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New copper(I) and silver(I) triazolato-complexes: Synthesis, reactivity and catalytic activity in olefin cyclopropanation

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Abstract

A new class of azolate ligands, deriving from the equimolar condensation of 3,5-diamino-1,2,4-triazole with salicylaldehyde (H_3L^1) and *o*-anisaldehyde (H_3L^2) was prepared. In their anionic form, these species act as bridging moieties upon coordination to Cu(I) and Ag(I), giving rise to the formation of dinuclear complexes with the ligand in the typical *N,N′*-exobidentate conformation. The copper derivative $[Cu(H_2L^1)(CH_3CN)]_2$ (**1**) showed attractive reactivity in the replacement of the labile acetonitrile molecules. In particular, it was possible to isolate a dinuclear copper(I)-carbonyl complex $[Cu(H_2L^1)(CO)]_2$ (**4**), by substitution of the nitrile with carbon monoxide. Moreover, the reaction of **1** with ethyl diazoacetate (EDA) in CH_2Cl_2 afforded a mono-carbene product, as established by ^{13}C NMR data. Finally, the copper derivative **1** proved to be a highly diastereoselective catalyst in olefin cyclopropanation in the presence of ethyl diazoacetate. In the case of internal alkenes a *trans*:*cis* ratio of up to 97:3 was reached. The X-ray structure of a dinuclear Ag(I) complex, namely $[Ag(H_2L^1)(PPh_3)]_2$ (**3**), obtained by reacting the polymeric $[Ag(H_2L^1)]_n$ (**2**), with triphenylphosphine, is also reported.
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1. Introduction

In the last decades, great attention has been dedicated to the synthesis of cyclopropylic moieties [1]. Indeed, cyclopropanes are versatile intermediates that can be converted into a variety of useful products by cleavage of the strained three-membered ring [2]. In addition, the occurrence in nature of molecules presenting interesting physiological properties and containing the cyclopropane moiety [3] is a continuous stimulus to develop new synthetic routes to functionalized cyclopropanes.

One of the most successful methods to achieve this purpose is the metal-assisted decomposition of diazo compounds in the presence of alkenes [4]. Among the others, copper complexes cover a crucial role in this field [5] and

both experimental [6] and theoretical [7] studies have been accomplished in order to elucidate the mechanism of olefin cyclopropanation promoted by Cu-based catalysts. A large variety of sp²-nitrogen based ligands, such as C_2-symmetric semicorrins [8], bis(oxazolines) [9], optically active bipyridines [10] polypyrazolylborates [11] and diiminophosphoranes [12], have been used with the aim of enhancing the selectivity. Recently, high enantioselectivities were reached with binaphthyldiimines [13] and chiral bispidines [14].

Our continuous interest in the coordination chemistry of azolate ligands [15] and in the applications of the corresponding coordination compounds in catalysis [16,18b] and in material science [15b], prompted us to investigate the synthesis and characterization of novel copper(I) and silver(I) triazolate complexes. To this purpose, two new ligands deriving from the condensation of 3,5-diamino-1,2,4-triazole with salicylaldehyde and *o*-anisaldehyde were prepared (respectively, H_3L^1 and H_3L^2, see Scheme 1) and used as bridging moiety in the synthesis of binuclear Cu(I)

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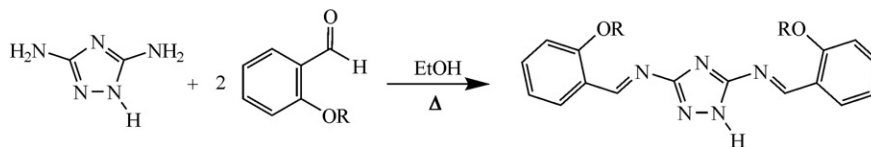
Scheme 1. Synthesis of ligands: R = OH, H_3L^1; R = OCH_3, H_3L^2.

and Ag(I) coordination compounds. Here we report the synthesis and characterization of H_3L^1 and H_3L^2 and of the resultant metal complexes, namely $[Cu(H_2L^1)(CH_3CN)]_2$, $[Cu(H_2L^2)(CH_3CN)]_2$ and $[Ag(H_2L^1)]_n$. The reactivity of the Cu(I) species towards CO or ethyl diazoacetate (EDA) and that of the Ag(I) compound towards PPh$_3$ is presented. The only air stable species obtained, $[Ag(H_2L^1)(PPh_3)]_2$, was isolated in the form of single crystals suitable for an X-ray analysis: its crystal and molecular structures are described. Eventually, the high *trans*-selectivity shown by the $[Cu(H_2L^1)(CH_3CN)]_2$ copper(I) derivative in the EDA-assisted cyclopropanation of olefins is discussed.

2. Results and discussion

2.1. Synthesis of ligand H_3L^1

Treatment of 3,5-diamino-1,2,4-triazole with an excess of salicylaldehyde at 170 °C gave a yellow compound. Using salicylaldehyde in a fourfold excess with respect to triazole prevented us from the formation of the mono-condensation product, as denoted from the presence of just the imine signal at 9.45 ppm in the ^1H NMR of the product (Scheme 1). In the IR spectrum (nujol mull), a sharp v_{N-H} band at 3258 cm^{-1} and $v_{C=N}$ stretchings at 1609 and 1567 cm^{-1} were detected; the absence of any broad band in the region between 3300 and 3500 cm^{-1} let us assume that the –OH groups of the H_3L^1 ligand were not involved in intermolecular O–H···N hydrogen bonds with the imine nitrogen [17]. Moreover, in the ^1H NMR, the singlet at 10.99 ppm ascribable to the –OH groups and that at 13.35 ppm due to the N–*H* proton of the heterocyclic ring confirmed the lack of any O–H···N interactions.

Noteworthy, the presence of four coordination sites makes H_3L^1 a very versatile species, which could potentially act even as a trianionic tetradentate (O–N–N–O) ligand, tuning its behaviour against the hard–soft properties of the metal involved.

2.2. Synthesis of $[Cu(H_2L^1)(CH_3CN)]_2$ (1)

When a suspension of $[Cu(CH_3CN)_4]BF_4$ in CH$_3$CN was treated with H_3L^1 in a 1:1 ratio in the presence of Et$_3$N, the formation of a yellow complex **1** immediately occurred. In this species, the –OH groups of the former salicylaldehyde are not involved in the coordination to the metal, as confirmed by the resonance at about 12 ppm in the ^1H NMR. This signal disappears after treatment with

D$_2$O, as a further evidence of the presence of free –OH groups. Moreover, the absence of any N–H stretching in the infrared spectrum let us ascertain that H_3L^1 acts as a mono-anionic ligand, the triazole moiety thus being the only coordination site of the molecule. Finally, the signal at 2.09 ppm in the ^1H NMR registered in CD$_2$Cl$_2$ was attributed to acetonitrile molecules bound to the metal centre. The labile acetonitrile ligands can easily be replaced, as the reactivity of species **1** with carbon monoxide suggested (see Section 2.4).

Unfortunately, the low stability towards oxidation shown by **1**, both in the solid state and when dissolved in common organic solvents, did not allow us to grow single crystals suitable for X-ray analysis. However, on the basis of the spectral data presented above and especially by comparison with the analogous Ag(I) complex (see Section 2.3), it was possible to propose a dimeric formulation to complex **1**, namely $[Cu(H_2L^1)(CH_3CN)]_2$, and to tentatively assign a structure to this species (Fig. 1). Despite uncommon among tricoordinated dinuclear compounds possessing a CuN$_3$ chromophore, the boat conformation of the hexa-atomic [Cu–NN–Cu–NN] ring was postulated according to our previous studies on similar Cu(I) and Rh(I) complexes containing azolate bridging ligands [18].

2.3. Synthesis and reactivity of $[Ag(H_2L^1)]_n$ (2)

The addition of H_3L^1 to a solution of AgNO$_3$ in CH$_3$CN, in the presence of Et$_3$N, afforded an orange species, postulated as $[Ag(H_2L^1)]_n$ (**2**). The polymeric nature of this derivative can be tentatively assumed from its remarkable insolubility in all organic solvents and from its reactivity, comparable to that of formerly reported pyrazolate and imidazolate silver(I) coordination compounds [19]. To prove this assumption, treatment of **2** with PPh$_3$ in CH$_2$Cl$_2$ was exploited and, as already observed with the analogous $[Ag(pz)]_n$ species (pz = pyrazolate) [20],
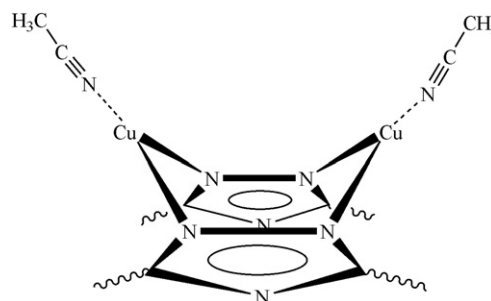
Fig. 1. Proposed molecular structure for complex **1**.

resulted into the cleavage of the polymeric chain and formation of the binuclear $[Ag(H_2L^1)(PPh_3)]_2$ compound (3), whose nature was confirmed by an X-ray analysis (see below). The single resonance at 6.44 ppm in the ^{31}P NMR spectrum of 3 was clearly attributed to the two phosphines bonded to the Ag(I) centres. In the ^1H NMR, the presence of a broad weak signal at 12.97 ppm, disappearing after treatment with D_2O, was related to the presence of free –OH groups on the H_2L^1 moiety, this suggesting a mono-anionic ligand coordinating in the N,N'-exobidentate mode. Species 3 was isolated in the form of single crystals suitable for an X-ray diffraction structural characterization.

The crystal structure of compound 3 is composed by dimers of $[Ag(H_2L^1)(PPh_3)]_2$ formula (Fig. 2) lying on a crystallographic twofold axis, the asymmetric unit being composed by one silver(I) ion, one H_2L^1 and one PPh_3 ligands. Each metal centre possesses a slightly distorted trigonal stereochemistry and is coordinated to two triazole nitrogen atoms of two distinct H_2L^1 moieties and to the phosphorous atom of one phosphine ligand. The two H_2L^1 ligands, acting in the N,N'-exobidentate mode, bridge metal centres 3.72 Å apart, and form dimers in which the six-membered rings composed by the four coordinated nitrogen atoms and the two silver(I) centres adopt a boat-shape disposition, as already encountered in the above mentioned Cu(I) and Rh(I) derivatives with 3,5-disubstituted pyrazolates [18]. The oxygen atoms of the –OH groups are not involved in the coordination to the metal centres, as expected for a metal with soft nature like Ag(I). Nevertheless, intermolecular hydrogen bonds of moderate strength (H–D···A 2.63 Å) are present between the hydroxy groups and the neighbouring iminic nitrogen atoms.

By analogy, we could assume that also in the Cu(I) derivative 1 the triazole moiety is the only one bonded to the metal, the residual coordination sites being occupied by CH_3CN.
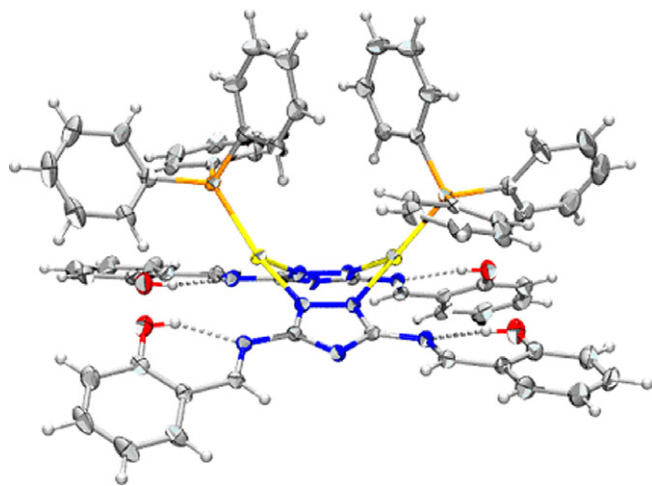

Fig. 2. Ortep representation, at a 20% probability level, of the dimeric $[Ag(H_2L^2)(PPh_3)]_2$ moiety present in species 3. O–H···N hydrogen bonds depicted with fragmented lines.

2.4. Reactivity of $[Cu(H_2L^1)(CH_3CN)]_2$ (1) with CO

Bubbling of CO for 4 h at room temperature through a suspension of species 1 in CH_2Cl_2 resulted in the formation of a Cu(I)-carbonyl complex derived from the substitution of both CH_3CN molecules with CO, as confirmed by the strong and sharp stretching visible in the IR spectrum (nujol mull) at 2105 cm^{-1}. The v_{CO} clearly speaks for a terminal CO bonded to a tri-coordinated copper centre, in accordance with other examples reported in the literature [18,21]. The presence of a single absorption is consistent with the complete replacement of CH_3CN by CO, giving rise to a binuclear symmetrical complex formulated as $[Cu(H_2L^1)(CO)]_2$ (4).

A first attempt to prepare complex 4 directly from a suspension of $[Cu(CH_3CN)_4]BF_4$ in CH_3CN, in the presence of H_3L^1 and Et_3N, under CO atmosphere, failed, complex 1 being the only species isolated. This could undoubtedly be attributed to the competition between CO and CH_3CN in binding to the metal centre, the latter being favoured due to its large excess. In contrast, when the same reaction was carried out using a less coordinating solvent, like acetone, instead of acetonitrile, a partial substitution took place. Better results could eventually be obtained by conducting the reaction in CH_2Cl_2, from which species 4 could be isolated in good yields. Unfortunately, the extremely low stability of $[Cu(H_2L^1)(CO)]_2$ in solution together with the rare affinity of Group 11 metals to carbon monoxide [22], did not allow us to fully characterize it with an X-ray analysis.

2.5. Reactivity of $[Cu(H_2L^1)(CH_3CN)]_2$ (1) with ethyl diazoacetate

The mechanism of diazoacetates decomposition in the presence of olefins and promoted by Cu(I) catalysts is still under investigation, and the isolation of the postulated Cu-carbene intermediate represents one of the main goals in this field [23]. Consequently, considering the preliminary information we had on the copper(I) derivatives, we investigated the reactivity of complex 1 with ethyl diazoacetate. When a suspension of 1 in CH_2Cl_2 was treated with an excess of EDA, the formation of a solution occurred and a brown solid 5 could be isolated in good yield after addition of Et_2O and pentane. The infrared spectrum (nujol mull) of 5 showed a strong absorption at 1744 cm^{-1}, attributable to the COOEt group of EDA. The same stretching was noted after registering the spectrum in solution (CH_2Cl_2), with only a slight downfield shift (1722 cm^{-1}), to be compared with the v_{CO} at 1692 cm^{-1} registered for a solution of the starting EDA in CH_2Cl_2. The change of the carbonyl frequency and the disappearing of the v_{NN} at 2114 cm^{-1} could be correlated to the formation of a carbene species. The ^1H NMR (CD_2Cl_2) did not provide any useful information, this complex being fluxional even at −90 °C. On the contrary, the $^{13}C\{^1H\}$ NMR gave satisfactory information thanks to the occurrence of a broad signal

at 169 ppm, attributable to the CH*C*OOEt group. It is worth mentioning that the resonance at 169 ppm in ^{13}C NMR could also derive from the insertion of the carbenic fragment into the O–H bond of the ligand [24].

In order to determine whether this side-reaction or the formation of the desired carbene took place, a new ligand bearing a –OCH$_3$ group instead of the –OH functionality was prepared. When 3,5-diamino-1,2,4-triazole was treated with an excess of *o*-anisaldehyde in refluxing ethanol, a yellow solid could be isolated (H$_3$L^2). The ^{1}H NMR revealed the occurrence of the resonance due to the iminic proton at 9.43 ppm, together with that of the OC*H*$_3$ group at 3.88 ppm. The broad signal at 12.02 ppm, disappearing after treatment with D$_2$O, was attributed to the N–H proton of the triazole portion. The typical H*C*=N resonance at 157.46 ppm in the ^{13}C NMR gave a final confirmation of the iminic nature of the ligand.

Treatment of a suspension of [Cu(CH$_3$CN)$_4$]BF$_4$ and H$_3$L^2 in CH$_3$CN, with Et$_3$N, resulted in the formation of an orange solid. On the basis of spectroscopic and analytical data it was identified as complex **6**. Complex **6** revealed to be comparable to the analogous species **1**, and was formulated as [Cu(H$_2$L^2)(CH$_3$CN)]$_2$. Specially, the resonances at 3.84 ppm (OCH$_3$ group) and 1.95 ppm (CH$_3$CN molecule) in the ^{1}H NMR of **6** registered in CD$_2$Cl$_2$, supported this structural assignment.

A dichloromethane suspension of [Cu(H$_2$L^2)(CH$_3$CN)]$_2$ treated with an excess of EDA afforded a brown solution from which, after addition of diethylether and pentane, a brown solid **7** could be recovered. The nature of complex **7** was conclusively established by spectroscopic data: the infrared spectrum (nujol mull) indicated a strong absorption at about 1740 cm^{-1}, while the ^{13}C{^{1}H} NMR gave a signal at 168 ppm. This could be easily attributed to the presence of a coordinated –COOEt group, the insertion into a –OCH$_3$ group being in this case impossible. The comparable reactivity with EDA of complex **6** and complex **1** strongly supported the carbenic nature of species **5**. The latter could thus be finally formulated as [Cu$_2$(H$_2$L^1)$_2$(CH-COOEt)(CH$_3$CN)], as depicted in Scheme 2. The two copper centres are both tri-coordinated, one of them with a carbenic CHCOOEt moiety on the apical position of the hexa-atomic Cu–N–N–Cu–N–N ring. The coordination of an acetonitrile molecule on the other metal centre was confirmed by the ^{13}C{^{1}H} NMR of **5** (CD$_2$Cl$_2$), showing a resonance at about 27 ppm (*C*H$_3$CN).

As a further piece of evidence for the presence of the CHCOOEt fragment in the molecular structure of **5**, we reacted it with cyclohexene in CH$_2$Cl$_2$. The stoichiometric formation of the corresponding cyclopropane esters took place, as detected via GC–MS analysis of the crude product. Moreover, after addition of an excess of EDA (**5**/EDA ratio: 1/20), the catalytic conversion of the olefin into the esters took place, thus suggesting the intermediate nature of derivative **5** into the catalytic cycle.

2.6. Cyclopropanation reactions

When complex **1** was suspended in dichloromethane under inert atmosphere, in the presence of EDA, the conversion of olefins into the corresponding cyclopropane derivatives took place. Together with the desired products, diethyl maleate and diethyl fumarate, deriving from EDA self-coupling [25], were always detected. In order to minimize these side-reactions, addition of a large excess of olefin (namely, a Cu:EDA:olefin = 1:100:250 molar ratio) was employed. As reported in Table 1, the yields in cyclopropane products were excellent in all the runs performed. Complex **1** showed to be a highly active catalyst in the cyclopropanation of both terminal (entries 1 and 2) and internal olefins (entries 3 and 4). As reported in the literature, in the conversion of styrene into the corresponding cyclopropane esters, most of the copper(I) catalysts provided the *trans* isomer as the main product [26], the common *trans:cis* ratio ranging from 50:50 to 75:25. Increasing the size of R on N$_2$CHCOOR enhances enantiocontrol, while the diastereoselectivity is not usually affected by steric effects, except when very bulky substituents are used, as in the case of 2,6-di-*tert*-butyl-4-methyl phenyl (BDA) diazoacetate [27]. Also species **1** confirmed this trend, providing a 70:30 *trans:cis* ratio in the catalytic cyclopropanation of styrene, as reported for other Cu(Schiff-base) catalysts with substituted salicylaldehydes [28]. Unfortunately, a lower *trans*-diastereoselectivity was observed using α-methylstyrene as substrate (entry 2).

On the contrary, complex **1** exhibited a remarkable diastereoselectivity in the cyclopropanation of internal olefins. In the case of cyclohexene, a 92:8 *exo:endo* ratio was achieved, while with 2-cyclohexen-1-one the *endo* isomer was detected only in traces. This behaviour could probably be ascribed to the higher steric hindrance of the internal double bond of the olefin with respect to the terminal
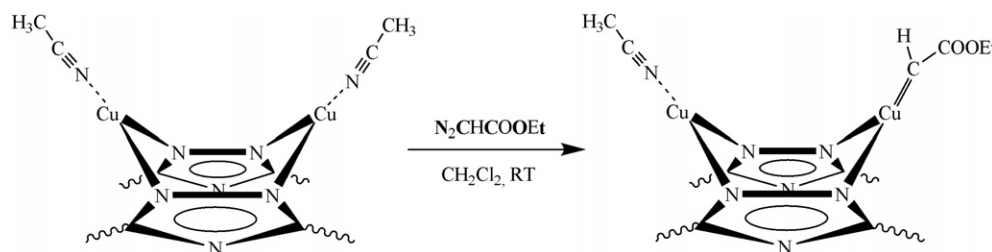
Scheme 2. Formation of the carbene complex **5**.

Table 1
Catalytic cyclopropanation of olefins mediated by complex 1[a]

Entry	Olefin	Yield (%)	trans:cis ratio
1	Styrene	84	70:30
2	α-Methylstyrene	92	55:45
3	Cyclohexene	88	92:8
4	2-Cyclohexen-1-one	85	97:3
5	2,5-Dimethyl-2,4-hexadiene	78	62:38

[a] *Reaction conditions:* CH_2Cl_2, RT, catalyst:EDA:olefin molar ratio 1:100:250.

one. As a result, in the substitution of the labile acetonitrile molecule, the internal olefin coordinates in a preferred direction to the copper.

In order to attain more insights about the possible mechanism, a competitive experiment was performed employing cyclohexene and 2-cyclohexen-1-one as substrates. Given that 2-cyclohexen-1-one exhibits better π-acidic properties, can be considered as a better coordinating olefin to the Cu(I) centre [29]; on the contrary, the presence of the withdrawing carbonyl group causes the deactivation of 2-cyclohexen-1-one towards the attack of an electrophilic carbene [1]. Monitoring (GC–MS) the formation of cyclopropanes from an equimolar solution of cyclohexene and 2-cyclohexen-1-one discloses better conversions of 2-cyclohexen-1-one with respect to cyclohexene (ratio about 1/3 of cyclopropanes derived from cyclohexene with respect to 2-cyclohexen-1-one). Moreover, parallel experiments carried out employing the pure olefins, reveal a reduction of the activity on cyclopropanation of 2-cyclohexen-1-one due to the presence of concurrent cyclohexene. However, a similar effect also occurs on conversion of cyclohexene: i.e. pure cyclohexene shows better conversion to the corresponding cyclopropanes with respect to a 1:1 cyclohexene/2-cyclohexen-1-one mixture. Indeed, when in mixture, cyclohexene shows a larger conversion decrement with respect to that observed for cyclohexen-1-one (−56% vs. −38% for cyclohexen-1-one).

The mutual interference of different olefins on the catalyst activity jointly to the high diastereoselectivity showed by both substrates, seem to suggest a mechanism involving attack of a copper carbene to a coordinated olefin, probably through an intermolecular path, rather than a mechanicistic pathway involving uncoordinated olefins. A mechanism that involves coordination of the olefin prior to the attack of the carbene moiety is probably also responsible of the high activity and diastereoselectivities showed in the cyclopropanation of a deactivated (but better coordinating) substrate as 2-cyclohexen-1-one.

Together with mono-alkenes, also dienes were employed as substrates in the copper-catalyzed cyclopropanation reactions. Indeed, 3-(1-isobutenyl)-2,2-dimethyl cyclopropanecarboxylic acid (chrysanthemic acid) is a key intermediate of pyrethroid insecticides [30] and the conversion of 2,5-dimethyl-2,4-hexadiene (DMHD) into the corresponding chrysantemate esters by means of diazoacetates continuously represents a fundamental target in industrial applicable processes [31].

Consistently with the behaviour observed for mono-olefins, when complex 1 was used to catalyze the conversion of conjugated diolefins into the corresponding cyclopropanes (entry 5), the *trans* isomer was always the major product. Indeed, on running parallel experiments (performed at 0 °C) using rhodium(II) acetate as a reference catalyst, similar selectivities were achieved, as supported by GC–MS analysis.

3. Conclusions

The synthesis, characterization and reactivity of new Cu(I) and Ag(I) complexes with triazolate ligands, namely $[Cu(H_2L^1)(CH_3CN)]_2$ (1) and $[Ag(H_2L^1)]_n$ (2), have been reported. Complex 1 proved to be an active catalyst in olefins cyclopropanation in the presence of EDA, under very mild conditions. Especially in the case of internal olefins, this compound revealed remarkably high selectivities towards the formation of the *trans* isomer. On the basis of spectroscopic and analytical evidences, the intermediate presence of a copper(I) carbene species has also been postulated.

4. Experimental

4.1. General procedures

All reactions were carried out under purified nitrogen using standard Schlenk techniques. The solvents were dried and distilled according to standard procedures prior to use. Alkenes employed in the catalytic reactions were taken from new bottles kept at −20 °C and their purity grade was confirmed by GC–MS control analysis. Salicylaldehyde, *o*-anisaldehyde, 3,5-diamino-1,2,4-triazole, triethylamine, triphenylphosphine, ethyl diazoacetate and silver nitrate (Aldrich) were used as purchased. $[Cu(CH_3CN)_4]BF_4$ was prepared as reported in the literature [32].

Infrared spectra were recorded on a Shimadzu Prestige 21 FTIR, NMR spectra were acquired on a Bruker 400 Avance instrument, elemental analyses were obtained with a Perkin–Elmer CHN Analyser 2400 Series II. Quantitative analyses of products were performed on a Shimadzu GC-17A gas chromatograph with a PS225 capillary column (25 m, 0.25 mm) equipped with a QP5000 mass selective detector.

4.2. Synthesis of ligand H_3L^1

A suspension of 2 g (0.02 mol) of 3,5-diamino-1,2,4-triazole in 9 ml (0.08 mol, $d = 1.146$ g/ml) of salicylaldehyde was heated at 170 °C for 6 h. The crude product was suspended in ethanol, and the resulting suspension was filtered. The resulting yellow solid (H_3L^1) was washed with diethylether and dried under vacuum. Yield: 60%.

^{1}H NMR (acetone-d_6, RT): 7.00 (d, 2H, $J_o = 8.3$ Hz), 7.03 (t, 2H, $J_o = 7.6$ Hz), 7.50 (t, 2H, $J_o = 7.3$ Hz), 7.73 (d, 2H, $J_o = 7.9$ Hz), 9.45 (s, 2H, *H*C=N), 10.99 (s, 2H,

OH), 13.35 (s, 1H, NH). ^{13}C NMR (acetone-d_6, RT): 117.50, 119.16 (CCH=N), 120.01, 133.96, 134.57, 155.48 (NCN), 162.02 (C–OH), 167.65 (HC=N). Anal. Calc. for C$_{16}$H$_{13}$N$_5$O$_2$: C, 62.53; H, 4.26; N, 22.79. Found: C, 62.14; H, 4.37; N, 22.35%.

4.3. Synthesis of ligand H_3L^2

A suspension of 1 g (0.01 mol) of 3,5-diamino-1,2,4-triazole and 5.5 g (0.04 mol) of *o*-anisaldehyde in 20 ml of ethanol was refluxed for 24 h. The light yellow solid (H$_3$L^2) was then filtered off and washed with hot ethanol and diethylether. Yield: 54%.

^{1}H NMR (DMSO-d_6, RT): 3.88 (s, 6H, OCH_3), 7.04 (t, 2H, $J = 7.5$ Hz), 7.12 (d, 2H, $J = 8.4$ Hz), 7.49 (dd, 2H, $J_o = 7.8$ Hz, $J_m = 1.3$ Hz), 8.03 (dd, 2H, $J_o = 7.7$ Hz, $J_m = 1.4$ Hz), 9.43 (s, 2H, HC=N), 12.02 (s, 2H, NH). ^{13}C NMR (DMSO-d_6, RT): 112.84, 121.59, 124.49 (CCH=N), 127.33, 134.20, 152.31 (NCN), 157.46 (HC=N), 160.36 (C–OCH$_3$). Anal. Calc. for C$_{18}$H$_{17}$N$_5$O$_2$: C, 64.47; H, 5.11; N, 20.88. Found: C, 64.10; H, 5.32; N, 20.47%.

4.4. Synthesis of $[Cu(H_2L^1)(CH_3CN)]_2$ (1) and $[Cu(H_2L^2)(CH_3CN)]_2$ (6)

To a suspension of the corresponding ligand (1.95 mmol) in 30 ml of CH$_3$CN kept under nitrogen flow, 500 mg (1.59 mmol) of [Cu(CH$_3$CN)$_4$]BF$_4$ and 300 μl of Et$_3$N (2.16 mmol, $d = 0.726$ g/ml) were added. The suspension was heated at 65 °C for 4 h, then filtered. The yellow **1** or orange **6** solid was washed with CH$_3$CN. The product was kept under nitrogen at −20 °C. Yield: 63% (**1**) and 57% (**6**). Anal. Calc. for C$_{36}$H$_{30}$Cu$_2$N$_{12}$O$_4$ (**1**): C, 52.62; H, 3.68; N, 20.45. Found: C, 52.32; H, 3.83; N, 20.29%. Anal. Calc. for C$_{40}$H$_{38}$Cu$_2$N$_{12}$O$_4$ (**6**): C, 54.73; H, 4.36; N, 19.15. Found: C, 54.39; H, 4.18; N, 18.93%.

4.5. Synthesis of complex $[Ag(H_2L^1)]_n$ (2)

To a solution of 0.5 g of AgNO$_3$ (2.94 mmol) in 10 ml of acetonitrile, 1.1 g of H$_3$L^1 (3.58 mmol) and 1 ml of Et$_3$N (7.19 mmol, $d = 0.726$ g/ml) were added. The suspension was stirred at room temperature for 2 h, then the orange solid (**2**) was filtered off and washed with acetonitrile. Yield: 79%. Anal. Calc. for C$_{16}$H$_{12}$AgN$_5$O$_2$: C, 46.40; H, 2.92; N, 16.91. Found: C, 46.20; H, 2.80; N, 16.87%.

4.6. Synthesis of complex $[Ag(H_2L^1)(PPh_3)]_2$ (3)

To a suspension of 200 mg of **2** (0.48 mmol) in 8 ml of dichloromethane, 260 mg of PPh$_3$ (0.99 mmol) were added. In about 1 h the suspension turned into an orange solution. The solution was stirred at room temperature for 4 h, the solvent was then removed under reduced pressure, diethylether was added and the resultant yellow solid (**3**) was filtered off and dried under vacuum. Yellow prismatic sin-

gle crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3** in diethylether. Anal. Calc. for C$_{68}$H$_{54}$Ag$_2$N$_{10}$O$_4$P$_2$: C, 60.37; H, 4.02; N, 10.35. Found: C, 60.18; H, 4.18; N, 10.13%.

4.7. Synthesis of $[Cu(H_2L^1)(CO)]_2$ (4)

(a) A suspension of 100 mg of **1** (0.27 mmol) in 20 ml of dichloromethane, previously degassed with CO, was kept under CO atmosphere at room temperature for 4 h. The suspension was then filtered off and the resultant yellow solid (**4**) was kept under N$_2$ at −20 °C.

(b) To a suspension of 600 mg of H$_3$L^1 (1.95 mmol) in 30 ml of acetone or dichloromethane kept under CO flow, 500 mg (1.59 mmol) of [Cu(CH$_3$CN)$_4$]BF$_4$ and 300 μl (2.16 mmol) of Et$_3$N were added. After standing for 4 h at room temperature, the solid was filtered off and kept under nitrogen at −20 °C.

Anal. Calc. for C$_{34}$H$_{24}$Cu$_2$N$_{10}$O$_6$: C, 51.32; H, 3.04; N, 17.60. Found: C, 51.12; H, 3.16; N, 17.21%.

4.8. Reaction of $[Cu(H_2L^1)(CH_3CN)]_2$ (1) with ethyl diazoacetate (EDA)

To a suspension of 200 mg of **1** (0.54 mmol) in 10 ml of dichloromethane, 1.14 ml of EDA (10.85 mmol, $d = 1.085$ g/ml) were added. After 1 h the suspension turned into a brown solution. The solution was stirred at room temperature for 4 h. The solvent was then removed under reduced pressure and the residue was redissolved in 1 ml of diethylether. The addition of 3 ml of pentane afforded a brown solid **5**, kept under inert atmosphere at −20 °C. The same procedure was carried out in reacting [Cu(H$_2$L^2)(CH$_3$CN)]$_2$ (**6**) with EDA, allowing the recovery of species **7** (see Section 2.5). Anal. Calc. for C$_{38}$H$_{33}$Cu$_2$N$_{11}$O$_6$ (**5**): C, 52.65; H, 3.84; N, 17.77. Found: C, 52.38; H, 3.89; N, 18.04%. Anal. Calc. for C$_{42}$H$_{41}$Cu$_2$N$_{11}$O$_6$ (**7**): C, 54.66; H, 4.48; N, 16.69. Found: C, 54.31; H, 4.11; N, 16.75%

4.9. Olefins cyclopropanation

In a standard experiment, to a solution of species **1** (0.01 mmol) in dichloromethane (10 ml) at room temperature and under inert atmosphere, EDA and olefin were added in one portion (catalyst:EDA:olefin molar ratio 1:100:250). The consumption of EDA was monitored by infrared spectroscopy. The mixture was then worked up by removing the solvent and the crude product was purified by column chromatography (dichloromethane:hexane = 6:4). All the cyclopropanes obtained were characterized by ^{1}H NMR and GC–MS. Diastereoselectivity (*trans:cis* ratio) was measured by GC–MS analysis. Competitive experiments were carried out in a similar manner, employing an equimolar solution of two olefins.

4.10. X-ray crystallography for $[Ag(H_2L^1)(PPh_3)]$ (**3**)

$C_{68}H_{54}Ag_2N_{10}O_4P_2$, fw = 1352.9 g/mol. Monoclinic, space group $C2/c$, $a = 15.929(1)$, $b = 21.649(2)$, $c = 18.010(1)$ Å, $\beta = 100.976(2)°$, $V = 6103.2(7)$ Å^3, $Z = 4$, $F(000) = 2752$, $\rho = 1.472$ g cm^{-3}, μ(Mo Kα) = 0.75 mm^{-1}. A total of 20980 collected, 2868 observed $[I > 2\sigma(I)]$, and 4004 unique reflections were acquired and reduced within the $3.2 < 2\theta < 45.1°$ sphere, by applying the ω-scan mode ($\Delta\omega = 0.3°$), on a Bruker AXS SMART automated diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorenz-polarization effects and absorption [33]. The structure was solved by direct methods [SIR-97] [34] and refined by full-matrix least-squares on F^2 (SHELX-97 [35], as implemented in the WinGX suite of programs). All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms (but those of the hydroxy groups) were made riding their parent atoms with an isotropic temperature factor 1.2 times that of their parent atoms. 396 parameters, no restraints. R_1 and wR_2 for the observed reflections 0.029 and 0.062, respectively; R_1 and wR_2 for all the unique reflections 0.059 and 0.069, respectively. Goodness-of-fit, highest peak and deepest hole reached values of 0.945, 0.29 e Å^{-3} and -0.20 e Å^{-3}, respectively.

5. Supplementary material

CCDC 665289 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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