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# Synthesis, characterization and study of the catalytic properties of Zn(II) camphor derived complexes



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# ABSTRACT

Zinc(II) complexes of general formula  $[ZnX_2(YNC_{10}H_{14}O)]$ ,  $[ZnX_2(YNC_{10}H_{13}NSO_2)]$ ,  $[ZnX_2(H_2NNC_{10}H_{14}O)_2]$ ,  $[\{ZnX_2\}_2(YNC_{10}H_{14}O)]$  and  $[\{ZnX_2\}_2(YNC_{10}H_{13}NSO_2)]$  were obtained from zinc halides (chloride or bromide) by reaction with the suitable camphor ligands.

In most of the complexes, the camphor ligands remain unchanged upon coordination, except in  $[{Zn(MeNNC_{10}H_{14}O)}_{2}(\mu-Cl)_{2}]$  where proton loss from MeHNNC<sub>10</sub>H<sub>14</sub>O occurs. The new complexes and camphor derivatives were characterized by IR, NMR (<sup>1</sup>H, <sup>13</sup>C{H}, DEPT, 2D) and elemental analysis. In some cases the surface composition was studied by X-ray photoelectron spectroscopy (XPS) and imaged by Scanning Electron Microscopy (SEM). Images of  $[ZnCl_{2}(Me_{2}NNC_{10}H_{14}O)]$  and  $[ZnCl_{2}(Me_{2}NNC_{10}H_{13}NSO_{2})]$  obtained by SEM show the solid particles have tubular structures capped in one or both extremities. The coordination of THF in  $[ZnCl_{2}(YNC_{10}H_{14}O)THF]$  was confirmed by X-ray diffraction analysis. The camphor derivatives  $YNC_{10}H_{14}NSO_{2}$  (Y = NMe<sub>2</sub>; NHMe) and *p*-C<sub>6</sub>H<sub>4</sub>(NC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub> were structurally characterized by X-ray diffraction analysis.

The ability of selected Zn(II) camphor complexes to catalyse the cyclization of 4-pentyn-1-ol was evaluated showing that the binuclear complex [ $\{ZnX_2\}_2(YNC_{10}H_{14}O)$ ] performs better than the mononuclear Zn(II) complexes.

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# 1. Introduction

Synthesis of several fine organic chemicals, rely, nowadays, on processes catalysed by transition metals or complexes. Thus, design of new and more efficient catalysts is an attractive topic for research on synthesis and catalysis. Under such perspective the design of catalysts able to activate CC triple bonds in processes with high *regio* selectivity and atom economy, difficult to promote in the absence of a catalyst [1–3]. Within our studies it was verified that camphor derived Pd and Pt complexes are efficient catalysts for alkynes cyclization or alkynols cycloisomerization [4–7] extending the role of the camphor ligands to processes other than the chirality control of reaction products [8–11].

The cyclization of alkynols promoted by palladium or platinum camphor complexes involves the activation of two molecules of alkynol forming O-heterocycles with a pending alkyne group (see Scheme 1 in the catalytic studies). Although other catalysts are known

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0022-328X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2013.10.040 to promote the cyclization of alkynols [12], the one-pot activation of a second alkynol molecule is characteristic of camphor derived Pd and Pt complexes. In order to verify whether this characteristic is also present in other camphor complexes, several zinc camphor derived complexes were synthesized and their reaction with 4-pentyn-1-ol was studied. Zinc looked a good choice because it is much cheaper than Pt or Pd, it is more environmental friendly, stabilizes coordination numbers four and five [13] and was recently considered outstanding for homogeneous catalysis [14]. Furthermore, there are reports on zinc complexes reacting under solvent free conditions [15,16] which is a type of process potentially interesting.

# 2. Results and discussion

# 2.1. Synthesis and structural characterization

Several Zn(II) complexes were obtained by reaction of zinc halides with camphor derivatives that were labelled with a number followed by a letter for clarity. Numbers refer to the metal to ligand ratio and the halide co-ligand; letters relate to the type of camphor





Scheme 1. Cyclization of 4-pentyn-1-ol catalysed by Zn(II) complexes.

ligand:  $[ZnX_2(YNC_{10}H_{14}O)] (X = Cl: Y = NMe_2$ **1a** $, Y = C_6H_4NH_2$ **1d** $, Y = NC_6H_4N$ **1e** $; X = Br: Y = NMe_2$ **2a** $, Y = C_6H_4NH_2$ **2d** $, Y = NC_6H_4N$ **2e** $, Y = m-C_6H_4NC_{10}H_{14}O$ **2j** $); <math>[ZnX_2(YNC_{10}H_{13}NSO_2)] (X = Cl: Y = NMe_2$ **1f** $; X = Br: Y = NMe_2$ **2f** $); <math>[ZnX_2(H_2NNC_{10}H_{14}O)_2] (X = Cl:$ **3b**, X = Br**4b** $); [{ZnX_2}(YNC_{10}H_{14}O)] (X = Cl: Y = p-C_6H_4NC_{10}H_{14}O$ **6j** $; X = Br: Y = p-C_6H_4NC_{10}H_{14}O$ **7i** $) and [{ZnX_2}(YNC_{10}H_{13}NSO_2)] (X = Cl: Y = NHMe$ **7h**).

Most of the complexes crystallize with solvent molecules in the lattice (see experimental). In the case of  $[ZnCl_2(Me_2NNC_{10}H_{14}O)(THF)]$  (**1a**') analysis by single crystal X-ray diffraction (XRD) showed that one molecule of THF coordinates the metal. Complex **1a**' crystallizes in the monoclinic P2<sub>1</sub> space group (Fig. 1) with a trigonal bipyramidal geometry. The camphor hydrazone (Me\_2NNC<sub>10</sub>H<sub>14</sub>O, a) coordinates the metal through the oxygen and the nitrogen atoms, although the distance between the nitrogen atom and zinc (2.54 Å) is among the longer Zn–N bond lengths reported [17–19]. The calculated Mulliken atomic overlap population (0.054) and bond order (0.096) are consistent with a weak Zn–N bonding.

The camphor ligand shares the equatorial position of the complex with the two chloride ligands. THF occupies one of the axial positions and the imine nitrogen atom the other one (Fig. 1).

Selected bond lengths and angles for **1a**' are in the expected ranges as displayed in Table 1.

In the structure of **1a**' it is worth to highlight that the amine nitrogen atom (N2) shows no pyramidalization (the three angles sum 360°). The bond length N1–N2 (1.305(2) Å) is shorter than the average for a single N–N bond length (1.425 Å) [20], pointing to an extended  $\pi$ -delocalization through the N2–N1–C12–C11–O system. DFT calculations show that the CO and CN (ca. 1.8) bond orders are lower and the CC and NN (ca. 1.1) bond orders higher, respectively, than the typical values for double and single bonds, in agreement with electron delocalization (Fig. 2). This also explains the shifts to lower values observed in the FTIR stretching frequency ( $\nu_{CO}$ ) of the coordinated camphor hydrazone (Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O, **a**) and the lower <sup>13</sup>C{H} NMR chemical shift of the imine carbon atom



Fig. 1. ORTEP drawing for  $[ZnCl_2(Me_2NNC_{10}H_{14}O)(THF)]$  (1a') showing atom labelling scheme. Hydrogen atoms were omitted for clarity. Ellipsoids are drawn at 50% probability.

Table 1
elected bond lengths and angles for [ZnCl <sub>2</sub> (Me <sub>2</sub> NNC <sub>10</sub> H <sub>14</sub> O)(THF)] ( <b>1a</b> ')

Bond lengths (Å)		Angles (°)	
Zn(1)-O(1)	2.044(1)	O(1)-Zn(1)-O(2)	84.06(5)
Zn(1) - O(2)	2.134(1)	O(1) - Zn(1) - Cl(2)	117.42(4)
Zn(1)-Cl(2)	2.218(1)	O(2) - Zn(1) - Cl(2)	98.64(3)
Zn(1)-Cl(1)	2.220(1)	O(1) - Zn(1) - Cl(1)	113.54(4)
O(1) - C(11)	1.244(2)	O(2) - Zn(1) - Cl(1)	97.57(3)
C(11)-C(12)	1.452(2)	Cl(2)-Zn(1)-Cl(1)	127.66(2)
C(12) - N(1)	1.307(2)	C(11) - O(1) - Zn(1)	117.0(1)
N(1)-N(2)	1.305(2)	N(2)-N(1)-C(12)	125.5(1)
N(2)-C(21)	1.454(2)	C(21)-N(2)-C(22)	117.9(1)
N(2)-C(22)	1.455(2)	N(1)-N(2)-C(21)	117.8(1)
		N(1)-N(2)-C(22)	124.3(1)

(138.8 ppm) compared to complexes Pd(II) (175.0 ppm) or Pt(II) (176.0 ppm) [21,22] or the free ligand (**a**, 143.8 ppm).

The elemental composition obtained by microanalysis (C, N, H, S) allows formulation of the new complexes, the spectroscopic IR and NMR data allow an insight into the coordination of the camphor ligands and the optical rotation shows that a selection of complexes keep the right-handed rotation of the ligands (see experimental). XPS provides information on the surface composition of the powders and SEM shows the respective image.

Camphor derived compounds used as ligands are shown in Fig. 3. The analytical and spectroscopic characterization of the new bi-camphor compounds (**i** and **j**) is displayed in the experimental section (5.1).

Complexes [ZnX<sub>2</sub>L] (X = Cl, L: **d** (1**d**); **e** (1**e**); **f**, (1**f**); X = Br, L: **a** (2a), d (2d), e (2e); f, (2f); j (2j)) and [ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)THF] (1a') obtained by reaction of  $ZnX_2$  (X = Cl, Br) with camphor ligands  $\text{YNC}_{10}\text{H}_{14}\text{O}$  (Y = NMe<sub>2</sub> (**a**), p-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (**d**)), camphor sulphonylimine  $(Me_2NNC_{10}H_{13}NSO_2 (\mathbf{f}))$ , camphorquinoxaline ( $\mathbf{e}$ ), or the bicamphor (j) have elemental compositions consistent with metal to ligand ratios 1:1. The FTIR and NMR spectra show that complexes 2a(X = Br) and 1a'(X = Cl), which essentially differ in the halide coligand, are spectroscopically similar, *i.e.* the values of the IR bands ( $\nu_{CO}$ ,  $\nu_{CN}$ , see Supplementary tables) and <sup>13</sup>C{H} NMR chemical shifts (C=N) decrease upon coordination pointing to an oxygen bound ligand in 2a such as observed by X-ray diffraction analysis in 1a'. In contrast, complexes 1d and 2d display IR bands ( $v_{CO}$ ,  $v_{CN}$ ) at higher values than those observed for the free ligands pointing to coordination through the oxygen and imine nitrogen atoms, the ligand behaving as chelating.

In complexes  $[ZnX_2\{(NC_6H_4)NC_{10}H_{14}O)\}]$  (X = Cl **1e** and X = Br **2e**) just one IR band (1516, and 1517 cm<sup>-1</sup>, respectively) is observed in the range assigned to the C=N bond pointing to equivalent stretching of the CN bonds in camphorquinoxaline (**e**). The values do not differ much from those for the free ligand (1514 cm<sup>-1</sup>). In the



Fig. 2. Bond orders calculated by DFT B3LYP with Grimme's dispersion.



Fig. 3. Camphor derivatives used as ligands.

<sup>13</sup>C{H} NMR spectrum, two signals attributed to the imine carbon atoms (**1e**, 167.4, 165.1; **2e**, 167.8, 165.4 ppm) at values slightly higher (ca. 2 ppm) than those in the free ligand [23] point to some deshielding upon coordination.

No complexes of general formula [ZnX<sub>2</sub>L] were obtained by reaction of  $H_2NNC_{10}H_{14}O$  or MeHNNC<sub>10</sub> $H_{14}O$  with zinc halides. In those cases there is formation of the complexes [ZnX<sub>2</sub>(H<sub>2</sub>NNC<sub>10</sub> $H_{14}O)_2$ ] (X = Cl **3b**, X = Br **4b**) and [{Zn(MeNNC<sub>10</sub> $H_{14}O)_2$ ]( $\mu$ -Cl)<sub>2</sub>] (**5c1**), respectively.

Hydrogen bonding involving the halide co-ligand, conceivably, inhibits ligand chelation thus enabling a second camphor ligand to coordinate in **3b** and **4b** and promoting HCl release to yield **5c1** (Eq. (1)). *In loco* formation of the anionic ligand (MeNNC<sub>10</sub>H<sub>14</sub>O<sup>-</sup>, **c1**) from MeHNNC<sub>10</sub>H<sub>14</sub>O was found in [Pd(MeNNC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>] [5].

$$2ZnCl_{2} + 2MeHNNC_{10}H_{14}O \rightarrow [{Zn(MeNNC_{10}H_{14}O)}_{2}(\mu-Cl)_{2}] + 2HCl$$
(1)

Complexes  $[ZnX_2(H_2NNC_{10}H_{14}O)_2]$  display two bands (**3b** 1636, 1584; **4b** 1634, 1581 cm<sup>-1</sup>) in the region attributed to the C=N stretching in the IR spectra that point to non-equivalent ligands. That is also the case in  $[{Zn(MeNNC_{10}H_{14}O)}_2(\mu-Cl)_2]$ , with a dinuclear formulation, that displays distinct C=O and C=N stretching frequencies for the two ligands (1709, 1689 ( $\nu_{CO}$ ), 1616, 1569 ( $\nu_{CN}$ ) cm<sup>-1</sup>). *E/Z* isomerization could also account for non-equivalent ligands such as reported for cis-[PtCl<sub>2</sub>(PhNC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>]

that exhibits one camphor ligand in the E and the other in the Z configuration [6]. One band in the IR spectrum would be expected for two equivalent ligands [24].

The above results show that the characteristics of the camphor substituent (Y) play a relevant role in the type of Zn complex formed. In order to evaluate the effect of the replacement of a ketone by an imine group in position 2 (see Fig. 3) and introduce more steric hindrance, reactions of zinc halides with camphor sulphonylimines ( $YNC_{10}H_{13}NSO_2$ ) were performed. Camphor sulphonylimines were chosen because they have coordinative bites that do not differ much from camphorimines ( $YNC_{10}H_{14}O$ ).

The structural analysis of camphor sulphonylimines  $Me_2NNC_{10}H_{13}NSO_2$  (**f**) and  $MeHNC_{10}H_{13}NSO_2$  (**h**) show they crystallize in the orthorhombic ( $P2_12_12_1$ ) space group in configurations (*Z*) (**f**) and (*E*) (**h**), respectively (Fig. 4, for bond lengths and angles, see Supplementary data).

The bite angles of (**f**) and (**h**) are very sensitive to the isomer type (*E* or *Z*) and less sensitive to their bicyclic or tricyclic character, as verified by comparing data herein with that reported for  $Me_2NNC_{10}H_{14}O(a)$  [25] (Fig. 5).

Complexes  $[ZnX_2(Me_2NNC_{10}H_{13}NSO_2)]$  (X = Cl **1f**; X = Br **2f**) obtained from camphor sulphonylimine ligands (YNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>) display two IR bands in the region assigned to the C=N stretching frequencies (**1f**, 1657, 1547 cm<sup>-1</sup>; **2f**, 1617, 1539 cm<sup>-1</sup>) that are shifted to values higher than those of the free ligand (Me<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>, 1584, 1521 cm<sup>-1</sup>) similarly to Zn(II) complexes



**Fig. 4.** ORTEP drawing for Me<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub> (**f**, left) and MeHNNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub> (**h**, right). Hydrogen atoms were omitted for clarity. Ellipsoids are drawn at 50% probability. See Supplementary data for details.



Fig. 5. Schematic structures of species a (E-isomer), h (E-isomer) and f (Z-isomer), showing bite angles.

derived from the camphor hydrazones (**b**, **d**). The band at higher value is attributed to the sulphonylimine group. IR data, together with the need for coordinative saturation, suggest the camphor derived ligands have a chelating character.

Camphor sulphonylimines (YNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>) with substituents such as Y = NHMe, **h** or Y = NH<sub>2</sub>, **g**, (Fig. 3) do not form complexes of type [ZnX<sub>2</sub>L]. Instead, complexes [{ZnCl<sub>2</sub>}<sub>2</sub>(H<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (**6g**) and [{ZnBr<sub>2</sub>}<sub>2</sub>(MeHNNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (**7h**) were obtained. Attempts to grow single crystals were unsuccessful and, consequently, structural information on ligand bonding in complexes **6g** and **7h** could not be obtained. Nevertheless, the shift of the IR bands ( $\nu_{C=N}$  and  $\nu_{C=NSO2}$ ) to higher values relative to the free ligands is consistent with coordination through the two nitrogen atoms.

Aiming to obtain complexes with structural motifs that include more than one metal atom *per* ligand,  $ZnX_2$  was reacted with the bicamphor species ( $NC_{10}H_{14}O$ )<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**i** and **j**, Fig. 3). From reaction of the bi-camphor ligand with the two camphor moieties in *para* position, the complexes [( $ZnCl_2$ )<sub>2</sub>{(p-NC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}] (**6i**) and [( $ZnBr_2$ )<sub>2</sub>{(p-NC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}] (**7i**) were obtained. [( $ZnCl_2$ )<sub>2</sub>{(m-NC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}] (**7j**) was obtained from the ligand in which the camphor moieties are in *meta* position. However, no such type of complex was obtained from reaction of  $ZnBr_2$  with m-NC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**j**), conceivably due to the steric hindrance by the bromide co-ligand.

The IR bands ( $\nu_{C=N}$  and  $\nu_{C=O}$ ) observed for complex **7i** (1685, 1756 cm<sup>-1</sup>) do not differ from those of the free ligand (1685, 1756 cm<sup>-1</sup>) whereas those observed for **6i** (1689, 1748 cm<sup>-1</sup>) and **6j** (1668, 1734 cm<sup>-1</sup>) differ slightly. The same tendency was observed by NMR suggesting a weaker coordination of the bi-camphor ligand in **7i** than in **6i** or **6j** which is attributed to the higher steric requirements of bromide.

No crystals of the complexes could be obtained. However, structural characterization by X-ray diffraction analysis of ligand **i** (*para*) was achieved (Fig. 6).  $(NC_{10}H_{14}O)_2C_6H_4$  crystallizes in the

orthorhombic  $P2_12_12_1$  space group. The two nitrogen atoms depict sp<sup>2</sup> geometry forming angles of 118.6(2)° (N2) and 121.7(2)° (N3) with the neighbour carbon atoms. The bridging phenyl group occupies a nearly orthogonal position to the two camphorimine moieties (angles between the nitrogen and phenyl planes are 82.5° (N2) and 78.3° (N3)) inhibiting extended electron delocalization between the camphor units through the  $\pi$ -system.

# 2.2. X-ray photoelectron spectroscopy studies (XPS)

The surface properties of selected compounds were studied by XPS (X-ray photoelectron spectroscopy) in the regions corresponding to the halogen (Cl 2p or Br 2p), to zinc  $(Zn 2p_{3/2})$ , to carbon (C 1s), to oxygen (O 1s) and, for some of them, sulphur (S 2p). Table 2 summarizes the data obtained for binding energies (BE) and respective assignments. A few XPS atomic ratios were included.

The Zn  $2p_{3/2}$  region was fit with a single peak centred at  $1022.5 \pm 0.2 \text{ eV}$  assigned to Zn(II) except for **1e**, where the amount of carbon exceeds the stoichiometric one by a factor of *ca*. 2. Since the binding energy of C 1s in C–C and **C**–H bonds was taken as reference for correcting binding energy charge shifts, the fact that in **1e** a lot of carbon coming from a different origin exists may be the reason for larger values found for Zn  $2p_{3/2}$ , Cl 2p and N 1s binding energy in this sample.

The XPS Cl 2p region was fit with a single doublet having a spinorbit split of  $1.6 \pm 0.1$  eV; its main component, Cl  $2p_{3/2}$  is centred at 198.8  $\pm 0.2$  eV a value very close to the one found in CuCl complexes [26]. However, when sample **1a**' was irradiated with 5 sweeps, a second small Cl 2p doublet, with the main component (Cl  $2p_{3/2}$ ) centred at BE = 200.4  $\pm$  0.2 eV, absent in the single sweep spectrum, was needed for a good fit. This BE value is typical of chlorine bound to carbon [27] suggesting that this bond is promoted by irradiation. This effect was not observed for **1a** that was washed



Fig. 6. ORTEP drawing for ligand (i). Hydrogen atoms were omitted for clarity. Ellipsoids are drawn at 50% probability. (see Supplementary for details).

Table 2				
XPS binding	energy ( $\pm 0.2$	eV) and	ratios	(±10%).

XPS region	( <b>1a</b> ′)	( <b>1</b> a)	( <b>1e</b> ) <sup>a</sup>	( <b>1f</b> )	( <b>2a</b> )	( <b>2f</b> )	( <b>7i</b> )	Assignments
Zn 2p <sub>3/2</sub>	1022.5	1022.5	1023.1	1022.7	1022.7	1022.5	1022.6	Zn <sup>2+</sup>
N 1s 1	(399.3)	(399.4)	400.1	399.6	(399.2)	399.5		-NC <sub>6</sub> H <sub>4</sub> N-
								-NSO <sub>2</sub> -
N 1s 2	401.0	401.0		400.7	401.1	400.8	400.5	-Me <sub>2</sub> NNC <sub>10</sub> -
Cl 2p <sub>3/2</sub> 1	198.7	198.7	199.0	198.7				Cl <sup></sup>
Cl 2p <sub>1/2</sub> 1	200.3	200.3	200.6	200.4				
Cl 2p <sub>3/2</sub> 2	200.4		200.1	199.7				C— <b>Cl</b>
Cl 2p <sub>1/2</sub> 2	202.1		201.7	201.4				
Br 2p <sub>3/2</sub>					182.7	182.4	182.7	Br—
Br 2p <sub>1/2</sub>					189.4	189.1	189.4	
S 2p <sub>3/2</sub>				168.3		168.4		$-SO_2-$
S 2p <sub>1/2</sub>				169.5		169.6		
O 1s	532.2	532.3	532.4	532.3	532.3	532.2	532.4	C- <b>O</b>
C 1s 1	285.0	285.0	285.0	285.0	285.0	285.0	285.0	С-С, С-Н
C 1s 2	286.7	285.9	286.1	286.1	286.9	286.1	285.9	$\mathbf{C}-\mathbf{N}+\mathbf{C}-\mathbf{O}$
C 1s 3	288.6	288.1	289.4	288.6			288.1	<b>C</b> =0
Halogen/Zn	2.5	2.0	2.5	2.3	2.2	2.1		
N/halogen	0.9	0.9	0.7	1.1	0.9	1.5		
C/N	8.5	7.7	15.1	7.9	10.6	7.0		
O/N	1.9	0.7	2.8	1.8	2.4	1.6		

<sup>a</sup> See text for a comment on the charge shift correction for this sample.

with dichloromethane. In sample **1f**, the same effect is noticed. However, chlorine is more labile than in sample **1a**' since it occurs even for the single sweep spectrum. The relative importance of the second doublet increases with the irradiation time. In compound **1e**, that was prepared in CH<sub>2</sub>Cl<sub>2</sub>, two doublets with similar intensities were needed to reach a good fit. These observations combined to the enormous difference between the measured C/N ratio and the stoichiometric one, suggest that occluded solvent stays in the sample.

Cl 2p<sub>3/2</sub> at higher binding energy comes mainly from the solvent. However the hypothesis that a part of it corresponds also to chlorine from the complex that bonds to carbon atoms, cannot be discarded since the relative importance of this second doublet increases with radiation time. Another explanation for this component increase is the diffusion of the occluded solvent towards the surface due to the sample heating induced by irradiation.

Analysis of the XPS Br 2p region in the samples with the Br coligand (**2a**, **2f**, **7i**) showed that, independently of the number of run sweeps, a single doublet with the main component Br  $2p_{3/2}$  centred at BE = 182.5  $\pm$  0.2 eV fitted the data in agreement with results reported for Cu(I) camphor derived complexes [21].

For samples **1a**' and **2a** the N 1s region displays one single component with BE around 401.0 eV denoting electron depletion in nitrogen, relatively to imine or amine nitrogen atoms [22]. A single component was fit also for sample **1e** at BE = 400 eV (or lower) denoting a higher electron density around the nitrogen atom. For samples **1f** and **2f** two components were fit at 399.5 and 400.7  $\pm$  0.2 eV the second one having an intensity which is twice the first one. The first component is attributed to the hydrazide group (NNMe<sub>2</sub>) and the second to the sulphonylimine (-NSO<sub>2</sub>) group (Fig. 7) showing that around the nitrogen atoms of the sulphonylimine group.

The N 1s components within brackets in Table 2, systematically at lower BE, are small components that appear with irradiation, meaning that the irradiation increases the electron density around some of the nitrogen atoms.

The few XPS atomic ratios included in Table 2 summarize the main quantitative observations. The nitrogen/halogen ratios are close to the expected ones, except for samples **1e** and **1f** where the ratios are lower than expected (beyond the experimental error). Since both samples were washed with dichloromethane, some solvent was probably retained accounting for the results obtained.

SEM pictures obtained from **1f** clearly show that the morphology of the powder consists of tubes with one or both capped extremities. Solvent retention is, therefore possible (Fig. 8) even in the XPS ultra-high vacuum conditions.

The experimental halogen/zinc atomic ratios are trendily higher than the stoichiometric ones which, combined with the fact that C/ N ratio is also much higher than the stoichiometric one, means that, at least partly, the extra carbon is due to a solvent layer retained near the surface of the sample. This layer leads to the attenuation of photoelectrons coming from the complex. Zn 2p having a much lower kinetic energy (=1486.6 eV-BE) are more attenuated than the



Fig. 7. XPS N 1s region for (from bottom to top) samples 1a', 1a, 1e, 1f, 2a, 2f and 7i.



Fig. 8. Images of complexes [ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (1f, top) and [ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)] (1a, bottom) obtained by SEM.

N 1s, C 1s or Cl 2p (or Br 2p) ones, decreasing the relative intensity of its photoelectrons. The amount of sample **7i** analysed by XPS was very small and, therefore, all the signals coming specifically from this sample had very low intensity; consequently, the relative errors in peak areas are large.

Regions C 1s and O 1s contain information coming also from the sample holder and, therefore will not be further discussed, mainly for sample **7i** where the relative contribution from the sample to the total signal is small.

#### 2.3. Scanning Electron Microscopy studies (SEM)

The data from XPS strongly suggest that some solvent molecules exist at the surface of zinc camphor complexes. Data from microanalysis also shows that, in the bulk, the complexes tend to keep solvent molecules. Thus, we decided to have a closer look into the surface characteristics of some complexes using SEM. Pictures obtained from complexes **1f** and **1a** are displayed in Fig. 7.

Particles **1f** and **1a** have tubular forms. Tubes are identified since a few of them are not capped in, at least, one of the extremities. Fig. 8 (top) shows the detail of one of the tubes that looks like one brick with a cavity (*ca.* 10  $\times$  10  $\mu$ m). In such cavities, solvent molecules can accommodate. Raise of temperature accompanying XPS irradiation can in principle promote release of solvent captured molecules, which under the ultra-high vacuum conditions used by XPS analysis would evaporate. However, if they are occluded in a closed cavity, they cannot escape. Instead, they migrate towards the surface this providing an explanation for the high content in carbon, oxygen and halogen measured by XPS.

The cavities observed in the particles of the Zn(II) complexes and the XPS results became a challenge to check whether there was a relation between the structure and the reactivity. To test that, reactions were undertaken in the absence of solvent.

# 2.4. Catalysis

The reaction of **1a** and **1f** with 4-pentyn-1-ol (**S**) was carried out in the absence of solvent and the composition of the mixture verified by <sup>1</sup>H NMR in CDCl<sub>3</sub>. After 3 days at 40 °C no products of cyclization were observed, discouraging further studies.

In solution (CDCl<sub>3</sub>), 4-pentyn-1-ol (**S**) reacts with complexes **1a**, **2a**, **3b** and **6i** at RT with formation of a compound which was identified by NMR (<sup>1</sup>H, <sup>13</sup>C{H}) as 2-methyl-2-(pent-4-yn-1-yloxy) tetrahydrofuran (**P**, Scheme 1) [5] and by HPLC as an unresolved mixture of *R* and *S* enantiomers (two signals with similar areas (52/48, RT = 6.35 and 6.70 min). The lack of chirality transfer was expected due to the weak chelating character of the ligand.

To confirm the complexes were the effective catalysts, the reaction of  ${\bf S}$  with ZnZl<sub>2</sub> was undertaken. No cyclization or other products were obtained.

Integration of the signal assigned to the methyl group of **P** (1.23 ppm in <sup>1</sup>H NMR) (normalized by the integration of the methyl signals of camphor) in spectra obtained from reactions of **S** with Zn complexes (**1a**, **2a**, **3b** and **6i**) shows that all the complexes enable cyclization of 4-pentyn-1-ol with addition of a second molecule of alkynol to the heterocycle, within a process similar to that promoted by Pd(II) or Pt(II) camphor derived complexes, that involves protonation and release of the camphor ligand to generate the active catalyst [5,7].

The catalytic activities of the mononuclear complexes (**1a**, **2a**, **3b**) are considerably lower at RT (100 mol **P** *per* (mol cat  $\times$  mol **S**  $\times$  hr)) than at 40 °C (*ca*. 400 mol **P** *per* (mol cat  $\times$  mol **S**  $\times$  hr). From the catalysts under study, the binuclear complex **6i** displays the highest catalytic activity (Fig. 9).

Relevant aspects concerning the catalytic activity of Zn complexes are: i) the halide co-ligand nature (chloride considerably enhances the catalytic activity), as verified for



**Fig. 9.** Data obtained by integration of the methyl signal of **P** (Scheme 1) in the <sup>1</sup>H NMR spectra. For eye guiding, a line connecting symbols is included.

[ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)] (**1a**) and [ZnBr<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)] (**2a**) and ii) the number of ligands, as verified for [ZnCl<sub>2</sub>(H<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>] (**3b**) that displays lower catalytic activity than [ZnCl<sub>2</sub>(Me<sub>2</sub>NN-C<sub>10</sub>H<sub>14</sub>O)] (**1a**). The weak chelate character of the ligand in **1a** (Fig. 2) favours coordination of 4-pentyn-1-ol enabling the catalytic process. The binuclear character of complex **6i** (two metal sites *per* molecule) accounts for the higher catalytic activity (*ca*. 1000 mol **P** *per* (mol cat × mol **S** × hr)) compared to the mononuclear complexes. Hydration of the triple bond of **P** by traces of water, leads to formation of 5-(2-methyltetrahydrofuran-2-yl)oxy)pentan-2-one in a competitive process responsible for no complete conversion of **S** into **P**, although the alkynol is fully consumed. The highest conversion of **S** into **P** (conversion *ca*. 60%) is attained after 70 h reaction at 40 °C using **6i** as catalyst.

Comparing the efficiency of the Zn(II) with that of Pd(II) or Pt(II) camphor derived complexes [5,7] for 4-pentyn-1-ol (**S**) cyclization it comes out that the Zn(II) complexes need longer reaction times to convert **S** into **P** (Scheme 1), thus they are less efficient. The higher basicity of the nitrogen atom of the coordinated ligands at Pd(II) or Pt(II) complexes is a key parameter, since deprotonation of **S** is necessary to enable interaction of the CC triple bond with the metal and promote cyclization.

Although the catalytic activity of  $[(ZnCl_2)_2\{(p-NC_{10}H_{14}O)_2C_6H_4\}]$ (**6i**) is lower than that of Pd(II) camphor derived complexes it can be considered as a good alternative for cyclization of 4-pentyn-1-ol (**S**) to form 2-methyl-2-(pent-4-yn-1-yloxy)tetrahydrofuran (**P**) due to the lower price and less environmental harmful properties of zinc compared to palladium.

The ability of  $[ZnCl_2(Me_2NNC_{10}H_{14}O)(THF)]$  (**1a**) to promote reaction of phenyl acetylene with aniline was also probed. No products of hydroamination were obtained due to complex decomposition. Replacement of the camphor ligand by aniline in the coordination sphere of zinc yields  $[ZnCl_2(NH_2C_6H_5)_2]$  (**8**) (Eq. (2)) which was characterized by elemental analysis, IR and NMR (see experimental).

$$\begin{split} & [\text{ZnCl}_2(\text{Me}_2\text{NNC}_{10}\text{H}_{14}\text{O})(\text{THF})] + 2\text{C}_6\text{H}_5\text{NH}_2 \rightarrow [\text{ZnCl}_2(\text{NH}_2\text{C}_6\text{H}_5)_2] \\ & + 2\text{Me}_2\text{NNC}_{10}\text{H}_{14}\text{O} + \text{THF} \end{split}$$

# 3. Conclusions

Zn(II) displays high ability to coordinate camphor imines  $(YNC_{10}H_{14}O)$  and camphor sulphonylimines  $(YNC_{10}H_{13}NSO_2)$  forming complexes with metal to ligand ratios that range from 1:1  $([ZnX_2(YNC_{10}H_{14}O)], [ZnX_2(YNC_{10}H_{13}NSO_2)])$  to 1:2  $([ZnX_2(H_2 NNC_{10}H_{14}O)_2])$  or 2:1  $([{ZnX_2}_2(YNC_{10}H_{14}O)])$ . The characteristics of

the Y group direct which type of complex forms, in particular when hydrogen atoms are involved (Y = NHMe, NH<sub>2</sub>). Metal to ligand ratio 1:2 was found just in the case of Y = NH<sub>2</sub> (**3b**, **4b**); ligand modification (Y = NHMe) induces formation of the dimer species [ $Zn(MeNNC_{10}H_{14}O)$ ]<sub>2</sub>(µ-Cl)<sub>2</sub>] (**5c1**).

Analysis by XPS of a selection of Zn camphor complexes showed that they have high tendency to keep solvent molecules in the structure. This behaviour was further investigated by Scanning Electron Microscopy. The images obtained by SEM (**1a**, **1f**) reveal tubular structures with cavities where solvent can accommodate and remain, even in ultra-high vacuum conditions. By temperature increase (e.g. irradiation) the solvent molecules migrate towards the surface of the powder, entering the range of depths probed by XPS. This may explain the high content of carbon and oxygen or halogen found by XPS depending on the solvent characteristics. The structural characterization of [ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)(THF)] made by single crystal X-ray diffraction analysis shows that one molecule of solvent (THF) coordinates the metal.

Evaluation of the ability of the complexes to activate CC triple bonds showed they catalyse the cyclization of 4-pentyn-1-ol with concomitant addition of a second molecule of alkynol forming 2methyl-2-(pent-4-yn-1-yloxy)tetrahydrofuran with activities that increase considerably by raising the temperature from *ca*. 20 to 40 °CC. The bi-camphor complexes (**6**, **7**) display higher catalytic activities than the camphor derived complexes (**1**, **2**, **3**, **4**).

#### 4. Experimental section

The synthesis of the zinc complexes were performed in the glove box. Other manipulations were undertaken under nitrogen atmosphere using vacuum and Schlenk techniques. The solvents were purchased from Lab-Scan purified by conventional techniques and distilled before use. Zinc bromide was purchased from BDH and zinc chloride from Aldrich. ZnCl<sub>2</sub> was recrystallized from THF before use.

The camphor derived compounds  $YNC_{10}H_{14}O$  (Y = NMe<sub>2</sub> (**a**), NH<sub>2</sub> (**b**), NHMe (**c**)) and camphorquinoxaline (**e**) were prepared by published methods [7,17,28–30]. The IR spectra were obtained from KBr pellets using a JASCO FT/IR 4100 spectrometer. NMR spectra (<sup>1</sup>H, <sup>13</sup>C{H}, DEPT, 2D) were obtained from CDCl<sub>3</sub> or MeOH-d<sub>4</sub> solutions using Bruker Avance II<sup>+</sup> Spectrometers (300 or 400 MHz) and referred to tetramethylsilane ( $\delta = 0$  ppm). The optical properties (rotation angle and enantiomers ratio) were measured using respectively an automatic Atago polarimeter and an HPLC equipment UHPLC<sup>+</sup> focused Dionex equipped with a column Lux 5 Cellulose-1 Phenpomenex (isopropanol/n-hexane (1/9); flow rate 0.5 mL/min) and a UV/Vis detector (working at 254 nm).

#### 4.1. Synthesis of bi-camphor compounds

#### 4.1.1. 3,3'-(1,4-Phenylenebis(azanylylidene)bis(1,7,7-

trimethylbicyclo[2.2.1]heptan-2-one-(p-NC<sub>10</sub>H<sub>14</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (i)

This synthetic procedure improves that in Ref. [31]. Acetic acid (0.5 mL) and camphorquinone (0.51 g, 3.0 mmol) were stirred in EtOH (5 mL) for 1hr. Then *p*-phenylenediamine (0.16 g, 1.51 mmol) was added and the mixture further stirred for 18 h at 50 °C affording a yellow suspension that was filtered off solution, washed with n-pentane (3 × 5 mL) and dried. Yield 79%. Elemental analysis for C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>- $^{3}/_{4}$  EtOH (%): Found C, 75.2; N, 6.9; H, 7.9. Calc. C, 75.2; N, 6.4; H, 8.3. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +18.5°, *c* 0.065, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1756 ( $\nu$ <sub>CO</sub>), 1685 ( $\nu$ <sub>CN</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 6.95 (s, 4H), 2.99 (d, *J* = 4.8, 1H), 2.11–1.63 (m, 4H), 1.08 (s, 3H), 0.98 (s, 3H), 0.89 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 206.5, 171.8, 146.9, 121.9, 58.3, 50.4, 44.8, 30.3, 24.5, 21.1, 17.7, 9.2.

# 4.1.2. 3,3'-(1,3-Phenylenebis(azanylylidene)bis(1,7,7-

# trimethylbicyclo[2.2.1]heptan-2-one - $(m-NC_{10}H_{14}O)_2C_6H_4$ (j)

Camphorquinone (0.31 g, 1.9 mmol) was stirred in EtOH (5 mL) acidified with acetic acid (0.5 mL) for 1 h. Then *m*-phenylenediamine (0.10 g, 0.93 mmol) was added and the mixture fluxed with nitrogen and stirred overnight at 50 °C. Extraction with CHCl<sub>3</sub> ( $3 \times 5$  mL) and drying the organic layer over anhydrous MgSO<sub>4</sub> the solution taken to dryness. The yellow solid was washed with n-pentane ( $2 \times 3$  mL) to afford the title yellow compound. Yield 91%. Elemental analysis for C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> (%): Found C, 76.5, N 6.8, H 8.0. Calc. C, 77.2; N, 6.9; H, 8.0. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +5.7°, *c* 0.070, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1748 ( $\nu$ <sub>CO</sub>), 1659 ( $\nu$ <sub>CN</sub>), 1578 ( $\nu$ <sub>CCarom</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.33 (t, *J* = 7.9 Hz, 1H), 6.70 (dd, *J*<sup>1</sup> = 7.8, *J*<sup>2</sup> = 1.9, 2H), 6.38 (t, *J* = 1.9, 1H), 2.81 (d, *J* = 4.0, 1H), 2.05–1.55 (m, 4H), 1.09 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 206.7, 172.7, 150.7, 129.8, 117.1, 111.4, 58.4, 50.3, 44.7, 30.3, 24.6, 21.1, 17.6, 9.2.

#### 4.2. Synthesis of complexes

All complexes, except **1a**, **2a** and **1d** were synthesized using the typical procedure described for **1e**. Slight changes in purification procedure are mentioned.

# 4.2.1. [ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>14</sub>O)(THF)] (**1a**)

ZnCl<sub>2</sub> (0.25 g, 1.8 mmol) and (*E*)-3-(2,2-dimethylhydrazono)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (**a**, 0.38 g, 1.8 mmol) were stirred in THF (6 mL) for 2 h. The solvent was partially evaporated and n-pentane (2 mL) added. The white crystalline precipitate was filtered off and dried under vacuum. A further crop of compound was obtained by evaporation of the residual solvent and washing with CH<sub>2</sub>Cl<sub>2</sub> (**1a**). Total yield 63%. Elemental analysis for ZnCl<sub>2</sub>C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub> (%): Found C, 46.1; N, 6.7; H, 7.0%. Calc: C, 46.1; N, 6.7; H, 6.8. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +3.3°, *c* 0.076, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1653 ( $\nu$ <sub>CO</sub>), 1535 ( $\nu$ <sub>CN</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 3.75 (m, 4H), 3.49 (s, 6H), 3.25 (d, *J* = 4.0, 1H), 2.15–1.60 (m, 4H), 1.83 (m, 4H), 1.10 (s, 3H), 1.01 (s, 3H), 0.93 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 211.6, 138.8, 68.2, 57.0, 50.8, 49.1, 29.8, 25.9, 25.7, 25.6, 21.3, 17.8, 8.5.

# 4.2.2. $[ZnCl_2\{(H_2NC_6H_4)NC_{10}H_{14}O\}]$ (1d)

ZnCl<sub>2</sub> (0.060 g, 0.43 mmol) and 3-((4-aminophenyl)imino)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (**d**, 0.10 g, 0.39 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) for 18 h. The unreacted ZnCl<sub>2</sub> was filtered and the solvent was fully evaporated. The orange solid obtained was washed with n-pentane, filtered and dried under vacuum. Yield 61%. Elemental analysis for ZnCl<sub>2</sub>Cl<sub>6</sub>H<sub>18</sub>N<sub>2</sub>O <sup>3</sup>/<sub>4</sub> H<sub>2</sub>O (%): Found C, 47.7; N, 7.0; H, 4.8. Calc. C, 47.5; N, 6.9; H, 4.8. IR (cm<sup>-1</sup>): 3444, 3364 ( $\nu$ <sub>NH</sub>), 1736 ( $\nu$ <sub>CO</sub>), 1624 ( $\nu$ <sub>CN</sub>), 1600 ( $\nu$ <sub>CCarom</sub>), 1507 ( $\nu$ <sub>NH</sub>). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>, δ ppm): 6.95 (d, *J* = 8.0, 2H), 6.77 (d, *J* = 8.0, 2H), 3.03 (d, *J* = 4.0, 1H), 2.26–1.61 (m, 4H), 1.07 (s, 3H), 1.05 (s, 3H), 0.83 (s, 3H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>, δ ppm): 208.4, 169.9, 148.6, 125.5, 116.6, 58.8, 52.1, 46.3, 31.6, 24.9, 21.1, 17.7, 9.2.

# 4.2.3. $[ZnCl_2\{(NC_6H_4)NC_{10}H_{14}\}]$ (1e)

A mixture of ZnCl<sub>2</sub> (0.057 g, 0.42 mmol) and camphorquinoxaline (**e**, 0.10 g, 0.53 mmol) were stirred in THF (3 mL) for 18 h. The solvent was evaporated and the orange precipitate was washed with CH<sub>2</sub>Cl<sub>2</sub> filtered off and dried under vacuum. Yield 78%. Elemental analysis for ZnCl<sub>2</sub>C<sub>16</sub>H<sub>18</sub>N<sub>2</sub> <sup>1</sup>/<sub>8</sub> CH<sub>2</sub>Cl<sub>2</sub> (%): Found C, 50.1; N, 7.4; H, 5.0. Calc. C, 50.3; N, 7.3; H, 4.7. [ $\alpha$ ]<sup>25</sup><sub>2</sub> +7.8°, *c* 0.064, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1625 ( $\nu$ <sub>CCarom</sub>), 1516 ( $\nu$ <sub>CN</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 8.57 (d, *J* = 7.6, 1H), 8.10 (d, *J* = 6.4, 1H), 7.72 (m, 2H), 3.75 (d, *J* = 3.2, 1H), 2.06–1.42 (m, 4.0 H), 1.42 (s, 3H), 1.10 (s, 3H), 0.62 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 167.4, 165.1, 142.4, 129.9, 129.7, 126.8, 55.0, 54.3, 53.8, 31.6, 24.7, 20.6, 18.4, 10.2.

#### 4.2.4. [ZnCl<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (1f)

ZnCl<sub>2</sub> (0.030 g, 0.22 mmol) and 7-(2,2-dimethylhydrazono)-8,8dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methanobenzo[c]isothiazole 2,2-dioxide (**f**, 0.055 g, 0.20 mmol) yielded 53% of **1f** as a light yellow precipitate. Elemental analysis for ZnCl<sub>2</sub>C<sub>12</sub>H<sub>19</sub>N<sub>3</sub>SO<sub>2</sub>· $^{3}/_{4}$ THF (%): Found C 39.3; N, 8.7; H, 5.6; S, 6.6. Calc. C, 39.2; N, 9.1; H, 5.4; S, 7.0. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +3.2°, *c* 0.046, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1657, 1547 ( $\nu$ <sub>CN</sub>), 1315 ( $\nu$ <sub>SO2assym</sub>); 1158, 1136 ( $\nu$ <sub>SO2sym</sub>); <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 3.36, (s, 6H), 3.17 (d, *J* = 4.1, 1H), 3.27, 3.24 (2d, *J* = 13.2, 2H), 2.10– 1.70 (m, 4H), 1.03 (s, 3H), 0.95 (s, 3H). <sup>13</sup>C{H} NMR (MeOH0-d<sub>4</sub>,  $\delta$  ppm): 188,6, 132.6, 63.6, 53.3, 50.5, 46.2, 29.4, 27.1, 26.5, 20.0, 19.1.

# 4.2.5. $[ZnBr_2(Me_2NNC_{10}H_{14}O)]$ (**2a**)

A procedure similar to that of **1a** was used. Camphor imine **a** (0.10 g, 0.50 mmol) and ZnBr<sub>2</sub> (0.11 g, 0.50 mmol) yielded 78% of **2a**. Elemental analysis for ZnBr<sub>2</sub>C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O·½THF (%): Found C 35.9, N 5.7, H 5.0. Calc. C, 35.8, N 6.0, H 5.1. IR (cm<sup>-1</sup>): 1657 ( $\nu_{CO}$ ), 1547 ( $\nu_{CN}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 3.42 (s, 6H), 3.24 (d, *J* = 4.4, 1H), 2.14–1.59 (m, 4H), 1.08 (s, 3H), 1.00 (s, 3H), 0.93 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 210.1, 140.3, 57.0, 51.0, 48.6, 46.6, 30.1, 26.1, 21.3, 18.2, 8.8.

#### 4.2.6. $[ZnBr_2\{(H_2NC_6H_4)NC_{10}H_{14}O\}]$ (**2d**)

ZnBr<sub>2</sub> (0.044 g, 0.19 mmol) and camphorimine **d** (0.050 g, 0.19 mmol) yielded 97% of **2d**. Elemental analysis (%) for ZnBr<sub>2</sub>C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O  $^{3}/_{4}$  H<sub>2</sub>O: Found: C, 38.7; N, 5.5; H, 4.1. Calc. C, 38.8; N, 5.7; H, 4.3. IR (cm<sup>-1</sup>): 3356, 3217 ( $\nu_{NH}$ ), 1739 ( $\nu_{CO}$ ), 1602 ( $\nu_{CN}$ ), 1507 (NH<sub>scissor</sub>). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 6.94 (d, *J* = 8.0, 2H), 6.75 (d, *J* = 8.0, 2H), 3.04 (d, *J* = 4.0, 1H), 2.25–1.60 (m, 4.0 H), 1.07 (s, 3H), 1.05 (s, 3H), 0.83 (s, 3H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 208.2, 169.8, 148.9, 148.9, 139.1, 125.4, 116.3, 58.7, 52.2, 46.2, 31.6, 24.9, 21.0, 17.8, 9.3.

#### 4.2.7. $[ZnBr_2\{(NC_6H_4)NC_{10}H_{14}\}]$ (**2e**)

ZnBr<sub>2</sub> (0.096 mg, 0.43 mmol) and camphorquinoxaline (**e**, 0.10 g, 0.43 mmol) yielded 97% of **2e**. Elemental analysis (%) for ZnBr<sub>2</sub>C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>·THF: Found: C, 45.1; N, 4.8; H, 5.2. Calc. C, 44.8; N, 5.2; H, 4.9. IR (cm<sup>-1</sup>): 1624 (νCC<sub>arom</sub>) 1517 (ν<sub>CN</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 8.69 (d, J = 8.0, 1H), 8.10 (d, J = 8.0, 1H), 7.71 (m, 2H), 2.61 (d, J = 4.0, 1H), 2.32–1.48 (m, 4.0 H), 1,42 (s, 3H), 1.10 (s, 3H), 0.63 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 167.8, 165.4, 142.4, 136,8, 129,9, 58.1, 55.0, 54.2, 31.4, 24.7, 20.6, 18.4, 10.2.

# 4.2.8. [ZnBr<sub>2</sub>(Me<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (2f)

ZnBr<sub>2</sub> (0.059 g, 0.26 mmol) and 7-(2,2-dimethylhydrazono)-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methanobenzo[c] isothiazole 2,2-dioxide (**f**, 0.055 mg, 0.20 mmol) yielded 42% of the whitish precipitate. Elemental analysis (%) for ZnBr<sub>2</sub>C<sub>12</sub>H<sub>19</sub>N<sub>3</sub>SO<sub>2</sub>·THF: Found: C, 33.9; N, 7.4; H, 5.0; S, 5.5. Calc: C, 33.9; N, 7.4; H, 4.8; S, 5.6.  $[\alpha]_D^{25}$  +4.0°, *c* 0.050, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1617, 1539 ( $v_{CN}$ ); 1316 ( $v_{SO2assym}$ ); 1159, 1136 ( $v_{SO2assym}$ ); 1159, 1136 ( $v_{SO2assym}$ ); 1216–1.77 (m, 4H), 1.03 (s, 3H), 0.86 (s, 3H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub> (due to low solubility in CDCl<sub>3</sub>) δ ppm): 188.1, 131.4, 60.2, 52.2, 51.5, 50.8, 47.0, 28.1, 26.2, 20.3, 19.4.

#### 4.2.9. $[ZnBr_2\{(m-NC_{10}H_{14}O)_2C_6H_4\}]$ (**2***j*)

ZnBr<sub>2</sub> (0.067 g, 0.030 mmol) and 3,3'-(1,3-phenylen ebis(azanylylidene)bis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (**j**, 0.10 g, 0.25 mmol) yielded 62% of **2j**. Elemental analysis (%) for ZnBr<sub>2</sub>C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> ¼THF: Found: C, 50.0; N, 4.0; H, 5.5. Calc. C, 50.0; N, 4.3; H, 5.3. IR (cm<sup>-1</sup>): 1752 ( $v_{CO}$ ), 1677 ( $v_{CN}$ ), 1593 ( $v_{CCarom}$ ). <sup>1</sup>H NMR (MeOH-d<sub>3</sub>,  $\delta$  ppm): 7.47 (t, *J* = 7.6, 1H), 6.84–6.82 (m, 2H), 6.51 (s, 1H), 2.86 (d, *J* = 4.8, 2H), 2.20–1.65 (m, 8.0 H), 1.09 (s, 6H), 1.04 (s, 6H), 0.91 (s, 6H). <sup>13</sup>C{H} NMR (MeOH-d<sub>3</sub>,  $\delta$  ppm): 207.4, 174.8, 151.2, 131.3, 118.8, 113.3, 59.2, 51.7, 45.6, 31.2, 25.2, 21.3, 17.6, 9.2.

#### 4.2.10. $[ZnCl_2(H_2NNC_{10}H_{14}O)_2]$ (**3b**)

ZnCl<sub>2</sub> (0.090 g, 0.66 mmol) and **b** (0.12 g, 0.68 mmol) yielded 19% of the white solid **3b**. Elemental analysis for ZnCl<sub>2</sub>C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>O·½CH<sub>2</sub>Cl<sub>2</sub> (%): Found C, 45.5; N, 10.1; H, 5.9. Calc. C, 45.6; N, 10.4; H, 6.1. IR (cm<sup>-1</sup>): 3406, 3283 ( $v_{NH}$ ), 1728 ( $v_{CO}$ ), 1636, 1584 ( $v_{CN}$ ). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 3.14 (d, *J* = 4.4, 1H), 2.05– 1.43 (m, 4H), 1.02 (s, 3H), 0.98 (s, 3H), 0.84 (s, 3H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 207.7, 148.7, 59.1, 46.9, 46.6, 32.6, 24.5, 20.6, 18.2, 9.3.

#### 4.2.11. $[ZnBr_2(H_2NNC_{10}H_{14}O)_2]$ (**4b**)

ZnBr<sub>2</sub> (0.059 g, 0.26 mmol) and camphorimine **b** (0.51 g, 0.28 mmol) reacted to yield 52%. Elemental analysis for ZnBr<sub>2</sub>C<sub>20</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub> (%): Found: C 41.2, N 9.4, H 5.7. Calc. C 41.0, N 9.6, H 5.5. IR (cm<sup>-1</sup>): 3397, 3274 ( $v_{NH}$ ), 1725 ( $v_{CO}$ ), 1634, 1581 ( $v_{CN}$ ). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 2.97 (d, J = 4.4, 1H), 2.04–1.44 (m, 4H), 1.00 (s, 3H), 0.97 (s, 3H), 0.83 (s, 3H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 207.5, 148.6, 58.9, 46.8, 46.4, 32.4, 24.3, 20.6, 18.2, 9.2.

#### 4.2.12. $[{Zn(MeNNC_{10}H_{14}O)}_{2}(\mu-Cl)_{2}]$ (5c1)

ZnCl<sub>2</sub> (0.070 g, 0.51 mmol) and 1,7,7-trimethyl-3-(methylhydrazinylidene) byciclo [2.2.1] heptan-2-one (**c**, 0.10 g, 0.51 mmol) reacted to form an oily solid that was washed with n-pentane (6 cm<sup>3</sup>) to yield a yellow precipitate that was filtered and dried under vacuum. Yield 49%. Elemental analysis for Zn<sub>2</sub>Cl<sub>2</sub>C<sub>22</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>·½THF (%): Found: C, 46.2; N, 9.0; H 6.5. Calc. C, 46.2; N, 9.0; H, 6.1. IR (cm<sup>-1</sup>): 1709, 1689 ( $\nu_{CO}$ ), 1616, 1569 ( $\nu_{CN}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 3.30 (s, 3H), 3.26 (d, *J* = 4.0, 1H), 3.10 (s, 3H), 2.44 (d, *J* = 4.0, 1H), 2.15–1.35 (m, 8H), 0.10 (s, 3H), 0.98 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H), 0.87 (s, 3H) 0.82 (s, 3H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 209.2, 203.5, 141.1, 140.9, 59.3, 57.3, 50.8, 48.6, 48.1, 38.1, 37.2, 30.9, 30.4, 26.3, 25.1, 21.0, 20.5, 18.7, 17.9, 8.9, 8.6.

# 4.2.13. [(ZnCl<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>NNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (**6g**)

Reaction of ZnCl<sub>2</sub> (0.058 g, 0.422 mmol) and **g** (0.102 g, 0.422 mmol) was performed using a procedure similar to **1d** affording a yellow precipitate. Yield 49%. Elemental analysis for Zn<sub>2</sub>Cl<sub>4</sub>C<sub>10</sub>H<sub>15</sub>N<sub>3</sub>SO<sub>2</sub> THF·H<sub>2</sub>O (%): Found: C, 28.0; N, 7.2; H, 4.8; S, 5.9. Cal. C, 27.8; N, 7.0; H, 4.1; S, 5.3; IR (cm<sup>-1</sup>): 3566, 3447 ( $\nu$ <sub>NH</sub>), 1623, 1559 ( $\nu$ <sub>CN</sub>). <sup>1</sup>H NMR (MeOD-d<sub>4</sub>,  $\delta$  ppm): 7.70 (s, 2H), 3.31–3.13 (d, *J* = 13.6, 2H), 2.68 (d, *J* = 3.6, 1H), 2.20–1.61 (m, 4H), 1.08 (s, 3H), 0.84 (s, 3H). <sup>13</sup>C{H} NMR (MeOD-d<sub>4</sub>,  $\delta$  ppm): 177.7, 138.2, 65.7, 53.2, 50.1, 29.4, 26.1, 24.3, 19.5, 19.3.

# 4.2.14. $[(ZnCl_2)_2\{(p-NC_{10}H_{14}O)_2C_6H_4\}]$ (**6***i*)

ZnCl<sub>2</sub> (0.067 g, 0.49 mmol) and 3,3'-(1,4-phenylenebis(azanylylidene)bis(1,7,7-trimethylbicyclo[2.2.1]hep-tan-2-one (**i**, 0.099 g, 0.245 mmol) yielded 53% of **6i**. Elemental analysis for Zn<sub>2</sub>Cl<sub>4</sub>C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> 1.5THF (%): Found C, 49.0; N, 3.8; H, 5.3. Calc. 48.9; N, 3.6; H, 5.6.  $[\alpha]_D^{25}$  +3.9°, *c* 0.051, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1748 ( $\nu_{CO}$ ), 1689 ( $\nu_{CN}$ ), 1589 (CC<sub>arom</sub>). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 7.07 (s, 4H), 2.92 (d, *J* = 4.8 Hz, 2H), 2.22–1.68 (m, 8.0 H), 1.09 (s, 6H) 1.05 (s, 6H), 0.90 (s, 6H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 207.6, 174.3, 147.9, 123.1, 59.1, 51.8, 45.7 31.3, 25.1, 21.2, 17.6, 9.2.

#### 4.2.15. $[(ZnCl_2)_2\{(m-NC_{10}H_{14}O)_2C_6H_4\}]$ (6j)

ZnCl<sub>2</sub> (0.072 g, 0.53 mmol) and 3,3'-(1,3-phenyle nebis(azanylylidene)bis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (**j**, 0.11 g, 0.27 mmol) yielded 57% of **6j** upon wash of the oily solid with n-pentane (6 cm<sup>3</sup>) to afford a precipitate that was filtered and dried under vacuum. Elemental analysis for Zn<sub>2</sub>Cl<sub>4</sub>C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> n-pentane (%): Found C, 49.5; N, 3.9; H, 5.6. Calc. C, 49.6; N, 3.7; H, 5.9. IR (cm<sup>-1</sup>): 1734 ( $v_{CO}$ ), 1668 ( $v_{CN}$ ), 1591 (CC<sub>arom</sub>). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 7.46 (t, *J* = 7.2, 1H), 6.81 (d, *J* = 7.2, 2H), 6.51 (s, 1H), 2.85 (sbrl, 2H), 2.17–1.63 (m, 8H), 1.09 (s, 6H), 1.04 (s, 6H), 0.91 (s, 6H).

<sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>, *δ* ppm): 206.0, 173.3, 149.8, 129.9, 117.4, 111.9, 57.8, 50.3, 44.2, 29.8, 23.8, 20.0, 16.3, 7.1.

# 4.2.16. [(ZnBr<sub>2</sub>)<sub>2</sub>(MeHNNC<sub>10</sub>H<sub>13</sub>NSO<sub>2</sub>)] (**7h**)

Procedure such as used for **1a**. Reaction of ZnBr<sub>2</sub> (0.27 g, 1.22 mmol) with 8,8-dimethyl-7-(2-methylhydrazono)-4,5,6,7-tetrahydro-3*H*-3a,6-methanobenzo [*c*]isothiazole 2,2-dioxide (0.15 g, 0.60 mmol) afforded 36% of the title compound. Elemental analysis for Zn<sub>2</sub>Br<sub>4</sub>C<sub>11</sub>H<sub>17</sub>N<sub>3</sub>·7/4THF: Found C, 25.7; N, 4.5; H, 4.0, S, 3.9. Calc. C, 26.0; N, 5.0; H, 3.7, S, 3.9. IR (cm<sup>-1</sup>): 3310 ( $v_{\text{NH}}$ ), 1617, 1551 ( $v_{\text{CN}}$ ), 1320, 1157 ( $v_{\text{SO2}}$ ). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 3.75 (m, 14 H), 3.20 (s, 3H), 3.31–3.13 (m, 2H), 2.98 (d, *J* = 4.4, 1H) 2.21–1.51 (m, 4H), 1.87 (m, 14 H), 1.09 (s, 3H), 0.88 (s, 3H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 186.3, 136.9, 64.9, 50.1, 38.0, 31.1, 29.5, 26.6, 24.7, 19.6, 18.9.

# 4.2.17. $[(ZnBr_2)_2\{(p-NC_{10}H_{14}O)_2C_6H_4\}]$ (7i)

ZnBr<sub>2</sub> (0.054 g, 0.24 mmol) and **i** (0.050 g, 0.124 mmol) yielded 96% of **7i**. Elemental analysis for Zn<sub>2</sub>Br<sub>4</sub>C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> 2CH<sub>2</sub>Cl<sub>2</sub> (%): Found C, 38.8; N, 3.1; H, 4.3. Calc. C, 38.9; N, 3.2; H, 4.2.  $[\alpha]_{D}^{25}$  +8.6°, *c* 0.064, CH<sub>2</sub>Cl<sub>2</sub>. IR (cm<sup>-1</sup>): 1756 ( $v_{CO}$ ), 1685 ( $v_{CN}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 6.99 (s, 4H), 2.91 (d, *J* = 4.7 2H), 2.15–1.65 (m, 8.0 H), 1.00 (s, 6H), 0.90 (s, 6H), 0.896 (s, 6H). <sup>13</sup>C{H} NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 206.7, 171.8, 146.8, 122.1, 58.2, 50.4, 45.0, 30.3, 24.6, 21.2, 17.7, 9.2.

# 4.2.18. [ZnCl<sub>2</sub>(NH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] (8)

Upon addition of aniline (138 µL, 1.5 mmol) to a mixture of **1a** (0.012 g, 0.030 mmol) and phenyl acetylene (120 µL, 1.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) a white suspension immediately formed. The mixture was stirred for 2 h, the white precipitate filtered off and washed with Et<sub>2</sub>O to afford the compound. Yield 42%. Elemental analysis for ZnCl<sub>2</sub>C<sub>12</sub>H<sub>14</sub>N<sub>2</sub> (%): Found C, 44.2; N, 8.5; H, 4.4. Calc. C, 44.7; N, 8.7; H, 4.3. IR (cm<sup>-1</sup>): 3262, 3222 ( $v_{NH}$ ), 1605 ( $v_{NH}$ ), 1577 ( $v_{CCarom}$ ). <sup>1</sup>H NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 7.01 (m, 4H), 6.74 (m, 4H), 6.68 (m, 2H). <sup>13</sup>C{H} NMR (MeOH-d<sub>4</sub>,  $\delta$  ppm): 148.3, 130.0, 119.5, 116.8.

#### 4.3. Catalytic experiments

The catalytic experiments were performed in sure seal NMR tubes using degassed  $CDCl_3$  (CIL) as solvent. Typically  $CDCl_3$  (ca. 0.3 mL) was added to the catalyst precursor.

(0.0050 g) and the <sup>1</sup>H NMR spectrum obtained. Then, 50  $\mu$ L of 4-pentyn-1-ol (**S**) were introduced into the tube through the septa and the reaction followed by <sup>1</sup>H NMR. The conversion was calculated by integration of the methyl signal of the product (**P**) using as internal standard the integration of the signals of the methyl groups of camphor.

From time to time <sup>13</sup>C{H} NMR was obtained to corroborate the presence of the products.

#### 4.4. XPS and SEM experiments

X-ray photoelectron spectra (XPS) were recorded using nonmonochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) and a power of 120 W (12 kV × 10 mA) from an XSAM800 (KRATOS) XPS dual anode spectrometer. Samples were fixed to the sample holder by a double-side tape. Data acquisition was performed in UHV (~10<sup>-7</sup> Pa) at room temperature, take-off-angle (TOA) of 45°, in FAT operation mode, with high magnification and pass energy of 20 eV. Spectra were recorded using a Sun SPARC Station 4 with Vision software (KRATOS) by steps of 0.1 eV. In order to detect possible degradation effects, all the samples were analysed using, firstly, a single sweep per XPS region and, then, five sweeps per region. Source satellites and a Shirley background were subtracted T.A. Fernandes et al. / Journal of Organometallic Chemistry 760 (2014) 186-196

	1a′	f	h	i
Empirical formula	C <sub>16</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Zn	C <sub>12</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> S	C <sub>11</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> S	C <sub>26</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	431.73	269.36	256.34	404.55
Crystal system	Monoclinic (vide text)	Orthorhombic	Orthorhombic	Orthorhombic
Space group	B2 <sub>1</sub> (vide text)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P212121
Unit cell dimensions				
a/Å	7.4657(6)	7.8568(3)	8.4107(5)	7.3718(4)
b/Å	13.795(1)	10.6301(3)	11.5410(7)	17.256(1)
c/Å	18.779(2)	16.1284(6)	12.5578(9)	17.841(1)
α/deg	90	90	90	90
α/deg	90	90	90	90
γ/deg	90	90	90	90
Volume (Å <sup>-3</sup> )	1934.0(3)	1197.3(2)	1219.0(1)	2269.6(2)
Z, Dcal (g/cm <sup>3</sup> )	8, 1.431	4, 1.328	4, 1.391	4, 1.184
Absorption coefficient (mm <sup>-1</sup> )	1.556	0.239	0.260	0.075
F(000)	872	576	544	872
Crystal size (mm <sup>3</sup> )	0.3  imes 0.2  imes 0.3	0.3 imes 0.2 imes 0.25	0.3 imes 0.2 imes 0.2	0.3 imes 0.2 imes 0.3
$\theta$ range for data collection (deg)	2.62 to 40.74	2.53 to 30.61	2.40 to 24.96	1.64 to 33.18
Index ranges	$-12 \le h \le 13, -24 \le k \le 25,$	$-8 \le h \le 11, -15 \le k \le 15,$	$-8 \le h \le 11, -15 \le k \le 15,$	$6 \le h \le 11, 26 \le k \le 24,$
-	$-34 \le l \le 33$	$-22 \le l \le 16$	$-22 \le l \le 16$	$-24 \le l \le 27$
Reflections collected/	18263/11442	8856/4069	4343/2125	20016/8551

[R(int) = 0.0342] 4069/0/167

R1 = 0.0643.wR2 = 0.1129

Table 3 The date for [7-C] (Ma NNC H. O)THE (1-() Ma NNC H. NCO (1) MALINNC H. NCO (1) and (NC H. O) C H. (1)

to all spectra. Gaussian-Lorentzian products were used to fit experimental curves with XPSPEAK Version 4.1 (freeware). No external charge compensation was used: the charge shift was corrected using as reference the binding energy of sp<sup>3</sup> C 1s bound to carbon and hydrogen. The sensitivity factors used in quantification analysis were: 0.25 for C 1s; 0.66 for O 1s; 0.42 for N 1s, 0.48 for Zn 2p<sub>3/2</sub>, 0.73 for Cl 2p, 1.39 for Br 2p and 0.54 for S 2p.

[R(int) = 0.0216] 11442/0/213

R1 = 0.0369.wR2 = 0.0621

SEM was acquired using a JEOL equipment, model JSM - 7001 with the accelerating voltage equal to 5.0 kV.

#### 4.5. X-ray diffraction analysis

unique Data/restraints/

parameters Final R (observed)

The X-ray crystallographic data for complex [ZnCl<sub>2</sub>(Me<sub>2</sub>NN- $C_{10}H_{14}O$ )THF] (1a') and the camphor derived species  $Me_2NNC_{10}H_{14}NSO_2$  (f) and  $(NC_{10}H_{14}O)_2C_6H_4$  (i) was collected at 150(2) K using a Bruker AXS-KAPPA APEX II area detector apparatus equipped with a graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) and were corrected for Lorentz polarization and, empirically, for absorption effects. The structures were solved by direct methods using SHELX97 [32] and refined by full matrix least squares against  $F^2$  using SHELX97 all included in the suite of programs WinGX v1.70.01 for Windows [33]. In the case of complex **1a** that crystallizes in the monoclinic P2<sub>1</sub> space group it was used the following sequence:  $\mathbf{c}(\text{new}) = \mathbf{a}(\text{old}) + 2 \mathbf{c}(\text{old})$  emulating a orthorhombic **B** centred space group. The structure was solved considering that the crystal depicts a twinning with components related by a binary axis (matrix  $1 \ 0 \ 0$ ;  $0 \ -1 \ 0$ ;  $0 \ 0 \ -1$ ). The crystal was refined using the twinning model (monoclinic B2<sub>1</sub>) with weights respectively 47.2 and 52.8%. The non-hydrogen atoms were refined anisotropically and the H atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Crystal data and refinement parameters are summarized in Table 3. Illustrations of the molecular structures were made with ORTEP3 [34].

# 4.6. Computational calculations

Computational calculations were made by DFT with GAMESS-US [35] version R3 and a B3LYP functional using an SBKJC basis set

supplemented with a Grimme's C6 dispersion correction term [36,37].

[R(int) = 0.0624] 8551/0/277

R1 = 0.0677, wR2 = 0.1588

[R(int) = 0.0313] 2125/0/154

R1 = 0.0389, wR2 = 0.0970

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# Appendix A. Supplementary material

CCDC 937765, 937766, 937767, 937768 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.

#### Appendix B. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2013.10.040.

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