

Copper catalysed 1,4-addition of organozinc reagents to α , β -unsaturated carbonyl compounds: a mechanistic investigation

Emma Gallo ^{a,*}, Fabio Ragaini ^a, Licia Bilello ^a, Sergio Cenini ^a, Cesare Gennari ^b,
Umberto Piarulli ^{b,c,*}

^a *Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università degli Studi di Milano, Istituto CNR di Scienze e Tecnologie Molecolari, Via Venezian 21, I-20133 Milano, Italy*

^b *Dipartimento di Chimica Organica e Industriale, Centro di Eccellenza CISI, Università degli Studi di Milano, Istituto CNR di Scienze e Tecnologie Molecolari, Via Venezian 21, I-20133 Milano, Italy*

^c *Dipartimento di Scienze Chimiche e Ambientali, Università degli Studi dell'Insubria, Via Valleggio 11, I-22100 Como, Italy*

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Abstract

A mechanistic study of the 1,4-addition of diethylzinc to 2-cyclohexenone catalysed by copper complexes of the Schiff base ligand **H₂L1** was performed. The kinetic law of this system was determined and the nature of the different copper complexes involved in the reaction was investigated. The experimental results indicate a first-order dependence of the reaction rate on 2-cyclohexenone concentration, a zero-order on diethylzinc concentration, and a first-order dependence with respect to the concentration of a 1:1.2 mixture of Cu(OTf)₂ and **H₂L1**. A sharp change in the kinetics of the reaction was observed at catalyst concentrations higher than 9 mM, indicating the possible formation of catalytically inactive species. An aggregate copper complex, with the molecular formula [(Cu**L1**)₂ · Cu(OTf)₂](TfOH)_{1/3} (**1**), is formed upon mixing Cu(OTf)₂ and ligand **H₂L1** in toluene. Complex **1** is reduced in situ to a catalytically active copper(I) species by addition of 12 equivalents of Et₂Zn. This species is able to perform the conjugate addition to 2-cyclohexenone under stoichiometric conditions and resumes its catalytic activity in the presence of 2-cyclohexenone and Et₂Zn. © 2004 Elsevier B.V. All rights reserved.

Keywords: Asymmetric catalysis; Michael addition; Mechanism; Copper; Zinc; Schiff base

1. Introduction

The 1,4-addition of organozinc reagents to electron-poor olefins (α , β -unsaturated carbonyl compounds and nitroolefins) [1] has recently raised a lot of interest, due to the mild conditions, the easy availability of a number of different organozinc reagents and the excellent enantioselectivity which can be attained. In the case of its catalytic asymmetric version [2], excellent enantioselectivities were obtained using chiral trivalent phosphorus compounds, such as chiral phosphoramidites (e.e. >98%) [3a], phosphites (e.e. up to 96%) [3b,3c], oxazoline-phosphite ligands (e.e. up to 90%) [3d], and

peptide based phosphine ligands (e.e. up to 98%) [3e,3f], which were used in combination with copper(I) or copper(II) salts. On the other hand, examples using non-phosphorus ligands are limited to the family of combinatorially exploited chiral Schiff base ligands of general structure **H₂L** (e.e. up to 91%) [4], chiral hydroxymethylene bis(oxazolines) (e.e. up to 94%) [5] and chiral *N*-heterocyclic carbenes (e.e. up to 93%) [6] (Chart 1).

The common feature of the Schiff base and hydroxymethylene bis(oxazolines) ligands is that they contain multiple metal binding sites (e.g. a phenolic OH, an imine nitrogen and a sulfonamide, in the case of ligands **H₂L**) and that such a multidentate array should favour the formation of organometallic complexes with well organised spatial arrangements.

Despite numerous mechanistic studies on the conjugate addition reaction using lithium or magnesium

* Corresponding authors. Tel.: +390250314372; fax: +390250314405 (E. Gallo); fax: +390312386449 (U. Piarulli).

E-mail addresses: emma.gallo@unimi.it (E. Gallo), umberto.piarulli@uninsubria.it (U. Piarulli).

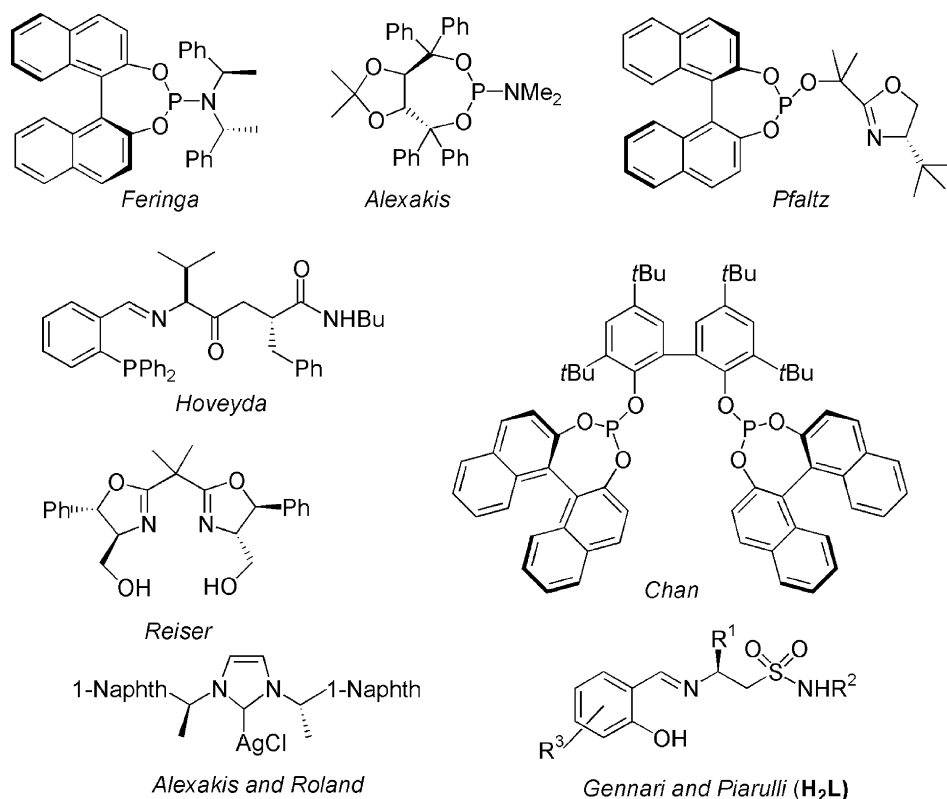
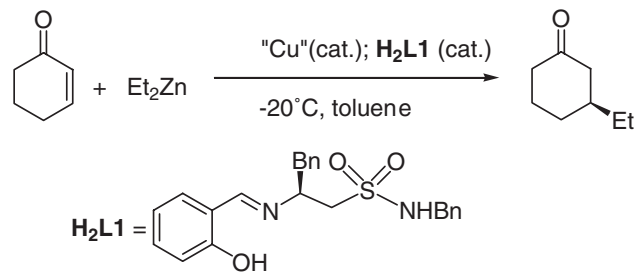


Chart 1.

cuprates [7], in the case of dialkylzinc reagents only two recent reports [8] deal with the kinetics and the mechanism of this reaction. In these reports, the authors used simple achiral sulfonamides (such as *N*-benzyl-benzenesulfonamide) as ligands for the metals (Cu and Zn). The principal results of this study are: (i) the reaction kinetics and its rate law were determined: a first-order dependence on the substrate, diethylzinc, and the catalytic system, formed by Cu^IOTf and *N*-benzyl-benzenesulfonamide, was found; (ii) based on the measurement of ¹²C/¹³C isotope effect, the 1,4-addition of diethylzinc to cyclohexenone was shown to occur through a concerted mechanism; (iii) the zinc enolate, which is formed in the conjugate addition step, has a dimeric structure. The proposed reactive intermediate, according to these authors, is represented in Fig. 1.

We report herein a mechanistic study of the 1,4-addition of diethylzinc to 2-cyclohexenone catalysed by the



Scheme 1.

copper complex of ligand **H₂L1** (Scheme 1). We have determined the kinetic law of our system (by ¹H NMR) and studied the nature of the different copper complexes involved in the reaction.

2. Results and discussion

2.1. Conjugate addition to 2-cyclohexenone

In order to study the kinetic law and the mechanism of this reaction, we decided to run all the kinetic experiments with ligand **H₂L1** (Scheme 1), which gave very good conversions albeit in a modest enantiomeric excess (24%). The reaction was run in toluene, preforming the copper complex in situ by stirring catalytic amounts of Cu(OTf)₂ and **H₂L1** at +20 °C. The addition of

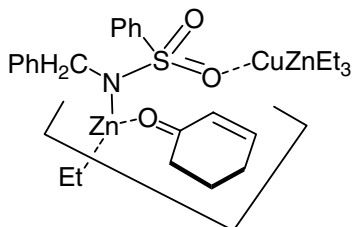


Fig. 1. Proposed reactive intermediate as discussed in [8].

diethylzinc (1.0 M in *n*-hexane) and of 2-cyclohexenone was then performed at $-20\text{ }^{\circ}\text{C}$, the reaction stirred for 3 h and quenched (aqueous NH_4Cl) at the same temperature. Conversions were measured by injection of the crude reaction mixtures in a gas chromatograph equipped with a chiral capillary column which also measured the enantiomeric excess of the reaction product [9]. An optimization of the ligand structure and reaction conditions, such as solvent, temperature, concentration and stoichiometry, was already reported elsewhere [4c]. A preliminary study, aimed at determining the influence of the source of copper on the yield and enantioselectivity of the reaction, revealed that these parameters are almost independent on the copper source [$\text{Cu}(\text{OTf})_2$ (yield 90%, e.e. 24%); $\text{Cu}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (yield 80%, e.e. 26%); CuCN (yield 85%, e.e. 22%)].

2.2. Kinetics

The reactions were performed in an NMR tube using d_8 toluene as solvent. The copper complex was preformed by mixing $\text{Cu}(\text{OTf})_2$ and $\text{H}_2\text{L1}$ which allowed to react for 30 min at RT. A molar ratio $\text{Cu}(\text{OTf})_2\text{:H}_2\text{L1} = 1\text{:}1.2$ was always used throughout the present investigation for consistency with the previous work in this area [4]. The resulting solution was cooled to $-78\text{ }^{\circ}\text{C}$ before addition of Et_2Zn and 2-cyclohexenone. In order to determine the rate law, the reaction rates were measured at $-20\text{ }^{\circ}\text{C}$ and at various concentrations of 2-cyclohexenone, diethylzinc and catalyst [10], by ^1H NMR spectroscopy. The reaction rates are expressed as the rate of the decrease of the 2-cyclohexenone concentration, as obtained from the integration of the ^1H NMR signal at 6.3 ppm belonging to the olefinic proton (H_β) in the β -position of 2-cyclohexenone (Fig. 2), relative to an internal standard (CH_2Cl_2) (see Section 4).

Considering I = integration value at time t of the ^1H NMR signal at 6.3 ppm and I_0 = integration value at time $t = 0$, the plot of $\ln(I/I_0)$ vs. time gives a straight line indicating a first-order dependence of the reaction rate on 2-cyclohexenone concentrations (Fig. 3(a)).

The reaction rate shows only a small dependence on diethylzinc concentration (Fig. 3(b)). However, since the catalyst is dissolved in toluene, but diethylzinc is added as an hexane solution, the solvent composition could not be held constant in the series. Thus, the small variation in k' value is most likely to be attributable to a solvent effect. A first-order dependence of k' with respect to diethylzinc concentration should give a much larger variation over the range investigated.

Finally, we measured the dependence of the reaction rate upon the catalyst concentration. A first-order rate constant with respect to the concentration of the 1:1.2 $\text{Cu}(\text{OTf})_2\text{:H}_2\text{L1}$ mixture was observed up to 9 mM. The reaction rate drastically decreased at higher catalyst concentration (Fig. 4).

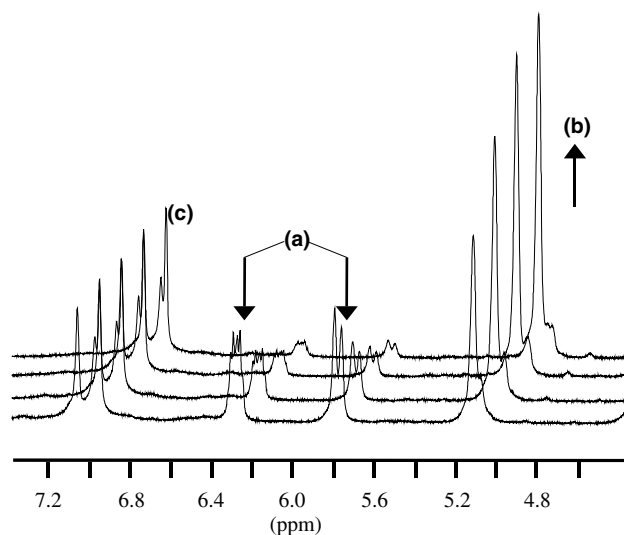


Fig. 2. Evolution of the ^1H NMR spectrum of a typical reaction with time. The reported signals are due to: 2-cyclohexenone (a) Znenolate [8a] (b); d_8 -toluene (c).

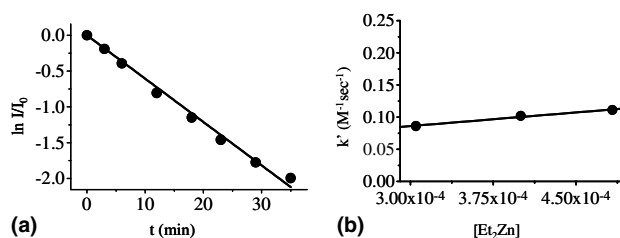


Fig. 3. Dependence of the reaction rate on 2-cyclohexenone concentration (a); dependence of the reaction rate on diethylzinc concentration (b).

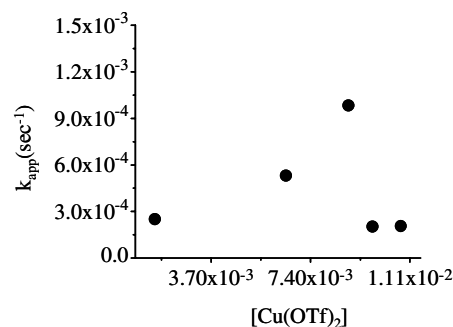


Fig. 4. Dependence of the reaction rate on copper(II) triflate concentration.

A possible rationale to this behaviour is the formation of a catalytically inactive aggregated species at higher $\text{Cu}(\text{OTf})_2$ and $\text{H}_2\text{L1}$ concentrations. This effect could also be responsible for the reduced enantioselectivity observed when performing the reaction at higher catalyst concentrations (e.g., e.e. 72% vs. 84% using H_2L with $R^1 = i\text{Pr}$, $R^2 = (\text{S})\text{-CH}(\text{Me})\text{Cy}$, $R^3 = 3,5\text{-Cl}_2$) (Chart 1) [4c].

On the basis of this kinetic study, the rate law of the reaction can be written as:

$$-d[2 - \text{cyclohexenone}]/dt = k'[\text{Cu}(\text{OTf})_2] \cdot [2 - \text{cyclohexenone}] \quad (1)$$

2.3. Synthesis of $[(\text{CuL1})_2 \cdot \text{Cu}(\text{OTf})_2](\text{TfOH})_{1/3}$ (**1**)

Having determined the kinetic law, we decided to investigate the nature and the composition of the copper species involved in the catalytic process, starting from the complex which is initially formed upon reaction of ligand **H₂L1** and $\text{Cu}(\text{OTf})_2$. This complex was isolated by stirring the ligand in the presence of $\text{Cu}(\text{OTf})_2$ in toluene and precipitating the product with *n*-hexane. Based on elemental analysis, the composition $[(\text{CuL1})_2 \cdot \text{Cu}(\text{OTf})_2](\text{TfOH})_{1/3}$ can be proposed for **1**. In support to this formulation, the FAB^+ mass spectrum showed a strong peak at $m/z = 939$, assignable to the fragment $[(\text{CuL1})_2 + \text{H}]^+$. The IR spectrum of complex **1** showed two sharp absorptions at 1651 and 1610 cm^{-1} that may be attributed to the imine bonds of the dimeric structure, and one absorption at 3249 cm^{-1} which was assigned to the –OH group of triflic acid present in the molecule. An absorption at 1281 cm^{-1} (stretching of the –SO₃ group) is indicative of a loosely bound $\text{Cu}(\text{OTf})_2$ [11].

The molecule of $\text{Cu}(\text{OTf})_2$ present in the molecular formula of **1** is in a coordinated status and is not coprecipitated with the copper(II) complex. In fact, complex **1** is completely soluble in non polar solvents such as toluene or diethyl ether, whereas cupric triflate is only soluble in more coordinating solvents, such as ethyl acetate or THF.

Due to the paramagnetism of complex **1** (a broad unresolved EPR signal centred at 2770 G was found), ^1H NMR spectroscopy was not helpful to confirm its formulation. ^{19}F NMR spectroscopy, conversely, gave very interesting informations: one signal was found at room temperature, whereas two different signals in a 1:6 ratio were observed at -50°C (Fig. 5). This evidence corroborates the presence in the molecular structure of $\text{Cu}(\text{OTf})_2$ and TfOH in a 3:1 ratio.

Other copper complexes of tri- or tetradentate N,O-ligands are known in the literature and were synthesised following a similar experimental procedure [12]. Their structure contains an oligomeric copper/ligand core and a bridging copper ion. In particular, the X-ray crystal structure [12a] of a trinuclear complex $[(\text{CuL}')_2 \cdot \text{Cu}(\text{OAc})_2]$ (Fig. 6(a)) has been reported, in which two CuL' units are bridged by one copper acetate molecule. Given the structural similarity between the ligand reported in Fig. 6(a) and **H₂L1**, we propose the structure in Fig. 6(b) for complex **1**.

Complex **1** was also obtained performing the reaction with the correct molar ratio $\text{Cu}(\text{OTf})_2\text{:H}_2\text{L1} = 3\text{:}2$.

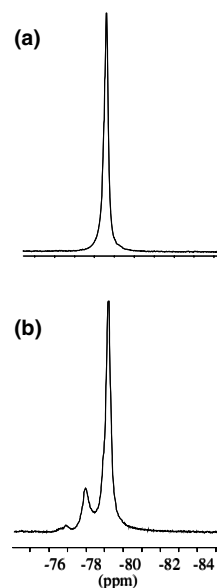


Fig. 5. ^{19}F NMR spectra of **1** at room temperature (a) and at -50°C (b).

Subsequently, in order to study the catalytic activity of complex **1**, the model reaction between 2-cyclohexenone and diethylzinc was run in the presence of isolated $[(\text{CuL1})_2 \cdot \text{Cu}(\text{OTf})_2](\text{TfOH})_{1/3}$ (**1**) in the ratio 2-cyclohexenone: $\text{Et}_2\text{Zn}:\mathbf{1} = 40\text{:}60\text{:}0.33$. Both the measured kinetic constant k' , as defined in Eq. (1), and the enantiomeric excess were comparable to those recorded for the catalytic reaction performed with the catalytic species obtained in situ ($0.89 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ vs. $0.93 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$; e.e. 25% vs. 24%). These data point to an active role of **1** in the catalytic reaction. (see also later, Scheme 2).

2.4. Analysis of the catalytically active intermediate

A number of different reports dealing with copper catalysed conjugate addition of organozinc reagents refer to the catalytically active species as a copper(I) complex, even when the copper source used as starting material is a copper(II) salt or a copper(II) complex. Although this is a generally accepted assumption, to the best of our knowledge, this intermediate was never isolated, nor characterised. In order to determine the oxidation states of the copper complexes formed under our conditions, we monitored the catalytic reaction by EPR spectroscopy. Fig. 7 shows the EPR signal of starting complex **1** (a), the spectrum of the same solution after addition of 2-cyclohexenone (b), and after addition of diethylzinc (c).

The EPR analysis of the reaction confirmed that upon addition of diethylzinc, reduction of copper(II) occurs with formation of a diamagnetic copper(I) complex.

The role of this copper(I) complex was investigated by ^1H NMR spectroscopy, running the reaction between

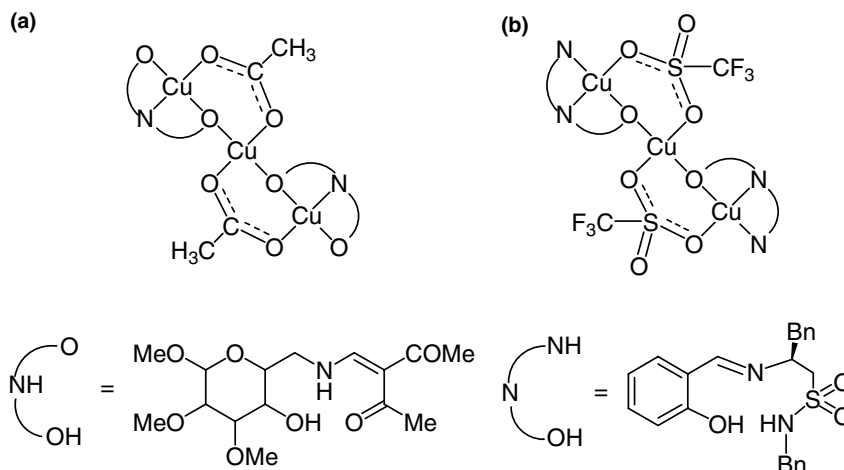
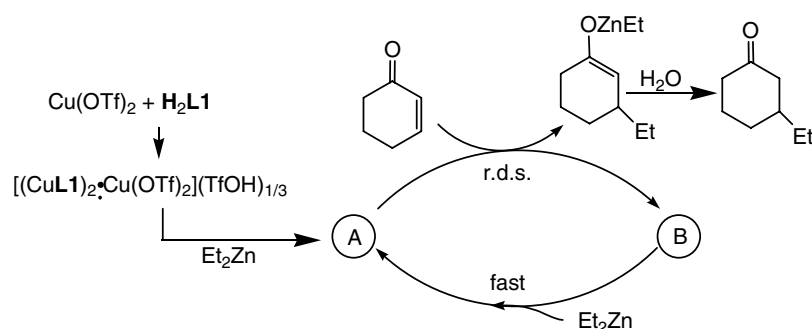


Fig. 6. The reported structure [12a] for a trinuclear complex $[(\text{CuL}')_2 \cdot \text{Cu}(\text{OAc})_2]$ (a) and the proposed structure for complex **1** (b).



Scheme 2. Proposed mechanism for the 1,4-addition of diethylzinc to 2-cyclohexenone catalysed by a 1:1.2 mixture of $\text{Cu}(\text{OTf})_2$ and $\text{H}_2\text{L1}$.

2-cyclohexenone, diethylzinc, $\text{H}_2\text{L1}$ and $\text{Cu}(\text{OTf})_2$, in the ratio 1.2:12:1.2:1. In this reaction, performed under almost stoichiometric conditions, up to 4.6 equivalents of Et_2Zn per equivalent of $\text{Cu}(\text{OTf})_2$ and ligand $\text{H}_2\text{L1}$ are calculated to be necessary to: (i) deprotonate the triflic acid which is formed upon Cu complexation and deprotonate the excess of $\text{H}_2\text{L1}$ (2.4 equivalents), (ii) reduce $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ (1 equivalent), and (iii) perform the alkylation (1.2 equivalents) [13]. Nonetheless, 12 equivalents of Et_2Zn were used to quench any adventitious water or dioxygen in the reaction medium. This reaction displayed the same kinetics and a similar k' value compared to the reactions with catalytic $\text{Cu}(\text{OTf})_2$ and ligand $\text{H}_2\text{L1}$ ($0.81 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ vs. $0.93 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$). The enone was completely transformed into the dimeric zinc enolate [8a] and the ^1H NMR spectrum did not reveal the presence of paramagnetic complex **1**. These results indicate that complex **1** is reduced to a copper(I) species in the presence of Et_2Zn , and that this is responsible for the alkylation of 2-cyclohexenone. When 40 equivalents of 2-cyclohexenone and 60 equivalent of diethylzinc were added to the mixture, the reaction restarted indicating that the reduced copper(I) species is a catalytically active intermediate.

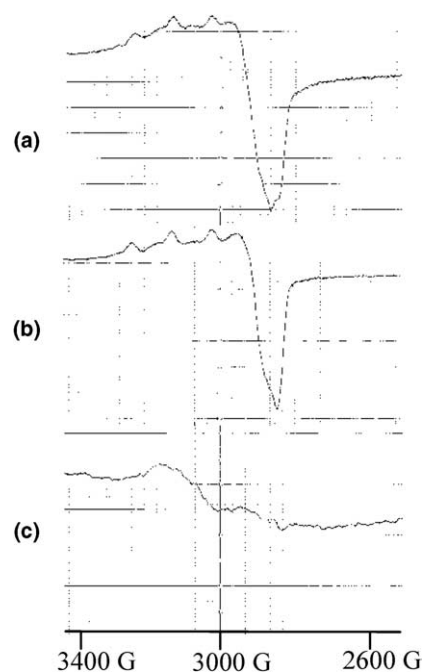


Fig. 7. The EPR signal of complex **1** (a), the spectrum of the same solution after addition of 2-cyclohexenone (b), and after addition of diethylzinc (c).

In order to isolate this copper(I) intermediate, the reaction between 2-cyclohexenone, diethylzinc, **H₂L1** and Cu(OTf)₂, in the ratio 1.2:12:1.2:1 was performed on a preparative scale. The reaction mixture was stirred at –20 °C for 2 h, the solvent was evaporated to dryness and the residue was washed with *n*-hexane to eliminate the excess of diethylzinc. The resulting solid was dissolved in d₈ toluene and ¹H NMR analysis of this solution showed the presence of the dimeric zinc enolate signals [8a]. The high complexity of the ¹H NMR spectrum indicates high nuclearity for this copper(I) complex but more details on the molecular structure could not be obtained. GC–MS analysis after quenching of a part of the solution with NH₄Cl confirmed the presence of 3-ethylcyclohexanone. The ¹⁹F NMR spectrum showed only one signal at both room temperature and –50 °C, indicating that only one type of fluorine species is present in the molecular structure. The FAB⁺ spectrum showed a strong peak at *m/z* = 470, assignable to the fragment [CuL1 + 1H]⁺ and the absence of the ion at *m/z* = 939 relative to complex **1**. The signals due to the triflate moiety are present in the IR spectrum and the EPR analysis showed the presence of diamagnetic species. These data support the hypothesis that the copper(I) complex contains in its structure the Schiff base ligand and the triflate anion. The low stability of this compound in solution hampers its storage and prevents a complete structural characterisation. The isolated complex, is indeed a catalytically active species and conjugate addition of diethylzinc to 2-cyclohexenone took place once the reaction conditions were restored.

In a separate control experiment, to one equivalent of complex **1** preformed in situ, diethylzinc (40 equivalents) was added and after aqueous quenching ligand **H₂L1** was recovered unchanged showing that no addition of an ethyl group to the imine double bond took place.

The experimental data allow us to propose the mechanism illustrated in Scheme 2.

Copper triflate reacts with the Schiff base to form complex **1** which, in the presence of an excess of diethylzinc, yields species A. This species transfers the ethyl group to the β-position of 2-cyclohexenone with a first-order kinetics and yields species B, a copper(I) complex in which the enone is not present. Compound B reacts with Et₂Zn with a zero-order kinetics to reform A.

3. Conclusions

In summary, we have reported a mechanistic study of the 1,4-addition of diethylzinc to 2-cyclohexenone catalysed by copper complexes of the Schiff base ligand **H₂L1**. We have determined the kinetic law of our system and studied the structure of the different copper complexes involved in the reaction. The experimental results indicate a first-order dependence of the reaction

rate on enone concentration, a zero-order on diethylzinc concentration, and a first-order dependence with respect to the concentration of a 1:1.2 mixture of Cu(OTf)₂ and **H₂L1**. A sharp change in the kinetic of the reaction is observed at catalyst concentration higher than 9 mM, indicating the possible formation of catalytically inactive species at higher concentrations. An aggregate copper complex is formed in the reaction medium upon mixing Cu(OTf)₂ and ligand **H₂L1**, whose composition is consistent with the formulation [(CuL1)₂·Cu(OTf)₂](TfOH)_{1/3} (**1**). Complex **1** is reduced in situ to a catalytically active copper(I) species by the addition of 12 equivalents of Et₂Zn, as witnessed by the absence of EPR signals. This species is able to perform the conjugate alkylation of 2-cyclohexenone under stoichiometric conditions, and resumes its catalytic activity in the presence of 2-cyclohexenone and Et₂Zn.

4. Experimental

4.1. General procedure

All operations were carried out under an atmosphere of purified dinitrogen using Schlenck techniques. Unless otherwise noted, laboratory reagents were used as received. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded on a Bio Rad FTS-7 FT-IR spectrophotometer, and NMR spectra using a Bruker 300-AC and 400-Avance instruments. EPR spectra were recorded on Varian E-109 spectrometer at X-band frequency with Receiver gain = 3.2×10^{-3} , Microwave power = 10 mW, Modulation amplitude = 0.5×10 G, Microwave frequency = 8.986 GHz, Time constant = 0.064 s, Temperature = –150 °C.

4.2. Kinetic measurements

4.2.1. Determination of the kinetic order with respect to 2-cyclohexenone

Cu(OTf)₂ (3.0 mg, 8.30×10^{-3} mmol) was dissolved in d₈ toluene (0.75 ml) in a NMR tube under N₂ with **H₂L1** (4.0 mg, 9.80×10^{-3} mmol) and CH₂Cl₂ (6 μl) as internal standard. The resulting yellow solution was stirred at room temperature for 15 min and a 1 M solution of Et₂Zn in *n*-hexane (0.5 ml, 5×10^{-1} mmol) and 2-cyclohexenone (32 μl, 3.32×10^{-1} mmol) were added at –78 °C. The consumption of 2-cyclohexenone was monitored by ¹H NMR spectroscopy measuring the decrease of the integration value of the signal at 6.3 ppm relative to the olefinic proton (H_β) in the β-position of 2-cyclohexenone at –20 °C every 5 min. The first-order rate constant $k_{app} = 6.16 \times 10^{-4}$ s^{–1} was obtained by a linear fit of ln(*I*/*I*₀) vs. time according to the equation

$\ln(I/I_0) = -k_{\text{app}}t$ where I_0 and I are the initial integration and the integration at the time t .

4.2.2. Determination of the kinetic order with respect to Et_2Zn

The reaction was run as described above for the determination of the kinetic order with respect to 2-cyclohexenone repeating it with three different amounts of Et_2Zn [(a) 0.33 ml, 3.30×10^{-1} mmol, $k' = 0.86 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$; (b) 0.50 ml, 5.00×10^{-1} mmol, $k' = 0.93 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$; (c) 0.70 ml, 7.00×10^{-1} mmol, $k' = 1.11 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$].

4.2.3. Determination of the kinetic order with respect to a 1:1.2 mixture of $\text{Cu}(\text{OTf})_2$ and $\text{H}_2\text{L1}$

The reaction was run as described above for the determination of the kinetic order with respect to 2-cyclohexenone repeating it with five different amounts of $\text{Cu}(\text{OTf})_2$ and $\text{H}_2\text{L1}$ [(a) $\text{Cu}(\text{OTf})_2$: 0.75 mg, 2.07×10^{-3} mmol, $\text{H}_2\text{L1}$: 0.93 mg, 2.23×10^{-3} mmol, $k_{\text{app}} = 2.50 \times 10^{-4} \text{ s}^{-1}$; (b) $\text{Cu}(\text{OTf})_2$: 3.00 mg, 8.30×10^{-3} mmol, $\text{H}_2\text{L1}$: 4.00 mg, 9.8×10^{-3} mmol, $k_{\text{app}} = 6.16 \times 10^{-4} \text{ s}^{-1}$; (c) $\text{Cu}(\text{OTf})_2$: 4.10 mg, 11.3×10^{-3} mmol, $\text{H}_2\text{L1}$: 4.90 mg, 11.9×10^{-3} mmol, $k_{\text{app}} = 9.83 \times 10^{-4} \text{ s}^{-1}$; (d) $\text{Cu}(\text{OTf})_2$: 4.50 mg, 12.4×10^{-3} mmol, $\text{H}_2\text{L1}$: 5.60 mg, 13.71×10^{-3} mmol, $k_{\text{app}} = 2.02 \times 10^{-4} \text{ s}^{-1}$; (e) $\text{Cu}(\text{OTf})_2$: 5.00 mg, 13.8×10^{-3} mmol, $\text{H}_2\text{L1}$: 6.10 mg, 14.9×10^{-3} mmol, $k_{\text{app}} = 2.05 \times 10^{-4} \text{ s}^{-1}$].

4.3. Preparation of $[(\text{CuL1})_2 \cdot \text{Cu}(\text{OTf})_2](\text{TfOH})_{1/3}(\text{I})$

$\text{Cu}(\text{OTf})_2$ (79.5 mg, 0.22 mmol) was added under an inert atmosphere to a solution of $\text{H}_2\text{L1}$ (97.0 mg, 0.24 mmol) in 50 ml of toluene. The resulting orange solution was stirred overnight at room temperature. The solution was concentrated to 15 ml and *n*-hexane (25 ml) was added. The precipitated yellow powder was collected by filtration and dried in vacuo (60.7 mg, 57%) Anal. Calc. for $\text{C}_{145}\text{H}_{133}\text{N}_{12}\text{O}_{39}\text{Cu}_9\text{F}_{21}\text{S}_{13}(\text{C}_{48.3}\text{H}_{44.3}\text{N}_4\text{O}_{13}\text{Cu}_3\text{F}_7\text{S}_{4.3})$ **1**: C, 42.52; H, 3.39; N, 3.79. Found: C, 42.95; H, 3.31; N, 4.14%. IR (nujol, $\nu_{\text{max}}/\text{cm}^{-1}$) 3369(w), 3249(w), 1652(s), 1610(s), 1281(s), 1226(s), 1170(m), 1029(s), 759(w). ^{19}F NMR (CDCl_3 298 K) δ : -78.394(s). ^{19}F NMR (CDCl_3 , 223 K), δ : -79.243(s), -78.012 (s). m/z (FAB^+): 939 $[(\text{CuL1})_2 + \text{H}]^+$, 470 $[\text{CuL1} + \text{H}]^+$, 409 $[\text{H}_2\text{L1} + \text{H}]^+$.

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