Phosphine-Mediated Cleavage of Sulfur−Sulfur Bonds

Phuong M. Tran, Yuzhong Wang, Yaoming Xie, Pingrong Wei, Mitchell E. Lahm, Henry F. Schaefer III, and Gregory H. Robinson*

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ABSTRACT: A series of phosphine-mediated reactions resulting in the cleavage of sulfur−sulfur bonds in the imidazole-based dithione dimer (**1**) have been investigated. **2**, the first X-ray structurally characterized 1,2,5-trithiepin, was synthesized through triphenylphosphine-mediated thermal extrusion of sulfur from **1**. While reaction of **1** with $P(NMe_2)_3$ gave a zwitterionic phosphine−dithiolene complex (**3**), through heterolytic cleavage of the sulfur−sulfur bonds in **1**, the thiophosphonate **4** was obtained when $P(OMe)_3$ was combined with **1**. Reaction of **2** with NHC^{iPr} produced **5**, containing a unique $S^+−C≡C−S−C=C−S^-$ zwitterionic core.
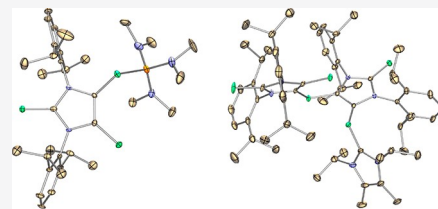
From biological systems to fundamental organic syntheses, the cleavage of sulfur−sulfur bonds has received considerable attention from disparate fields.[1−3] For instance, the enzyme thiolate has been shown to repair misconnected disulfides in polypeptides, *in vivo*, through a thiol−disulfide interchange process,[4] while transition metal complexes can catalyze addition of disulfides to alkenes and alkynes.[2] Beyond transition metals,[2,5] main group element-based nucleophiles and electrophiles have also played a remarkable role in this field.[1,3,6−9] Phosphine,[1,10,11] phosphine/H_2O,[12−17] or phosphine-based frustrated Lewis pairs (FLPs)[18] molecular systems have been studied regarding the cleavage of sulfur−sulfur bonds. Inspired by carbene-insertion into the sulfur−sulfur bond,[19−22] we recently investigated reactions of N-heterocyclic carbene (NHC) and cyclic (alkyl)(amino)carbene (CAAC) ligands[23−25] with an imidazole-based dithione dimer (**1**)[26] (Scheme 1). This resulted in cleavage of sulfur−sulfur bonds in **1** and ultimately afforded carbene-stabilized dithiolene zwitterions.[27] Proceeding from this work, we investigate the reactions of **1** with a series of phosphines [i.e., PPh_3, $P(NMe_2)_3$, and $P(OMe)_3$]. Herein, we report the syntheses,[28] molecular structures,[28] and computations[28] of compounds **2**−**5**. While the imidazole-based 1,2,5-trithiepin (**2**), zwitterionic phosphine−dithiolene complex (**3**), and thiophosphonate (**4**) were obtained via phosphine-mediated cleavage of the sulfur−sulfur bonds in **1**, zwitterionic **5** was prepared via NHC-mediated cleavage of the sulfur−sulfur bond in **2**.

1 was synthesized via a one-electron oxidation of the corresponding lithium dithiolene radical[29] (Scheme 1).[26] Notably, analogues of **1** have been synthesized by sulfurization of an imidazole-based dione and bromine oxidation of a nickel bis-dithiolene complex.[30−32] While combining **1** with PPh_3 in toluene at room temperature did not result in reaction, the 1:2 reaction of **1** with triphenylphosphine at 125 °C gave **2** (as a red powder in 67.0% yield) (Scheme 1).[28] X-ray single crystals of **2** were obtained by recrystallization from toluene/hexane

mixed solvent. Moreover, isolation of triphenylphosphine sulfide, $Ph_3P=S$, supports a mechanism involving phosphine-mediated thermal extrusion of sulfur in the **1**-to-**2** conversion.[33−35] It has been reported that photolysis of the benzene-based dithione dimer gives the 1,2,5-trithiepin derivative as an unstable intermediate in the formation of the corresponding thianthrene.[36,37] Interestingly, at elevated temperatures, **2** may be converted back to **1** by reaction with excess S_8.[28] Encouraged by the carbene-mediated cleavage of sulfur−sulfur bonds in **1**,[27] we further investigated the 1:1 reaction of **2** with NHC^{iPr},[23] which afforded the carbene-stabilized 2,2′-thiobis(ethene-1-thiolene) zwitterion (**5**) as an orange power in a quantitative yield (Scheme 1).[28]

The electronic properties of phosphines (PR_3) may be conveniently tuned by changing the R group. Thus, we investigated the reaction of **1** with $P(NMe_2)_3$, a stronger phosphine base.[38] This reaction produced a zwitterionic phosphine−dithiolene complex **3**, via $P(NMe_2)_3$-mediated heterolytic cleavage of the sulfur−sulfur bonds in **1** (Scheme 1).[28] Compound **3** was recrystallized in 1,2-difluorobenzene and subsequently isolated as colorless crystals (66.7% yield). The $^{31}P\{^1H\}$ spectrum of **3** reveals a singlet resonance at 58.3 ppm, which is shifted upfield compared to that of free $P(NMe_2)_3$ (123.5 ppm). This may be due to coordination of $P(NMe_2)_3$ to the sulfur atom which, in turn, induces the three amino substituents to donate more electron density to the phosphorus atom. Repeated attempts to obtain the ^{13}C NMR spectrum of **3** (and **5**) were unsuccessful due to their poor solubility in common organic solvents.
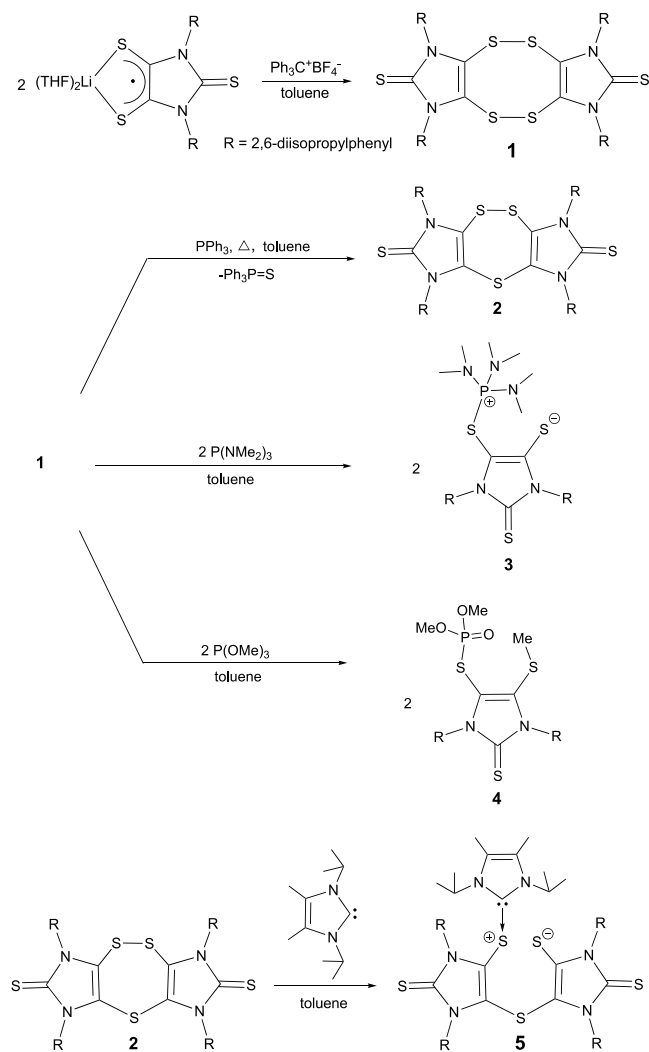
Scheme 1. Synthesis of 2−5

Figure 1. Proposed mechanism of the formation of **4** (R = 2,6-diisopropylphenyl).

The 19.91 ppm ^{31}P NMR resonance of **4** compares well to that (18.86 ppm) of the reported thiophosphonate.[40]

While the parent 1,2,5-trithiepin (Figure 2) has previously been synthesized and reported as a 10 π-electron multi-sulfur-

parent 1,2,5-trithiepin   lissoclinotoxin F
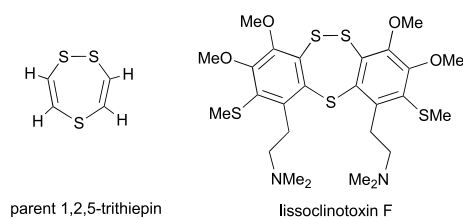
Figure 2. 1,2,5-Trithiepin and lissoclinotoxin F.

heteroaromatic system,[41] lissoclinotoxin F (Figure 2), a naturally occurring 1,2,5-trithiepin-based alkaloid, has exhibited cytotoxicity against the PTEN-deficient cell line.[37,42] Considering the paucity of the X-ray structural information on 1,2,5-trithiepin and its derivatives,[41,43] it is appropriate to probe the solid-state structure of **2** via single-crystal X-ray diffraction.[28] The asymmetric unit contains two molecules of **2** (for clarity, only one molecule of **2** and its bonding parameters are shown in Figure 3). The S−S bond in **2** [2.114(3) Å, av] is only marginally longer than that in **1** [2.0728(9) Å].[26] The C−S single bonds (1.738 Å, av) and C=C double bonds (1.349 Å, av) in the C_4S_3 ring of **2** are comparable with those for **1** (d_{C-S} = 1.739 Å, av; $d_{C=C}$ = 1.348 Å, av).[26] The seven-membered 1,2,5-trithiepin core in **2** is nonplanar with the C(3)−S(3)−S(4)−C(30) torsion angle of 82.5°, which compares to the theoretical values of the simplified **2-Me** model (85.8°) and of the parent 1,2,5-trithiepin (79.7°) (Figure S12).[28] The obvious nonplanarity of the seven-membered S_3C_4 ring in the parent 1,2,5-trithiepin (Figure S12, computed at the B3LYP/6-311G** level) does not support the "10 π-electron multi-sulfur-heteroaromatic system" depiction.[41]

Similar to carbene-stabilized neutral dithiolene zwitterions,[27] **3** also exists as an enantiomeric pair in the solid state (for clarity, only one enantiomer of **3** and its bonding parameters are shown in Figure 3).[28] By comparison with that (−180°) of the simplified **3-Ph** model,[28] the S(2)−C(2)−C(3)−S(3) torsion angle (−19.5°, av) of **3** should be ascribed to packing effects. The four-coordinate phosphorus atom in **3** adopts a distorted tetrahedral geometry (τ = 0.92, av).[44] The P−S bond distance in **3** [2.078(2) Å, av] is comparable with those [2.0694(4) Å for R = iPr; 2.0916(13) Å for R = p-tolyl] of the [RSP(tBu)$_3$]$^+$ cations.[18] The 0.78 Wiberg bond index (WBI) value of the P−S bond in **3-Ph** indicates its single bond character. The P−S bond in **3-Ph** is only marginally polarized toward the sulfur atom (49.1% toward P and 50.9% toward
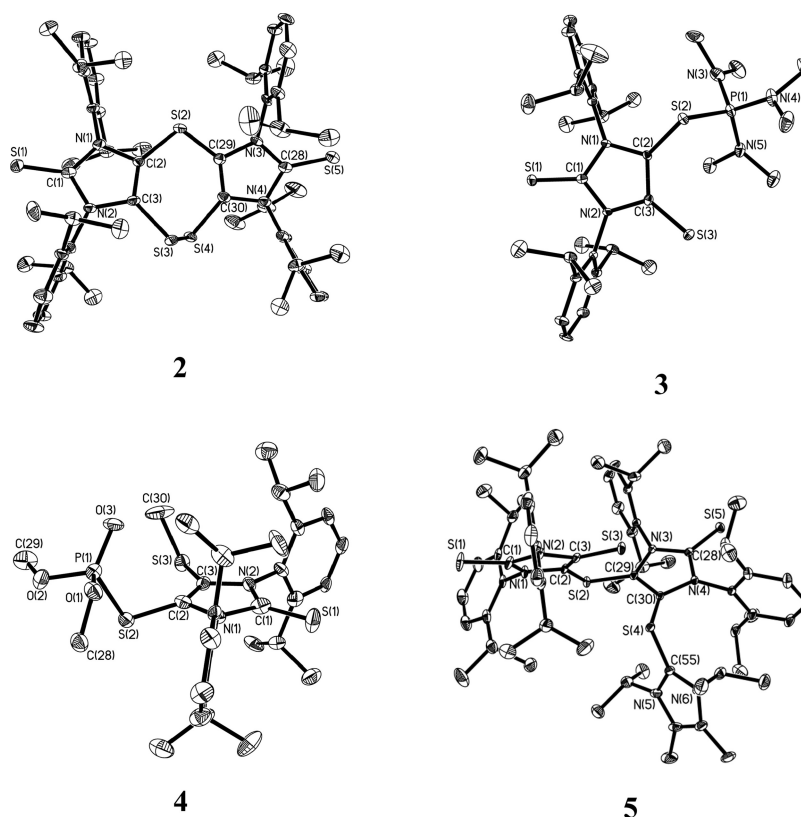
According to the Tolman electronic parameter (TEP)[38] P(OMe)$_3$ is a weaker electron donor than PPh$_3$. However, reaction of **1** with an excess of P(OMe)$_3$ over 4 days at room temperature resulted in formation of the thiophosphonate, **4** (isolated as pale-yellow solid in 86.9% yield) (Scheme 1).[28] The formation of a phosphonium intermediate has been proposed for the reaction of triethyl phosphite with diethyl disulfide.[1,39] However, in terms of the ^{1}H and ^{31}P NMR-monitored reactions of **1** and P(OMe)$_3$ (in toluene-d_8), the formation of P(OMe)$_3$-based analogue of **3** as a stable intermediate was not observed, supporting the direct conversion of **1** to **4**. Although the mechanistic details regarding the formation of **4** remain obscure, a plausible route for the formation of **4** could involve two synergic nucleophilic attacks (Figure 1): nucleophilic attack of P(OMe)$_3$ to one "sulfur−sulfur bonded" sulfur atom in **1**; followed by nucleophilic attack of the other sulfur atom of the S$_2$-bridge in **1** to one methyl group of P(OMe)$_3$. This results in cleavage of the S−S bond and C−O bond and concomitant formation of the P=O unit, giving thiophosphonate **4** as the product. A similar P(OMe)$_3$ activation reaction has been reported for the C$_6$S$_{12}$ carbon sulfide, which contains a 10-membered C$_4$S$_6$ ring.[40] The ^{1}H NMR spectrum of **4** exhibits a singlet resonance at 2.09 ppm for the SMe unit and a doublet resonance at 3.16 ppm for the (MeO)$_2$PO unit ($^3J_{PH}$ = 13 Hz).

Figure 3. Molecular structures of **2**–**5**. Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity. Selected bond distances (Å) and angles (deg): For **2**, C(1)–S(1) 1.657(7), C(2)–C(3) 1.345(8), C(2)–S(2) 1.739(6), C(3)–S(3) 1.740(6), S(3)–S(4) 2.112(2), C(2)–C(3)–S(3) 128.0(5), C(3)–S(3)–S(4) 98.1(2), C(2)–S(2)–C(29) 107.2(3). For **3**, C(1)–S(1) 1.674(6), C(2)–C(3) 1.390(7), C(2)–S(2) 1.727(5), C(3)–S(3) 1.694(5), P(1)–S(2) 2.078(2), C(3)–C(2)–S(2) 126.9(4), C(2)–S(2)–P(1) 107.50(19). For **4**, C(1)–S(1) 1.630(11), C(2)–C(3) 1.339(12), C(2)–S(2) 1.750(10), C(3)–S(3) 1.750(10), P(1)–S(2) 2.093(4), P(1)–O(3) 1.455(6), S(3)–C(30) 1.791(11), C(3)–C(2)–S(2) 127.3(9), C(2)–C(3)–S(3) 130.3(9), C(2)–S(2)–P(1) 102.8(3), O(3)–P(1)–S(2) 113.6(3), C(3)–S(3)–C(30) 101.3(5). For **5**, C(1)–S(1) 1.690(4), C(2)–C(3) 1.365(5), C(2)–S(2) 1.769(4), C(3)–S(3) 1.712(4), C(29)–S(2) 1.750(3), C(29)–C(30) 1.356(5), C(30)–S(4) 1.746(3), C(55)–S(4) 1.763(4), C(2)–C(3)–S(3) 134.0(3), C(30)–S(4)–C(55) 104.35(16).

S).[28] Among the three C–S bonds in **3**, the C(2)–S(2) bond [1.727(5) Å] is the longest, which compares to those [1.7137(15) and 1.718(2) Å] in carbene-stabilized dithiolene zwitterions.[27] NBO natural population analysis shows that, in zwitterionic **3-Ph**,[45] while the S(3) atom bears a negative charge of −0.32, the S(2) atom only has a positive charge of +0.06. The positive charge in **3-Ph** mainly resides at the phosphorus atom (+1.92). The DFT computations of **3-Ph** at the B3LYP/6-311G** level[28] show that while the LUMO involves a phosphorus–sulfur σ-antibonding orbital, the HOMO is mainly dithiolene-based, containing both polarized C–C π-bonding and C–S π-antibonding character (Figure 4).

X-ray structural analysis reveals that **4** exists as a pair of enantiomers (for clarity, only one enantiomer of **4** and its bonding parameters are shown in Figure 3).[28] In **4**, the two sulfur atoms of the C_2S_2 unit bear a methyl and a $(MeO)_2PO$ unit, respectively. Both the CH_3 and $(MeO)_2PO$ groups reside at the same side of the imidazole plane. The four-coordinate phosphorus atom in **4** also adopts a distorted tetrahedral geometry ($\tau = 0.91$).[44] The P–S bond in **4** [2.093(4) Å] is marginally longer than that in **3** [2.078(2) Å, av]. While being somewhat shorter than that for triphenyl phosphine oxide (1.48 Å),[46] the P–$O_{terminal}$ bond in **4** [1.455(6) Å] is obviously shorter than the P–O single bonds of the $P(OMe)_2$ fragment in **4** [1.559(7) and 1.566(7) Å]. The WBI value (1.32) of the
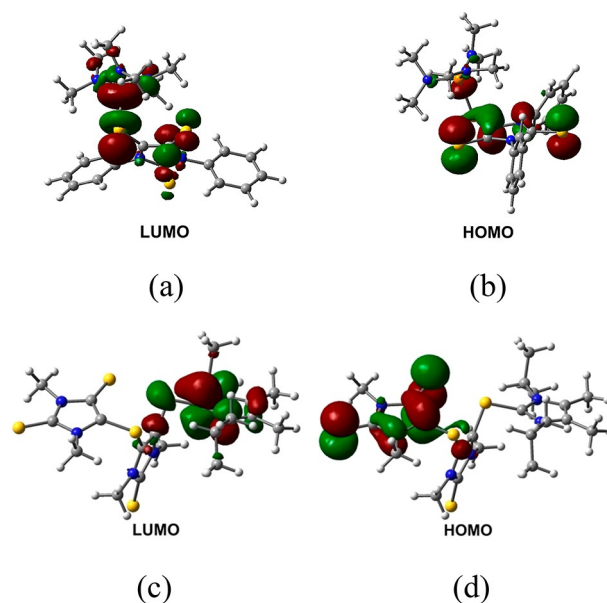
Figure 4. Frontier orbitals of the simplified **3-Ph** (a, b) and **5-Me** (c, d) models.

P–$O_{terminal}$ bond in the **4-Ph** model indicates multiple bond character.

X-ray structural analysis of **5** (Figure 3) shows that with carbene coordination, the sulfur−sulfur bond in **2** is cleaved (rendering to the nonbonding $d_{S\cdots S}$ = 3.163 Å in **5**). The carbene-mediated cleavage of sulfur−sulfur bond should be due to carbene donating an electron pair to the S−S σ-antibonding orbital (i.e., LUMO, Figure S11) of **2**.[28] The carbene coordination results in the heterolytic cleavage of the sulfur−sulfur bond in **2**. NBO natural population analysis of the simplified **5-Me** model shows that the sulfur atom [i.e., S(4)] complexed by the NHC^{iPr} ligand has a positive charge of +0.36, while the terminal sulfur atom [i.e., S(3)] of the C_4S_3 backbone bears a negative charge of −0.35.[28] The charge separation observed for **5** compares well to those of carbene-stabilized neutral dithiolene zwitterions [when carbene = ^{Me}CAAC, S(2) (+0.43) and S(3) (−0.35); when carbene = NHC^{iPr}, S(2) (+0.33) and S(3) (−0.35)].[27] Although the C_{NHC}−S bond in **5-Me** (WBI = 1.06) is only marginally polarized toward the carbene carbon (52.0% toward carbon and 48.0% toward sulfur), its essence is a dative bond, which is supported by our very recent observation of the releasing of the carbene ligand when **5** is combined with main group species. The terminal C(3)−S(3) bond in **5** [1.712(4) Å] is somewhat shorter than the other three C−S bonds in the C_4S_3 unit of **5** [1.746(3)−1.769(4) Å]. The 1.26 WBI reveals the modest double bond character of the terminal C(3)−S(3) bond in **5**. The two C_2S_2 units in **5** exhibit a C(2)−S(2)−C(29)−C(30) torsion angle of 75.3°. The DFT computations of **5-Me** at the B3LYP/6-311G**level[28] indicate that while the LUMO is largely NHC ligand-based with C_{NHC}−N π-antibonding character, the HOMO is predominantly the "terminal" dithiolene unit-based with C−C π-bonding and C−S π-antibonding character (Figure 4).

The phosphine-mediated cleavage of sulfur−sulfur bonds in the imidazole-based dithione dimer (**1**) have been explored. The first X-ray structurally characterized 1,2,5-trithiepin derivative (**2**) was prepared via triphenylphosphine-mediated thermal extrusion of sulfur from **1**. Compound **2** can be converted back to **1** by reacting with excess S_8 at elevated temperatures. Subsequent reaction of **2** with carbene gave a carbene-stabilized 2,2′-thiobis(ethene-1-thiolene) zwitterion (**5**). Additionally, reactions of **1** with $P(NMe_2)_3$ and $P(OMe)_3$ also resulted in the cleavage of sulfur−sulfur bonds, giving a zwitterionic phosphine−dithiolene complex (**3**) and thiophosphonate (**4**), respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00271.

> Syntheses, computations, and X-ray crystallography (PDF)

> Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 2157790, 2157791, 2174421, and 2174422 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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Notes

The authors declare no competing financial interest.

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