Inorganica Chimica Acta 383 (2012) 105–111

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

Investigation of the structure and catalytic activity in olefin cyclopropanation of neutral and cationic dicopper complexes of 3,5-bis(pyridinylimino)benzoic acid

Dimitrios Tzimopoulos [a], Stefano Brenna [b], Agnieszka Czapik [c], Maria Gdaniec [c,*], Attilio Ardizzoia [b,*], Pericles D. Akrivos [a,*]

[a] Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of Inorganic Chemistry, P.O. Box 135, 541 24 Thessaloniki, Greece
[b] Dipartimento di Scienze Chimiche ed Ambientali, Universita' degli Studi dell'Insubria, Via Valleggio 11, 22100 Como, Italy
[c] Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60 780 Poznań, Poland

ARTICLE INFO

Article history:
Received 6 August 2011
Received in revised form 15 October 2011
Accepted 21 October 2011
Available online 29 October 2011

Keywords:
Copper complexes
Crystal structure
Catalytic cyclopropanation
Iminopyridine complexes

ABSTRACT

Three neutral and one cationic copper(I) complexes with 3,5-bis(pyridinylimino)benzoic acid are synthesized and characterized in solution and in the solid state by a variety of spectroscopic techniques and X-ray crystallography. The compounds are monomeric in nature possessing two Cu(I) centers each coordinated to one of the two diimine sites of the ligand. The chromophores are either N_2PX, where X is a halide (Cl, Br or I) for the neutral or N_2P_2 for the ionic compounds, respectively. The phosphorus donor is triphenylphosphane. The crystal structures of the isostructural bromido and iodido compounds are solved and discussed. The compounds are tested for their catalytic activity in olefin cyclopropanation reactions by means of ethyl diazoacetate decomposition and prove to be moderately active with the ionic one being the most active and the most promising since for cyclohexene it reveals a considerable diastereoselectivity and a 90:10 *exo*:*endo* ratio of the final product.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Transition metal catalyzed C–C bond-forming reactions always represent a primary goal for organometallic chemists [1–7], and among the others cyclopropanation of alkenes has attracted enormous research interest due to the importance of cyclopropanes as starting materials or intermediates in a wide range of organic synthetic reactions [8]. Thus, the search for new synthetic routes to functionalized cyclopropanes is a continuous stimulus, especially as regards the synthesis of new transition metal-based catalytic systems. Actually, one of the most effective method to convert olefins into the corresponding cyclopropanes is the metal-assisted decomposition of diazocompounds [9–12] and very often the catalytic system incorporates copper because it offers, besides high efficiency [13,14], relatively low cost with respect to other second-row transition metals. Both experimental [15,16] and theoretical [17–21] studies have been accomplished in order to elucidate the mechanism of olefin cyclopropanation promoted by Cu-based catalysts and it is well known and established that the active catalyst is a Cu(I) system either introduced directly or formed *in situ* from an appropriate Cu(II) pre-catalyst [22].

A large variety of sp^2-nitrogen based ligands [23–28] have been used with the aim of enhancing the selectivity. Recently, high enantioselectivities were reached with binaphthyldiimines [29] and chiral bispidines [30]. Copper(I) species containing azolate bridging ligands [31,32] or imine-type ligands [33], which proved to be highly selective towards the formation of the *trans* isomer in both terminal and internal olefin cyclopropanation, were also recently reported by some of us.

Herein we report on the synthesis and full characterization of new bisimine copper(I) complexes containing 3,5-bis(pyridinylimino)benzoic acid as building block (Fig. 1). All these compounds proved to be active catalysts in olefin cyclopropanation reactions, in mild conditions. Specially, the cationic species **4** demonstrated to be the most active among the series considered. Finally, the X-ray crystal structure of the iso-structural compounds **2** and **3** is reported.

2. Experimental

2.1. Reagents and methods

The starting reagents were obtained from ACROS and were used without any further purification. The solvents used were of reagent grade and were not subjected to any further drying process prior to their use. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240B elemental analyzer. Infrared spectra were

* Corresponding authors. Tel.: +30 2310997706; fax: +30 2310997738 (P.D. Akrivos).
E-mail addresses: magdan@amu.edu.pl (M. Gdaniec), attilio.ardizzoia@uninsubria.it (A. Ardizzoia), akrivos@chem.auth.gr (P.D. Akrivos).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.10.055

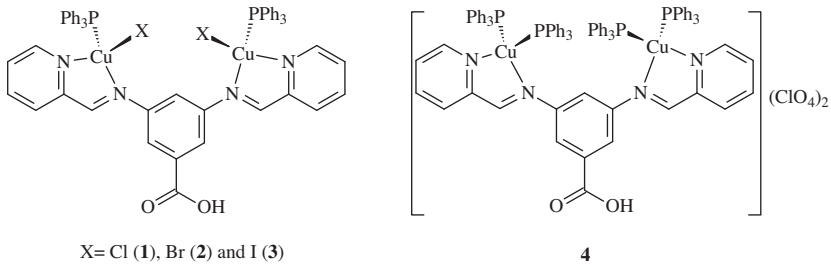

Fig. 1. Schematic representation of the studied compounds.

recorded in KBr pellets on a Perkin–Elmer Spectrum One FTIR spectrometer with a resolution of 2 cm^{-1} following the collection of 16 scans over the range 4000–360 cm^{-1}. Solution NMR for ^1H and ^{13}C were measured at 300 and 75 MHz, respectively in $CDCl_3$ solutions on a Bruker 300 spectrometer using TMS as internal standard. Absorption spectra were recorded with a Perkin–Elmer Spectrum One spectrophotometer.

2.2. Synthesis of the compounds

The pyridinylimino substituted benzoic acids were synthesized according to literature method [34] with slight variations, which include the use of ethanol as the single solvent and without use of formic acid as catalyst. The compounds were identified by elemental analyses and IR spectra.

The copper precursor complexes $[Cu(MeCN)_4][ClO_4]$ and $[Cu(MeCN)_2(PPh_3)_2][ClO_4]$ were prepared according to literature methods [35,36].

2.3. Synthesis of complexes **1**–**3**

In a typical procedure, to a suspension of the appropriate copper(I) halide (1.0 mmol) in 10 mL of acetonitrile, an equimolar amount of triphenylphosphane was added, and the oligomeric $[CuX(PPh_3)]_n$ formed as a white precipitate. Then a suspension of the acid (1.0 mol) in dichloromethane (10 mL) was added and the resulting dark red solution was left stirring for 1 h at room temperature. The deposited precipitate was filtered and recrystallized from dichloromethane–diethylether. Samples for subsequent studies were obtained after prolonged stay under vacuum while crystals were deposited after slow evaporation of the solvent in the dark.

Complex ***1***: Yield: 82%. *Anal.* Calc. for $C_{55}H_{44}Cl_2Cu_2N_4O_2P_2$: C, 56.71; H, 5.95; N, 6.01. Found: C, 56.60; H, 5.82; N, 6.06%. IR (KBr, cm^{-1}): 3422 (O–H), 1636 (C=N), 1715, 1434 (COO). ^1H NMR (DMSO-d_6, δ): 12.01 (COOH), 8.87 (CH=N), 7.66 (o-C_6H_3), 7.16 (p-C_6H_3). ^{13}C-NMR (DMSO-d_6, δ): 166.4 (COOH), 160.8 (CH=N), 132.8 (C–COOH). ^{31}P NMR (DMSO-d_6, δ): −3.80 ppm (s).

Complex ***2***: Yield: 86%. *Anal.* Calc. for $C_{55}H_{44}Cl_2Cu_2N_4O_2P_2$: C, 51.77; H, 5.43; N, 5.49. Found: C, 51.60; H, 5.30; N, 5.56%. IR (KBr, cm^{-1}): 3432 (O–H), 1636 (C=N), 1718, 1435 (COO). ^1H NMR (DMSO-d_6, δ): 11.14 (COOH), 8.93 (CH=N), 7.55 (o-C_6H_3), 7.03 (p-C_6H_3). ^{13}C NMR (DMSO-d_6, δ): 166.1 (COOH), 159.8 (CH=N), 132.9 (C–COOH).. ^{31}P NMR (DMSO-d_6, RT): −3.78 ppm (s).

Complex ***3***: Yield: 88%. *Anal.* Calc. for $C_{55}H_{44}Cl_2Cu_2N_4O_2P_2$: C, 47.41; H, 4.97; N, 5.03. Found: C, 47.52; H, 4.82; N, 4.98%. IR (KBr, cm^{-1}): 3442 (O–H), 1636 (C=N), 1700, 1435 (COO). ^1H NMR (DMSO-d_6, δ): 11.86 (COOH), 9.03 (CH=N), 7.56 (o-C_6H_3), 7.08 (p-C_6H_3). ^{13}C NMR (DMSO-d_6, δ): 165.49 (COOH), 158.9 (CH=N), 132.9 (C–COOH). ^{31}P NMR (DMSO-d_6, RT): −3.87 ppm (s).

2.4. Synthesis of complex **4**

The synthetic procedure was identical to the above except that 2.0 mmol of $[Cu(MeCN)_2(PPh_3)_2][ClO_4]$ were used. Yield: 78%. *Anal.* Calc. for $C_{91}H_{74}Cl_2Cu_2N_4O_{10}P_4$: C, 64.09; H, 4.37; N, 3.29. Found: C, 63.84; H, 4.30; N, 3.20%. IR (KBr, cm^{-1}): 3442 (O–H), 1618 (C=N), 1724, 1435 (COO). ^1H NMR (DMSO-d_6, δ): 11.87 (COOH), 9.10 (CH=N), 7.69 (o-C_6H_3), 7.05 (p-C_6H_3). ^{13}C NMR (DMSO-d_6, δ): 165.2 (COOH), 162.2 (CH=N), 132.7 (C–COOH). ^{31}P NMR (DMSO-d_6, δ): 0.43 ppm (s).

2.5. Olefin cyclopropanation

In a standard experiment, to a solution of copper catalyst (0.006 mmol) and olefin (3 mmol) in dichloromethane (10 mL) at room temperature and under inert atmosphere, EDA (1.2 mmol) was added dropwise. 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 ^1H NMR and GC–MS. Quantitative analyses of products were performed on a Finningan Trace GC with a DB-5MS UI capillary column (30 m, 0.25 mm) equipped with a Finningan Trace MS.

2.6. X-ray crystal structure analysis

The crystal structures were determined using an Oxford Diffraction Xcalibur E diffractometer. Data collection and cell refinement were carried out with CRYSALIS PRO [37]; SHELX-97 programs [38] were used to solve and refine the structures. In the crystal structure of **2** it was not possible to model solvent molecules due to their extensive disorder. Since the solvent molecules are beyond the scope of

Table 1
Catalytic cyclopropanation of olefins mediated by copper complexes.[a]

Entry	Olefin	Catalyst	Yield (%)[b]	*cis*:*trans* ratio
1	styrene	**4**	78	32:68
2	styrene	**1**	62	31:69
3	styrene	**2**	63	31:69
4	styrene	**3**	46	30:70
5	styrene	**1**/Cl^-	<5	–
6	α-methylstyrene	**4**	75	44:56
7	1-octene	**4**	72	21:79
8	ethyl vinyl ether	**4**	69	26:74
9	cyclohexene	**4**	81	10:90[c]
10	2-cyclohexen-1-one	**4**	<5	-
11	*trans*-β-nitrostyrene	**4**	<5	-

[a] Reaction conditions: solvent CH_2Cl_2, 25 °C, Cu:EDA:olefin molar ratio 1:100:250.
[b] Based on EDA conversion into products.
[c] In this specific case, the diastereoselectivity is referred to *endo*:*exo* ratio.

this study, the SQUEEZE procedure implemented in PLATON [39] was used to remove solvent contribution to the structure factors. In the unit cell of **2** the solvent molecules are enclosed in centrosymmetric voids having the volume of 502 Å^3. In the crystal structure of **3** the solvent molecules, acetonitrile and five water molecules, are disordered and were refined with partial occupancies. The N atom of acetonitrile and water molecule O1W occupy the same position in which they accept hydrogen bond from the carboxylic group. In structures **2** and **3** the carbon bound hydrogen atoms were added in calculated positions and refined as riding on their carrier atoms. The carboxylic group H atoms were located in difference Fourier maps and in case of **2** refined in riding model approximation. In **3** the carboxylic H atom was freely refined. Positions of the H atoms from disordered solvent molecules were not determined. Some further details concerning crystal data and structure refinement are given in Table 2. Selected bond lengths and angles are listed in Table 3. Molecular graphics were generated with ORTEP-3 for Windows [40].

3. Results and discussion

3.1. Syntheses of complexes

When a suspension of the appropriate halide CuX (X = Cl, Br, I) in acetonitrile is treated with an equimolar amount of PPh_3, the precipitation of the white oligomeric $[CuX(PPh_3)]_n$ immediately occurs. This intermediate species can be easily converted into the desired dinuclear copper(I) complexes **1–3**, formulated as $[Cu_2X_2(PPh_3)_2(3,5\text{-pybac})]$ (3,5-pybac = 3,5-bis(pyridinylimino) benzoic acid ligand; **1**, X = Cl; **2**, X = Br; **3**, X = I), by addition of a dichloromethane suspension of the ligand. The work up of the resulting dark red solution allowed the isolation of complexes **1–3** as orange crystalline powders.

Compound **4** is prepared from a solution of $[Cu(MeCN)_2(PPh_3)_2][ClO_4]$ in dichloromethane, by replacement of the acetonitrile molecules with one equivalent of 3,5-bis(pyridinylimino)benzoic acid ligand.

Table 3
Selected bond lengths (Å) and angles (°).

*(a) Compound **2***	
Cu3–N3 2.0622(17)	Cu5–N5 2.0974(19)
Cu3–N33 2.0880(18)	Cu5–N53 2.0781(18)
Cu3–P3 2.1825(7)	Cu5–P5 2.1947(7)
Cu3–Br3 2.4123(4)	Cu5–Br5 2.4451(4)
N33–Cu3–N3 79.72(7)	N53–Cu5–N5 78.86(7)
N33–Cu3–P3 108.14(5)	N53–Cu5–P5 125.46(5)
N3–Cu3–P3 129.28(5)	N5–Cu5–P5 109.79(5)
N33–Cu3–Br3 108.99(5)	N53–Cu5–Br5 105.54(5)
N3–Cu3–Br3 111.67(5)	N5–Cu5–Br5 108.68(5)
P3–Cu3–Br3 112.27(2)	P5–Cu5–Br5 120.19(2)
*(b) Compound **3***	
Cu3–N3 2.062 (2)	Cu5–N5 2.093(2)
Cu3–N33 2.083(2)	Cu5- N53 2.075(2)
Cu3–P3 2.1895(9)	Cu5–P5 2.2074(9)
Cu3–I3 2.5765(4)	Cu5–I5 2.5955(4)
N33–Cu3–N3 80.05(9)	N53–Cu5–N5 78.97(9)
N33–Cu3–P3 109.34(7)	N53–Cu5–P5 126.48(8)
N3–Cu3–P3 130.36(7)	N5–Cu5–P5 110.35(7)
N33–Cu3–I3 109.46(7)	N53–Cu5–I5 109.52(8)
N3–Cu3–I3 111.36(6)	N5–Cu5–I5 108.39(6)
P3–Cu3–I3 110.58(3)	P5–Cu5–I5 115.91(3)

3.2. Spectroscopic investigation

The infrared spectra of the compounds are indicative of their stoichiometry. They all present the characteristic bands due to the hydroxyl group 3420–3440 cm^{-1} and the imine C=N bond in the region 1620–1635 cm^{-1}, respectively [41]. These values are very close to the ones observed for the free ligand (observed at 3410 and 1635 cm^{-1}, respectively) and indicate that the coordination is rather weak and occurs through the diimine site and not the carboxylic group. The asymmetric carboxylic band is observed in the region 1700–1724 cm^{-1} in a small margin around the value of 1704 realized for the free acid. For compound **4** there is observed a broad and featureless intense band with an approximate peak at 1094 cm^{-1} revealing that the perchlorate anion is not coordinated

Table 2
Crystallographic data and refinement details for **2** and **3**.

	2	**3**
Empirical formula	$[Cu_2Br_2[P(C_6H_5)_3]_2(C_{19}H_{14}N_4O_2)]\cdot$solvent	$[Cu_2I_2[P(C_6H_5)_3]_2(C_{19}H_{14}N_4O_2)]\cdot 0.62\ (CH_3CN)\cdot 1.89(H_2O)$
Formula weight	998.69	1291.93
T (K)	130	130
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	13.6330(2)	13.7035(5)
b (Å)	15.5608(3)	15.6164(6)
c (Å)	15.8732(4)	15.9500(5)
α (°)	60.999(2)	61.391(4)
β (°)	70.612(2)	72.566(3)
γ (°)	86.583(2)	86.708(3)
Volume (Å^3)	2757.1(1)	2843.8(2)
Z, Z'	2, 1	2, 1
Absorption coefficient (mm^{-1})	2.332	1.936
Reflections collected	37236	47251
Independent reflections	11195	11582
Completeness up to theta (max) = 26.37° (%)	99.4	99.7
Data/restraints/parameters	11195/0/608	11582/0/642
Goodness-of-fit (GOF) on F^2	0.995	0.883
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0271, wR_1 = 0.0674	R_1 = 0.0315, wR_1 = 0.0623
R indices (all data)	R_2 = 0.0409 wR_2 = 0.0699	R_2 = 0.0561 wR_2 = 0.0653
Largest difference in peak and hole	0.460, −0.410	1.044, −0.785

to the metal and does not participate in any kind of electrostatic interaction with any other part of the molecule [42]. The compounds are probably monomeric since the hydroxyl group bond stretch is observed as a well defined band of medium intensity for all the studied compounds indicating that the carboxylate region is not involved in the typical hydrogen bonding of carboxylic acids. Furthermore, the asymmetric COO band appears at higher wavenumbers than when the group is involved in hydrogen bonding [43]. This has been observed in the spectra of the corresponding compounds with the 3-pyridinylimino derivatives where the analogous frequencies are observed around 1680 cm^{-1} [44].

The resonances in the ^1H solution NMR spectra are observed in the expected regions. The imine proton resonance in particular, which in the free acid is observed at 8.70 ppm as a singlet is shifted downfield and appears at 8.87, 8.94 and 9.03 for compounds **1**–**3** in order with the expected halide atom effect [45]. The resonance appears even more downfield shifted for compound **4** at 9.10 ppm. In all cases the signal is a single sharp line indicating symmetric environment for both regions due to the fluxional character of the methylimino group. The ^{13}C NMR signals are again indicative of the coordination to the metal center [46]. The carboxylic carbon resonance remains very close to the free ligand value of 166.60 ppm indicating no significant change in the carboxylate region upon coordination to the metal center. Very small shifts are observed also for the imino carbon atoms in the complexes relative to the free ligand value of 162.40 ppm. The resonances realized for compounds **1**–**3** are 158.9, 159.8 and 160.8 ppm, respectively, revealing again the halide influence to the shielding while for 4 the corresponding signal is at 162.2 ppm.

The visible spectra of the compounds were recorded in methanol and dichloromethane solutions. The spectra recorded in dichloromethane are presented in Fig. 2. In every case the spectra are dominated by the intense π–π^* ligand centered (LC) transitions but their common feature extends further to the existence of a broad low energy charge transfer absorption extending from 350 to 600 nm [47] as it is inferred by the calculated excitation coefficients (ε). This envelope is known to incorporate several discrete excitations from mainly metal-based HOMOs to mainly diimine-centered LUMOs [48]. This was further verified by semi-empirical calculations carried out by means of the PM6 Hamiltonian [49] as implemented in the MOPAC2009 package [50].

Calculations were carried out at the ground electronic state assuming a single molecule in the gas phase and the structural optimization was full except for the assumption of perfectly planar aromatic rings. The octet of frontier molecular orbitals obtained for compound **4** are presented in Fig. 3. As it is evident the occupied orbitals are mainly metal-centered with some delocalization towards the phosphorus and the halide atoms, while the virtual ones are located over the entire or in part of the bis(imino) benzoate. Subsequent configuration interaction taking into consideration the above frontier MOs revealed, in agreement with the experimental findings, that the CT bands in the halide compounds are considerably extended towards the lower energy side of the visible spectrum reaching even 610 nm whereas the first excitation for the ionic complex is calculated to be at 415 nm, in close analogy to the experimental findings.

3.3. Crystal structures of *2* and *3*

The solvated forms of compounds **2** and **3**, crystallising in the $P\bar{1}$ space group are, to a large extent, isostructural. The asymmetric unit of **2** consists of the dinuclear $[Cu_2Br_2[P(C_6H_5)_3]_2(C_{19}H_{14}N_4O_2)]$ complex molecules (Fig. 4a) and unidentified solvent molecules. In turn the asymmetric unit of **3** contains dinuclear $[Cu_2I_2[P(C_6H_5)_3]_2$-$(C_{19}H_{14}N_4O_2)]$ molecules (Fig. 4b) and disordered solvent molecules that were identified as acetonitrile and water molecules. The two Cu(I) centers with the N_2PX (X = Br, I) donor set show a strongly distorted tetrahedral coordination geometry (Table 3) and intramolecular distances between the metal centers are 7.867 and 7.861 Å in **2** and **3**, respectively. Moreover, they constitute two independent chirality centers as the Cu atoms have four different substituents. Owing to the identical configuration of the two chiral centers in the studied molecules, the compounds **2** and **3** are racemic. The complex molecules adopt an asymmetric shape with one of the planar pyridylimino groups strongly twisted relative to the plane of the central C1–C6 benzene ring (dihedral angles 65.9° in **2** and 65.0° in **3**) and

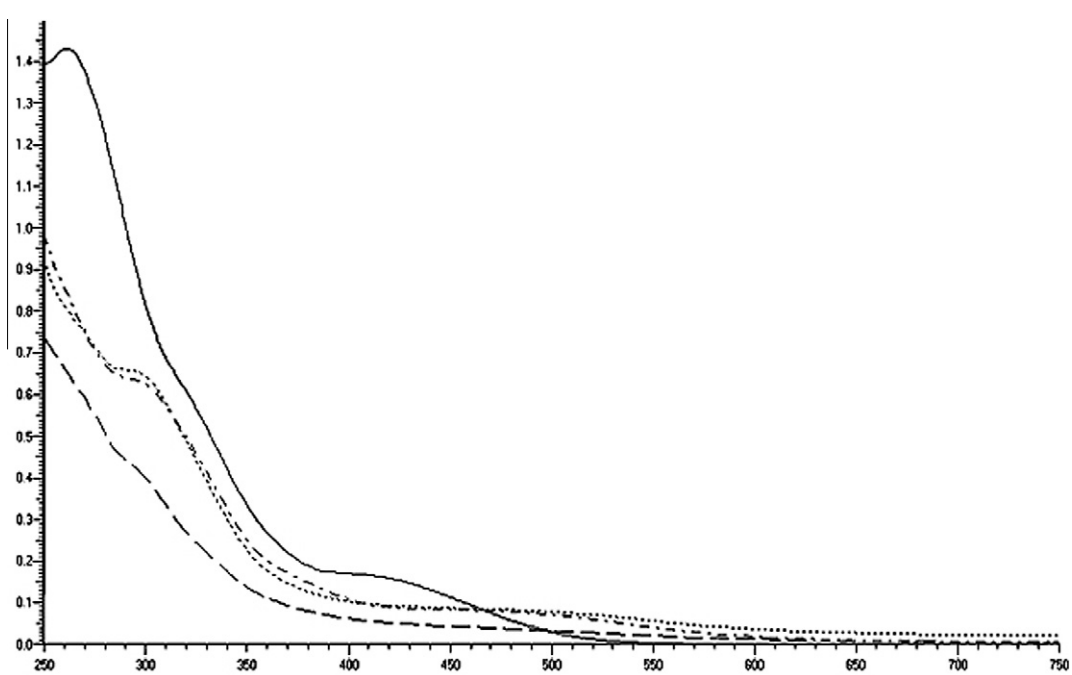

Fig. 2. Visible spectra of the studied compounds recorded in 1×10^{-4} M solutions in CH_2Cl_2. **1** dashed line; **2** dotted line; **3** mixed line and **4** solid line.

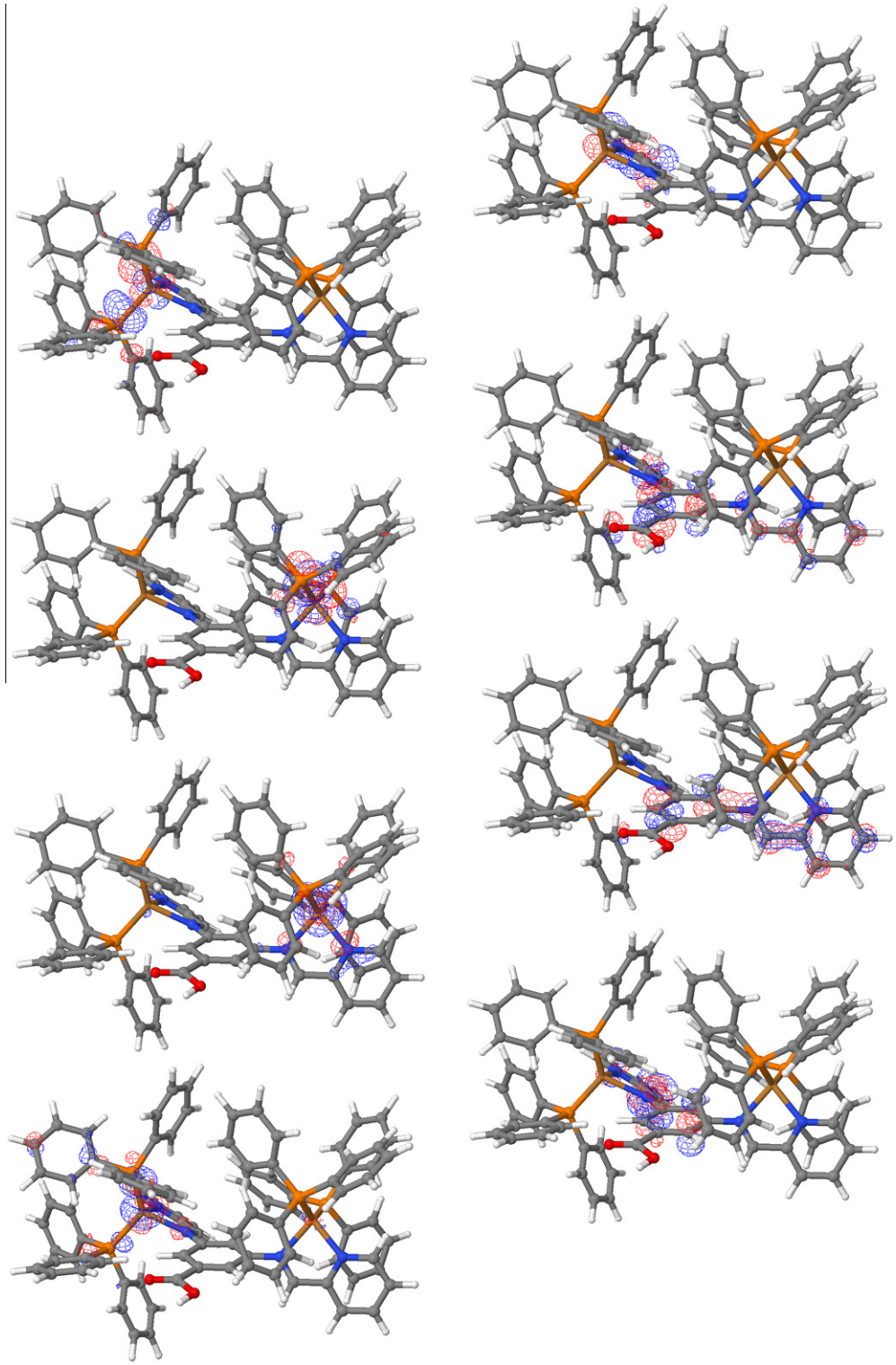

Fig. 3. Schematic representation of the four HOMOs (left column) and four LUMOs (right column) of the optimized structure of compound **4**. The orbitals are placed in order of increasing energy from bottom to top.

the other group approximately coplanar (dihedral angles 4.0 in **2** and 5.3° in **3**). The bulky substituent at the benzoic acid unit incorporating the coordinated Cu3 atom is oriented *syn* relative to the carboxylic group resulting in a short intramolecular contact Cu3···H2 contact (2.67 Å in **2** and 2.69 Å in **3**). In turn, owing to a strong twist relative to the benzoic acid unit, the substituent at position 5 of the benzene ring, incorpoprating the Cu5 atom, is able to place one of its triphenylphosphane phenyl rings directly above the aromatic ring of the benzoic acid fragment. The geometrical parameters of the intramolecular π–π stacking interactions between the rings C1–C6 and C5A1–C5A6 in **2** and **3**, respectively, are as follows: dihedral angles between the aromatic rings are 2.0° and 2.4°**,** the centroid-to-centroid distances 3.57 and 3.56 Å and the ring offset 0.46 and 0.42 Å.

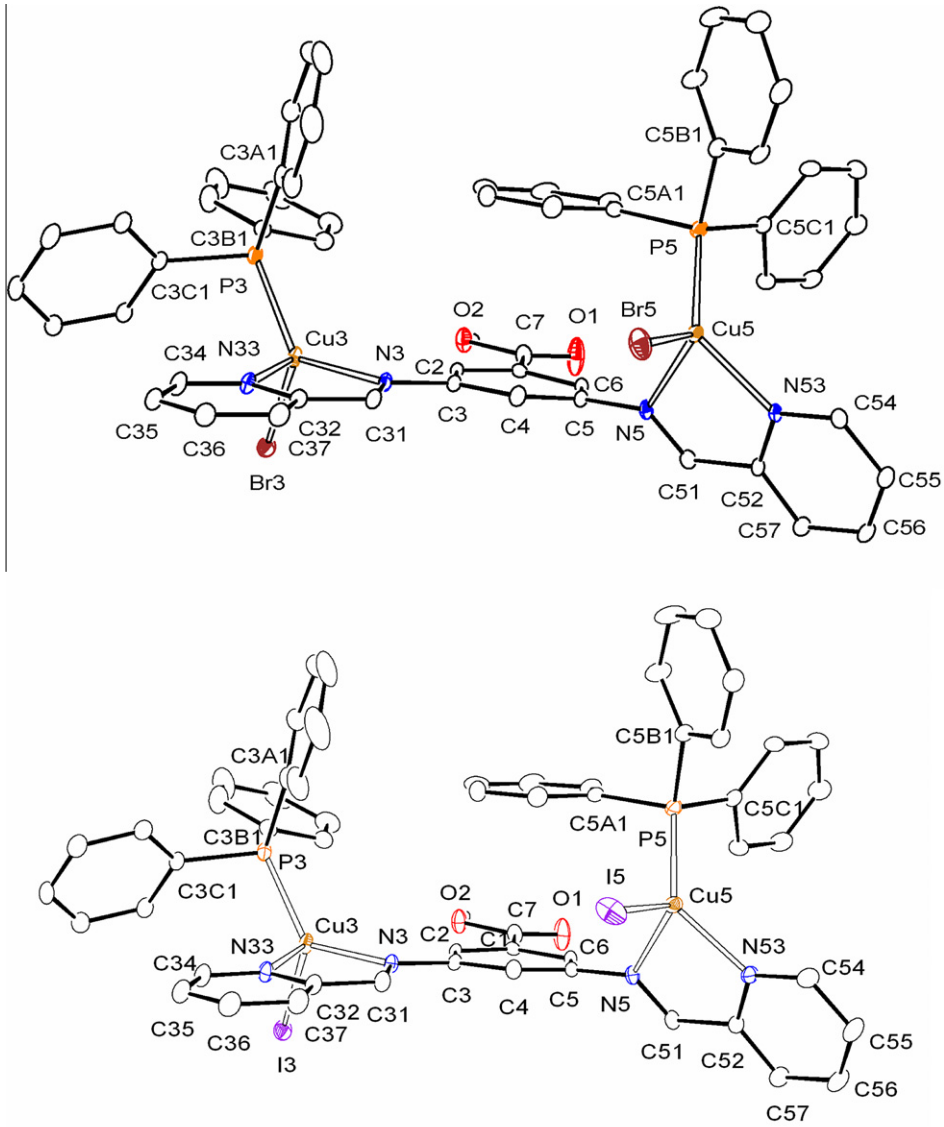

Fig. 4. Molecular structures of compound **2** (top) and **3** (bottom). All hydrogen atoms except carboxylic H atom have been omitted for clarity. Only one C atom in each phenyl ring of the triphenylphosphane ligand is labeled. Displacement ellipsoids are drawn at the 50% probability level.

The intramolecular π–π stacking interactions in **2** and **3** are more pronounced than in the coordination cation in **4** [44] where the interacting aromatic rings formed dihedral angle of 16.8° and their centroids were at a distance of 4.36 Å.

3.4. Cyclopropanation reactions

The catalytic activity of complexes **1**–**4** in olefin cyclopropanation was finally tested. In order to monitor the possibility to employ the studied complexes as catalysts, styrene was first used as reference substrate, and all the compounds demonstrated to be active in olefin cyclopropanation (see entries 1–4 in Table 1), giving moderate-to-high yields under mild conditions. However, together with the desired products, diethyl maleate and diethyl fumarate, deriving from ethyl diazoacetate self-coupling [51], were always detected. In order to minimize these side-reactions, a large excess of olefin (namely, a Cu:EDA:olefin = 1:100:250 M ratio) was employed and EDA was added dropwise during a 15-min period. The copper (I) compounds showed comparable diastereoselectivities, the *cis*:*trans* ratio being about 30:70 in all the runs. 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 [18,52], 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 less affected by steric effects, except when very bulky substituents are used, as in the case of 2,6-di-*tert*-butyl-4-methyl phenyl (BDA) diazoacetate [9,53]. The studied species confirmed this trend, providing a 70:30 *trans*:*cis* ratio in the catalytic cyclopropanation of styrene.

The cationic species **4** displayed the highest activity, the consumption of EDA being complete within 4 h, whereas the **1–3** species all required a longer reaction time (>7 h), with an initial induction period necessary to reach the complete dissolution. Moreover, when employing the halide-containing compounds the yields obtained were lower, especially in the case of **3**. As discussed hereafter, this could probably be ascribed to the relative strength of the Cu–X bonds (Cl < Br < I). In fact, among the halide-containing ones we observed an interesting trend related to the nature of the anion: the induction period increase moving from chlorine to

iodine. Probably, taking into account the activity of the ionic species **4**, and the relative strength of the Cu–X bonds (Cl < Br < I), a prerequisite in order to have the catalytic active species is the dissociation of the halide ion from the copper centers.

To prove this assumption, we performed a catalytic run in the presence of exogenous chloride anions (entry 5). In fact, when ethyl diazoacetate was added to a CH_2Cl_2 solution containing styrene, complex **4** as catalyst and an equivalent (with respect to metal) of benzyltriethylamonium chloride, no formation of cyclopropanation products was detected even after a long reaction time (48 h). This outcome corroborated the supposition that the first step in the catalytic cycle involving the halide complexes is most probably the anion dissociation, in this specific case prevented by the presence of exogenous chloride.

We then decided to deepen the activity of the most active species, **4**, in the presence of different olefins as substrate. Thus, complex **4** was tested as catalyst in the cyclopropanation of both terminal (entries 6–8) and internal olefins (entries 9–11). The diastereoselectivities reached using terminal olefins ranged from 44:56 *cis*:*trans* ratio in the case of α-methylstyrene (entry 6) to 21:79 in the cyclopropanation of 1-octene. On the contrary, in the case of an internal olefin like cyclohexene, species **4** showed a higher diastereoselectivity and a 90:10 *exo*:*endo* ratio was achieved. Unfortunately, with deactivated internal olefins such as 2-cyclohexen-1-one (entry 10) or *trans*-β-nitrostyrene (entry 11), the cyclopropanation products were detected only in traces, thus limiting the activity of **4** to not deactivated substrates.

4. Conclusion

The neutral and one cationic dicopper(I) complexes with 3,5-bis(pyridinylimino)benzoic acid are synthesized and their structure studied. The proximity of the copper centers give rise to asymmetric compounds as far as the orientation of the diimine sites of the bridging ligand. The compounds are potential catalysts in olefin cyclopropanation reactions and in fact they reveal overall moderate-to-high yields when tested with styrene. The cationic complex is the better and is further applicable to analogous reactions where it proves to be efficient with internal olefins affording a high diastereoselectivity of 90:10 with cyclohexene.

Appendix A. Supplementary material

CCDC 821562 and 821563 contain 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.2011.10.055.

References

[1] K. Huang, C.-L. Sun, Z.-J. Shi, Chem. Soc. Rev. 40 (2011) 2435.
[2] S. Dastgir, K.S. Coleman, M.L.H. Green, Dalton Trans. 40 (2011) 661.
[3] I.D. Gridnev, M. Watanabe, H. Wang, T. Ikariya, J. Am. Chem. Soc. 132 (2010) 16637.
[4] S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green, Organometallics 29 (2010) 4858.
[5] S. Reimann, J.-D. Grunwaldt, T. Mallat, A. Baiker, Chem. Eur. J. 16 (2010) 9658.
[6] J.R. Khusnutdinova, N.P. Rath, L.M. Mirica, J. Am. Chem. Soc. 132 (2010) 7303.
[7] T. Ikariya, I.D. Gridnev, Top. Catal. 53 (2010) 894.
[8] H.N.C. Wong, M.-Y. Hon, C.-W. Tse, Y.-C. Yip, J. Tanko, T. Hudlicky, Chem. Rev. 89 (1989) 165.
[9] A. Caballero, A. Prieto, M.M. Díaz-Requejo, P.J. Pérez, Eur. J. Inorg. Chem. (2009) 1137.
[10] A. de Meijere, Chem. Rev. 103 (2003) 931.
[11] M.P. Doyle, A. McKervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides, Wiley, Chichester, 1998.
[12] T. Ye, A. McKervey, Chem. Rev. 94 (1994) 1091.
[13] A. Pfaltz, Cyclopropanation and C–H Insertion with Cu, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 2, Springer-Verlag, Berlin, 1999, pp. 513–538.
[14] W. Kirmse, Angew. Chem., Int. Ed. 42 (2003) 1088.
[15] T. Rasmussen, J.F. Jensen, N. Østergaard, D. Tanner, T. Ziegler, P. Norrby, Chem. Eur. J. 8 (2002) 177.
[16] B.F. Straub, P. Hofmann, Angew. Chem., Int. Ed. Engl. 40 (2001) 1288.
[17] J.I. García, G. Jiménez-Osés, J.A. Mayoral, Chem. Eur. J. 17 (2011) 529.
[18] J.M. Fraile, J.I. García, A. Gissibl, J.A. Mayoral, E. Pires, O. Reiser, M. Roldán, I. Villalba, Chem. Eur. J. 13 (2007) 8830.
[19] Q. Meng, M. Li, J. Mol. Struct. THEOCHEM 765 (2006) 13.
[20] J.A.S. Howell, Dalton Trans. (2006) 545.
[21] Q. Meng, M. Li, D. Tang, W. Shen, J. Zhang, J. Mol. Struct. THEOCHEM 711 (2004) 193.
[22] J.M. Fraile, J.I. García, V. Martínez-Merino, J.A. Mayoral, L. Salvatella, J. Am. Chem. Soc. 123 (2001) 7616. and references therein.
[23] H. Fritschi, U. Leutenegger, A. Pfaltz, Helv. Chim. Acta 71 (1988) 1553.
[24] A.J. Burke, E. da Palma Carreiro, S. Chercheja, N.M.M. Moura, J.P.P. Ramalho, A.I. Rodrigues, C.I.M. dos Santos, J. Organomet. Chem. 692 (2007) 4863.
[25] C. Ricardo, T. Pintauer, J. Organomet. Chem. 692 (2007) 5165.
[26] G. Chelucci, R.P. Thummel, Chem. Rev. 2002 (102) (2002) 3129.
[27] M.M. Diaz-Requejo, A. Caballero, T.R. Belderrain, M.C. Nicasio, S. Trofimenko, P.J. Perez, J. Am. Chem. Soc. 124 (2002) 978.
[28] L. Beaufort, A. Demonceau, A.F. Noels, Tetrahedron 61 (2005) 9025.
[29] H. Suga, A. Kakehi, S. Ito, T. Ibata, T. Fudo, Y. Watanabe, Y. Kinoshita, Bull. Chem. Soc. Jpn. 76 (2003) 189.
[30] G. Lesma, C. Cattenati, T. Pilati, A. Sacchetti, A. Silvani, Tetrahedron: Asymmetry 18 (2007) 659.
[31] G.A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, C. Marelli, N. Masciocchi, J. Organomet. Chem. 693 (2008) 1870.
[32] A. Maspero, S. Brenna, S. Galli, A. Penoni, J. Organomet. Chem. 672 (2003) 123.
[33] G.A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, Inorg. Chim. Acta 362 (2009) 3507.
[34] B.P. Buffin, E.B. Fonger, A. Kundu, Inorg. Chim. Acta 355 (2003) 340.
[35] P. Hemmerich, C. Sigwart, Experentia 19 (1963) 488.
[36] P.F. Barron, J.C. Dyason, L.M. Engelhardt, P.C. Healy, A.H. White, Aust. J. Chem. 38 (1985) 261.
[37] Oxford Diffraction, CRYSALIS CCD and RED, Ver. 1.171.33, Oxford Diffraction Ltd., Yarnton, Oxfordshire, UK, 2009.
[38] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[39] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2009.
[40] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[41] D. Tzimopoulos, A. Czapik, M. Gdaniec, T. Bakas, A.A. Isab, A.-C. Varvogli, P.D. Akrivos, J. Mol. Struct. 965 (2010) 56. and references therein.
[42] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Complexes, fourth ed., John Wiley & Sons, USA, 1992.
[43] I. Wolfs, H.O. Desseyn, Appl. Spectrosc. 50 (1996) 1000.
[44] S. Shakhatreh, J. Mohanraj, A. Czapik, D. Tzimopoulos, S. Kotoulas, M. Gdaniec, P.D. Akrivos, J. Mol. Struct. 1002 (2011) 51.
[45] A.M. Kantola, P. Lantto, J. Vaara, J. Jokisaari, Phys. Chem. Chem. Phys. 12 (2010) 2679.
[46] R.J. Abraham, M. Mobli, R.J. Smith, Magn. Reson. Chem. 42 (2004) 436.
[47] W.-F. Fu, X. Gan, J. Jiao, Y. Chen, M. Yuan, S.-M. Chi, M.-M. Yu, S.-X. Xiong, Inorg. Chim. Acta 360 (2007) 2758. and references cited therein.
[48] N. Armaroli, G. Accorsi, F. Cardinali, A. Listorti, Top. Curr. Chem. 280 (2007) 69.
[49] J.J.P. Stewart, J. Mol. Mod. 13 (2007) 1173.
[50] MOPAC2009, James J.P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, 2009, <http://www.OpenMOPAC.net>.
[51] I. Shepperson, S. Quici, G. Pozzi, M. Nicoletti, D. O'Hagan, Eur. J. Org. Chem. (2004) 4545.
[52] M.P. Doyle, W. Hu, J. Org. Chem. 65 (2000) 8839.
[53] M.P. Doyle, V. Bagheri, T.J. Wandless, N.K. Harn, D.A. Brinker, C.T. Eagle, K.-L. Loh, J. Am. Chem. Soc. 112 (1990) 1906.