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Phosphorus-Chalcogen Ring Expansion and Metal Coordination

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Supporting Information

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 6membered 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 6membered rings were found to react with coinage metals, giving the same products: (RPCh)₃ rings bound to the metal center from the phosphorus atom in tripodal fashion.

coinage metals Ch Ar Ch Lewis Bas coinage metals

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 co-workers.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 P_2Ch_2 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 transformations^{14–18} and material applications.^{19,20} Although 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) center (Figure 1B-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

Although select examples of $(RPCh)_n$ have been reported since the early 1980s, 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 synthesized and isolated via cyclocondensation of Ar^*PCl_2 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 $7_{Ch}M$ (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. HNEt₂ was purchased from Sigma-Aldrich and distilled from KOH. PCl₃ was purchased from Sigma-Aldrich and distilled/degassed prior to use. Gaseous HCl was prepared in situ by dropping neat H_2SO_4 to CaCl₂ powder, bubbled through H₂SO₄ then through the reaction mixture and ultimately through a NaHCO₃ outlet bubbler to neutralize

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Figure 1. Left: Previously reported phosphorus-chalcogen rings, (A) Woollins' and Lawesson's reagents with P(V), (B-D) (RPCh)_n with P(III), and (E) polynuclear Ag sandwich complex. 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-(tBu)₃C₆H₂, Im = imidazolium-2-yl.

excess HCl. $Ch(TMS)_2$ (Ch = S, Se)²⁷ and Ar*PCl₂²⁸⁻³¹ were made following known literature procedures. CuCl, AgOTf, (Me₂S)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 (CDCl₃ and C₆D₆) 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, ³¹P{¹H} 161.8 MHz) or 600 MHz (¹³C{¹H} 150.8 MHz) spectrometers. All samples for ¹H NMR spectroscopy were referenced to the residual protons in the deuterated solvent relative to tetramethylsilane (CDCl₃; δ = 7.26, C₆D₆; δ = 7.16). The chemical shifts for ${}^{31}P{}^{1}H{}$ NMR spectroscopy were referenced using an external standard (85% H₃PO₄; δ = 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 $7_{Ch}M$ and **8Ch** are light-sensitive. $7_{Ch}M$ 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 $^{13}C\{^{1}H\}$ 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 25. 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 h 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 (C₆D₆, 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_{H-H} = 7.4 Hz, Aromatic

C–H), 6.83 (br s, 12 H, Mesityl C–H), 7.02 (t, 3 H, ${}^{3}J_{H-H} = 7.4$ Hz, Aromatic C–H). ${}^{31}P{}^{1}H$ NMR (C₆D₆, 161.8 MHz, δ): 96.7 (s). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 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*, C₇₂H₇₅P₃S₃Na [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*PCl₂ (487 mg, 1.17 mmol, 20 mL THF) portionwise over 3 h. The volatiles were removed in vacuo, leading to an orange oil. The oil was washed with pentane $(3 \times$ 10 mL) and insoluble 1Se was filtered and collected (yield: 348 mg, 86%). The pentane fractions were combined, concentrated in vacuo, and 1 mL of DCM was added to the oil, which resulted in the precipitation of a yellow powder when left at -35 °C for 2 h. X-ray quality single crystals of 2Se were grown via vapor diffusion using DCM/Toluene (yield: 49 mg, 10%). mp: decomposes at 215 °C (turns dark brown). ¹H NMR (C₆D₆, 600 MHz, δ): 2.08 (s, 36 H, Mesityl o-CH₃), 2.30 (s, 18 H, Mesityl p-CH₃), 6.78 (d, 6 H, ${}^{3}J_{H-H} =$ 7.5 Hz, Aromatic C–H), 6.84 (br s, 12 H, Mesityl C–H), 7.03 (t, 3 H, ${}^{3}J_{H-H} = 7.5$ Hz, Aromatic C–H). ${}^{31}P{}^{1}H$ NMR (C₆D₆, 161.8 MHz, δ): 87.8 (s, ${}^{1}J_{P-Se}$ = 136.6 Hz). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 150.8 MHz, δ): 21.6, 21.8, 128.3, 130.1, 130.3, 137.0, 138.0, 146.0. ${}^{77}Se$ NMR (C₆D₆, 114.4 MHz, δ): 421.0 (ddd, ${}^{1}J_{Se-P}$ = 202.6, 133.3 Hz, ${}^{3}J_{Se-P}$ = 67.1 Hz). EI-MS: 1271.3 m/z, $C_{72}H_{75}P_{3}Se_{3}$ [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 Anal. Calcd 68.08% C, 5.95% H. Exptl 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 h. The volatiles were removed in vacuo and the crude powder was washed with diethyl ether $(3 \times 5 \text{ mL})$, giving an insoluble powder that was collected.

Synthesis of 7₅Cu. 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 vapor 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), 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),

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



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.

907 (5), 1030 (10), 1374 (8), 1448 (2), 1480 (14), 1562 (9), 1611 (3), 2853 (13), 2915 (1), 2944 (15), 2968 (11).

Synthesis of 7₅Ag. 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 vapor diffusion using DCM/ pentane. **mp**: decomposes at 141 °C (turns dark gray). 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), 7.53 (t, 3 H, δ): 109.0 (br s). ¹³C{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. ¹⁹F{¹H} **NMR** (CDCl₃, 376.3 MHz, δ): -77.4 (s). **EI-MS**: 1237.3 *m*/*z*, C₇₂H₇₅P₃S₃Ag [M - 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 7_{se} **Cu.** Reagents: **1Se** (40 mg, 0.047 mmol, 5 mL DCM) and CuCl (3.0 mg, 0.032 mmol, 5 mL DCM). ³¹P NMR spectra of crude reaction mixture showed formation of 7_{se} **Cu** ($\delta_P = 72$) and free **2Se** ($\delta_P = 88$). Attempts to separate **2Se** and 7_{se} **Cu** by fractional crystallization were unsuccessful. Attempts to convert **2Se** to 7_{se} **Cu** resulted in multiple products in the ³¹P NMR spectrum, including **8Se** (Figure S3).

Synthesis of 7_{se}Ag. 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 vapor diffusion using DCM/ pentane. **mp**: decomposes at 171 °C (turns dark gray). ¹**H NMR** (CDCl₃, 400 MHz, δ): 1.92 (s, 36 H, Mesityl *o*-CH₃), 2.27 (s, 18 H, Mesityl *p*-CH₃), 7.03 (d, 6 H, ³J_{H-H} = 7.6 Hz, Aromatic C-H), 7.15 (s, 12 H, Mesityl C-H), 7.63 (t, 3 H, ³J_{H-H} = 7.6 Hz, Aromatic C-H). ³¹**P**{¹**H**} **NMR** (CDCl₃, 161.8 MHz, δ): 113.3 (d, ¹J¹⁰⁹_{Ag-P} = 213.2 Hz, ¹J¹⁰⁷_{Ag-P} = 185.8 Hz, ¹J_{Se-P} = 151.8 Hz). ¹³**C**{¹**H**} **NMR** (CDCl₃, 150.8 MHz, δ): 20.9, 21.4, 129.7, 131.3, 133.7, 135.1, 136.8, 140.5, 1464. ¹⁹**F**{¹**H**} **NMR** (CDCl₃, 376.3 MHz, δ): -76.4 (s). **EI-MS**: 1379.2 *m*/*z*, C₇₂H₇₅P₃Se₃Ag [M - 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: **IS** (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 vapor diffusion using DCM/pentane. **mp**: decomposes at 119 °C (turns brown). ¹**H 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, ³J_{H-H} = 6.4 Hz, Aromatic C–H), 7.46 (t, 3 H, ³J_{H-H} = 6.4 Hz, Aromatic C–H). ³¹**P**{¹**H**} **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 vapor diffusion using DCM/ pentane. **mp**: decomposes at 160 °C (turns black). ¹**H 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 Ch-(TMS)₂ (Figure 2). Although the sulfur chemistry proceeds cleanly, multiple products are present in the crude reaction



Figure 4. Reaction coordinate diagram for DMAP-induced (RPS)_n ring expansion (phosphorus atoms are colored 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**.

mixture for Ch = Se. The major product **1Se** ($\delta_{\rm p}$ = 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 °C ($\delta_{\rm p}$ = 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 (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

After successfully isolating 1Ch, we endeavored 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 2,3dimethyl-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 ³¹P{¹H} NMR spectrum at δ_P = 97, an upfield shift from the parent 1S ($\delta_{\rm P}$ = 127), and significantly downfield shifted from 5S ($\delta_{\rm P}$ = 28). Slowly concentrating a DCM solution at -35 °C resulted in pale-yellow single crystals. Single-crystal Xray 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. ³¹P{¹H} NMR spectra obtained from solutions containing redissolved crystals of 2S showed the same distinct singlet ($\delta_{\rm P} = 97$) observed in the crude reaction mixture, whereas the ¹H NMR spectra showed a single set of terphenyl protons, indicating equivalence of aromatic substituents on the NMR time scale.

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 ³¹P{¹H} 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 ($\delta_p = 88$). Other structurally related Lewis bases such as pyridine and 2,6-lutidene also generated **2Se**, but again with multiple other side products (Figure S1). Alternatively to nitrogen bases, phosphine-based donors (PEt₃, PCy₃, and PPh₃) produced multiple products as determined by ³¹P{¹H} NMR spectroscopy. Interestingly, there was no evidence for a ring expansion product **2Se**, however evidence for the corresponding phosphine-selenides were present in the ³¹P{¹H} NMR spectra (R₃P=Se; Figure S2), 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.

The reaction pathway for forming **2S** was examined using density functional theory at the PBE1PBE/TZVP level 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-

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Figure 5. Ring expansion of 1Ch (Ch = S, Se) using coinage metals (MX = CuCl, AgOTf) resulting in $7_{Ch}M$. 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.



Figure 6. Stack plot of ${}^{31}P{}^{1}H$ NMR spectra of different sulfur derivatives reported herein: parent 1S and ring expansion products 2S, $7_{s}Cu$, $7_{s}Ag$, and 8S.

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 breakup of one P-S bond in 1S to give 1Sb 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



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

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

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 a pathway is not feasible in practice because of 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 Ch = 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 onward reactivity, especially metal coordination. Our initial approach was to explore their reactivity as ligands to transition metals, first with Group 16 metal carbonyls (M = Cr, Mo, W). However, no reaction occurred upon reaction of the ($M(CO)_5THF$) precursor to either 1Ch/2Ch, even after prolonged reaction times and varying reaction conditions. We hypothesized that the steric demand imposed by the *m*-terphenyl ligands prevented coordination. We then turned to the coinage metals (M = Cu, Ag, 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 ³¹P{¹H} NMR spectra (Ch = S: Cu δ_P = 89, Ag δ_P = 109; Ch = Se: Ag δ_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 (7_{Ch}M). 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 center.

Although the addition of **1Ch** with MX proceeds cleanly for $7_{s}M$ and $7_{se}Ag$, the addition of **1Se** to CuCl resulted in multiple products. However, a major product at $\delta_p = 72$, which has been hypothesized to be $7_{se}Cu$ based on the similarity of the shift to $7_{s}Cu$, 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 $7_{se}Cu$ did not proceed cleanly but resulted in multiple phosphorus containing products (Figure S3). Attempts to use a different Cu⁺ source CuOTf[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 $7_{Ch}M$ that were isolated in yields comparable to those



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

obtained for reactions performed with 1Ch. Similar to the reactions with Cu and Ag, the low temperature addition of 1S to Me₂SAuCl resulted in one major product ($\delta_{\rm P} = 82$). Leaving a solution state sample at -35 °C for overnight in an attempt to grow single crystals resulted in numerous phosphorus-containing products (Figure S4) and repeated attempts to isolate the observed major product were met only with evidence for decomposition.

Compounds $7_{s}M$ contain a single resonance in the ${}^{31}P{}^{1}H$ NMR spectrum (Figure 6) as well as one set of terphenyl signals in the ${}^{1}H$ NMR spectrum, indicating 3-fold symmetry among the 6-membered ring in solution. The ${}^{19}F{}^{1}H$ NMR of $7_{Ch}Ag$ contained singlets with the chemical shifts reminiscent of a covalent cation—anion interaction (Ch = S: $\delta_{\rm F} = -77.4$; Ch = Se: $\delta_{\rm F} = -76.4$; *c.f.* [Bu₄N][OTf]: $\delta_{\rm F} = -79.0$ (ionic) and MeOTf: $\delta_{\rm F} = -74.1$ (covalent)).^{33,34} The ${}^{31}P{}^{1}H$ NMR spectrum of $7_{\rm S}Ag$ displayed a broad singlet, likely indicating a dynamic process in solution (Figure 6). In contrast, the selenium congener $7_{\rm Se}Ag$ showed two sharp doublets with selenium satellites (${}^{107}Ag$: ${}^{1}J_{Ag-P} = 185.8$ Hz; ${}^{109}Ag$: ${}^{1}J_{Ag-P} =$ 213.2 Hz; ${}^{1}J_{Se-P} = 151.8$ Hz; Figure 7).

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 ³¹P{¹H} NMR spectrum (Ch = S: $\delta_p = 61$; Ch = Se: $\delta_p = 46$; Figures 6 and 7). After removing the volatiles in vacuo and washing the crude powder with Et₂O, the slow layering of a DCM solution with pentane at -35 °C resulted in single crystals that confirmed the product to be **8Ch**. Redissolving the single crystals in CDCl₃ gave the same broad ³¹P{¹H} 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 time scale. 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) centers, where the cage is charge-neutral.

Recently, the synthesis of polynuclear silver complexes stabilized by macrocyclic (PNPCh)₂ ligands and accommodating up to four metal centers 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 $7_{Ch}M$ 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 $7_{Ch}M$ 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 $7_{s}M$ where structure solutions were refined anisotropically and confirmed the ring expansion products. A structure solution of $7_{se}Ag$ was obtained that verified atom connectivity, however the data was of poor quality and could only be refined isotropically (Figure S31) 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 P_2Ch_2 rings, and were observed to have alternating P/Ch atoms that adopt a chair conformation with P–S– $P_{avg} = 90.19(7)^{\circ}$ and S–

	28	2Se	7 _s Cu	7 _S Ag	85	8Se
Bond Length (Å)						
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)		
Bond Angle (deg)						
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)		

 $P-S_{avg} = 102.15(7)^{\circ}$ for **2S** and $P-Se-P_{avg} = 87.07(7)^{\circ}$ and $Se-P-Se_{avg} = 102.37(7)^{\circ}$ 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 S31). The solid-state structures of **2Ch** resemble those previously reported.^{23,25,26}

The structures of 7_s M 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 7_s M, the metal is bound by each phosphorus atom from within the 6membered ring. 7_s Cu has $P-S-P_{avg} = 89.32(7)^\circ$ and $S-P-S_{avg}$ = 104.15(7)°, whereas 7_s Ag 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 7_s Cu, 7_s Ag, and **2S**: 2.1334(16), 2.128(2) and 2.1393(2) Å, respectively. Compound 7_s Cu 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 7_s Ag 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 4coordinate phosphorus atoms, four μ^3 -chalcogen centers, four 3-coordinate copper centers, and two μ^2 -chalcogen centers. Compounds 8Ch crystallize in the space group I-4 and sit on a crystallographic center 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 $P-Ch(\mu^2)$ 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 $(\text{RPCh})_3$ rings **2Ch**: the sulfur derivative through ring expansion of the parent 4membered rings **1Ch** by the addition of DMAP, and the selenium derivative by cyclocondensation of Ar*PCl_2 and $\text{Se}(\text{TMS})_2$. The mechanism for the formation of **2S** was

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examined computationally, which leads 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 coinagemetal induced ring expansion of 1Ch to $7_{Ch}M$ 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 $7_{\rm Ch}M$. Compounds 2Ch were found to be thermodynamically and thermally more stable than 1Ch, and they are also unreactive toward both Nheterocyclic 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

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02217.

Figures S1–S31, Table S1, computational details, complete experimental section and associated spectroscopic data not included in the manuscript (PDF) Optimized structures of investigated compounds (XYZ)

Accession Codes

CCDC 1569577–1569582 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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

Notes

The authors declare no competing financial interest.

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