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Structural variations and chemical bonding in platinum complexes of Group 14 heavier tetrylene homologues (germylene to plumbylene)

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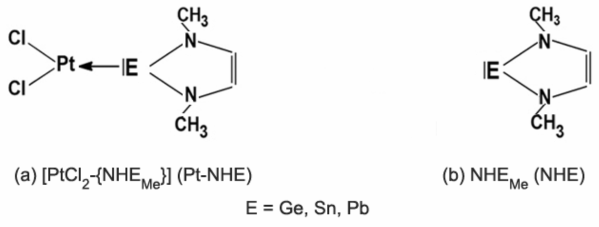
The structures of Pt(II) complexes containing the heavier homologues of germylene, stannylene, and plumbylene [$PtCl_2$-{NHE_{Me}}] (Pt-NHE) with E = Ge to Pb, in which the ligand {NHE_{Me}} retains one lone pair at the E central atom, have been computed using density functional theory calculations at the BP86 level with def2-SVP, def2-TZVPP, and TZ2P+ basis sets. The bonding of the complexes has been analyzed by charge and energy decomposition analysis methods. The results of bonding analysis show that NHE_{Me} ligands exhibit donor-acceptor bonds with the σ lone pair electrons of heavier NHE_{Me} donated into the vacant orbital of the metal fragment, and the Pt-E bonds having $PtCl_2 \leftarrow NHE_{Me}$ strong σ-donation. The divalent heavier tetrylenes(II) have the same role as the divalent heavier tetrylones(0) character since the ligand can retain the two lone pairs at E atom. Currently experimental efforts are directed towards the synthesis of tetrylenes Pt(II) complexes from natural products. Hence, the results in this study will provide an insight into the properties and chemical bonding of complexes being synthesised.

Keywords: Theoretical chemistry, Density functional calculations, Bonding analysis, Carbenes, Germylenes, Stannylenes, Plumbylenes, Platinum.

The coordination chemistry of the heavier analogues of carbene-NHCs (silylenes, germylenes, and stannylenes) has attracted considerable attention during the last 20 years[1-3], although less developed than that of carbenes which was facilitated by the increasing propensity towards adopting divalent states as the group was descended[4]. A large variety of N-heterocyclic silylenes (NHSi)[5], germylenes (NHGe)[6], and stannylenes (NHSn) derived from different heterocycles which are stable at ambient temperature has been prepared[7]. NHC complexes including those of platinum, gold, silver, ruthenium, nickel and copper have been used in catalytic reaction[8-11], including C-C-coupling reactions[12], olefin metathesis[13], hydroformylation[14], polymerization reactions[15] and CH activation[16]. Many NHCs derived from heterocycles are moisture stable[17], generally less toxic than those with similar donor characteristics (phosphines and carbonyls) and less susceptible to dissociation[8]. Electronically, the NHC ligand is considered to be a better σ donor, and a weaker π acceptor, than the phosphine ligand[18]. A similar bonding situation has been suggested for the heavier analogues, germylene, stannylene, plumbylene[19-21]. However, divalent plumbylene (NHPb) is more stable than divalent carbon and has been considered as complexes featuring terminal ligands as reported recently by Heitmann *et al.*[22], and Arp *et al.*[23] From the lighter to the heavier elements of Group 14, both the nucleophilicity and directionality of the lone pair on the divalent atom decrease as there is increase in the s character and become more spherical[24]. Platinum complexes that carry NHCs ligands have been used for the reductive cyclization of diynes and enynes[25], the catalytic diboration of unsaturated molecules[26] and the tandem hydroboration–cross coupling reaction[27]. In addition, platinum complexes having antimicrobial activity have also been reported recently[28-30]. The complexes of heavier analogues of carbene, i.e., germylene, stannylene, and plumbylene, with platinum complexes have also been reported in the recent past[4,19,23,24,31]. In view of the above, we have studied the [($PtCl_2$-{NHE_{Me}}] (Pt-NHE) complexes with E = Ge to Pb, for an insight into the nature of the unusual bonding between $PtCl_2$ and heavier tetrylenes. We have investigated the donor-acceptor complexes shown in Scheme 1. To the best of our knowledge, the present work is the first detailed study of the structures and bonding of the complexes [$PtCl_2$-{NHE_{Me}}]. The electronic structure of the molecules has also been analyzed by the charge and energy decomposition methods.

Computational Methods

The geometries of the molecules were calculated without symmetry constraints using the Gaussian 09[32] optimizer together with Turbomole 7.0[33] energies and gradients at the BP86[34]/def2-SVP[35] level of theory. For the heavier Group 14 atoms, Sn and Pb, and the Pt element of $PtCl_2$ fragment, small-core quasi-relativistic effective core potentials (ECPs) were used[36]. The RI approximation was used for all structure optimizations by using the appropriate auxiliary basis sets. All structures presented in this study were optimized to the minima on the potential energy surface (PES). The nature of the stationary points on the PES was also confirmed as energy minima by frequency calculations. The bond dissociation energy (BDE), D_e (kcal/mol), was calculated at BP86/def2-TZVPP[37]//BP86/def2-SVP level using the NBO 3.1 program[38]. The Wiberg bond orders, natural partial charges, and molecular orbitals with orbital energies were analysed at the BP86/def2-TZVPP//BP86/def2-SVP level using the natural bond orbital (NBO 3.1 program) method available in Gaussian 09. The parent compounds and free ligands were re-optimized for the energy decomposition analysis with the program package ADF 2013.01[39] with BP86 in conjunction with a triple-zeta-quality basis set using un-contracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons[40]. 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[41]. Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA)[42]. A thorough insight into the nature of chemical bonding and properties of complexes was obtained using the EDA-NOCV method[43] under the C1 symmetric geometries (without symmetry) at the BP86/TZ2P+ level of theory.


(a) [$PtCl_2$-{NHE_{Me}}] (Pt-NHE) (b) NHE_{Me} (NHE)

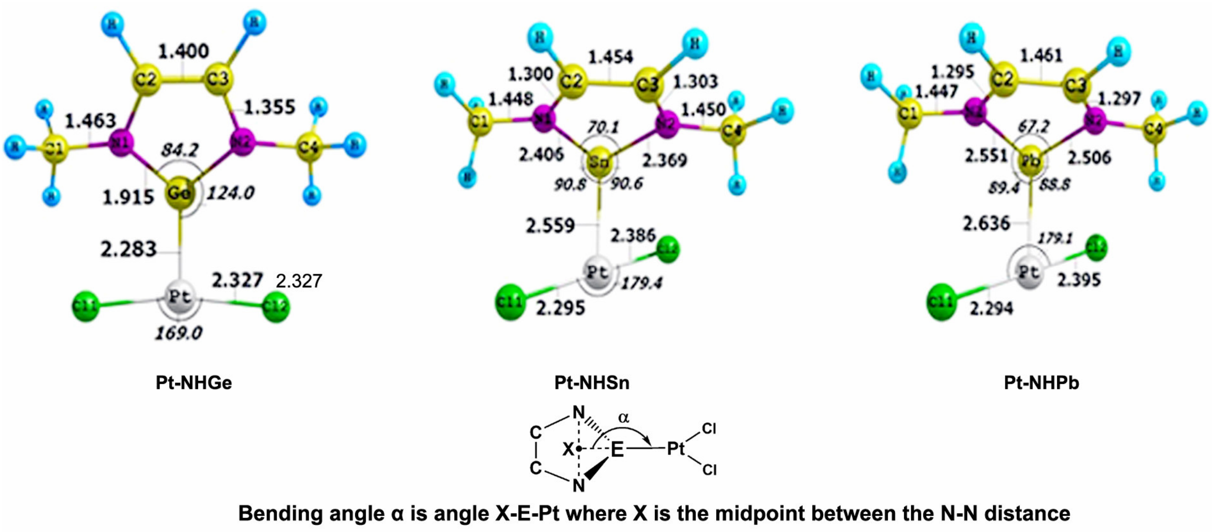
E = Ge, Sn, Pb

Scheme 1

Results and Discussion

Structures and energies

The optimized structures of complexes Pt-NHGe to Pt-NHPb are illustrated in Fig. 1 and the calculated geometry parameters of molecules are presented in Table 1. There are no experimental values available for these complexes. The theoretically predicted Pt-E bond lengths show the shortest value for Pt-NHGe (2.283 Å) which increases from 2.283 to 2.559 Å for



Bending angle α is angle X-E-Pt where X is the midpoint between the N-N distance

Fig. 1 – Optimized geometries of Pt-NHGe to Pt-NHPb complexes at the BP86/def2-SVP level. [Bond lengths are given in Å; angles in degrees].

Pt-NHSn (2.559 Å), while the longest value is 2.636 Å for Pt-NHPb. The germylene complex [$(Cy_3P)_2$Pt-$GeCl_2$][44] has an experimental Pt-Ge bond length of 2.397 Å. Note that the experimental results obtained by X-ray structural analysis of [$(PPh_3)_2$Pt (bisstannylene)][45] give Pt-Sn bond lengths in the range of 2.5735 to 2.5868 Å which are quite similar to that in the stannylene complex studied herein. However, the experimental Pt-Pb bond length (2.8558 Å) in complex [Pt(NHPb)-$(PPh_3)_3$][46] is much longer than the $PtCl_2$-NHPb distance in the plumbylene complex Pt-NHPb.

DFT calculations show that in the equilibrium structures of complexes all the heavier ligands NHE_{Me} are bonded in a tilted orientation relative to the metal fragment $PtCl_2$ in Pt-NHE (Table 1) wherein the bending angle, α, is 138.9° for Pt-NHGe. Note that the Pt-NHSn and Pt-NHPb complexes exhibit a significantly different bonding mode of the ligand as compared with the germylene complex, and have α = 90.9° and 88.9°, respectively. Regarding the tilted orientation between the ligands NHE_{Me} and the metal fragment $PtCl_2$, the bending angle of the heavier tetrylene adducts (Pt-NHGe to Pt-NHPb) in this study shows the same trend as the bending angle values of the heavier tetrylene species, ($W(CO)_5$-NHGe to $W(CO)_5$-NHPb), and particularly the heavier tetrylone complexes, ($W(CO)_5$-{$Ge(PPh_3)_2$} to $W(CO)_5$-{$Pb(PPh_3)_2$}), reported in a previous paper[48]. Table 1 shows that the bond lengths E-N in the complexes increase from Ge-N to Pb-N and are shorter than the bond lengths in the free ligands ($NHGe_{Me}$ to $NHPb_{Me}$)[47]. Table 1 also gives the increase in the theoretically predicted bond dissociation energies (BDEs) for the Pt-E bonds of complexes from 60.0 kcal/mol (Pt-NHGe) to 64.8 kcal/mol (Pt-NHSn) and 69.6 kcal/mol (Pt-NHPb). The data thus suggest that the heavier complexes have stronger bonds than the lighter homologues[48]. As mentioned above, of the theoretically predicted Pt-Ge bond lengths, the shortest value is 2.283 Å for Pt-NHGe and the longest value is 2.636 Å for Pt-NHPb. It may be noted that stronger bonds for heavier complexes do not correlate with the bond dissociation energy and longer Pt-E bonds do not mean that the bonds become weaker[48]. Note that the trend of the theoretically predicted $PtCl_2$-heavier tetrylenes BDEs in this study is opposite to that reported for the complexes of tetrylenes recently[47-50]. The BDEs of complexes Pt-NHE (E = Ge to Pb) in this study follow the same trend as the tetrylones E(0) investigated in an earlier study; [$W(CO)_5$-{$Ge(PPh_3)_2$}] to [$W(CO)_5$-{$Pb(PPh_3)_2$}] (39.7 to 44.6 kcal/mol)[48], [$W(CO)_4$-{$Ge(PPh_3)_2$}] to [$W(CO)_4$-{$Pb(PPh_3)_2$}] (48.3 to 50.0 kcal/mol)[50], wherein the ligand {$E(PPh_3)_2$} retains the two lone pairs at the E central atom i.e., tetrylones E(0). From this, it may be noted that the platinum complexes with divalent heavier tetrylenes E(II) in this study have the same features as the divalent heavier tetrylones E(0) in which the ligands may retain the two lone pairs at the E atom of NHE_{Me}.

Bonding analysis

Table 2 gives the results of the NBO analysis with the Wiberg bond orders (WBI) and the partial charges (NPA) of Pt-NHGe to Pt-NHPb at the BP86/def2-TZVPP//BP86/def2-SVP level. The partial charge of the $PtCl_2$ fragment is always negative showing an increase from Pt-NHGe (-0.83 e) to Pt-NHSn (-1.03 e) and remains at -1.08 e for Pt-NHPb. The partial atomic charges of the acceptor platinum atom are negative between -0.03 e (E = Ge) and -0.19 e (E = Pb). The germanium donor atom in Pt-NHGe has a positive charge of 1.24 e and decreases from the germylenes complex to the stannylene adduct (0.98 e) and plumbylene complex (1.00 e). The Wiberg bond order for the Pt-E bond in Pt-NHGe is larger (0.94)

Table 1 – Bond length, bond angle, and bending angle for the optimized neutral molecules of Pt-NHGe to Pt-NHPb calculated at the BP86/def2-SVP level, and calculated bond dissociation energy, for the dissociation of one molecule of $PtCl_2$ from Pt-NHGe to Pt-NHPb at the BP86/def2-TZVPP//BP86/def2-SVP level

Molecule	Bond (Å)	Bond angle (°)	D_e (kcal/mol)	Bending angle α (°)
Pt-NHGe	Ge-Pt = 2.283 Ge-N = 1.915 Pt-Cl = 2.327	N1-Ge-N2 = 84.2 Pt-Ge-N1 = 124.0 Pt-Ge-N2 = 124.0	60.0	138.9
Pt-NHSn	Sn-Pt = 2.559 Sn-N1/N2 = 2.406/2.369 Pt-Cl1/Cl2 = 2.295/2.386	N1-Sn-N2 = 70.1 Pt-Sn-N1 = 90.8 Pt-Sn-N2 = 90.6	64.8	90.9
Pt-NHPb	Pb-Pt = 2.636 Pb-N1/N2 = 2.551/2.506 Pt-Cl1/Cl2 = 2.294/2.395	N1-Pb-N2 = 67.2 Pt-Pb-N1 = 89.4 Pt-Pb-N2 = 88.8	69.6	88.9

than in Pt-NHSn (0.80) and then is 0.82 in Pt-NHPb. The NBO results, suggest that the NHE_{Me} ligands are strong σ-donors and weak π-acceptors. This is possible because the ligands NHE_{Me} have only one lone-pair orbital available for donation[18, 48]. This indicates that the bonding of the Pt-NHE compounds is associated with the strength of the π donation $PtCl_2 \leftarrow NHE_{Me}$ which may be expected from the π lone-pair orbital of the ligands NHE_{Me} into the metal fragment $PtCl_2$. As pointed out in the computational details, the molecules have C1 symmetry with no genuine σ and π orbitals since there is no mirror plane in the molecular structure[50]. Therefore, the structures had to be re-calculated with the donor, and acceptor fragments in one plane in which the NHE_{Me} ligands in the complexes are bonded end-on to the $PtCl_2$ fragment with the bending angle for all adducts as 180.0°. Then the visual inspection of the shape of the orbitals could easily identify the σ-type and π-type molecular orbitals in the complexes. The occupied orbitals of the complexes associated with $PtCl_2 \leftarrow NHE_{Me}$ σ donation and π donation, and also showing occupied molecular orbitals π of ligand NHE_{Me} are clearly given in Fig. 2. The energy levels of the π-type donor orbitals of ligands and complexes Pt-NHGe to Pt-NHPb are higher than the σ-type donor orbitals, while as mentioned ealier also NHC is usually considered to be a strong σ donor and a weak π acceptor. However, in the Pt-NHE complexes, the shape of the MOs indicates that not only σ donation but also $PtCl_2 \leftarrow NHE_{Me}$ π donation is important. From the frontier orbital plot of the energy levels of the σ and π orbitals (Fig. 2), it can be affirmed that the Pt-E bond has a significant contribution from the strong σ-donation and π-donation of $PtCl_2 \leftarrow NHE_{Me}$. This is contrary to the above statement that the NHE_{Me} ligands are strong σ-donors and weak π-acceptors and will be further explained and clarified in the following parts.

Table 2 – NBO results with Wiberg bond indices and natural population analysis at the BP86/def2-TZVPP//BP86/def2-SVP level for complexes, Pt-NHGe to Pt-NHPb

Molecule	Bond	WBI	$q[PtCl_2]$ (e)	Atom	NPA
Pt-NHGe	Pt-Ge	0.94	-0.83	Pt	-0.03
	Ge-N1	0.69		Ge	1.24
	Ge-N2	0.69		N	-0.60
	Pt-Cl	0.69		Cl	-0.40
Pt-NHSn	Pt-Sn	0.80	-1.03	Pt	-0.17
	Sn –N1	0.30		Sn	0.98
	Sn –N2	0.33		N	-0.42
	Pt-Cl1/Cl2	0.71/0.54		Cl	-0.43
Pt-NHPb	Pt-Pb	0.82	-1.08	Pt	-0.19
	Pb-N1	0.24		Pb	1.00
	Pb-N2	0.27		N	-0.40
	Pt-Cl1/Cl2	0.53/0.71		Cl1/ Cl2	-0.45/ -0.44

To investigate whether or not the complexes of platinum with divalent tetrylenes E(II) in this study have the same features as the divalent heavier

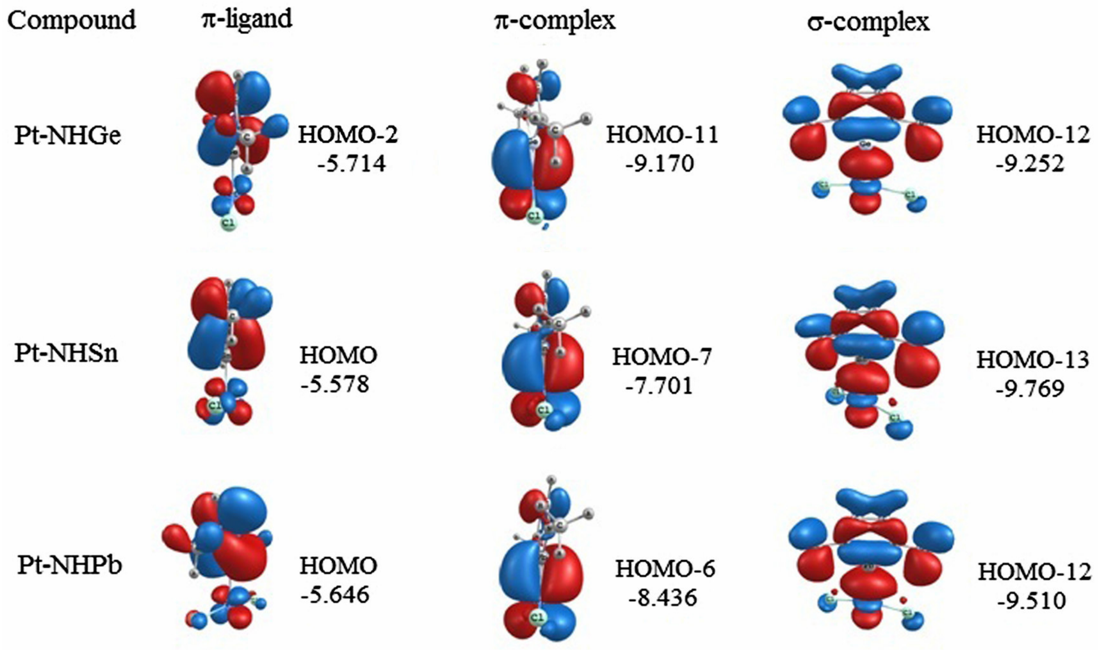


Fig. 2 – Molecular orbitals and orbital energies of σ-type and π-type MOs from Pt-NHGe to Pt-NHPb. [Orbital energies are given in eV].

tetrylones(0) character, we first considered that the $PtCl_2$ fragment is highly symmetrical, and optimized the complexes using Gaussian 09 optimizer with Turbomole 7.0. Herein, the problem was that we were unable to distinguish which of the two bonds, Pt-Cl1 or Pt-Cl2, allows the system to rotate freely. We checked again by re-optimizing the molecules for the energy decomposition analysis with the ADF 2013.01 program package with the energy decomposition analysis for optimization. Interestingly, we found that the spacing effect between heavier tetrylene ligands (Pt-NHGe to Pt-NHPb) and fragment $PtCl_2$ may lead to significant difference between the Pt-Cl1 and Pt-Cl2 bond lengths in the parent compounds since Pt-Cl1 and Pt-Cl2 bonds in the heavier complexes Pt-NHE (E = Sn, Pb) may not be totally identical. We analyzed the nature of the donor-acceptor bonds of the equilibrium structures of Pt-NHGe to Pt-NHPb with the EDA-NOCV method also. Table 3 shows that the Pt-NHE (E = Ge to Pb) molecules are divided into the two fragments, NHE_{Me} and $PtCl_2$, and both are in the singlet state. The EDA-NOCV results demonstrate that the bond dissociation energies (ΔE (= $-D_e$)) increases from E = Ge (-58.9 kcal/mol) to E = Pb (-70.1 kcal/mol). The increase in the metal-ligand bonding is due to the interaction energy ΔE_{int}, which increases from Pt-NHGe (-77.0 kcal/mol) to Pt-NHPb (-98.9 kcal/mol) and is as steep as the BDEs. This is because $\Delta E_{prep,}$ the main component increases from Pt-NHGe (ΔE_{prep} = 18.1 kcal/mol) to Pt-NHPb (ΔE_{prep} = 28.8 kcal/mol).

Table 3 – EDA-NOCV results at the BP86/TZ2P + level for Pt-NHGe to Pt-NHPb using the moieties [$PtCl_2$] and [NHE_{Me}] as interacting fragments. [The complexes are analyzed with C1 symmetry]

Energy (kcal/mol)	Pt-NHGe	Pt-NHSn	Pt-NHPb
ΔE_{int}	-77.0	-91.3	-98.9
ΔE_{Pauli}	281.9	249.8	248.3
$\Delta E_{elstat}{}^{a}$	-206.5 (57.5 %)	-187.3 (54.9 %)	-184.5 (53.1 %)
$\Delta E_{orb}{}^{a}$	-152.5 (42.5 %)	-153.8 (45.1 %)	-162.7 (46.9 %)
$\Delta E_{\sigma}{}^{b}$	-110.2 (72.3 %)	-137.6 (89.5 %)	-146.6 (90.1 %)
$\Delta E_{\pi}{}^{b}$	-41.8 (27.4 %)	-14.6 (9.5 %)	-15.1 (9.3 %)
$\Delta E_{rest}{}^{b}$	-0.5 (0.3 %)	-1.6 (1.0 %)	-1.0 (0.6 %)
ΔE_{prep}	18.1	26.4	28.8
ΔE (= $-D_e$)	-58.9 (-60.0)^{c}	-64.9 (-64.8)^{c}	-70.1 (-69.6)^{c}

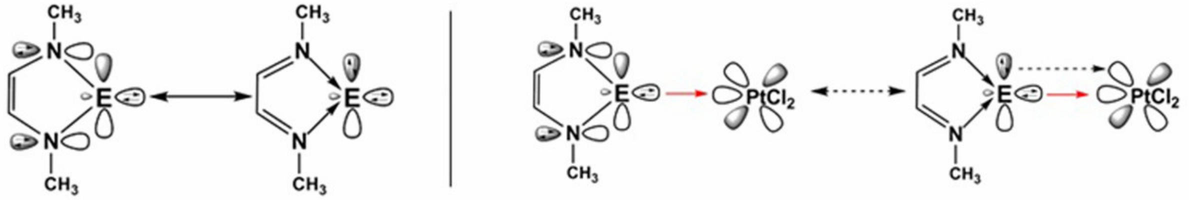
[a] The values in parentheses are the percentage contributions to the total attractive interaction ΔE_{elstat}+ ΔE_{orb}.

[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/def2-SVP level.

The three main terms, ΔE_{Pauli}, ΔE_{elstat}, and ΔE_{orb}, are considered to contribute to the interaction energy (ΔE_{int}) of the molecules. The Pauli repulsion, ΔE_{Pauli}, has the largest value for Pt-NHGe (281.9 kcal/mol) and becomes smaller for the heavier homologues. The same trend is observed for the electrostatic term, ΔE_{elstat}, which continuously decreases from Pt-NHGe (-206.5 kcal/mol) to Pt-NHPb (-184.5 kcal/mol). In contract, a different trend is seen for the orbital interactions, which show an increase from Pt-NHGe (-152.5 kcal/mol) to Pt-NHPb (-162.7 kcal/mol) with the percentage contribution of the orbital interactions as 42.5% in Pt-NHGe and stays nearly the same from Pt-NHSn (45.1%) to Pt-NHPb (46.9%). The increase in the attractive interaction, ΔE_{orb}, of the heavier tetrylene ligands can be traced back to the σ lone-pair orbital[48]. The σ-orbital contribution ΔE_{orb} is much stronger for the heavier complexes (-110.2 kcal/mol for Pt-NHGe) with the largest value for Pt-NHPb (-146.6 kcal/mol), whereas the π-orbital contribution ΔE_{π} is much weaker than that of ΔE_{σ} in heavier tetrylene complexes. The NBO and EDA-NOCV results not only offer an insight into the optimized structures and energies as well as the chemical bonding investigated complexes, but also explain the interesting trend of the bond strength in [$PtCl_2$-{NHE_{Me}}] where the BDEs of complexes exhibit the same trend as the BDEs of tetrylone complexes [$W(CO)_5$-{$E(PPh_3)_2$}][48] and [$W(CO)_4$-{$E(PPh_3)_2$}][50]. Thus, we have proposed the structures of [$PtCl_2$-{NHE_{Me}}] complexes to understand more clearly bond formation in these complexes. We propose the existence of extreme resonance complexes to clarify further the unusual bonding of the Pt-NHE complexes (Schemes 2–4).

The possible resonance forms of NHE_{Me} showing the divalent element E(II) character and the divalent element E(0) character (E = Ge, Sn, Pb), as well as the donor-acceptor interactions of NHE_{Me} with the metal fragment $PtCl_2$[47] are shown in Scheme 2. Furthermore, Scheme 3 shows that classical heavier tetrylenes NHE_{Me} can be considered to have a resonance form in which the central E atom has two lone pairs; the resonance form may be ignored due to delocalization of the π-type lone pair. This leads to the loss of aromaticity in the NHE ring and may show the characteristics of E(0) compounds in Pt-NHE complexes with E = Ge to Pb. In this case, we have suggested a schematic representation of NHE_{Me} showing the corresponding probable resonance forms

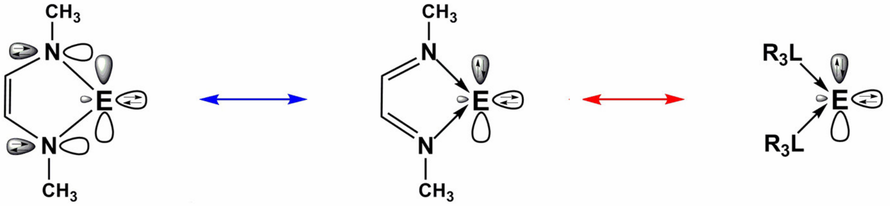


(a) Probable resonance forms of NHE$_{Me}$ showing divalent element E(II) character and divalent element E(0) character

(b) Schematic representation of the probable bonding in PtCl$_2$$\leftarrow$NHE$_{Me}$ donor-acceptor interactions

E = Ge, Sn, Pb

Scheme 2



(a) NHE$_{Me}$ showing divalent element E(II) character

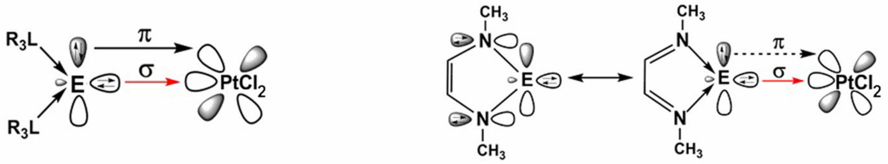
(b) NHE$_{Me}$ showing divalent element E(0) character

(c)

(b) and (c) are the corresponding probable resonance forms of tetrylene and tetrylone ligands showing the divalent element E(0) character

E = Ge, Sn, Pb

Scheme 3



(a) Bonding in PtCl$_2$$\leftarrow$E(LR$_3$)$_2$

(b) Bonding in PtCl$_2$$\leftarrow$NHE$_{Me}$

E = Ge, Sn, Pb

Scheme 4

of tetrylone and tetrylene ligands displaying the divalent element E(II) and the divalent element E(0) characters with E = Ge to Pb in Scheme 3. From this, it follows that the heavier tetrylenes NHE$_{Me}$ in Pt-NHE can be considered to have a resonance heavy tetrylones form in which the central E atom has two lone pairs and thus be able to show the characteristics of divalent E(0) compounds (Scheme 4)[47,51]. This also shows that the ligand NHE$_{Me}$ in Pt-NHE complexes is a strong σ-donor and π donor. The above discussion shows that the tetrylenes ligands in Pt-NHE can act as the tetrylones ligands in Pt-NHE. This explains why the trend of BDEs of Pt-NHE increases from germylene to plumbylene, exhibiting the same trend as two other complexes, [W(CO)$_5$-{E(PPh$_3$)$_2$}][48] and [W(CO)$_4$-{E(PPh$_3$)$_2$}][50].

Conclusions

The equilibrium geometries of the heavier tetrylene complexes [PtCl$_2$-{NHE$_{Me}$}] (Pt-NHE) possess side-on-bonded NHE$_{Me}$ ligands (E = Ge, Sn, Pb). The order of the calculated BDEs is: Pt-NHGe < Pt-NHSn < Pt-NHPb. The donation of the second pair of electrons does not play a role in the trend in the dissociation energies, and the longest bond length of Pb-Pt bond does not correlate with the trend of BDEs.

The EDA-NOCV results indicate that the ligand NHE_{Me} in Pt-NHE complexes is a strong σ-donor and π-donor and the trend of the Pt-E bond strength is due to the increase in $PtCl_2 \leftarrow NHE_{Me}$ donation and also from the strong preparation energy, and orbital interactions. The possible resonance forms and the suggested schematic representation of the bonding situation in complexes, highlight the existence of divalent heavier tetrylones(0) character in the divalent heavier tetrylenes(II) in Arduengo type N-heterocyclic cabenes[17] and analogues. The theoretical results point toward new directions for experimental research in the field of low-coordinate heavier tetrylene compounds.

Supplementary Data

Cartesian coordinates and energies of the optimized molecules are available as supplementary data in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(03)269-276_SupplData.pdf.

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