

Heteroaromatic Substituted Phosphoranes with Enhanced Hemilabile Character

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New ligands with enhanced hemilabile character compared to iminophosphoranes known in the literature are presented. When diphenyl-2-picolyolphosphane was oxidized with elemental sulfur or gray selenium, the new ligands $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2\text{Py})$ (**1**) and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2\text{Py})$ (**2**) were obtained. In addition, the calcium complex $[(\text{thf})_2\text{Ca}\{(\text{PyCH})(\text{Se})\text{PPh}_2\}_2]$ (**3**), based on **2**, is presented. This is only the second example of a molecular structure displaying a direct calcium–selenium contact. A structural comparison of the parent ligands and the related motifs in the organometallic complex reveals the bonding to the central phosphorus atom to be mostly strengthened by electrostatic means rather than by any double bonding. The spectroscopic data of **3** show features similar to those of iminophosphoranes, despite small differences in electronegativity. All of the compounds presented are accessible in good yields and high purity. The DTA analysis of **3** points to possible CVD applications to form CaSe from the gas phase.

Introduction

Alkaline-earth-metal and alkali-metal chalcogenolates have gained increasing attention over the last few years, since they are useful in technical applications. In particular, alkaline-earth-metal oxygen compounds are suitable precursors for high-temperature superconductors and ferroelectrics. Much less attention has been paid to the alkaline-earth-metal thiolates and selenates, although many heavier chalcogenates are known as potential dopants for chalcogen-based semiconductors.¹ In the past, chelating ligands such as the aminoiminophosphoranes $\text{Ph}_2\text{P}(\text{NSiMe}_3)_2$,² diiminosulfates $\text{PhS}(\text{NSiMe}_3)_2$,³ and benzamidates $\text{PhC}(\text{NSiMe}_3)_2$ ⁴ have proved to be versatile ligands, because they supply enough bulk to sufficiently shield the metal atom and give solubility even in nonpolar hydrocarbons. Synthetic and structural studies of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{Py}$ (Py = 2-pyridyl) showed the monoanionic ligand to have (O,N)-chelating properties.⁵ Now we introduce the new ligands $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2\text{Py})$ (**1**) and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2\text{Py})$ (**2**), derived from the known diphenyl-2-picolyolphosphane, with (S(Se),N)-chelating coordination sites. In deprotonation reactions of the methylene group of the picolyl substituent these neutral ligands can be converted to monoanionic hemilabile ligands. In this context, the calcium selenium containing complex $[(\text{thf})_2\text{Ca}\{(\text{PyCH})(\text{Se})\text{PPh}_2\}_2]$ (**3**) is presented, which is available in good yield

and high purity. This is a *conditio sine qua non* for chemical vapor deposition processes.⁶ DTA analysis suggests **3** to be a suitable candidate to give CaSe in the CVD process.

Over the last few years only a few calcium selenides have been reported, such as $[(\text{TMEDA})_2\text{Ca}(\text{SeSi}(\text{SiMe}_3)_3)]$,⁷ but to date only the solid-state structure of $[(\text{thf})_4\text{Ca}(\text{SeMes}^*)_2]$ has been reported.⁸ The complex reported herein, $[(\text{thf})_2\text{Ca}\{(\text{PyCH})(\text{Se})\text{PPh}_2\}_2]$ (**3**), is the second fully characterized such compound, including the solid-state structure, with a direct selenium–calcium contact.

The newly introduced ligands $\text{Ph}_2\text{P}(\text{S})(\text{CH}_2\text{Py})$ (**1**) and $\text{Ph}_2\text{P}(\text{Se})(\text{CH}_2\text{Py})$ (**2**) are typical hemilabile ligands. According to the concept of Jeffrey and Rauchfuss, hemilabile ligands provide different electronegativities at their coordination sites.⁹ This is of special interest for catalytic processes. Werner et al. transformed the ubiquitous chelating ligands 1,2-bis(diphenylphosphanyl)ethane (dppe) and 1,2-bis(dimethylphosphanyl)ethane (dmpe) into hemilabile ligands by switching one phosphanyl donor group to an arsanyl or antimonyl site.¹⁰ Our ligands provide a less dangerous approach to coordination site selective chelating ligands compared to the arsenic- or antimony-based species. In particular, phosphorus-based hemilabile ligands show outstanding results in catalytic processes,¹¹ i.e., allylic substitution, hydrosilylation, hydroboration, and hydrogen-transfer reactions.¹² With this in mind, we embarked upon the improvement of the hemilabile character to facilitate even better catalytic features. The reported compounds are potential new

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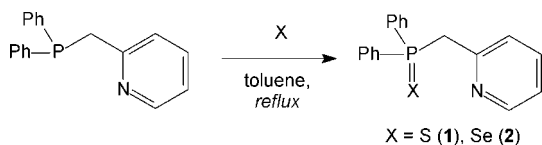
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ligands in catalytic application. In addition, their solid-state structures give further insight into the selenium–calcium interaction.

Results and Discussion

Aiming for a new coordination site with a Lewis hardness different from that of the known diphenyl-2-picolyiminophosphorane,¹³ we oxidized diphenyl-2-picolyolphosphane with sulfur and gray selenium (Scheme 1). The resulting ligands are thought to have similar properties according to the concept of Langmuir, since iminophosphoranes are isoelectronic with thiophosphoranes.¹⁴ By means of the lowered hardness, we gained an even stronger hemilabile character of the ligand while descending group 16. Sulfur is softer and selenium is much softer than nitrogen.

Scheme 1. Syntheses of Ph₂P(S)(CH₂Py) (1) and Ph₂P(Se)(CH₂Py) (2) by Oxidation



The oxidation of diphenyl-2-picolyolphosphane was carried out with elemental sulfur in refluxing toluene over a period of 4 h. Washing with diethyl ether gave **1** as the product in excellent purity. Crystals suitable for X-ray diffraction analysis were obtained at room temperature after 7 days from a saturated solution of **1** in THF. Accordingly, we used gray selenium in toluene at reflux for the synthesis of **2**, following the oxidation of triphenylphosphane¹⁵ reported by Allen and Taylor. Again, washing with diethyl ether gave the product in excellent purity. Crystals suitable for X-ray diffraction analysis (Table 1) were grown from THF within 10 days at room temperature.

1 crystallizes in the monoclinic space group $P2_1/n$. The solid-state structure is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The phosphorus atom is tetrahedrally coordinated. The average C_{ipso}–P1–C13 angle is slightly smaller and the C–P–S angle is marginally larger than the ideal tetrahedral angle. The P1–C13 bond at the methylene bridge is 0.02 Å longer than the other two P–C bonds. This

Table 1. Crystallographic Data of Compounds 1–3

	1	2	3
CCDC no.	682152	682153	682154
formula	C ₁₈ H ₁₆ NPS	C ₁₈ H ₁₆ NPSe	C ₅₂ H ₆₂ CaN ₂ O ₄ P ₂ Se ₂
fw	309.35	356.25	1038.98
cryst size (mm)	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.30	0.18 × 0.10 × 0.04
space group	$P2_1/n$	$P2_1/n$	$C2/c$
<i>a</i> (Å)	12.413(1)	12.6149(7)	27.690(2)
<i>b</i> (Å)	7.3039(5)	7.2983(4)	9.1573(7)
<i>c</i> (Å)	17.165(1)	17.401(1)	19.484(1)
β (deg)	99.485(5)	100.102(1)	96.946(1)
<i>V</i> (nm ³)	1.5350(2)	1.5772(2)	4.9042(6)
<i>Z</i>	4	4	4
ρ_c (Mg m ⁻³)	1.339	1.500	1.407
μ (mm ⁻¹)	0.307	2.474	1.724
<i>F</i> (000)	648	720	2152
θ range (deg)	1.89–24.83	2.38–26.37	2.11–26.39
<i>R</i> _{int}	0.0467	0.0247	0.0275
no. of rflns measd	16 794	37 857	25 988
no. of unique rflns	2642	3220	5030
no. of restraints	0	0	602
no. of refined params	190	190	443
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.0268	0.0179	0.0280
w <i>R</i> 2 (all data)	0.0670	0.0502	0.0686
highest diff peaks (e Å ⁻³)	0.202/–0.226	0.362/–0.282	0.464/–0.512

can easily be rationalized by the smaller radius of a sp²-hybridized carbon atom compared to a sp³-hybridized one.¹⁶ The P=S bond distance of 1.9608(6) Å is comparable with the related distance in Ph₃P=S (1.9554(7) Å).¹⁷

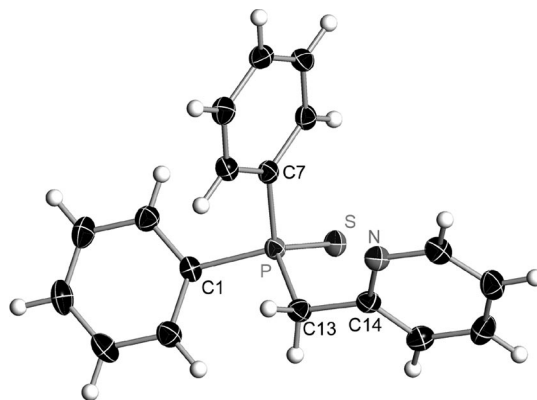


Figure 1. Solid-state structure of Ph₂P(S)(CH₂Py) (**1**). Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths and angles are given in Table 2.

2 is isostructural to compound **1** and the solid state structure is depicted in Figure 2. Selected bond lengths and angles are listed in Table 2. The P=Se bond distance of 2.1112(4) Å is comparable with the related distance in Ph₃P=Se (2.112(1) Å).¹⁸ The increase in P=X bond distances by about 0.15 Å from X = S to Se reflects the increase in radii.¹⁹

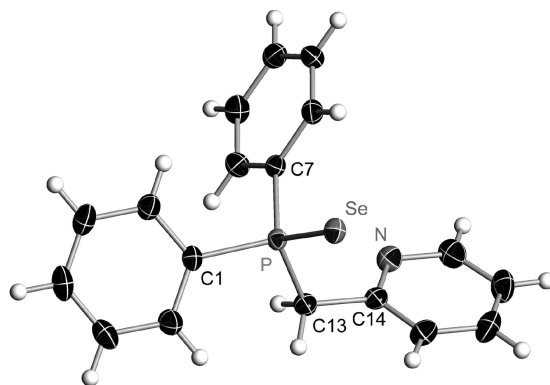
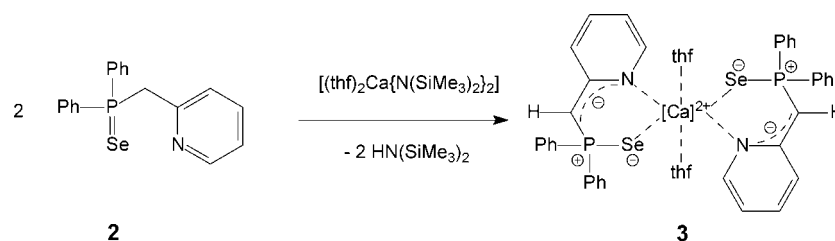


Figure 2. Solid-state structure of Ph₂P(Se)(CH₂Py) (**2**). Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths and angles are given in Table 2.

According to the successful preparation of related ligands, the best way to introduce a metal is to employ metal bis(tri-

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1–3

	1	2	3
Ca1–N1			2.470(2)
Ca1–Se1			2.945(1)
P1–S1/Se1	1.961(1)	2.111(1)	2.161(1)
P1–C1	1.813(2)	1.815(1)	1.822(2)
P1–C7	1.812(2)	1.812(1)	1.831(2)
P1–C13	1.832(2)	1.836(1)	1.721(2)
C13–C14	1.501(2)	1.506(2)	1.399(3)
C14–N1	1.345(2)	1.339(2)	1.377(2)
C13–P1–C1	104.58(7)	104.85(6)	104.02(9)
C13–P1–C7	105.51(7)	105.81(6)	110.65(9)
C1–P1–C7	104.35(7)	104.87(6)	104.30(8)
S1/Se1–P1–C1	114.46(5)	113.99(5)	109.29(8)
S1/Se1–P1–C7	113.74(5)	113.49(5)	106.60(6)
S1/Se1–P1–C13	113.22(6)	112.97(5)	120.82(7)
P1–C13–C14	113.50(11)	113.44(10)	127.26(15)

Scheme 2. Preparation of [(thf)₂Ca{(PyCH)(Se)PPh₂}]₂ (**3**) by Deprotonation of Ph₂P(Se)(CH₂Py) (**2**) with [(thf)₂Ca{N(SiMe₃)₂}]₂

methylsilyl)amides to obtain the monoanionic ligand in deprotonation reactions.²⁰ The main advantages of this synthetic route are the straightforward accessibility of the starting materials in high purity, the high basicity, and the formation of volatile bis(trimethylsilyl)amine, easily removable under vacuum. In contrast, the preparation via a metal exchange reaction from the lithiated phosphorane and alkaline-earth-metal halides always formed crude inseparable products, presumably due to cocoordinated lithium halides.

[(thf)₂Ca{N(SiMe₃)₂}]₂²¹ and **2** were mixed in a 1:2 ratio at room temperature in THF in an argon glovebox (Scheme 2). Slightly better yields and purity of **3** were gained using ligand and metal in equimolar amounts. Crystallization from THF yielded crystals suitable for X-ray diffraction analysis. The thermal decomposition of **3** was monitored by DTA analysis. After removal of the coordinated solvent, the complex loses the first diphenyl-2-picolyphosphane up to 385 °C and subsequently the second ligand is lost on heating to 591 °C. The residual calcium diselenide could be transformed to calcium selenide by heating the sample to 1400 °C.

The complex crystallizes in the monoclinic space group *C2/c* with a half-molecule in the asymmetric unit. The solid-state structure is shown in Figure 3, and selected bond lengths and angles are given in Table 2. The calcium atom resides on a special position of the 2-fold axis. The distorted-octahedral coordination sphere is completed by two THF molecules. Each ligand is chelating the calcium atom with the nitrogen and the selenium atom to give a facial orientation.

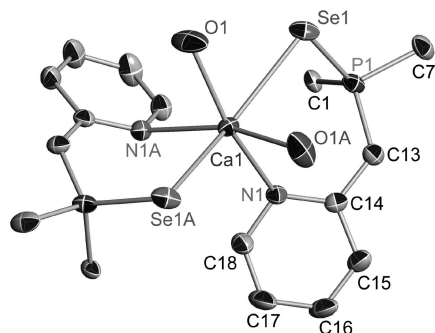


Figure 3. Molecular structure of [(thf)₂Ca{(PyCH)(Se)PPh₂}]₂ (**3**). Anisotropic displacement parameters are depicted at the 50% probability level. Carbon atoms of the THF ligands, the phenyl ring atoms (except the C_{ipso} atoms), and the hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 2.

As in [(thf)₂Ca{(NSiMe₃)₂SPh}]₂,^{3b} the two ligands in **3** provide enough space for two additional THF donor molecules. Interestingly, they are orientated to the same side of the coordination octahedron. With the bulkier ligands in [(thf)₂Ca{(NSiMe₃)₂PPh₂}] there is only space for one thf molecule.² On comparison of the solid-state structures of the free phosphoranes **1** and **2** to that of the ligand in the metal

complex **3**, a contraction of the P–C13 and C13–C14 bonds of more than 0.1 Å is observed. Thus, these bond lengths are halfway between a formal single and double bond. The wider P–C13–C14 angle indicates the change in the hybridization of C13 from sp³ to sp². However, in light of recent charge density investigations it seems unlikely that there is any P=C double-bond character involved.²²

With regard to the phosphorus atom, the coordination geometry resembles a distorted tetrahedron in **3** compared to **1** and **2**. While the Se1–P1–C_{ipso} angles are decreased, the P1–C_{ipso} bond length increases slightly. Regarding the phosphorus–selenium interaction, we found a widening of the Se1–P1–C13 angle by about 8° but a marginal elongation of the P1–Se1 bond by only 0.05 Å in the metal complex **3** compared to the free ligand **2**. The Ca–Se distance of 2.945(1) Å is almost identical with the only other reported distance in [(thf)₄Ca(SeMes*)₂] of 2.934(1) Å.⁸

The NMR data reveal a downfield shift for C13, C14, and Se1 of **3** related to the signals for **2**, suggesting the deshielding of the nuclei by the metal complexation. The decrease of the selenium–phosphorus coupling constant by 206 Hz can be taken as a hint of the weakening of the bond. In contrast, we found an upfield shift for H5 and P1, as well as an increased P1–C13 NMR coupling constant, indicating a strengthened P1–C13 bond. This is in accordance with the reduced bond distance.

However, neither the decrease in the P–Se NMR coupling constant nor the slight bond elongation upon metalation would be enough evidence for P=Se double bonding in **2**. As for the polarized ⁺P–N[−] bond in metalated iminophosphoranes,²³ we suggest an electrostatically strengthened ⁺P–Se[−] bond in **2** and **3**. The calcium atom in **3** competes with the phosphorus atom for the charge density at the selenium atom, and thus, the P–Se

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bond is elongated. If there was a P=Se double bond in the hypervalent species of **2**, a much more pronounced bond elongation would have been found upon metalation. The same is valid for the bonding around C13. Although there is considerable P–C13 and C13–C14 bond shortening, it remains questionable whether there is P=C double bonding involved. The same increase in the P1–C13 NMR coupling constant and bond shortening would be observed with a polarized $^+P-C^-$ bond. Recent experimental charge density investigations of a benzyllithium derivative show the negative charge mostly accumulated at the benzylic carbon atom and only marginally coupled into the phenyl ring.^{22a} Thus, in **3** the charge is mainly shifted from the deprotonated C13 to N1 to facilitate the calcium metal coordination.

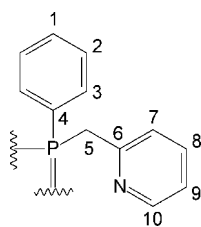
Conclusion

In oxidation reactions of the phosphane Ph₂P(CH₂Py) with elemental sulfur and selenium the two phosphoranes Ph₂P(X)(CH₂Py), with X = S (**1**), Se (**2**), are available in high yields. They offer two potential donor sites to a metal in an (X,N)-hemilabile chelating ligand. Moreover, they can be converted to monoanionic ligands in deprotonation reactions of the bridging methylene group. Exactly this anticipated coordination mode is observed in the calcium complex [(thf)₂Ca{(PyCH)(Se)PPh₂}₂] (**3**). The structural comparison of the parent phosphanes and the related ligands in the organometallic complex reveals the bonding to the central phosphorus atom to be strengthened mostly by electrostatic means rather than by any double bonding. Accordingly, the Lewis diagram with $^+P-Se^-$ describes the bonding more correctly than a P=Se double bond. Similarly, there is no ylenic P=C bonding but a $^+P-C^-$ bond that is polarized. The negative charge is partially transferred to the ring nitrogen atom to give an attractive metal donor site. DTA analysis indicates **3** to be a promising candidate to form CaSe from the gas phase.

Experimental Section

All experiments were performed under a dry argon gas atmosphere by using modified Schlenk²⁴ techniques or a drybox. Solvents were freshly distilled from sodium–potassium alloy prior to use. ¹H, ¹³C, ³¹P, and ⁷⁷Se NMR spectra were recorded at room temperature in dry THF-*d*₈ using a Bruker Avance DRX 500 spectrometer. All signals were unambiguously assigned via H,H-COSY and C,H-correlation spectra. The assignment of the signals is depicted in Scheme 3. EI mass spectra were measured with a MAT 95 instrument. Melting points were determined with a Büchi B-540 instrument. Elemental analyses and DTA studies were performed by the Analytisches Labor, Institut für Anorganische Chemie of the Georg-August-Universität Göttingen. The latter were performed on a Netzsch STA 409 with a heating rate of 10 K min⁻¹. All starting materials were commercially available or were synthesized according to the cited literature procedures.^{21,25}

Scheme 3. Numbering Scheme for the NMR Signal Assignment



Ph₂P(S)(CH₂Py) (1). 5.00 g (18.0 mmol) of Ph₂P(CH₂Py) in 100 mL of toluene and 0.87 g (27.0 mmol) of sulfur were refluxed for 4 h. After the mixture was cooled to room temperature and filtered over Celite, the solvent was removed under vacuum. Washing with diethyl ether gave the product as a pale yellow solid. Crystallization from THF yielded colorless blocks suitable for X-ray structure analysis (room temperature, 7 days). Yield: 5.13 g, 16.6 mmol, 92%. Mp: 113–114 °C. ¹H NMR (500.13 MHz): δ 4.14 (d, 2H, ²J_{PH} = 14.5 Hz, 5); 7.03–7.07 (m, 1H, 9); 7.37–7.46 (m, 6H, 1, 2); 7.46–7.55 (m, 2H, 7, 8); 7.94–8.00 (m, 4H, 3); 8.27–8.30 (d, 1H, ³J_{HH} = 5.26 Hz, 10). ¹³C NMR (125.76 MHz): δ 43.8 (d, ¹J_{CP} = 50.1 Hz, 5); 122 (s, 9); 126 (s, 7); 129 (s, 2); 131 (s, 1); 132 (s, 3); 135 (d, ¹J_{CP} = 80.5 Hz, 4); 136 (s, 8); 149 (s, 10); 154 (s, 6). ³¹P NMR (202.46 MHz): δ 43.9 (s). EI-MS (70 eV): *m/z* (%) 309 (42) [M]⁺, 276 (30) [M – S]⁺, 217 (78) [M – (CH₂Py)]⁺, 200 (38) [M – S – Ph]⁺, 183 (80) [PPh₂]⁺, 169 (100) [Ph(CH₂Py)]⁺, 217 (78) [M – (CH₂Py) – Ph]⁺. Anal. Found (calcd): C, 69.4 (69.88); H, 5.3 (5.21); N, 4.5 (4.53).

Ph₂P(Se)(CH₂Py) (2). 5.00 g (18.0 mmol) of Ph₂P(CH₂Py)²⁶ and 2.13 g (27.0 mmol) of gray selenium in 100 mL of toluene were refluxed for 4 h. After the mixture was cooled to room temperature and filtered over Celite, the solvent was removed under vacuum. Washing with diethyl ether gave the product as a yellow solid. After storage of a saturated solution in THF at room temperature for 10 days, pale yellow crystals suitable for X-ray structure analysis were obtained. Yield: 5.46 g, 15.3 mmol, 85%. Mp: 125–126 °C. ¹H NMR (500.13 MHz): δ 4.30 (d, 2H, ²J_{PH} = 14.5 Hz, 5); 7.03–7.08 (m, 1H, 9); 7.48–7.52 (m, 6H, 1, 2); 7.52–7.55 (m, 2H, 7, 8); 7.95–8.01 (m, 4H, 3); 8.27–8.29 (m, 1H, 10). ¹³C NMR (125.76 MHz): δ 43.7 (d, ¹J_{CP} = 43.1 Hz, 5); 122 (s, 9); 126 (s, 7); 128 (s, 2); 132 (s, 1); 133 (s, 3); 134 (s, 4); 136 (s, 8); 150 (s, 10); 154 (s, 6). ³¹P NMR (202.46 MHz): δ 36.6 (s). ⁷⁷Se NMR (95.38 MHz): δ –337 (d, ¹J_{SeP} = 756 Hz). EI-MS (70 eV): *m/z* (%) 357 (100) [M]⁺, 277 (30) [M – Se]⁺, 265 (78) [M – (CH₂Py)]⁺, 200 (66) [M – Se – Ph]⁺, 183 (80) [PPh₂]⁺, 169 (100) [Ph(CH₂Py)]⁺. Anal. Found (calcd): C, 60.3 (60.68); H, 4.4 (4.53); N, 3.9 (3.93).

[(thf)₂Ca{(PyCH)(Se)PPh₂}₂] (3). A 0.71 g portion (1.41 mmol) of [(thf)₂Ca{N(SiMe₃)₂}₂]²¹ was added to a solution of 1.00 g (2.81 mmol) of **2** in 40 mL of THF, and the mixture was stirred at room temperature for 18 h. After removal of all volatile components crystallization from THF gave the product as yellow blocks suitable for X-ray structure analysis. Yield: 1.08 g, 1.21 mmol, 81%. ¹H NMR (500.13 MHz): δ 3.19 (d, 1H, ²J_{PH} = 20.1 Hz, 5); 5.64 (dd, 1H, ³J_{HH} = 6.5, 7.6 Hz, 9); 6.42 (d, 1H, ³J_{HH} = 8.2 Hz, 7); 6.78 (dd, 1H, ³J_{HH} = 7.6, 8.2 Hz, 8), 7.24–7.32 (m, 6H, 1, 2); 7.46–7.55 (m, 1H, 10); 7.83–7.91 (m, 4H, 3). ¹³C NMR (125.76 MHz): δ 54.1 (d, ¹J_{CP} = 109 Hz, 5); 108 (s, 9); 120 (s, 7); 128 (s, 2); 130 (s, 1); 133 (s, 3); 134 (s, 8); 139 (d, ¹J_{CP} = 109 Hz, 4); 148 (s, 10); 167 (s, 6). ³¹P NMR (202.46 MHz): δ 14.3 (s). ⁷⁷Se NMR (95.38 MHz): δ –106 (d, ¹J_{SeP} = 550 Hz). Anal. Found (calcd): C, 56.7 (58.93); H, 5.3 (5.39); N, 2.9 (3.12).

Crystallographic Data. All data were measured at 100 K with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) from oil-coated shock-cooled crystals.²⁷ Data for **1** were collected on a Stoe IPDS II diffractometer with an image plate detector. Cell determination, cell refinement, and integration of the data were performed with the X-AREA program package.²⁸ Data for **2** and **3** were collected on a Bruker D8 diffractometer with an APEX2 detector. Cell determinations and cell refinements were performed

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with the APEX 2 software v2.1-0.²⁹ The data were integrated with SAINT V7.23A and corrected for absorption with SADABS-2004/1 (2) res. SADABS-2007/5 (3). All structures were solved by direct methods using SHELXS 97 and were refined by full-matrix least-squares procedures on F^2 using SHELXL-97.³⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were refined using standard distance and orientation restraints and riding model constraints. The only exception was the crucial hydrogen atom H13 in **3**, which was refined by employing only the riding model constraint. The X-ray crystallographic data, bond lengths, angles, atom coordinates, and thermal parameters are given in

additional CIF files which have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are given in Table 1.

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Supporting Information Available: CIF files and tables and figures giving further refinement details, crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of all structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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