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Palladium(II) and Platinum(II) Bis(stibinidene) Complexes with Intramolecular Hydrogen-Bond Enforced Geometries

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The coordination capability of two *N,C,N* pincer coordinated stibinidenes, *i.e.* bis(imino)- [2,6-(DippN=CH)₂C₆H₃]Sb (**1**) or imino-amino- [2-(DippN=CH)-6-(DippNHCH₂)C₆H₃]Sb (**2**) toward palladium(II) and platinum(II) centers was examined. In the course of this study, seven new square-planar bis(stibinidene) complexes were synthesized and characterized by NMR, IR, Raman, UV-vis spectroscopy and single crystal (sc)-X-ray diffraction analysis. In all cases, both stibinidene ligands **1** or **2** adopt *trans* positions, but differ significantly in the torsion angle describing mutual orientation of aromatic rings of the stibinidenes along the Sb–Pd/Pt–Sb axes. Furthermore, majority of complexes form isomers in solution most probably due to a

hindered rotation around Sb–Pd/Pt bonds caused by bulkiness of **1** and **2**. This phenomenon also seems to be influenced by the absence/presence of a pendant –CH₂NH– group in **1/2** that is able to form intramolecular hydrogen bonds with the adjacent chlorine atom(s) attached to the metal centers. The whole problem was subjected to a theoretical study focusing on the role of hydrogen bonds in structure architecture of the complexes. To describe the UV-vis spectra of these highly coloured complexes, TD-DFT calculations were employed. These outline differences between the stibinidene ligands, the transition metals as well as between the charge of the complexes (neutral or anionic).

Introduction

The coordination chemistry of neutral triorganostibines R₃Sb (R stands for *C*-monoanionic substituent), as heavier analogues of ambiguous phosphines, is a continuously developing area of inorganic chemistry and their complexes with a variety of transition metals (TMs) have been well documented. These ligands usually behave as 2e (L) donors (Figure 1A), albeit they are considered as weaker σ -donor in comparison with their phosphorus counterparts. The feature that is mostly ascribed to energetically more separated 5s and 5p orbitals of the antimony atom that leads to a significant *p*-character of the Sb–C bonds

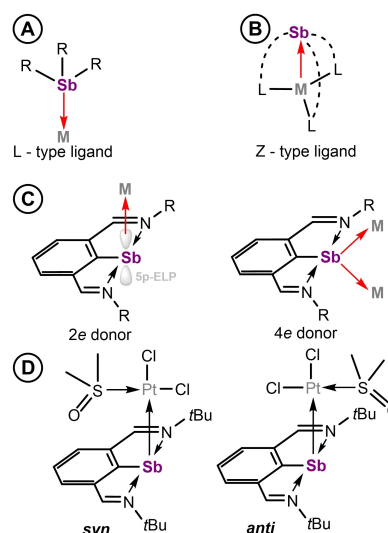


Figure 1. A – triorganostibines as 2e donors, L-type ligands; B – antimony serving as a Z-type ligand; C – stibinidenes and their coordination ability preferably via 5p electron lone pair (ELP) as 2e donor or as 4e donor; D – rotamers formed in stibinidenes complexes of platinum.

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in R₃Sb. Consequently, the lone pair of Sb possesses a high *s*-character and lacks any directional properties resulting in weaker bonding with TMs.^[1]

Nevertheless, a remarkable potential of the antimony centre to serve as a Lewis acidic Z-type ligand for TMs,^[2] a concept originally developed for inherently acidic group 13 elements,^[3] was discovered by the group of Gabbai among others.^[4]

Sophisticated systems containing one (or more) L ligands are, however, utilized to keep the antimony centre close to the particular TM, thereby facilitating the Z-type coordination

(Figure 1B). It is to note that such complexes found remarkable applications in catalysis.^[5]

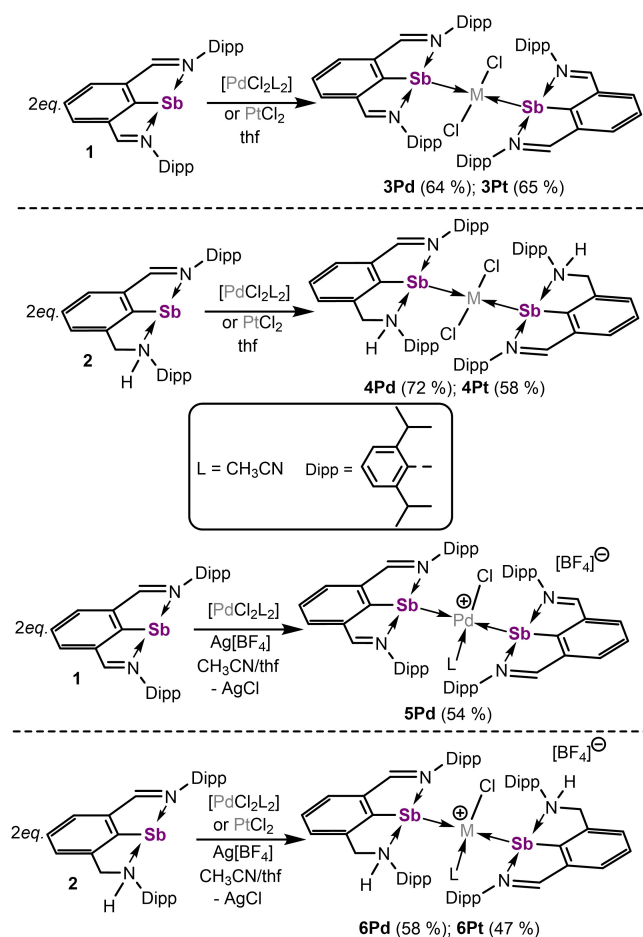
Previously, we have used *N,C,N*-pincer ligands for the stabilization of the first example of stibinidenes (Figure 1C).^[6] They inherently exhibit reducing properties,^[7] but due to a tight coordination of two imino- functions to the Sb atom a closure of aromatic 5-membered ring is feasible and they may behave as hidden heterodienes as well.^[8] Furthermore, the antimony centre carries two lone pairs of predominantly 5s and 5p character and therefore can be used either as 2e^[9] or 4e^[10] type ligand for the coordination of various TMs. In this regard, it is also to note that several other stibinidene complexes including those with a bridging antimony atom, *i.e.* [μ -RSb(TM)₂], were reported.^[11] Nevertheless, the geometry of stibinidene complexes is also remarkable. The TM is coordinated perpendicularly to the main plane of the ligand using the 5p lone pair (Figure 1C) and it might lead to the formation of rotamers (*syn*- or *anti*-) in solution for example in square-planar Pt(II) complexes (Figure 1D).^[12]

In the present contribution, we report our achievement in coordinating of two stibinidene ligands toward a single Pd(II) or Pt(II) ion. We have used two types of stibinidenes containing either a bis(imino)- ([2,6-(DippN=CH)₂C₆H₃]Sb; **1**, Dipp = 2,6-*i*Pr₂-C₆H₃) or imino-amino- ([2-(DippN=CH)-6-(DippNHCH₂)C₆H₃]Sb; **2**) pincer ligand (Scheme 1), the latter is for the first time used in the coordination chemistry. It turned out that the formation of isomers in solution, similar to those mentioned in Figure 1D, seems to be influenced by the presence or absence of intramolecular NH-Cl hydrogen bonds in the case of complexes containing **2** with a pendant -CH₂NH- function or stibinidene **1**, respectively. DFT calculations were employed to study the geometrical aspects of these complexes, and the unusual colours of these species were interpreted by TD-DFT calculations.

Results and Discussion

Starting stibinidenes **1** (*i.e.* [2,6-(DippN=CH)₂C₆H₃]Sb)^[13] and **2** (*i.e.* [2-(DippN=CH)-6-(DippNH-CH₂)C₆H₃]Sb)^[13] were synthesized by published procedures. Both **1** and **2** were treated with [PdCl₂(CH₃CN)₂] or PtCl₂ yielding neutral complexes *trans*-[MCl₂(κ^1 -Sb-**1**)₂] (**3Pd** and **3Pt**) and *trans*-[MCl₂(κ^1 -Sb-**2**)₂] (**4Pd** and **4Pt**) that were isolated as crystalline solids (Scheme 1). It contrasts to our previous finding with the stibinidene [2,6-(*t*BuN=CH)₂C₆H₃]Sb, in the case of which we were neither able to attach two of the stibinidenes to a single platinum atom, nor synthesize the palladium complexes, because the reaction with [PdCl₂(CH₃CN)₂] resulted only in the reduction of the Pd(II) center to Pd(0).^[12] This finding is in agreement with a more reducing behavior of the stibinidene [2,6-(*t*BuN=CH)₂C₆H₃]Sb in comparison with **1** and **2** as recently shown by cyclic voltammetry experiments.^[7]

We were further curious if cationic Pd and/or Pt center can be also stabilized using **1** or **2** as ligands. Using a two-step procedure including treatment of [PdCl₂(CH₃CN)₂] or PtCl₂ with 1 eq. of Ag[BF₄] in acetonitrile followed by the addition of 1 eq.



Scheme 1. Synthesis of the studied complexes.

of **1** or **2** indeed allowed isolation of [PdCl(CH₃CN)(κ^1 -Sb-**1**)₂][BF₄] (**5Pd**) and *trans*-[MCl(CH₃CN)(κ^1 -Sb-**2**)₂][BF₄] (**6Pd** and **6Pt**, Scheme 1). Unfortunately we were unable to crystallize pure sample of *trans*-[PtCl(CH₃CN)(κ^1 -Sb-**1**)₂][BF₄] (hypothetical **5Pt**, *vide infra*) as a platinum analogue of **5Pd**. It is to note that all our attempts to abstract the second chloride from **5Pd** or **6Pd**/Pt by Ag[BF₄] failed in our hands. All of the obtained compounds were characterized by IR, Raman, UV-vis and NMR spectroscopy (*vide infra*) and by sc-X-ray diffraction analysis, except for **5Pd** that revealed only data of poor quality (see ESI, Figure S21). Unfortunately, due a very high sensitivity of all complexes, we were not able to obtain satisfactory combustion analysis for these complexes.

The molecular structures of all complexes are shown in Figures 2–4, except for low-quality structure of **5Pd** (Figure S21). Selected structural parameters are collected in Table 1. All compounds adopt typical distorted square-planar environment at the Pd or Pt centres, with *trans* coordinated stibinidene ligands. The Sb–M–Sb bonding angles (M = Pd or Pt) are quite deviated from linearity in neutral complexes **3Pd**/Pt and **4Pd**/Pt (164.47(3)–169.04(3)°) reflecting the bulkiness of the ligands, but these angles become more linearized in ionic complexes **6Pd**/Pt (*cf.* 174.14(2) and 174.09(2)°). The Cl(1)–M–X bonding angles (X = Cl(2) or N(acetonitrile)) approach the ideal value in

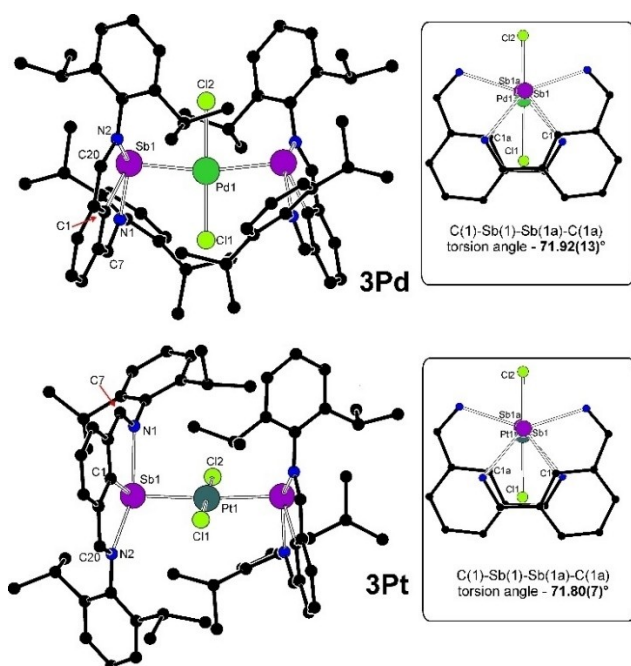


Figure 2. PLUTON drawings of molecular structures of compounds **3Pd/Pt** with projections along the Sb–Sb axis. The hydrogen atoms, benzene solvate molecules are omitted for clarity.

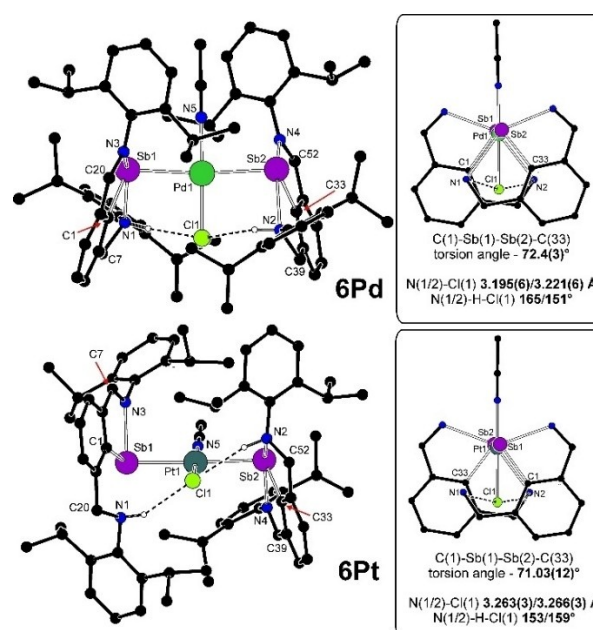


Figure 4. PLUTON drawings of molecular structures of compounds **6Pd/Pt** with projections along the Sb–Sb axis. The hydrogen atoms, the $[\text{BF}_4]^-$ counter anion, dichloromethane (**6Pd**) and thf solvate molecules (**6Pt**) are omitted for clarity.

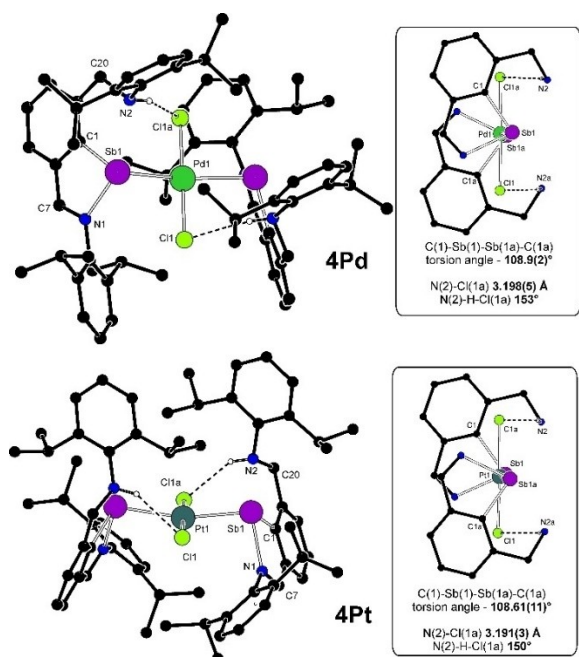


Figure 3. PLUTON drawings of molecular structures of compounds **4Pd/Pt** with projections along the Sb–Sb axis. The hydrogen atoms are omitted for clarity. The symmetry operator for **4Pd**: $a = 1-x, y, 1/2-z$, for **4Pt**: $a = 1-x, y, 3/2-z$.

the interval 178.02(3)–180.00(1)°. The Sb–Pd(1) bond lengths of 2.6167(3) and 2.6165(6) Å in **3/4Pd** are shorter than those found in the ionic complex **6Pd** (2.6466(7) and 2.6530(7) Å); nevertheless, all values well correspond to $\Sigma_{\text{cov}}(\text{Sb}–\text{Pd}) = 2.63$ Å.^[14] A similar trend is also obtained for platinum complexes with

Sb–Pt(1) bond lengths of 2.6025(3), 2.6059(3) and 2.6413(5)/2.6377(5) Å, for **3/4Pt** and **6Pt**, respectively, $\Sigma_{\text{cov}}(\text{Sb}–\text{Pt}) = 2.63$ Å.^[14] All these values are also larger in comparison with other neutral Pd(II) and Pt(II) complexes in which the R_3Sb ligands adopt *trans*-orientation, *i.e.* $\text{trans}[\text{PdCl}_2(\kappa^1\text{-R}_3\text{Sb})_2]$ (where $\text{R} = \text{o-tolyl}$ ^[15a] 2.5658(3) or $i\text{Pr}$ ^[15b] 2.5721(7) Å) and $\text{trans}[\text{PtCl}_2(\kappa^1\text{-R}_3\text{Sb})_2]$ (where $\text{R} = [2\text{-(EtO)}_2\text{CH}]\text{C}_6\text{H}_4$ ^[15c] 2.5821(7) Å), as well as in cationic complexes $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2][\text{PF}_6]$ (2.506(1) and 2.527(1) Å)^[16a] and $[\text{Pt}(\text{[9]aneS}_3)(\text{SbPh}_3)][\text{PF}_6]_2$ (2.5486(9) and 2.5447(8) Å).^[16b]

As a consequence of the coordination of the antimony atom *via* its 5p lone pair, the pincer ligands are orientated almost perpendicularly to the Sb–M(1)–Sb linkage, leading to a steric clash between bulky Dipp groups that is reflected in formation of isomers in solution as described below.

The mutual orientation of both pincer moieties may be described using the $\text{C}(\textit{ipso})\text{--Sb--Sb--C}(\textit{ipso})$ torsion angles. These are 71.92(13) and 71.80(7)° for **3Pd/Pt**, but amount to 108.9(2) and 108.61(11)° for **4Pd/Pt**, respectively (Figures 2 and 3). This finding is most probably caused by the presence of two $\text{NH}\cdots\text{Cl}$ hydrogen bonds involving both chlorine atoms in **4Pd/Pt** (Figure 3), which influences the mutual orientation of the pincer systems. Interestingly, the same torsion angle shrinks back to 72.4(3) and 71.03(12)° for the ionic compounds **6Pd/Pt**, respectively, but in this case both NH groups are now connected to a single Cl atom. This fact only underlines how significant are these $\text{NH}\cdots\text{Cl}$ interactions for the geometry in complexes containing **2**.

Solid-state infrared spectra of **4Pd/Pt** showed broadened bands in the region 3225–3185 cm^{-1} pointing to the presence of N–H groups involved in hydrogen bonding; and the band in

Table 1. Relevant bond lengths [Å] and angles [°] of the studied compounds from sc-XRD measurements, M(1) = Pd(1) or Pt(1) and Wiberg Bond Indices (in parentheses) obtained at the ω B97X–D/def2-SVP level of theory.

Bond lengths [Å]			Bonding angles [°]		
Comp.	Sb(1)–N(1/2)	Sb(1)–M(1)	M(1)–Cl(1/2)	Sb(1)–M(1)–Sb(1a)	Cl(1)–M(1)–Cl(2) ^[a]
3Pd	2.429(3)/2.405(3) (0.28/0.30)	2.6167(3) (0.58)	2.2869(12)/2.3059(12) (0.62/0.56)	168.79(3)	180.00(1)
4Pd	2.4084(17)/2.4314(17) (0.29/0.28)	2.6025(3) (0.68)	2.2910(8)/2.3084(8) (0.71/0.66)	169.04(3)	180.00(1)
3Pt	2.285(5)/2.574(4) (0.38/0.19)	2.6165(6) (0.59)	2.3138(15) ^[a] (0.55)	164.47(3)	178.65(6) ^[a]
4Pt	2.300(3)/2.573(3) (0.36/0.20)	2.6059(3) (0.68)	2.3146(6) ^[a] (0.66)	165.28(1)	178.02(3) ^[a]
6Pd	Sb(1)–N(1/3) Sb(2)–N(2/4)	Sb(1)–M(1) Sb(2)–M(1)	M(1)–Cl(1) M(1)–N(5)	Sb(1)–M(1)–Sb(2)	Cl(1)–M(1)–N(5)
	2.536(3)/2.317(5) (0.24/0.34) ^[b] 2.526(5)/2.303(5) (0.24/0.34) ^[b]	2.6466(7) (0.60) 2.6530(7) (0.60)	2.2999(16) 1.998(7)	174.14(2)	178.85(17)
6Pt	2.548(3)/2.310(3) (0.24/0.33) ^[c] 2.524(3)/2.325(3) (0.24/0.33) ^[c]	2.6413(5) (0.68) 2.6377(5) (0.68)	2.2919(9) 1.979(3)	174.09(2)	179.66(9)

[a] Cl(2) = Cl(1a) for **4Pd/Pt**, [b] calculated for **6Pd**⁺, [c] calculated for **6Pt**⁺.

both **4Pd/Pt** is split by 23 cm^{−1} due to site-symmetry effects. IR spectroscopic measurements of **4Pt** in various solvents (CH₂Cl₂, THF and benzene) at different concentrations proved that the environment of N–H group in the complex remains identical even in solution, as the energy and shape of ν_{NH} band did not change. For each of the ionic compounds **6Pd/Pt**, a single broadened absorption corresponding to the NH stretching mode was observed at 3206 and 3220 cm^{−1}, respectively. A slightly broadened band of ν_{NH} motion was also observed at 3232 cm^{−1} in the solution of **6Pt**; we note that acquiring of solution IR spectra for **6Pd** was not possible due to its fast hydrolysis during measurement. Two bands of $\nu_{\text{C}\equiv\text{N}}$ at 2323 and 2286 cm^{−1} in both **6Pd/Pt** are indicative of terminal N-coordinated acetonitrile ligands with little π -backbond stabilization.^[17]

The structure of all compounds in solution was examined using NMR spectroscopy. The ¹H and ¹³C{¹H} NMR spectra of **3Pd/Pt** revealed two sets of closely related signals including two signals for the CH=N groups: $\delta(^1\text{H})=8.75$ (overlap) and 8.65/8.70; $\delta(^{13}\text{C})=163.3/164.8$ and 163.2/165.3 ppm, for **3Pd/Pt**, respectively. Both sets of signals were obtained in nearly ideal 1:1 mutual ratio and this finding is reminiscent to other stibinidene platinum(II) complexes reported earlier (Figure 1D), where the formation of two rotamers due to a hindered rotation around the Sb–Pt bond was described (*vide infra*).^[12] Similarly, two sets of signals were obtained in the ¹H and ¹³C{¹H} NMR spectra of **4Pd/Pt** including CH=N groups: $\delta(^1\text{H})=8.35/8.40$ and 8.26/8.31; $\delta(^{13}\text{C})=164.8/165.5$ and 165.2/165.8 ppm, for **4Pd/Pt**, respectively. The AMX spin systems obtained for the pendant CH₂NH moieties also represent diagnostic features of the ¹H NMR spectra (see Figures S7 and S10). It is to note that the signal of the NH group within this spin system is quite

significantly downfield shifted (found in the range 7.03–7.51 ppm, *cf.* for starting **2** at 4.46 ppm^[13]) probably pointing to its involvement in a hydrogen bonding as described above in molecular structures and by IR spectroscopy in solution. More importantly, the mutual ratio between both rotamers of **4Pd/Pt** amounts to *ca.* 1:0.3 pointing to a preference of one of them which contrasts to the situation established for **3Pd/Pt** (*vide infra*).

The situation becomes even more interesting in the case of the ionic complexes **5Pd** and **6Pd/Pt**. The ¹H and ¹³C{¹H} NMR spectra of **5Pd**, lacking any NH group for possible hydrogen bond formation, again showed two set of signals, but the non-symmetric substitution at the palladium atom bearing one chlorine and one acetonitrile resulted in the observation of two magnetically non-equivalent CH=N groups for each rotamer (Figure S11). Consequently, four signals for CH=N moieties are found in both ¹H and ¹³C{¹H} NMR spectra in the range $\delta(^1\text{H})=8.82\text{--}9.00$ ppm and $\delta(^{13}\text{C})=164.2\text{--}167.1$ ppm. Furthermore, the mutual ratio between both rotamers of **5Pd** is *ca.* 1:0.65, which contrasts to **3Pd/Pt** with their equal presentation and may be most probably caused by a heterogenic coordination sphere of the palladium atom. Finally, the ¹H and ¹³C{¹H} NMR spectra of **6Pd/Pt** showed only one set of signals with the typical AMX spin systems (Figures S16 and S20) for the CH₂NH group ($\delta(^1\text{H}\text{--}NH)=6.73/6.66$ ppm) and one signal for the CH=N functionality $\delta(^1\text{H})=8.69/8.75$; $\delta(^{13}\text{C})=165.9/165.3$ ppm, for **6Pd/Pt**, respectively. This points to the presence of only one isomer in solution and may be a result of two NH groups connected *via* hydrogen bonds to a single Cl atom similarly to the situation in the solid state (Figure 4) that effectively suppresses a formation of another rotamer.

To gain deeper insight into the bonding situation, geometry optimizations were performed for both neutral (**3Pd/Pt** and **4Pd/Pt**) and cationic complexes (**5Pd** and **6Pd/Pt**) using several functionals: ω B97X-D, M06-2X, B3LYP, B3LYP-D3 and CAM-B3LYP in combination with the def2-SVP basis set. Among these, the ω B97X-D and M06-2X functionals show the best agreement with the experimental results, based on the smallest average absolute deviation for the characteristic bonds (see Table S8). The other functionals deliver slightly larger deviations, however, these can still be considered minor (see Table S2–S7). Regarding the cationic complexes, since the $[\text{BF}_4]^-$ anion is weakly coordinating, the calculations were performed without a counter-anion. Because the bond lengths of these cationic models differ only slightly from those of the ionic pairs **5Pd** and **6Pd/Pt**, the cationic complexes **5Pd**⁺, **6Pd**⁺ and **6Pt**⁺ will be discussed in detail (see Table S3). To describe the bonding situations, Wiberg bond indices (WBI), natural population analysis (NPA) charges and charge transfer (CT)-values were also employed. Note the WBI values account primarily for the covalent character of the bonds and their comparison is more straightforward than those of bonds distances, as the bonds between different elements can be simply compared using WBIs, and no reference values are needed (such as for distances). Therefore, in the following we will focus on WBI values. The CT values quantify the transferred NPA charges from the ligand toward the PdCl_2 or PtCl_2 moieties.

As we outlined in our previous work,^[7] the bis(imino)- ligand **1** can be described with so called “bell-clapper type” equilibrium, while the structure of the imino-amino- ligand **2** can be better characterized as an azastibole ring with a pendant amino-arm, which establishes a weak pnictogen interaction with the Sb centre. According to the WBI values, upon complex formation significant changes occur in the structure of the ligands, because the antimony centre behaves as a donor in the Sb–M (M=Pd, Pt) dative bond and therefore, the acceptor properties of the Sb atoms toward the two N-donors also undergo changes. The Sb–M bonds have rather high covalent dative character, which is supported by the remarkable WBI values of 0.58 to 0.68. Further evidence for the high covalency of the Sb–M bonds are the charge transfer values, which are rather similar for the Pd and Pt complexes (for neutral Pd: 0.54e, Pt: 0.59e and for cationic Pd: 0.66–0.67e, Pt: 0.71e, respectively), and in line with the WBIs, they indicate slightly stronger interactions in the Pt complexes than in Pd counterparts (see Table S2 and S10). First, we compare the WBIs of the complexes with the analogous values of the free ligands (Table S2). In the case of the bis(imino)- ligand **1**, the metric parameters around the antimony centre in its complexes change less considerably upon complexation (compared with the free ligand **1**): the two Sb–N bonds become slightly weaker ($\Delta\text{WBI} \approx -0.07$), but they are still similar to each other. In the case of the complexation ligand **2** leads to more substantial changes around the Sb: the Sb–N_{amino} bond gets somewhat stronger ($\Delta\text{WBI} \approx 0.10$) while, the Sb–N_{imino} bonds significantly weaken ($\Delta\text{WBI} \approx -0.22$) compared to the free ligand. Altogether the differences between the donor properties of the imino- and amino- groups become less remarkable in comparison with starting **2**.

These observations led us to the conclusion that the coordination of the Sb centres toward a metal has a different impact on the two types of Sb–N bonds, because the Sb centres are Lewis bases toward the metals, but at the same time, they also behave as acceptors to the lone pairs of the N donors. Furthermore, the sum of WBI values around the Sb centres (natural valences) are highly similar in the different complexes ($\Sigma\text{WBI} = 1.95$ to 2.06) regardless of the nature of the metal or the type of ligand, and these values are also comparable with those of the free ligands ($\Sigma\text{WBI} = 1.82$ and 1.75 for **1** and **2**, respectively). This “conservation” of valences indicates that the appearance of the Sb–M interaction in the complexes strongly affects the covalency of the Sb–N bonds, and therefore, the cumulative strength of the latter needs to decrease (albeit the amino- and imino- donors behave differently). Note that, similar effects have previously been reported for bismuth complexes with chelating ligands.^[18] Furthermore, similar observations can be made for the cationic complexes as well, but the cationic complexes feature even more similar WBIs for the amino- and imino- dative bonds compared to the neutral counterparts.

The marked difference between the complexes **3Pd/Pt** and **4Pd/Pt** (containing ligands **1** and **2**, respectively) is the absence or presence of NH...Cl weak interactions, respectively. To shed more light on this point, the atoms-in-molecule analysis of the electron density was examined and revealed bond critical points (see Figure S32–S35) between the relevant Cl and H centres, in complexes **4Pd/Pt** with electron densities indicating secondary van der Waals interactions ($\rho = 0.157$ and $0.156 \text{ e} \text{ \AA}^{-3}$, respectively). Due to the symmetry in the complexes, the two H-bonds are practically equal and independent of the metal. The rotation along the $\text{C}_{\text{ipso}}\text{--Sb--Sb--C}_{\text{ipso}}$ torsion angle of complex **4Pd** results in a rotamer **4Pd'** (minimum on the potential energy surface, Figure S29), in which both NH...Cl interactions are cleaved completely, lying 7.0 kcal/mol higher in energy. A similar rotamer **4Pt'** can be found for complex **4Pt** (Figure S30). As might be expected even complexes of ligand **1**, *i.e.* **3Pd/Pt**, cations **5Pd**⁺ and the hypothetical (non-isolated) **5Pt**⁺ are able to form rotamers as illustrated in Figures S28 and S31, but in this case no H-bonds are present. All these findings support our conclusions that various isomers are formed for these compounds in solution as suggested by NMR spectroscopy above. Nevertheless, the bulkiness and high conformation flexibility of ligands **1** and **2** did not allowed us to definitely distinguish between possible rotamers for the particular complexes.

Another remarkable feature of studied complexes is their intense colouring obtained in solution ranging from green-blue to dark blue (see ESI, Table 2 and further discussion). This finding contrasts with Pd(II) and Pt(II) stibinidene complexes reported by us^[10,12] previously, that revealed yellow to orange colour, which is also usually obtained for other structurally characterized Pd(II) and Pt(II) chloro- complexes bearing two triorganostibines in their coordination spheres.^[15,19] The ionic blue complex $[\text{Pd}(\eta^5\text{-Cp})(\kappa^1\text{-Ph}_3\text{Sb})_2][\text{PF}_6]$ constitutes a remarkable exception in this regard.^[16a]

To shed more light on their optical properties, all isolated complexes containing either ligand **1** (*i.e.* **3Pd/Pt**, **5Pd**) or **2** (*i.e.*

Table 2. Experimental and calculated spectral data for neutral and cationic complexes ^[a]				
λ_{max} [nm]	3Pd	3Pt	4Pd	4Pt
Experimental	662	580	705	617
Calculated	656	595	695	637
	5Pd ^[b]	5Pt ^[b]	6Pd ^[b]	6Pt ^[b]
Experimental	645	n. a. ^[c]	671	571
Calculated	645	575	661	600

[a] Absorption wavelength (λ_{max} , dichloromethane), [b] The calculated values of complexes 5Pd/Pt and 6Pd/Pt correspond to the cationic species 5Pd⁺, 5Pt⁺, 6Pd⁺ and 6Pt⁺, [c] Not isolated.

4Pd/Pt and 6Pd/Pt) were studied by UV-vis spectroscopy (Figures S29, S30, Table 2). In order to bolster the experimental observations and understand the nature of the electronic excitations, TD-DFT calculations including 30 excitations were performed with four different functionals: ω B97XD, M06-2X, B3LYP and CAM-B3LYP at different equilibrium geometries (see Table 2 and for further results Table S12). Since the experimental spectra were obtained in a dichloromethane solution, a PCM model with the same solvent was applied. The values of the maximum absorption wavelengths corresponding to the first excitations ($S_1 \leftarrow S_0$), which strongly impact the colours of complexes, are shown in Table 2. The TD-B3LYP/def2-TZVP//B3LYP/def2-SVP level of theory has the lowest deviation from the experimental data, see Figures 5 and 6 (as well as Figures S36–S42), for other methods see Table S12.

On the basis of the experimental and calculated data, the λ_{max} values markedly depend on the type of the ligand. The complexes with ligand 1 exhibit blue-shifted absorption with respect to the analogues containing ligand 2. Moreover, the platinum complexes also show blueshift compared to the corresponding palladium complexes. Therefore, a general trend of λ_{max} values follows the order: 3Pt < 4Pt < 3Pd < 4Pd. Furthermore, the maximum absorption wavelengths of the cations are

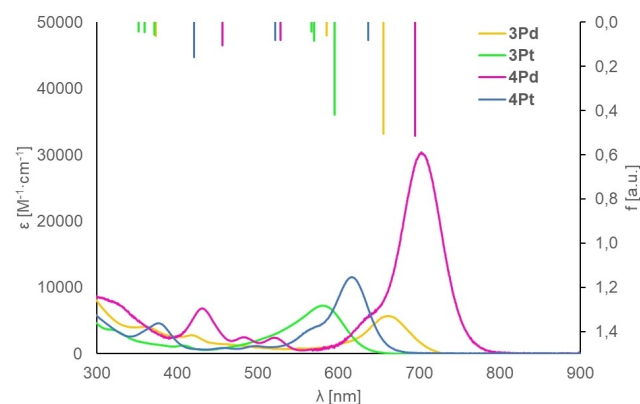


Figure 5. Experimental UV-Vis spectra of 3Pd/Pt and 4Pd/Pt, the lines above denote the calculated oscillator strengths of the corresponding compounds (from the 30 calculated excitations only those exceeding $f = 0.04$ a.u. are plotted for clarity).

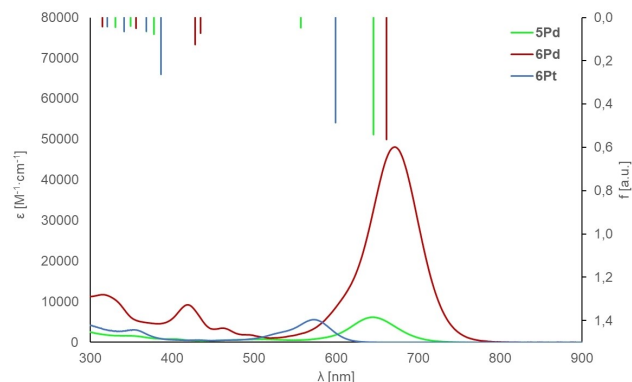


Figure 6. Experimental UV-Vis spectra of 5Pd and 6Pd/Pt, the lines above denote the calculated oscillator strengths of the corresponding compounds (5Pd⁺ and 6Pd⁺/Pt⁺ (from the 30 calculated excitations only those exceeding $f = 0.04$ a.u. are plotted for clarity)).

typically 20–40 nm smaller, than observed for the neutral counterparts, again leading to a blueshift.

According to the TD-DFT results, the lowest energy excitations correspond to pure HOMO→LUMO transitions in all of these cases, both for the neutral and cationic complexes (the only exception is complex 3Pt, which will be discussed separately below). Thus, these excitation processes can be well interpreted with the help of frontier molecular orbitals (FMOs). To decipher and explain the excitations, the relative energies of selected molecular (Kohn-Sham) orbitals are presented in Figure 7 and Figure 8. In addition to a visual assessment, Mulliken

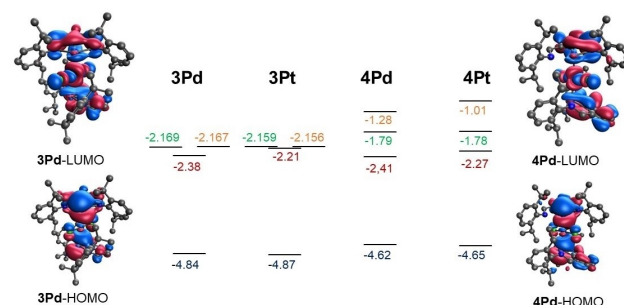


Figure 7. Energy diagram (in eV) of frontier molecular orbitals of 3Pd/Pt and 4Pd/Pt. (Blue, red, green, and yellow colours denote the HOMO, LUMO, LUMO+1 and LUMO+2 orbitals, respectively.)

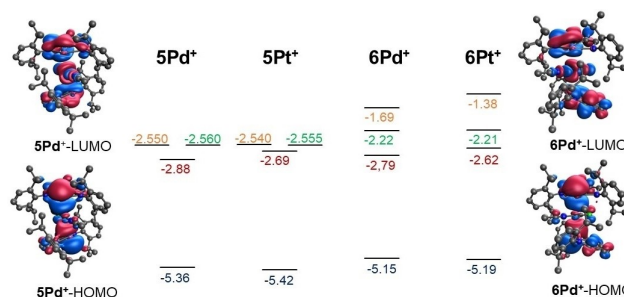


Figure 8. Energy diagram (in eV) of frontier molecular orbitals of 5Pd⁺, 5Pt⁺, 6Pd⁺ and 6Pt⁺. (Blue, red, green, and yellow colours denote the HOMO, LUMO, LUMO+1 and LUMO+2 orbitals, respectively.)

atomic decomposition of the frontier molecular orbitals were also determined.

First, we discuss the FMOs of the neutral complexes with the bis(imino)- and imino-amino- ligands. In general, the appearances of the orbitals show negligible variations upon the metal, and for simplicity the two prototype Pd-containing complexes are compared. The HOMOs in complexes **3/4Pd** are ligand-centred and are composed mainly from the p_z -type orbital of antimony and π -contributions at the backbone. In contrast, the LUMOs are composed of the σ^* orbitals at the PdCl_2 moiety involving the d-orbital of Pd and the π -system of the ligand, located on the central phenyl moieties. Similar statements can be obtained for the Pt complexes **3/4Pt** and also for the cationic analogues (**5Pd**⁺, **5Pt**⁺, **6Pd**⁺ and **6Pt**⁺, respectively).

Altogether, the HOMO-LUMO gaps ($\Delta\epsilon(\text{H-L})$) show a good agreement with the experimental results (Figures 5 and 6 and Tables S13 and S14), that is, the sequence of HOMO-LUMO gaps follow the reversed trend of λ_{max} values. In general, complexes with ligand 1, exhibit a blue shift compared to the corresponding complexes with ligand 2, both in neutral and cationic forms and this observation can be explained by the $\Delta\epsilon(\text{H-L})$ values. As the HOMOs are ligand centred, their energies depend on the type of the ligand. Indeed, the HOMOs with the ligand 1 lie lower at energy (−4.84 and −4.87 eV for **3Pd/Pt**) than those with ligand 2 (−4.62 and −4.65 eV for **4Pd/Pt**) and in both cases these energies are practically independent of the metal. However, as the LUMOs have significant contributions at the metal fragments, their energies for a given metal are nearly identical (e.g. −2.38 and −2.41 eV for **3/4Pd**; −2.21 and −2.27 eV for **3/4Pt** respectively), independent of the ligand type (1 or 2). Therefore, the complexes with ligand 1 have larger HOMO-LUMO gaps, and consequently blue-shifted absorption compared to those with ligand 2. Importantly, the LUMO energies of the Pd-containing complexes are lower than those containing Pt, since Pt has higher energy orbitals with higher principal quantum number. Thus, the Pt-containing complexes **3/4Pt** have larger HOMO-LUMO gaps compared to the corresponding ones with Pd, leading again to a blueshift.

The energies of the frontier orbitals in the cationic complexes deepen significantly compared to the corresponding neutral complexes. This energy lowering, however, is different for the HOMO and LUMO orbitals. To explain the trend, we discuss the most significant blueshift in the absorption of $\Delta\lambda_{\text{max}}=46$ nm, which is obtained between complexes **4Pt** and **6Pt** (note that the difference between these complexes is that a chloride is replaced by an acetonitrile molecule). The HOMO of **6Pt**⁺ lies 0.54 eV lower in energy compared to complex **4Pt**. In contrast, the LUMO energies are less different, the cationic complex **6Pt**⁺ exhibits only 0.35 eV lower LUMO than the neutral **4Pt**. Therefore, the HOMO-LUMO gap of complex **6Pt**⁺ is significantly larger ($\Delta\epsilon(\text{H-L})=2.57$ eV) compared to complex **4Pt** ($\Delta\epsilon(\text{H-L})=2.38$ eV). This difference in the HOMO-LUMO gaps results in a blueshift for the cationic species compared to the neutral analogues, but the $\Delta\epsilon(\text{H-L})$ values of the cations follow the same trends as observed for the neutral counterparts.

The unusual case of Pt-complex **3Pt** deserves further explanation, because the $S_1\leftarrow S_0$ excitations of this species is not a HOMO→LUMO transition. In this case, the TD-DFT calculations deliver three excitations that can be found in a relatively narrow regime (~13 nm): The first and second lowest energy excitation are the HOMO→LUMO+1 ($\lambda_{\text{max}}=573$ nm, $f=0.0182$), and the HOMO→LUMO+2 transitions ($\lambda_{\text{max}}=571$ nm, $f=0.0500$) having very low oscillator strengths. The third excitation at $\lambda_{\text{max}}=560$ nm, which is mainly a HOMO→LUMO (73.5%) transition with a minor contribution of a HOMO-1→LUMO (23.4%) transition, has a remarkable oscillator strength of 0.337. This unique situation can be explained by the resemblance of orbital energies shown in Figure 7. For complex **3Pt** the energy differences between the LUMO, LUMO+1 and LUMO+2 orbitals are negligible, approximately 0.05 eV. Thus, three excitations arise at similar wavelengths, and the difference of 13 nm between them is practically within the error of TD-DFT methods. In contrast to complex **3Pt**, in the cases of the neutral Pd-analogue **3Pd** or the cationic counterpart **5Pt**⁺, the energy differences between the LUMO and the LUMO+1 orbitals are much larger, 0.14 eV and 0.19 eV, respectively. Hence, complexes **3Pd** and **5Pt**⁺ does not exhibit near-lying HOMO-LUMO+1 excitations, and the $S_1\leftarrow S_0$ excitations are pure HOMO→LUMO transitions.

Conclusions

We have prepared a set of bis(stibinidene) palladium(II) or platinum(II) complexes bearing two types of antimony(I) donor ligands that differ by the presence/absence of a pendant $-\text{CH}_2\text{NH}-$ function in the structure of N,C,N -pincer ligand used. The stibinidene containing this amino- function was used for the first time in coordination chemistry in this study. Albeit all complexes adopt expected distorted square planar geometries at the metal centers, the influence of the NH-moiety becomes obvious as it forms intramolecular $\text{NH}\cdots\text{Cl}$ hydrogen bond(s). These contacts influence the mutual orientation of both stibinidene ligands in the structure of the complexes. Additionally, the two different ligands undergo structural changes upon complexation in comparison with the free forms. The optical properties of the complexes were investigated by combined experimental (UV-vis) – theoretical (TD-DFT) techniques and allowed us to in detail describe their orbital structure. These results outline that the unusual colours of these complexes are tuned by the type of the ligand (bis(imino) or amino/imino), the nature of metal and the charges of the complexes.

We have thus recognized the potential of the stibinidene ligand armed with the $-\text{CH}_2\text{NH}-$ function to influence the structure of the resulting complexes by possible formation of H-bonds. Therefore, our next effort will be devoted to an extension of this approach to other transition metals. We will also examine the potential of $-\text{CH}_2\text{NH}-$ group for attachment of harder Lewis acids by its deprotonation.

Experimental Section

Materials and methods: Standard Schlenk technique using argon as an inert gas was applied for all synthesis. Solvents were dried using a MD7 Pure Solv instrument (Innovative Technology, MA, USA), degassed and stored in Young-valve containers. Deuterated solvents were dried by standard procedures and stored in the Young-valve containers. Starting compounds **1** and **2**^[13] were synthesized according to the literature. Other chemicals were purchased from commercial companies and used as delivered. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker 500 MHz spectrometer, using 5 mm cryoprobe Prodigy. Chemical shifts in the ¹H and ¹³C{¹H} NMR spectra were referenced to the residual solvent signals (C₆D₆: δ(¹H)=7.16 ppm, δ(¹³C)=128.39 ppm, CDCl₃: δ(¹H)=7.27 ppm, δ(¹³C)=77.23 ppm, acetonitrile-d₃: δ(¹H)=1.94 ppm, δ(¹³C)=1.39 ppm). The values for particular integrals in ¹H NMR spectra in the case of compounds **3Pd/Pt**, **4Pd/Pt** and **5Pd** are not listed in the synthetic protocols below, because it might be confusing as all compounds contain two isomers with many overlapping signals. All spectra including integrals can be found in SI. Infrared (single-bounce diamond ATR) and Raman (vacuum-sealed capillary, excitation laser 1064 nm) spectra were recorded on a Nicolet iS50 FTIR spectrometer equipped with an iS50 Raman module. Solution IR spectra of **4Pd/Pt** and **6Pt** were measured in 110 μm KBr cuvette. We note that Raman spectrum of **6Pd** was not obtained due to sample decomposition under laser irradiation. Electronic absorption spectra (CH₂Cl₂ solutions, 230–1100 nm) were run on Maya 2000Pro concave grating spectrometer using transmission dip probes with optical path 2.5 and 10 mm, respectively.

Synthesis of 3Pd: 265 mg (0.46 mmol) of **1** was dissolved in thf (10 mL) and 60 mg (0.23 mmol) of solid [PdCl₂(CH₃CN)₂] was added to this solution. It was stirred for 1 h at room temperature and the solution turned to dark blue. Then, it was evaporated and extracted with benzene (10 mL). The dark blue extract was concentrated to ca 1/2 of the original volume. Following storage of this mixture at 5 °C provided crystalline material with metallic lustre of **3Pd**, that was collected by decantation and dried *in vacuo*. Yield 195 mg, 64%, m.p. 148 °C (dec.). ¹H NMR (400 MHz, CDCl₃): δ 0.35 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.69 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.75 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.93 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.01 [d, ³J_{H,H}=6.8 Hz, *iPr*-CH₃]; 1.03 [d, ³J_{H,H}=6.8 Hz, *iPr*-CH₃]; 1.18 [d, ³J_{H,H}=6.8 Hz, *iPr*-CH₃]; 3.00 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.13 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.19 [h, ³J_{H,H}=6.8 Hz, *iPr*-CH]; 6.99 [d, ³J_{H,H}=7.7 Hz, *Ar*-H]; 7.03 [d, ³J_{H,H}=7.4 Hz, *Ar*-H]; 7.10 [t, ³J_{H,H}=7.7 Hz, *Ar*-H]; 7.14 [m, *Ar*-H]; 7.20 [t, ³J_{H,H}=7.5 Hz, *Ar*-H]; 7.60 [t, ³J_{H,H}=7.4 Hz, *Ar*-H]; 7.92 [d, ³J_{H,H}=7.5 Hz, *Ar*-H]; 7.98 [d, ³J_{H,H}=7.4 Hz, *Ar*-H]; 8.65 [s, CH=N]; 8.75 [overlap of two signals, CH=N] ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 22.6 [*iPr*-CH₃]; 24.0 [*iPr*-CH₃]; 24.8 [*iPr*-CH₃]; 24.9 [*iPr*-CH₃]; 25.5 [*iPr*-CH₃]; 25.8 [*iPr*-CH₃]; 26.3 [*iPr*-CH₃]; 26.8 [*iPr*-CH]; 27.5 [*iPr*-CH₃]; 28.5 [*iPr*-CH]; 28.6 [*iPr*-CH]; 28.8 [*iPr*-CH]; 122.9 [Ar-C]; 123.4 [Ar-C]; 123.8 [Ar-C]; 125.0 [Ar-C]; 125.6 [Ar-C]; 126.5 [Ar-C]; 126.6 [Ar-C]; 133.0 [Ar-C]; 133.4 [Ar-C]; 138.3 [Ar-C]; 140.3 [Ar-C]; 140.6 [Ar-C]; 140.8 [Ar-C]; 141.6 [Ar-C]; 143.8 [Ar-C]; 143.9 [Ar-C]; 163.3 [CH=N]; 164.8 [CH=N]; 171.8 [Ar-C] ppm.

Synthesis of 3Pt: 152 mg (0.26 mmol) of **1** was dissolved in thf (10 mL) and 35 mg (0.13 mmol) of solid PtCl₂ was added to this solution. It was stirred for 1 h at room temperature and the solution turned to dark purple. Then, it was evaporated and extracted with benzene (10 mL). The dark purple extract was concentrated to ca 1/2 of the original volume and layer by hexane. Following storage of this mixture at 5 °C provided crystalline material with metallic lustre of **3Pt**, that was collected by decantation and dried *in vacuo*. Yield 121 mg, 65%, m.p. 246 °C (dec.). ¹H NMR (400 MHz, CDCl₃): δ 0.36 [d, ³J_{H,H}=6.6 Hz, *iPr*-CH₃]; 0.67 [d, ³J_{H,H}=6.6 Hz, *iPr*-CH₃]; 0.72 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.93 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.02 [m, *iPr*-CH₃]; 1.18 [m, *iPr*-CH₃]; 3.00 [h, ³J_{H,H}=6.7 Hz,

iPr-CH]; 3.20 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.31 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 6.98 [d, ³J_{H,H}=7.7 Hz, *Ar*-H]; 7.02 [d, ³J_{H,H}=7.4 Hz, *Ar*-H]; 7.08–7.15 [m, *Ar*-H]; 7.20 [t, ³J_{H,H}=7.4 Hz, *Ar*-H]; 7.60 [t, ³J_{H,H}=7.4 Hz, *Ar*-H]; 7.92 [d, ³J_{H,H}=7.4 Hz, *Ar*-H]; 7.95 [d, ³J_{H,H}=7.4 Hz, *Ar*-H]; 8.65 [s, CH=N]; 8.70 [s, CH=N] ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 22.4 [*iPr*-CH₃]; 23.9 [*iPr*-CH₃]; 24.7 [*iPr*-CH₃]; 24.9 [*iPr*-CH₃]; 25.4 [*iPr*-CH₃]; 25.5 [*iPr*-CH₃]; 26.2 [*iPr*-CH₃]; 26.8 [*iPr*-CH]; 27.5 [*iPr*-CH₃]; 28.0 [*iPr*-CH]; 28.6 [*iPr*-CH]; 28.8 [*iPr*-CH]; 122.8 [Ar-C]; 123.3 [Ar-C]; 123.7 [Ar-C]; 125.0 [Ar-C]; 125.8 [Ar-C]; 126.4 [Ar-C]; 126.6 [Ar-C]; 132.5 [Ar-C]; 133.4 [Ar-C]; 138.5 [Ar-C]; 140.6 [Ar-C]; 140.7 [Ar-C]; 140.8 [Ar-C]; 141.5 [Ar-C]; 141.6 [Ar-C]; 143.9 [Ar-C]; 144.0 [Ar-C]; 163.2 [CH=N]; 165.3 [CH=N]; 170.8 [Ar-C] ppm.

Synthesis of 4Pd: 263 mg (0.46 mmol) of **2** was dissolved in thf (10 mL) and 59 mg (0.23 mmol) of solid [PdCl₂(CH₃CN)₂] was added to this solution. It was stirred for 1 h at room temperature and the solution turned to dark green. Then, it was evaporated and extracted with benzene (10 mL). The dark green extract was concentrated to ca 1/2 of the original volume. Following storage of this mixture at 5 °C provided crystalline material with metallic lustre of **4Pd**, that was collected by decantation and dried *in vacuo*. Yield 220 mg, 72%, m.p. 139 °C (dec.). ¹H NMR (500 MHz, C₆D₆): δ 0.73 [s(br), *iPr*-CH₃]; 0.82 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.95 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.04 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.08 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.12 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.16 [s(br), *iPr*-CH₃]; 1.23 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.37 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.45 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 3.05 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.29 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.37 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.44 [s(br), *iPr*-CH]; 3.50 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.75 [s(br), *iPr*-CH]; 3.86 [s(br), *iPr*-CH]; 3.84, 4.77 and 7.51 [AMX pattern, NCH₂NH]; 4.05, 4.62 and 7.03 [AMX pattern, NCH₂NH]; 6.71 [d, ³J_{H,H}=7.6 Hz, *Ar*-H]; 6.86 [d, ³J_{H,H}=7.4 Hz, *Ar*-H]; 6.96 [m, *Ar*-H]; 7.00–7.15 [m, *Ar*-H]; 7.38 [d, ³J_{H,H}=7.6 Hz, *Ar*-H]; 7.42 [d, ³J_{H,H}=7.5 Hz, *Ar*-H]; 8.35 [s, CH=N]; 8.40 [s, CH=N] ppm. ¹³C{¹H} NMR (125.76 MHz, C₆D₆): δ 23.1 [*iPr*-CH₃]; 24.0 [*iPr*-CH₃]; 24.7 [*iPr*-CH₃]; 25.1 [*iPr*-CH₃]; 25.5 [*iPr*-CH₃]; 25.6 [*iPr*-CH₃]; 25.9 [*iPr*-CH₃]; 28.0 [*iPr*-CH₃]; 28.3 [*iPr*-CH₃]; 28.6 [*iPr*-CH₃]; 29.0 [*iPr*-CH]; 29.1 [*iPr*-CH]; 29.2 [*iPr*-CH]; 29.3 [*iPr*-CH]; 29.4 [*iPr*-CH]; 57.8 [NCH₂]; 58.6 [NCH₂]; 123.5 [Ar-C]; 123.6 [Ar-C]; 124.5 [Ar-C]; 124.6 [Ar-C]; 125.3 [Ar-C]; 125.6 [Ar-C]; 126.3 [Ar-C]; 126.5 [Ar-C]; 126.6 [Ar-C]; 127.7 [Ar-C]; 127.9 [Ar-C]; 128.9 [Ar-C]; 131.1 [Ar-C]; 131.8 [Ar-C]; 139.2 [Ar-C]; 139.5 [Ar-C]; 140.9 [Ar-C]; 141.6 [Ar-C]; 141.6 [Ar-C]; 142.4 [Ar-C]; 142.7 [Ar-C]; 142.8 [Ar-C]; 143.9 [Ar-C]; 144.2 [Ar-C]; 144.5 [Ar-C]; 146.3 [Ar-C]; 147.4 [Ar-C]; 164.6 [Ar-C]; 164.8 [CH=N]; 165.5 [CH=N]; 165.8 [Ar-C] ppm. IR (solid, cm⁻¹): 3211 m-br, 3188 m-br (ν_{NH}). IR (THF, cm⁻¹): 3216 m-br.

Synthesis of 4Pt: 108 mg (0.19 mmol) of **2** was dissolved in thf (10 mL) and 25 mg (0.09 mmol) of solid PtCl₂ was added to this solution. It was stirred for 1 h at room temperature and the solution turned to dark blue. Then, it was evaporated and extracted with benzene (10 mL). The dark green extract was concentrated to ca 1/2 of the original volume and layered with hexane. Following storage of this mixture at 5 °C provided crystalline material with metallic lustre of **4Pt**, that was collected by decantation and dried *in vacuo*. Yield 77 mg, 58%, m.p. 220–226 °C. ¹H NMR (500 MHz, C₆D₆): δ 0.75 [s(br), *iPr*-CH₃]; 0.82 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.94 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 0.97 [s(br), *iPr*-CH₃]; 1.05 [m, *iPr*-CH₃]; 1.13 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.15 [s(br), *iPr*-CH₃]; 1.23 [d, ³J_{H,H}=6.7 Hz, *iPr*-CH₃]; 1.32 [s(br), *iPr*-CH₃]; 1.36 [d, ³J_{H,H}=6.8 Hz, *iPr*-CH₃]; 1.45 [m, *iPr*-CH₃]; 3.19 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.37 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.51 [h, ³J_{H,H}=6.7 Hz, *iPr*-CH]; 3.76 [s(br), *iPr*-CH]; 3.85 [s(br), *iPr*-CH]; 3.95, 4.69 and 7.45 [AMX pattern, NCH₂NH]; 4.09, 4.58 and 7.03 [AMX pattern, NCH₂NH]; 6.72 [d, ³J_{H,H}=7.5 Hz, *Ar*-H]; 6.87 [d, ³J_{H,H}=7.5 Hz, *Ar*-H]; 6.95 [m, *Ar*-H]; 6.99–7.12 [m, *Ar*-H]; 7.38 [d, ³J_{H,H}=7.8 Hz, *Ar*-H]; 7.42 [d, ³J_{H,H}=7.8 Hz, *Ar*-H]; 8.26 [s, CH=N]; 8.31 [s, CH=N] ppm. ¹³C{¹H} NMR (125.76 MHz, C₆D₆): δ 22.8 [*iPr*-CH₃]; 23.7 [*iPr*-CH₃]; 24.7 [*iPr*-CH₃]; 25.0 [*iPr*-CH₃]; 25.2

[*i*Pr-CH₃]; 25.5 [*i*Pr-CH₃]; 25.7 [*i*Pr-CH₃]; 25.9 [*i*Pr-CH₃]; 28.1 [*i*Pr-CH₃]; 28.5 [*i*Pr-CH₃]; 28.6 [*i*Pr-CH₃]; 28.7 [*i*Pr-CH₃]; 28.8 [*i*Pr-CH₃]; 29.3 [*i*Pr-CH₃]; 29.5 [*i*Pr-CH₃]; 58.1 [NCH₂]; 59.1 [NCH₂]; 123.5 [Ar-C]; 123.6 [Ar-C]; 124.4 [Ar-C]; 124.7 [Ar-C]; 125.3 [Ar-C]; 125.4 [Ar-C]; 125.6 [Ar-C]; 126.0 [Ar-C]; 126.4 [Ar-C]; 126.6 [Ar-C]; 126.7 [Ar-C]; 127.7 [Ar-C]; 127.8 [Ar-C]; 128.9 [Ar-C]; 131.1 [Ar-C]; 131.8 [Ar-C]; 139.4 [Ar-C]; 139.7 [Ar-C]; 140.8 [Ar-C]; 141.5 [Ar-C]; 141.6 [Ar-C]; 142.3 [Ar-C]; 142.6 [Ar-C]; 142.7 [Ar-C]; 144.0 [Ar-C]; 144.3 [Ar-C]; 144.5 [Ar-C]; 146.4 [Ar-C]; 147.4 [Ar-C]; 162.7 [Ar-C]; 164.1 [Ar-C]; 165.2 [CH=N]; 165.8 [CH=N] ppm. IR (solid, cm⁻¹): 3222 m-br, 3199 m-br (ν_{NH}). IR (THF or benzene, cm⁻¹): 3226 m-br. IR (CH₂Cl₂, cm⁻¹): 3230 m-br.

Synthesis of 5Pd: 47 mg (0.18 mmol) of [PdCl₂(CH₃CN)₂] and 35 mg (0.18 mmol) of Ag[BF₄] was mixed and dissolved in acetonitrile (5 mL). The reaction mixture was stirred for 4 h at 50 °C and solid AgCl precipitated. Afterwards, this suspension was filtered and the filtrate was directly added into thf (10 mL) solution of 208 mg (0.36 mmol) of **1**. Stirring of this mixture for 1 h at room temperature was accompanied by a colour change to dark blue. Then, it was filtrated and concentrated to minimum and layered by Et₂O. Storage of this mixture at -30 °C provided crystalline material with metallic lustre of **5Pd**, that was collected by decantation and dried in vacuo. Yield 138 mg, 54%, m.p. 170 °C (dec). ¹H NMR (500 MHz, CDCl₃): δ 0.20 [d, ³J_{H,H}=6.6 Hz, *i*Pr-CH₃]; 0.38 [d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 0.56 [d, ³J_{H,H}=6.6 Hz, *i*Pr-CH₃]; 0.61 [d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 0.76 [d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 0.83 [d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 0.96 [m, *i*Pr-CH₃]; 1.01 [m, *i*Pr-CH₃]; 1.06 [d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 1.18 [m, *i*Pr-CH₃]; 2.41 [h, ³J_{H,H}=6.7 Hz, *i*Pr-CH]; 2.79 [1H, h, ³J_{H,H}=6.7 Hz, *i*Pr-CH]; 2.85–3.08 [m, *i*Pr-CH]; 6.98 [d, ³J_{H,H}=7.6 Hz, Ar-H]; 7.06 [d, ³J_{H,H}=7.7 Hz, Ar-H]; 7.11 [d, ³J_{H,H}=7.7 Hz, Ar-H]; 7.12–7.22 [m, Ar-H]; 7.25–7.29 [m, Ar-H]; 7.78 [t, ³J_{H,H}=7.6 Hz, Ar-H]; 7.84 [t, ³J_{H,H}=7.6 Hz, Ar-H]; 8.10 [m, Ar-H]; 8.17 [d, ³J_{H,H}=7.6 Hz, Ar-H]; 8.46 [d, ³J_{H,H}=7.6 Hz, Ar-H]; 8.82 [s, CH=N]; 8.83 [s, CH=N]; 8.85 [s, CH=N]; 8.99 [s, CH=N] ppm. ¹³C{¹H} NMR (125.76 MHz, CDCl₃): δ 0.83 [CH₃CN-coord]; 22.5 [*i*Pr-CH₃]; 23.6 [*i*Pr-CH₃]; 23.9 [*i*Pr-CH₃]; 24.0 [*i*Pr-CH₃]; 24.6 [*i*Pr-CH₃]; 24.7 [*i*Pr-CH₃]; 24.8 [*i*Pr-CH₃]; 25.2 [*i*Pr-CH₃]; 25.3 [*i*Pr-CH₃]; 25.4 [*i*Pr-CH₃]; 25.5 [*i*Pr-CH₃]; 26.1 [*i*Pr-CH₃]; 26.8 [*i*Pr-CH₃]; 27.2 [*i*Pr-CH₃]; 27.7 [*i*Pr-CH]; 28.4 [*i*Pr-CH]; 28.8 [*i*Pr-CH]; 28.9 [*i*Pr-CH]; 29.1 [*i*Pr-CH]; 29.2 [*i*Pr-CH]; 123.4 [Ar-C]; 123.9 [Ar-C]; 124.2 [Ar-C]; 124.3 [Ar-C]; 124.5 [Ar-C]; 124.6 [Ar-C]; 125.1 [Ar-C]; 126.9 [CH₃CN]; 127.3 [Ar-C]; 127.4 [Ar-C]; 127.6 [Ar-C]; 127.8 [Ar-C]; 128.0 [Ar-C]; 128.2 [Ar-C]; 134.5 [Ar-C]; 134.8 [Ar-C]; 134.9 [Ar-C]; 135.6 [Ar-C]; 137.8 [Ar-C]; 138.5 [Ar-C]; 138.7 [Ar-C]; 139.4 [Ar-C]; 140.0 [Ar-C]; 140.4 [Ar-C]; 140.7 [Ar-C]; 140.9 [Ar-C]; 141.1 [Ar-C]; 141.4 [Ar-C]; 141.4 [Ar-C]; 141.5 [Ar-C]; 142.2 [Ar-C]; 142.6 [Ar-C]; 142.7 [Ar-C]; 143.1 [Ar-C]; 164.2 [CH=N]; 164.7 [CH=N]; 166.1 [Ar-C]; 166.6 [CH=N]; 166.9 [Ar-C]; 167.1 [CH=N] ppm. ¹¹B{¹H} NMR (160.5 MHz, CDCl₃): -1.36 ppm.

Synthesis of 6Pd: 53 mg (0.21 mmol) of [PdCl₂(CH₃CN)₂] and 40 mg (0.21 mmol) of Ag[BF₄] was mixed and dissolved in acetonitrile (5 mL). The reaction mixture was stirred for 4 h at 50 °C and solid AgCl precipitated. Then, this suspension was filtered and the filtrate was directly added into thf (10 mL) solution of 237 mg (0.41 mmol) of **2**. Stirring of this mixture for 1 h at room temperature was accompanied by a colour change to dark blue-green. Then, it was filtrated and concentrated to minimum and layered by Et₂O. Storage of this mixture at -30 °C provided crystalline material with metallic lustre of **6Pd**, that was collected by decantation and dried in vacuo. Yield 173 mg, 58%, m.p. 176 °C (dec). ¹H NMR (500 MHz, CDCl₃): δ 0.40 [6H, d, ³J_{H,H}=6.6 Hz, *i*Pr-CH₃]; 0.52 [6H, d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 0.75 [3H, s, CH₃CN]; 0.84 [6H, d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 1.09 [12H, d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 1.15 [12H, m, *i*Pr-CH₃]; 1.19 [6H, d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 2.80 [1H, h, ³J_{H,H}=6.7 Hz, *i*Pr-CH]; 2.89 [1H, h, ³J_{H,H}=6.7 Hz, *i*Pr-CH]; 3.09 [1H, h, ³J_{H,H}=6.8 Hz, *i*Pr-CH];

3.45 [1H, h, ³J_{H,H}=6.8 Hz, *i*Pr-CH]; 4.07, 4.71 and 6.73 [3H, AMX pattern, NCH₂NH]; 7.06 [2H, d, ³J_{H,H}=8.0 Hz, Ar-H]; 7.08 [2H, d, ³J_{H,H}=7.7 Hz, Ar-H]; 7.15 [2H, d, ³J_{H,H}=7.7 Hz, Ar-H]; 7.21 [4H, m, Ar-H]; 7.30 [2H, t, ³J_{H,H}=7.7 Hz, Ar-H]; 7.40 [2H, d, ³J_{H,H}=7.6 Hz, Ar-H]; 7.59 [2H, d, ³J_{H,H}=7.6 Hz, Ar-H]; 7.95 [2H, d, ³J_{H,H}=7.6 Hz, Ar-H]; 8.69 [2H, s, CH=N] ppm. ¹³C{¹H} NMR (125.76 MHz, CDCl₃): δ 0.78 [CH₃CN]; 23.5 [*i*Pr-CH₃]; 24.3 [*i*Pr-CH₃]; 24.6 [*i*Pr-CH₃]; 25.2 [*i*Pr-CH₃]; 25.3 [*i*Pr-CH₃]; 25.4 [*i*Pr-CH₃]; 27.3 [*i*Pr-CH₃]; 28.2 [*i*Pr-CH]; 28.4 [*i*Pr-CH]; 28.9 [*i*Pr-CH]; 29.1 [*i*Pr-CH]; 56.5 [NCH₂]; 124.4 [Ar-C]; 124.5 [Ar-C]; 124.9 [Ar-C]; 126.0 [Ar-C]; 126.6 [Ar-C]; 128.1 [Ar-C]; 128.6 [CH₃CN]; 128.8 [Ar-C]; 133.3 [Ar-C]; 138.0 [Ar-C]; 138.5 [Ar-C]; 141.2 [Ar-C]; 141.7 [Ar-C]; 142.1 [Ar-C]; 142.8 [Ar-C]; 143.4 [Ar-C]; 145.2 [Ar-C]; 158.5 [Ar-C]; 165.9 [CH=N] ppm. ¹¹B{¹H} NMR (160.5 MHz, CDCl₃): -1.6 ppm. IR (solid, cm⁻¹): 3206 m-br (ν_{NH}), 2323w, 2285w (ν_{C≡N}), 1053vs (ν_{BF}). Raman (cm⁻¹): 2291w (ν_{C≡N}), 1034 s (ν_{BF}).

Synthesis of 6Pt: 49 mg (0.18 mmol) of PtCl₂ was suspended in acetonitrile (5 mL) and this suspension was stirred overnight. This was followed by filtration into CH₃CN (5 mL) solution of 36 mg (0.18 mmol) Ag[BF₄]. The reaction mixture was stirred for 4 h at 50 °C and simultaneously solid AgCl was precipitated. Afterwards, the solution was filtrated into thf (10 mL) solution of 213 mg (0.37 mmol) of **2**. Stirring of this mixture for 1 h at room temperature was accompanied by a colour change to dark blue-green. Then it was filtrated and concentrated to minimum and layered by Et₂O. Storage of this mixture at -30 °C provided crystalline material with metallic lustre of **6Pt**, that was collected by decantation and dried in vacuo. Yield 128 mg, 47%, m.p. 165 °C (dec.). ¹H NMR (500 MHz, CD₃CN): δ 0.49 [6H, d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 0.51 [6H, d, ³J_{H,H}=6.7 Hz, *i*Pr-CH₃]; 0.62 [3H, s, CH₃CN]; 0.82 [6H, d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 1.03 [12H, m, *i*Pr-CH₃]; 1.12 [6H, d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 1.14 [6H, d, ³J_{H,H}=6.8 Hz, *i*Pr-CH₃]; 1.20 [6H, d, ³J_{H,H}=6.6 Hz, *i*Pr-CH₃]; 2.86 [1H, h, ³J_{H,H}=6.7 Hz, *i*Pr-CH]; 2.97 [1H, h, ³J_{H,H}=6.7 Hz, *i*Pr-CH]; 3.12 [1H, h, ³J_{H,H}=6.8 Hz, *i*Pr-CH]; 3.44 [1H, h, ³J_{H,H}=6.8 Hz, *i*Pr-CH]; 4.15, 4.75 and 6.66 [3H, AMX pattern, NCH₂NH]; 7.13 [4H, m, Ar-H]; 7.20 [8H, m, Ar-H]; 7.45 [2H, d, ³J_{H,H}=7.6 Hz, Ar-H]; 7.59 [2H, t, ³J_{H,H}=7.6 Hz, Ar-H]; 8.04 [2H, d, ³J_{H,H}=7.6 Hz, Ar-H]; 8.75 [2H, s, CH=N] ppm. ¹³C{¹H} NMR (125.76 MHz, CD₃CN): δ 23.6 [*i*Pr-CH₃]; 24.6 [*i*Pr-CH₃]; 24.7 [*i*Pr-CH₃]; 24.8 [*i*Pr-CH₃]; 25.3 [*i*Pr-CH₃]; 25.5 [*i*Pr-CH₃]; 27.4 [*i*Pr-CH₃]; 28.7 [*i*Pr-CH]; 28.8 [*i*Pr-CH]; 29.7 [*i*Pr-CH]; 30.0 [*i*Pr-CH]; 57.5 [NCH₂]; 125.3 [Ar-C]; 125.4 [Ar-C]; 126.8 [Ar-C]; 127.4 [Ar-C]; 127.8 [Ar-C]; 128.9 [Ar-C]; 129.0 [Ar-C]; 133.3 [Ar-C]; 139.5 [Ar-C]; 139.7 [Ar-C]; 142.2 [Ar-C]; 142.8 [Ar-C]; 143.1 [Ar-C]; 143.5 [Ar-C]; 144.3 [Ar-C]; 146.3 [Ar-C]; 156.5 [Ar-C]; 168.3 [CH=N] ppm. IR (solid, cm⁻¹): 3220 m-br (ν_{NH}), 2324w, 2287w (ν_{C≡N}), 1054vs (ν_{BF}). Raman (cm⁻¹): 2292w (ν_{C≡N}), 1035 s (ν_{BF}). IR (THF, cm⁻¹): 3232 m-br.

DFT calculations: All the geometry optimizations were performed with the Gaussian 16 suite of programs.^[20] All structures were optimized using the B3LYP,^[21] B3LYP-D3,^[22] CAM-B3LYP,^[23] M06-2X^[24] and ωB97X-D^[25] functionals combined with the def2-SVP basis set.^[26,27,28] Each of the optimized structures were characterized by obtaining second derivatives to check whether the stationary point located is a minimum on the potential energy hypersurface (no imaginary frequencies were obtained). Using TD-DFT calculations the first 30 excitations were calculated. For charge transfer, WBI and NPA charges, NBO analysis was carried out with the NBO 5.9 program.^[29] The molecular orbitals were visualised using the IQmol 2.15.3. program.^[30] For the atoms-in-molecules analysis of the hydrogen bonds and Mulliken partition analysis of the frontier molecular orbitals the Multiwfn program was employed.^[31] The plotting of the UV-Vis spectra was performed with the GaussSum program.^[32]

Crystallography: The X-ray data for crystals of studied compounds were obtained at 150 K using Oxford Cryostream low-temperature

device with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K α radiation; $\lambda = 0.71073$ Å) microfocus X-ray (I μ S) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection. Obtained data were treated by XT-version 2019/1 and SHELXL-2019/1 software implemented in APEX3 v2016.9-0 (Bruker AXS) system.^[33] The frames for all complexes were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structures were solved and refined using the Bruker SHELXTL Software Package. Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure uniformity of treatment of crystal, most of the hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom) or of $1.5 U_{eq}$ (methyl). H atoms in methyl, methylene or methane moieties and C–H in aromatic rings were placed with C–H distances of 0.96, 0.97, 0.98 and 0.93 Å. N–H bonds were refined freely. In **5Pd** and **6Pd**, the disordered solvent molecules are responsible for the major disorder and residual electron densities. PLATON/SQUEZZE^[34] was used to correct the data for the presence of disordered solvent in **6Pd**. A potential solvent volume of $388 \text{ \AA}^3$ was found. 106 electrons per unit cell worth of scattering were located in the void, to which $2.5 \text{ CH}_2\text{Cl}_2$ was modelled, which gives 106e with the overall stoichiometry **6Pd** $\cdot 3.25\text{CH}_2\text{Cl}_2$. Furthermore, in **6Pt**, minor positional disorder (~30%) of three fluorine atoms of [BF $_4$] anion, as well as, the disordered [BF $_4$] anion and dichloromethane solvent in **6Pd** were treated by splitting them into two positions. The low-quality structure of **5Pd** is presented only in ESI (Figure S20) for imagination of the molecule composition. Crystallographic data for all structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2263904 (**3Pd**), 2263910 (**3Pt**), 2263905 (**4Pd**), 2263908 (**4Pt**), 2263909 (**5Pd**), 2263906 (**6Pd**), 2263907 (**6Pt**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: stibinidene · palladium · platinum · hydrogen-bond · TD-DFT

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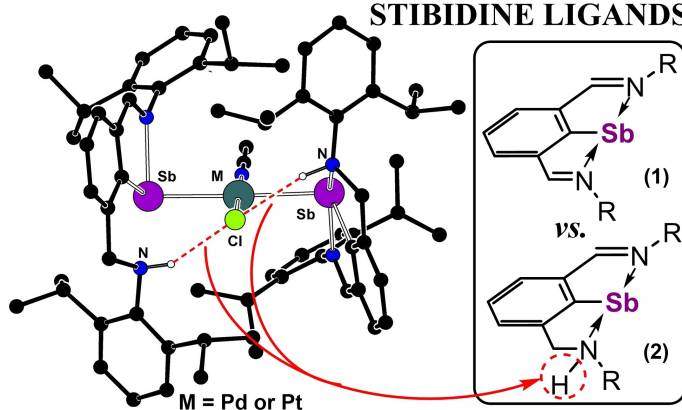
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STIBIDINE LIGANDS



The coordination capability of two *N,C,N* pincer chelated stibinidenes (1 and 2) toward palladium(II) and platinum(II) centres is reported. This study reveals significant structural dif-

ferences between these ligands caused mainly by the formation of hydrogen bonds *via* pendant NH groups of 2.

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Palladium(II) and Platinum(II) Bis(Stibinidene) Complexes with Intramolecular Hydrogen-Bond Enforced Geometries

