

Coordination Complexes of $\text{Ph}_3\text{Sb}^{2+}$ and $\text{Ph}_3\text{Bi}^{2+}$: Beyond Pnictonium Cations**

Alasdair P. M. Robertson, Neil Burford,* Robert McDonald, and Michael J. Ferguson

Abstract: The syntheses of salts containing ligand-stabilized $\text{Ph}_3\text{Sb}^{2+}$ and $\text{Ph}_3\text{Bi}^{2+}$ dications have been realized by *in situ* formation of $\text{Ph}_3\text{Pn}(\text{OTf})_2$ ($\text{Pn} = \text{Sb}$ or Bi) and subsequent reaction with OPPh_3 , *dmap* and *bipy*. The solid-state structures demonstrate diversity imposed by the steric demands and nature of the ligands. The synthetic method has the potential for broad application enabling widespread development of the coordination chemistry for Pn^{V} acceptors.

The 1809 report of the amine-borane adduct $\text{H}_3\text{N}\cdot\text{BF}_3$ ^[1] defines the origin of coordination chemistry. Nevertheless, coordination complexes of p-block acceptors are rare beyond the elements of Group 13, and are insignificant in comparison to the extensive coordination chemistry of transition metals, in which p-block elements are often the Lewis basic centers of the ligands. Cationic frameworks exhibit an enhanced Lewis acidity compared with neutral analogues and recent reports of cationic complexes of p-block acceptors represent a new direction for coordination chemistry.^[2,3] For example, complexes of mono-,^[4] di-,^[5] and tricationic^[6] Sb^{III} centers have been reported with the generic formula $[\text{X}_{3-n}\text{PnL}_n]^{n+}$, where X represents a notional anionic substituent and L is a neutral $2e^-$ donor. With this precedent, we envisage the formation of a more extensive series of coordination complexes involving Pn^{V} acceptors with the generic formulae $[\text{X}_{4-n}\text{PnL}_n]^{n+}$, $[\text{X}_{4-n}\text{PnL}_2]^{n+}$, $[\text{X}_{4-n}\text{PnL}_3]^{n+}$, etc., representing derivatives of pnictonium cations, $[\text{PnX}_4]^+$, through sequential replacement of an anionic substituent (X) by neutral ligand(s) (L). Indeed, a number of cationic complexes containing tetrahedral P^{V} acceptor centers have been structurally characterized,^[7–11] although in all but a single case^[7] ligand coordination is facilitated by a low coordination number at a phosphorus center involved in multiple bonding.

Here we report the synthesis and comprehensive characterization of complexes with the generic formula $[\text{Ph}_3\text{PnL}_2]^{2+}$ for $\text{Pn} = \text{Sb}$ or Bi , and $\text{L} = \text{OPPh}_3$ or 4-(dimethylamino)pyridine (*dmap*), which demonstrate a preference for axial

coordination of the L donors. In addition, we report analogous complexes of $\text{Ph}_3\text{Pn}^{2+}$ for $\text{Pn} = \text{Sb}$ or Bi , with the chelating donor 2,2'-bipyridine (*bipy*). The results confirm the cations of general formula $[\text{R}_3\text{PnL}_2]^{2+}$ ($\text{Pn} = \text{Sb}$ or Bi) that were postulated on the basis of spectroscopic and conductivity measurements.^[12,13]

Treatment of a solution of Ph_3SbCl_2 or Ph_3BiCl_2 in CH_2Cl_2 with two equivalents of AgOTf yielded $\text{Ph}_3\text{Sb}(\text{OTf})_2$ (**1a**) and $\text{Ph}_3\text{Bi}(\text{OTf})_2$ (**1b**), respectively, which were spectroscopically and crystallographically characterized (Figure 1). Addition of

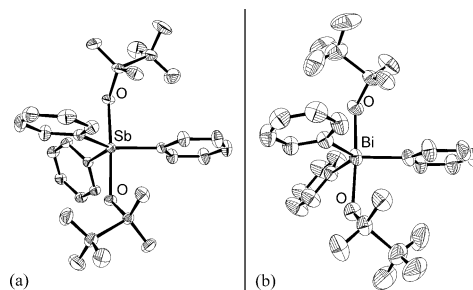
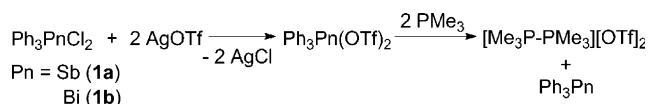


Figure 1. Solid-state structures of a) $\text{Ph}_3\text{Sb}(\text{OTf})_2$ (**1a**) and b) $\text{Ph}_3\text{Bi}(\text{OTf})_2$ (**1b**). All hydrogen atoms omitted for clarity.

two equivalents of PMe_3 to **1a** or **1b**, generated *in situ* in CH_2Cl_2 at ambient temperature resulted in the immediate precipitation of a colorless solid characterized by multinuclear NMR spectroscopy as $[\text{Me}_3\text{P}-\text{PMe}_3][\text{OTf}]_2$.^[14,15] The filtrate was shown by ^1H NMR spectroscopy to contain almost exclusively Ph_3Pn ($\text{Pn} = \text{Sb}$ or Bi), suggesting that oxidation of PMe_3 is associated with consequential reduction of **1a/b** (Scheme 1). Formation of $[\text{Me}_3\text{P}-\text{PMe}_3][\text{OTf}]_2$ is independent of reaction stoichiometry such that the presence of limited



Scheme 1. Chloride/triflate exchange at Ph_3PnCl_2 to give $\text{Ph}_3\text{Pn}(\text{OTf})_2$ [$\text{Pn} = \text{Sb}$ (**1a**) or Bi (**1b**)], and subsequent redox reaction with two equivalents of PMe_3 .

PMe_3 effects incomplete consumption of **1a/b**. Also, formation of the diposponium dication has been previously observed through reductive elimination from $[\text{Sb}(\text{PMe}_3)_3]^{3+}$.^[15] The direction of the observed redox couple, however, is counter to that reported previously for reactions

[*] Dr. A. P. M. Robertson, Prof. N. Burford
Department of Chemistry, University of Victoria
P.O. Box 3065, Stn. CSC, Victoria, BC (Canada)
E-mail: nburford@uvic.ca

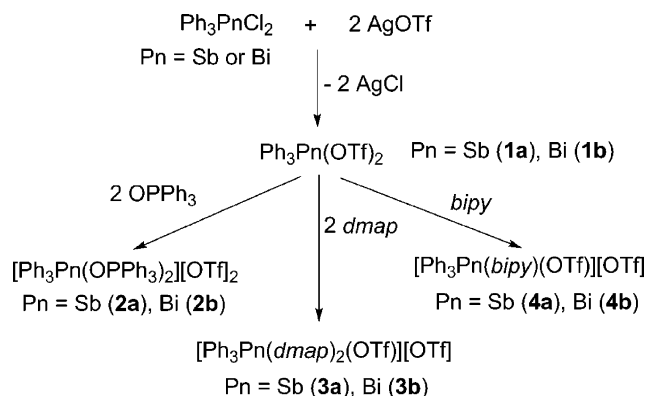
Dr. R. McDonald, Dr. M. J. Ferguson
X-Ray Crystallography Laboratory, Department of Chemistry
University of Alberta
11227 Saskatchewan Drive NW, Edmonton, AB (Canada)

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of Ph_3Sb with dihalophosphines in the presence of a halide abstracting agent, which leads to oxidation of Ph_3Sb and reductive coupling of two phosphine centers.^[16]

In contrast, reactions of **1a** and **1b** with the oxidation-resistant ligands OPPh_3 , *dmap* or *bipy* led to the corresponding derivatives of $\text{Ph}_3\text{PnL}_2(\text{OTf})_2$ ($\text{L} = \text{OPPh}_3$ or *dmap*) or $\text{Ph}_3\text{Pn}(\text{bipy})(\text{OTf})_2$, respectively (Scheme 2).^[17] Reaction



Scheme 2. Synthesis of $[\text{Ph}_3\text{Pn}(\text{OPPh}_3)_2][\text{OTf}]_2$, $[\text{Ph}_3\text{Pn}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ and $[\text{Ph}_3\text{Pn}(\text{bipy})(\text{OTf})][\text{OTf}]$.

mixtures of **1a/b** with OPPh_3 show a single resonance [$\delta_{\text{P}} = 48.7$ (Sb) and 43.1 ppm (Bi)] in the ^{31}P NMR spectra. Spectroscopic, analytical, and crystallographic data show the compounds to be salts of the form $[\text{Ph}_3\text{Pn}(\text{OPPh}_3)_2][\text{OTf}]_2$, containing $\text{Ph}_3\text{Pn}^{2+}$ dications bearing two OPPh_3 ligands in an axial configuration (Figure 2). Analogous reactions of **1a/b** with two equivalents of *dmap* or an equivalent of *bipy* at ambient temperatures quantitatively furnish salts of the form $[\text{Ph}_3\text{Pn}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ and $[\text{Ph}_3\text{Pn}(\text{bipy})(\text{OTf})][\text{OTf}]$ the cations of which are shown in Figure 3 and 4, respectively.

In the solid-state, $[\text{Ph}_3\text{Sb}(\text{OPPh}_3)_2][\text{OTf}]_2$ (**2a**) and $[\text{Ph}_3\text{Bi}(\text{OPPh}_3)_2][\text{OTf}]_2$ (**2b**) each contain a dication (Figure 2) and two distinct anions in the asymmetric unit, the pnictogen center adopts a trigonal bipyramidal geometry. The two statistically identical $\text{Ph}_3\text{PO-Sb}$ bonds in **2a** [average $2.102(2)$ Å] are similar in magnitude to the sum of the

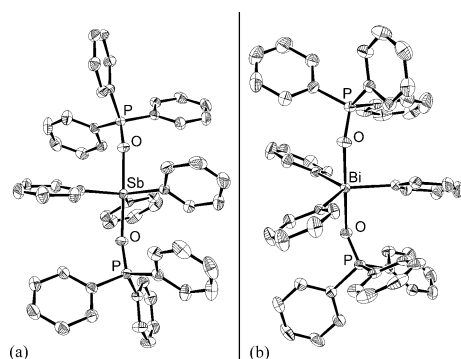


Figure 2. Solid-state structures of the dications in a) $[\text{Ph}_3\text{Sb}(\text{OPPh}_3)_2][\text{OTf}]_2$ (**2a**) and b) $[\text{Ph}_3\text{Bi}(\text{OPPh}_3)_2][\text{OTf}]_2$ (**2b**). All hydrogen atoms omitted for clarity.

covalent radii [$\Sigma_{\text{CR}} 2.05$ Å]^[18] and those in other cationic and neutral adducts of phosphine oxides and antimony [2.15 – 2.23 Å].^[19,20] The shortest cation–anion Sb–O distance [$4.998(3)$ Å] is well in excess of the sum of the van der Waals radii [3.61 Å].^[21] The $\text{Ph}_3\text{PO-Bi}$ bonds in **2b** [average $2.265(2)$ Å] are slightly greater than the sum of the covalent radii [$\Sigma_{\text{CR}} 2.14$ Å]^[22] but shorter than other examples of O–Bi coordinate bonds,^[23,24] possibly due to the greater Lewis acidity of the dicationic acceptor in this case.^[23,24] As for the antimony analogue, the shortest cation–anion Bi–O contact [$4.922(3)$ Å] is significantly greater than the sum of the van der Waals radii [3.61 Å].^[21]

In contrast to derivatives of $[\text{Ph}_3\text{Pn}(\text{OPPh}_3)_2][\text{OTf}]_2$, the pnictogen centers in the solid-state structures of $[\text{Ph}_3\text{Pn}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ [$\text{Pn} = \text{Sb}$ (**3a**), Bi (**3b**)] involve a close Pn–O contact with one triflate anion (Figure 3) [Sb-OTf

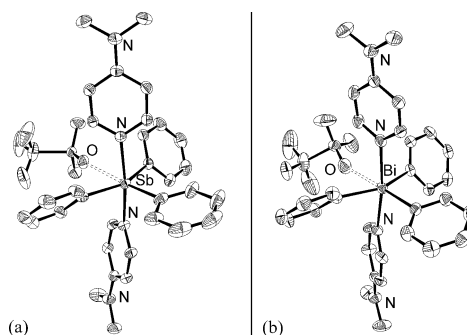


Figure 3. Solid-state structures of the dication and one anion in a) $[\text{Ph}_3\text{Sb}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ (**3a**) and b) $[\text{Ph}_3\text{Bi}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ (**3b**). All hydrogen atoms omitted for clarity.

$2.714(2)$ Å, cf. **1a** $2.172(2)$ Å and $\Sigma_{\text{CR}} \text{Sb-O}$ 2.05 Å]^[22] [Bi-OTf $2.888(2)$ Å, cf. **1b** $2.325(2)$ Å and $\Sigma_{\text{CR}} \text{Bi-O}$ 2.14 Å]^[22] These Pn–O contacts impose a distorted octahedral geometry at the pnictogen center, with the two *dmap* ligands in a *trans* configuration. In each case, the second triflate anion is > 5 Å from the pnictogen center. The N–Pn coordinate bonds [N-Sb $2.222(2)$ Å; N-Bi $2.373(2)$ Å] in both cases are greater in magnitude than the sum of the covalent radii of the two elements [$\Sigma_{\text{CR}} \text{N-Sb}$ 2.10 Å; $\Sigma_{\text{CR}} \text{N-Bi}$ 2.19 Å], but shorter than other examples of N-Sb^+ [2.23 – 2.81 Å].^[6,20,25–27] and N-Bi^+ bonds [2.50 – 2.84 Å],^[20,27–30] respectively. We interpret the cations in **3a/b** as ligand-stabilized pseudo-dications, with a short contact to a triflate anion.

The distinct structural differences between the OPPh_3 and *dmap* complexes reflect the different steric bulk of the ligands, with the planarity of *dmap* enabling interaction of the triflate anion. Interestingly, spectroscopic evidence for the formation of the *dmap* complexes **3a/b** was also apparent on the treatment of **2a/b** with two equivalents of *dmap* over 18 h in CH_2Cl_2 , with quantitative release of Ph_3PO apparent by ^{31}P NMR spectroscopy ($\delta_{\text{P}} = 28.3$ ppm). This ligand-exchange process is in line with the interpretation of these compounds as coordination complexes of $\text{Ph}_3\text{Pn}^{2+}$ acceptors.

Reaction of **1a** or **1b** with an equivalent of *bipy* in CH_2Cl_2 solution results in quantitative formation of $[\text{Ph}_3\text{Pn}(\text{bipy})(\text{OTf})][\text{OTf}]$ [$\text{Pn} = \text{Sb}$ (**4a**), Bi (**4b**)] based on ^1H and

^{13}C NMR spectra and elemental microanalyses. X-ray crystallographic characterization of **4a** provided information about connectivity and configuration (Figure 4), but loss of solvent precluded determination of definitive structural

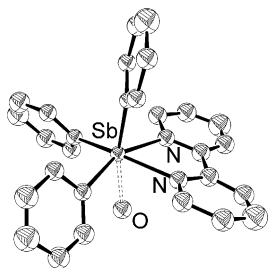


Figure 4. Preliminary structure of the cation in $[\text{Ph}_3\text{Sb}(\text{bipy})(\text{OTf})][\text{OTf}]$ (**4a**). All hydrogen atoms omitted for clarity, along with all but the bound oxygen atom of a disordered triflate anion.

parameters. A distorted octahedral environment at antimony is imposed by a triflate anion, three phenyl rings and a chelating bipy ligand. The inherent binding constraints of the bipy ligand preclude the axial configuration of the nitrogen donors that is observed for dmap complex **3a** and the *cis* configuration of triflate and bipy imposes a facial configuration of the phenyl substituents in contrast to the OPPh_3 and dmap complexes **2a** and **3a**. Given the structural consistency for the antimony and bismuth derivatives of **2** and **3**, it is reasonable to postulate that the spectroscopically characterized bismuth complex **4b** adopts a similar structure to its antimony analogue **4a** in the solid state.

In conclusion, the first structurally characterized examples of ligand-stabilized $\text{Ph}_3\text{Sb}^{2+}$ and $\text{Ph}_3\text{Bi}^{2+}$ acceptors have been prepared by displacement of triflate anions in $\text{Ph}_3\text{Pn}(\text{OTf})_2$ [$\text{Pn} = \text{Sb}$ (**1a**) or Bi (**1b**)] by the neutral donors, OPPh_3 , dmap and bipy. The new complexes exhibit structural diversity dictated by the steric demands and the nature of the ligands. Future research will target complexes with alternative substituents and ligands with a view to increasing the observed structural diversity, and will assess complexes bearing 3+, 4+ and 5+ charges, with a view towards potential catalytic activity.

Experimental Section

The syntheses of all six compounds were carried out by analogous method, presented as a representative example for $[\text{Ph}_3\text{Sb}(\text{OPPh}_3)_2][\text{OTf}]_2$ (**2a**): To a solution of Ph_3SbCl_2 (0.25 g, 0.59 mmol) in CH_2Cl_2 (4 mL) was added AgOTf (0.30 g, 1.18 mmol) and the mixture was stirred for 1 h at 20°C. The mixture was filtered and solid OPPh_3 (0.33 g, 1.18 mmol) then added to the filtrate. The resulting solution was stirred for 1 h before removing all volatiles under high vacuum to furnish a colorless solid, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -30°C. Yield: 0.51 g, 71% (crystalline); ^1H NMR (300 MHz, CD_2Cl_2): $\delta_{\text{H}} = 7.71\text{--}7.63$ (15H, m, Ph), $7.55\text{--}7.46$ (6H, m, Ph), $7.45\text{--}7.36$ (12H, m, Ph), $7.08\text{--}6.98$ (12H, m, Ph); ^{31}P { ^1H } NMR (202 MHz, CD_2Cl_2): $\delta_{\text{P}} = 48.40$ ppm (s, $\text{Ph}_3\text{Sb}(\text{OPPh}_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_{\text{F}} = -78.75$ ppm (s, OTf); FT-IR (Nujol Mull, ranked intensities): 1262(1), 1150(3), 1115(4), 1030(2), 1009(6), 993(5), 687(7), 636(8), 534(9), 516(10), 456(11); elemental analysis: calcd: C 55.69, H 3.76; found: C 55.41, H 3.57; Mp. 196–198°C.^[31]

$[\text{Ph}_3\text{Sb}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ (**3a**): Colorless solid; yield: 0.38 g, 71% (powder); ^1H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 7.79\text{--}7.69$ (15H, m, Ph), 7.59 (4H, d, $J_{\text{HH}} = 7.6$ Hz, Ar-H [dmap]), 6.56 (4H, d, $J_{\text{HH}} = 7.6$ Hz, (Ar-H [dmap]), 3.09 ppm (12H, s, NMe_2); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_{\text{C}} = 156.8$ (s), 145.0 (s), 135.3 (s), 134.5 (s), 132.1 (s), 130.0 (s), 121.3 (q, $J_{\text{CF}} = 321.2$ Hz, CF_3), 108.7 (s), 40.2 ppm (s, $\text{N}(\text{CH}_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_{\text{F}} = -78.80$ ppm; FT-IR (Nujol Mull, ranked intensities): 1621(7), 1258(1), 1228(4), 1150(5), 1028(2), 1008(6), 995(8), 739(10), 725(9), 635(3); elemental analysis: calcd: C 45.60, H 3.94, N 6.26; found: C 45.32, H 3.97, N 6.22; Mp. 200–202°C.

$[\text{Ph}_3\text{Sb}(\text{bipy})(\text{OTf})][\text{OTf}]$ (**4a**): Colorless solid; yield: 0.29 g, 61% (crystalline); ^1H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 9.12$ (2H, d, $J_{\text{HH}} = 8.3$ Hz, bipy), 8.65 (2H, d, $J_{\text{HH}} = 6.0$ Hz, Ar-H [bipy]), 8.62 (2H, t, $J_{\text{HH}} = 8.0$ Hz, Ar-H [bipy]), 7.93 (2H, t, $J_{\text{HH}} = 6.8$ Hz, Ar-H [bipy]), 7.71 (6H, $J_{\text{HH}} = 7.6$ Hz, Ph), $7.66\text{--}7.61$ (3H, m, Ph), $7.61\text{--}7.56$ ppm (6H, m, Ph); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_{\text{C}} = 146.7$ (s), 144.1 (s), 141.8 (s), 136.3 (s), 135.1 (s), 133.4 (s), 131.4 (s), 130.1 (s), 126.5 (s), 120.5 ppm (q, $J_{\text{CF}} = 320.3$ Hz, CF_3); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_{\text{F}} = -78.59$ ppm (s, OTf); FT-IR (Nujol Mull, ranked intensities): 1601(11), 1261(1), 1232(4), 1201(5), 1157(2), 1030(3), 987(7), 734(8), 723(9), 691(10), 631(6), 517(12); elemental analysis: calcd: C 44.63, H 2.87 N 3.47; found: C 44.60, H 2.87, N 3.47; Mp. 180–182°C.

$[\text{Ph}_3\text{Bi}(\text{OPPh}_3)_2][\text{OTf}]_2$ (**2b**): Colorless solid; yield: 0.32 g, 63% (crystalline); ^1H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 7.86\text{--}7.80$ (6H, m, Ph), $7.68\text{--}7.59$ (15H, m, Ph), $7.45\text{--}7.39$ (12H, m, Ph), $7.30\text{--}7.20$ ppm (12H, m, Ph); ^{31}P { ^1H } NMR (202 MHz, CD_2Cl_2): $\delta_{\text{P}} = 43.08$ (br. s, $\text{Ph}_3\text{Bi}(\text{OPPh}_3)_2$); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_{\text{C}} = 158.9$ (s), 134.7 (s), 134.6 (br. s), 134.2 (s), 133.8 (s), 132.7 (d, $J_{\text{PC}} = 11.3$ Hz, PPh), 130.0 ppm (d, $J_{\text{PC}} = 13.2$ Hz, PPh); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_{\text{F}} = -78.61$ ppm (s); FT-IR (Nujol Mull, ranked intensities): 1273(1), 1258(2), 1148(8), 1117(3), 1030(4), 1021(8), 995(9), 984(7), 636(6), 542(9), 536(5), 515(10); elemental analysis: calcd: C 51.93, H 3.50; found: C 52.40, H 3.61; Mp. 164–166°C.

$[\text{Ph}_3\text{Bi}(\text{dmap})_2(\text{OTf})][\text{OTf}]$ (**3b**): Bright yellow solid; yield: 0.26 g, 41% (crystalline); ^1H NMR (360 MHz, CD_2Cl_2): $\delta_{\text{H}} = 7.91$ (4H, br. s, Ar-H [dmap]), $7.84\text{--}7.56$ (15H, m, Ph), 6.58 (4H, d, $J_{\text{HH}} = 6.7$ Hz, Ar-H [dmap]), 3.09 ppm (12H, s, NMe_2); ^{13}C NMR (91 MHz, CD_2Cl_2): $\delta_{\text{C}} = 154.6$ (s), 135.1 (s), 134.5 (s), 133.8 (s), 133.7 (s), 132.8 (s), 40.0 ppm (s, $\text{N}(\text{CH}_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_{\text{F}} = -78.89$ ppm; FT-IR (Nujol Mull, ranked intensities): 1621(5), 1550(9), 1283(4), 1220(3), 1141(8), 1027(1), 1003(7), 978(6), 817(10), 634(2); elemental analysis: calcd: C 41.55, H 3.59, N 5.70; found: C 41.46, H 3.33, N 5.73; Mp. 134–136°C.

$[\text{Ph}_3\text{Bi}(\text{bipy})(\text{OTf})][\text{OTf}]$ (**4b**): Colorless solid; yield: 0.31 g, 54% (crystalline); ^1H NMR (500 MHz, CD_2Cl_2): $\delta_{\text{H}} = 8.63$ (2H, d, $J_{\text{HH}} = 4.8$ Hz, Ar-H [bipy]), 8.56 (2H, d, $J_{\text{HH}} = 7.6$ Hz, Ar-H [bipy]), 8.18 (2H, br. s, Ar-H [bipy]), 7.95 (6H, d, $J_{\text{HH}} = 7.6$ Hz, Ph), 7.81 (6H, t, $J_{\text{HH}} = 8.0$ Hz, Ph), 7.67 (3H, t, $J_{\text{HH}} = 7.6$ Hz, Ph), 7.57 ppm (2H, br. s, Ar-H [bipy]); ^{13}C NMR (126 MHz, CD_2Cl_2): $\delta_{\text{C}} = 141.8$ (very broad singlet), 134.5 (s), 134.0 (s), 133.9 (s), 127.3 (very broad singlet), 124.7 ppm (very broad singlet); ^{19}F NMR (283 MHz, CD_2Cl_2): $\delta_{\text{F}} = -78.31$ ppm; FT-IR (Nujol Mull, ranked intensities): 1594(14), 1554(12), 1256(1), 1235(2), 1205(3), 1160(4), 1030(5), 1008(6), 980(8), 770(10), 730(9), 647(11), 637(7), 514(13); elemental analysis: calcd: C 40.28, H 2.59 N 3.13; found: C 40.13, H 2.59, N 3.10; Mp. > 138 (decomposed).

Full experimental information and details of X-ray crystallographic studies can be found in the Supporting Information. CCDC 975311 (**2a**), 975312 (**2b**), 975313 (**3a**), 975314 (**3b**), 975315 (**1a**) and 975316 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cam-

bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [17] At the suggestion of a reviewer we also investigated the reactivity of the N-heterocyclic carbene (NHC) 1,3-di-*tert*-butyl-4,5-dihydroimidazol-2-ylidene (as an oxidation resistant ligand) with $\text{Ph}_3\text{Pn}(\text{OTf})_2$, and observed a complicated mixture of products, which are now under investigation.
- [18] Σ_{CR} values reported throughout are calculated from the values reported by Alvarez and co-workers: B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–3838.
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