

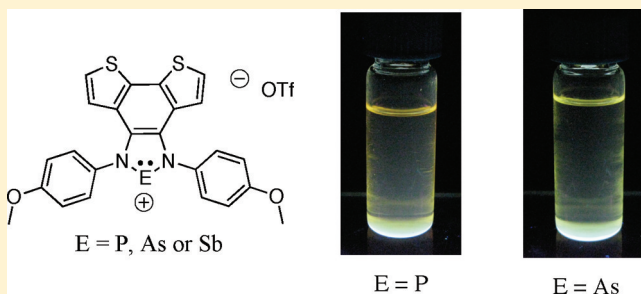
Group 15 Pnictenium Cations Supported by a Conjugated Bithiophene Backbone

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S Supporting Information

ABSTRACT: Thiophene based polymers and oligomers have attracted considerable attention because they can be functionalized to alter the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which enables the design of tunable light emitting materials. One area, which has been less explored, is the incorporation of low coordinate, low oxidation state main group elements into these systems. We have currently developed a novel π -conjugated ligand containing two contiguous thiophene rings in which we have demonstrated its ability to support both pnictogen cations and their metal complexes.



INTRODUCTION

The current renaissance in p-block chemistry has borne witness to some remarkable developments for main group elements, with many of the breakthroughs centering on new structure, bonding, and reactivity.^{1–7} An emerging tenet in this area of research is to use these novel molecules and their unique reactivity to bridge the gap into functional or applied chemical processes. Excellent examples have surfaced in the past few years including efforts in organic light-emitting devices (OLEDs), catalysis, and small molecule activation.^{5–9} One of the limitations to further expanding p-block chemistry into the realm of the applied has been the challenge of developing novel frameworks with which to support low coordinate and low oxidation state main group element centers. New directions could be realized by installing various functionalities onto these supporting ligands and by taking advantage of the inherent electronic influence as well as the chemical versatility of the p-block elements. Combined, these can have a significant impact on the resulting materials that are not always possible in exclusively organic systems.^{7,10}

It has been well established that thiophene based materials lend themselves to the design of tunable, light emitting polymers and materials.¹¹ Related efforts in this area by other research groups have realized the synthesis of both a polythiophene with orthogonal carbenes and a redox active thiophene substituted diazabutadiene ligand for the construction of phosphonium cations.^{12–14} Although each development is novel, a key drawback to the utility of these systems has been the lack of a conjugated system between the thiophene rings and the rest of the molecule. In this context, we have undertaken an effort to model a wholly new ligand system where two contiguous thiophene rings occupy the supporting backbone (Figure 1). The corresponding diaminochloropnictine

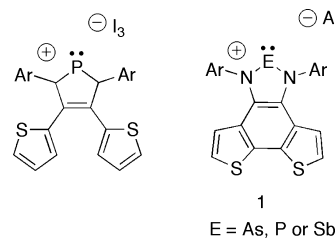


Figure 1. Previously reported phosphonium cation with the triiodide salt and the reported new pnictenium cations (1) reported in this work.

and pnictenium cations were readily synthesized using established dehydrohalogen coupling protocols between diamine ligands and p-block halides in high yields, and a platinum complex of both the phosphonium and arsenium cation were prepared. These achievements represent a unique opportunity to bring together the known and emerging chemistry of low coordinate p-block cations, with the alluring photophysical properties of thiophene based materials.

RESULTS AND DISCUSSION

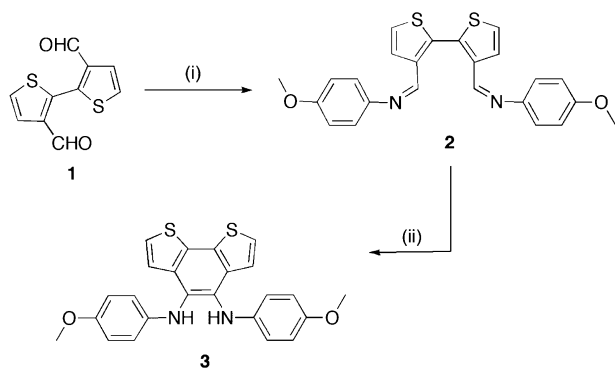
Synthesis. Our entry into the new thiophene-based systems (Scheme 1) rested on the known 2,2'-bithiophene-3,3'-biscarboxaldehyde (1).¹⁵

Compound 2 was made by a condensation reaction between a yellow ethanolic suspension of 1 with 2.1 stoichiometric equivalents of *p*-anisidine. Upon addition of the amine, the solution turned from yellow to black, and during the 4 h reflux a yellow solid precipitated. The slurry was then cooled to room

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Scheme 1. Synthesis of 3^a

^a(i) *p*-OMe-C₆H₄NH₂, EtOH, reflux 4 h, 82%; (ii) NaCN, DMF, r.t. 48 h, 80%.

temperature, and the yellow solid was isolated by filtration. The ¹H NMR spectrum of the redissolved yellow powder revealed the disappearance of the aldehyde proton at $\delta_{\text{H}} = 9.85$ ppm and the appearance of a singlet at $\delta_{\text{H}} = 8.35$ ppm consistent with an imine, along with the protons corresponding to the *p*-MeOPh group. Coupling of the diimine to form the corresponding

diamine target (3) was carried out by the addition of dimethylformamide (DMF) to solid NaCN and 2. The mixture immediately became dark green, and was stirred at room temperature for 2 days. The reaction mixture was diluted with CH₂Cl₂ and washed with water. Removal of the volatiles and the subsequent addition of MeOH caused precipitation of a bright orange solid. A sample of the bulk material was redissolved for ¹H NMR spectroscopy, which revealed the disappearance of the aldimine proton and no significant change in the aryl groups, indicating that the cyclization was likely successful. Single crystals suitable for X-ray diffraction studies (Figure 2) were grown from a solution of MeOH at room temperature confirming the successful synthesis of 3, isolated in 86% yield.

A 3:1:1 stoichiometric reaction between *N*-methylmorpholine (NMM), PCl₃, and 3 in tetrahydrofuran (THF) resulted in an immediate color change from brown/orange to a bright orange. The reaction was monitored by ³¹P{¹H} NMR spectroscopy, which showed the reaction was complete after 4 days by the disappearance of PCl₃ ($\delta_{\text{p}} = 220$ ppm), and the appearance of a new peak ($\delta_{\text{p}} = 136$ ppm) was tentatively assigned to the chlorophosphine 4a. X-ray quality, orange crystals were grown by CH₂Cl₂/pentane liquid diffusion at room temperature, and subsequent X-ray diffraction analysis confirmed the production

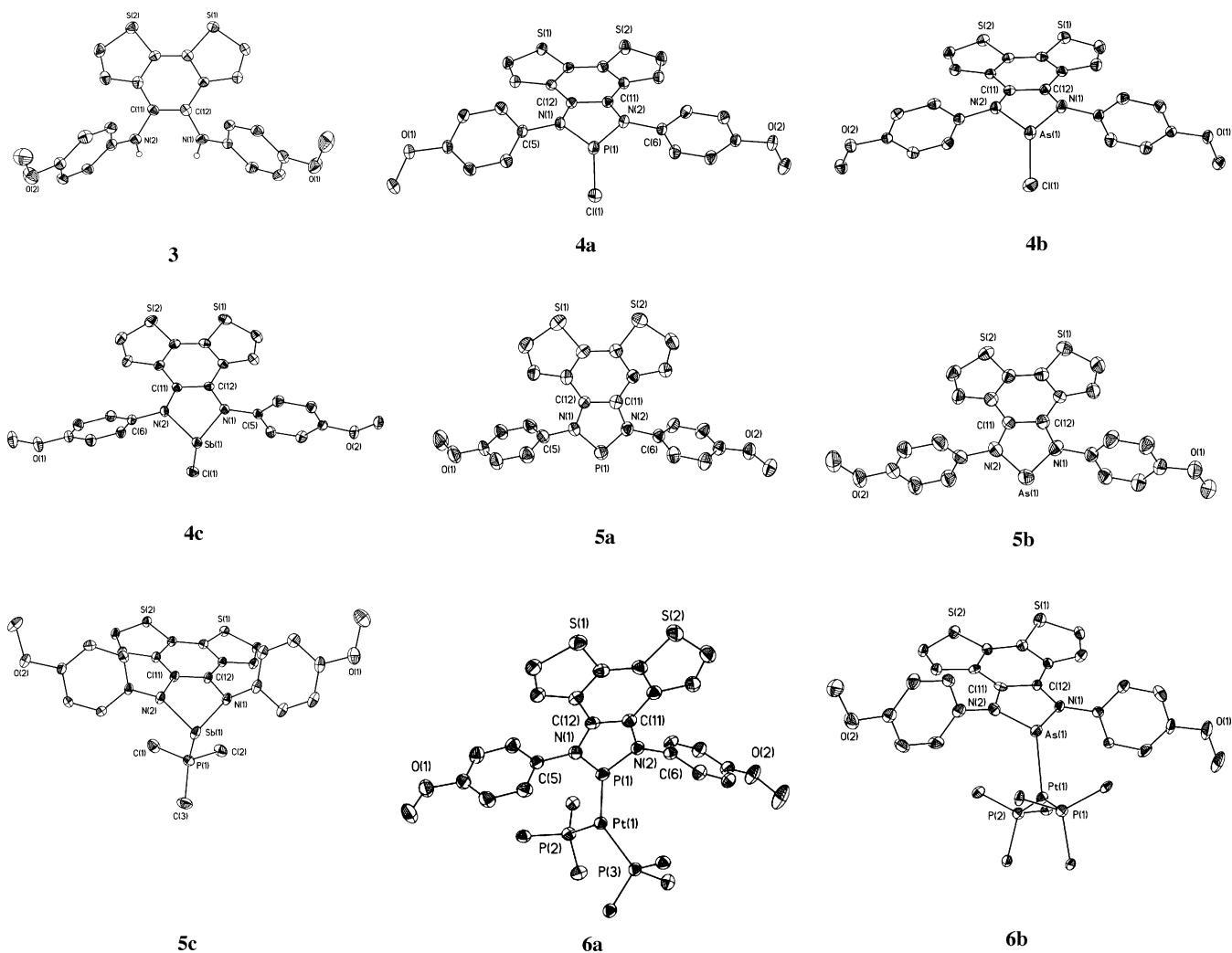
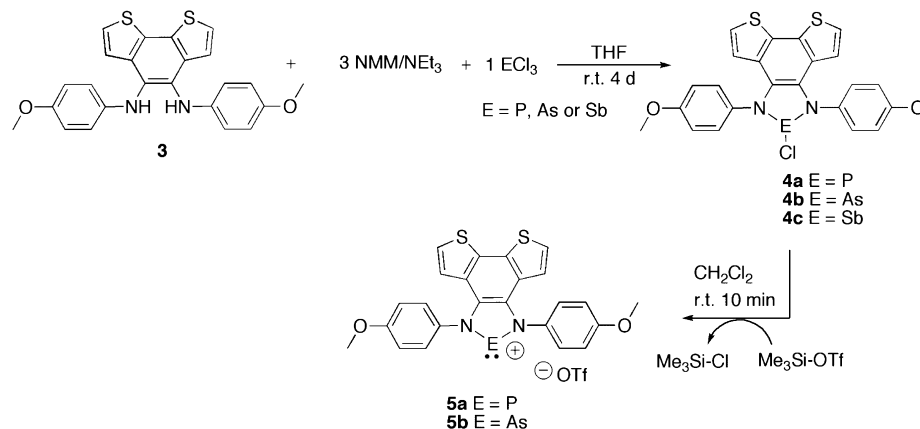
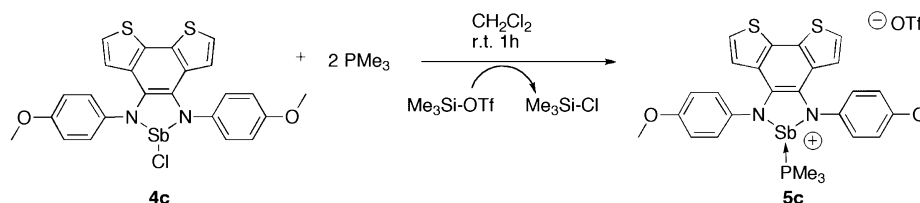


Figure 2. Solid-state structures of 3 to 6. Ellipsoids are drawn to 50% probability. Hydrogen atoms are removed except on the nitrogen atoms for compound 3 for clarity. Compounds 3, 4a, and 5a, one of two formula units within the asymmetric unit is shown. Compounds 5–6, the triflate anion has been removed for clarity. Compounds 6a and 6b, all but the ipso-C in the PPh₃ has been removed for clarity.

Scheme 2. Synthesis of 4a, 4b, and 4c, and the Subsequent Halide Abstraction Yielding 5a and 5b



Scheme 3. Synthesis of 5c



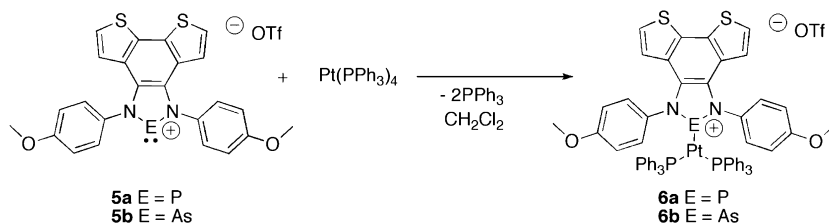
of the cyclic diaminochlorophosphine (**4a**), isolated in 83% yield (Figure 2). The corresponding diaminochloroarsine, **4b** was synthesized using a similar procedure of a 3:1:1 stoichiometric reaction between NMM, AsCl_3 , and **3** in THF, and resulted in a slight color change from an orange to a red solution. The reaction was complete after 4 days, denoted by the proton shifts in the ^1H NMR spectrum (Scheme 2). The protons belonging to the thiophene ring shifted significantly upfield **4b** ($\delta_{\text{H}} = 7.04$ and 6.20 ppm) compared to the proligand **3** ($\delta_{\text{H}} = 7.18$ and 7.04 ppm). Whereas the resonances in the phenyl rings were further split in compound **4b** ($\delta_{\text{H}} = 7.48$ and 6.98 ppm; $\Delta\delta = 0.50$) compared to the free ligand, **3** ($\delta_{\text{H}} = 6.69$ and 6.62 ppm; $\Delta\delta = 0.07$). Another indication that the desired chloroarsine was synthesized was the disappearance of the NH peak in the ^1H NMR spectrum ($\delta_{\text{H}} = 5.63$). X-ray quality, orange crystals were grown by CH_2Cl_2 /pentane liquid diffusion at room temperature, and subsequent X-ray analysis confirmed the production of **4b** isolated in 54% yield (Figure 2). The 3:1:1 stoichiometric reaction between NMM, SbCl_3 , and **3** resulted in no reaction so the reaction mixture was heated to 50°C for 48 h, and 3 stoichiometric equivalents Et_3N were added. Upon completion of the reaction as detected by proton NMR spectroscopy, X-ray quality, red crystals were grown from CH_2Cl_2 / Et_2O liquid diffusion at room temperature confirming the synthesis of the diaminochlorostibine (Figure 2).

To convert **4a** to the corresponding phosphonium cation, (**5a**) two stoichiometric equivalents of trimethylsilyltrifluoromethanesulfonate (Me_3SiOTf) were added to **4a** in CH_2Cl_2 . The solution immediately turned from orange to red, and after a few minutes a yellow solid precipitated from the reaction mixture. The red liquid was decanted and the yellow powder dried in vacuo. A phosphorus-31 NMR spectrum of the redissolved yellow solid revealed a singlet at $\delta_{\text{P}} = 191$ ppm and ionic triflate was detected in $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum ($\delta_{\text{F}} = -78.5$ ppm cf. $[\text{Bu}_4\text{N}]\text{OTf}$ $\delta_{\text{F}} = -78.7$ ppm);¹⁶ thus the solid was assigned as the triflate salt of the phosphonium cation (**5a**).

Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of pentane into a CH_2Cl_2 solution of **5a**, confirming the production of the title compound, which was isolated in 90% yield (Figure 2). To convert **4b** to the corresponding arsenium cation, **5b**, one stoichiometric equivalent of Me_3SiOTf was added in CH_2Cl_2 (Scheme 2). The solution remained red in color; however after 15 min of stirring an orange solid began to precipitate from the reaction mixture. To this mixture 5 mL of Et_2O was added, and the supernatant was decanted off leaving an orange solid, which was dried in vacuo. The Fluorine-19 NMR spectrum revealed an ionic triflate, and in the ^1H NMR spectrum, both signals belonging to thiophene and phenyl rings were shifted downfield by 0.1 ppm. Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of Et_2O into CH_2Cl_2 solution of **5b**, confirming the synthesis of the desired product in 93% yield (Figure 2).

The corresponding stibonium cation could not be isolated, and only decomposition products were observed by ^1H NMR spectroscopy when halide-abstracting agents TMS-OTf or GaCl_3 were added to a CH_2Cl_2 solution of the diaminochlorostibine; however, the stibonium cation could be trapped using a Lewis base. To a CH_2Cl_2 solution of chlorostibine (**4c**), 2 stoichiometric equivalents of PMe_3 and 1 stoichiometric equivalent of Me_3SiOTf were added (Scheme 3). A yellow solid precipitated from the orange solution after 15 min of stirring, and the orange solution was decanted off. The yellow solid was isolated in 37% yield. Upon examination of the yellow solid by ^{31}P NMR spectroscopy a peak at -1.2 ppm was observed along with ionic triflate at $\delta_{\text{F}} = 78.7$ indicating the target product was likely synthesized. A doublet in the ^1H NMR spectrum at 1.55 ppm corresponding to the methyl groups on the PMe_3 was also observed providing further evidence that the desired product was isolated. Single crystals were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the product, and single X-ray quality crystals were obtained confirming the target compound (Figure 2).

Scheme 4. Synthesis of Pnictogenium Metal Complexes



The ability to readily modify the pnictogenium framework is important for the successful manipulation of the photophysical and electronic properties of the thiophene system; metalation strategies are often useful in this regard.¹⁷ This was probed by the addition of a CH_2Cl_2 solution of $\text{Pt}(\text{PPh}_3)_4$ to a CH_2Cl_2 solution of **5a** (both yellow), causing an immediate color change to deep red. The reaction mixture was concentrated in vacuo to a red oil. Diethylether was added to precipitate a bright orange powder. A $^{31}\text{P}\{^1\text{H}\}$ spectrum of the redissolved solid revealed an upfield doublet and a downfield triplet, each with corresponding ^{195}Pt satellites, in an approximate 2:1 integration ratio that were assigned to two PPh_3 and one phosphonium ligand, respectively ($\delta_{\text{P}} = 47$ ppm, $^1J_{\text{Pt-P}} = 2358$ Hz, $^2J_{\text{PP}} = 490$ Hz; $\delta_{\text{P}} = 249$ ppm, $^1J_{\text{PtP}} = 2326$ Hz, $^2J_{\text{PP}} = 490$ Hz). Single crystals were grown by vapor diffusion of pentane into a CH_2Cl_2 solution of the product, and subsequent X-ray diffraction studies revealed the coordinatively unsaturated $\text{Pt}(0)$ phosphonium complex (**6a**) isolated in 77% yield (Figure 2). The reactivity of **5b** was also explored by the addition of 1 equiv of $\text{Pt}(\text{PPh}_3)_4$ in CH_2Cl_2 causing an immediate color change from red to dark purple (Scheme 4). The reaction mixture was concentrated in vacuo to give a purple oil, to which 3 mL of Et_2O was added precipitating a purple solid. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the purple powder displayed a single peak at $\delta_{\text{P}} = 41.8$ ppm with ^{195}Pt satellites ($^1J_{\text{Pt-P}} = 3579.6$ Hz) and the disappearance of the Pt precursor at $\delta_{\text{P}} = 23.0$ ppm. Upon examination of the ^1H NMR spectrum, again the protons on the thiophene backbone are very diagnostic and have shifted upfield from $\delta_{\text{H}} = 6.28$ in **5b**, to $\delta_{\text{H}} = 6.01$ ppm in the metal complex **6b**. Single crystals were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the product, and X-ray diffraction studies revealed the $\text{Pt}(0)$ arsenic complex, **6b** (Figure 2; 90%).

Photophysical properties. The photophysical properties of compounds **3–6b** were examined by UV–vis and fluorescence spectroscopy (Table 1). In comparison to the ligand **3** ($\lambda_{\text{abs}} = 279$, $\lambda_{\text{em}} = 450$), upon the addition of the pnictogen center, phosphorus (**4a**, $\lambda_{\text{abs}} = 266, 373$ nm), arsenic (**4b**, $\lambda_{\text{abs}} = 271, 373$), and antimony (**4c**, $\lambda_{\text{abs}} = 252, 276, 372, 465$), the absorption was blue-shifted to shortened wavelengths with antimony having an absorption maxima at the highest energy. Absorption maxima for the pnictenium cations are shifted to a higher energy as the charge is increased on the five membered ring; phosphorus (**5a**, $\lambda_{\text{abs}} = 258, 377$), arsenic (**5b**, $\lambda_{\text{abs}} = 256, 282$) however the base stabilized stibenium cation, the λ_{abs} was shifted to a lower energy (**5c**, $\lambda_{\text{abs}} = 279, 386$). Although as one goes down group 15, both the maximum absorption wavelength and the maximum absorption emission wavelengths of these compounds were similar in dichloromethane solutions. This suggests that the substitution did not cause significant changes in the conjugation of the molecular structure, and the photophysical properties are dominated by the bithiophene backbone. The solvatochromatic effects of the pnictenium compounds were investigated, and upon changing

the solvent composition from acetonitrile to ether in about 10 vol % increments, there was no dramatic shift in the UV–vis absorption; however, the absorption coefficient decreased as

Table 1. Optical Properties of Compounds **2–6^a**

compound	λ_{abs} nm (ϵ_{max} L mol ⁻¹ cm ⁻¹)	λ_{em} (nm)	ϕ_{FL}
2	273 (3.5×10^4)		
	333 (3.3×10^4)		
3	279 (2.7×10^4)	450	0.011
4a	266 (3.1×10^4)	400	0.023
	373 (7.1×10^3)		
4b	271 (3.1×10^4)		
	383 (1.3×10^3)		
4c	252 (4.8×10^5)	450	0.011
	276 (4.6×10^5)		
	372 (8.0×10^4)		
	465 (4.0×10^4)		
5a	258 (2.5×10^4)	400	0.019
	377 (8.2×10^3)		
5b	256 (5.6×10^4)		
	282 (2.9×10^4)		
5c	423 (3.9×10^3)		
	279 (6.6×10^4)	450	0.010
6a	386 (1.2×10^4)		
	259 (5.9×10^4)		
6b	394 (1.3×10^4)		
	466 (9.5×10^3)		
	276 (3.2×10^4)		
	576 (2.7×10^4)		

^aFluorescence quantum yields measured in CH_2Cl_2 solution using 9,10 diphenylanthracene ($\phi_{\text{FL}} = 0.90$ in CH_2Cl_2) as a standard, excited at 260 nm.¹⁸

the vol % of ether increased. The quantum yields were calculated against diphenylanthracene, which were low, ranging from 0.01% to 0.02%.¹⁸

X-ray Crystallography. Compounds **3–6b** have been characterized by single X-ray diffraction studies. Views of the solid state structures are shown in Figure 2, and refinement details can be found in Table 2. Key bond lengths and angles are summarized in Table 3.

An examination of the solid-state structures of compounds **3–6b** revealed that the metrical parameters for the C_2N_2 ring were all consistent with two C–N single bonds (1.388–1.415 Å cf. 1.420 Å (ave.) in the free ligand) and a C–C double bond (1.386–1.399 Å cf. 1.382 Å (ave.) in **3**). The C–N bonds are slightly shortened upon coordination to pnictogen, and the C–C double bond in the backbone remained the same as in the free ligand (**3**).

Compound **4a** is isostructural with **4b** and **4c**, and all feature long E(1)–Cl(1) bonds and are all pyramidal at the pnictogen center. Upon examination of the pnictogen halogen linkage the

Table 2. Crystal Data for Compounds 3 to 6b

	3	4a	4b	4c	5a	5b	5c	6a	6b
empirical formula	C ₂₄ H ₂₀ N ₂ O ₂ S ₂	C ₂₄ H ₁₈ N ₂ O ₂ S ₂ PCl	C ₂₄ H ₁₈ N ₂ O ₂ S ₂ AsCl	C ₂₄ H ₁₈ N ₂ O ₂ S ₂ SbCl	C ₂₃ H ₁₈ F ₃ N ₂ O ₂ PS ₃	C ₂₃ H ₁₈ F ₃ N ₂ O ₂ AsS ₃	C ₂₈ H ₂₇ F ₃ N ₂ O ₂ P ₃ S ₃ Sb	C ₆₂ H ₄₉ Cl ₃ F ₃ N ₂ O ₂ P ₃ PtS ₃	C ₆₂ H ₄₉ Cl ₃ F ₃ N ₂ O ₂ P ₃ AsS ₃
FW (g/mol)	432.54	496.94	540.89	587.72	610.56	654.51	862.34	1449.56	1374.14
crystal system	orthorhombic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	P2 ₁ 2 ₁ 2 ₁	P $\bar{1}$	P2 ₁	P $\bar{1}$	P2 ₁	P2 ₁	P $\bar{1}$	P2 ₁ /c	P $\bar{1}$
a (Å)	5.6639(4)	8.8245(18)	8.7034(4)	9.8620(4)	10.270(2)	10.342(2)	9.1339(5)	19.897(4)	11.5899(8)
b (Å)	18.2454(12)	10.045(2)	13.3155(6)	14.3596(6)	11.016(2)	10.994(2)	11.8823(7)	11.949(2)	13.2732(10)
c (Å)	19.7061(13)	13.898(3)	19.5851(9)	17.3069(7)	12.460(3)	12.477(3)	16.8352(10)	25.874(5)	17.7278(13)
α (deg)	90.00	80.52(3)	90.00	66.669(2)	90.00	90.00	81.367(2)	90.00	85.961(2)
β (deg)	90.00	74.17(3)	101.340(2)	89.298(2)	112.43(3)	111.88(3)	79.485(2)	98.91(3)	83.564(2)
γ (deg)	90.00	67.92(3)	90.00	86.426(2)	90.00	90.00	71.365(2)	90.00	84.914(2)
V (Å ³)	2036.4(2)	1095.7(4)	2225.41(18)	2245.92(16)	1303.0(5)	1316.4(5)	1694.01(17)	6078(2)	2694.3(3)
D _c (mg m ⁻³)	1.411	1.506	1.861	1.559	1.556	1.651	1.691	1.584	1.694
R1 [I > 2 σ (I)] ^a	0.0359	0.0411	0.0224	0.0222	0.0632	0.0501	0.0311	0.0388	0.0498
wR2(F ²) ^a	0.0860	0.1177	0.0603	0.0576	0.1439	0.1234	0.0673	0.1009	0.0669
^a R1[F(I > 2 σ (I))] = $\sum F_o - F_c / \sum F_o $; wR2(F ² [all data]) = $[w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$; S(all data) = $[w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; w = 1/[$\sigma^2(F_o^2) + (aP)^2 + bP$]) where P = (F _o ² + 2F _c ²)/3 and a and b are constants suggested by the refinement program.									

bond length increases down the group from 2.2123(9) Å for compound **4a**, 2.3296(5) for **4b**, and 2.5129(6) for **4c**, corresponding to the increase in size of the central element. The pnictogen atom is pyramidal which is expected from a three coordinate pnictogen center with a lone pair; however, the Cl(1)–Pn(1)–N(1) angle decreases as one goes down the group from **4a** ($\Sigma_{\text{ang}} = 102.81(7)^\circ$), **4b** ($\Sigma_{\text{ang}} = 100.85(5)^\circ$) to **4c** ($\Sigma_{\text{ang}} = 92.70(6)^\circ$) because of the decrease in hybridization at the pnictogen.

Upon examination compound **5a** (**5b** is isostructural) the thiophene–P(1) portion deviates from planarity only by 0.0348 Å. The *p*-MeOPh rings are twisted out of the plane by 96.0(7) $^\circ$ and are almost perpendicular to the plane of the bithiophene backbone. In general, the metrical parameters of the phosphonium cation (**5a**) are comparable to those reported for other NHP systems. Upon formation of the arsenium cation there is a contraction in the C–N bond from 1.405(2) Å for compound **4b** to C(11)–N(2) 1.369(6) Å and C(12)–N(1) 1.372(6) Å. This contraction was also observed in the P–N bond, P(1)–N(1) 1.683(2) Å; P(1)–N(2) 1.6942(19) Å for compound **4a** and P(1)–N(1) 1.649(5) Å; P(1)–N(2) 1.655(5) Å for **5a**. The structural changes that were observed with the formation of the trimethylphosphine stabilized stibonium cation **5c** from **4c** are summarized in Table 3. There is a slight increase in the Sb–N bond lengths (Sb–N(1) = 2.057(2) Å, Sb–N(2) = 2.053 Å), and is slightly longer than previously reported examples of N-heterocyclic stibonium cations.^{19,20} The Sb–P bond is elongated at 2.6171(11) Å and is outside the sum of the covalent radii (cf. 2.50 Å)²¹ and is in line with other values reported for P→Sb bonding modes.^{22,23} Figure 3 shows the crystal structure and packing motifs of compound **5b** forming an extended network of zigzag chains. When viewed down the *c*-axis the molecules are π -stacked in a head to tail cation conformation orientated in a perpendicular fashion with the pnictogenium center in one cation directed toward the centroid of the bithiophene unit on an adjacent cation. They are packed in four nonequivalent stacks that are nearly vertical to each other (ca. 75.49 $^\circ$) because of the occurrence of As $\cdots\pi$ intermolecular contacts with an interplanar distance of 6.18 Å. This packing motif is most likely attributed to the existence of C–H $\cdots\pi$ and As $\cdots\pi$ interactions and is not observed in any of the other pnictogen complexes. These interactions are similar to those reported between three coordinate As(III) centers and arenes^{24–26} and other arsenium cations.²⁷

The Pt complex **6a** is trigonal planar at the metal ($\Sigma_{\text{ang}} = 360.00^\circ$). The geometry at the phosphonium P-atom is almost trigonal planar ($\Sigma_{\text{ang}} = 356.87^\circ$). The N(1)–P(1)–N(2) plane of the phosphonium makes a torsion angle of 78.9(2) $^\circ$ with the coordination plane of the metal likely because of the bulky nature of the triphenylphosphine ligands. The Pt–NHP bond P(1)–Pt(1) (2.1157(12) Å) is shorter than the Pt(1)–P(2) (2.3315(13) Å) and Pt(1)–P(3) bonds (2.2935(12) Å) suggesting strong backbonding from the Pt to the phosphonium similar to that observed in related phosphonium→Pt complexes (cf. 2.116(3) Å; 2.107(3) Å).^{28,29} Upon examination of the solid state structure of **6a**, it consists of a central Pt center with two triphenylphosphine ligands. In contrast to **6a**, compound **6b** is pyramidal at the pnictenium center and has a coordination geometry ($\Sigma_{\text{ang}} = 307.24^\circ$) consistent with a nonbonding lone pair still present on the arsenium and can be described as primarily M → L bonding.³⁰ Progressing down group 15 from P to As, the bonding changes from the filled sp² hybrid orbital on phosphorus interacting with the empty

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Compounds 3–6

compound bond	3	4a	4b	4c	5a	5b	5c	6a	6b
N(1)–C(12)	1.404(4)	1.413(3)	1.405(2)	1.406(3)	1.396(8)	1.372(6)	1.417(4)	1.401(6)	1.394
N(2)–C(11)	1.434(4)	1.415(3)	1.406(2)	1.396(3)	1.388(8)	1.369(6)	1.423(4)	1.395(5)	1.388(7)
C(11)–C(12)	1.379(4)	1.399(3)	1.395(2)	1.412(3)	1.396(7)	1.408(6)	1.391(4)	1.386(6)	1.408(7)
Pn(1)–X(1)	N/A	2.2123(9)	2.3296(5)	2.5129(6)	N/A	N/A	2.6171(11)	N/A	N/A
N(1)–Pn(1)	N/A	1.683(2)	1.8224(13)	2.0203(19)	1.649(5)	1.790(4)	2.057(2)	1.660(4)	1.835(4)
N(2)–Pn(1)	N/A	1.6942(19)	1.8255(13)	2.0091(18)	1.655(5)	1.798(4)	2.053(3)	1.666(4)	1.825(5)
Pn(1)–Pt(1)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2.1157(12)	2.4462(7)
N(1)–Pn(1)–N(2)	N/A	89.79(10)	85.72(6)	79.67(7)	91.3(3)	85.89(17)	81.52(10)	90.90(18)	84.5(2)
N(1)–Pn(1)–X(1)	N/A	102.81(7)	100.85(5)	92.70(6)	N/A	N/A	89.17(8)	N/A	N/A
N(2)–Pn(1)–X(1)	N/A	100.40(7)	101.12(5)	95.81(6)	N/A	N/A	89.69(8)	N/A	N/A
N(1)–Pn(1)–Pt(1)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	134.49(14)	107.78(14)
N(2)–Pn(1)–Pt(1)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	131.48(14)	114.98(15)

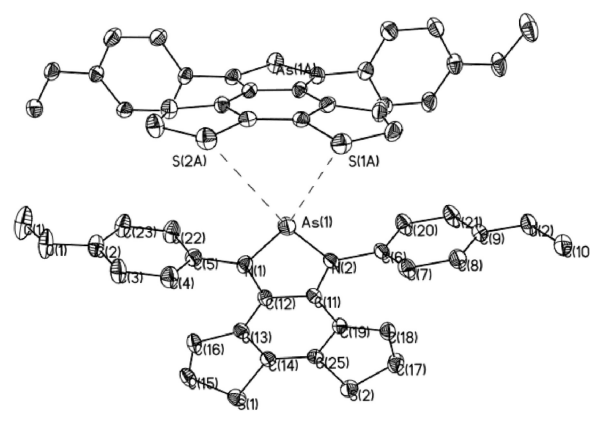
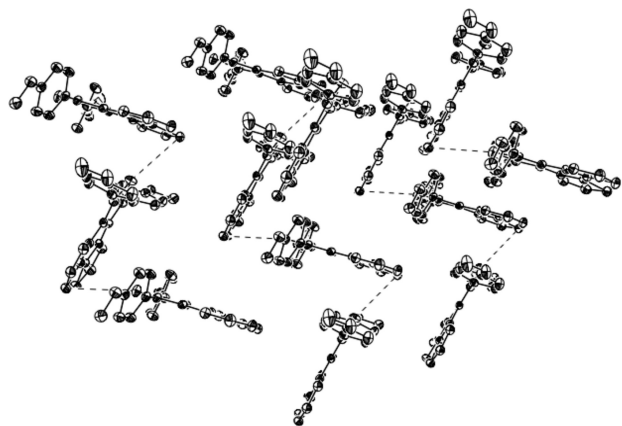


Figure 3. Crystal packing of 5b.

d-orbitals on Pt^0 , and metal backbonding to the empty p orbital on phosphorus leading to a coplanar arrangement. However for As, only the metal is donating into the empty p orbital on As leading to a pyramidal geometry. This bonding is similar to the heavy N-heterocyclic plumblylenes observed by Hahn. The metal (Pt^0 or Pd^0) acts as a d-electron donor to the empty p orbital on Pb^{II} , and the lone pair of electrons on Pb, located in the sp^2 hybrid orbital, do not participate in bonding to the metal center. By going down group 14 in synthesizing the heavier group 14 NHC metal complexes, the geometry at the coordinating atom changes from coplanar to tetrahedral.³¹

CONCLUSION

The successful synthesis of a new diamine ligand with a conjugated fused bithiophene backbone was achieved and subsequently converted to the diaminochloropnictine and pnictenium cations. These complexes are the first examples of pnictogens containing a conjugated bithiophene backbone and the first example of a pnictogen containing a thiophene heterocycle complexed to a transition metal. These new complexes did not display any solvatochromic properties. Compounds 3, 4a, 4c, 5a, and 5c did display fluorescence; however, the efficiencies were low. This new ligand system opens the door to the preparation of other p-block derivatives, which could have new electronic or photophysical properties, and is a step toward narrowing the gap between pure and applied chemistry.

EXPERIMENTAL SECTION

All manipulations were performed under N_2 atmosphere using standard Schlenk or glovebox techniques unless stated otherwise.

Reagents were obtained from commercial sources. Phosphorus(III) chloride was distilled prior to use while all other reagents were used without purification. CDCl_3 was dried over calcium hydride. Solvents were dried and deoxygenated by using an MBraun controlled-atmosphere solvent purification system and stored in Straus flasks under N_2 atmosphere or over 4 Å molecular sieves in the glovebox. All NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer (^1H = 399.76 MHz, ^{13}C = 100.52 MHz, ^{19}F = 376.15 MHz, ^{31}P = 161.85 MHz). All $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded relative to an external standard (85% H_3PO_4 , δ 0.00). X-ray diffraction data were collected on a Nonius Kappa-CCD area detector or Bruker Kappa Apex II using Mo_α radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on glass fibers or scoops, and immediately placed in a cold stream of N_2 . Structures were solved by direct methods and refined using full matrix least-squares of F^2 . Hydrogen-atom positions were calculated. UV–visible absorption spectra were recorded over a range of 250–600 nm using a Varian Cary 300 spectrometer in CH_2Cl_2 . Emission spectra were recorded on a Fluorolog (QM-7/2005) instrument with a slit width of 0.5 nm in CH_2Cl_2 . High resolution mass spectrometry data were collected by Mr. Doug Hairsine (UWO) using a Finnigan MAT 8400 instrument. Synthesis of 2,2'-bithiophene,³² 3,3',5,5'-tetrabromo-2,2'-bithiophene,³² 3,3'-dibromo-2,2'-bithiophene,³² and 2,2'-bithiophene-3,3'-biscarboxaldehyde¹⁵ were synthesized following literature procedures.

Compound 2. A solution of 2,2'-bithiophene-3,3'-biscarboxaldehyde (1.50 g, 6.70 mmol) in EtOH (40 mL) was cooled to 0 °C and a solution of *p*-anisidine (1.74 g, 14.1 mmol) in EtOH (10 mL) was added dropwise. The reaction mixture was warmed to room temperature and then heated to reflux for 4 h. The solvent was concentrated, and the resulting yellow powder was collected by filtration and washed with cold EtOH (3×5 mL). Yield: 86% (2.50 g, 5.78 mmol); mp 148–149 °C (dec). ^1H NMR (CDCl_3): δ 8.38 (s, 2H, CH), 7.81 (d, 2H, aryl, $^3J_{\text{HH}}$ = 5.2), 7.45 (d, 2H, aryl, $^3J_{\text{HH}}$ = 5.2),

7.08 (d, 4H, aryl, $^3J_{\text{HH}} = 8.8$), 6.83 (d, 4H, aryl, $^3J_{\text{HH}} = 9.2$), 3.78 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 55.4, 114.3, 122.1, 127.0, 127.3, 136.2, 139.1, 144.6, 151.7, 158.4. FT-IR (relative intensities) $\nu = 533(14)$, 630(9), 715(11), 728(13), 781(7), 826(4), 1034(2), 1105(12), 1207(6), 1251(1), 1293(10), 1458(8), 1500(3), 1611(5), 2360(15) cm^{-1} . FT-Raman (relative intensities) $\nu = 160(3)$, 679(12), 788(15), 968(13), 1166(7), 1209(4), 1247(14), 1295(11), 1355(8), 1392(9), 1462(5), 1501(6), 1592(1), 1624(2), 3101(15). HRMS: $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2$ calcd (found) 432.0966 (432.0955).

Compound 3. A DMF (5 mL) solution of **2** (2.50 g, 5.78 mmol) and sodium cyanide (0.28 g, 5.78 mmol) stirred at room temperature for 48 h. To the reaction mixture 10 mL of CH_2Cl_2 was added and washed with water (3×5 mL). The CH_2Cl_2 layer was then dried with MgSO_4 and concentrated. The product was then precipitated with MeOH and isolated by filtration. The resulting orange powder was washed with MeOH (3×5 mL). Yield: 80% (2.05 g, 4.62 mmol); mp 173–175 °C (dec). ^1H NMR (CD_3CN): δ 7.39 (d, 2H, aryl, $^3J_{\text{HH}} = 5.6$), 7.10 (d, 2H, aryl, $^3J_{\text{HH}} = 5.6$), 6.69 (d, 4H, aryl, $^3J_{\text{HH}} = 8.8$), 6.62 (d, 4H, aryl, $^3J_{\text{HH}} = 8.8$), 6.28 (s, 2H, NH), 3.66 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 55.6, 114.6, 117.5, 123.5, 123.9, 128.84, 130.5, 134.5, 139.8, 153.7. FT-IR (relative intensities) $\nu = 653(9)$, 732(4), 806(6), 901(10), 1033(3), 1107(15), 1167(11), 1179(12), 1245(2), 1297(13), 1356(14), 1397(8), 1449(5), 1507(1), 3336(7) cm^{-1} . FT-Raman (relative intensities) $\nu = 1314(4)$, 1462(2), 1499(1), 1587(3), 2061(15), 2076(13), 2146(14), 2157(7), 2171(12), 2205(11), 2220(10), 2243(9), 2265(8), 2732(5), 3059(6). HRMS: $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2$ 432.0966 (432.0955).

Compound 4a. A THF (5 mL) solution of **3** (0.30 g, 0.69 mmol) and *n*-methylmorpholine (0.29 mL, 2.08 mmol) stirred for 10 min at room temperature. PCl_3 (0.06 mL, 0.69 mmol) was added to the solution. The reaction then stirred for 4 days at room temperature. The white precipitate was removed by centrifuge, and the resulting orange solution was concentrated in vacuo yielding an orange solid. Yield: 83% (0.28 g, 0.57 mmol); mp 207–211 °C (dec). ^1H NMR (CDCl_3): δ 7.62 (br. s, 4H, aryl), 7.16 (d, 2H, aryl, $^3J_{\text{HH}} = 6.0$), 7.07 (d, 4H, aryl, $^3J_{\text{HH}} = 7.6$), 6.28 (d, 2H, aryl, $^3J_{\text{HH}} = 5.2$), 3.92 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 55.5, 114.8, 120.9, 124.2, 125.2, 129.1, 129.4, 129.9, 130.0, 130.3, 159.9. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 136.53. FT-IR (relative intensities) $\nu = 532(12)$, 724(2), 817(7), 918(10), 978(5), 1031(9), 1104(13), 1124(4), 1167(8), 1247(2), 1280(11), 1437(15), 1463(14), 1363(6), 1508(1) cm^{-1} . FT-Raman (relative intensities) $\nu = 215(2)$, 384(3), 795(8), 1238(5), 1365(1), 1500(6), 2619(7), 3321(7) cm^{-1} . HRMS: $[\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{PS}_2]^+$ calcd (found) 461.0547 (461.0547). Elemental Analysis (%) calc for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{PS}_2\text{Cl}$: C 58.00, H 3.65, N 5.64; found C 57.86, H 3.70, N 5.44.

Compound 4b. A THF (40 mL) solution of **3** (1.0 g, 23 mmol) and *n*-methylmorpholine (0.76 mL, 69 mmol) stirred for 10 min at room temperature. AsCl_3 (0.20 mL, 23 mmol) was added to the solution. The reaction then stirred for 4 days at room temperature. The white precipitate was removed by centrifuge, and the resulting red solution was concentrated in vacuo yielding a red solid. Yield: 54% (0.67 g, 12.4 mmol); mp 208.4–213.2 °C (dec). ^1H NMR (CDCl_3): δ 7.48 (d, 4H, aryl, $^3J_{\text{HH}} = 8.8$), 7.04 (d, 2H, aryl, $^3J_{\text{HH}} = 5.2$), 6.98 (d, 4H, aryl, $^3J_{\text{HH}} = 8.8$), 6.20 (d, 2H, aryl, $^3J_{\text{HH}} = 5.6$), 3.84 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 55.5, 114.8, 121.5, 123.5, 126.0, 129.0, 129.8, 131.1, 132.2, 142.2, 159.6. FT-IR (relative intensities) $\nu = 485(15)$, 521(6), 642(5), 728(3), 812(10), 912(8), 945(12), 1028(4), 1116(13), 1244(1), 1277(11), 1363(7), 1455(14), 1505(2), 1602(9) cm^{-1} . HRMS: $[\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{As}]^+$ calcd (found) 505.0026 (505.0029). Elemental Analysis (%) calc for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{AsS}_2\text{Cl}$: C 53.29, H 33.35, N 5.18; found C 53.29, H 33.3, N 5.15.

Compound 4c. In a pressure tube a THF (30 mL) solution of **3** (1.0 g, 23 mmol) and NEt_3 (0.96 mL, 0.0069 mmol) stirred for 10 min at room temperature. A THF solution (5 mL) of SbCl_3 (0.52 g, 0.0023 mmol) was added to the solution. The reaction was then heated to 60 °C for 48 h. The precipitate was removed by centrifuge, and the resulting red solution was concentrated in vacuo yielding a red solid. Yield: 95% (1.27 g, 21 mmol); decomp. 152 °C (dec). ^1H NMR (CDCl_3): δ 7.33 (d, 4H, aryl, $^3J_{\text{HH}} = 8.4$), 7.03 (d, 2H, aryl, $^3J_{\text{HH}} = 5.6$), 6.96 (d, 4H, aryl, $^3J_{\text{HH}} = 8$), 6.32 (d, 2H, aryl, $^3J_{\text{HH}} = 4.8$),

3.88 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 45.7, 55.5, 110.7, 114.7, 122.5, 128.0, 134.6, 136.5, 158.2. FT-IR (relative intensities) $\nu = 638(10)$, 704(8), 722(4), 814(11), 909(5), 942(14), 1030(6), 1102(12), 1178(8), 1241(2), 1274(7), 1349(3), 1450(9), 1503(1), 1601(15). FT-Raman (relative intensities) $\nu = 96.7(5)$, 173(11), 195(13), 227(4), 245(1), 676(8), 784(10), 1098(12), 1224(3), 1270(6), 1307(9), 1348(2), 1388(14), 1449(15), 1496(7).

Compound 5a. To a solution of **3** (0.10 g, 0.20 mmol) in CH_2Cl_2 (4 mL) the halide-abstracting agent Me_3SiOTf (0.04 mL, 0.22 mmol) was added dropwise. The solution was stirred for 10 min at room temperature during which time a yellow solid precipitated from the solution. The red solution was decanted off, and the remaining yellow solid was dried in vacuo. The product was washed with Et_2O (2×3 mL) and dried. Yield: 90% (0.11 g, 0.18 mmol); mp >300 (dec) °C. ^1H NMR (CDCl_3): δ 7.84 (d, 4H, aryl, $^3J_{\text{HH}} = 8.4$), 7.36 (d, 2H, aryl, $^3J_{\text{HH}} = 5.2$), 7.20 (d, 4H, aryl, $^3J_{\text{HH}} = 8.8$), 6.41 (d, 2H, aryl, $^3J_{\text{HH}} = 5.2$), 3.97 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (pyridine- d_5): δ 54.3, 114.5, 119.5, 123.8, 125.2, 127.6, 127.8, 128.2, 128.3, 129.7, 159.4. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 191.00. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3): δ -78.5. FT-IR (relative intensities) $\nu = 527(13)$, 635(5), 649(11), 724(12), 740(9), 824(8), 1030(2), 1159(3), 1174(6), 1221(7), 1257(1), 1307(10), 1325(15), 1509(3), 1608(14) cm^{-1} . FT-Raman (relative intensities) $\nu = 633(9)$, 709(10), 736(12), 794(13), 1029(6), 1180(5), 1325(14), 1366(15), 1433(7), 1491(1), 1605(4), 1892(8), 2115(3), 2609(2), 3081(11) cm^{-1} . HRMS: $[\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{PS}_2]^+$ calcd (found) 461.0547 (461.0538). Elemental Analysis (%) calc for $\text{C}_{25}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_5\text{PS}_3\text{C}_{0.25}\text{H}_{0.5}\text{Cl}_{0.5}$: C 48.00, H 2.95, N 4.43, S 15.23; found C 47.91, H 3.03, N 4.43, S 15.39.

Compound 5b. To a solution of **4b** (0.18 g, 0.33 mmol) in CH_2Cl_2 (4 mL) the halide-abstracting agent Me_3SiOTf (0.11 mL, 0.66 mmol) was added dropwise. The solution was stirred for 45 min at room temperature during which time the solution turned red and a dark yellow solid precipitated from the solution. The red solution was decanted off, and the remaining yellow solid was dried in vacuo. The product was washed with Et_2O (2×3 mL) and dried. Yield: 93% (0.20 g, 0.31 mmol); mp >300 (dec) °C. ^1H NMR (CDCl_3): δ 7.68 (d, 4H, aryl, $^3J_{\text{HH}} = 8.0$), 7.27 (d, 2H, aryl, $^3J_{\text{HH}} = 8.0$), δ 7.15 (d, 4H, aryl, $^3J_{\text{HH}} = 8.4$), 6.34 (d, 2H, aryl, $^3J_{\text{HH}} = 4.8$), 3.94 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 55.7, 115.3, 116.3, 122.2, 124.9, 125.7, 128.9, 129.3, 135.1, 136.4, 161.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3): δ -78.2. FT-IR (relative intensities) $\nu = 521$ (8), 635 (4), 715 (10), 738 (7), 819 (5), 1029 (3), 1157 (5), 1173 (14), 1221 (15), 1256 (10), 1458 (13), 1508 (2), 1540 (11), 1606 (9), 3084 (12) cm^{-1} . HRMS: $[\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{AsS}_2]^+$ calcd (found) 505.0020 (505.0003). Elemental Analysis (%) calc for $\text{C}_{25}\text{H}_{18}\text{AsClF}_3\text{N}_2\text{O}_5\text{S}_3$: C 45.88, H 2.77, N 4.28; found C 45.72, H 2.49, N 4.12.

Compound 5c. To an orange solution of **5c** (0.1 g, 0.17 mmol) in CH_2Cl_2 (3 mL) was added PMe_3 (0.035 mL, 0.034 mmol) and Me_3SiOTf (0.031 mL, 0.17 mmol). The reaction mixture stirred at room temperature for 1 h and was then concentrated. The CH_2Cl_2 was decanted off leaving a yellow solid, which was washed (2×5 mL) with pentane. Yield: 36% (0.135 g, 0.061 mmol); decomp. 223–225 (dec) °C. ^1H NMR (CDCl_3): δ 7.15 (m, 6H, aryl), 6.82 (d, 4H, aryl, $^3J_{\text{HH}} = 8.4$), 6.68 (d, 2H, $^3J_{\text{HH}} = 5.4$), 3.78 (s, 6H, CH_3), 1.55 (d, 9H, CH_3 , $^2J_{\text{PH}} = 12$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 9.5 (CP, $^1J_{\text{PC}} = 106.8$), 55.1, 114.2, 123.0, 124.4, 125.6, 141.5, 137.8, 140.8, 156.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3): δ -78.2. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ -1.19. FT-IR (relative intensities) $\nu = 510(6)$, 633(4), 704(14), 732(6), 810(13), 901(9), 956(8), 1024(3), 1109(12), 1161(7), 1237(1), 1291(5), 1386(10), 1453(15) cm^{-1} . FT-Raman (relative intensities) $\nu = 87(3)$, 194(10), 244(2), 674(12), 780(6), 1025(11), 1221(8), 1262(15), 1312(7), 1361(5), 1387(9), 1452(13), 1497(1), 1606(4), 2914(14) cm^{-1} . Elemental Analysis (%) calc for $\text{C}_{28}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_5\text{PS}_3\text{Sb}\text{-C}_{0.5}\text{H}_{1.5}\text{Cl}_1$: C 41.75, H 3.44, N 3.42, S 11.73; found C 41.48, H 3.61, N 3.47, S 11.71.

Compound 6a. To a solution of **5a** (0.015 g, 0.032 mmol) in CH_2Cl_2 (2 mL) was added a CH_2Cl_2 (2 mL) solution of $\text{Pt}(\text{PPh}_3)_4$ (0.04 g, 0.032 mmol). The solution turned from yellow to red and was stirred for 10 min at room temperature. The CH_2Cl_2 was removed in vacuo, yielding a red oil. After triturating the red oil with Et_2O (3 mL)

for 10 min an orange solid precipitated from solution. The Et₂O was decanted off and dried under reduced pressure. Yield: 77% (0.028 g, 0.024 mmol); mp 146–148 °C (dec). ¹H NMR (CDCl₃): δ 7.29 (t, 6H, aryl, ³J_{HH} = 7.6), 7.21 (d, 2H, ³J_{HH} = 5.6), 7.10 (t, aryl, 12H, ³J_{HH} = 8), 6.91 (br. 15H, aryl), 6.82 (pseudo d, 2H, aryl, ³J_{HH} = 8.8), 3.85 (s, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃): 55.8, 115.4, 120.6, 123.6, 125.9, 127.5, 127.6, 128.7, 128.8, 129.3, 130.9, 131.6, 133.4, 160.9. ³¹P{¹H} NMR (CDCl₃): 47.45 (²J_{PP} = 490.8, ¹J_{PPt} = 2358), 249.5 (²J_{PP} = 492.4, ¹J_{PPt} = 2326). ¹⁹F {¹H} NMR (CDCl₃): δ 78.41. FT-IR (relative intensities) ν = 514(5), 528(2), 636(3), 693(3), 743(9), 922(11), 998(14), 1030(4), 1094(10), 1130(8), 1248(1), 1435(7), 1478(15), 1507(2), 1605(12) cm⁻¹. FT-Raman (relative intensities) ν = 174(6), 363(7), 999(3), 1027(12), 1096(14), 1131(2), 1236(3), 1375(1), 1494(11), 1321(15), 1585(5), 1887(8), 2112(13), 2560(10), 3057(9) cm⁻¹.

Compound 6b. To a solution of **5b** (0.015 g, 0.032 mmol) in CH₂Cl₂ (2 mL) was added a CH₂Cl₂ (2 mL) solution of Pt(PPh₃)₄ (0.04 g, 0.032 mmol). The solution turned from orange to purple and was stirred for 10 min at room temperature. The CH₂Cl₂ was removed in vacuo, yielding a purple oil. After triturating the purple oil with Et₂O (3 mL) for 10 min a purple solid precipitated from solution. The Et₂O was decanted off and dried under reduced pressure. Yield: 92% (0.035 g, 0.029 mmol); decomp. 225(dec) °C. ¹H NMR (CDCl₃): 7.28 (m, 6H, aryl), 7.20 (m, 15H, aryl), 7.07 (m, 15H, aryl), 6.81 (d, 4H, aryl, ³J_{HH} = 8.8), 5.97 (d, 2H, aryl, ³J_{HH} = 5.6), 3.87 (s, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 55.8, 114.5, 122.9, 123.9, 124.5, 128.5, 129.1, 131.3, 134.6, 156.6. ³¹P{¹H} NMR (CDCl₃): 41.9 (t, ¹J_{PPt} = 5347.6). ¹⁹F {¹H} NMR (CDCl₃): δ -78.3. FT-IR (relative intensities) ν = 515(2), 538(10), 636(6), 695(4), 744(7), 1025(5), 1097(11), 1157(8), 1222(12), 1263(1), 1303(13), 1386(14), 1435(9), 1478(15), 1506(3).

■ ASSOCIATED CONTENT

● Supporting Information

Spectroscopic data for compounds **3–6b**. This material is available in free of charge via the Internet at <http://pubs.acs.org>.

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