Olefin-copper(I) complexes and their properties

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The synthesis, structure and the novel chemical and physical properties of olefin-copper(I) complexes are the focus of this review. Particular emphasis is placed on the molecular assembly of these compounds and their potential applications as homogeneous catalysts in solution and as solids possessing unusual physical functional properties.

KEY WORDS: olefin-copper(I) complexes; catalysis; chemical reactivates; optoelectronics; physical functional properties.

1. Introduction

Olefin-copper(I) complexes are known to play an important role in biochemistry and modern organometallic chemistry and employed as active species in homogeneous catalysis or resting state in copper-catalyzed chemical reactions. At the beginning of the 20th century, it was shown that olefins reacted with cuprous salts in solution or the solid state. Manchot and Brandt [1] found that ethylene reacts with cuprous chloride to form an unstable compound which may be regarded as the first olefin-copper(I) complex. Since then many olefin-copper(I) complexes have been studied [2]. However their structures were unknown until a report of a cuprous chloride-1,5-cyclocatadine (COD) complex by van Den Hende and Baird [3]. The pioneering work of Thompson and co-workers demonstrated the first stable copper(I)-olefin complexes in 1983 [4]. In the following years the area has experienced a rapid development, and this has led to the synthesis and structural characterization of a large number of olefin-copper(I) complexes. The published crystal structures of olefin-copper(I) complexes via years are shown in figure 1.

Olefin-copper(I) complexes have attracted considerable attention[5]. Interest in the area has not been restricted to basic research on the nature of the bonding between copper(I) and olefin but also to the potential applications of these species. The air-stable olefin-copper(I) complexes have shown their usefulness with its chemical properties (such as asymmetric cyclopropanation or aziridination, the sensitization of olefin in photoreactions including rearrangement, cycloaddtion, and molecular fragmentation, copper(I) promoted conjugate addition reactions of α,β-unsaturated carbonyl compounds, separation of olefins via the formation of olefin-copper(I) complexes) and physical properties (such as fluorescence, ferroelectric behaviour, chiral separation and models for the active sites of ethylene in biological systems).

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In this review, the synthesis and structures of complexes of copper(I) salts with ethylene and its derivatives are presented. In particular emphasis is placed on the role of olefin-copper(I) complexes in homogeneous catalysis reactions and its opto-electronics physical functions.

2. Synthesis of olefin-copper(I) complexes

Olefin-copper(I) complexes can be prepared by using a variety of techniques including traditional solution reactions, solvothermal. synthesis and electrochemical methods.

2.1. Solution method

In general, the reactions involving heating and stirring of solutions are carried out under an atmosphere of purified nitrogen in order to prevent oxidation of the Cu(I). Crystallization is generally achieved using solvent diffusion techniques or evaporation of solvent under normal or reduced pressure. [6, 7] Munakata group used biL (biL = the derivatives of 2,2′-bipyridine and 1,10-phenanthroline (phen); olefin = ethylene and derivatives) and Cu(CH$_3$CN)$_4$ClO$_4$ to afford twenty-five new olefin-copper(I) complexes using solution method. One of example is shown in equation (1).

2.2. Solvothermal method

(1) Typically, the solvent, olefin ligand and copper(I) salt are placed in a thick Pyrex tube (typically 20 cm long), frozen using liquid nitrogen and then flame sealed under vacuum. The tube is then heated in an oven for a period up to several days. Crystals isolated from the solution are then washed and dried. The use of the sealed tube aids in the prevention of oxidation of the Cu(I). Xiong et al. synthesized a number of highly stable olefin-copper (I) coordination polymers [8] by this method. For example, they have studied the reactions of triallyl-1,3,5-triazine-2,4,6(1H,3H,SH)-trione (TTT) with CuBr at different temperatures and afforded two
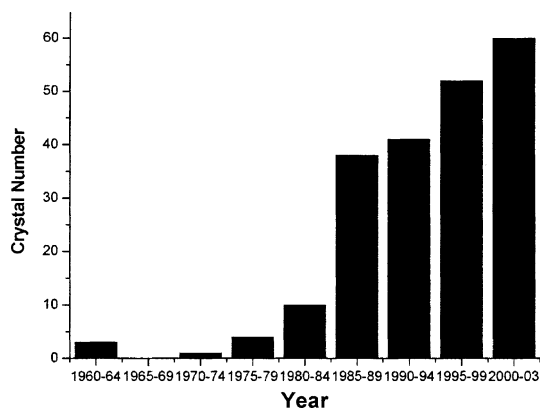
Figure 1. Numbers of crystal structures of olefin-copper(I) complexes via years (taken from CCDC).
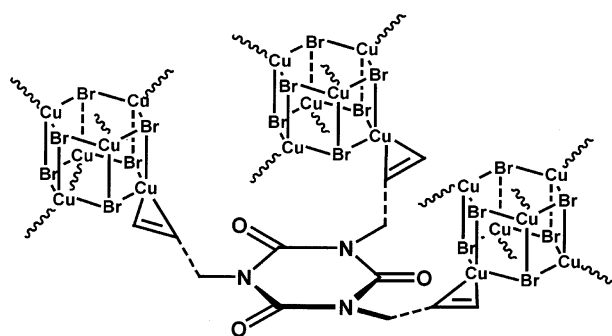
Figure 3. An asymmetry unit of the complex $[Cu_6Br_6(TTT)_2]_n$.

$$(1)$$

$$(2)$$
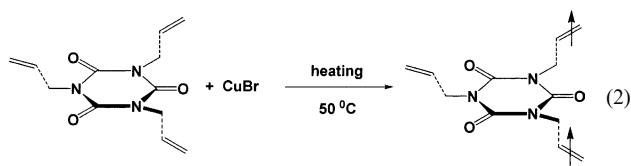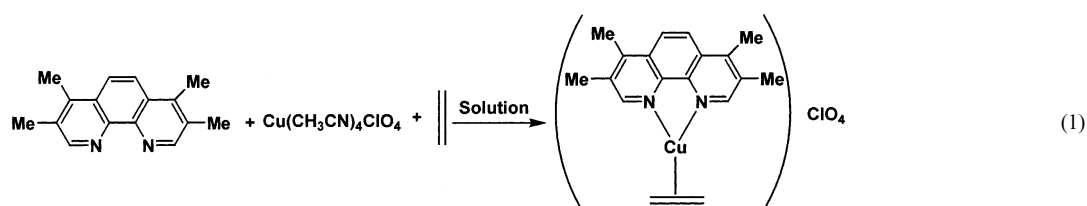
olefin-copper(I) complex $[Cu_4Br_4(TTT)_2]_n$ (equation (2), figure 2 and $[Cu_6Br_6(TTT)_2]_n$ (equation (3), figure 3) [9], which have some electrochemical properties (figures 4 and 5) and perhaps many novel properties such as

gas-storage capabilities as well as exhibiting magnetic and catalytic properties.

(2) Olefin ligand, copper(II) salt and solution are placed in a Teflon-lined autoclave (Parr bomb), sealed, and placed in a furnace for several days. After cooling,
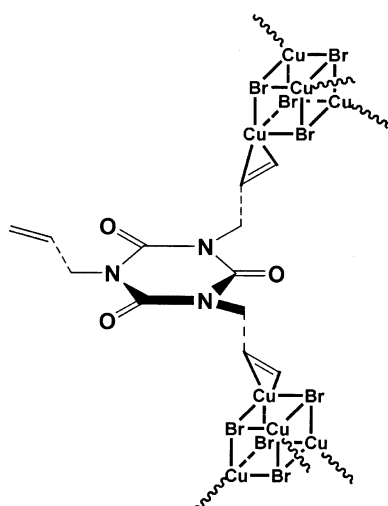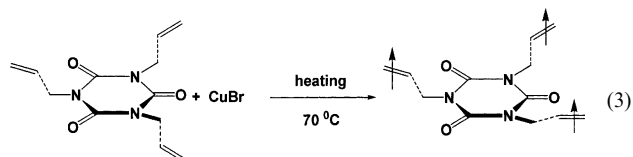

$$(3)$$

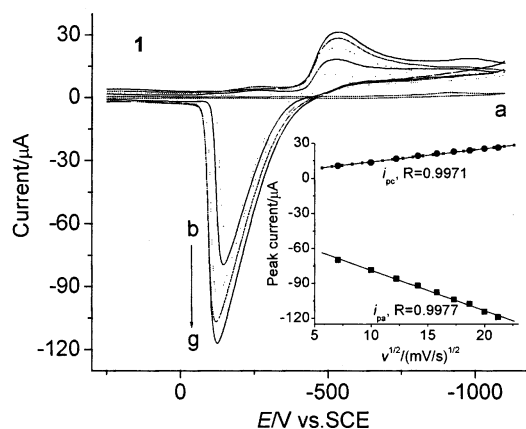Figure 2. An asymmetry unit of the complex $[Cu_4Br_4(TTT)_2]_n$.

Figure 4. Cyclic voltammagrams of 1.0 mm TTT in 0.1 m Bu_4NClO_4 solution (CH_3CN) at 150 mV s^{-1} of 1.0 mm of $[Cu_4Br_4(TTT)_2]_n$ in 0.1 m Bu_4NClO_4 solution (CH_3CN) at 50, 150, 250, 350, and 450 mV s^{-1} (from b to g) at a platinum disc working electrode. Insert: plots of anodic and cathodic peak currents versus v$^{1/2}$.

Figure 5. Cyclic voltammagrams of 1.0 mm TTT in 0.1 m Bu_4NClO_4 solution (CH_3CN) at 150 mV s^{-1} of 0.5 mm of $[Cu_6Br_6(TTT)_2]_n$ in 0.1 m Bu_4NCLO_4 solution (CH_3CN) at 50, 150, 250, 350, and 450 mV s^{-1} (from b to g) at a platinum disc working electrode. Insert: plots of anodic and cathodic peak currents versus v$^{1/2}$.

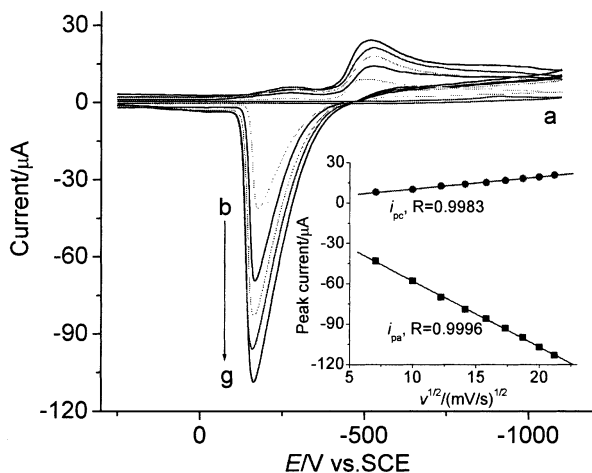the crystals were isolated from a clear solution, washed with distilled water, and air-dried. Schultz group [10] used $Cu(CH_3CO_2)_2 \cdot H_2O$ and fumaric acid (*trans*-$HO_2CCHCHCO_2H$) in a 1:2 ratio in 7 mL of distilled water to afford a olefin-copper(I) complex Cu_2(*trans*-$O_2CCHCHCO_2$) (equation (4)). This is the first olefin-copper(I) complex which was synthesized by the solovthermal method.

2.3. Electrochemical method

In this method a solution of the olefin ligand and copper(II) salt are placed into a small test-tube along with copper-wire electrodes. After applying an alternating current (frequency 50 Hz) or a direct current at a potential between −0.3 V and ~0.3 V for several days, colorless crystals of the desired compounds appear on the copper electrodes. Electrochemical method have

been used by Olijnik, Mys'kiv etc. to afford a number of olefin-copper(I) complexes. [11–13] Goreshnik group used $CuBr_2$ or $CuCl_2 \cdot 2H_2O$ of and 1-allyl-4-aminopyridium bromide in ethanol solution to afford olefin-copper(I) complexes under alternating-current electrochemical synthesis (equation (5)).

An alternative synthesis can be performed using a photochemical method, in which a sealed tube, prepared as described in 2.2 is irradiated with UV light at room temperature until the solution turns red. The tube is then heated in an oven for several days to give crystals, which are different from those prepared by the direct solvothermal synthesis. The products prepared by this method display dimeric structures, rather than polymeric structures, quite different from those prepared by the solvothermal reaction [8–10]. Three dimeric olefin-copper(I) complexes [14] (equation(6)), $[(2-H_2PYA)_2-Cu^+{}_2Cl_4]$ (figure 6), $[(3-H_2PYA)_2Cu^+{}_2Cl_4]$ (figure 7) and $[(4-H_2PYA)_2Cu^+{}_2Cl_4]$ (figure 8) under photochemical method were obtained by Xiong and co-workers by reactions of 2-, 3-, and 4-pyridylacrylic acid (*n*-H_2PYA) with CuCl. Some electrochemical properties of those complexes are shown in figure 9.

Some of the new crystal structures are list in table 1.

3. Crystal structures and bonding of olefin-copper complexes

The properties and the classification of olefin-copper complexes are dependent on their structures and bonding in the complexes.

3.1. General structural types

The structural types of olefin-copper(I) complexes have been examined by single crystal X-ray diffraction. Often the local coordination environment of the Cu(I) ions within the complexes can best be described as a

(4)

(5)

(6)
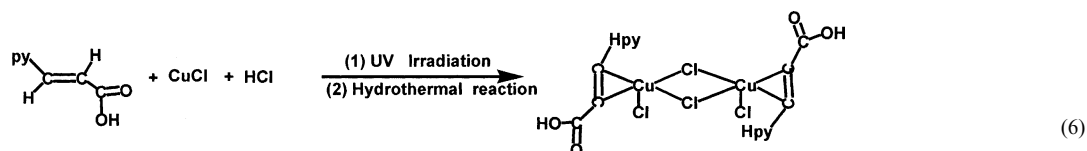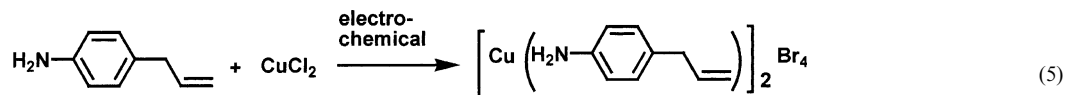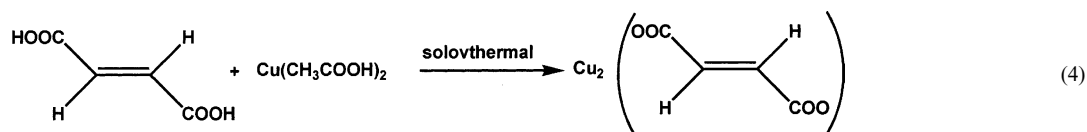
py = 2-pyridyl, 3-pyridyl and 4-pyridyl
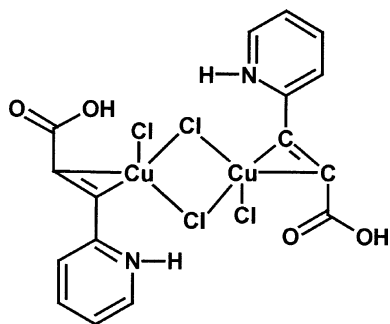
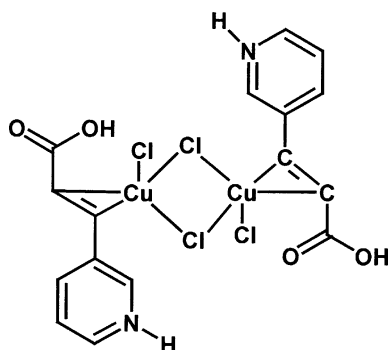Figure 6. Dimer molecular structural representation of [(2-H_2PYA)$_2$
Cu$^+_2$Cl$_4$].

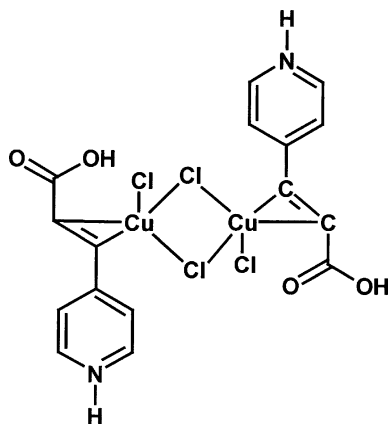Figure 7. Dimer molecular structural representation of [(3-H_2PYA)$_2$
Cu$^+_2$Cl$_4$].

Figure 8. Dimer molecular structural representation of [(4-H_2PYA)$_2$
Cu$^+_2$Cl$_4$].

distorted tetrahedron by the nature of a sp^3 or dsp^2
hybride as shown in figure 10. In Mode I [37], a single
olefin and three other atoms **a**, **b** and **c** acting as donors.
In Mode II [38], two halide ions serve as bridges and a
single olefin together with another atom a complete an
approximately tetrahedral coordination environment. A
single halide bridge in Mode III [39] links Cu(I) centers,
each of which is bound to a terminal halide, an olefin
and another donor **a**. In Mode IV [40], triply bridging
halides and Cu(I) centers combine to form a polymeric
"pleated ladder". The olefin in this case serves as the
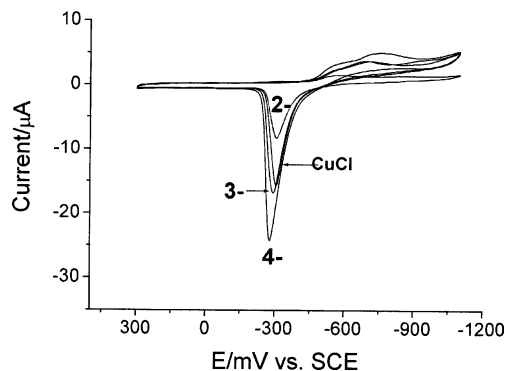only non-bridging ligand in an approximately tetrahe-

Figure 9. Cyclic voltammograms of 0.1 M Bu$_4$NClO$_4$ acetonitrile
solutions containing 1.0 mM CuCl, complexes [(n-H_2PYA)$_2$Cu$^+_2$ZCl$_4$]
at 100 mV/s at a platinum disk working electrode.

dral metal coordination enviromnent. The coordination
environment of the Cu(I) center in Mode V [41]
comprises only four olefins while in mode VI [42], two
olefins and two other atoms (**a, b**) are bond to the
tetrahedrally coordinated Cu(I) center. Other motifs
such as those depicted in the prismane, VII [43] and the
cluster VIII [44], have also been observed. In both VII
and VIII a tetrahedral coordination environment is
completed by binding to olefin ligands.

The steric effect of bulky ligands can encourage the
formation of three coordinate copper(I) centers through
sp^2 or dp^2 hybridization usually in trigonal planar shape
as shown in figure 11. Examples of 3-coordinate Cu(I)
centers are presented in Modes IX[45] and X [46], where
the metal center is bound to one or two olefin molecules
respectively. In Mode XI[22] the 3-coordinate Cu(I)
center is part of a or eight-membered ring while in
Model XII[47], 3-coordinate Cu(I) centers in similar
coordination environments are present in chains.

3.2. The nature of bonding

The nature of coordination between the metal and
olefin can be generally described qualitatively by the
Dewar–Chatt–uncanson model as shown in figure 12.
[48] which includes both contributions of the filled
π-MO of the olefin donates σ electron to empty d or σ
hybrid valence orbital of the metal, and a d π-p π back
donation of electron from a filled valence d-orbital on
metal to the empty π* MO on the alkene. Since both
population of the alkene π MO and population of the
alkene π* MO decrease the C=C bond order, leading to
increase in the olefin C=C distance upon coordination.
Many observations such as the effects of oxidation state
of M, ancillary ligands, olefin substations and the
reactivity, could be explained by this model. For weekly
basic olefin, the Cu$^+$ ion (and other d^{10} ions, such as
Ag$^+$, Hg^{2+}, Pt^0, which without empty d orbital) is the
best acid to form the complexes. In fact, some evidence
[4,7] suggests that the π-back-donation from the d π-
orbital of the Cu(I) to the anti-bonding π* orbital of

Table 1
The crystal structure in CCDC (since year 2000)

CCDC name	Complex name	Synthesis model	Coordination number	Coordination mode	Ref.
BUCGOV	(N, N′-bis(2,6-Dimethylphenyl)-2,4-pentanedi–iminato-N,N′)-(η2-ethene)-copper(i) pentane solvate	Solution	3	IX	[15]
BUCGUB	(N, N′-bis(2,6-Dimethylphenyl)-2,4-pentanedi–iminato-N,N′)-(η2-phenylethene)-copper(i)	Solution	3	IX	[15]
CALKEG	Tetrakis(μ3-η2-2-Allyl-6-methylphenoxo-O,O,O)-tetra-copper(i)	Solution	4	VII	[16]
DUFQAW	Catena-((μ2-η2-trans-3-(4-Pyridyl)acrylic acid-N)-(1,10-phenanthroline-N,N′)-copper(i) tetrafluoroborate	Solovthermal	4	I	[8]
DUFQEA	Catena-((μ2-η2-trans-3-(3-Pyridyl)acrylic acid-N)-(2,2̇-bipyridine-N,N′)-copper(i) tetrafluoroborate monohydrate	Solovthermal	4	I	[8]
ECEVUD	Catena-((N,N′-bis-(η2-Allyl)-S-ethylisothiouronium)-dibromo-chloro-dicopper(i)	Electrochemical	4	II	[17]
ECICAU	Catena-(tetrakis(μ3-Chlora)-chloro-(tetrakis(η2-allylox) silane)-pentacopper(i)	Electrochemical	3	VIII	[18]
GUKRAF	(η2-Allylammonium)-aqua-bis(sulfamato-N)-copper(i)	Solution	4	I	[19]
GUPBEY	Catena-((μ2-η2-4-Allylthiosemicarbazide-N,S,S)-copper(i)sulfamate)	Electrochemical	4	I	[20]
GUPBIC	Catena-(bis(μ2-η2-4-Allylthiosemicarbazide-N,S,S)-bis(μ2-η2-4-allylthiosemicarbazide-N,S)-bis(sulfato-O)-tetra-copper(i))	Electrochemical	4	I	[20]
GUZKAN	(η2-Methyl acrylate)-(N,N,N′,N″,N″pentamethyldiethyl-enetriamine-N,N′,N″)-copper(i) tetraphenylborate		4	I	[21]
LOZJEP	Catena-((μ3-Bromo)-(μ2-bromo)-(μ2-η2,η2-1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione)-di-copper(i))	Solovthermal	3	VIII	[22]
LOZJIT	Catena-(tris(μ3-Bromo)- (μ3-η2,η2,η2-1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione)-tri-copper(i))	Solovthermal	4	VII	[22]
MIDPUK	Catena-(bis(μ2-Chloro)-bis(μ2-η2-4-vinylpyridine-N)-di-copper(i))	Solovthermal		II	[9]
MITWIV	(η2-Ethylene)-(hydrogen tris(3.5-bis(trifluoromethyl) pyrazol-1-yl)borate)-copper(i)benzene solvate	Solution	4	I	[23]
MITWOB	(η2-Ethylene)-(hydrogen tris(5-phenyl-3-(trifluoromethyl) pyrazol-1-yl)borate)-copper(i)	Solution	4	I	[23]
MITUH	(η2-Ethylene)-(hydrogen tris(3-(trifluoromethyl) pyrazol-1-yl)borate)-copper(i)	Solution	4	I	[23]
OFANAK	Catena-((μ2-η2-η2-Isoprene)-bis(μ2-trifluoromet hanesulfonato)-bis(triphenylphosphine)-di-copper(i))	Solution	4	I	[24]
OFANEO	Catena-((μ3-Chloro)-(μ2-chloro)-(μ2-η2,η2-isopropenylacetylene)-dicopper(i))	Solution	4	II	[24]
OFANIS	Catena-(bis(μ3-Chloro)-(μ2-η2,η2-1,3-dimethylbuta-1,3-diene)-dicopper(i))	Solution	4	IV	[24]
OFANOY	Catena-(bis(μ3-Chloro)-(μ2-η2,η2-trans-1,5-pentadiene)-di-copper(i))	Solution	4	IV	[24]
QAYBEX	Catena-((μ2-η2-trans-4-Pyridylacrylicacid)-(2,2′-bipyridine)-copper(i)tetrafluoroborate)	Solovthermal	4	I	[12]
QEFJAM	Aqua-(η2,η2-diallylformamide)-(sulfamate-N)-copper(i)	Electrochemical	4	VI	[25]
QENJEY	((3R)-η2-Buten-3-ol)-((1S,2S)-N,N′-bis(mesitylmethyl)-1,2-diphenylethane-1,2, diamine-N,N′)-copper(i) perchlorate acetone solvate	Solution	3	IX	[26]
QEQPUX	Catena-((μ3-Sulfato)-(η2-allylammonium)-copper(i))	Electrochemical	4	II	[27]
QICFUD	((R,R-(-)-(μ2-η5,η5-4,4′-demethyl-2,2′-bi(cylolpentena(e) pyridine))-bis(η5y-pentamethylcyclopentadienyl) -iron)-(η2-styrene)-copper(i)hexafluorophosphate	Solution	3	IX	[28]
QUSTUT	(μ2-η2,η2-2-Methyl-l-hexen-3-yne)-bis(hexafluoroacetylacetonato-O.O′)-d-copper(i)	Solution	3	IX	[29]
QUSVAB	(μ2-η2,η2-1-Hexen-3-yne)-bis(hexafluoroacetyl acetonato-O.O′)-dicopper(i)	Solution	3	IX	[29]
TUXKOM	Tetrakis(μ2-η2-2-Allyl-6-methylphenoxo)-tri-copper(i,ii) toluene solvate	Solution	4	VI	[30]
UDAXEC	(η2,η2-8,8′-bis(allyl)-5,7:5′,7′-bis(methano)-8,8,8′-tetram ethyl-5,5′, 6,6′,7,7′,8,8′-octahydro-2,2′-biquinoline)-copper(i)hexafluorophosphate ethanol solvate	Solution	4	VI	[31]

Table 1
(Continued)

CCDC name	Complex name	Synthesis model	Coordination number	Coordination mode	Ref.
WUCQUG	(η2-2-(Allythio)benzimidazole-N)-chloro-copper(i)	Electrochemical	3	IX	[32]
WUCRAN	bis((μ2-Bromo)-(η2-2-(allylthio)benzimidazole-N)–copper(i))	Electrochemical	4	II	[32]
WITCUX	Catena (tris(μ2-Bromo)-(η2-1,3-diallylbenzimidazole)-di-copper(i))	Solovthermal	4	II	[11]
WITVAW	Catena ((μ3-chloro)-tris(μ2-chloro)-(η2-N-allyl-4-(N,N′-dimethylamino) benzaldiminium)-tetrachloro-tri-copper)	Electrochemical	4	VII	[33]
XEPMAG	Tetrakis(μ2-Bromo)-bis(μ2-η2-N-(2-furylmethylidene)-2-propenamine)-tetracopper(i)	Electrochemical	3	XI	[34]
XIFMII	Catena-((μ2-η2,η2-Diallyformamide-O)-aqua-copper(i) tetrafluoroborate)	Electrochemical	3	X	[35]
XIFMOO	Catena-((μ2-η2,η2-Diallyformamide-O)-copper(i) perchlorate)	Electrochemical	3	X	[35]
XIRZON	Bis((μ2-Chloro)-bis((η2-5-(E)-propyl-4,7-octadien-4-yl) diphenylphosphine)-di-copper(i)	Solution	4	II	[36]
XIRZUT	Bis((μ2-Chloro)-bis((η2-1,2-diphenyl-1,4-penetadien-1-yl) diisopropylphosphine)-di-copper(i)	Solution	4	II	[36]

olefin is responsible for the lengthening of the C=C bond. An unusual structure feature of complex [Cu(-Phen)(C$_2$H$_4$)]ClO$_4$ is that the C=C bond distance of the coordinated olefin (~1.347 Å) is approximately the same as that in the free molecule. The spectroscopic results appear to be in conflict with the crystal structure. This anomaly may, however, be resolved by applying the concept of a molecular Rydberg state [49] to the ethylene molecular bound to the metal ion. The Rydberg orbital of the ethylene molecule is 3d$_\pi$-orbital with its core at the center of the ethylene molecule. This orbital overlaps with the 3d$_\pi$ orbital of the copper(I) ion, and back-donation from the metal 3d$_\pi$ orbital to the Rydberg 3d$_\pi$ orbital is then possible. The lengthening of the C=C bond distance does not occur owing to this back-donation, because this Rydberg 3d$_\pi$ orbital is a non-bonding orbital from the C=C bond.

Many reaction mechanisms have been proposed by the quantum chemical calculations. For instance, Mori and Nakamura [50] studied the reaction pathway of the conjugate addition of a dimeric cuprate (Me$_2$CuLi)$_2$ to 2-cyclohexenone by means of the B3LYP hybrid density functional method, and determined intermediates and transition structures on the potential surface of the reaction. The models are the closest to the experimental examples, and provide the first molecular picture of the nature of the diastereoselectivity of the cuprate addition.

4. Chemical properties of olefin-copper complexes

4.1. As catalysis in organic reactions

The transformation of unsaturated substrates into useful or "value-added" products represents one of the main goals of modern chemistry. Transition metal complexes are often employed as the catalysts in such reactions. One of these reactions is the conversion into three-membered rings such as cyclopropanes, aziridines and epoxides, compounds that possess several desirable properties.

4.1.1. olefin-copper(I) complexes as catalysts for asymmetric cyclopropanation or aziridination

The Srookhart and Templeton groups [51] have prepared a η^2-ethylene-copper(I) complex [Tp' Cu(C$_2$H$_4$)] [Tp' = hydrotris (3,5-dimethyl-1-pyrazolyl) borate] (figure 13) which was found to be a highly efficient catalyst, under mild conditions, for carbene transfer from ethyl diazoacetate to alkenes (equation (7)) and for the coversion of alkynes to cyclopranes and cyclopropenes. Furthermore, this complex also catalyzes, again under mild conditions, nitrene transfer from (N-(p-toluenesulfonyl)imino)- phenyliodinane PhI=NTs to alkenes to produce aziridines.

The Rasika Dias group [52] has prepared three η^2-ethylene-copper(I) complexes HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu (C$_2$H$_4$), [HB(3-(CF$_3$),5-(C$_6$H$_5$)Pz)$_3$]Cu (C$_2$H$_4$), and [HB (3-(CF$_3$)Pz)$_3$]Cu(C$_2$H$_4$) by reacting the corresponding sodium derivative with CF$_3$SO$_3$Cu in the presence of ethylene. The former two complexes were evaluated as aziridination catalysts utilizing a variety of olefins and N-tosyliodinane as the nitrene source (equation (8)).

Hofmann and co-workers [53] have synthesized a novel highly stable copper(I) ethylene complex [Bu$^t_2$P(NSiMe$_3$)$_2$-κ_2N]Cu(η^2-C$_2$H$_4$) (equation (9)), which can catalyze cyclopropanation of styrene with α-carbonyl diazoalkanes at room temperature. The presence of a number of NMR active nuclei (^{1}H, ^{13}C,
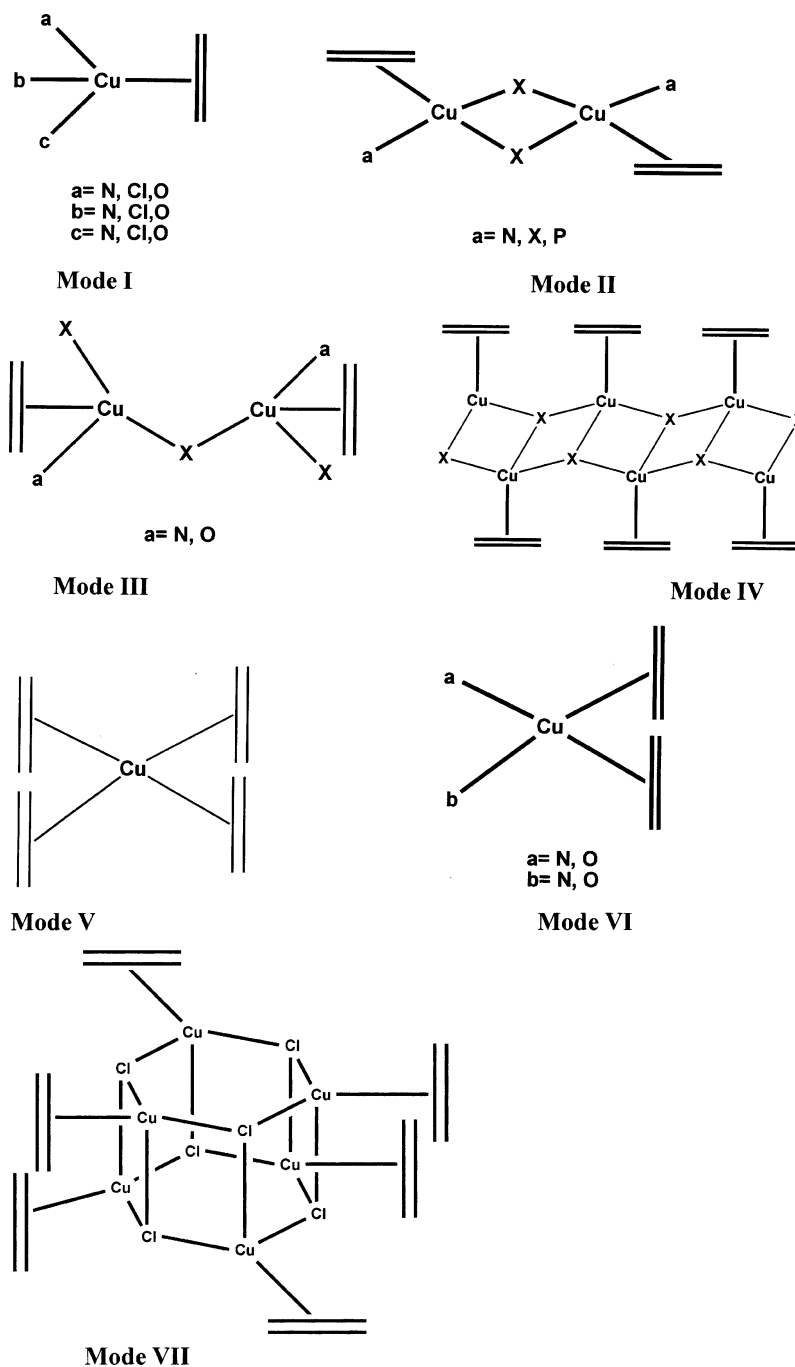
a= N, Cl,O
b= N, Cl,O
c= N, Cl,O

Mode I

a= N, X, P

Mode II

a= N, O

Mode III

Mode IV

Mode V

a= N, O
b= N, O

Mode VI

Mode VII

Figure l0. The modes of olefin-copper(I) complex (Coordination numbers four).

^{29}Si and especially ^{31}P) and the high solubility of the complex (even in alkanes) provides an opportunity to investigate mechanistic aspects of organometallic copper(I) chemistry, especially copper(I)-catalyzed cyclopropanation.

Pe'rez and co-workers [54–60] used polypyrazolylb-orate ligands (figure 14), copper(I) salts and assistant ligands to synthesise copper(I) complexes. They investigated the catalytic capabilities of their copper(I) complexes and, after a comprehensive kinetic study, proposed a reasonable mechanism (figure 15).

Copper complexes Tp^{X}Cu (Tp^X = homoscorpio-nate)[61] prepared in situ catalyze the olefin cycloprop-anation reaction using ethyl diazoacetate as the carbene source. High activity and diastereoselectivity toward the *cis*-isomer have been obtained for styrene, r-methylsty-rene, 1-hexene,1-octene, vinyl acetate, n-butyl vinyl ether, 2,5-dimethyl-2,4-hexadiene, and 3,3-dimethyl-l-butene. The effect of the temperature in the diastereose-lectivity was almost negligible within the range −10 to + 3 °C. Kinetic studies allowed the authors to propose that the homoscorpionate ligand may act in a dihapto
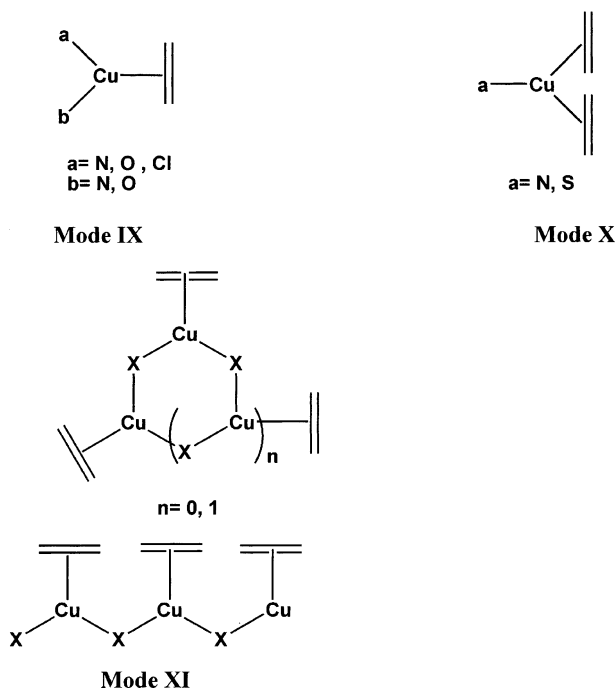
Mode IX

a= N, O , Cl
b= N, O

Mode X

a= N, S

n= 0, 1

Mode XI

Figure 11. The modes of olefin-copper(I) complex (Coordination numbers three).

Figure 13. The molecular for [Tp′ Cu(C$_2$H$_4$)].

have been obtained with a group of representative substrates, including nonactivated terminal olefins. The high activity of these catalysts has allowed the use of equimolar amounts of PhINTs and olefins, avoiding the requirement of excess olefin. Particularly effective is the perbromo catalyst TpBr^{3}Cu, which has provided high yields of aziridines, even with equimolar mixtures of the olefin and PhINTs and low (1%) catalyst loading. In an effort to eliminate nondesired by products, chloramine-T has been employed as the nitrene source, in a reaction that produces sodium chloride as the sole residue, with high degrees of conversions also being obtained.

Doyle and Forbes [63] reviewed the use of copper(I) complexes of C$_2$-symmetric bis-oxazolines (figure 16), bis(pyrazolyl)pyridine bipyridine (figure 17) and chiral C$_3$-symmetric pyrazolylborate (figure 18) as catalysts for the conversion of olefins into cyclopropanes.

Figure 12. A qualitative orbital description of metal-alkene bonding.

form during the catalytic process. This transformation seems to operate under kinetic control, where the formation of the *cis*-isomer governs the reaction rate.

A series of complexes Tp^{X}Cu [62] have been tested as catalysts for the olefin aziridination reactions using PhINTs as the nitrene source. High yields of aziridines

$$(7)$$
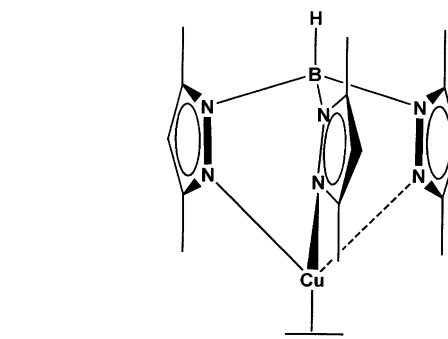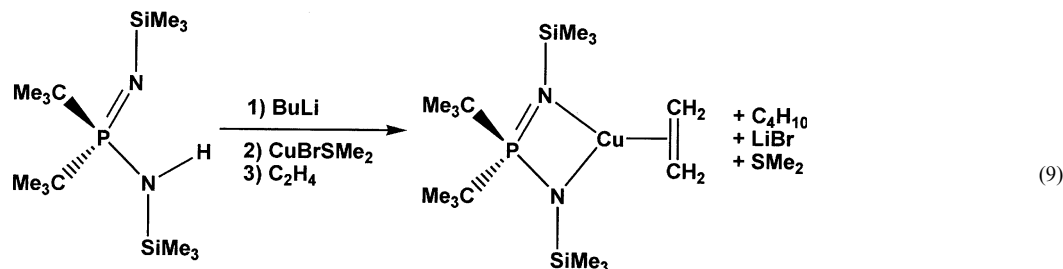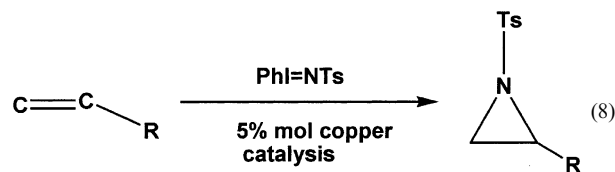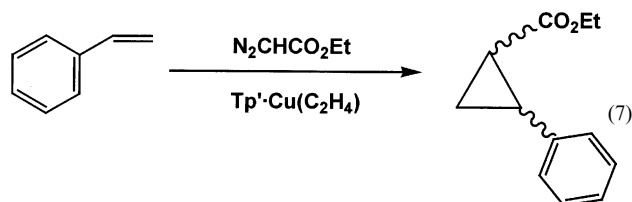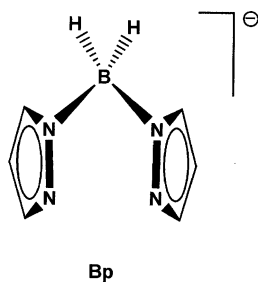

$$(8)$$

$$(9)$$

Figure l4. Polypyrazolylborate ligands.

Based on previous studies, Lo and Fu [64] synthesized a $C2$-symmetric bi-sazaferrocene (figure 19) as a ligand for copper(I) complexes. The copper(I) complex is an efficient catalyst not only for the asymmetric cyclopropanation of aryl-substituted olefins but also for alkyl- and silyl-substituted olefins (equation (10)). It was found that allylbenzene and 1-octene react with the diazoester to produce the *trans*-cyclopropane with a high enantiomeric excess. Furthermore, vinyltrimethylsilane undergoes addition with excellent diastereo- and enantioselectivity.

Zeolite-supported copper(I) complexes with C2-multidentate nitrogen ligands (figure 20) were synthesized by Iglesias and co-workers [65]. These heterogeneous catalysts promote a high degree of enantioselective hydrogenation and cyclopropanation of olefins (equation (11), table 2). It was found that the activity of homogeneous catalysts for different substrates was increased by heterogenisation on USY-zeolite (containing supermicropores and a large quantity of silanol groups) and MCM41. These catalysts can be recovered and reused (table 3), with retention of most of their catalytic activity. Moreover, the heterogenised copper(I) complexes are significantly more stable than the corresponding homogeneous complexes over prolonged reaction times and were handled without special care under standard conditions. Zeolite-supported copper(I)

complexes show interesting catalytic properties in different reactions. This is due to changes in the microenvironment (solvent, site isolation, dimensionality) of the metal-complex within the supporting zeolite structure.

4.1.2. Sensitization of olefin to photoreactions including rearrangement, cycloaddtion, and molecular fragmentation

The copper(I) can sensitize a diverse assortment of olefin photoreactions including rearrangement, cycloaddition, and molecular fragmentation. Using the normal solvent method Srinivasan [66] reacted 1,5-cyclooctadiene with CuCl to prepare a olefin-copper(I) complex. He examined the photochemical behavior of the complex and suggested a mechanism for the conversion of coordinated 1,5-cyclooctadiene to tricylooctane upon exposure to light (equation (12)).

Kutal [67–70] investigated the role of assistions in the photoconversion of norbornadiene (NBD) to quadricyclene (Q) (equation (13)) and answered a number of relevant questions.

The appropriate coordination environment of copper(I) binding NBD has so far been disregarded; To date the light source employed in the (NBD) → (Q) metal assisted photo conversion is not quite in the visible region, and no data are available using light with $I > 400$ nm; The copper(I)-assisted (NBD) → (Q) photoconversion is usually characterized by limited turnover numbers; The search for a catalyst for the reverse (Q) → (NBD) thermal reaction has been overlooked.

Floriani and co-workers [71] used either metathesis reaction involving CuCl or reactions of the monoprotic ligands with Cu_5Mes_5 (Mes = 2,4,6-$Me_3C_6H_2$) (equation (14)) in the presence of norbornadien to generate four olefin-copper(I) complexes. The complexes were designed as photosensitizers which would permit the (NBD) → (Q) isomierization. The reactions were performed using visible light and a high NBD/photocatalyst
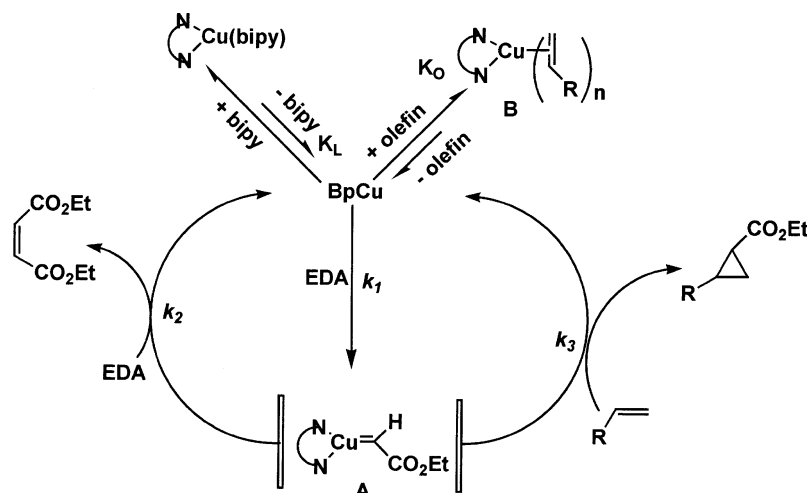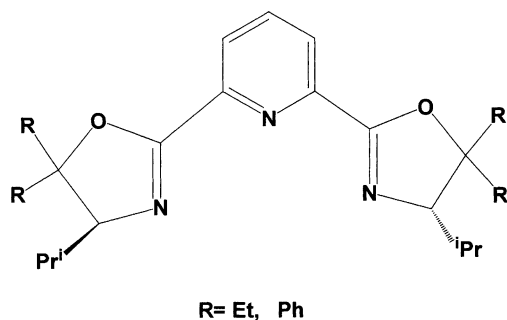

Figure 15. Proposing a reasonable mechanism by a complete kinetic study.
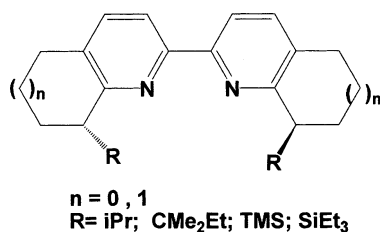
Figure 16. bis-oxazolines ligands.

n = 0 , 1
R= iPr; CMe₂Et; TMS; SiEt₃
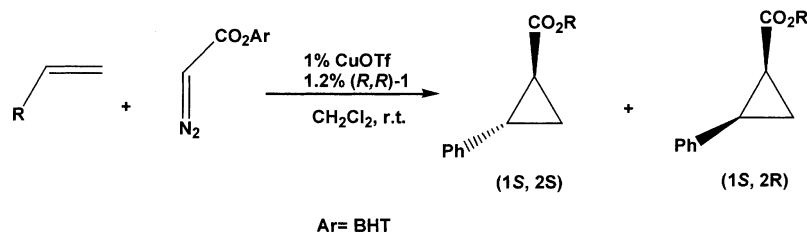
Figure 17. bis(pyrazolyl)pyridine bipyridine ligands.

R= R'=

Figure l8. chiral C3-symmetric pyrazolylborate ligands.

Figure 19. *C*2-symmetric bisazaferrocene ligands.

4.1.3. Copper(I) promoted conjugate addition reactions of α,β-unsaturated carbonyl compounds

Conjugate addition of organocuprates occupies a unique and important position in organic synthesis because of the ability of the system to stereoselectively deliver a carbanionic center in order to create a new chiral center. Olefin-copper(I) complexes formed between copper(I) and α,β-unsaturated carbonyl compounds are of interest in connection with the tendency of copper(I) to promote conjugate addition reactions. Ullenius' group [73] has studied lithium dimethylcuprate and methyl or t-butyl *trans*-cinnamate by NMR. The NMR results suggest that the copper-olefin complex and lithium-carbonyl complex are formed and co-exist in equilibrium, and that the former is the major component at low temperature in the presence of an excess LiMe₂Cu. Accordingly, they suggested that the π -complex is present in the reaction pathway, which ends at the formation of the enolate (equation (16)). The initial formation of a π -complex between the reactants can be equally well accommodated by the mechanisms suggested for conjugate addition of cuprates to enones or enoates which form a complex in the first step between the reactants.

4.2. The separation of olefins via the formation of the olefin-copper (I) complexes

Cuprous halides used to absorb and purify olefins have been reported by Gilliland [74]. The Reger

turnover was achieved. All complexes show absorption in the visible spectrum, which provides some promise in regard to improved solar energy storage systems[72]. They suggested two distinct mechanisms (equation (15)).
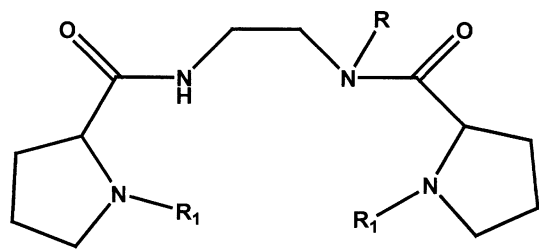

(10)

Ar= BHT

1a: R=R$_1$ = H;
1b: R=(CH$_2$)$_3$Si(OEt)$_3$, R$_1$=H
2a: R=H, R$_1$ = Bz
2b: R=(CH$_2$)$_3$Si(OEt)$_3$, R$_1$=Bz

Figure 20. *C*2-multidentate nitrogen ligands.

Table 2
Catalytic results for the cyclopropanation reaction involving styrene and alkyl diazoacetates

N$_2$CHCO$_2$R	Catalyst	Selectivity (% yield, h)	Trans–cis
R = Et	Cula	49(74, 2)	2.0
	USY-Culb	100(32, 20)	1.88
	MCM-Culb	100(60, 21)	2.0
	MCM-lbCu	100(20, 20)	1.89
R = *t*-Bu	Cula	49(74, 4)	2.0
	USY-Culb	100(23, 19)	2.13
	MCM-Culb	100(57, 19)	2.04
	MCM-lbCu	85(37, 21)	2.17

Table 3
Recycling of MCM-Cu1b

CN$_2$CHCOOR	Run	Selectivity (% yield)	Tran—cis	%ee
R = Et	1	100(50)	2.0	15
	2	100(57)	2.02	15
	3	100(53)	2.03	14
	4	100(52)	2.0	13
R = *t*-Bu	1	100(37)	2.04	< 5
	2	100(47)	2.13	< 5
	3	100(41)	2.02	< 5
	4	100(39)	2.04	< 5

group[75] has synthesized a series of polyolefin copper(I) trifluoroacetate complexes which all release the olefins in the presence of water. This property had been used to recover the olefin in ca. 95% yield by simply adding water to the complexes and extracting the olefin with organic solvents.

Recently, Vitagliano and co-workers [26] have reacted the chiral Corey diamine and a Cu(I) salt with olefins, as well as with allylic alcohols and ethers in order to generate trigonal copper(I) complexes (equation (17)). The complexes were investigated using ^{1}H NMR and computational methods – combined quantum mechanics and molecular mechanics (QM/MM). It was found that prochiral olefins are coordinated with high enantioface selection, although the complexes exist as rapidly equilibrated mixtures of stereoisomers. The [(S,S)−1]-Cu fragment selectively recognizes the R enantiomer of secondary allylic alcohols and ethers (table 4), This has been confirmed by the X-ray crystal structure analysis of the adduct with (R)-1-buten-3-ol. They elucidated the reasons for the observed selectivities which lead to the enantioselection observed in catalytic cyclopropanation reactions promoted by copper complexes of the same ligand.

Jacobsen and co-workers [76] used C2-symmetric 1,2-diimines, olefin ligands and a copper salt to construct a series of olefin-copper(I) complexes (equation (18)), which demonstrate enantiofacial selectivity of olefin.

Using NMR the enantiofacial selectivity of olefin complexation was extended to other series of alkenes (table 5). Enantiofacial selectivity in binding of 2,4,6-trimethylstyrene to copper complex which based on C2-symmetric 1,2-diimines (87:13) was almost identical to that of 2,6-difluorostyrene, reinforcing the notion that edge-face interactions with the chiral ligand are precluded for both substrates. Interestingly, the presence of electron-donating or electron-withdrawing substituents on the styrene derivative (e.g. *p*-methoxystyrene and *m*-nitrostyrene) had no detrimental effect on binding selectivity. Aliphatically substituted alkenes such as vinylcyclohexane were found to bind with no measurable selectivity. The solution and solid-state structures of olefin-copper(I) complexes thus provide strong evidence that attractive edge-face and face-face aromatic

(11)

$$(12)$$
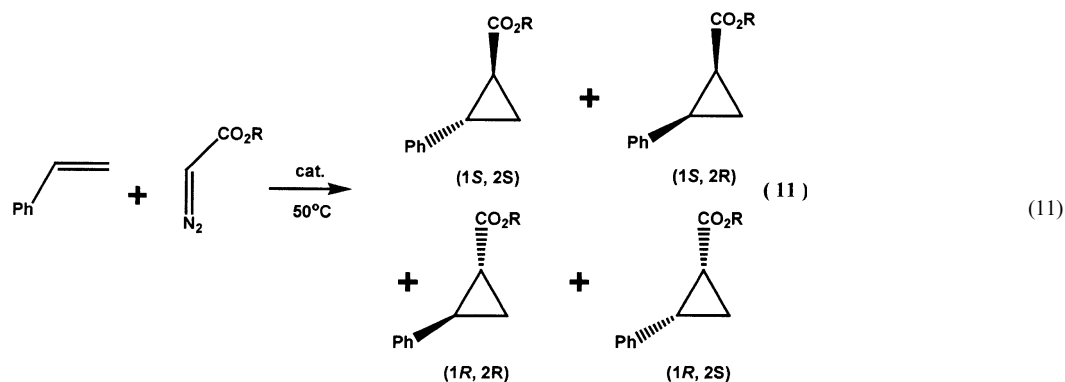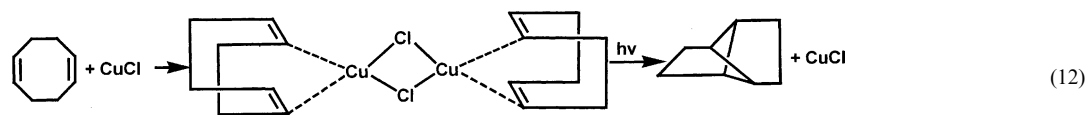
interactions can play a determining role in enantioface discrimination in the binding of prochiral substrates to this class of chiral catalysts. Such secondary catalyst-substrate interactions may also play an important role in catalysis.

5. Physical properties of olefin-copper complexes

Molecular-based materials with potential opto-electronics application are developed recently, but less on the metal-olefin compounds, we attempt to promote the application complexes in this field. [77]

5.1. Chiral seperation

It is more likely that the binding selectivity is often the controlling factor in stoichiometric processes but not in metal-catalyzed asymmetric reactions [78]. The rational design and construction of hybrid organic-inorganic zeolite analogues for enantioseparation and catalysis are of intense current interest [79,80]. The inclusion of enantiomerically pure chiral compounds
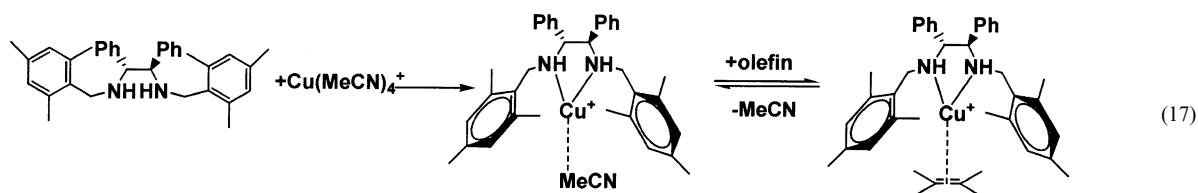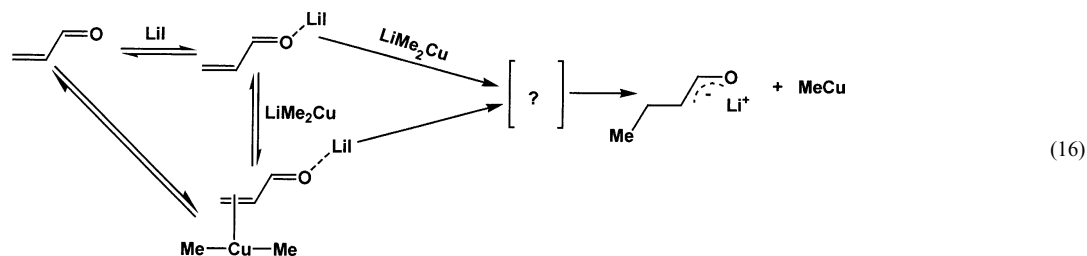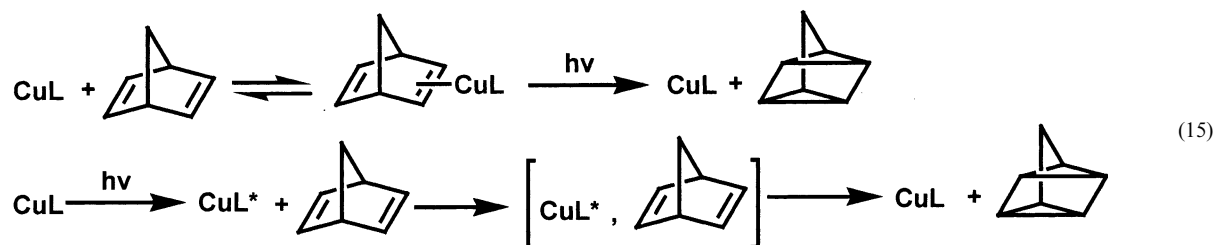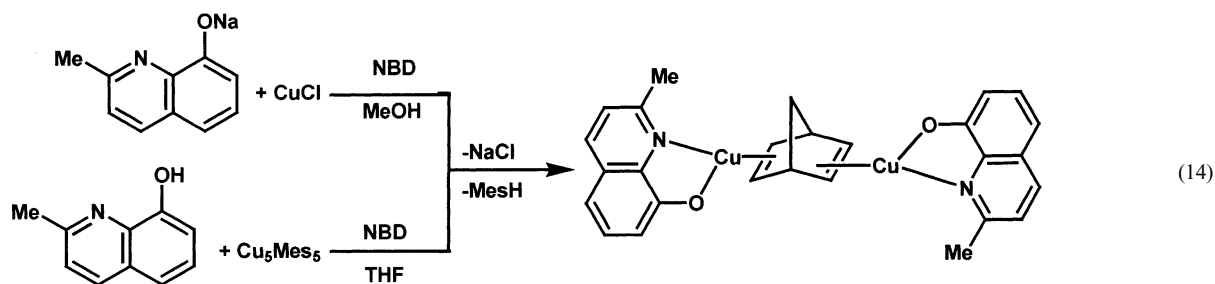
$$(13)$$

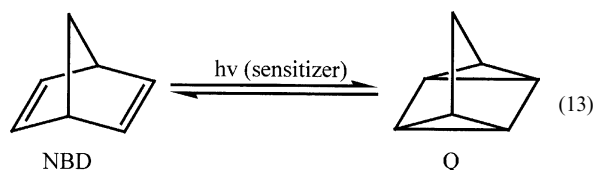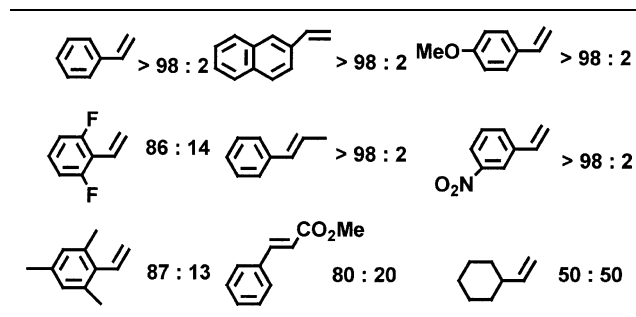$$(14)$$

$$(15)$$

$$(16)$$

$$(17)$$

Table 4
Diastereomeric distribution of [Cu((S,S)-1)(olefin)] complexes

Complex	Olefin	% at 243 K	N,N configuration	Coordinatd enantioface
2a	ethylene	70	R, R	–
2b	ethylene	30	R, S	–
3a	propene	86	R, R	re
3b	propene	8	R, S	re
3c	propene	6	R, S	si
4a	1-pentene	83	R, R	si
4b	1-pentene	10	R, S	si
4c	1-pentene	7	R, S	re
5a	E-2-butene	> 97	R, R	re
6b	E-2-butene	≈75	R, S	–

Table 5
Enantiofcial selectivity of Complexation of Selected Olefins to 1 As
Determined by 1H NMR at −90°C (CD$_2$Cl$_2$)

into microporous materials (zeotypes) for enantiomer separation, as well as chiral synthesis and catalysis, has been a continuing challenge and represents an ambitious goal for chemists [81,82]. Currently known materials capable of offering enantiomeric separation and catalysis tend to be 2-D layer-type structures that are able to intercalate guests [83,84]. Chiral recognition in the coordination of olefins to chiral transition metal fragments is a topic of interest [85], especially in relation to metal-promoted enantioselective syntheses.
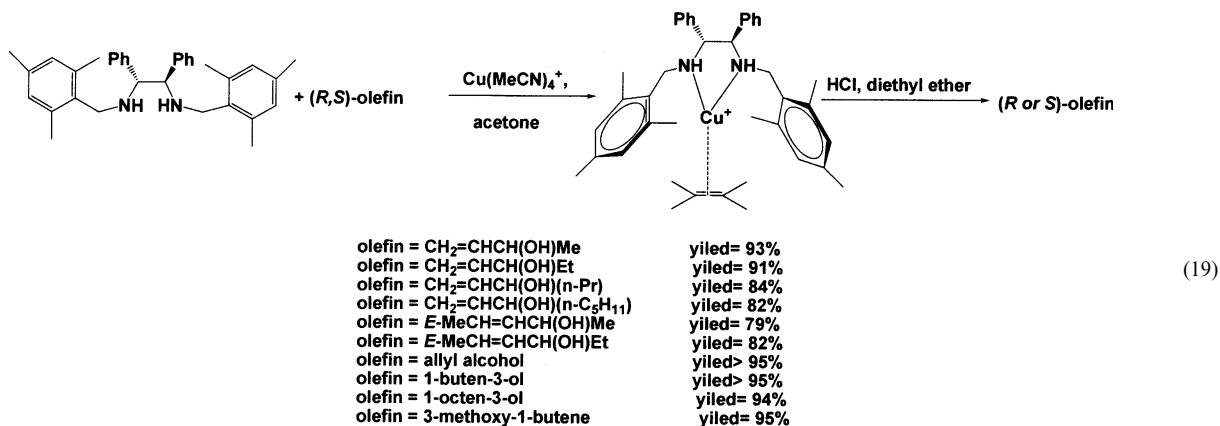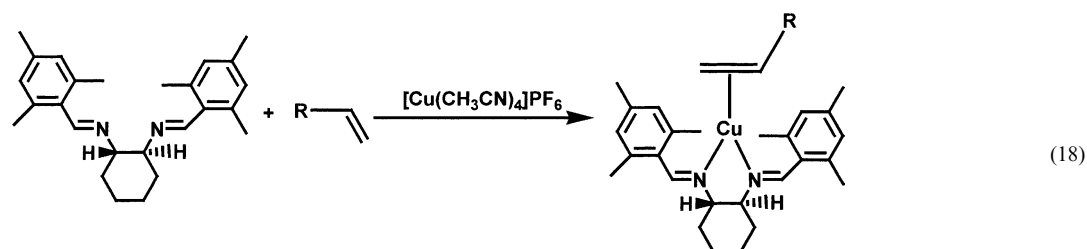
Olefin-copper(I) complexes with chiral ligands can be used for the resolution of racemic mixtures of olefins. Vitagliano and co-workers [26,86] used Corey diathine 1,2-diphenyl-N,N'-bis[(2,4,6-trimethylphenyl)methyl]-1,2-diaminoethane, Cu(I) salt and chiral olefin ligands to form olefin-copper(I) complexes. When the olefin is a racemic allylic alcohol, the olefins are coordinated

with high enantioface selection. Cleavage with aqueous HCl or NaCN allows a two-step resolution affording excellent enantiomeric excess (equation (19)). Compared to olefin platinum complexes, olefin-copper(I) complexes are cheaper and more labile, which are important factors in the separation of racemic olefins.

Vinylbenzylcinchonidinium chloride ([VB-N-CIN]Cl) is a chiral phase transfer catalyst (CPTC), which can be prepared from the corresponding cinchona alkaloid. We [87] have found that ([VB-N-CIN]Cl) and 4-vinylbenzyl chloride in refluxing acetone and N,N-dimethylformamide (equation (20), figure 21a), solvo-thermally react with CuCl to form an unprecedented 2-D layered homochiral copper(I)-olefin coordination polymer of formula, Cu$_5$Cl$_6$(VB-N-CIN)$_2$•C$_2$H$_5$OH (1•EtOH) (equation (21) figure 21b). It is noteworthy that two adjacent layers are in an AA type arrangement

(18)

olefin = CH$_2$=CHCH(OH)Me   yiled= 93%
olefin = CH$_2$=CHCH(OH)Et   yiled= 91%
olefin = CH$_2$=CHCH(OH)(n-Pr)   yiled= 84%
olefin = CH$_2$=CHCH(OH)(n-C$_5$H$_{11}$)   yiled= 82%
olefin = E-MeCH=CHCH(OH)Me   yiled= 79%
olefin = E-MeCH=CHCH(OH)Et   yiled= 82%
olefin = allyl alcohol   yiled> 95%
olefin = 1-buten-3-ol   yiled> 95%
olefin = 1-octen-3-ol   yiled= 94%
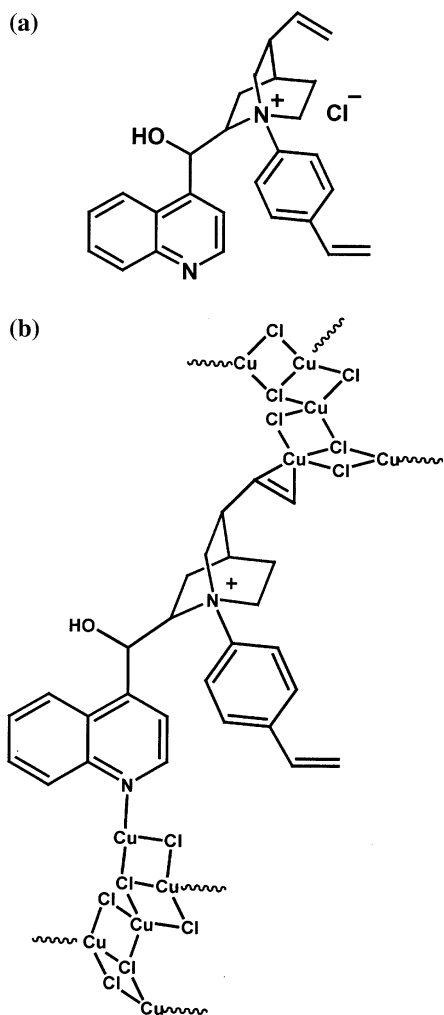olefin = 3-methoxy-1-butene   yiled= 95%

(19)

(a)

(b)

Figure 21. [VB-N-CIN]Cl and an asymmetric unit of compound Cu$_5$Cl$_6$(VB-N-CIN)$_2$

and one ethanol molecule is intercalated between layers of **1**. A preliminary enantioseparation investigation shows that the 2-D layered network in **2** is capable of

selectively intercalating (R)-2-butanol. This is the first example of a homochiral olefin-copper coordination polymer, which may be useful for enantioseparation, proposed resolution process by intercalation is shown figure 22.

5.2. Fluorescent properties

A reaction of CuCl and 4-vinylpyridine in CH$_3$CN solution at 90 °C under hydrothermal reaction results in the formation of a novel luminescent 2-D rectangular neutral grid, [Cu(4-vinylpyridine Cl]$_n$, (equation (22)), The rectangle has dimensions of approximately 10.576 Å × 7.322 Å (figure 23). The luminescence spectrum of the compound in the solid state at room temperature is shown in figure 24. The compound exhibits a strong yellow fluorescent emission. [88]

The solvothermal reactions of 3-pyridylacrylic acid and 2-pyridylacrylic acid with Cu(CH$_3$CN)$_4$BF$_4$ yield two novel, highly stable copper(I)-olefin coordination polymers[89] (equation (23), equation (24)), [(3-pyridyl-acrylicacid)Cu(I)]$_n$ and {[(2-pyridylacrylic acid)-Cu(I)]•(H$_2$O)}$_n$ (figure 25), respectively. Both polymers display 2-D layered structures and yellow fluorescent emission in the solid state (figure 26) in addition to high thermal stability.

Under solvothermal conditions, the reaction of 4-pyridylacrilic acid and 2,2′-bipyridine with Cu(Me-CN)$_4$BF$_4$ gives rise to an unprecedented, stable copper(I)-olefin coordination polymer {[(2,2′-bipyridine)(4-pyridylacrilic acid)Cu(I)] (BF$_4$)}$_n$ (equation (25)) (figure 27) which displays a strong red fluorescent emission in the solid state (figure 28). [90]

5.3. Ferroelectric properties [91,92]

The reactions of quinine with CuCl and CuBr afford Cu$_8$Cl$_{10}$(HQuinine)$_2$ (**1**) and Cu$_8$Br$_{10}$(HQuinine)$_2$ (**2**) (figure 29), respectively. The 2-D layer networks are
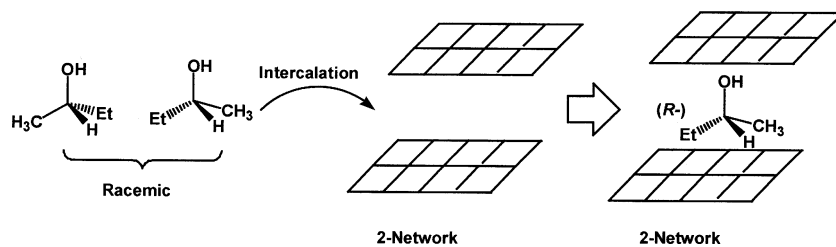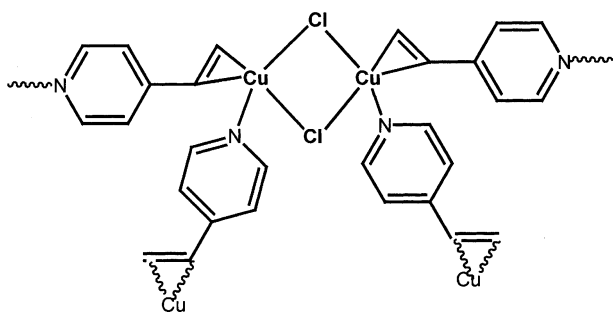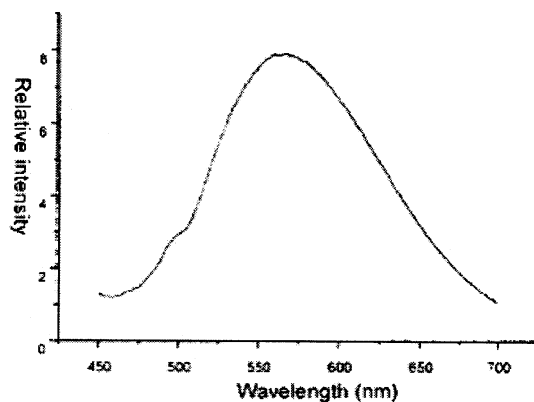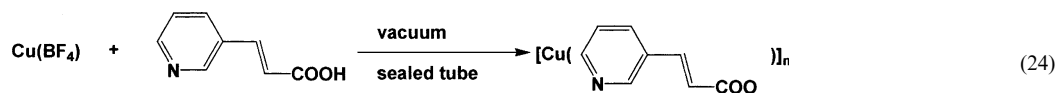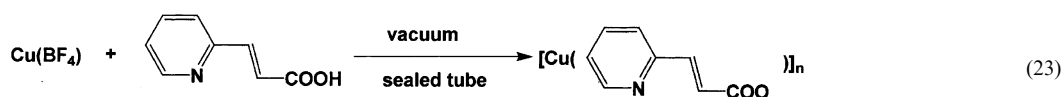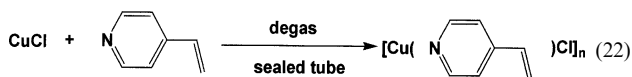

(20)

(21)
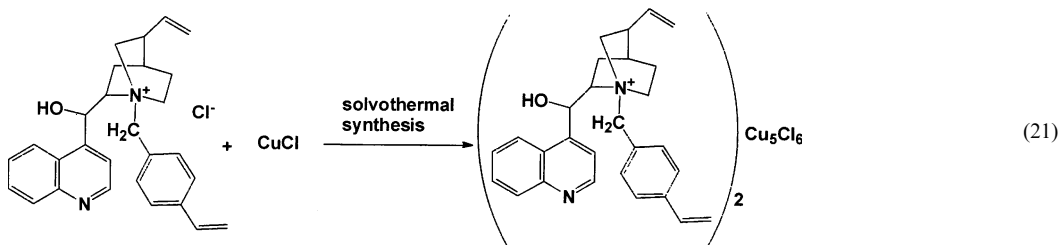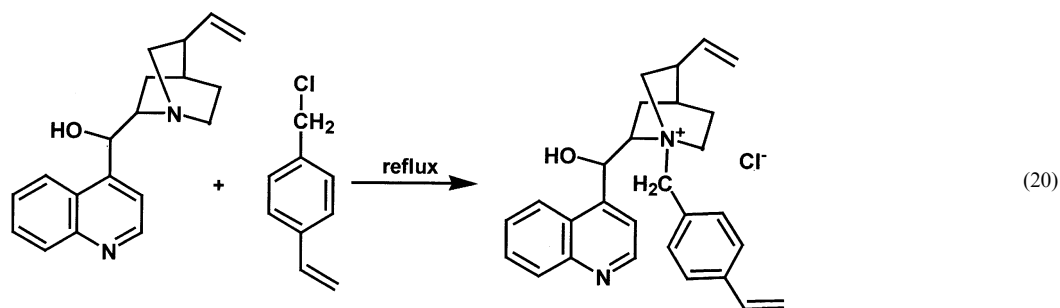
Figure 22. Proposed resolution process by intercalation.

Figure 23. An asymmetry unit of complex [CuC(4-Vinylpyridine) Cl]$_n$.

Figure 24. Luminescent spectrum of [Cu(4-vinylpyridine) Cl]$_n$ in the solid state at room temperature.

isostructural (equation (26)). The space group *C2* is associated with the point group C_2, one of the 10 polar point groups (C_1, C_s, C_2, C_{2v}, C_3, C_{3v}, C_4, C_{4v}, C_6, C_{6v}) required for ferroelectric behavior. Experimental results indicate that **1** does indeed display good ferroelectric behavior. An electric hysteresis loop (a typical ferroelectric feature) is produced by compound **1**, with a remnant polarization (Pr) of 0.12 μC cm^{-2} and a coercive field (Ec) of 5.0 kV cm^{-1}. The saturation spontaneous polarization (Ps) of (1) is ca. 30 μC cm^{-2} compared to ferroelectric KDP is 5.0 μC cm^{-2}. **1** is the first homochiral olefin-copper(I) coordination polymer exhibiting ferroelectric behavior (figure 30) [93].

5.4. *Mimic the active sites of ethylene in biological systems*

Of all the metals involved in biological systems only Cu(I) reacts with olefins. Ethylene is a plant hormone that plays a critical role in virtually every phase of

development in most plants: germination, growth, sex expression, fruit ripening, senescence, and abscission, [94–96] Considerable research has suggested the copper(I) is the binding site for ethylene action. The role of the copper ion has been suggested in the metabolism of ethylene to ethylene oxide and other products. Other olefins, such as propene, 1-butene etc also exhibit similar behavior to ethylene. The Thompson group [4,97] prepared series of stable olefin-copper(I) complexes with imidazole-like ligands and di-pyridylamine ligands (equations (27) and (28)). Their work demonstrated for the first time that the coordination chemistry of monoolefin-copper(I) complexes was consistent with the proposed role of Cu at the ethylene receptor site of plants. This work established that Cu(I) complexes with imidazole-like ligands formed stable adducts with the biological active olefins. Furthermore, the geometries observed for the low molecular weight complexes are plausible for Cu(1)-olefin adducts present at the active site of proteins, which have established or proposed tetrahedral and lower coordinate geometries. The struc-
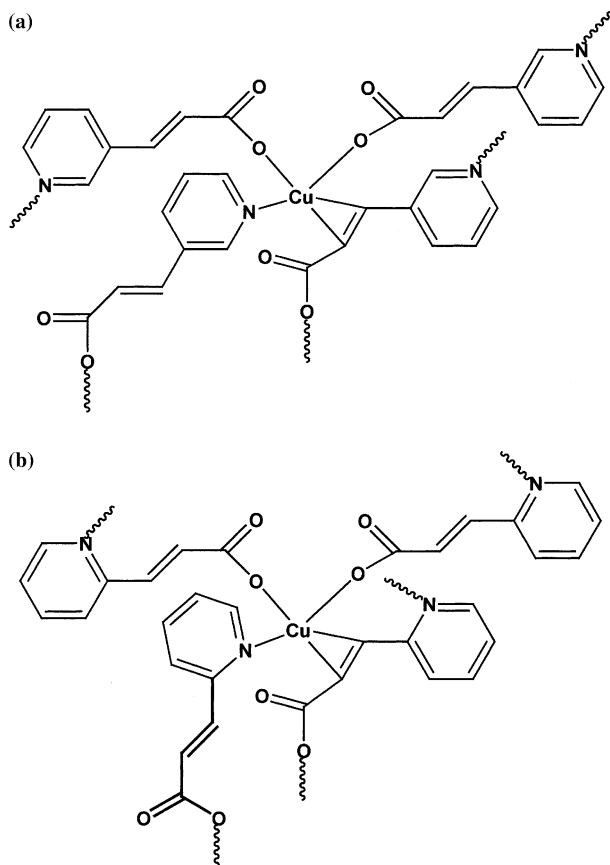

$$\text{CuCl} + \text{N}\diagdown\diagdown \xrightarrow[\text{sealed tube}]{\text{degas}} [\text{Cu(N}\diagdown\diagdown\text{)Cl}]_n \quad (22)$$

$$\text{Cu(BF}_4) + \text{(pyridyl-CH=CH-COOH)} \xrightarrow[\text{sealed tube}]{\text{vacuum}} [\text{Cu(pyridyl-CH=CH-COO)}]_n \quad (23)$$

$$\text{Cu(BF}_4) + \text{(pyridyl-CH=CH-COOH)} \xrightarrow[\text{sealed tube}]{\text{vacuum}} [\text{Cu(pyridyl-CH=CH-COO)}]_n \quad (24)$$

(a)

(b)

Figure 25. An asymetry unit of complex [(3-pyridylacrylicacid)Cu(I)]$_n$ (a) and {[(2-pyridylacrylic acid)Cu(I)]·(H$_2$O)}$_n$ (b).
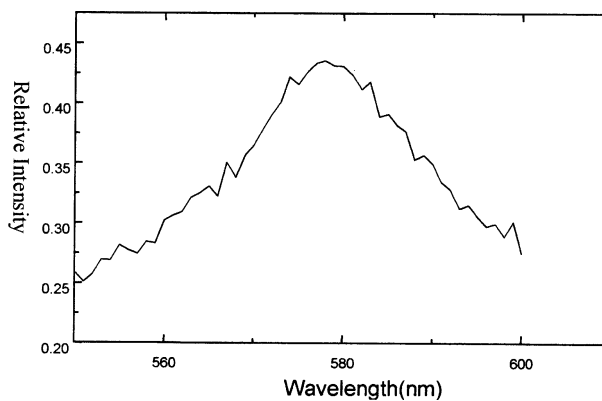
Figure 26. Fluorescent emission spectrum of [(3-pyridylacrylic-acid)Cu(I)]$_n$ and {[(2-pyridylacrylic acid)Cu(I)]·(H$_2$O)}n in the solid state at room temperature.

ture of these complexes suggested that σ-bonding between the cuprous ion and the coordinated olefin is the dominant interaction. This would account, at least in part, for the observed decrease in biological activity relative to ethylene for olefins with electron-withdrawing groups. Steric interactions with other metal ligands would be expected to impact on the olefin coordination in tetrahedral complexes. This may explain why biological activity is reduced with increasing size of the olefin. It has been found that activity decreases from ethylene, propylene, 1-butene, 2-butene.
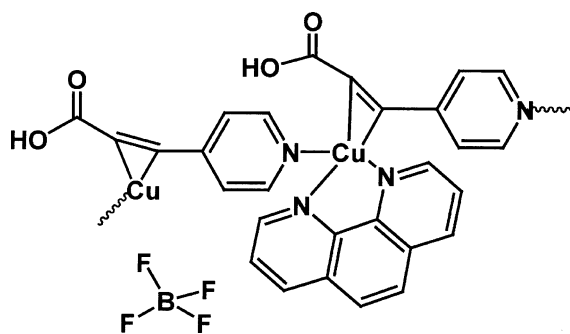

(25)

(26)

(27)

(28)
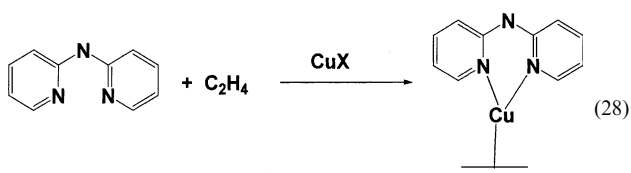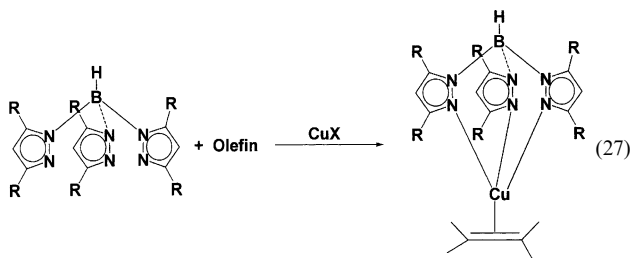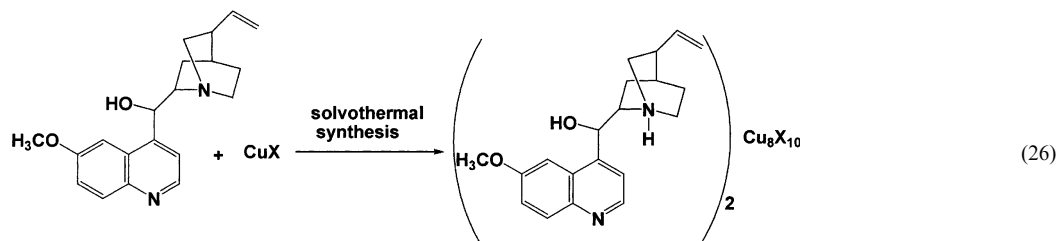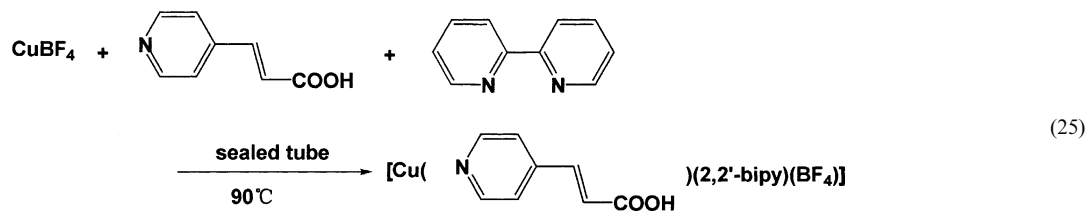
Figure 27. The asymmetric unit of {[(2,2'-bipyridine)(4-pyridylacrilic acid)Cu(I)](BF$_4$)}$_n$.

Figure 28. Fluorescent emission spectrum of {[(2,2'-bipyridine)(4-pyridylacrilic acid)Cu(I)](BF$_4$)}$_n$ in the solid state.

6. Conclusion

The interaction between oleofin and copper(I) centers results in complexes that exhibit a range of useful properties. As a consequence, both coordination and organometallic chemists are continuing to develope the rich and diverse chemistry in this system and offers a view to exploit such complexes in a range of applications. Although the area has progressed impressively over the past few decades, there remains wonderful opportunities for further development. Future work can be expected to yield novel olefin-copper(I) complexes that may have useful applications.
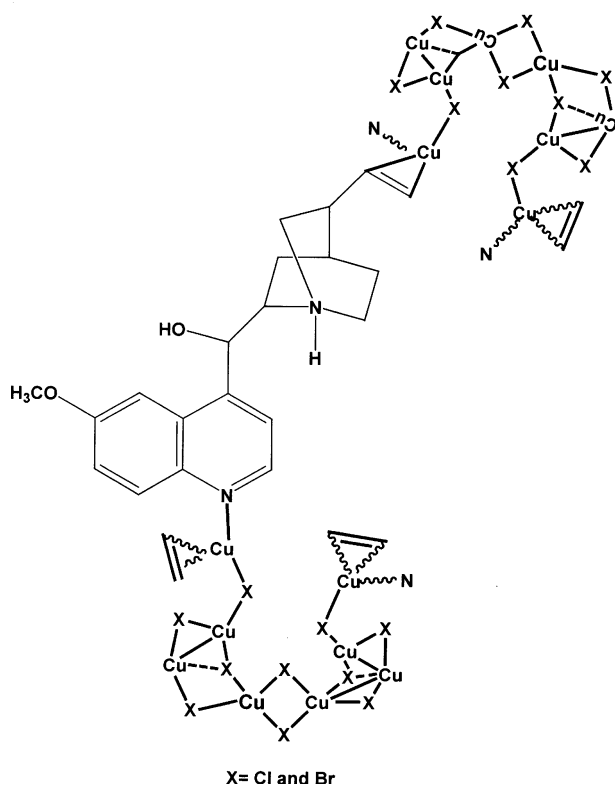

Figure 30. Electric hysteresis loop of Cu$_8$Cl$_{10}$(HQuinine)$_2$ in the form of a pellet, obtained in Virtual Ground Mode at room temperature.

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X= Cl and Br

Figure 29. An asymmetry unit of the complex Cu$_8$Cl$_{10}$(HQuinine)$_2$.

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