

# Synthetic Applications of Lawesson's Reagent in Reactions with Cu<sup>I</sup> Alkoxides

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*Dedicated to Prof. Reinhart Ahlrichs on the occasion of his 65th birthday*

**Keywords:** Metal alkoxide / P ligands / S ligands / Elimination

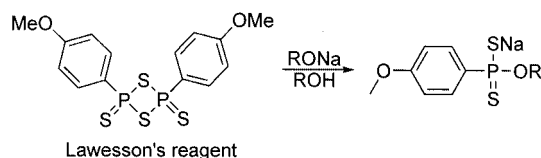
The reaction of Lawesson's reagent with CuOtBu and tertiary phosphanes produced the complexes [Cu<sub>2</sub>(μ<sub>2</sub>-ArS<sub>2</sub>P-O-PS<sub>2</sub>Ar)(PPh<sub>3</sub>)<sub>4</sub>] (**1**) (Ar = *p*-C<sub>6</sub>H<sub>4</sub>OMe) and [Cu<sub>4</sub>{Ar(μ<sub>2</sub>-S)<sub>2</sub>P-O-P(μ<sub>2</sub>-S)<sub>2</sub>Ar}<sub>2</sub>(dppa)<sub>2</sub>] (**2**) (dppa = Ph<sub>2</sub>PNHPPH<sub>2</sub>) in high

yields. The ligand [ArS<sub>2</sub>P-O-PS<sub>2</sub>Ar]<sup>2-</sup> is the first of a new family of dianionic P/S ligands.

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## Introduction

Coordination chemistry with phosphorus- and sulfur-containing ligands is still an active area of research.<sup>[1]</sup> The motivation for research in this field is diverse and includes the use of thio-functionalised organophosphorus compounds as additives to vulcanisation processes, as precursors for CVD processes and as insecticides.<sup>[2–4]</sup> Recent activities in this field made use of silyl esters of diphenylphosphanyldithioic and phenyltrithiophosphonic acid as starting materials for coinage metal clusters.<sup>[5]</sup> Also the coordination chemistry of other P/S-containing anions, e.g., phosphorodithioato and -selenolato anions [(RO)<sub>2</sub>PE<sub>2</sub>]<sup>-</sup> (R = organic group; E = S, Se), with transition metal cations has received much attention.<sup>[6]</sup> Lawesson's reagent,<sup>[7]</sup> widely known as a powerful thionation reagent in organic synthesis, offers another route to complexes containing P/S-based anionic ligands (Scheme 1).<sup>[8]</sup>



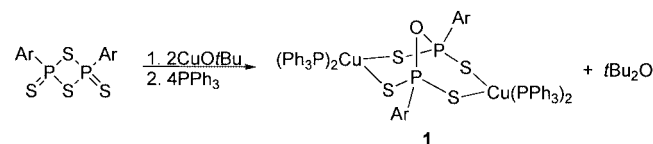
Scheme 1. Synthesis of sodium phosphonodithioate salts (R = Me, Et, *i*Pr).

Metathesis of the sodium phosphonodithioate salts (Scheme 1) gave rise to several metal complexes.<sup>[8]</sup> The gen-

erated *O*-alkyl (4-methoxyphenyl)phosphonodithioato ligands are bidentate and chelate metal atoms via the S atoms, whilst the introduced alkoxide group is not involved in coordination. As part of a wider study of the reactivity of late transition metal alkoxides, we have studied reactions of CuOtBu with Lawesson's reagent in aprotic solvents and report here the first results.

## Results and Discussion

When Lawesson's reagent was heated with 2 equiv. of CuOtBu in toluene, a yellow precipitate was formed which dissolved upon addition of PPh<sub>3</sub>. Crystallization from a mixture of dichloromethane and pentane gave, to our surprise, no phosphane-stabilised copper(I) phosphonodithioate, which could have been regarded as analogous compound to the sodium phosphonodithioate salts prepared by Woollins et al. (Scheme 1).<sup>[8]</sup> Instead, the Cu<sup>I</sup> pyrophosphonodithioate [Cu<sub>2</sub>(μ<sub>2</sub>-ArS<sub>2</sub>P-O-PS<sub>2</sub>Ar)(PPh<sub>3</sub>)<sub>4</sub>] (**1**) (Ar = *p*-C<sub>6</sub>H<sub>4</sub>OMe) was obtained in 80% yield (Scheme 2).



Scheme 2. Synthesis of **1** (Ar = *p*-C<sub>6</sub>H<sub>4</sub>OMe).

The structure of **1** was initially determined by X-ray analysis (Figure 1). The dianionic ligand [ArS<sub>2</sub>P-O-PS<sub>2</sub>Ar]<sup>2-</sup> generated in the reaction of CuOtBu with Lawesson's reagent bridges two [Cu(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ions. Compound **1** is consists of two puckered annulated six-membered [CuS<sub>2</sub>P<sub>2</sub>O] rings and an organic shell of phenyl rings of the PPh<sub>3</sub>

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ligands (each one disordered over two positions; 50:50) and *p*-C<sub>6</sub>H<sub>4</sub>OMe groups from Lawesson's reagent. The Cu<sup>I</sup> centres show a distorted tetrahedral coordination environment.

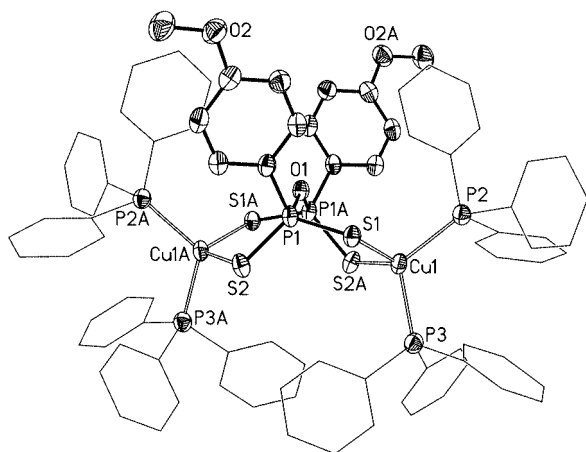
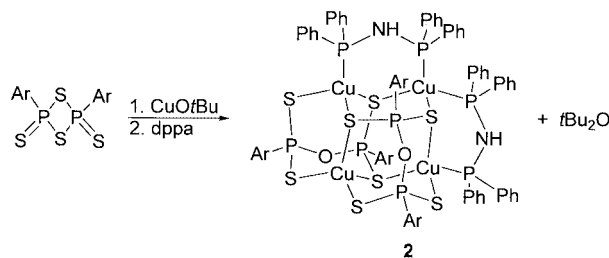


Figure 1. Molecular structure of **1** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity; label A denotes symmetry operation  $-x + 1, y, -z - 1/2$ ). Selected bond lengths [Å] and angles [°]: Cu(1)–P(3) 2.3181(15), Cu(1)–P(2) 2.3193(14), Cu(1)–S(1) 2.3643(14), Cu(1)–S(2A) 2.3749(15), P(1)–O(1) 1.640(2), P(1)–S(2) 1.9909(17), P(1)–S(1) 1.9927(16); O(1)–P(1)–S(2) 110.33(12), O(1)–P(1)–S(1) 110.01(7), S(2)–P(1)–S(1) 117.41(8), P(1A)–O(1)–P(1) 130.3(3).

The P–O and P–S distances in **1** are in good agreement with values observed in [K<sub>2</sub>(C<sub>10</sub>H<sub>6</sub>)PS<sub>2</sub>(μ-O)PS<sub>2</sub>], which is the closest related compound to **1**.<sup>[9]</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was recorded from crystals of **1** dissolved in CDCl<sub>3</sub> (verified by redetermination of the unit cell). Resonances at  $\delta = 91.5$  ppm for the generated [ArS<sub>2</sub>P–O–PS<sub>2</sub>Ar]<sup>2-</sup> dianion and at  $\delta = -3.6$  ppm for coordinated PPh<sub>3</sub> ligands were observed and the IR spectrum showed a strong band at  $\tilde{\nu}_{\text{as}}(\text{P–O–P}) = 841 \text{ cm}^{-1}$ . The detailed mechanism of the formation of the [ArS<sub>2</sub>P–O–PS<sub>2</sub>Ar]<sup>2-</sup> dianion in **1** is difficult to confirm. We propose the initial formation of an intermediate Cu<sup>I</sup> phosphonodithioate salt [ArP(O*t*Bu)S<sub>2</sub>Cu], which instantly decomposes to form *t*Bu<sub>2</sub>O and **1**. It was impossible to isolate and characterize intermediate complexes. The separation of *t*Bu<sub>2</sub>O from the solvent toluene cannot be achieved by distillation, and in GC/MS experiments *t*Bu<sub>2</sub>O was not detected due to large solvent excess. The reaction was therefore performed in C<sub>6</sub>D<sub>6</sub> and all volatile products were distilled off. Redistillation into an NMR tube afforded a sample containing *t*Bu<sub>2</sub>O formed in the reaction (Supporting Information; for Supporting Information see also the footnote on the first page of this article). Reactions of CuO*t*Bu with Lawesson's reagent in the presence of several different phosphane ligands were also performed. Addition of dppa (dppa = Ph<sub>2</sub>PNHPPH<sub>2</sub>) afforded the tetranuclear complex [Cu<sub>4</sub>{Ar(μ<sub>2</sub>-S)<sub>2</sub>P–O–P(μ<sub>2</sub>-S)<sub>2</sub>Ar}<sub>2</sub>(dppa)<sub>2</sub>] (**2**) (Scheme 3, Figure 2).



Scheme 3. Synthesis of **2** (Ar = *p*-C<sub>6</sub>H<sub>4</sub>OMe; dppa = Ph<sub>2</sub>PNHPPH<sub>2</sub>).

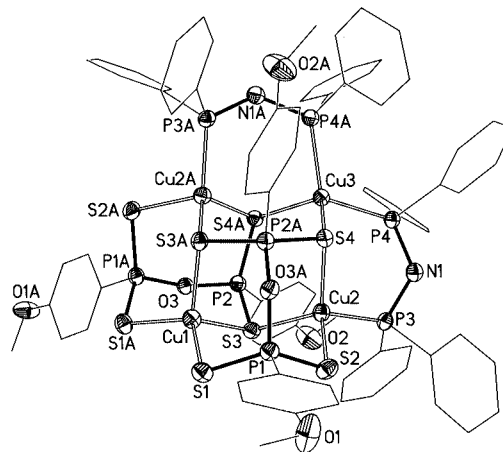


Figure 2. Molecular structure of **2** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Label A denotes symmetry operation  $-x - 1, y, -z + 3/2$ . Selected bond lengths [Å] and angles [°]: Cu(1)–S(1) 2.2958(16), Cu(1)–S(3) 2.3394(19), Cu(2)–P(3) 2.2209(19), Cu(2)–S(3) 2.3178(16), Cu(2)–S(4) 2.337(2), Cu(2)–S(2) 2.3570(17), Cu(3)–P(4) 2.3318(18), Cu(3)–S(4) 2.3641(16), S(1)–P(1) 1.994(2), S(2)–P(1) 1.990(3), S(3)–P(2) 2.011(2), S(4)–P(2A) 2.027(2), P(1)–O(3A) 1.662(5), P(2)–O(3) 1.613(4), P(2)–S(4A) 2.027(2), P(3)–N(1) 1.707(6), P(4)–N(1) 1.709(5); O(3A)–P(1)–S(2) 109.66(19), O(3A)–P(1)–S(1) 110.14(17), S(2)–P(1)–S(1) 118.99(12), O(3)–P(2)–S(3) 108.20(18), S(3)–P(2)–S(4A) 119.43(10), P(3)–N(1)–P(4) 127.3(3), P(2)–O(3)–P(1A) 136.3(3).

In the solid state **2** consists of two fused adamantane cage frameworks in which two [ArS<sub>2</sub>P–O–PS<sub>2</sub>Ar]<sup>2-</sup> dianions coordinate the Cu atoms Cu(1,2,2A). Cu(3) is located in the periphery of the cluster and two dppa ligands complete the remaining coordination sites of Cu(2,2A,3). Like in **1**, Cu atoms in **2** exhibit distorted tetrahedral coordination environments but the new ligand [Ar(S)<sub>2</sub>P–O–PS<sub>2</sub>Ar]<sup>2-</sup> now bridges two Cu atoms via the S atoms S(3,3A,4,4A), whilst the remaining S atoms S(1,1A,2,2A) are coordinated to one Cu atom each. Spectroscopic data and observed bond lengths in **2** verify the uniform composition of crystals of **2** and can be compared with **1** or [K<sub>2</sub>(C<sub>10</sub>H<sub>6</sub>)PS<sub>2</sub>(μ-O)PS<sub>2</sub>].<sup>[9]</sup>

## Conclusions

The results presented here show that the reaction of the Cu<sup>I</sup> alkoxide CuO*t*Bu and Lawesson's reagent in toluene produces Cu<sup>I</sup> complexes containing the new dianionic ligand

[ArS<sub>2</sub>P–O–PS<sub>2</sub>Ar]<sup>2–</sup> in high yield. Currently, investigations in this area are extended to different Lawesson-type reagents, metal alkoxides and phosphane ligands. Studies of the influence of organic substituents of transition metal alkoxides on the fragmentation of Lawesson-type reagents will be the subject of future work in this area. Compounds **1** and **2** are the first representatives of a range of metal complexes currently prepared using these ligands and illustrate that a variety of coordination modes is to be expected.

## Experimental Section

**General Remarks:** All operations were carried out under purified dinitrogen. Toluene was dried with sodium, dichloromethane was dried with CaH<sub>2</sub>, pentane was dried with LiAlH<sub>4</sub> and freshly distilled. Chemicals were purchased from Aldrich. CuOtBu and dppa were prepared according to published procedures.<sup>[10,11]</sup>

**1:** To a solution of Lawesson's reagent (202 mg, 0.50 mmol) in toluene (12 mL) was added dropwise a solution of CuOtBu (136 mg, 1.00 mmol) in toluene (10 mL). The resulting yellow solution was refluxed for about 5 h during which time a color change to brown and the formation of a yellow precipitate was observed. The precipitate was dissolved by addition of a solution of PPh<sub>3</sub> (524 mg, 2.0 mmol) in toluene (10 mL). The solvent was removed under reduced pressure. Addition of CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and pentane (5 mL) and storage of the solution at room temp. for 1 d produced colorless crystals; yield 0.68 g (81%); m.p. 194 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.9–6.7 (m., 19 H, ar. H), 3.8 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C): δ = 161.5–113.1 (ar. C), 55.3 (s, OCH<sub>3</sub>) ppm. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>, 25 °C, 65% H<sub>3</sub>PO<sub>4</sub>): δ = 91.2 (s, ArPS<sub>2</sub>O), –3.6 (s, CuPPh<sub>3</sub>) ppm. IR (KBr): ν̄ = 3046 w, 1593 s, 1431 (P–C), 1250 s, 1105 s, 841 s (P–O–P), 657 s (P=S) cm<sup>–1</sup>. C<sub>86</sub>H<sub>74</sub>Cu<sub>2</sub>O<sub>3</sub>P<sub>6</sub>S<sub>4</sub> (1594.2): calcd. C 64.6, H 4.6; found C 64.4, H 4.6.

**2:** To a solution of Lawesson's reagent (202 mg, 0.50 mmol) in toluene (12 mL) was added dropwise a solution of CuOtBu (136 mg, 1.00 mmol) in toluene (10 mL). The resulting yellow solution was refluxed for about 5 h during which time a colour change to brown and the formation of a yellow precipitate was observed. The precipitate was dissolved by addition of a solution of dppa (385 mg, 1.00 mmol) in toluene (10 mL). The solvent was removed under reduced pressure. Addition of CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and pentane (5 mL) and storage of the solution at room temp. for 1 d produced colorless crystals of **2**; yield 0.42 g (79%); m.p. 201 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 8.1–6.9 (m., 24 H, ar. H), 5.4 (s, 1 H, NH, next to peak of CH<sub>2</sub>Cl<sub>2</sub>), 3.9–3.8 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 162.2–113.5 (10 C, ar. C), 55.8 (s, 1 C, OCH<sub>3</sub>) ppm. <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, 65% H<sub>3</sub>PO<sub>4</sub>): δ = 89.1 (s, ArPS<sub>2</sub>O), 38.3 (br. s, NPPH<sub>2</sub>) ppm. IR (KBr): ν̄ = 3297 w (N–H), 3051 w, 1596 s, 1435 s (P–C), 1258 s, 1107 s, 880 bs (P–O–P), 694 s (P=S) cm<sup>–1</sup>. C<sub>76</sub>H<sub>68</sub>Cu<sub>4</sub>N<sub>2</sub>O<sub>6</sub>P<sub>8</sub>S<sub>8</sub> (1859.8): calcd. C 48.9, H 3.7; found C 49.3, H 3.8.

**X-ray Crystallographic Study:** Data for **1** and **2** were collected with a STOE IPDS II diffractometer using graphite-monochromated Mo-K<sub>α</sub> radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares on F<sup>2</sup> (all data) using the SHELXTL program package.<sup>[12]</sup> Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components were refined with isotropic thermal parameters. Crystal data for **1**:

C<sub>86</sub>H<sub>74</sub>Cu<sub>2</sub>O<sub>3</sub>P<sub>6</sub>S<sub>4</sub>CH<sub>2</sub>Cl<sub>2</sub>; M = 1681.52; monoclinic, space group C2/c; Z = 4; a = 22.431(5), b = 13.711(3), c = 26.435(5) Å, β = 104.20(3)°; V = 7882(3) Å<sup>3</sup>; T = 100(2) K; F(000) = 3472; D<sub>calcd.</sub> = 1.417 g cm<sup>–3</sup>. 29604 reflections measured, of which 8548 were unique (R<sub>int</sub> = 0.0485); 238 parameters; final wR<sub>2</sub> = 0.2063 (all data); R<sub>1</sub> = 0.0742 [I > 2σ(I)]; largest difference peak/hole 2.446/–1.145 e<sup>–</sup> Å<sup>–3</sup>. Crystal data for **2**: C<sub>76</sub>H<sub>68</sub>Cu<sub>4</sub>N<sub>2</sub>O<sub>6</sub>P<sub>8</sub>S<sub>8</sub>3CH<sub>2</sub>Cl<sub>2</sub> M = 2130.51; monoclinic, space group C2/c, Z = 4; a = 18.457(4), b = 19.747(4), c = 24.311(5) Å, β = 93.66(3)°; V = 8843(3) Å<sup>3</sup>; T = 100(2) K; F(000) = 4328; D<sub>calcd.</sub> = 1.600 g cm<sup>–3</sup>. 13293 reflections measured, of which 7876 were unique (R<sub>int</sub> = 0.0460); 509 parameters; final wR<sub>2</sub> = 0.2042 (all data); R<sub>1</sub> = 0.0682 [I > 2σ(I)]; largest difference peak/hole 0.995/–1.633 e<sup>–</sup> Å<sup>–3</sup>. CCDC-263199 and -263200 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): NMR spectra of tBu<sub>2</sub>O formed during the reaction.

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