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Note

Synthesis, characterization and crystal structures of silver(I)– and gold(I)–*N*-heterocyclic carbene complexes having benzimidazol-2-ylidene ligands

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ABSTRACT

A series of *N*,*N*′-disubstituted benzimidazolium salts (**1**–**3**) were prepared *via* the successive *N*-alkylation method. Cationic, linearly coordinated silver(I)–NHC complexes (**4**–**6**) were synthesized in good yield by the reaction of Ag_2O with salts **1**–**3**. The corresponding cationic gold(I)–NHC complexes (**7**–**9**) of silver(I)–NHC derivatives were prepared by the technique of transmetallation at mild reaction condition. The new azolium salts and their carbene complexes were characterized by ^1H and ^{13}C NMR and FTIR spectroscopy, and elemental analysis. Additionally, benzimidazolium salts **2** and **3**, silver(I)–carbene complexes **4a** and **6a**, and gold(I)–carbene complex **8** were structurally characterized by single crystal X-ray diffraction technique.

1. Introduction

N-Heterocyclic carbenes (NHCs) are interesting class of ligands in modern organometallic chemistry with diverse ligational behaviors. Numerous NHC transition metal complexes are employed on a huge scale to produce catalytically and biologically relevant agents, which are demonstrated by several recently published articles [1]. Among others, silver(I)–NHC complexes gained special and considerable attention by the organometallic chemists due to their versatile applications in catalysis [2] as well as in biology [3]. Wang and Lin were the first to report the use of NHC–silver(I) complexes to prepare other NHC-transition metal complexes *via* carbene transfer method [4]. This transfer route provided acceptable way of preparing transition metal carbene complexes that are hard to obtain by free carbene method. Nowadays, the use of NHC–silver(I) complexes for the preparation of other complexes is becoming much better than conventional methods especially, for the preparation of late transition metal carbene complexes [5]. Transmetallation using silver(I)–NHC complexes is advantageous over free carbene method as this can be performed in air with no decrease in yield, and affords easy metal complex formation. The metals to which silver(I)–NHCs are most widely transferred are gold(I) and palladium(II) [6].

On the other hand, bioorganometallic chemistry of silver(I)– and gold(I)–NHC complexes is a significant area in both therapeutic and diagnostic medicine. Development of transition metal carbene complexes as metal-based drugs is a much focused task, and great efforts are required to get a compound of interest. In spite of all limitations and side effects of periodic table metal complexes, transition metal complexes are still the most widely used chemotherapeutic agents and make a large contribution to medicinal therapeutics. Even though platinum-based complexes had been in primary focus of research on chemotherapeutic agents [7], the interests in this field have shifted to non-platinum based agents [8] in order to find different metal complexes with less side effects and similar cytotoxicity. Thus, a wide variety of metal carbene complexes based on silver, palladium and gold are being intensively studied as platinum replacements. Among these, silver(I)– and gold(I)–NHC complexes displayed significant results for anticancer activity against a number of human derived cancer cell lines [9]. As a consequence, intense research on the structure activity relationship of these metal carbene complexes has emerged during the past five years using sterically and electronically modulated carbene systems [10]. In this article, we present the synthesis, structure and transmetallation studies of biologically relevant benzimidazole-based salts and their respective silver(I)– and gold(I)–NHC complexes.

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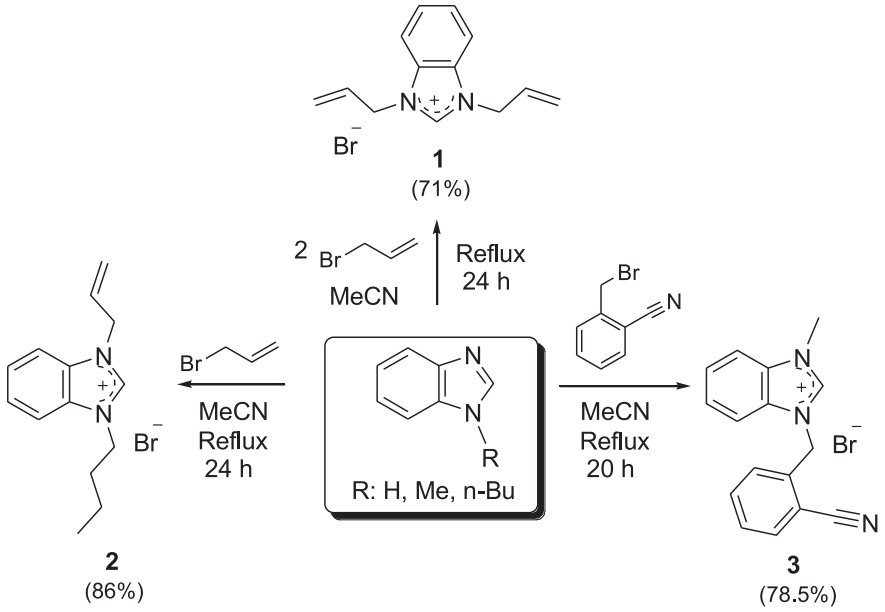


Scheme 1. Preparation of carbene ligand precursors **1**–**3**.

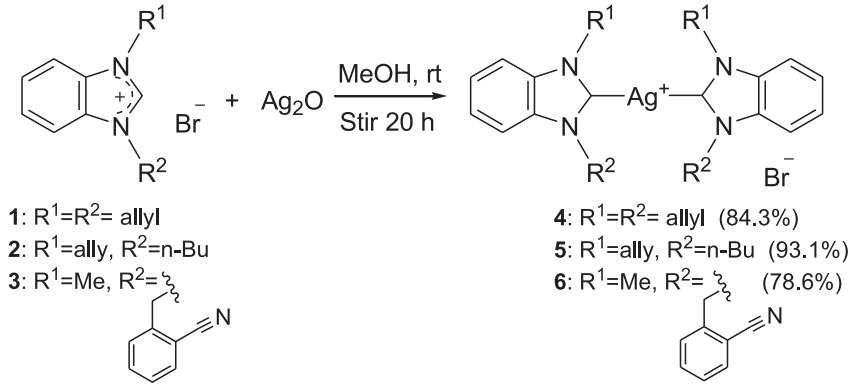
2. Results and discussion

Considering the practical advantages and wide availability of simple bis-NHC silver(I)– and gold(I)-complexes of the type $[(NHC)–M–(NHC)]^{+}X^{-}$ (M = Ag, Au and X = Cl, Br), we were prompted to study the effect of a steric modulation of the NHCs on their structure. Among the few spectacular categories of sterically tuned (benz)imidazole-based NHC–silver(I) and palladium(II) complexes, we were logically inclined to opt for members of our previously reported series of similar backbones [11], however, with different N-substitutions and the metal center. The NHC precursors and their carbene complexes reported herein are thermally stable up to their decomposition temperature and are nonhygroscopic in nature. The complexes are insoluble in water, but are readily soluble in DMSO, DMF, (m)ethanol and acetonitrile. Elemental analysis data is in well agreement with the structures of compounds.

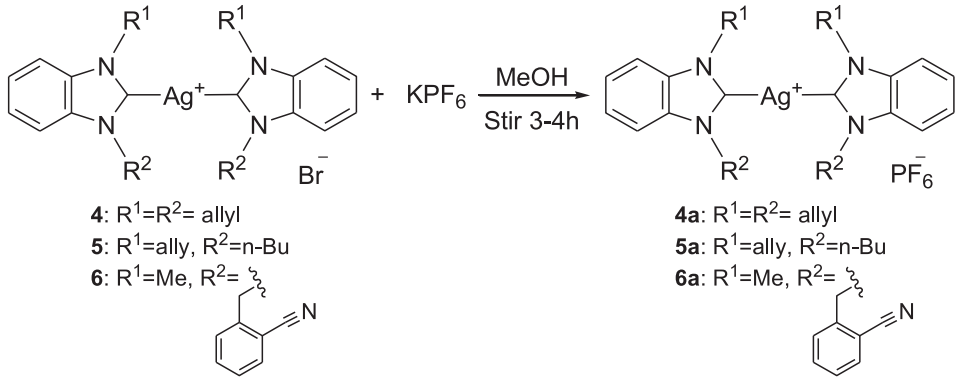
2.1. Syntheses

Successive *N*-alkyl/arylation of benzimidazole allowed a desirable, wide-ranging tunability to access NHC precursors with various steric and electronic properties. Reported benzimidazolium salts **1**–**3** were prepared by the successive *N*-alkylation method as shown in Scheme 1. For the symmetrical carbene ligand precursor **1**, allylation at both N-terminals of benzimidazole was carried out at once by refluxing a solution of benzimidazole and allyl bromide (1:2 ratio) in acetonitrile for 24 h. However, in the case of carbene ligand precursors **2**/**3**, *N*-butyl/methyl benzimidazole was treated with allyl bromide/2-bromomethylbenzonitrile in acetonitrile at refluxing temperature for 24/20 h, respectively affording the benzimidazolium salts with reasonable yields.

In the corresponding complexes, the silver(I)–NHCs having bromide counter ion **4**–**6** were prepared in good yields *via* the *in situ* deportation of benzimidazolium salts by silver(I) oxide. Benzimidazolium salts **1**–**3** were treated with silver(I) oxide in methanol at mild reaction conditions to afford silver(I)–NHC complexes **4**–**6** with 78–93% yields (Scheme 2). These reactions were carried out in equipment wrapped with aluminum foil to avoid the light. Owing to the fact that, silver(I)–NHC complexes with bulkier counterions such as, hexafluorophosphate, tetrafluoroborate, perchlorate, among others are easy to crystallize, complexes **4**–**6** were subjected to salt metathesis reactions using KPF_6 in methanol to afford silver(I)–NHC hexafluorophosphate complexes **4a**–**6a** in good yields (Scheme 3). These complexes were found stable to light for few days.



Scheme 2. Synthetic pathway to silver(I)–NHC complexes (**4**–**6**) from NHC precursors **1**–**3**.



Scheme 3. Salt metathesis reactions of silver-carbene complexes **4**–**6**.

Following the transmetallation reactions using silver(I)–NHC bromide complexes **4**–**6**, gold(I)–NHC complexes **7**–**9** were obtained with 77–88% yields after having filtered off the silver(I) bromide precipitate from a dichloromethane solution as shown in Scheme 4. The reactions for gold(I)–NHC complexes were conducted at room temperature using gold(I) chloride dimethyl sulfide as a gold source. This method allows for the preparation of NHC–gold(I) complexes **7** and **8** having symmetrically and non-symmetrically substituted benzimidazole-2-ylidenes, respectively. Whereas, nitrile-functionalized gold(I)–NHC complex **9** was prepared straightforwardly at the same complexation conditions. Nevertheless, efficient purification could be achieved by the repeated precipitation of gold(I) complexes in methanol using diethyl ether.

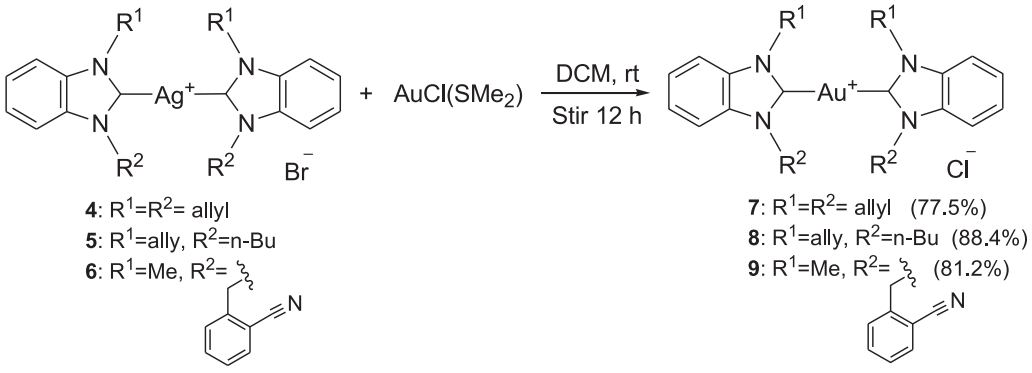
2.2. NMR spectral studies

All new compounds were fully characterized in solution by NMR spectroscopic methods and for five of them, namely **2**, **3**, **4a**, **6a** and **8**, by an X-ray structure analysis. In the ^{1}H NMR spectra of the carbene precursors **1**–**3**, the NC*H*N protons resonate at ca. 9.75 ppm, approximately 1.5 ppm more downfield shifted compared to that of the corresponding acidic C2 proton in the monosubstituted *N*-alkyl benzimidazoles. Apart from this, spectra also evidenced the peaks in the range 1.0–5.5 and 6.9–7.9 ppm, which are attributed to resonance of aliphatic and aromatic protons, respectively. The corresponding NCHN carbon signals in the ^{13}C NMR spectra of carbene precursors were also observed at more downfield positions at ca. 142 ppm compared to those of the more acidic *C*2H carbons in the respective monosubstituted *N*-alkyl benzimidazoles. This observation along with crystal structure determinations is an indicative of the successful carbene precursor formation [12].

Successful formation of silver(I)–NHC complexes **4**–**6** was indicated by the complete disappearance of NC*H*N proton signal at ca. 9.75 ppm in their ^{1}H NMR spectra, with respect to that of the carbene precursors. Further, it is also worth notice that the respective values of the carbon chemical shifts of their NCHN carbon center are downfield shifted at ca. 190 ppm, nearly 42 ppm more compared to their corresponding carbene precursors. These two observations along with the crystal structure determinations collectively evidenced the successful formation of the desired silver(I)–NHC complexes. Whereas in the case of the anionic carbene complexes of gold(I) **7**–**9**, carbon chemical shifts of NCHN carbon center is still more downfield shifted at ca. 191 ppm, which could be due to the more electropositive nature of the gold(I) center. This observation along with the crystal structure determination of gold(I) complex collectively confirmed the formation of target complexes [13]. On the other hand, aliphatic and aromatic carbon resonances in carbene complexes were almost similar to that of corresponding carbene precursors with negligible differences in peak position and intensity. All carbene complexes and their precursors were stable in solution; exhibiting good solubility in common deuterated organic solvents.

2.3. FT-IR spectral studies

All compounds were characterized using FT-IR spectral technique though carbene precursors **1** and **2**, and their carbene complexes do not contain any functional group. However, carbene precursor **3** and its silver(I)– and gold(I)–carbene complexes



Scheme 4. Synthetic pathway to gold(I)–NHC complexes (**7**–**9**) from silver(I)–NHC complexes **4**–**6** *via* transmetallation method.

Table 1
Crystal data and structure refinement details for compounds **2**, **3**, **4a**, **6a** and **8**.

	2	**3**	**4a**	**6a**	**8**
Formula	$C_{14}H_{21}N_2BrH_2O$	$C_{16}H_{14}N_3Br$	$C_{26}H_{28}AgN_4F_6P$	$C_{32}H_{26}AgN_6F_6P$	$C_{28}H_{36}AuN_4ClO$
Formula weight	315.24	328.20	649.36	747.43	663.02
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P1, (No. 1)	P21/c, (No. 14)	Cc, (No. 9)	P-1, (No. 2)	P21/c, (No. 14)
a, *b*, *c* [Å]	8.5628(19) 9.773(2), 10.250(2)	8.2554(4) 10.5079(6), 17.1114(9)	10.1366(14), 18.235(3), 15.753(2)	10.1513(3), 12.0531(3), 14.7855(4)	16.8881(4), 14.7745(4), 23.5643(6)
α, β, γ [°]	68.477(4), 84.455(4), 75.437(4)	90.00, 96.392(1), 90.00	90.00, 103.087(2), 90.00	66.742(1), 71.660(2), 72.434(2)	90.00, 94.272(1), 90.00
V [Å^3]	772.3(3)	1475.13(14)	2836.2(7)	1544.59(8)	5863.3(3)
Z	2	2	4	2	4
D (calc) [g/cm^3]	1.656	1.478	1.521	1.607	1.552
Mu (MoKα] [/mm]	2.654	2.780	0.828	0.774	5.137
F(000)	328	664	1312	752	2720
Crystal size [mm]	0.10 × 0.19 × 0.34	0.14 × 0.26 × 0.44	0.14 × 0.37 × 0.49	0.05 × 0.08 × 0.38	0.23 × 0.24 × 0.74
Temperature (K)	100	100	100	100	100
Radiation [Å]	MoK α 0.71073	MoKa α 0.71073	MoK α 0.71073	MoKa α 0.71073	MoK α 0.71073
θ Min–Max [°]	2.14–29.40	2.3–30.1	2.2–30.1	1.9–29.0	1.2–27.5
Tot.; Uniq. Data	11030, 4698	16033, 4316	11808, 7011	32708, 8094	46570, 13445
R_{int}	0.042	0.028	0.028	0.057	0.042
Nref; Npar	10685, 303	4316, 181	7011, 373	8094, 417	13445, 635
R, wR_2, *S*	0.0468, 0.0719, 1.056	0.0221, 0.0581, 1.05	0.0479, 0.1619, 0.98	0.0526, 0.0909, 1.06	0.0472, 0.1474, 1.03

possess a nitrile-functionality, which can take part in the coordination or can make a weak attraction with metal centers. This possibility can be easily traced by FT-IR spectral technique [14]. The FT-IR stretching vibrational bands for the benzimidazolium ring in carbene precursors **1**–**3** were observed at ca. 1550 and 1100 cm^{-1}, whereas aliphatic and aromatic C–H vibrations at ca. 2930 and 2860 cm^{-1}, respectively. The former vibrations shifted to lower energy region in the corresponding carbene complexes indicating the formation of the carbene complexes. This shift is due to the presence of electropositive metal center, which affects the C=N and C–N bond vibrations by dragging electron density towards itself. The nitrile stretching vibrations in the carbene precursor **3** was observed at 2224 cm^{-1}. Interestingly, in the respective carbene complexes this band remains almost unaltered with peak intensity and position, suggesting its noninvolvement in the coordination. This observation is further supported by the single crystal structure determination of the silver(I)–carbene complex **6**. Observed stretching vibrational bands and their assignments are in well agreement with the previous reports [15].

2.4. Single crystal X-ray diffraction studies

The crystal structures for carbene precursors **2** and **3**, silver(I)–carbene complexes **4a** and **6a**, and gold(I)–carbene complex **8** were obtained, and the crystal data and structure refinement details are provided in Table 1. Single crystals of these compounds suitable for X-ray diffraction analysis were obtained either by slow evaporation of their methanolic solution or by slow diffusion of diethyl ether into a solution of compound in methanol/acetonitrile at room temperature. Carbene precursor **2** crystallized in the triclinic space group *P*1 having two crystallographically independent structural units. A perspective view of carbene precursor **2** is shown in Fig. 1. Pertinent bond distances and angles of **2** are tabulated in Table 2. An asymmetric unit of **2** consists of two crystallographically independent units of benzimidazolium cations, two bromide anions and two water molecules. While, both benzimidazole rings are coplanar with slightly different geometric parameters. The internal ring angle of benzimidazole (N1–C1–N2) at the carbene carbon center is 109.5(11)° for N1A–C1A–N2A and 112.0(7)° for N2B–C1B–N1B. These bond angles are in well agreement with those

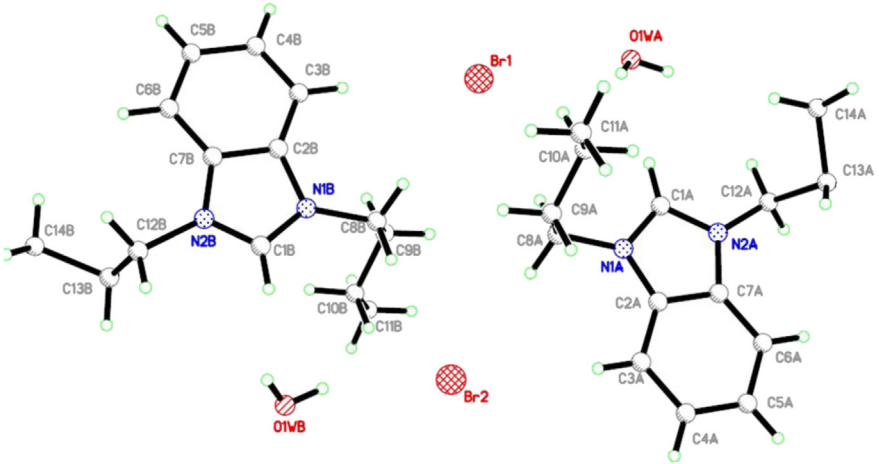


Fig. 1. Molecular structures of two crystallographically units of **2** with displacement ellipsoids drawn at 50% probability.

Table 2
Selected bond distances (Å) and angles (°) for **2**.

Bond distance (Å)			
N1A–C8A	1.473(12)	N1B–C8B	1.507(12)
N1A–C1A	1.315(16)	N1B–C1B	1.313(12)
N2A–C1A	1.382(15)	N2B–C1B	1.284(12)
N2A–C12A	1.425(13)	N2B–C12B	1.532(13)
N2A–C7A	1.370(10)	N2B–C7B	1.376(8)
N1A–C2A	1.334(9)	N1B–C2B	1.411(9)
C6A–C7A	1.3900(11)	C6B–C7B	1.3900(7)
Bond angle (°)			
N1A–C8A–C9A	114.2(9)	N1B–C8B–C9B	109.4(8)
C8A–N1A–C1A	123.3(9)	C8B–N1B–C1B	129.8(8)
N1A–C1A–N2A	109.5(11)	N1B–C1B–N2B	112.0(7)
C1A–N2A–C12A	126.1(11)	C1B–N2B–C12B	125.1(8)
N2A–C12A–C13A	114.3(11)	N2B–C12B–C13B	108.1(10)

observed in the related benzimidazolium salts [16]. In the extended structure, benzimidazolium cations and bromide anions of **2** are connected *via* OH_{water}–Br (3.286 Å), $CH_{benzimi}$–O (3.315 Å) and $CH_{benzimi}$–Br (3.131 Å) intermolecular hydrogen bonds to form a three dimensional array.

Carbene precursor **3** is a well ordered bromide salt crystallized in the monoclinic space group of *P*21/c comprising one benzimidazolium cation and one bromide anion in an asymmetric unit. A perspective view of the salt is shown in Fig. 2, and the selected bond distances and angles are tabulated in Table 3. Planes of benzimidazole are benzonitrile rings are almost perpendicular to each other with a dihedral angle of 113.28(10)° for N1–C8–C9 module. The angle at nitrile carbon is found almost linear with the bond angle of 178.60(17) for N3–C15–C10, which is accordance with our previous reports on nitrile-functionalized azolium salts [17]. Like **2**, carbene precursor **3** shows comparable bond angle (110.23(12)° for N1–C7–N2) at carbene carbon center, illustrating the successful salt formation. In the crystal packing of **3**, two types of intermolecular hydrogen bonds, C–H–Br (2.868 Å) and C–H–$N_{nitrile}$ (3.189 Å) are observed.

Silver(I)–carbene complex **4a** (Fig. 3) crystallized in the monoclinic space group *Cc*, while complex **6a** (Fig. 4) crystallized in the triclinic space group *P*1. Pertinent bond distances and angles of complexes **4a** and **6a** are tabulated in Tables 4 and 5, respectively. These complexes possess one bis–carbene complex cation and one hexafluorophosphate anion in their asymmetric unit. Both complexes show a slightly distorted linear coordination geometry around the silver(I) center with the bond angle of 172.58(15) (C1–Ag1–C8) and 176.09(13)° (C1–Ag1–C17) for **4a** and **6a**, respectively. The internal ring angles at carbene carbon centers are decreased to 104.9(5)° (N1–C1–N2), 105.3(5)° (N3–C8–N4) and 106.0(3)° (N1–C1–N2), 105.6(3)° (N4–C17–N5) in both cases respectively, which is attributed to the formation carbene-silver(I) bonds [18]. Carbene-silver-carbene module found almost

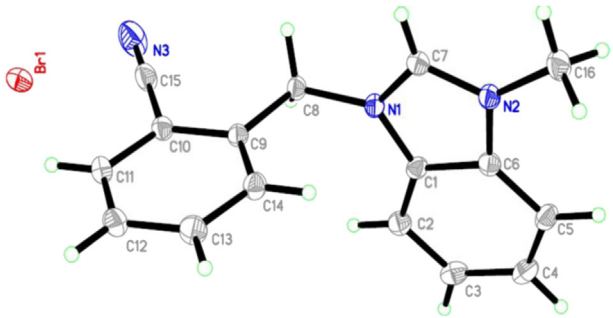


Fig. 2. Molecular structure of **3** with displacement ellipsoids drawn at 50% probability.

Table 3
Selected bond distances (Å) and angles (°) for **3**.

Bond distance (Å)			
N2–C16	1.4576(17)	N1–C1	1.3943(16)
N2–C7	1.3291(16)	N1–C8	1.4627(16)
N2–C6	1.3954(17)	C10–C15	1.4427(19)
N1–C7	1.3365(16)	N3–C15	1.142(2)
Bond angle (°)			
C16–N2–C7	125.38(12)	N1–C8–C9	113.28(10)
C16–N2–C6	125.99(11)	C8–C9–C10	118.89(11)
N2–C7–N1	110.23(12)	C9–C10–C15	119.73(11)
C7–N1–C8	125.30(11)	C9–C10–C11	121.72(12)
C7–N1–C1	108.38(11)	N3–C15–C10	178.60(17)

perpendicular to the *bc*-plane. In the case of complex **4a**, one of the allyl wingtip is disordered over two sets along with fluorides of hexafluorophosphate unit. However, complex **6a** is a well ordered structure, having almost coplanar benzimidazole units. Both carbene ligands adopt a *syn*-arrangement around the silver(I) center, which is due to the sterically demanding nature of the benzonitrile substituents. Similarly, both benzonitrile arms were twisted out of the C–Ag–C module on the side pointing nitrile-functionalities away from the metal center. This observation is in agreement with the assignment based on FT-IR spectral analysis. Similar observations were found in the previously reported nitrile-functionalized silver(I) carbene and coordination complexes [17,19,20]. In the extended crystal structure, both complexes showed similar type of intermolecular hydrogen bonds of C–H–F (2.560–2.665 Å) connecting the complex units into three dimensional networks.

Single crystal X-ray diffraction results of gold(I)–carbene complex **8** revealed that the crystals are comprised of monoclinic unit cells in the space group P21/c having two crystallographically independent structural units possessing slightly different geometric parameters. Molecular structures of complex **8** are depicted in Figs. 5 and 6. Selected bond distances and angles of complex 8 are tabulated in Table 6. Gold(I)–carbene complex **8** comprises two crystallographically independent gold(I) bis–carbene complex cations along with two chloride ions and four water molecules in an asymmetric unit. The central gold(I) ion adopts a distorted linear

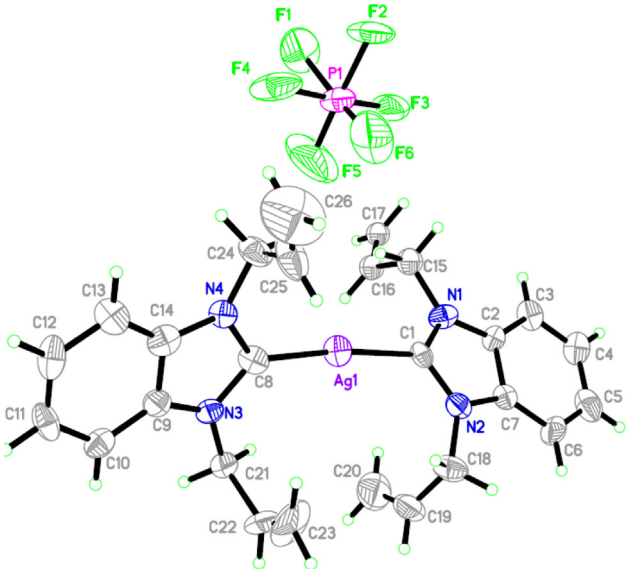


Fig. 3. Molecular structure of **4a** with displacement ellipsoids drawn at 50% probability.

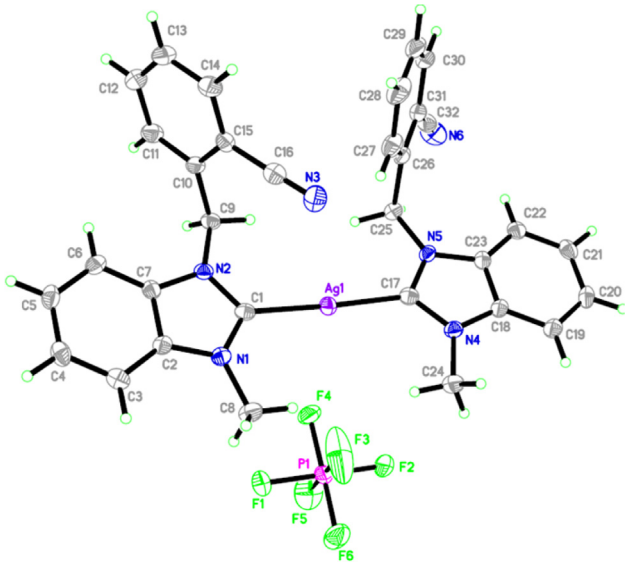


Fig. 4. Molecular structure of **6a** with displacement ellipsoids drawn at 50% probability.

coordination sphere with 176.1(3)o for C1A–Au1A–C8A and 178.4(3)° for C1B–Au1B–C8B. The internal ring angles [106.8(6)° for N1A–C1A–N2A, 107.0(6)° for N3A–C8A–N4A, 105.7(7)° for N1B–C1B–N2B and 106.3(6)° for N3B–C8B–N4B] at carbene carbon centers are comparable with that of silver(I)–carbene complexes and are much lesser than carbene precursors. On the other hand, gold(I)–carbene carbon bond lengths were found in the range 2.019(7)–2.026(7) Å, which are comparable with that of the other gold(I)–carbene complexes [21]. Like silver(I)-carbene complexes **4a** and **6a**, in the case of gold(I) complex **8** the carbene ligands adopt a *syn*-arrangement around the metal center. In the crystal packing of complex **8**, two types of intermolecular hydrogen bonds OH_{water}–Cl (3.253 Å) and CH–Cl (3.202 Å) were observed along with other short contacts leading to the three dimensional network.

3. Conclusion

A series of sterically modulated carbene complexes of silver(I) and gold(I) were prepared and their solid (**2**, **3**, **4a**, **6a** and **8**) as well as solution state structures were studied. Gold(I)–carbene complexes were prepared by the technique of transmetallation using silver(I)–carbene complexes. Single crystal X-ray diffraction studies of carbene complexes revealed the presence of distorted linear coordination geometry around the metal center with *syn*-arrangement of the carbene ligands. Reported benzimidazolium salts and their silver(I)– and gold(I)–NHC complexes displayed similar structure with the biologically relevant complexes showing potential anticancer activity.

Table 4
Selected bond distances (Å) and angles (°) for **4a**.

Bond distance (Å)			
Ag1–C1	2.105(5)	N4–C24	1.485(7)
Ag1–C8	2.056(6)	N1–C2	1.379(5)
N1–C1	1.327(7)	N2–C7	1.396(5)
N2–C1	1.328(6)	N3–C9	1.333(5)
N1–C15	1.349(13)	N4–C14	1.347(5)
N2–C18	1.518(8)	P1–F1	1.570(10)
N3–C21	1.413(8)	P1–F2	1.613(8)
Bond angle (°)			
C1–Ag1–C8	172.58(15)	Ag1–C8–N4	129.8(4)
Ag1–C1–N1	129.9(4)	N1–C1–N2	104.9(5)
Ag1–C1–N2	124.9(4)	N3–C8–N4	105.3(5)
Ag1–C8–N3	124.9(4)	F1–P1–F6	163.9(8)

Table 5
Selected bond distances (Å) and angles (°) for **6a**.

Bond distance (Å)			
Ag1–C1	2.080(3)	N2–C9	1.467(4)
Ag1–C17	2.072(3)	N4–C24	1.463(4)
N1–C1	1.350(4)	N5–C25	1.463(4)
N2–C1	1.358(4)	N3–C16	1.148(4)
N4–C17	1.350(4)	N6–C32	1.144(5)
N5–C17	1.364(4)	P1–F1	1.602(2)
N1–C8	1.463(4)	P1–F2	1.605(2)
Bond angle (°)			
C1–Ag1–C17	176.09(13)	N1–C1–N2	106.0(3)
Ag1–C1–N1	126.6(2)	N4–C17–N5	105.6(3)
Ag1–C1–N2	127.2(2)	N2–C9–C10	114.3(3)
Ag1–C17–N4	128.0(2)	C15–C16–N3	179.0(4)
Ag1–C17–N5	126.3(2)	C31–C32–N6	176.8(4)

4. Experimental

4.1. Reagents and instruments

All chemicals and solvents were obtained from commercial sources and all reagents and solvents were of analytical grade and used without further purifications. Benzimidazole, 1-methylbenzimidazole, ally bromide, 2-bromomethylbenzonitrile, *n*-butyl bromide, silver(I) oxide, potassium hexafluorophosphate and gold(I)chloride(dimethyl sulfide) were purchased from Sigma–Aldrich. The carbene ligand precursors were prepared according to an established procedure. Nuclear magnetic resonance spectra were recorded in d_6-DMSO or $CDCl_3$ using a Bruker 500 MHz Ascend spectrometer at room temperature. The ^1H and ^{13}C NMR peaks were labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). Chemical shifts were referenced with respect to solvent signals. Elemental analysis was carried out on a Perkin Elmer Series II, 2400 microanalyzer. The FT-IR spectra of the

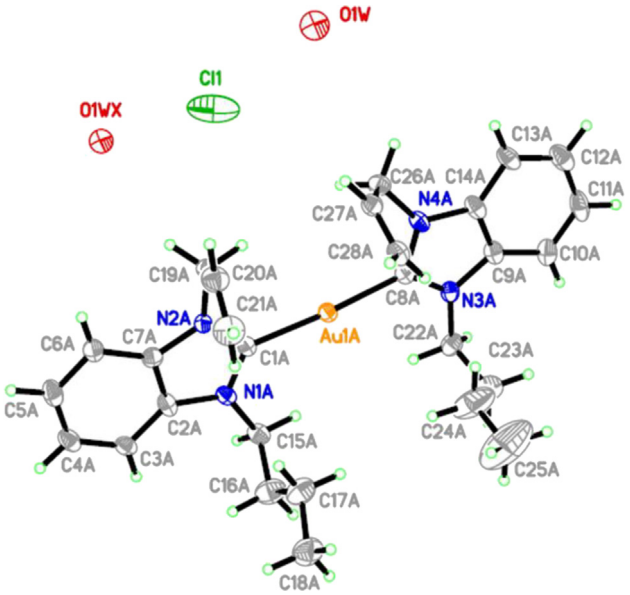


Fig. 5. Molecular structure of a crystallographically independent unit (A) of **8** with displacement ellipsoids drawn at 50% probability.

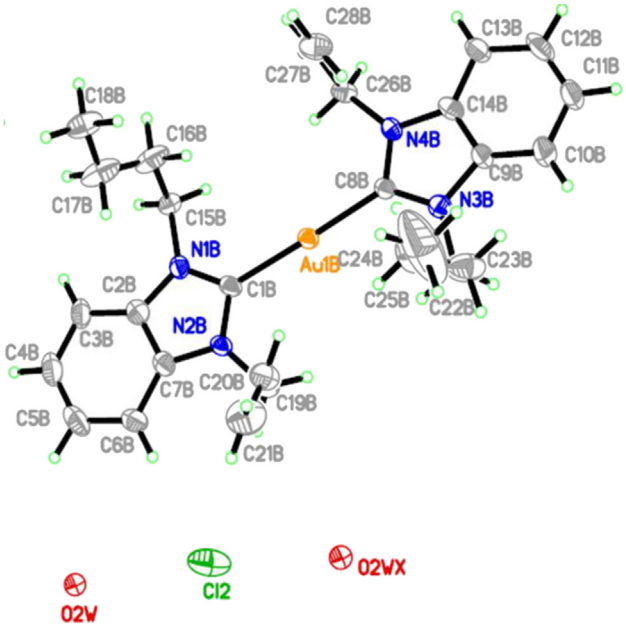


Fig. 6. Molecular structure of a crystallographically independent unit (B) of **8** with displacement ellipsoids drawn at 50% probability.

compounds were recorded in potassium bromide disks using a Perkin Elmer 2000 system spectrometer in the range 4000 to 400 cm^{-1}. The instruments are available at The School of Chemical Sciences, Universiti Sains Malaysia (USM). The X-ray diffraction data were collected using a Bruker SMART APEX2 CCD area-detector diffractometer. Structures were solved by direct methods and refined by full-matrix least-squares against F^2. Calculations, structure refinement, molecular graphics and the material for publication were performed using the SHELXTL and PLATON (Spek, 2009) software packages available at The School of Physics, USM.

4.2. Synthesis of benzimidazolium salts

4.2.1. Synthesis of 1,3-bis-(allyl)benzimidazolium bromide (*1*)

To a stirred solution of benzimidazole (0.25 g, 2.1 mmol) in dioxane (10 mL), allyl bromide (0.51 g, 4.2 mmol) was added in one portion and the mixture was stirred at reflux for one day. A brown colored oily product was formed, after cooling, the solvent was removed under a vacuum. The oily residual was then washed thoroughly with fresh dioxane (2 × 3 mL) and diethyl ether (2 × 3 mL) to yield a viscous brown liquid. Yield: 71%. ^{1}H NMR (500 MHz, d_6-DMSO): δ 5.41 (4H, s, N–CH_2), 5.18 (4H, d, J = 13 Hz, =CH_{cis}–), 5.43 (4H, m, =CH_{trans}–), 6.12 (2H, m, CH=CH$_2$), 7.71–8.02 (4H, m, benzimi-ArH) and 9.75 (1H, s, benzimi-$H2'$); ^{13}C {^{1}H}NMR (125 MHz, d_6-DMSO): δ 49.23 (N–CH_2), 113.49 (CH$_2$=CH–), 120.70 (CH=CH_2), 126.89, 127.90, 129.20, 131.36 (benzimi-ArC) and 140.86 (benzimi-$C2'$). FT-IR (KBr disc) in cm^{-1}: 2881, 2939 ν(C–H), 1524, 1146 ν(benzimidazole ring).

4.2.2. Synthesis of 1-allyl-3-butylbenzimidazolium bromide (*2*)

To a solution of butyl benzimidazole (0.50 g, 1.9 mmol) in acetonitrile (20 mL), allyl bromide (0.24 g, 1.9 mmol) was added and refluxed for 20 h. The mixture turned brownish like salt **1** after completion of reaction. Then the solvent was removed under a vacuum giving the product as brown solid, washed thoroughly with diethyl ether (2 × 5 mL) and recrystallized using methanol. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the salt solution in methanol at room temperature. Yield: 86%, M.P.: 161–163 °C. ^{1}H NMR (500 MHz, d_6-DMSO): δ 0.93 (3H, t, J = 7.2 Hz, CH_3), 1.35 (6H, m, CH$_2$–CH_2–CH$_3$), 1.91 (5H, m, CH_2–CH$_2$–CH$_3$), 4.50 (2H, t, J = 7.2 Hz, N–CH_2Bu), 5.15 (2H, d, J = 5.8 Hz, N–CH_2), 5.39 (2H, d, J = 5.8 Hz, =CH_{trans}–), 5.43 (2H, s, =CH_{cis}–), 6.24 (2H, m, CH=CH$_2$), 8.00–8.12 (4H, m, benzimi-ArH) and 9.75 (1H, s, benzimi-$H2'$); ^{13}C{^{1}H}NMR (125 MHz, d_6-DMSO): δ 13.00 (CH_3), 19.50 (CH$_3$–CH_2–CH$_2$), 30.05 (CH$_3$–CH$_2$–CH_2), 46.50 (N–CH_2Bu), 49.00 (N–CH_{2allyl}), 113.50, 120.50, 126.50, 131.00 (benzimi-ArC) and 142.10 (benzimi-$C2'$). FT-IR (KBr disc) in cm^{-1}: 2875, 2937 ν(C–H), 1522, 1141 ν(benzimidazole ring). Anal. Calcd for $C_{14}H_{19}N_2Br$: C, 56.9; H, 6.5; N, 9.5%. Found: C, 55.5, H, 6.7, N, 9.0%.

4.2.3. Synthesis of 1-methyl-3-{(2′-nitrile)benzyl}benzimidazolium bromide (*3*)

This compound was prepared in a manner analogous to that for **2**, only with 1-methylbenzimidazole (0.23 g, 1.5 mmol) and 2-bromomethylbenzonitrile (0.30 g, 1.5 mmol) instead of 1-butylbenzimidazole and allyl bromide. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into the methanolic solution of salt at room temperature. Yield: 78.5%, M.P.: 140–141 °C. ^{1}H NMR (500 MHz, d_6-DMSO): δ 4.14 (3H, s, N–CH_3), 6.05 (2H, s, benzylic-CH_2), 7.45, 7.55–7.76 (4H, m, benzyl Ar-H), 7.89, 7.96, 8.10 (4H, m, benzimi-ArH) and 9.85 (1H, s, benzimi-$H2'$); ^{13}C {^{1}H} NMR (125 MHz, d_6-DMSO): δ 36.10 (N–CH_3), 51.00 (benzylic-CH_2), 111.10, 112.75, 124.70, 134.81 (benzimi-ArC), 118.63 (N≡C), 112.40, 125.10, 130.03 (benzyl-ArC), 141.01 (benzimi-$C2'$). FT-IR (KBr disc) in cm^{-1}: 2935, 2862 ν(C–H), 2224 ν(C≡N), 1534, 1118 ν(benzimidazole ring) Anal. Calc. for $C_{16}H_{15}BrN_3$: C, 58.4; H, 4.6; N, 12.7%. Found: C, 58.1; H, 4.7; N, 12.5%.

4.3. Synthesis of silver(I)–NHC complexes

4.3.1. Synthesis of bis{1,3-bis-(allyl)benzimidazolium}silver(I) bromide (*4*)

To a suspension of Ag_2O (0.33 g, 1.4 mmol) in methanol (20 mL), was added **1** (0.20 g, 0.7 mmol)) and stirred at room temperature for 16 h in the equipment wrapped with aluminum foil to avoid light. The reaction mixture was filtered through a pad of Celite, and the resulted colorless filtrate was concentrated to 5 mL under a vacuum. A white solid was afforded by addition of 75 mL diethyl ether to the filtrate. So obtained solid was redissolved in acetonitrile and 150 mL of diethyl ether was added to reprecipitate the solid, which was isolated by filtration and dried. Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion

Table 6
Selected bond distances (Å) and angles (°) for **8**.

Bond distance (Å)			
Au1A–C1A	2.024(7)	Au1B–C1B	2.020(8)
Au1A–C8A	2.026(7)	Au1B–C8B	2.019(7)
N1A–C1A	1.356(9)	N1B–C1B	1.341(11)
N2A–C1A	1.330(9)	N2B–C1B	1.349(10)
N3A–C8A	1.332(9)	N3B–C8B	1.357(10)
N4A–C8A	1.359(10)	N4B–C8B	1.353(10)
N1A–C15A	1.466(10)	N1B–C15B	1.485(10)
N2A–C19A	1.468(9)	N2B–C19B	1.480(11)
N3A–C22A	1.465(10)	N3B–C22B	1.469(11)
N4A–C26A	1.480(10)	N4B–C26B	1.469(10)
Bond angle (°)			
C1A–Au1A–C8A	176.1(3)	C1B–Au1B–C8B	178.4(3)
Au1A–C1A–N1A	127.2(5)	Au1B–C1B–N1B	127.7(6)
Au1A–C1A–N2A	126.1(5)	Au1B–C1B–N2B	126.6(6)
Au1A–C8A–N3A	129.8(6)	Au1B–C8B–N3B	127.2(6)
Au1A–C8A–N4A	123.1(5)	Au1B–C8B–N4B	122.3(8)
N1A–C1A–N2A	106.8(6)	N1B–C1B–N2B	105.7(7)
N3A–C8A–N4A	107.0(6)	N3B–C8B–N4B	106.3(6)

of diethyl ether into the methanolic solution of the complex. Yield: 84.3%, M.P.: 144–146 °C. ^{1}H NMR (500 MHz, d_6-DMSO): δ 5.15 (4H, m, N–CH_2), 5.22 (2H, s, 2× = CH_{trans}–), 5.32 (2H, s, 2× = CH_{cis}–), 6.19 (2H, m, CH=CH_2), 7.49, 7.70 (4H, m, benzimi-ArH); ^{13}C{^{1}H} NMR (125 MHz, d_6-DMSO): δ 51.00 (N–CH_2), 112.07 (CH_2=CH–), 123.90 (CH=CH_2), 125.21, 133.08, 133.61 (benzimi-ArC), 189.03 ($C_{carbene}$–Ag). FTIR (KBr disc) cm^{-1}: 2868, 2923 ν(C–H), 1476, 1192 ν(benzimidazole ring). Anal. Calc. for $C_{26}H_{28}N_4AgBr$: C, 53.3; H, 5.2; N, 9.6%. Found: C, 53.2; H, 5.4; N, 9.3%.

4.3.2. Synthesis of bis{1-allyl-3-butylbenzimidazolium}silver(I) bromide (**5**)

This complex was prepared in a manner analogous to **4**, only with **2** (0.19 g, 0.7 mmol) instead of **1**. Yield: 93.1%. M.P.: 230–231 °C. ^{1}H NMR (500 MHz, d_6-DMSO): δ 1.00 (3H, t, J = 8.1 Hz, CH_3), 1.45 (6H, m, CH_2–CH_2–CH_3), 1.97 (5H, m, CH_2–CH_2–CH_3), 4.53 (2H, t, J = 6.7 Hz, N–CH_2Bu), 5.13 (2H, s, N–CH_2CH), 5.17 (1H, t, J = 5.5 Hz, =CH_{trans}–), 5.33 (1H, t, J = 5.5 Hz, =CH_{cis}–), 6.15 (2H, m, CH=CH_2), 7.45–7.55 (4H, m, benzimi-ArH); ^{13}C{^{1}H}NMR (125 MHz, d_6-DMSO): δ 13.31 (CH_3), 20.20 (CH_3–CH_2–CH_2), 33.52 (CH_3–CH_2–CH_2), 50.08 (N–CH_2Bu), 53.21 (N–CH_2CH), 113.31, 118.65 (CH=CH_2), 125.61, 127.93, 132.81, 134.20 (benzimiAr–C) and 187.41 ($C_{carbene}$–Ag). FTIR (KBr disc) cm^{-1}: ~2860, 2925 ν(C–H), 1488, 1187 ν(benzimidazole ring). Anal. Calc. for $C_{28}H_{36}N_4AgBr$: C, 54.4; H, 6.2; N, 9.1%. Found: C, 54.7; H, 6.4; N, 8.8%.

4.3.3. Synthesis of bis[1-methyl-3-{(2′-nitrile)benzyl} benzimidazolium]silver(I) bromide (**6**)

This complex was prepared in a manner analogous to **4**, only with **3** (0.23 g, 0.7 mmol) instead of **1**. Yield: 78.6%, M.P.: 205–206 °C. ^{1}H NMR (500 MHz, d_6-DMSO): δ 4.05 (3H, s, N–CH_3), 5.93 (2H, s, benzylicCH_2), 7.20 (2H, d, J = 7.8 Hz, benzimi-ArH), 7.47 (4H, m, benzimi-ArH), 7.57 (2H, d, J = 6.0 Hz, benzyl-ArH), 7.86–7.94 (4H, m, benzyl-ArH); ^{13}C {^{1}H} NMR (125 MHz, d_6-DMSO): δ 35.42 (N–CH_3), 50.00 (benzylic-CH_2), 117.31 (C≡N), 110.42, 124.44, 134.27 (benzimi-ArC), 121.11, 128.10, 129.30, 139.41 (benzyl-ArC), 191.80 ($C_{carbene}$–Ag). FTIR (KBr disc) cm^{-1}: 2882, 2937 ν(C–H), 2221 ν(C≡N), 1466, 1183 ν(benzimidazole ring). Anal. Calc. for $C_{32}H_{26}N_6AgBr$: C, 56.2; H, 4.1; N, 12.3%. Found: C, 56.4; H, 4.4; N, 11.9%.

4.3.4. Salt metathesis of silver(I)–NHC bromide complexes (**4**–**6**) to silver(I)–NHC hexafluorophosphate complexes (**4a**–**6a**)

A solution of silver(I)–NHC complex **4** (0.30 g, 0.5 mmol) in methanol (20 mL) was added KPF_6 (0.092 g, 0.5 mmol) and stirred for 3–4 h at room temperature. The solvent was removed under a vacuum to afford white solid of **4a**. This residual solid was thoroughly washed with water to remove unreacted KPF_6, and was isolated by filtration and dried. In the same manner, silver bromide complexes **5** and **6** were converted into their hexafluorophosphate counterparts **5a** and **6a**, successfully. Further, NMR and FTIR spectral data of the hexafluorophosphate derivatives are as same as their bromide derivatives. Elemental analysis results of these complexes are in well agreement with their structure.

4.4. Synthesis of gold(I)–NHC complexes

4.4.1. Synthesis of bis{1,3-bis-(allyl)benzimidazolium}gold(I) chloride (**7**)

A mixture of silver(I)–carbene complex **4** (0.3 g, 0.5 mmol) and $AuCl(SMe_2)$ (0.15 g, 0.5 mmol) in dichloromethane (20 mL) was stirred at room temperature for 12 h in an equipment wrapped with aluminum foil to exclude light. It was then filtered through a pad of Cilite and the solvent was removed under a vacuum to obtain an off-white solid. So obtained complex was recrystallized by repeated precipitation in methanol using diethyl ether. Yield: 77.5%, M.P.: 171 °C. ^{1}H NMR (500 MHz, d_6-DMSO): δ 5.11 (4H, m, N–CH_2), 5.34 (2H, s, 2× = CH_{trans}–), 5.47 (2H, s, 2× = CH_{cis}–), 6.28 (2H, m, CH=CH_2), 7.86–7.94 (4H, m, benzimi-ArH); ^{13}C{^{1}H}NMR (125 MHz, d_6-DMSO): δ 51.71 (N–CH_2), 111.60 (CH_2=CH–), 121.00 (CH=CH_2), 123.87, 133.11, 134.61 (benzimi-ArC), 184.33 ($C_{carbene}$–Au). FTIR (KBr disc) cm^{-1}: 2873, 2936 ν(C–H), 1467, 1131 ν(benzimidazole ring). Anal. Calc. for $C_{26}H_{28}N_4AuCl$: C, 49.6; H, 4.5; N, 8.9%. Found: C, 50.2; H, 4.9; N, 9.3%.

4.4.2. Synthesis of bis{1-allyl-3-butylbenzimidazolium}gold(I) chloride (**8**)

This complex was prepared in a manner analogous to **7**, only with **5** (0.35 g, 0.5 mmol) instead of **4**. Single crystals of gold(I) complex **8** suitable for X-ray diffraction studies were grown by the slow diffusion of ethyl ether into the methanolic solution of the complex at room temperature. Yield: 88.4%, M.P.: 249–250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (3H, t, J = 7.5 Hz, CH_3), 1.44 (2H, m, CH_2–CH_2–CH_3), 2.04 (2H, m, CH_2–CH_2–CH_3), 4.63 (2H, t, J = 7.2 Hz, N–CH_2), 5.31 (2H, m, N–CH_{2allyl}), 5.25 (1H, s, =CH_{cis}–), 5.38 (1H, s, =CH_{trans}–), 6.16 (1H, m, –CH=CH_2) and 7.63 (4H, m, benzimi-ArH), 7.92 (4H, d, J = 7.0 Hz, benzimi-ArH); ^{13}C {^{1}H} NMR (125.0 MHz, $CDCl_3$): δ 13.30 (CH_3), 20.04 (CH_3–CH_2–CH_2), 32.41 (CH_3–CH_2–CH_2), 49.67 (N–CH_2Bu), 51.51 (N–CH_2CH), 112.45 (CH=CH_2), 119.30 (CH=CH_2), 124.72, 131.90, 133.24 (benzimi-ArC) and 190.90 ($C_{carbene}$–Au). FTIR (KBr disc) cm^{-1}: 2865, 2928 ν(C–H), 1470, 1184 ν(benzimidazole ring). Anal. Calc. for $C_{28}H_{36}N_4AuCl$: C, 50.7; H, 5.8; N, 8.5%. Found: C, 51.3; H, 5.9; N, 8.3%.

4.4.3. Synthesis of bis[1-methyl-3-{(2′-nitrile)benzyl} benzimidazolium]gold(I) chloride (**9**)

This complex was prepared in a manner analogous to **7**, only with **6** (0.34 g, 0.5 mmol) instead of **4**. Yield: 81.2%, M.P.: 221–222 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.47 (3H, s, N–CH_3), 5.32 (2H, s, benzylic-CH_2), 6.94 (2H, d, J = 7.0 Hz, benzimi-ArH), 7.16–7.23 (4H, m, benzimi-ArH), 7.40 (2H, d, J = 7.2 Hz, benzyl-ArH), 7.64–7.73 (4H, m, benzyl-ArH); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 27.52 (N–CH_3), 42.39 (benzyl-CH_2), 110.38 (C≡N), 112.31, 125.40, 129.31, 140.00 (benzimi-ArC), 122.04, 128.10, 133.24 (benzyl-ArC), 191.50 ($C_{carbene}$–Au). FTIR (KBr disc) cm^{-1}: 2874, 2927 ν(C–H), 2222 ν(C≡N), 1476, 1192 ν(benzimidazole ring), Anal. Calc. for $C_{32}H_{26}N_6AuCl$: C, 52.8; H, 3.7; N, 11.5%. Found: C, 53.0; H, 4.1; N, 11.3%.

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Appendix A. Supplementary material

CCDC 849996, 849997, 849998, 962984, and 862525 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.

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