

Structures, Energies, and Bonding Analysis of Monoaurated Complexes with N-Heterocyclic Carbene and Analogues

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In this work, we computationally investigated from quantum chemical calculations (DFT) at the BP86 level with the various basis sets def2-SVP, def2-TZVPP, and TZ2P+, chemical bonding issues of the recently described carbene-analogues gold(I) complexes AuCl-NHE_{Me} (AuI-NHE) with E = C – Pb. The optimized structures and the metal-ligand bond dissociation energy (BDE) were calculated, and the nature of the E→Au bond was studied with charge and energy decomposition methods. The equilibrium structures of the system showed that there were major differences in the bonded orientation from the ligands NHC-NHPb to gold(I) complex between the lighter and the heavier homologues. The BDEs results showed that the metal-carbene analogues bonds were very strong bonds and the strongest bond was calculated for AuI-NHC which had the bond strength $D_e = 79.2$ kcal/mol. Bonding analysis of AuI-NHE showed that NHE ligands exhibited donor-acceptor bonds with the σ lone pair electrons of NHE donated into the vacant orbital of the acceptor fragment (AuCl). The EDA-NOCV results indicated that the ligand NHE in AuI-NHE complexes were strong σ -donors and very weak π donor and the bond order in complexes was AuI-NHC > AuI-NHSi > AuI-NHGe > AuI-NHSn > AuI-NHPb. We also realised that the gold-ligand bond was characterized by a π back-donation component from the Au to the ligand. All investigated complexes in this study were suitable targets for synthesis and gave a challenge in designing Au nano-crystals of narrow size distribution from gold(I) complexes that carried versatile N-heterocyclic carbene-analogues NHE.

Key words: N-heterocyclic carbene ligands; bond dissociation energy; EDA-NOCV; gold; DFT calculations

The first direct synthesis of metal complexes with N-heterocyclic carbenes (NHCs) as ligand was pendently presented by Hans Werner Wanzlick (Wanzlick 1968) and Karl Öfele (1968). After that the break through result of the isolation of stable carbenes was reported by Arduengo *et al.* (1991). It has been known that NHCs have emerged as an essential class

of ligands in inorganic and organometallic chemistry (Bourissou *et al.* 2000; Hahn & Jahnke 2008; Herrmann 2002). In the report of Jacobsen (Jacobsen *et al.* 2009) showed that NHCs display particular properties across the wide family of neutral ligands used in catalysis due to strong σ -donating character. Furthermore, ligand NHCs exhibit a special

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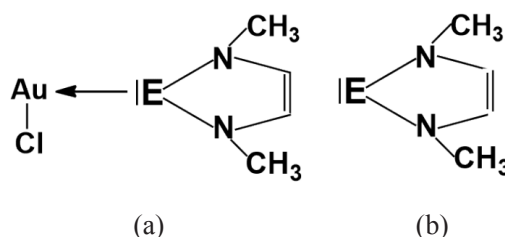
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geometry associated with a flexible structure allowing fine-tuning of their steric properties (Poater *et al.* 2009). In addition to this, NHCs can be very popular used for a large variety of reactions of high synthetic interest and these two-coordinate forms of carbon with two unpaired electrons have been considered as “new” ligands for bioactive coordination compounds (Hermann *et al.* 2002; Nemcsok *et al.* 2004). It has been noted that NHCs ligands can be stabilized by two nitrogens and form stable complexes with transition metals (Ag, Au) and with main-group elements (Nemcsok *et al.* 2004). Although the first stable transition metal carbene complex was investigated in 1964 (Fischer & Maasböl 1964), but after a long time, the metal-ligand bonding in complexes of mixed carbene-halogen complexes (NHC-TMX with TM = Cu, Ag, Au and X = F – I) was published for using a charge decomposition analysis which was noticed for the first time by Frenking and Boehme (1998) and group 11 elements (Cu, Ag, Au) called as coinage metals, have aroused intense interest (Zhu *et al.* 2012). The chemical bonding between NHCs and group 11 metals have been investigated theoretically (Nemcsok *et al.* 2004; Hu *et al.* 2004). Moreover, theoretical studies of the electronic structure of transition metal complexes with NHCs ligand have been recently carried out by other group (Schwarz *et al.* 2000; Weskamp *et al.* 1999; Lee *et al.* 2004). The fact was that, the type of NHC ligands that have been developed by Arduengo *et al.* [1991] have found recent use in the synthesis of molecular gold(I) fluoride and chloride complexes. Particularly in recent years, it has been known that gold could form stable coordination complexes with NHC ligand (Marion & Nolan 2008; Nolan 2011; Zhu *et al.* 2012). The nature of the Au-NHC binding has been presented from the structures and properties of the complexes (Nemcsok *et al.* 2004). In this study, we want to choose NHC_{Me} and to extend to the heavier homologues in order to give insight into the structures and bonding situation using NBO and energy

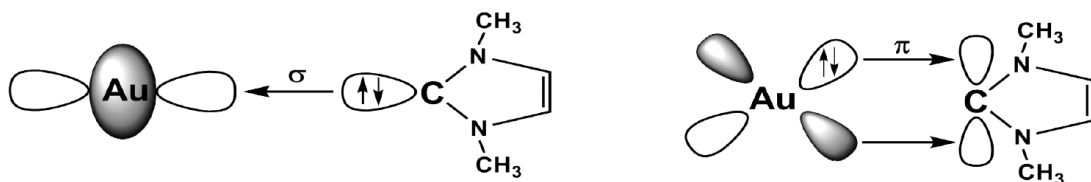
decomposition analysis (EDA) with the set of orbitals — the natural orbitals for chemical valence (NOCV) methods. The main purpose of this study was to investigate in details the bond strength of Au-E bond; the nature of the Au-E bond in AuCl-ligands; and the differences in the Au-ligand bonding from the carbene to plumblylene complexes. *Scheme 1* shows the overview of the compounds investigated in the presented work and the schematic representation of a donor-acceptor bonding in Fischer-type carbene complex is shown in *Scheme 2*. The C atom in NHC_{Me} ligand retains one lone pairs which is formally formed from a carbene ligand in a triplet state to a triplet AuCl fragment. To understand the gold-chloride and NHE ligands interactions in complexes, we have carried out density functional theory calculations. We investigated the bonding situation in complexes and the electronic structure of the molecules was analyzed with charge- and energy-decomposition methods.



Scheme 1. Overview of the compounds investigated in the present work: (a) Complexes [AuCl- $\{NHE_{Me}\}$] (AuI-NHE) and (b) Ligand NHE_{Me} (NHE) with E = C, Si, Ge, Sn, Pb.

COMPUTATIONAL DETAILS AND THEORETICAL ASPECTS

The geometries of the gold(I) carbene-analogues complexes [AuCl- $\{NHC_{Me}\}$] – [AuCl- $\{NHPb_{Me}\}$] (AuI-NHC – AuI-NHPb) were carried out at the gradient corrected DFT level of theory using Beck’s exchange functional (Becke 1998) in conjunction with Perdew’s correlation functional (BP86) (Perdew 1986). The calculations were carried out using



Scheme 2. Schematic representation of donor-acceptor bonding in Fischer-type of AuCl complex that carries NHC ligand.

the program package Gaussian03 (Frisch *et al.* 2004) optimized together with Turbomole 6.01 (Ahlich *et al.* 1989). All geometries were fully optimized without any symmetry constraints. A triple zeta valence basis set (def2-SVP) (Schäfer *et al.* 1992) was used for all of the main group elements and the relativistic of effective core potentials (ECPs) (Weigend & Ahlich *et al.* 2005) were applied for the heavier group-14 atoms Sn, Pb, and atom Au. The nature of the stationary points was checked by frequency calculations at the same level of theory (BP86/def2-SVP). All the structures of the complexes were verified as minimum by confirming that their respective Hessians were real on the BP86/def2-SVP level. The calculation of the bond dissociation energies (BDEs) and the charge analysis with Wiberg bond indices (WBI) as well as the natural partial charges at the BP86/def2-TZVPP (Snijders *et al.* 1981) //BP86/def2-SVP level of theory were carried out by using NBO 3.1 partitioning method in Gaussian03. Next, the bonding analysis was considered by using the Ziegler-Rauk-type energy decomposition analysis (EDA) (Ziegler & Rauk 1977) and natural orbital for chemical valence (NOCV). All complexes on the BP86/def2-SVP optimized structures were re-optimized by using the BP86/TZ2P+ of core functional/basis set combination as implemented in ADF 2013.01 (Velde *et al.* 2001). An auxiliary set of *s*, *p*, *d*, *f*, and *g* STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle (Krijn & Baerends 1984). Relativistic effects were taken by means of the zeroth-order regular approximation

(ZORA) Hamiltonian (Velde *et al.* 2001; Lenthe *et al.* 1993; Lenthe *et al.* 1996) with a small frozen core. The nature of the Au-E bonds in Au1-NHC–Au1-NHPb were investigated at BP86/TZ2P+ with the EDA-NOCV (Mitoraj & Michalak 2007a; Mitoraj & Michalak 2007b; Mitoraj *et al.* 2009) method which combines the EDA (Nemcsok *et al.* 2004) with the NOCV (Mitoraj & Michalak 2007b; Mitoraj *et al.* 2009) under C1 symmetric geometries (without symmetry).

Herein, we want to present a detailed theoretical aspect about the EDA-NOCV method. The EDA gave very well-defined energy terms for the chemical bonds in molecules. In the EDA developed independently by different groups (Morokuma 1971; Ziegler & Rauk 1979), and the recently introduced EDA-NOCV, the bond dissociation energy, D_e , of a molecule was divided into the instantaneous interaction energy ΔE_{int} and the preparation energy ΔE_{prep} :

$$\Delta E (= -D_e) = \Delta E_{int} + \Delta E_{prep} \quad (1)$$

The preparation energy ΔE_{prep} was the energy which was required to promote the fragments from their equilibrium geometries in the electronic ground state to the geometries and electronic reference state which they had in the molecule. The interaction energy ΔE_{int} could be further divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{pauli} + \Delta E_{orb} \quad (2)$$

where, ΔE_{elstat} is the quasiclassical electrostatic interaction energy between the fragments,

calculated by means of the frozen electron density distribution of the fragments in the geometry of the molecules. ΔE_{Pauli} was referred to the repulsive interactions between the fragments which were caused by the fact that two electrons with the same spin could not occupy the same region in space, and could be calculated by enforcing the Kohn–Sham determinant on the superimposed fragments to obey the Pauli principle by anti-symmetrisation and renormalisation. The stabilising orbital interaction term ΔE_{orb} was calculated in the final step of the energy partitioning analysis when the Kohn–Sham orbitals relaxed to their optimal form. The EDA-NOCV method

combined the charge (NOCV) and energy (EDA) partitioning schemes to decompose the deformation density which was associated with the bond formation, $\Delta\rho$, into different components of the chemical bond. Furthermore, the EDA-NOCV calculations also provided pair wise energy contributions for each pair or interacting orbitals to the total bond energy. NOCV is defined as the eigenvector of the valence operator, v , given by *Equation 4*:

$$v \psi_i = v \psi_i \quad (4)$$

In the EDA-NOCV scheme the orbital interaction term, ΔE_{orb} , is given by *Equation 5*:

$$\Delta E_{orb} = \sum_{k=1}^{N/2} \Delta E_k^{orb} = \sum_{k=1}^{N/2} v_k \left[-F_{-k,-k}^{TS} + F_{k,k}^{TS} \right] \quad (5)$$

in which $F_{-k,-k}^{TS}$ and $F_{k,k}^{TS}$ were diagonal transition-state Kohn–Sham matrix elements corresponding to NOCVs with the eigenvalues $-v_k$ and v_k , respectively. The ΔE_k^{orb} term of a particular type of bond was assigned by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV scheme thus provided information about the strength of orbital interactions in terms of both, charge ($\Delta\rho_{orb}$) and energy contributions (ΔE_{orb}) in chemical bonds.

RESULTS AND DISCUSSION

Structures and Energies

The theoretically predicted geometries of Au1-NHC–Au1-NHPb with bond length, bond angle, and bending angle are shown in *Figure 1* together with *Table 1*. Complexes Au1-NHC–Au1-NHPb clearly feature η^1 coordinated AuCl at the central E atom (E = C – Pb). To the best of our knowledge, there was no experimental geometries for gold(I) complex that carried NHE_{Me}. Note that the theoretical study with geometries and bond dissociation energies of less bulky N-heterocyclic carbene, silylene,

and germylene complexes of MCl (M = Cu, Ag, Au) have been investigated by Boehme and Frenking (1998) for the first time in the recent past. Moreover, we have found somewhere else that the theoretical as well as the experimental geometries of related carbene complexes where the substituents at nitrogen was R = hydrogen, benzyl, benzoyl, were in good agreement with our calculated values (Boehme & Frenking 1998; Bovio *et al.* 1993). The calculated Au–C bond length of Au1-NHC gives the shortest value (1.997 Å) and the theoretically predicted Au–E bond lengths of complexes Au1-NHC–Au1-NHPb in this study increased from 1.997 to 2.708 Å. This could be easily explained by the increasing radii of the group-14 atoms. The calculated equilibrium structures of complexes Au1-NHC–Au1-NHPb in *Table 1* show that lighter ligands NHE (E = C – Ge) were bonded in a head-on way to the metal fragment AuCl in which the bending angle was 180°. A comparison of the bending angle of the theoretical structures of Au1-NHC_H – Au1-NHGe_H indicates that our calculated values are quite similar (Boehme & Frenking 1998). In contrast to that the bending angle of Au1-NHE

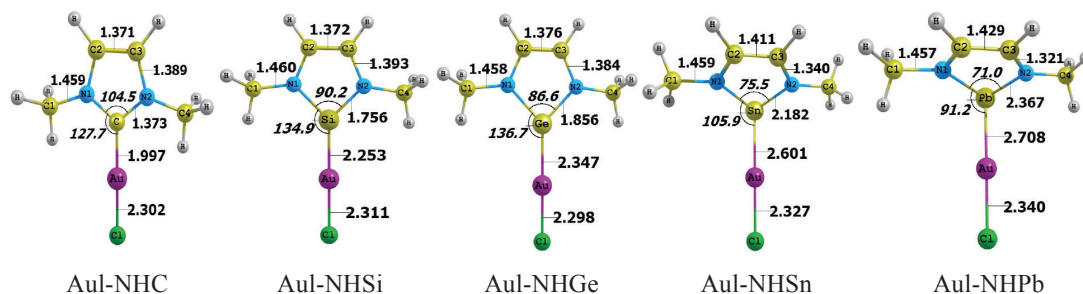
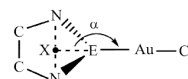


Figure 1. Optimized geometries of complexes AuI-NHC–AuI-NHPb at the BP86/def2-SVP level. Bond lengths are given in Å; angles in degrees. The bending angle, α , is the angle X-E-Au where X is the mid-point between the N-N distance:



became much more acute when E was heavier (bending angles α of AuI-NHSn = 110.3° and AuI-NHPb = 91.5°). We want to discuss the changes in the geometries of free ligands and AuCl in complexes. Table 1 shows that the bond lengths E-N in the complexes increased from C-N to Pb-N and those were shorter than in the free ligands in which the calculated values for the free ligands NHC_{Me} – NHPb_{Me} have recently been discussed by us (Nguyen *et al.* 2015). The increase of Au-Cl distances from the lighter to the heavier complexes exhibits the same trend compared with the values in the AuCl-NHE_H (E = C – Pb) complexes (Boehme & Frenking 1998).

Table 1 also shows the calculated BDEs for the Au-NHE_{Me} bonds. There was a significant decrease from the carbene complex AuI-NHC ($D_e = 79.2$ kcal/mol) to the silylene AuI-NHSi complex ($D_e = 67.0$ kcal/mol) and continuous decrease for the BDEs of the heavier group-14 ligands (51.9 – 42.7 kcal/mol). The calculations suggest that the NHC_{Me} ligand in AuI-NHC is the strongest bonded while the heavier homologues AuI-NHE where E = Si, Ge, Sn, Pb have weaker bonds which are not much different compared with the BDEs of the complexes in the previous studies (Boehme & Frenking 1998; Nguyen & Frenking 2012). The trend of the theoretically predicted AuCl-carbene and analogues bond

energy in this study was significantly higher than the calculated values for the borane-NHE_{Me} complexes ($D_e = 59.8 – 13.8$ kcal/mol) (Nguyen *et al.* 2015), the classical Fischer complex (CO)₅W-CH(OH) ($D_e = 75.0$ kcal/mol) (Vyboishchikov & Frenking 1998) as well as the (CO)₅W-carbene ($D_e = 54.4$ kcal/mol) and analogues ($D_e = 44.3 – 25.5$ kcal/mol) {(CO)₅W-NHE with E = C – Pb} (Nguyen & Frenking 2012). This was quite suitable because the metal-NHE_{Me} interactions of NHE_{Me}-AuCl had small NHE_{Me}←AuCl π -back-donation in complexes. From this, it follows that the monoaurated donor-acceptor complexes with carbene, silylene, and germylene ligands could have very strong bonds and the appearance of a small contribution in free ligands←AuCl π -back-donation in complexes would be further explained in bonding analysis.

Analysis of the Bonding Situation

The bonding situation in the complexes AuI-NHC–AuI-NHPb was analyzed using charge- and energy-decomposition methods. Table 2 shows the results of the NBO partitioning scheme and the Wiberg bond indices as well as the natural partial charges. The calculated partial charges showed that the metal fragment AuCl in the complexes carried always a negative charge which increases from AuI-NHC (−0.31 e) to AuI-NHPb (−0.53 e).

Table 1: Bond length (\AA), bond angle ($^\circ$), and bending angle (α°) for the optimized neutral molecules of Au1-NHC – Au1-NHPb calculated at the BP86/def2-SVP level, and calculated bond dissociation energy, D_e (kcal/mol) for the dissociation of one molecule of AuCl from Au1-NHC to Au1-NHPb at the BP86/def2-TZVPP//BP86/def2-SVP level of theory.

Molecule	Bonding (\AA)	Bonding angle ($^\circ$)	Bending angle (α°)	D_e (kcal/mol)
Au1-NHC	C-Au = 1.997	N1CN2 = 104.5	180.0	79.2
	C-N = 1.373	N1CAu = 127.7		
	Au-Cl = 2.302			
Au1-NHSi	Si-Au = 2.253	N1SiN2 = 90.2	180.0	67.0
	Si-N = 1.756	N1SiAu = 134.9		
	Au-Cl = 2.311			
Au1-NHGe	Ge-Au = 2.347	N1GeN2 = 86.6	180.0	51.9
	Ge-N = 1.856	N1GeAu = 136.7		
	Au-Cl = 2.298			
Au1-NHSn	Sn-Au = 2.601	N1SnN2 = 75.5	110.3	44.2
	Sn-N = 2.182	N1SnAu = 105.9		
	Au-Cl = 2.327			
Au1-NHPb	Pb-Au = 2.708	N1PbN2 = 71.0	91.5	42.7
	Pb-N = 2.367	N1PbAu = 91.2		
	Au-Cl = 2.340			

Table 2. NBO results with Wiberg bond indices (WBI) and natural population analysis (NPA) at the BP86/def2-TZVPP//BP86/def2-SVP level for complexes Au1-NHC – Au1-NHPb. The partial charges, q , are given in electrons [e].

Molecule	Bond	WBI	$q[\text{AuCl}]$	Atom	NPA (q)
Au1-NHC	Au-C	0.70	-0.31	Au	0.22
	C-N1	1.25		C	0.13
	C-N2	1.25		N	-0.31
Au1-NHSi	Au-Si	0.88	-0.43	Au	0.10
	Si-N1	0.82		Si	1.16
	Si-N2	0.82		N	-0.71
Au1-NHGe	Au-Ge	0.75	-0.37	Au	0.14
	Ge-N1	0.80		Ge	1.07
	Ge-N2	0.80		N	-0.68
Au1-NHSn	Au-Sn	0.62	-0.47	Au	0.04
	Sn -N1	0.61		Sn	0.86
	Sn -N2	0.61		N	-0.56
Au1-NHPb	Au-Pb	0.61	-0.53	Au	-0.01
	Pb-N1	0.49		Pb	0.74
	Pb-N2	0.49		N	-0.49

The amount of charge donation to the AuCl fragment is always smaller than the donation to other transition metal moieties such as $W(CO)_5$ and $Mo(CO)_4$ that carry the similar NHE_{Me} ligands in the complexes which have been calculated in the previous papers (Nguyen & Frenking 2012; Nguyen *et al.* 2014a; Nguyen *et al.* 2014b) in which the more negative charges in transition metal fragments $W(CO)_5$ and $Mo(CO)_4$ are between -0.47 and -0.77 e from the lighter to the heavier homologues.

The Wiberg bond orders for the Au-E bond in Au1-NHC was 0.70 and increased in the Au1-NHSi (0.88) and then decreased from Au1-NHGe to Au1-NHPb which were from 0.75 to 0.61. The bond order for the E-N bond became clearly larger in the complexes Au1-NHC–Au1-NHPb compared with the free ligands NHC_{Me} – $NHPb_{Me}$. This is in agreement with the change in the E-N bonds which become shorter in the complexes than in the free ligands (Nguyen 2015; Nguyen *et al.* 2014b). The natural population analysis carried out for complexes found that the electrostatic charges of carbon atom in the NHC_{Me} fragment of Au1-NHC complex was nearly neutral whereas Si and Ge carried large positive charges which were 1.16 and 1.07 e and then slightly decreased in the heavier homologues (Sn = 0.86 e and Pb = 0.74 e).

As mentioned in the computational methods, all complexes were considered under without any symmetry constraints meant the molecules had C1 symmetry. So there were no genuine σ and π orbitals because there was no mirror plane in the molecular structure. Although the lighter complexes Au1-NHE exhibited the end-on bonded in the NHE_{Me} ligands (E = C – Ge) whereas the heavier ligands $NHSn_{Me}$ and $NHPb_{Me}$ were bonded side-on to the metal fragment AuCl. In order to consider the strength of the π donation $NHE_{Me} \rightarrow AuCl$ which might be expected from the σ - and π lone-pair orbital of the ligand NHE_{Me} into the second

vacant coordination side of metal fragment AuCl, we had to visually keep the shapes of Au1-NHSn and Au1-NHPb in one plane to identify σ - and π -type molecular orbitals. *Figure 2* shows two occupied molecular orbitals and orbital energies of σ -type and π -type MOs from Au1-NHC–Au1-NHPb at the BP86/TZVPP level. The energy levels of the π -type donor orbitals of complexes were higher lying than the σ -type donor orbitals. The orbital energy values were particularly large in the Au1-NHC in both σ - and π -type MOs and decreased in the silylene and germylene as well as in the heavier analogues. Especially, the shape of the molecular orbitals which indicated that $NHE_{Me} \rightarrow AuCl$ not only had significant σ donation but also exhibited a bit π donation in complexes. We can explain that the π donation in complexes due to the strong $N \rightarrow E$ π donation at the ring of the NHE_{Me} ligands.

We showed the frontier orbitals with the plot of the energy levels of the energetically highest lying σ and π orbital of the isolated NHE ligands (*Figure 3*) in order to know whether the ligands had an occupied π -orbital in the E center atom. The HOMO of NHE ligand had π symmetry, except for NHC, in which the HOMO has σ symmetry whereas the HOMO-1 and HOMO-2 had π symmetry. The σ orbitals of NHE ligand were uniformly lone-pair molecular orbitals (MOs), but the π orbitals were delocalized over the NHE ring atoms. *Figure 3* also shows that the energy level of the π orbital increased, whereas that of the σ orbital decreased as atom E became heavier. The trend of the energy levels of the energetically highest-lying σ and π orbitals of NHE ligand rationalize the preference of the heavier ligands NHSn to NHPb for side-on co-ordination to the metal, in which the σ -donation takes place through the π orbital of the ligand (Nguyen & Frenking 2012). The end-on coordination of the lighter homologues NHC to NHGe could be explained by various factors that also influence the bending angle α of the ligands (*Table 1*).

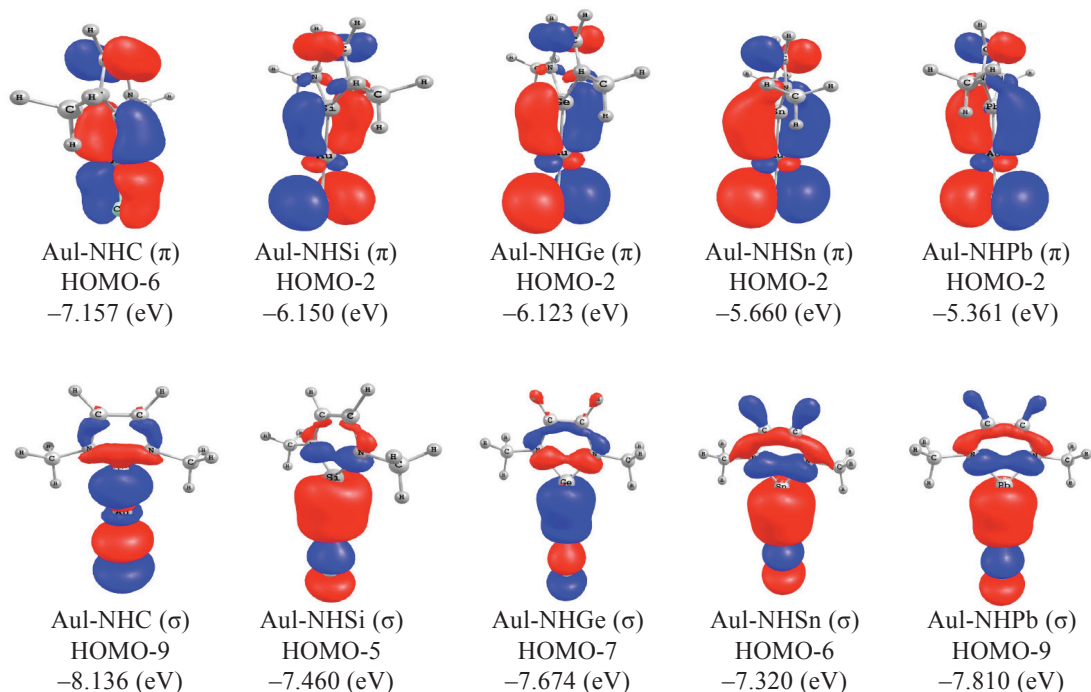


Figure 2. Molecular orbitals and orbital energies of σ -type and π -type MOs from AuI-NHC–AuI-NHPb at the BP86/TZVPP level. Orbital energies are given in eV.

We also want to point out the orbitals at the Au side carried a little $\text{NHE}_{\text{Me}} \leftarrow \text{AuCl}$ back-donation and mainly exhibited $\text{NHE}_{\text{Me}} \rightarrow \text{AuCl}$ σ -donation. We suggested the scheme illustration showing the mixing of the empty s and occupied d_z^2 orbitals of Au(I) which was graphically shown in *Figure 4a*. Note that the Au cation had an $s^0 d^{10}$ electron configuration but the s orbital was mostly filled in AuCl due to the ionic $\text{Au}^+ \text{Cl}^-$ bond and the lowest lying empty orbitals were at the Au might be p orbitals. Although in the gold(I) complex, the relativistic effects were responsible for the very small charge transfer from Au to Cl but when the AuCl-NHE_{Me} was formed, there was no further charge transfer from the Au atom to chlorine. From this it could be asserted that there was the mixing of the valence s orbital with occupied d_z^2 orbital of the Au. The competition for the empty Au s orbital between donation from chlorine and the carbene-analogues σ -lone pair might

lead to the longer Au-Cl bonds in the complexes (*Figure 1*).

Furthermore, the three filled orbitals arose from the E atom to Au and to Cl (E–Au–Cl) σ -interactions which were illustrated in *Figure 4b*. The highest energy had d_z^2 symmetry along the Au-Cl axis which could be considered as σ -antibonding character toward chlorine. The middle level of energy showed an anti-state combination of the Cl p_z and an sp_2 hybrid on the E atom and also revealed that there was no bonding toward Au. The lowest energy of E–Au–Cl σ -bonding orbitals exhibited a constructive overlap of the Au(I) $5d_z^2$ orbital that carried the σ -symmetry on Cl and E atoms. We could point out that the covalent part of the metal bonding in AuCl-NHE_{Me} had the patent of the familiar 6-electron-3 center interactions with the fully important d_z^2 orbital which significantly contributed to the Au-Cl

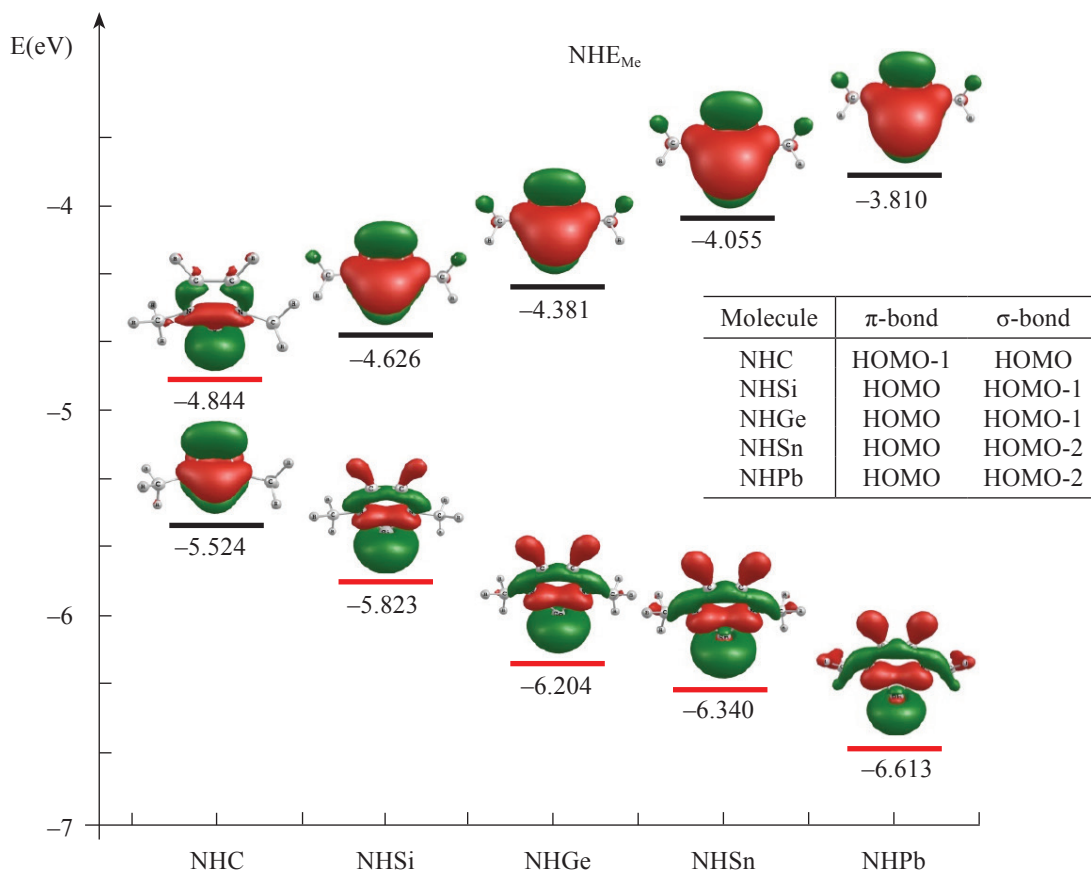


Figure 3. Plot of the energy levels of the energetically highest lying σ and π orbital of ligands NHE ($E = C - Pb$).

and AuCl-NHE_{Me} bonding (Figure 4b). Note that the transition metal complexes MCl with M = Au, Ag, Cu that carry the less bulky NHC ligand has been recently described by Nemcsok *et al.* (2004) using EDA method. In this study, we used the EDA-NOCV calculations in order to give a thorough insight into the nature of the metal-ligand bonding in Au1-NHE. This led to a donor-acceptor description of the Au-E bond in the system. Table 3 showed the results of EDA-NOCV when considering NHC_{Me} as the donor fragments and AuCl as the acceptor fragment. Table 3 shows that EDA-NOCV results at the BP86/TZ2P+ level for compound Au1-NHC–Au1-NHPb using the moieties [AuCl] and [NHE_{Me}] as interacting fragments.

The Au-E bond dissociation energies trend in Au1-NHE decreased from the lighter to the heavier homologues (Au1-NHC: $D_e = 78.1$ kcal/mol; Au1-NHPb: $D_e = 42.6$ kcal/mol).

The trend of the bond dissociations energies (BDEs) D_e for the Au-E bond in Au1-NHE system was Au1-NHC > Au1-NHSi > Au1-NHGe > Au1-NHSn > Au1-NHPb. The decrease of the BDEs from the lighter to heavier adduct was determined by the intrinsic strength of the Au-ligand bonds ΔE_{int} . The carbene adduct had a smaller preparation energy of the interacting fragments ($\Delta E_{prep} = 1.2$ kcal/mol) and stays nearly the same in the heavier homologues ($\Delta E_{prep} = 2.0 - 2.5$ kcal/mol) and the largest

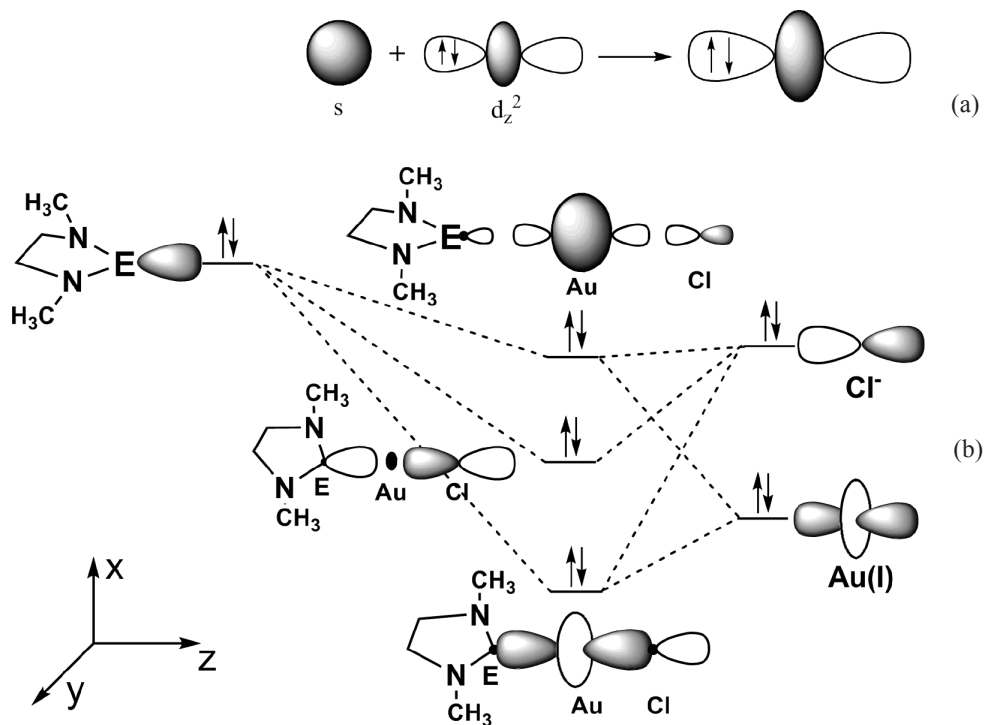


Figure 4. (a) Scheme illustration showing the mixing of the empty s and occupied d_z^2 orbitals of $Au(I)$; (b) Qualitative diagram of the interaction of the Au^+ d_z^2 orbital with Cl^- and σ -donor orbital of E atom with $E = C - Pb$.

Table 3. EDA-NOCV results at the BP86/TZ2P+ level for compound $AuI-NHC-AuI-NHPb$ using the moieties $[AuCl]$ and $[NHE_{Me}]$ as interacting fragments. The complexes are analyzed with C_1 symmetry. Energy values in kcal/mol.

Compound	$AuI-NHC$	$AuI-NHSi$	$AuI-NHGe$	$AuI-NHSn$	$AuI-NHPb$
Fragment	$[AuCl]$ $[NHC_{Me}]$	$[AuCl]$ $[NHSi_{Me}]$	$[AuCl]$ $[NHGe_{Me}]$	$[AuCl]$ $[NHSn_{Me}]$	$[AuCl]$ $[NHPb_{Me}]$
ΔE_{int}^*	-79.3	-68.5	-52.2	-47.2	-50.0
ΔE_{Pauli}	212.1	186.9	124.9	95.5	84.8
$\Delta E_{elstat}^{[a]}$	-219.3 (75.3 %)	-182.0 (71.3 %)	-118.5 (66.9%)	-87.2 (61.1 %)	-78.3 (58.1 %)
$\Delta E_{orb}^{[a]}$	-72.1 (24.7 %)	-73.3 (28.7 %)	-58.6 (33.1 %)	-55.5 (38.9 %)	-56.5 (41.9 %)
$\Delta E_{\sigma}^{[b]}$	-51.3 (71.2 %)	-50.0 (68.2 %)	-42.6 (72.8 %)	-45.4 (81.7 %)	-49.0 (86.7 %)
$\Delta E_{\pi}^{[b]}$	-17.0 (23.5 %)	-20.8 (28.4 %)	-13.7 (23.4 %)	-7.9 (14.3 %)	-4.9 (8.7 %)
$\Delta E_{rest}^{[b]}$	-3.8 (5.3 %)	-2.5 (3.4 %)	-2.3 (3.8 %)	-2.2 (4.0 %)	-2.6 (4.6 %)
ΔE_{prep}	1.2	2.4	2.0	2.5	7.4
$\Delta E (= -D_e)$	-78.1 (79.2) ^[c]	-66.0 (67.0) ^[c]	-50.2 (51.9) ^[c]	-44.7 (44.2) ^[c]	-42.6 (42.7) ^[c]

[a] The values in parentheses are the percentage contributions to the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb}$.

[b] The values in parentheses are the percentage contributions to the total orbital interaction ΔE_{orb} .

[c] The values in parentheses give the dissociation energy at the BP86/def2-TZVPP//BP86/def-SVP level.

value preparation energy was 7.4 kcal/mol which gave the smallest BDE for AuI-NHPb. Inspection of the three main terms which contributed to the interaction energy ΔE_{int} indicated that the Pauli repulsion ΔE_{Pauli} and the electrostatic attraction ΔE_{elstat} were smaller for the heavier group-14 atoms AuI-NHSi–AuI-NHPb than for AuI-NHC. The largest contributions to the ΔE_{int} values of the system always came from the electrostatic interaction term ΔE_{elstat} which contributed more than 60% in complexes except for the less than that in AuI-NHPb (58.1%). In contrast to this, the orbital term contributed < 30% in the lighter complexes which were 24.7% and 28.7% for AuI-NHC and AuI-NHSi. The strength of the total orbital interactions ΔE_{orb} decreased from the lighter to the heavier homologues. Note that the most important information which was provided by the EDA-NOCV calculations concerned the strength of the σ and π bonding. *Table 3* also shows that the contribution of ΔE_{σ} to ΔE_{orb} was rather large for all complexes where the values were between 68.2% – 86.7%. For all complexes holds that the contribution of ΔE_{π} to ΔE_{orb} is significantly smaller than in other transition metal complexes of tungsten pentacarbonyl and tetracarbonyl complexes [W(CO)₅-NHE] (with E = C – Pb) (Nguyen & Frenking 2012). Thus, the EDA-NOCV calculations showed that the Au-E bonding in the complexes AuI-NHC–AuI-NHPb had a small contribution which might come from $NHE_{Me} \rightarrow AuCl$ π -donation and $NHE_{Me} \rightarrow AuCl$ π -back-donation. We continue determining the charge transfer between the donor and acceptor fragments by plotting of the pairs of orbitals, the associated deformation densities, and stabilization energies. The fact was that, the plots of the pairs of orbitals ψ_k/ψ_{-k} that yield the NOCVs provided the largest contributions to the σ - and π -orbital terms ΔE_{σ} and ΔE_{π} in AuI-NHE (E = C, Si) and the associated deformation densities $\Delta\rho$ and stabilization energies were shown in *Figure 5*. The shape of pairs for AuI-NHSi and AuI-NHGe were quite similar with the carbene complex, while the shape of pairs

for the heavier specie shape of pairs for AuI-NHSn possessed the same shapes compared with the shape of pairs for AuI-NHPb, and there for were not shown in *Figure 5*.

Note that the white/blue colours in the small figures for ψ_k/ψ_{-k} indicated the sign of the orbitals, and the black/yellow colours in the deformation density $\Delta\rho$ designate charge depletion, and the yellow areas point to charge accumulation. The charge flow $\Delta\rho$ occurred in the direction from black to yellow. *Figure 5(a)* shows that the σ -type interaction was clearly from the donating NHC_{Me} fragment to the accepting AuCl fragment which was the deformation density $\Delta\rho_1$ which showed that stabilization of energy was –42.0 kcal/mol. The shapes of the NOCV pairs ψ_2/ψ_{-2} and the deformation density $\Delta\rho_2$ showed that stabilization of –11.1 kcal/mol could be assigned to $ClAu \leftarrow NHC_{Me}$ π -donation while the stabilization of also came from relaxation of the acceptor fragment AuCl in AuI-NHC. *Figure 5(c,d)* shows significantly different EDA-NOCV results for AuI-NHPb because of the surprising structure of the plumbylene ligand which was bonded through its π -electron density. Note that the structures and orbitals pairs of the lighter homologues AuI-NHE with E = C, Si, Ge had head-on modes between the ligands and metal fragment, whereas the heavier species AuI-NHE with E = Sn, Pb exhibited a side-on bonded ligands to the AuCl fragment. *Figure 5(c)* clearly shows that the σ -type interaction had the direction of the charge flow of $ClAu \leftarrow NHPb_{Me}$. The deformation density ψ_1 exhibited an area of charge donation (black area) at the $NHPb_{Me}$ moiety associated with the deformation density $\Delta\rho_1$ and stabilization energy was –46.1 kcal/mol. *Figures 5(d)* show that the very weak π -type orbital interactions in AuI-NHPb came from typical π -back-donation $ClAu \rightarrow NHPb_{Me}$ with the charge flow ψ_2/ψ_{-2} which indicated stabilization at –2.9 kcal/mol. Thus, the bonding in AuI-NHE complexes exhibited the typical feature in terms of strong σ -donation and weak π -back-donation. From

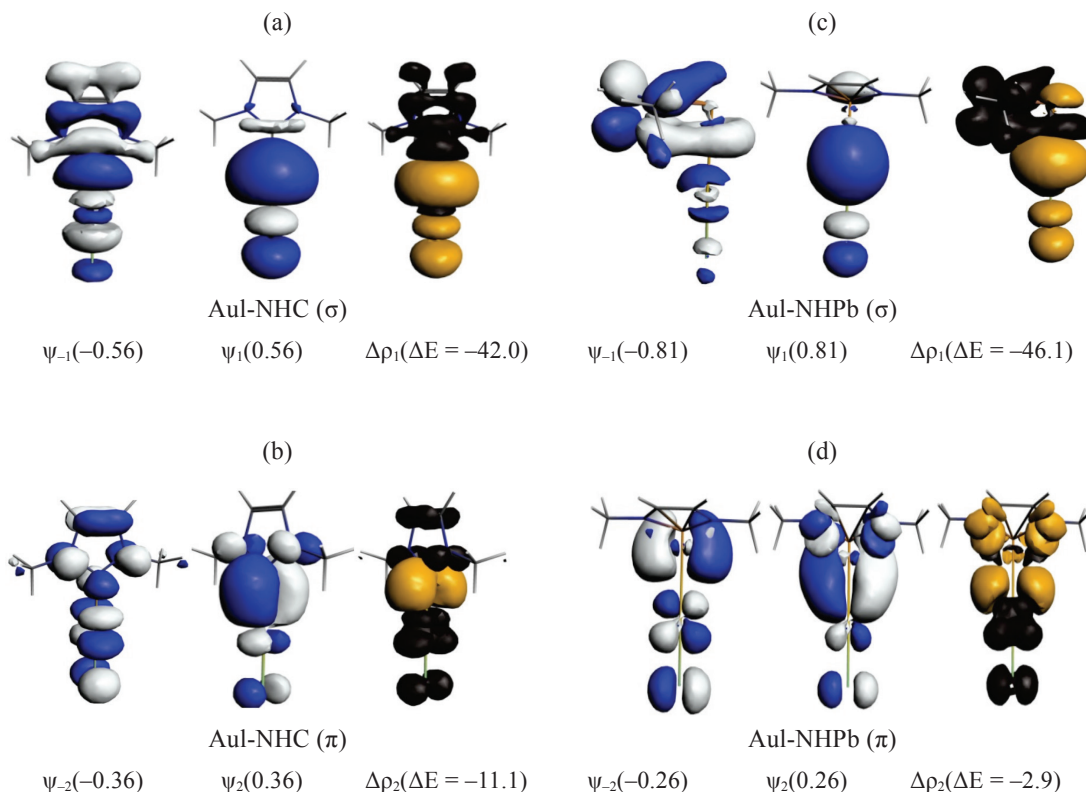


Figure 5. Most important NOCV pairs of orbitals Ψ_{-k} , Ψ_k with their eigenvalues $-v_k$, v_k given in parentheses, and the associated deformation densities $\Delta\rho_k$ and orbital stabilization energies ΔE for the complexes AuI-NHC and AuI-NHPb. The charge flow in the deformation densities is from the black \rightarrow yellow region. (a) σ -NOCV of AuI-NHC; (b) π -NOCV of AuI-NHC; (c) σ -NOCV AuI-NHPb; (d) π -NOCV of AuI-NHPb. Energy values in kcal/mol.

the above results, it could be asserted that the decrease in the donation $\text{ClAu} \leftarrow \text{NHE}_{\text{Me}}$ which was manifested in the calculated values for ΔE_σ and in the electrostatic attraction, ΔE_{elstat} , provided a rationale for the weaker bonding of the heavier atoms E. The π -interactions in $[\text{ClAu-NHE}_{\text{Me}}]$ were due to very weak π -back-donation and were also irrelevant for the bond strength. The ligand \leftarrow Au π -back-donation in the complexes was very small and the Au-ligand bonds had strong ionic character which came from the electrostatic attraction between the positively charged Au atom and the σ -electron pair of the E donor atom.

CONCLUSIONS

In summary, the full isolable carbene analogues-stabilized gold(I) chloride was structurally characterized in this work. DFT calculations found that the equilibrium structures of the AuI-NHE system showed major differences in the bonded orientation from the ligands NHC to NHPb of gold(I) complex between the lighter and the heavier homologues. The calculated structures of carbene-analogues complexes AuI-NHE of the lighter complexes AuI-NHE possessed end-on-bonded NHE_{Me} ligands (E = C-Ge) with the bending angles, α , were 180° . In contrast, the heavier species

AuI-NHSn and AuI-NHPb exhibit side-on-bonded ligands which the bending angle, α , became more acute (110.3° for AuI-NHSn and 91.5° for AuI-NHPb). The trend of the bond dissociation energy of Au-ligands in AuI-NHE show for the ligands NHE order is: AuI-NHC > AuI-NHSi > AuI-NHGe > AuI-NHSn > AuI-NHPb. Bonding analysis of AuI-NHE showed that NHE ligands exhibited donor- acceptor bonds with the σ lone pair electrons of NHE donated into the vacant orbital of the acceptor fragment (AuCl). The EDA-NOCV results indicated that the ligand NHE in AuI-NHE complexes were strong σ -donors and very weak π donors. The Au-NHE bonds were mainly held together by electrostatic energy, which contributed >60% of the binding interactions for the lighter homologues (AuI-NHC – AuI-NHGe). The NOCV pairs of the bonding showed small π -back donation from the Au to the NHE ligands.

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