



# Axially chiral benzimidazolium based silver(I) and gold(I) *bis*-NHC complexes of R-BINOL scaffold: synthesis, characterization and DFT studies

SONALI RAMGOPAL MAHULE\*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra 400 076, India  
E-mail: sonalimahule@chem.iitb.ac.in

MS received 11 May 2017; revised 8 July 2017; accepted 18 July 2017; published online 4 September 2017

**Abstract.** The axially chiral ligand of R-BINOL scaffold was synthesized by a series of manipulations which involved different chemical reactions to obtain the desired silver(I) and gold(I)  $\{[L(L'-NHC)_2]M\}Cl$  ( $L = 3,3'$ -dimethyl-2,2'-dimethoxy-1,1'-binaphthyl,  $L' = i$ -propyl-benzo[d]imidazole) ( $M = Ag$  and  $Au$ ) complexes. Enantiopure R-BINOL was employed as a basic unit to synthesize a benzimidazole based *bis*-NHC ligand **1g** which was obtained through the formation of different intermediate **1(a-f)** compounds. The newly synthesized *bis*-NHC ligand precursor (**1g**) and its corresponding  $\{[L(L'-NHC)_2]Ag\}Cl$  (**1h**) and  $\{[L(L'-NHC)_2]Au\}Cl$  (**1i**) complexes were characterized by different spectroscopic techniques. The geometries of the optimized structure of the complexes **1h** and **1i** were computed at the B3LYP/SDD, 6-31G(d) level. Low temperature fluorescence spectroscopic studies did not show any evidence for the weak metal-metal interaction in these complexes.

**Keywords.** Chiral *bis*-N-heterocyclic carbene ligand; Ag(I) complex; Au(I) complex; computational study; electronic property.

## 1. Introduction

The development of chiral N-heterocyclic carbene (NHC) has been a very exciting topic in coordination chemistry for the last two decades. This trend is expanding day by day but, it is less likely to be explored in other interesting areas for their applications beyond the asymmetric catalysis.<sup>1-7</sup> At the same time, achiral NHCs have widely been studied for their different properties<sup>8-11</sup> and applications in the fields of medicine for drug designing,<sup>12-14</sup> nanosciences<sup>15,16</sup> and materials.<sup>17</sup> Herein, we developed a new benzimidazole based chiral *bis*-N-heterocyclic carbene ligand (**1g**) and its silver(I) (**1h**) and gold(I) (**1i**) complexes for their future perspective of studying their properties and applications.

A phenomenal progress has been made in synthesis, characterization and reactions of NHCs with unique electronic and steric properties. The structures can easily be modified by change in functional group in imidazolium ring, principally at the nitrogen, with different

organic and inorganic moieties.<sup>18-22</sup> The functionalization of the NHC ligand can be utilized in different ways depending upon the metal and also on the oxidation state of the metal coordinated to NHC ligand.<sup>23</sup> Therefore, the chemistry of NHCs has become mainstream in organometallics, challenging the popular *tert*-phosphine ligands.<sup>18,24-26</sup> However, the importance of optically active transition metal complexes of NHC ligands is interestingly increasing because of the current attraction in the preparation of new optical devices.<sup>27</sup>

Furthermore, in asymmetric catalysis, N-heterocyclic carbene ligands are popular as a growing class of ligands that can be a substituent to a phosphine ligand and produce more efficient metal complexes owing to their stability to air and moisture with strong  $\sigma$ -donor and poor  $\pi$ -acceptor properties.<sup>28,29</sup> In light of these facts, many N-heterocyclic carbene ligands are designed with different structural motifs, coordinated with various transition metals like copper(I), silver(I), gold(I), mercury(II), palladium(II), rhodium(III), ruthenium(II), etc., and are employed not only for various organometallics<sup>30,31</sup> but for organocatalytic

\*For correspondence

transformations.<sup>32</sup> Herein, we report and discuss one such versatile chiral structural motif, BINOL and its benzimidazole based N-heterocyclic carbene complexes. *R* and *S* enantiomers of BINOL have been extensively used as chiral ligands in a number of asymmetric reactions.<sup>33</sup> Their chirality is based on the blocked rotation around the C-C axis linking the two naphthyl units giving configurationally stable atropisomers.<sup>34</sup> Excellence in enantioselectivity of BINOL-type chiral N-heterocyclic ligand is its inflexible backbone and rigid chiral pocket, which allow only one face of substrate for attack and binding. The binaphthyl backbone imposes  $C_2$  symmetry upon the *bis*-carbene ligand and mutual anti-orientation of N-alkyl substituent with respect to the plane into which chelate ring is inscribed.<sup>35</sup>

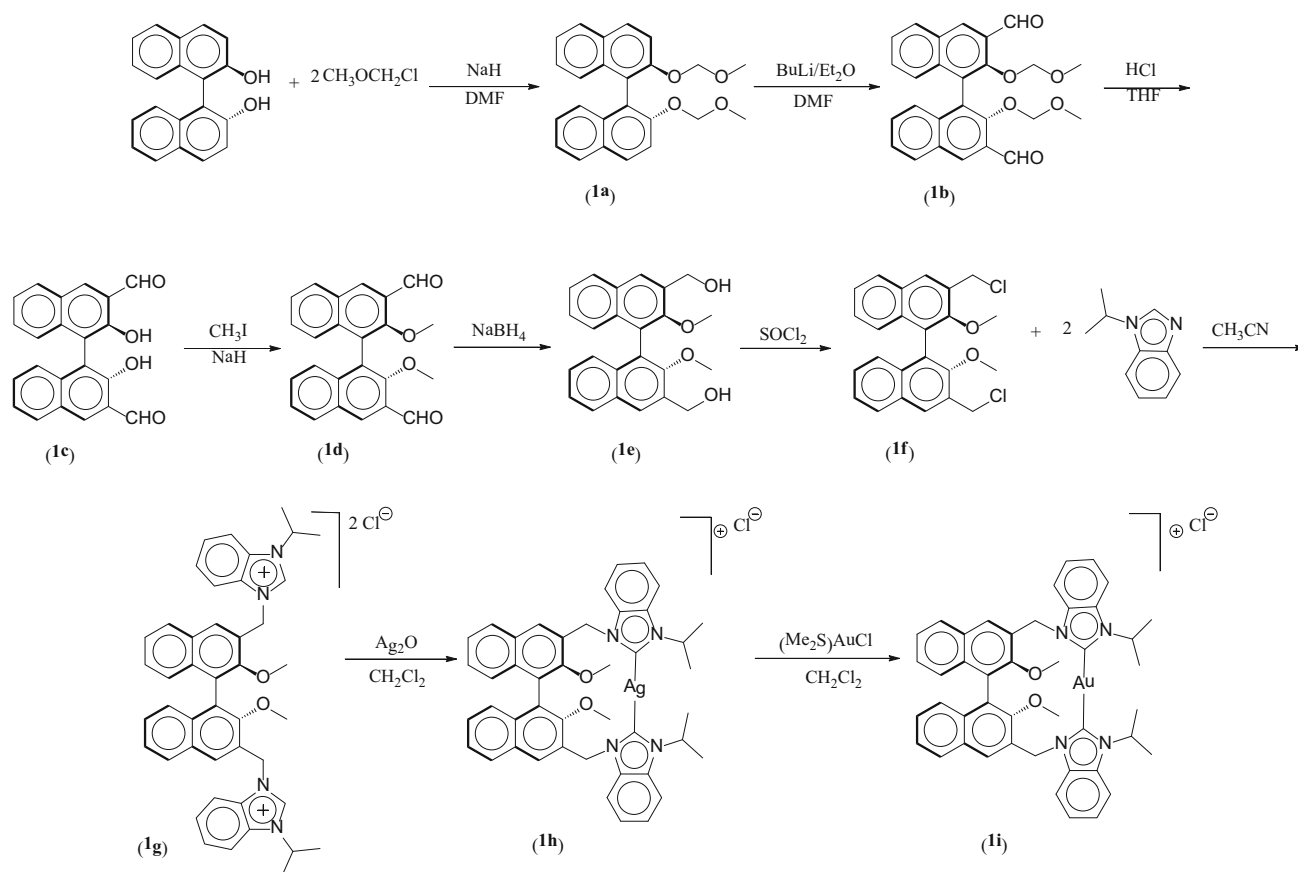
However, a very fascinating interaction between the closed shells of many organometallic or inorganic compounds of  $d^2$ ,  $d^8$  and  $d^{10}$  systems are interestingly being recognized as important determinants of solid-state structures as well as potential sources of useful materials.<sup>36-38</sup> These closed shell contacts are commonly known as metallophilic interactions and are experimentally observed by X-ray diffraction studies and by the electronic properties of complexes in its solid state.

In this work, we studied the electronic properties of Ag(I) and Au(I) complexes to check such M-M interactions in the solid state structure of the complexes of  $\{[L(L'-NHC)_2]M\}Cl$  type.

## 2. Experimental

### 2.1 General procedures

All manipulations were carried out using standard Schlenk techniques. Solvents were purified by standard procedures. *R*-BINOL and *n*-BuLi were purchased from Spectrochem (India) and used without any further purification. The compounds, *viz.*, **1(a-f)**<sup>39</sup> (see Scheme 1) were synthesized by manipulations of the procedures, reported in the literature. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub>, and CD<sub>3</sub>OD on a Bruker 400 and 500 MHz NMR spectrometers. <sup>1</sup>H NMR peaks are labelled as singlet (s), doublet (d), triplet (t), triplet of doublets (td) and multiplet (m). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-ToF spectrometer and Bruker maxis impact spectrometer. Elemental analysis was carried out on Thermo Finnigan Flash EA 112 SERIES (CHNS) Elemental analyser. Specific optical rotation experiments



**Scheme 1.** Synthetic pathway for the *R*-BINOL based axially chiral silver(I) and gold(I) complexes.

were performed with Autopol IV, Serial #82083 polarimeter. Absorption spectra were recorded on a Varian UV-Vis spectrophotometer in the range of 200–800 nm at room temperature whereas fluorescence studies were performed at 77 K using Horiba Fluoromax-4 spectrophotometer in a glassy solution of EtOH:CHCl<sub>3</sub> (4:1, v/v).

## 2.2 Synthesis of (*R*)-1,1'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methylene)bis(3-*i*-propylbenzo[d]imidazol-1-ium) chloride (1g)

A mixture of (*R*)-3,3'-bis(chloromethyl)-2,2'-dimethoxy-1,1'-binaphthyl (**1f**) (0.500 g, 1.21 mmol) and 1-*i*-propylbenzo[d]imidazole (0.48 g, 3.04 mmol) was refluxed in CH<sub>3</sub>CN (*ca.* 20 mL) for one day, after which the solvent was evaporated *in vacuo*. The product was purified by column chromatography using silica gel as a stationary phase eluted with CH<sub>2</sub>Cl<sub>2</sub>:MeOH (5:1 v/v) to give the product **1g** (0.473 g, 53%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C): δ 9.81 (s, 2H, NHCHN of C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 8.22 (s, 2H, C<sub>10</sub>H<sub>5</sub>), 8.00 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.93 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 7.88 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 7.63 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 7.54 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 7.38 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.20 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 6.96 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 5.98 (d, 2H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, CH<sub>2</sub>), 5.92 (d, 2H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, CH<sub>2</sub>), 5.05 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.00 (s, 6H, CH<sub>3</sub>), 1.66 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (CD<sub>3</sub>OD, 125 MHz, 25°C): δ 155.6 (C<sub>10</sub>H<sub>5</sub>), 141.8 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 135.8 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 132.9 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 132.8 (C<sub>10</sub>H<sub>5</sub>), 132.4 (C<sub>10</sub>H<sub>5</sub>), 131.7 (C<sub>10</sub>H<sub>5</sub>), 129.7 (C<sub>10</sub>H<sub>5</sub>), 128.7 (C<sub>10</sub>H<sub>5</sub>), 128.2 (C<sub>10</sub>H<sub>5</sub>), 128.1 (C<sub>10</sub>H<sub>5</sub>), 127.7 (C<sub>10</sub>H<sub>5</sub>), 126.8 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 126.3 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 125.2 (C<sub>10</sub>H<sub>5</sub>), 115.1 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 115.05 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 61.3 (CH<sub>2</sub>), 52.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 48.8 (CH<sub>3</sub>), 22.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.2 (CH(CH<sub>3</sub>)<sub>2</sub>). HRMS (ES): *m/z* 330.1725 [M-2Cl]<sup>2+</sup> calcd. 330.1727. IR data in KBr pellet, ν/cm<sup>-1</sup>: 2979 (s), 1621 (m), 1557 (s), 1499 (m), 1318 (m), 1242 (s), 1206 (s), 1147 (m), 1097 (s), 1039 (m), 1002 (m), 893 (m), 798 (m), 750 (s), 496 (m). Anal. Calc. for C<sub>44</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> • CHCl<sub>3</sub>: C, 63.50; H, 5.33; N, 6.58%. Found: C, 62.33; H, 5.89; N, 7.54%.

## 2.3 Synthesis of [(*R*)-1,1'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methylene)bis(3-*i*-propylbenzo[d]imidazol-2-ylidene)Ag] [Cl] (1h)

A mixture of (*R*)-1,1'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methylene)bis(3-*i*-propylbenzo[d]imidazol-1-ium) chloride (**1g**) (0.250 g, 0.340 mmol) and Ag<sub>2</sub>O (0.078 g, 0.340 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 10 mL) was stirred at room temperature in dark for overnight. The reaction mixture was filtered through a pad of celite to remove excess inorganic salt and then the solvent was removed *in vacuo* to obtain the product

**1h** as a white solid (0.256 g, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C): δ 7.75 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.65 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>4</sub>), 7.55 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.38 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.35 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.32 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.25 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.16 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 5.89 (s, 2H, CH<sub>2</sub>), 5.16 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.20 (s, 6H, CH<sub>3</sub>), 1.79 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (CDCl<sub>3</sub>, 125 MHz, 25°C): δ 187.3 (Ag-C), 153.9 (C<sub>10</sub>H<sub>5</sub>), 134.3 (C<sub>10</sub>H<sub>5</sub>), 134.1 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 132.7 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 130.2 (C<sub>10</sub>H<sub>5</sub>), 128.9 (C<sub>10</sub>H<sub>5</sub>), 128.5 (C<sub>10</sub>H<sub>5</sub>), 128.2 (C<sub>10</sub>H<sub>5</sub>), 127.3 (C<sub>10</sub>H<sub>5</sub>), 125.6 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 125.4 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 124.3 (C<sub>10</sub>H<sub>5</sub>), 124.2 (C<sub>10</sub>H<sub>5</sub>), 124.0 (C<sub>10</sub>H<sub>5</sub>), 112.6 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 112.5 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 61.5 (CH<sub>2</sub>), 53.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 48.9 (CH<sub>3</sub>), 22.7 (CH(CH<sub>3</sub>)<sub>2</sub>). HRMS (ES): *m/z* 766.2433 [M-Cl]<sup>+</sup> calcd. 766.2432. IR data in KBr pellet, ν/cm<sup>-1</sup>: 3056 (m), 2973 (m), 2934 (m), 1671 (m), 1622 (m), 1597 (m), 1498 (m), 1476 (s), 1387 (s), 1240 (s), 1147 (m), 1088 (m), 1006 (m), 886 (m), 746 (s), 668 (m), 527 (m). Anal. Calc. for C<sub>44</sub>H<sub>42</sub>AgClN<sub>4</sub>O<sub>2</sub>: C, 65.88; H, 5.28; N, 6.98%. Found: C, 66.80; H, 5.08; N, 7.55%.

## 2.4 Synthesis of [(*R*)-1,1'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methylene)bis(3-*i*-propylbenzo[d]imidazol-2-ylidene)Au] [Cl] (1i)

A mixture of [(*R*)-1,1'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methylene)bis(3-*i*-propylbenzo[d]imidazol-2-ylidene)Ag] [Cl] (**1h**) (0.200 g, 0.249 mmol) and Au(SMe<sub>2</sub>)Cl (0.073 g, 0.244 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 10 mL) was stirred in dark at room temperature for overnight. The reaction mixture was filtered through a pad of celite to remove excess inorganic salt and then the solvent was removed *in vacuo* to obtain a crude product which was purified by column chromatography using silica gel as a stationary phase and eluted with CH<sub>2</sub>Cl<sub>2</sub>:MeOH (99:1 v/v) to give a product **1i** as white powder (0.093 g, 42%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25°C): δ 7.78 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.75 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.68 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.58 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.340 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 6 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.36 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 6 Hz, C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 7.32 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, C<sub>10</sub>H<sub>5</sub>), 7.26 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, C<sub>10</sub>H<sub>5</sub>), 7.16 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, C<sub>10</sub>H<sub>5</sub>), 6.12 (d, 2H, <sup>2</sup>J<sub>HH</sub> = 16 Hz, CH<sub>2</sub>), 5.98 (d, 2H, <sup>2</sup>J<sub>HH</sub> = 16 Hz, CH<sub>2</sub>), 5.60 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 3.28 (s, 6H, CH<sub>3</sub>), 1.83 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (CDCl<sub>3</sub>, 100 MHz, 25°C): δ 177.9 (Au-C), 154.0 (C<sub>10</sub>H<sub>5</sub>), 134.2 (C<sub>10</sub>H<sub>5</sub>), 134.0 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 132.0 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 130.4 (C<sub>10</sub>H<sub>5</sub>), 129.1 (C<sub>10</sub>H<sub>5</sub>), 128.4 (C<sub>10</sub>H<sub>5</sub>), 128.2 (C<sub>10</sub>H<sub>5</sub>), 127.4 (C<sub>10</sub>H<sub>5</sub>), 125.7 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 125.6 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 124.7 (C<sub>10</sub>H<sub>5</sub>), 124.4 (C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>), 112.9 (C<sub>10</sub>H<sub>5</sub>), 112.9 (C<sub>10</sub>H<sub>5</sub>), 112.8 (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>), 61.5 (CH<sub>2</sub>), 54.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 48.1 (CH<sub>3</sub>), 22.0 (CH(CH<sub>3</sub>)<sub>2</sub>). HRMS (ES): *m/z* 891.2744 [M-Cl]<sup>+</sup> calcd. 891.2735. IR data in KBr pellet, ν/cm<sup>-1</sup>: 2927 (m), 1623 (m), 1438 (s), 1399 (s),

1241 (m), 1091 (m), 1007 (m), 747 (s). Anal. Calc. for  $C_{44}H_{42}AuClN_4O_2$ : C, 59.30; H, 4.75; N, 6.29%. Found: C, 58.59; H, 4.32; N, 6.58%.

## 2.5 Computational Methods

Density functional theory (DFT) calculations were performed on all the metal complexes **1h** and **1i** using GAUSSIAN 09<sup>40</sup> suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee-Yang-Parr correlation functional (B3LYP) was employed in the study.<sup>41,42</sup> The polarized basis set 6-31G(d)<sup>43-45</sup> was used to describe chlorine, oxygen, carbon, nitrogen and hydrogen atoms. The Stuttgart-Dresden effective core potential (ECP) along with valence basis sets (SDD) was used for the silver,<sup>46-48</sup> and gold<sup>49,50</sup> atoms. Frequency calculations were performed for both the optimized structures to characterize the stationary points as minima.

## 3. Results and Discussion

New axially chiral *bis*-NHC ligand of *R*-BINOL framework was efficiently synthesized in overall yield of *ca.* 87% and was characterized unambiguously by NMR, IR, mass, elemental analysis and polarimetry (Scheme 1). Starting from the commercially available *R*-BINOL, to prepare the ligand, different precursors **1(a-f)** (Scheme 1) were synthesized which involved a series of manipulations in the procedures which were reported in the literature.<sup>39</sup> The straightforward process for the synthesis of ligand precursor **1g** (Scheme 1) started from the protection of phenolic hydroxyl group of BINOL with the chloromethyl methyl ether obtained (*R*)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl (**1a**) in quantitative yields. The compound **1a** on formylation in the presence of *n*-BuLi and DMF afforded (*R*)-2,2'-*bis*(methoxymethoxy)-1,1'-binaphthyl-3,3'-dicarbaldehyde (**1b**) which was then subjected to deprotection and again protection with methyl iodide gave (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarbaldehyde (**1c**) and (*R*)-2,2'-dimethoxy-1,1'-binaphthyl-3,3'-dicarbaldehyde (**1d**), respectively. The reduction of **1d** with  $NaBH_4$  gave **1e**, which was followed by chlorination with  $SOCl_2$ , which gave (*R*)-3,3'-*bis*(chloromethyl)-2,2'-dimethoxy-1,1'-binaphthyl (**1f**). The desired compound **1g** was finally obtained by refluxing **1f** and 1-*i*-propyl-benzo[d]imidazole in acetonitrile.

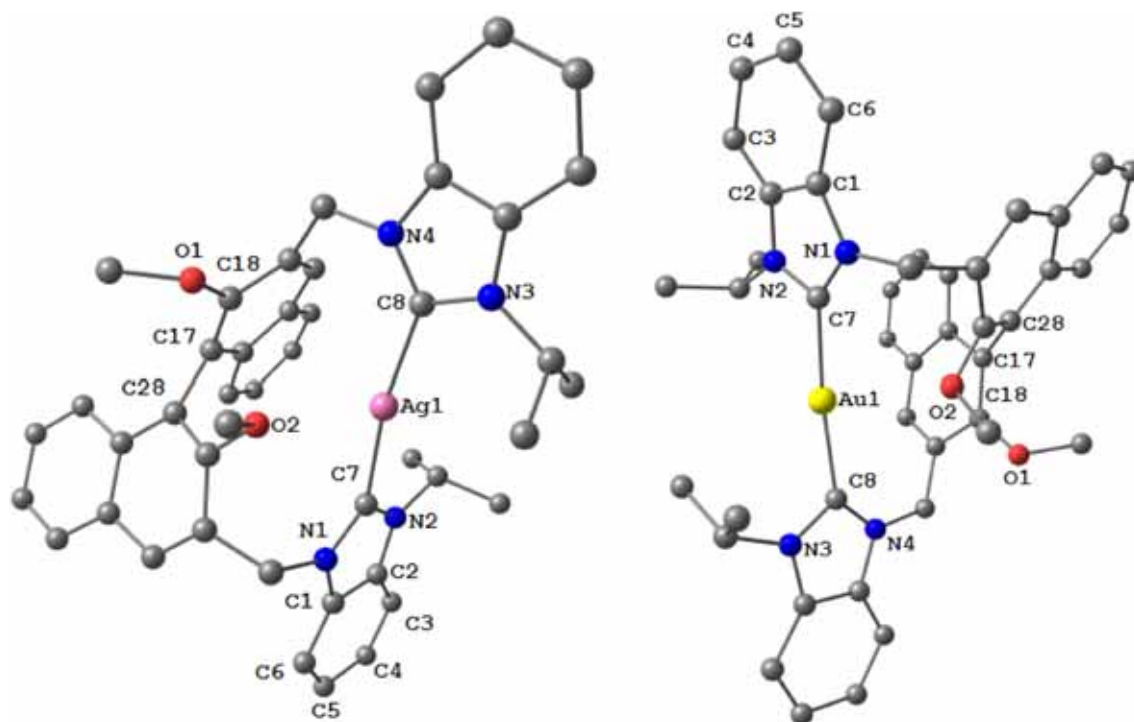
The downfield shift at 9.81 ppm of benzimidazolium proton in  $^1H$  NMR spectrum of **1g** confirmed its formation which was further supported by the high resolution electrospray mass spectrum (HRMS) which showed a

peak at  $m/z$  330.1725 corresponding to dicationic  $[M-2Cl]^{2+}$  species (calculated mass  $m/z$  330.1727).

The Ag(I)-*bis*-NHC complex,  $\{[L(L'-NHC)_2]Ag\}Cl$  ( $L = 3, 3'$ -dimethyl-2,2'-dimethoxy-1,1'-binaphthyl,  $L' = i$ -propyl-benzo[d]imidazole) (**1h**) was synthesized by metallation of benzimidazolium salt **1g** with  $Ag_2O$  as the metal precursor in *ca.* 93% yield. In particular, Ag(I)-*bis*-NHC complex (**1h**) was observed with highly downfield chemical shift at 187.13 ppm in  $^{13}C\{^1H\}$ NMR spectrum attributed to  $Ag-C_{carbene}$  and the HRMS showed peak at 766.2433 corresponding to  $[M-Cl]^+$  species (calculated mass  $m/z$  766.2432).

The  $\{[L(L'-NHC)_2]Au\}Cl$  ( $L = 3, 3'$ -dimethyl-2,2'-dimethoxy-1,1'-binaphthyl,  $L' = i$ -propyl-benzo[d]imidazole) (**1i**) complex was obtained by transmetallation of **1h** with the gold precursor  $Au(SMe_2)Cl$  in *ca.* 42% yield. Interestingly, the peak at 177.92 ppm of  $Au-C_{carbene}$  was observed in its  $^{13}C\{^1H\}$  NMR spectrum with no peak at 187.13 ppm of  $Ag-C_{carbene}$  of its corresponding Ag-*bis*-NHC (**1h**) complex. Similarly, HRMS peak was seen at 891.2744 belonging to  $[M-Cl]^+$  species (calculated mass  $m/z$  891.2735). Furthermore, Ag-*bis*-NHC (**1h**) and Au-*bis*-NHC (**1i**) complexes were characterized by NMR, IR, mass, elemental analysis and polarimetry. These studies of Au(I)-*bis*-NHC complex designated it to be the structural mimic of its corresponding parent Ag(I)-*bis*-NHC complex (**1h**).

As the X-ray structure for these compounds was difficult to obtain even after applying several tricks and methods of crystal growth as well as by changing counter anion. To overcome this problem, we came up with the solution of designing the **1h** and **1i** complexes in 'Chemcraft' and to optimize it using GAUSSIAN 09 quantum chemical computations at the B3LYP/SDD, 6-31G(d) level of theory (Figure S25 in Supporting information). In this regard, the atomic coordinates were adopted from two different X-ray structures<sup>51</sup> CCDC 818680 and CCDC 258234 (Figure S25 in Supporting information), by combining these coordinates the  $\{[L(L'-NHC)_2]Ag\}Cl$  ( $L = 3, 3'$ -dimethyl-2,2'-dimethoxy-1,1'-binaphthyl,  $L' = i$ -propyl-benzo[d]imidazole) (**1h**) molecule was constructed using Chemcraft software with hypothetical bond length and bond angles. Finally, the coordinates of this newly designed molecule were fed into the DFT calculations which gave the output of geometry of the optimised structure **1h** (Figure 1) and (Table S1 in Supporting information). A comparison of the adopted solid state crystal structures with that of geometry optimised structure reveals the good conformity in them in terms of measured and calculated bond lengths and bond angles (Table 1).



**Figure 1.** Computed structures of **1h** (left) and **1i** (right) at B3LYP/SDD, 6-31G(d) level of theory.

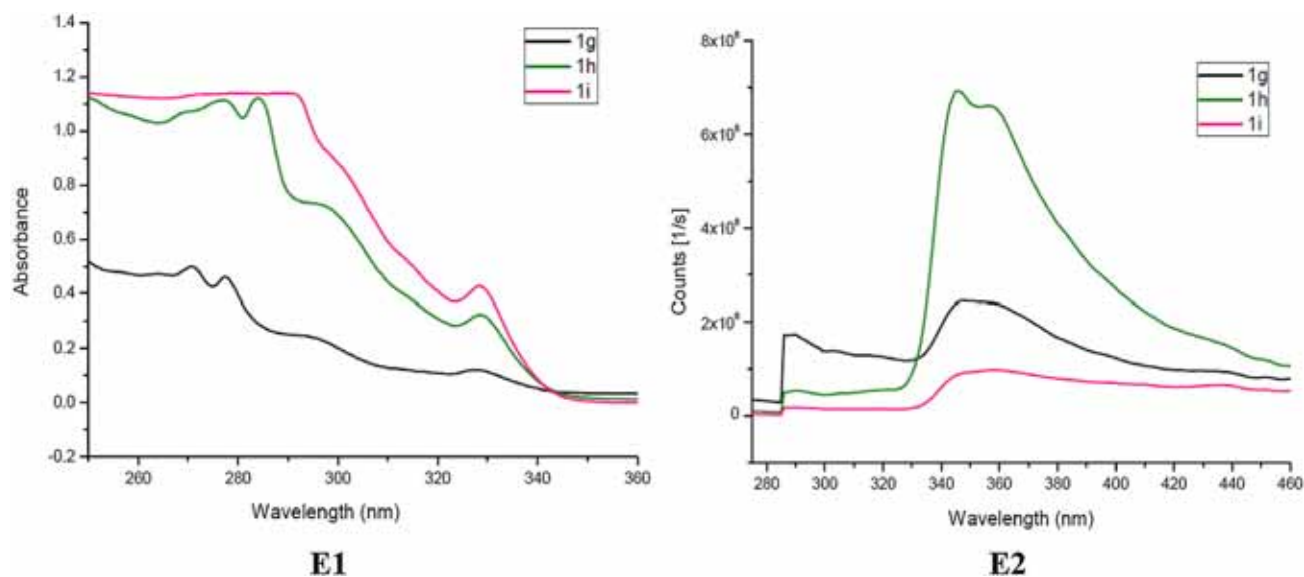
**Table 1.** Comparison of X-ray crystal of fragments and computed structures of **1h** and **1i** complexes at B3LYP/SDD, 6-31G(d) level of theory (Supporting information: Figure S25<sup>51</sup>).

Selected bond lengths (Å) and angles (°) of <b>1h</b>		Selected bond lengths (Å) and angles (°) of <b>1i</b>		Selected bond lengths (Å) and angles (°) of fragments <sup>51</sup>	
C7–Ag1	2.19421	C7–Ag1	2.210182	C7–Ag1	2.10687
C7–N2	1.36275	C7–N2	1.37171	C7–N2	1.35611
C17–C28	1.4995	C17–C28	1.50035	C29–C40	1.49989
C7–Ag1–C8	170.147	C7–Au1–C8	173.769	C7–Ag1–C12	171.603
N1–C7–N2	105.856	N1–C7–N2	106.280	N1–C7–N2	105.715
C18–C17–C28	120.475	C18–C17–C28	120.194	C28–C29–C40	121.015

The computed structure of  $\{[L(L'-NHC)_2]Au\}Cl$  ( $L = 3,3'$ -dimethyl-2,2'-dimethoxy-1,1'-binaphthyl,  $L' = i$ -propyl-benzo[d]imidazole) (**1i**) complex (Figure 1) was generated by using the coordinates of geometry optimized structure of its corresponding Ag-*bis*-NHC (**1h**) complex. These computed structures showed good agreement with the experimental data which was obtained from different spectroscopic and analytical means. The coordinates obtained from the DFT study of Au-*bis*-NHC complex (**1i**) are shown in Supporting information (Table S2 in Supplementary Information).

The electronic properties of these complexes further gave an idea that both the silver(I) and gold(I) complexes **1h** and **1i** do not show evidence for metal-metal

interactions in their molecular structures. The photoluminescence studies were performed on these complexes in a saturated, glassy solution of EtOH:CHCl<sub>3</sub> (4:1, v/v) at 77 K which showed emission peaks at 346 nm when excited at 255 nm for **1g**, **1h** and **1i** (E2 in Figure 2). There was no fluorescent peak observed in the emission spectra of **1h** and **1i** complexes, even on excitation at different wavelengths, corresponding to their electronic spectra. Before performing the fluorescence experiments, the absorption spectra were recorded for all these compounds. The UV spectrum of the ligand precursor (**1g**) showed absorption peaks at 228, 271, 277 and 330 nm. Ag-*bis*-NHC (**1h**) and Au-*bis*-NHC showed (**1i**) bathochromic shift in their absorption spectra: for **1h** at 246, 276 and 284 nm, and for **1i** at 246,



**Figure 2.** (E1) An overlay plot of UV spectra of ligand **1g** and *bis*-NHC complexes **1h** and **1i** recorded in MeOH and  $\text{CHCl}_3$  ( $1 \times 10^{-6}$  M), respectively. (E2) An overlay plot of emission spectra of **1(g-i)** measured in a saturated glassy solution of EtOH: $\text{CHCl}_3$  (4:1, v/v) at 77 K upon excitation at 255 nm.

280 and 290 nm, but there was no change in the peak at 330 nm which is associated with the absorption related to ligand (E1 in Figure 2).

#### 4. Conclusions

In summary,  $\{[L(L'\text{-NHC})_2]M\}\text{Cl}$  ( $M = \text{Ag}$  and  $\text{Au}$ ) type complexes, **1h** and **1i**, were synthesized from the *bis*-N-heterocyclic carbene ligand of *R*-BINOL and benzimidazole framework. The ligand **1g** and the complexes **1h** and **1i** were characterized by using various spectroscopic and analytical techniques. These studies conspicuously revealed that in both the complexes **1h** and **1i**, one metal ion was linearly chelated to a bidentate N-heterocyclic carbene carbons of ligand **1g**. In addition, the DFT studies also support the several electronic parameters related to metal-carbene interactions and its orientation with respect to *R*-BINOL scaffold in these Ag(I) and Au(I) complexes. Photoluminescence studies were performed on these compounds to check the possibility of metal-metal interactions in these complexes; it gave no proof about such interactions which lend further support to the monometallic molecular structures.

#### Supplementary Information (SI)

Spectroscopic and analytical data for **1g**, **1h** and **1i** (Figures S1–S25) and the computational data, B3LYP/SDD, 6-31G(d) level optimized coordinates of the complexes, **1h** and **1i** (Tables S1 and S2) are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

#### Acknowledgements

Author thanks the Ph.D supervisor Prof. Prasenjit Ghosh for his guidance and support, and IIT Bombay for research fellowship. Author is grateful to the Department of Chemistry, IIT Bombay for Central Facility and Computational facilities.

#### References

1. Yoon T P and Jacobsen E N 2003 Privileged Chiral Catalysts *Science* **299** 1691
2. Cesar V Bellemin-Lapponnaz, S Gade 2004 Chiral N-heterocyclic carbenes as stereodirecting ligands in asymmetric catalysis *Chem. Soc. Rev.* **33** 619
3. Garrison J C and Youngs W J 2005 Ag(I) N-Heterocyclic Carbene Complexes: Synthesis, Structure, and Application *Chem. Rev.* **105** 3978
4. Hahn F E and Jahnke M C 2008 Heterocyclic Carbenes: Synthesis and Coordination Chemistry *Angew. Chem. Int. Ed.* **47** 3122
5. Fortman G C and Nolan S P 2011 N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: a perfect union *Chem. Soc. Rev.* **40** 5151
6. Velazquez H D and Verpoort F 2012 N-heterocyclic carbene transition metal complexes for catalysis in aqueous media *Chem. Soc. Rev.* **41** 7032
7. Liu W and Gust R 2013 Metal N-heterocyclic carbene complexes as potential antitumor metallodrugs *Chem. Soc. Rev.* **42** 755
8. Yam V W-W and Lo K K-W 1999 Luminescent polynuclear d10 metal complexes *Chem. Soc. Rev.* **28** 323
9. Pugh V J H and Zuo Q S 2001 Optically Active BINOL Core-Based Phenyleneethynylene Dendrimers

- for the Enantioselective Fluorescent Recognition of Amino Alcohols *J. Org. Chem.* **66** 6136
- Ray L, Shaikh M M and Ghosh P 2008 Shorter Argentophilic Interaction than Auophilic Interaction in a Pair of Dimeric (NHC)MCl<sub>2</sub> (M = Ag, Au) Complexes Supported over a N/O-Functionalized N-Heterocyclic Carbene (NHC) Ligand *Inorg. Chem.* **47** 230
  - Liu X Y, Fu X and Zhu Y and Cheng C Y 2011 Novel fluorescent sensor for Ag<sup>+</sup> and Hg<sup>2+</sup> based on the BINOL-pyrene derivative via click reaction *Tetrahedron* **67** 3181
  - Wang D and Lippard S J 2005 Cellular processing of platinum anticancer drugs *Nat. Rev. Drug Discov.* **4** 307
  - Ray S, Mohan R S, Samantaray J K, Shaikh M K, Panda M M and Ghosh P 2007 Anticancer and Antimicrobial Metallopharmaceutical Agents Based on Palladium, Gold, and Silver N-Heterocyclic Carbene Complexes *J. Am. Chem. Soc.* **129** 15042
  - Jakupec M A, Galanski M A, Hartinger V B, Keppler C G and Bernhard K 2008 Antitumour metal compounds: more than theme and variations *Dalton Trans.* **2** 183
  - Yasukawa T, Miyamura H and Kobayashi S 2014 Chiral metal nanoparticle-catalyzed asymmetric C-C bond formation reactions *Chem. Soc. Rev.* **43** 1450
  - Chen Y, Cheng, Li G, Shelar K, Lu D P and Che W 2014 Phosphorescent polymeric nanomaterials with metallophilic d10...d10 interactions self-assembled from [Au(NHC)<sub>2</sub>]<sup>+</sup> and [M(CN)<sub>2</sub>] *Chem. Sci.* **5** 1348
  - Mercs L and Albrecht M 2010 Beyond catalysis: N-heterocyclic carbene complexes as components for medicinal, luminescent, and functional materials applications *Chem. Soc. Rev.* **39** 1903
  - Glorius F 2007 N-Heterocyclic Carbenes in Catalysis—An Introduction *Top. Organomet. Chem.* **21** 13
  - Bourissou D, Guerret O, Gabbai F P and Bertr G 2000 Stable Carbenes *Chem. Rev.* **100** 39
  - Arduengo A J, Harlow R L and Kline M 1991 A stable crystalline carbene *J. Am. Chem. Soc.* **113** 361
  - Enders D N and Henseler A 2007 Organocatalysis by N-Heterocyclic Carbenes *Chem. Rev.* **107** 5606
  - Marion N and Nolan S P 2007 N-Heterocyclic Carbenes as Organocatalysts *Angew. Chem. Int. Ed.* **46** 2988
  - Visbal R and Gimeno M C 2014 N-heterocyclic carbene metal complexes: photoluminescence and applications *Chem. Soc. Rev.* **43** 3551
  - Crabtree R H 2005 NHC ligands versus cyclopentadienyls and phosphines as spectator ligands in organometallic catalysis *J. Organomet. Chem.* **690** 5451
  - Dove A P, Pratt R C, Lohmeijer B G G, Li H, Hagberg E C, Waymouth R M and Hedrick J L 2006 In *N-Heterocyclic Carbenes as Organic Catalysts*, in *N-Heterocyclic Carbenes in Synthesis* S P Nolan (Ed.) (Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA) p. 163
  - Kuhl O 2007 The chemistry of functionalised N-heterocyclic carbenes *Chem. Soc. Rev.* **36** 592
  - Cui Y Y, Qian Y and Chen G 2012 Luminescent Functional Metal–Organic Frameworks *Chem. Rev.* **112** 1126
  - Brendgen T F and Schatz J M 2006 The Suzuki Coupling of Aryl Chlorides in Aqueous Media Catalyzed by in situ Generated Calix[4]arene-Based N-Heterocyclic Carbene Ligands *Eur. J. Org. Chem.* **2006** 2378
  - Hillier A C, Grasa G A, Viciu M S, Lee H M, Yang C and Nolan S P 2002 Catalytic cross-coupling reactions mediated by palladium/nucleophilic carbene systems *J. Organomet. Chem.* **653** 69
  - Wang Y M and Toste A D 2014 Development of Catalysts and Ligands for Enantioselective Gold Catalysis *Acc. Chem. Res.* **47** 889
  - Normand A T and Cavell K J 2008 Donor-Functionalised N-Heterocyclic Carbene Complexes of Group 9 and 10 Metals in Catalysis: Trends and Directions *Eur. J. Inorg. Chem.* **2008** 2781
  - Weselinski L S and Jurczak J 2011 The highly enantioselective 1,3-dipolar cycloaddition of alkyl glyoxylate-derived nitrones to E-crotonaldehyde catalyzed by hybrid diamines *Tetrahedron Lett.* **52** 381
  - Bolm C and Gladysz J A 2003 Introduction: Enantioselective Catalysis. *Chem. Rev.* **103** 2761
  - Grill J M, Reibenspies J H and Miller S A 2005 Racemic and chiral expanded salen-type complexes derived from biphenol and binaphthol: Salbip and salbin *J. Organomet. Chem.* **690** 3009
  - Shi M and Duan W L 2005 Synthesis of an axially chiral Ir–NHC complex derived from BINAM *Appl. Organomet. Chem.* **19** 40
  - Pyykko P 1997 Strong Closed-Shell Interactions in Inorganic Chemistry *Chem. Rev.* **97** 597
  - Bauer A and Schmidbaur H 1996 Self-Assembly of [(Me<sub>2</sub>PhP)<sub>2</sub>Au]<sup>+</sup>[Au(GeCl<sub>3</sub>)<sub>2</sub>]<sup>-</sup> into Linear Ion Quadruples with an Unusual [+–+] Sequence *J. Am. Chem. Soc.* **118** 5324
  - Sluch I M, Miranda A J, Elbjairami O, Omary M A and Slaughter L M 2012 Interplay of Metallophilic Interactions, π–π Stacking, and Ligand Substituent Effects in the Structures and Luminescence Properties of Neutral PtII and PdII Aryl Isocyanide Complexes *Inorg. Chem.* **51** 10728
  - Yang L, Qin S, Yang X, You F, Hu J, Xie C and Lan J 2010 1,1[prime or minute]-Binaphthyl-based imidazolium chemosensors for highly selective recognition of tryptophan in aqueous solutions *Org. Biomol. Chem.* **8** 339
  - Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr J A, Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas O, Foresman J B, Ortiz J V, Cioslowski J, Fox D J 2009 *Gaussian 09, Revision A.1* (Gaussian, Inc.: Wallingford CT)
  - Becke A D 1988 Density-functional exchange-energy approximation with correct asymptotic behavior *Phys. Rev. A: Atom. Mol. Opt. Phys.* **38** 3098

42. Lee C, Yang W and Parr R G 1988 Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density *Phys. Rev. B: Condens. Matter* **37** 785
43. Hehre W J, Ditchfield R and Pople J A 1972 Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules *J. Chem. Phys.* **56** 2257
44. Petersson G and Al-Laham M A 1991 A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms *J. Chem. Phys.* **94** 6081
45. Petersson G A, Bennett A, Tensfeldt T, G Al-Laham M A, Shirley W A and Mantzaris J 1988 A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements *J. Chem. Phys.* **89** 2193
46. Dolg M, Wedig U, Stoll H and Preuss H 1987 Energy-adjusted abinitio pseudopotentials for the first row transition elements *J. Chem. Phys.* **86** 866
47. Andrae D H, Dolg U, Stoll and Preub M H 1990 Energy-adjusted abinitio pseudopotentials for the second and third row transition elements *Theoret. Chim. Acta* **77** 123
48. Alkauskas A, Baratoff A and Bruder C 2004 Gaussian Form of Effective Core Potential and Response Function Basis Set Derived from Troullier-Martins Pseudopotential: Results for Ag and Au *J. Phys. Chem. A* **108** 6863
49. Wang X and Andrews L 2001 Gold Hydrides AuH and (H<sub>2</sub>)AuH and the AuH<sub>3</sub> Transition State Stabilized in (H<sub>2</sub>)AuH<sub>3</sub>: Infrared Spectra and DFT Calculations *J. Am. Chem. Soc.* **123** 12899
50. Faza, O N, Alvarez C S and Lera A R 2006 Mechanism of the Gold(I)-Catalyzed Rautenstrauch Rearrangement: A Center-to-Helix-to-Center Chirality Transfer *J. Am. Chem. Soc.* **128** 2434
51. Wang L Q, Zhao H, Yao X J, Wang Z Q, Chen Z Q and Wang X G 2012 N-Heterocyclic carbene silver(i), palladium(ii) and mercury(ii) complexes: synthesis, structural studies and catalytic activity *CrystEngComm* **14** 5330