# Oxorhenium Complexes as Aldehyde-Olefination Catalysts

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**Abstract:** Several oxorhenium compounds in the formal oxidation states v and vii are examined as catalysts for the aldehyde-olefination starting from diazo compounds, phosphines, and aldehydes. Of these, [$ReMeO_2(\eta^2$-alkyne)] complexes provide the simplest catalysts to study, although [$ReOCl_3(PPh_3)_2$] still remains the most efficient rhenium catalyst for aldehyde-olefination described to date. Prior to the reaction with the Re catalysts the phosphine and the diazo compound react to form a phosphazine. No catalytic reaction occurs in cases where no phosphazine formation is observed. The first step of the catalytic cycle involves the formation of a carbene intermediate by the reaction of 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. Excess of alkyne as well as the presence of ketones slows down the catalytic reaction. The olefination of 4-nitrobenzaldehyde with diazomalonate is possible with these Re catalysts. In contrast, this reaction does not take place either in the classical Wittig fashion from $Ph_3P{=}C(CO_2Et)_2$ and aldehyde or by use of all other catalysts for aldehyde olefination reactions reported to date. Catalytic ylide formation from diazo compounds seems therefore not to be the only pathway through which catalytic aldehyde-olefination reactions can proceed.

**Keywords:** aldehydes · homogeneous catalysis · olefination · rhenium · Wittig reactions

## Introduction

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 such as the Wittig reaction and its several variations,[1,2] a selective catalytic system would be highly desirable to speed up reactions, shorten experimental multistep procedures, and avoid the use of expensive reagents difficult to handle.[3]

The quest for effective catalysts has been developing slowly since the late 1980s.[4] Presently, several efficient catalytic aldehyde-olefination reactions have been reported based on Re,[5,6] Ru,[7,8] Rh,[8a] Fe,[9a–e] and Co[9f] 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.[6,9] 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,[10] whereas in other cases evidence suggests that they give rise to free ylides that perform the Wittig reaction in a classical, uncatalyzed 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[5,11] have shown that [$ReMeO_3$] (MTO) and [$ReOCl_3(PPh_3)_2$] are good catalysts for aldehyde-olefination according to Equation (1).

$$RHCO + N_2CH(CO_2Et) + PPh_3 \rightarrow RHC{=}CH(CO_2Et) + N_2 + OPPh_3 \quad (1)$$

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They also showed that [Cp*$ReO_3$], [$CpReO_3$] and [($tBu_2$-bipy)$ReO_3$] display a lower activity in aldehyde-olefination. In the case of these trioxo complexes it was also shown that $PPh_3$ is necessary to reduce the trioxorhenium(VII) species to an active dioxorhenuim(V) species, which in the case of MTO was isolated as [$ReMeO_2(PR_3)_2 \cdot ReMeO_3$] (R = Ph, Cy). In a preliminary communication, we were able to confirm the activity of these dioxorhenuim(V) complexes, by using [$MeReO_2(\eta^2$-RC≡CR)] as efficient catalysts for olefination of activated aldehydes.[6a] We also proposed that reaction (1) is initiated by the intermediate formation of a phosphazine, $Ph_3PN{=}NCH(CO_2Et)$.

In the present study we explore the activity of other types of $Re^{VII}O_3$, $Re^{V}O_2$, and $Re^{V}O$ complexes in this reaction and present detailed investigations on the influence of changing the nature of the reaction components and conditions on catalytic activity, to attempt to establish a better understanding of the olefination reaction catalyzed by oxorhenium complexes.

## Results and Discussion

### Survey of oxorhenium complexes for aldehyde-olefination catalysis

The complexes **1**–**19** were preliminarily screened as catalysts in aldehyde-olefination according to Equation (1), with 4-nitrobenzaldehyde (4-nba), ethyldiazoacetate (eda), and $PPh_3$. A selection of these complexes was further tested under controlled standardized conditions to allow meaningful comparisons. These latter results for **1**–**9** are summarized in Table 1 for the olefination of 4-nitrobenzaldehyde (4-nba) with ethyldiazoacetate and $PPh_3$ at room temperature, and a reaction time of 2 h. TOF values were recorded after a reaction time of 5 min. Details are given in the Experimental Section.

The trioxorhenium(VII) complexes **4** and **5** show similar yields and TOF values. These are, however, only about half of those observed for MTO, a coordinatively unsaturated

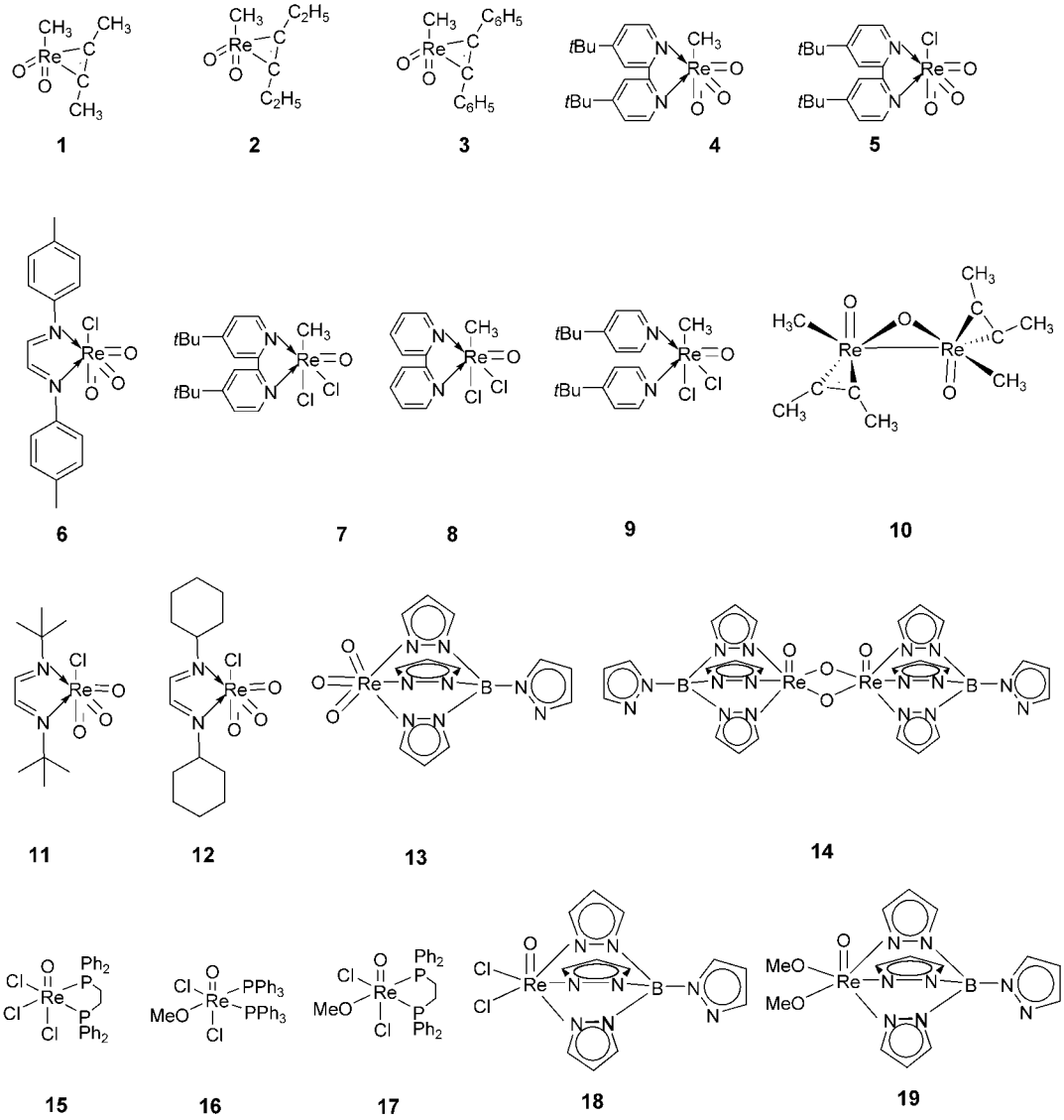



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Table 1. Catalytic results for compounds **1–9** in the olefination of 4-nba at room temperature; 5 mol% catalyst. The yields obtained with compounds **10–19** are below 5% and therefore are considered negligible, the TOFs are below 10 $mol\,mol^{-1}\,h^{-1}$.

| Catalyst | Yield [%][a] | TOF[b] [$mol\,mol^{-1}\,h^{-1}$] |
|---|---|---|
| **1** | 80 | 150 |
| **2** | 77 | 150 |
| **3** | 70 | 120 |
| **4** | 41 | 70 |
| **5** | 46 | 95 |
| **6** | 82 | 150 |
| **7** | 14 | 30 |
| **8** | 12 | 30 |
| **9** | 68 | 120 |

[a] Yield calculated after a reaction time of 2 h. [b] Calculated after a reaction time of 5 min.

molecule. The influence of the electronegativity of the chlorine ligand is felt in slightly higher yield/activity counts for Cl over $CH_3$. 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 a weaker donor than $t$Bu$_2$-bipy. In fact, it is likely that the diazabutadiene ligand is at least partially removed from the metal during the catalytic reaction.[12] Indeed, the reaction of **6** is slowed down by addition of $OPPh_3$; the yield decreases to 53%. Exploratory experiments carried out with other diazabutadiene complexes, [(DAB)$ReClO_3$], **11,12** have shown virtually no activity. DAB derivatives with saturated organic ligands on the nitrogen centers are known to coordinate more strongly to metal atoms in high oxidation states.[12] A marginal activity was also observed for the neutral complex [$ReO_3\{\kappa^3$-B(pz)$_4\}$] (**13;** pz = pyrazole ) analogue of [Cp*$ReO_3$]. These results show that reduced Lewis acidity and coordinative saturation of the metal centre hamper the catalytic reaction. Unfortunately, the extreme reactivity of [$ClReO_3$], the limiting reagent in this series, does not allow its use as catalyst.

The $Re^V$ complexes are divided in two groups: $ReXO_2$ and $ReX_3O$ derivatives.

The [$ReMeO_2(\eta^2$-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 $Me_2C_2 > Et_2C_2 > Ph_2C_2$. Excess alkyne slows down the reaction. In the case of **3** the yield goes down from 70 to 50% when excess $Ph_2C_2$ 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 **1** < **2** < **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.[13]

Interestingly, both the dimeric $Re^V$ complex [{Re[$\kappa^3$-B(pz)$_4$)]O(μ-O)}$_2$], (**14**) and the $Re^{IV}$ dimer **10** are totally inactive. The formation of a similar dimer in the reaction of [Cp*$ReO_3$] with $PPh_3$, namely [{Cp*ReO(μ-O)}$_2$] has been held responsible for the lack of aldehyde-olefination reactivity of [Cp*$ReO_3$].[14] Dimerization is not favored for the [$MeReO_2$] (MDO) complex.[15]

The prototypical catalyst in the $ReX_3O$ family is [$ReOCl_3(PPh_3)_2$], by far the most active Re catalyst for aldehyde-olefination. Under appropriate circumstances (reaction temperature: 50°C, catalyst/substrate = 1:1000) it can reach TOF values of $1200\,h^{-1}$. Replacement of $PPh_3$ by the bidentate dppe, as in complex (**15**), totally blocks catalysis suggesting the importance of $PPh_3$ dissociation as a condition for forming an active species. Also devoid of any catalytic action in aldehyde-olefination are the complexes [ReO(OMe)$Cl_2(PPh_3)_2$] (**16**), [ReO(OMe)$Cl_2$(dppe)] (**17**: dppe = 1,2-bis(diphenylphosphino)ethane), [Re(O)$Cl_2\{\kappa^3$-B(pz)$_4\}$] (**18**), and [Re(O)(OMe)$_2\{\kappa^3$-B(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 aldehyde-olefination 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 $PPh_3$ groups in [$ReOCl_3(PPh_3)_2$], the $R_2C_2$ 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*$ReO_3$] or the $\{\kappa^3$-B(pz)$_4\}$ ligands in the compounds **13**, **14**, **18**, and **19**, bidentate aliphatic diimines (as in **11** and **12**), bidentate phoshines (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 catalysts for the olefination of aldehydes.

### The influence of the substrates on the catalytic performance of [$ReMeO_2(\eta^2$-alkyne)] complexes

Equation (1) represents a complex multicomponent 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 to identify their action and influence in the outcome of the reaction.

**The diazo compounds**: In our previous study[6a] we used 4-nba as aldehyde, $PPh_3$ 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 $Ph_3P{=}NN{=}CH(CO_2Et)$ from $PPh_3$ and eda precedes and triggers the catalytic reaction. The formation of phosphazine is fast, as can be observed conveniently by $^{31}P$ NMR spectroscopy (see below). Addition of **3** to a solution of phosphazine preformed from $PPh_3$ and eda leads to a very exothermic reaction and liberation of $N_2$. If 4-nba is present, catalysis is then observed (see below for the characterization of this interaction).

In contrast, the use of trimethylsilyldiazomethane $N_2CH(TMS)$ instead of eda leads to no formation of olefination products, neither for aldehydes nor for ketones with selected Re complexes (**1**,**3**). $^{31}P$ NMR spectroscopy also

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shows that no phosphazine, $Ph_3P{=}NN{=}CH(TMS)$ is formed from $N_2CH(TMS)$ and $PPh_3$: the only signal present in the $^{31}P$ NMR spectrum of a 1:1 mixture of these compounds, even after several hours, belongs to free $PPh_3$.[8e] Other catalysts, however, for example, Ru-based systems[4c,9] generate aldehyde-olefination products starting from phosphines, $N_2CH(TMS)$, 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 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 24 h. $^{31}P$ NMR experiments have shown that in this case the corresponding phosphazine is formed but at a much slower rate than with eda, even after two 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 [$ReMeO_2(\eta^2$-alkyne)] catalysts. Without formation of phosphazine complexes **1**–**3** are seemingly unable to catalyze aldehyde-olefination.

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 uncatalyzed Wittig fashion. This possibility has been clearly observed in other metal-catalyzed olefination reactions according to Equation (1).[6b,9b]

There is, however, an important additional set of experiments that 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 $Ph_3P{=}C(CO_2Et)_2$ in the absence of catalyst. Furthermore, when a catalytic amount of compound **3** is added to the mixture $Ph_3P{=}C(CO_2Et)_2$/4-nba, no olefination products are obtained even after a reaction time of four days. As described already above, however, compound **3** catalyzes the reaction of 4-nba, $PPh_3$, and diazomalonate. This reaction is slow, but reaches good yields after several days. Accordingly, compound **3** does not initiate or catalyze the reaction of $Ph_3P{=}C(CO_2Et)_2$ with 4-nba and an olefination mechanism operating by the catalytic formation of ylides and the further reaction of these ylides with aldehydes (both catalyzed or uncatalyzed) can be excluded at least for $Ph_3P{=}C(CO_2Et)_2$. Therefore, it is important to point out that olefination of 4-nba with $N_2C(CO_2Et)_2/PPh_3$ 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.[6b,9b] We have selected some of those $Ru^{II}$- and $Fe^{II}$-based aldehyde-olefination catalysts, namely $[Cp^*RuCl(PR_3)_2]$[16] and [Fe(TPP)Cl][9c–e] (TPP = tetra(*p*-tolyl)porphyrin), and observed that they catalyze (very efficiently) the Wittig reaction of $PPh_3{=}CHCO_2Et$ with various aldehydes, but *do not catalyze* either the reaction of $PPh_3{=}C(CO_2Et)_2$ with aldehydes or the four-component reaction of $N_2C(CO_2Et)_2$ with aldehyde and $PPh_3$.

Taken together, these observations show that: 1) 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. 2) The four-component reaction catalyzed by $ReMeO_2(\eta^2$-alkyne) is able to form olefins from $N_2C(CO_2Et)_2$ that are not available by the Wittig reaction of $Ph_3PC(CO_2Et)_2$ with aldehyde nor by the action of other, usually more active catalysts, such as [Fe(TPP)Cl] that operate via an ylide intermediate.[9c–e] Therefore, the $ReMeO_2$ catalysts have the important advantage of being able to catalyze aldehyde-olefination reactions that are not feasible under classical or catalyzed Wittig conditions, that is, 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 rhena-oxethane 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.[6c] Although it has been convincingly shown to operate in other catalytic aldehyde-olefination systems, a catalytic reaction yielding an ylide can be by no means the only way to get to aldehyde-olefination products. Furthermore, for the $MeReO_2$ systems examined in this work we never observed the formation of significant amounts of ylides (by $^{31}P$ NMR spectroscopy) during the course of the catalytic reactions.

**The phosphines**: The type of phosphines used for oxygen abstraction is also a factor of major influence on the catalytic performance of Equation (1). The reaction of the phosphine with the diazo compound is fast in the case of ethyldiazoacetate (eda) and $PPh_3$. In less than 5 min all starting materials are completely consumed. Phosphazine, $Ph_3P{=}NN{=}CH(CO_2Et)$ is the only product formed according to $^{31}P$ NMR spectroscopy. The chemical shift observed in the $^{31}P$ NMR spectrum, $\delta(^{31}P) = 23.3$ ppm is identical within the error range to the value found in the literature for this phosphazine.[17] The signal for the $\alpha$ proton of eda at $\delta(^1H) = 4.69$ ppm is replaced by a new signal at $\delta(^1H) = 7.70$ ppm, in full accordance with the literature data for such reactions.[18] 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 $N_2CH(TMS)$, which does not react with $PPh_3$ to form a phosphazine under the conditions applied, also fails to start the catalytic cycle, although—of course—plenty of free $PPh_3$ and $N_2CH(TMS)$ is available. When **3** is added to a solution containing the phosphazine in a 1:10 ratio, a rapid reaction


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ensues with liberation of $N_2$ and an increase in temperature. Already after 5 min the $^{31}P$ NMR spectrum of the mixture reveals a significant decrease of the peak corresponding to the phosphazine as well as the appearance of a new peak at $\delta(^{31}P) = 29$ ppm (triphenylphosphine oxide). The peak corresponding to the $OPPh_3$ increases with time, limited in growth by the amount of catalyst present. Small peaks at $\delta(^{31}P) = 18.68$ and 17.10 ppm indicate the formation of ylides $Ph_3P{=}CH(CO_2Et)$ (*cis*oid and *trans*oid 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 $OPPh_3$. Therefore, again, the catalytic ylide formation can not be the major reaction with the Re catalysts of type $[ReMeO_2(\eta^2\text{-alkyne})]$. It should be noted that all these reactions occur quickly and the $^{31}P$ NMR spectra do not change significantly from a reaction of 10 min to 4 h, 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 $^{31}P$ NMR spectrum, correspond to the following species: unreacted phosphazine, triphenylphosphine oxide and the ylides, $Ph_3P{=}CHCO_2Et$, with signals of low intensity.[9a] The ylides are formed in small amounts either by decomposition of the phosphazine[17] or by reaction of $PPh_3$ with some $Re{=}CH(CO_2Et)$ species formed during the course of the reaction, that cannot be consumed otherwise in the absence of aldehydes.

To confirm the latter point, the reaction was also monitored in the presence of an aldehyde by $^{31}P$ and $^{1}H$ NMR spectroscopy. The reaction mixture consisted of $PPh_3$, eda, **3**, 4-nba, 1.1:1:0.07:1, which were added in this order. In the $^{31}P$ NMR spectrum recorded after a reaction time of 5 min only one significant signal is present, corresponding to $OPPh_3$. The ylides are not observed even in trace amounts, and within 4 h no further changes are detected in the spectrum.

MTO and compounds **3** and **5** were tested by using $P(OEt)_3$ as deoxygenating agent in catalytic aldehyde-olefinations according to Equation (1) with 4-nba and eda under the same conditions as described above for $PPh_3$. The catalytic activity decreases significantly (Table 2). An analogous observation was made with $[ReOCl_3(PPh_3)_2]$ as the catalyst. This is very likely due to the fact that phosphazine formation is much slower with triethylphosphite than with $PPh_3$, as can be seen from $^{31}P$ NMR measurements.

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

| Compound | $PPh_3$ | *cis*/*trans* | $P(OC_2H_5)_3$ | *cis*/*trans* |
|---|---|---|---|---|
| MTO | 77 | 10/90 | 17 | 22/78 |
| **3** | 70 | 5/95 | 7 | 29/71 |
| **5** | 46 | 10/90 | 15 | 10/90 |

In fact, reacting triethylphosphite with eda gives rise in the $^{31}P$ NMR spectra to the appearance of a new signal at $\delta(^{31}P) = 20.2$ ppm, assigned to the corresponding phosphazine, the signal corresponding to the triethylphosphite being found at $\delta(^{31}P) = 139$ ppm. However, in this case the reaction is not complete, even after days.

Summarizing the above results it can be again said that formation of phosphazine is essential to start aldehyde-olefination in the four-component system eda, $PR_3$, 4-nba, $ReO_xL_n$ catalyst. Free ylides are only detected in small amounts at high catalyst concentration in the absence of aldehyde.

**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/$PPh_3$/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 than with 4-nitrobenzaldehyde as substrate under the same reaction conditions. After a reaction time of 24 h, however, in both cases high yields of 70–82% are reached. In the case of benzaldehyde the yields after 24 h are about 50% both with complex **2** and **3** as the catalysts. Interestingly, in the case of 4-nitrobenzaldehyde the product yield increase from 2 to 24 h is only marginal (5% or less), whereas in the case of 4-bromobenzaldehyde and benzaldehyde the yield approximately doubles in the same period of time (see Figure 1).

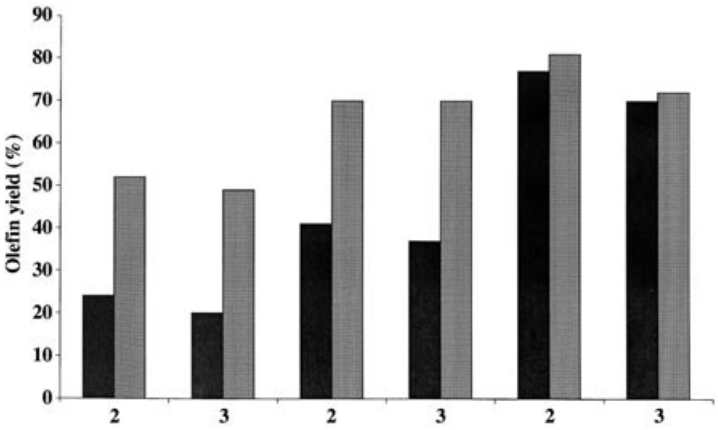


Figure 1. Catalytic activity of compounds **2** and **3** with benzaldehyde, 4-bromobenzaldehyde and 4-nba, respectively. Black columns: yield after 2 h, grey columns: yield after 24 h.

The reason for this observation in the case of 4-nitrobenzaldehyde may be related to the fast accumulation of the by-product $OPPh_3$ that significantly blocks the reaction at an early stage. In fact, if extra $OPPh_3$ 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, acetone, and benzophenone as substrates instead of the aldehydes does not lead to significant olefin yields within a reaction time of 24 h with both catalysts **2** and **3**. Notably, benzophenone does not react with the ylide $Ph_3P{=}CHCO_2Et$ even after a reaction time of eight days, whereas, this ylide reacts

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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.

The interaction of different aldehydes with catalyst **3** was also examined by $^{1}H$ and $^{13}C$ NMR spectroscopy in $CDCl_3$. 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 $\delta(^{1}H) = 2.61$ ppm in the free molecule to $\delta(^{1}H) = 2.49$ ppm in the mixture) and the $CH_3$ protons of the ketone from $\delta(^{1}H) = 2.55$ ppm to $\delta(^{1}H) = 2.51$ ppm. To examine this behavior 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, $PPh_3$ as the substrates) with compound **3** as catalyst in an acetophenone/catalyst ratio of 1:1, 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 $Re^{V}$ center of $[ReMeO_2(\eta^2\text{-alkyne})]$ in competition with the substrates of catalysis, namely the phosphazine, thus blocking the catalytic site.

**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, $RC_6H_4CH{=}NN{=}CH(CO_2Et)$ 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 Equation (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 a reaction time of two hours (78% instead of 70%). The ratios of the substrate were changed and runs with 4-nba/$PPh_3$/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 $PPh_3$ or eda. In the presence of an excess of eda the formation of diethyl maleate as by-product is observed.

**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 2 h. The results in $CH_2Cl_2$, $CHCl_3$, and $CH_3CN$ were 26, 24, and 38% respectively after 2 h. 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 $CHCl_3$ and $CH_3CN$. 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 h 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 a reaction time of 5 min) increases from about $120\,h^{-1}$ at 20 °C to about $170\,h^{-1}$ at 50 °C. A further raise in the reaction temperature, however, does not accelerate the reaction significantly, the TOF staying below $200\,1\,h^{-1}$.

**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, $N_2$ and $OPPh_3$ 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 $^{17}O$-NMR spectroscopy from a reaction with $^{17}O$-labeled **3*** published previously.[6a]

In the case of catalyst **3** at −30 °C, the carbene species was characterized by the signals at $\delta(^{13}C) = 323$ ppm and $Re{=}C{-}H$ at $\delta(^{1}H) = 16.32$ ppm both in accordance with the values reported in the literature for related complexes, such as $[RuClCp(=CHCO_2Et)(PPh_3)]$.[19] 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 complex 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 carbene complexes in the catalytic aldehyde-olefination has independently been confirmed by Chen et al. for $Re_2O_7$-based, cationic catalysts in the gas phase by mass spectrometry, although in their systems a catalytic ylide formation (following the carbene formation) seems to take place.[6b]


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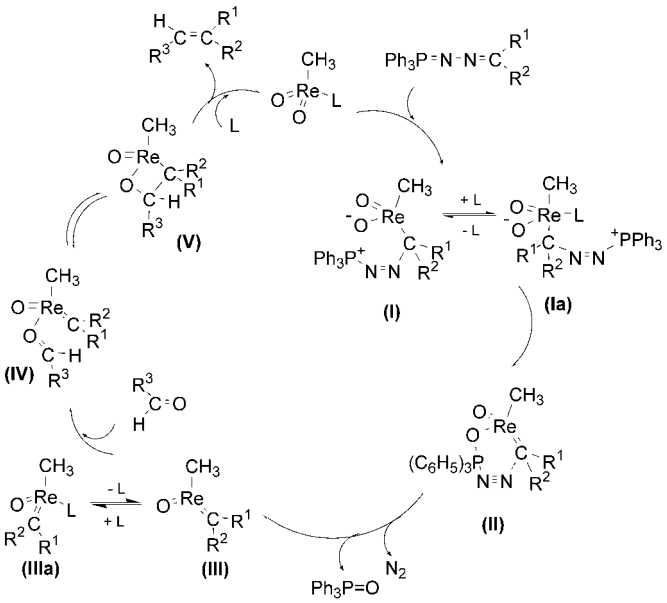

Scheme 1. Catalytic cycle for aldehyde-olefination with [$ReMeO_2L$] complexes (L = alkyne, $PPh_3$) with $PPh_3$ and $N_2CR^1R^2$.

**The catalytic cycle for aldehyde-olefination with [$ReMeO_2L$] 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**, $PPh_3$, eda and 4-nba as reaction partners. An 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 aldehydes, diazo compounds, ylides, or $PPh_3$, whereas a rapid reaction is observed between these and phosphazine.

Therefore, the first step is the interaction of [$ReMeO_2(\eta^2$-alkyne)] with the phosphazine $Ph_3P{=}N{-}N{=}CR^1R^2$] 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 of **II** that precedes $Ph_3PO$ elimination. A six-membered ring is formed in which 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) leading to the formation of **IIIa**. $^{13}C$ NMR spectroscopy 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. 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 atom facilitating the formation of the metalla-oxetane 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 triphenylphosphine in **IIIa** leads to the formation of an ylide, as has been suggested by Chen et al.[6b,c] 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 large 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 $N_2C(CO_2Et)_2$. Since a phosphazine is formed from $PPh_3$ and $N_2C(CO_2Et)_2$, 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 by ylide formation, it would not take place since $Ph_3P{=}C(CO_2Et)_2$ does not react with aldehydes, even 4-nba. Moreover, $Ru^{II}$ and $Fe^{II}$ catalysts known to operate by ylide formation are not active catalysts for olefination with $N_2C(CO_2Et)_2$. Therefore, this catalytic system, although not being as 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 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 incapable of promoting ketone-olefination and of activating electron-rich diazo compounds, for example, the synthetically useful $N_2CH(TMS)$. 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 $Re^VO_2$ derivatives for enlarging their scope of applications in olefination reactions.

## Conclusion

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 [$ReMeO_2(\eta^2$-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

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as intermediates is not observed. Furthermore, the olefination of diazomalonate can be catalyzed, whereas 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 $ReMeO_2$ type catalysts. This does, of course, not exclude that other catalysts lead to olefin formation by an entirely or partially different pathway in which ylide intermediates play a prominent role.

## Experimental Section

All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under nitrogen before use. All compounds were purchased from Aldrich unless stated otherwise. The ligand *p*-tolyl-DAB,[20] compounds **1**–**3**,[13] **4**,[21] **5**,[22] **7**–**9**,[23] **10**,[13] $[ReOCl_3(PPh_3)_2]$,[24] $[ReOCl_3(dppe)]$,[25] **13**,[26] **14**,[27] **15**,[25] **16**,[28] **17**,[25] **18**,[27] and **19**[27] were synthesized according to published procedures. Complexes **13**–**19** were a kind offer from Dr. Isabel Santos and Dr. António Paulo from the Instituto de Tecnologia Nuclear, Sacavém, Portugal. Elemental analysis were obtained at the ITQB by Conceição Almeida. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer by using KBr pellets as the IR matrix. $^1H$, $^{31}P$, and $^{13}C$ NMR spectra were obtained by using a 400 MHz Bruker Avance DPX-400 and a 300 MHz Bruker CPX 300 spectrometer. 85% $H_3PO_4$ was used as an internal standard for the $^{31}P$ NMR measurements.

**Preparation of $[ReClO_3(DAB)]$ complexes**

All these complexes were prepared in a similar fashion described in detail for DAB = 4-$MeC_6H_4N$=CHCH=$NC_6H_4$Me-4) (**6**)

**Preparation of 6**: A solution of $Re_2O_7$ (0.400 g, 0.826 mmol) in THF (15 mL) was treated with $Me_3SiCl$ (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 diethyl ether and dried under vacuum. Yield 63%. IR selected (KBr pellets): $\tilde{\nu} = 1597$ m, 1500 s, 947 s, 922 vs, 910 s, 896 vs, 858 s, 814 $cm^{-1}$ s; $^1$HNMR ($CDCl_3$, 300 MHz, RT): $\delta = 8.12$ (s, 2H), 7.65–7.12 (m, 8H), 2.41–2.24 ppm (m, 6H); elemental analysis calcd (%) for $C_{16}H_{16}N_2O_3ClRe$ (505.978): C 37.98, H 3.19, N 5.54; found: C 37.78, H, 3.34, N 5.45.

**Complexes 11–13**: These complexes were prepared in a similar fashion by using the corresponding ligands, respectively $Me_3CN$=CHCH=$NCMe_3$ and $(C_6H_{11})$N=CHCH=N$(C_6H_{11})$.

Data for compound **11**: IR selected (KBr pellets): $\tilde{\nu} = 3080$ m, 2980 vs, 2928 s, 2893 s, 983 s, 947 s, 923 vs, 902 vs, 877 $cm^{-1}$ s; $^1$HNMR ($CDCl_3$, 300 MHz, RT): $\delta = 7.51$ (s, 2H), 1.19–1.69 ppm (m, 18H); elemental analysis calcd (%) for $C_{10}H_{20}N_2O_3ClRe$ (437.94): C 27.43, H 4.60, N, 6.40; found: C 27.44, H, 5.00, N 6.39.

Data for compound **12**: IR selected (KBr pellets): $\delta = 3203$ m, 2939 vs, 2858 s, 935 s, 922 vs, 908 s, 898 $cm^{-1}$ vs; $^1$HNMR ($CDCl_3$, 300 MHz, RT): $\delta = 7.72$–7.09 (m, 2H), 2.24–1.26 ppm (m, 22H); elemental analysis calcd (%) for $C_{14}H_{24}N_2O_3ClRe$ (490.02): C 34.32, H 4.94, N 5.72; found: C 34.45, H 5.05, N 6.01.

**Catalytic aldehyde-olefination using diazoacetate**: 4-Nitrobenzaldehyde (0.6 g, 3.9 mmol), $PPh_3$ (1.12 g, 4.3 mmol), fluorene (0.4 g, internal standard), 5 mol% (if not indicated otherwise) of compounds **1**–**19** and eda (0.40 mL, 3.9 mmol) were dissolved in dry THF (20 mL) and allowed to react at room temperature. For benzaldehyde and 4-bromobenzaldehyde the same molar amounts (if not indicated otherwise) were used. Samples were taken after the first 5 min and then every 30 min for 2 h. The conversion of aldehyde (4-nitrobenzaldehyde, benzaldehyde, and 4-bromobenzaldehyde) and the formation of ethyl-4-nitrocinnamate, ethylcinnamate, and ethyl-4-bromocinnamate were monitored by GC and calculated from calibration curves ($r^2 = 0.999$, internal standard fluorene) recorded prior to the reaction course.

**Catalytic ketone-olefination**: Dry acetone (15.82 g, 0.272 mol), $PPh_3$ (1.88 g, 7.2 mmol), compound **3** (0.148 g, 0.36 mmol), and eda (0.904 g, 7.92 mmol) were refluxed at 100 °C for 48 h. The reaction mixture was distilled until no more acetone came out and the residue was treated with dry hexane and cooled. The solution was filtered and concentrated to yield a crude oil. The oil was chromatographed in silica gel over hexane, and the product was obtained from the required fractions as a colorless oil.

**Catalytic aldehyde-olefination using diazomalonate**: 4-nba (0.5 g, 3.3 mmol), $PPh_3$ (0.95 g, 3.6 mmol), fluorene (0.4 g, internal standard), compound **3** (0.068 g, 0.166 mmol), and ethyl diazomalonate (0.739 g, 3.97 mmol), were dissolved in dry THF (20 mL) and allowed to react at room temperature.

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