Inorganica Chimica Acta 362 (2009) 3507–3512

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Copper(I)-imine complexes: Synthesis and catalytic activity in olefin cyclopropanation

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ARTICLE INFO

Article history:
Received 2 December 2008
Received in revised form 16 March 2009
Accepted 24 March 2009
Available online 31 March 2009

Keywords:
Copper
Cyclopropanation
Imines
Homogeneous catalysis

ABSTRACT

Different imine-type ligands, prepared by the condensation of anilines or of α-methylbenzylamine with 2-pyridinecarboxaldehyde (pyim^{1,2}) or 2-quinolinecarboxaldehyde (quim^{1,2}) were prepared. These species act as *N,N′*-bidentate, chelating ligands upon coordination to Cu(I): treatment of [Cu(PPh$_3$)$_3$Cl] with an equimolar amount of the ligands resulted in the displacement of two molecules of PPh$_3$, giving rise to the formation of [Cu(pyim^{1,2})(PPh$_3$)Cl] (**1**–**2**) and [Cu(quim^{1,2})(PPh$_3$)Cl] (**3**–**4**), respectively. The copper derivatives **1**–**4** proved to be highly active catalysts in olefin cyclopropanation in the presence of ethyl diazoacetate, even using deactivated olefins (namely, 2-cyclohexen-1-one) as substrate. The X-ray structure of complex **2**, [Cu(pyim^2)(PPh$_3$)Cl], is also reported.

1. Introduction

Transition metal complexes-catalyzed cyclopropanation of alkenes has attracted enormous research interest [1]. In fact, cyclopropanes are versatile intermediates that can be converted into a variety of useful products by cleavage of the strained three-membered ring [2]. Moreover, the occurrence in nature of molecules presenting interesting physiological properties and containing the cyclopropane moiety [3] is a continuous stimulus to develop new synthetic routes to functionalized cyclopropanes. One of the most effective methods to convert olefins into the corresponding cyclopropane derivatives is the metal-assisted decomposition of diazocompounds [4]. Among the others, copper complexes cover a crucial role in this field [5] and both experimental [6] and theoretical [7] studies have been accomplished in order to elucidate the mechanism of olefin cyclopropanation promoted by Cu-based catalysts. A large variety of sp^2-nitrogen based ligands, such as C_2-symmetric semicorrins [8], bis(oxazolines) [9], bipyridines [10], polypyrazolylborates [11] and diiminophosphoranes [12], have been used with the aim of enhancing the selectivity. Recently, high enantioselectivities were reached with binaphthyldiimines [13] and chiral bispidines [14]. We previously reported on copper(I) species containing pyrazolate [15] or triazolate [16] bridging ligands, which proved to be extremely selective towards the formation of the *trans* isomer in both terminal and internal olefin cyclopropanation. Here we report on the synthesis and spectroscopic characterization of the [Cu(pyim^{1,2})(PPh$_3$)Cl] (**1**–**2**) and [Cu(quim^{1,2})(PPh$_3$)Cl] (**3**–**4**) complexes, obtained by reacting [Cu(PPh$_3$)$_3$Cl] with different imines, containing a pyridine (pyim$^{1-2}$) or a quinoline (quim$^{1-2}$) core (Chart 1), and coordinating as neutral, bidentate ligands. These compounds showed high activity and acceptable diastereoselectivity in the conversion of terminal and internal olefins into cyclopropanes. Moreover, they proved to be highly active towards a deactivated substrate like 2-cyclohexen-1-one. Finally, the X-ray crystal structure of compound **2**, [Cu(pyim^2)(PPh$_3$)Cl], is described.

2. Experimental

2.1. General procedures

All reactions were carried out under purified nitrogen using standard Schlenk techniques. The solvents were dried and distilled according to standard procedures prior to use. Alkenes employed in the catalytic reactions were taken from new bottles kept at −20 °C and their purity grade was confirmed by GC–MS control analysis. Ethyl diazoacetate, 2-pyridinecarboxaldehyde, 6-methylpyridine-2-carboxaldehyde, 2-quinolinecarboxaldehyde, 4-chloroaniline, *p*-toluidine, (rac)α-methylbenzylamine (Aldrich) were used as purchased. [Cu(PPh$_3$)$_3$Cl] was prepared as reported in the literature [17].

Infrared spectra were recorded on a Shimadzu Prestige 21 FTIR, NMR spectra were acquired on a Bruker 400 Avance instrument, elemental analyses were obtained with a Perkin–Elmer CHN Analyser 2400 Series II. Quantitative analyses of products were

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doi:10.1016/j.ica.2009.03.038

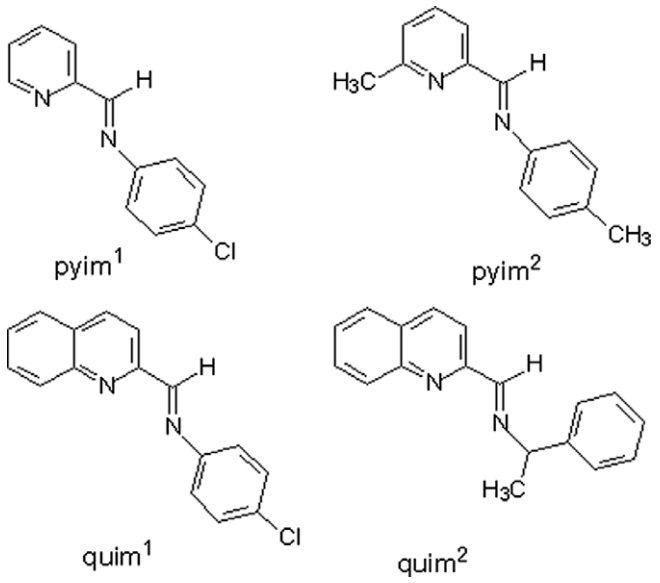


Chart 1.

performed on a Shimadzu GC-17A gas chromatograph with a PS225 capillary column (25 m, 0.25 mm) equipped with a QP5000 mass selective detector.

2.2. Synthesis of pyim[1]

To a solution of 2.25 g (21 mmol) of 2-pyridinecarboxaldehyde in 10 ml of methanol, 2.95 g (23 mmol) of 4-chloroaniline were added. The solution was stirred at 40 °C for 8 h, then it was reduced to half the volume and chilled in an ice-bath. A yellow solid was formed, which was filtered and dried in vacuum. Yield: 78%.

^{1}H NMR ($CDCl_3$, RT): 7.23 (d, 2H, *J* = 6.6 Hz), 7.37 (d, 2H, *J* = 6.7 Hz), 7.38 (t, 1H, *J* = 5.0 Hz), 7.81 (t, 1H, *J* = 7.7 Hz), 8.18 (d, 1H, *J* = 7.9 Hz), 8.58 (s, 1H, *H*C=N), 8.72 (d, 1H, *J* = 4.7 Hz). ^{13}C NMR ($CDCl_3$, RT): 121.50, 123.71, 125.08, 129.16, 131.37, 137.48, 139.45, 151.12, 152.36, 162.02, 162.65 (H*C*=N). *Anal.* Calc. for $C_{12}H_9ClN_2$: C, 66.52; H, 4.19; N, 12.93. Found: C, 66.39; H, 3.97; N, 12.79%.

2.3. Synthesis of pyim[2]

To a solution of 0.50 g (4.13 mmol) of 6-methylpyridine-2-carboxaldehyde in 10 ml of ethanol, 0.48 g (4.48 mol) of *p*-toluidine was added. The solution was stirred at 80 °C for 6 h, then it was reduced to half the volume and a yellow solid formed. It was filtered and dried in vacuum. Yield: 81%.

^{1}H NMR ($CDCl_3$, RT): 2.38 (s, 3H), 2.64 (s, 3H), 7.21 (d, 1H, *J* = 7.6 Hz), 7.23 (d, 2H, *J* = 8.6 Hz), 7.25 (d, 2H, *J* = 8.7 Hz), 7.68 (t, 1H, *J* = 7.7 Hz), 8.02 (d, 1H, *J* = 7.7 Hz), 8.62 (s, 1H, *H*C=N). ^{13}C NMR ($CDCl_3$, RT): 21.46 (*C*H$_3$), 24.78 (*C*H$_3$), 119.31, 121.57, 125.09, 130.22, 137.02, 137.25, 148.85, 154.60, 158.76, 160.36 (H*C*=N). *Anal.* Calc. for $C_{14}H_{14}N_2$: C, 79.67; H, 6.79; N, 13.32. Found: C, 79.95; H, 6.72; N, 13.33%.

2.4. Synthesis of quim[1]

To a solution of 0.50 g (3.18 mmol) of 2-quinolinecarboxaldehyde in 10 ml of toluene, 0.37 g (3.45 mol) of *p*-toluidine were added. The solution was stirred at 70 °C for 8 h, during which time a yellow solid formed. It was filtered and dried in vacuum. Yield: 88%.

^{1}H NMR ($CDCl_3$, RT): 2.42 (s, 3H), 7.27 (d, 2H, *J* = 8.0 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.62 (t, 1H, *J* = 7.5 Hz), 7.79 (t, 1H, *J* = 7.6 Hz), 7.89 (d, 1H, *J* = 8.1 Hz), 8.19 (d, 1H, *J* = 8.5 Hz), 8.27 (d, 1H, *J* = 8.6 Hz), 8.39 (d, 1H, *J* = 8.6 Hz), 8.84 (s, 1H, *H*C=N). ^{13}C NMR ($CDCl_3$, RT): 20.66 (CH_3), 118.59, 120.56, 126.90, 127.48, 127.83, 129.50, 129.75, 130.13, 131.90, 136.77, 144.99, 147.79, 154.51, 163.67 (H*C*=N). *Anal.* Calc. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.60; H, 5.65; N, 11.29%.

2.5. Synthesis of quim[2]

To a solution of 0.50 g (3.18 mmol) of 2-quinolinecarboxaldehyde in 10 ml of toluene, 0.42 g (3.47 mol) of α-methylbenzylamine were added. The solution was stirred at 70 °C for 8 h, then the solvent was removed under reduced pressure and the crude product suspended in 2 ml of methanol. An orange solid was isolated after filtration. Yield: 72%.

^{1}H NMR ($CDCl_3$, RT): 1.68 (d, 3H, *J* = 6.6 Hz), 4.74 (q, 1H, *J* = 6.6 Hz), 7.29 (t, 1H, *J* = 8.1 Hz), 7.39 (t, 2H, *J* = 7.4 Hz), 7.50 (d, 2H, *J* = 7.6 Hz), 7.61 (t, 1H, *J* = 7.5 Hz), 7.76 (t, 1H, *J* = 7.6 Hz), 7.86 (d, 1H, *J* = 8.1 Hz), 8.14 (d, 1H, *J* = 8.5 Hz), 8.21 (d, 1H, *J* = 8.5 Hz), 8.29 (d, 1H, *J* = 8.5 Hz), 8.66 (s, 1H, *H*C=N). ^{13}C NMR ($CDCl_3$, RT): 24.43 (CH_3), 54.76 (CH), 120.61, 125.67, 126.77, 126.84, 127.80, 128.39, 128.53, 129.54, 129.70, 136.72, 143.97, 147.84, 157.84, 162.96 (H*C*=N). *Anal.* Calc. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.50; H, 6.22; N, 10.74%.

2.6. Synthesis of copper(I) complexes ***1*–*4***

In a typical experiment, a suspension of 0.50 g (0.565 mmol) of $[Cu(PPh_3)_3Cl]$ in diethylether was treated with an equimolar amount of the corresponding imine. The resulting suspension was stirred at room temperature for 18 h, after which time a brick-red precipitate formed. The solid was filtered off and dried in vacuum. Yield: 77% (**1**); 81% (**2**); 86% (**3**); 91% (**4**).

[Cu(pyim[1])(PPh$_3$)Cl], ***1****:* ^{1}H NMR (CD_2Cl_2, RT): 7.31–7.44 (m, 19H), 7.61 (t, 1H, *J* = 6.2 Hz), 8.01 (t, 1H, *J* = 6.7 Hz), 8.14 (d, 1H, *J* = 5.9 Hz), 8.68 (s, 1H, *H*C = N), 8.70 (d, 1H, *J* = 4.9 Hz). ^{13}C NMR (CD_2Cl_2, RT): 120.87, 123.22, 124.92, 128.16, 128.35, 129.54, 130.96, 133.49, 137.28, 137.56, 139.12, 150.85, 151.98, 161.38, 164.14 (H*C*=N). ^{31}P NMR (CD_2Cl_2, RT): −4.08 ppm (s). *Anal.* Calc. for $C_{30}H_{24}N_2Cl_2PCu$: C, 62.34; H, 4.19; N, 4.85. Found: C, 62.22; H, 4.31; N, 4.64%.

[Cu(pyim[2])(PPh$_3$)Cl], ***2****:* ^{1}H NMR (CD_2Cl_2, RT): 2.38 (s, 3H), 2.60 (s, 3H), 7.13 (d, 2H, *J* = 7.4 Hz), 7.23–7.34 (m, 17H), 7.48 (d, 1H, *J* = 5.6 Hz), 7.54 (d, 1H, *J* = 5.4 Hz), 7.75 (t, 1H, *J* = 5.5 Hz), 8.41 (s, 1H, *H*C=N). ^{13}C NMR (CD_2Cl_2, RT): 20.46 (*C*H$_3$), 25.98 (*C*H$_3$), 118.73, 120.38, 124.76, 128.12, 128.38, 131.11, 133.43, 136.69, 137.22, 137.87, 147.99, 155.10, 158.01, 162.49 (H*C*=N). ^{31}P NMR (CD_2Cl_2, RT): −4.30 ppm (s). *Anal.* Calc. for $C_{32}H_{29}N_2ClPCu$: C, 67.24; H, 5.11; N, 4.90. Found: C, 67.09; H, 5.28; N, 4.77%.

Brick-red crystals suitable for X-ray analysis of species **2** were obtained by slow diffusion of diethylether into a dichloromethane solution of the complex.

[Cu(quim[1])(PPh$_3$)Cl], ***3****:* ^{1}H NMR (CD_2Cl_2, RT): 2.39 (s, 3H), 7.16 (d, 2H, *J* = 8.1 Hz), 7.22 (t, 1H, *J* = 7.4 Hz), 7.28–7.37 (m, 16H), 7.53–7.56 (m, 4H), 7.58 (d, 1H, *J* = 7.6 Hz), 8.27 (d, 1H, *J* = 8.3 Hz), 8.65 (s, 1H, *H*C=N). ^{13}C NMR (CD_2Cl_2, RT): 19.71 (CH_3), 117.99, 121.06, 126.31, 126.76, 127.43, 128.09, 128.31, 129.15, 129.39, 130.81, 132.07, 133.51, 136.12, 137.18, 144.74, 146.89, 156.62, 165.07 (H*C*=N). ^{31}P NMR (CD_2Cl_2, RT): −5.56 ppm (s). *Anal.* Calc. for $C_{35}H_{29}N_2ClPCu$ (**3**): C, 69.19; H, 4.81; N, 4.61. Found: C, 69.57; H, 4.98; N, 4.20%.

[Cu(quim[2])(PPh$_3$)Cl], ***4****:* ^{1}H NMR (CD_2Cl_2, RT): 1.81 (d, 3H, *J* = 6.7 Hz), 4.91 (q, 1H, *J* = 6.6 Hz), 7.24–7.39 (m, 20H), 7.52 (d, 1H, *J* = 6.3 Hz), 7.65 (t, 1H, *J* = 6.8 Hz), 7.79 (t, 1H, *J* = 6.4 Hz), 7.84

(d, 1H, J = 5.8 Hz), 8.24 (d, 1H, J = 7.9 Hz), 8.33 (d, 1H, J = 6.9 Hz), 8.48 (s, 1H, *HC*=N). ^{13}C NMR (CD_2Cl_2, RT): 20.83 (CH_3), 58.90 (CH), 119.82, 125.12, 126.88, 127.65, 127.92, 128.21, 128.38, 128.44, 128.47, 129.50, 129.85, 133.63, 135.30, 137.20, 144.17, 145.13, 158.91, 164.70 (HC=N). ^{31}P NMR (CD_2Cl_2, RT): −5.52 ppm (s). *Anal.* Calc. for $C_{36}H_{31}N_2ClPCu$ (**4**): C, 69.56; H, 5.03; N, 4.51. Found: C, 69.85; H, 4.97; N, 4.33%.

2.7. Olefin cyclopropanation

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

2.8. X-ray crystallography

The single crystal X-ray diffraction data for **2** were acquired on an Enraf Nonius CAD-4 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A brick-red platelet single crystal of approximate 0.25 × 0.25 × 0.10 mm dimensions was mounted on top of a goniometer head. The unit cell was determined on the basis of the setting angles of 25 randomly distributed reflections in the 9.0° < θ < 11.0° range. The data collection was performed in the 3.0° < θ < 25.3° range by applying the ω-scan mode [$\Delta\omega = 1.4 + (0.35\tan\theta)$]. A total of 2604 unique and 2418 observed [$I > 2\sigma I$)] reflections were collected [R_{int} = 0.012, $R(\sigma)$ = 0.020], and used for the structure solution and the structure refinement (against 334 parameters).The data were corrected for absorption and Lorenz-polarization effects. The structure was solved by direct methods [18] and refined by full-matrix least-squares on F^2 [19]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were made riding their parent atoms with an isotropic temperature factor 1.2 times that of their parent atoms. Details on the crystal data and on the refinement results are collected in Table 1.

Table 1
Crystallographic data and refinement parameters for species **2**.

Formula	$C_{32}H_{29}CuN_2ClP$
Formula weight (g mol^{-1})	571.53
T (K)	298(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	8.712(3)
b (Å)	14.877(8)
c (Å)	10.612(3)
β (°)	87.20(2)
V (Å^3)	1383(1)
Z	2
ρ_{calc} (Mg m^{-3})	1.382
μ (Mo Kα, mm^{-1})	0.974
F(000)	592
Sample size (mm^3)	0.25 × 0.25 × 0.10
θ range (°)	3.0–25.3
hkl range	$-10 \leqslant h \leqslant 10$ $0 \leqslant k \leqslant 17$ $0 \leqslant l \leqslant 12$
Unique, observed reflections	2604, 2418
R_{int} = 0.012, $R(\sigma)$	0.012, 0.0
Data, restrains, parameters	2604, 0, 334
$\chi(F^2)$[a]	1.070
$R(F)$, $wR(F^2)$ for $I > 2\sigma(I)$[a]	0.025, 0.059
$R(F)$, $wR(F^2)$ for all reflections[a]	0.030, 0.061
Highest peak, deepest hole (e Å^{-3})	0.31, −0.16

[a] $\chi(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ where n is the number of reflections, p the number of parameters and $w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 1.88P]$ with $P = (F_o^2 + 2F_c^2)/3$. $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

3. Results and discussion

3.1. Synthesis of ligands

When 2-pyridinecarboxaldehyde or 6-methylpyridine-2-carboxaldehyde was treated with a slight excess of the appropriate amine, the formation of the corresponding ligands pyim$^{1-2}$ took place (Scheme 1). The reaction was performed in alcohol (methanol or ethanol) and was monitored via ^{1}H NMR. Actually, the occurrence of the desired product was confirmed by the disappearing of the signal associated to the aldehyde and the parallel appearance of the typical imine resonance, at about 8–9 ppm. The infrared spectra (nujol mull) of the ligands showed the expected absorptions in the range 1550–1690 cm^{-1} usually attributed to the C=N stretching.

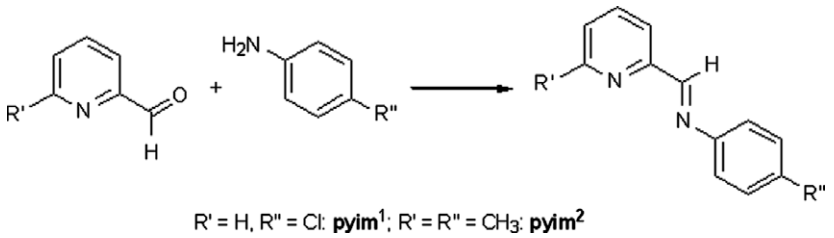
Similarly, when 2-quinolinecarboxaldehyde was treated with a slight excess of *p*-toluidine or α-methylbenzylamine in toluene, it was possible to isolate pure, crystalline yellow (quim^1) or orange (quim^2) imines, as confirmed by spectroscopic data (Scheme 2). Indeed, the formation of the C=N iminic moiety was proved both by the resonances at 8.84 and 8.66 ppm in the ^{1}H NMR ($CDCl_3$) and by the stretching at about 1600 cm^{-1} in the infrared spectra of the solids.

3.2. Synthesis of copper(I) complexes

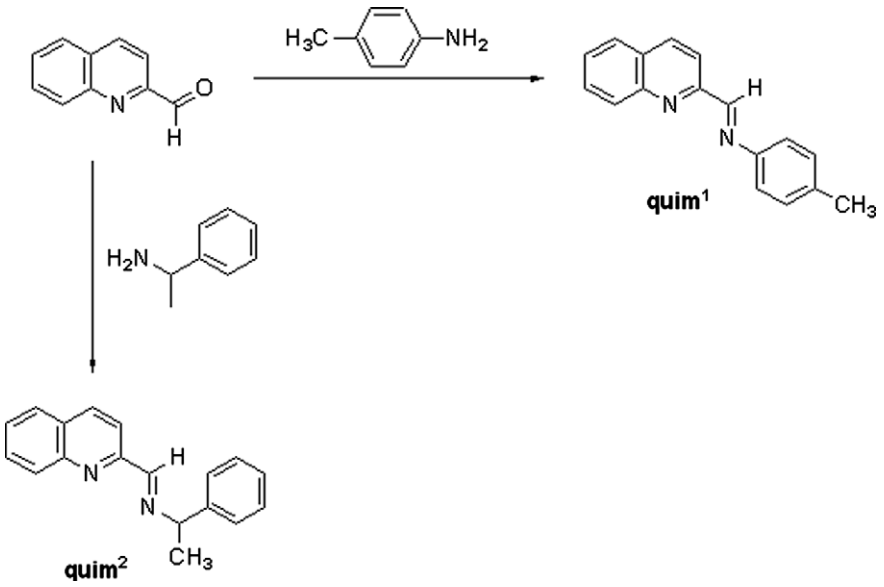
Treatment of a suspension of $[Cu(PPh_3)_3Cl]$ in diethylether with an equimolar amount of one of the previously isolated iminic ligands (pyim$^{1-2}$–quim$^{1-2}$), at room temperature, resulted in the formation of an orange suspension, from which it was possible to isolate a brick-red solid (species **1**–**4**, respectively). The relatively long reaction time (18 h) was due to the slow substitution of two molecules of triphenylphosphine by the ligand in the heterogeneous system. However, the high solubility of PPh_3 in diethylether favoured its dissociation, and the subsequent replacement by the imine. On the basis of spectroscopic data and elemental analysis, the copper(I) species **1**–**4** were formulated as [Cu(N–N)(PPh_3)Cl] (where N–N represents the chelating imine ligand). The presence of a remaining PPh_3 molecule in **1**–**4** was confirmed by their ^{31}P NMR spectra, showing a single resonance in the range between −5.56 and −4.08 ppm (see Section 2 for details). As described for previously reported complexes of general formula $[M_2(CO)_6(\alpha\text{-diimine})]$ (M = Fe, Ru; α-diimine = pyridine-2-carbaldehyde-imines) [20], the pyim$^{1-2}$ and quim$^{1-2}$ ligands in compounds **1**–**4** reasonably chelate the copper(I) centre by means of the two nitrogen donor atoms (Scheme 3). These features find proper support in the crystal structure characterization of complex **2** (see below).

3.3. Crystal structure of [Cu(pyim^2)(PPh_3)Cl], **2**

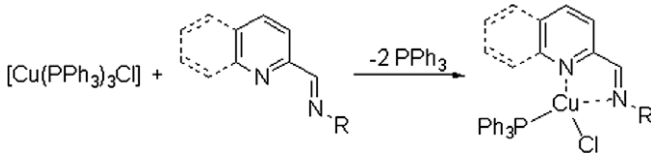
Compound **2** crystallizes in the monoclinic $P2_1$ space group and is composed by mononuclear complexes of [Cu(pyim^2)(PPh_3)Cl] formula. In each complex, the Cu(I) metal centre possesses a slightly distorted tetrahedral geometry of the $CuClN_2P$ kind. The two nitrogen atoms of the coordination sphere belong to one pyim^2 ligand, exhibiting a *N*,*N*′-endo-bidentate coordination mode. The metal ion coordination is completed by one chlorine atom and by



Scheme 1. Synthesis of ligands pyim[1–2].



Scheme 2. Synthesis of ligands quim[1–2].



Scheme 3. Formation of the copper(I) complexes **1**–**4**.

Table 2
Significant bond distances (Å) and angles (°) at the metal centre in species **2**.

Cu–Cl	2.310(1)
Cu–N	2.101(3), 2.134(3)
Cu–P	2.204(1)
Cl–Cu–N	107.53(8), 109.34(8)
Cl–Cu–P	111.78(4)
N–Cu–N	78.9(1)
N–Cu–P	118.35(8), 126.15(8)

the phosphorous atom of one PPh_3 ligand. A search through the Cambridge Structural Database (Version August 2008) evidenced that only a few Cu(I) monomeric complexes possessing a *N*,*N*′-chelating ligand and showing, on the whole, a $CuClN_2P$ coordination, have been structurally characterized. As expected, their bond distances and angles at the metal are nicely met by those present in species **2**. Significant bond distances and angles at the metal centre are gathered in Table 2 (see Fig. 1).

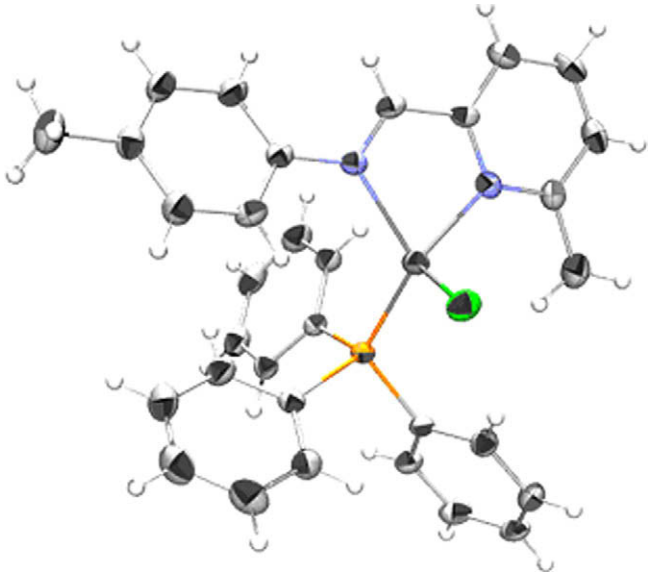


Fig. 1. Ortep representation (at a 20% probability level) of the mononuclear complex present in the crystal structure of **2**. Carbon, grey; hydrogen, light grey; chlorine, light green; copper, magenta; nitrogen, light blue; phosphorous, orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4. Cyclopropanation reactions

When complexes **1**–**4** were dissolved in dichloromethane under inert atmosphere, in the presence of ethyl diazoacetate (EDA), the

conversion of olefins into the corresponding cyclopropane derivatives took place. Together with the desired products, diethyl maleate and diethyl fumarate, deriving from EDA self-coupling [21], were always detected. In order to minimize these side-reactions, addition of a large excess of olefin (namely, a Cu:EDA:olefin = 1:100:250 molar ratio) was employed. As reported in Table 3, the yields in cyclopropane products were excellent in all the runs performed. Complexes **1**–**4** showed to be highly active catalysts in the cyclopropanation of both terminal and internal olefins. As reported in the literature, in the conversion of styrene into the corresponding cyclopropane esters, most of the copper(I) catalysts provided the *trans* isomer as the main product [22], the common *trans*:*cis* ratio ranging from 50:50 to 75:25. Increasing the size of R on $N_2CHCOOR$ enhances enantiocontrol, while the diastereoselectivity is not usually affected by steric effects, except when very bulky substituents are used, as in the case of 2,6-di-*tert*-butyl-4-methylphenyl (BDA) diazoacetate [23]. Species **1**–**4** confirmed this trend in the catalytic cyclopropanation of styrene (Table 3, entries 1–4), in accord with some previously reported Cu(Schiff-base) catalysts [24]. A similar tendency was noted using different terminal olefins, such as α-methylstyrene or 1-hexene, as substrates (Table 3, entries 5–12).

Compounds **1**–**4** exhibited to be active in internal olefin cyclopropanation as well. In fact, the conversion of cyclohexene into its corresponding cyclopropylic derivatives took place in high yields (Table 3, entries 13–16).

Moreover, as reported by Zhang and co-workers [25], cyclopropanes containing electron-withdrawing groups have shown to be valuable synthetic intermediates for various applications. According to this, the cyclopropanation of 2-cyclohexen-1-one (presenting a deactivated C=C bond because of the presence of the carbonyl group) was also investigated. All catalysts **1**–**4** provided high conversion yields, together with slightly better diastereoselectivities when compared to other substrates.

Unfortunately, despite their elevated catalytic activity, complexes **1**–**4** showed an ordinary selectivity when compared to our previously reported copper(I) species [15,16]. This is probably attributable to the absence of steric effects: the first step after dissolution in CH_2Cl_2 is the dissociation of the triphenylphosphine (as evidenced by ^{31}P NMR), which reduces the steric hindrance around the metal centre. The imine ligands alone cannot force the substrates to coordinate to copper with a favoured approaching direction, thus reducing diastereoselectivity. To improve the selectivity, the synthesis of some new imine-type ligands and corresponding copper(I) complexes is under investigation.

Table 3
Catalytic cyclopropanation of olefins mediated by complexes **1**–**4**.[a]

Entry	Catalyst	Olefin	Yield (%)	*trans*:*cis* ratio
1	**1**	styrene	80	55:45
2	**2**		81	58:42
3	**3**		77	60:40
4	**4**		88	55:45
5	**1**	α-	91	50:50
6	**2**	methylstyrene	87	55:45
7	**3**		89	55:45
8	**4**		94	50:50
9	**1**	1-hexene	82	50:50
10	**2**		78	60:40
11	**3**		76	50:50
12	**4**		85	55:45
13	**1**	cyclohexene	88	55:45
14	**2**		85	65:35
15	**3**		84	60:40
16	**4**		92	60:40
17	**1**	2-cyclohexen-	90	58:42
18	**2**	1-one	87	70:30
19	**3**		88	65:35
20	**4**		91	68:32

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

4. Conclusions

The syntheses and characterization of copper(I) complexes containing chelating imines have been reported. Complexes **1**–**4**, of general formula [Cu(N–N)(PPh_3)Cl] (where N–N represents the bidentate imine), proved to be active catalysts in olefin cyclopropanation in the presence of EDA, under very mild conditions. These compounds also converted internal deactivated olefins such as 2-cyclohexen-1-one into the corresponding esters derivatives. The X-ray crystal structure of one of these copper(I) species, [Cu(pyim^2)(PPh_3)Cl], (**2**) (pyim^2 = [1-(6-methyl-pyridin-2-yl)-methylene]-*p*-tolyl-amine) has also been described.

Finally, the preliminary results achieved using complex **4** as catalyst, encourage us to investigate the potential enantioselectivity of similar species containing the imines obtained by means of enantiopure α-benzylamine.

Appendix A. Supplementary data

CCDC 710251 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.03.038.

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