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Note

The 2,2′-diindolylmethane dianion supporting scaffold for group 15 compounds

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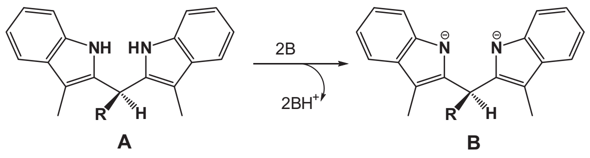
ABSTRACT

Deprotonated 2,2′-diindolylmethane functions as a dianionic chelating ligand for the isolation and characterization of the group 15 species $\{ArCH(3\text{-}MeC_8H_4N)_2\}PCl$ (**2**) and $\{ArCH(3\text{-}MeC_8H_4N)_2\}SbNMe_2$ (**6**, Ar = p-C_6H_4Br). The single crystal X-ray structure of **2** revealed a six-membered heterocycle featuring an N–P–N bonding motif and a terminal P–Cl function. The antimony complex **6** is a rare example of an N-heterocyclic aminostibine. DFT computations were used to examine the energies of isomers for these compounds and to describe the bonding features of the diindolyl fragment with the group 15 cation.

1. Introduction

The alteration of the electronic and geometric environment of transition metal and main group element centres can be achieved through supporting ligand design, modification and substituent variation. Indolate anions represent variants of amido ligands in which the N centre resides in a fused, planar aromatic framework. Like common amido ligands, these anions possess two potential donor pairs of electrons. However, indolates differ from simple amido ligands due to the fact that one of the nitrogen-centred lone electron pairs is incorporated into the aromatic π-system which leads to reduced donating ability by the coordinated N centre. Bridging two indoles at the 2-position with a single carbon linkage generates 2,2′-diindolylmethanes such as **A** [1]. Double deprotonation of the two indole N–H functions of **A** would produce a dianionic species, **B** (Eq. (1)), that is capable of chelate formation and generation of a six-membered heterocycle compound. Despite the relatively direct synthetic access to 2,2′-diindolylmethane compounds, *via* the condensation of 3-methylindole with an aldehyde, examples of comprehensively reported complexes with these species as ligands are scarce. Structurally characterized diindolylmethane complexes of **B** are limited to the group 4 amido compounds $(NEt_2)_2Ti[(NC_8H_4Me)_2CHAr]$ and $(NEt_2)_2(THF)Zr[(NC_8H_4Me)_2CHAr]$ (Ar = C_6H_5, p-C_6H_4Br) [2a,b], the group 4 metallocene compounds $Cp_2M[(NC_8H_4Me)_2CHAr]$ (M = Ti, Ar = C_6H_5; M = Zr, Ar = C_6H_5, p-$C_6H_4(OCH_3)$) [3] and a single group 14 complex $(C_6H_5)_2Si[(NC_8H_4Me)_2CHAr]$ (Ar = p-C_6H_4OMe) [2a]. The steric bulk of the ligand and relatively low π-donating ability of the indole nitrogen atoms affords the possibility of synthesizing π-acidic group 15 complexes and to probe their Lewis-acid/base properties. Furthermore, such species may also serve as synthetic reagents, providing access to group 15 cations or new metal complexes. Herein we present the first application of deprotonated 2,2′-diindolylmethane as dianionic chelating ligands for the isolation and characterization of the group 15 species $\{ArCH(3\text{-}MeC_8H_4N)_2\}PCl$ and $\{ArCH(3\text{-}MeC_8H_4N)_2\}SbNMe_2$ (Ar = p-C_6H_4Br)



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2. Results and discussion

The *in situ* deprotonation of di(3-methylindolyl)-4-bromophenylmethane with dimethylaminopyridine (DMAP) in the presence of PCl_3 in CH_2Cl_2 yielded compound **2** in moderate yield (55%) after removal of volatiles and extraction with THF (Eq. (2)). The ^1H and ^{13}C NMR spectra of this product exhibited the resonances for two diastereomeric compounds, in an approximate 5:1 ratio each consistent with the proposed formulation of **2** and each possessing doubly deprotonated 2,2′-diindolylmethane substituents. These features were further supported by the appearance of two ^{31}P NMR resonances at δ 90.3 ppm (major) and 96.0 ppm (minor). These two isomers arise from the disposition of the P–Cl group and the

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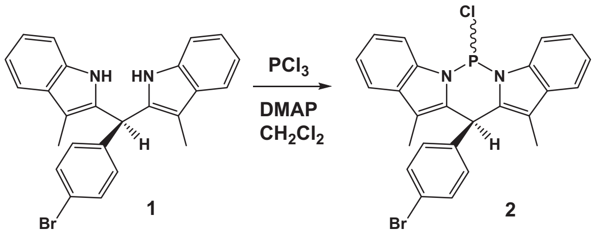
p-C_6H_4Br substituent relative to the six-membered heterocyclic ring. Variation of the reaction stoichiometry did not result in an appreciable reduction of the minor product in the NMR spectra and gave poorer overall yields. Furthermore, attempts to separate the isomers by extraction or recrystallization methods have not met with success.



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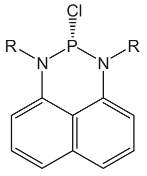
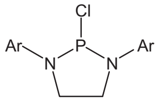
Compound **2** represents a new member of the 2-halo-1,3,2-diazaphospholene class of compounds and possesses a unique scaffold provided by the diindolylmethane framework. Although these species have a rich history, the synthetic approaches to these compounds have received significant current attention [4–7]. In addition, most of these diaminophospholenes consist of five-membered cycles while compound **2** has the P centre in a six-membered ring [4a,6–8]. As a result we obtained the single crystal X-ray structure of compound **2** using crystals that were prepared by slow diffusion of hexanes into a saturated CH_2Cl_2 solution of **2**. The results of this analysis are summarized in Fig. 1 and Table 1. The trigonal pyramidal P centre in **2** is defined by a stereochemically active lone electron pair, the two N centres of the chelating di(indolyl)methane ligand and a chloride group. In this structure the P–Cl group and the p-C_6H_4Br substituent are oriented on the same side of the heterocyclic ring ("*cis*" conformation). This relative orientation of the two centres defines one of the possible isomers for the structure of compound **2**. The two tetrahedral centres P(1) and C(10) of the resulting six-membered heterocycle are directed to the same side of the ring plane to give a boat-like conformation.

The P–N bond lengths of **2**, at 1.689(6) and 1.676(6) Å are comparable to other previously reported structures of similar N-heterocyclic phosphines. For example, the six-membered heterocyclic compound **3** displayed P–N bond lengths of 1.678(2) and 1.681(2) and the bond distance of **4** was 1.670(2) Å [8a]. These distances are slightly longer than the bond lengths of 1.6684(13) and 1.6678(13) Å for **5** [6,7]. Furthermore, the P–Cl bond length of 2.108(2) Å in **2** is slightly shorter than the P–Cl bond lengths of 2.148(1) Å of **3**, 2.1723(9) Å of **4**, and 2.1993(6) Å of **5**.



R = ^iPr, **3**; Ph, **4**



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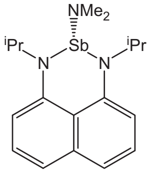
Ar = pMeOPh



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In order to explore the electronic structure and relative energies of the two isomers of compound **2**, DFT optimizations were carried out using B3LYP and a mixed TZVP/DZVP basis set. The energy difference between the two isomers was found to be only 3.3 kcal/mol with the crystallographically observed isomer being more stable. For comparison between the computed and experimental features, selected structural parameters from the optimization are presented alongside the crystallographic data in Table 1. Owing to these computational results we propose that the crystallographically characterized isomer obtained for **2** is the major isomer observed in the NMR spectra.

The details of the bonding interactions between the dianionic di(indolyl)methane ligand and the PCl dication fragments were next examined. As expected, a strong energy of interaction (−709.8 kcal/mol) and high bond order (2.15) between these two species were observed, which correspond to a charge transfer from the diindolyl ligand to PCl fragment of 1.78 electrons. The di(indolyl) ligand has four significant donor orbitals that interact with the cation. The highest occupied fragment orbitals (HOFO) and their relative contributions are HOFO, HOFO − 1, HOFO − 2, and HOFO − 5 and are shown in Fig. 2. The P–Cl cation fragment accepts this electron density into three lowest unoccupied fragment orbitals LUFO, LUFO + 1 and LUFO + 2. The LUFO and LUFO + 1 orbitals are dominated by phosphorus p orbital (80%) character. The LUFO + 2 orbital is mixture of phosphorus p (63%) and Cl p (32%) and is essentially a σ P–Cl orbital. The fragment interactions are a mix of σ (LUFO with HOFO/HOFO-2 and LUFO + 2 with HOFO − 5) and π (LUFO + 1 with HOFO − 1) in nature. In order to compare the electronic interactions observed in **2** with the related compound **3**, similar DFT computations were carried out on **3**(Fig. S1).[1] Similar to **2**, a strong energy of interaction between the PCl and $(^iPrN)_2C_{10}H_6$ fragments and high bond order were obtained. In the case of **3**, the interaction energy and bond order were larger than for **2** with values of −771.3 kcal/mol and 2.28, respectively. These corresponded to a charge transfer of 1.83 electrons from the diamido fragment to PCl. The diamidonapthalene ligand fragment donates from the highest four occupied orbitals (relative charge transfer in brackets): HOFO (11.7%), HOFO − 1 (17.3%), HOFO − 2 (33.5%), HOFO − 3 (30.2%). These orbitals have analogous spatial distributions to those seen for the di(indolyl)methane fragment of **2**. Furthermore, similar acceptor orbitals on the PCl fragment were obtained from the fragment bonding analysis of **3**. Specifically the major acceptor orbitals were LUFO (34.8%), LUFO + 1 (57.0%) LUFO + 2 (11.6%). There was a small acceptor contribution from LUFO + 10 (4.0%) which is a P centred orbital with d character.

Overall, the bonding analysis supports the experimental bond lengths obtained from X-ray analysis. For example, compound **3** displayed slightly shorter P–N bond distances than **2**. This appears to be due largely to a reduced π-donation of the di(indolyl)meth-

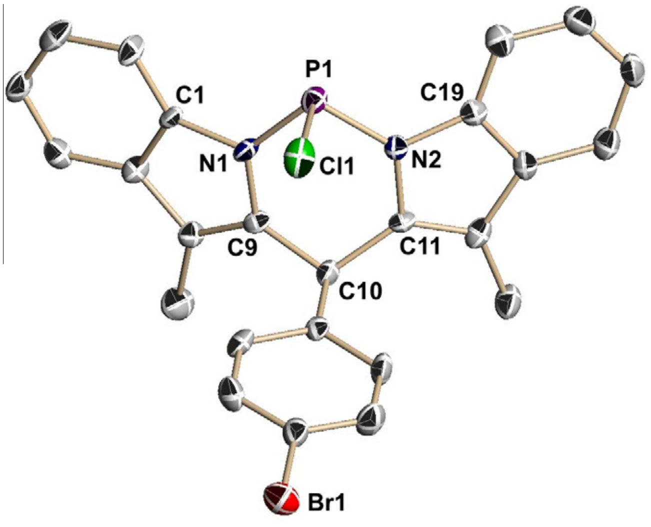

Fig. 1. Thermal ellipsoid representation and numbering scheme for **2**. Hydrogen atoms and a co-crystallized toluene molecule have been omitted for clarity.

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[1] A figure providing the fragment orbitals for the interaction of the ligand and the PCl2+ fragments, similar to Fig. 2, is provided in the supporting information.

Table 1
Selected bond distances and angles for **2** derived from single crystal X-ray analysis and computation.

Selected bonds	SS[a] BL[b] (Å)	Comp[c] BL[b] (Å)	Selected angles	SS[a] angles (deg)	Comp[c] angle (deg)
P–Cl	2.108(3)	2.154	N–P–N	96.8(3)	96.15
P–N1	1.689(6)	1.725	N1–P–Cl	101.5(2)	102.33
P–N2	1.676(6)	1.725	N2–P–Cl	101.0(2)	
			P–N1–C1	122.9(5)	123.47
			P–N2–C19	123.5(5)	
			P–N1–C9	128.3(9)	128.26
			P–N2–C11	129.5(5)	

[a] SS = solid state.
[b] BL = bond lengths.
[c] Comp = computed.

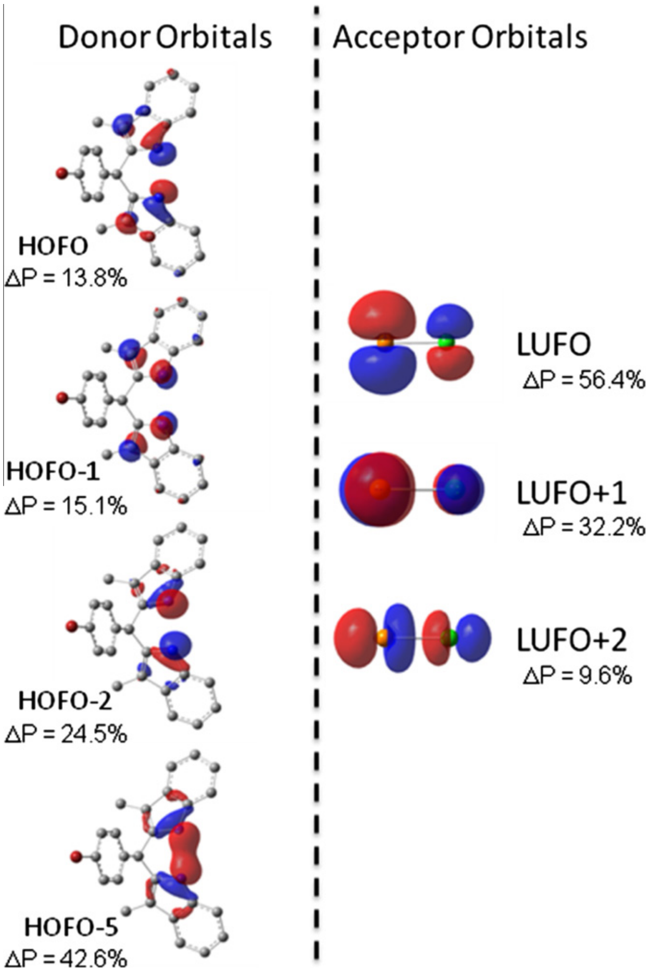
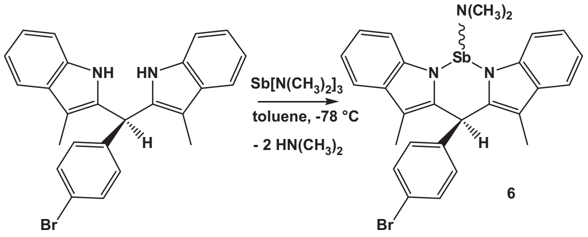


Fig. 2. Fragment orbitals for optimized **2**. The FOs with the largest contributions to bonding are shown. The change in the orbital population (%) due to the fragment interactions is provided by ΔP values and indicate the relative charge transfer for the orbital.

ane ligand into the LUFO + 1 relative to the diamidonaphthalene ligand in **3**. The slightly shorter P–Cl distance for **2** is consistent with the lower degree of ligand donation into the LUFO + 2, an antibonding P–Cl orbital.

In order to apply the di(indolyl)methane ligand scaffold to the heavier congeners of group 15, Sb[N(CH$_3$)$_2$]$_3$ was reacted with {ArCH(3-MeC$_8$H$_4$NH)$_2$} (Eq. (3)). This transamination reaction was carried out at −78 °C in toluene, followed by gradual warming to room temperature and removal of volatiles to produce the white amidostibine **6** in 88% yield within 6 h. ^{1}H and ^{13}C NMR spectra showed the expected resonances for the protons and carbon atoms of the deprotonated and coordinated 2,2′-diindolylmethane ligand. Single resonances in the ^{1}H and ^{13}C NMR spectra were assigned to the methyl protons and carbon atoms of the remaining dimethylamido substituent. The proposed mononuclear structure is consistent with reported five-membered 2-X-1,3,2-stibolenes (X ·Cl, Br) [9] and with the only reported stibolene with the Sb centre captured in a six-membered ring, **7** [8a,10]. Confirmation of the chemical formula of **6** was obtained by elemental analysis



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In spite of repeated attempts, crystals of **6** suitable for structural elucidation were not forthcoming. The mononuclear structure of **6** was, therefore, modeled with a DFT computational study using the B3LYP functional and the mixed DZVP/TZVP basis set. As observed in the case of **2**, isomers with two relative orientations of the Sb-NMe$_2$ to the ligand reached satisfactory minima with only a very slight energy difference (2.1 kcal/mol). In contrast to the optimized structure of **2**, in this case the lower energy structure displayed the Sb–NMe$_2$ and the *p*-C$_6$H$_4$Br moieties in a "*trans*" conformation with respect to the metallacyclic ring (Fig. S2). Examining the bonding between the di(indolyl) anionic fragment and the SbNMe$_2$ dication revealed a high degree of interaction with a bond order of 1.97 and charge transfer of 1.58 electrons from the ligand to the antimony-amido fragment. This corresponded to a large energy of interaction of −531.3 kcal/mol.

The in-depth bonding features of **6** displayed major donation from five di(indolyl)methane donor orbitals to the SbNMe$_2$ fragment. As in the case of **2**, the most significant were HOFO − 2 with 24.8% and HOFO − 5 with 38.6% donation respectively (Fig. S3). The HOFO (5.1% donation), HOFO − 1 (7.4% donation) and HOFO − 3 (3% donation) each make important but smaller contributions to bonding. The acceptor orbital array on the SbNMe$_2$$^{2+}$ fragment is also similar to that observed with **2**. However, there are some interesting differences. Specifically, the Sb–NMe$_2$$^{2+}$ LUFO is the largest accepting orbital (47.2%) and is an Sb-centred *p* orbital. The LUFO + 1 is the next largest accepting orbital (34.5%) and is dominated by Sb *p* orbital character (58.2%) but has very significant N-centred *p* nature (29.3%). Like compound **2**, the LUFO + 2 accepts a smaller percentage (3.8%) from the di(indolyl)methane donor group. Furthermore, this orbital is a mix of 68.1% Sb *p* orbital and 8.9% N *p* character and is Sb–NMe$_2$ antibonding in nature. This orbital is, in fact, the analogy to the LUFO + 2 of the PCl dication fragment of **2**. However, a significant difference in the nature of this orbital arises from the fact that LUFO + 2 has 10.4% contribution from an antimony *d* orbital. Finally, the Sb amido cation accepts 3.1% of the electron density into the LUFO + 8, an orbital that is predominantly of Sb *d* orbital character. This increased importance of acceptor *d* orbitals would be an anticipated feature of the heavier members of group 15.

3. Conclusion

This report expands on the small number of known di(indolyl)methane compounds to include the first examples featuring group 15 elements. Two new compounds of 2,2′-diindolylmethane have been obtained using two distinct synthetic methodologies; (i) substitution of two chlorophosphine groups by di(indolyl)methane in the presence of base and (ii) use of metal amido base to doubly deprotonate the indolyl groups with concomitant coordination of the resulting anionic ligand. One of the products, a six-membered heterocycle featuring an N–P–N bonding motif and a terminal P–Cl function, is an interesting material for further synthesis of phosphorus compounds. The antimony complex **6** is a rare example of an N-heterocyclic aminostibine and provides the first definitive evidence that diindolylmethane ligands can effectively support heavier main-group elements to form stable compounds, and that these compounds are obtainable in high yields. The intimate bonding features of the diindolyl fragment with the group 15 cation were revealed through computational analysis and several common aspects will assist in defining our future goals. Continued exploration of the unique steric and electronic properties of the di(indolyl)methane ligand promise to add significantly to chemistry of these chelating diamido ligands.

4. Experimental section

4.1. General Considerations

All manipulations were carried out under nitrogen atmosphere employing standard drybox or Schlenk line techniques. Dichloromethane was distilled over CaH_2 prior to use. All other solvents were sparged with nitrogen and dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated benzene, chloroform and dichloromethane were dried by addition of molecular sieves. Di-(3-methylindol-2-yl)-4-bromophenylmethane was prepared according to a previously reported procedure [2a]. Tris(dimethylamido)antimony was purchased from Strem Chemicals and used as received. All other reagents were purchased from Aldrich and used as received. NMR spectra were run on Bruker Avance 300 and 500 MHz spectrometers with deuterated benzene, chloroform or dichloromethane as the solvent using residual protons of the deuterated solvent for reference. Elemental analysis was performed by Midwest Microlabs, Indianapolis, Indiana.

4.1.1. Di-(3-methylindol-2-yl)chlorophosphine-4-bromophenylmethane (2)

PCl_3(0.050 mL, 0.57 mmol) was added dropwise to a solution of di-(3-methylindolyl)-4-bromophenylmethane (0.189 g, 0.440 mmol in 2 mL dichloromethane), followed immediately by addition of 0.140 g (1.15 mmol) DMAP. The resulting clear yellow solution was allowed to stir for 72 h before removal of the solvent *in vacuo*. The product was extracted with THF (3 × 1.5 mL), filtered through a glass frit and solvent was removed *in vacuo*. The resultant off-white solid was washed with hexanes (3 × 1.5 mL) and diethyl ether (3 × 1.5 mL) and the resulting white solid was recrystallized from dichloromethane at −22 °C. Yield: 0.119 g (54.8%) $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): 90.3 (major isomer), 96.0 (minor isomer). ^1H NMR(C_6D_6, major isomer, ppm): 2.11 (s, 6H, 2 CH_3), 5.60 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 7.16 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.1 Hz) 7.22 (t, 2H, *H*Ar, $^3J_{HH}$ = 8.1 Hz), 7.25 (m, 4H, *H*Ar, $^3J_{HH}$ = 8.4 Hz), 7.53 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz), 7.65 (m, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz) Minor isomer: ^1H NMR($CDCl_3$, minor isomer, ppm): 2.17 (s, 6H, 2 CH_3), 5.78 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 7.08 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.1 Hz) 7.24 (t, 2H, *H*Ar, $^3J_{HH}$ = 8.1 Hz), 7.38 (m, 4H, *H*Ar, $^3J_{HH}$ = 8.4 Hz), 7.50 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz), 7.81 (m, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz) ^{13}C NMR ($CDCl_3$, major isomer, ppm): 9.03(CMe), 36.60 (CH(3-methylindolyl)2), 106.47 (CAr), 110.54 (CAr), (CAr), 115.84 (CAr), 115.92 (CAr), 119.15 (CAr), 122.29 (CAr), 123.68 (CAr), 129.31 (CAr), 129.23 (CAr), 130.76 (CAr), 138.28 (CAr), 139.57 *Anal.* Calc. for $C_{25}H_{19}$ N_2BrPCl: C, 60.81; H, 3.88; N, 5.67. Found: C, 60.47; H, 3.79; N, 5.43.

4.1.2. Di-(3-methylindol-2-yl)dimethylamidoantimony-4-bromophenylmethane (6)

To a Schlenk flask containing a suspension of 0.336 g (0.783 mmol) di-(3-methylindolyl)-4-bromophenylmethane in 2 mL toluene cooled to −78 °C in a dry ice/acetone bath was added a solution of 0.225 g (0.88 mmol) tris(dimethylamido)antimony in 2 mL toluene. The resultant white suspension was allowed to warm to room temperature over a period of 3 h, with stirring, by which point it had become a slightly cloudy, colourless solution. Volatiles were then removed *in vacuo* and the resulting white solid was washed with hexanes (2 × 1.5 mL) to yield **6** (0.407 g, 88% yield) ^1H NMR ($CDCl_3$, ppm): 2.48 (s, 6H, NC*H*$_3$), 2.77 (s, 6H, 2 C*H*$_3$), 5.84 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.69 (d of quartets, 2H, *H*Ar, $^3J_{HH}$ = 8.6 Hz), 7.16 (m, 4H, *H*Ar, $^3J_{HH}$ = 8.1 Hz),), 7.31 (m, 4H, *H*Ar, $^3J_{HH}$ = 7.9 Hz),), 7.63 (m, 2H, *H*Ar, $^3J_{HH}$ = 8.6 Hz) ^{13}C NMR ($CDCl_3$, ppm): 9.21 (*C*Me), 38.11 (N*C*H$_3$), 41.02 (*C*H(3-methylindolyl)$_2$), 110.95 (*C*Ar), 111.43 (*C*Ar), 118.68 (*C*Ar), 119.21 (*C*Ar), 119.60 (*C*Ar), 121.30 (*C*Ar), 121.84 (*C*Ar), 129.76 (*C*Ar), 131.46 (*C*Ar), 132.00 (*C*Ar), 137.04 (*C*Ar), 141.31 (*C*Ar) *Anal.* Calc. For $C_{27}H_{25}BrN_3Sb$: C, 54.67; H, 4.35; N, 7.08. Found: C, 54.52; H, 4.34; N, 7.01.

EI-MS *m/z* 593.03 [0.4%, M^+], 547.97 [14%, $C_{25}H_{19}BrN_2SbH^+ = LSbH^+$], 546.98 [3.9%, $C_{25}H_{19}BrN_2Sb^+ = LSb^+$], 428.09 [50%, $C_{25}H_{21}BrN_2^+ = L^+$].

4.3. Computations

Density Functional Theory (DFT) calculations have been performed using the GAUSSIAN 09 package [11]. Wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the electronic ground state. The structures of all species were optimized using the B3LYP exchange-correlation (XC) functional with the mixed basis set (DZVP on Br and Sb and TZVP on all other atoms). Tight SCF convergence criteria (10^{-8} a.u.) were used for all calculations. Harmonic frequency calculations with the analytic evaluation of force gradients were used to determine the nature of the stationary points.

The analysis of the molecular orbital (MO) compositions in terms of occupied and unoccupied orbitals of the fragment species (HOFOs and LUFOs, respectively), the construction of MO diagram (Figs. 2, S1and S3) and Mayer bond orders were calculated using the AOMix program [12,13]. Atomic charges and Wiberg bond orders in the natural atomic orbital basis were evaluated by using the natural population analysis (NPA) [14].

4.4. Crystallography

Crystals of compound **2** were mounted on thin glass fibers using paraffin oil and the sample were cooled to 200 °K prior to data collection. Data were collected on a Bruker AXS SMART (3-circle) single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and SMART 1 K CCD detector. Raw data collection and processing were performed with Smart software package from Bruker axs (Bruker axs: Smart – Bruker Molekular Analysis Research Tool, version 5.632, Bruker AXS Inc., Madison, WI, USA 1997)The crystals were weakly diffracting at high angles. Since the R(sigma) was exceeding 35% beyong 1.1 Å resolution limit, the data set was trimmed in order to improve signal to noise ratio and achieve better refinement convergence.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.06.019.

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