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Iron(II) N-heterocyclic carbene complexes in catalytic one-pot Wittig reactions: Mechanistic insights

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ABSTRACT

An iron(II) N-heterocyclic carbene (NHC) complex is applied as catalyst for aldehyde olefination with ethyl diazoacetate (EDA) in the presence of triphenylphosphine. The reaction leads to high olefin yields with very good *E*-selectivities. The key step of the reaction is the catalytic *in situ* generation of a phosphorus ylide. Mechanistic studies reveal two possible pathways for the formation of the Wittig reagent with respect to the carbene source being the metal carbene (NHC)Fe^{IV}=CH(CO_2Et), and phosphazine, Ph_3P=N–N=CH(CO_2Et). Based on the experimental observations a new mechanism for the transformation of phosphazine is proposed.

1. Introduction

During the last years iron complexes have attracted increasing attention as catalysts for a variety of organic reactions [1,2]. Prominent among these reactions are iron-mediated carbon-carbon bond formations. The element iron bears numerous advantages in comparison with other (transition) metals, such as abundance, low cost and non-toxicity in many complexes. Accordingly, iron is in several cases considered as a promising substitute of the still widespread application of expensive or toxic metals such as Pd, Ni or Sn [3–7]. Other than coupling reactions, olefinic C—C bonds can be generated by the olefination of carbonyl motifs in e.g. the Horner-Wadsworth-Emmons reaction, the Peterson reaction and the Kocienski-Julia reaction [8–10]. Among these, non-catalytic Wittig-type reactions are still predominantly used for both small and large reaction scales; however, such reactions necessitate multiple steps, starting with the generation of a nucleophilic reagent [11–18].

Catalytic Wittig reaction variations are known with transition metals such as Mo, Re, Ru and Fe [19–42]. Many of these systems require high catalyst loadings while providing only moderate olefin yields under quite harsh reaction conditions. The first highly active catalyst was presented by Woo et al. using an iron(II) porphyrin complex in low concentrations at ambient temperature [29–31]. These results prompted the question for the reaction mechanism of catalytic Wittig reactions. Depending on the catalyst system three main mechanistic proposals (Scheme 1) emerged, assuming either a direct carbene transfer *via* a metallaoxetane species (pathway A), the catalytic formation of a Wittig reagent *via* a metal carbene complex (pathway B), or *via* a pre-coordination of the diazo compound (pathway C) [29–42]. Based on pathway A, which was postulated by Herrmann et al. for a Re based organometallic catalyst, Kühn et al. proved the presence of a rhenium carbene intermediate by *in situ* NMR spectroscopy [32–39]. On the other hand isolation of a phosphorus ylide and indication of an unstable iron carbene intermediate suggested pathway B for iron porphyrin systems [29–31,40]. However, the catalytic formation of a Wittig reagent from phosphazine, Ph_3P=N–N=CHR, as illustrated in pathway C was spectroscopically observed for Mo and Fe complexes [41,42].

In order to broaden the scope and to elucidate the iron-mediated aldehyde olefination, two iron(II) complexes bearing tetradentate bis(N-heterocyclic carbene)-bis(pyridine) (**1**) and cyclic tetra(N-heterocyclic carbene) (**2**) ligands are examined in this work (Fig. 1) [43–45]. These compounds have been shown to be active catalysts in, e.g. epoxidation of olefins, hydroxylation of aromatic compounds, and oxidation of cyclohexane [46–49]. So far iron-catalyzed olefination of aldehydes is known for porphyrin or corrole ligands but has never been performed with N-heterocyclic carbene ligated compounds [29–31,40,42]. Elucidating the catalytic behavior is targeted in this work, together with

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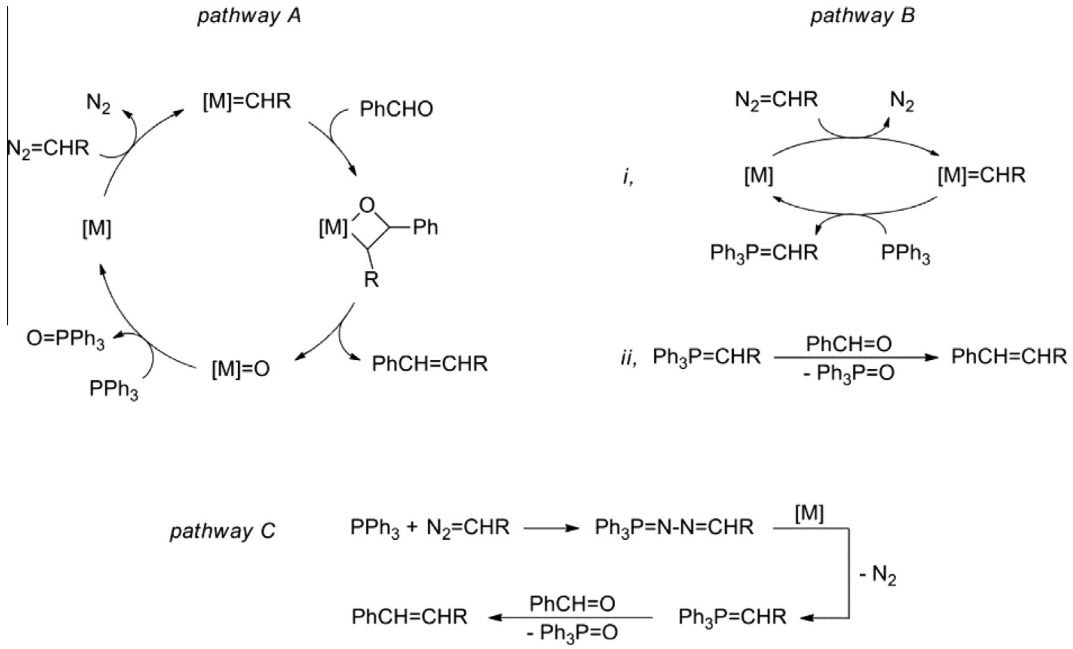


Scheme 1. Different mechanistic pathways in the catalytic aldehyde olefination postulated by Herrmann et al. (A), Woo et al. (B) and Lu et al. (C) [29–42].

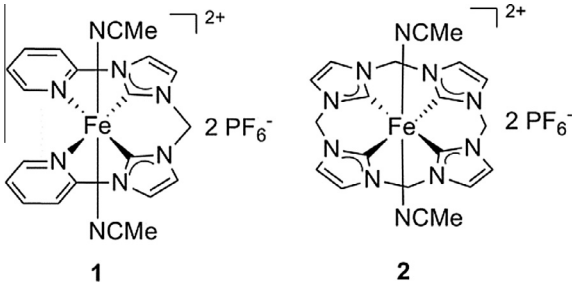


Fig. 1. Dicationic iron(II) complexes with square-planar bis(N-heterocyclic carbene)-bis(pyridine) (**1**) and cyclic tetra(N-heterocyclic carbene) (**2**) ligand systems applied in the catalytic aldehyde olefination [43–45].

the examination of the catalytic mode of action in comparison with literature-known mechanisms.

2. Experimental section

2.1. General remarks

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were obtained water-free from an Mbraun solvent purification system. Acetonitrile-d_3 was dried over P_4O_{10} and degassed by two freeze-pump-thaw cycles prior use. All other reagents, including ethyl diazoacetate (EDA, contains ⩾13 wt.% dichloromethane; Sigma Aldrich), were purchased from commercial suppliers and were used without further purification. Complexes **1** and **2** as well as the phosphazine compound were synthesized according to published procedures [38,43,44]. For the characterization of compounds and the time-dependent monitoring of catalytic reactions NMR spectra were recorded on a Bruker Avance III 400 and a Bruker Avance DPX 400, respectively. Chemical shifts are given in parts per million (ppm) and the spectra were referenced by using the residual solvent shifts as internal standards (^{1}H NMR: $CDCl_3$, δ 7.26, CD_3CN, δ 1.94; ^{13}C NMR: $CDCl_3$, δ 77.16, CD_3CN, δ 1.32). Electrospray ionization (ESI) mass spectrometry (MS) data were acquired on an LCQ-Fleet from Thermo Scientific. GC–MS analysis was performed by using a 7890B GC System (Agilent Technologies) and a 5977A (Agilent Technologies) mass-selective detector equipped with a HP-5 ms UI column (30 m × 0.250 mm; 0.25 μm film, Agilent Technologies).

2.2. Catalytic synthesis of E-ethyl cinnamate (*3*)

Triphenylphosphine (430 mg, 1.64 mmol, 1.2 equiv.) was added to a solution of **1** (0.10 mg, 10 mol%) in MeCN (15 mL) and stirred until complete dissolution. Then benzaldehyde (140 μL, 1.4 mmol, 1.0 equiv.) and ethyl diazoacetate (200 μL, 1.64 mmol, 1.2 equiv.) were added and the reaction mixture was stirred over night at 70 °C. After cooling to room temperature, the crude product was purified by column chromatography using hexane/EtOAc (10/1). Upon drying in vacuo, a colorless oil was obtained (220 mg, 1.25 mmol, 91%). ^{1}H NMR (400 MHz, CD_3CN, 296 K): δ 7.67 (d, $^3J_{H-H}$ = 16.1 Hz, 1H, =C*H*C$_6$H$_5$), 7.65–7.61 (m, 2H, —C*H*), 7.42–4.41 (m, 3H, —C*H*), 6.50 (d, $^3J_{H-H}$ = 16.1 Hz, 1H, =C*H*CO$_2$Et), 4.21 (q, 2H, —C*H*$_2$), 1.29 (t, 3H, —C*H*$_3$). ^{13}C NMR (101 MHz, CD_3CN, 296 K): δ 167.5, 145.2, 135.4, 131.3, 129.9, 129.1, 119.3, 61.2, 14.6.

2.3. Preparation of PhCH=N—N=CHCO$_2$Et (*4*) [41]

A solution of benzaldehyde (739 μL, 7.30 mmol, 1.0 equiv.), PPh_3 (1.92 g, 7.30 mmol, 1.0 equiv.) and ethyl diazoacetate (884 μL, 7.30 mmol, 1.0 equiv.) in MeCN (15 mL) was stirred over night at 50 °C. After cooling to r.t. the solvent was evaporated in vacuo. The resulting crude product was purified by column chromatography using hexane/EtOAc (15/1) as eluent. The product was yielded as yellow crystals (1.3 g, 6.4 mmol, 88%) after drying in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ 8.60 (s, 1H, =C*H*Ph), 7.91 (s, 1H, =C*H*CO$_2$Et), 7.84–7.81 (m, 2H, —C*H*), 7.53–7.43 (m, 3H, —C*H*), 4.40 (q, 2H, —C*H*$_2$), 1.39 (t, 3H, —C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, 296 K): δ 164.9, 163.3, 151.7, 133.2, 132.4, 129.3, 129.0, 62.1, 14.3.

2.4. Synthesis of compound **5**

To a solution of complex **2** (10 mg, 13 μmol, 1.0 equiv.) in MeCN (5 mL) ethyl diazoacetate (3.2 μL, 26 μmol, 2.0 equiv.) in MeCN (2 mL) was slowly added at −30 °C. The mixture was slowly warmed to r.t. and stirred for 4 h. After the mixture was concentrated to 3 mL at r.t., 7 mL of diethyl ether was added. The mixture was filtered and the residue was dried in vacuo to give **5** as a gray solid. ^{1}H NMR (400 MHz, CD_3CN, 296 K): δ 8.34 (s, 2H, NC*H*N), 7.39 (m, 4H, —C*H*), 6.83 (s, 4H, —C*H*), 6.82 (d, $^2J_{H-H}$ = 14.7 Hz, 4H, —CH_2), 5.89 (d, $^2J_{H-H}$ = 14.7 Hz, 4H, —CH_2), 4.27 (s, 2H, =C*H*($CO_2CH_2CH_3$)), 4.11 (q, 4H, —CH_2CH$_3$), 1.25 (t, 6H, —CH$_2$CH_3). ESI-MS: m/z 930.60 $[5 + 2H^+ + PF_6^-]^+$, 784.89 $[5 + H^+]^+$, 638.90 $[5 - PF_6^-]^+$.

2.5. Catalytic synthesis of Ph_3P=CH(CO_2Et)

A solution of PPh_3 (431 mg, 1.64 mmol, 1.0 equiv.) and **1** (0.1 g, 0.17 mmol, 10 mol%) in MeCN (12 mL) was heated at 70 °C. Subsequent addition of ethyl diazoacetate (0.2 mL, 1.64 mmol, 1.0 equiv.) resulted in gas evolution for approximately ten minutes. The reaction mixture was then stirred for 4 h at this temperature. The solvent was evaporated and the residue was dissolved in 10 mL of EtOAc. After the solution was filtered over Al_2O_3 and washed using EtOAc as eluent, the solvent was removed at 40 °C. The yellow crude product was stirred in 50 mL of petroleum ether and the resulting white solid was filtered. Residual solvent was evaporated in vacuo, yielding the phosphorus ylide as a white solid (360 mg, 1.00 mmol, 63%). ^{1}H NMR (400 MHz, CD_3CN, 296 K): δ 7.67–7.60 (m, 9H, —C*H*), 7.53–7.49 (m, 6H, —C*H*), (3.87, major + 3.69, minor) (b-s, 2H, —CH_2), (2.80, major + 2.50, minor) (b-s, 1H, =C*H*), (1.13, major + 0.67, minor) (b-s, 3H, —CH_3). ^{31}P NMR (162 MHz, CD_3CN, 296 K): δ 17.7 (s, *cisoid*), 16.2 (s, *transoid*). ESI-MS: m/z 349.3 $[C_{22}H_{22}O_2P]^+$.

2.6. Experimental procedure for the catalytic aldehyde olefination

Under standard conditions (4 mol% relative catalyst concentration), benzaldehyde (7.6 μL, 75 μmol, 1.0 equiv.) and a respective amount of PPh_3 were added to 0.4 mL of a 7.5 mM stock solution of **1** or **2** in acetonitrile-d_3 and dissolved completely in a J. Young NMR tube. After the reaction was started by addition of ethyl diazoacetate (11 μL, 90 μmol, 1.2 equiv.) under argon atmosphere the sealed tube was shaken and immediately placed in the NMR spectrometer monitoring the reaction progress for several hours. For catalyst concentrations 1 mol% and 10 mol%, 1.9 mM and 18.8 mM stock solutions of complex **1** in acetonitrile-d_3 were prepared, providing the same reaction volume for each reaction.

By means of ^{1}H NMR the respective reactants and products were quantified using the solvent of the diazo reagent (CH_2Cl_2 δ 5.45) as internal standard. The following signals were used for the quantification of the respective substrates in acetonitrile-d_3: benzaldehyde δ 10.03 (1H, PhC*H*O), *E*-ethyl cinnamate δ 6.50 (1H, PhCH=C*H*(CO_2Et)), *Z*-ethyl cinnamate δ 5.98 (1H, PhCH=C*H*(CO_2Et)), azine **4** δ 8.45 (1H, PhC*H*=N—N=C*H*CO_2Et), phosphorus ylide δ 3.89 (2H, Ph_3P=CH($CO_2CH_2CH_3$)), 4-nitrobenzaldehyde δ 10.15 (1H, NO_2PhC*H*O), 4-anisaldehyde δ 9.86 (1H, MeOPhC*H*O), ethyl 4-nitrocinnamate δ 6.63 (1H, NO_2PhCH=C*H*(CO_2Et)), ethyl 4-methoxycinnamate δ 6.36 (1H, MeOPhCH=C*H*(CO_2Et)).

2.7. GC–MS analysis of cyclopropanation reaction

The experiment was conducted according to a modified procedure by Woo et al. [30]. Under argon atmosphere ethyl diazoacetate (22.6 μL, 0.02 mmol, 1.0 equiv.) was added to a solution of **1** (14.6 mg, 0.02 mmol, 1.0 equiv.) and styrene (256 μL, 1.60 mmol, 80 equiv.) in MeCN (1 mL) at −40 °C. The reaction mixture was allowed to warm to r.t. and stirred for 1 h. For qualitative analysis 100 μL of the reaction solution was diluted with 1500 μL MeCN and characterized by GC-MS. Next to the main product 1-carbethoxy-2-phenylcyclopropane, dimerization products of EDA, ethyl maleate and ethyl fumarate, were detected (see SI for spectra).

3. Results and discussion

The catalytic performance of complexes **1** and **2** as potential catalysts for aldehyde olefination using benzaldehyde, ethyl diazoacetate (EDA) and triphenylphosphine is evaluated. Time-dependent yield studies show high aldehyde consumption for both complexes. Application of 4 mol% of **1** affords *E*-ethyl cinnamate in 46% yield and 20% azine, PhCH=N—N=CHCO_2Et, after 4 h at 70 °C. In contrast, no olefin formation takes place in the presence of complex **2**, leading to the selective accumulation of (usually unwanted) azine (63%; Fig. 2) by a non-catalytic reaction. A [2 + 2]-cycloaddition reaction between aldehyde and phosphazine, Ph_3P=N—N=CHCO_2Et, an intermediate which is formed from EDA and PPh_3 *in situ*, leads to azine as (by-)product **4** (Scheme 2) [19–42,50].

In other catalytic reactions, e.g. epoxidations, complexes **1** and **2** do not differ so noticeably in their reactivity, prompting further investigations into their difference in performance in aldehyde olefination [43–49]. Reaction of **2** solely with EDA reveals decomposition of **2** to a defined metal-free species **5**, which can be identified by ^{1}H NMR spectroscopy and by ESI-MS analysis (Scheme 3). The formation of this compound might take place *via* an unstable iron(IV) carbene species as it is known for a series of iron complexes [29–31,51,52]. Substrate olefination therefore does not take place as complex **2** decomposes by ligand olefination. An analogous decomposition product was not identified for **1**.

3.1. Catalytic aldehyde olefination

Complex **1** was further investigated as olefination catalyst (see Table S1, Supporting Info). Key goals for the optimization of catalyst performance were high catalytic activity, e.g. high conversion of aldehyde, and high selectivity, which in the following text is indicated by the ratio of *E*-olefin to (unwanted) azine. Control reactions lacking one of the reagents (catalyst **1**, PPh_3, EDA,

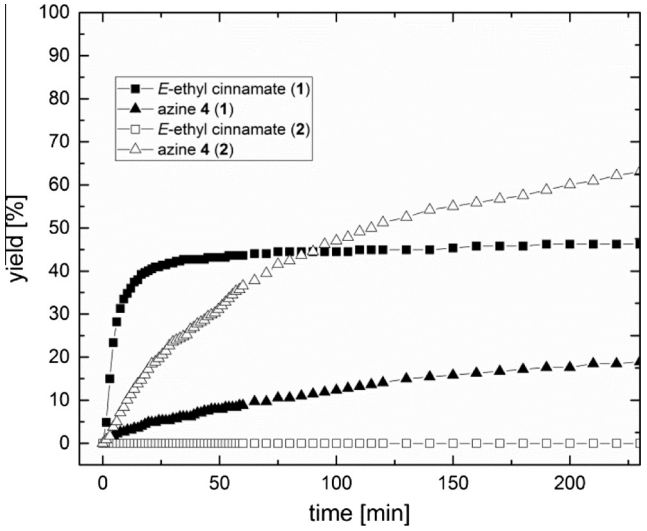
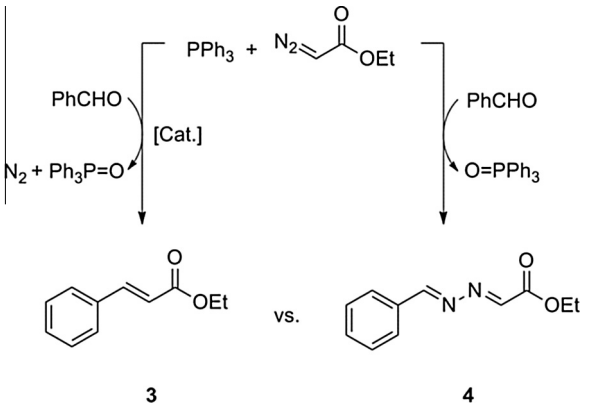


Fig. 2. Performance of iron(II) NHC complexes **1** and **2** as aldehyde olefination catalysts. Reaction conditions: benzaldehyde (75 μmol, 1.0 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (90 μmol, 1.2 equiv.), catalyst (3 μmol, 4 mol%) in CD_3CN at 70 °C. Time-dependent yields were determined *via* ^{1}H NMR spectroscopy.



Scheme 2. Catalytic aldehyde olefination (left) and non-catalytic parallel reaction (right) forming the desired *E*-ethyl cinnamate (**3**) and the undesired azine (**4**), respectively [19–42].

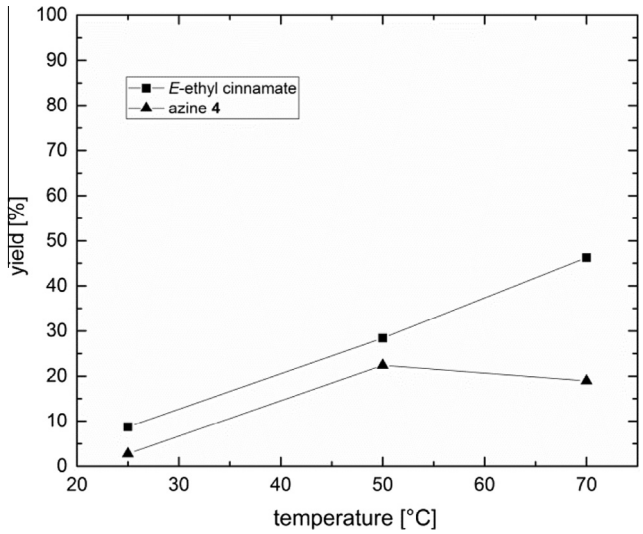


Fig. 3. Temperature dependence of the catalytic aldehyde olefination using **1** as catalyst. Reaction conditions: benzaldehyde (75 μmol, 1.0 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (90 μmol, 1.2 equiv.), **1** (3 μmol, 4 mol%) in CD_3CN. Yields were determined *via* ^1H NMR spectroscopy after 4 h.

benzaldehyde) yielded in all cases no olefin. In the absence of catalyst **1** azine **4** was observed as end-product (see Scheme 2, right) whereas the absence of PPh_3 led to the decomposition of **1** by EDA. Omitting EDA had no major effect on the reaction mixture. It should be noted that the use of other phosphines (e.g. PEt_3) led to no olefin formation.

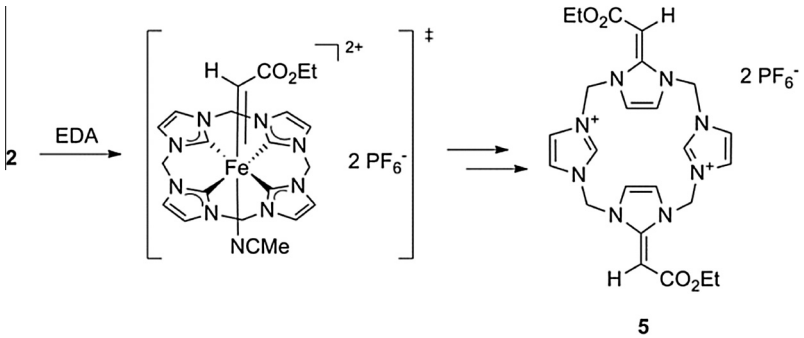
The first parameter to be evaluated in olefination catalysis using **1** was the reaction temperature. The activity and selectivity of reactions at ambient conditions and elevated temperatures were monitored. The conversion of aldehyde increases at higher reaction temperatures with 12% at r.t., 53% at 50 °C and 68% at 70 °C. Parallel to increasing conversion, the yield of olefin increases from 9% at r.t. and 28% at 50 °C to 46% at 70 °C; this corresponds to selectivities of 75%, 53% and 68%, respectively. It should be noted, that **1** selectively catalyzes the formation of *E*-olefin (⩾94%), whereas only small amounts of *Z*-olefin are detected. The azine yield shows different temperature dependence with an increase in azine yield from 3% at r.t. to 23% at 50 °C with a subsequent decrease in yield to 20% at 70 °C (Fig. 3). Hence, at increased temperature a higher activity and selectivity of the catalyst system are observed. This indicates that the productive olefination reaction is accelerated to a higher degree at increased temperatures than the unwanted azine side reaction.

A significant increase in *E*-ethyl cinnamate yield is observed when increasing the catalyst concentration from 1 mol% (4%) to 4 mol% (46%) and 10 mol% (63%), corresponding to the selectivities of 7%, 68% and 79% at 70 °C. A parallel decrease is observed for the azine yield reaching a minimum of 2% at a catalyst concentration of 10 mol%. The slower reaction velocity at room temperature apparently hampers the catalytic reaction. Accordingly, the *E*-olefin/azine ratio can be effectively controlled by variation of the catalyst concentration (Fig. 4).

Further investigations on the olefin formation were performed by variation of the substrate ratios. Product yield decreases when the concentration of PPh_3 is lowered relative to EDA. When using 1.0 equiv. of PPh_3 and 0.5 equiv. of PPh_3 in the presence of 1.2 equiv. of EDA, the olefin yield is – relatively low – with 24% and 18%, respectively. In the case of 1.5 equiv. and 2.5 equiv. of PPh_3, however, *E*-ethyl cinnamate yields increase significantly in a sigmoidal fashion to 50% and 72%, respectively (Fig. 5). The highest amount of by-product is obtained for $PPh_3 \approx$ EDA, since a stoichiometric reaction to phosphazine, the precursor of azine, can occur. In contrast to the catalytic reaction, a further increase in the amount of PPh_3 has a negative effect on the side reaction. Consequently, aldehyde olefination is strongly favored in the presence of excess PPh_3, but not in the presence of excess of EDA.

This result can be explained by the catalyst stability. ^1H NMR experiments suggest decomposition of **1** in the presence of excess EDA, while it is known that excess PPh_3 does not lead to complex decomposition [45]. By doubling the EDA amount, a faster catalyst deactivation is observed, correlating with a lower olefin yield.

Based on these results, an optimized protocol was established for the catalytic olefination using **1** (Fig. 6). Yields up to 90% of *E*-ethyl cinnamate and only 2% of the by-product were obtained after 2 h, corresponding to a selectivity of 95%. This shows that



Scheme 3. Possible oxidative addition reaction of complex **2** and EDA indicated by the formation of **5**.

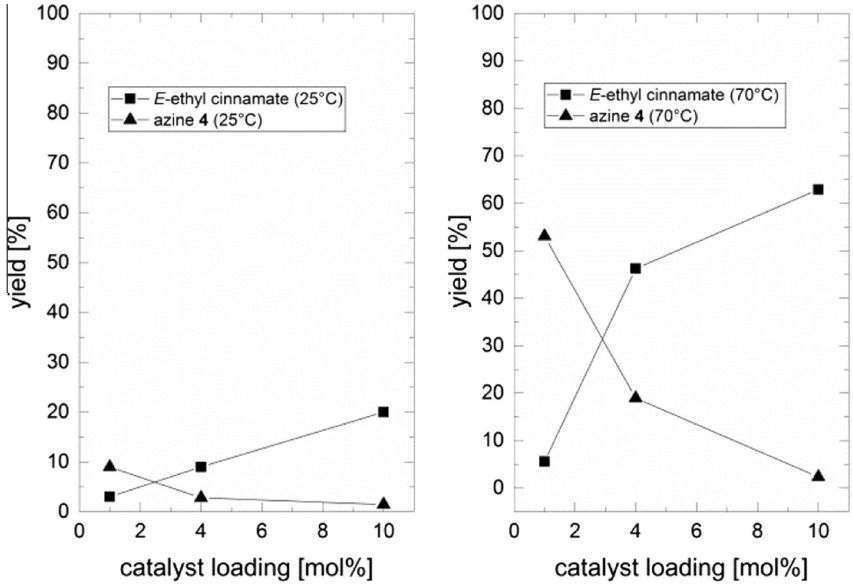


Fig. 4. Effects of increasing concentrations of **1** in the catalytic aldehyde olefination at 25 °C and 70 °C. Reaction conditions: benzaldehyde (75 μmol, 1.0 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (90 μmol, 1.2 equiv.), **1** (0.75 μmol, 1 mol%), **1** (3 μmol, 4 mol%) and **1** (7.5 μmol, 10 mol%), respectively, in CD_3CN. Yields were determined *via* ^1H NMR spectroscopy after 4 h.

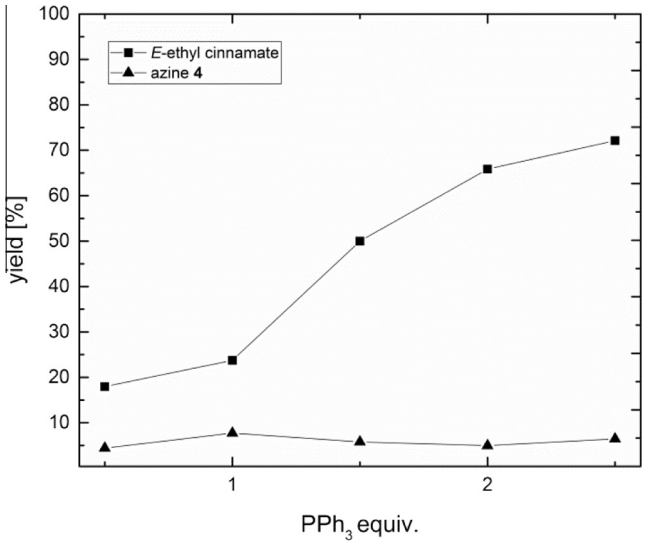


Fig. 5. Influence of the variation of the PPh_3 amount in the catalytic aldehyde olefination. Reaction conditions: benzaldehyde (75 μmol, 1.0 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (37.5 μmol, 0.5 equiv.; 75 μmol, 1.0 equiv.; 112.5 μmol, 1.5 equiv.; 150 μmol, 2 equiv.; 187.5 μmol, 2.5 equiv.), **1** (3 μmol, 4 mol%) in CD_3CN at 70 °C. Yields were determined *via* ^1H NMR spectroscopy after 1 h.

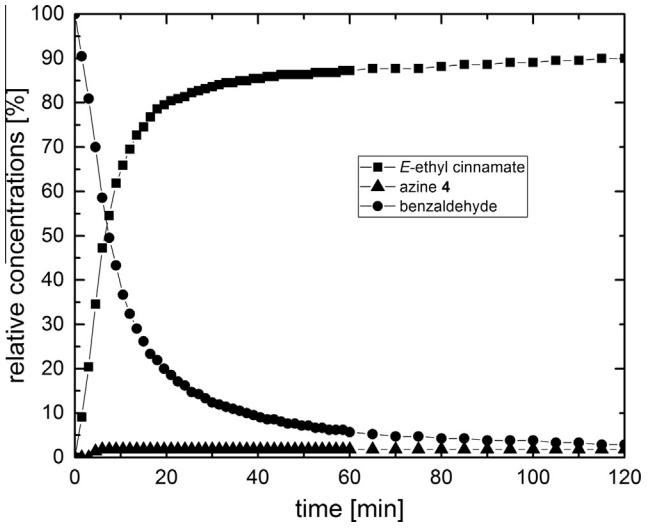


Fig. 6. Time-dependent conversion of benzaldehyde yielding an excellent olefin/azine ratio at optimized reaction conditions: benzaldehyde (75 μmol, 1.0 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (150 μmol, 2 equiv.), **1** (7.5 μmol, 10 mol%) in CD_3CN at 70 °C. Relative concentrations were determined *via* ^1H NMR spectroscopy.

under improved reaction conditions azine side reactions can be effectively suppressed.

3.2. Mechanistic studies

In order to rationalize the discussed trends in catalyst behavior, investigations on the catalytic mode of action of **1** in aldehyde olefination were performed considering previously published pathways (Scheme 1). According to the catalytic cycle published by Herrmann et al. for Re(VII/V) as shown in pathway A, stoichiometric olefin formation should be observable in the absence of PPh_3 as the phosphine is only necessary to regenerate the Re(V)-catalyst in the last reaction step [32–39]. However, stoichiometric reactions of **1**, benzaldehyde and EDA yielded no olefin, thus ruling out reaction pathway A for compound **1**.

The key step in pathway B is the formation of a metal carbene intermediate [Fe]=CH(CO_2Et). Most likely due to its high reactivity the iron carbene complex was not detectable *via* ^1H and ^{13}C NMR at r.t. and lower temperatures to −40 °C in this work. Therefore, a typical method for its indirect detection, namely a cyclopropanation reaction which was also successfully applied by Woo et al., was attempted to find an analogous intermediate for **1** [29–31,51]. By means of GC-MS analysis 1-carbethoxy-2-phenylcyclopropane was found in the reaction mixture styrene/EDA/**1** = 80/1/1 at r.t. Moreover, dimerization by-products of EDA, ethyl maleate and ethyl fumarate, deriving from metal carbenes were observed (see Supporting Information). As common reactivity patterns for metal carbenes, the addition of carbene to olefin and

carbene dimerization, were observed, an iron carbene intermediate of **1** is likely to be formed in the aldehyde olefination mixture. A series of experiments were then set up in order to examine the potential of the iron(II) NHC system to oxidize phosphine to phosphorus ylide in a catalytic manner as shown in pathway B.

From recent studies it is known that acetonitrile ligands, which coordinate axially to **1** can be readily exchanged with PPh_3, leading to a product mixture of mono- (**1a**) and di-substituted (**1b**) analogs (Scheme 4). Dissolved in MeCN, only **1b** releases a PPh_3 ligand whereas no transformation from **1a** to **1** occurs [45]. Therefore, it is assumed that **1a** predominantly exists in the reaction mixture. In order to follow further *in situ* generated phosphorus compounds, ^{31}P NMR experiments were performed. In the resulting spectrum of the typical four-component mixture (PhCHO/EDA/PPh_3/**1** = 1.0/1.2/1.2/0.1) large amounts of O=PPh_3 (26.1 ppm) are found, as well as small quantities of non-coordinating PPh_3 (−5.8 ppm) and substituted complex species **1a** (60.4 ppm) and **1b** (43 ppm). Furthermore, a small peak appears at 20.7 ppm, which corresponds to residual phosphazine.

More interestingly, in the absence of aldehyde, no O=PPh_3 is observed, whereas large signals emerge at 16.1 and 17.7 ppm, which derive from the phosphorus ylide $Ph_3P{=}CH(CO_2Et)$ (*transoid* and *cisoid* form) [53]. The catalytic synthesis of a phosphorus ylide from EDA and PPh_3 is further confirmed by ^1H NMR spectroscopy and ESI-MS analysis. The reaction of the catalytically formed phosphorus ylide from EDA/PPh_3/**1** and benzaldehyde to give *E*-ethyl cinnamate could be monitored by time-dependent ^1H NMR, which corresponds to a Wittig-type reaction (Fig. 7). Due to overlapping peaks in the aromatic range of ^1H NMR spectra a reliable quantification of either PPh_3 or phosphazine was not possible.

The replacement of benzaldehyde by 4-nitrobenzaldehyde and 4-methoxybenzaldehyde, respectively, leads to different reaction rates. Time-dependent studies show that the olefination reaction is faster with an aldehyde exhibiting an electron-withdrawing substituent (—NO_2) whereas an electron-donating group (—OCH_3) in *para* position slows the reaction down (Fig. 8). These findings correspond well to the trend received in classic (non-catalyzed) Wittig reactions.

Overall, the observation that complex **1** can catalyze the synthesis of a Wittig reagent and that the time-dependent decrease in phosphorus ylide correlates with the olefin formation, strongly suggests that the olefination proceeds *via* catalyzed Wittig reaction. It is therefore possible for iron(II) NHC complex **1** to follow the mode of action described in pathway B.

Nevertheless further investigations on whether the Wittig reagent can also derive from the catalytic transformation of phosphazine, as shown in pathway C for iron(IV) corrole complexes, were performed. Results show that when a catalytic amount of **1** is added to a freshly prepared solution of phosphazine, in the presence of residual PPh_3, phosphorus ylide signals appear, while the phosphazine peak disappears completely in the ^{31}P NMR spectrum. Control reactions show that this transformation does not occur when heating the phosphazine compound at 70 °C for several hours. This strongly suggests that in addition to pathway B also pathway C is a likely mode of action for **1**.

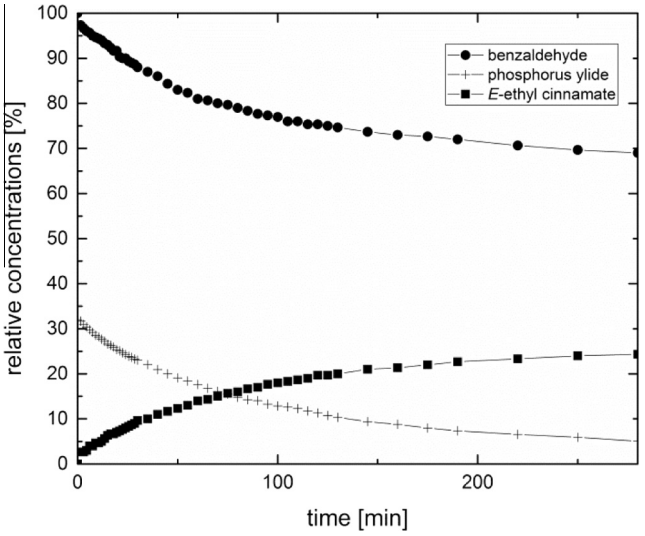


Fig. 7. Time-dependent product formation corresponding to conversion of aldehyde and *in situ* generated phosphorus ylide. Reaction conditions: benzaldehyde (75 μmol, 1 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (90 μmol, 1.2 equiv.), **1** (7.5 μmol, 10 mol%) in CD_3CN at r.t. Relative concentrations were determined *via* ^1H NMR spectroscopy.

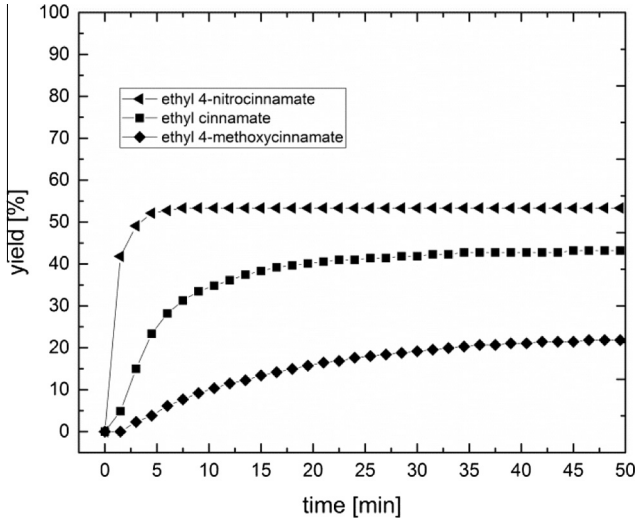
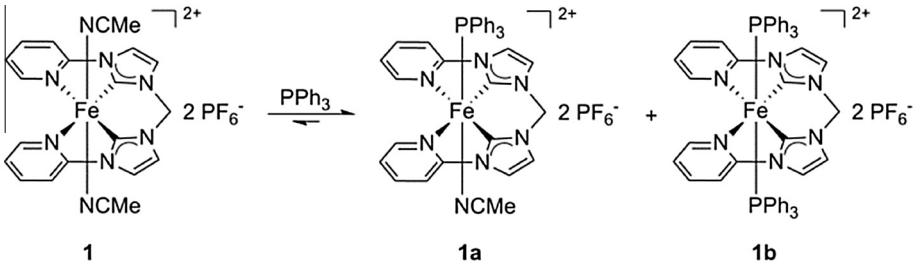
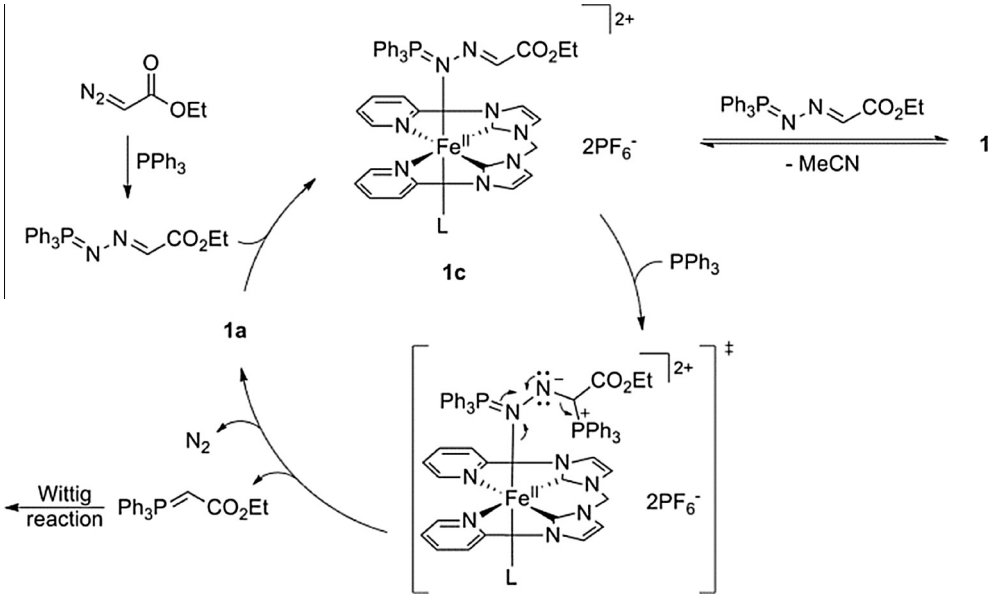


Fig. 8. Influence of the aldehyde variation on the catalytic reaction rate. Reaction conditions: aldehyde (75 μmol, 1 equiv.), EDA (90 μmol, 1.2 equiv.), PPh_3 (90 μmol, 1.2 equiv.), **1** (3 μmol, 4 mol%) in CD_3CN at 70 °C. Time-dependent yields were determined *via* ^1H NMR spectroscopy.



Scheme 4. Exchange reaction of axially coordinating acetonitrile ligands in **1** with triphenylphosphine leading to the mono- and bis-substituted complexes **1a** and **1b** [45].



Scheme 5. Proposed catalytic pathways for the synthesis of the phosphorus ylide; L = MeCN/PPh_3.

Pathway C as shown in Scheme 1 indicates the formation of phosphorus ylide from the stoichiometric reaction of catalyst and phosphazine. However, the reaction mixture **1**/Ph_3P=N–N=CH(CO_2Et) = 1/1 yielded no such result whereas after the addition of PPh_3 (**1**/Ph_3P=N–N=CH(CO_2Et)/PPh_3 = 1/1/1) signals of the phosphorus ylide were observed in the ^{31}P NMR spectrum. This result broadens the function of PPh_3 in the catalytic reaction with **1** aside from its role as the Wittig reagent.

In 2001, Grubbs et al. proved the existence of low valent iron(II) phosphazine complexes [54]. In analogy, complex **1c** is suggested to be generated during the reaction. The latter might play a key role in the catalytic formation of the phosphorus ylide as shown in Scheme 5. A possible pathway for the formation of **1c** is the coordination of the *in situ* generated excess phosphazine. The catalytic conversion continues with the reaction of an additional PPh_3 equivalent with **1c** in a nucleophilic fashion, initiating the subsequent release of N_2 and the phosphorus ylide followed by a classic Wittig-type reaction with the aldehyde. This proposed catalytic route relates to the results depicted in Fig. 5 that an excess of PPh_3 over EDA leads to a distinct increase in *E*-ethyl cinnamate potentially by using PPh_3 as a nucleophile in the reaction. Furthermore, this proposed cycle might explain why the stoichiometric reaction of **1** and phosphazine yields no Wittig reagent in the absence of free PPh_3 as experimentally shown (see above). A previously reported similar mechanism following pathway C, suggested an internal ylide formation *via* a cyclic intermediate from a stoichiometric reaction of phosphazine and catalyst [42]. This stands in contrast to the observations described above for compound **1**, where PPh_3 > 1 equiv. is necessary to form the ylide. Overall the observations summarized in this work show that both, pathway B and a variation of pathway C are likely to occur in parallel during the catalytic aldehyde olefination with complex **1**.

4. Conclusion

Iron(II) N-heterocyclic carbene complexes can be applied as catalysts for aldehyde olefination reactions with EDA and PPh_3. The examined Fe(II) NHC compound provides a clean, selective Wittig-type olefination in a one-pot fashion without the necessity of the preformation of an ylide needed in a classic un-catalyzed Wittig reaction. Complex **1** catalyzes aldehyde olefination reactions with yields of up to 90% with very good *E*-selectivity ($\geqslant$94%).

Mechanistic investigations reveal that the catalytic formation of phosphorus ylide is likely to proceed *via* two different pathways. On the one hand, intermediate (NHC)Fe=CH(CO_2Et) potentially serves as carbene donor for PPh_3 as described by Woo et al. [29–31]. On the other hand, the transformation of phosphazine in the presence of uncoordinated PPh_3 is observed. The dependence of the olefin yield on PPh_3 suggests a mechanism in which non-coordinating PPh_3 acts as nucleophile in the formation of the phosphorus ylide.

Based on the obtained results a two-step mechanism appears to be responsible for the overall reaction: i, the catalytic formation of phosphorus ylide followed by ii, a Wittig-type conversion of the aldehyde to the respective olefin. Based on positive results of a possible iron carbene intermediate, a catalytic metal centered redox reaction is likely in the aldehyde olefination with **1**. Furthermore, it is proposed that the catalytic behavior of **1** is also caused by Lewis acid catalysis, explaining the need for further nucleophiles in the crucial phosphazine conversion step in aldehyde olefination.

Acknowledgments

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.09.029.

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