

# Macrocycles of axially chiral and racemic *N*-heterocyclic carbene silver(I), gold(I) and palladium(II) complexes: synthesis, characterization and computational structures

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**In this study, Ag(I), Au(I) and Pd(II) *bis-N*-heterocyclic carbene (NHC) complexes derived from axially chiral *R*-1,1'-binaphthyl-2,2'-diol (*R*-BINOL) and racemic biphenyl-2,2'-diol scaffolds have been synthesized. The metallation of these *bis*-imidazolium and *bis*-triazolium types of ligand precursors of *R*-BINOL and biphenol unit, viz. (1–4)d has been achieved using standard procedure. The  $\{[L(L'-NHC)_2]Ag\}Cl$ -type, chiral (1–2)e and racemic (3–4)e complexes have been obtained by the treatment of ligand with  $Ag_2O$ . Similarly, chiral Pd(II) (1f) and Au(I) (1g) complexes have been synthesized and analysed using spectroscopic techniques. The geometry-optimized structures obtained through the density functional theory display good proximity with the reported X-ray structures of similar type of Ag(I), Au(I) and Pd(II) complexes.**

**Keywords:** Axial chirality, density functional theory, ligands, racemic complex.

AXIAL chirality in 1,1'-binaphthyl-2,2'-diol (BINOL) is due to restricted rotation around the C–C axis linking two naphthyl units that give the two configurationally stable atropisomers. Consequently, BINOL have been widely used as a structural motif for designing chiral catalysts for various asymmetric transformations<sup>1–3</sup>. The chelating effect provides stability to *bis-N*-heterocyclic carbene (NHC)-based metal complex and constitutes a key component for the successful designing of a homogeneous catalyst; hence the same phenomenon works in developing several *bis*-NHC-type catalysts of axially chiral NHC ligands. However, the successful designing of NHC for homogeneous catalysts requires thermal stability and strong M–NHC bond, which is often achieved through chelation<sup>4,5</sup>.

The coordination chemistry and synthesis of the first axially chiral NHC of BINOL moiety with two imidazole rings linked to it was reported by Clyne *et al.*<sup>6</sup>. Thereafter, several NHC ligands of BINOL-based scaffolds have been evaluated for their strong  $\sigma$ -donor and weak  $\pi$ -acceptor

characters, and utility in several catalytic reactions. The gradual changes in designing different types of NHC ligands began from the year 2000, with major contributions from Shi and co-workers<sup>7–9</sup> and Hoveyda and co-workers<sup>10,11</sup>, who mainly studied the catalytic tendency of various transition metal–NHC complexes and ligands as well as their chiral induction in many asymmetric catalytic transformations. The most popular examples of such reactions are Heck reactions<sup>12</sup>, Suzuki coupling<sup>13</sup>, Sonogashira coupling<sup>11</sup>, and asymmetric ring-opening cross-metathesis (AROM/CM)<sup>10,14</sup>, and other reactions<sup>2,15–23</sup>. Moreover, Au and Au–NHC complexes are gaining popularity not only in homogeneous catalysis<sup>24</sup>, but also in medicinal chemistry for their anticancer and antimicrobial properties<sup>25</sup>.

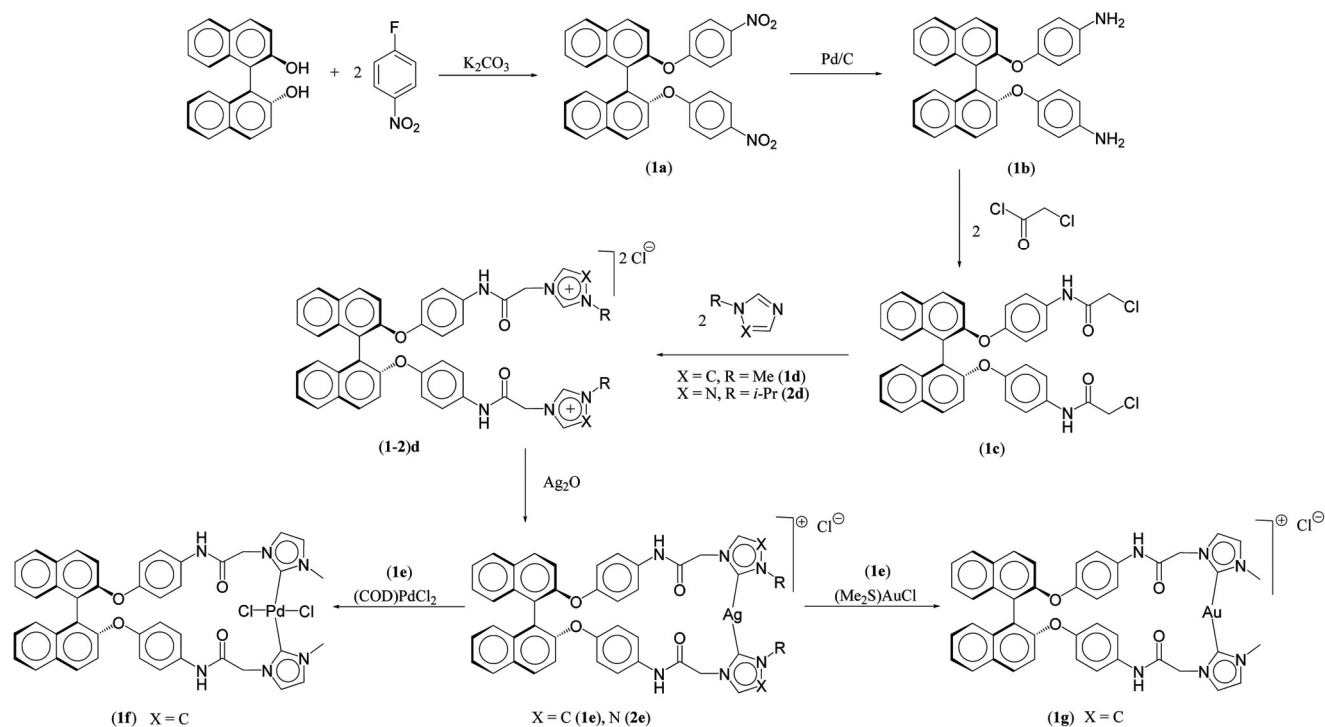
Several types of *N*-heterocyclic carbenes of BINOL scaffolds have been studied but this type of comparative study of chiral moiety (BINOL) and its achiral counterpart (2,2'-biphenol) is reported here first time. Therefore, here we have designed and synthesized different Ag(I), Au(I) and Pd(II) complexes (Schemes 1 and 2) of these two scaffolds. We have examined them based on characterization data and developed computational structures of each of these complexes.

## Experimental

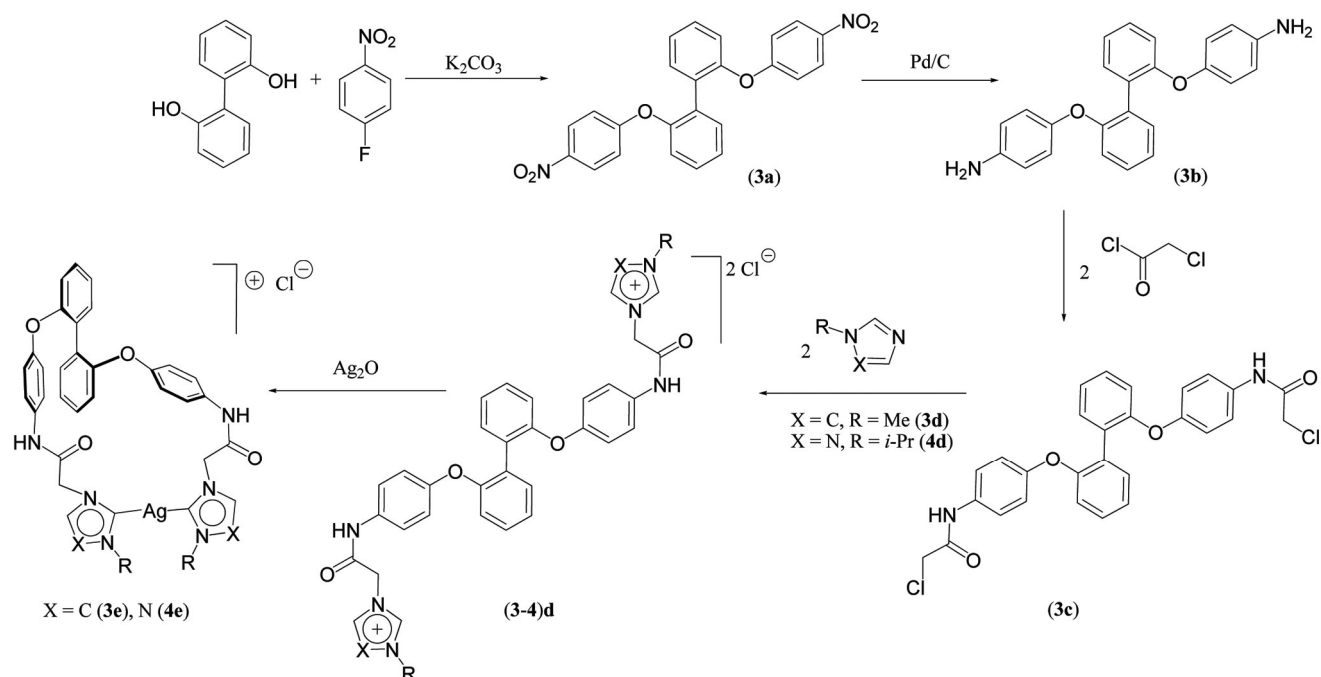
### General procedure

All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. *R*-BINOL, chloroacetyl chloride, 1-methyl-imidazole and  $Ag_2O$  were purchased from Spectrochem (India) and used without any further purification. 1-*i*-Propyl-1*H*-1,2,4-triazole (ref. 26), (COD)PdCl<sub>2</sub> and (SMe<sub>2</sub>)AuCl (ref. 27), and other intermediates<sup>28</sup>, viz. **1a**, **1b**, **3a** and **3b** were synthesized by some amendments 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 (Bruker 400 and 500 MHz NMR spectrometer). <sup>1</sup>H NMR peaks were labelled as singlet (s),

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**Scheme 1.** Synthetic pathway for the *R*-BINOL-based axially chiral silver(I), gold(I) and palladium(II) complexes of *bis*-NHC ligands.



**Scheme 2.** Synthetic pathway for the biphenyl-2,2'-diol based racemic silver(I) complexes of *bis*-NHC ligands.

doublet (d), triplet (t), a triplet of doublets (td) and multiplet (m). Infrared spectra were recorded (Perkin–Elmer Spectrum One FT-IR Spectrometer) and mass spectrometry measurements were made (Micromass Q-T of Spectrometer and Bruker Maxis Impact Spectrometer).

Elemental analysis was carried out (Thermo Finnigan Flash EA 112 SERIES (CHNS) Elemental Analyzer) and specific optical rotation experiments were performed (JASCO P-2000 polarimeter and Autopol IV, Serial #82083 Polarimeter).

### Computational methods

Density functional theory (DFT) calculations were performed on all the metal complexes (**1–4**) using GAUSSIAN 09 suite of quantum chemical programs<sup>29</sup>. The Becke three-parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) was employed in the study<sup>30,31</sup>. The polarized basic set 6-31G(d) was used to describe chlorine, oxygen, carbon, nitrogen and hydrogen atoms<sup>32–34</sup>. The Stuttgart–Dresden effective core potential (ECP) along with valence basis sets (SDD) were used for the silver<sup>35–37</sup>, gold<sup>38,39</sup> and palladium<sup>39–43</sup> atoms. Frequency calculations were performed for all the optimized structures to characterize the stationary points as minima.

### Results and discussion

#### *BINOL-based chiral bis-imidazolium and bis-1,2,4-triazolium chloride salts*

A series of axially chiral *bis*-imidazolium and *bis*-triazolium salts (**1–2**)**d** (Scheme 1) were synthesized in four steps. Designing the ligand precursors included a series of manipulations that commenced with the framework of *R*-BINOL as described below.

(*R*)-2,2'-*bis*(4-nitrophenoxy)-1,1'-binaphthyl (**1a**) was prepared by nucleophilic aromatic substitution with addition–elimination reaction between *R*-BINOL and *p*-fluoronitrobenzene in the presence of base in quantitative yields, which on reduction with Pd/C yielded (*R*)-4,4'-(1,1'-binaphthyl-2,2'-diyl-*bis*(oxy))dianiline (**1b**) in 90–95% yield. The compound **1b** showed broad resonance at 3.00–4.00 ppm for  $\text{NH}_2$  moiety, while the aromatic resonances appeared in the range 6.50–7.70 ppm in the <sup>1</sup>H NMR spectra.

Subsequently, the reaction of chloroacetyl chloride with the precursor **1b** gave the compound **1c** in 85% yield. The compound **1c** showed chemical shift at 8.00 ppm for  $\text{NH}$  as a broad singlet and 4.00–4.20 ppm as a singlet for  $\text{CH}_2$  moiety. The amide (–CONH) stretching frequencies for **1c** appeared at 1670 and 1593  $\text{cm}^{-1}$  in the infrared spectrum.

The compound **1c** on further alkylation with *N*-methylimidazole gave **1d** and with 1-*i*-propyl-1,2,4-triazole gave **2d** in quantitative yields<sup>44</sup>. In the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the highly downfield  $\text{NCHN}$  resonance at 9.17–11.0 ppm and 137.9–138.0 ppm respectively, is for the *bis*-imidazolium salt **1d** and the corresponding *bis*-triazolium salts appeared at 10.0 and 145.0 ppm for **2d** (ref. 45). Optical activity [ $\alpha$ ]<sub>D</sub><sup>25</sup> of these chiral ligand precursors was found to be +23.8° (c 1.0, MeOH) and +301.3° (c 1.0, CHCl<sub>3</sub>) for **1d** and **2d** respectively. These intermediates were further characterized by HRMS data and elemental analysis.

#### *Biphenol-based racemic bis-imidazolium and bis-1,2,4-triazolium chloride salts*

The 2,2'-biphenol based racemic ligand precursors (**3–4**)**d** (Scheme 2) were synthesized following the same method as that of its corresponding chiral precursors **1(a–d)** and **2d**. Interestingly, these intermediates were obtained with almost same yields as those for compounds **1a**, **1b**, **1c**, **1d** and **2d**. On interpreting and comparing various data, the results were quite similar to the chiral counterparts; for example, **3b** showed broad resonance at 3.00–4.00 ppm for  $\text{NH}_2$  in the <sup>1</sup>H NMR spectrum as that of **1b**, while **3d** showed the same  $\text{NCHN}$  resonance at 9.17–11.0 ppm like **1d** and in *bis*-triazolium salt **4d**, the  $\text{NCHN}$  resonance appeared at 10.0–11.0 ppm as in **2d** (ref. 45). On comparison between the chiral and racemic moieties, the main difference was observed in <sup>1</sup>H NMR spectra of  $\text{CH}_2$  splitting pattern. These protons split as double of doublet for diastereotopic protons in (**1–2**)**c** and (**1–2**)**d**, and singlet for homotopic protons in (**3–4**)**c** and (**3–4**)**d**.

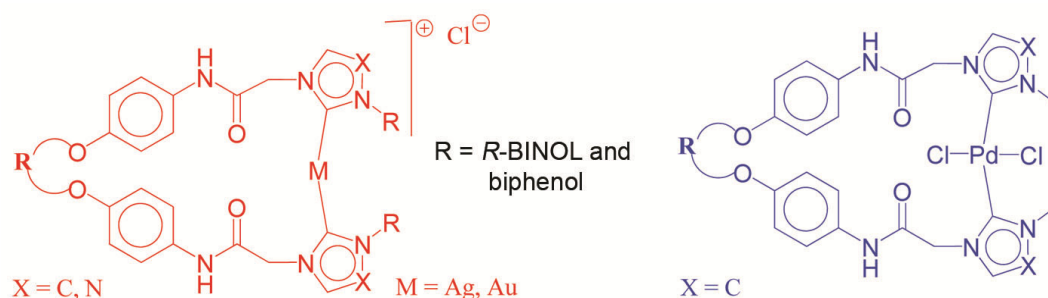
#### *Axially chiral Ag, Au, Pd, and racemic Ag bis-NHC complexes*

The formation of chiral (**1–2**)**e** {[L(L'-NHC)<sub>2</sub>]Ag}Cl (L = 2,2-dioxo-binaphthyl, L' = phenyl-acetamido) and racemic (**3–4**)**e** [L(L'-NHC)<sub>2</sub>]Ag}Cl (L = 2,2-dioxo-biphenyl, L' = phenyl-acetamido) complexes was achieved through *in situ* deprotonation of their respective *bis*-azolium salts, viz. (**1–4**)**d** with two equivalents of Ag<sub>2</sub>O in dichloromethane (Schemes 1 and 2). The disappearance of resonance at 9.17–11.0 ppm of the starting carbene precursors in <sup>1</sup>H NMR spectrum and appearance of a peak at 180.0–181.0 ppm in <sup>13</sup>C{<sup>1</sup>H} NMR spectrum confirmed the formation of compounds **1e** and **3e**. Similarly, no corresponding resonances at 10.0–11.0 ppm in the <sup>1</sup>H NMR spectrum of the starting carbene precursors and presence of a peak at 180.0–181.0 ppm in <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed the formation of **2e** and **4e** {[L(L'-NHC)<sub>2</sub>]Ag}Cl complexes<sup>46</sup>.

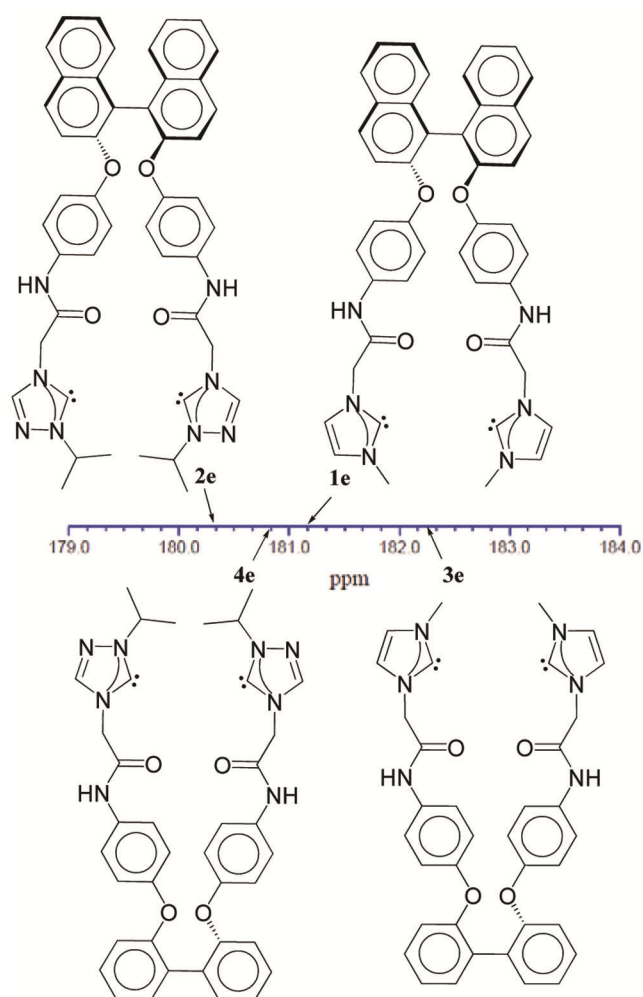
However, the change in stoichiometry of ligand–metal precursors with the above-mentioned synthetic conditions has not resulted in a mixture of complexes or any other type of complex.

The axially chiral BINOL-based [L(L'-NHC)<sub>2</sub>]PdCl<sub>2</sub> (L = 2,2-dioxo-biphenyl, L' = phenyl-acetamido) complex (**1f**) was synthesized by the transmetallation of Ag-*bis*-NHC complex (**1e**) with the metal precursor (COD)PdCl<sub>2</sub> in 29–35% yield<sup>47</sup>. The complex (Figure 1) **1f** showed the characteristic Pd– $\text{NCN}$  resonance at 169.5 ppm in <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the compound upfield shifted from its respective Ag-*bis*-NHC complex (**1e**).

The chiral {[L(L'-NHC)<sub>2</sub>]Au}Cl (L = 2,2-dioxo-binaphthyl, L' = phenyl-acetamido (**1g**)) complex was synthesized from its Ag-*bis*-NHC analogue (**1e**) with the



**Figure 1.**  $\{[L(L'-NHC)_2]M\}Cl$  ( $M = Ag, Au$ ) and  $\{[L(L'-NHC)_2]Pd\}Cl_2$ -type complexes.



**Figure 2.** Donor ability of *bis*-N-heterocyclic carbenes (NHCs) on  $^{13}C\{^1H\}$  NMR scale.

metal precursor  $(SMe_2)AuCl$  in 44% yield. The formation of this complex is evident from the upfield shift of the  $Au-N\bar{C}N$  resonance at 171.2 ppm in the  $^{13}C\{^1H\}$  NMR spectrum compared to the corresponding  $Ag-NHC$  complex that appeared at 180.0–181.0 ppm. Further, these NHC complexes have been characterized using other techniques like HRMS studies and elemental analysis.

Interestingly, the four different imidazole and triazole-based ligands containing BINOL and biphenol units in chelated (**1–4**)e complexes were employed as a  $^{13}C\{^1H\}$  NMR spectroscopic probe to determine the donor strength of *bis*-NHC ligand<sup>48</sup>, whereby strong donating ligands lead to a more downfield shift (Figure 2). Amongst the NHCs studied herein, the weakest ligand in complex **2e** led to the most upfield carbeneid signal, while the strongest ligand in complex **3e** gave rise to the most downfield carbene signal. This order of the values of  $^{13}C\{^1H\}$  NMR was also practically observed with the ease of formation of silver(I) complexes from their respective ligands, the **3e** synthesized fastest whereas the **2e** was the slowest.

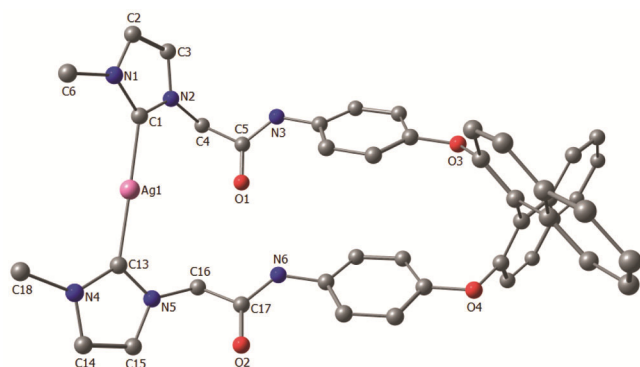
### Computational studies

Although efforts have been made to obtain the crystal structure of the synthesized NHC complexes as well as ligands using various methods of crystallization in different solvents and by changing counter ions of the ligand, not a single X-ray crystal structure was acquired through these experiments. This prompted us to take up computational studies of these complexes. Therefore, we derived the molecular structures from already obtained X-ray structures of similar types of complexes by DFT. To obtain insight on the electronic structure of all the silver(I), gold(I) and palladium(II) NHC complexes **1–4**, their molecular structures were designed based on their different spectroscopic and analytical data. The X-ray structure of CCDC-928696 was rearranged and designed into a hypothetical molecule according to the spatial arrangement and proximity of the donor site of the *bis*-NHC ligand with the metal centre. Then DFT study was carried out using coordinates adopted from these hypothetically designed structures. The electronic structure of this hypothetical molecule was computed at the B3LYP/SDD, 6-31G(d) level of theory and single-point calculation was performed at the same level of theory for detailed prediction of the electronic properties, obtained with the output of geometry-optimized structure of complex **1e** (Figure 3). After designing the hypothetical computed molecular

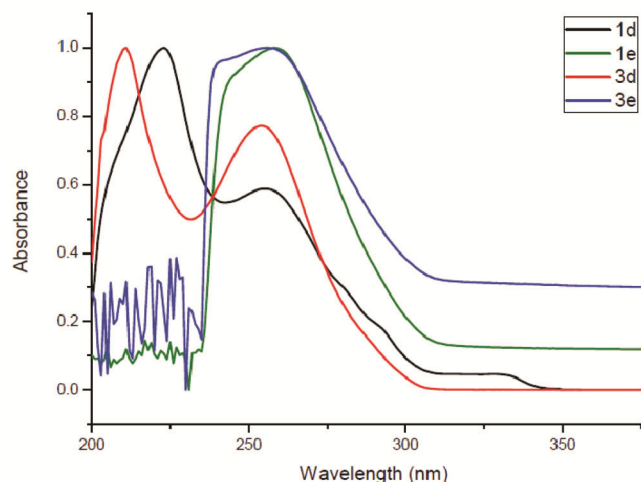
structures of all other complexes, similar computational studies were performed on them using the coordinates of their respective hypothetical structures. Finally, the output was geometry-optimized structures of their respective complexes.

The Ag(I) and Au(I) complexes exhibit linear geometry, whereas the Pd(II) complex fits into the square planar geometry where all the ligands are bidentate, which bind to a single metal ion in a chelated fashion. These were obtained with the general formula for such types of complexes as  $\{[L(L'-NHC)_2]M\}Cl$  ( $M = Ag, Au$ ) and  $\{[L(L'-NHC)_2]Pd\}Cl_2$ , and hence the ligands were designated as the chelating *bis*-NHC-type.

In general, the optimized bond lengths and bond angles of the computed output structure are in good agreement with those of the adopted X-ray crystallographic structures as well as the reported structures of such types of silver(I)<sup>48–51</sup>, gold(I)<sup>21,52–55</sup> and palladium(II)<sup>16,43,48,56–59</sup> complexes. Moreover, the geometry-optimized electronic structures for (**1e–g**), **2e**, **3e**, and **4e** were obtained along with their characteristic bond lengths and bond angles using computational method.



**Figure 3.** Computed structure of **1e** selected bond lengths (Å) and bond angles (°): Ag1–C1 2.12, Ag1–C13 2.11, C13–N4 1.35, C13–N5 1.36, C1–Ag1–C13 178.60, N4–C13–N5 104.40, N1–C1–N2 104.15.



**Figure 4.** An overlay plot of ultraviolet spectra of ligand precursor **1d** and **3d** and *bis*-NHC–silver(I) complexes **1e** and **3e** in a solution of MeOH and CHCl<sub>3</sub> respectively.

### Electronic properties

Electronic spectra of complexes **1e** and **3e** were measured in chloroform solution (Figure 4). Both the complexes display an intense absorption band at 255 nm that is similar in position and band shape to their carbene precursors **1d** and **3d**, which show absorption at 210–220 and 255 nm respectively. Therefore, these bands can be assigned to  $\pi$ – $\pi^*$  aromatic intraligand transitions<sup>60</sup>.

The experimental part includes synthetic procedures for all the compounds of Schemes 1 and 2, which are presented in the supplementary information. It also covers spectroscopic and analytical data of these compounds (Supplementary Figures S1–S102), computational structures of the complexes (Supplementary Figures S103–S107) and coordinates (Supplementary Tables A1–A5).

### Conclusion

In summary, axially chiral and racemic ligand precursors and Ag, Au and Pd *bis*-NHC complexes have been prepared from the scaffolds of enantiopure *R*-BINOL and racemic biphenol. These chiral *bis*-NHC complexes **1e**, **2e**, **1f** and racemic complexes **3e** and **4e** were characterized and analysed using <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H}NMR spectra, HRMS data and elemental analysis. Studies of Ag(I), Au(I) and Pd(II) complexes based on their different characterization data reveal the formation of axially chiral BINOL-based and achiral biphenol-based *bis*-NHC chiral and racemic complexes. Computational studies further reveal the geometry-optimized molecular structures of these complexes.

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