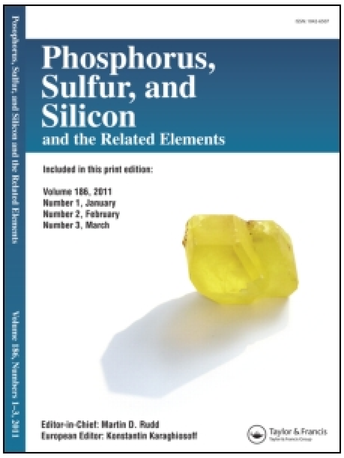
This article was downloaded by:
On: *27 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of New Schiff Base Metal Complexes and Their Use as Catalysts for Olefin Cyclopropanation

Nabil S. Youssef[a]; Eman A. El-Zahany[a]; Ahmed M. A. El-Seidy[a]
[a] Inorganic Chemistry Department, National Research Centre, Dokki, Giza, Egypt

Online publication date: 23 March 2010

To cite this Article Youssef, Nabil S. , El-Zahany, Eman A. and El-Seidy, Ahmed M. A.(2010) 'Synthesis and Characterization of New Schiff Base Metal Complexes and Their Use as Catalysts for Olefin Cyclopropanation', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 4, 785 — 798

To link to this Article: DOI: 10.1080/10426500902967904

URL: http://dx.doi.org/10.1080/10426500902967904

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 185:785–798, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902967904

SYNTHESIS AND CHARACTERIZATION OF NEW SCHIFF BASE METAL COMPLEXES AND THEIR USE AS CATALYSTS FOR OLEFIN CYCLOPROPANATION

Nabil S. Youssef, Eman A. El-Zahany, and Ahmed M. A. El-Seidy
Inorganic Chemistry Department, National Research Centre, Dokki, Giza, Egypt

New transition metal complexes of Co^{II}, Cu^{II}, Ni^{II}, and Fe^{III} of the ligands 2N,2-bis((7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromen-6-yl)methylene)hydrazinecarbo-thioamide H_3L^1 and (E)-2-((7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromen-6-yl)methylene)-N-phenylhydrazinecarbothioamide H_2L^2 have been prepared and characterized. Mass spectra and NMR assignments for the ligands, 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 square pyramidal or octahedral. The structures are consistent with the IR and UV-VIS, as well as conductivity and magnetic moments measurements. Cyclopropanation reactions of unactivated olefins by ethyldiazoacetate (EDA) in the presence of $H_3L^1Cu_2.Cl_4.H_2O$ as catalyst proceed with excellent turn over numbers (TON: up to 12556).

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** *to view the free supplemental file.*

Keywords Condensation reactions; cyclopropanation reactions; homogeneous catalysis; metal complexes; Schiff bases; thiosemicarbazide

Downloaded At: 16:45 27 January 2011

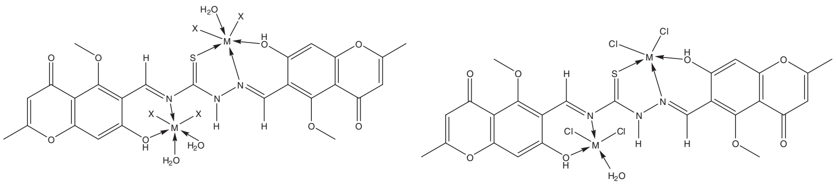
INTRODUCTION

A large number of Schiff base compounds are often used as ligands in coordination chemistry as they readily form stable complexes. Metal complexes with these Schiff bases have the ability to reversibly bind oxygen in epoxidation reactions,[1] catalytic activity in hydrogenation of olefins[2,3] and photochromic properties.[4] Moreover, the chemistry of metal complexes of Schiff base ligands having nitrogen, oxygen, and sulfur at their donor sites has been extensively studied in the last decades.[5–31] Also, these complexes have numerous applications, such as, in the treatment of cancer,[32] as antibactericide agents,[33] as antiviral agents,[34] as fungicide agents,[35] and for their other biological properties.[36] All these advantages make Schiff bases very good candidates in the effort to synthesize metal complexes of interest in bioinorganic chemistry, catalysis, encapsulation, transport

Received 23 October 2008; accepted 14 April 2009.

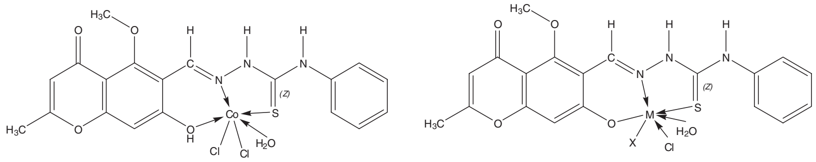
Address correspondence to Nabil S. Youssef, Inorganic Chemistry Department, National Research Centre, Dokki, Giza, Egypt. E-mail: nabilyoussef@hotmail.com

Downloaded At: 16:45 27 January 2011



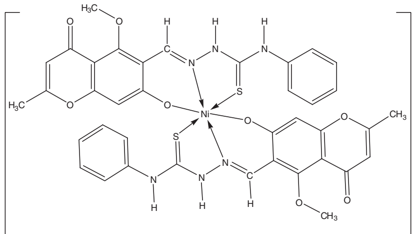
Complex **2:** $H_3L^1Co_2Cl_4(H_2O)_3$, X=Cl
Complex **3** : $H_3L^1Ni_2Cl_4(H_2O)_3$,X=Br
Complex **4:** $H_3L^1Co_2Br_4(H_2O)_3$,X=Cl

Complex **5:**$H_3L^1Cu_2Cl_4H_2O$



Complex **7:** $H_2L^2CoCl_2.H_2O$

Complex **8:** $L^2Ni.Cl(H_2O)_2$, X=H_2O
Complex **10:** $L^2FeCl_2.H_2O$, X=Cl

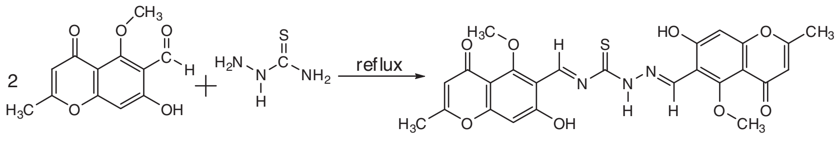


Complex **9:** $[(L^2)_2Ni]H_2O$

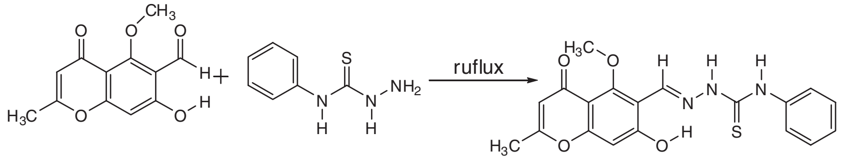
Figure 1 The proposed structures of metal complexes.

and separation processes, magnetochemistry,[37,38] and heterogeneous and homogeneous catalysis for oxidation and polymerization of organic compounds.[39–42] Cyclopropanation of olefins with diazo reagents catalyzed by metal complexes has attracted great research interest because of its fundamental and practical importance.[43–46] Carbene intermediates can be easily generated starting from diazo alkane derivatives, in the presence of different metals. Copper,[47–49] rhodium,[50–52] and ruthenium[53,54] complexes have proven to be among the most effective and with general applicability.[55,56] The resulting cyclopropanes are of biological and industrial importance and serve as versatile precursors in organic synthesis.[44–46,57–60]

In view of the above facts and in continuation of our recent research[61] on the synthesis and characterization of new Schiff bases complexes and their use as catalysts for cyclopropanation of olefins, we report in this article the synthesis and identification of the Schiff base ligands 2N,2-bis((7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromen-6-yl)methylene)hydrazi necarbothioamide H_3L^1 and (E)-2-((7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromen-6-yl)methylene)-N-phenylhydrazine-carbothioamide H_2L^2 and their Co^{II}, Cu^{II}, Ni^{II}, and Fe^{III} complexes. ^{13}C NMR spectra were also obtained to determine the structure of the ligands and some of their complexes. The catalytic activity of complexes $H_3L^1Cu_2.Cl_4.H_2O$ (**5**) toward the decomposition of ethyl diazoacetate (EDA) in the presence of olefins to yield cyclopropane products has also been investigated. Although various methodologies are available today, the cycloaddition of carbenoids to C=C double bonds is the most practical one to construct this class of compounds. Stereochemical control of these reactions, such as differentiation of the enantiotopic faces of the double bond or *cis-trans* selectivity imposed on the cyclopropanation reaction by the presence of a substituent at the carbenoid carbon, are the main issues.[62,63] However, another issue of the cyclopropanation is the chemoselectivity of the reaction: Very often catalysts that are fast in the activation of the approaching carbenoid, namely diazoacetates, give olefins derived by coupling reactions as major byproducts. Rarely, metal complexes can give high selectivities in cyclopropanation reactions together with high turnover number (TON). We report in this article that $H_3L^1Cu_2Cl_4H_2O$ (**5**) is a competent catalyst for the cyclopropanation of olefins, even the underlying examination of the copper complex prepared from the ligand that was prepared from a (1:1) condensation of hydrazinecarbothioamide and 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde showed similar activity (Schemes 1 and 2).



Scheme 1 Schematic representation for the formation of the Schiff base ligand H_3L^1.



Scheme 2 Schematic representation for the formation of the Schiff base ligand H_2L^2.

Downloaded At: 16:45 27 January 2011

RESULTS AND DISCUSSION

The elemental and physical data of the ligands $H_3L^1$and H_2L^2 and their complexes (Table I) showed that the stoichiometry of the complexes obtained is 1:1, 1:2, or 2:1 (metal:ligand) (see Figure 1).

Mass Spectra of the Ligands

The mass spectra of the Schiff base ligands H_3L^1 and H_2L^2 revealed the molecular ion peaks at *m/e* 523 and 383, which are coincident with the formula weights (523.51) and (383.42), respectively, for these ligands support the identity of their structures. The pathway fragmentation patterns of the mass spectra of these ligands are depicted in Schemes S1 and S2 (available online in the Supplemental Materials).

Infrared Spectra

The IR bands for the metal complexes derived from Schiff bases H_3L^1 and H_2L^2, which are most useful in attempting to determine the mode of coordination, are listed in

Downloaded At: 16:45 27 January 2011

Table I Analytical and physical data of the ligands H_3L^1, H_2L^2 and their metal complexes

No.	Ligand/complexes	Color	FW	Yield (%)	Analysis (%)/Found (calcd) C	H	N	M	Molar Conductance Λ_m ($\Omega^{-1}cm^2\,mol^{-1}$)
1	H_3L^1	Yellow	523.51	65	56.95 (57.36)	4.10 (4.04)	8.12 (8.03)	—	—
2	$H_3L^1Co_2Cl_4(H_2O)_3$	Brown	865.29	73	37.30 (37.48)	3.73 (3.61)	5.05 (4.86)	13.55 (13.62)	11
3	$H_3L^1Ni_2Cl_4(H_2O)_3$	Beige	864.81	86	37.39 (37.50)	3.77 (3.61)	5.09 (4.86)	13.48 (13.57)	13
4	$H_3L^1Co_2Br_4(H_2O)_3$	Brown	1043.09	69	30.98 (31.09)	3.20 (3.00)	4.22 (4.03)	11.64 (11.30)	9
5	$H_3L^1Cu_2Cl_4\ H_2O$	Green	773.97	81	39.05 (38.80)	3.00 (2.87)	5.65 (5.43)	16.30 (16.42)	14
6	H_2L^2	Yellow	383.09	72	59.59 (59.52)	4.51 (4.47)	10.67 (10.96)	—	—
7	$H_2L^2CoCl_2(H_2O)$	Brown	545.30	79	43.95 (44.05)	3.99 (3.88)	7.85 (7.71)	10.65 (10.81)	13
8	$L_2Ni.Cl(H_2O)_2$	Beige	512.59	75	44.41 (44.52)	4.85 (3.93)	8.36 (8.20)	11.30 (11.45)	8
9	$[(L^2)_2Ni]H_2O$	Beige	841.53	83	54.46 (54.24)	3.97 (4.07)	9.86 (9.99)	6.85 (6.97)	10
10	$L^2FeCl_2(H_2O)$	Brown	541.21	71	44.30 (44.39)	3.71 (3.72)	7.84 (7.76)	10.21 (10.32)	17

Table II IR frequencies of the bands (cm^{-1}) of ligand H_3L^1, H_2L^2, their metal complexes, and their assignments

No.	Ligand/complexes	$\nu(H_2O)$	$\nu(OH)$	$\nu(NH)$	$\nu(C{-}O)$	$\nu(C{=}S)$	$\nu(C{=}N)$	$\nu(N{-}N)$
1	H_3L^1	—	3295 s	3160 m	1219	886 m	1648 v.s	1108 m
2	$H_3L^1Co_2Cl_4(H_2O)_3$	3484 br	3286 m	3164 m	1211	880 m	1633 m	1115 m
3	$H_3L^1Ni_2Cl_4(H_2O)_3$	3380 br	3289 m	3166 m	1210	879 m	1624 m	1116m
4	$H_3L^1Co_2Br_4(H_2O)_3$	3463 br	3286 m	3164 m	1212	881 m	1628 m	1119 m
5	$H_3L^1Cu_2Cl_4\ H_2O$	3440 br	3282 m	3175 m	1232	883 v.w	1626 s	1118 m
6	H_2L^2	—	3276 s	3249 m 3150 w	1221	845 s	1605 s	1110 m
7	$H_2L^2CoCl_2(H_2O)$	3451 br	3270 m	3148 w 3199 w	1228	828 w	1600 sh	1157 m
8	$L_2Ni.Cl(H_2O)_2$	3450 br	—	3155 w	1234	837 m	1598 sh	1174 m
9	$[(L^2)_2Ni]H_2O$	3440 br	—	3172 w	1225	838 w	1597 sh	1140 m
10	$L^2FeCl_2(H_2O)$	3430 br	—	—	1220	835 m	1599 sh	1171 m

Table II. The assignments were made by comparison with the vibrational frequencies of the free ligand.

The most characteristic vibrational frequencies and their tentative assignments for the ligand H_3L^1, H_2L^2 and their transition metal complexes are listed in Table II. The assignments were made by comparison with the vibrational frequencies of the free ligand.

The IR data obtained for the ligand H_3L^1 showed that the ligand behaves as a neutral pentadentate (ONSNO) ligand coordinating through C—OH, C=N, and C=S groups. In these complexes, the mode of coordination was suggested by the following pieces of evidence: i) the band due to the hydroxyl group is shifted to lower wave number by 6–13 cm^{-1}, which is further supported by the shift in the stretching frequency of phenolic oxygen υ(C—O) in the complexes,[64] indicating the subsequent deprotonation of the phenolic proton prior to coordination. ii) The imines bands are shifted to lower wave number by 15–24 cm^{-1},[65,66] with iii) the negative shift and weakness of the band assigned to the thioketone group; iv) the shift of υN–N band to higher wave number by 7–11 cm^{-1}; v) the simultaneous appearance of new bands in the 345–384, 419–455, and 500–540 cm^{-1} regions due to the υ(M–S), υ(M—N), and υ(M—O) vibrations, respectively.[67,68]

On the other hand, the IR data obtained for the H_2L^2 ligand suggested that this ligand can behave as either of the following:

1) Mononegative tridentate ligand coordinating through the C—O, C=N, and C=S groups. In these complexes, the mode of coordination was suggested by the following pieces of evidence: (i) the disappearance of the band due to the hydroxyl oxygen, indicating the subsequent deprotonation of the phenolic proton prior to coordination[64]; ii) the shift of the two imine bands to lower wave number by 5–8 cm^{-1} with a decrease in their intensities[65,66]; iii) the band due to the thioketone group is weakened and shifted to lower wave number by 8–10 cm^{-1}; iv) the positive shift of υN–N band by 30–64 cm^{-1}; v) the simultaneous appearance of new bands in the 355–391, 420–447, and 477–519 cm^{-1} regions due to the υ(M–S), υ(M—N), and υ(M—O) vibrations, respectively.[67,68]
2) Neutral tridentate ligand coordinating via the C—OH, C=N, and C=S groups in complex **7**. In this complex, the mode of coordination was suggested by the following pieces of evidence: (i) the weakness and shift of υOH band to lower wave number by 6 cm^{-1}; ii) the red shift of the imine bands by 5 cm^{-1} with a weak appearance[65,66]; iii) the

Downloaded At: 16:45 27 January 2011

red shift of band due to the thioketone group by 17 cm^{-1} with a decrease in intensity; iv) the blue shift of the υN–N band by 47 cm^{-1}; v) the simultaneous appearance of new bands in the 370, 432, and 507 cm^{-1} regions attributable to the υ(M–S), υ(M—N), and υ(M—O) vibrations, respectively.[67,68]

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. The conductance data, reported in Table I, indicate that all the metal complexes have conductivity values in the range characteristics for the non-electrolytic nature of these complexes due to absence of counter ions in the proposed structures of these complexes.

Electronic Spectra and Magnetic Moments

Cobalt (II) complexes. The electronic spectrum of the cobalt(II) complex (**7**) gave three bands at 1092, 679, and 529 nm, which can be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν1) and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν3), respectively, whereas the spectra of complexes (**2**) and (**4**) showed the last two transitions at 1096–1165 and 602–672 nm, and the first transition is masked by the more intense charge transfer band, suggesting an octahedral[69–72] geometry around Co(II) ion. The magnetic moment of complex (**7**) is 4.72 B.M. in consistent with octahedral geometry,[73], while complexes (**2**) and (**4**) show magnetic moment values in the range 2.64–3.84 B.M., which is smaller than the calculated value for two Co(II) ions in octahedral geometries, and this may be due to antiferromagnetism between the two ion centers (Table S1, Supplemental Materials).

Downloaded At: 16:45 27 January 2011

Copper (II) complex. The UV-Vis spectra of the Cu complex $H_3L^1Cu_2.Cl_4.H_2O$ showed a single band at 632 nm, which indicates a normal distorted square pyramidal geometry at Cu(II).[74]

Nickel (II) complexes. The absorption spectral bands of nickel(II) complexes (**3**, **8**, **9**) 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 1198–1100, 894–877, and 620–578 nm, consistent with a typical Ni(II) in an octahedral environment.[70,71] The magnetic moment values for complexes **8** and **9** were found in the range 3.15–3.5 B.M.[70,71] expected for octahedral nickel complexes, but in the case of the complex (**3**), the value is 2.64 B.M., which indicates antiferromagnetism between the two Ni centers.

Iron (III) complex. The electronic spectra of Fe(III) complex showed broad bands at 766 and 527 nm. The former band may be due to the spin forbidden transition $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, which may gain intensity as a result of the vibronic mechanism in the octahedral field around ferric ion. The second band may be attributed to $^6A_1 \rightarrow {}^4T_1(G)$ transitions. In addition, a third absorption band with high intensity observed at 440 nm assigned for charge transfer transition. The magnetic moment of complex is 5.14 B.M.[75]

Catalytic Activity

The catalytic activity of complex $H_3L^1Cu_2Cl_4H_2O$ (**5**) in cyclopropanation reactions has been investigated. As a model reaction, we choose the cyclopropanation of α-methyl

Downloaded At: 16:45 27 January 2011

styrene by EDA (EDA = ethyl diazoacetate) (Scheme S3, Supplemental Materials). Catalytic reactions were run by adding the EDA to a stirred solution containing the olefin and the metal complex in dichloroethane under dinitrogen.

The copper complex $H_3L^1Cu_2.Cl_4.H_2O$ (**5**) exhibited an interesting catalytic capability toward the decomposition of ethyl diazoacetate and the subsequent transfer of the carbene moiety to the C=C double bond. To evaluate the catalytic activity of $H_3L^1Cu_2.Cl_4.H_2O$ (**5**), we used the complex as a catalyst in our model reaction. Conditions of the catalytic reaction were examined by varying the temperature and relative ratio of **5**/EDA/olefin. Results are summarized in Table S2 (Supplemental Materials).

The copper complex $H_3L^1Cu_2Cl_4H_2O$ (**5**) exhibited excellent catalytic capability toward the decomposition of ethyl diazoacetate, and the subsequent transfer of the carbene moiety to the C=C double bond.

According to the results (Table S2), it can be seen that $H_3L^1Cu_2Cl_4.H_2O$ (**5**) is a very active catalyst for cyclopropanation reactions. The catalyst was examined with 1:1.1, 1:2, and 1:5 ratios of EDA/olefin, and it was found that a large excess of the olefin is not required for the reaction to proceed: even if equimolar amounts of EDA and olefin were used, the cyclopropane products were obtained in reasonable yields (70–78%); the rest of the starting EDA is consumed to form the well-known coupling byproducts (maleate and fumarate) normally obtained in cyclopropanation reactions (Table S2). The temperature plays an important role in these reactions: the catalyst at room temperature is inactive (Table S2, entry 5), but as soon as the temperature is increased to 65°C it becomes active (Table S2, entry 6). Reaction times can be almost reduced to a half just by increasing the temperature at 75°C (Table S2, entry 7). After complete consumption of the starting EDA, the catalytic cycle can be restored just by addition of both reactants. In the second and third runs, we observed even shorter reactions times (see later in this section). The *cis:trans* ratio is not affected to a large extent by changing the conditions, and nearly equal amounts of both cyclopropanes have always been obtained. The best result in terms of cyclopropane yield (93% based on EDA) was obtained at 65°C at a 5/EDA/olefin ratio of 1:500:2500 (Table S2, entry 6). In contrast to the prolonged EDA addition time generally required to reduce the formation of coupling products in cyclopropanation, we found complex **5** to be very active: 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 converted EDA) in less than 100 min (TON 1000, Table S2, entry 9). The turnover number (TON) reached 12556 at a **5**/EDA/olefin ratio of 1:20000:40000 at 75°C; in this case we observed a 73% conversion based on converted EDA in just 5 h, 20 min (Table S2, entry 10). Although, the catalyst $H_3L^1Cu_2Cl_4.H_2O$ (**5**) has shown a very high selectivity (93%, Table S2, entry 6), it showed a low diastereoselectivity (*cis:trans* = 41:59, Table S2, entries 5 and 8).

To examine the generality of the complex $H_3L^1Cu_2Cl_4H_2O$ (**5**) as a cyclopropanation catalyst, several alkenes were employed to determine the substrate scope of the complex $H_3L^1Cu_2Cl_4H_2O$ (**5**). At a **5**/EDA/olefin ratio of 1:1000:2000 at 75°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 S3 (Supplemental Materials).

When styrene is employed as substrate, we observed a slight decrease in the quantitative conversion of the starting EDA to what was observed in the case of α-methyl styrene with an increase of the conversion rate. However, in this case, the diastereoselectivity is improved (*cis:trans* = 29:71, compare entry 1, Table S3 and entry 4, Table S2). Slightly better yields in cyclopropane products, although with slightly longer reaction times, are obtained when electron-donating substituents are present in the para position of the aromatic ring (entry 2, Table S3). If 4-chloro-α-methylstyrene is employed as substrate, the catalytic rate increases with a slight decrease in the yield (entry 3, Table S3). It can be seen that in the absence of an α substituent on the styrene derivative, the formation of the trans cyclopropane is slightly favored. Steric hindrance at the α position does not hamper the reaction, and good yields are obtained even with 1,1-diphenyl ethylene (entry 4, Table S3). On the other hand, steric hindrance at the β-position of the styrene greatly affected the reactivity. In case of cis-stilbene a dramatic drop in the cyclopropanation products was observed (entry 6, Table S3).

Even aliphatic double bonds that are generally less reactive towards cyclopropanation gave excellent results. Though the time of the cyclopropanation reaction for these substrates increased slightly if compared to what is observed for styrenic derivatives, very good yields were always obtained (entries 8–11, Table S3). Even in these cases, *trans* cyclopropane compounds are obtained as major products, and a remarkable diastereoselectivity (*trans:cis* = 10.1) has been observed in the case of cyclohexene (entry 9, Table S3). With 2,5-dimethyl-2,4-hexadiene, an important precursor to chrysanthemic acid,[76] the catalytic reaction yielded the desired cyclopropanes in very good yields (84%) and with reasonable diastereoselectivities (entry 10, Table S3), without the need of a large excess of the olefin.

Downloaded At: 16:45 27 January 2011

Copper(I) complexes 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. 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. 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.[77] A detailed mechanistic study of the cyclopropanation reaction catalyzed by complex $H_3L^1Cu_2Cl_4H_2O$ (**5**) has not been undertaken yet due to the very high reactivity of this complex; any attempt to isolate it 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 to monitor the disappearance of the band due to the stretching of the N_2 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 increasing 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. 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 color of the solution, due to the dissolved copper complex, changed from green (due to copper(II) complex) to light yellow. The time needed for the change in color 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. All this data, together with the data reported in literature,[78] suggest that the catalyst is activated during the induction period and that the initial reduction of copper(II) to copper(I) is necessary for the catalysis to take place.

Usually, good catalysts give TON around 400,[79–92] and excellent ones give TON around 10.000.[61,93–102] If we compare our catalyst activity to some other catalysts reported in literature, we will find that our catalyst lies in the range reported for catalysts with excellent TON (up to 12556).

CONCLUSIONS

Two new tridentate and pentadentate Schiff base ligands [H_3L^1] and [H_2L^2] containing the ONS and ON-ONS donor set and their corresponding Co^{II}, Cu^{II}, Ni^{II}, and Fe^{III} complexes have been synthesized and spectrally characterized. The study revealed octahedral geometry around Ni(II), Co(II), and Fe(III) complexes. However, distorted square pyramidal geometry is suggested for copper ion in the binuclear Cu(II) complex. In all H_2L^2 complexes, the ligand acts either as monobasic, neutral, or tridentate ligand coordinating through ONS coordination sites. Olefins cyclopropanation reactions by ethyldiazoacetate (EDA) in the presence of $H_3L^1Cu_2Cl_3.H_2O$ as catalyst proceed with excellent TON (up to 12556).

EXPERIMENTAL

Materials

All the reagents employed for the preparation of the ligand and its complexes were of analytical grade and used without further purification. Unless otherwise stated, all catalytic tests were carried out under an atmosphere of purified dinitrogen using modified Schlenk techniques. Solvents employed were dried and distilled before use by standard methods.[103] Benzene, cyclohexene, and 1-octene were distilled over sodium; styrene and α-methyl styrene were distilled over calcium hydride and stored under dinitrogen.

Physical Measurements

The ligands and their metal complexes were analyzed for C, H, N, and M contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. Analytical and physical data of the ligand H_3L^1, H_2L^2 and their metal complexes are reported in Table I. The metal ion contents of the complexes were also determined[104–106] by the previously reported methods.[107,108] 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 ^{13}C NMR spectra were obtained on Bruker Avance 300-DRX or Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. The mass spectra were run at 70 eV with HP Model MS 5988A and/or GCMS Cap 1000 EX SHIMADZU spectrometer using Electron Impact Technique. 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: $\Lambda = V \times K \times Mw/g \times \Omega$, where Λ, molar conductivity ($ohm^{-1}\ cm^2\ mol^{-1}$); 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 a calibrant. Mass spectra of the solid ligand were recorded using a JEUL JMS-AX-500 mass spectrometer.

Downloaded At: 16:45 27 January 2011

Downloaded At: 16:45 27 January 2011

Synthesis of the Schiff Base Ligands

Synthesis of the Schiff base ligand H_3L^1. The solid hydrazinecarbothioamide (0.194 g, 2.13 mmol) was added to a hot solution (75°C) containing 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde (chromone) (0.500 g, 2.13 mmol) in ethanol (60 mL). A few drops of acetic acid were added to the reaction mixture, which was then refluxed for 10 h. The reaction was then followed by TLC using ethylacetate/n-hexane as an eluent until the disappearance of the chromone spot. A hot (75°C) solution of chromone (0.500 g, 2.13 mmol) in methanol (60 mL) was then added to the reaction mixture and refluxed for a further 85 h. The reaction mixture was then again followed by TLC (same condition) until the disappearance of the spot of chromone. The reaction is very sensitive to temperature (maximum 80°C) and also to the quantity of acetic acid (adjust the pH to 5.5), as exceeding these conditions leads to the formation of undesired product. The mixture was then concentrated to 25 mL, and the yellow product was then filtered off, washed with cold methanol, recrystallized from ethanol, and dried under vacuum over anhydrous $CaCl_2$ (65% yield). ^1H NMR (300 MHz, DMSO): $\delta = 11.95$ and 11.50 [s, broad, H(45) and H(46)], 10.60 [s, broad, H(40)], 10.26 and 8.59 [S, 2H, H(22) and H(39)], 6.79 [d, 2H, H(42), H(43)], 6.08 and 6.03 [S, 2H, H(41), H(44)], 3.93 and 3.80 [S, 6H, $-OCH_3(20)$ and $-OCH_3(37)$], 2.31 [d, 6H, $CH_3(19)$ and $CH_3(36)$]. ^{13}C NMR (300 MHz, DMSO, 300 K): C(3) 175.39, C(21) and C(38) 142.70 and 142.76, C(15) and C(32) 111.32 and 111.47, C(6) and C(23) 100.62 and 100.70, C(20) and C(37) 63.52 and 64.70, C(19) and C(36) 19.69 and 19.73. (See Scheme 1 and Figure S for numbering.)

Synthesis of the Schiff base ligand H_2L^2. A few drops of glacial acetic acid were added to a hot solution (75°C) of 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde (1.00 g, 4.27 mmol) in ethanol (25 mL). The reaction mixture was then added to a hot solution (75°C) of N(4)-phenylthiosemicarbazide (0.714 g, 4.27 mmol) in dioxane (10 mL). The reaction mixture was refluxed for 15 h. After cooling, water was added, and a yellow precipitate started to form which was filtered off, and washed with water and then with ethanol. The product was recrystallized from ethanol and dried under vacuum over anhydrous $CaCl_2$ (75% yield). ^1H NMR (300 MHz, DMSO): $\delta = 11.86$ [s, 1H, H(30)], 10.19 [s, 1H, H(29)], 8.68 [S, 1H, H(28)], 7.53 [d, 2H, J = 7.6, H(32) and H(22)], 7.38 [t, 2H, J = 7.6, H(33) and H(35)], 7.21 [t, 1H, J = 7.6, H(34)], 6.80 [S, 1H, H(37)], 6.04 [S, 1H, H(38)], 3.83 [S, 3H, $-OCH_3(26)$], 2.30 [S, 3H, $-CH_3(25)$]. ^{13}C NMR (300 MHz, DMSO, 300 K): C(14) 175.41, C(27) 142.03, C(20) 125.67, C(5) 111.35, C(26) 63.58, C(21) and C(19) 128.83, C(22) and C(32) 125.27, C(7) 100.77 and C(25) 19.75. (See Scheme 2; Figure S2 for numbering.)

Synthesis of the metal complexes. The metal complexes of the ligands were prepared by mixing a hot methanolic solution of the metal salt with the required amount of a hot ethanolic solution of the ligand to form 1:1, 1:2, or 2:1 M/L (metal/ligand) complexes, as shown in Table III. The reaction mixture was then refluxed for a time depending on the transition metal salt used. The precipitates formed were filtered off, washed with ethanol then with diethyl ether, and dried under vacuum over anhydrous $CaCl_2$.

Typical Procedure for the Catalytic Cyclopropanation of Olefins by $H_3L^1Cu_2Cl_4H_2O$ (5)

EDA (see caption of Tables S2 and S3 for quantities) was added to a suspension of $H_3L^1Cu_2Cl_4$ H_2O (**5**) (5.0 mg, 1.15×10^{-2} mmol) and the olefin (see caption of Tables S2

Table III Amounts of the reactants used in the formation of the metal complexes

			Metal chloride, or bromide in 10–20 mL methanol		ligand in 10–25 mL ethanol	
No.	Ligand/Complexes	Metal salt used	Mass(g) × 10^{-3}	mmol × 10^{-3}	Mass(g) × 10^{-3}	mmol × 10^{-3}
1	H_3L^1					
2	$H_3L^1Co_2Cl_4(H_2O)_3$	$CoCl_2.6H_2O$	195	821	215	411
3	$H_3L^1Ni_2Cl_4(H_2O)_3$	$NiCl_2$ $6H_2O$	199	840	220	420
4	$H_3L^1Co_2Br_4(H_2O)_3$	$CoBr_2$ $6H_2O$	266	936	245	468
5	$H_3L^1Cu_2Cl_4$ (H_2O)	$CuCl_2$	190	1417	371	709
6	H_2L^2					
7	$H_2L^2CoCl_2(H_2O)$	$CoCl_2.6H_2O$	149	626	240	626
8	$L_2Ni.Cl(H_2O)_2$	$NiCl_2$ $6H_2O$	186	783	300	783
9	$[(L^2)_2Ni].H_2O$	$NiCl_2$ $6H_2O$	87	365	280	731
10	$L^2FeCl_2(H_2O)$	$FeCl_3.6H_2O$	211	783	300	783

and Tables S3 for quantities) in dichloroethane (10 mL). The resulting pale green solution was heated at the required temperature under stirring; depending on the olefin used and its concentration, after a few minutes, the solution turned to colorless and dinitrogen started to evolve from the system. The reaction was followed until total consumption of the EDA (IR absorbance, $\nu_{\max} = 2114$ cm^{-1}, < 0.025) was observed. The final solution was analyzed by GC-MS after the addition of 2,4-dinitrotoluene as an internal standard.

REFERENCES

1. M. Samir, El-Medani, A. M. A. Omyana, and R. N. Ramaden, *J. Mol. Struct.*, **738,** 171 (2005).
2. J. Colman and L. S. Hegedu, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, California, 1980).
3. J. Zhan, B. Zhan, J. Liu, W. J. Xu, and Z. Wang, *Spectrochim. Acta, Part A*, **57,** 149 (2001).
4. W. Liu, Y. Zou, Y. Li, Y. Yao, and Q. J. Meng, *Polyhedron*, **23,** 849 (2004).
5. R. Abu-Eittah, A. Osman, and G. Arafa, *J. Inorg. Nucl. Chem.*, **41,** 555 (1979).
6. G. Contreras and R. Schmidt, *J. Inorg. Nucl. Chem.*, **32,** 1295 (1970).
7. B. Beecroft, M. J. M. Campbell, and R. Grzeskowiak, *J. Inorg. Nucl. Chem.*, **36,** 55 (1974).
8. L. El-Sayed, M. F. Iskander, and A. El-Toukhy, *J. Inorg. Nucl. Chem.*, **36,** 1739 (1974).
9. M. J. M. Campbell, *Coord. Chem. Rev.*, **15,** 279 (1975).
10. M. C. Jain, A. K. Srivastava, and P. C. Jain, *Inorg. Chim. Acta*, **23,** 199 (1977).
11. M. Akbar Ali and S. G. Teoh, *J. Inorg. Nucl. Chem.*, **40,** 2013 (1978).
12. K. Ballschmiter, H. Greber, and H.-G. Steinhäuser, *J. Inorg. Nucl. Chem.*, **40,** 631 (1978).
13. J. C. J. Bart, I. W. Bassi, M. Calcaterra, and M. Pieroni, *Inorg. Chim. Acta*, **28,** 201 (1978).
14. N. C. Mishra, B. B. Mohapatra, and S. Guru, *J. Inorg. Nucl. Chem.*, **41,** 408 (1979).
15. G. Atassi, P. Dumont, and J. C. E. Harteel, *Eur. J. Cancer*, **15,** 451 (1979).
16. S. Chandra, K. B. Pandeya, and R. P. Singh, *J. Inorg. Nucl. Chem.*, **42,** 1075 (1980).
17. S. P. Mital, R. V. Singh, and J. P. Tandon, *J. Inorg. Nucl. Chem.*, **43,** 3187 (1981).
18. Y. K. Bhoon, *Polyhedron*, **2,** 365 (1983).
19. K. Weller, G. Horn, and T. X. Gian, *J. Electroanal. Chem.*, **156,** 173 (1983).
20. B. Thimme Gowda and D. S. Mahadevappa, *Microchem. J.*, **28,** 374 (1983).
21. A. Gallardo Cespedes, D. Perez Bendito, and M. Valcarcel, *Microchem. J.*, **30,** 105 (1984).
22. S. Chandra and R. Singh, *Spectrochim. Acta, Part A*, **41,** 1109 (1985).
23. S. S. Djbbar, B. O. Benali, and J. P. Deloume, *Polyhedron*, **16,** 2175 (1997).

Downloaded At: 16:45 27 January 2011

24. P. Bhattacharyya, J. Parr, and A. T. Ross, *J. Chem. Soc., Dalton Trans.*, 3149 (1998).
25. J. C. Wu, N. Tang, W. S. Liu, M. Y. Tan, and A. C. S. Chan, *Chin. Chem. Lett.*, **12,** 757 (2001).
26. L. He, S. H. Gou, and O. F. Shi, *J. Chem. Crystallogr.*, **29,** 207 (1999).
27. E. Pereira, L. R. Gomes, J. N. Low, and B. de Castro, *Polyhedron*, **27,** 335 (2008).
28. M. K. Koley, S. C. Sivasubramanian, B. Varghese, P. T. Manoharan, and A. P. Koley, *Inorg. Chim. Acta*, **361,** 1485 (2008).
29. M. A. Ali, H. J. H. Abu Bakar, A. H. Mirza, S. J. Smith, L. R. Gahan, and P. V. Bernhardt, *Polyhedron*, **27,** 71 (2008).
30. L. T. YildIrIm, R. Kurtaran, H. Namli, A. D. Azaz, and O. Atakol, *Polyhedron*, **26,** 4187 (2007).
31. K. P. Balasubramanian, R. Karvembu, R. Prabhakaran, V. Chinnusamy, and K. Natarajan, *Spectrochim. Acta, Part A*, **68,** 50 (2007).
32. M. Wang, L. F. Wang, Y. Z. Li, Q. X. Li, Z. D. Xu, and D. Q. Qu, *Trans. Met. Chem.*, **26,** 307 (2001).
33. N. N. Gulerman, S. Rollas, H. Erdeniz, and M. Kiraj, *J. Pharm. Sci.*, **26,** 1 (2001).
34. P. Tarasconi, S. Capacchi, G. Pelosi, M. Corina, R. Albertini, A. Bonati, P. P. Dall'Aglio, P. Lunghi, and S. Pinelli, *Bioorg. Med. Chem.*, **8,** 154 (2000).
35. J. Charo, J. A. Lindencrona, L. M. Carlson, J. Hinkula, and R. Kiessling, *J. Virol.*, **78,** 1132 (2004).
36. V. Mishra, S. N. Pandeya, and S. Anathan, *Acta Pharm. Turc.*, **42,** 139 (2000).
37. A. J. Atkins, D. Black, A. J. Blake, A. Marin-Bocerra, S. Parsons, L. Ruiz-Ramirez, and M. Schröder, *Chem. Commun.*, 457 (1996).
38. M. Sakamoto, K. Maneski, and H. Okawa, *Coord. Chem. Rev.*, **379,** 219 (2001).
39. M. Kanthimathi, A. Dhathathreyan, and B. U. Nair, *Chem. Phys. Lett.*, **324,** 43 (2000).
40. H. Zhang, Y. Zhang, and C. Li, *J. Catal.*, **238,** 369 (2006).
41. B. Bahramian, V. Mirkhani, M. Moghadam, and S. Tangestaninejad, *Appl. Catal. A*, **301,** 169 (2006).
42. J. Wen, J. Zhao, X. Wang, J. Dong, and T. You, *J. Mol. Catal. A: Chem.*, **245,** 242 (2006).
43. P. A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, **248,** 1717 (2004).
44. H. Lebel, J.-F. Marcoux, C. Molinaro, and A. B. Charette, *Chem. Rev.*, **103,** 977 (2003).
45. H. M. L. Davies and E. Antoulinakis, *Org. React.*, **57,** 1 (2001).
46. M. P. Doyle and D. C. Forbes, *Chem. Rev.*, **98,** 911 (1998).
47. H. Fritschi, U. Leutenegger, and A. Pfaltz, *Angew. Chem., Int. Ed. Engl.*, **25,** 1005 (1986).
48. D. A. Evans, K. A. Woerpel, M. M. Hinman, and M. M. Faul, *J. Am. Chem. Soc.*, **113,** 726 (1991).
49. M. M.-C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, **120,** 10270 (1998).
50. J. L. Maxwell, S. O'Malley, K. C. Brown, and T. Kodadek, *Organometallics*, **11,** 645 (1992).
51. M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen, and R. Ghosh, *J. Am. Chem. Soc.*, **115,** 9968 (1993).
52. H. M. L. Davies, P. R. Bruzinski, D. H. Lake, N. Kong, and M. J. Fall, *J. Am. Chem. Soc.*, **118,** 6897 (1996).
53. H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, and K. Itoh, *J. Am. Chem. Soc.*, **116,** 2223 (1994).
54. C. M. Che, J.-S. Huang, F.-W. Lee, Y. Li, T.-S. Lai, H.-L. Kwong, P.-F. Teng, W.-S. Lee, W.-C. Lo, S.-M. Peng, and Z.-Y. Zhou, *J. Am. Chem. Soc.*, **123,** 4119 (2001).
55. A. G. H. Wee, *Curr. Org. Synth.*, **3,** 499 (2006).
56. G. Maas, *Chem. Soc. Rev.*, **33,** 183 (2004).
57. J. Pietruszka, *Chem. Rev.*, **103,** 1051 (2003).
58. L. A. Wessjohann, W. Brandt, and T. Thiemann, *Chem. Rev.*, **103,** 1625 (2003).
59. W. A. Donaldson, *Tetrahedron*, **57,** 8589 (2001).
60. J. Salaun, *Chem. Rev.*, **89,** 1247 (1989).
61. N. S. Youssef, E. El-Zahany, A. M. A. El-Seidy, A. Caselli, S. Fantauzzi, and S. Cenini, *Inorg. Chim. Acta*, **362**, 2006 (2009).

Downloaded At: 16:45 27 January 2011

62. H. Lebel, J. F. Marcoux, C. Molinaro, and A. B. Charette, *Chem. Rev.*, **103,** 977 (2003).
63. H. Pellissier, *Tetrahedron*, **64,** 7041 (2008).
64. K. Naresh Kumar and R. Ramesh, *Polyhedron*, **24,** 1885 (2005).
65. R. Ramesh and S. Maheswaran, *J. Inorg. Biochem.*, **96,** 457 (2003).
66. S. N. Pal and S. Pal, *J. Chem. Soc., Dalton Trans.*, 2102 (2002).
67. S. Chandra and U. Kumar, *Spectrochim. Acta, Part A*, **61,** 219 (2005).
68. K. Nakamato, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley Interscience, New York, 1971).
69. K. Singh, M.S. Barwa, and P. Tyagi, *Eur. J. Med. Chem.*, **41,** 147 (2006).
70. M. Shakir, Y. Azim, H. T. N. Chishti, and S. Parveen, *Spectrochim. Acta, Part A*, **65,** 490 (2006).
71. K. G. Kumar and K. Saji John, *React. Funct. Polym.*, **66,** 1427 (2006).
72. G. G. Mohamed and Z. H. A. El-Wahab, *Spectrochim. Acta, Part A*, **61,** 1059 (2005).
73. N. Mondal, D. K. Dey, S. Mitra, and K. M. A. Malik, *Polyhedron*, **19,** 2707 (2000).
74. X. Wang, J. Ding, and J. J. Vittal, *Inorg. Chim. Acta*, **359,** 3481 (2006).
75. K. S. Abou-Melha, *Spectrochim. Acta, Part A*, **70,** 162 (2008).
76. M. Itagaki and K. Suenobu, *Org. Process Res. Dev.*, **11**(3), 509 (2007).
77. J. M. Fraile, J. I. Garcia, V. Martinez-Merino, J. A. Mayoral, and L. Salvatella, *J. Am. Chem. Soc.*, **123,** 7616 (2001).
78. R. L. Safiullin, V. A. Dokichev, L. R. Yakupova, R. M. Sultanova, S. L. Khurasan, R. N. Zaripov, and Yu. V. Tomilov, *Kinet. Catal.*, **49,** 43 (2008).
79. S. Shylesh, C. Srilakshmi, A. P. Singh, and B. G. Anderson, *Micropor. Mesopor. Mat.*, **108**(1–3), 29 (2008).
80. C. N. Kato and W. Mori, *C.R. Chim.*, **10,** 284 (2007).
81. M. Bagherzadeh, L. Tahsini, and R. Latifi, *Catal. Commun.*, **9,** 1600 (2008).
82. J. M. Crosthwaite, V. A. Farmer, J. P. Hallett, and T. Welton, *J. Mol. Catal. A: Chem.*, **279,** 148 (2008).
83. K. Kervinen, H. Korpi, M. Leskelä, and T. Repo, *J. Mol. Catal. A: Chem.*, **203,** 9 (2003).
84. M. Klahn, C. Fischer, A. Spannenberg, U. Rosenthal, and I. Krossing, *Tetrahedron Lett.*, **48,** 8900 (2007).
85. M. V. Kirillova, J. A. L. da Silva, J. J. R. Fraôsto da Silva, and A. J. L. Pombeiro, *Appl. Catal., A*, **332,** 159 (2007).
86. T. M. Suzuki, T. Nakamura, K. Fukumoto, M. Yamamoto, Y. Akimoto, and K. Yano, *J. Mol. Catal. A: Chem.*, **280,** 224 (2008).
87. J. Hájek, M. Dams, C. Detrembleur, R. Jérôme, P. A. Jacobs, and D. E. De Vos, *Catal. Commun.*, **8,** 1047 (2007).
88. P. Roy, K. Dhara, M. Manassero, and P. Banerjee, *Inorg. Chem. Commun.*, **11,** 265 (2008).
89. D. Zois, C. Vartzouma, Y. Deligiannakis, N. Hadjiliadis, L. Casella, E. Monzani, and M. Louloudi, *J. Mol. Catal. A: Chem.*, **261,** 306 (2007).
90. G. Budroni, A. Corma, H. García, and A. Primo, *J. Catal.*, **251,** 345 (2007).
91. D. Chatterjee, *Coord. Chem. Rev.*, **252,** 176 (2008).
92. C.-T. Yeung, H.-L. Yeung, C.-S. Tsang, W.-Y. Wong, and H.-L. Kwong, *Chem. Commun.*, 5203 (2007).
93. H. Nakagawa, Y. Sei, K. Yamaguchi, T. Nagano, and T. Higuchi, *J. Mol. Catal. A: Chem.*, **219,** 221 (2004).
94. V. Dragutan, I. Dragutan, L. Delaude, and A. Demonceau, *Coord. Chem. Rev.*, **251,** 765 (2007).
95. D. J. Darensbourg, E. B. Frantz, and J. R. Andreatta, *Inorg. Chim. Acta*, **360,** 523 (2007).
96. W. Chen, C. Xi, and Y. Wu, *J. Organomet. Chem.*, **692,** 4381 (2007).
97. H.-U. Blaser, B. Pugin, and F. Spindler, *J. Mol. Catal. A: Chem.*, **231,** 1 (2005).
98. P.-F. Teng, T.-S. Lai, H.-L. Kwong, and C.-M. Che, *Tetrahedron: Asymmetry*, **14,** 837 (2003).
99. K. A. Chatziapostolou, K. A. Vallianatou, A. Grigoropoulos, C. P. Raptopoulou, A. Terzis, I. D. Kostas, P. Kyritsis, and G. Pneumatikakis, *J. Organomet. Chem.*, **692,** 4129 (2007).

Downloaded At: 16:45 27 January 2011

100. M. K. Tse, H. Jiao, G. Anilkumar, B. Bitterlich, F. G. Gelalcha, and M. Beller, *J. Organomet. Chem.*, **691,** 4419 (2006).
101. A. Fihri, P. Meunier, and J.-C. Hierso, *Coord. Chem. Rev.*, **251,** 2017 (2007).
102. V. Dragutan, I. Dragutan, L. Delaude, and A. Demonceau, *Coord. Chem. Rev.*, **251,** 765 (2007).
103. D. D. Perrin, W. L. F. Armarego, And D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed. (Pergamon, Oxford, UK, 1980).
104. F. J. Welcher, *The Analytical Use of EDTA* (Van Nostrand, USA, 1958).
105. A. I. A. Vogel, *Text Book of Quantitative Inorganic Analysis*, 4th ed. (Longmans, London, 1978).
106. Z. Holzbecher, L. Divis, M. Kral, L. Sucha, and F. Lecil, *Handbook of Organic Reagents in Inorganic Analysis* (John Wiley, New York, 1976).
107. A. M. G. McDonald and P. Sirichanya, *Microchem. J.*, **14,** 199 (1969).
108. N. S. Youssef, *Synth. React. Inorg. Met.-Org. Chem.*, **30,** 225 (2000).

Downloaded At: 16:45 27 January 2011