

An Unexpected Sequence: From Phosphole Sulfide to Phosphole- and Thiophene-Annulated 1,2-Dithiole-3-thiones

Ana Ciric and François Mathey*

Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

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Summary: The deprotonation of 1-phenyl-3,4-dimethylphosphole sulfide by a bulky base, followed by the reaction of S_2Cl_2 , unexpectedly yields a phosphole-annulated 1,2-dithiole-3-thione. The complexation of this product by $[W(CO)_5]$ takes place at C=S as expected on the basis of theoretical calculations. Another product results from the unprecedented replacement of the P(S)Ph unit by sulfur, giving the corresponding thiophene derivative.

The easily accessible 3H-1,2-dithiole-3-thiones¹ display an interesting redox chemistry, can serve as ligands for transition metals, and have a lot of interesting biological properties. It would be quite interesting to combine this structure with a modulating phosphino group, but, to the best of our knowledge, no phosphino-substituted dithiolethione has ever been described in the literature until now. We describe herein how we found an original phosphole-annulated dithiolethione while trying to link two phosphole units by a sulfur bridge.

Our starting point was the delocalized anion obtained by deprotonation of 1-phenyl-3,4-dimethylphosphole sulfide (1) by a bulky base (here the sodium hexamethyldisilazide).² We investigated the reaction of this anion with disulfur dichloride with the aim of creating a S-S link between two phosphole units. In fact, we obtained a complicated mixture of products, among which a readily eluted deep red compound (2) was especially noteworthy (eq 1).



The formula of **2** was established as follows. The measured mass, m/z 312.9398 (MH⁺), was very close to the computed mass for C₁₂H₁₀PS₄ (312.9403). The proton NMR spectrum showed only one olefinic α -proton at δ 6.19 ppm (²J_{H-P} = 32.24 Hz) and one methyl at δ 2.61 ppm (CD₂Cl₂). The most prominent feature of the ¹³C NMR spectrum was a C=S doublet at δ 209.61 ppm (J_{C-P} = 16.5 Hz). Classical dithiolethiones show a C=S resonance in the range 206–216 ppm.¹ The characterization of **2** was completed by the X-ray crystal structure analysis of the complex (see later). In order to have a more precise understanding of the electronic structure of **2**, we

performed a DFT calculation on the model compound **3** at the B3LYP/6-311+G(d,p) level.³ The computed structure is very close to the experimental structure of the complex. The HOMO (Figure 1) is essentially localized on the dithiolethione ring with no participation of phosphorus. The coefficient at the C=S sulfur is huge, indicating that it will be the reactive site toward electrophiles, as is the case for normal dithiolethiones. The participation of the phosphole ring is more significant in the LUMO. At -5.1, the NICS(1) index⁴ indicates that the sulfur ring is only weakly aromatic.



The UV/vis spectrum of **2** (Figure 2) shows a characteristic band at 483 nm (ε 8339). In the parent dithiolethione, this band occurs at 410 nm (ε 6400) and corresponds to a $\pi^* \leftarrow \pi$



Figure 1. HOMO and LUMO of compound 3 as computed at the B3LYP/6-311+G(d,p) level.

^{*}Corresponding author. E-mail: fmathey@ntu.edu.sg.

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Figure 2. UV/vis spectrum of 2 in dichloromethane (λ in nm).

transition.⁵ So it seems that the phosphole annulation slightly increases the delocalization within the dithiolethione ring.

The yields of our initial experiments were quite low and erratic, so it was necessary to improve both the reproducibility and the productivity of the transformation. A logical mechanism is proposed in eq 2.



On this basis, it seemed clear that 1 equiv of a strong and bulky base was necessary to produce the anion derived from 1 that serves to build the initial C–S link and that three additional equivalents of a weaker base were necessary to close the sulfur ring and create the thiocarbonyl group. This second base must be inert toward the S–Cl bonds. Thus we devised an optimized procedure starting by the condensation of 1 equiv of 1, 1 equiv of (Me₃Si)₂NNa, and 1 equiv of S₂Cl₂ at low temperature, followed by the addition of a second equivalent of S₂Cl₂ and 3 equiv of triethylamine at 0 °C. In doing so, we obtained a reproducible 10% yield.

In order to fully establish the structure of 2 and to see what is its preferential coordination site (C=S or P=S), we investigated the reaction of 2 with tungsten pentacarbonyl. The theoretical study favored a complexation at C=S. Besides a lot of oligomers, the reaction produces two welldefined compounds in low yields. The first one is, indeed, the C=S complex 4, whose structure was confirmed by X-ray analysis (Figure 3).



The dithiolethione and phosphole rings are not strictly coplanar: P-C-C-C(S) dihedral angle = 6.5°. The sulfur ring does not display a sizable aromatic character, in agreement with the previously reported structures⁶ and theoretical computations.⁷ But the most exciting finding was the for-



Figure 3. X-ray crystal structure analysis of the complex of the phosphole-annulated 1,2-dithiole-3-thione with tungsten pentacarbonyl 4. Ellipsoids are scaled to enclose 50% of the electronic density. Significant distances (Å) and angles (deg): P1–S1 1.9428(15), P1–C1 1.788(4), P1–C5 1.825(3), P1–C7 1.793(4), C1–C2 1.350(5), C2–C4 1.501(5), C4–C5 1.367(5), C4–C6 1.430(5), C5–S2 1.696(4), C6–S3 1.731(4), S3–S2 2.0713(12), C6–S4 1.668(4), S4–W1 2.5185(10); C1–P1–C5 90.47(17), P1–C5–S2 129.1(2), C4–C5–S2 120.5(3), C5–S2–S3 92.79(13), S2–S3–C6 97.19(12), S3–C6–S4 119.4(2), S3–C6–C4 113.4(3), C4–C6–S4 127.2(3), C5–C4–C6 115.9(3), C6–C4–C2 130.9(3), C6–S4–W1 114.67(13).

mation of another product (5) that does not contain phosphorus. It, apparently, results from the unprecedented conversion of a phosphole sulfide into a thiophene ring. At the moment, we are unsure of how this conversion proceeds and if it is possible to generalize it. Complex 5 was unambiguously characterized by X-ray analysis (Figure 4). The two rings are strictly coplanar. The thiophene ring is sharply dissymmetrized by annulation with the dithiolethione. The parameters of the dithiolethione ring in 4 and 5 are very similar. It is interesting to note that the HOMO-LUMO gap of the free ligand in 5 is exactly the same as the gap of TTF at the same level of theory, but both the HOMO and the LUMO are shifted to lower energies by 1.5 eV in the thiophene derivative by comparison with TTF.

Experimental Section

Synthesis of Phosphole-Annulated 1,2-Dithiole-3-thione (2). To a solution of 1-phenyl-3,4-dimethylphosphole sulfide (0.5 g, 2.27 mmol) in 10 mL of THF at -80 °C and under argon was added sodium bis(trimethylsilyl)amide (2.4 mL of 1 M solution in THF) via syringe. The color immediately turned from pale yellow to dark red. This solution was stirred for \sim 5 min, after which freshly⁸ distilled S₂Cl₂ (0.2 mL, 2.4 mmol) was added via syringe and the solution was warmed to 0 °C and stirred for \sim 20 min. At this point the color of the solution turned lighter red. Still at 0 °C, triethylamine (0.97 mL, 6.96 mmol) was added to

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Figure 4. X-ray crystal structure analysis of the complex of the thiophene-annulated 1,2-dithiole-3-thione with tungsten pentacarbonyl **5**. Ellipsoids are scaled to enclose 50% of the electronic density. Significant distances (Å) and angles (deg): S1–C1 1.733(3), S1–C5 1.708(2), C1–C2 1.359(3), C2–C4 1.441(3), C4–C5 1.387(3), C5–S2 1.723(2), S2–S3 2.0711(8), S3–C6 1.728(2), C6–C4 1.425(3), C6–S4 1.669(2), S4–W1 2.5274(6); C1–S1–C5 90.59(11), S1–C5–S2 127.83(14), C5–S2–S3 92.61(8), S2–S3–C6 97.79(8), S3–C6–C4 113.99(16), S3–C6–S4 119.52 (12), C6–C4–C5 115.89(19), C4–C5–S2 119.72(16), C6–S4–W1 114.64(8).

the mixture followed by another equivalent of S_2Cl_2 (0.2 mL, 2.4 mmol). The color turned brown. The solution was then warmed to room temperature. The reaction was monitored by ³¹P NMR and TLC (50:50 petroleum ether/CH₂Cl₂), proving the presence of the red compound **2**. The solvent was removed *in vacuo*, and the mixture was purified by column chromatography on silica gel using 75:25 petroleum ether/methylene chloride as the eluent, yielding 73 mg (10.3%) of **2**. Black crystals were formed spontaneously overnight.

crystals were formed spontaneously overlight. ¹H NMR (CD₂Cl₂): $\delta 2.61$ (dd, 3H, ⁴J_{PH}=1.7 Hz, ⁴J_{HH}=1.1 Hz, Me), 6.19 (dd, 1H, ²J_{PH} = 32.2 Hz, ⁴J_{HH} = 1.1 Hz, =CH-P), 7.56 (m, 2H, Ph *meta* H), 7.64 (m, 1H, Ph *para* H), 7.87 (m, 2H, Ph *ortho* H). ¹³C NMR (CD₂Cl₂): δ 18.90 (d, ³J_{PC} = 16.2 Hz, Me), 126.94 (d, ¹J_{PC}=83.7 Hz, Ph *ipso* C), 128.03 (d, ¹J_{PC}=83.3 Hz, = CH-P), 129.87 (d, ³J_{PC} = 14.4 Hz, Ph *meta* CH), 131.34 (d, ²J_{PC} = 12.7 Hz, Ph *ortho* CH), 133.95 (s, Ph *para* CH), 150.24 (d, ²J_{PC} = 28.7 Hz, Me-C=), 153.65 (s, =C-C=S), 175.75 (d, ${}^{1}J_{PC} = 64.8$ Hz, P-C-S), 209.61 (d, ${}^{3}J_{PC} = 16.6$ Hz, C=S). ${}^{31}P$ NMR (CD₂Cl₂): δ 31.6. Mass spectrum: m/z 312.9398 (MH⁺, 100%). Anal. Calcd for C₁₂H₉PS₄: C, 46.13; H, 2.90. Found: C, 46.21; H, 3.00.

Complexation of 2 by Tungsten Pentacarbonyl. Tungsten pentacarbonyl was made in situ by dissolving 86 mg (0.24 mmol) of tungsten hexacarbonyl in 12 mL of acetonitrile, then adding 27 mg (0.24 mmol) of trimethylamine-N-oxide dihydrate as a solid. The solution turned bright yellow immediately and was stirred for ~30 min. Acetonitrile was removed in vacuo, and the remaining bright yellow solid was then redissolved in 10 mL of dry THF. This solution was stirred for 20 min and cooled to 0 °C, and the 24 mM solution of 2 (76 mg in 10 mL of THF) was added dropwise via a syringe. The mixture was stirred overnight, and in the morning, the solution appeared dark blue. One pink and one blue spot were observed by TLC (50:50 petroleum ether/dichloromethane). The crude mixture was initially filtered quickly through silica gel, after which it was further purified using another silica gel column chromatography (100% petroleum ether \rightarrow 100% dichloromethane). The pink fraction (5) was eluted with a 70:30 solvent mixture in 2.3% yield (3 mg), and the blue fraction (4) with a 50:50 solvent mixture in 1% yield (1.6 mg). Both fractions were left overnight in test tubes, and pink and blue crystals were obtained spontaneously. Elemental analyses were not obtained for 4 and 5 due to insufficient quantities of products.

Complex 4: ¹H NMR (CD₂Cl₂): δ 2.66 (dd, 3H, ⁴J_{PH} \approx ⁴J_{HH} = 1.8 Hz, Me), 6.29 (dd, 1H, ²J_{PH} = 32.0 Hz, ⁴J_{HH} = 1.8 Hz, = CH-P), 7.55 (m, 2H, Ph *meta* H), 7.64 (m, 1H, Ph *para* H), 7.87 (m, 2H, Ph *ortho* H). ¹H NMR (CD₂Cl₂): δ 19.79 (d, ³J_{PC} = 16.1 Hz, Me), 125.57 (d, ¹J_{PC} = 84.2 Hz, Ph *ipso* C), 129.32 (d, ¹J_{PC} = 83 Hz, =CH-P), 129.64 (d, ³J_{PC} = 13.4 Hz, Ph *meta* CH), 130.93 (d, ²J_{PC} = 12.0 Hz, Ph *ortho* CH), 133.87 (s, Ph *para* CH), 151.49 (s, =C-C=S), 196.91 (s, *cis*-CO), 201.04 (s, *trans*-CO), 207.70 (d, ³J_{PC} = 13.4 Hz, C=S). ³¹P NMR (CDCl₃): δ 38.0.

Complex 5: ¹H NMR (CDCl₃): δ 2.62 (s, Me), 7.09 (s, =CH-S). ¹³C NMR (CDCl₃): δ 15.67 (s, Me), 128.23 (s, =CH-S), 134.92 (s, Me-C=), 197.26 (s, *cis*-CO), 201.08 (s, *trans*-CO), 207.11 (s, C=S). Mass spectrum: m/z 203.94 (base peak). Theory for M-W(CO)₅: 203.92.

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Supporting Information Available: X-ray crystal structure analysis of compounds 4 and 5. NMR spectra of 2, 4, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.