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(η^2-Alkyne)methyl(dioxo)rhenium Complexes as Aldehyde-Olefination Catalysts

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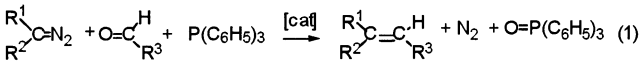
The olefination of aldehydes and ketones is a very important transformation in organic synthesis.[1] Although the Wittig reaction as well as its modified versions provide a highly effective and general method, they still have several drawbacks.[2] Useful organometallic stoichiometric reagents based on titanium and zinc are, however, expensive, difficult to handle, and not completely devoid of unwanted side reactions.[3] The search for reagents that carry out the olefination reaction in a catalytic manner has produced some promising results with Ru,[2c] Rh,[2c] Fe,[4] Mo,[5] and Re complexes[6] as catalysts (eq 1). In the Re case, both complexes $ReOCl_3(PPh_3)_2$ and CH_3ReO_3 (MTO) show a remarkable catalytic activity, but the reaction mechanism remains speculative.[7] In the MTO-catalyzed reaction, it was proposed that the first step is oxygen atom abstraction by PPh_3 to form "CH_3ReO_2" (MDO). This then reacts with eda (ethyldiazoacetate) to form a carbene complex, $CH_3ReO_2(CHCO_2Et)$, which reacts further with the aldehyde, forming the olefin and regenerating MTO. Accordingly, Re(V) MDO derivatives should be suitable precursors for catalytic aldehyde olefination.



(1)

This is indeed the case for adducts of MDO with acetylenes, $CH_3ReO_2(R{\equiv}R)$ (R = C_6H_5 (**1**), R = C_2H_5 (**2**), R = CH_3 (**3**)). Spectroscopic studies clarifying the mechanism and the nature of the active species as well as a new mechanism for oxygen abstraction by PPh_3 are presented.

The catalytic activity of the Re(V) compounds **1**−**3**[8a] was tested, using 4-nitrobenzaldehyde (4-nba), eda, and PPh_3. The reactions were conducted at room temperature in THF with the reaction ratios of PPh_3:eda:4-nba:catalyst 1.1:1.2:1.0:0.05.[8b] The reaction is clearly catalytic because no olefination products are formed in the absence of **1**−**3**. Moreover, PPh_3 is also necessary, and no olefination products are formed in its absence even with **1**−**3** being present. Additional catalytic runs, with new charges of substrate, lead to the same product yields, indicating that the catalyst is stable under catalytic conditions. Complexes **1**−**3** show a very similar behavior in the catalytic runs: after 2 h of reaction time, there is no more formation of olefin, and the yields are around 75%, the cis/trans selectivity is ca. 5/95, and the TOFs are up to 150 mol/(mol × h). The aldehyde conversion is in all cases 100%. The azine ($4\text{-}NO_2{-}C_6H_4CH{=}N{-}N{=}CH(CO_2Et)$) is the only significant byproduct. Excess alkyne in the catalytic reaction mixture leads to less than one-half of the usual olefin yield. The reaction proceeds quickly, and, in all cases, the yield after the first 5 min is over 25% of the total yield after 2 h.

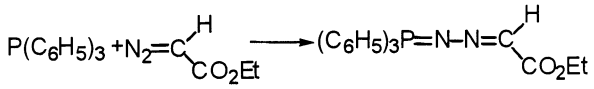
To elucidate the mechanism, spectroscopic studies were performed using in situ ^{31}P, ^{17}O, ^{13}C, and ^{1}H NMR spectroscopy (see Supporting Information). Compound **1** was selected as the catalyst for these tests. For the NMR measurements, the amounts of catalyst used were higher than those used in the catalytic runs, to enable the observation of the changes of the catalytic active species during the course of the reaction. Because the catalytic reaction involves four different reagents (**1**, PPh_3, eda, 4-nba), we considered it necessary to identify possible initial reactions between sets of two and three of the reagents involved.

As mentioned above, the olefination reaction requires both **1** and PPh_3. In the absence of **1**, no olefin is formed, but a slow reaction takes place under formation of azine and $OPPh_3$ (eq 2).

$$4\text{-}O_2NC_6H_4CHO + PPh_3 + N_2CHCO_2Et \rightarrow 4\text{-}O_2NC_6H_4CH{=}N{-}N{=}CHCO_2Et + O{=}PPh_3 \quad (2)$$

This reaction is already known to take place when PPh_3, an aldehyde, and eda are reacted in benzene under reflux conditions.[5] Most important, however, is the fact that this azine does not react with **1**. Addition of **1** to a mixture of eda, 4-nba, and PPh_3, which was previously allowed to react for some hours, does not change the NMR spectra of the organic product compounds (azine and $OPPh_3$) and does not lead to evolution of N_2. Therefore, the reaction presented in eq 2 can be envisaged as a side reaction with respect to the catalytic reaction in eq 1. It consumes aldehyde and PPh_3 but does not lead to olefination products and does not involve **1**.

Aldehyde (4-nba) and PPh_3 do not react, and no $OPPh_3$ is formed (^{31}P NMR). Catalyst **1** also does not react with PPh_3 (^{31}P, ^{17}O NMR evidence). Catalyst **1** furthermore does not react with eda (^{13}C, ^{1}H, ^{17}O NMR evidence). This is a surprising observation because the formation of carbene complexes has been postulated upon similar reactions between MTO and eda in olefination catalysis.[6c,9] In fact, the ^{13}C, ^{1}H, and ^{17}O NMR spectra of a 1:1 mixture of eda and **1** in $CDCl_3$ showed no indication of any reaction. Most notably, no ^{13}C peak was observed around $\delta(^{13}C)$ = 300 ppm (Re=C carbene signal).[10] Furthermore, no evidence was found for a metallacyclopropene oxide species postulated as an alternative possible intermediate for aldehyde olefination with MTO-derived catalysts.[7a,11] PPh_3 and eda react rapidly to form the phosphazine according to eq 3.



(3)

When PPh_3 is reacted with eda at room temperature, the instantaneous and quantitative formation of the corresponding

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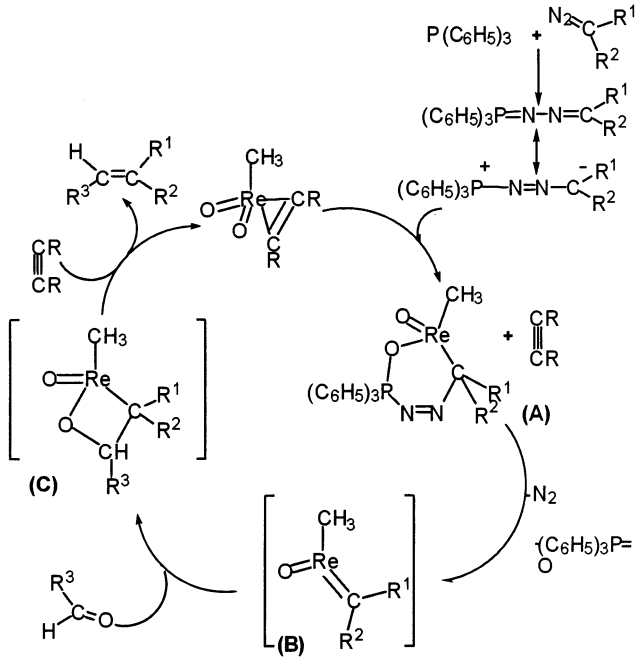
Scheme 1



phosphazine[12,13] is observed. This strongly suggests that the formation of phosphazine precedes and triggers the catalytic olefination reaction because this is the only fast reaction that ensues between the reagents in the beginning of the olefination reaction. In accordance with this hypothesis, addition of a substoichiometric amount of **1** to a mixture of PPh_3 and eda (phosphazine) results in immediate, vigorous liberation of N_2 with a significant temperature rise and the formation of $OPPh_3$. It can be concluded that $OPPh_3$ is formed by the reaction of phosphazine (not PPh_3) with **1**. This was confirmed by separate ^{17}O NMR experiments with ^{17}O labeled **1** in a stoichiometry of phosphazine:**1** = 1.2:1. A Re intermediate with a ^{17}O NMR signal at 676 ppm is formed. This chemical shift indicates a compound with a terminal, not a bridging, oxygen ligand.[14] The ^{17}O NMR signal of **1** (δ = 731 ppm) disappears completely. After one of the terminal oxygens is abstracted from the catalyst without replacement (no other oxygen source such as the aldehyde is present), the intermediate decomposes quickly (the $Re-CH_3$ signal disappears as well as the remaining terminal oxygen signal), and no further phosphazine is consumed. During the decomposition, a dark brownish precipitate is formed (EA shows high Re and O content), while the $OPPh_3$ signal is not significantly increasing (^{31}P, ^{17}O NMR evidence). The amount of catalyst originally present is therefore equivalent (within the measurement error) with the formed $OPPh_3$, meaning that only one, not two, oxygen of **1** is transferred to the PPh_3.

If aldehyde is present and lower amounts of catalyst are used (aldehyde:phosphazine:**1** = 5:5:1), however, the reaction cycle is completed, and the unstable intermediate is transformed into **1**. During this process, the ^{17}O NMR signal at 731 ppm decreases quickly, while two new signals at 45 ($^{17}OPPh_3$) and 676 ppm are rising. While the signal at 676 ppm diminishes with time, the signal at 45 ppm increases until the signal at 676 ppm has completely vanished. The $Re-CH_3$ signals, however (compound **1**: $\delta(^1H)$ = 2.64 ppm; intermediate $\delta(^1H)$ = 2.88 ppm), do not disappear in this case in contrast to the aldehyde-free system, and only minor amounts of brownish precipitate are formed until the catalytic reaction comes to an end.

On the basis of these findings, we propose the mechanism shown in Scheme 1 for the olefination reaction: Phosphazine is rapidly formed at the beginning of the reaction and reacts with the metal dioxide complex. The α-carbon atom attacks the electron-deficient metal center, presumably setting free the η^2-alkyne ligand. As the α-carbon atom of the phosphazine interacts with the Re atom, the electron-deficient phosphorus atom interacts with one of the terminal oxygen atoms of the catalyst, forming a six-membered metallacycle intermediate **A**. This process leads to an abstraction of one of the terminal oxygen atoms of the Re complex and in due course to the liberation of both $OPPh_3$ and N_2. (Using ^{17}O-labeled **1** leads to the formation of ^{17}O-labeled $OPPh_3$.) Control experiments have shown that **1** does not exchange oxygen with any reaction partner. The intramolecular rearrangement is very fast (vigorous liberation of N_2). ^{17}O NMR experiments show that the intermediate compound **B** has one terminal Re=O bond ($\delta(^{17}O)$ = 676 ppm). In the absence of aldehyde, **B** decomposes quickly. The carbene carbon Re=*C* atom is observed at $\delta(^{13}C)$ = 323 ppm. However, in the presence of aldehyde, **B** recaptures oxygen (forming an oxo-metallacyclobutane species **C**) and then liberates the olefin and **1** (^1H, ^{17}O NMR evidence), thus completing the catalytic cycle. The generality of this mechanism for other rhenium-oxo catalysts is currently being investigated.

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Supporting Information Available: Selected NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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