



Synthesis and characterization of some transition metal complexes with a novel Schiff base ligand and their use as catalysts for olefin cyclopropanation

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ARTICLE INFO

Article history:

Received 4 February 2009

Received in revised form 3 April 2009

Accepted 3 April 2009

Available online 14 April 2009

Keywords:

Schiff bases

Metal complexes

Cyclopropanation reactions

Homogeneous catalysis

Thiosemicarbazide

ABSTRACT

A novel ligand HL (**1**), N,2-bis(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide was synthesized through the condensation of 3-acetyl-2H-chromen-2-one and hydrazinecarbothioamide. This ligand was used to prepare new transition metal complexes of Cu(II), Ni(II) and Co(II). Characterization of the HL (**1**) ligand and its complexes is also reported. Mass spectra and NMR assignments for the ligand, using COSY, NOESY homonuclear and HMQC and HMBC heteronuclear correlation techniques were carried out. Electronic and magnetic moments of the complexes indicate that the geometries of the metal centers are either distorted octahedral, or square planar. The structures are consistent with the IR, UV–vis, ESR, as well as conductivity measurements. The catalytic activity of the copper complex, [HLCu₂Cl₃]Cl·H₂O (**2**), in cyclopropanation reactions of unactivated olefins with ethyldiazoacetate (EDA) was studied. Cyclopropanes were obtained in high yield (up to 97%, TON up to 16,900) with moderate to good diastereoselectivities (50–91%).

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1. Introduction

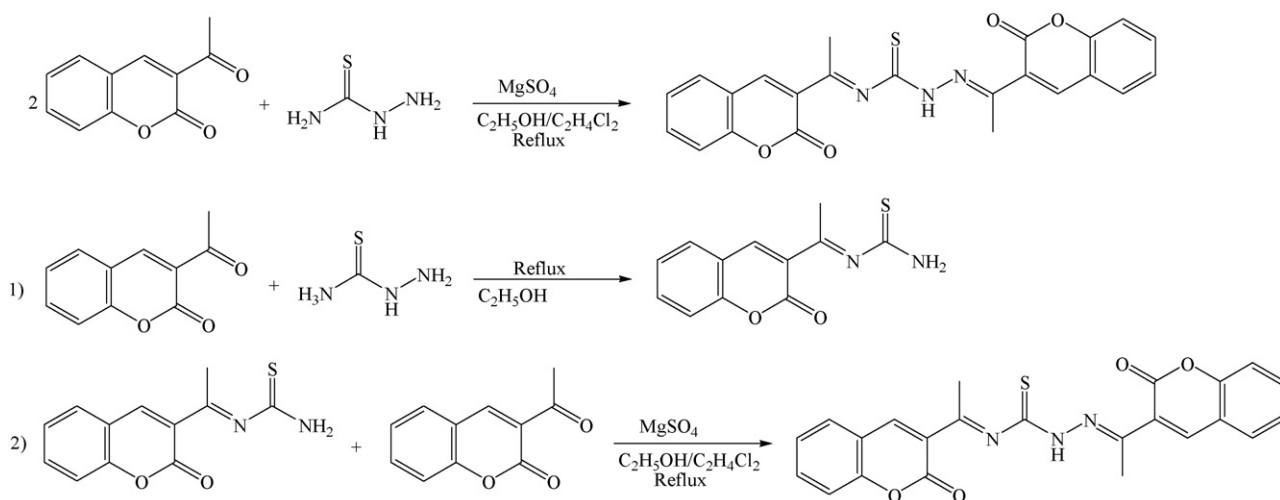
Thiosemicarbazide and its derivatives as ligands with potential sulphur and nitrogen donors are interesting and have gained special attention not only because of the structural chemistry of their multifunctional coordination modes, but also of their importance in medicinal and pharmaceutical field; they show biological activities including antibacterial [1–3], antifungal [4,5], anticancer [6,7] and herbicidal activities [8]. Schiff bases represent an important class of compounds as they are utilized as starting materials in the synthesis of industrial products [9]. Moreover, Schiff bases are regarded as “privileged ligands” [10] due to their capability to form complexes with different transition metals that can act as catalysts for many different reactions [11–20] and their relation to synthetic and natural oxygen carriers [21] and biological compounds such as β-lactons [22].

The structure of the thiosemicarbazide moiety confers a good chelating capacity and this property can be increased in thiosemicarbazone by inserting suitable aldehyde or ketone possessing a further donor atom to render the ligand polydentate [23]. On the other hand, Schiff bases derived from coumarin and its metal complexes have been found to exhibit biological activities and plant regulating activities [9,24].

Cyclopropanation of olefins with diazo reagents catalyzed by metal complexes has attracted great research interest because of its fundamental and practical importance [25–28]. Carbene intermediates can be easily generated starting from diazo alkane derivatives, in the presence of different metals. Copper [29–31], rhodium [32–34] and ruthenium [35,36] complexes have proven to be among the most effective and with general applicability [37,38]. The resulting cyclopropanes are of biological and industrial importance and serve as versatile precursors in organic synthesis [26–28,39–42]. In view of their importance, in the present paper we report the synthesis and characterization of a novel Schiff base derivative ligand HL (**1**), N,2-bis(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide (Scheme 1), and its binary as well as ternary complexes resulting from the interaction with 1,10-phenanthroline (phen) as a secondary ligand. The evaluation of the catalytic activity of the prepared copper complex has also been carried out. The distinctive structure of the [(histidine)₇Cu₄(μ₄-S)] cluster in the “Cu₂” active site of nitrous oxide reductase [43,44] and the intriguing proposals for its redox [45,46] and catalytic reactivity [47–50] have inspired the synthesis of the dicopper complex [HLCu₂Cl₃]Cl·H₂O (**2**) under study, with the aim of understanding the properties of copper complexes supported by N, O and S donor ligands [51]. We have recently discovered that a copper(II) complex of the ligand 3-acetylcoumarin-N(4)-phenylthiosemicarbazone derived from the condensation of N(4)-phenylthiosemicarbazide with 3-acetyl-2H-chromen-2-one is a competent catalyst for the cyclopropanation reaction of olefins [52]. Rarely, metal complexes can give high selectivities in cyclopropanation reactions together

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Scheme 1. Schematic representation for the formation of the Schiff base ligand HL (1).

with high turnover number (TON). We report here that **(1)** is a suitable ligand for copper salts and that the complexes derived are competent catalysts for the cyclopropanation of olefins with ethyldiazoacetate (EDA).

2. Results and discussion

2.1. Synthesis of the ligand

The ligand was prepared either by the condensation of 3-acetyl-2H-chromen-2-one with hydrazinecarbothioamide (2:1) or the condensation of 3-acetyl-2H-chromen-2-one with (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide (1:1), which was previously prepared by the condensation of 3-acetyl-2H-chromen-2-one with hydrazinecarbothioamide (1:1). A mixture of ethanol/1,2-dichloroethane (1:3) was used as a solvent in the presence of anhydrous magnesium sulphate as a dehydrating agent [53]. The addition of 1,2-dichloroethane was necessary to avoid the precipitation of (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide (see Section 4).

2.2. Mass spectra of the ligand

The mass spectra of the Schiff base ligand HL (**1**) showed the molecular ion peak at m/e 431, which is coincident with the formula weight (431.5) for this ligand and supports the identity of the structure. The pathway fragmentation pattern of the mass spectrum of the ligand is depicted in Scheme 2.

2.3. Synthesis of the metal complexes

The metal complexes of the ligand HL (**1**) were prepared by mixing a hot methanolic solution of the metal salts with the required amount of a hot ethanolic solution of the ligand to form 1:1 or 2:1 M/L (metal/ligand) complexes, or other derivatives in the presence of 1-10-phenanthroline (phen) as a secondary ligand, as detailed in Section 4 (Scheme 3).

2.4. Infrared spectra of the complexes

The IR spectra of all complexes, except complex (**7**), showed that the ligand HL (**1**) behaves as a neutral pentadentate of the type ONSNO with two coordinating sites (ON and SNO). This

behaviour was proved by: (i) the shift of $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{S})$, $\nu(\text{C}=\text{N})$ signals to lower frequencies (4–18, 2–17, and 12–39 cm^{-1} , respectively) together with their weak appearance; (ii) the occurrence of the $\nu(\text{N}-\text{N})$ band at higher wave numbers; (iii) the simultaneous appearance of new bands in the 340–390, 422–467, and 487–530 cm^{-1} regions due to the $\nu(\text{M}-\text{S})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ vibrations, respectively [54] and (iv) the presence of the NH group indicating the neutrality of the ligand.

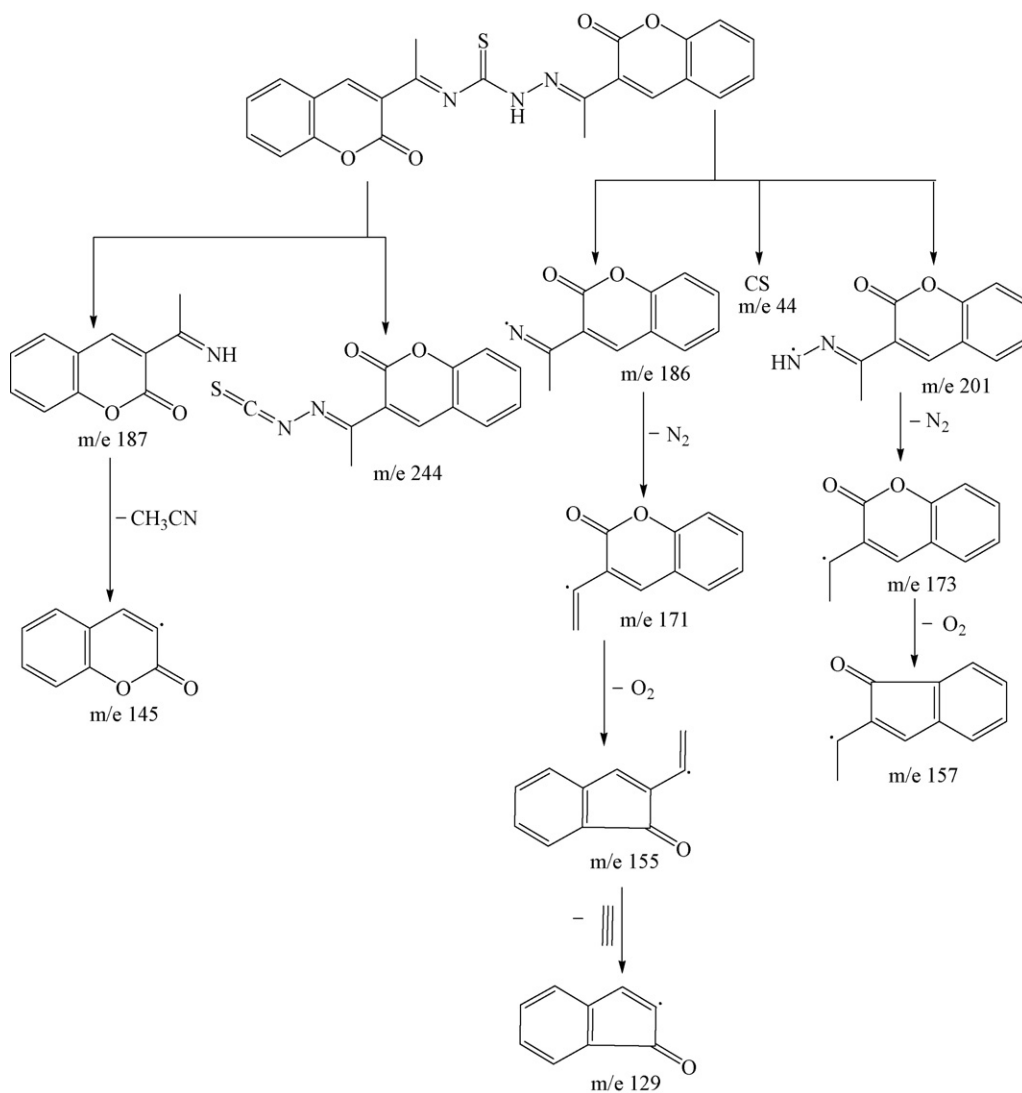
In the case of complex (**7**), the ligand behaves as a neutral tridentate coordinating through $\text{C}=\text{S}$, $\text{C}=\text{N}$, $\text{C}=\text{O}$. This mode of coordination was proved by: (i) the shift of one of the two $\text{C}=\text{O}$ groups to lower wave number (18 cm^{-1}) with a decrease in the intensity while the other retains its original position and intensity; (ii) the shift of $\nu(\text{C}=\text{S})$, $\nu(\text{C}=\text{N})$ signals to lower frequencies by (8 and 37 cm^{-1} , respectively) together with their weak appearance; (iii) the occurrence of the $\nu(\text{N}-\text{N})$ band at higher wave numbers; (iv) the simultaneous appearance of new bands in the 360, 457, and 490 cm^{-1} regions due to the $\nu(\text{M}-\text{S})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ vibrations, respectively [54] and (iv) the presence of the NH group indicating the neutrality of the ligand.

The characteristic bands of phenanthroline [55] appear in the IR spectra of the ternary complex **6** suggesting phenanthroline coordination in these complexes.

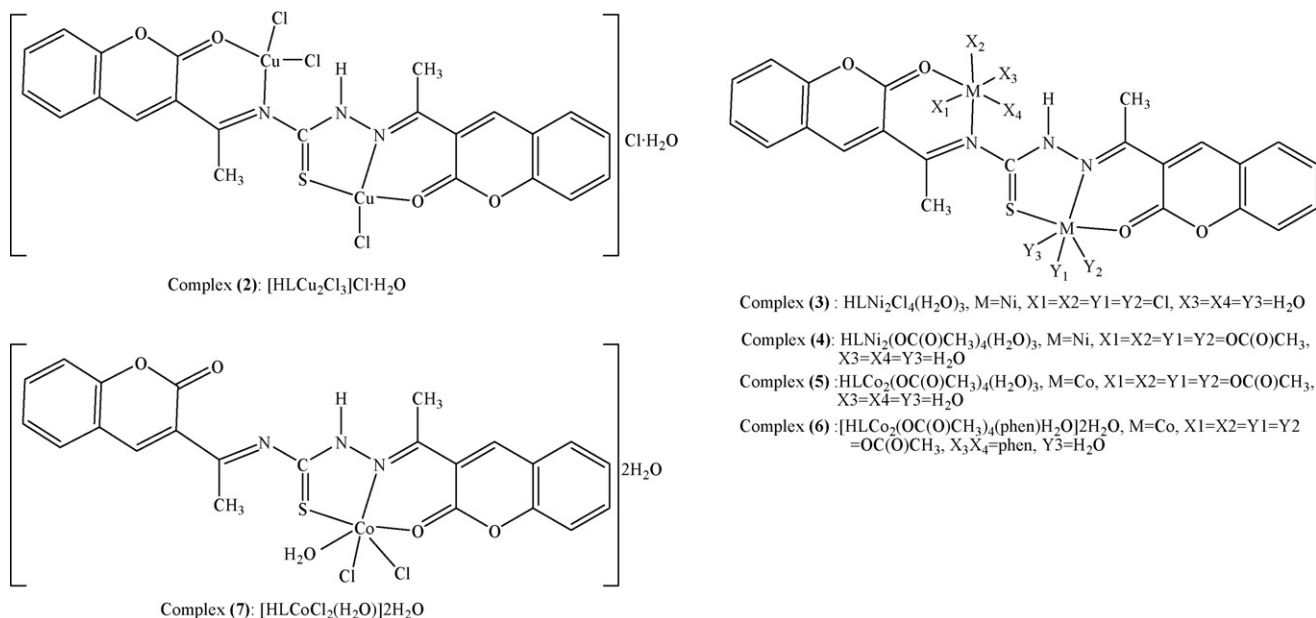
The appearance of two characteristic bands in the ranges 1561–1559 cm^{-1} and 1370–1367 cm^{-1} in the case of complexes **4**, **5** and **6** was attributed to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$. The separation value, $\Delta\nu(\text{COO}^-)$, between $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, in these complexes were more than 190 cm^{-1} (191–193 cm^{-1}) suggesting the coordination of carboxylate group in a monodentate fashion [55].

2.5. Molar conductance data

The metal complexes discussed herein were dissolved in DMF or DMSO and the molar conductivities of their solutions (10^{-3} M) at room temperature were measured to establish the charge of the metal complexes. All complexes behave as non-electrolytes (**3–7**) except complex (**2**), which showed a conductance typical of an ionic compound (see Section 4).



Scheme 2. The pathway fragmentation pattern of the mass spectrum of the ligand HL (1).



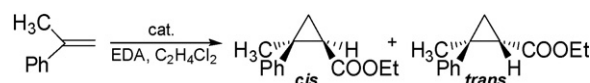
Scheme 3. Proposed structures for the metal complexes.

2.6. Magnetic, electronic and electron spin resonance spectral studies

The electronic spectrum of the copper complex (**2**) shows single broad d–d band centered at 500 nm, as expected for square planar geometry as encountered for related copper(II) complexes [56]. The ESR spectrum of this complex is of axial shape with $g_{\parallel} > g_{\perp}$ characteristic of complexes with $^2B_{1(dx^2-y^2)}$ ground state. The average g values were calculated according to the equation $g_{av} = 1/3[g_{\parallel} + 2g_{\perp}]$. Complex (**2**) exhibits $g_{\parallel} < 2.3$, suggesting covalent characters of the copper–ligand bonding in this complex. The parameter $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$ shows the possibility of exchange interaction in the Cu(II) complex. The G values for the complex ($G > 4$) indicate that there is no direct copper–copper interaction in the solid state [57]. The $g_{\parallel}/A_{\parallel}$ is taken as an indication for the stereochemistry of the copper(II) complexes. Addison [58] has suggested that this ratio may be an empirical indication of the tetrahedral distortion of the square planar geometry. The values lower than 135 cm are observed for square planar structures and those higher than 150 cm for tetrahedrally distorted complexes. The value of $g_{\parallel}/A_{\parallel}$ quotient for the complex under investigation lies below 135 cm, indicating square planar geometry around copper in this complex. The magnetic moment value for this complex was found to be 1.76 B.M. per Cu ion [57] which is in the usual range for square planar copper complexes and indicating no direct interaction between the two copper centers in the solid state at room temperature [57].

The absorption spectral bands of nickel(II) complexes **3**, **4** showed three spin allowed transitions: $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ appearing in the ranges 1145–1054, 706–695 and 461–443 nm, respectively consistent with a typical Ni(II) in an octahedral environment [59]. The magnetic moment values for these complexes were found in the range 3.10–3.14 B.M. [59] expected for octahedral nickel complexes.

The electronic spectra of the cobalt(II) complexes (**5**), (**6**) and (**7**) gave three bands at 1200–1051, 700–622 and 489–433 nm, which can be assigned to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F) (\nu_1)$ and $^4T_{1g}(F) \rightarrow ^4A_{2g}(F) (\nu_2)$ and $^4T_{1g}(F) \rightarrow ^4T_{2g}(P) (\nu_3)$, respectively, suggesting an octahedral geometry around Co(II) ion [60]. The magnetic moment of complex (**7**) is 4.96 B.M., indicating octahedral geometry [61] while complexes **5** and **6** show magnetic moment values in the range 3.2–3.5 B.M., which is smaller than the calculated value



Scheme 4.

for two Co(II) ions in octahedral geometries and this may be due to antiferromagnetism between the two ion-centers.

2.7. Application to catalytic olefin cyclopropanation

To evaluate the catalytic activity of $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**), we choose the cyclopropanation of α -methyl styrene by EDA (EDA = ethyl diazoacetate) (Scheme 4) as a model reaction. Conditions of the catalytic reaction were examined by varying the temperature and relative ratio **2**/EDA/olefin. Results are summarized in Table 1. Catalytic reactions were run by adding the EDA to a stirred solution containing the olefin and the metal complex in 1,2-dichloroethane under dinitrogen.

The copper complex $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**), exhibited excellent catalytic capability towards the decomposition of ethyl diazoacetate, and the subsequent transfer of the carbene moiety to the C=C double bond.

As it can be seen from data reported in Table 1, $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**), is a very active catalyst for cyclopropanation reactions. The catalyst showed a medium activity at room temperature at a **2**/EDA/olefin ratio of 1/500/2500 and gave a conversion of 99% in 345 min, but if the temperature was raised from 28 to 65 °C the reaction time necessary to have a complete conversion decrease from 345 to 10 min (entries 1 and 2, Table 1) indicating a very high change in activity with temperature. Equimolar amounts of EDA and olefin can be used without the need for an excess of the olefin (entry 4, Table 1). The catalyst activity decreases with increasing the amount of the olefin, though this leads to a slight improvement in the yield of the cyclopropanation reaction (compare entry 2 with entry 4, Table 1). The formation of the cyclopropanes is accompanied by the formation of the well-known coupling by-products (maleate and fumarate), normally obtained in cyclopropanation reactions, but only as minor products. The catalyst showed a good stability and after complete consumption of the starting EDA, the catalytic cycle can be restored just by the addition of both reactants. The times of the second and third runs are shorter (see later). The *cis*:*trans*

Table 1
Cyclopropanation of α -methylstyrene with EDA catalyzed by $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**)^a.

Entry	2 /EDA/olefin	T (°C)	Time (min)	Conversion (%) ^b	Yield (%) ^c	<i>cis</i> : <i>trans</i> ^c
1	1/500/2500	28	345	>99	91	43:57
2 ^d		65	10	>99	90	46:54
3		75	5	>99	90	43:57
4	1/500/500	65	7	>99	87	43:57
5	1/1000/5000	65	10	>99	92	44:56
6 ^e	1/10,000/11,000	65	320 780	81 91	67 76	43:57
7 ^f	1/20,000/21,000	65	325 780	67 84	53 66	42:58
8 ^g	1/26,900/40,000	65	1560	63	46	48:52

^a Experimental conditions: EDA was added to a solution of $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**) (2 mg, 2.8×10^{-3} mmol) and α -methyl styrene in 1,2-dichloroethane (10 mL).

^b Conversion of the starting EDA.

^c Yield, based on conversion of EDA, and *cis*/*trans* ratio determined by GC–MS analysis.

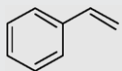
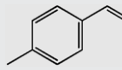
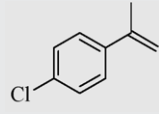
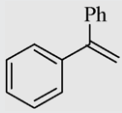
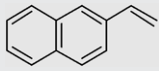
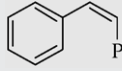
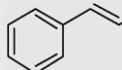
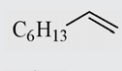
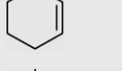
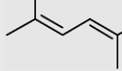
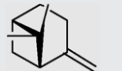
^d After complete consumption of the starting EDA, the catalytic cycle was restored twice by addition of EDA and α -methyl styrene; overall yield is reported.

^e EDA was added to a solution of $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**) (0.6 mg, 8.4×10^{-4} mmol) and α -methyl styrene in 1,2-dichloroethane (10 mL).

^f EDA was added to a solution of $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**) (0.4 mg, 5.6×10^{-4} mmol) and α -methyl styrene in 1,2-dichloroethane (10 mL).

^g EDA was added to a solution of $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**) (0.12 mg, 1.7×10^{-4} mmol) and α -methyl styrene in 1,2-dichloroethane (10 mL). These solutions were prepared by dilution of a solution prepared by dissolving $[HLCu_2Cl_3]Cl \cdot H_2O$ (**2**) (1 mg, 1.4×10^{-3} mmol) in 1,2-dichloroethane (10 mL).

Table 2
Cyclopropanation of olefins with EDA catalyzed by [HLCu₂Cl₃]Cl·H₂O (**2**)^a.

Entry	Olefin	Time (min)	Conversion (%) ^b	Yield (%) ^c	cis:trans ^c
1		15	>99	85	32:68
2		13	>99	89	31:69
3		9	>99	97	46:54
4		6	>99	66	One product
5		20	>99	89	33:67
6		5	>99	17	28:72
7		11	>99	63	32:68
8		24	>99	80	32:68
9		13	>99	88	9:91
10		11	>99	89	35:65
11		10	>99	93	56:43:1 ^d

^a Experimental conditions: EDA was added to a solution of [HLCu₂Cl₃]Cl·H₂O (**2**) (2 mg, 2.8 × 10⁻³ mmol) and olefin in 1,2-dichloroethane (10 mL) with [Cu]/EDA/olefin ratio of 1/500/2500 at 65 °C.

^b Conversion of the starting EDA.

^c Determined by GC–MS (yield based on EDA).

^d Only traces of the fourth diastereoisomer were detected by GC–MS.

ratio is not affected to a large extent by changing the conditions and nearly equal amounts of both cyclopropanes have always been obtained. Best results in terms of cyclopropane yield (92% based on EDA) were obtained at 65 °C at a **2**/EDA/olefin ratio of 1/1000/5000 (entry 5, Table 1). In contrast to the prolonged EDA addition time generally required to reduce the formation of coupling products in cyclopropanation, we found complex (**2**) to be rather insensitive to this: a loading of 0.01 mol% of the catalyst and one pot addition of EDA completely consumed all the EDA and afforded cyclopropane products with good selectivity (76% based on EDA) in 13 h (TON 9100, entry 6, Table 1). Note that the same catalyst loading (entry 6, Table 1) after 320 min gave a conversion of 81% (TON 8100) with almost the same selectivity. Further decrease of the catalyst loading (entries 6 and 7, Table 1) causes a slight drop in selectivity, but cyclopropanes are still obtained in reasonable yields (66% after 13 h). The catalyst keeps its activity for prolonged times and at a **2**/EDA/olefin ratio of 1/26,900/40,000 (entry 8, Table 1) 63% of the starting EDA is converted in 26 h (TON = 16,947).

To determine the general applicability of complex [HLCu₂Cl₃]Cl·H₂O (**2**), cyclopropanation reactions of a series

of styrene derivatives with varied electronic and steric properties were carried out, using ethyl diazoacetate (EDA) as carbene source (Table 2). At a **2**/EDA/olefin ratio of 1/500/2500 at 65 °C, the complex catalyzed the cyclopropanation of a range of substrates with quantitative conversion in short reaction times and with selectivities ranging from good to excellent. The results are summarized in Table 2.

When styrene was employed as substrate, we observed the quantitative conversion of the starting EDA in a comparable rate to what observed in the case of α -methyl styrene (entry 2, Table 1 and entry 1, Table 2). Better yields in cyclopropane products, with slightly shorter reaction times, were obtained when electron-donating substituents are present in the *para* position of the aromatic ring (entry 2, Table 2). The highest yield in cyclopropane derivatives (97%) was obtained with *p*-chloro- α -methyl styrene (entry 3, Table 2). It can be seen that in the absence of a α -substituent on the styrene derivative the formation of the *trans* cyclopropane is slightly favored (compare entries 1 and 2, Table 2 with entry 3 Table 2 and entry 2 Table 1). However, steric hindrance at the alpha position does not hamper the reaction and

Table 3
Cyclopropanation of α -methylstyrene with EDA catalyzed by different copper salts in the presence of HL (**1**)^a.

Entry	Catalyst	Ratio (HL/"Cu")	Time (min)	Conversion (%) ^b	Yield (%) ^c	cis : trans ^c
1	HL + Cu ^{II} Cl ₂	1:2	8 ^d /4 ^e /4 ^f	>99	89	44:56
2 ^g		1:1	16 ^d /6 ^e /6 ^f	>99	90	45:55
3	HL + Cu ^{II} (CH ₃ COO) ₂ ·H ₂ O	1:2	14 ^d /9 ^e /13 ^f	>99	93	43:56
4 ^h	HL + [Cu ^I (OTf)] ₂ ·C ₆ H ₆	1:2	3 ^d /3 ^e /3 ^f	>99	88	45:55

^a Experimental conditions: HL/[Cu] is prepared by adding the required amount of copper salt (5.6×10^{-3} mmol) to a hot (65 °C) solution of HL (**1**) (1.2 mg, 2.8×10^{-3} mmol) in 1,2-dichloroethane (10 mL) and stirring was maintained until colour change from yellow to green or brown according to the salt was observed, then EDA and olefin (1/EDA/olefin ratio of 1/500/2500) were added to the reaction mixture at 65 °C. After complete consumption of the starting EDA, the catalytic cycle was restored twice by addition of EDA and olefin; overall yield is reported.

^b Conversion of the starting EDA.

^c Determined by GC-MS (yield based on EDA).

^d First run.

^e Second run.

^f Third run.

^g Cu^{II}Cl₂ (0.38 mg, 2.8×10^{-3} mmol) was used.

^h [Cu^I(OTf)]₂·C₆H₆ (1.4 mg, 2.8×10^{-3} mmol) was used.

good yields were obtained even with 1,1-diphenyl ethylene (entry 4, Table 2). On the other hand, steric hindrance at the β -position of the styrene greatly affected the reactivities. *Trans*- β -methyl styrene gave lower reaction yields (63%) although with a good diastereoselectivity (entry 7, Table 2), while with *cis*-stilbene a dramatic drop in the cyclopropanation products was observed (entry 6, Table 2).

Even aliphatic double bonds that are generally less reactive towards cyclopropanation, gave excellent results. Though the time of the cyclopropanation reaction for these substrates increase slightly if compared to what observed for styrene derivatives, very good yields were always obtained (entries 8–11, Table 2). Even in these cases *trans* cyclopropane compounds were obtained as major products and a remarkable diastereoselectivity (*cis:trans* = 9:91) has been observed in the case of cyclohexene (entry 9, Table 2). With 2,5-dimethyl-2,4-hexadiene, an important precursor to the chrysanthemoid acid synthesis [62], the catalytic reaction yielded the desired cyclopropanes in very good yields (89%) and with reasonable diastereoselectivities (entry 10, Table 2), without the need of a large excess of the olefin. Out of the four possible diastereoisomers that could be obtained in the cyclopropanation of (–) β -pinene, two major isomers were obtained, along with minor amounts of a third one. The fourth diastereoisomer was detected only in small traces upon GC/MS analysis of the reaction mixture (entry 11, Table 2).

To determine the effect of the oxidation state of copper and of the counter anion on the activity of the catalyst in the cyclopropanation reactions, different copper salts were used. If the catalyst was prepared *in situ* by adding 2 equiv. of anhydrous CuCl₂ to the ligand (**1**) and then the mixture was allowed to stir at 65 °C before the addition of the olefin and EDA with a 1/EDA/olefin ratio of 1/500/2500, similar selectivity and diastereoselectivity, within the experimental error, to what obtained when employing isolated complex (**2**) were observed (compare entry 1, Table 3 with entry 2, Table 1). However, we noticed a slight decrease in the reaction time that can be due to the fact that in this case we used an anhydrous salt to prepare the catalyst, while complex (**2**) has been prepared starting from dihydrated copper(II) chloride (see Section 4). For this reason, the effect of water on the catalytic reaction has been studied. Different amounts of H₂O were added to a reaction mixture at a 2/EDA/olefin ratio of 1/500/2500, retaining a constant volume of 10 mL as the sum of the volume of H₂O and C₂H₄Cl₂. The catalyst showed high stability to H₂O content even at a H₂O/C₂H₄Cl₂ ratio of 1/1, with a quantitative conversion of the starting EDA in 10 min but with a decrease in the selectivity (73% yield of cyclopropanes).

Complex (**2**) contains two coordinated copper ions in different coordination sites, but no direct interaction between the two copper centers in the solid state at room temperature is observed. To

better understand the role played by each copper atom in the catalysis, different metal/ligand ratios were used. When the amount of copper was halved (HL/"Cu" = 1:1), the same selectivity of the reaction outcome was observed, but the reaction time is almost doubled (entry 2, Table 3). Under these conditions it is reasonable to assume that a 1 to 1 complex is formed and thus it is tempting to suggest that each copper ion independently contribute to the reaction, but without any cooperative effect.

The catalyst prepared from Cu^{II}(CH₃COO)₂·H₂O is slightly less active than [HLCu₂Cl₃]Cl·H₂O (**2**) and again showed a decrease in the time of cyclopropanation in the second run (see later), but an increase of the time of the third run was observed (entry 3, Table 2), indicating that the presence of the acetate ion renders the catalyst less stable.

When copper(I) trifluoromethane sulfonate benzene complex was used for the preparation of the catalyst the reaction time dropped sharply and exactly the same time was obtained for three consecutive runs (entry 4, Table 3). This is consistent with the fact that copper(II) must be reduced to copper(I) before entering the catalytic cycle (see below). If only the copper(I) trifluoromethane sulfonate benzene complex was used as a catalyst in the absence of any ligand [63], the time of the reaction increased in the second and more in the third runs indicating a fast decrease in reactivity. If the copper complex of hydrazinecarbothioamide was used as a catalyst the cyclopropanation reaction did not take place and only the coupling products (maleate and fumarate) were formed.

Copper(I) compounds are known to be more efficient cyclopropanation catalysts than copper(II) compounds. It has been observed that Cu(II) complexes are reduced to Cu(I) derivatives by the diazo compound under the reaction conditions [63]. This has led to general agreement that the active catalyst is a Cu(I) species, irrespective of the oxidation state of the copper complex used as the precatalyst [64]. It is also generally accepted that transition metal-catalyzed cyclopropanation reactions proceed via a metal-carbene complex, which is formed by association of the diazo compound and the catalyst with concomitant extrusion of nitrogen [64]. Due to the very high reactivity of this complex, any attempt to isolate this copper(I) complex met with failure. We can anyway note the following: (i) All the catalytic reactions tested need an induction period before the nitrogen evolution due to the EDA decomposition was observable. All the reactions were also followed by IR spectroscopy monitoring the disappearance of the band due to the stretching of the N₂ moiety of the EDA ($\nu = 2114 \text{ cm}^{-1}$). The consumption of the diazoacetate always started after an induction period. This explains why the catalytic cycle is faster in the second and third runs. This induction period depends also on the concentration of the olefin and increases with the increase of the

olefin concentration. (ii) When the EDA conversion reached completion, it was possible to restore the catalytic cycle just by adding new EDA and olefin to the reaction mixture. In this case no induction period was necessary to the system and the reactions always proceeded to give cyclopropanes with almost identical yields. (iii) During the reaction the colour of the solution, due to the dissolved copper complex changed from brown (due copper(II) complex) to colourless. The time needed for the change in colour was always coincident with the induction period. (iv) The induction period observed depends also on the olefin employed and longer times are observed for *trans*- β -methyl styrene or non-conjugated double bonds (see also Table 2). (v) If the reaction was run in air, longer reaction times were needed and we never obtained a full conversion of the starting EDA in these cases. (vi) If a copper(I) source was used instead, no induction period was necessary to the system.

All these data, together with the data reported in the literature [65] suggest that the catalyst is activated during the induction period and that the initial reduction of copper(II) to copper(I) is necessary to the catalysis to take place.

3. Conclusions

The straightforward condensation of 3-acetyl-2H-chromen-2-one and hydrazinecarbothioamide to yield the novel Schiff base N,2-bis(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide (**1**) has been reported. Its flexible back bone, together with the presence of N, S and O donor atoms, renders this compound interesting for studying its coordination behaviour with transition metals ion. In this work some complexes with copper, nickel and cobalt have been characterized and all the data collected are in agreement with the proposed structures. The spectral data indicate that when equimolar amounts of ligand and metal are used, the ligand can behave as a neutral tridentate ligand to coordinate a single metal ion through the C=N, C=O and C=S groups, as is the case for the cobalt complex (**7**). When the stoichiometry of the reaction is changed and a double amount of metallic salt is used instead, the ligand behaves as a neutral pentadentate ligand, with two different coordinating sites, one provided by a nitrogen and an oxygen donor atoms and one by the C=N, C=O and C=S groups, each one accommodating a metal ion.

The copper(II) complex, [HLCu₂Cl₃]Cl·H₂O (**2**), showed excellent catalytic activity in cyclopropanation reaction and we have observed that TON up to 16,900 can be obtained. In contrast to the prolonged EDA addition time generally required to reduce the formation of coupling products in cyclopropanation, we found this complex to be very active and one pot addition of EDA is allowed to yield the desired cyclopropanes with excellent selectivity. Moreover, the catalyst is very robust and no decrease in yield was observed even after three catalytic runs. It has been shown that the present system tolerates water and that the initial reduction step from copper(II) to copper(I) is required to start the catalytic cycle.

4. Experimental

4.1. Materials and methods

All the reagents and solvents employed for the preparation of the ligand and its complexes were of the best grade available and used without further purification. Unless otherwise stated, all catalytic tests were carried out under an atmosphere of purified dinitrogen using modified Schlenk techniques. Benzene, cyclohexene, and 1-octene were distilled over sodium, styrene, α -methyl styrene and 1,2-dichloroethane were distilled over calcium hydride and stored under dinitrogen.

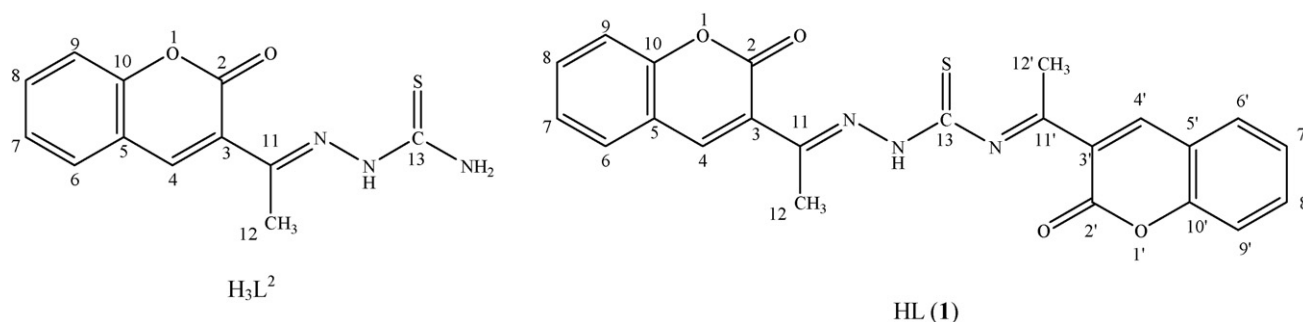
The ligand and its metal complexes were analyzed for C, H, N and M contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. The metal ion contents of the complexes were also determined [66–68] by the previously reported methods [69,70]. Mass spectra of the ligand and its metal complexes were recorded using JEUL JMS-AX-500 mass spectrometer provided with data system. IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400–4000 cm⁻¹ and in the 500–100 cm⁻¹ region using polyethylene-sandwiched nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. ¹H and ¹³C{¹H} NMR spectra were obtained on Bruker Avance 300-DRX or Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. The electronic spectra of the ligands and their complexes were obtained in Nujol mulls and in saturated DMSO solutions using a Shimadzu UV-240 UV-Visible recording spectrophotometer. Molar conductivities of the metal complexes in DMSO (10⁻³ M) were measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in ohms and the molar conductivities were calculated according to the equation: $\Delta = V \times K \times Mw/g \times \Omega$, where Δ , molar conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$); V , volume of the complex solution (mL); K , cell constant 0.92 cm⁻¹; Mw , molecular weight of the complex; g , weight of the complex; and Ω , resistance measured in ohms. Magnetic moments at 298 K were determined using the Gouy method with Hg[Co(SCN)₄] as calibrant. The solid ESR spectra of the complexes were recorded with ELEXSYS E500 Bruker spectrometer in 3-mm Pyrex Tubes at 298 K. Diphenylpicrylhydrazide (DPPH) was used as a g -marker for the calibration of the spectra. GC-MS analyses were performed on a Shimadzu GCMS-QP5050A instrument.

4.2. Synthesis of the Schiff base ligand HL (**1**) and its metal complexes

4.2.1. Synthesis of the Schiff base ligand HL (**1**)

The synthesis of the ligand was made in two different ways.

4.2.1.1. One step formation of the ligand HL (1**).** Hydrazinecarbothioamide (218.0 mg, 2.4 mmol) was added to a hot solution (75 °C) of 3-acetyl-2H-chromen-2-one (900.0 mg, 4.8 mmol) in ethanol (25 mL), the solid hydrazinecarbothioamide dissolved gradually to yield a clear solution. The solution was stirred at 75 °C and after 4 h a heavy yellow precipitate started to form. 1,2-Dichloroethane (40 mL) was added to the mixture to dissolve the formed 1:1 condensation product, (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide, H₃L², then anhydrous magnesium sulphate (250.0 mg, 2.5 mmol) was added to the mixture. The reaction mixture was refluxed for 108 h, then 1,2-dichloroethane (40 mL) was added and the solution was filtered and dried, recrystallized from ethanol and dried under vacuum in a desiccator over anhydrous CaCl₂ (0.7145 g, 58% yield). ¹H NMR (300 MHz, DMSO): δ = 10.43 (bs, 1H, NH), 8.65 (s, 1H, H(4')), 8.46 (s, 1H, H(4)), 7.95 (d, J = 7.7 Hz, 1H, H(6')), 7.77 (d, J = 7.7 Hz, 1H, H(6)) overlapping with 7.75 (pst, 1H, H(8')), 7.65 (t, J = 7.7 Hz, 1H, H(8)), 7.48/7.37 (m, 4H, H(7), H(7'), H(9) and H(9')), 2.60 (s, 3H, CH₃(12')), 2.26 (s, 3H, CH₃(12)). ¹³C NMR (300 MHz, DMSO, 300 K): 196.0 (C=S), 180.1 (C=N), 160.0 (C=O), 155.5 (C=O), 154.2 (C=N), 147.9, 146.8, 142.8, 135.3, 133.2, 131.6, 130.0, 126.7, 125.8, 125.6, 125.3, 119.8, 119.0, 117.0, 116.8, 30.9, (CH₃), 16.5 (CH₃). One quaternary carbon was not detected. UV/vis (Nujol mul (nm)): λ = 280, 330, 340. UV/vis (1×10^{-4} mol, DMSO): λ = 270, 290, 345. IR (KBr): ν (N²H) 3245 m, ν (C=O), 1719 s, ν (C=S) 861 s, ν (C=N) 1678 s, ν (N–N) 1115 s cm⁻¹. Elemental analysis for C₂₃H₁₇N₃O₄S (431.46): calcd. C 64.03, H 3.97, N 9.74; found C 64.21, H 4.24, N 9.81.



Scheme 5. Numbering scheme employed for H_3L^2 and HL (**1**).

4.2.1.2. Two step formation of the ligand HL (**1**).

(1) Synthesis of (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide, H_3L^2 . hydrazinecarbothioamide (218.0 mg, 2.4 mmol) was added to a hot solution (75 °C) of 3-acetyl-2H-chromen-2-one (450.0 mg, 2.4 mmol) in ethanol (20 mL), the solid hydrazinecarbothioamide dissolved gradually to yield a clear solution. The solution was stirred at 75 °C and after 4 h a heavy yellow precipitate started to form. The reaction mixture was refluxed for 8 h, then the product was filtered off and dried under vacuum in a desiccator over anhydrous $CaCl_2$. This compound is readily crystallized from dichloromethane giving yellow crystals of (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide, H_3L^2 . ¹H NMR (400 MHz, DMSO): δ = 10.43 (s, 1H, NH), 8.47 (s, 1H, H(4)), 8.39 (bs, 1H, NH), 7.94 (bs, 1H, NH), 7.77 (d, J = 8.0 Hz, 1H, H(6)), 7.64 (t, J = 8.0 Hz, 1H, H(8)), 7.41 (d, J = 8.0 Hz, 1H, H(9)), 7.39 (t, J = 8.0 Hz, 1H, H(7)), 2.27 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO, 300 K): 179.8 (C=S), 159.6 (C=O), 153.8 (C=N), 146.4, 142.4, 132.8, 129.6, 126.3, 125.2, 119.4, 116.4, 16.5 (CH₃).

(2) Preparation of the ligand HL (**1**): a solution of 3-acetyl-2H-chromen-2-one (450.0 mg, 2.4 mmol) in 1,2-dichloroethane (40 mL) was added to a solution of (E)-2-(1-(2-oxo-2H-chromen-3-yl)ethylidene)hydrazinecarbothioamide, H_3L^2 , (624.9 mg, 2.4 mmol) in ethanol/ 1,2-dichloroethane 1/3 (60 mL) and then anhydrous magnesium sulphate (150.0 mg, 1.5 mmol) was added to the mixture. The reaction mixture was refluxed for 95 h. After the completion of the reaction, 1,2-dichloroethane (40 mL) was added, the solution was filtered off and dried, the residue was recrystallized from ethanol and dried under vacuum in a desiccator over anhydrous $CaCl_2$. Yield and characterization of the product were identical to those reported for Section 4.2.1.1 (Scheme 5).

4.2.2. Synthesis of the metal complexes

4.2.2.1. Synthesis of $[HLCu_2Cl_3]Cl \cdot H_2O$ complex (**2**). A solution of $CuCl_2 \cdot 2H_2O$ (0.292 g, 1.716 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of HL (**1**) (0.37 g, 8.58×10^{-1} mmol) in ethanol (25 mL), then the reaction mixture was refluxed for 2 h. The brown solution was then concentrated under vacuum (8 mL). The precipitate was then filtered off, washed with methanol and dried under vacuum over anhydrous $CaCl_2$ (0.419 g, 68% yield). Conductance Λ_m : $79 \Omega^{-1} cm^2 mol^{-1}$. UV/vis (Nujol mul (nm)): 260, 280, 300, 500. IR (KBr): $\nu(H_2O)$ 3411 (br), $\nu(N^2H)$ 3277 (br), $\nu(C=O)$ 1714 (w), $\nu(C=S)$ 847 (m), $\nu(C=N)$ 1644 (m), $\nu(N-N)$ 1122 cm^{-1} (w). ESR (CD Disk): g_{\parallel} 2.216, g_{\perp} 2.038, G = 5.99. Elemental analysis for $C_{23}H_{19}Cl_4Cu_2N_3O_5S$ (718.38): calcd. C 38.45, H 2.67, N 5.85, Cu 17.69; found C 38.77, H 2.9, N 5.65, Cu 17.19.

4.2.2.2. Synthesis of $HLNi_2Cl_4(H_2O)_3$ complex (**3**). A solution of $NiCl_2 \cdot 6H_2O$ (0.341 g, 1.437 mmol) in methanol (15 mL) was added

to a hot solution (75 °C) of HL (**1**) (0.310 g, 7.19×10^{-1} mmol) in ethanol (16 mL) then the reaction mixture was refluxed for 4 h. The precipitate was then filtered off, washed with methanol and dried under vacuum over anhydrous $CaCl_2$ (0.433 g, 81% yield). Conductance Λ_m : $11 \Omega^{-1} cm^2 mol^{-1}$. UV/vis (Nujol mul (nm)): λ = 260, 279, 320, 445, 706, 1145. IR (KBr): $\nu(H_2O)$ 3440 (br), $\nu(N^2H)$ 3265 (br), $\nu(C=O)$ 1715 (s), $\nu(C=S)$ 845 (m), $\nu(C=N)$ 1650 (s), $\nu(N-N)$ 1146 cm^{-1} (s). Elemental analysis for $C_{23}H_{23}Cl_4N_3Ni_2O_7S$ (744.71): calcd. C 37.09, H 3.11, N 5.64, Ni 15.76; found C 37.02, H 3.20, N 5.72, Ni 15.70.

4.2.2.3. Synthesis of $HLNi_2(OC(O)CH_3)_4(H_2O)_3$ complex (**4**). A solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.415 g, 1.669 mmol) in methanol (10 mL) was added to a hot solution (75 °C) of HL (**1**) (0.360 g, 8.34×10^{-1} mmol) in ethanol (23 mL) then the reaction mixture was refluxed for 4 h. The precipitate was then filtered off, washed with methanol and dried under vacuum over anhydrous $CaCl_2$ (0.484 g, 78% yield). Conductance Λ_m : $8 \Omega^{-1} cm^2 mol^{-1}$. UV/vis (Nujol mul (nm)): λ = 255, 270, 340, 461, 676 and 1135. IR (KBr): $\nu(H_2O)$ 3340 (br), $\nu(N^2H)$ 3260 (br), $\nu(C=O)$ 1706 (s), $\nu(C=S)$ 859 (w), $\nu(C=N)$ 1657 (s), $\nu(N-N)$ 1123 (m), $\nu_{sym}(OC(O)CH_3)$ 1559 (m), $\nu_{asym}(OC(O)CH_3)$ 1368 cm^{-1} (m), ($\Delta\nu$ = 191 cm^{-1}). Elemental analysis for $C_{31}H_{35}N_3Ni_2O_{15}S$ (839.07): calcd. C 44.37, H 4.20, N 5.01, Ni 13.99; found C 44.30, H 4.28, N 5.25, Ni 13.69.

4.2.2.4. Synthesis of $HLCu_2(OC(O)CH_3)_4(H_2O)_3$ complex (**5**). A solution of $Co(OAc)_2 \cdot 4H_2O$ (0.450 g, 1.808 mmol) in methanol (12 mL) was added to a hot solution (75 °C) of HL (**1**) (390 mg, 9.04×10^{-1} mmol) in ethanol (26 mL) then the reaction mixture was refluxed for 6 h. The precipitate was then filtered off, washed with methanol and dried under vacuum over anhydrous $CaCl_2$ (0.478 g, 71% yield). Conductance Λ_m : $17 \Omega^{-1} cm^2 mol^{-1}$. UV/vis (Nujol mul (nm)): λ = 255, 270, 340, 433, 622, 1051. IR (KBr): $\nu(H_2O)$ 3344 (br), $\nu(N^2H)$ 3263 (br), $\nu(C=O)$ 1705 (s), $\nu(C=S)$ 854 (w), $\nu(C=N)$ 1639 (s), $\nu(N-N)$ 1122 (w), $\nu_{sym}(OC(O)CH_3)$ 1560 (m), $\nu_{asym}(OC(O)CH_3)$ 1367 cm^{-1} (m) [$\Delta\nu$ = 193 cm^{-1}]. Elemental analysis for $C_{31}H_{35}Co_2N_3O_{15}S$ (839.55): calcd. C 44.35, H 4.20, N 5.01, Co 14.04; found C 44.51, H 3.90, N 5.19, Co 14.11.

4.2.2.5. Synthesis of $[HLCu_2(OC(O)CH_3)_4(phen)H_2O]2H_2O$ complex (**6**). A solution of $Co(OAc)_2 \cdot 4H_2O$ (0.346 g, 1.391 mmol) in methanol (12 mL) was added to a hot solution (75 °C) containing HL (**1**) (0.300 g, 6.95×10^{-1} mmol) and 1,10-phenanthroline (0.251 g, 1.391 mmol) in ethanol (25 mL) then the reaction mixture was refluxed for 6 h. The precipitate was then filtered off, washed with methanol and dried under vacuum over anhydrous $CaCl_2$ (0.475 g, 67% yield). Conductance Λ_m : $14 \Omega^{-1} cm^2 mol^{-1}$. UV/vis (Nujol mul (nm)): λ = 260, 331, 468 and 700. IR (KBr): $\nu(H_2O)$ 3406 (br), $\nu(N^2H)$ 3286 (br), $\nu(C=O)$ 1707 (vw), $\nu(C=S)$ 856 (w), $\nu(C=N)$ 1651 (m), $\nu(N-N)$ 1121 (w), $\nu_{sym}(OC(O)CH_3)$ 1561 (m),

$\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$ 1370 (m) [$\Delta\nu = 191 \text{ cm}^{-1}$], 1560, 770, 640 cm^{-1} . Elemental analysis for $\text{C}_{43}\text{H}_{43}\text{Co}_2\text{N}_5\text{O}_{15}\text{S}$ (1019.76): calcd. C 50.65, H 4.25, N 6.87, Co 11.56; found C 50.78, H 4.11, N 6.65, Co 11.25.

4.2.2.6. Synthesis of $[\text{HLCuCl}_2(\text{H}_2\text{O})]2\text{H}_2\text{O}$ complex (7). A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.193 g, 8.11×10^{-1} mmol) in methanol (12 mL) was added to a hot solution (75 °C) of HL (1) (0.350 g, 8.11×10^{-1} mmol) in ethanol (20 mL) then the reaction mixture was refluxed for 6 h. The reddish brown solution was then concentrated under vacuum (8 mL). The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl_2 (0.375 g, 71% yield). Conductance Λ_m : $15 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. UV/vis (Nujol mul (nm)): $\lambda = 265, 280, 330, 489, 636, 1200$. IR (KBr): $\nu(\text{H}_2\text{O})$ 3419 (br), $\nu(\text{N}^2\text{H})$ 3277 (br), $\nu(\text{C}=\text{O})$ 1717 (s) and 1701 (m), $\nu(\text{C}=\text{S})$ 853 (m), $\nu(\text{C}=\text{N})$ 1641 (m), $\nu(\text{N}-\text{N})$ 1122 cm^{-1} (m). Elemental analysis for $\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{CoN}_3\text{O}_7\text{S}$ (630.38): calcd. C 44.89, H 3.77, N 6.83, Co 9.58; found C 45.15, H 4.05, N 6.89, Co 9.48.

4.3. Typical procedure for the catalytic cyclopropanation of olefins with 2

EDA (see caption of Tables 1 and 2 for quantities) was added to a suspension of $[\text{HLCu}_2\text{Cl}_3]\text{Cl} \cdot \text{H}_2\text{O}$ (2) (2.00 mg, 2.78×10^{-3} mmol) and the olefin (see caption of Tables 1 and 2 for quantities) in 1,2-dichloroethane (10 mL). The resulting pale brown solution was heated at the required temperature under stirring; depending on the olefin used and its concentration, after few minutes the solution turned to colourless and dinitrogen started to evolve from the system. The reaction was followed until total consumption of the EDA (IR absorbance, $\nu_{\text{max}} = 2114 \text{ cm}^{-1}$, <0.025) was observed. The final solution was analyzed by GC–MS after the addition of 2,4-dinitrotoluene as internal standard.

4.4. Typical procedure for the catalytic cyclopropanation of olefins with in situ formed catalyst

The required amount of copper salt (see caption of Table 3 for quantities) was added to a hot (65 °C) solution of HL (1) (1.4 mg, 3.1×10^{-3} mmol) in 1,2-dichloroethane (10 mL) then the mixture was maintained under stirring until the colour of the solution changed from yellow to brown or yellowish brown. The olefin was added to the solution and finally EDA was added to the resulting solution heated at 65 °C. The reaction was followed until total consumption of the EDA (IR absorbance, $\nu_{\text{max}} = 2114 \text{ cm}^{-1}$, <0.025) was observed. After complete consumption of the starting EDA, the catalytic cycle was restored twice by addition of EDA and olefin. The final solution was analyzed by GC–MS after the addition of 2,4-dinitro-toluene as internal standard.

Acknowledgement

We thank MiUR (Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale PRIN2007HMTJWP.004) for financial support.

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