aldehydes). To increase the reaction rates benzoic acid (0.5 eq) was added as co-catalyst.

The yields obtained with aromatic ketones range from 92% for 4-nitroacetophenone to 57% for 4-methoxy acetophenone. Activated ketone **IX** reacts relatively fast (44 h) and shows the best selectivity observed for the aromatic ketones under examination, with an *E:Z* ratio of 35:65. Ketones **VIII** (entry 9) and **X** (entry 11) require long reaction times to obtain moderate yields, 78% and 57%, respectively, having very similar *E:Z* ratios. Moreover, the use of an initial excess of ketone **VIII** (3 eq) produces a 72% olefin yield with an *E:Z* ratio of 42:58, after 72 hours of reaction time, which is not an improvement over our standard reaction conditions. The lack of electron withdrawing groups seems to be responsible for the lack of reactivity of this type of ketones.

Cyclic ketones can also be olefinated by this method. Cyclohexanone is olefinated with 84% yield (entry 12) within 24 h, while for **XII** as substrate only a moderate yield of 58% is achieved.

Complex **7** catalyses efficiently the aldehyde olefination, giving high yields and excellent selectivities in short reaction times, while for the olefination of some ketones only moderate yields could be obtained, even in the presence of benzoic acid as co-catalyst. With respect to selectivity the results obtained with  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  for ketone olefination are in the same order of magnitude of those obtained by other good catalysts,<sup>6d,4g</sup> unlike the case of aldehyde olefination, where compound **7** is clearly the most selective system reported so far.



### 4.3 Conclusions

Several ruthenium compounds bearing phosphane ligands act as catalysts for the aldehyde olefination starting from diazo compounds, phosphanes and aldehydes. The phosphane structure has a strong effect on the catalyst performance, bulkier phosphanes leading to better yields and higher selectivities. The replacement of the Cl ligand by a more electron withdrawing group such as  $-\text{OC}(\text{O})\text{CF}_3$  has a negative effect on the catalyst performance. On the other hand, the replacement of the Cp ligand by bulkier  $\pi$ -ligands such as Cp\* or Indenyl has a remarkable positive effect on the catalyst activity. Particularly Cp\*RuCl(PPh<sub>3</sub>)<sub>2</sub> leads to excellent yields and particularly high *E:Z* ratios, the latter being the best reported so far. This compound was also found to be a good catalyst for the olefination of activated ketones and a moderate catalyst for the olefination of non-activated ketones using benzoic acid as co-catalyst.

## 5. Investigations on the reaction mechanism of catalytic carbonyl olefination with $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$

### 5.1 Background

The mechanism of the metal catalyzed aldehyde olefination with diazo compounds and phosphanes is still under debate. In what concerns ester stabilized diazo compounds most authors suggest the existence of a metal carbene intermediate species.<sup>1</sup>

The subsequent steps change according to the metal center: (a) Fe,<sup>2</sup> Ru<sup>2c,3</sup> and Co<sup>4</sup> complexes originate quantitative amounts of phosphorus ylides and electrophilic attack of the phosphane at the carbene is considered to be the decisive step; (b) Re (MTO<sup>5</sup> and derivatives) although producing phosphorus ylides, usually they cannot account for the total olefin yield and the reaction is thought of proceeding through a metaloxetane intermediate. This would explain the observed olefination with extremely stable diazo compounds such as  $\text{N}_2=\text{C}(\text{CO}_2\text{Et})$ .<sup>5a</sup>

The high catalytic activity of the Fe, Ru and Co catalysts has eluded the detection of metal carbene intermediates under catalysis conditions, but they are known to produce such intermediates with other diazo compounds under similar conditions.<sup>6,7</sup>

In this work a comprehensive study of the reaction mechanism of catalytic aldehyde olefination with  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  confirms the presence of a catalytically active mixed phosphane/carbene Ru species  $\text{Cp}^*\text{RuCl}(\text{=CHCO}_2\text{Et})(\text{PPh}_3)$ . Subsequent NMR spectroscopic studies confirm the identity of the latter compound formed during the catalytic cycle and elucidate the way substrates and catalysts react to produce the desired olefin.

The effect of benzoic acid over the Wittig reaction with un-reactive ketones was also investigated as most studies don't address this subject and the assumptions made lack experimental support.

### 5.2 Results and discussion

In a previous communication<sup>8</sup> we suggested a possible mechanism for the aldehyde olefination with  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  type complexes based on published results<sup>9</sup> and our own <sup>31</sup>P-NMR spectroscopy studies. The proposed mechanism involves a  $\text{Cp}^*\text{RuCl}(\text{=CHCO}_2\text{Et})(\text{PPh}_3)$  (**8**) carbene intermediate.

Following the reaction of complex **7** with EDA by  $^1\text{H-NMR}$  and  $^{31}\text{P-NMR}$  in  $\text{CD}_2\text{Cl}_2$  at low temperatures, the existence of complex **8** is evident. At  $-15\text{ }^\circ\text{C}$  a doublet at  $\delta_{\text{H}} = 14.88\text{ ppm}$  appears in the  $^1\text{H-NMR}$ , suggesting the formation of a  $\text{Cp}^*\text{RuCl(=CHCO}_2\text{Et)(PPh}_3\text{)}$  carbene.<sup>9</sup> Simultaneously the intensity of the methyl groups peak of  $\text{Cp}^*$  of complex **7** ( $\delta_{\text{H}}(\text{Cp}^*) = 0.98\text{ ppm}$ ) decreases while a new one appears around  $\delta_{\text{H}} = 1.30\text{ ppm}$ . At the same temperature the  $^{31}\text{P-NMR}$  shows a steady decrease of the peak of complex **7** ( $\delta_{\text{P}} = 41\text{ ppm}$ ) while two new peaks arise: a peak at  $50.3\text{ ppm}$  for carbene complex **8** and a somewhat broader peak at  $17.9\text{ ppm}$ , which splits into two peaks after 20 minutes at  $-10\text{ }^\circ\text{C}$ . The latter peaks, at  $\delta_{\text{P}} = 18.4$  and  $\delta_{\text{P}} = 16.7\text{ ppm}$  correspond to the *cis* and *trans* isomers of the phosphorus ylide,<sup>10</sup> as further confirmed by the  $^1\text{H-NMR}$ .

At  $-10\text{ }^\circ\text{C}$  the conversion of complex **7** is quite fast since in less than 30 min it is completely absent from the  $^1\text{H}$  and  $^{31}\text{P-NMR}$ . Performing the same procedure in deuterated toluene or THF produces very similar results, with the exception that complex **7** is never fully consumed due to its lower solubility in these solvents.

The reactive complex **8** is isolated in 68 % yield by performing all operations at low temperature ( $-5\text{ }^\circ\text{C}$  or below), because at higher temperatures a carbene-carbene coupling reaction easily occurs, leading to diethyl maleate, **7** and other uncharacterized ruthenium complexes. The properties of **8** can be compared with those of the related compounds **9**<sup>8b</sup> and **10**<sup>11</sup> (chart 1), which have previously been reported by Baratta *et al.*

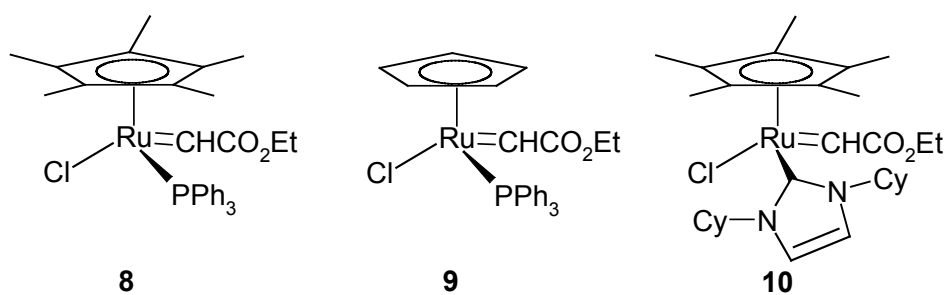
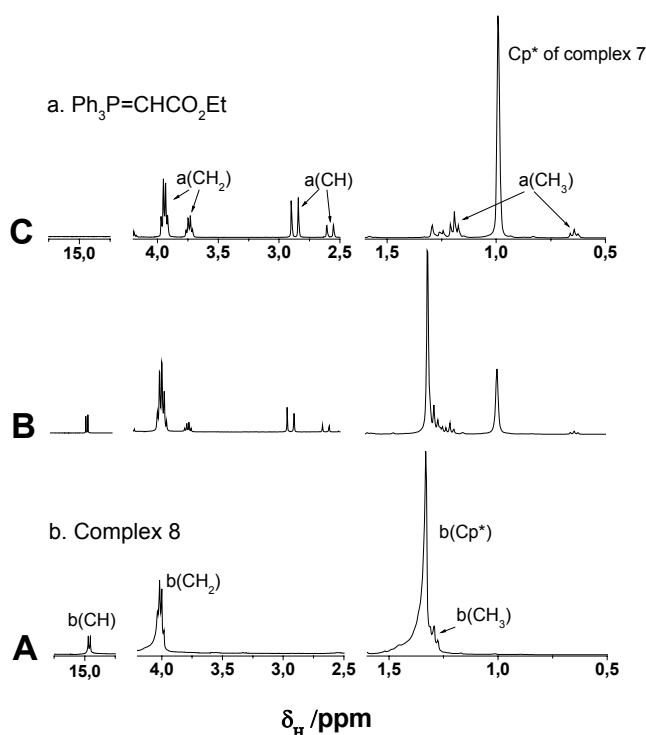


Chart 1

Thus, complex **8** is more stable than compound **9**, which was only observed in solution, due to the stabilizing effect of the  $\text{Cp}^*$  moiety, but less stable than complex **10**, containing a stabilizing N-heterocyclic carbene, which was isolated at RT and decomposes in solution after many hours. Complex **8** displays hindered rotation of the phosphane and carbene ligands. At  $-20\text{ }^\circ\text{C}$  the phenyl peaks are broad ( $^1\text{H}$  and  $^{13}\text{C}$ -

NMR) while at  $-70\text{ }^{\circ}\text{C}$  the peaks are resolved and the fine structure of the phenyl carbons is observed. The peaks of the carbene ligand change from definite peaks to broad peaks on going from  $-20$  to  $-90\text{ }^{\circ}\text{C}$ , indicating also a rotation barrier. The rotation restriction is more pronounced for the phosphane ligand, in agreement with its larger bulk.

Complex **8** reacts, as expected, with  $\text{PPh}_3$  (fig. 1): the outcome of adding less than one equivalent of phosphane is a mixture of complex **8**, complex **7** and  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ ; when using more than 2 eq of  $\text{PPh}_3$ , complex **7** is the only Ru species present plus the phosphorus ylide (in a predictable 1:1 ratio), and the excess phosphane.



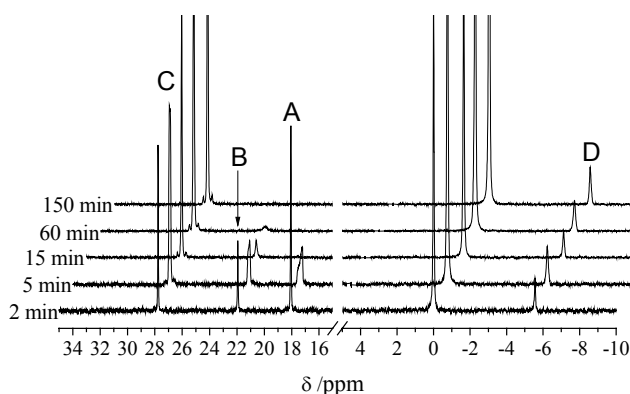
**Fig. 1** -  $^1\text{H}$ -NMR of the reaction of complex **8** with  $\text{PPh}_3$  in  $\text{CD}_2\text{Cl}_2$  at  $-30\text{ }^{\circ}\text{C}$ . (A) Complex **8**. (B) Complex **8** after addition of less than 1 eq of  $\text{PPh}_3$ . (C) Complex **8** with 2.5 eq of  $\text{PPh}_3$ . The aromatic region is excluded for simplicity purposes.

Noteworthy is the fact that this reaction occurs even at  $-50\text{ }^{\circ}\text{C}$ . The mixture reacts quantitatively with 2 eq of 4-nba within 20 min (starting at  $-30\text{ }^{\circ}\text{C}$  then proceeding to RT) to produce the corresponding olefin with a final *E:Z* ratio of 97:3 (determined by GC-MS). For comparison purposes the olefination of 4-nba, using complex **7** as catalyst in  $\text{CH}_2\text{Cl}_2$  at RT produces the same results – within the measurement error of the GC-MS technique - being the final *E:Z* ratio 96:4. The agreement between the results renders it likely complex **8** to be the active intermediate of the catalytic cycle.

Following a catalytic run by  $^1\text{H}$  and  $^{31}\text{P}$ -NMR in both the absence and in the presence of benzaldehyde in  $\text{CD}_2\text{Cl}_2$ , the identity of the species formed during the catalytic cycle becomes clearer (see experimental part for details). In the absence of aldehyde in less than 5 min the quantitative formation of phosphorus ylide and the phosphazine  $\text{Ph}_3\text{P}=\text{N}-\text{N}=\text{CHCO}_2\text{Et}$  (**XIII**) in an 86:14 ratio (by integration of  $^1\text{H}$ -NMR peaks, available as supplementary material), is observed.

The  $^{31}\text{P}$ -NMR has three main peaks besides the free  $\text{PPh}_3$  (excess): a singlet at  $\delta_{\text{P}} = 21.1$  ppm and two broad peaks corresponding to the geometrical isomers of the ylide ( $\delta_{\text{P}} = 18.0$  and  $16.4$  ppm), which, as the temperature increases, almost coalesce to a single broad peak at  $\delta_{\text{P}} = 17.9$  ppm.<sup>10</sup> It is necessary to wait 24 h until the phosphazine is almost entirely consumed, leaving ylide as the main product, observable in both  $^{31}\text{P}$  and  $^1\text{H}$ -NMR spectra.

The same reaction in the presence of benzaldehyde (fig. 2) shows some particular features: the ylide has a single sharp peak ( $\delta_{\text{P}} = 18.1$  ppm) in the  $^{31}\text{P}$ -NMR, a result of its interaction with the aldehyde;<sup>10</sup> the formation of  $\text{O}=\text{PPh}_3$  ( $\delta_{\text{P}} = 28.0$  ppm) is fast and it is present almost since the beginning of the catalysis; the ylide is consumed completely within 15 min, during which phosphazine **XIII** ( $\delta_{\text{P}} = 22.6$  ppm) scarcely reacts. After 150 min at RT the reaction is complete, as there is only the peak of  $\text{O}=\text{PPh}_3$  in the  $^{31}\text{P}$ -NMR.



**Fig. 2** -  $^{31}\text{P}$ -NMR of a catalytic benzaldehyde olefination with complex **7** at RT in  $\text{CD}_2\text{Cl}_2$ . A. Phosphorus ylide; B. Phosphazine **XIII**; C.  $\text{O}=\text{PPh}_3$ ; D.  $\text{PPh}_3$ .

These observations lead to two conclusions: a) the ylide formation is much faster than the phosphazine **XIII** formation and **XIII** is also less reactive; b) the phosphazine reaction is promoted by the presence of aldehyde.

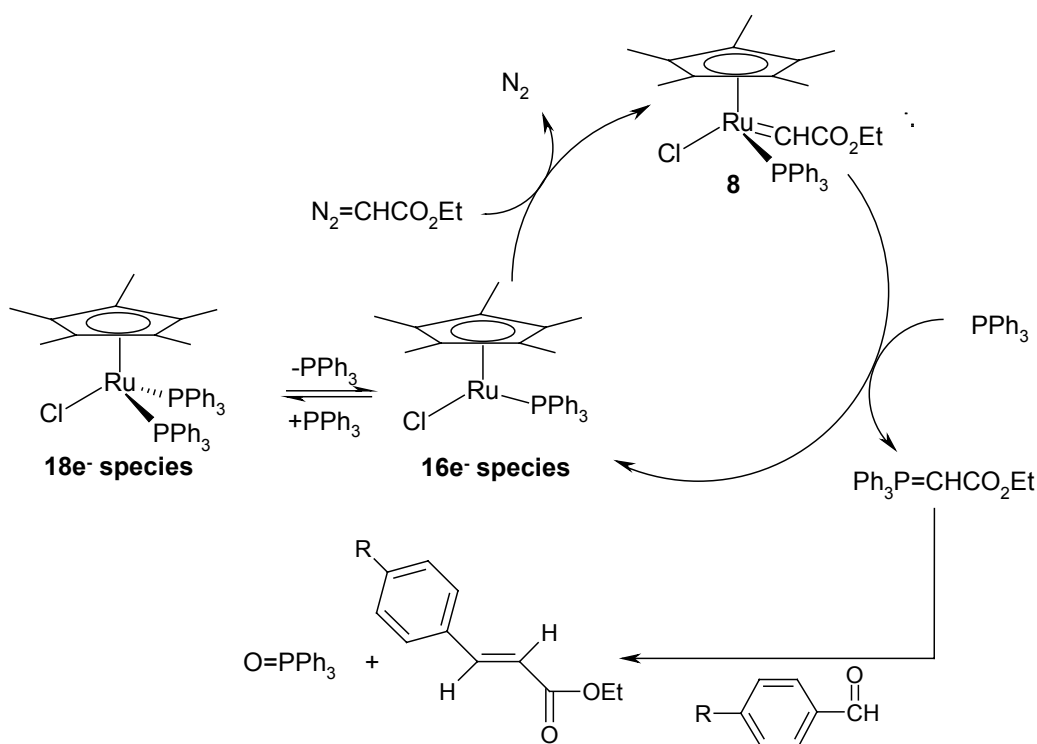
Bestmann and Göthlich<sup>12</sup> proved that in solution resonance stabilized phosphazines exist in equilibrium with the original phosphane and diazo starting compounds (Scheme 1). This suggests that even in the presence of phosphazine the actual reaction partner is EDA.



Scheme 1

A mixture of phosphazine and complex **7** (ratio 2:1) in  $\text{CD}_2\text{Cl}_2$  does not show any changes in the  $^{31}\text{P}$  or  $^1\text{H}$ -NMR between  $-30$  and  $10$  °C. At  $15$  °C a small doublet at  $\delta_{\text{H}} = 14.9$  ppm in the  $^1\text{H}$ -NMR can be observed, evidencing the presence of complex **8** in solution. At  $20$  °C there is a small peak at  $\delta_{\text{P}} = 51$  ppm in the  $^{31}\text{P}$ -NMR (complex **8**). However, it is necessary to let the sample react for 20 minutes at  $20$  °C to observe the first peak of  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$  in the  $^{31}\text{P}$ -NMR.

The conversion of phosphazine into phosphorus ylide should be faster as the equilibrium is shifted to the starting materials. This explains why the presence of aldehyde in solution - which pushes the reaction forward through the formation of the olefin - or a temperature increase, enhance the conversion rate since they drive the equilibrium toward the right side of scheme 1.



For highly active catalysts like complex **7**, the phosphazine formation is strongly suppressed and should only become significant at very low catalyst loadings, therefore, the main reaction pathway for complex **7** should be the one described in scheme 2.

Therefore, the best catalysts promote the direct formation of  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$  from EDA and  $\text{PPh}_3$ , avoiding the production of phosphazine **XIII**, a comparatively sluggish reactant. The first step, release of phosphane and formation of complex **8** by reaction with EDA, occurs at temperatures above  $-10\text{ }^\circ\text{C}$ . The second step, formation of the phosphorus ylide through reaction of complex **8** with  $\text{PPh}_3$  is considerably easier and occurs even at  $-50\text{ }^\circ\text{C}$ . The third step, reaction of the phosphorus ylide with the aldehyde was considered above in terms of ylide structure and reactivity. For this class of ruthenium complexes the different *E:Z* ratios obtained with catalysts **1**, **6** and **7** (table 1, entries 1, 6 and 7, respectively) show that the catalyst might play a certain role in the third step influencing the reactions selectivity. The *E:Z* selectivity obtained with complex **7** is (within the experimental error) for several tested aldehydes (**I**, **II** and **III**) equal to the selectivity obtained in the non-catalysed Wittig reaction using similar reaction conditions. The NMR studies also did not show any noticeable interaction between this catalyst and the phosphorus ylide so that it may be concluded the role of complex **7** in the third step being negligible to the reaction outcome.

To the best of our knowledge, the reaction rate enhancement effected by benzoic acid was never fully understood. Some authors suggest the carbonyl to be protonated by the acid making it more electrophilic and prone to a nucleophilic attack by the ylide.<sup>2d</sup>

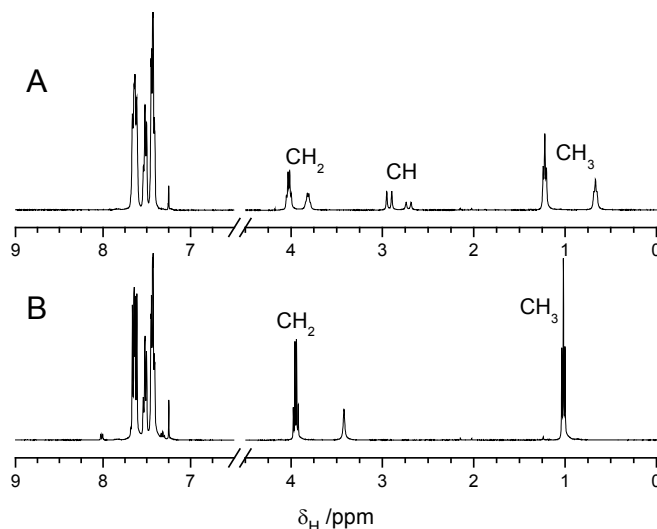
A  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of a mixture of acetophenone:benzoic acid (1:0.5) resembles the arithmetic sum of the spectra of the individual compounds, therefore excluding a significant interaction between the compounds and less likely any activation toward the olefination reaction.

Addition of benzoic acid to the phosphorus ylide changes their NMR spectra considerably (fig. 3 and 4).

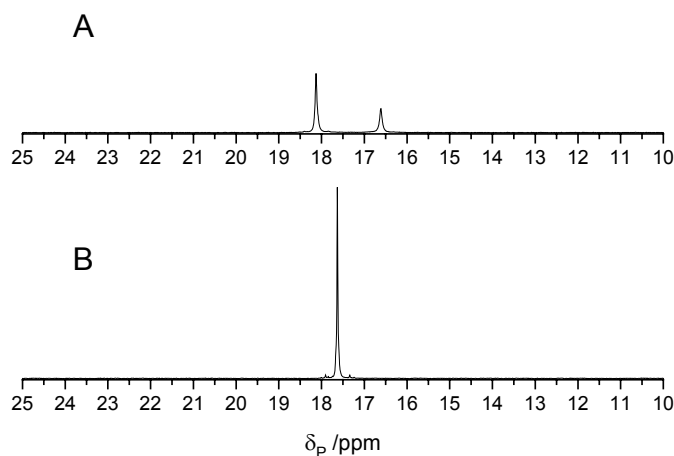
One of the main features is the collapse of the peaks of the ylide's cis and trans isomers. This pattern is similar to that observed on addition of benzaldehyde to the ylide.<sup>10a-b</sup> The collapse of the peaks indicates that the interconversion between cis and trans isomers is very fast (on the NMR timescale).

Hooper *et al.*<sup>10b</sup> suggested that during the Wittig reaction neither the cis nor trans isomers of the phosphorus ylide seem to readily react with the carbonyl group. Instead the reaction is carried by an intermediate present during the interconversion of the two

isomers, which bears a negative charge on the methine carbon (scheme 3).<sup>10b</sup> In the presence of traces of water or acidic protons (to promote the protonation of the isomers), the carbonyl of benzaldehyde easily “traps” this reactive intermediate and thereby the peaks collapse.



**Fig. 3** –  $^1\text{H}$ -NMR spectra of the phosphorus ylide: (A) dried over  $\text{CaH}_2$ ; (B) after addition of *ca.* 0.1 eq of benzoic acid to A.

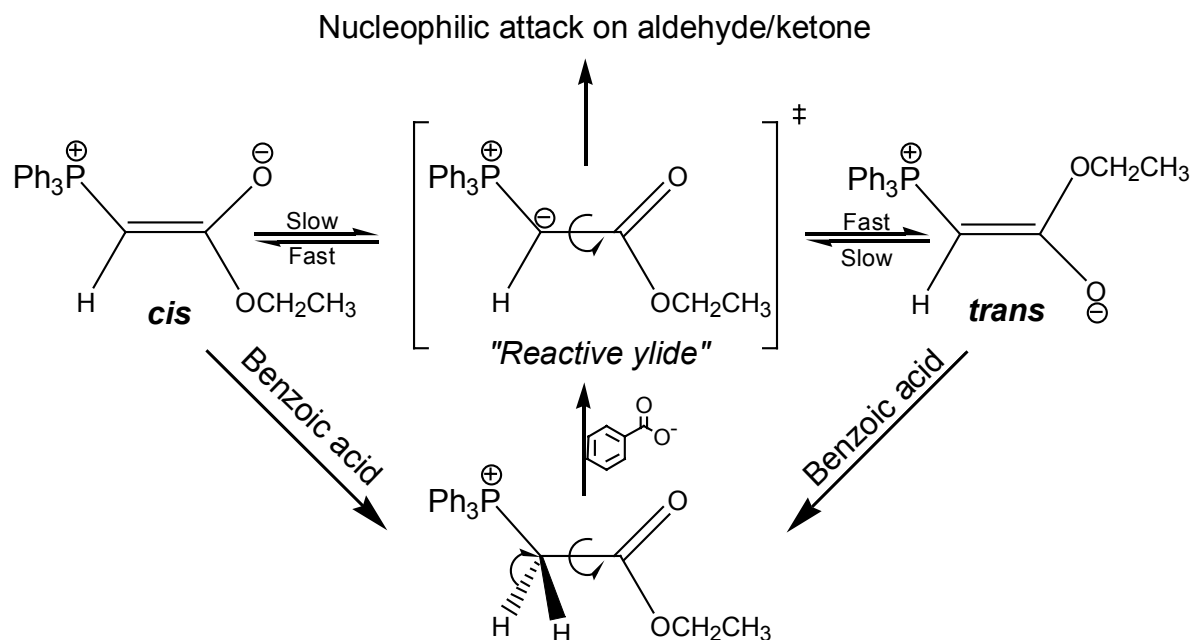


**Fig. 4** –  $^{31}\text{P}$ -NMR spectra of the phosphorus ylide: (A) dried over  $\text{CaH}_2$ ; (B) after addition of *ca.* 0.1 eq of benzoic acid to A.

Mixing acetophenone with the ylide (1:1) no such collapse is observed, indicating that the ketone cannot “trap” the reactive intermediate due to its low electrophilic character. The benzoic acid, however, greatly increases the concentration of the “reactive ylide” in solution, while not reacting with it (scheme 3), making it available to



nucleophilic attack on a carbonyl group. Still the carbonyl group of ketones is much less electrophilic than the carbonyl of aldehydes and concomitantly the reactions are considerably slower with ketones than with aldehydes. Nevertheless the trend is clear, the more electrophilic is the ketone's carbonyl, the higher is the reaction rate.



Other interesting features observed in fig. 3 are the position of the methine proton and its lack of coupling with the phosphorus. While the position of the methylene and methyl protons appear to be the average of the initial positions and relative amounts of each isomer existing before the addition of the benzoic acid, the methine proton is considerably shifted towards lower fields. Further experiments using different amounts of benzoic acid unveil that this peak shifts to lower fields as the relative amount of benzoic acid increases. We conclude that the proton must be switching between the two ylide isomers and the benzoic acid and the result peak is an average of these three contributions. A calculation of the expected position of this peak simply based on the amounts of each component and the peaks original positions leads to  $\delta_{\text{H}}(\text{CH}) = 3.48$  ppm as the expected chemical shift of the methine proton and is in very good agreement with the experimental result  $\delta_{\text{H}}(\text{CH}) = 3.42$  ppm (fig. 3), thus confirming the above described suggestion. The lack of coupling with phosphorus of the resulting peak stems from this same process, since the proton while coordinated to benzoic acid does not couple with the phosphorus.

### 5.3 Conclusion

Investigations on the mechanism show the existence of a mixed carbene/phosphane ruthenium intermediate, complex **8**, which was isolated and characterized. The catalytic cycle is triggered by EDA, and the ylide  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$  is formed by reaction of complex **8** with  $\text{PPh}_3$ . Under catalytic conditions phosphazine **XIII**, a less reactive reaction partner, is also formed and exists in equilibrium with its precursor compounds. Highly active catalysts like complex **7** largely suppress phosphazine formation.

Benzoic acid promotes the catalytic reaction with both aldehydes and ketones, by facilitating the transition between cis and trans isomers of the phosphorus ylide and hence increasing the presence of the “reactive ylide” in solution, making it available to react with otherwise unreactive ketones.

## 6. Heterogenization of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ and its catalytic application for cyclopropanation of styrene using ethyl diazoacetate

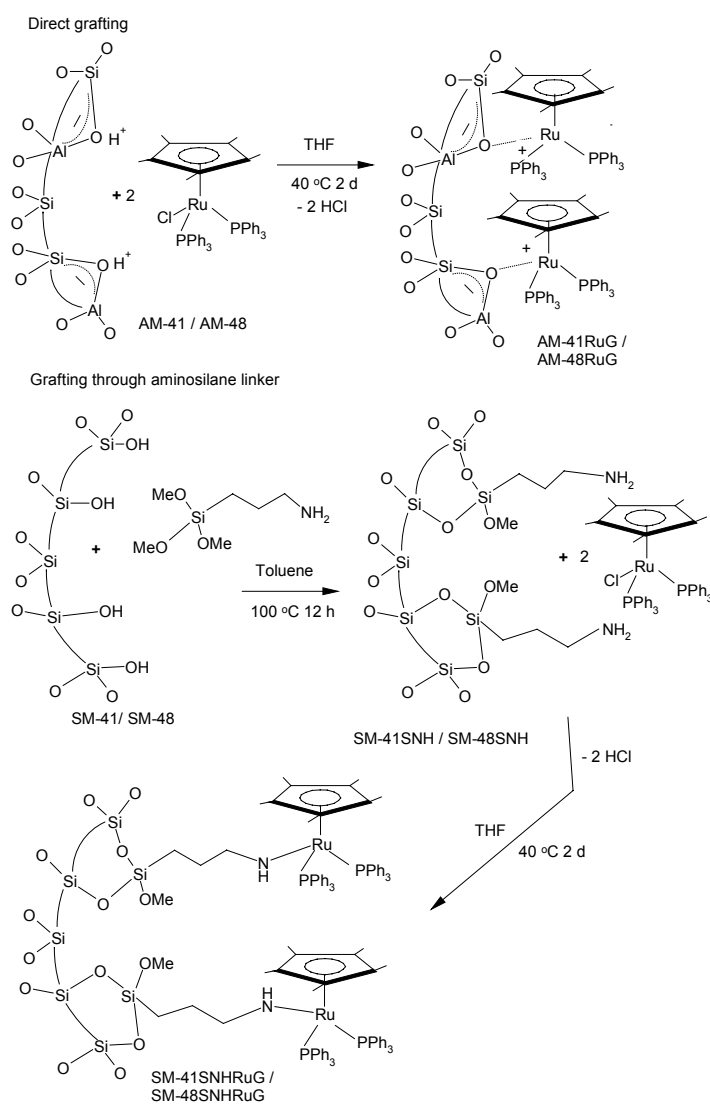
### 6.1 Background

The implementation of organometallic complexes as catalysts for organic synthesis is a continuously developing field. The trends clearly point to a growing demand for efficient, selective, and low cost catalysts that can be easily separated from the product(s). Ruthenium compounds of the general formula  $\text{Cp}'\text{RuX}(\text{PR}_3)_2$  found widespread applications in catalysis.<sup>1,2</sup> The ease of their synthesis, the wide array of ligands available to coordinate with the metal centre and their general high stability makes them a versatile class of catalysts. Recently, various research groups have started to apply this compound family for aldehyde olefination<sup>1-3</sup> and more recently for cyclopropanation reactions.<sup>4</sup> Aldehyde olefination is an important transformation for the production of carbon-carbon double bonds. The catalytic approach is a valid alternative to the Wittig type reactions since it allows generation of phosphorus ylides in non-basic and generally mild conditions, suitable for base sensitive substrates.<sup>5</sup> Ruthenium complexes, such as  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  (**1**) besides displaying a high activity, are among the most selective catalysts for this reaction reported to date.<sup>3</sup> Cyclopropanation of olefinic bonds using diazo compounds as a carbene source is among the best developed and most useful transformations available to the synthetic organic chemist.<sup>6,7</sup> Cyclopropane derivatives are basic structural elements in a wide range of naturally occurring and biologically active compounds and they are versatile synthetic intermediates in the synthesis of functionalised cycloalkanes and acyclic compounds. Strained cycloalkanes have also been prepared to test their bonding features and to study enzyme mechanisms and their inhibition. The ruthenium-catalysed cyclopropanation reaction envisaged an exponential development in recent years. The main reasons for that development lay in the lower price of the ruthenium based catalysts, when compared to rhodium derivatives, and their richer reaction chemistry, providing a wide array of ruthenium complexes.<sup>7</sup>

Catalyst heterogenization, i.e. the immobilization of the catalyst on a supporting material allowing an easy product isolation and catalyst recycling, attracts also considerable industrial attention,<sup>8</sup> since cost-reducing advantages are very important, particularly at industrial scale production. Among the various supporting materials studied, the mesoporous silicates known as MCM-41 and MCM-48<sup>9</sup> with regular pore size, large

surface areas, large number of surface silanol groups, and high chemical and thermal stability, are potential and promising candidates as both catalysts and catalyst supports.<sup>10,11</sup> To the best of our knowledge the only extensive studies published on ruthenium catalyst heterogenization deal with Ru(II) porphyrin and amine derivatives.<sup>12</sup> These particularly effective immobilized catalysts were mainly applied in alkene epoxidation<sup>12b,5g</sup> and in a few cases also in intermolecular cyclopropanation.<sup>12f</sup> As a rule, the performance of the immobilized catalysts surpassed, in these cases, that obtained with their homogeneous phase counterparts.

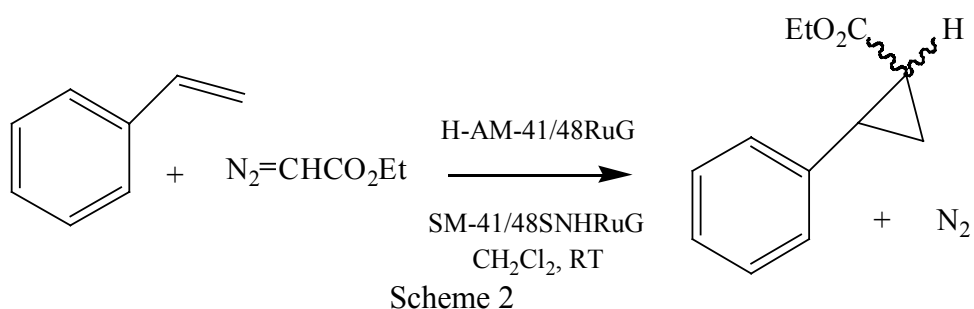
In the present work, complex **1** is grafted on the surface of mesoporous materials by direct reaction with mesoporous aluminosilicate (H-AMCM-41 and H-AMCM-48) or with aminosilane linker modified mesoporous silicate materials (designated as SM-41SNH, and SM-48SNH) (Scheme 1).



Scheme 1

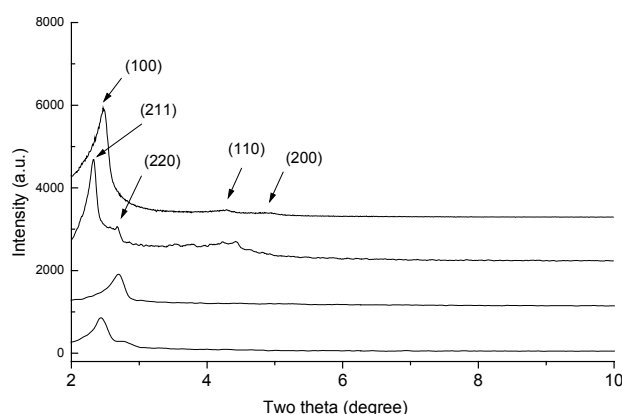
Complex **1** grafted in H-AlMCM-41, H-AlMCM-48, SM-41SNH, and SM-48SNH samples are designated as HAM-41RuG, HAM-48RuG, SM-41SNHRuG, and SM-48SNHRuG, respectively.

The grafted materials obtained from the heterogenization of the compound **1** were systematically characterized by powder X-ray diffraction (XRD), N<sub>2</sub> adsorption/desorption (BET), TEM analysis, thermogravimetry coupled with mass spectroscopy (TG-MS), FT-IR and NMR spectroscopic methods. The grafted samples are applied in the catalytic styrene cyclopropanation (Scheme 2).



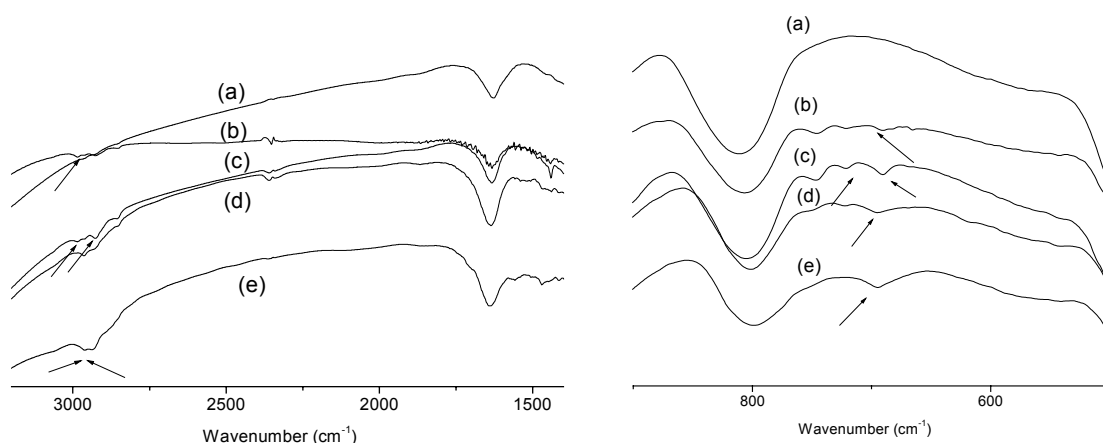
## 6.2 Results and Discussion

The powder XRD pattern of complex **1** grafted MCM-41 and MCM-48 samples are in full agreement with reported pattern,<sup>8-10</sup> indicating the samples to be well ordered (Fig. 1).<sup>9,10</sup> Several distinct Bragg peaks are observed in the  $2\theta = 2-8^\circ$  region, which can be indexed to different hkl reflections for a hexagonal unit cell (using the strongest reflection,  $d_{100}$ ) and a cubic unit cell (using the strongest reflection,  $d_{211}$ ), respectively.



**Fig. 1** - XRD pattern of (a) HAM-41RuG; (b) HAM-48RuG; (c) SM-41SNHRuG; (d) SM-48SNHRuG.

Even after grafting bulky complex **1** on mesoporous surfaces (Fig. 1) the higher  $2\theta$  peaks are still observed, indicating the retention of long-range hexagonal and cubic symmetry. Compared to parent MCM-41 and MCM-48,<sup>10e</sup> the grafted samples show a decrease in the relative intensities of the XRD reflections and there is a clear shift to higher  $2\theta$  values (for the decrease in inter-planar distances and unit cell parameters, see Table 1). These changes originate from the immobilization of the bulky organometallic Ru complexes inside the channels of MCM-41 and MCM-48.<sup>9-11</sup>



**Fig. 2** - FT-IR spectra of (a) MCM-41, (b) HAM-41RuG, (c) HAM-48RuG, (d) SM-41SNHRuG and (e) SM-48SNHRuG.

Fig. 2 depicts the FT-IR spectra of parent calcined mesoporous MCM-41, MCM-48 and of the grafted samples. The bands at 1206, 1060, and 794  $\text{cm}^{-1}$  are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). New, comparatively weak bands around 3000, 2957, and 2927  $\text{cm}^{-1}$  can be assigned to cyclopentadienyl (Cp), and triphenylphosphane group vibrations of the grafted compounds. Additional bands appear for SM-41SNHRuG, and SM-48SNHRuG samples in the range of 2853  $\text{cm}^{-1}$  due to C-H stretching vibrations, originating from the  $\text{CH}_2$  groups present in the silane ligand. Additional bands appear at 690 and 745  $\text{cm}^{-1}$ , due to C-C bending vibration from the phenyl ring.<sup>13</sup> Elemental analyses (EA) indicate (Table 1) that aluminium containing MCM-41/48 show a relative low Ru content (0.2-0.4 wt.%) when compared to the amino silane linker modified MCM-41/48 (0.9-1.8 wt. %). The presence of more Ru in the amino silane linker containing mesoporous samples compared to pure aluminium samples is attributed to the ease of the reaction of the Ru complex with the amino func-

tional group of the linker (0.12-0.25 mol % of linker on the surface based on C, H, N elementary analysis), as shown in Scheme 1.

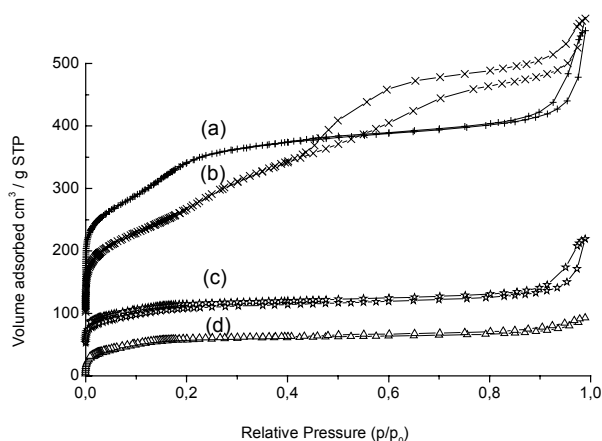
The low temperature N<sub>2</sub> adsorption/desorption isotherm is of type IV according to the IUPAC<sup>14</sup> and characteristic for mesoporous solids. However, compared to parent mesoporous samples (Table 1),<sup>10e</sup> the samples bearing grafted Ru complex (Fig. 3) exhibit a drastic decrease in N<sub>2</sub> uptake and surface area (10-70 %; Table 1) due to both the presence of quite large amounts of the comparatively bulky organometallic molecules and to bridging silane moieties on the surface of the mesoporous channels.

**Table 1** Textural properties of MCM-41/MCM-48 and the samples grafted with the Cp<sup>\*</sup>Ru complexes.

Sample	Ru wt. %	Interplane distance (nm) <sup>a</sup>	Unit cell parameter $\bar{a}$ (nm) <sup>b</sup>	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore diameter (nm)
MCM-41	—	3.80	4.39	839	2.74
MCM-48	—	3.97	9.72	1043	2.41
H-AM-41RuG	0.2	3.59	4.14	770	2.1-3.0
H-AM-48RuG	0.35	3.78	9.28	680	2.1-3.5
SM-41SNHRuG	0.9	3.26	3.76	211	1.5-5.0
SM-48SNHRuG	1.8	3.60	8.82	200	1.4-5.1

<sup>a</sup>  $d_{100}$  for MCM-41 and  $d_{211}$  for MCM-48.

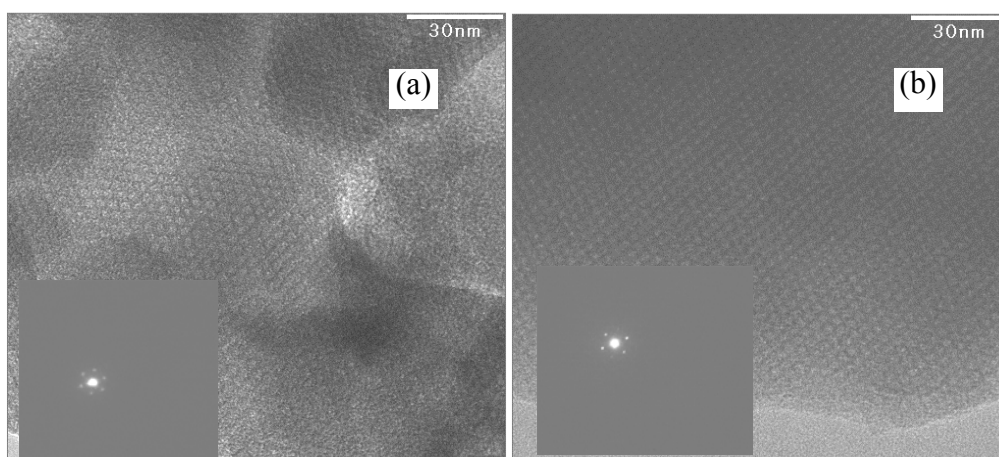
<sup>b</sup>  $\bar{a} = 2d_{100}/\sqrt{3}$  for MCM-41;  $\bar{a} = d_{hkl} (h^2+k^2+l^2)^{1/2}$  for MCM-48.



**Fig. 3** - N<sub>2</sub> adsorption/desorption isotherms of (a) HAM-41RuG, (b) HAM-48RuG, (c) SM-41SNHRuG and (d) SM-48SNHRuG.

The parent MCM-41 and MCM-48 samples exhibit narrow pore size distributions with average pore diameters of 2.7 and 2.4 nm respectively. The grafted materials exhibit a broader pore size distribution (1.4-3.0 nm) and also display a decrease in surface area and unit cell parameter (see Table 1) compared to parent MCM-41 and MCM-48.<sup>10e</sup> The decrease of the unit cell value and the broad pore size distribution evidences that the organometallic complexes in the grafted mesoporous samples are mainly located on internal surfaces of the mesoporous materials.<sup>9-11</sup>

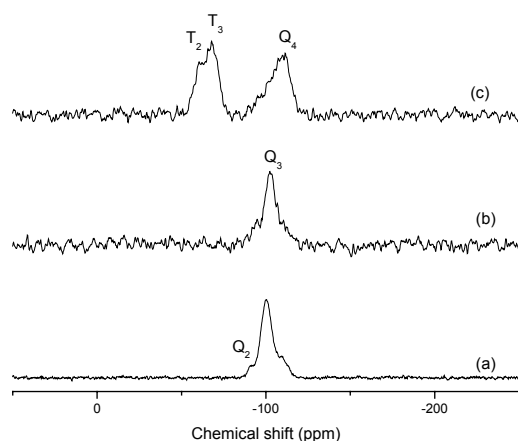
The TEM images (see Fig. 4) of the grafted samples (SM-41SNHRuG, and SM-48SNHRuG) provide strong evidence that the mesoporous structure of the support retains its long range ordering<sup>9,10</sup> throughout the grafting process and that the channels remain accessible. The ED pattern of the grafted samples shows the reflection of the (100) plane, which further supports the presence of long range ordering in the samples, even after blocking of some pores by linker molecules and Ru complexes.



**Fig. 4** - TEM image and electron diffraction pattern of (a) SM-41SNHRuG and (b) SM-48SNHRuG.

The parent MCM-48 and the grafted samples were examined by solid-state <sup>29</sup>Si CP MAS NMR spectroscopy. The parent MCM-48 exhibits two broad elaborate resonances (Fig. 5a) in the <sup>29</sup>Si CP MAS NMR spectrum at  $\delta = -113.0$  and  $-103.8$  ppm, assigned to Q<sub>4</sub> and Q<sub>3</sub> species of the silica framework, respectively, [Q<sub>n</sub> = Si(OSi)<sub>n</sub>(OH)<sub>4-n</sub>].<sup>9-11</sup> A weak shoulder is also observed at  $\delta = -94.5$  ppm for the Q<sub>2</sub> species. After grafting of complex **1** (Fig. 5b) there is an increase of Q<sub>4</sub> and Q<sub>3</sub> intensities and a corresponding Q<sub>2</sub> species decrease, which indicates the successful grafting of complex **1** on AIMCM-41/48.



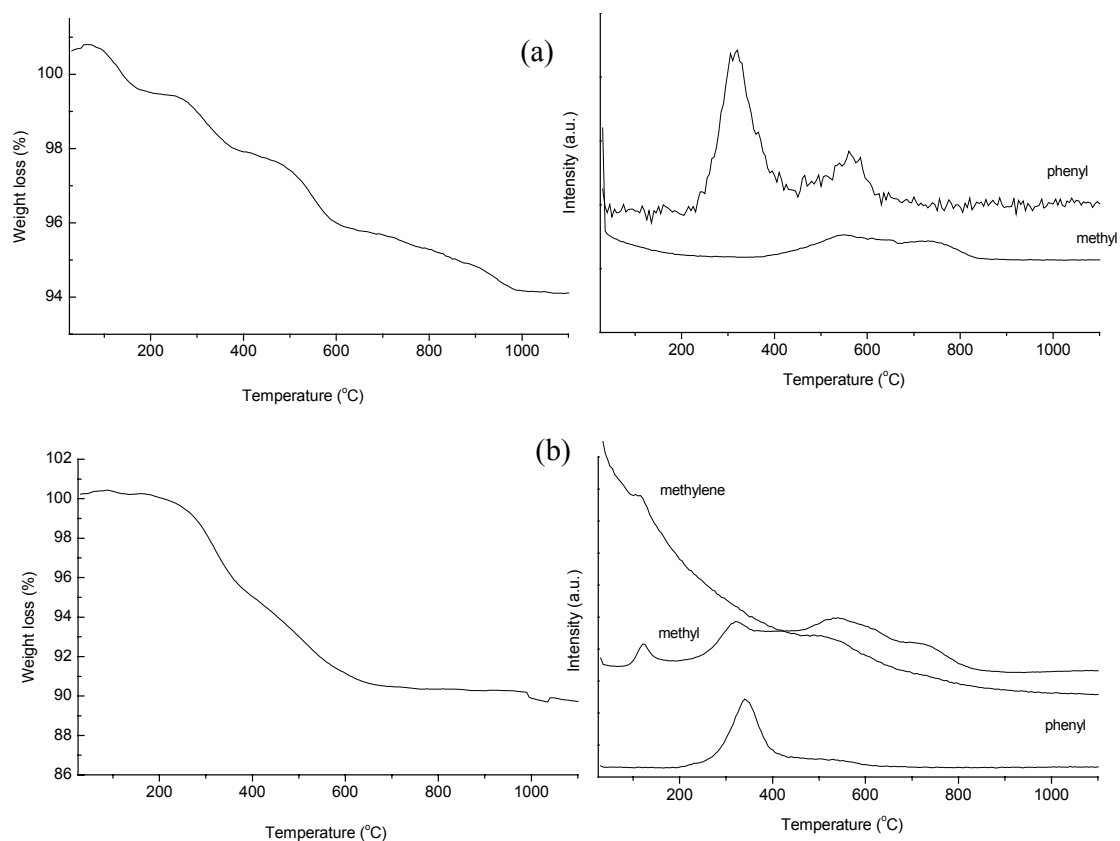


**Fig. 5** -  $^{29}\text{Si}$  CP MAS NMR spectrum of (a) MCM-48, (b) HAM-48RuG, and (c) SM-48SNHRuG.

The grafting of  $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$  also results in the reduction of the  $\text{Q}_2$  and  $\text{Q}_3$  resonances, and a concurrent increase of the  $\text{Q}_4$  resonance. The changes of the  $\text{Q}_4$  resonances are more pronounced due to the higher loading. This is consistent with an esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atoms in the organic ligand.<sup>10</sup> The  $^{29}\text{Si}$  CP MAS NMR spectra also exhibit two additional signals at  $\delta = -61.4$  and  $-67.4$  ppm assigned to  $\text{T}_2$  and  $\text{T}_3$  organosilica species, respectively, [ $\text{T}_m = \text{RSi}(\text{OSi})_m(\text{OR})_{3-m}$ ]. However, as expected, the silylated but not Ru-containing and the Ru grafted samples show (nearly) identical  $^{29}\text{Si}$  CP MAS NMR signals, thus indicating that during the *in-situ* grafting process there is no significant change in the silicon environment. The observed changes in the  $^{29}\text{Si}$  CP MAS NMR spectra arise during the silylating procedure using the aminosilane. The  $^1\text{H}$  MAS NMR spectra of all the samples show signals at  $\delta = 7.7$ ,  $7.2$ ,  $6.8$  and  $1.92$  ppm, characteristic for the Cp, phenyl and methyl groups of complex **1**. The additional peak at  $3.30$  ppm for SM-41SNHRuG, and SM-48SNHRuG samples is due to the residual OMe groups attached to silane. All the above-described studies support the successful grafting of complex **1** in the mesoporous channels of MCM-41 and MCM-48.

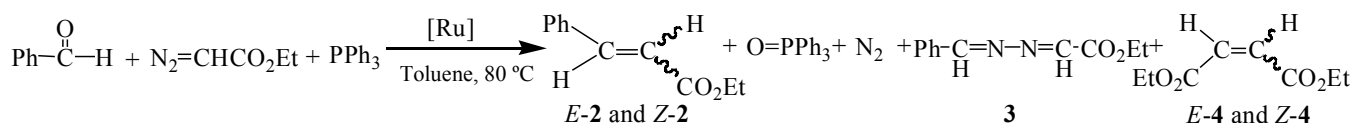
The TG-MS spectra of HAM-41RuG and SM-41SNHRuG (Fig. 6) show about 2.5 and 8.5 % weight loss up to  $1000$  °C, due to decomposition of the  $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2$  moiety. The observed mass values  $m/z^+ = 77$  and  $15$  are corresponding to a phenyl and methyl group of complex **1**, which once again confirms the presence of Ru-complexes in the mesoporous channels. In addition, the presence of mass values  $m/z^+ = 14$  and  $31$

in the SM-41SNHRuG sample are characteristic of methylene (CH<sub>2</sub>) and residual methoxy groups of silane.



**Fig. 6** - TG-MS spectrum of (a) (HAM-41RuG, and b) SM-41SNHRuG.

Applying materials with the grafted complex **1** to benzaldehyde olefination with ethyl diazoacetate (EDA) and triphenylphosphine (PPh<sub>3</sub>) (scheme 3) shows two different types of behavior: SM-41SNHRuG and SM-48SNHRuG display almost no catalytic activity with only trace amounts of *E*-**2** being formed, being azine **3** the major product along with traces of **4**; HAM-41RuG and HAM-48RuG afford olefin yields of 15-20 % with an *E* : *Z* ratio of 99:1. The reaction profiles for the latter materials follow a similar trend: a steady olefin formation until *ca.* one hour of reaction time followed by no olefin yield improvement during the rest of the reaction time with concomitant build up of azine **3**.



Scheme 3

According to scheme 3, the pores of the grafted materials have to accommodate not only the quite bulky complex **1**, bearing two PPh<sub>3</sub> ligands, but an extra PPh<sub>3</sub> for oxygen abstraction of the aldehyde and the resulting triphenylphosphane oxide.

The N<sub>2</sub> adsorption/desorption data show that in the case of SM41-SNHRuG and SM48-SNHRuG with complex loadings of 0.9 and 1.8 %, respectively, already 75% of the pores are occupied, thus preventing the incoming PPh<sub>3</sub> to reach the catalytic center, thus blocking any catalytic activity. Materials HAM-41RuG and HAM-48RuG, having much lower Ru complex loadings (0.2 and 0.35 %, respectively) are initially catalytically active, but after a while (ca. 1 hour of reaction time) the pores are also blocked, preventing the olefination reaction to further proceed. To overcome these problems it is essential to use supporting materials with bigger pore dimensions and to keep the catalyst loading at low levels to avoid complete pore blocking.

The grafted MCM-41 and MCM-48 materials were additionally applied in the styrene cyclopropanation with EDA at room temperature (Scheme 2) and the results are displayed in table 2. The grafted materials show medium to good activity in the cyclopropanation reaction, when compared to their homogeneous phase counterpart, with prevailing *E*-selectivity, as expected.

The three-dimensional pore structure of MCM-48 is beneficial to the reaction, since these grafted materials achieve better performances than the ones grafted on the one-dimensional MCM-41, regarding both activity and *E*-selectivity, for both immobilization techniques.

**Table 2** Cyclopropanation of styrene over Cp<sup>\*</sup>Ru complex grafted samples <sup>a</sup>

Samples	Isolated yield (%) <sup>b</sup>	Product distribution	
		Cis- ( <i>Z</i> )	Trans- ( <i>E</i> )
Compound <b>1</b>	56.3	31.3	68.7
H-AM-41RuG	28.1	39.4	60.6
H-AM-48RuG	36.0	34.8	65.2
SM-41SNHRuG	49.2	22.4	77.6
SM-48SNHRuG 1 <sup>st</sup> run	68.5	8.4	91.6
SM-48SNHRuG 2 <sup>nd</sup> run	56.8	27.0	73.0
SM-48SNHRuG 3 <sup>rd</sup> run	55.5	26.9	72.1

<sup>a</sup> Catalyst : Styrene = 1 : 250; <sup>b</sup> Based on EDA conversion; Time = 16 h; Temperature = RT.

The yields are considerably higher when complex **1** is grafted through the aminosilane linker, especially for SM-48SNHRuG, rather than when immobilized by direct grafting.

The higher catalyst loadings might be the cause for these activity differences. The fact that SM-48SNHRuG is considerably more active and selective than complex **1**, when used in homogeneous catalysis conditions, lead us to reuse it for two additional runs. There is a slight decrease of activity on the second run, but the fact that it remains active for the third run shows that grafted compound **1** is stable on the surface and remains active for several catalytic cycles. The slight decrease in activity and selectivity in the recycled catalyst is possibly due to some adsorption of organic molecules on the channels of the mesoporous materials. The inexistence of Ru in the filtrate, as well as the absence of catalytic conversion in the filtrate, indicate that the catalyst is stable and the leaching of complex **1** is insignificant. The reaction can be conveniently performed in CH<sub>2</sub>Cl<sub>2</sub> avoiding the use of styrene itself as solvent for the reaction, which is favourable regarding both starting materials usage and product isolation. There are also no C-H insertion side products, which were observed in homogeneous catalysis.<sup>4b</sup> These features are obvious advantages over the homogeneous catalysis system.

### 6.3 Conclusions

A ruthenium complex of formula ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl (**1**) was successfully grafted on the surface of mesoporous MCM-41 and MCM-48 either by direct grafting or by an aminosilane linker. The obtained materials are stable and the structures of the supporting materials remain intact. The heterogenized catalysts are active in the cyclopropanation of styrene with EDA, especially SM-48SNHRuG whose activity and selectivity are both higher than in homogeneous catalysis. This catalyst is active even after several recycling cycles, with just a slight activity decrease.

## 7. Grafting of Cyclopentadienyl Ruthenium Complexes on aminosilane linker modified mesoporous SBA-15 silicates

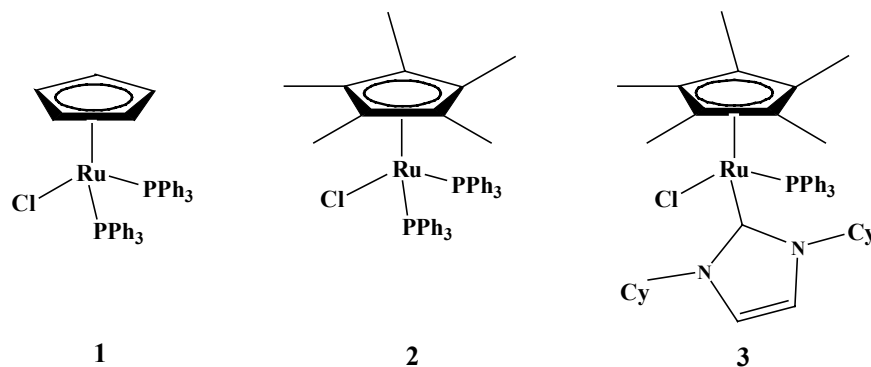
### 7.1 Background

Organic synthesis has made remarkable progress due to transition metal catalysts in recent decades.<sup>1</sup> In particular, the implementation of organometallic complexes as catalysts for organic syntheses is a continuously developing field. Ruthenium compounds of the general formula  $\text{Cp}^*\text{RuX}(\text{PR}_3)_2$ ,  $\text{Cp}^*\text{RuX}(\text{PR}_3)(\text{C}_3\text{N}_2\text{R}_5)$ , etc., have found widespread applications in catalysis.<sup>2-5</sup> Recently, various research groups have started to apply this compound family for aldehyde olefination<sup>2-6</sup> and more recently for cyclopropanation reactions.<sup>7,8</sup> Aldehyde olefination is an important transformation for the production of carbon-carbon double bonds.<sup>8</sup> Ruthenium complexes, such as  $\text{CpRuCl}(\text{PPh}_3)_2$ ,  $\text{Cp}^*\text{RuX}(\text{PR}_3)_2$ ,  $\text{Cp}^*\text{RuX}(\text{PR}_3)(\text{C}_3\text{N}_2\text{R}_5)$ , (**1-3**) besides displaying a high activity, are among the most selective catalysts for this reaction reported to date.<sup>6</sup> On the other hand cyclopropanation of olefinic bonds utilizing diazo compounds as a carbene source is one of the best developed and most useful transformations available to the synthetic organic chemist.<sup>9,10</sup> The ruthenium-catalysed cyclopropanation reaction experienced a fast development in recent years. The main reasons for this lay in the lower price of the ruthenium based catalysts, when compared to rhodium derivatives, and their richer reaction chemistry.<sup>10</sup>

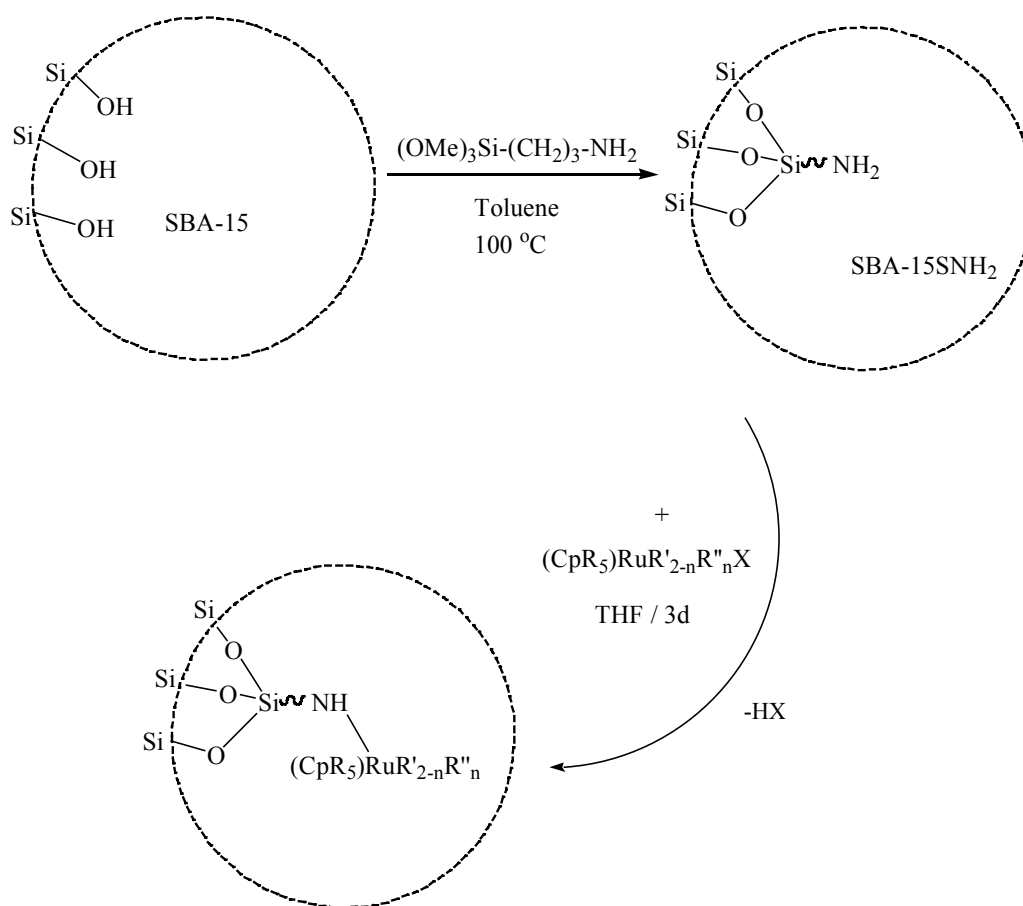
Catalyst heterogenization, i.e. the immobilization of the catalyst on a supporting material allowing an easy product isolation and catalyst recycling, attracts also considerable industrial attention.<sup>11</sup> Among the various supporting materials studied, the mesoporous silicate known as SBA-15<sup>12</sup> with a regular pore size, a large surface area, a large number of surface silanol groups, and a high chemical and thermal stability, is a potential and promising candidate as both catalyst and catalyst support.<sup>13,14</sup> To the best of our knowledge the only extensive studies published on ruthenium catalysts heterogenization deal with Ru(II) porphyrin and amine derivatives, which were also exclusively heterogenized on hydro-thermally less stable mesoporous MCM-41 materials.<sup>15</sup> These particularly effective immobilized catalysts were mainly applied in alkene epoxidation<sup>15b,8g</sup> and in a few cases also in intermolecular cyclopropanation.<sup>15f</sup>

In the present work, cyclopentadienyl ruthenium phosphane complexes **1-3** are grafted on the surface of aminosilane linker modified mesoporous SBA-15 silicate material (designated as SBA-15SNH<sub>2</sub>) (Scheme 1). Complexes **1-3** grafted in samples

of SBA-15SNH<sub>2</sub> are designated as SBA-15SNH<sub>2</sub>CpRu, SBA-15SNH<sub>2</sub>Cp\*Ru and SBA-15SNH<sub>2</sub>Cp\*RuNHC, respectively. The grafted materials were systematically characterized and applied as catalysts for benzaldehyde olefination as well as styrene cyclopropanation using ethyl diazoacetate (EDA).



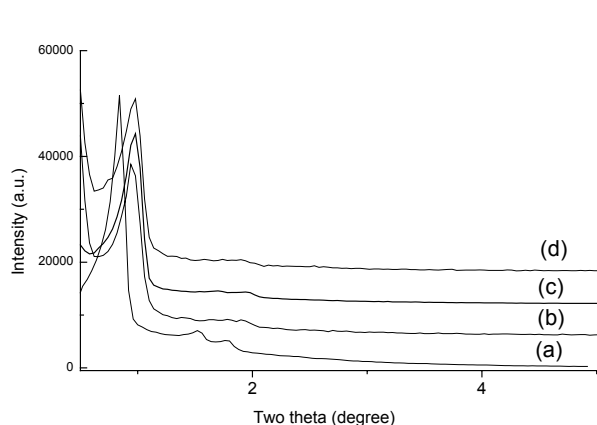
(CpR<sub>5</sub>)RuR'<sub>2-n</sub>R''<sub>n</sub>X where R = H (or) CH<sub>3</sub>; R' = PPh<sub>3</sub>; R'' = carbene; X = Cl; Cy = cyclohexyl



Scheme 1

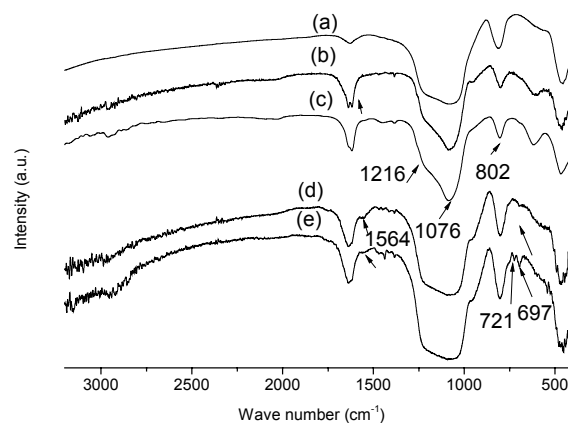
## 7.2 Results and Discussion

The low angle powder XRD pattern of the grafted Ru complex samples are depicted in Fig. 1. The XRD pattern of SBA-15 (Fig. 1a), where the main reflection corresponds to a hexagonal unit cell<sup>12,13d</sup> is observed at a  $2\theta$  range of  $0.84^\circ$ , and two other weak reflections are found in the  $2\theta$  range of  $1-2^\circ$ , with an indexing referring to the (110) and (200) planes. The grafted ruthenium complex samples exhibit a main reflection corresponding to the (100) plane. However, compared to parent SBA-15 (Fig. 1a),<sup>13d</sup> the grafted samples show a decrease in the relative intensities and line broadenings of the XRD reflections and there is a clear shift to higher  $2\theta$  values ( $2\theta$  range  $0.94^\circ$ ,  $0.97^\circ$  and  $0.98^\circ$  for SBA-15SNH<sub>2</sub>CpRu, SBA-15SNH<sub>2</sub>Cp\*Ru and SBA-15SNH<sub>2</sub>Cp\*RuNHC, respectively) and also a decrease in inter-planar distance (see Table 1). These changes originate from the immobilization of the bulky organometallic Ru complexes inside the



channels of SBA-15.<sup>13,14</sup>

**Fig. 1.** Low angle powder XRD pattern of (a) SBA-15, (b) SBA-15SNH<sub>2</sub>CpRu, (c) SBA-15SNH<sub>2</sub>Cp\*Ru and (d) SBA-15SNH<sub>2</sub>Cp\*RuNHC.

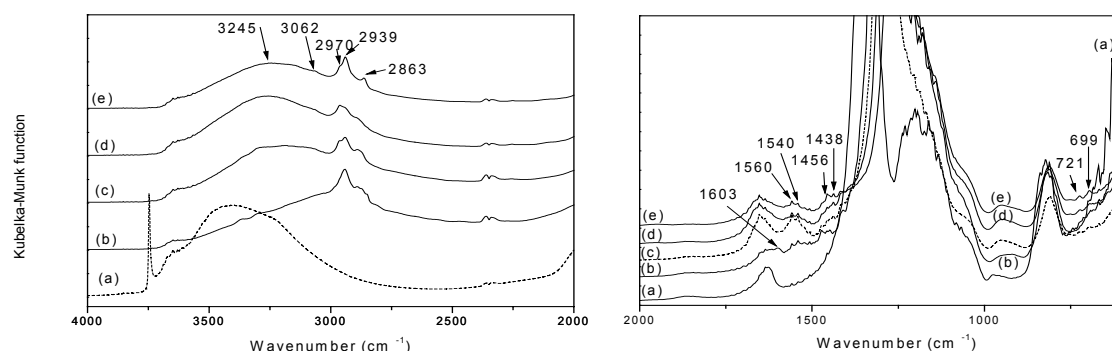


**Fig. 2.** FT-IR spectra of (a) SBA-15, (b) SBA-15SNH<sub>2</sub>, (c) SBA-15SNH<sub>2</sub>CpRu, (d) SBA-15SNH<sub>2</sub>Cp\*Ru and (e) SBA-15SNH<sub>2</sub>Cp\*RuNHC.

Fig. 2 depicts the FT-IR spectra of parent calcined mesoporous SBA-15, aminosilane grafted SBA-15 and of the grafted samples. The bands at 1216, 1076, and  $802\text{ cm}^{-1}$  are attributed to stretching vibrations of the mesoporous framework (Si-O-Si). The presence of weak bands around  $1564\text{ cm}^{-1}$  is due to amino group of the linker, which is largely masked by the hydroxyl vibrations. New, comparatively weak bands around  $3000$ ,  $2957$ , and  $2927\text{ cm}^{-1}$  can be assigned to the cyclopentadienyl (Cp, Cp\*)

moiety, and triphenylphosphane group vibrations of the grafted compounds. Furthermore, the presence of another band in the range of  $2853\text{ cm}^{-1}$  is due to C-H stretching vibrations, originating from the  $\text{CH}_2$  groups present in the silane ligand. Additional bands appear at  $697$  and  $721\text{ cm}^{-1}$ , due to C-C bending vibration from the phenyl ring.<sup>16</sup>

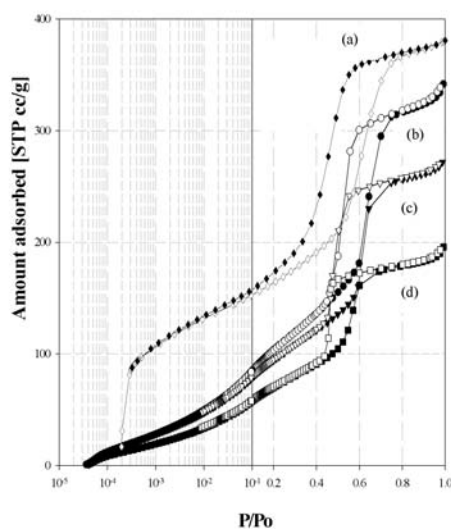
The DRIFT spectra of SBA-15, aminosilane grafted SBA-15 and of the grafted samples are shown in Figure 3. After the aminosilane grafting new bands appear at  $2863$ ,  $2939$ ,  $2970$ ,  $1438$ ,  $1456$ ,  $1540$  and  $1560\text{ cm}^{-1}$ , characteristic of C-H vibrations, further evidencing the  $\text{CH}_2$  group vibration of the aminosilane ligand. The appearance of broad bands at  $3062$  and  $1603\text{ cm}^{-1}$  are typical of NH vibrations. The broadening of peak areas near  $3245\text{ cm}^{-1}$  and also appearance of weak band at  $699$  and  $721\text{ cm}^{-1}$  are observed from phenyl groups of the phosphane ligand. Elemental analyses (EA) indicate (Table 1) that the RuCp complex **1** shows relatively low loading in comparison to the RuCp\* complex, which may probably be due to the enhancement of the leaving ability of the chloride ions by the Cp\* moiety, thus favouring very high loadings in the case of compounds **2** and **3**.



**Fig. 3.** DRIFT-IR spectra of (a) SBA-15, (b) SBA-15 $\text{NH}_2$ , (c) SBA-15 $\text{NH}_2\text{CpRu}$ , (d) SBA-15 $\text{NH}_2\text{Cp}^*\text{Ru}$  and (e) SBA-15 $\text{NH}_2\text{Cp}^*\text{RuNHC}$ .

The low temperature  $\text{N}_2$  adsorption/desorption isotherms are of type (IV) according to the IUPAC<sup>17</sup> and characteristic for mesoporous solids. However, compared to the parent mesoporous sample (Fig. 4a),<sup>13d</sup> the samples bearing grafted Ru complexes (Fig. 4b – 4d) exhibit a drastic decrease in  $\text{N}_2$  uptake due to the presence of aminosilane linkers and the relatively bulky organometallic compounds on the surface of the mesoporous channels.





**Fig. 4.** N<sub>2</sub> adsorption-desorption analysis of (a) SBA-15, (b) SBA-15SNH<sub>2</sub>CpRu, (c) SBA-15SNH<sub>2</sub>Cp\* Ru and (d) SBA-15SNH<sub>2</sub>Cp\* RuNHC.

**Table 1.** Textural properties of SBA-15 and the grafted Ru samples.

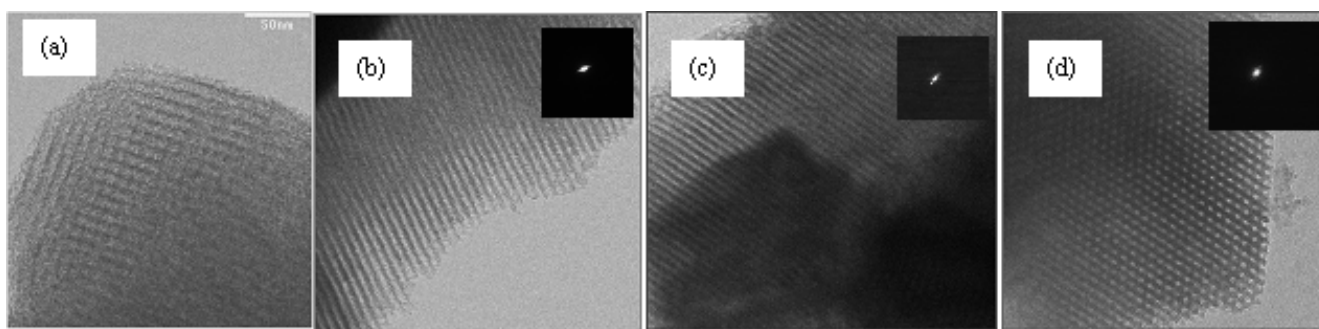
Sample	Ru wt. %		Interplane distance (nm)	BET surf. area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter (nm)
	Fresh	Recycled				
SBA-15	—	—	10.5	750	1.1	7.4
SBA-15SNH <sub>2</sub> CpRu	0.3	0.3	9.39	380	0.5	6.5
SBA-15SNH <sub>2</sub> Cp* Ru	1.9	1.7	9.04	340	0.4	6.0
SBA-15SNH <sub>2</sub> Cp* RuNHC	2.8	2.0	8.99	260	0.3	5.5

Furthermore, the parent SBA-15 sample exhibits a narrow pore size distribution with average pore diameters of 7.4 nm. The grafted materials exhibit an overall decrease of pore size and a broadening of the pore size (6.5-5.5 nm) distribution.

Additionally they display a decrease in surface area and pore volume (see Table 1). The decrease of pore volume and the pore size evidences that the aminosilane linker and the organometallic complexes in the grafted mesoporous samples are mainly located on

the internal surfaces of the mesoporous materials. However, the micropore volume is not affected much after grafting, which might be due to the difficulty of bulky organometallic complexes to access small micropores.

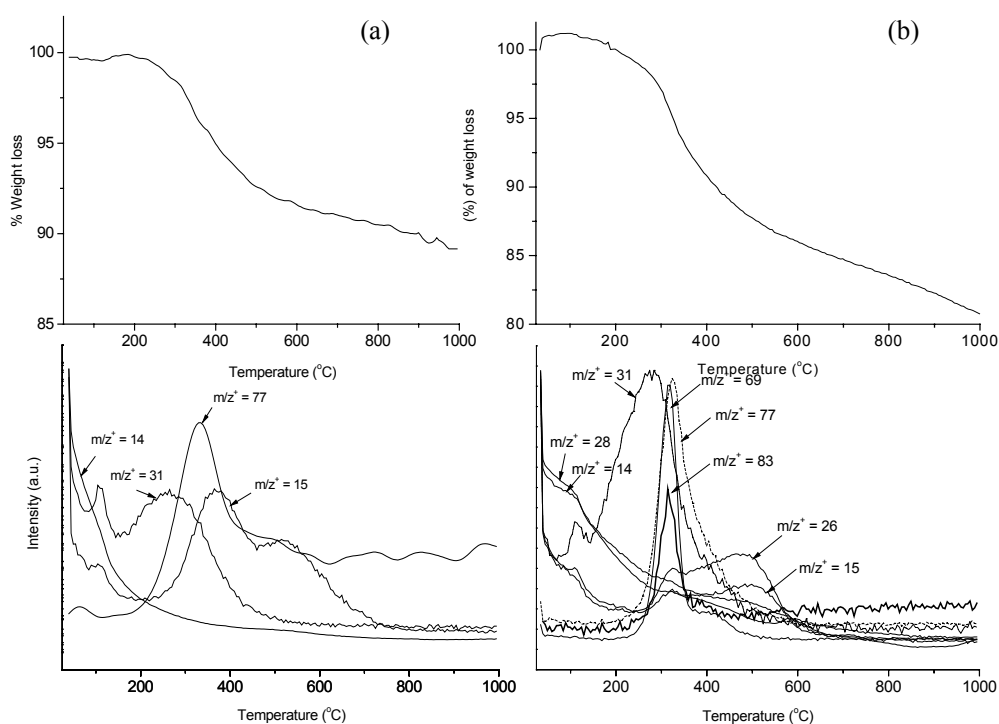
The TEM images (see Fig. 5) of the parent and grafted samples (SBA-15NH<sub>2</sub>CpRu, SBA-15NH<sub>2</sub>Cp<sup>\*</sup>Ru and SBA-15NH<sub>2</sub>Cp<sup>\*</sup>RuNHC) provide strong evidence that the mesoporous structures have a uniform pore size distribution and a well ordered pore structure. The long range ordering<sup>12,13</sup> is kept throughout the grafting process and the channels remain accessible. The well resolved ED pattern spots of the grafted samples, typical of (110) and (100) planes, further supports the presence of long range ordering in the samples, even after blocking of some pores by linker molecules and Ru complexes.



**Fig. 5.** TEM images of (a) SBA-15, (b) SBA-15NH<sub>2</sub>CpRu, (c) SBA-15NH<sub>2</sub>Cp<sup>\*</sup>Ru and (d) SBA-15NH<sub>2</sub>Cp<sup>\*</sup>RuNHC.

The parent SBA-15 and the grafted samples were examined by solid-state <sup>29</sup>Si CP MAS NMR spectroscopy. The parent SBA-15 material exhibits two broad elaborate resonances in the <sup>29</sup>Si CP MAS NMR spectrum at  $\delta = -110.3$  and  $-100.5$  ppm, assigned to the Q<sub>4</sub> and Q<sub>3</sub> species of the silica framework, respectively, [Q<sub>n</sub> = Si(OSi)<sub>n</sub>(OH)<sub>4-n</sub>].<sup>11-14</sup> A weak shoulder is also observed at  $\delta = -96.2$  ppm for the Q<sub>2</sub> species. The grafting of (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> also results in the reduction of the Q<sub>2</sub> and Q<sub>3</sub> resonances, and a concurrent increase of the Q<sub>4</sub> resonance. The changes of the Q<sub>4</sub> resonances are more pronounced due to the comparatively high loading. This is consistent with an esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atom of the organic ligand.<sup>13</sup> The <sup>29</sup>Si CP MAS NMR spectra also exhibit two additional signals at  $\delta = -59.2$  and  $-64.3$  ppm assigned to T<sub>2</sub> and T<sub>3</sub> organosilica species, respectively, [T<sub>m</sub> = RSi(OSi)<sub>m</sub>(OR)<sub>3-m</sub>]. However, as expected, the silylated samples show (nearly) identical <sup>29</sup>Si CP MAS NMR spectra before and after the grafting with the organo-ruthenium samples, thus indicating that during the grafting

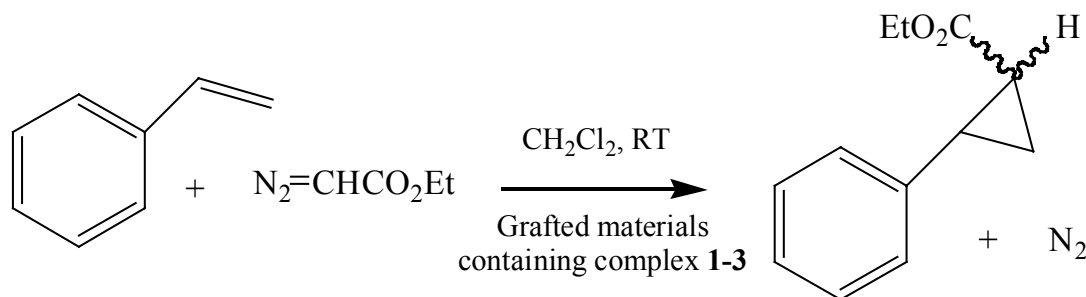
process no significant changes in the silicon environment take place. The observed changes in the  $^{29}\text{Si}$  CP MAS NMR spectra arise only during the silylating procedure using aminosilane. The  $^1\text{H}$  MAS NMR spectra (see supplementary information) of all the samples show broad signals between  $\delta = 8.1\text{-}4.5$  (centre at 5.2, 7.3 ppm) and 1.9 ppm characteristic for the Cp, phenyl and methyl groups of the complexes **1-3**. The additional peak at 3.30 ppm for the grafted samples is due to the residual OMe groups attached to silane.



**Fig. 6.** TG-MS spectra of (a) SBA-15SNH<sub>2</sub>Cp\* Ru and (b) SBA-15SNH<sub>2</sub>Cp\* RuNHC.

TG-MS spectra of SBA-15SNH<sub>2</sub>Cp\* Ru and SBA-15SNH<sub>2</sub>Cp\* RuNHC show (Fig. 6) 12 % and 18 % of weight loss up to 1000 °C, due to decomposition of the Cp\*Ru(PPh<sub>3</sub>)<sub>2</sub> and the Cp\*Ru(PPh<sub>3</sub>)(C<sub>3</sub>N<sub>2</sub>H<sub>2</sub>(Cy)<sub>2</sub>) moieties. The expected mass loss for SBA-15SNH<sub>2</sub>Cp\* Ru and SBA-15SNH<sub>2</sub>Cp\* RuNHC is 14 and 19 %, respectively, based on the TG-MS spectra of the organometallic complexes, the TG-MS of the SBA support with aminosilane linker and the complex loadings. The observed mass values  $m/z^+ = 77$ , 31 and 15 are corresponding to the phenyl, phosphorous and methyl groups of complexes **2** and **3**. The observed mass values  $m/z^+ = 83$ , 69, 14 in case of SBA-15SNH<sub>2</sub>Cp\* RuNHC originates from the carbene ligand, the peak  $m/z^+ = 83$  being characteristic of the cyclohexyl group. In addition, the presence of mass values  $m/z^+ = 14$  and 31 in the grafted sample are characteristic of methylene (CH<sub>2</sub>) and residual

methoxy groups of the silane linker. All the above-described observations support the successful grafting of complex **1-3** in the mesoporous channels of the SBA-15 molecular sieves.



Scheme 2

The homogeneous catalysts (**1-3**) and the grafted materials containing complexes **1-3** are applied in styrene cyclopropanation with EDA at room temperature for 24 h (Scheme 2) and the results are displayed in table 2. The catalytic activities increase in the order **1** < **2** < **3**.

**Table 2.** Cyclopropanation of styrene over the grafted ruthenium complexes<sup>a</sup>

Samples	Ru content (atom / nm <sup>2</sup> )	Isolated yield (%) <sup>b</sup>	Product distribution	
			Cis- ( <i>Z</i> )	Trans- ( <i>E</i> )
Compound <b>1</b>	—	47	47.8	52.2
Compound <b>2</b>	—	56	31.3	68.7
Compound <b>3</b>	—	77	24.9	75.1
SBA-15SNH <sub>2</sub> CpRu	0.047	21	46.7	53.3
SBA-15SNH <sub>2</sub> Cp* <sup>*</sup> Ru	0.33	50	30.1	69.9
1 <sup>st</sup> recycle	—	42	29.1	70.9
2 <sup>nd</sup> recycle	—	46	23.7	76.3
SBA-15SNH <sub>2</sub> Cp* <sup>*</sup> RuNHC	0.637	73	20.1	79.9
1 <sup>st</sup> recycle	—	63	22.3	77.1
2 <sup>nd</sup> recycle	—	66	19.9	80.1

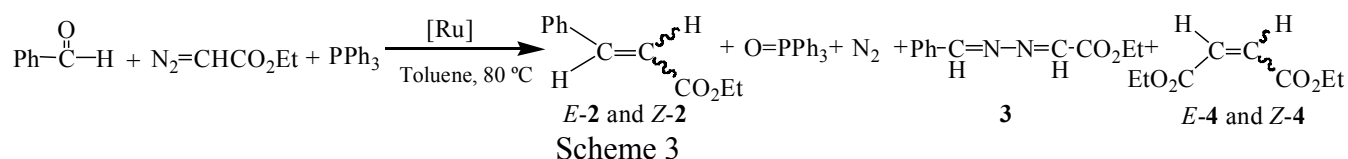
<sup>a</sup> Catalyst : styrene = 1 : 250; <sup>b</sup> Based on EDA conversion; Temperature = 298 K; Time = 24 h.

The grafted materials show comparable activity to their homogeneous counterparts (see table 2),<sup>7b</sup> with prevailing *E*-selectivity, as expected. However, in the case of SBA-15SNH<sub>2</sub>CpRu the catalyst reaches only relatively low yields as well as an equivalent amount of *E*- and *Z*-isomers, possibly due to the relatively low ruthenium content and therefore a significant diffusion limitation slowing down the reaction.

The yields are considerably higher, after the same period of time, in the case of SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>Ru and SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>RuNHC. The presence of more ruthenium atoms per nm<sup>2</sup> of the catalyst promotes the higher activities. Importantly, all the catalysts are re-usable for several catalytic runs. There is a slight decrease of activity on the second run, but the fact that the catalysts remain equally active for a third run shows that the grafted compounds are stable on the surface. The small decrease in catalytic activity during the first catalytic run (5-8 %) may be due to slight leaching of the ruthenium complexes on the surface of the SBA-15 materials, which is supported by elemental analysis of the residual ruthenium content in the filtrate. However, the lack of Ru in the filtrate solution of subsequent runs, as well as the absence of catalytic conversion in the filtrate, indicate that the catalysts are then stable and the leaching is insignificant after the first run.

There are no C-H insertion side products, which are observed in homogeneous catalysis.<sup>7b</sup> This is a clear advantage over the homogeneous catalyst system. It is noteworthy the similarity between the homogeneous and heterogeneous results, regarding both selectivity and overall yield, showing that the silica mesopores are not imposing significant structural or electronic perturbations on the immobilized metal centre.

Complexes **1-3** and the corresponding grafted materials are applied for the benzaldehyde olefination (using the same catalyst : benzaldehyde ratio based on the Ru content on the samples), with ethyldiazoacetate (EDA) in the presence of triphenylphosphane (PPh<sub>3</sub>) (Scheme 3). Again the homogeneous catalysts show the same general trend as observed for cyclopropanation, i.e. the olefin yields are higher in the case of the Cp<sup>\*</sup> compounds when compared to the Cp derivatives due to the better leaving ability of phosphane from the more electron rich ruthenium complexes.<sup>6b</sup>



**Table 3.** Benzaldehyde olefination over the heterogenized ruthenium complexes.<sup>a</sup>

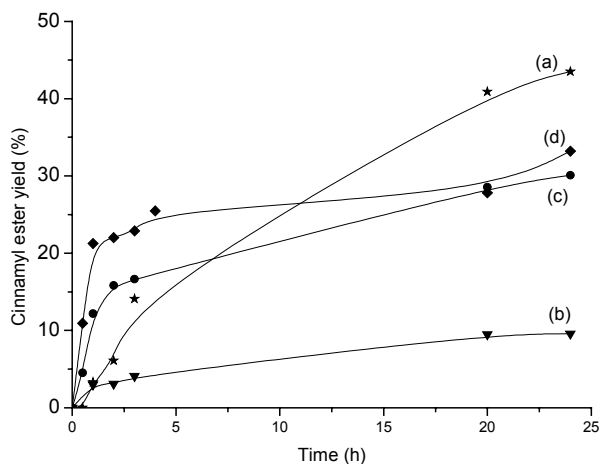
Catalysts	Yield (%) <sup>b</sup>	Ratio of olefin	
		Cis	Trans
Compound 1	25	8	92
Compound 2	73	10	90
Compound 3	35	9	91
SBA-15SNH <sub>2</sub> CpRu	43	5	95
SBA-15SNH <sub>2</sub> CpRu-PPO	10	14	86
SBA-15SNH <sub>2</sub> Cp <sup>*</sup> Ru	30	4	96
SBA-15SNH <sub>2</sub> Cp <sup>*</sup> RuNHC	33	4	96

<sup>a</sup> Catalyst : benzaldehyde = 1 : 325; Temperature = 298 K; Time = 24 h.

<sup>b</sup> The error range in the GC results is  $\pm 2$  %.

The heterogeneous catalysts show comparable yields with considerable azine formation. Both SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>Ru and SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>RuNHC show similar olefin yields, in the range 30-33 %, with an *E:Z* ratio of 96:4 in the olefinic products. In case of SBA-15SNH<sub>2</sub>CpRu the initial activity is lower, however, slightly higher olefin yields of ca. 43 % are reached after 24 h with an *E:Z* ratio of 95:5. Although the ruthenium content is quite low, the overall yield is better than in the case of the other two catalysts. As can be seen from figure 7, the initial catalytic activity is high in the case of SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>Ru and SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>RuNHC, probably due to the high ruthenium loading per unit volume.

However, the reaction velocity slows down during the course of the reaction. The observed slowing down of the catalytic process during the course of time seems to be due to adsorption of the bulky triphenyl phosphine or triphenyl phosphine oxide (PPh<sub>3</sub> or PPh<sub>3</sub>O) molecules on the surface of the supporting material. This is evident from the phosphorus elemental analysis of fresh and used catalysts, where the phosphorus content is increased from 0.4-0.6 to 0.8-3.4 wt %. The adsorption of phosphine on the surface of SBA-15 is further confirmed by treatment of SBA-15 with PPh<sub>3</sub> or PPh<sub>3</sub>O under identical reaction conditions, which results in adsorptions of 6-8 wt. % of PPh<sub>3</sub> or PPh<sub>3</sub>O (TGA and EA).



**Fig. 7.** Kinetic profiles for benzaldehyde olefination reaction over (a) SBA-15SNH<sub>2</sub>CpRu, (b) SBA-15SNH<sub>2</sub>CpRu-PPO, (c) SBA-15SNH<sub>2</sub>Cp\* Ru and (d) SBA-15SNH<sub>2</sub>Cp\* RuNHC.

Thus, the PPh<sub>3</sub> or PPh<sub>3</sub>O molecules block the SBA-15 channels and reduce the reaction rate resulting in an overall low yield. However, in case of SBA-15SNH<sub>2</sub>CpRu although the initial activity is lower the kinetic curve shows a steady increase in yield during the course of the reaction. Due to the higher amounts of supporting material necessary (337 mg in case of **1** compared to 49 and 36 mg in the case of **2** and **3**) to reach the same catalyst amount, higher amounts of phosphine or phosphine oxide can be adsorbed before the pores get blocked and the catalytic reaction comes to a halt. This result is supported by the catalytic reaction carried out on PPh<sub>3</sub>O pre-treated SBA-15SNH<sub>2</sub>CpRu catalyst (designated as SBA-15SNH<sub>2</sub>CpRuPPO). Such pre-treated samples give only very low yield (9.6 %) and the kinetic curve also shows no significant improvement in yield with time (see Fig. 7b).

### 7.3 Conclusions

Ruthenium phosphine and carbene complexes are successfully grafted on the aminosilane modified surface of SBA-15 materials. The grafted samples are stable and the structures of the supporting materials remain intact. The heterogenized catalysts are active in the aldehyde (benzaldehyde) olefination and cyclopropanation of styrene with EDA. The catalytic activities remain in the same order of magnitude even after three catalytic runs for the cyclopropanation reactions, therefore catalyst leaching can be considered as being minimal. In the case of benzaldehyde olefination, however, the catalytic reaction is hampered by adsorption of PPh<sub>3</sub> or PPh<sub>3</sub>O on the carrier material.

## 8. Experimental section

### 8.1 General procedure

#### 8.1.1 Inert gas atmosphere

All reactions and preparations were carried out under an Argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under nitrogen before use. All compounds were purchased from Aldrich, Acros Organics and Lancaster Synthesis unless otherwise stated; all the chemicals were used as received by the supplier. The glassware was washed in an isopropanol/KOH bath followed by HCl bath to remove traces of base and then rinsed with distilled water. All glassware was dried in an oven at 150 °C and then cooled under oil pump vacuum.

#### 8.1.2 Solvents

All solvents were dried and stored under inert gas atmosphere and molecular sieves (4 Å or 3 Å for acetonitrile and methanol). Hexane, pentane, dichloromethane, tetrahydrofuran (THF), diethyl ether and toluene were dried in a Grubbs apparatus. THF was collected immediately before use and the solvent moisture content was analysed by a Karl-Fisher titrator. Methanol was dried with Mg, ethanol was dried with Na, acetone was dried with K<sub>2</sub>CO<sub>3</sub> and acetonitrile with CaH<sub>2</sub>.

Deuterated solvents were dried under molecular sieves and degassed prior to use.

### 8.2 Characterization methods

Elemental analyses were measured at the Mikroanalytisches Labor of the TU München (M. Barth and co-workers). Metal analyses were determined with a Vario EL metal analyzer. Atomic absorption spectroscopy (Varian SpectrAA-400 spectrometer) was used to determine the metal content.

FT-IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using KBr pellets as matrix. DRIFT spectra were recorded at room temperature in the spectral range of 400–4000 cm<sup>-1</sup> with a Nicolet Impact 410 spectrophotometer equipped with a DRIFT chamber. The fine powders were loaded into a sample cell equipped with a CaF<sub>2</sub> window.

NMR measurements (<sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C and <sup>19</sup>F-NMR) were made with a 400 MHz Bruker Avance DPX-400 and a 400 MHz Jeol JNM-GX 400.



$^{29}\text{Si}$  CP MAS NMR spectra are recorded at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with  $5.5 \mu\text{s}$   $^1\text{H}$   $90^\circ$  pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays.  $^1\text{H}$  MAS NMR spectra were recorded at 300 MHz using a Bruker Avance 300 spectrometer with  $3.0 \mu\text{s}$   $^1\text{H}$   $90^\circ$  pulses and a spinning rate of 8 kHz.

Thermogravimetric analyses were performed using a Netzsch TG209 system at a heating rate of  $10 \text{ K min}^{-1}$  under argon.

Powder XRD data were collected with a Philips X'pert diffractometer using Cu-K $\alpha$  radiation filtered by Ni.

Nitrogen adsorption-desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 and SBA-15 samples were degassed at 723 K overnight to a residual pressure of ca. 10-24 mbar. A degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the  $\text{N}_2$  uptake at  $p/p_0 = 0.95$ , using the liquid nitrogen density of  $0.8081 \text{ g cm}^{-3}$ . The pore size distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls.

Transmission electron microscopy (TEM) was recorded on a JEOL JEM2010 operated at 120 kV.

### 8.3 Synthesis and characterization of the compounds described in this work

#### 8.3.1 Chapter 2

Complexes **1-3**,<sup>1</sup> **4**,<sup>2</sup> **5**,<sup>3</sup> **7-9**,<sup>4</sup> **10**,<sup>1</sup>  $\text{ReOCl}_3(\text{PPh}_3)_2$ ,<sup>5</sup>  $\text{ReOCl}_3(\text{dppe})$ ,<sup>6</sup> **13**,<sup>7</sup> **14**,<sup>8</sup> **15**,<sup>6</sup> **16**,<sup>9</sup> **17**,<sup>6</sup> **18**,<sup>8</sup> and **19**,<sup>8</sup> were synthesized according to published procedures. Complexes **13-19** were a kind offer from Dr. Isabel Santos and Dr. António Paulo from Instituto de Tecnologia Nuclear, Sacavém, Portugal. Complexes **6**, **11** and **12** were prepared by I. S. Lucas and C. C. Romão at the Instituto de Tecnologia Química e Biológica (ITQB) from the Universidade Nova de Lisboa.

*Preparation of ReClO<sub>3</sub>(L-L) complexes 6, 11 and 12*

All these complexes were prepared in a similar fashion described in detail for DAB = 4-MeC<sub>6</sub>H<sub>4</sub>N=CHCH=NC<sub>6</sub>H<sub>4</sub>Me-4) (**6**)

Preparation of **6**: A solution of Re<sub>2</sub>O<sub>7</sub> (0.400 g, 0.826 mmol) in 15 mL THF was treated with Me<sub>3</sub>SiCl (0.210 mL, 1.652 mmol, d = 0.856). Two equivalents of the ligand were then added (0.389 g, 1.652 mmol). The orange precipitate that formed immediately was filtered from the red mother liquor, washed with diethylether and dried under vacuum. Yield 63%. IR selected (KBr pellets, cm<sup>-1</sup>): 1597 m, 1500 s, 947 s, 922 vs, 910 s, 896 vs, 858 s, 814 s. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz, rt, δ ppm): 8.12 (s, 2H), 7.65-7.12 (m, 8H), 2.41-2.24 (m, 6H). Anal. Calc. % for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>ClRe (Mw.: 505.978); C 37.98, H 3.19, N, 5.54. Exp: C 37.78, H, 3.34, N 5.45.

Complexes **11-12** were prepared in a similar fashion using the corresponding ligands, respectively Me<sub>3</sub>CN=CHCH=NCMe<sub>3</sub> and (C<sub>6</sub>H<sub>11</sub>)N=CHCH=N(C<sub>6</sub>H<sub>11</sub>).

Data for compound **11**: IR selected (KBr pellets): 3080 m, 2980 vs, 2928,s, 2893 s, 983 s, 947 s, 923 vs, 902 vs, 877 s. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz, rt) δ 7.51 (s, 2H), 1.19-1.69 (m, 18 H). Anal. Calc. % for C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>ClRe (Mw.: 437.94); C 27.43, H 4.60, N, 6.40. Exp: C 27.44, H, 5.00, N 6.39.

Data for compound **12**: IR selected (KBr pellets): 3203 m, 2939 vs, 2858 s, 935 s, 922 vs, 908 s, 898 vs. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 300 MHz, rt): δ 7.72-7.09 (m, 2H), 2.24-1.26 (m, 22 H). Anal. Calc. % for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>ClRe (Mw.: 490.02); C 34.32, H 4.94, N, 5.72. Exp: C 34.45, H 5.05, N 6.01.

**8.3.2 Chapter 3**

MTO was synthesized following the literature procedure.<sup>10</sup>

**8.3.3 Chapter 4**

Compounds **1**,<sup>11</sup> **2**,<sup>12</sup> **3**,<sup>12</sup> **4**,<sup>12</sup> **6**<sup>13</sup> and **7**<sup>14</sup> were synthesized following literature procedures.

**CpRu(OC(O)CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (5)**

CpRuCl(PPh<sub>3</sub>)<sub>2</sub> (0.298 g, 0.41 mmol) and AgOC(O)CF<sub>3</sub> (0.1 g, 0.45 mol) were dissolved in 20 mL of THF. The mixture was stirred for 16 h under exclusion of light.

The solution was slowly filtered followed by partial removal of the volatiles under vacuum. Addition of 15 mL of *n*-heptane and stirring afforded a yellow precipitate after a few minutes. The solution was filtered and the CpRu(OC(O)CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (0.244 g, 74 %) was washed twice with *n*-heptane. Anal. Calcd for C<sub>43</sub>H<sub>35</sub>O<sub>2</sub>F<sub>3</sub>P<sub>2</sub>Ru: C, 64.26; H, 4.39 %. Found: C, 63.97; H, 4.39 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.22-7.08 (30 H, m, C<sub>6</sub>H<sub>5</sub>), 4.30 (5 H, s, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.1 (1 C, weak q, <sup>2</sup>J(F,C) 35.1 Hz, OC(O)CF<sub>3</sub>), 137.3 (1 C, t, C<sub>6</sub>H<sub>5</sub>) 133.5 (2 C, t, C<sub>6</sub>H<sub>5</sub>) 129.0 (1 C, s, C<sub>6</sub>H<sub>5</sub>) 127.7 (2 C, m, C<sub>6</sub>H<sub>5</sub>), 113.2 (1 C, weak t, <sup>1</sup>J(F,C) 292.7 Hz, CF<sub>3</sub>), 79.1 (5 C, s, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, standard 85% H<sub>3</sub>PO<sub>4</sub>): δ 41.1; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, standard CFCl<sub>3</sub>): δ -75.7.

### 8.3.4 Chapter 5

#### Cp\*RuCl(=CHCO<sub>2</sub>Et)(PPh<sub>3</sub>) (8)

Cp\*RuCl(PPh<sub>3</sub>)<sub>2</sub> (0.305 g, 0.38 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) and cooled to -12 °C in a dry ice/isopropanol bath. Ethyldiazoacetate (0.217 g, 1.9 mmol) was added to the solution and the mixture was stirred between -12 and -6 °C until the evolution of nitrogen ceased (which occurred usually within *ca.* 2 h). The solvent was concentrated in vacuum to approximately 5 cm<sup>3</sup> maintaining the temperature below -10 °C. The solution was cooled down to -30 °C and cold *n*-hexane (*ca.* 40 cm<sup>3</sup> at -30 °C) was added through a cannula to the solution. Stirring the solution produces a green precipitate, which was filtered and dried under vacuum. The product was dissolved in cold, dry toluene (2 cm<sup>3</sup> at -30 °C) and precipitated by adding cold, dry *n*-hexane (50 cm<sup>3</sup> at -30 °C). The precipitate (0.162 g, 68 %) was dried in vacuum. For characterization the product was recrystallized from toluene/*n*-hexane (2/40 cm<sup>3</sup>) and dried under vacuum for 2 hours. Anal. calcd for C<sub>32</sub>H<sub>36</sub>O<sub>2</sub>ClPRu: C, 61.98; H, 5.85 %. Found: C, 62.74; H, 5.60 %. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -20 °C): δ 14.90 (1 H, d, <sup>3</sup>J(H, P) 12.26 Hz, CH) 7.88-7.15 (15 H, br m, C<sub>6</sub>H<sub>5</sub>) 3.99 (2 H, q, <sup>3</sup>J(H,H) 7.35 Hz, CH<sub>2</sub>) 1.30 (15 H, s, C<sub>5</sub>Me<sub>5</sub>), 1.26 (3 H, t, <sup>3</sup>J(H,H) 7.35 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -20 °C): δ 264.5 (1 C, d, <sup>2</sup>J(C,P) 14.8 Hz, Ru=CHCO<sub>2</sub>Et), 182.9 (1 C, s, CO) 135.7-127.7 (6 C, br m, C<sub>6</sub>H<sub>5</sub>) 104.0 (5 C, s, C<sub>5</sub>Me<sub>5</sub>) 59.1 (1 C, s, CH<sub>2</sub>CH<sub>3</sub>), 13.8 (1 C, s, CH<sub>2</sub>CH<sub>3</sub>), 8.8 (5 C, s, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -20 °C, standard 85 % H<sub>3</sub>PO<sub>4</sub>): δ 49.6.

$\text{Ph}_3\text{P}=\text{N}=\text{N}=\text{CHCO}_2\text{Et}$  (Phosphazine **XIII**)<sup>15</sup>

$\text{PPh}_3$  (1.311 g, 5 mmol) was dissolved in 20 cm<sup>3</sup> of *n*-pentane. Ethyl diazoacetate (0.571 g, 0.5 mmol) was added to the mixture and the solution was stirred for 8 hours. The resulting solid was filtered and washed three times with cold pentane, producing a white powder (1.675 g, 89 %). Anal. calcd for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$ : C, 70.20; H, 5.62; N, 7.44%. Found: C, 69.43; H, 5.74; N, 7.12%. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (1 H, d, <sup>3</sup>*J*(H,P) 2.0 Hz, N=CH), 7.68-7.46 (15 H, m,  $\text{C}_6\text{H}_5$ ), 4.19 (2 H, q, <sup>3</sup>*J*(H,H) 7.20 Hz,  $\text{CH}_2$ ), 1.26 (3 H, t, <sup>3</sup>*J*(H,H) 7.20 Hz,  $\text{CH}_3$ ). <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.4 (1 C, s, C(O)), 138.1 (1 C, d, *J*(C,P) 47.6 Hz, N=CH) 133.5 (6 C, d, *o*- $\text{C}_6\text{H}_5$ ), 132.5 (3 C, s, *p*- $\text{C}_6\text{H}_5$ ), 128.7 (6 C, t, *m*- $\text{C}_6\text{H}_5$ ), 127.7 (3 C, d, *J*(C,P) 93.8 Hz, C-P) 59.7 (1 C, t,  $\text{CH}_2$ ) 14.4 (1 C, q,  $\text{CH}_3$ ). <sup>31</sup>P NMR (162 MHz,  $\text{CDCl}_3$ , standard 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  22.7.

### 8.3.5 Chapter 6

**MCM-41 and MCM-48:** The following materials, colloidal silica ( $\text{SiO}_2$ ), fumed silica ( $\text{SiO}_2$ ), hexadecyl-trimethyl ammonium bromide (CTABr), polyoxyethylen(4)-laurylether (Brij-30), tetramethyl ammonium hydroxide (TMAOH, 25 wt.%), aluminium nitrate nano-hydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and sodium hydroxide (NaOH) were used without purification for the synthesis of the mesoporous materials.

Na-**AlMCM-41** with a Si/Al (molar) ratio of 100 is synthesized as described in the literature,<sup>16</sup> having a typical molar gel composition of 1  $\text{SiO}_2$  : 0.2 NaOH : 0.27 TMAOH : 0.27 CTABr : 60  $\text{H}_2\text{O}$  : 0.005  $\text{Al}_2\text{O}_3$ . A typical synthetic procedure is as follows: first TMAOH is dissolved in water and stirred for 5 min. To this solution fumed silica is slowly added (the resulting solution is designated as A). Another solution, B, is prepared by mixing CTABr and NaOH in distilled water and stirred for about 30 min. Both these solutions, A and B, are mixed together and a gel is formed. Aluminium nitrate is then added to the resulting clear solution and the mixture is stirred for one hour. The pH of the resulting gel is adjusted to 11.0 with dilute sulphuric acid, and is aged for 16 h. The gel is transferred into a polyethylene bottle and kept in an oven under air for crystallization at 373 K for 3 days. The obtained solid product is washed repeatedly, filtered, and dried at 353 K for 12 h. The as-synthesized sodium form of the material (Na-**AlMCM-41**) is calcined at 823 K for 2 h in  $\text{N}_2$  followed by drying under air for 6 h.

Na-**AIMCM-48** is prepared<sup>17</sup> by the following procedure with a molar gel composition of 5.0 SiO<sub>2</sub> : 2.5 NaOH : 0.87 CTABr : 0.13 Brij-30 : 0.025 Al<sub>2</sub>O<sub>3</sub> : 400 H<sub>2</sub>O. First, a surfactant mixture solution is prepared by dissolving both CTABr (7.74 g) and Brij-30 (1.35 g) simultaneously in distilled water (60 mL). Then, a sodium hydroxide solution (2.5 g in 5 mL water) is added to the surfactant solution and stirred for 0.5 h. The silica solution is then added to the solution described above and the resulting mixture is shaken vigorously for 0.5 h. The resulting gel is kept at 373 K for crystallization. After two days, the mixture is cooled to room temperature (298 K) and the pH of the solution is adjusted to 10 with acetic acid. This procedure is repeated twice. Then, aluminium nitrate is added to the gel and the resulting mixture is kept at 373 K for 7 days. The resulting final product is filtered and washed with an ethanol/water mixture and dried in an oven at 373 K, followed by calcination in air at 823 K for 6 h.

**H-**AIMCM-41** and H-**AIMCM-48****: The protonated forms of both Na-**AIMCM-41** and Na-**AIMCM-48** are prepared by the following procedure. About 1 g of the calcined sample is treated with 30 ml of (1 M) NH<sub>4</sub>NO<sub>3</sub> solution and refluxed at 343 K for 6 h. The process is repeated thrice to obtain maximum exchange and then washed, filtered and dried at 373 K. It was then calcined at 773 K in air for 6 h to obtain H-**AIMCM-41** and H-**AIMCM-48**.

**SM-41SNH, and SM-48SNH**: Aminosilanes were introduced on siliceous mesoporous materials by the following procedure: first siliceous mesoporous materials were prepared by a similar procedure as Na-**AIMCM-41** and Na-**AIMCM-48** without addition of aluminium salt. The SiMCM-41 and SiMCM-48 (1 g) were pre-activated at 473 K under vacuum (10<sup>-3</sup> mbar) for 4 h to remove physisorbed water. The physisorbed water free SiMCM-41 and SiMCM-48 (1 g) is silylated with aminopropyl trimethoxy silane (2 mmol) using dry toluene (30 ml) as solvent under argon atmosphere at 383 K for 24 h. Then excess silane is removed by filtration followed by washing several times with dichloromethane. The resulting solid is dried under vacuum at room temperature. The samples silylated with aminopropyl trimethoxy silane are designated as SM-41SNH, and SM-48SNH respectively.

**HAM-41RuG, HAM-48RuG, SM-41SNHRuG, and SM-48SNHRuG**: Grafting experiments are carried out using standard Schlenk techniques under argon atmosphere

with the following procedure:  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}(\text{PPh}_3)_2$  (**1**) is synthesized as described earlier.<sup>14</sup> The mesoporous molecular sieves H-**AlMCM-41**, H-**AlMCM-48** and aminosilane modified molecular sieves **SM-41SNH**, and **SM-48SNH** (1 g) are again pre-activated at 473 K under vacuum ( $10^{-3}$  mbar) for 4 h to remove any physisorbed water. Then, the samples (1 g) were treated with 0.6 mmol of complex **1** in 30 ml dry THF under an argon atmosphere. The mixtures were stirred at 313 K for 3 days. The resulting solutions were filtered off and the white solids were repeatedly washed with THF until all physisorbed complex was removed from the surfaces. The washed samples were dried under vacuum at RT.

### 8.3.6 Chapter 7

**SBA-15**: SBA-15 silicas were synthesized in a similar way as originally reported by Zhao *et al.*<sup>18,19</sup> using Pluronic 123 triblock copolymers (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide); (Aldrich))  $\text{EO}_n\text{PO}_{70}\text{EO}_n$  as templates. In a typical synthesis, 4.0 g of the  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  copolymer was dissolved in 150 g of 1.6 M HCl. To this solution 8.50 g of TEOS (tetraethyl orthosilicate), was added and the resulting mixture was stirred until TEOS was dissolved. The final molar gel composition of the synthesis mixture was  $6.89 \times 10^{-4}$  P123 triblock copolymers: 0.24 HCl : 0.041 TEOS : 7.88  $\text{H}_2\text{O}$ . The mixture was placed in an oven for 24 h at 308 K and then additional 24 h at 373 K under static condition. Silica products were filtered, dried, and calcined at 823 K.

**SBA-15SNH<sub>2</sub>**: The SBA-15 molecular sieve was heated at 523 K under vacuum ( $10^{-3}$  mbar) for 6 h to remove physisorbed water. The activated mesoporous molecular sieve (SBA-15; 1 g) was treated with aminopropyl trimethoxy silane (2 mmol) using dry toluene (30 mL) as solvent under argon atmosphere at 383 K for 24 h. Then excess silane was removed by filtration followed by repeatedly washing with dichloromethane. The resulting solid was dried under vacuum at room temperature. The aminosilane modified sample is designated as SBA-15SNH<sub>2</sub>.

**SBA-15SNH<sub>2</sub>CpRu**, **SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>Ru** and **SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>RuNHC**: Grafting experiments were carried out using standard Schlenk techniques under argon atmosphere with the following procedure: The cyclopentadienyl ruthenium complexes **1**, **2** and **3** were synthesized as described in the literature.<sup>20,21</sup> SBA-15SNH<sub>2</sub> is again pre-

activated at 473 K under vacuum ( $10^{-3}$  mbar) for 4 h to remove any physisorbed water. Then, the sample (1 g) was treated with 0.6 mmol of complexes **1-3** in 30 mL of dry THF under an argon atmosphere. The mixtures were stirred at 313 K for 3 days. The resulting solutions were filtered off and the white solids are repeatedly washed with THF until all physisorbed complexes are removed from the surfaces. The washed samples were dried under vacuum at RT. Complexes **1-3** grafted in samples of SBA-15SNH<sub>2</sub> are designated as SBA-15SNH<sub>2</sub>CpRu, SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>Ru and SBA-15SNH<sub>2</sub>Cp<sup>\*</sup>RuNHC, respectively.

## 8.4 Catalytic reactions

### 8.4.1 General procedure for aldehyde olefination

Aldehyde (1 eq, typically 2 - 4 mmol), PPh<sub>3</sub> (1.2 eq) and catalyst (0.3 – 2 mol % for Ru catalysts, 1 - 5 mol % for Re catalysts) were dissolved in the appropriate solvent (10 – 20 cm<sup>3</sup>) and taken to the desired reaction temperature. Ethyl diazoacetate (0.274 g, 2.4 mmol) was added in one portion and allowed to react while monitoring the reaction progress by GC-MS. Afterwards the solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was taken into a small amount of toluene and chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1) affording the olefin(s). The identity of the olefins was determined by GC-MS and NMR.

For 4-nitrobenzaldehyde, benzaldehyde and 4-dimethylamino-benzaldehyde the yield was determined by GC-MS using a previously recorded calibration curve ( $R^2 > 0.999$ ), using fluorene as internal standard.

*Catalytic aldehyde olefination using diethyl diazomalonate:* 4-nba (0.5 g, 3.3 mmol), PPh<sub>3</sub> (0.95 g, 3.6 mmol), fluorene (0.4 g, internal standard), CH<sub>3</sub>ReO<sub>2</sub>(PhC=CPh) (0.068 g, 0.166 mmol) and ethyldiazomalonate (0.739 g, 3.97 mmol), were dissolved in 20 cm<sup>3</sup> of dry THF and allowed to react at RT. The yield was determined by GC-MS using a previously recorded calibration curve ( $R^2 > 0.999$ ), using fluorene as internal standard.

### 8.4.2 General procedure for ketone olefination

Ketone (2 mmol), PPh<sub>3</sub> (0.577g, 2.2 mmol), catalyst (1-5 mol %) and benzoic acid (0.122 g, 1 mmol) were dissolved in toluene (10 cm<sup>3</sup>) and heated to the desired reaction

temperature. For MTO as catalyst, EDA (0.274g, 2.4 mmol) dissolved in toluene (1 cm<sup>3</sup>) was added dropwise to the reaction mixture. For Ru catalysts EDA (0.274 g, 2.4 mmol) was added in one portion. The reaction progress was monitored by GC-MS. Afterwards the solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was taken into a small amount of toluene and chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1) affording the olefin(s). The identity of the olefins was determined by GC-MS and NMR.

### 8.4.3 General procedure for styrene cyclopropanation

EDA (0.114 g, 1.0 mmol) in 2.0 cm<sup>3</sup> of dichloromethane was slowly added (addition time 1 h) to a 4.0 cm<sup>3</sup> dichloromethane solution of styrene (0.520 g, 5.0 mmol) and catalyst (0.02 mmol; based on Ru content) over 60 min. The reaction was followed by GC-MS. After the reaction was completed the products were identified by GC-MS. Products were isolated by flash chromatography using a silica gel column with *n*-hexane/ethyl acetate (20:1).

### 8.4.4 Mechanistic studies

*Catalysis without aldehyde:*

( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)RuCl(PPh<sub>3</sub>)<sub>2</sub> (2 mg, 2.5  $\mu$ mol) and PPh<sub>3</sub> (36 mg, 0.138 mmol) were dissolved in 0.6 cm<sup>3</sup> of CD<sub>2</sub>Cl<sub>2</sub>. The resulting solution was transferred via cannula to the NMR tube and cooled to -70 °C. EDA (14.3 mg, 0.125 mmol) was added and the NMR tube was kept at -70 °C until the beginning of the measurements, which were performed at RT.

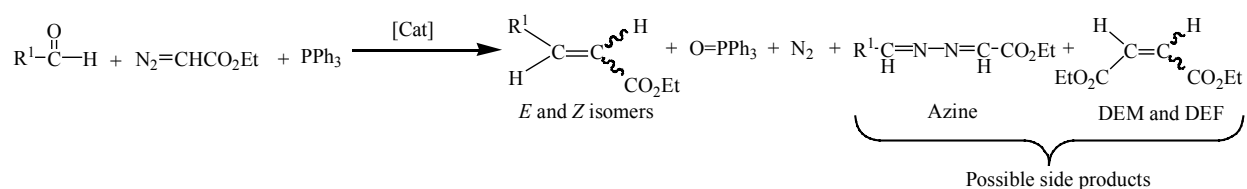
*Catalysis with aldehyde:*

( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)RuCl(PPh<sub>3</sub>)<sub>2</sub> (2 mg, 2.5  $\mu$ mol), PPh<sub>3</sub> (36 mg, 0.138 mmol) and benzaldehyde (26.5 mg, 0.25 mmol) were dissolved in 0.6 cm<sup>3</sup> of CD<sub>2</sub>Cl<sub>2</sub>. The resulting solution was transferred via cannula to the NMR tube and cooled down to -70 °C. EDA (14.3 mg, 0.125 mmol) was added and the NMR tube was kept at -70 °C until the beginning of the measurements, which were performed at RT.



## 9. Summary

The work performed showed the ability of high oxidation rhenium complexes and Cp'RuClXL<sup>1</sup>L<sup>2</sup> ruthenium compounds to catalyse aldehyde olefination with phosphanes and diazo compounds (scheme 1). The structural diversity of the studied complexes allowed a comprehensive catalyst optimisation, which coupled with the investigations on the optimal reaction conditions brought further light into the reaction mechanisms.

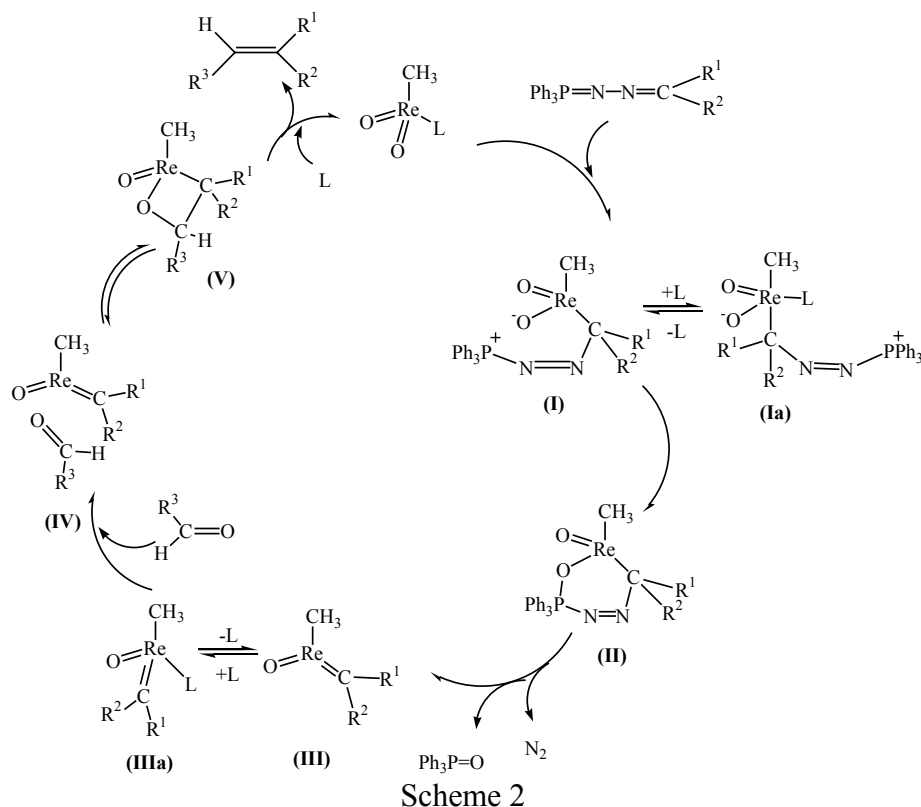


Scheme 1

The rhenium complexes range from completely inactive to good catalysts for aldehyde olefination. The best catalysts have high oxidation states and contain electron-withdrawing groups, such as CH<sub>3</sub>ReO<sub>2</sub>(alkyne), which produces olefin yields within the range of 70-80 % in the olefination of 4-nitrobenzaldehyde (4-nba), using a 5 % mol catalyst loading in THF at RT. The crucial factors for a high catalytic activity seem to be a high Lewis acidity of the metal center and either a sterically unhindered compound (like MTO) or weakly coordinating “protecting ligands” that can be easily displaced and in consequence trigger the catalytic activity.

The reaction with diazo compounds other than ethyl diazoacetate (EDA), such as trimethylsilyldiazomethane (N<sub>2</sub>CH(TMS)) afforded no olefins and olefination with diethyl diazomalonate required longer reaction times (24 hours for 22 % olefin yield).

It was observed that PPh<sub>3</sub> and EDA react very fast to produce a phosphazine (Ph<sub>3</sub>P=N-N=CHCO<sub>2</sub>Et). In contrast, no phosphazine formation was observed when reacting N<sub>2</sub>CH(TMS) with PPh<sub>3</sub> and diethyl diazomalonate produced phosphazine at a very slow rate, the reaction being after 24 h still incomplete. Therefore the formation of a phosphazine from a diazo compound and a phosphane seems to be critical for the beginning of the catalytic cycle. Catalytic amounts of CH<sub>3</sub>ReO<sub>2</sub>(alkyne) complexes slowly convert the phosphazine into phosphorus ylide (Ph<sub>3</sub>P=CHCO<sub>2</sub>Et), but do not further catalyse the Wittig reaction with the aldehyde. Since a typical olefination reaction is finished within minutes there should be an alternative reaction pathway involving the phosphazine and the rhenium catalyst (scheme 2). The mechanism also accounts for the olefin production when using diethyl diazomalonate, since the correspondent phosphorus ylide does not react under the classic Wittig conditions.



Under the typical reaction conditions the rhenium compounds do not catalyse the olefination of ketones. The olefination of ketones with MTO is possible when using benzoic acid (0.5 eq) as co-catalyst. The olefination was tested in the absence of co-catalyst and in the presence of Lewis acids, but only vestigial amounts of olefins could be obtained after long reaction times. After a careful study of the reaction conditions it was found higher temperatures (80 °C in toluene), 0.5 eq of co-catalyst and 5 mol % catalyst loading to be the optimal settings to achieve the best results.

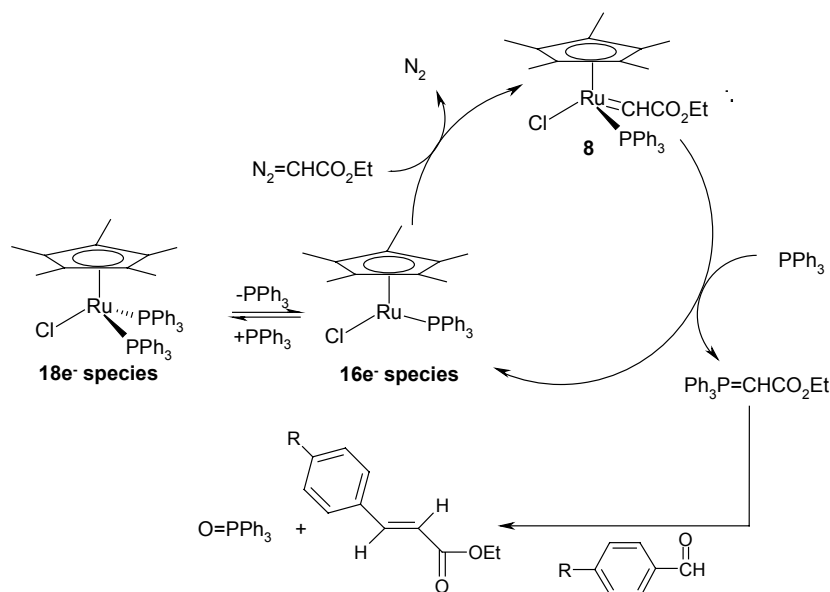
The developed system catalyses the olefination of aromatic, aliphatic and cyclic ketones (30 – 70 % olefin yield), while trifluoroketones can be olefinated even in the absence of co-catalyst (>90% yield). The olefination reaction comes faster to completeness when the ketone contains electron withdrawing groups and the selectivity trends point to a slight preference for the *Z*-isomer.

Several ruthenium catalysts of the type  $\text{Cp}^*\text{RuXL}^1\text{L}^2$  ( $\text{X} = \text{Cl}, \text{OCOCF}_3, \text{L}^1 = \text{PR}_3, \text{L}^2 = \text{PR}_3, \text{N-heterocyclic carbene}$ ) were successfully applied to the olefination of 4-nitro-benzaldehyde with EDA and  $\text{PPh}_3$ . Through careful tuning of the ligands coordinating to the metal, it was possible to turn a medium performance catalyst  $\text{CpRuCl}(\text{PPh}_3)_2$  into a very good catalyst  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  combining fast reaction rates with high *E*-olefin selectivity. The system developed for the latter compound catalyses the olefination of aromatic, aliphatic and cyclic aldehydes under relatively smooth

reaction conditions (optimised in toluene at 80 °C with 1 % mol of catalyst loading). The yields are usually above 90 % within a few hours of reaction time (just 5 minutes for 4-nba) and the selectivity is strongly geared toward the *E*-isomer (>90 %), being the highest reported so far. Cp\*RuCl(PPh<sub>3</sub>)<sub>2</sub> was also found to be a good catalyst for the olefination of activated ketones (yields > 85 %) and a moderate to good catalyst for the olefination of non-activated ketones using benzoic acid (0.5 eq) as co-catalyst (yields within the 57 - 92 % range). This system presents an average *Z*-selectivity of the same order of magnitude of the best-known catalysts.

Overall electron releasing and bulky ligands increase the catalysts activity as they decrease the Ru-P bond strength, which seems to be crucial to trigger the reaction.

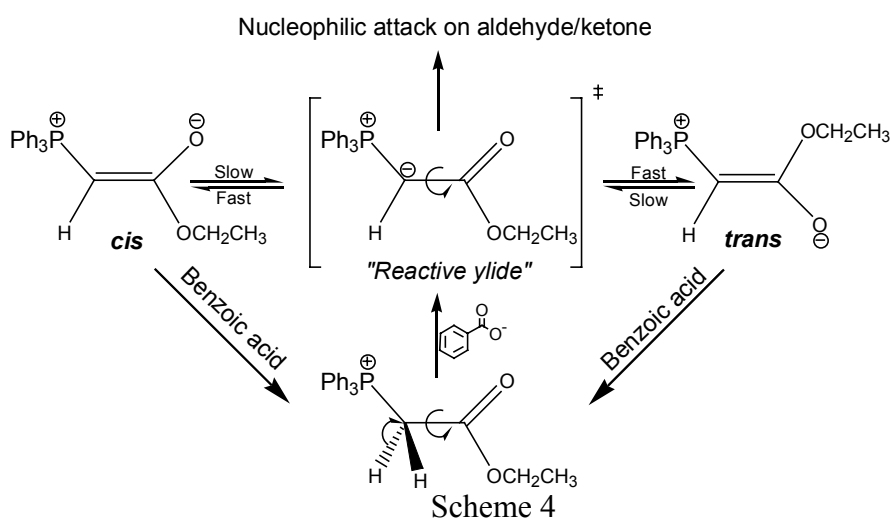
Investigations on the reaction mechanism disclosed the existence of the complex Cp\*RuCl(=CHCO<sub>2</sub>Et)(PPh<sub>3</sub>), resulting from the reaction of Cp\*RuCl(PPh<sub>3</sub>)<sub>2</sub> with EDA at -10 °C. Cp\*RuCl(=CHCO<sub>2</sub>Et)(PPh<sub>3</sub>) reacts quantitatively with PPh<sub>3</sub> to produce the phosphorus ylide Ph<sub>3</sub>P=CHCO<sub>2</sub>Et even at -50 °C.



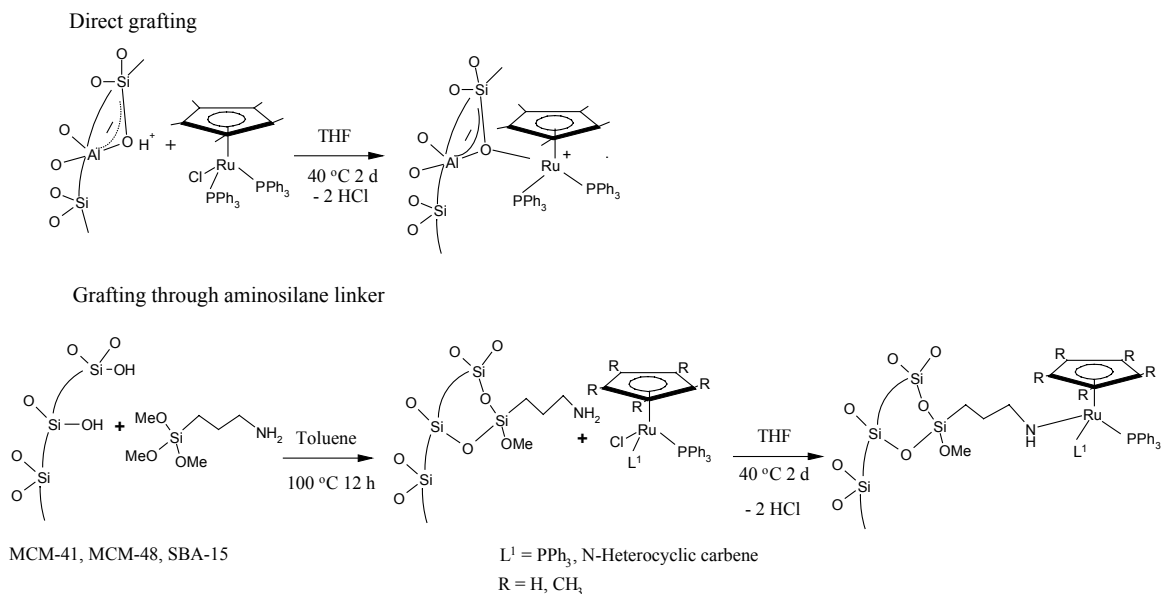
Such observations lead us to establish the reaction mechanism (scheme 3) of this type of ruthenium catalysts: the first step is the release of phosphane and formation of complex Cp\*RuCl(=CHCO<sub>2</sub>Et)(PPh<sub>3</sub>) by reaction with EDA; the second step is the formation of the phosphorus ylide through reaction of this complex with PPh<sub>3</sub>. The third step, reaction of the phosphorus ylide with the aldehyde produces the desired olefin(s).

The best catalysts promote the direct formation of Ph<sub>3</sub>P=CHCO<sub>2</sub>Et from EDA and PPh<sub>3</sub>, avoiding the production of significant amounts of phosphazine, Ph<sub>3</sub>P=N=N=CHCO<sub>2</sub>Et, a comparatively sluggish reactant.

The role of benzoic acid in the ketone olefination was investigated to explain its singular activation effect (scheme 4). No evidence of interaction of the acid with the ketone was found, but instead benzoic acid promotes the interconversion between the *cis* and *trans* forms of the phosphorus ylide. It is accepted that this interconversion proceeds through an intermediate that bears a negative charge on the ylidic carbon. This same reactive intermediate is responsible for the nucleophilic attack on the carbonyl during the Wittig reaction. Nevertheless due to the lack of electrophilicity of the ketones carbonyl, they still require longer reaction times than aldehydes.



The organometallic complex  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ , was immobilized on the surface of modified mesoporous MCM-41 and MCM-48 by direct grafting on mesoporous aluminosilicates and through aminosilane linker modified materials. The complexes  $\text{CpRuCl}(\text{PPh}_3)_2$ ,  $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$  and  $\text{Cp}^*\text{RuCl}(\text{C}_3\text{N}_2\text{Cy}_2)(\text{PPh}_3)$  (Cy = cyclohexyl) were also heterogenized on the surface of aminosilane linker modified mesoporous SBA-15 molecular sieves (scheme 5). All the materials were fully characterized, the metal loading determined and applied as heterogeneous catalysts in aldehyde olefination (scheme 1) and styrene cyclopropanation (scheme 6). The heterogeneous catalysts kept the long range ordering of the parent materials and were quite stable to leaching. The grafting procedure greatly influenced the metal loading of the heterogeneous materials: direct grafting on aluminosilicates afforded very low ruthenium contents (0.2-0.35 Ru wt. %), while the grafting on surfaces modified with the aminosilane linker usually afforded higher catalyst loadings (0.9-2.8 Ru wt. %). The loading also improved with increasing pore diameter and extended three dimensional pore structure of the parent materials in the order  $\text{MCM-41} < \text{MCM-48} < \text{SBA-15}$ .



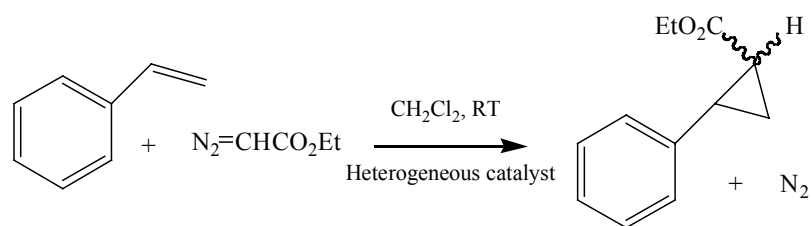
Scheme 5

The heterogeneous catalysts were applied for benzaldehyde olefination with EDA and  $PPh_3$ . The catalysts immobilized on MCM-41 and MCM-48 by direct grafting afforded olefin yields of 15-20 % with an  $E : Z$  ratio of 99:1. The materials synthesized using an aminosilane linker, the heterogeneous catalysts displayed distinct results: the ones immobilized on MCM-41 and MCM-48 yielded only traces of olefin, azine being the main product; the ones immobilized on SBA-15 produce 30 – 43 % olefin yield, with very good  $E:Z$  ratios ( $> 95:5$ ) and can be recycled for further catalysis with negligible activity decline.

Materials with higher Ru content display the lower catalytic activities due to the obstruction of the heterogeneous catalysts pores by the bulky organometallic complex, the aminosilane linker and the side products formed during the reaction, which prevent the access of the reactants to the catalytic sites. The wider pores of the SBA-15 molecular sieves combined with lower Ru loadings produces materials less prone to deactivation by pore blocking and thus obtain the highest olefin yields.

Applied in styrene cyclopropanation (scheme 6) with EDA the grafted materials show comparable activity to their homogeneous counterparts with cyclopropane yields ranging the 50 – 70 % and high  $E$ -selectivity ( $> 80$  %), and can be reused with insignificant leaching and little activity decrease. The yields are considerably higher when the complex is grafted through the aminosilane linker due to the higher catalyst loadings. The three-dimensional pore structure of MCM-48 is beneficial to the reaction

as well as the larger pore width of the SBA-15 molecular sieves, when compared to the one-dimensional structure of MCM-41.



Scheme 6

## References

### References for chapter 1:

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3. **Filipe M. Pedro**, Sebastian Hirner, Fritz E. Kühn, *Tetrahedron Lett.* **2005**, 46, 7777-7779.
4. Ayyamperumal Sakthivel, **Filipe E. Pedro**, Anthony S. T. Chiang, Fritz E. Kühn, *Synthesis* **2006**, 10, 1682-1688.
5. Sofia M. Bruno, Bernardo Monteiro, Maria Salete Balula, **Filipe M. Pedro**, Marta Abrantes, Anabela A. Valente, Martyn Pillinger, Paulo Ribeiro-Claro, Fritz E. Kühn, Isabel S. Gonçalves, *J. Mol. Catal. A. Chem.* **2006**, 260, 11-18.
6. Ayyamperumal Sakthivel, **Filipe M. Pedro**, Anthony S. T. Chiang, Fritz E. Kühn, *Dalton Trans.* **2007**, 320-326.
7. **Filipe M. Pedro**, Ana. M. Santos, Walter Baratta, Fritz E. Kühn, *Organometallics* **2007**, 26, 302-309.

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