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Title: Phosphorus-Chalcogen Ring Expansion and Metal Coordination

Year: 2017

Version:

Please cite the original version:

Graham, C. M. E., Valjus, J., Pritchard, T. E., Boyle, P. D., Tuononen, H., & Ragogna, P. J. (2017). Phosphorus-Chalcogen Ring Expansion and Metal Coordination. *Inorganic Chemistry*, 56(21), 13500-13509. <https://doi.org/10.1021/acs.inorgchem.7b02217>

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Phosphorus-chalcogen ring expansion and metal coordination

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Keywords: Main-Group Chemistry, Inorganic Rings, Phosphorus-Chalcogen Rings,
Coordination Chemistry, Coinage Metals, Ring-Expansion

Abstract

The reactivity of 4-membered (RPCh)₂ rings (Ch = S, Se) that contain phosphorus in the +3 oxidation state is reported. These compounds undergo ring expansion to (RPCh)₃ with the addition of a Lewis base. The 6-membered rings were found to be more stable than the 4-membered precursors, and the mechanism of their formation was investigated experimentally and by density functional theory calculations. The computational work identified two plausible mechanisms involving a phosphinidene chalcogenide intermediate, either as a free species or stabilized by a suitable base. Both the 4- and 6-membered rings were found to react with coinage metals, giving the same products: (RPCh)₃ rings bound to the metal centre from the phosphorus atom in tripodal fashion.

Introduction

Small inorganic ring systems have been of interest to chemists for decades as they normally offer a window into unique structure, bonding, and reactivity.¹⁻⁴ A comprehensive review regarding the breadth of these compounds was recently published by Rivard and coworkers.⁵ Inorganic rings containing phosphorus-p-block element cores have been extensively explored and reported in the literature. Of this large collection of phosphorus-containing main group rings, phosphorus-chalcogen (P-Ch) heterocycles have been a particular focus area because of their widespread application as ligands for transition metals,^{6,7} and “P” or “Ch” transfer reagents.⁸ Major developments in P-Ch heterocyclic chemistry feature P(V) compounds, with noteworthy examples being Lawesson’s (Ch = S)⁹ and Woollins’ (Ch = Se)¹⁰ reagents (Figure 1, **A**) that contain P₂Ch₂ rings with each phosphorus further oxidized by an additional sulfur or selenium atom, respectively.¹¹⁻¹³ These have proven to be indispensable reagents in a variety of synthetic transformations¹⁴⁻¹⁸ and material applications.^{19,20} While there have been extensive studies on P(V)-Ch derivatives, examples of P(III) within the ring core are more uncommon, especially in regards to those with a general formula (RPCh)_n. Examples of (RPCh)_n have been reported for n = 2, 3, and 4, where bulky R groups are required to kinetically stabilize the P(III) centre (Figure 1, **B-D**).²¹⁻²⁶ In particular, our group has recently reported the syntheses of strained (RPCh)₂ rings **1Ch** (Ch = S, Se) with P in the +3 oxidation state, the first representatives of these strained compounds, by installing *m*-terphenyl substituents at phosphorus.²⁴

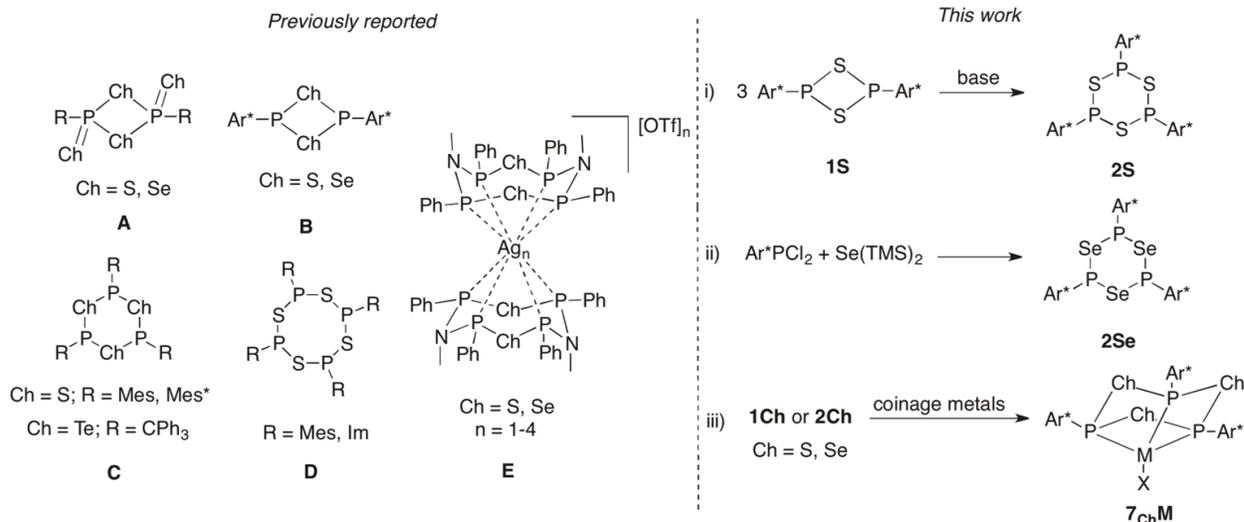


Figure 1. Left: Previously reported phosphorus-chalcogen rings, Woollins' and Lawesson's reagents with P(V) (**A**), (RPCh)_n with P(III) (**B-D**), and polynuclear Ag sandwich complex (**E**). Right: i) Synthesis of **2S** via base-induced ring expansion, ii) Synthesis of **2Se** by cyclocondensation of Ar*PCl₂ and Se(TMS)₂, iii) Ring expansion and/or metal coordination to coinage metals. Ar* = 2,6-Mes₂C₆H₃, Mes = 2,4,6-(CH₃)₃C₆H₂, Mes* = 2,4,6-(*t*Bu)₃C₆H₂, Im = imidazolium-2-yl.

Although select examples of (RPCh)_n have been reported since the early 1980's, a thorough examination of their chemistry has not been published, though related P(III)-Ch-N macrocycles have been reported to form polynuclear Ag(I) sandwich complexes upon reaction with various amounts of AgOTf (Figure 1, **E**).⁷ In this context, we report herein on the chemistry of **1Ch** and the possibility to use them to access larger (RPCh)₃ rings **2Ch** (Ch = S, Se). Although consistent reactivity between **1S** and **1Se** is not observed, identical derivatives can still be prepared using different synthetic approaches. In particular, the reaction of **1S** with Lewis bases gives **2S**, whereas the selenium analogue **2Se** can be synthesised and isolated via cyclocondensation of Ar*PCl₂ and Se(TMS)₂. We have also discovered that by introducing coinage-metals Cu and Ag to **1Ch**, ring expansion products (RPCh)₃ are observed for both chalcogens. The rings were found to be further bound to the employed metal cation in a tripodal fashion through phosphorus,

giving coordination complexes 7ChM (Ch = S, Se; M = Cu, Ag); the same coordination complexes can also be prepared directly from 2Ch .

Experimental Methods

All manipulations were performed under an inert atmosphere either in a nitrogen-filled MBraun Labmaster 130 glovebox or on a Schlenk line. HNEt_2 was purchased from Sigma Aldrich and distilled from KOH. PCl_3 was purchased from Sigma Aldrich and distilled/degassed prior to use. Gaseous HCl was prepared *in situ* by dropping neat H_2SO_4 to CaCl_2 powder, bubbled through H_2SO_4 then through the reaction mixture and ultimately through a NaHCO_3 outlet bubbler to neutralize excess HCl. $\text{Ch}(\text{TMS})_2$ (Ch = S, Se)²⁷ and Ar^*PCl_2 ²⁸⁻³¹ were made following known literature procedures. CuCl , AgOTf , $(\text{Me}_2\text{S})\text{AuCl}$, and DMAP were purchased from Sigma Aldrich and used as received. 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 activated 4 Å molecular sieves. Solvents for NMR spectroscopy (CDCl_3 and C_6D_6) were stored in the drybox over activated 4 Å molecular sieves. Nuclear Magnetic Resonance (NMR) spectroscopy was recorded on Varian INOVA 400 MHz (^1H 400.09 MHz, $^{31}\text{P}\{^1\text{H}\}$ 161.8 MHz) or 600 MHz ($^{13}\text{C}\{^1\text{H}\}$ 150.8 MHz) spectrometers. All samples for ^1H NMR spectroscopy were referenced to the residual protons in the deuterated solvent relative to tetramethylsilane (CDCl_3 ; $\delta = 7.26$, C_6D_6 ; $\delta = 7.16$). The chemical shifts for $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy were referenced using an external standard (85 % H_3PO_4 ; $\delta = 0.0$). FT-IR spectroscopy was performed on samples as KBr pellets using a Bruker Tensor 27 FT-IR spectrometer with 4 cm^{-1} resolution. Mass spectrometry was recorded in positive- and negative-ion modes using an electrospray ionization Micromass LCT spectrometer. Melting or

decomposition points were determined by flame-sealing samples in capillaries and heating using a Gallenkamp variable heater. Elemental analyses were performed at the University of Montreal and are reported as an average of two samples weighed under air and combusted immediately thereafter. Multiple samples of spectroscopically pure **2S** were sent away for elemental analysis, however we could not obtain chemically sensible data. For this case, we have omitted EA data for this compound.

Note: Metal-coordination reactions were prepared with strict exclusion from ambient light as compounds **7ChM** and **8Ch** are light-sensitive. **7ChM** and **8Ch** decomposed when left in solution overnight at room temperature or in the solid-state at room temperature for more than 2 days. These challenges precluded obtaining accurate elemental analyses and quaternary carbons in the corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR spectra could not be identified. In the case of **8Ch**, multiple samples were prepared for mass spectroscopic characterization, including the use of different ionization methods, however we could not obtain chemically sensible data.

Synthesis of **2S**

Solid 4-dimethylaminopyridine (6.5 mg, 0.053 mmol) was added to a solution of **1S** (20 mg, 0.027 mmol, 2 mL THF) and the mixture was heated for 16 hours at 50 °C. The volatiles were removed *in vacuo* and the yellow powder was dissolved in 1 mL DCM and slowly concentrated leading to single crystals of **2S** (yield: 13 mg, 70 %). Alternatively, the reaction mixture could be heated at 35 °C for 7 days, which resulted in increased yields (>90 %). **mp**: 210-211 °C. ^1H NMR (C_6D_6 , 400 MHz, δ): 2.02 (s, 36 H, Mesityl *o*-CH₃), 2.27 (s, 18 H, Mesityl *p*-CH₃), 6.77 (d, 6 H, $^3J_{\text{H-H}} = 7.4$ Hz, Aromatic C-H), 6.83 (br s, 12 H, Mesityl C-H), 7.02 (t, 3 H, $^3J_{\text{H-H}} = 7.4$ Hz, Aromatic C-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 161.8 MHz, δ): 96.7 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.8

MHz, δ): 21.5, 21.8, 29.9, 130.1, 130.7, 133.6, 136.9, 137.8, 146.4. **EI-MS**: 1151.4 m/z , $C_{72}H_{75}P_3S_3Na$ $[M + Na]^+$. **FT-IR** (cm^{-1} (ranked relative intensities), KBr): 625 (11), 732 (4), 750 (14), 807 (1), 845 (8), 906 (6), 1016 (5), 1216 (7), 1261 (13), 1374 (12), 1445 (2), 1559 (9), 1610 (10), 1643 (15), 2915 (3).

Synthesis of 2Se

A solution of $Se(TMS)_2$ (264 mg, 1.17 mmol, 10 mL THF) was added to a solution of Ar^*PCl_2 (487 mg, 1.17 mmol, 20 mL THF) portionwise over 3 hours. The volatiles were removed *in vacuo*, leading to an orange oil. The oil was washed with pentane (3 x 10 mL) and insoluble **1Se** was filtered and collected (yield: 348 mg, 86 %). The pentane fractions were combined, concentrated *in vacuo*, and 1 mL DCM was added to the oil, which resulted in the precipitation of a yellow powder when left at $-35\text{ }^\circ C$ for 2 hours. X-ray quality single crystals of **2Se** were grown *via* vapour diffusion using DCM/Toluene (yield: 49 mg, 10 %). **mp**: decomposes at $215\text{ }^\circ C$ (turns dark brown). **1H NMR** (C_6D_6 , 600 MHz, δ): 2.08 (s, 36 H, Mesityl *o*- CH_3), 2.30 (s, 18 H, Mesityl *p*- CH_3), 6.78 (d, 6 H, $^3J_{H-H} = 7.5$ Hz, Aromatic C-H), 6.84 (br s, 12 H, Mesityl C-H), 7.03 (t, 3 H, $^3J_{H-H} = 7.5$ Hz, Aromatic C-H). **$^{31}P\{^1H\}$ NMR** (C_6D_6 , 161.8 MHz, δ): 87.8 (s, $^1J_{P-Se} = 136.6$ Hz). **$^{13}C\{^1H\}$ NMR** (C_6D_6 , 150.8 MHz, δ): 21.6, 21.8, 128.3, 130.1, 130.3, 137.0, 138.0, 146.0. **^{77}Se NMR** (C_6D_6 , 114.4 MHz, δ): 421.0 (ddd, $^1J_{Se-P} = 202.6$, 133.3 Hz, $^3J_{Se-P} = 67.1$ Hz). **EI-MS**: 1271.3 m/z , $C_{72}H_{75}P_3Se_3$ $[M^+]$. **FT-IR** (cm^{-1} (ranked relative intensities), KBr): 85 (4), 159 (15), 236 (12), 321 (9), 391 (7), 414 (13), 576 (3), 738 (11), 1035 (6), 1302 (2), 1381 (8), 1576 (10), 1611 (5), 2915 (1), 3037 (14). **Elemental Analysis**: Calculated 68.08 % C, 5.95 % H; Experimental 67.60 % C, 6.48 % H.

General Methods for Coordination Chemistry with Coinage Metals

A solution of **1Ch** in DCM was added to a suspension of MX in DCM and the mixture let stir at room temperature for 1 hour. The volatiles were removed *in vacuo* and the crude powder was washed with diethyl ether (3 x 5 mL), giving an insoluble powder that was collected.

Synthesis of **7sCu**

Reagents: **1S** (75 mg, 0.097 mmol, 4 mL DCM) and CuCl (6.0 mg, 0.067 mmol, 4 mL DCM); yield: 55 mg, 61 %. Single crystals were grown *via* vapour diffusion using DCM/pentane. **mp**: decomposes at 131 °C (turns brown). **¹H NMR** (CDCl₃, 600 MHz, δ): 1.80 (s, 36 H, Mesityl *o*-CH₃), 2.24 (s, 18 H, Mesityl *p*-CH₃), 6.81 (br s, 12 H, Mesityl C-H), 6.90 (d, 6 H, ³*J*_{H-H} = 7.8 Hz, Aromatic C-H), 7.43 (t, 3 H, ³*J*_{H-H} = 7.8 Hz, Aromatic C-H). **³¹P{¹H} NMR** (CDCl₃, 161.8 MHz, δ): 88.6 (s). **¹³C{¹H} NMR** (CDCl₃, 150.8 MHz, δ): 21.4, 21.6, 129.1, 130.8, 131.8, 136.3, 137.5, 146.0. **EI-MS**: 1191.4 *m/z*, C₇₂H₇₅P₃S₃Cu [M - Cl]⁺. **FT-IR** (cm⁻¹ (ranked relative intensities), KBr): 733(4), 749 (12), 809 (7), 845 (6), 907 (5), 1030 (10), 1374 (8), 1448 (2), 1480 (14), 1562 (9), 1611 (3), 2853 (13), 2915 (1), 2944 (15), 2968 (11).

Synthesis of **7sAg**

Reagents: **1S** (75 mg, 0.097 mmol, 4 mL DCM) and AgOTf (16 mg, 0.065 mmol, 4 mL DCM); yield: 45 mg, 50 %. Single crystals were grown *via* vapour diffusion using DCM/pentane. **mp**: decomposes at 141 °C (turns dark grey). **¹H NMR** (CDCl₃, 400 MHz, δ): 1.82 (s, 36 H, Mesityl *o*-CH₃), 2.25 (s, 18 H, Mesityl *p*-CH₃), 6.87 (br s, 12 H, Mesityl C-H), 6.97 (d, 6 H, ³*J*_{H-H} = 7.6 Hz, Aromatic C-H), 7.53 (t, 3 H, ³*J*_{H-H} = 7.6 Hz, Aromatic C-H). **³¹P{¹H} NMR** (CDCl₃, 161.8 MHz, δ): 109.0 (br s). **¹³C{¹H} NMR** (CDCl₃, 150.8 MHz, δ): 21.2, 21.5, 128.8, 131.1, 132.8,

136.6, 138.6, 146.2. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376.3 MHz, δ): -77.4 (s). **EI-MS**: 1237.3 m/z , $\text{C}_{72}\text{H}_{75}\text{P}_3\text{S}_3\text{Ag}$ $[\text{M} - \text{OTf}]^+$. **FT-IR** (cm^{-1} (ranked relative intensities), KBr): 635 (9), 749 (13), 807 (11), 852 (7), 1027 (4), 1113 (14), 1162 (10), 1182 (15), 1232 (2), 1305 (8), 1377 (6), 1449 (3), 1563 (12), 1610 (5), 2918 (1).

Synthesis of 7SeCu

Reagents: **1Se** (40 mg, 0.047 mmol, 5 mL DCM) and CuCl (3.0 mg, 0.032 mmol, 5 mL DCM). ^{31}P NMR spectra of crude reaction mixture showed formation of 7SeCu ($\delta_{\text{P}} = 72$) and free **2Se** ($\delta_{\text{P}} = 88$). Attempts to separate **2Se** and 7SeCu by fractional crystallization were unsuccessful. Attempts to convert **2Se** to 7SeCu resulted in multiple products in the ^{31}P NMR spectrum, including **8Se** (Figure S-3).

Synthesis of 7SeAg

Reagents: **1Se** (50 mg, 0.039 mmol, 4 mL DCM) and AgOTf (6.7 mg, 0.026 mmol, 4 mL DCM); yield: 27 mg, 69 %. Single crystals were grown *via* vapour diffusion using DCM/pentane. **mp**: decomposes at 171 °C (turns dark grey). ^1H NMR (CDCl_3 , 400 MHz, δ): 1.92 (s, 36 H, Mesityl *o*- CH_3), 2.27 (s, 18 H, Mesityl *p*- CH_3), 7.03 (d, 6 H, $^3J_{\text{H-H}} = 7.6$ Hz, Aromatic C-H), 7.15 (s, 12 H, Mesityl C-H), 7.63 (t, 3 H, $^3J_{\text{H-H}} = 7.6$ Hz, Aromatic C-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 161.8 MHz, δ): 113.3 (d, $^1J_{\text{Ag-P}} = 213.2$ Hz, $^1J_{\text{Ag-P}} = 185.8$ Hz, $^1J_{\text{Se-P}} = 151.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150.8 MHz, δ): 20.9, 21.4, 129.7, 131.3, 133.7, 135.1, 136.8, 140.5, 146.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376.3 MHz, δ): -76.4 (s). **EI-MS**: 1379.2 m/z , $\text{C}_{72}\text{H}_{75}\text{P}_3\text{Se}_3\text{Ag}$ $[\text{M} - \text{OTf}]^+$. **FT-IR** (cm^{-1} (ranked relative intensities), KBr): 634 (3), 731 (5), 807 (8), 854 (6), 910 (13), 1024 (1), 1164 (10), 1213 (15), 1231 (2), 1303 (12), 1378 (11), 1448 (4), 1562 (14), 1608 (9), 2917 (7).

Synthesis of 8S

Reagents: **1S** (25 mg, 0.033 mmol, 5 mL DCM) and CuCl (4.3 mg, 0.043 mmol, 5 mL DCM).
yield: 12 mg, 61 %. Single crystals were grown *via* vapour diffusion using DCM/pentane. **mp**:
decomposes at 119 °C (turns brown). **¹H NMR** (CDCl₃, 400 MHz, δ): 1.92 (s, 36 H, Mesityl *o*-
CH₃), 2.12 (s, 18 H, Mesityl *p*-CH₃), 6.78 (br s, 12 H, Mesityl C-H), 6.88 (d, 6 H, ³*J*_{H-H} = 6.4 Hz,
Aromatic C-H), 7.46 (t, 3 H, ³*J*_{H-H} = 6.4 Hz, Aromatic C-H). **³¹P{¹H} NMR** (CDCl₃, 161.8 MHz,
δ): 61.3 (s). **¹³C{¹H} NMR** (CDCl₃, 150.8 MHz, δ): 21.4, 22.2, 130.1, 130.8, 131.7, 132.1, 137.0,
146.7. **FT-IR** (cm⁻¹ (ranked relative intensities), KBr): 728 (3), 748 (12), 807 (5), 850 (2), 908
(6), 1031 (7), 1113 (13), 1182 (11), 1377 (9), 1443 (1), 1561 (10), 1609 (8), 2854 (14), 2914 (4),
2946 (15).

Synthesis of 8Se

Reagents: **1Se** (50 mg, 0.0590 mmol, 7 mL DCM) and CuCl (7.8 mg, 0.0788 mmol, 7 mL
DCM); yield: 32.6 mg, 80 %. Single crystals were grown *via* vapour diffusion using
DCM/pentane. **mp**: decomposes at 160 °C (turns black). **¹H NMR** (CDCl₃, 400 MHz, δ): 1.94 (s,
36 H, Mesityl *o*-CH₃), 2.24 (s, 18 H, Mesityl *p*-CH₃), 6.82 (br s, 12 H, Mesityl C-H), 6.86 (d, 6
H, ³*J*_{H-H} = 7.6 Hz, Aromatic C-H), 7.45 (t, 3 H, ³*J*_{H-H} = 7.6 Hz, Aromatic C-H). **³¹P{¹H} NMR**
(CDCl₃, 161.8 MHz, δ): 45.9 (br s). **¹³C{¹H} NMR** (CDCl₃, 150.8 MHz, δ): 21.5, 22.0, 130.0,
130.8, 131.7, 132.0, 135.8, 136.9, 138.9, 146.5. **FT-IR** (cm⁻¹ (ranked relative intensities), KBr):
719 (15), 748 (5), 807 (1), 846 (6), 1030 (2), 1090 (14), 1110 (10), 1183 (12), 1263 (7), 1376 (9),
1445 (3), 1562 (11), 1610 (8), 1720 (13), 2964 (4).

Results and Discussion

Formation of P/Ch heterocycles

The synthesis of **1Ch** resulted from the cyclocondensation of Ar^*PCl_2 with $\text{Ch}(\text{TMS})_2$ (Figure 2). Although the sulfur chemistry proceeds cleanly, multiple products are present in the crude reaction mixture for $\text{Ch} = \text{Se}$. The major product **1Se** ($\delta_{\text{P}} = 23$) could be isolated by washing the crude reaction mixture with pentane, yielding an orange powder. A minor product from this reaction was isolated by precipitating out a yellow powder from a DCM solution at $-35\text{ }^\circ\text{C}$ ($\delta_{\text{P}} = 88$). Slowly concentrating a DCM solution resulted in single crystals suitable for X-ray diffraction that confirmed the preparation of **2Se**. Although numerous examples of $(\text{RPS})_3$ are known, **2Se** represents the first selenium derivative, and is one of the few known examples of heavier chalcogens in such a ring system.²³

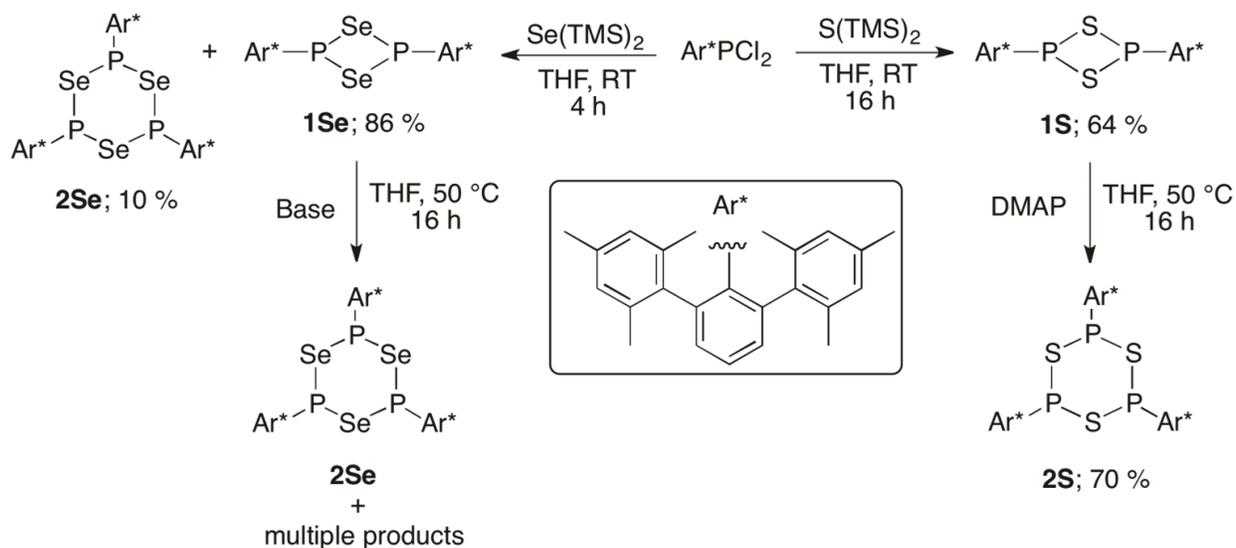


Figure 2. Cyclocondensation of Ar^*PCl_2 with $\text{Ch}(\text{TMS})_2$ yielding **1S** (right), **1Se**, and **2Se** (left). While base induced ring expansion yields **2S** from **1S** in high yield, the addition of a base to **1Se** results in multiple products, including **2Se**.

After successfully isolating **1Ch**, we endeavoured to utilize these strained compounds as precursors to the monomeric R-P=Ch, which have been elusive intermediates in low valent phosphorus-chalcogen chemistry. In our initial work (Figure 3, top), **1Ch** could be monomerized by gentle heating, giving solution accessible R-P=Ch that could be trapped using 2,3-dimethyl-1,3-butadiene (dmbd) to give **4Ch**. Alternatively, monomerization of **1S** could be induced through the addition of 1,3-isopropyl-4,5-dimethylimidazol-2-ylidene (NHC), which resulted in the formation of the adduct **5S** even without heating.²⁴ Taking our lead from these results, the reaction of DMAP with **1S** in 2:1 stoichiometry yielded one major product in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{P}} = 97$, an upfield shift from the parent **1S** ($\delta_{\text{P}} = 127$), and significantly downfield shifted from **5S** ($\delta_{\text{P}} = 28$). Slowly concentrating a DCM solution at $-35\text{ }^{\circ}\text{C}$ resulted in pale-yellow single crystals. Single crystal X-ray diffraction experiments revealed that the product is not a simple DMAP adduct of **1S** but instead the 6-membered ring expansion species **2S**, analogous to **2Se**. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained from solutions containing redissolved crystals of **2S** showed the same distinct singlet ($\delta_{\text{P}} = 97$) observed in the crude reaction mixture, while the ^1H NMR spectra showed a single set of terphenyl protons, indicating equivalence of aromatic substituents on the NMR timescale.

Although the ring expansion product was the only species obtained from the reaction between **1S** and DMAP, the analogous reaction using **1Se** gave numerous products, as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Even though none of these products could be isolated and characterized, the NMR spectroscopic data clearly indicated that ring expansion to **2Se** did occur ($\delta_{\text{P}} = 88$). Other structurally related Lewis bases such as pyridine and 2,6-lutidine also generated **2Se**, but again with multiple other side products (Figure S-1). Alternatively to nitrogen bases, phosphine-based donors (PEt_3 , PCy_3 , and PPh_3) produced multiple products as determined by

$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Interestingly, there was no evidence for a ring expansion product **2Se**, however evidence for the corresponding phosphine-selenides were present in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra ($\text{Se}=\text{PR}_3$; Figure S-2), indicative of a competing process upon addition of alkyl/aryl phosphines.

Taking all of the above into account, a possible mechanism for the formation of **2Ch** can be envisioned (Figure 3, bottom). The reaction most likely begins by breaking up of **1Ch** that is induced either by the employed base (*cf.* formation of **5S**) or simply by heating (*cf.* formation of **4Ch**). In the presence of excess DMAP, the initial product should in both cases be the adduct **6Ch** that could subsequently undergo insertion into **1Ch**, leading to dissociation of DMAP and formation of **2Ch** (Figure 3, bottom). This mechanism is experimentally supported by the appearance of free DMAP in the crude reaction mixture once **1S** is fully consumed. Furthermore, heating samples of **1S** without DMAP does not lead to the formation of **2S**. However, as **2Se** is formed even during the synthesis of **1Se**, the potential energy surface for the formation of **2Ch** is obviously not completely independent of the chalcogen atom.

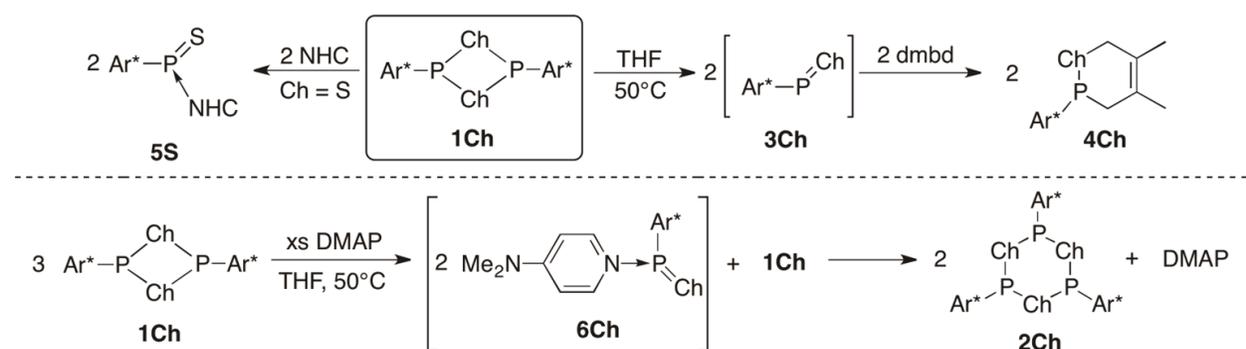


Figure 3. Top: Using **1Ch** as sources of monomeric phosphinidene chalcogenides, trapping **3Ch** with dmbd (**4Ch**, dmbd = 2,3-dimethyl-1,3-butadiene) or by addition of an NHC (**5S**, NHC = 1,3-isopropyl-4,5-dimethylimidazol-2-ylidene). Bottom: Proposed reaction pathway for ring expansion of **1Ch** induced by DMAP/heating and proceeding through the suggested intermediate **6Ch**.

The reaction pathway for forming **2S** was examined using density functional theory at the PBE1PBE/TZVP level of theory augmented with an empirical dispersion correction. The calculations show that DMAP does not monomerize **1S** as efficiently as was observed earlier in the case of an N-heterocyclic carbene. However, the calculated activation barrier for the formation of two stoichiometric equivalents of **6S** (95 kJ mol⁻¹) is in any case considerably lower than that found for the direct, heat induced, monomerization of **1S** to two equivalents of **3S** (124 kJ mol⁻¹).³² Furthermore, while the formation of **3S** is highly endergonic (118 kJ mol⁻¹), the base-assisted monomerization of **1S** to two equivalents of **6S** is only slightly so (44 kJ mol⁻¹). This shows that DMAP efficiently stabilizes the R-P=S unit, as expected, but does it so that further reactivity of the monomer is not hindered. This is in contrast to what was observed for the NHC adduct **5S**, the formation of which was calculated to be exergonic by as much as 106 kJ mol⁻¹.

Having established the possible role of DMAP in stabilizing the transient R-P=S monomer, we turned our attention to the formation of **2S**. Many different mechanisms can be envisioned for this process, but the most likely one is a direct reaction between **1S** and **6S**. Computational work showed that the lowest energy pathway on this particular potential energy surface involves the break-up of one P-S bond in **1S** to give **1S-b** that then binds **6S** and forms a 6-membered acyclic intermediate **Int1** (Figure 4). This reaction is almost energy neutral and proceeds through a transition state that is comparable in energy (**TS1**, 103 kJ mol⁻¹) to that found for the formation of **6S**. The intermediate **Int1** can subsequently close in on itself (**TS2**, 75 kJ mol⁻¹), dissociating the coordinated DMAP and forming **2S**. The calculations showed that **2S** can adopt several conformers that are interconnected *via* low-energy transition states, with the experimentally observed chair conformer of **2S** as the global energy minimum. In total, a reaction energy of -127 kJ mol⁻¹ were obtained for the overall transformation of three equivalents of **1S** to two

equivalents of **2S**, which confirms that the 6-membered rings are more stable than their 4-membered precursors.

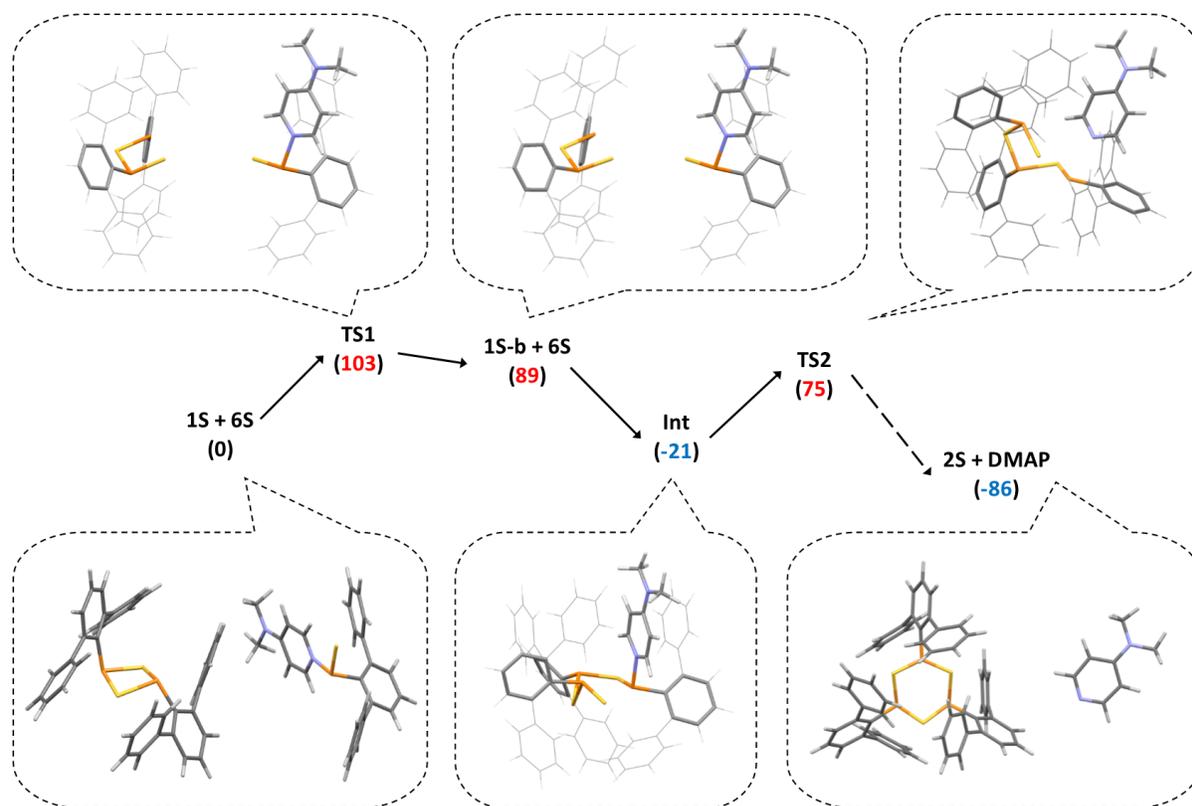


Figure 4. Reaction coordinate diagram for DMAP-induced (RPS)_n ring expansion (phosphorus atoms are coloured orange, sulfur being yellow, and nitrogen blue). For simplicity, interconversion of different conformers of **2S** is omitted (dashed arrow). Gibbs energies are reported in kJ mol⁻¹ and relative to **1S + 6S**.

As **2Se** was found to form even during the synthesis of **1Se**, there must also be a base-free mechanism for the formation of **2Ch**. To allow comparison to extant data, we examined this possibility for **2S** with computational methods. The results show that **3S**, being a highly reactive species, binds very easily to **1S** *via* formation of two P-S interactions. This gives a stable intermediate **Int2** that is 33 kJ mol⁻¹ lower in energy compared to free **3S** and **1S**. The intermediate **Int2** can subsequently form **2S** *via* simple rearrangement of its P-S bonds (**TS3**, 57

kJ mol^{-1}). Even though all of these transformations involve only low-energy transition states, such pathway is not feasible in practice due to the instability of the monomer **3S**, in particular with respect to the dimer **1S**; the conversion of two equivalents of **3S** to **1S** has a calculated barrier of only 6 kJ mol^{-1} . Thus, simply heating **1Ch** is unlikely to lead to the formation of significant amounts of **2Ch**. However, as the synthesis of **1Ch** proceeds *via* **3Ch**, it is possible that some **2Ch** forms during the process, as observed experimentally for $\text{Ch} = \text{Se}$.

Reactivity of P/Ch heterocycles with Coinage Metals

Both **1Ch** and **2Ch** have a lone pair of electrons on each phosphorus, leaving a functional group for onwards reactivity, especially metal coordination. Our initial approach was to explore their reactivity as ligands to transition metals, firstly with Group 16 metal carbonyls ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). However, no reaction occurred upon reaction of the $(\text{M}(\text{CO})_5\text{THF})$ precursor to either **1Ch/2Ch**, even after prolonged reaction times and varying reaction conditions. We hypothesised that the steric demand imposed by the *m*-terphenyl ligands prevented coordination. We then turned to the coinage metals ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) because of their linear coordination modes and affinity for soft, phosphine donors (Figure 5).

The addition of **1Ch** to a metal salt (CuCl or AgOTf) in 3:2 stoichiometry at room temperature showed single resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra ($\text{Ch} = \text{S}$: $\text{Cu } \delta_{\text{P}} = 89$, $\text{Ag } \delta_{\text{P}} = 109$; $\text{Ch} = \text{Se}$: $\text{Ag } \delta_{\text{P}} = 113$; Figures 6 and 7). Slow layering of pentane onto a DCM solution resulted in single crystals suitable for X-ray diffraction, which confirmed the structures to be ring-expansion products from the parent **1Ch**, with the metal being bound to the phosphorus atoms in tripodal fashion (**7ChM**). The mechanism of this transformation was not examined computationally, but it can be easily envisaged that the coordination of a metal fragment to **1Ch** leads to weakening of

P-S bonds, which provides a pathway for the formation of **3Ch** stabilized by the coordinated metal centre.

Although the addition of **1Ch** with MX proceeds cleanly for **7sM** and **7seAg**, the addition of **1Se** to CuCl resulted in multiple products. However, a major product at $\delta_P = 72$, which has been hypothesized to be **7seCu** based on the similarity of the shift to **7sCu**, and a minor product at $\delta_P = 88$ (**2Se**), with a relative integration of 60:40, were dominant (Figure 7). The addition of more CuCl to the crude reaction mixture in an attempt to convert **2Se** to **7seCu** did not proceed cleanly but resulted in multiple phosphorus containing products (Figure S-3). Attempts to use a different Cu^+ source $\text{CuOTf}[\text{MeCN}]_4$ yielded similar results as reactions performed with CuCl. As an alternative to the coinage metal induced ring expansion of **1Ch**, the parent 6-membered rings **2Ch** could be reacted directly with the metal species (CuCl, AgOTf) in 1:1 stoichiometry to yield **7ChM** that were isolated in yields comparable to those obtained for reactions performed with **1Ch**. Similar to the reactions with Cu and Ag, the low temperature addition of **1S** to Me_2SAuCl resulted in one major product ($\delta_P = 82$). Leaving a solution state sample at $-35\text{ }^\circ\text{C}$ for overnight in an attempt to grow single crystals resulted in numerous phosphorus-containing products (Figure S-4) and repeated attempts to isolate the observed major product were met only with evidence for decomposition.

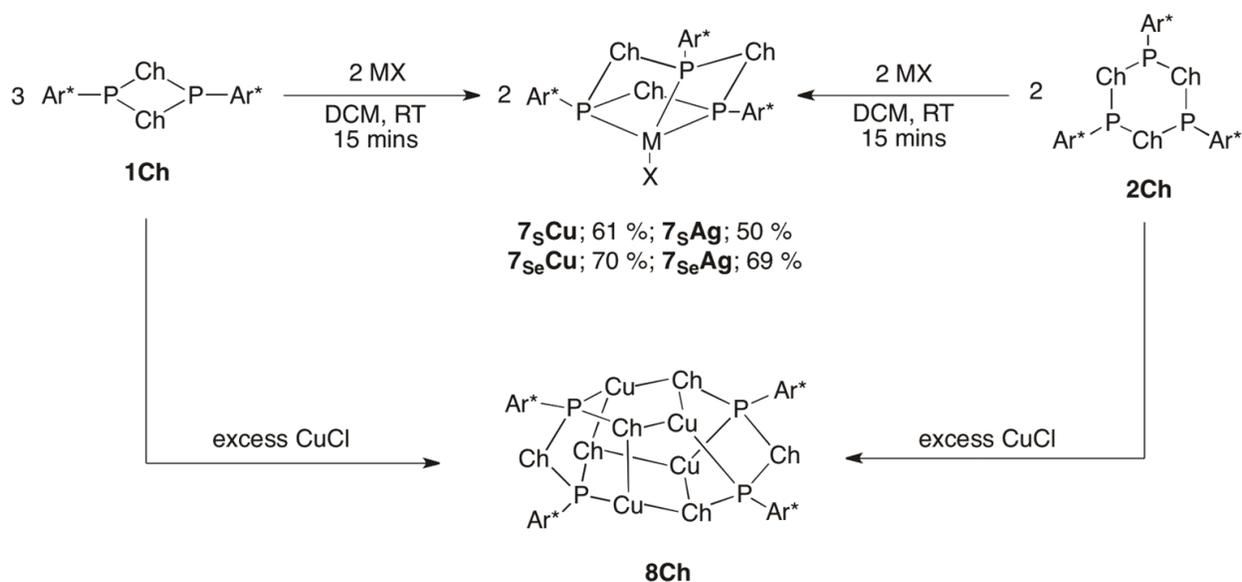


Figure 5. Ring expansion of **1Ch** (Ch = S, Se) using coinage metals (MX = CuCl, AgOTf) resulting in **7ChM**. Similar products were obtained from the addition of **2Ch** to MX. Addition of excess CuCl to either **1Ch** or **2Ch** resulted in the formation of **8Ch**.

Compounds **7sM** contain a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure 6) as well as one set of terphenyl signals in the ^1H NMR spectrum, indicating 3-fold symmetry amongst the 6-membered ring in solution. The $^{19}\text{F}\{^1\text{H}\}$ NMR of **7ChAg** contained singlets with the chemical shifts reminiscent of a covalent cation-anion interaction (Ch = S: $\delta_{\text{F}} = -77.4$; Ch = Se: $\delta_{\text{F}} = -76.4$; *c.f.* $[\text{Bu}_4\text{N}][\text{OTf}]$: $\delta_{\text{F}} = -79.0$ (ionic) and MeOTf: $\delta_{\text{F}} = -74.1$ (covalent)).^{33,34} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7sAg** displayed a broad singlet, likely indicating a dynamic process in solution (Figure 6). In contrast, the selenium congener **7seAg** showed two sharp doublets with selenium satellites (^{107}Ag : $^1J_{\text{Ag-P}} = 185.8$ Hz; ^{109}Ag : $^1J_{\text{Ag-P}} = 213.2$ Hz; $^1J_{\text{Se-P}} = 151.8$ Hz; Figure 7).

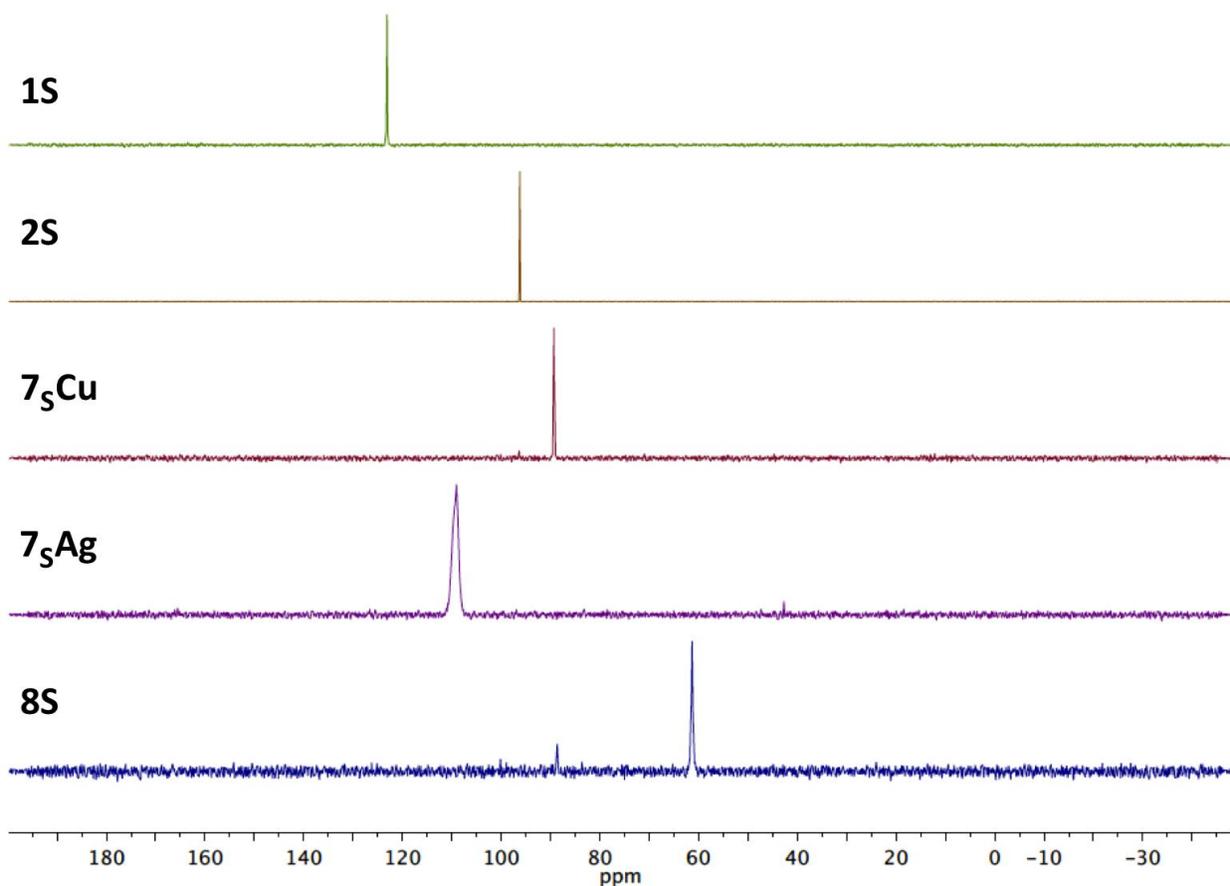


Figure 6. A stack plot of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of different sulfur derivatives reported herein: parent **1S** and ring expansion products **2S**, **7SCu**, **7SAg**, and **8S**.

The addition of excess CuCl to either **1Ch** or **2Ch** in DCM resulted in the consumption of the starting material and the appearance of a broad resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum ($\text{Ch} = \text{S}$: $\delta_{\text{P}} = 61$; $\text{Ch} = \text{Se}$: $\delta_{\text{P}} = 46$; Figures 6 and 7). After removing the volatiles *in vacuo* and washing the crude powder with Et_2O , the slow layering of a DCM solution with pentane at -35 $^{\circ}\text{C}$ resulted in single crystals that confirmed the product to be **8Ch**. Redissolving the single crystals in CDCl_3 gave the same broad $^{31}\text{P}\{^1\text{H}\}$ NMR resonance, consistent with the crude reaction mixture, and a ^1H NMR spectrum that shows one distinct set of *m*-terphenyl signals indicating a symmetrical core on the NMR timescale. The structures are unexpected, but a close

examination shows insertion of Cu(I) into **1Ch** with Cu₂Ch₂ bridging another P₂Ch₂Cu. Compound **8Ch** can be interpreted as containing two bridging sulfur sites, four 3-coordinate sulfides and four Cu(I) centres, where the cage is charge neutral.

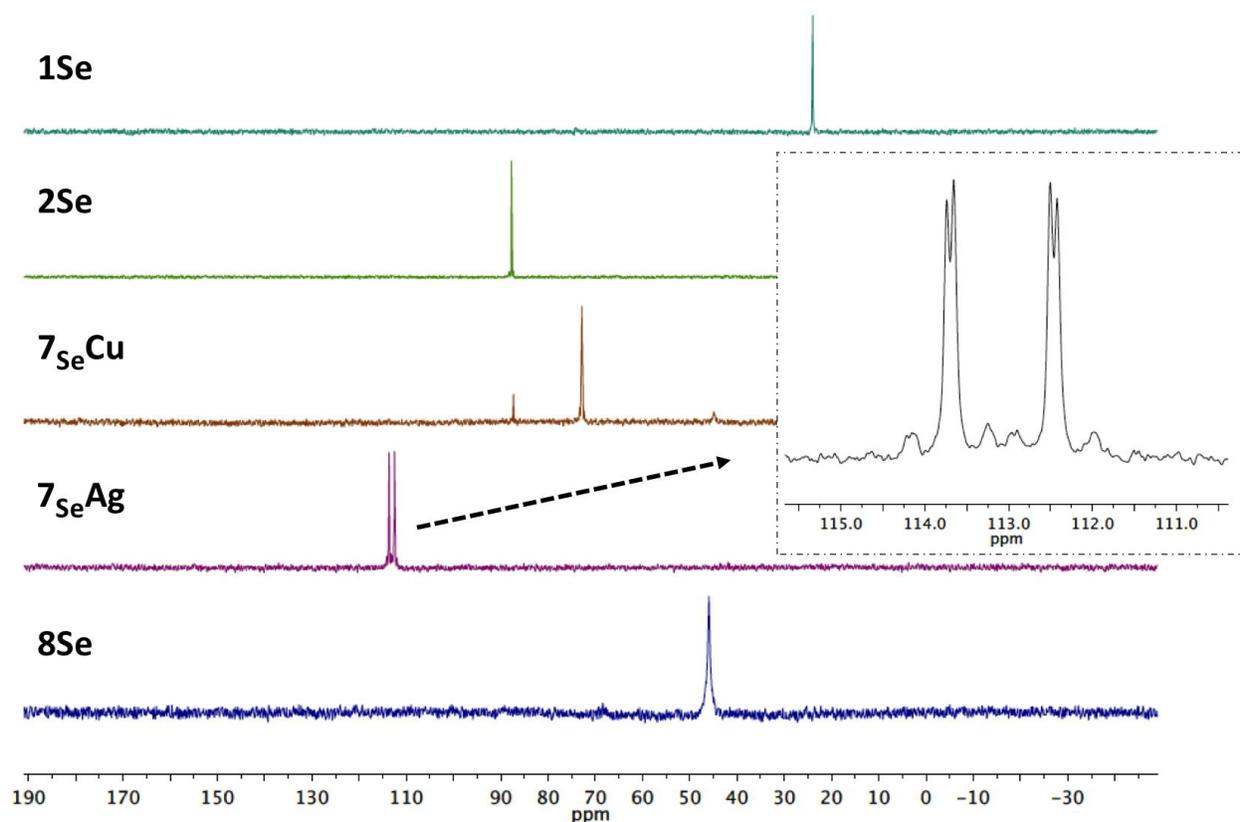


Figure 7. A stack plot of ³¹P{¹H} NMR spectra of different selenium derivatives reported herein: parent **1Se** and ring expansion products **2Se**, **7_{Se}Cu**, **7_{Se}Ag**, and **8Se**.

Recently the synthesis of polynuclear silver complexes stabilized by macrocyclic (PNPCh)₂ ligands and accommodating up to four metal centres have been reported by varying the metal:ligand ratio.⁷ In this respect, attempts to use a large excess of either AgOTf or **1Ch** did not influence the outcome of the reaction, and **7_{Ch}Ag** were the only appreciable products formed alongside **8Ch**. The increased steric bulk at phosphorus (terphenyl vs. phenyl) could rationalize why sandwich metal complexes could not be formed.

Although **2Ch** showed long-term stability when stored under ambient conditions (no decomposition after 2 months at room temperature for either chalcogen derivative) and high thermal stability (**2S** mp = 210-211°C; **2Se** decomposes at 215°C), the metal-containing compounds **7ChM** and **8Ch** were found to be unstable at room temperature, with decomposition occurring either in the solid state or in solution (Figures S-5 and S-6). This inherent instability of **7ChM** and **8Ch** precluded our ability to fully characterize these compounds.

X-ray Crystallography

Images of the solid-state structures are shown in Figure 8, metrical parameters are listed in Table 1, and important X-ray parameters are found in Table S-1. X-ray diffraction experiments were performed on **2Ch** and **7SM** where structure solutions were refined anisotropically and confirmed the ring expansion products. A structure solution of **7SeAg** was obtained that verified atom connectivity, however the data was of poor quality and could only be refined isotropically (Figure S-31) and therefore an in-depth analysis of this particular structure is not appropriate.

The solid-state structures of **2Ch** confirmed the production of 6-membered ring expansion products from the parent P₂Ch₂ rings, and were observed to have alternating P/Ch atoms that adopt a chair conformation with P-S-P_{avg} = 90.19(7)° and S-P-S_{avg} = 102.15(7)° for **2S** and P-Se-P_{avg} = 87.07(7)° and Se-P-Se_{avg} = 102.37(7)° for **2Se**. The average P-Ch bond length for **2S** is 2.1393(2) Å, whereas significant lengthening of P-Ch occurred in **2Se** with an average P-Se bond length of 2.285(2) Å. The 6-membered P₃Ch₃ cores in both **2Ch** were found to be occupationally disordered, with the major component occupying 79 % for **2S** and 78 % for **2Se** (see Figure S-31). The solid-state structures of **2Ch** resemble those previously reported.^{23,25,26}

Table 1. Selected metrical parameters of the reported compounds.^a

	2S	2Se	7SCu	7SAg	8S	8Se
P(1)-Ch(1)	2.1459(18)	2.3021(19)	2.1320(17)	2.131(3)	2.1258(10)	2.2569(16)
P(1)-Ch(3)	2.1367(19)	2.273(2)	2.1318(17)	2.125(3)	-	-
P(2)-Ch(1)	2.1352(17)	2.278(2)	2.1364(17)	2.128(4)	-	-
P(2)-Ch(2)	2.1556(19)	2.283(2)	2.1305(18)	2.132(3)	-	-
P(3)-Ch(2)	2.1395(17)	2.286(2)	2.1322(17)	2.141(3)	-	-
P(3)-Ch(3)	2.1455(18)	2.290(2)	2.1343(17)	2.112(4)	-	-
P(1)-Ch(2)	-	-	-	-	2.1458(10)	2.2757(15)
Ch(1)-Cu(1) (avg)	-	-	-	-	2.3098(9)	2.3948(10)
P(1)-C(1)	1.854(4)	2.273(2)	1.850(4)	1.846(10)	1.859(3)	1.867(6)
P(2)-C(25)	1.855(4)	2.278(2)	1.853(4)	1.828(9)	-	-
P(3)-C(49)	1.860(4)	2.283(2)	1.862(5)	1.825(10)	-	-
P(1)-M(1)	-	-	2.4535(16)	2.689(3)	2.2864(9)	2.2881(17)
P(2)-M(1)	-	-	2.4179(15)	2.705(3)	-	-
P(3)-M(1)	-	-	2.5095(16)	2.746(3)	-	-
Ag(1)-O(1)	-	-	-	2.259(8)	-	-
P(1)-Ch(1)-P(2)	90.31(7)	86.36(8)	89.07(6)	91.10(14)	-	-
P(2)-Ch(2)-P(3)	90.39(7)	85.77(7)	89.56(6)	91.20(13)	-	-
P(3)-Ch(3)-P(1)	89.88(7)	89.09(7)	89.34(7)	91.61(13)	-	-
Ch(1)-P(2)-Ch(2)	102.01(7)	102.94(8)	104.16(7)	103.44(13)	-	-
Ch(2)-P(3)-Ch(3)	101.83(7)	102.55(8)	103.93(7)	103.74(15)	-	-
Ch(3)-P(1)-Ch(1)	102.62(7)	101.67(8)	104.37(7)	102.88(13)	-	-
P(1)-Ch(2)-P(1C)	-	-	-	-	92.92(9)	90.55(8)
C(1)-P(1)-Ch(1)	98.41(14)	96.83(15)	106.07(15)	107.0(13)	-	-
C(1)-P(1)-Ch(3)	105.84(14)	107.54(16)	99.74(16)	101.3(3)	-	-
C(25)-P(2)-Ch(1)	105.81(14)	106.73(16)	100.14(14)	100.9(3)	-	-
C(25)-P(2)-Ch(2)	99.02(14)	100.65(17)	106.12(15)	107.7(13)	-	-
C(49)-P(3)-Ch(2)	106.98(14)	107.23(17)	99.80(14)	100.2(3)	-	-
C(49)-P(3)-Ch(3)	98.03(14)	96.88(16)	106.15(16)	106.3(3)	-	-
P(1)-M-X	-	-	135.49(6)	148.9(2)	-	-
P(2)-M-X	-	-	136.68(6)	130.3(2)	-	-
P(3)-M-X	-	-	133.59(6)	138.1(2)	-	-

^a Bond lengths and angles are given in Ångstroms (Å) and degrees (°), respectively.

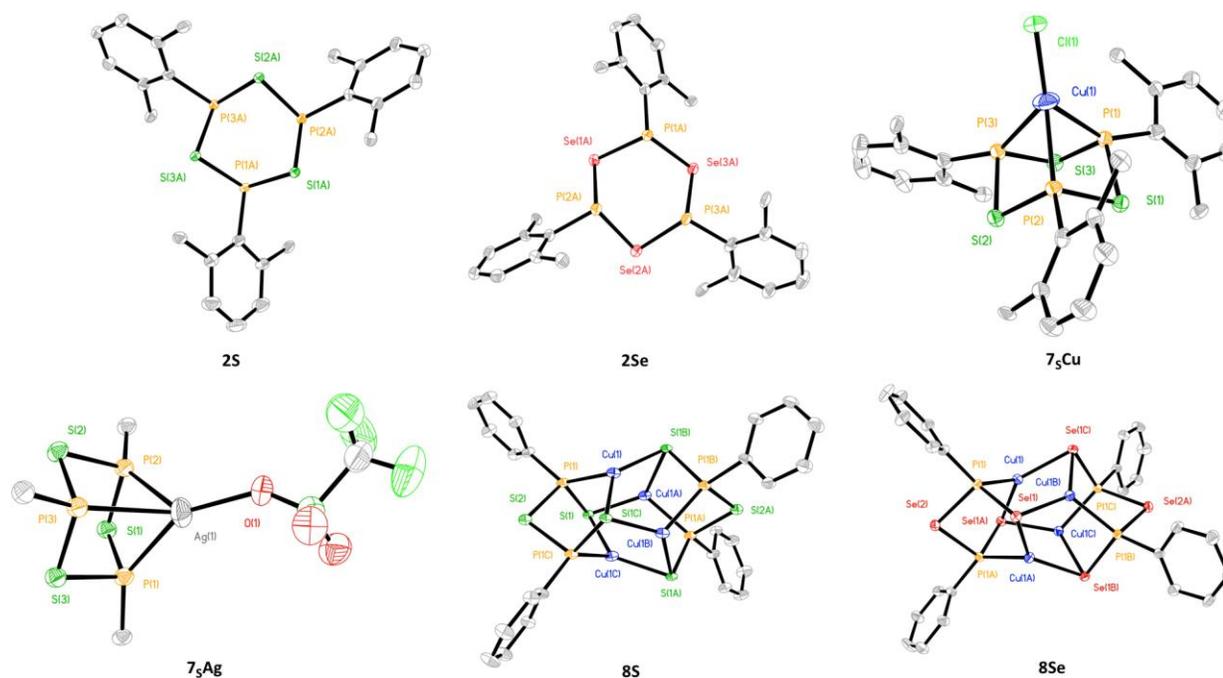


Figure 8. Solid-state structures of the reported compounds. From left to right, top to bottom, **2S**, **2Se**, **7sCu**, **7sAg**, **8S**, and **8Se**. Thermal ellipsoids are drawn at 50 % probability level. Mesityl (2,4,6-trimethylphenyl) rings are omitted from **2S**, **2Se**, **7sCu**, and **8S** for clarity. Terphenyl ligands are omitted from **7sAg** for clarity.

The structures of **7sM** confirm the formation of a ring expansion product from the parent 4-membered ring, and possess the same P_3Ch_3 cores as **2Ch**. However, in **7sM** the metal is bound by each phosphorus atom from within the 6-membered ring. **7sCu** has $P-S-P_{avg} = 89.32(7)^\circ$ and $S-P-S_{avg} = 104.15(7)^\circ$, whereas **7sAg** has $P-S-P_{avg} = 91.30(13)^\circ$ and $S-P-S_{avg} = 103.35(13)^\circ$. This data is similar to that found for **2S**. The same is true also for P-Ch bond distances in **7sCu**, **7sAg**, and **2S**: 2.1334(16), 2.128(2) and 2.1393(2) Å, respectively. Compound **7sCu** has an average P-Cu distance of 2.4603(16) Å that is considerably longer than that found for other tripodal phosphine complexes bound to CuCl (2.246-2.359 Å).^{35–39} Compound **7sAg** has an average P-Ag bond distance of 2.713(3) Å that is considerably longer than that found for one other reported

tripodal phosphine-AgOTf complex (2.537 Å)⁴⁰ and longer than P-Ag bonds in polynuclear silver(I)-phosphine compounds (average P-Ag bond distance of 2.676 Å).⁷

The structures of **8Ch** are isomorphous and contain four 4-coordinate phosphorus atoms, four μ^3 -chalcogen centres, four 3-coordinate copper centres, and two μ^2 -chalcogen centres. Compounds **8Ch** crystallize in the space group *I*-4, and sit on a crystallographic centre of symmetry with Ar*PCh₂Cu as the asymmetric unit. **8Ch** has P-Ch(μ^3) bond distances (S: 2.1258(10) Å, Se: 2.2559(16) Å) that are slightly different from P-Ch(μ^2) distances (S: 2.1458(10) Å, Se: 2.2757(15) Å), but which all fall in the range of typical P-Ch single bond lengths (the sum of Pyykkö & Atsumi single bond covalent radii for P and S/Se is 2.14/2.27 Å)^{41,42} and vary only slightly from the parent **1Ch** (**1S**, P-S_{avg} = 2.1461(2) Å; **1Se**, P-Se_{avg} = 2.303(2) Å)²⁴. The P-Cu bond lengths in **8Ch** are not significantly different (S: 2.2864(9) Å, Se: 2.2881(17) Å), whereas the Ch-Cu distances (S-Cu = 2.3098(9) Å and Se-Cu = 2.3948(10) Å) naturally depend on the identity of the employed chalcogen atom.

Conclusion

We have shown the successful synthesis of (RPCh)₃ rings **2Ch**: the sulfur derivative through ring expansion of the parent 4-membered rings **1Ch** by the addition of DMAP, and the selenium derivative by cyclocondensation of Ar*PCl₂ and Se(TMS)₂. The mechanism for the formation of **2S** was examined computationally, which lead to the identification of a feasible low-energy pathway in which DMAP functions to stabilize the fleeting monomeric R-P=S unit. The calculations also suggested that the formation of **2Se** involves a reaction between R-P=Se and (RPSe)₂. We have also showed coinage-metal induced ring expansion of **1Ch** to **7ChM** by the addition of CuCl or AgOTf, and the formation of **8Ch** through the addition of excess CuCl to

1Ch/2Ch. The 6-membered (RPCh)₃ rings could undergo direct coordination to coinage metals that also resulted in the formation of **7ChM**. Compounds **2Ch** were found to be thermodynamically and thermally more stable than **1Ch**, and they are also unreactive towards both N-heterocyclic carbenes and dimethylbutadiene, Consequently, the synthesized 6-membered (RPCh)₃ rings could not be used as sources of the monomeric R-P=Ch unit unlike the smaller 4-membered P₂Ch₂ rings.

ASSOCIATED CONTENT

Computational details, complete experimental section and associated spectroscopic data not included in the manuscript can be found in the supporting information. The crystallographic data for the compounds reported can be found using CCDC numbers 1569577-1569582, all of which are available free of charge.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

We thank the Natural Science and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation, Ontario Ministry of Research and Innovation, Western University, and University of Jyväskylä for funding. We also acknowledge grants of computer capacity from the Finnish Grid and Cloud Infrastructure (persistent identifier [urn:nbn:fi:research-infras-2016072533](https://nbn-resolving.org/urn:nbn:fi:research-infras-2016072533)).

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