5-2017

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As submitted: Final article published in *Dalton Trans*. 2017, **46**, 9769 - 9776

Synthesis of Trithiobisphosphines by Oxidative Transfer of Phosphorus (I)

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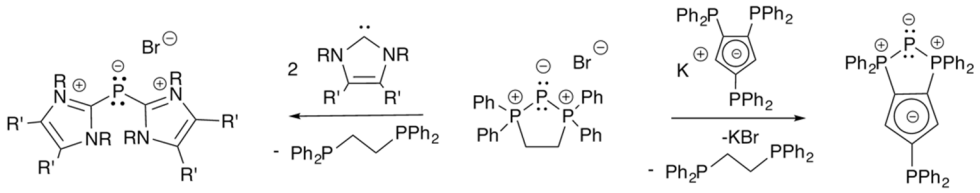
Abstract

The synthesis of novel trithiobisphosphines is achieved by oxidative addition of tetrathiocins to the phosphorus(I) reagent [P^{I}dppe][Br] in good yields under ambient conditions. These trithiobisphosphines and the related intermediate diphosphine species are characterized by X-ray diffraction and multinuclear NMR and a mechanism is proposed for the formation of these molecules.

Introduction

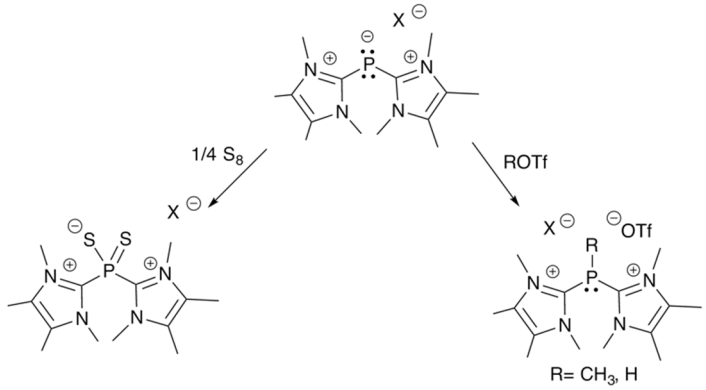
The chemistry of stable, low valent main group elements has been one of the principal themes underlying the renaissance of main group chemistry,[1,2] and – as part of this special collection in honour of the 100th anniversary of the Canadian Society for Chemistry – it is worth noting that many research groups in Canada have been at the forefront of such research.[3–8] Molecules containing elements in low valent and low oxidation states exhibit diverse, interesting, and sometimes unique patterns of reactivity and some of these compounds have proven useful in areas including: materials precursor chemistry, as ligands in coordination chemistry, organic synthesis, and catalysis.[5,9–18] Our research group amongst others has been investigating the isolation of stable compounds featuring low valent and low oxidation state group 13, 14 and 15 environments over the past decade.[19–21]

Typically, molecules containing low valent atoms are synthesized using protocols that include the use of harsh reagents such as strong reducing agents and bases. However, in several reports, we have described the facile generation of new molecules containing low-valent phosphorus(I) fragments *via* the versatile "P^+" transfer agent [P^Idppe][Br] (Scheme 1) through substitution of the diphenylphosphinoethane (dppe) molecule by a different set of ligands.[22–24] This approach has proven to be "P" atom efficient in many cases – the transfer of P^I atoms from the starting material is often quantitative – and no unnecessary or unexpected by-products are generated.[25]



Scheme 1. Synthesis of molecules containing a low valent phosphorus centre recently reported by our group using the P^+ transfer agent, [P^Idppe][Br].

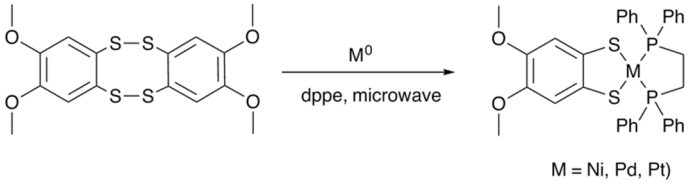
One of the most obvious potential reactivity patterns of low valent elements exploits their ability to undergo oxidation. In this context, we had previously demonstrated the oxidation chemistry of some of these P^I molecules by employing oxidants such as sulfur, methylating agents and acids (Scheme 2). These reactions selectively oxidize phosphorus(I) ions to yield phosphorus(III)- or phosphorus(V)-containing species.[26,27]



Scheme 2. Selected examples of oxidation reactions of a phosphorus(I) compound reported by our group.

Cognizant of the reactivity of P^I fragments towards oxidation and the ligand exchange chemistry of the [P^Idppe][Br] molecule, we reasoned that this compound should be capable of undergoing other oxidative addition reactions with or without loss of the chelating phosphine. Indeed we have previously noted that the concepts of cycloaddition and electron transfer can be used to rationalize the formation of *N*-heterocyclic phosphines and phosphenium species[28,29] *in a formal sense*, although the actual mechanism through which these compounds are actually formed does not likely involve any low-valent phosphorus intermediates.[30]

Recent work by Rawson and co-workers has included the investigation of the oxidative addition chemistry of 1,2,5,6-tetrathiocins to zero-valent group 10 metal complexes to afford a range of monometallic metal dithiolate complexes[21] (Scheme 3) as well as dimetallic and hexametallic clusters.[22] The tetrathiocin precursors are readily formed in multi-gram quantities[31] and the oxidative addition chemistry often occurs quantitatively by NMR with recovered crystalline yields up to 89% (Scheme 3).

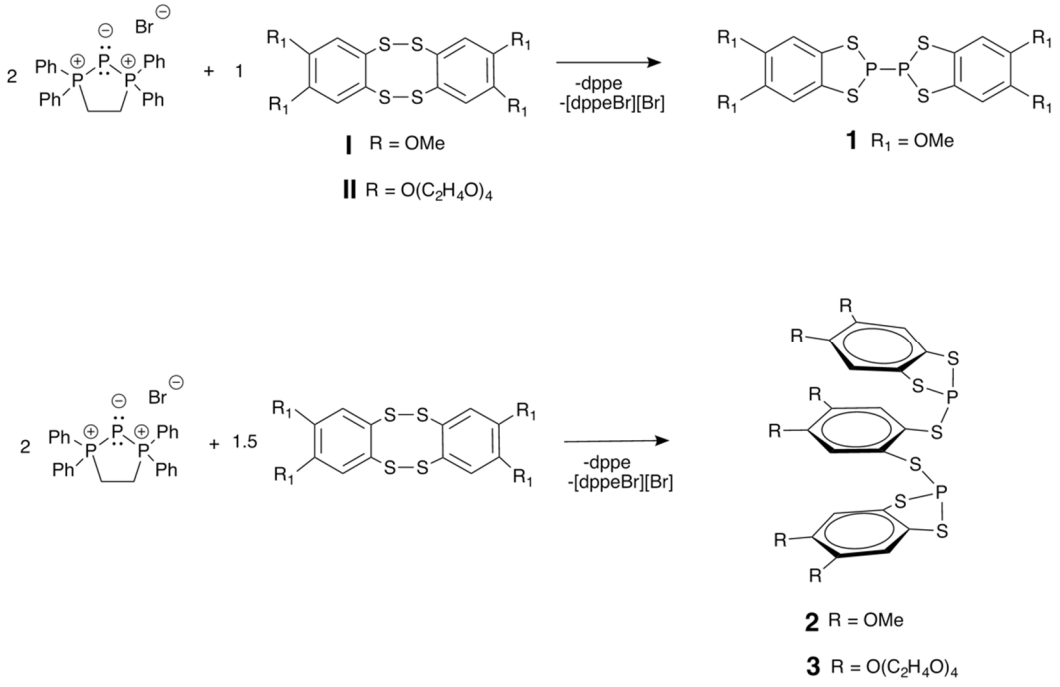


Scheme 3. Oxidative addition chemistry of tetrathiocins to zero valent group 10 metal complexes

In a collaborative effort, our groups have commenced an examination of such tetrathiocins as reagents with which to explore the oxidative addition chemistry to a range of low oxidation state complexes of main group elements. In the current work we describe our first foray into this area where we examine the oxidative addition of tetrathiocins to the phosphorus(I) transfer agent,

[P^{I}dppe][Br], to generate the benzo-dithiophosphinyl framework (Scheme 4, **1**) containing formal phosphorus(II) centres in addition to compounds **2** and **3** which feature formal phosphorus(III) environments. It should be noted that work on such benzo-fused C_2S_2P heterocycles was initially reported by Baudler[32] and subsequent studies by Burford focused on the structure and Lewis acidity of divalent benzodithiaphosphenium cations derived .[33–36]

Related classes of thiophosphines have been shown to have many industrial applications such as antioxidants for lubricants and oils,[37] and are traditionally synthesized from highly reactive and poisonous white phosphorus.[38] We reasoned that the use of our easily handled, air- and moisture stable phosphorus(I) sources coupled with the readily prepared tetrathiocins might provide a more convenient and safer route to such compounds.



Scheme 4. Oxidative addition chemistry of tetrathiocins to [P^{I}dppe][Br] to generate **1**, **2** and **3**.

Results & Discussion

The 1,2,5,6-tetrathiocin ring is a convenient source of 1,2-disulfides and can be prepared in multi-gram quantities from the treatment of electron-rich aromatics with S_2Cl_2 in acetic acid.

These molecules have proven successful in regard to oxidative addition reactions with various late transition metals.[39–42] In this context, we suspected that these soft donors would be excellent candidates for oxidative addition reactions to the phosphorus(I) fragment in [P^Idppe][Br].

The addition of bis(dimethoxybenzo)tetrathiocin (Scheme 4, **I**) with [P^Idppe][Br] was investigated initially using a stoichiometric ratio of 1:2, anticipating the formation of the *P*-bromo-benzo-1,3,2-dithiaphosphole. In spite of the low solubility of the tetrathiocins in most common laboratory solvents, the reactions proceeded smoothly within 1 – 2 hours in dichloromethane to produce a pale yellow solution. The progress of the reaction was followed using ^{31}P NMR spectroscopy. In each case, the signals corresponding to the starting material, [P^Idppe][Br], (δ 64 ppm (doublet), and -220 ppm (triplet)) decreased as the reaction proceeded and singlets corresponding to dppe (-12 ppm) and trace amounts of dppeS (+32 ppm) appeared alongside two other products at *ca.* 50 ppm and 120 ppm. The singlet at *ca*. 50 ppm is comparable to those of other tetrathiodiphosphines reported by both Woollins[43] and Rawson[44] which feature ^{31}P NMR resonances in the 40 – 70 ppm region and were tentatively assigned to the coupled product **1**. The major product **2** at 120 ppm was more difficult to attribute. *Post facto* analysis, however, showed that the 120 ppm peak observed for **2** was in good agreement with that predicted based on ^{31}P NMR chemicals shift correlations for C_2S_2P-X systems (*ca*. 161 ppm). Confirmation of the structure of **1** and unambiguous identification of **2** were made on the basis of single crystal X-ray diffraction studies of crystals grown from the slow evaporation of the dichloromethane reaction mixture.

Compound **1** crystalizes in the monoclinic space group $P2_1/c$ with half a molecule in the asymmetric unit (Fig. 1). The P-P distance, 2.2350(16) Å is indicative of a single bond, and is well within the typical range (2.22 – 2.27 Å) observed for P-P bonds in other diphosphines.[45] It is

indistinguishable from the only other reported dithiaphosphinyl dimer (2.2306(13)) and the only other example of a diphosphine bearing organosulfur substituents.[43] The P-S bond lengths [2.1017(11) Å and 2.1110(11) Å] fall in the range of reported bond lengths for P-S single bonds within the Cambridge Structural Database (CSD)[46] (1.90 – 2.66 Å). The S-P-S angle of 95.90(4)° is also unexceptional. The C-C bond lengths within the carbocycles of the molecule range from 1.378(4)-1.411(4) Å and are consistent with the presence of an aromatic system, rather than a more diene-like system (which would suggest non-innocent behavior of the ligand). The heterocyclic ring in **1** is non-planar with a slight envelope effect observed such that the C_6S_2 and S_2P mean planes form a fold angle of 31.1°, similar to that observed in the parent derivative, $(C_6H_4S_2P)_2$ (33.03°).[44]

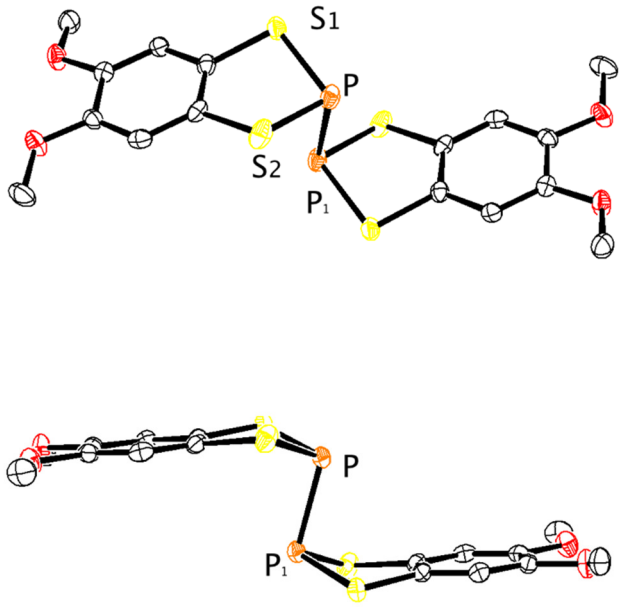


Figure 1. Thermal ellipsoid plot of **1,** hydrogen atoms omitted for clarity and ellipsoids drawn at 50% probability. The top down (top) and side on (bottom) views are depicted. Selected bond lengths (Å) and angles (°): P-P^1: 2.2350(16), P-S_1: 2.1017(11), P-S_2: 2.1110(11), S1-P-S2: 95.90(4).

We repeated the reaction with the appropriate stoichiometry (tetrathiocin:[P^{I}dppe]Br = 1.5:2) to prevent excess [P^{I}dppe][Br] remaining in the reaction, and monitored the reaction by ^{31}P

NMR spectroscopy. In this case, the reaction proceeds to completion relatively quickly (within 1 – 2 hours depending on the amounts of the reagents used) and affords **2** as the major product. The ^{31}P NMR spectrum of the reaction mixture contains a singlet at 120 ppm corresponding to **2**, as well as a mixture of by-products, mainly [dppeBr][Br],[47] dppeS_2(C_6H_2(OMe)$_2$), and dppe. The product was isolated by adding an equal volume of diethyl ether to the CH_2Cl_2 reaction mixture and cooling the mixture to -20° C overnight to precipitate by-products. The remaining CH_2Cl_2/Et_2O solution was decanted and left to crystalize by slow evaporation. This method was the only convenient protocol for the purification and isolation of **2** in analytically pure form and all characterization and further chemistry involving compound **2** was conducted with crystalline material obtained in that manner. We were able to confirm the formation of dppeS_2(C_6H_2(OMe)$_2$)- *i.e* the product of the addition of half an equivalent of tetrathiocin to one molecule of dppe- by adding the bis(dimethoxybenzo)tetrathiocin ligand to dppe as an NMR scale reaction. This reaction proceeds overnight to form dppeS_2(C_6H_2(OMe)$_2$) as the sole product observed apart from some remaining dppe (δ 56 ppm, SI Fig 16).

Compound **2** crystallizes in the space group $P2_1/c$ with one molecule and two dichloromethane solvent molecules in the asymmetric unit. The structure of **2** comprises two C_2S_2P heterocycles linked *via* a 1,2-dithiolate bridge (Fig. 2). The compound adopts a step-like structure featuring π-π stacking of the electron-rich dimethoxybenzo groups such that the centroid···centroid distances are 3.4490(18) Å. The P-S bond distances within the heterocycle range from 2.1095(10)-2.1152(10) Å and are essentially identical, within experimental error, to the lengths described above for **1**. In contrast, the P-S bond lengths within the "bridging" thiocin moiety are significantly longer – ranging from 2.1425(10) Å to 2.1527(10) Å – which might be a

consequence of hyperconjugation within the terminal phosphine fragments of the kind that has been described for analogous phosphorus heterocycles.[48] The S-P-S angles are similar to those in diphosphine **1** and range from 94.58(4)-94.43(4)°.

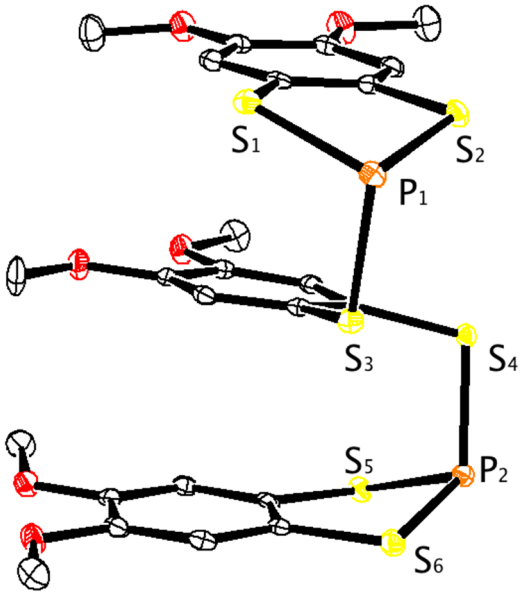


Figure 2. Thermal ellipsoid plot of **2**, hydrogen atoms and solvent molecules omitted for clarity and ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): P1-S1: 2.1151(10), P1-S2: 2.1095(10), P-S3: 2.1527(10), P2-S4: 2.1425(10), P2-S5: 2.1152(10), P2-S6: 2.1112(10), S1-P1-S2: 94.58(4), S5-P2-S6: 94.43(4).

There is a single crystallographically characterized example analogous to **2**, reported by Finder *et al.* which features an ethylene dithiione linker between C_2S_2P heterocycles. The P-S bond lengths in that complex, which range from 2.102 to 2.126 Å, are consistent with those in **2** and the S-P-S angle of 95.5° is also similar.[49] Notably, a handful other examples of related structures in which P is replaced by heavier group 15 elements (As, Sb, Bi) have been described[50,51,52] but this structural motif is surprisingly rare.

The reaction of [P^{I}dppe][Br] with the dibenzo-15-crown-5-functionalized tetrathiocin Scheme 4, II) under identical conditions (1.5:2 mole ratio) yielded the analogous molecule, **3**. The ^{31}P NMR spectrum of the reaction mixture features a dominant signal at a similar frequency (+119 ppm) to **2**, and also features additional signals indicative of the anticipated by-products of the reaction. Product **3** can be isolated as crystalline material by washing the material with diethyl ether, using the same methodology employed for **2** (*vide supra*). Compound **3** crystalizes in the triclinic space group *P*-1 with one molecule in the asymmetric unit (Fig. 3). The P-S bond distances within the structure are similar to the analogous distances in compound **2**, and range from 2.111(2) – 2.133(2) Å, but in contrast to the methoxy-substituted variant, the P-S lengths *exo* to the heterocycle are not significantly longer than the heterocyclic P-S bonds.

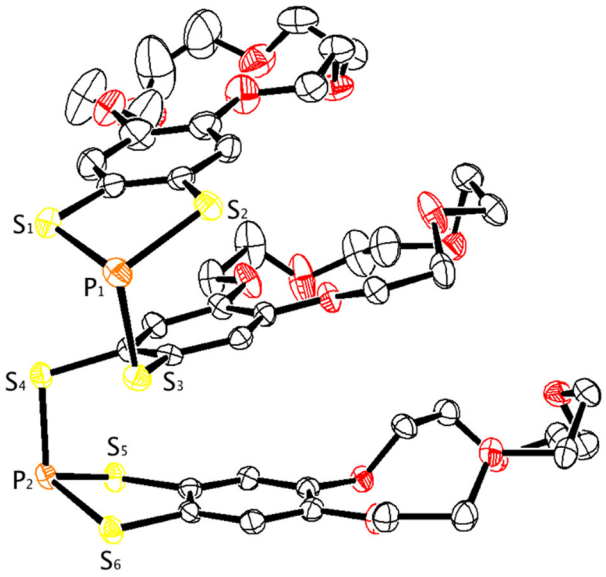
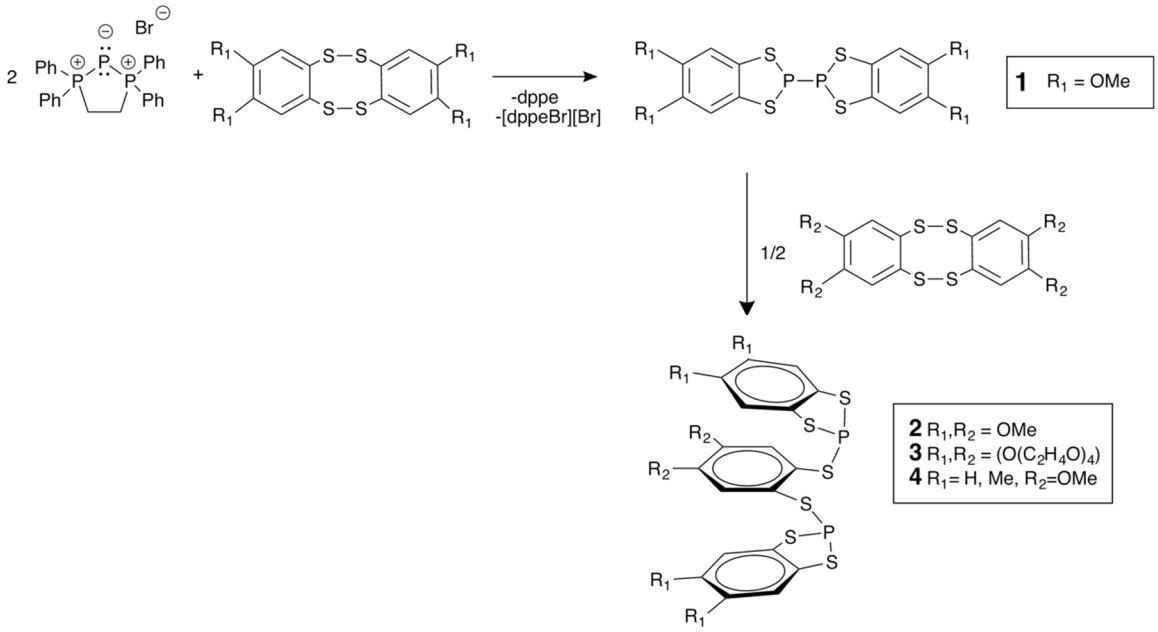


Figure 3. Thermal ellipsoid plot of **3**, hydrogen atoms omitted for clarity and ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): P1-S1: 2.1117(2), P1-S2: 2.111(2), P-S3: 2.118(2), P2-S4: 2.133(2), P2-S5: 2.112(2), P2-S6: 2.116(2), S1-P1-S2: 94.24(8), S5-P2-S6: 94.44(9).

All of our attempts to isolate tetrathiodiphopsphines such as **1** as the sole product, either by using the slow addition of tetrathiocin to [P^{I}dppe][Br], by washing the reaction mixture containing excess [P^{I}dppe][Br], or with decreased reaction temperatures have proven unsuccessful

to date. Regardless of the stoichiometry or conditions employed in the reaction, we observe the selective formation of compound **2** or **3**, while the appropriate intermediate diphosphine **1** can be identified while following the reaction progress by ^{31}P NMR spectroscopy. In our hands, this diphosphine is only able to be isolated as single crystals grown from reactions containing excess [P^{I}dppe][Br]. This observation suggests that the tetrathiocin initially undergoes oxidative addition to the P^{I} centre followed by a dimerization with the formal elimination of Br_2 to generate the diphosphine **1**. Although $C_6H_4S_2PBr$ has been identified as a stable product from oxidation of $(C_6H_4S_2P)_2$, the presence of electron donating alkoxy groups may promote such disproportionation reactions. The diphosphine **1** can then react with additional tetrathiocin to form **2** (Scheme 5). Our inability to isolate intermediate **1** as the major product suggests that the kinetics of the subsequent addition process are at least comparable with the initial rate of formation of **1**. In an effort to substantiate this mechanistic hypothesis, we treated half an equivalent of the bis(dimethoxybenzo)tetrathiocin with a sample of $(MeC_6H_3S_2P)_2$ (prepared using an alternative procedure) in dichloromethane. Previous studies indicate this diphosphine undergoes facile oxidation with even milder oxidants such as I_2.[44] The reaction mixture was left to stir for several hours until completion as identified by the disappearance of the solid reagent in the reaction flask. Analysis of the reaction mixture using ^{31}P NMR revealed the absence of starting material (δ 40 ppm) and observation of a new singlet at *ca.* 115 ppm, consistent with formation of the bridged species **4** (Scheme 5).



Scheme 5. Reaction of [P^{I}dppe][Br] and a substituted tetrathiocin to generate diphosphine **1**. Subsequent addition of tetrathiocin generates the bis-trithiophosphines **2** – **4**.

To further investigate the observed oxidative additions of disulfide ligands with [P^{I}dppe][Br], we treated the "P^{+}" reagent with diphenyl disulfide in both 1:1 and 2:1 stoichiometric ratios of disulfide:[P^{I}dppe][Br] in an effort to generate acyclic analogs of compounds **1-3**. We posited that the 1:1 mixture would generate an analogous diphosphine (*i.e.* $(PhS)_2P\text{-}P(SPh)_2$) either selectively, or as an intermediate, however there was no evidence for the formation of this diphosphine during the reaction by ^{31}P NMR. Instead, we observed exclusively the generation of the known tris(phenylthio)phosphine[53] (132 ppm) and the by-product [dppe(SPh)][Br] (55 ppm). The observation of the former suggests that, assuming a similar mechanistic pathway, that the oxidative addition of the disulfide to the diphosphine $(PhS)_2P\text{-}P(SPh)_2$ is considerably more rapid than in the case of the tetrathiocin chemistry. One explanation might be the poor solubility of tetrathiocin which could potentially slow the final step to form the bridged compound.

Based on the required 2:1 (disulfide: [P^{I}dppe][Br]) stoichiometry to form $(PhS)_3P$, it was unsurprising that the 1:1 stoichiometric reaction left additional unreacted starting material -

[P^Idppe][Br]- evidenced by the signals at 65 ppm (d) and -225 ppm (t). However, the reaction of a 2:1 ratio of disulfide to [P^Idppe][Br] results in the selective formation of tris(phenylthio)phosphine, and the by-product, [dppe(SPh)][Br]. During the progress of the reaction, the intermediate phosphonium salt [dppe(SPh)][Br] is visible in the ^{31}P NMR spectrum (doublets at -55 ppm and -11 ppm, $^3J_{p\text{-}p}$= 95 Hz) (Fig. 4). However, upon completion, only [dppe$(SPh)_2$][$Br]_2$ and dppe are observed. There are also small peaks at *ca.* 40 ppm and 85 ppm that appear upon consumption of [P^Idppe][Br], which do not correspond to the expected dimer, or the bromodithiophosphine, Ph_2S_2PBr, (150-180 ppm); to date, we have been unable to identify these minor products. Typically tris(phenylthio) phosphine is synthesized from the reaction of $PhSPCl_2$ and thiophenol,[53] however we present this as an alternative synthetic approach to obtain thiophosphines, particularly where the corresponding disulfides are readily available. This phosphine can easily be isolated by extraction with non-polar solvents such as hexanes or pentane from the reaction mixture also containing dppe and [dppeSPh][Br].

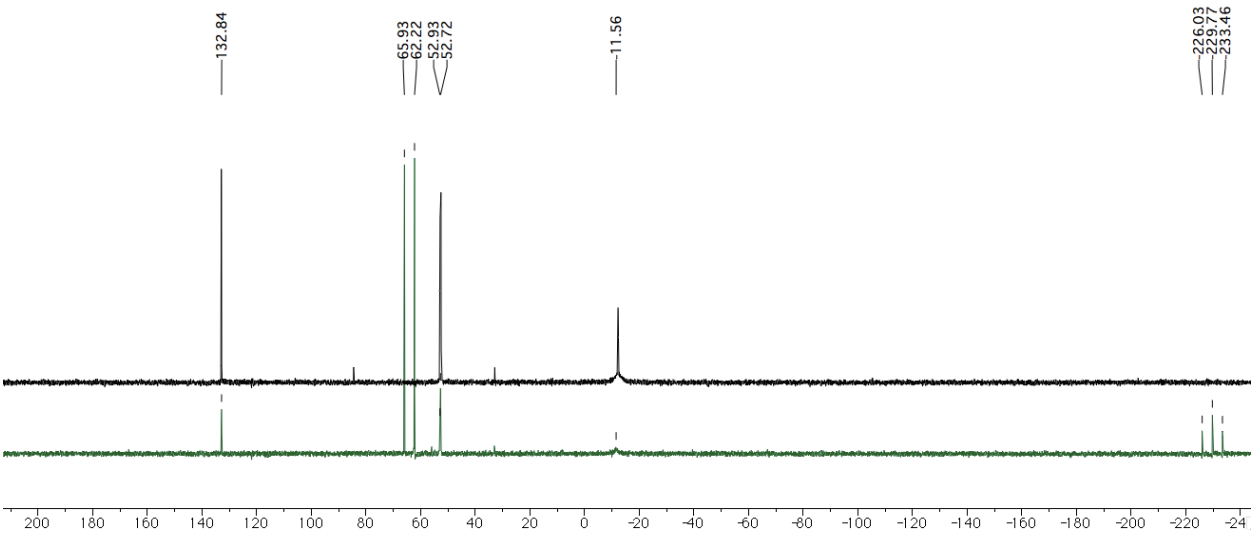


Figure 4. ^{31}P NMR of the reaction of 1:1 (bottom) and 2:1 (top) diphenyl disulfide:[P^{I}dppe][Br]. The product, tris(phenylthio)phosphine appears at 132 ppm, the by-product [dppeSPh][Br] at 53 ppm and dppe at -11 ppm. In the bottom spectrum, some of the starting material, [P^{I}dppe][Br], remains (65 ppm (d) and -229 ppm (t)).

With our more convenient preparation of these types of phosphines, experiments are on-going to assess the donor ability of these molecules for the coordination of metals, as these trithiobisphosphine molecules can potentially be used as multidentate donors, featuring both hard and soft donor sites. In this context it is worth noting the bimetallic gold(I) complex in which the related ligand$\{(CH_2)_2S_2P\}SCH_2CH_2S\{PS_2(CH_2)_2\}$ coordinates to two AuC_6F_5 groups through the two phosphine centres.[54]

Conclusion

We have synthesized and characterized a new series of bis-trithiophosphines through the oxidative addition of tetrathiocins with the P^+ transfer agent, [P^{I}dppe][Br]. The isolation of the intermediate- diphosphine (**1)-** during this reaction, coupled with the stoichiometric reaction of an isolated diphosphine with tetrathiocin to form the bis-trithiophosphine provides insight into the mechanistic pathway for formation of these bis-trithiophosphines which therefore appears to

progress through a formal sequence of oxidation steps from P^{I} to P^{II} to P^{III}. The use of ^{31}P NMR to track the progress of the reaction coupled with single crystal X-ray diffraction was used to characterize these unusual bis-trithiophosphine compounds, as well as identify the reaction intermediate. The analogous reactions of [P^{I}dppe][Br] with acyclic disulfides leads directly to the useful phosphorus tris(thiolates) with no evidence for diphosphine intermediates. Further studies are on-going to evaluate the propensity of these molecule for the coordination of metals, or the generation of stable radicals.

Acknowledgements

S.C.K thanks Justin Wrixon and Zeinab Ahmed of the Rawson research group for providing tetrathiocin. CLBM and JMR thank NSERC and CFI for generous financial support.

Experimental

General Procedures

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried according to literature procedures when necessary, and all other solvents were dried over a series of Grubbs'-type columns and degassed prior to use. The ligands, 1, 2- methoxy-tetrathiocin and benzo-15-crown-5-tetrathiocin were synthesized according to literature procedures.[55] NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz or Bruker Avance Ultrashield 300 MHz spectrometer. Chemical shifts are reported in ppm relative to internal standards for ^{1}H and ^{13}C (for the given deuterated solvent) and external standard for ^{31}P (85% H_3PO_4 = 0 ppm). Elemental Analysis was performed at the University of Windsor using a Perkin Elmer 2400 combustion CHN analyser.

Crystallographic Details

Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXIII software suite[56] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK_α radiation ($\lambda = 0.71073$ Å). For each sample, data were collected at low temperature. APEXIII software was used for data reductions and SADABS[57] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX[58] software suite as implemented in the WinGX[59] program suites. Validation of the structures was conducted using PLATON.[60] Details are provided in Table 1.

Specific Procedures

Isolation of the reaction Intermediate: 1

1,2-dimethoxy-tetrathiocin (0.150 g, 0.374 mol, 1 eq) and [P^Idppe][Br] (0.381g, 0.749 mol, 2 eq) were added together in a Schlenk flask to which 15 mL of dichloromethane was added. Upon addition, a cloudy yellow solution appeared as the tetrathiocin is insoluble in DCM. The reaction was left to stir for several hours until a clear yellow solution was obtained. The solution was placed under reduced pressure until a yellow oil remained. Storage of a concentrated DCM solution of this mixture yielded pale yellow single crystals of **1** (in addition to colourless crystals of dppe and [P^Idppe][Br]). As indicated in the text, we were fortunate enough to isolate this molecule as single crystals from a reaction mixture, and all our subsequent attempts to isolate this reaction intermediate have been unsuccessful.

Synthesis of 2

1,2-dimethoxybenzotetrathiocin (0.267g, 0.67 mol, 1.5 eq) and [P^Idppe][Br] (0.438g, 0.86 mol, 2 eq) were loaded into a Schlenk flask, to which 25 mL of dichloromethane (DCM) was added. The resulting cloudy yellow was left to stir until a clear yellow solution was obtained after about 1hr. The DCM was removed under reduced pressure and the resulting oil was redissolved in 5 mL of DCM and 15 mL of diethyl ether was added. The solution was then left at -30 °C overnight to aid in the precipitation of by-products. This washing procedure was repeated until no by-products remained. The resulting pale yellow solution

was collected and left for slow evaporation to afford yellow single crystals (Isolated Yield 0.170g, 60%). **$^{31}P\{^{1}H\}$ NMR** (CD_3CN): 120.9 (s) **^{1}H NMR** (CD_3CN): δ 6.92 (s, 3H, *Ar*), 6.83 (s, 3H, *Ar*), 3.76 (s, 18H O*CH₃*); **$^{13}C\{^{1}H\}$ NMR** (CD_2Cl_2) δ 149.3-108 ppm (s, aromatic), 56.1 ppm (s, O*C*H_3). **Anal. Calcd for**:$C_{24}H_{24}O_6S_6P_2$: C, 43.49; H, 3.65; N, 0; found: C, 43.0; H 3.73, N, -0.01.

Synthesis of 3. Benzo 15-crown-5- tetrathiocin (0.100g, 0.151 mol) and [P^{I}dppe][Br] (0.077g, 0.151 mol) were added together under an inert atmosphere and left to stir in approximately 15mL of dichloromethane. Upon addition of dichloromethane, a cloudy yellow solution initially appeared which cleared on stirring for approximately 1 hr to afford a clear yellow solution. The yellow solution was concentrated and 5 mL of diethyl ether was added. The solution was stored at -30 °C to form a white precipitate, a mixture of: [dppeS_2(O(C_2H_4O)$_4$)], and dppe, identified by ^{31}P NMR. The remaining yellow solution was decanted and pale single crystals were obtained via slow evaporation of this concentrated solution. (Isolated Yield 0.083g 52%) δ **$^{31}P\{^{1}H\}$ NMR** ($CDCl_3$): 122.7ppm (s). **^{1}H NMR** ($CDCl_3$): δ 6.9-7.1 (m, 2 H, Ar), 4.18 (*m,* 4H, $C_{10}H_{16}O_5$), 3.97 (*s,* 4H, $C_{10}H_{16}O_5$), 3.8 (s, 8 H, $C_{10}H_{16}O_5$); **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$) δ 149 (s, Ar (*C*-O)), 121(s, Ar *C*-S), 114 (s, Ar *C*-H), 69-71 (s, $C_{10}H_{16}O_5$) **Anal. Calcd for**:$C_{42}H_{54}O_{15}S_6P_2$•3/2 CH_2Cl_2: C, 44.25; H, 4.87; N, 0; found: C, 43.99; H, 5.01; N, 0.03. The presence of CH_2Cl_2 was confirmed by ^{1}H NMR (SI Fig 5)

Synthesis of 4. To a Schlenk flask containing 4′-methyl-1,3,2-benzodithiaphosphole (0.083g, 0.022 mol) was added half of an equivalent of 1,2-dimethoxybenzotetrathiocin (0.045g, 0.112 mol) suspended in 15 mL of dichloromethane. Upon addition of DCM, a cloudy yellow solution resulted which was left to stir for approximately 1 hr to afford a clear yellow solution. The reaction was quantitative by ^{31}P NMR. (Isolated Yield 0.0436 g, 77%). **$^{31}P\{^{1}H\}$ NMR** ($CDCl_3$): δ 111, 113, 114 ppm (s) **^{1}H NMR** ($CDCl_3$): δ 128-136 ppm (*Ar*), 55.8 ppm (s, O*C*H_3), 20.5 (s, CH_3) **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$) δ 149 (s, Ar (*C*-O)), 137-111 (s, Ar), 56.1 ppm (s, O*C*H_3), 20.5 ppm (s, *C*H_3). **Anal. Calcd for**: $C_{20}H_{16}O_2S_6P_2$ C, 44.26; H, 2.97; N, 0; found: C, 44.69; H, 3.19; N, 0.05.

Synthesis of Tris(phenylthio)phosphine

To a dichloromethane solution of [P^{I}dppe][Br] (0.100 g, 0.196 mmol) was added diphenyl disulfide (0.085 g, 0.392 mmol). The mixture was left to stir for approximately 1 hr during which time it became pale yellow. ^{31}P NMR confirmed the generation of tris(phenylthio)phosphine as well as the necessary by-product, [dppeSPh][Br]. The product was isolated by extraction with pentane. The pentane was removed to afford a white precipitate. (0.063g, 90%) **^{31}P{^{1}H} NMR** ($CDCl_3$): δ 132.9 (s, ***P***$(SPh)_3$, **^{1}H NMR** ($CDCl_3$): δ 7.05-8.17 (m, *Ar*), **^{13}C{^{1}H} NMR** ($CDCl_3$) δ 128.5-136.9 (s, *Ar*)

Table 1: Summary of Crystallographic Data

Compound	**1**	**2**	**3**
CCDC	1543742	1543743	1543744
Empirical formula	$C_{16}H_{16}O_4P_2S_4$	$C_{26}H_{28}Cl_4O_6P_2S_6$	$C_{42}H_{54}O_{15}P_2S_6$
Formula weight	462.47	832.58	1053.15
Temperature/K	172.8	100(2)	170(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	11.6592(5)	10.0951(3)	8.3950(13)
b/Å	8.9815(4)	25.1596(8)	14.979(2)
c/Å	10.3322(5)	14.0295(4)	19.671(3)
α/°	90	90	85.760(6)
β/°	115.786(2)	1063.6580(10)	78.209(5)
γ/°	90	90	74.703(6)
Volume/Å^3	974.22(8)	3462.57(18)	2335.1(6)
Z	2	4	2
ρ_{calc} / g/cm^3	1.577	1.597	1.498
μ/mm^{-1}	0.672	0.836	0.430
F(000)	467	1704.0	1104.0
Crystal size/mm^3	0.145 × 0.11 × 0.051	0.5× 0.4 × 0.3	0.361 × 0.329 × 0.208
2θ range for data collection/°	5.97 to 54.986	5.704 to 52.84	5.156 to 54.998
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -13≤ l ≤ 13	-12 ≤ h ≤ 12, -31≤ k ≤ 31, -17≤ l ≤ 17	-10 ≤ h ≤ 10 -19 ≤ k ≤ 19, -25≤ l ≤ 25
Reflections collected	11795	91341	54870
Independent reflections	2233 [R_{int} = 0.0646]	7103 [R_{int} = 0.0884]	9698 [R_{int} = 0.0419
Data/restraints/parameters	2233/ 0 / 120	7103/ 0 / 403	9698/ 84 / 642
Goodness-of-fit on F^2	1.035	1.129	1.186
Final R indexes [I>=2σ (I)]	R_1 = 0.0434 wR_2 = 0.0871	R_1 = 0.0413 wR_2 = 0.0834	R_1 = 0.0847 wR_2 = 0.2164
Final R indexes [all data]	R_1 = 0.0718 wR_2 = 0.0980	R_1 = 0.0563 wR_2 = 0.0894	R_1 = 0.1098, wR_2 = 0.2352
Largest diff. peak/hole / e Å-3	0.79/-0.37	0.76/-0.73	1.42/-0.85
Refinement method	Full-matrix least-squares on F^2		
Data completeness	1.00	0.997	0.904

$R_1 = \Sigma(|Fo| - |Fc|) / \Sigma F_o$, $wR2 = [\Sigma(\mathbf{w}(F_o^2 - F_c^2)^2) / \Sigma(\mathbf{w}F_o^4)]$., GOF = $[\Sigma(\mathbf{w}(F_o^2-F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.

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