

Hexacoordinated Pnictines

Synthesis and Molecular Structure of Pseudo-Hexacoordinated Pnictines Bearing 2-Phenylpyridine Ligands

Masato Sakabe,^[a] Akihisa Ooizumi,^[a] Wataru Fujita,^[b] Shinobu Aoyagi,^[c] and Soichi Sato*^[a]

Abstract: The pseudo-hexacoordinated organo-pnictogen(III) compounds tris[2-(2-pyridyl)phenyl]stibine [(ppy)₃Sb, **1**] and tris[2-(2-pyridyl)phenyl]bismuthine [(ppy)₃Bi, **2**], which bear three 2-phenylpyridine (ppy) ligands, were prepared and isolated from the reaction of 2-(2-lithiophenyl)pyridine with the corresponding pnictogen(III) chloride (PnCl₃; Pn = Sb, Bi). Compounds **1** and **2** were characterized using NMR spectroscopy, mass spectrometry, and elemental analysis. Their solid-state structures were determined using single-crystal X-ray diffraction analysis, which revealed similar pseudo-hexacoordinated,

Introduction

In recent years, the chemistry of organoantimony and organobismuth compounds has seen significant progress^[1-6] especially toward their use as Lewis-acid catalysts,^[7-17] as anionsensing molecules,^[18-24] and as non-innocent ligands for transition-metal complexes.^[25-30] Heavy triorganopnictines of the type R₃Pn (Pn = Sb and Bi) are well-known organopnictogen(III) compounds that obey the octet rule and that can be classified as 8-Pn-3 chemical species.^[31] In general, heavy pnictines adopt a trigonal pyramidal coordination geometry with three covalent bonds and a lone pair (LP) of electrons on the central atom.^[2,4] Due to the diminished propensity toward hybridization of heavy atoms, the three covalent bonds and the LP consist predominantly of contributions from the p- and s-orbitals of the bonding atoms. In addition, the Allred-Rochow electronegativity values (χ) of antimony and bismuth (χ_{Sb} = 1.82; χ_{Bi} = 1.67) are much smaller than that of carbon ($\chi_{c} = 2.50$), which renders the central atom of the heavy pnictines cationic and means that the heavy pnictines form polarized $\text{Pn}^{\delta +}\text{-}\text{C}^{\delta -}$ bonds. Therefore, the LPs of heavier pnictines are more weakly coordinating than those of their corresponding lighter analogues

[a]	M. Sakabe, A. Ooizumi, Prof. Dr. S. Sato
	Department of Chemistry, Graduate School of Science, Tokyo Metropolitan
	University,
	1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan
	E-mail: ssato@tmu.ac.jp
[b]	Prof. Dr. W. Fujita
	Faculty of Science and Technology, Seikei University,
	3-3-1 Kichijoji-kitamachi, Musashino, Tokyo 180-8633, Japan
[c]	Prof. Dr. S. Aoyagi
	Department of Information and Basic Science, Nagoya City University,
	Nagoya 467-8501, Japan
	Supporting information and ORCID(s) from the author(s) for this article are

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distorted *facial* octahedral bonding geometries around the central pnictogen atoms, wherein the three pyridyl groups coordinate to the pnictogen atoms via three weak LP(N) $\rightarrow \sigma^*(Pn-C)$ donor-acceptor interactions. Natural bond orbital (NBO) and atoms in molecules (AIM) analyses were used to characterize the weak ionic interactions between the nitrogen and pnictogen atoms. The HOMOs of **1** and **2** correspond to the lone pairs of electrons on the central pnictogen atom, which indicates that these compounds can be classified as 14–Pn–6 chemical species.

(phosphines and arsines). Furthermore, the $\sigma^*(Pn-C)$ orbitals in heavy pnictines behave as Lewis acceptors and interact easily with the LPs of nucleophiles.^[5] The resulting compounds become hypervalent species that bear three-center four-electron (3c-4e) bonds. The introduction of a bidentate ligand with an intramolecular donor moiety (pendant-arm ligands) to a heavy pnictogen element is a commonly used method to generate relatively stable hypercoordinated pnictines that have valence electrons beyond the octet rule.^[32,33] However, due to the steric hindrance between ligands, there are not many reports of hexaor higher coordinated compounds. Hitherto reported neutral (pseudo-)hexacoordinated stibines (R₃Sb) and bismuthines (R₃Bi) contain either amino (**A**),^[34-38] formyl (**B**),^[39] imino (**C**),^[40]



Figure 1. (a) Previously reported examples of (pseudo-)hexacoordinated heavy pnictines (Pn = Sb, Bi). (b) Previously reported example of monomeric hexacoordinated telluronium cation. (c) (Pseudo-)hexacoordinated pnictines reported in this work.



or phosphino (**D**)^[27,41] groups as the intramolecular donor (Figure 1a). Although these (pseudo-)hexacoordinated pnictines can be classified as rare 14–Pn–6-type chemical species, detailed investigations into the bonding character and reactivity of these hypervalent species remain scarce.

Recently, Singh and co-workers have synthesized the asymmetrical telluronium salt [(ppy)₃Te][Br], which contains three 2-phenylpyridine (ppy) ligands (Figure 1b).^[42] This cationic hexacoordinated chalcogen species (14–Te–6) resembles the (valence-)isoelectronic molecules of the neutral hexacoordinated pnictines (14–Pn–6, Pn = Sb or Bi). Similar to the 14–Te–6-type species, the novel hexacoordinated heavy pnictines, which bear various bidentate ligands, are of great interest due to their unique structure, bonding character, and electrochemical properties.

Herein, we report the synthesis and molecular structures of stibine $[(ppy)_3Sb]$ (1) and bismuthine $[(ppy)_3Bi]$ (2), which contain three ppy ligands (Figure 1c), together with detailed calculations on the electronic properties of these 14–Pn–6 chemical species.

Results and Discussion

2-(2-Lithiophenyl)pyridine (ppy-Li) was prepared via a halogenlithium exchange reaction of 2-(2-iodophenyl)pyridine with *n*-butyllithium in Et₂O at low temperature to give a yellow suspension. As shown in Scheme 1, the ppy-Li suspension was added to a solution of 0.3 equivalents of pnictogen(III) chloride $(PnCl_3; Pn = Sb, Bi)$ in Et₂O to give **1** and **2** as moderately airstable solids in reasonable yield [1: pale yellow, 59 %, 2: beige, 52 %]. Products 1 and 2 were easily isolated by elution from the respective residues with dry toluene. Compounds 1 and 2 exhibit decomposition points of 208 °C and 188-190 °C, respectively. The ¹H and ¹³C NMR spectra of **1** and **2** show that the three ppy ligands on the pnictogen atoms are magnetically equivalent at room temperature. Equivalency of these resonances is also encountered for most other reported hexacoordinated pnictines (Figure 1a) and (valence-)isoelectronic [(ppy)₃Te]⁺ molecules.^[42] The exception to this rule are geminally substituted tris(acenaphthyl)pnictines (Figure 1a; D, R = *i*Pr).^[41] The identification of **1** and **2** was completed via the use of atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) and elemental analyses.

$$\begin{array}{c} \begin{array}{c} 1) \ 1.2 \ eq. \ ^{n} BuLi \\ \underline{2) \ 0.3 \ eq. \ PnCl_{3}} \\ Et_{2}O, \ -70 \ ^{\circ} C \ ^{\circ} r.t. \end{array} \begin{array}{c} 1 \ (Pn = Sb, \ 59\%) \\ 2 \ (Pn = Bi, \ 52\%) \end{array}$$

Scheme 1. Synthesis of 1 and 2.

Single crystals of 1 and 2 suitable for X-ray crystallographic analysis were prepared by slow evaporation of solvent from an ethanol/chloroform solution of 1 or from a toluene solution of 2 at room temperature. The crystal data are summarized in Table S1. The crystal structures of 1 and 2 are very similar and show two independent molecules per asymmetric unit. These independent molecules can be classified as type A and B molecules. In **1B** and **2B**, one of the three ppy groups (that carrying the N2' and C12' atoms) is disordered over two positions with relative occupancies of 0.695(7)/0.305(7) (**1B**) or 0.652(7)/0.348(7) (**2B**). The structures are shown in Figure 2 with the type **A** structures presented on top and the type **B** structures presented below. The packing structures are shown in Figure 55 and selected structural parameters obtained from around the central pnictogen atoms are summarized in Table 1. Al-



Figure 2. Molecular structure of **1** (left) and **2** (right) in the solid state [type **A** molecules (top) and type **B** molecules (bottom)]. Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms are omitted for clarity and in the disordered part, only the positions with higher occupancy are shown.

Table 1. Selected bond lengths [Å] and bond angles [°] of 1 and 2 (values in brackets correspond to the positions with lower occupancy in the disordered part).

	1 (Pn = Sb)			2 (Pn = Bi)		
Parameters	1A	1B	1 _{calcd}	2A	2B	2 _{calcd}
Pn–C1	2.191(3)	2.191(3)	2.203	2.299(5)	2.294(6)	2.312
Pn–C12	2.169(3)	2.238(7)		2.262(5)	2.36(1)	
		[2.07(2)]			[2.17(2)]	
Pn–C23	2.212(4)	2.206(4)		2.301(5)	2.306(5)	
Pn•••N1	2.779(3)	2.815(3)	2.871	2.853(5)	2.880(5)	2.906
Pn····N2	2.808(3)	2.834(7)		2.840(5)	2.878(8)	
		[2.76(1)]			[2.84(2)]	
Pn····N3	3.044(3)	3.002(3)		3.031(5)	3.018(5)	
C1-Pn-C12	97.6(1)	93.2(2)	94.8	96.2(2)	91.2(3)	93.2
		[100.4(5)]			[98.9(6)]	
C12–Pn–C23	91.1(1)	92.6(2)		90.4(2)	91.5(3)	
		[91.9(5)]			[90.2(6)]	
C23-Pn-C1	92.8(1)	96.4(1)		92.3(2)	96.0(2)	
N1PnN2	112.33(9)	117.3(1)	113.7	112.7(1)	119.0(2)	114.7
		[122.0(3)]			[123.1(3)]	
N2•••Pn•••N3	91.02(9)	115.4(1)		90.5(1)	117.9(2)	
		[106.3(3)]			[108.2(3)]	
N3PnN1	137.01(9)	114.00(9)		139.6(1)	114.0(1)	

though it seems that intramolecular repulsion exists between the LPs of the central pnictogen atom and the donor nitrogen atoms, all nitrogen atoms are directed toward the pnictogen atom, commensurate with a *facial* configuration. The Pn–C bond lengths observed in **1** [2.169(3)–2.212(4) Å] and **2** [2.262(5)–2.36(1) Å] are slightly longer than the average Pn–C bond length of the analogous molecules Ph₃Sb (av. 2.155 Å)^[43] and Ph₃Bi (av. 2.237 Å).^[44] Although the values found for the C–Pn–C angles in **1** [91.1(1)–97.6(1)°] and **2** [90.4(2)–96.2(2)°] vary widely due to their asymmetric structures, the averages of these angles are slightly smaller than those of Ph₃Sb [95.1(3)– 98.0(3)] and Ph₃Bi [92(1)–96(1)°].

In addition, the Pn ... N3 bond, depicted with dotted lines in Figure 2, is ca. 0.2 Å longer than the other Pn...N bonds. Thus, 1 and 2 can be described as having a pseudo-hexacoordinated and distorted octahedral bonding geometry. However, the Sb...N bond lengths of 1 [2.76(1)-3.044(3) Å] and the Bi...N bond lengths of 2 [2.84(2)-3.031(5) Å] are significantly shorter than the sum of the van der Waals radii $[\Sigma r_{vdW}(Sb,N) = 3.61 \text{ Å};$ $\Sigma r_{vdW}(Bi,N) = 3.62$ Å],^[45,46] supporting the presence of $LP(N) \rightarrow \sigma^{*}(Pn-C)$ intramolecular donor-acceptor interactions. The Sb---N bond lengths of 1 are shorter than those of other known (pseudo-)hexacoordinated stibines that possess three Sb---N interactions.^[27,34,35,37,38,40,41] Similarly, the Bi---N bond lengths of 2 are shorter than those of other known (pseudo-)hexacoordinated bismuthines such as (Et₂NCH₂C₆H₄)₃Bi [3.214(7) Å].^[36] These results are interesting because the basicity of the pyridyl group is much lower than that of the amino or imino group. These short Pn...N bond lengths in 1 and 2 are due to the lower steric hindrance between the ppy ligands relative to that of pendant-arm ligands that contain amino or imino groups. As supported by theoretical calculations (vide infra), 1 and 2 contain relatively short Pn...N bonds and three sets of weak three-center four-electron (3c-4e) bonds formed by three $LP(N) \rightarrow \sigma^{*}(Pn-C)$ donor-acceptor interactions.

Compounds 1 and 2 crystallize exclusively in *facial* configurations and a racemic mixture of Δ and Λ isomers. The most significant difference between the structures of the two independent molecules (type **A** and **B**) is the set of three N····Pn···N angles in each molecule (Table 1). In the more distorted **A** molecules, these angles are approximately 90°, 110°, and 140°, whereas in the **B** molecules, all three angles are ca. 115°.

Space-filling models of the type **B** molecules (**1B** and **2B**) are shown in Figure 3. There is no significant difference between the type **A** and type **B** space-filling models and thus only the type **B** illustrations are depicted in Figure 3. This figure shows that both **1** and **2** contain a larger space on the NNN-face side than on the CCC-face side. These results indicate that the LP on the central pnictogen atom in **1** and **2** should be located on the NNN-face side.

The structure and the electronic states of **1** and **2** were investigated by density functional theory (DFT) calculations at the B3PW91/aug-cc-pVTZ-PP [Sb, Bi]/6-31G(d) [C, H, N] level of theory. The optimized structures of **1**_{calcd} and **2**_{calcd} show C₃ symmetry, which differs from their respective crystal structures (Table 1). The optimized Pn–C bonds (**1**_{calcd}: 2.203 Å; **2**_{calcd}: 2.312 Å) are in good agreement with those in the correspond-



Figure 3. Space-filling models of 1B (left) and 2B (right).

ing crystal structures, and slightly longer than those of Ph₃Sb (2.160 Å) and Ph₃Bi (2.258 Å) when calculated at the same level of theory. The optimized Pn···N bonds (1_{calcd} : 2.871 Å; 2_{calcd} : 2.906 Å) fall in the middle of the range of Pn···N bond lengths found in the crystal structure [1: 2.76(1)–3.044(3) Å; 2: 2.84(5)–3.031(5) Å]. The crystal structures of the type **B** molecules are closer to the optimized structures than those of the type **A** molecules. The differences between the optimized structures and the X-ray crystal structures probably originate from crystal-packing effects. The small deferent energy gap (< 3 kcal/mol) between these structures is supported by theoretical calculations (Tables S4 and S5).

Furthermore, the Pn···N bonds in $(R_2NCH_2C_6H_4)_3Pn$ (Pn = Sb or Bi; R = Me or Et) optimized at the same level of theory are significantly longer than $\mathbf{1_{calcd}}$ or $\mathbf{2_{calcd}}$ (Table S6). These results are consistent with the results of the X-ray diffraction analyses, supporting that the shorter Pn···N bonds in $\mathbf{1_{calcd}}$ or $\mathbf{2_{calcd}}$ relative to those of other known (pseudo-)hexacoordinated pnictines are due to the small steric hindrance between the ppy ligands.

An analysis of the molecular orbitals of the optimized structures of $\mathbf{1}_{calcd}$ and $\mathbf{2}_{calcd}$ showed that the HOMOs correspond to the LP on the NNN-face side of each central pnictogen atom (Figure 4), and this result agrees with the space-filling models (Figure 3). The LPs occupy orbitals that have high s-character (1_{calcd}: Sb 5s orbital, 74.03 %; 2_{calcd}: Bi 6s orbital, 84.07 %) due to the non-hybridization effect of the heavier pnictogen atoms. A natural bond orbital (NBO) analysis^[47] of **1**_{calcd} and **2**_{calcd} revealed that the Pn···N interactions result from LP(N) $\rightarrow \sigma^*(Pn-C)$ donor-acceptor interactions with weak second order perturbation energies [$\mathbf{1}_{calcd}$: $E^{(2)} = 7.84$ kcal/mol; $\mathbf{2}_{calcd}$: 9.05 kcal/mol]. The Wiberg bond indexes (WBIs) for the Pn---N interactions [1_{calcd}: 0.0849; 2_{calcd}: 0.0853] confirm that these interactions can be expected to be very weak. Each central pnictogen atom exhibits a higher positive charge [1_{calcd}: +1.21; 2_{calcd}: +1.23] than the central atom in the corresponding triphenylphictine [Ph₃Sb: +1.08; Ph₃Bi: +1.07]. When the X-ray structures were optimized with fixed Pn ... N geometries (Table S5), slightly different second



order perturbation energies and WBIs were obtained at the same level of theory.



Figure 4. (a) HOMOs calculated for 1_{calcd} (left) and 2_{calcd} (right). (b) AIM plots of 1_{calcd} (left) and 2_{calcd} (right).

In order to better understand the bonding situation around the central atoms in **1** and **2**, these compounds were analyzed using the atoms-in-molecules (AIM) method^[48] based on a C_3 -symmetric optimized structure (**1**_{calcd} and **2**_{calcd}). Six bond critical points (BCPs) were found around the central pnictogen atom of **1**_{calcd} and **2**_{calcd}. The electron density (ρ_{bcp}), Laplacian of the electron density ($\nabla^2 \rho_{bcp}$), and total energy (*H*) of each BCP are summarized in Table 2. At the same level of theory, the calculated Pn–C bond parameters do not show any substantial differences between (ppy)₃Pn (**1**_{calcd} and **2**_{calcd}) and Ph₃Pn (Pn = Sb, Bi). The small positive $\nabla^2 \rho_{bcp}$ values observed for the Pn···N bonds are indicative of weak associative ionic interactions. Given the results of the DFT calculations and the AIM analyses, **1**_{calcd} and **2**_{calcd} can be classified as 14–Pn–6 (Pn = Sb, Bi) chemical species.

Table 2. Selected AIM parameters for the optimized structures of $\mathbf{1}_{calcd}$ and $\mathbf{2}_{calcd}$

Parameters			1 _{calcd}
Pn–C	$\rho_{\rm bcp} \ ({\rm e}/{\rm a_0}^3)$	0.1022	0.0913
	$\nabla^2 \rho_{\rm bcp}$ (e/a ₀ ⁵)	0.0639	0.0846
	$H_{\rm bcp}$ (au)	-0.0453	-0.0330
Pn•••N	$\rho_{\rm bcp}$ (e/a ₀ ³)	0.0232	0.0231
	$\nabla^2 \rho_{\rm bcp}$ (e/a ₀ ⁵)	0.0530	0.0599
	H _{bcp} (au)	-0.0003	+0.0003

To investigate the oxidative behavior of **1** and **2**, the electrochemical oxidation potentials of these pnictines were measured using cyclic voltammetry in $CH_2Cl_2/0.1 \text{ M} [nBu_4N][PF_6]$, which revealed irreversible oxidation potentials at 0.07 V (1) and 0.40 V (2) (vs. the ferrocene/ferrocenium couple) (Figure 5). Interestingly, the oxidation value of 1 is much lower than the corresponding value found for Ph₃Sb [1.22 V vs. SCE (= 1.06 V vs. Fc/Fc⁺)],^[49,50] which indicates that the LP on the central antimony atom of 1 is electrochemically more easily oxidized than that in Ph₃Sb. This is probably due to the presence of three intramolecular donor-acceptor interactions. In fact, the calculated HOMO level of 1 (-5.09 eV) is higher than that of Ph₃Sb (-6.13 eV), which is in agreement with the experimentally observed oxidation behavior of 1. As far as we know, there have so far been no reports on the electrochemical behavior of Ph₂Bi. but the results of the DFT calculations suggest a similar tendency for the HOMO levels of the bismuth analogues (2: -5.42 eV; Ph₃Bi: -6.28 eV). The observed irreversible waves likely occur because the corresponding radical cations ([1]⁺⁺ or [2]⁺⁺), generated by the one-electron oxidation, are unstable. Due to the lanthanide contraction and the relativistic effects,^[51] 2 exhibits a higher oxidation potential than 1. Indeed, DFT calculations show that the HOMO energy level of 2 (-5.42 eV) is lower than that of 1 (-5.09 eV).



Figure 5. Cyclic voltammograms of 1 (red) and 2 (green), recorded in CH_2Cl_2 with 0.10 ${\rm M}~[nBu_4N][PF_6]$ at room temperature.

Conclusions

We have described the new stibine 1 and the new bismuthine 2, which bear three 2-phenylpyridine (ppy) pendant-arm ligands. The three ppy ligands of 1 and 2 are magnetically equivalent in solution, as evident by NMR spectroscopy. However, in the crystalline state, the structures of 1 and 2 are distorted, probably due to packing forces. Each crystal contains two independent molecules (A and B), both of which adopt a pseudohexacoordinated facial octahedral coordination geometry. DFT calculations revealed three relatively weak intramolecular donor-acceptor interactions [LP(N) $\rightarrow \sigma^*(Pn-C)$] and an LP on the central pnictogen atom, indicating that 1 and 2 can be classified as 14-Pn-6 (Pn = Sb, Bi) chemical species. Cyclic voltammetry measurements revealed that the first oxidation potentials of 1 and 2 are relatively low, suggesting that these LPs are easily oxidized. While several (pseudo-)hexacoordinated pnictines that bear three pendant-arm ligands have previously been reported, their reactivity has not been studied systematically. The low oxidation potentials of 1 and 2 suggest promising potential to be converted into new cationic chemical species. Investigations



into oxidation reactions of these 14-Pn-6 chemical species are currently in progress in our laboratory.

Experimental Section

General: All reactions were performed under an atmosphere of dry argon. Unless otherwise stated, reagents were purchased from commercial suppliers and used as supplied. 2-Phenylpyridine (ppy-H) was dried with CaH₂, distilled under reduced pressure and kept under argon. Dry diethyl ether and dichloromethane were purchased from Kanto chemical (dehydrated). Toluene was dried with CaH₂ and distilled prior to use. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 500 (1H: 500 MHz; 13C: 126 MHz) spectrometer. Chemical shifts (δ) are reported in ppm. The chemical shifts of the ¹H and ¹³C{¹H} NMR spectra in CDCl₃ are reported relative to the internal standard Me₄Si (0 ppm). The absolute values of the coupling constants (J) are giving in Hertz (Hz). Multiplicities are abbreviated to singlet (s), doublet (d), triplet (t), and multiplet (m). The assignment of the ¹H and ¹³C{¹H} resonance signals was based on the corresponding COSY and HSQC spectra. Atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) measurements were collected on a Bruker micrOTOF II mass spectrometer for a minute and averaged. Melting points were determined on a Yanako MP-J3 apparatus and are uncorrected. Elemental analyses were carried out in the Elemental analysis room at Tokyo Metropolitan University.

Synthesis of (2-lodophenyl)pyridine (ppy-l): 2-(2-lodophenyl)pyridine (ppy-I) was prepared on a large scale using a modified literature procedure.^[52] In a 100 mL flask, distilled 2-phenylpyridine (5.76 g, 37 mmol), Copper(II) acetate monohydrate (7.39 g, 37 mmol), and I₂ (9.39 g, 37 mmol) were dissolved in 1,2-dichloroethane (40 mL) under atmospheric air. The mixture was then heated to reflux (100 °C) and stirred overnight. Subsequently, the reaction mixture was filtered, and the filtrate was washed consecutively with saturated aqueous Na2S2O3 (40 mL), saturated aqueous Na2S (40 mL), and brine (40 mL). The organic layer was filtered, dried with Na₂SO₄, and concentrated under reduced pressure. The resulting brown oil was purified by column chromatography on silica gel using hexane/ethyl acetate (2:1, v/v) as the eluent to afford ppy-l as a pale-yellow oil (3.72 g, 35 %). Unfortunately, ppy-I contains a small amount of inseparable 2-(2-chlorophenyl)pyridine (ppy-Cl) as a by-product. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 7.09 (ddd, J = 8.0, 6.9, 2.2, 1H), 7.30 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 7.43 (dt, J = 7.4, 1.2 Hz, 1H), 7.46 (dd, J = 7.8, 2.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.77 (dt, J = 7.8, 1.8 Hz, 1H), 7.97 (dd, J = 8.0, 0.8 Hz, 1H), 8.71 (d, J = 4.8 Hz, 1H). These spectroscopic data are consistent with literature values.

Synthesis of Tris[2-(2-pyridyl)phenyl]stibine, (ppy)₃Sb (1): *n*-Butyllithium (5.4 mL, 8.64 mmol, 1.60 m in *n*-Hexane) was added dropwise to a solution of ppy-l (2.16 g, 7.68 mmol) in dry diethyl ether (25 mL) under a dry argon atmosphere at -70 °C, and stirring was continued for 2 h at this temperature. The resulting yellow suspension was added via cannula to a solution of SbCl₃ (0.540 g, 2.37 mmol) in dry diethyl ether (40 mL) at -70 °C, where stirring was continued for 2 h. Then, the reaction mixture was allowed to slowly warm to room temperature, where stirring was continued overnight. The resulting mixture was filtered and the dark solid was washed with diethyl ether. The thus obtained brown residue was eluted with toluene, filtered, and the filtrate was concentrated under reduced pressure to afford **1** (0.82 g, 59 %) as a pale-brown solid. M.p. 208 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 7.01 (ddd, J = 7.4, 4.8, 1.1 Hz, 1H, py), 7.11 (dt, J = 7.4, 1.1 Hz, 1H, Ph), 7.34 (dt, J = 7.4, 1.1 Hz, 1H, Ph), 7.53 (dd, J = 7.4, 1.1 Hz, 1H, Ph), 7.59 (dt, J = 7.4, 1.8 Hz, 1H, py), 7.65 (d, J = 8.0 Hz, 1H, py), 7.78 (d, J = 7.7 Hz, 1H, Ph), 8.26 (d, J = 4.8 Hz, 1H, py); ¹³C NMR (126 MHz, CDCl₃, 25 °C) $\delta = 121.7$ (s, py), 121.7 (s, py), 127.3 (s, Ph), 127.5 (s, Ph), 128.6 (s, Ph), 136.3 (s, py), 138.6 (s, Ph), 144.5 (s, Ph), 147.8 (s, py), 148.4 (s, Ph), 159.1 (s, py); MS (APCI, pos) m/z 582 ([M – 1]⁺), 429 {[M – (ppy)]⁺}, 275 {[M – 2(ppy)]⁺}; elemental analysis calcd. (%) for C₃₃H₂₄N₃Sb: C, 67.83; H, 4.14; N, 7.19; found C, 67.64; H, 4.10; N, 7.17.

Synthesis of Tris[2-(2-pyridyl)phenyl]bismuthine, (ppy)₃Bi (2): A yellow suspension of ppy-Li was prepared by treatment of ppy-I (2.17 g, 7.7 mmol) with *n*-butyllithium (5.4 mL, 8.6 mmol, 1.60 м in n-hexane) in dry diethyl ether (20 mL) at -70 °C under an atmosphere of dry argon. After stirring for 2 h at -70 °C, the yellow suspension of ppy-Li was added via cannula to a solution of BiCl₃ (0.650 g, 2.06 mmol) in dry diethyl ether (30 mL) at -70 °C, where stirring was continued for 2 h. Then, the reaction mixture was allowed to slowly warm to room temperature, where stirring was continued overnight. The resulting mixture was filtered and the dark solid was washed with diethyl ether under an atmosphere of dry argon. The thus obtained brown residue was eluted with toluene, filtered, and the filtrate was concentrated under reduced pressure to afford 2 (0.715 g, 52 %) as a brown solid. The signal of the ipso carbon atoms bound to the Bi atom (172.8 ppm) were not observed at room temperature. Therefore, the corresponding ¹³C{¹H} NMR spectrum was measured at -20 °C. M.p. 188-190 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 7.00–7.03 (m, 1H, py), 7.10 (dt, J = 7.3, 1.3 Hz, 1H, Ph), 7.33 (dt, J = 7.3, 1.3 Hz, 1H, Ph), 7.60-7.65 (m, 2H, py), 7.85 (dd, J = 7.4, 1.3 Hz, 1H, Ph), 8.04 (dd, J = 7.4, 1.3 Hz, 1H, Ph), 8.27 (md, J = 4.8 Hz, 1H, py); ¹³C NMR (126 MHz, CDCl₃, –20 °C) δ = 121.4 (s, py), 121.5 (s, py), 126.6 (s, Ph), 127.9 (s, Ph), 130.7 (s, Ph), 136.4 (s, py), 141.4 (s, Ph), 145.0 (s, Ph), 148.2 (s, py), 160.8 (s, py), 172.8 (s, Ph); MS (APCI, pos) m/z 670 ([M - 1]+), 517 {[M - (ppy)]⁺}, 363 {[M - 2(ppy)]⁺}; elemental analysis calcd. (%) for C₃₃H₂₄N₃Bi: C, 59.02; H, 3.60; N, 6.26; found C, 58.72; H, 3.55; N, 6.13.

Electrochemical Measurements: Cyclic voltammograms (CV) were recorded at room temperature on a BAS-ALS620B apparatus under atmospheric air. Dry dichloromethane and [nBu_4N][PF₆] were used as the solvent and the supporting electrolyte, respectively, under the following conditions. Working electrode: glassy carbon; reference electrode: Ag/AgCl; counter electrode: platinum wire; concentration of the analyte: 1 mm; concentration of the supporting electrolyte: 0.1 m; scan rate: 100 mV/s. Ferrocene was used as an internal standard, and all potentials are referenced with respect to the $E_{1/2}$ of the Fc/Fc⁺ redox couple.

X-ray Crystallographic Analyses: Single crystals of **1** and **2** were prepared by slow evaporation of solvent from an ethanol/chloroform solution of **1** or from a toluene solution of **2** at room temperature. These crystals were coated with mineral oil and put on a MacroMountTM (MiTeGen, LLC), before they were mounted on a Rigaku Mercury CCD detector, where data were collected using Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Structures were solved by a dual space method using the SHELXT program^[53] and refined by a leastsquares method using SHELXL vers. 2018/1.^[54] All hydrogen atoms were put at calculated positions, while all other atoms were refined anisotropically.

Deposition Numbers 1997509 (for **1**) and 1997510 (for **2**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.



Theoretical Calculations: Geometry optimization and frequency calculations on **1** and **2** were carried out using the Gaussian 09 (Revision D.01) program package.^[55] These calculations were performed at the B3PW91^[56,57] /aug-cc-pVTZ-PP [Sb, Bi],^[58,59] 6-31G(d) [C, H, N]^[60] level of theory.^[61–63] Second order perturbation energies, Wiberg bond indexes (WBI), and natural population charges were calculated using the natural bond orbital (NBO) method via the NBO 3.1 program implemented in Gaussian 09.^[47,64] The QTAIM analysis was carried out using the AIMAII program package^[65] with a wavefunction file based on the optimized structure generated by Gaussian 09.

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