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Preparations of Metal Trichalcogenophosphonates from Organophosphonate Esters

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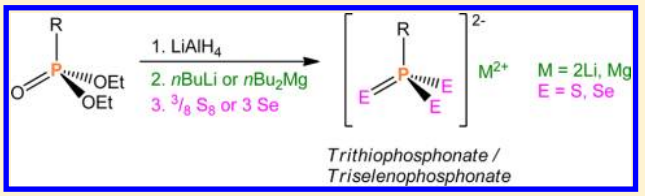
Supporting Information

ABSTRACT: A new method for the preparation of metal trichalcogenophosphonates is presented wherein organophosphonate esters are first reduced with $LiAlH_4$ and subsequently treated with an organometallic reagent and elemental sulfur or selenium to give the desired trichalcogenophosphonate complex. Using this synthetic protocol with ^{n}BuLi as the organometallic reagent, the lithium trithiophosphonate complexes $[Li_2(S_3PCH_2Ph)(THF)(TMEDA)]_2$ (**1**) and $[Li_4(S_3P^nPr)_2(TMEDA)_3]_\infty$ (**3**), where THF = tetrahydrofuran and TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, have been prepared. In both cases, the formation of byproducts is also evident, including, for **1**, the tetrathiohypodiphosphonate complex $[(PhCH_2P(S_2))_2Li_2(THF)_4]$ (**2**), which has been structurally characterized. Replacement of ^{n}BuLi with ^{n}Bu$_2$Mg as the metallating agent led to much cleaner products and improved yields, with the new trithio- and triselenoorganophosphonate complexes $[Mg(S_3PCH_2Ph)(TMEDA)]_2$ (**4**) and $[Mg(Se_3P^nPr)(TMEDA)]_2$ (**5**) reported. All trichalcogenophosphonate complexes have been structurally characterized in the solid state: **1** adopts a dimer structure in which the $[PhCH_2PS_3]^{2-}$ ligand exhibits a unique μ_3-η^2,η^2,η^2-coordination mode; **3** is polymeric comprising of $[Li_4(S_3P^nPr)_2(TMEDA)_2]$ dimers linked via additional bridging bis(monodentate) TMEDA molecules; **4** and **5** both adopt dimeric motifs with μ_2-η^2,η^2 coordination of the magnesium centers.

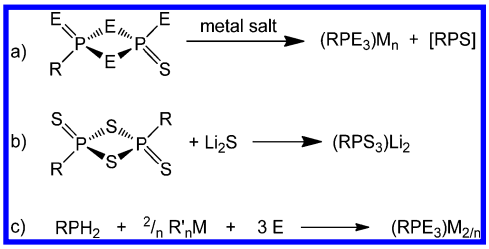


INTRODUCTION

Despite their potential wide-ranging applications, studies on metal trichalcogenophosphonates $[RPX_3]^{2-}$ (X = S, Se) remain sparse in the scientific literature, primarily because of the lack of a reliable and generally applicable synthetic route to these compounds. In stark contrast, salts and complexes of the analogous oxygen-containing organophosphonates, $[RPO_3]^{2-}$, have been subjected to extensive investigations. Thus, metal organophosphonates have shown potential and realized applications in many fields including catalysis, guest intercalation, sorbents, ion exchange, proton conduction, nonlinear optics, photochemically active materials, and sensors.[1] The wide applicability of organophosphonate materials is, in part, due to the ability of the organophosphonate ligands to act as versatile building blocks in the design of layered structures and cages.[1] Analogous behavior in trichalcogenophosphonates might lead to new materials with similarly useful or novel properties. Additionally, in common with other metal organophosphorus−chalcogen complexes, trichalcogenophosphonates have potential applications as single-source precursors to metal chalcogenide thin films and quantum dots, lubricant additives, catalysts or chalcogen-exchange reagents in organic synthesis, biological agents, and heavy-metal extractants.[2] Hence, a better understanding of the synthesis, structure, and properties of trichalcogenophosphonates is highly desirable and is the focus of this work.

Preparations of metal trichalcogenophosphonates to date have mainly employed dichalcogenodiphosphetane dichalcogenides $[\{RP(E)(\mu\text{-}E)\}_2]$ (such as Lawesson's or Woollins' reagents with E = S, R = 4-anisyl and E = Se, R = Ph, respectively) in reactions with metal salts or complexes. This approach has been reported by the groups of Woollins,[3−6] Rothenberger,[7,8] and others,[9−14] and usually proceeds via the asymmetric cleavage of dichalcogenodiphosphetane dichalcogenides (Scheme 1a). However, the scope of the reaction has been somewhat limited both by the availability of dichalcogenodiphosphetane dichalcogenide starting materials and also by competition from the associated symmetric cleavage reaction. An alternative route to trithiophosphonates uses thiometal reagents to induce symmetric cleavage of dithiodiphosphetane disulfides (Scheme 1b).[10,11] Other reported syntheses of trichalcogenophosphonates include a gallium trithiophosphonate prepared by Cowley et al. via the reaction of P_4S_{10} with

Scheme 1. Representative Synthetic Routes to Metal Trichalcogenophosphonates (E = S, Se)



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$^{t}Bu_3Ga$,[15] platinum trithiophosphonate complexes formed from the reaction of $[Pt(SP(=NPh)(Ph)(NPh))(L_2)]$ (L_2 = $2PPh_3$, dppp) with phenyl isothiocyanate or carbon disulfide by Kemmitt et al.,[16] and a tungsten trithiophosphonate complex isolated from the reaction of $[PPh_4]_2[WS_4]$ with $PhPCl_2$ by Garner and co-workers.[17] Transmetalation,[7,12,18] ion exchange,[19−22] and silyl ester cleavage[10,17,23,24] protocols have also been used to introduce a metal center to an existing RPS_3 group. Moreover, and particularly salient to this work, we have previously reported on the reaction of primary phosphines with an organometal deprotonating agent and elemental chalcogen to give metal trithio- and triselenophosphonate complexes (Scheme 1c).[25−27]

We now report on a significant extension of this final synthetic route using organophosphonate esters, $RP(O)(OR'')_2$, as starting materials and thus taking advantage of the widespread commercial availability of such esters with a large variety of organo R groups. In a "one-pot" reaction, organophosphonate esters are first reduced by lithium aluminum hydride to the corresponding primary phosphine followed by the reaction with an organometallic metallating reagent and elemental chalcogen to give the desired metal trichalcogenophosphonate. The employment of such a protocol avoids any risk associated with the isolation and handling of neat primary phosphines, which are often malodorous and highly pyrophoric, and significantly simplifies the reaction protocol. In addition to providing a new route to these complexes, the coordination chemistry of trichalcogenophosphonates is further elaborated upon in this work.

EXPERIMENTAL SECTION

General Procedures. All experimental work was carried out under an inert atmosphere of nitrogen using standard Schlenk double-manifold techniques for the synthesis, and a glovebox for the storage, of the reported complexes. Purification and drying of the solvents was carried out following standard methods or using an Innovative Technologies PureSolv Solvent Purification System with purification-grade solvents. The reduction of organophosphonate esters using $LiAlH_4$ is based upon an adaptation of published procedures.[28,29] ^1H, ^{31}P, and ^7Li NMR spectra were recorded on a Bruker DPX400 spectrometer with internal standards. ^{77}Se NMR spectra were recorded on a JOEL EX270 Delta Upgrade spectrometer with an external standard (Me_2Se). Melting points were measured in capillaries sealed under nitrogen, and microanalytical data were obtained from the Science Technical Support Unit, London Metropolitan University.

Preparation of $[Li_2(S_3PCH_2Ph)(THF)(TMEDA)]_2$ (1) and $[(PhCH_2P(S_2))_2Li_2(THF)_4]$ (2). $PhCH_2P(O)(OEt)_2$ (3.15 mL, 7.5 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.42 g, 11 mmol) in toluene (15 mL) at 0 °C. The mixture was stirred for 16 h and then quenched with thoroughly degassed saturated aqueous Na_2SO_4 (15 mL) at 0 °C. The white mixture was filtered and the organic layer separated. The remaining aqueous layer was washed with toluene (2 × 4.0 mL), and the combined organic layers were dried over $MgSO_4$. NMR studies on the resultant solution show complete conversion to $PhCH_2PH_2$: $^{31}P\{^1H\}$ NMR (162 MHz, toluene/C_6D_6) δ/ppm −122.5 (lit.[30] −120.9). The phosphine solution was cooled to 0 °C, and ^{n}BuLi (2.5 M in hexanes, 6.0 mL, 15 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 2.3 mL, 15 mmol) were added. The solution was then transferred onto S_8 (0.720 g, 2.8 mmol) and stirred at room temperature for 16 h. Removal of the solvent under vacuum and recrystallization from tetrahydrofuran (THF)/hexane (8 mL/3 mL) at −35 °C gave a crystalline precipitate (1.36 g) that was shown by ^{31}P NMR analysis to be an approximately equimolar mixture of **1** (∼15% yield) and **2** (∼18% yield). Further concentration of the filtrate and storage at −35 °C for 2 weeks gave a small (0.07 g) batch of colorless block crystals of **1**: mp >250 °C; ^1H NMR (400 MHz, DMSO-d_6) δ/ppm 7.41 (d, $^3J_{HH}$ = 6.8 Hz, 2H, *o*-C_6H_5), 7.09 (m, 2H, *m*-C_6H_6), 7.03 (m, 1H, *p*-C_6H_6), 3.60 (m, 4H, THF), 3.34 (d, $^2J_{HP}$ = 13.5 Hz, 2H, CH_2), 2.28 (s, 4H, TMEDA), 2.12 (s, 12H, TMEDA), 1.75 (m, 4H, THF); ^{31}P NMR (162 MHz, DMSO-d_6) δ/ppm 83.9 (t, $^2J_{PH}$ = 13.5 Hz); ^7Li NMR (156 MHz, DMSO-d_6) δ/ppm −0.9. A spectroscopically pure sample of **2** was obtained as colorless crystals by the slow cooling to room temperature of a hot THF (8.0 mL) and hexane (3.0 mL) solution of the original **1** + **2** mixture: mp 120 °C (dec); ^1H NMR (400 MHz, DMSO-d_6) δ/ppm 7.36 (d, $^3J_{HH}$ = 7.3 Hz, 4H, *o*-C_6H_5), 7.18 (dd, $^3J_{HH}$ = 7.1 and 7.3 Hz, 4H, *m*-C_6H_5), 7.10 (t, $^3J_{HH}$ = 7.1 Hz, 2H, *p*-C_6H_5), 3.61 (m, 16H, THF), 3.52 (dd, $^2J_{HP}$ = 6.5 Hz, $^3J_{HP}$ = 3.8 Hz, 4H, CH_2), 1.76 (m, 16H, THF); $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6) δ/ppm 82.0; ^7Li NMR (156 MHz, DMSO-d_6) δ/ppm −1.0.

Preparation of $[Li_4(S_3P^nPr)_2(TMEDA)_3]_\infty$ (3). ^{n}PrP(O)$(OEt)_2$ (0.88 mL, 5 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.28 g, 7.4 mmol) in toluene (15 mL) at 0 °C. The mixture was stirred for 16 h and then quenched with thoroughly degassed saturated aqueous Na_2SO_4 (10 mL) at 0 °C. The white mixture was then filtered and the organic layer separated. The remaining aqueous layer was washed with toluene (2 × 3.0 mL), and the combined organic layers were dried over $MgSO_4$. NMR studies on the resultant solution show complete conversion to ^{n}PrPH_2: $^{31}P\{^1H\}$ NMR (162 MHz, toluene/C_6D_6) δ/ppm −139.9 (lit.[31] −138). The phosphine solution was cooled to −78 °C, and TMEDA (1.5 mL, 10 mmol) and ^{n}BuLi (2.5 M in hexanes, 4.0 mL, 10 mmol) were added. This solution was then transferred onto S_8 (0.480 g, 1.9 mmol), stirred for 16 h at room temperature, and filtered through Celite. Removal of the solvent under vacuum and recrystallization from hexane/toluene (2 mL/4 mL) at −35 °C for 4 days gave a batch of colorless block crystals of **3** along with a small amount of red solid (see the Results and Discussion section): yield 0.334 g, 20%; mp 108 °C; ^1H NMR (400 MHz, C_6D_6) δ/ppm 2.91 (m, 4H, CH_2), 2.50 (m, 4H, CH_2), 2.32 (s, 36H, TMEDA), 2.01 (s, 12H, TMEDA), 1.23 (t, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ/ppm 84.8; ^7Li NMR (156 MHz, C_6D_6) δ/ppm 1.5.

Preparation of $[Mg(S_3PCH_2Ph)(TMEDA)]_2$ (4). A solution of $PhCH_2PH_2$ (2.5 mmol) in toluene (∼10 mL) was prepared from $PhCH_2P(O)(OEt)_2$ and $LiAlH_4$ using a procedure identical with that described in the preparation of **1** above. ^{n}Bu$_2$Mg (1.0 M in heptane, 2.5 mL, 2.5 mmol) and TMEDA (0.60 mL, 4.0 mmol) were then added to the phosphine solution. The resultant cloudy yellow solution was transferred onto S_8 (0.255 g, 0.94 mmol) and stirred for 16 h to yield a batch of pale-yellow solid **4**: yield 0.922 g, 52%; mp >250 °C; ^1H NMR (400 MHz, DMSO-d_6) δ/ppm 7.41 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-C_6H_5), 7.08 (dd, $^3J_{HH}$ = 7.2 and 7.5 Hz, 2H, *m*-C_6H_5), 6.99 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_5), 3.31 (d, $^2J_{HP}$ = 13.9 Hz, 2H, CH_2), 2.23 (s, 4H, TMEDA), 2.12 (s, 12H, TMEDA); ^{31}P NMR (162 MHz, DMSO-d_6) δ/ppm 84.1 (t, $^2J_{PH}$ = 12.0 Hz). Calcd for $C_{26}H_{46}Mg_2N_4P_2S_6$: C, 43.51; H, 6.46; N, 7.81. Found: C, 43.51; H, 6.51; N, 7.87. Recrystallization from THF at 5 °C gave colorless crystals of **4** suitable for X-ray crystallographic studies.

Preparation of $[Mg(Se_3P^nPr)(TMEDA)]_2$ (5). A solution of ^{n}PrPH_2 (2.5 mmol) in toluene (∼10 mL) was prepared from ^{n}PrP(O)$(OEt)_2$ and $LiAlH_4$ using a procedure identical with that described in the preparation of **3** above. ^{n}Bu$_2$Mg (1.0 M in heptane, 2.5 mL, 2.5 mmol) and TMEDA (0.75 mL, 5.0 mmol) were then added to the phosphine solution. The resultant cloudy yellow solution was transferred onto Se (0.592 g, 7.5 mmol) at 0 °C and stirred for 16 h to give the white solid **5**: yield 0.662 g, 37%; mp 221 °C (dec); ^1H NMR (400 MHz, DMSO-d_6) δ/ppm 2.27 (s, 2H, TMEDA), 2.24−2.20 (m, 2H, CH_2), 2.11 (s, 12H, TMEDA), 1.84−1.72 (m, 2H, CH_2), 0.90 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3); $^{31}P^{10}$ NMR (162 MHz, DMSO-d_6) δ/ppm −18.5 (s + d satellites, $^1J_{PSe}$ = −542 Hz); ^{77}Se NMR (95.4 MHz, DMSO-d_6) δ/ppm 353.6 (d, $^1J_{SeP}$ = −542 Hz). Calcd for $C_{18}H_{46}Mg_2N_4P_2Se_6$: C, 23.94; H, 5.14; N, 6.21. Found: C, 23.87; H, 5.12; N, 6.54. Recrystallization from dichloromethane at 30 °C gave crystals of **2** suitable for X-ray crystallographic studies.

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Table 1. Crystal Data, Data Collection, and Refinement Parameters for the Structures of 1−5

	1	2	3	4	5
formula	$C_{34}H_{62}Li_4N_4O_2P_2S_6$	$C_{30}H_{46}Li_2O_4P_2S_4$	$C_{24}H_{62}Li_4N_6P_2S_6$	$C_{26}H_{46}Mg_2N_4P_2S_6$	$C_{18}H_{46}Mg_2N_4P_2Se_6$
solvent	C_4H_8O			$2(C_4H_8O)$	$2(CH_2Cl_2)$
fw	913.04	674.73	716.86	861.80	1072.76
color, habit	colorless, blocks	colorless, tablets	colorless, blocks	colorless, prisms	colorless, tablets
temp/K	173	173	173	173	173
cryst syst	triclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	8.8544(4)	10.8127(8)	10.5462(5)	10.0755(3)	10.1998(3)
b/Å	10.7325(5)	12.1431(6)	10.7732(5)	18.8928(4)	10.2810(4)
c/Å	14.0520(6)	13.4353(7)	10.9125(6)	12.4849(4)	10.4612(4)
α/deg	94.743(4)	88.900(4)	117.717(5)		68.813(4)
β/deg	91.093(4)	84.026(5)	105.696(5)	109.942(3)	76.831(3)
γ/deg	110.391(4)	88.591(5)	95.638(4)		86.348(3)
V/Å^3	1245.76(10)	1753.70(18)	1019.47(11)	2234.05(12)	995.75(6)
Z	1[a]	2[b]	1[a]	2[a]	1[a]
D_c/g cm^{-3}	1.217	1.278	1.168	1.281	1.789
radiation used	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Mo Kα
μ/mm^{-1}	0.375	0.394	0.437	4.046	5.911
$2\theta_{max}$/deg	65	66	61	145	63
no. of unique reflns					
measd (R_{int})	8173 (0.0188)	15098 (c)	5379 (0.0167)	4402 (0.0259)	5969 (0.0185)
obsd $\|F_o\| > 4\sigma(\|F_o\|)$	6262	9568	4044	3774	4127
no. of variables	285	401	207	269	172
R1 (obsd), wR2 (all)[d]	0.0388, 0.1062	0.0666, 0.1942	0.0345, 0.0827	0.0383, 0.1056	0.0250, 0.0488

[a]The complex has crystallographic C_i symmetry. [b]The structure contains two crystallographically independent C_i-symmetric complexes. [c]Not applicable because of twinning; see the Supporting Information for more details. [d]R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

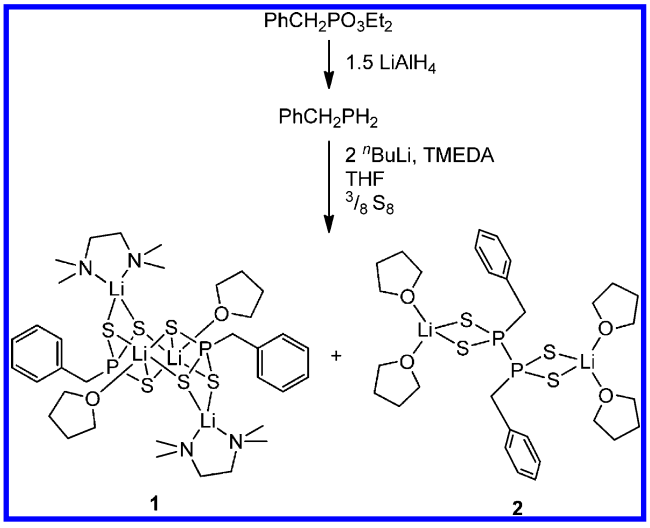
Crystallographic Studies. Crystals to be analyzed by X-ray diffraction were taken directly from the mother liquor, covered with a perfluorinated ether, and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. Table 1 provides a summary of the crystallographic data for the structures of **1**−**5**. Data were collected using Oxford Diffraction Xcalibur 3 (**1**−**3** and **5**) and Xcalibur PX Ultra (**4**) diffractometers, and the structures were refined based on F^2 using the *SHELXTL* and *SHELX-97* program systems.[32] The THF molecules in **1** and **2** and the TMEDA molecules in **3** and **4** all exhibit some disorder in the crystal structures; see the Supporting Information for full details. The crystal structure data have been deposited with the Cambridge Crystallographic Data Center under deposition numbers CCDC 878883−878887. This material can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.

RESULTS AND DISCUSSION

The diethyl phosphonate esters ^{n}PrPO$_3$Et$_2$ and PhCH$_2$PO$_3$Et$_2$ were used in these reactions because of their commercial availability and lack of any additional functionalization. In both cases, reduction with LiAlH$_4$ in toluene (with rigorous exclusion of oxygen) gave conversions in 95+% yield to the corresponding primary phosphines (PhCH$_2$PH$_2$ or ^{n}PrPH$_2$). After an aqueous workup using a deoxygenated sodium sulfate solution under an atmosphere of nitrogen, the organic layer was separated (again under nitrogen) and dried to give a toluene solution of the phosphine. ^{31}P NMR studies on this solution showed clean formation of the primary phosphines in both cases (δ −122.5 and −139.9 for PhCH$_2$PH$_2$ and ^{n}PrPH$_2$ respectively), with no other phosphorus-containing species present. No further purification of the phosphine solutions was undertaken, thus avoiding any complications associated with the handling and storage of neat primary phosphines, which are often malodorous and pyrophoric.

Immediate reaction of the toluene solution of PhCH$_2$PH$_2$ with 2 equiv of ^{n}BuLi and $^3/_8$ equiv of elemental S$_8$ in the presence of TMEDA gave a mixture of products (Scheme 2),

Scheme 2. Synthesis of 1 and 2



showing that the reaction had not proceeded cleanly to the trithiophosphonate complex as desired. Two compounds were identified in the product mixture, the targeted trithiophosphonate **1** and tetrathiohypodiphosphonate **2** (^{31}P NMR in C$_6$D$_6$: δ 83.9 and 82.0, respectively), each of which was subsequently purified using differing crystallization conditions and charac-

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terized using single-crystal X-ray diffraction (see the Experimental Section).

X-ray structure elucidation reveals complex **1** to exist as a centrosymmetric dimer in the solid state in which each dianionic trithiophosphonate ligand bonds to three of the four lithium centers present via μ_3-η^2,η^2,η^2 coordination (Figure 1 and Table 2). Although observed in triselenophosphonate

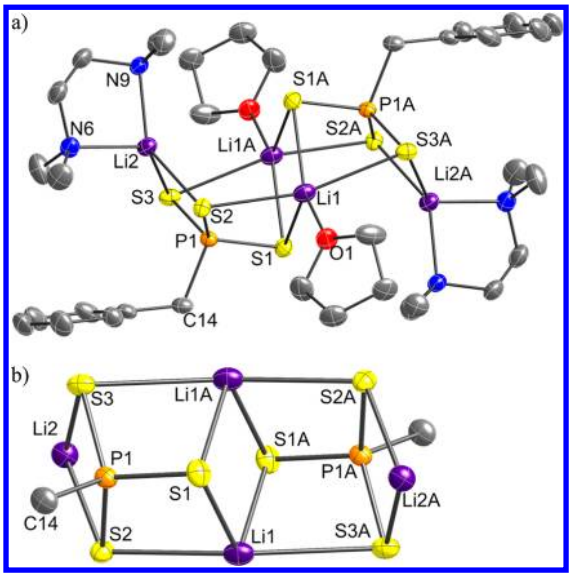

Figure 1. (a) Molecular structure of **1**, with hydrogen atoms and disorder in the THF molecules omitted for clarity. (b) Central core unit of **1**. Thermal ellipsoids are displayed at the 40% probability level.

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

P1−S1	2.0218(5)	Li1−S2	2.697(3)
P1−S2	2.0213(4)	Li1−S3A	2.854(3)
P1−S3	2.0153(5)	Li2−S2	2.445(2)
P1−C14	1.8464(14)	Li2−S3	2.462(2)
Li1−O1	2.001(2)	Li2−N6	2.093(3)
Li1−S1	2.529(3)	Li2−N9	2.107(3)
Li1−S1A	2.646(2)		
S2−P1−S1	112.34(2)	S1A−Li1−S3A	74.04(7)
S3−P1−S1	110.43(2)	O1−Li1−S2	95.29(10)
S3−P1−S2	111.30(2)	O1−Li1−S3A	92.24(10)
C14−P1−S1	104.90(5)	O1−Li1−S1A	152.12(13)
C14−P1−S2	108.14(5)	S2−Li1−S3A	166.05(10)
C14−P1−S3	109.47(5)	S2−Li2−S3	85.56(8)
S1−Li1−S1A	97.92(8)	S2−Li2−N6	113.20(11)
S1−Li1−S2	79.91(7)	S2−Li2−N9	137.83(12)
S1−Li1−S3A	108.55(9)	S3−Li2−N6	118.35(11)
O1−Li1−S1	109.54(11)	S3−Li2−N9	118.44(11)
S1A−Li1−S2	94.10(8)	N6−Li2−N9	86.66(10)

complexes,[33] this coordination mode is, to the best of our knowledge, previously undocumented for trithiophosphonate ligands. The phenyl groups are oriented such that the C14−C_{ipso} bond is anti to the P1−S1 bond. The central lithium atom, Li1, is coordinated by both trithiophosphonate ligands and is bridged to Li1A by S1 and S1A to give a SLiSLi four-membered ring. Li1 adopts a distorted square-pyramidal-based geometry (τ = 0.23),[34] with S1 in the apical position and the outward-facing basal coordination site occupied by a THF molecule. The other lithium atom, Li2, is coordinated by just one $[PhCH_2PS_3]^{2-}$ ligand and is additionally chelated by a TMEDA molecule, resulting in distorted tetrahedral geometry at the metal center.

Within complex **1**, the P−S bonds are intermediate in length between the expected P−S single (2.13 Å[35]) and double (1.88 Å[35]) bonds, suggesting delocalization of the double negative charge over the PS_3 group. Nonetheless, the phosphorus bond to S3 is marginally shorter at 2.0153(5) Å than those to S1 and S2, 2.0218(5) and 2.0213(4) Å, respectively. There is an associated variation in the S−Li bond lengths, with S3−Li2 being slightly longer than S2−Li2 [2.462(2) vs 2.445(2) Å] and S3−Li1A being longer than S1−Li1A [2.854(3) vs 2.646(2) Å]. The longer bonds to Li1 relative to Li2 are to be expected, given the differing coordination numbers of these metal centers (5 and 4, respectively).

X-ray structural studies on the other reaction product **2** reveal a monomeric tetrathiohypodiphosphonate complex (Figure 2 and Table 3). This complex is most likely formed

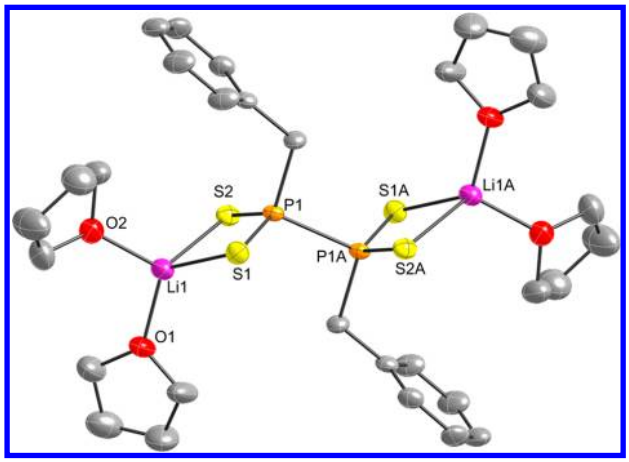

Figure 2. Molecular structure of one (**2-A**) of the two similar but independent C_i-symmetric complexes present in the crystals of **2**. Hydrogen atoms and disorder in the THF molecules are omitted for clarity. Thermal ellipsoids are displayed at the 40% probability level.

through condensation of two $PhCH_2PS_3Li_2$ species (present in **1**) with the elimination of lithium sulfide. A similar mechanism has been previously documented for the reaction of $[Al_2(S_2P(H)C_6H_{11})_2(S_3PC_6H_{11})_2]$ with ^{n}BuLi to give $[(C_6H_{11}P(S_2))_2Li_2(TMEDA)_2]$.[27]

The unit cell of **2** contains two independent complexes, **2-A** and **2-B**, both of which adopt the same structure with just minor variations in the bonding parameters (see Table 3). Within each complex, the $[PhCH_2P(S)_2P(S)_2CH_2Ph]^{2-}$ ligand coordinates the two metal centers in a doubly bidentate manner, with each PS_2 moiety chelating a lithium center to create two four-membered PSLiS rings. Two THF molecules also coordinate each lithium, resulting in a distorted tetrahedral geometry at the metal centers. Chelation of the lithium atoms by the PS_2 units is symmetrical with P1−S1 and P1−S2, and also Li1−S1 and Li1−S2, equal in length within experimental error. Further analysis of the P−S bond lengths in **2** [range 1.9888(10)−1.9927(11) Å] indicates complete delocalization of the single negative charge within the PS_2 unit. Notably, the formally higher bond order of the P−S bonds in **2** ($1^1/_2$) relative to those in **1** ($1^1/_3$) is reflected in their shorter bond lengths (mean 1.990 Å in **2** vs 2.019 Å in **1**). The P−P bond is rotated such that the benzyl groups are staggered with respect

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Complexes 2-A and 2-B Present in 2[a]

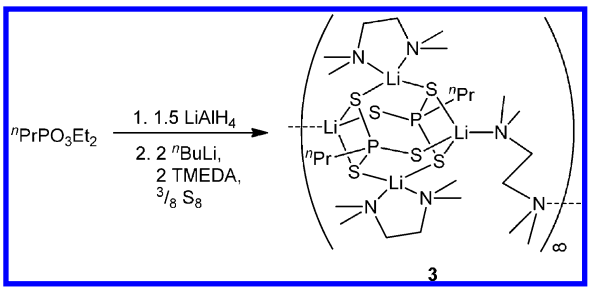
	2-A	2-B		2-A	2-B
P1−S1	1.9927(11)	1.9906(11)	Li1−S1	2.499(7)	2.500(6)
P1−S2	1.9896(11)	1.9888(10)	Li1−S2	2.500(7)	2.491(6)
P1−C11	1.842(3)	1.831(3)	Li1−O1	1.907(7)	1.929(6)
P1−P1A	2.2321(13)	2.2339(13)	Li1−O6	1.908(8)	1.931(6)
S1−P1−S2	114.87(5)	114.69(5)	P1−S2−Li1	80.41(16)	80.62(14)
S1−P1−C11	112.06(12)	111.77(11)	S1−Li1−S2	84.34(18)	84.35(16)
S1−P1−P1A	109.20(6)	109.26(5)	S1−Li1−O1	120.0(3)	118.8(3)
S2−P1−C11	111.19(11)	111.54(11)	S1−Li1−O6	115.7(5)	114.2(3)
S2−P1−P1A	108.97(6)	109.08(5)	S2−Li1−O1	119.1(4)	119.8(3)
C11−P1−P1A	99.39(10)	99.37(9)	S2−Li1−O6	112.2(4)	113.2(3)
P1−S1−Li1	80.36(17)	80.35(13)	O1−Li1−O6	105.0(4)	105.8(3)

[a]Phosphorus atoms labeled with an A are related to their parent atoms by a center of symmetry; full details of symmetry operations for **2-A** and **2-B** are given in the Supporting Information.

to one another. The "end-on" coordination mode observed in **2** is very different from the "side-on" coordination observed in tetrathiohypodiphosphonate $[(C_6H_{11}P(S_2))_2Li_2(TMEDA)_2]$,[27] in which two five-membered PPSLiS chelate rings are present, both of which include the P−P bond. To our knowledge, the only other example of similar "end-on" coordination as featured in **2** is in the tetraselenohypodiphosphonate complex $[(PhP(Se_2))_2Li_2(TMEDA)_2]$.[36]

Attempts to prepare the trithiophosphonate **1** in higher purity and yield by lowering the reaction temperature to −78 °C in order to minimize the occurrence of the condensation reaction proved unsuccessful, with ^{31}P NMR showing tetrathiohypodiphosphonate **2** to still be present in the product mixture in appreciable quantity. However, substitution of $PhCH_2PO_3Et_2$ with $^nPrPO_3Et_2$ did lead to an improvement in yield and purity with the trithiophosphonate **3** obtained in 20% yield as colorless crystals (Scheme 3). Nevertheless, even in this

Scheme 3. Synthesis of 3



case, a small quantity of insoluble red powder (<5% yield), thought to be the corresponding tetrathiohypodiphosphonate complex, was also formed in the reaction. Preparation of the homologous lithium triselenophosphonate ($^nPrPSe_3Li_2$) was also attempted via substitution of the sulfur reagent in Scheme 3 with elemental selenium; however, the reaction yielded a number of inseparable phosphorus- and selenium-containing products as determined by ^{31}P NMR, with the major product (δ 55.9) thought to be the tetraselenohypodisphosphonate $[(^nPrP(Se_2))_2Li_2]$.

X-ray diffraction experiments reveal **3** to form a polymeric chain in the solid state, comprising dimeric $[Li_2(S_3P^nPr)(TMEDA)]_2$ cages linked together by bridging bis(monodentate) TMEDA molecules (Figure 3 and Table 4). Independent centers of symmetry are present at the centers of the cage and the bridging TMEDA molecule. Within each dimeric cage, the $[^nPrPS_3]^{2-}$ trithiophosphonate ligands are staggered with respect to each other, with two ligand sulfur atoms, S1 and S2, each bridging two lithium centers and the remaining sulfur, S3, binding to a single lithium to give an overall μ_4-η^2,η^1,η^1,η^1-coordination mode. Both lithium environments within the structure are distorted tetrahedral: Li1 is coordinated to two sulfur and two nitrogen atoms from a chelating TMEDA molecule, while Li2 is coordinated by three sulfur and one nitrogen atoms from a bridging TMEDA molecule. All P−S bonds in **3** are of similar length and are intermediate between those expected for single and double P−S bonds, again suggesting charge delocalization (vide supra). However, the P1−S3 bond involving the nonbridging sulfur atom is, at 2.0113(6) Å, slightly shorter than the P1−S1 and P1−S2 bonds, 2.0406(6) and 2.0391(6) Å, which both involve bridging sulfur atoms. The difference in coordination modes of the sulfur atoms is also reflected in the S−Li bond lengths, with lithium bonds to S3 being slightly shorter than those to S1 and S2, 2.405(3) Å vs 2.427(3)−2.486(3) Å. Similar but discrete lithium trithiophosphonate dimer cages have previously been reported for $[Li_4(S_3PC_6H_{11})_2(THF)_2(TMEDA)_2]$ in which THF molecules can be considered to formally replace the bridging TMEDA molecules in **3**.[26]

A significant improvement to the reaction protocol was further realized by the replacement of ^{n}BuLi with $^nBu_2Mg$ as the organometallic agent. This change in the metallating agent resulted in inhibition of the condensation reaction (with no tetrathiohypodiphosphonate byproduct detected) and led to increased yields of the desired metal trithiophosphonate complex. In addition, using this protocol, it was also possible to prepare the homologous triselenophosphonate complex. Thus, magnesium trithiophosphonate and triselenophosphonate complexes **4** and **5**, respectively, were prepared from diethylphosphonate ester starting materials via a reaction protocol involving reduction with $LiAlH_4$ followed by a reaction with dibutylmagnesium and either elemental sulfur or selenium (Scheme 4).

Reduction of $^nPrP(O)(OEt)_2$ followed by treatment with 1 equiv of $^nBu_2Mg$ and $^3/_8$ equiv of S_8 in the presence of TMEDA gave **4** as a crystalline solid in 51% overall yield (^{31}P NMR in DMSO-d_6: δ 84.1). The yield of **4** from the phosphonate ester starting material is therefore directly comparable to that obtained for the only previously reported magnesium trithiophosphonate complex $[Mg(S_3PC_6H_{11})(THF)_2]_2$ (52%),

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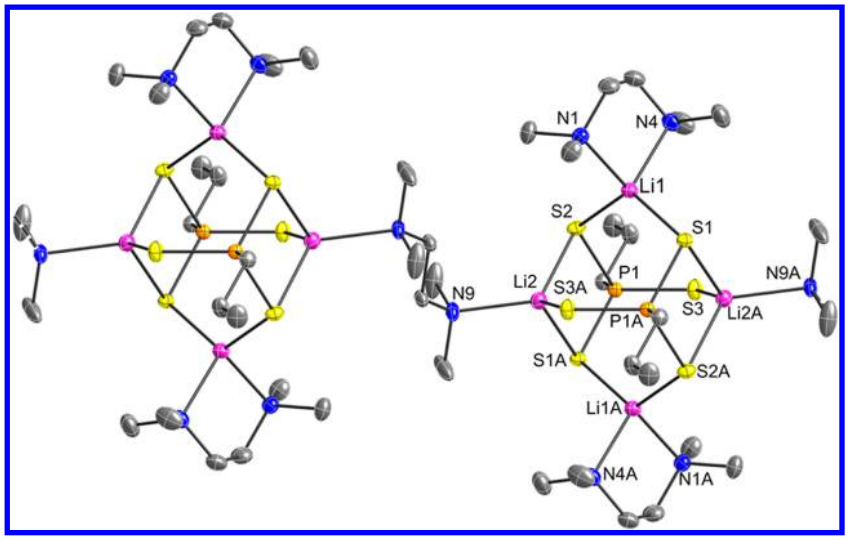
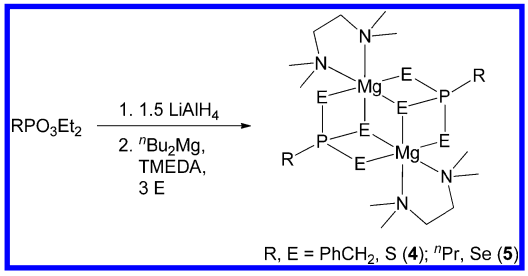


Figure 3. View of a section of the polymeric structure of **3**. Hydrogen atoms and disorder in the bridging TMEDA molecule are omitted for clarity. Thermal ellipsoids are displayed at the 40% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

P1−S1	2.0406(6)	Li2−S1	2.486(3)
P1−S2	2.0391(6)	Li2−S2	2.469(3)
P1−S3	2.0113(6)	Li2−S3A	2.405(3)
P1−C13	1.8242(16)	Li1−N1	2.117(3)
Li1−S1	2.444(3)	Li1−N4	2.123(3)
Li1−S2A	2.427(3)	Li2−N9	2.185(6)
S2−P1−S1	108.40(3)	P1−S1−Li1	109.83(8)
S3−P1−S1	115.40(3)	P1−S1−Li2	81.83(7)
S3−P1−S2	115.50(3)	P1−S2−Li2	82.28(8)
C13−P1−S1	105.03(6)	P1−S2−Li1A	110.52(8)
C13−P1−S2	105.46(6)	P1−S3−Li2A	114.01(8)
C13−P1−S3	106.01(6)		

Scheme 4. Synthesis of 4 and 5



formed in the much more direct reaction of $C_6H_{11}PH_2$ with $^nBu_2Mg$ and S_8.[26] Similarly, the reaction of a prepared toluene solution of $^nPrPH_2$ with 1 equiv of $^nBu_2Mg$ and 3 equiv of elemental gray selenium proceeded cleanly to give triselenophosphonate **5** in 37% overall yield [^{31}P NMR in DMSO-d_6 δ −18.5 ($^1J_{PSe}$ = −542 Hz)].

Following recrystallization from either THF (**4**) or dichloromethane (**5**), both trichalcogenophosphonates complexes were structurally characterized by single-crystal X-ray diffraction and shown to exhibit similar molecular structures in the solid state, forming dimeric aggregrates with comparable core bonding motifs (Figure 4 and Table 5).

Complexes **4** and **5** adopt C_i-symmetric dimeric structures, with two ligands bridging the two metal centers via μ_2-η^2,η^2 coordination. One chalcogen atom from each ligand coordinates to both metal centers, while the remaining two donors bind to a single magnesium only. The orientation of the ligands in both complexes is staggered with respect to one another, and in **4**, the orientation of the C1−C_{ipso} bond of the benzyl groups is anti to the P1−S3 bond. Chelating TMEDA molecules occupy the outward-facing coordination sites around the magnesium centers. Inspection of the P−E (E = S, Se) bond lengths in both complexes shows the bonds to the bridging chalcogens, S2 or Se2, to be longer than those involving nonbridging chalcogens [**4**, 2.0390(7) vs 2.0090(8) and 2.0181(8) Å; **5**, 2.1948(6) vs 2.1716(6) and 2.1720(6) Å]. Nevertheless, all P−E bonds are intermediate in length between the expected P−E single (P−S, 2.13 Å; P−Se 2.24 Å[35]) and double (P═S, 1.88 Å[35]; P═Se, 1.96 Å[35]) bond lengths, suggesting delocalization of the double negative charge over the PE_3 group similar to **1** and **3**. The Mg−E bond lengths also vary depending on the chalcogen atom environment, with magnesium distances to bridging chalcogens longer than those to the other chalcogens [**4**, 2.6811(9) and 2.6856(9) vs 2.5780(9) and 2.5899(9) Å; **5**, 2.8219(7) and 2.8383(7) vs 2.7297(7) and 2.7111(7) Å]. A comparable core structure, exhibiting similar variation in the P−E and E−Mg bond lengths, has also been observed in the THF-solvated magnesium trithiophosphonate $[Mg(S_3PPh)(THF)_2]_2$.[26]

^{31}P and ^{77}Se NMR spectroscopic studies on **5** in dimethyl sulfoxide (DMSO)-d_6 suggest that on the NMR time scale all of the selenium atoms are identical: only one doublet is observed in the ^{77}Se NMR spectrum, and one set of ^{77}Se satellites is observed in the ^{31}P NMR spectrum. A feasible explanation for this is the breakup of the complex in DMSO to give an ion-separated species comprised of a $[^nPrPSe_3]^{2-}$ anion and a solvated magnesium cation. The ^{31}P NMR signal for **5** is, at −18.5 ppm, within the range reported for triselenophosphonates (13.4[4] to −29.4[7] ppm). The $^1J_{PSe}$ coupling constant (−542 Hz) is, however, slightly larger than those previously reported for similar complexes (−477[25] to −504[7,33] Hz) but is still consistent with a P−Se bond order of $1^1/_3$ (which is indicative of complete charge delocalization over the PSe_3 moiety), being between values reported for P−Se single (−405 Hz)[37] and $1^1/_2$ bonds (−585 Hz).[25] The ^{77}Se NMR

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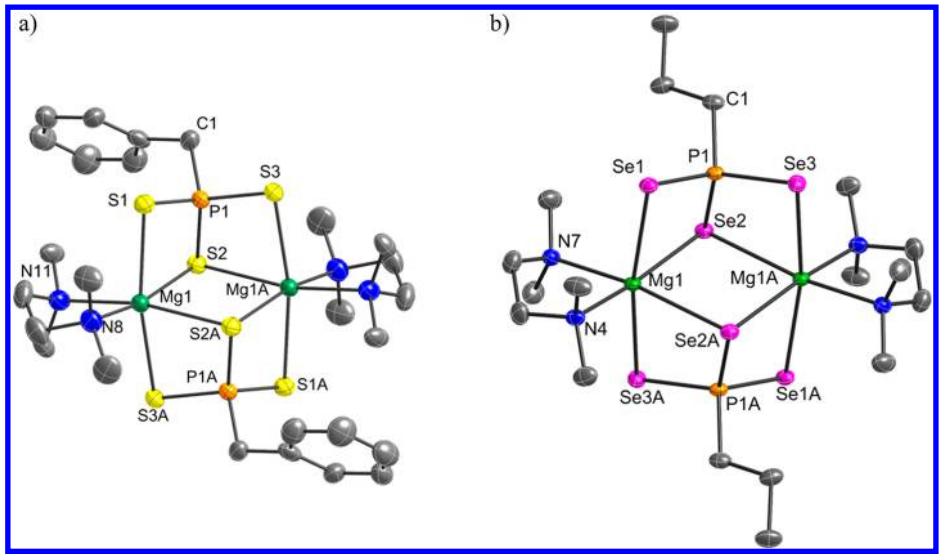

Figure 4. Molecular structures of (a) **4** and (b) **5**. Hydrogen atoms in **4** and **5** and disorder in the TMEDA molecule in **4** are omitted for clarity. Thermal ellipsoids are displayed at the 40% probability level.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4 and 5

	4 (E = S)	**5** (E = Se)		**4** (E = S)	**5** (E = Se)
P1–E1	2.0090(8)	2.1720(6)	E1–Mg1	2.5899(9)	2.7297(7)
P1–E3	2.0181(8)	2.1948(6)	E2–Mg1	2.6856(9)	2.8219(7)
P1–E2	2.0390(7)	2.1716(6)	E2–Mg1A	2.6811(9)	2.8383(7)
P1–C1	1.848(2)	1.821(2)	E3–Mg1A	2.5780(9)	2.7111(7)
E1–P1–E3	114.13(4)	113.48(3)	P1–E1–Mg1	86.43(3)	85.10(2)
E1–P1–E2	109.06(3)	109.84(2)	P1–E2–Mg1	83.32(3)	82.47(2)
E3–P1–E2	109.34(3)	109.04(2)	P1–E2–Mg1A	83.53(3)	82.08(2)
C1–P1–E1	109.27(9)	109.35(8)	P1–E3–Mg1A	86.67(3)	85.57(2)
C1–P1–E2	109.14(9)	109.71(8)			
C1–P1–E3	105.78(8)	105.33(7)			

spectrum shows a doublet signal at 353.6 ppm with $^{1}J_{SeP}$ = −542 Hz. This is consistent with chemical shift values reported for similar $[RPSe_3]^{2-}$ triselenophosphonate ligands: 166 (R = C_6H_{11})[25] and 364 (R = Ph)[7,33] ppm.

CONCLUDING REMARKS

This work has demonstrated a new synthetic route to metal trichalcogenophosphonates from readily available organophosphonate esters. An all-in-one protocol involving reduction of the organophosphonate ester using $LiAlH_4$ followed by an aqueous workup under nitrogen and immediate reaction with a metallating agent and elemental chalcogen gave the titled compounds. The use of *n*-butyllithium as the metallating agent yielded the lithium trithiophosphonate complexes **1** and **3**, although contamination from the tetrathiohypodiphosphonate condensation product (**2**) was evident. Switching from *n*-butyllithium to di-*n*-butylmagnesium as the metallating reagent avoided the formation of condensation byproducts, giving the trithiophosphonate **4** in moderate yield and also allowing access to the triselenophosphonate homologue **5**. Structures of metal trichalcogenophosphonates are still rare in the literature; thus, all four trichalcogenophosphonates in this paper have been structurally characterized and discussed.

Trichalcogenophonate materials are promising candidates for a range of future potential applications both as homologues to metal organophosphophosphonates and as phosphorus–chalcogen ligand systems in their own right. The synthetic protocol pioneered in this work will allow access to a wide range of new trichalcogenophosphonate systems with differing organo groups thanks to the commercial availability and easy accessibility of the organophosphonate ester starting materials. Work to prepare and exploit these materials is currently ongoing in our group.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and X-ray crystal structures of **1**–**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Clearfield, A. Metal Phosphonate Chemistry. *Progress in Inorganic Chemistry*; John Wiley & Sons, Inc.: New York, 2007; pp 371–510.
(2) Davies, R. P.; Chalcogen–Phosphorus (and Heavier Congeners) Chemistry. In *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*; Devillanova, F. A., Ed.; Royal Society of Chemistry: Cambridge, U.K., 2007; pp 286–343.
(3) Jones, R.; Williams, D. J.; Wood, P. T.; Woollins, J. D. *Polyhedron* **1987**, *6*, 539–542.
(4) Parkin, I. P.; Pilkington, M. J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Polyhedron* **1990**, *9*, 987–990.

(5) Foreman, M. R. S. J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 3653−3657.
(6) Wood, P. T.; Woollins, J. D. *Transition Met. Chem.* **1987**, *12*, 403−405.
(7) Shi, W.; Shafaei-Fallah, M.; Anson, C. E.; Rothenberger, A. *Dalton Trans.* **2006**, 2979−2983.
(8) Shi, W.; Shafaei-Fallah, M.; Anson, C. E.; Rothenberger, A. *Dalton Trans.* **2005**, 3909−3912.
(9) Kourkine, I. V.; Glueck, D. S. *Inorg. Chem.* **1997**, *36*, 5160−5164.
(10) Hahn, J.; Nataniel, T. *Z. Anorg. Allg. Chem.* **1986**, *543*, 7−21.
(11) Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Lomeli, V.; McBurnett, B. G. *Chem. Commun.* **1998**, 243−244.
(12) Zank, G. A.; Rauchfuss, T. B. *Organometallics* **1984**, *3*, 1191−1199.
(13) van Zyl, W. E.; Staples, R. J.; Fackler, J. P. *Inorg. Chem. Commun.* **1998**, *1*, 51−54.
(14) van Zyl, W. E.; López-de-Luzuriaga, J. M.; Mohamed, A. A.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* **2002**, *41*, 4579−4589.
(15) Cowley, A. H.; Hellert, D.; Gabbai, F. P.; Olbrich, F. *Inorg. Chem.* **1995**, *34*, 3127−3129.
(16) Henderson, W.; Kemmitt, R. D. W.; Mason, S.; Moore, M. R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1992**, 59−66.
(17) Slater, J. M.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1990**, 281−282.
(18) Preisenberger, M.; Pyykkö, P.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1999**, *38*, 5870−5875.
(19) Fluck, E.; Binder, H. *Z. Anorg. Allg. Chem.* **1970**, *377*, 298−&.
(20) Barrau, J.; Amine, M. E.; Rima, G.; Satgé, J. *Can. J. Chem.* **1986**, *64*, 615−620.
(21) Barrau, J.; Et, G. R.; Satge, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *54*, 23−29.
(22) Barrau, J.; Rima, G.; Satge, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *107*, 99−105.
(23) Fenske, D.; Rothenberger, A.; Fallah, M. S. *Z. Anorg. Allg. Chem.* **2004**, *630*, 943−947.
(24) Preisenberger, M.; Bauer, A.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 4753−4758.
(25) Davies, R. P.; Martinelli, M. G. *Inorg. Chem.* **2002**, *41*, 348−352.
(26) Bjernemose, J. K.; Davies, R. P.; Jurd, A. P. S.; Martinelli, M. G.; Raithby, P. R.; White, A. J. P. *Dalton Trans.* **2004**, 3169−3170.
(27) Davies, R. P.; Gimenez, M. A.; Patel, L.; White, A. J. P. *Dalton Trans.* **2008**, 5705−5707.
(28) Gali, H.; Prabhu, K. R.; Karra, S. R.; Katti, K. V. *J. Org. Chem.* **2000**, *65*, 676−680.
(29) Pillarsetty, N.; Raghuraman, K.; Barnes, C. L.; Katti, K. V. *J. Am. Chem. Soc.* **2004**, *127*, 331−336.
(30) Maier, L. D.; Peter, J.; Tebby, J. C. ^{31}P NMR of Three Coordinate ($\lambda^3\sigma^3$) Phosphorus Compounds Containing Phosphorus Bonds to Group IV Elements and Hydrogen Only. In *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1991; pp 121−176.
(31) Van Hooijdonk, M. C. J. M.; Gerritsen, G.; Brandsma, L. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *162*, 39−49.
(32) *SHELXTL PC*, version 5.1; Bruker AXS: Madison, WI, 1997. Sheldrick, G. *SHELC-97*; Institut Anorganische Chemie: Gottingen, Germany, 1998.
(33) Shi, W.; Shafaei-Fallah, M.; Zhang, L.; Anson, C. E.; Matern, E.; Rothenberger, A. *Chem.—Eur. J.* **2007**, *13*, 598−603.
(34) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.
(35) Corbridge, D. E. C. *Phosphorus World: Chemistry, Biochemistry and Technology*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005.
(36) Lux, K.; Eckstein, K.; Schön, O.; Karaghiosoff, K. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1208−1213.
(37) Parveen, S.; Kilian, P.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2006**, 2586−2590.