Ladder-Type π-Conjugated 4-Hetero-1,4-dihydrophosphinines: A Structure–Property Study

Yi Ren and Thomas Baumgartner*[a]

Abstract: π-Conjugated six-membered 1,4-dihydrophosphinines containing a heteroatom (Si, P, S) at the 4 position were synthesized and systematically studied. X-ray crystallographic analyses showed that the central six-membered heterocyclic rings are almost planar. The sum of the angles around the phosphorus atom increases by 23° from the trivalent phosphorus to the phosphonium atom in the thiaphosphinine system, which is consistent with the NMR spectroscopic studies. UV/Vis spectroscopy and theoretical calculations revealed that the communication between the phosphorus center and the benzothiophene moiety is enhanced by the incorporation of a sulfur atom into the molecular scaffold. The increased conjugation endows the thiaphosphinines with interesting emission properties. Theoretical calculations supported the postulation that the orbital coupling between the π system and a σ* orbital could be enhanced in the thiaphosphinine system, especially through a phosphonium center. Cyclic voltammetry studies revealed that the thiaphosphinine oxide, thiaphosphonium, and cis-diphosphinine oxide exhibit quasi-reversible reduction processes, which demonstrate that simple changes in the bridge heteroatoms help to efficiently tune the redox properties of the ladder-type 4-hetero-1,4-dihydrophosphinines.

Keywords: organic electronic materials · π interactions · phosphorus heterocycles · solid-state structures · sulfur heterocycles

Introduction

In recent years, organic π-conjugated compounds have become an important class of materials owing to their semiconducting properties.[1,2] In particular, ladder-type heteroacenes[3] have attracted a lot of attention as their rigidified, planar structure makes them promising candidates for a variety of applications that include, for example, organic field-effect transistors (OFETs).[1,2] The fusion of ring-systems generally provides a high degree of π-conjugation, which intrinsically affords smaller band gaps in the materials; fused arenes can generally impart quinoid character into the oligomer/polymer and thus lower the band gap relative to, for example, simple polyarylenes or polythiophenes, where twisting from planarity can easily disrupt conjugation.[1c,3e] To further improve the properties of these materials, ladder-type oligothiophene and acene analogues that incorporate main-group atoms, such as boron,[4] silicon,[5] and phosphorus,[6] have recently become desirable targets. The main-group elements in these materials were found to introduce some intriguing photophysical properties, such as high quantum yields, tunable emission color, and high charge-carrier mobility. These effects can be attributed to the inherent electronic structure and chemical versatility of the inorganic centers, and can generally not be observed in such complexity with purely carbon-based π-conjugated materials.[1–3] Whereas boron atoms provide an empty π orbital that can efficiently interact with π-conjugated systems,[4] silicon and phosphorus show σ–π hyperconjugation between the π* system of the conjugated scaffold and the σ* orbital of exocyclic Si/P–C bonds.[5,6] Both of these interactions have a significant impact on the frontier orbitals of the materials, and thus on the photophysical properties of the materials as a whole. We previously observed these beneficial features for the dithieno[3,2-b:2′,3′-d]phosphole system (1, Figure 1).[7] Using extended dithienophosphole heteropentacenes (1, A = C3H5), we recently reported that the presence of a phosphorus center also enhances the desirable n-type semiconducting characteristics in these systems.[8]

Importantly, the photophysical properties and solid-state organization can be efficiently addressed through simple
modification at the phosphorus center (E; Figure 1). This is a staple of organophosphorus π-conjugated materials and further illustrates the beneficial features of main-group element-based electronic materials. In an expansion of our work on dithienophospholes, we have recently reported our preliminary studies on ladder-type systems that contain a central 1,4-dihydro-1,4-phosphasilin ring (II; Figure 1).[9]

Our studies revealed that the incorporation of an additional silicon center into the scaffold of the dithienophosphate system significantly changes the photophysics of the scaffold, largely owing to the electronic effect of increasing the band gap of the system by approximately 1 eV.

To further evaluate the suitability of ladder-type systems that contain central six-membered rings for π-conjugated organophosphorus electronic materials, we now report our systematic structure–property studies on a series of extended 1,4-dihydrophosphinine-based pentacenes containing a 1,4-P,S or 1,4-P,P substitution pattern. For comparison, we have also included the P/C0 Si system in our studies. We report that the tuning of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels, that is, the electronic structure of systems, the solid-state organization, and the π-conjugation within the molecular scaffolds can be controlled efficiently by the nature, as well as the chemical modification of the heteroatoms. This experimental study is further supported by theoretical calculations to provide a detailed understanding of these new classes of ladder-type organophosphorus materials.

**Results and Discussion**

**Synthesis of Extended Ladder-Type 4-Heterophosphinines**

Our initial studies involving dithieno[2,3-b:2′,3′-d][1,4-dihydro-1,4-phosphasilin]-based ladder-type materials (Scheme 1).[9] The heteroatom-bridged bis-(benzo[b]thiophene)es 1a–1c were obtained from the reaction between their corresponding heteroatomic reagents (Me3SiCl2, PhPCl2, (PhSO2)2S) and 2-lithio-3-bromobenzothiophene, which was generated by monolithiation of 2,3-dibromobenzothiophene at −78°C with nBuLi in THF or diethyl ether. Subsequent lithiation of compounds 1a–1c with nBuLi at −78°C in THF or diethyl ether afforded the 4-heteroatomic 1,4-dihydrophosphinine rings in good yields after the addition of PhPCl2 with the assistance of TMEDA; compound 2a could also be obtained without the addition TMEDA. Owing to the expected occurrence of the cis- and trans-isomers of the diphosphinine 2b in various ratios depending on the solvent ratio used (THF/Et2O),[10] the trivalent phosphorus species was oxidized with hydrogen peroxide in situ to provide dioxide 3b (Scheme 2). The latter allowed for the clean separation into cis- and trans-species by column chromatography, owing to their significantly different dipole moments, as recently shown by Yamaguchi and co-workers for a π-conjugated ladder bis(phosphole).[6f] On the other hand, 4-thia-1,4-dihydrophosphinine species 2c was isolated and its electronic structure systematically modified in a series of subsequent reactions at the tri-
valent phosphorus center (Scheme 3). These representative modifications involved oxidation with hydrogen peroxide, methylation with methyl triflate (MeOTf), and complexation with [Au(tht)]Cl (tht = tetrahydrothiophene).\[^{7-9,11}\] to afforded the corresponding products 3c, 4c, and 5c, respectively, in good yields (Scheme 3).

Scheme 3. Functionalization of the sulfur-based system 2c.

Owing to the intriguing optical properties afforded by potential Au–Au interactions, the complexation of 1,4-dihydrodiposphinine 2b with [Au(tht)Cl] was also carried out using a mixture of cis/trans-2b containing about 90% cis-2b.\[^{10}\] The cis-configured gold complex cis-5b could then be isolated by washing the product mixture with acetone. These simple modifications provided us with a family of materials that were either different in terms of the electronic nature of the phosphorus center, or, in the case of the P–P system, in terms of cis/trans-isomerism as well. Differential scanning calorimetry (DSC) studies on the heteroatomic dihydrodiphosphinines also showed good thermal stability for these compounds (\(T_m = 230.6 ^\circ\text{C}\) for 3c, 273.9 \(^\circ\text{C}\) for 4c, 322.2 \(^\circ\text{C}\) for cis-3b, and 333.6 \(^\circ\text{C}\) for trans-3b) with no decomposition observed at up to 350 \(^\circ\text{C}\), except for gold complexes 5c and cis-5b that did not show clear melting transitions in this range. The obtained materials were then investigated in detail to elucidate how the degree of \(\pi\)-conjugation within the molecular scaffold impacts the optical/electronic properties, as well as their solid-state organization.

**NMR Studies**

Our studies involving the phosphasilin system 2a have indicated that its degree of \(\pi\)-conjugation is minimal, although the silicon center should theoretically allow for negative hyperconjugation, and as such for delocalization throughout the whole scaffold; the same is true for the oxidized phosphoranyl unit. Even participation of the lone pair of trivalent phosphorus species 2a in the \(\pi\) conjugation is limited. The phosphasilin ring unit was found to essentially isolate the two benzo[\(b\)]thiophene chromophores of the scaffold.\[^{9}\]

To further investigate this feature in more detail, we analyzed the \(^{31}\)P NMR shifts of three families of compounds with P–Si, P–P, and P–S central rings. Chemical shifts in the NMR spectra are generally indicative of the delocalization effect of atoms. According to previous studies, the \(^{31}\)P NMR shift can give an indication of the electronic shielding at a phosphorus center, particularly in its trivalent state.\[^{13}\] The trivalent phosphorus compounds 2a–c have high-field-shifted \(^{31}\)P NMR resonances, when compared with the bis(benzothieno)phosphole system (1, A = C\(_4\)H\(_4\)).\[^{8a}\] which indicates the lone pair on the phosphorus atom may not be efficiently delocalized in the heterocyclic phosphinine systems. It is worth pointing out that thiaphosphinine compound 2c has the most high-field-shifted \(^{31}\)P NMR resonance of this series (\(\delta = -60.2 \text{ ppm}\)), which is consistent with a strongly pyramidal P-center (see below). Upon oxidation and methylation of the trivalent phosphorus center, the \(^{31}\)P NMR signal shifts to lower fields at \(\delta = -4.1 \text{ ppm}\) (3c), or \(\delta = -4.1 \text{ ppm}\) (4c), as expected. Notably, the chemical shift difference between the trivalent, the oxidized, and methylated phosphorus species of the thiaphosphinine compounds is much larger (\(\Delta\delta = 68.4 \text{ ppm for P=O, } \Delta\delta = 56.1 \text{ ppm for } \text{P=Me}\) than for the dithienophosphole system reported previously (\(\Delta\delta = 53.5 \text{ ppm for P=O, } \Delta\delta = 33.5 \text{ ppm for } \text{P=Me}\)).\[^{8b,8a,11}\] which indicates a more significant electronic structural change in the phosphinine system after oxidation/methylation. In the \(^{13}\)C NMR spectrum of compound 4c, the ipso(P)-carbon atoms of the thieno-units experienced a strong shielding (\(\delta^{13}\text{C}=103.6 \text{ ppm}\); cf. 2c \(\delta^{13}\text{C}=141.7 \text{ ppm}\); 3c \(\delta^{13}\text{C}=134.3 \text{ ppm}\); 5c \(\delta^{13}\text{C}=112.5 \text{ ppm}\); cis-3b \(\delta^{13}\text{C}=143.3 \text{ ppm}\) and 139.7 ppm; trans-3b \(\delta^{13}\text{C}=143.2 \text{ ppm}\) and 139.2 ppm). This indicates that the phosphonium center polarizes the molecule considerably when compared to the other thiaphosphinine compounds (see below). As for diphasphinine gold complex cis-5b, the P–P coupling constant (\(J = 7.9 \text{ Hz}\)) is smaller than those of the diphasphinine oxides (cis-3b \(J = 36.6 \text{ Hz}\); trans-3b \(J = 22.8 \text{ Hz}\)), which points towards the absence of Au–Au intramolecular interactions, owing to a weaker communication between the two P centers (see below).

**Molecular Structures and Solid-State Organization Studies**

We were able to obtain single crystals of compounds 2c, 3c, 4c, 5c, cis-3b, and trans-3b that were suitable for X-ray crystallographic studies. As has already been observed in the structure of the oxidized P–Si compound 3a (Scheme 1), the six-membered rings of all new compounds are almost planar. Thiaphosphinine 2c has a single molecule in the unit cell (Figure 2). Compared with those of the benzo-extended system 1 (A = C\(_4\)H\(_4\)), the endocyclic C7–C8 and C9–C10 bonds (both 1.36 \(\text{Å}\)) are significantly shorter than the C5–C6 and C11–C12 bonds (both 1.41 \(\text{Å}\)) of the benzene rings, which indicates the conjugation within the molecular framework decreases when an additional sulfur atom is placed in the phosphole ring. The small sum of the angles around the phosphorus atom may not be efficiently delocalized in the heterocyclic phosphinine systems. It is worth pointing out that thiaphosphinine compound 2c has the most high-field-shifted \(^{31}\)P NMR resonance of this series (\(\delta = -60.2 \text{ ppm}\)), which is consistent with a strongly pyramidal P-center (see below). Upon oxidation and methylation of the trivalent phosphorus center, the \(^{31}\)P NMR signal shifts to lower fields at \(\delta = -4.1 \text{ ppm}\) (3c), or \(\delta = -4.1 \text{ ppm}\) (4c), as expected. Notably, the chemical shift difference between the trivalent, the oxidized, and methylated phosphorus species of the thiaphosphinine compounds is much larger (\(\Delta\delta = 68.4 \text{ ppm for P=O, } \Delta\delta = 56.1 \text{ ppm for } \text{P=Me}\) than for the dithienophosphole system reported previously (\(\Delta\delta = 53.5 \text{ ppm for P=O, } \Delta\delta = 33.5 \text{ ppm for } \text{P=Me}\)).\[^{8b,8a,11}\] which indicates a more significant electronic structural change in the phosphinine system after oxidation/methylation. In the \(^{13}\)C NMR spectrum of compound 4c, the ipso(P)-carbon atoms of the thieno-units experienced a strong shielding (\(\delta^{13}\text{C}=103.6 \text{ ppm}\); cf. 2c \(\delta^{13}\text{C}=141.7 \text{ ppm}\); 3c \(\delta^{13}\text{C}=134.3 \text{ ppm}\); 5c \(\delta^{13}\text{C}=112.5 \text{ ppm}\); cis-3b \(\delta^{13}\text{C}=143.3 \text{ ppm}\) and 139.7 ppm; trans-3b \(\delta^{13}\text{C}=143.2 \text{ ppm}\) and 139.2 ppm). This indicates that the phosphonium center polarizes the molecule considerably when compared to the other thiaphosphinine compounds (see below). As for diphasphinine gold complex cis-5b, the P–P coupling constant (\(J = 7.9 \text{ Hz}\)) is smaller than those of the diphasphinine oxides (cis-3b \(J = 36.6 \text{ Hz}\); trans-3b \(J = 22.8 \text{ Hz}\)), which points towards the absence of Au–Au intramolecular interactions, owing to a weaker communication between the two P centers (see below).
bis(benzo[b]thieno)-1,4-dithiins that contain two sulfur atoms in the central ring.[13] Both isomeric bis-

In addition to efficient intramolecular conjugation, strong π–π intermolecular interactions are also very important for facilitating the charge transport in the bulk material. Unlike the 1,4-dihydro-1,4-phosphasilin oxide 3a, which has two methyl groups on the silicon center that prevent efficient intermolecular overlap of the π-conjugated scaffolds,[9] 2c crystallizes in a “sandwich” herringbone arrangement with two different kinds of π–π stacking motifs (distance = 3.6 Å; see the Supporting Information).

The oxidation of the phosphorus atom changes the geometric parameters significantly (Figure 3). The endocyclic P–C bonds (P1–C7/C10 both 1.79 Å) of the thiophosphinine oxide 3c are shorter than those of 2c (cf. P1–C7/C10 1.82 Å); the S–C bonds in the central six-membered ring also shortened upon oxidation of the phosphorus atom. The sum of angles around phosphorus center is increased to 315.4° supporting an enhancement of the electronic coupling between the phosphorus center and the π system by oxidation. In the solid state, 3c shows a herringbone motif, with molecules showing π–π stacking interaction of 3.5 Å within each layer (see the Supporting Information).

The molecular structure of the gold complex 5c in the solid state shows two independent molecules in the unit cell (Figure 4). The geometries of the two molecules are very similar. The gold center shows a relatively linear coordination (P1-Au1-Cl1 173.3°, P1A-Au1A-Cl1A 178.7°) in both molecules with bond lengths of 2.23 Å for Au1-P1, 2.30 Å for Au1–Cl1, 2.24 Å for Au1A–P1A, and 2.30 Å for Au1A–Cl1A, which are typical for (phosphanyl)gold(I) chlorides.[8c,11b,14] As with 3c, shortened endocyclic P–C bonds (P1-C7/C10 both 1.79 Å) are also found in gold complex 5c; the sum of the angles around the phosphorus atom (313.1°) is similar to that of compound 3c (315.4°). Remarkably, instead of aurophilic Au−Au interactions, three short intermolecular Au−S contacts (Au−S 3.72 Å, 3.27 Å, and 3.43 Å) induce two different kinds of π–π intermolecular interactions (3.6 Å and 3.8 Å), thereby leading to a dimeric associa-
tion of cis-5c in the solid state (see the Supporting Information). The latter is also the reason for different non-linear geometries around the two gold centers (Au1 and Au1A).

The structure of the phosphonium salt 4c in the solid state is shown in Figure 5. Notably, the positively charged phosphorus center further planarizes the central six-membered ring, which results not only in an increased sum of the angles around phosphorus (323.7°), but also increased endohedral angles around sulfur (4c: C9-S3-C10 102.8°; cf. 2c 101.4°, 3c 101.6°, 5c 101.7°). The endocyclic P–C bonds (P1-C8/C11 both 1.76 Å) are noticeably even shorter when compared to the other thiaphosphinines, whilst the carbon bonds of the central six-membered ring are elongated (C8–C9 1.38 Å, C10-C11 1.37 Å). The structural information of 4c suggests that the communication between phosphorus center and the aromatic ring is further enhanced by methylation of the phosphorus center, which is consistent with the observation in the NMR studies (see above). Strong π–π stacking interactions are also observed in 4c (3.5 Å and 3.6 Å; see the Supporting Information).

On the other hand, the additional phosphorus atom in cis-3b (Figure 6) and trans-3b (Figure 7) elongates the endocyclic P1/P2–C bonds, which indicates that the incorporation of a second phosphorus atom in the central six-membered ring decreases the communication between phosphorus atoms and the π system, as opposed to the incorporation of a sulfur atom. The trans-isomer 3b has a structure similar to cis-3b, but with a bigger sum of angles around P1 (cis-3b 319.7°, trans-3b 314.7°). Interestingly, the intermolecular π–π interactions are also strongly influenced by the small change in the orientation of the two phosphorus centers. For cis-3b, two kinds of π–π interactions, with distances of 3.5 Å and 3.6 Å, can be observed in the solid state (see the Supporting Information). However, in the case of trans-3b the two bulky phenyl rings on the opposite sides of the planar molecular scaffold prevent the molecules from efficiently forming π–π interactions. Here, only short contacts between two sulfur (3.2 Å), and one sulfur and one oxygen atom (3.3 Å) of neighboring molecules can be observed.

The very diverse molecular structures of compounds 2c, 3c, 4c, cis-trans-3b, and 5c in the solid state clearly show that the nature of the central six-membered heterocyclic ring has a significant impact on the molecular structure and the solid-state organization, thus highlighting the versatility that can be introduced by these main group element atoms.

### Optical Spectroscopy Studies

Optical spectroscopy can also be used to determine the degree of conjugation within a molecular scaffold. In order to study the effect of the heteroatoms in these new S–P and P–P systems, we have systematically investigated their ab-
sorption and photoluminescence properties. We have further compared the photophysics of the new heteropentacenes to those of the phosphasilin system, which has been found to show only negligible conjugation across the central six-membered ring.[9] The photophysical properties are summarized in Table 1. The diphosphinines, cis- and trans-3b, show similar absorption spectra to that of the phosphasilin system (2a: \( \lambda_{\text{max}} = 310 \) nm, 3a: \( \lambda_{\text{max}} = 311 \) nm)[9] with these lowest energy absorptions at \( \lambda_{\text{max}} = 301 \) nm and \( \lambda_{\text{max}} = 309 \) nm, respectively; these absorptions are assigned to \( \pi-\pi^* \) transitions according to the TD-DFT calculations (see below). The gold complex cis-5b shows a hypsochromic shift (\( \lambda_{\text{max}} = 294 \) nm) compared to the absorption of cis-3b, possibly owing to the greater electronegativity of oxygen versus gold, which increases the LUMO energy level and the band gap.

**Figure 6.** Top: Molecular structure of cis-3b in the solid state (50% probability level); hydrogen atoms and a dichloromethane solvent molecule are omitted for clarity. Selected bond lengths [\( \AA \)] and angles [\(^\circ \)]: P1–O1 1.483(4), P1–C7 1.815(5), P1–C10 1.805(5), P1–C21 1.806(5), P2–O2 1.487(3), P2–C8 1.781(5), P2–C9 1.792(5), P2–C31 1.793(5), C7–C8 1.366(7), C9–C10 1.367(7), S1–C8 1.732(5), S2–C9 1.730(5); C7–P1–C10 104.7(2), C7–P1–C21 104.9(2), C21–P1–C10 105.9(2), C8–P2–C9 102.6(2), C9–P2–C31 106.2(2), C8–P1–C10 104.7(2), C8–P1–C21 104.9(2), C21–P1–C10 105.9(2), C7–P2–C9 102.6(2), C9–P2–C31 106.2(2). Bottom: Molecular packing of 3b.

**Figure 7.** Top left: Molecular structure of trans-3b in the solid state (50% probability level); hydrogen atoms are omitted for clarity. Selected bond lengths [\( \AA \)] and angles [\(^\circ \)]: P1–O1 1.477(3), P1–C8 1.797(3), P1–C10 1.805(4), P1–C21 1.797(4), P2–O2 1.486(3), P2–C7 1.794(4), P2–C9 1.794(4), P2–C31 1.792(4), C7–C8 1.371(5), C9–C10 1.375(5), S1–C7 1.742(4), S2–C9 1.732(4); C8–P1–C10 105.02(17), C8–P1–C21 107.23(18), C21–P1–C10 107.39(17), C7–P2–C9 102.38(17), C9–P2–C31 105.09(18), C8–P1–C10 104.7(2), C8–P1–C21 104.9(2), C21–P1–C10 105.9(2), C7–P2–C9 102.6(2), C9–P2–C31 106.2(2). Bottom right: Molecular packing of trans-3b.

**Table 1.** UV/Vis, fluorescence, and cyclic voltammetry data, and TD-DFT calculations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) [nm][a]</th>
<th>( \lambda_{\text{agg}} ) [nm][b]</th>
<th>Transition[c]</th>
<th>( E_{\text{HOMO}} ) [eV][f]</th>
<th>( E_{\text{LUMO}} ) [eV][f]</th>
<th>LUMO [eV][f]</th>
<th>HOMO [eV][f]</th>
<th>( \Delta E ) [eV][f]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>289, 310</td>
<td>298.2 (0.059)</td>
<td>HOMO–LUMO</td>
<td>nd</td>
<td>nd</td>
<td>–1.07</td>
<td>–5.64</td>
<td>4.57</td>
</tr>
<tr>
<td>3a</td>
<td>301 (3.81), 311 (3.71)</td>
<td>306.2 (0.001)</td>
<td>HOMO–LUMO</td>
<td>–0.87</td>
<td>1.12</td>
<td>–1.38</td>
<td>–5.98</td>
<td>4.60</td>
</tr>
<tr>
<td>cis-3b</td>
<td>277 (4.12), 301 (4.24)</td>
<td>325.1 (0.001)</td>
<td>HOMO–LUMO</td>
<td>–1.15</td>
<td>NA</td>
<td>–1.89</td>
<td>–6.23</td>
<td>4.34</td>
</tr>
<tr>
<td>trans-3b</td>
<td>299 (4.56), 309 (4.51)</td>
<td>322.9 (0.009)</td>
<td>HOMO–LUMO</td>
<td>–1.16</td>
<td>NA</td>
<td>–1.90</td>
<td>–6.16</td>
<td>4.26</td>
</tr>
<tr>
<td>cis-5b</td>
<td>294 (3.63), 322(sh)</td>
<td>nd</td>
<td>nd</td>
<td>–1.26</td>
<td>NA</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>trans-5b</td>
<td>294 (3.63), 322(sh)</td>
<td>nd</td>
<td>nd</td>
<td>–1.26</td>
<td>NA</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

of cis-5b. The spectrum of gold complex cis-5b also exhibits shoulders and broad bands, owing to the presence of multiple conformations of the central six-membered ring in solution.\cite{14} Compared to the phosphasilin and diphosphinine systems, the absorptions of the thiaphosphinines are further bathochromically shifted (2c: $\lambda_{max}=336$ nm, 3c: $\lambda_{max}=335$ nm, 4c: $\lambda_{max}=350$ nm, and 5c: $\lambda_{max}=354$ nm), thus supporting an increased conjugation in the sulfur-bridged system. Furthermore, the bathochromic trend (from $\lambda_{max}=336$ nm for 2c to $\lambda_{max}=354$ nm for 5c) of the functionalized phosphorus center illustrates how the different electronic nature of phosphorus center can further tune the communication between the heteroatom center and $\pi$-system. Interestingly however, the absorption of the gold complex 5c is red-shifted from that of the thiaphosphinine oxide 3c, despite the greater electronegativity of oxygen. To investigate this unusual observation, theoretical calculations have been performed (see below).

The trivalent thiaphosphinine 2c also shows blue fluorescence in dichloromethane with an emission maximum at $\lambda_{em}=476$ nm, but with a low quantum yield of $\phi_{PL}=0.03$.\cite{15} A large Stokes shift of $\Delta\lambda=7143$ cm$^{-1}$ indicates that its electronic structure in the ground state is significantly different from that in the excited state. Similar results have also been found in triphenylphosphane and phosphane-substituted oligothiophene systems.\cite{16} In MeOH, the emission of 2c shows a hypsochromic shift of $\Delta\lambda=30$ nm ($\phi_{PL}=0.02$; Figure 8). These features indicate the presence of a fast geometrical conversion of the phosphorus center from a pyramidal ground state into a more planar excited state in CH$_2$Cl$_2$, whereas this geometrical conversion could be hindered by hydrogen bond interactions between the phosphorus center and protic solvents.\cite{16} By contrast, the oxidized compound 3c only shows a weak emission at $\lambda_{em}=372$ nm ($\phi_{PL}=0.001$)\cite{15} in CH$_2$Cl$_2$ (378 nm in MeOH), probably owing to the absence of the geometrical conversion of the oxide phosphorus center.

Interestingly, the cationic phosphonium compound 4c also shows yellow fluorescence at $\lambda_{em}=535$ nm in the solid state, whereas the other heteroatomic phosphinine compounds do not show any noticeable solid-state fluorescence. In order to gain some deeper insight into this different behavior, we have studied the concentration dependent fluorescence emission of 4c in solution. At low concentration ($c=1.4 \times 10^{-5}$ M), an emission at $\lambda_{em}=387$ nm was observed. A lower energy emission ($\lambda_{em}=513$ nm, $\phi_{PL}=0.023$)\cite{15} emerges as the concentration increases to $c=1.0 \times 10^{-3}$ M (Figure 9). However, the absorption features of 4c did not change with concentration in CH$_2$Cl$_2$ solution. Therefore, the concentration-dependant emission can be assigned to the formation of an excimer, which is induced by the polarized electronic structure of 4c in the excited state.\cite{17} The excimer formation also explains the solid-state fluorescence of 4c that is not observed for the other thiaphosphinine derivatives.

Furthermore, cis- and trans-3b did not show any fluorescence in solution or in the solid state, presumably owing to the reduced conjugation in the diphosphinines, as well as their bulkiness thus preventing an excimer formation. For gold complexes cis-5b and 5c, low energy emissions originating from Au–Au interactions in the solid state\cite{18} were also not observed. This result was supported by the lack of Au–Au interactions in the molecular organization of 5b in the solid-state (see above), and is consistent with the observations made with the analogous phosphasilin gold complex.\cite{18}

**Electrochemical Studies**

Recently, we and others were able to show that the incorporation of phosphorus centers into $\pi$-conjugated materials allows for facile electrochemical reduction, which emphasizes their $n$-type characteristics.\cite{9,16} To verify if this is also true for the series of new materials reported here, the redox
properties of the heteroatomic phosphinine systems were investigated using cyclic voltammetry. 2,3-Dibromobenzol[e]-thiophene, which was used as a benchmark compound for the CV studies, only exhibited an irreversible oxidation at \( E = 1.22 \text{ V} \). By contrast, an irreversible reduction peak was observed for the oxidized phosphasilin 3a at relatively low potential \( E = -0.87 \text{ V} \), thus indicating that addition of the phosphoranyl center endows the scaffold with \( n \)-type characteristics. In the thiaphosphinine series, trivalent compound 2c only shows an irreversible oxidation peak at \( E = 1.54 \text{ V} \), which can be attributed to the electron-rich sulfur and phosphorus heteroatoms. Modification of the phosphorus center, however, changes the redox properties and switches the character of the material from \( p \)-type to \( n \)-type. Both compounds 3c and 4c now show quasi-reversible reduction at \( E = -1.14 \text{ V} \) and \( E = -1.10 \text{ V} \), respectively; the more positive reduction potential of compound 4c indicates that the cationic phosphonium center can further decrease the LUMO energy level of the thiaphosphinine system. This is in line with the results obtained for the related bis(benzothieno)phospholes (I, \( \text{A} = \text{C}_2\text{H}_3 \)). On the other hand, gold complex 5c not only shows an irreversible reduction at \( E = -1.10 \text{ V} \), but also an irreversible oxidation at \( E = 0.67 \text{ V} \), which can be attributed to the electron richness of the gold center. Surprisingly, gold complex cis\(_5\)bm only shows an irreversible reduction at \( E = -1.26 \text{ V} \), which is in contrast to the redox behavior of 5c. This difference could be rationalized by the different electronic nature of the heteroatoms (S and P) in the molecular scaffold of cis\(_5\)bm and 5c. As for the isomers of 3b, cis\(_3\)bm has a quasi-reversible reduction peak at \( E = -1.15 \text{ V} \), whilst trans\(_3\)bm shows one irreversible reduction peak at \( E = -1.16 \text{ V} \). The corresponding oxidation processes were not observed for these two compounds. These results complement the work of other groups that have reported similar heteroatom systems, such as N-phenylphenothiazine\(^{[10]} \) bis-(benzo[\( b \)]thieno)-1,4-dithiins\(^{[13]} \) and thiophene-based heteroacenes\(^{[22-24]} \) that only exhibit reversible oxidation processes. Our observations clearly demonstrate that replacing the N/S heteroatoms with phosphorus centers in a \( \pi \)-conjugated scaffold affords systems with considerably altered electrochemical features.

**Theoretical Studies**

The five-membered phosphole is a weak aromatic system, owing to the pyramidal geometry of the phosphorus center (A, B, Figure 10). However, the hyperconjugation between the \( \pi^* \) system of the butadiene moiety and the \( \sigma^* \) orbital of exocyclic P–C bond induces a low LUMO energy level in the phosphole system.\(^{[25]} \) Compared with the extended dithiophosphole heteropentacenes (I, \( \text{A} = \text{C}_2\text{H}_3 \), Figure 1),\(^{[26]} \) the heteroatomic phosphinine systems exhibit larger band gaps (Table 1) that can be attributed to reduced conjugation through the additional heteroatoms in the scaffold.

Similar \( \sigma^*–\pi^* \) hyperconjugation effects are also observed in the phosphasilin and the diphosphinine systems (DFT calculations, B3LYP/6-31G(d) level of theory,\(^{[28]} \) see the Supporting Information). The LUMO energy levels (and band gaps) of the phosphinines cis\(_{\text{trans}}\)bm, (cis: \( E_{\text{LUMO}} = -1.89 \text{ eV}, \text{trans}: E_{\text{LUMO}} = -1.90 \text{ eV} \)) are significantly lower than those of the phosphasilin system (2a: \( E_{\text{LUMO}} = -1.07 \text{ eV} \) and 3a: \( E_{\text{LUMO}} = -1.38 \text{ eV} \)) owing to the stronger electron-withdrawing effect of the two phosphoranyl moieties and a more pronounced hyperconjugation from the two phosphoranyl centers, which is consistent with the observed red-shifted absorption shoulders in the diphosphinine system.

The trivalent thiaphosphinine 2c exhibits a smaller band gap (\( E_{\text{bg}} = 4.11 \text{ eV} \)) and higher lying LUMO energy level (\( E_{\text{LUMO}} = -1.16 \text{ eV} \)) than those of both the phosphasilin and diphosphinine systems (3a: \( E_{\text{bg}} = 4.60 \text{ eV}, \text{cis-bm}: E_{\text{bg}} = 4.34 \text{ eV}, \text{trans-bm}: E_{\text{bg}} = 4.26 \text{ eV} \)). The lone pairs of the phosphorus and sulfur centers in the central six-membered rings largely contribute to the HOMO level, but not to the LUMO levels. This charge transfer between heteroatoms and the benzothiophene \( \pi \)-system is consistent with the large Stokes shift of 2c in dichloromethane (aprotic solvent). The oxidation of the phosphorus center in the thiaphosphinine oxide 3c brings down both the LUMO and HOMO levels (\( \Delta E_{\text{LUMO}} = 0.30 \text{ eV}; \Delta E_{\text{HOMO}} = 0.62 \text{ eV} \)). The molecular orbitals reveal that the \( \sigma^* \) orbital of the exocyclic P–C bond couples with the \( \pi \) orbitals of the two thiophene moieties, thereby lowering the HOMO level significantly, which is also consistent with the significantly shortened endocyclic P–C bonds of 3c. The phosphonium center in 4c further enhances this \( \sigma^*–\pi^* \) interaction (Figure 10, C), thus lowering both the LUMO and HOMO levels even more; this enhancement agrees very well with the redox properties of the thiaphosphinines. Kawashima and co-workers have recently reported the somewhat related dibenzothiaborins and TD-DFT calculations have indicated that the HOMO–LUMO transition in these systems can be attributed to an intramolecular charge transfer from a sulfur atom to the boron center that, however, is not the strongest transition.\(^{[21]} \) Both LUMO and HOMO energy levels have a contribution from the boron center in Kawashima’s system, whereas the phosphonium center in 4c only contributes to the HOMO energy level, but not the LUMO level. The different electronic contribution of the phosphonium center to the HOMO and LUMO levels can thus explain the enhanced \( \pi–\pi^* \) transition in the thiaphosphinine system, and consequently also the stronger fluorescence intensity of 4c, compared to its congeners.

\[ \text{A} \]
\[ \text{B} \]
\[ \text{C} \]

Figure 10. Schematic molecular orbitals of phospholes and thiaphosphinine as derived from theoretical calculations.
The calculations also revealed the reasons for the unexpected observation in terms of absorption shifts for compounds 2c-5c. In contrast to the phosphasilin and diphosphinine systems, where the $\sigma^*\pi$ orbital of the oxycyclic P–C bond couples with the $\pi^*$ system (LUMO) of the molecular scaffold, the opposite is true for the thiaphosphinine oxide 3c and the thiaphosphonium 4c. Here the $\sigma^*$ orbital interacts with the $\pi$ system (HOMO), leading to a lowered HOMO instead of a lowered LUMO energy level in the thiaphosphinine system (see Figure 11 and the Supporting Information). This in turn, increases the band gap of 3c and is likely the cause of the hypsochromic shift compared to the gold complex 5c.

According to our previous studies, changing the environment around the phosphorus center in the dithiophosphole system can control the electronic nature of the whole material, particularly through the interaction of the $\sigma^*$ orbital of the oxycyclic P–C bond(s) with the LUMO of the $\pi$-conjugated system. This study now confirms that the additional heteroatoms in the 4-position (Si, S, P), under the right conditions (that is, the nature of the phosphorus center), can enhance this effect as they also have a significant influence on the electronic coupling between the $\sigma^*$ orbital of the oxycyclic P–C bond and the $\pi/\pi^*$ system.

**Conclusions**

In conclusion, we have synthesized a series of 4-heteroatom-1,4-dihydroporphinophosphate heteropentacenes. The electronic structures of these molecules can be tuned by changing heteroatoms (Si, S, and P) in the central six-membered ring, as supported by multinuclear NMR studies and optical spectroscopy. The thiaphosphinine system exhibits a stronger conjugation than the phosphorus- and silicon-based systems. Functionalization of the phosphorus center, particularly its quaternization into a phosphonium species, further enhances the communication between the phosphorus center and the $\pi$ system in the thiaphosphinine heteroacene scaffold. This induces intriguing optical properties that are considerably distinct from other hetero (Si and P) phosphinines. Changing the central heteroatoms also dramatically alters the organization of heteroatomic phosphinines in the solid state. Even small geometric changes on the phosphorus centers can provide different packing-motifs, such as $\pi$ stacking along the long axis of molecules as observed in cis-3b, whilst no such packing was observed in trans-3b. More importantly, the redox properties of the $\pi$ systems can also be modified with additional heteroatoms. The theoretical studies have shown that modification of the heteroatoms in the phosphinine ring helps to decrease the HOMO-LUMO energy gap. Owing to the increased orbital coupling between the $\pi$ orbitals of the two thiophene moieties and the $\sigma^*$ orbital of the oxycyclic P–C bond in the thiaphosphinine system, the conjugation within the molecules is enhanced, which is consistent with the optical properties of these systems.

**Experimental Section**

**General:** All manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques. Solvents were dried using a MBraun Solvent Purification System. nBuLi (2.5 M in n-hexane), bis(phenylsulfanyl)sulfide, methyl triflate, and hydrogen peroxide were used as received. N,N,N,N-tetramethylthlylenediamine (TMEDA), dichlorophenylphosphine, and dichloromethylsilane were freshly distilled prior to use. 2,3-Dibromobenzo[3,4]thieno[3,2-b]thiophene, cis-[Au(tht)(C≡N)] and bis[benzo[4]thieno]phosphasilin oxide (3a) were prepared according to literature procedures. cis$^{[1]}$[H] NMR, 1$H$ NMR and 13$C$[1]H NMR spectra were recorded on Bruker DRX400, DMAX1000, or Avance(-H)-III 400 spectrometers. Chemical shifts were referenced to external 85% H$_3$PO$_4$ (H$^3$PO$_4$) and, external TMS (CDCl$_3$, H). Elemental analyses were performed at the Department of Chemistry at the University of Calgary. Mass spectra were run on a Finnigan SQQ 7000 spectrometer, or a Bruker Daltonics AUTOFLX III system. Crystal data and details of the data collection are provided in Table 2. Diffraction data for 2c, 3c, 4c, 5c, cis-3b, and trans-3b were collected on a Nonius Kappa CCD diffractometer, using Mo K$\alpha$ radiation (λ) 0.71073 Å (graphite monochromator). The structures were solved by direct methods (SHELXTL) and refined on $F^2$ by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding model. CCDC 769137 (cis-3b), CCDC 769138 (trans-3b), CCDC 769139 (2c), CCDC 769140 (5c), CCDC 769141 (4c), and CCDC 769142 (3c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif. Melting points were determined on a TA-TQ200 DSC instrument. All fluorescence experiments were recorded in a Jasco FP-6600 spectrofluorometer and UV/VIS/NIR Cary 5000 spectrophotometer. Electrochemical studies were performed on an Autolab PGSTAT302 instrument with a platinum rod as working electrode, platinum wire as counter electrode, and Ag/AgCl/KCl$_{sat}$ as reference electrode; the supporting electrolyte was NBF$_4$PF$_6$. Scan rate was 100 mVs$^{-1}$.

**Bis(3-bromobenzo[4]thiophen-2-yl)(phenyl)phosphine (1b):** nBuLi (2.12 mL, 5.29 mmol) was added dropwise at −78°C to a solution of 2,3-dibromobenzo[4]thiophene (1.534 g, 5.29 mmol) in Et$_2$O. After stirring for 1 h, PhPCl$_2$, 0.474 g, 2.65 mmol) was added dropwise at −78°C and the reaction was gradually warmed to room temperature and stirred overnight. The mixture was then quenched with water, and extracted three times with CH$_2$Cl$_2$. The organic layer was collected and dried under
Table 2. Crystal data and structure refinement for 2c, 3c, 4c, 5c, and cis-3b and trans-3b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2c</th>
<th>3c</th>
<th>4c</th>
<th>5c</th>
<th>trans-3b</th>
<th>cis-3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₂₁H₂₉P₂S₁₀</td>
<td>C₂₁H₂₉OPS,C₂H₅O</td>
<td>C₂₁H₂₉F₂O₂P₂S₁₀</td>
<td>C₂₁H₂₉AuClP₂S₁₀</td>
<td>C₂₁H₂₉O₂P₂S₁₀</td>
<td>C₂₁H₂₉O₂P₂S₁₀</td>
</tr>
<tr>
<td>Mᵣ</td>
<td>404.51</td>
<td>478.58</td>
<td>568.58</td>
<td>636.89</td>
<td>512.48</td>
<td>512.48</td>
</tr>
<tr>
<td>T [K]</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>χ [Å]</td>
<td>0.70173</td>
<td>0.70173</td>
<td>0.70173</td>
<td>0.70173</td>
<td>0.70173</td>
<td>0.70173</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2₁/c</td>
<td>Pca2₁</td>
<td>P-1</td>
<td>P-1</td>
<td>C2</td>
<td>P2/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>10.074(3)</td>
<td>11.209(2)</td>
<td>9.039(4)</td>
<td>12.485(2)</td>
<td>20.176(7)</td>
<td>16.629(4)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>9.092(4)</td>
<td>15.907(3)</td>
<td>10.537(4)</td>
<td>13.705(3)</td>
<td>8.198(4)</td>
<td>11.637(6)</td>
</tr>
<tr>
<td>α [°]</td>
<td>90</td>
<td>90</td>
<td>105.106(2)</td>
<td>111.334(1)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β [°]</td>
<td>103.667(2)</td>
<td>90</td>
<td>99.025(2)</td>
<td>104.909(1)</td>
<td>120.527(2)</td>
<td>111.006(3)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90</td>
<td>90</td>
<td>99.886(2)</td>
<td>99.238(1)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>1810.66(11)</td>
<td>4364.64(14)</td>
<td>1195.94(8)</td>
<td>2069.39(7)</td>
<td>2370.09</td>
<td>2497.69(19)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρcalc (Mg/m³)</td>
<td>1.485</td>
<td>1.457</td>
<td>1.579</td>
<td>2.044</td>
<td>1.436</td>
<td>1.476</td>
</tr>
<tr>
<td>μ [mm⁻¹]</td>
<td>0.501</td>
<td>0.434</td>
<td>0.514</td>
<td>0.764</td>
<td>0.385</td>
<td>0.475</td>
</tr>
<tr>
<td>F(000)</td>
<td>832</td>
<td>1984</td>
<td>580</td>
<td>1216</td>
<td>1056</td>
<td>1140</td>
</tr>
<tr>
<td>crystal size [mm3]</td>
<td>0.47 ± 0.04</td>
<td>0.23 ± 0.19</td>
<td>0.19 ± 0.12</td>
<td>0.10</td>
<td>0.25 ± 0.18</td>
<td>0.22 ± 0.19</td>
</tr>
<tr>
<td>θ range [°]</td>
<td>2.06 ± 0.28</td>
<td>2.46 ± 0.27</td>
<td>2.50</td>
<td>1.60 ± 0.27</td>
<td>1.40</td>
<td>1.66 ± 0.27</td>
</tr>
<tr>
<td>index ranges</td>
<td>–13 &lt; h &lt; 13</td>
<td>–14 &lt; l &lt; 14</td>
<td>–11 &lt; k &lt; 11</td>
<td>–16 &lt; h &lt; 14</td>
<td>–26 &lt; h &lt; 25</td>
<td>–21 &lt; h &lt; 21</td>
</tr>
<tr>
<td>reflections collected</td>
<td>7464</td>
<td>9344</td>
<td>9980</td>
<td>17332</td>
<td>5123</td>
<td>9802</td>
</tr>
<tr>
<td>independent reflections</td>
<td>4111</td>
<td>4993</td>
<td>5352</td>
<td>9448</td>
<td>4292</td>
<td>5675</td>
</tr>
<tr>
<td>completeness to θ [°]</td>
<td>27.48 (99.3%)</td>
<td>27.50 (96.8%)</td>
<td>27.40 (98.1%)</td>
<td>27.55 (98.9%)</td>
<td>27.48 (98.1%)</td>
<td>27.43 (99.5%)</td>
</tr>
<tr>
<td>max./min. transmission</td>
<td>0.9010/0.885</td>
<td>0.9220/0.9067</td>
<td>0.9504/0.9086</td>
<td>0.3407/0.2516</td>
<td>0.9304/0.9201</td>
<td>0.9279/0.9027</td>
</tr>
<tr>
<td>data/restraints/parameters</td>
<td>4111/0/235</td>
<td>4993/0/280</td>
<td>5352/0/280</td>
<td>9448/0/506</td>
<td>4292/0/280</td>
<td>5675/0/280</td>
</tr>
<tr>
<td>GoF on F²</td>
<td>1.123</td>
<td>1.152</td>
<td>1.074</td>
<td>1.161</td>
<td>1.176</td>
<td>1.158</td>
</tr>
<tr>
<td>final R indices</td>
<td>R₁ = 0.0529, wR₁ = 0.1173</td>
<td>R₁ = 0.0624, wR₁ = 0.1705</td>
<td>R₁ = 0.1318, wR₁ = 0.0764</td>
<td>R₁ = 0.0279, wR₁ = 0.1307</td>
<td>R₁ = 0.0506, wR₁ = 0.1996</td>
<td></td>
</tr>
<tr>
<td>I &gt; 2σ(I)</td>
<td>R₁ = 0.0274, wR₁ = 0.0868, wR₁ = 0.1391</td>
<td>R₁ = 0.0626, wR₁ = 0.1504</td>
<td>R₁ = 0.0819, wR₁ = 0.1440</td>
<td>wR₁ = 0.2263</td>
<td></td>
<td></td>
</tr>
<tr>
<td>largest diff. peak/hole [eÅ⁻³]</td>
<td>0.390 – 0.374</td>
<td>1.306 – 0.534</td>
<td>1.894 – 0.504</td>
<td>0.742 – 1.525</td>
<td>0.524 – 0.589</td>
<td>0.615 – 0.889</td>
</tr>
</tbody>
</table>

Vacuum. The pure white product was obtained after washing the solid three times with pentane (yield: 1.00%, 71.1%). ¹H NMR (400 MHz, CDCl₃): δ = 7.87 (dd, J₆₇ = 6.0 Hz, J₆₈ = 1.2 Hz, J₇₈ = 0.8 Hz, 2H, benzo), 7.72 (dd, J₆₇ = 6.0 Hz, J₆₈ = 2.0 Hz, J₇₈ = 1.2 Hz, 2H, benzo), 7.60 – 7.55 (m, 4H, Ph), 7.51 – 7.39 ppm (m, 4H, Ph); ¹³C[¹H] NMR (100 MHz, CDCl₃): δ = 139.3 (s, thiophene), 130.8 (s, thiophene), 130.5 (s, thiophene), 126.3 (s, benzol), 123.8 (s, benzol), 122.2 (s, benzol), 114.5 ppm (s, thiophene). Bis(benzyl)(thieno-2-yl)bis(diphosphin-1-yl)phosphane 1c: nBuLi (1.47 mL, 3.67 mmol) was added dropwise at –78°C to the solution of 2,3-dibromo-benzyl[thiophene (1.065 g, 3.67 mmol) in THF. After stirring for 1 h at this temperature, bis(phenylisothiophene)sulfide (0.578 g, 1.84 mmol) in THF was added dropwise and the reaction was gradually warmed to room temperature and stirred overnight. The mixture was quenched with water, and extracted with three times with CH₂Cl₂. The organic layer was collected and dried under vacuum. The pure light yellow product was obtained after washing the solid three times with pentane (yield: 0.61 g, 73.3%). ¹H NMR (400 MHz, CDCl₃): δ = 7.80 (dd, J₆₇ = 6.0 Hz, J₆₈ = 1.6 Hz, J₇₈ = 0.8 Hz, 2H, benzo), 7.69 (dd, J₆₇ = 6.0 Hz, J₆₈ = 0.8 Hz, J₇₈ = 0.4 Hz, 2H, benzo), 7.47 – 7.37 ppm (m, 4H, benzo); ¹³C[¹H] NMR (100 MHz, CDCl₃): δ = 139.9 (s, thiophene), 130.8 (s, thiophene), 130.5 (s, thiophene), 126.3 (s, benzol), 125.4 (s, benzol), 123.8 (s, benzol), 122.2 (s, benzol), 114.5 ppm (s, thiophene). Bis(benzyl)(thieno-2-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)diphosphin-1-yl)
126.1 (s, benzo), 122.7 ppm (s, benzo); 31P{1H} NMR (100 MHz, CDCl3): δ = 6.54 (d, J = 7.9 Hz, 3P, CHCl3); elemental analysis (%) calcd. for C14H13O3PS3: C 51.76, H 2.80; found: C 51.65, H 2.80.

**Bis(benzothieno)-4-thiaphosphinine gold(I) chloride 5c** [Au(tht)Cl] (0.197 g, 0.4 mmol) was added to a solution of 2c (0.500 g, 1.24 mmol) in CHCl3 (20 mL). The reaction mixture was stirred for 5 h at room temperature. Then all volatile materials were removed under vacuum, and the remaining solid was washed with pentane and diethyl ether. The product was obtained as white solid by recrystallization from a concentrated acetonitrile solution at room temperature (yield: 0.460 g, 65.2%). 1H NMR (400 MHz, CDCl3): δ = 8.25 ppm (s); 19F NMR (282 MHz, CDCl3): δ = 78.0 ppm (s). 1H NMR (400 MHz, CDCl3): δ = 8.25 (m, J = 11.9 Hz, Ar) ppm; 13C{1H} NMR (162 MHz, CDCl3): δ = 138.7 (d, J = 11.9 Hz, Ar), 136.5 (d, J = 11.1 Hz, m-Ph), 128.7 (d, J = 13.2 Hz, o-Ph), 125.5 (s, benzo), 125.4 (s, benzo), 123.9 (s, benzo), 121.5 (s, benzo), 120.4 ppm (s, thiophene); 31P{1H} NMR (162 MHz, CDCl3): δ = 41.0 ppm (s); elemental analysis (%) calcd. for C14H13O3PS3: C 51.65, H 2.80; found: C 51.60, H 2.84.

**Acknowledgements**

Financial support from the NSERC of Canada and the Canada Foundation for Innovation (CFI) is gratefully acknowledged. We also thank Alberta Innovates Technological Futures for a graduate scholarship (Y.R.) and a New Faculty Award (T.B.). Thanks to Prof. Laszlo Nyulasi (Budapest) for helpful discussions regarding the theoretical calculations, and Prof. Todd Sutherland (Calgary) for his help with the electrochemical studies.


96.89255 [M+Na]+, calcd. 96.89762.


[15] Fluorescence quantum yield, relative to quinine sulfate (0.1 m H₂SO₄ solution).


Received: March 13, 2010
Published online: June 11, 2010