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Preparation and Characterization of P_2BCh Ring Systems (Ch = S, Se) and their Reactivity with N-Heterocyclic Carbenes

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Abstract: Four-membered rings with a P_2BCh core (Ch = S, Se) have been synthesized via reaction of phosphinidene chalcogenide (**Ar*P=Ch**) and phosphaborene (**Mes*P=BNR$_2$**). The mechanistic pathways towards these rings are explained by detailed computational work that confirmed the preference for the formation of P–P, not P–B, bonded systems, which seems counterintuitive given that both phosphorus atoms contain bulky ligands. The reactivity of the newly synthesized heterocycles, as well as that of the known $(RPCh)_n$ rings (n = 2, 3), was probed by the addition of N-heterocyclic carbenes, which revealed that all investigated compounds can act as sources of low-coordinate phosphorus species.

Introduction

The ability of low-coordinate and low-valent main group compounds to mimic the reactivity of transition metal complexes has pushed research in this area to the top of the inorganic chemistry agenda over the last decade.[1] One strategy to isolate these reactive species is through donor stabilization of the low-valent main group centre, offering a doorway to explore the chemistry of these elusive intermediates. A common group of two electron σ-donors that have been used exhaustively over the last decade is N-heterocyclic carbenes (NHCs). NHCs have stabilized p-block frameworks in many unusual bonding arrangements,[2] including some noteworthy examples such as the homodiatomic main group allotropes (Figure 1, **A** & **B**),[3–5] carbon (0) in carbodicarbenes/bent allenes (**C**),[6] phosphinidenes (**D**),[7–16] phosphaborenes (**E**),[17] and phosphinidene sulfides (**F**).[18] While NHCs offer thermodynamic stabilization, they are often used in conjunction with bulky substituents that aid in kinetic stability, rendering the low-coordinate and low-valent main group compounds "bottleable" and ready for onwards transformations.

While the interest in small strained inorganic rings is important for exploring the structural chemistry of main group heterocycles, these compounds have routinely acted as precursors to low-coordinate main group species that are otherwise difficult to isolate. The approach of using cyclic

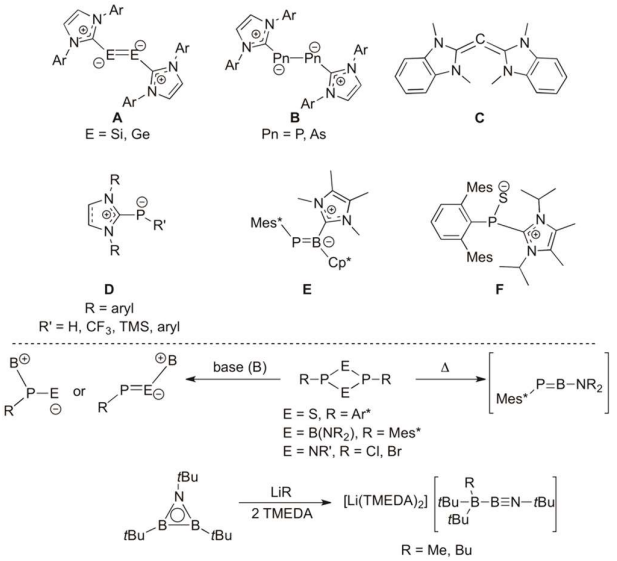

Figure 1. Top: Examples of NHC-stabilized main group compounds: homodiatomic main group allotropes (**A** & **B**), bent allenes (**C**), phosphinidenes (**D**), phosphaborenes (**E**), and phosphinidene sulfides (**F**) (Ar = 2,6-diisopropylphenyl, TMS = trimethylsilane, Cp* = pentamethylcyclopentadiene, Mes* = 2,4,6-(tBu)$_3$C$_6$H$_2$, Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$). Bottom: Examples of base-/thermal-induced degradation of inorganic heterocycles yielding low-coordinate main group compounds (NR$_2$ = TMP = 2,2,6,6-tetramethylpiperidine, TMEDA = tetramethylethylenediamine, Ar* = 2,6-Mes-C$_6$H$_3$).

structures to gain access to otherwise inaccessible species has been successful for P_2B_2,[19,20] P_2N_2,[21] P_2S_2,[18] and $B_2N^{[22]}$ rings that upon thermolysis or addition of a Lewis base lead to degradation of their inorganic cores and formation of compounds with low-coordinate PB, PN, PS, and BN moieties (Figure 1, bottom).

In recent years, we have been focused on incorporating pnictogen and chalcogen atoms into unique cyclic structures. While small phosphorus heterocycles with symmetrical cores dominate the literature,[23] there are fewer examples of phosphorus-chalcogen rings.[18,24,25] Moreover, small phosphorus-chalcogen heterocycles that display asymmetry with respect to the 4-membered core are even rarer. These include P-S-P-E (Figure 2, **G**),[26–28] P-Ch-P-C (Ch = S, Se, **H**),[29–31] P-S-C-S (**I**),[32] and P-S-C-C structures (**J**),[33] amongst others.[34–39] Small ring cores that contain asymmetry in the presence of a P-P bond are by far the rarest, with published examples limited to only three species: P-P-C-N (**K**),[40] P-P-C-O (**L**),[37] and P-P-Si-N (**M**).[41] In this context, we report the synthesis of small main group heterocycles containing a P_2BCh core (**3Ch**; Ch = S, Se) that possess a P–P bond. Compounds **3Ch** were prepared

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through the combination of monomeric phosphinidene chalcogenides (**Ar*P=Ch**) and phosphaborenes (**Mes*P=BNR$_2$**) via formation of a P–P bond. One could consider this an expected outcome with the phosphorus in **Ar*P=Ch** as the electrophilic site and the phosphorus in the **Mes*P=B-NR$_2$** the nucleophilic one. However, the formation of a P–P bond is counterintuitive when considering the steric demand imposed by both phosphorus atoms as well as the electrophilicity of the boron atom in **Mes*P=B-NR$_2$**. In agreement with these notions, density functional theory (DFT) calculations showed that the reaction begins with a P→B attack after which the resulting intermediate can follow multiple pathways with the most favourable ones lead to the formation of a P–P bond. The synthesized P$_2$BCh main group rings can be monomerized at elevated temperatures in the presence of NHCs, reforming **Ar*P=Ch** and **Mes*P=BNR$_2$** as well as giving access to NHC-stabilized phosphinidenes.[20]

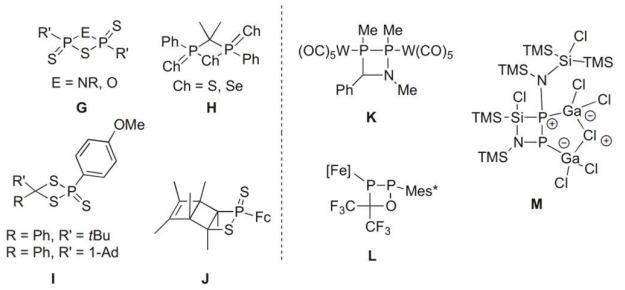


Figure 2. Left: Examples of small asymmetric P–Ch heterocycles (**G**-**J**) (1-Ad = 1-adamantyl, Fc = ferrocenyl). Right: Examples of small phosphorus heterocycles that contain an asymmetric core in the presence of a P–P bond (**K**-**M**) ([Fe] = Fe(Cp*)(CO)$_2$).

Results and Discussion

The 1:1 stoichiometric reaction of **1Ch** and **2** in toluene at 80 °C resulted in the consumption of both starting materials after 2 hours and the appearance of two doublets in the $^{31}P\{^1H\}$ NMR spectrum. Removing the volatiles *in vacuo* and slowly concentrating a pentane solution of the crude reaction mixture produced single crystals suitable for X-ray diffraction, which confirmed the products as **3Ch**, four-membered heterocycles formed from the incorporation of monomeric units from **1Ch** and **2** (Scheme 1). $^{31}P\{^1H\}$ NMR spectra of the redissolved single crystals of **3Ch** displayed the same doublets as observed in the crude reaction mixture (**3S**: δ_P = -29.8; -13.6, $^1J_{P\text{-}P}$ = 184.0 Hz; **3Se**: δ_P = -33.5, $^1J_{Se\text{-}P}$ = 91.8 Hz, $^1J_{P\text{-}P}$ = 181.7 Hz; -31.5, $^1J_{P\text{-}P}$ = 181.7 Hz), with both doublets shifted upfield from **1Ch** and downfield from **2**. The ^{11}B NMR spectra of both **3Ch** display similar chemical shifts (**3S**: δ_B = 44.2; **3Se**: δ_B = 42.3), as one would expect, and are indicative of three-coordinate boron centers. The solid-state structures of **3Ch** confirmed the presence of P-P-B-Ch cores in butterfly conformation with P–Pbond lengths of 2.2371(9) and 2.243(1) Å, and P–B bonds of 1.955(2) and 1.957(2) Å for **3S** and **3Se**, respectively (Figure 3). The B–Ch bond lengths in **3S** and **3Se** are 1.850(3) and 1.985(2) Å, respectively, whereas the corresponding P–Ch bond distances are 2.1301(8) and 2.267(1) Å.

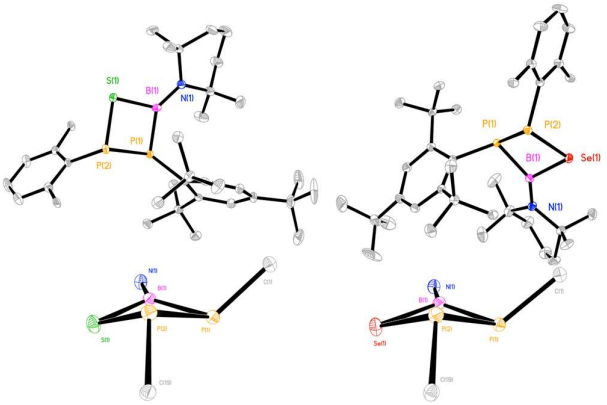
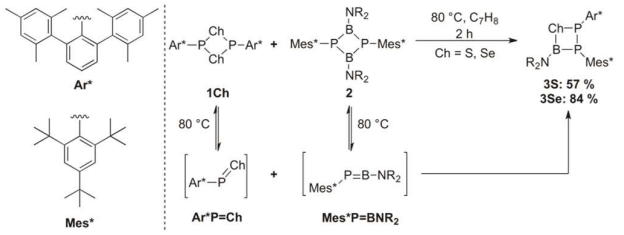


Figure 3. Solid-state structures of **3S** (left) and **3Se** (right) with thermal ellipsoids at 50 % probability. Hydrogen atoms and mesityl rings from terphenyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]. **3S**: C(1)-P(1) 1.875(3), P(1)-P(2) 2.2371(9), P(1)-B(1) 1.955(2), P(2)-C(19) 1.862(2), P(2)-S(1) 2.1301(8), S(1)-B(1) 1.850(3), B(1)-N(1) 1.405(3), C(1)-P(1)-P(2) 118.15(8), C(1)-P(1)-B(1) 113.8(1), B(1)-P(1)-P(2) 83.50(8), P(1)-P(2)-S(1) 81.38(3), P(1)-P(2)-C(19) 110.69(8), P(2)-S(1)-B(1) 89.08(9), S(1)-B(1)-P(1) 96.9(1), S(1)-B(1)-N(1) 124.1(2), N(1)-B(1)-P(1) 138.7(2), C(19)-P(2)-S(1) 106.82(8). **3Se**: C(1)-P(1) 1.885(2), P(1)-P(2) 2.243(1), P(1)-B(1) 1.957(2), P(2)-C(19) 1.861(2), P(2)-Se(1) 2.267(1), Se(1)-B(1) 1.985(2), B(1)-N(1) 1.414(2), C(1)-P(1)-P(2) 117.05(6), C(1)-P(1)-B(1) 113.03(9), P(1)-P(2)-C(19) 111.47(6), P(1)-P(2)-Se(1) 81.66(2), P(1)-B(1)-Se(1) 96.84(9), C(19)-P(2)-Se(1) 107.36(6), P(2)-Se(1)-B(1) 85.19(6), Se(1)-B(1)-P(1) 96.84(9), Se(1)-B(1)-N(1) 124.1(1), N(1)-B(1)-P(1) 138.6(2), B(1)-P(1)-P(2) 86.49(6).



Scheme 1. Synthesis of mixed main group rings **3Ch** by combining monomeric **Ar*P=Ch** and **Mes*P=BNR$_2$** units (NR$_2$ = 2,2,6,6-tetramethylpiperidine (TMP)).

The structures of **3Ch** revealed the formation of a P–P bond, which is counterintuitive based on the steric demand at both phosphorus atoms and the electronic predisposition to form a P–B bond. In order to ascertain the mechanism of forming **3Ch**, we turned to the aid of DFT calculations (Figure 4). For reasons of computational efficiency, the parent ligands Ar (*m*-diphenylbenzene) and Mes (2,4,6-trimethylphenyl) were used in the calculations and the formation of **3Ch** was assumed to involve only monomeric **ArP=S** and **MesP=B−NMe$_2$** units.

The addition of **ArP=S** to **MesP=B−NMe$_2$** was found to proceed via transition state **TS1** with a barrier of only 6 kJ mol^{-1} (38 kJ mol^{-1} without dispersion correction). The transition state shows an initial P→B attack that subsequently leads to the formation of the intermediate **INT1** with a cyclic P−P−B core. This is understandable as the phosphorus atom in **ArP=S** is both nucleophilic and electrophilic, whereas the boron and phosphorus atoms in **MesP=B−NMe$_2$** are electrophilic and nucleophilic, respectively. The optimized structure of **INT1** shows that the Mes and Ar groups reside on opposite side of the plane of the three-membered ring, with the sulfur atom located on the same side of the plane as the Mes ligand.

From the intermediate **INT1**, a one-step pathway to **3S** was found that proceeds via **TS2** with a barrier of 67(71) kJ mol^{-1}. The reaction involves a straightforward insertion of the dangling sulfur atom into the P–B bond, forming the experimentally observed 2,3-isomer of **3S**. Interestingly, no simple one-step pathway connecting **INT1** to the 2,4-isomer of **3S** was found. Instead, the intermediate three-membered ring first changes conformation from anti to syn via **TS2b** with a barrier of 53(56) kJ mol^{-1}. The resulting intermediate **INT2** can then undergo an insertion of the sulfur atom into the P−P bond via **TS3** with a barrier of 111(89) kJ mol^{-1}, giving **INT3** that still needs to undergo an additional low-energy syn to anti conformation flip to form 2,4-**3S** via **TS4**. The calculations show that, despite the lower steric demand, 2,4-**3S** is 62(65) kJ mol^{-1} higher in energy than 2,3-**3S**, presumably due to the favourable S–B bond in 2,3-**3S**. This interaction also lowers the energy of the transition state **TS2**, bringing it significantly below that of **TS3**, the highest transition state on the path leading to 2,4-**3S**. Furthermore, while **INT2** is an intermediate en route to 2,4-**3S**, it can also form 2,3-**3S** via transition state **TS3b** that is 48(36) kJ mol^{-1} lower in energy than **TS3**. Consequently, the formation of 2,4-**3S** seems highly unlikely when considering the thermodynamic and kinetic favourability of the two competing pathways leading to 2,3-**3S**.

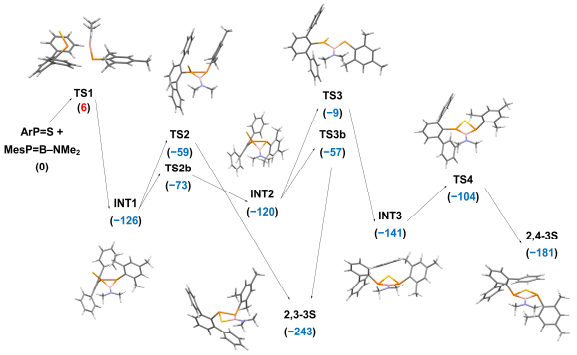
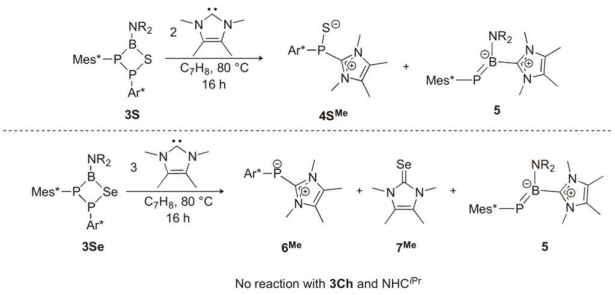


Figure 4. Reaction coordinate diagram for the formation of 2,3 and 2,4 isomers of **3S**. The structures of **TS2b** and **TS3b** are omitted for clarity. Gibbs energies are reported in kJ mol^{-1} and relative to **ArP=S** + **MesP=B−NMe$_2$**.

Upon making the unique mixed main group rings **3Ch**, we opted to explore their reactivity with strong Lewis bases, namely NHCs. Monitoring the addition of **NHC^{iPr}** to **3Ch** by ^{31}P{^{1}H} NMR spectroscopy revealed no reaction, even after heating the mixture at 80 °C for 3 days (Scheme 2). We hypothesized that the bulky aryl groups on phosphorus in combination with the sterically encumbered NHC resulted in "molecular frustration" and turned to an NHC with a lower steric demand.

Heating a solution of **NHC^{Me}** and **3Ch** at 80 °C for 16 hours resulted in consumption of the starting material and appearance of two phosphorus-containing products in the ^{31}P{^{1}H} NMR spectra: two singlets at δ_P = 32 and 151 for Ch = S, corresponding to **4S^{Me}** and **5**, and two singlets at δ_P = -77 and 151 for Ch = Se, corresponding to **6^{Me}** and **5** (Figure 5). The NHC-stabilized phosphaborene **5** has been reported as the product from the reaction of **2** with **NHC^{Me}** and was therefore easily identified.[20] Similarly, a derivative of an NHC-stabilized phosphinidene sulfide has also been reported,[18] with ^{31}P{^{1}H} NMR chemical shifts similar to that observed for **4S^{Me}**.[18] While **4S^{Me}** is stable and can be observed by NMR spectroscopy in crude reaction mixtures, there is no direct evidence of the analogous selenide **4Se^{Me}** (Figure 5). Instead, we observed the formation of an NHC-stablized phosphinidene **6^{Me}** and selenourea **7^{Me}**, as confirmed by NMR spectroscopy and X-ray crystallography.[43] The inherently weak "P=Se" moiety of **Ar*P=Se** likely makes **4Se^{Me}** an unstable intermediate that easily forms **6^{Me}** and **7^{Me}** in presence of excess NHC (Scheme 2).

Scheme 2. Accessing low-coordinate phosphorus compounds from reacting **3S** (top) and **3Se** (bottom) with **NHC^{R}** (NR$_2$ = TMP = 2,2,6,6-tetramethylpiperidine).[44]



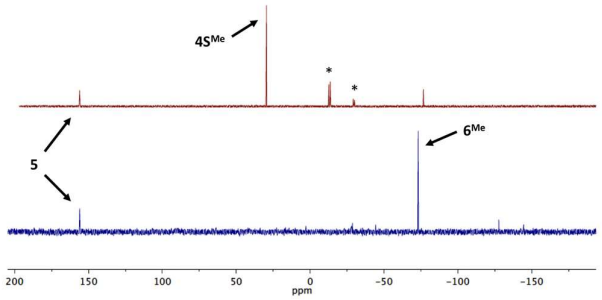
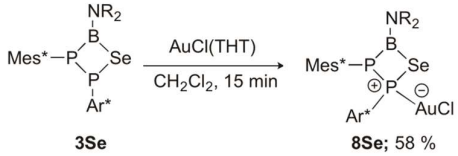


Figure 5. ^{31}P{^{1}H} NMR spectra recorded from the crude reaction mixtures of the addition of **NHC^{Me}** to **3S** (top) and **3Se** (bottom). Products of the reactions are labelled corresponding to their phosphorus NMR chemical shifts and leftover **3S** is indicated by asterisks.

Attempting the Lewis acid stabilization of low-coordinate phosphorus species, the addition of AuCl(THT) (THT = tetrahydrothiophene) to **3S** resulted in no reaction even after a prolonged period. However, the addition of one stoichiometric equivalent of AuCl(THT) to **3Se** resulted in full consumption of the starting material and the appearance of two new doublets in the ^{31}P{^{1}H} NMR spectrum that were shifted downfield from the starting material (δ_P = -8.4, $^{1}J_{Se\text{-}P}$ = 169.9 Hz, $^{1}J_{P\text{-}P}$ = 246.4 Hz; 10.3, $^{1}J_{P\text{-}P}$ = 246.4 Hz). Removing the volatiles *in vacuo* and leaving a concentrated solution in MeCN at -35 °C overnight resulted in single crystals suitable for X-ray diffraction that confirmed the product to be **8Se** in which AuCl is coordinated by the P-Se phosphorus site (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of the redissolved single crystals displayed the same doublets as observed in the crude reaction mixture while a broad singlet was noted in the ^{11}B NMR spectrum (δ_B = 44). The solid-state structure revealed that the P$_2$BSe core had remained intact retaining its butterfly conformation with relevant bond distances consistent with the parent structure **3Se** (Figure 6). Compound **8Se** is unstable if left in solution, giving a black precipitate along with a wide range of decomposition products, as indicated by

$^{31}P\{^{1}H\}$ NMR spectroscopy. This instability is a marked departure from that of the parent ring **3Se** that was found to be indefinitely stable, even at higher temperatures.

Scheme 3. Addition of Lewis acidic AuCl(THT) to **3Se**, resulting in metal coordination.



3Se **8Se**; 58 %

Upon observing that the addition of an NHC to **3Ch** resulted in dissociation of the rings and formation of base-stabilized low-coordinate phosphorus compounds **4S^{Me}** and **6^{Me}**, we then wondered if similar reactivity could also be observed with the parent P-Ch rings, **1Ch**. Consequently, the 4:1 addition of **NHC^{R}** (R = Me, *i*Pr) to a THF solution of **1Se** at room temperature resulted in the consumption of starting material and the appearance of a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum (δ_P = -76.7, R = Me; δ_P = -75.0, R = *i*Pr). Removing the volatiles *in vacuo*, dissolving the crude reaction mixture in a minimal amount of pentane, and leaving the solutions overnight at -35 °C resulted in single crystals suitable for X-ray diffraction. A subsequent structure analysis confirmed the products as NHC-stabilized phosphinidenes **6^{Me}** and **6^{iPr}** (Figure 6), that is, similar species that were obtained via addition of **NHC^{Me}** to **3Se**.

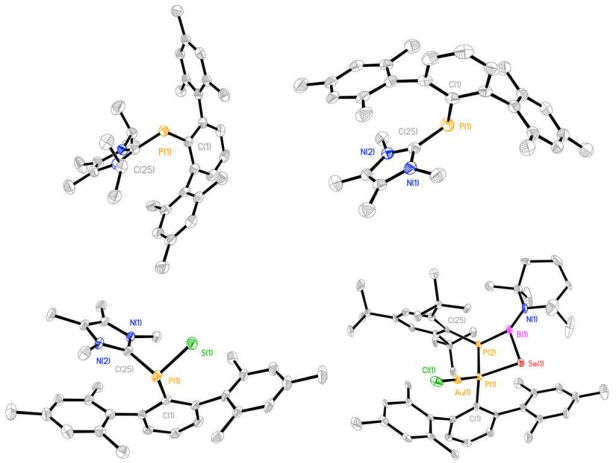
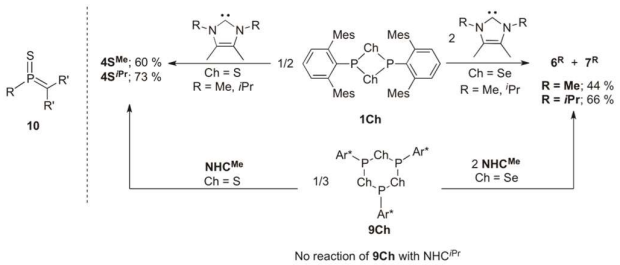


Figure 6: Solid state structures of **6^{iPr}** (top left), **6^{Me}** (top right), **4S^{Me}** (bottom left), and **8Se** (bottom right) with thermal ellipsoids at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]. **6^{iPr}**: P(1)-C(1) 1.843(3), P(1)-C(25) 1.799(3), C(1)-P(1)-C(25) 101.53(11). **6^{Me}**: P(1)-C(1) 1.832(4), P(1)-C(25) 1.786(4), C(1)-P(1)-C(25) 99.10(17). **4S^{Me}**: P(1)-C(1) 1.867(3), P(1)-C(25) 1.852(3), P(1)-S(1) 2.0186(15), C(1)-P(1)-C(25) 97.01(14), C(1)-P(1)-S(1) 111.62(11), C(25)-P(1)-S(1) 100.48(12). **8Se**: C(1)-P(2) 1.840(6), P(2)-P(1) 2.201(2), P(1)-C(25) 1.863(6), P(1)-B(1) 1.952(7), B(1)-N(1) 1.393(8), B(1)-Se(1) 2.007(7), P(2)-Se(1) 2.2492(18), P(2)-Au(1) 2.2344(17), Au(1)-Cl(1) 2.2978(17), C(1)-P(2)-Au(1)114.09(19), C(1)-P(2)-P(1)106.43(19), C(1)-P(2)-Se(1) 114.8(2), P(2)-P(1)-C(25) 112.66(18), P(2)-P(1)-B(1) 89.0(2), P(1)-B(1)-N(1) 137.1(5), P(1)-B(1)-Se(1) 96.7(3), B(1)-Se(1)-P(2) 86.3(2), Se(1)-P(2)-P(1) 83.33(7).

The $^{31}P\{^{1}H\}$ NMR spectra of **6^{R}** displayed a single resonance, consistent with the other reported NHC-stabilized phosphinidenes.[45] The $^{31}P\{^{1}H\}$ chemical shifts of **6^{R}** were found to be shifted significantly upfield from the parent **1Se** ($\Delta\delta_P$ = 98), indicating the presence of an electron-rich phosphorus site. The ^{1}H NMR spectra of **6^{R}** display a symmetric environment at phosphorus, indicated by one set of signals for the *o*-CH_3 and *p*-CH_3 groups on the terphenyl ligand, integrating to 12 and 6 hydrogen atoms, respectively, along with one set of signals for the NHC.[46,47] The solid-state structures of **6^{R}** (Figure 6) display typical features for NHC-stabilized phosphinidenes, with a bent geometry at phosphorus (C^{Ar}-P-C^{NHC} = 101.53(1) and 99.10(17)° for **6^{iPr}** and **6^{Me}**, respectively) and a short P–C^{NHC} bond (1.799(3) and 1.786(4) Å for **6^{iPr}** and **6^{Me}**, respectively). In addition to the formation of **6^{R}**, selenoureas **7^{R}** were concomitantly formed during the reaction and their identities confirmed using X-ray diffraction and NMR spectroscopy.[43]

While we have already reported that the reaction of **1S** and **NHC^{iPr}** yields the NHC-stabilized phosphinidene sulfide **4S^{iPr}**,[18] we repeated the same chemistry with the more sterically accommodating **NHC^{Me}** (Scheme 4). In doing so, the 2:1 addition of **NHC^{Me}** to **1S** at -50 °C resulted in the consumption of starting material and appearance of one signal in the crude $^{31}P\{^{1}H\}$ NMR spectrum (δ_P = 30.0) with a similar chemical shift as found for **4S^{iPr}** (δ_P = 29.0). After removing the volatiles *in vacuo*, dissolving the crude reaction mixture in toluene, and slowly layering the solution with ether at -35 °C, single crystals suitable for X-ray diffraction were obtained that confirmed the product to be **4S^{Me}** (Figure 6). The metrical parameters of **4S^{Me}** revealed two essentially identical P–C bond lengths (P–C^{NHC} = 1.852(3) Å and P–C^{Ar} = 1.867(3) Å) and a short P–S bond of 2.0186(15) Å, that is, bond parameters that are similar to those in **4S^{iPr}**. The NHC-adduct **4S^{Me}** has a strikingly similar structure to the known methylenethioxophosphoranes (**10**, Scheme 4),[48] however **4S^{Me}** contains a longer P–S bond (2.0186(15) Å vs. 1.928 Å)[49] and a significantly longer P–C bond (P–C^{NHC} in **4S^{Me}** 1.852(3) Å vs. 1.656 Å).[49] The P–C^{NHC} bond length is longer than expected for P=C,[50–52] thus describing **4S^{Me}** as containing a multiply bound phosphorus atom is not appropriate.

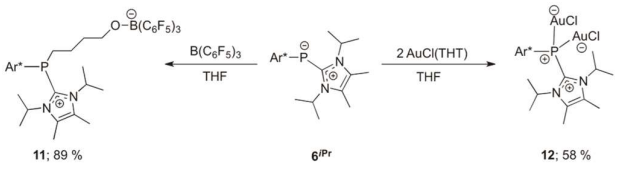
The recently reported 6-membered phosphorus-chalcogen rings **9Ch**[53] (Scheme 4, bottom) contain the same general formula as **1Ch** (*i.e.* $(RPCh)_n$) and have long been considered as precursors to phosphinidene chalcogenides,[54] although no experimental evidence has supported this claim. We utilized the same approach employed for **1Ch** and **3Ch**, and attempted the degradation of these larger P-Ch heterocycles into base-stabilized phosphinidene chalcogenides using NHCs. Similar to **3Ch**, the addition of **NHC^{iPr}** to **9Ch** at room temperature or



Scheme 4. Top: Reactivity of **1Ch** with **NHC^{R}** yields NHC-stabilized phosphinidene sulfides (left, **4S^{R}**) and phosphinidenes (right, **6^{R}**) as well as selenoureas (right, **7^{R}**). Bottom: Reactivity of **9Ch** with **NHC^{Me}** yields similar products as observed with **1Ch**. Left: Structure of literature known methylenethioxophosphoranes (**10**).

elevated temperatures resulted in no reaction, even after prolonged reaction times. The use of a more sterically accommodating carbene **NHC^{Me}** in 4:1 (Ch = S) or 6:1 (Ch = Se) stoichiometry, however, resulted in the formation of **4S^{Me}** (Ch = S) or **6^{Me}** and **7^{Me}** (Ch = Se) even at room temperature, indicating that strong sterically accommodating donors can indeed degrade these larger P-Ch heterocycles into their base-stabilized monomers.

Upon obtaining NHC-stabilized phosphinidenes **6^{R}** via multiple routes, we opted to test their onwards reactivity towards Lewis acids (Scheme 5). Although reports of such reactivity studies have been previously published,[10–16] the coordination chemistry of NHC-stabilized phosphinidenes containing bulky terphenyl groups is currently unknown. The addition of **6^{iPr}** to tris(pentafluorophenyl)borane in THF resulted in immediate colour change from yellow to colourless. After concentrating the crude reaction mixture, precipitation with *n*-pentane gave an off-white powder that shows a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum (δ_P = -25), a singlet in the ^{11}B NMR spectrum (δ_B = -3), indicating a four-coordinate boron centre, and three resonances in the ^{19}F NMR spectrum, consistent with the *ortho*-, *meta*-, and *para*-fluorine resonances for tris(pentafluorophenyl)borane. An X-ray diffraction experiment on single crystals grown via THF/pentane vapour diffusion confirmed the structure of **11**, indicating that a controlled ring-opening of THF by **6^{iPr}** had occurred in the presence of the strongly Lewis acidic $B(C_6F_5)_3$ (Figure 7). The ring-opened product **11** had a B–O bond length of 1.495(5) Å and two similar P–C bonds (C^{Ar*}–P = 1.843(4) Å and C^{NHC}–P = 1.839(4) Å), both of which are comparable to corresponding bond distances in **6^{iPr}**.



Scheme 5. Reactivity of NHC-stabilized phosphinidene **6^{iPr}** with $B(C_6F_5)_3$ results in a controlled ring-opening of THF (left, **11**), while reaction with two equivalents of Lewis acidic AuCl(THT) gives a coordination complex (right, **12**).

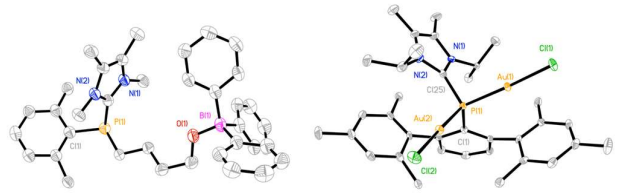


Figure 7: Solid state structures of **11** (left) and **12** (right) with thermal ellipsoids at 50 % probability. Mesityl groups of **11** and hydrogen atoms of both **11** and **12** are omitted for clarity. Selected bond lengths [Å] and angles [°]: **11**: P(1)-C(1) 1.843(4), P(1)-C(25) 1.839(4), P(1)-C(36), O(1)-B(1) 1.459(5), C(1)-P(1)-C(25) 100.59(16), C(1)-P(1)-C(36) 109.40(17), C(25)-P(1)-C(36) 99.36(17). **12**: P(1)-C(1) 1.849(4), P(1)-C(25) 1.856(4), P(1)-Au(1) 2.2452(13), P(1)-Au(2) 2.2451(13), C(1)-P(1)-C(25) 102.64(18), C(1)-P(1)-Au(1) 115.96(14), C(1)-P(1)-Au(2) 111.54(13), C(25)-P(1)-Au(1) 103.71(14), C(15)-P(1)-Au(2) 111.54(13), Au(1)-P(1)-Au(2) 108.81(4).

Direct coordination of a Lewis acidic transition metal was performed by adding two stoichiometric equivalents of AuCl(THT) to a solution of **6^{iPr}** (Scheme 5). After stirring for one hour at room temperature, the starting material was fully consumed and one major product was observed in the $^{31}P\{^{1}H\}$ NMR spectrum (δ_P = -41.9). After removing the volatiles of the crude reaction mixture *in vacuo*, a DCM/pentane vapourn diffusion of the crude reaction mixture yielded X-ray quality single crystals of **12**. The structure of **12** shows that the phosphorus atom is bound to two AuCl fragments (Figure 7) with a coordination environment reminiscent of other NHC-stabilized phosphinidene compounds with a tetrahedral geometry at phosphorus.[14,55] Significant lengthening of the C^{NHC}–P bond from 1.799(3) Å in **6^{iPr}** to 1.856(4) Å in **12** was observed, which is likely induced by an increase in steric interactions along with complete loss of backbonding with the inclusion of two AuCl units.

Conclusion

In summary, we have demonstrated the synthesis of unique inorganic heterocycles containing group 13, 15, and 16 elements as 4-membered P_2BCh rings (**3Ch**). The synthesis of **3Ch** was accomplished via reaction between two highly reactive monomers: phosphinidene chalcogenide and phosphaborene. The P_2BCh rings **3Ch** were found to be a source for low-coordinate phosphorus products, phosphinidene sulfides **4S** and phosphinidenes **6**, from their reaction with NHCs at elevated temperatures. Similar reactivity was also observed for the 4- and 6-membered $(RPCh)_n$ rings **1Ch** and **9Ch**. The coordination chemistry of NHC-stabilized phosphinidenes **6** was also explored, demonstrating their ability to ring-open THF and coordinate to Lewis acids via both lone pairs at phosphorus. Consequently, the controlled reactivity of monomeric **Ar*P=Ch** and **Mes*P=BNR$_2$** units, accessed from their parent dimers **1Ch** and **2**, has led to unique p-block rings that have eluded characterization until now. This method of forming novel heterocycles should allow for the synthesis of more asymmetric rings as well as the production of new low-coordinate main group compounds with possibly unforeseen structures and reactivity.

Experimental Section

All manipulations were performed under an inert atmosphere either in a nitrogen-filled MBraun Labmaster 130 glovebox or on a Schlenk line. **1Ch**,[18] **2**,[19] **9Ch**,[53] AuCl(THT),[56] and NHCs[57] were made following literature methods. Trispentafluorophenylborane was purchased from Strem Chemicals and sublimed overnight prior to use (50 °C, 0.01 mmHg, -10 °C cold finger). Solvents were obtained from Caledon and dried using an MBraun solvent purification system. Dried solvents were collected under vacuum in a flame dried Straus flask and stored over 4 Å molecular sieves. Solvents for Nuclear Magnetic Resonance (NMR) spectroscopy ($CDCl_3$, C_6D_6, and THF-d_8) were stored in the glovebox over 4 Å molecular sieves. NMR spectra were recorded on a Varian INOVA 400 MHz (^{1}H 400.09 MHz, $^{31}P\{^{1}H\}$ 161.8 MHz, ^{19}F 376.3 MHz), Bruker PRO 500 MHz (^{1}H 500 MHz, ^{11}B 160 MHz, $^{13}C\{^{1}H\}$ 126.0 MHz, $^{31}P\{^{1}H\}$ 202.1 MHz), or Varian INOVA 600 MHz spectrometer (^{1}H 600.1 MHz, $^{31}P\{^{1}H\}$ 242.3 MHz, $^{13}C\{^{1}H\}$ 126.0 MHz). All samples for ^{1}H and ^{13}C NMR spectroscopy were referenced to the residual protons in the deuterated solvent relative to tetramethylsilane ($CDCl_3$: ^{1}H δ = 7.26, ^{13}C δ = 77.16; C_6D_6: ^{1}H δ = 7.16, ^{13}C δ = 128.06; THF-d^8: ^{1}H δ = 1.72 and 3.58,

^{13}C δ = 67.21, 25.31). The samples for ^{31}P, ^{11}B, and ^{19}F NMR spectroscopy were referenced externally to phosphoric acid, trimethyl borate, and trifluorotoluene, respectively. Mass spectrometry was recorded in house in positive- and negative-ion modes using electrospray ionization Micromass LCT spectrometer. Melting or decomposition points were determined by flame-sealing the sample in capillaries and heating using a Gallenkamp variable heater. Elemental analysis was performed at the University of Montreal and is reported as an average of two samples weighed under air and combusted immediate thereafter.

General method for synthesis of 3Ch

A mixture of **1Ch** and **2** in benzene was heated at 80 °C for 2 hours after which the crude ^{31}P{^{1}H} NMR spectrum showed complete consumption of starting materials and appearance of two doublets. The volatiles were removed *in vacuo* and the crude reaction mixture was redissolved using 3 mL pentane and placed at -35 °C for 1 hour, leading to precipitation of a yellow powder.

3S: Reagents: **1S** (130 mg, 0.173 mmol) and **2** (148 mg, 0.173 mmol) in 5 mL benzene. Yield: 157 mg (57 %). **m.p.** (argon sealed capillary): 254 °C. **^{1}H NMR** (THF-*d*^{8}, 500 MHz, δ): 0.92 (s, 6H; TMP C(C**H**$_3$)$_2$), 1.12 (s, 9H; Mes* *ortho*-C(C**H**$_3$)$_3$), 1.21 (s, 6H; TMP C(C**H**$_3$)$_2$), 1.29 (s, 9H; Mes* *para*-C(C**H**$_3$)$_3$), 1.29-1.36 (m, 2H; TMP C**H**), 1.46-1.53 (m, 4H; TMP C**H**), 1.55 (s, 9H; Mes* *ortho*-C(C**H**$_3$)$_3$), 1.70 (br s, 6H; Mes *ortho*-C**H**$_3$), 2.22 (s, 6H; Mes *para*-C**H**$_3$), 2.28 (br s, 6H; Mes *ortho*-C**H**$_3$), 6.64 (s, 2H; Mes C-**H**), 6.82 (s, 2H; Mes C**H**), 6.89 (br d, ^{3}*J*(H,H) = 7.5 Hz, 2H; Ar* *meta*-**H**), 7.32 (br s, 2H; Mes* C**H**), 7.37 (t, ^{3}*J*(H,H) = 7.5 Hz, 1H; Ar* *para*-**H**). **^{13}C{^{1}H} NMR** (THF-*d*^{8}, 125 MHz, δ) 158.2, 156.7 (d, ^{2}J(C,P) = 30 Hz), 150.6, 148.8 (br d, ^{1}*J*(C,P) = 19 Hz), 139.6, 137.4 (br s), 136.6, 134.4 (br s), 130.7 (br s), 130.3, 128.2 (br s), 125.3, 122.8 (br s), 56.8, 40.7, 40.4, 39.9, 35.3, 35.2 (br s), 35.0 (br s), 33.5, 31.4, 22.9, 21.8, 21.0, 16.2. **^{31}P{^{1}H} NMR** (THF-*d*^{8}, 160 MHz, δ) -13.6 (d, ^{1}*J*(P,P) = 184 Hz; P-**P**-S), -29.8 (d, ^{1}*J*(P,P) = 184 Hz; P-**P**-B). **^{11}B NMR** (THF-*d*^{8}, 160 MHz, δ) 44.2 (br s). **EI-MS**: 803.49 *m/z* $C_{51}H_{72}BNP_2S$ [M]$^{+}$. **Elemental Analysis**: Calculated (%) for $C_{51}H_{72}BNP_2S$: C 76.19, H 9.03, N 1.74; Found: C 76.32, H 9.15, N 1.80.

3Se: Reagents: **1Se** (31 mg, 0.0366 mmol) and **2** (32 mg, 0.0366 mmol) in 3 mL of benzene. Yield: 26 mg (84 %). Single crystals suitable for X-ray diffraction were obtained by slowly concentrating a pentane solution via vapour diffusion. **m.p.**(nitrogen sealed capillary): 210-211 °C. **^{1}H NMR** (C_6D_6, 600 MHz, δ): 1.08 (s, 6H; TMP C(C**H**$_3$)$_2$), 1.29 (br s, 14H), 1.36 (s, 16H), 1.74 (s, 9H; Mes* *ortho*-C(C**H**$_3$)$_3$), 1.84 (s, 6H; Mes *ortho*-C**H**$_3$), 2.29 (s, 6H; Mes *ortho*-C**H**$_3$), 2.54 (s, 6H; Mes *para*-C**H**$_3$), 6.76 (s, 2H; Mes C**H**), 6.88 (d, ^{3}*J*(H,H) = 7.6 Hz, 2H; Ar* *meta*-**H**), 6.95 (s, 2H; Mes C**H**), 7.09 (t, ^{3}*J*(H,H) = 7.6 Hz, 1H; Ar* *para*-**H**), 7.49 (br s, 1H; Mes* C**H**), 7.54 (br s, 1H; ; Mes* C**H**). **^{13}C{^{1}H} NMR** (C_6D_6, 150.1 MHz, δ): 14.3, 15.8, 21.2, 21.9, 22.7, 23.2, 31.4, 32.0, 33.6, 34.9, 35.0, 35.4, 39.8, 40.0, 40.6, 57.4, 122.6 (br), 126.1, 128.4, 129.8, 130.0, 136.3, 136.9, 137.0, 137.2, 137.5, 139.7, 148.6, 148.7, 148.8, 150.1, 155.1, 155.2, 155.4, 157.8. **^{31}P{^{1}H} NMR** ($CDCl_3$, 242.3 MHz, δ): -33.5 (d, ^{1}*J*(P,P) = 181.7 Hz, ^{1}*J*(P,Se) = 91.8 Hz, 1P; P-**P**-Se), -31.5 (d, ^{1}*J*$_{P\text{-}P}$ = 181.7 Hz, 1P; P-**P**-B). **^{11}B NMR** ($CDCl_3$, 192.5 MHz, δ): 42.3 (br s). **ESI-MS**: 874.4 *m/z* $C_{51}H_{72}BNP_2SeNa$ [M + Na]$^{+}$. **Elemental Analysis**: Calculated (%) for $C_{51}H_{72}BNP_2Se$: C 71.99, H 8.53, N 1.65; Found: C 70.90, H 9.09, N 1.74.

Synthesis of 4S^{Me}: A solution of **NHC^{Me}** (21 mg, 0.173) in 3 mL THF was added to a stirred solution of **1S** (65 mg, 0.0863) in 4 mL THF at -50 °C and let stir for 30 minutes before letting warm to room temperature. The volatiles were removed *in vacuo*, the crude powder was washed with cold pentane (3 x 5 mL), and the resulting yellow solid was collected. Yield: 52 mg (60 %). **m.p.** (nitrogen sealed capillary): 218-219 °C. **^{1}H NMR** (C_6D_6, 400 MHz, δ): 1.07 (s, 6H; NHC C=C-C**H**$_3$), 2.12 (s, 6H; Mes *ortho*-C**H**$_3$), 2.18 (s, 6H; Mes *ortho*-C**H**$_3$), 2.43 (s, 6H; Mes *para*-C**H**$_3$), 3.02 (br s, 6H; NHC N-C**H**$_3$), 6.69 (br s, 2H; Mes C**H**), 6.81 (br s, 2H; Mes C**H**), 6.89 (d, ^{3}*J*(H,H) = 7.6 Hz, 2H; Ar* *meta*-C**H**), 7.11 (t, ^{3}*J*(H,H) = 7.6 Hz, 1H; Ar* *para*-C**H**). **^{13}C{^{1}H} NMR** (C_6D_6, 100.5 MHz, δ): 7.7, 21.2, 21.5, 21.6, 21.9, 22.0, 130.1, 135.4, 136.2, 136.4, 140.4, 145.0 (br). **^{31}P{^{1}H} NMR** (C_6D_6, 161.8 MHz, δ): 30.0 (s). **ESI-MS**: 1023.5 *m/z* $C_{62}H_{74}P_2N_4S_2$ [(2 x M) + Na]$^{+}$, 523.2 *m/z* $C_{31}H_{37}PN_2S$ [M + Na]$^{+}$, 469.3 *m/z* $C_{31}H_{37}PN_2$ [M - S]$^{+}$.

General method for synthesis of 6^{R}

A solution of **NHC^{R}** in THF was added to a solution of **1Se** or **9Se** in THF. The mixture was left to stir for 15 minutes after which the initial orange solution had changed to dark red. The volatiles were removed *in vacuo* and the crude reaction mixture was dissolved in 5 mL pentane and left at -35 °C overnight, giving orange crystals.

6^{iPr}: Reagents: **NHC^{iPr}** (38 mg, 0.213 mmol) in 3 mL THF and **1Se** (45 mg, 0.053 mmol) in 3 mL THF. Yield: 37 mg (66 %). Single crystals suitable for X-ray diffraction were obtained by leaving a concentrated pentane solution at -35 °C overnight. **m.p.** (nitrogen sealed capillary): 198 °C (orange powder turns red-orange at 155 °C). **^{1}H NMR** (C_6D_6, 400 MHz, δ): 0.87 (d, ^{3}*J*(H,H) = 6.8 Hz, 12H; *i*Pr C**H**$_3$), 1.54 (s, 6H; NHC C=C-C**H**$_3$), 2.22 (s, 6H; Mes *para*-C**H**$_3$), 2.41 (s, 12H; Mes *ortho*-C**H**$_3$), 5.24 (sept, ^{3}*J*(H,H) = 7.2 Hz, 1H; *i*Pr C**H**), 5.26 (sept, ^{3}*J*(H,H) = 7.2 Hz, 1H; *i*Pr C**H**), 6.87 (br s, 4H; Mes C**H**), 7.08 (overlapping multiplet, 3H). **^{13}C{^{1}H} NMR** (C_6D_6, 150.8 MHz, δ): 10.5 (br s), 21.5 (m), 52.3 (m), 123.4, 124.0, 129.2, 135.0, 136.1, 142.7, 147.3 (d, ^{1}*J*(C,P) = 54.9 Hz), 149.3, 149.7, 171.0, 171.6. **^{31}P{^{1}H} NMR** (C_6D_6, 161.8 MHz, δ): -75.0 (s). **ESI-MS**: 525.3 *m/z*, $C_{35}H_{45}PN_2$ [M^{+}]. **Elemental Analysis**: Calculated (%) for $C_{35}H_{45}PN_2$: C 80.11, H 8.64, N 5.34; Found: C 78.55, H 8.65, N 5.29.

6^{Me}: Reagents: **NHC^{Me}** (36 mg, 0.283 mmol) in 3 mL THF and **9Se** (60 mg, 0.0472 mmol) in 3 mL THF. Yield: 30 mg (44 %). Single crystals suitable for X-ray diffraction were obtained by leaving a concentrated ether solution at -35 °C overnight. **m.p.** (nitrogen sealed capillary): 241-242 °C. **^{1}H NMR** (C_6D_6, 400 MHz, δ): 1.22 (s, 6H; NHC C=C-C**H**$_3$), 2.17 (s, 6H; Mes *para*-C**H**$_3$), 2.42 (s, 12H; Mes *ortho*-C**H**$_3$), 2.84 (s, 6H; NHC N-C**H**$_3$), 6.79 (s, 4H; Mes C**H**), 7.03 (overlapping multiplet, 3H). **^{13}C{^{1}H} NMR** (C_6D_6, 150.8, MHz, δ): 8.5, 21.1, 21.2, 21.3, 33.8, 33.9, 122.0, 122.1, 122.2, 128.7, 134.4, 135.9, 142.4 (d, ^{1}*J*(C,P) = 4.8 Hz), 144.4 (d, ^{1}*J*(C,P) = 20.1 Hz). **^{31}P{^{1}H} NMR** (C_6D_6, 161.8 MHz, δ): -76.7 (s). **ESI-MS**: 469.3 *m/z*, $C_{31}H_{37}PN_2$ [M^{+}]. **Elemental Analysis**: Calculated (%) for $C_{31}H_{37}PN_2$: C 79.45, H 7.96, N 5.98; Found: C 78.38, H 7.63, N 6.04.

Synthesis of 8Se: A solution of **3Se** (40 mg, 0.0470 mmol) in 3 mL dichloromethane was added to a solution of AuCl(THT) (15 mg, 0.0470 mmol) in 3 mL dichloromethane. The reaction vial

was wrapped in aluminum foil to keep out ambient light. The reaction was let stir for 30 minutes and the volatiles were removed *in vacuo*. The crude reaction mixture was redissolved in 4 mL ether, passed through a Celite® filter, and the filtrate was collected. The volatiles were removed *in vacuo* to yield **8Se** (29 mg, 58 %). Leaving a concentrated solution of **8Se** in MeCN at -35 °C overnight yielded single crystals suitable for X-ray diffraction. **m.p.** (nitrogen sealed capillary): 118-119 °C (decomp., turns black). **^{1}H NMR** ($CDCl_3$, 600 MHz, δ): 1.09 (s, 6H; TMP C(CH_3)$_2$), 1.17 (s, 3H; TMP C(CH_3)), 1.29 (s, 6H), 1.33 (s, 9H; Mes* *ortho*-C(CH_3)$_3$), 1.42 (s, 9H; Mes* *ortho*-C(CH_3)$_3$), 1.50-1.55 (br m, 6H; TMP C**H**), 1.64 (s, 9H; Mes* *para*-C(CH_3)$_3$), 1.75 (3H; Mes *ortho*-CH_3), 1.87 (s, 3H; Mes *ortho*-CH_3), 2.28 (s, 3H; Mes *ortho*-CH_3), 2.38 (s, 3H; Mes *para*-CH_3), 2.70 (s, 3H; Mes *para*-CH_3), 6.55 (s, 1H; Mes C**H**), 6.80 (s, 1H; Mes C**H**), 6.92 (br, 3H), 7.13 (br d, ^{3}J(H,H) = 7.6 Hz, 1H; Ar* *meta*-C**H**), 7.35 (br d, ^{3}J(H,H) = 7.6 Hz, ^{4}J(P,H) = 1.2 Hz, 1H; Ar* *meta*-C**H**), 7.43 (dt, ^{3}J(H,H) = 7.6 Hz, ^{5}J(P,H) = 1.2 Hz, 1H; Ar* *para*-C**H**), 7.57 (s, 1H; Mes* C**H**). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.1 MHz, δ): 15.7, 16.5, 21.0, 21.4, 22.0, 22.5, 23.4, 27.9, 31.3, 33.8, 34.4, 34.5, 35.2, 35.3, 36.6, 36.7, 39.7, 39.8, 40.6, 41.2, 57.4, 58.1, 123.6, 123.7, 127.6, 127.9, 128.1, 129.1, 131.0, 131.2, 131.7, 132.3, 132.4, 132.4, 135.7, 136.3, 137.1, 137.6, 138.0, 138.4, 138.5, 138.6, 147.0, 147.9 (d, ^{1}J(C,P) = 22.6 Hz), 152.2, 154.5 (d, ^{2}J(C,P) = 4.9 Hz), 154.8 (d, ^{2}J(C,P) = 4.9 Hz), 157.6. **^{31}P{^{1}H} NMR** ($CDCl_3$, 161.8 MHz, δ): -8.4 (d, ^{1}J(P,P) = 245.6 Hz, ^{1}J-(P,Se) = 169.9 Hz, 1P; P-**P**-Se), 10.3 (d, ^{1}J(P,P) = 246.4 Hz, 1P; P-**P**-B). **^{11}B NMR** ($CDCl_3$, 192.5 MHz, δ): 43.8 (br s).

Synthesis of 11: A solution of **6^{iPr}** (50 mg, 0.0953 mmol) in 3 mL THF was added to a solution of trispentafluorophenylborane (49 mg, 0.0953 mmol) in 3 mL THF. After 30 minutes, the initial orange solution had turned colourless and the volatiles were removed *in vacuo*. The crude powder was washed with pentane (3 x 3 mL) and the resulting white solid was collected. Yield: 94 mg (89 %). Single crystals suitable for X-ray diffraction were obtained by pentane/THF vapour diffusion at -35 °C overnight. **m.p.** (nitrogen sealed capillary): 212-213 °C (decomp., turns grey). **^{1}H NMR** ($CDCl_3$, 600 MHz, δ): 0.80 (d, ^{3}J(H,H) = 6.6 Hz, 3H; *i*Pr CH_3), 1.13 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 3H; *i*Pr CH_3), 1.20 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 3H; *i*Pr CH_3), 1.32 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 3H; *i*Pr CH_3), 1.75-1.84 (br m, 6H; CH_2), 2.21 (br s, 9H), 2.26 (s, 3H; ; Mes *ortho*-CH_3), 2.28 (s, 6H; Mes *ortho*-CH_3), 2.29 (s, 6H; Mes *para*-CH_3), 2.78 (br m, 1H; alkyl C**H**), 2.89 (br m, 1H; alkyl C**H**), 4.61 (septet, ^{3}J(H,H) = 6.6 Hz, 1H; *i*Pr C**H**), 4.77 (septet, ^{3}J(H,H) = 6.6 Hz, 1H; *i*Pr C**H**), 6.82 (br s, 2H), 6.96 (br s, 4H), 7.44 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H; Ar* *para*-C**H**). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.5 MHz, δ): 10.5, 10.8, 14.2, 20.0, 21.0, 21.1, 21.2, 21.9, 22.4, 22.5, 22.9, 24.5, 24.6, 24.8, 34.3, 53.3, 53.6, 62.2, 129.0, 129.2, 129.7, 129.8, 130.4, 132.0, 132.2, 132.6, 137.6, 138.8, 145.7, 146.3, 147.0 (br), 149.1 (br). **^{31}P{^{1}H} NMR** ($CDCl_3$, 161.8 MHz, δ): -24.7 (s). **^{11}B NMR** ($CDCl_3$, 128.3 MHz, δ): -2.87 (s). **^{19}F NMR** ($CDCl_3$, 376.3 MHz, δ): -168.1 (br t, ^{3}J(F,F) = 20.0 Hz, 6F; *ortho*-C**F**), -165.2 (t, ^{3}J(F,F) = 20.0 Hz, 3F; *para*-C**F**), -133.4 (br d, ^{3}J(F,F) = 20.0 Hz, 6F; *meta*-C**F**). **ESI-MS**: 1131.4 *m/z*, $C_{57}H_{53}BF_{15}N_2OPNa$ [M + Na]$^{+}$, 597.4 *m/z*, $C_{39}H_{53}N_2OP$ [M – B(C_6F_5)$_3$]$^{+}$. **Elemental Analysis**: Calculated (%) for $C_{57}H_{53}BF_{15}N_2OP$: C 60.07, H 4.69, N 2.46; Found: C 60.83, H 5.29, N 2.43.

Synthesis of 12: A solution of **6^{iPr}** (65 mg, 0.124 mmol) in 3 mL THF was added dropwise to a well stirred solution of AuCl(THT) (30 mg, 0.248 mmol) in 3 mL THF. After the addition of **6^{iPr}** was complete, the orange colour had disappeared and the crude reaction mixture remained colourless. After 30 minutes, the volatiles were removed *in vacuo*, the crude powder was washed with pentane (3 x 3 mL), and the resulting white solid was collected. Yield: 71 mg (58 %). Single crystals suitable for X-ray diffraction were grown via dichloromethane/ether vapour diffusion at -35 °C. **m.p.** (nitrogen sealed capillary): 184-185 °C (decomp., turns black). **^{1}H NMR** ($CDCl_3$, 600 MHz, δ): 1.14 (br s, 6H; NHC C=C-CH_3), 1.39 (br s, 6H; *i*Pr CH_3), 2.29 (s, 18H; Mes CH_3), 2.32 (s, 3H; *i*Pr CH_3), 2.45 (s, 3H; *i*Pr CH_3), 5.56 (br m, 2H; *i*Pr C**H**), 6.98 (br m, 3H), 7.11 (br s, 2H; Mes C**H**), 7.34 (br s, 1H; Mes C**H**), 7.52 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1H; Ar* *para*-C**H**). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.8 MHz, δ): 11.5, 14.2, 20.7 (br), 22.5, 22.8, 29.5, 29.8, 31.4, 32.1, 34.3, 38.3, 54.0, 128.4, 129.2, 130.0, 130.6, 130.7, 130.9, 131.4, 131.7, 132.6, 137.9, 139.5, 143.8, 144.1, 146.6, 148.1. **^{31}P{^{1}H} NMR** ($CDCl_3$, 161.8 MHz, δ): -41.9 (s). **ESI-MS**: 1195.1 *m/z*, $C_{35}H_{45}PN_2Au_2I_2Na$ [M - 2 Cl + 2 I + Na]$^{+}$, 1011.2 *m/z*, $C_{35}H_{45}PN_2Au_2Cl_2Na$ [M + Na]$^{+}$.

X-ray Crystallography

CCDC 1573801-1573808 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The single crystal X-ray diffraction studies were performed at the Western University X-Ray facility. Samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil, at a temperature of 110 K for data to be collected on a Bruker Apex II detector using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å). The Bruker and Nonius instrument operate SMART[58] and COLLECT[59] software, respectively. The data collection strategy was a number of ϕ and ω scans which collected data up to 2θ. The frame integration was performed using SAINT.[60] The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[61] The structure was solved by using a dual space methodology using the SHELXT program.[62] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on *F*. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the SHELXL program from the SHELXTL suite of crystallographic software.[61,63] For all compounds reported (**3Ch**, **4S^{Me}**, **6^{R}**, **8Se**, **11**, and **12**), the non-hydrogen atoms were well ordered and refined with anisotropic thermal parameters. In the case of **8Se**, a MeCN solvate was found in the asymmetric unit that could not be refined anisotropically but isotropically.

Computational Details

Calculations were performed using the PBE1PBE[64–67] density functional with the Gaussian09[68] program package. Ahlrichs' TZVP basis sets were used for all atoms.[69] The importance of dispersion interactions was examined by performing optimizations both with and without Grimme's GD3BJ empirical dispersion correction.[70,71] The bulky Ar* and Mes* groups were replaced with Ar (*m*-diphenylbenzene) and Mes (2,4,6-trimethylphenyl), respectively, to speed up the calculations. Similarly, 2,2,6,6-tetramethylpiperidine was replaced with dimethylamine throughout calculations.

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