Copper-mediated cleavage of disulfides by tertiary phosphines: a new route to As–S anions \dagger

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The synthesis of [(PhAs)₂(μ -S₂)(μ -S)] and its reactions to form novel Cu(I) complexes are reported, together with a new cleavage reaction of disulfides by Cu(I) thiolates and tertiary phosphines.

In comparison to the chemistry of phosphorus chalcogenides the related area of arsenic chalcogenides is less developed. This is illustrated by a large number of ca. 1750 compounds containing P-E-metal (E = S, Se, Te) structural motifs in comparison to less than 100 hits for analogous arsenic compounds [As-E-metal (E = S, Se, Te)].^{1,2} Amongst the metal complexes containing arsenic-chalcogenide-based ligands, As-S ligands are predominant. Synthetic routes to metal complexes with As-S ligands include the transformation of As-S precursors in the coordination sphere of a transition metal or synthesis in melts.³⁻⁹ Alternatively, preformed As-S ligands can directly be reacted with metal complexes in ligand exchange reactions.10-12 The interest in this type of chemistry has so far been motivated mainly by structural features of previously unknown compounds in addition to the biological role of arsenic which is known to bind to S atoms of cysteine sites in proteins.¹³⁻¹⁶ The present investigation builds on recent results where metal salts containing P-S and P-Se anions were obtained in one-pot syntheses from metal salts and chalcogen transfer reagents.¹⁷⁻¹⁹ In the following at first the optimised synthesis of an arsenic compound analogous to Lawesson's reagent (L. R.) $[ArP(S)(\mu-S)]_2$ (Ar = 4-anisyl) is described and then, the transformation of an As-S heterocyclic compound to the first representatives of coinage metal complexes containing As-S anions is demonstrated.

The phosphorus chalcogenide heterocyclic compounds L. R. or Woollins' reagent (W. R.) [PhP(Se)(μ -Se)]₂ are easily accessible (Scheme 1).²⁰⁻²² For arsenic analogs, however, compounds of the type [RAs(S)(μ -S)]₂ (R = organic group) are unknown. [(PhAs)₂(μ -S₂)(μ -S)] is the closest related As–S reagent to L. R. and it is obtained by treating solutions of PhAs(O)(OH)₂ with H₂S(g) (Scheme 1).^{23,24} In the course of the reaction H₂S is partially oxidised to unidentified polysulfanes whilst As(v) is reduced to As(III). The formation of As–S heterocyclic compounds containing As=S double bonds has so far not been observed (and a theoretical study describes hypothetical As–S double bonds as polarized σ -bonds, with the bond strength depending on the electrostatic interactions between the As and S atoms rather than on π -

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Scheme 1 Synthesis of Group 15 chalcogen transfer reagents.

back-donation).²⁵ The high-yield preparation of $[(PhAs)_2(\mu-S_2)(\mu-S)]$ was achieved by an adapted procedure, originally used for the preparation of As₄S₅, in which PhAs(O)(OH)₂ was dissolved in concentrated hydrochloric acid and reacted with H₂S at low temperature.²⁶

When $[(PhAs)_2(\mu-S_2)(\mu-S)]$ is reacted with the Cu(1) thiolate CuSCy (Cy = Cyclohexyl, C₆H₁₁) in the presence of the tertiary phosphine PEt₃, $[Cu_4{Ph(S)As-As(S)Ph}_2(PEt_3)_4]$ (1) is formed in moderate yield (Scheme 2). The structural analysis showed that 1 consists of a centrosymmetric arrangement of four $[Cu(PEt_3)]$ units held together by two [Ph(S)As-As(S)Ph]-dianions (Fig. 1).[‡]§

$$\begin{array}{c} S \xrightarrow{S} \\ I \\ Ph \xrightarrow{As-S} \end{array} \xrightarrow{S} \left[CuSCy, PEt_3 \xrightarrow{} [Cu_4[Ph(S)As-As(S)Ph]_2(PEt_3)_4] (1) \\ THF \end{array} \right]$$

Scheme 2 Synthesis of 1.

The phenyl substituents at As(1,2) are in a *gauche*-conformation and form the organic shell of **1** together with ethyl substituents of the tertiary phosphine. S(1) and S(2) each bridge two Cu atoms. Cu(1) is four-coordinated, interacting with the stereochemically active lone-pair at As(1), two S atoms and one phosphine ligand. Cu(2) is three-coordinated by S atoms and one phosphine ligand. The lone-pair at As(2) is not involved in metal coordination and is pointing towards the periphery of the arrangement. The formation of $[Ph(S)As-As(S)Ph]^{2-}$ anions in the course of the reaction was surprising and a comparison of starting materials and product reveals that in **1** the bridging S atom between arsenic atoms is missing. Instead, formation of a As-As bond and cleavage of the disulfide bridge, present in the starting material, were observed. This rather complex transformation can be regarded

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Fig. 1 Solid-state structure of **1** (disordered components of one PEt₃ ligand are omitted). Selected bond lengths [Å] and angles [°]: As(1)–Cu(1) 2.4533(8), As(1)–As(2) 2.4648(8), As(1)–S(1) 2.2096(15), As(2)–S(2) 2.2185(16), Cu(1)–P(1) 2.201(3), Cu(2)–P(2) 2.2089(19), Cu(1)–S(1A) 2.3201(17), Cu(1)–S(2A) 2.3450(16), Cu(2)–S(1) 2.2542(15), Cu(2)–S(2A) 2.3121(16); S(1)–As(1)–Cu(1) 111.65(4), S(1)–As(1)–As(2) 102.90(4), Cu(1)–As(1)–As(2) 116.17(3), S(2)–As(2)–As(1) 95.32(4). Symmetry operations: -x + 1, -y + 1, -z (A).

as a multiple reduction of the neutral As–S starting material in which desulfuration and formation of the As–As bond can be explained by oxidation of the tertiary phosphine PEt₃ to Et₃P=S (solid samples of **1** were contaminated with Et₃P=S).²⁷ Similar reactions were observed for trithiophosphonates.²⁸ In order to study the cleavage of the disulfide bridge in [(PhAs)₂(μ -S₂)(μ -S)] and to understand the role of the anions in Cu(1) thiolates, several reactions of [(PhAs)₂(μ -S₂)(μ -S)] with tertiary phosphines and a range of Cu(1) thiolates were performed. In the case of a mixture of [(PhAs)₂(μ -S₂)(μ -S)], CuSEt and PPh₃ this resulted in the formation of crystals of [Cu₄{Ph(S)As–S–As(S)Ph}₂(PPh₃)₄] (**2**) (Scheme 3, Fig. 2).

$$\begin{array}{c} S \xrightarrow{S} \\ As - Ph \xrightarrow{CuSEt, PPh_3} \\ As \xrightarrow{S} S \xrightarrow{} Ph \xrightarrow{As \xrightarrow{S}} Ph \xrightarrow{THF} Ph_3^{P(SEt)]^+} (EtS)^- \end{array}$$

Scheme 3 Synthesis of 2.

In the solid state **2** forms a cage arrangement consisting of four [Cu(PPh₃)]-units, in which the Cu atoms are chelated by [Ph(S)As–S–As(S)Ph]^{2–} anions. The core composition found in **2** can be described as two dimerised norbornane-like [Cu₂{Ph(S)As–S–As(S)Ph}(PPh₃)₂}]-arrangements consisting of five-membered [Cu₂As₂] and [Cu₂S₂As] rings (with additional organic groups and phosphine ligands). In contrast to **1** where formation of a As–As bond and cleavage of the disulfide bridge were observed now the reaction of [(PhAs)₂(μ -S₂)(μ -S)], CuSEt and PPh₃ resulted in the formation of [Ph(S)As–S–As(S)Ph]^{2–} anions. During the reaction the disulfide bridge in [(PhAs)₂(μ -S₂)(μ -S)] was cleaved but the sulfur bridge between As atoms was retained. Mechanistically this observation can be rationalised by oxidation of PPh₃ and



Fig. 2 Solid-state structure of 2 (phenyl groups of triphenylphosphine ligands were omitted). Selected bond lengths [Å] and angles [°]: As(1)–Cu(1) 2.4144(9), As(2)–Cu(2) 2.4122(9), As(3)–Cu(3) 2.4076(9), As(4)–Cu(4) 2.4331(9), As(1)–S(1) 2.2548(16), As(1)–S(2) 2.2106(14), As(2)–S(3) 2.2104(14), As(2)–S(1) 2.2549(15), As(3)–S(5) 2.2167(15), As(3)–S(4) 2.2608(15), As(4)–S(6) 2.2069(16), As(4)–S(4) 2.2614(15), Cu–P 2.2390(18)–2.2504(17), Cu–S 2.3171(14)–2.3793(16); S(2)–As(1)–S(1) 104.55(5), S(3)–As(2)–S(1) 103.89(5), S(5)–As(3)–S(4) 103.72(6), S(6)–As(4)–S(4) 103.82(6), S(2)–As(1)–Cu(1) 110.87(4), S(1)–As(1)–Cu(1) 104.40(5), S(3)–As(2)–Cu(2) 110.91(4), S(1)–As(2)–Cu(2) 105.05(5), S(5)–As(3)–Cu(3) 111.11(4), S(4)–As(3)–Cu(3) 103.47(5), S(6)–As(4)–Cu(4) 111.34(4), S(4)–As(4)–Cu(4) 102.95(4), As(2)–S(1)–As(1) 90.44(5).

formation of $[Ph_3P(SEt)]^+(SEt)^-$ and **2**. The $[Ph_3P(SEt)]^+$ -ion was observed in MALDI-TOF experiments. A broader application of these findings could be the copper-mediated cleavage of all kinds of disulfides. In this context a couple of model reactions were performed (Scheme 4). The cleavage of MeS–SMe by CuSEt/PEt₃ or CuSEt/PPh₃ was investigated and the ³¹P NMR of reaction mixtures recorded. Several P-containing species $[R_3P=S,^{27}R_3P(SEt)^+, R_3PCu (R = Et, Ph)]$ were detected in the two separate reactions indicating that the nature of the organic substituent of phosphines does not seem to have an influence on the course of the reaction. Clearly, more studies are required in order to optimise this Cumediated reductive cleavage reaction of disulfides for synthetic purposes.^{29,30}

$$\begin{tabular}{|c|c|c|c|} \hline Me_2S + R_3P=S \\ \hline MeS-SMe \begin{tabular}{c|c|c|c|c|} \hline PR_3, CuSEt \\ \hline \begin{tabular}{|c|c|} \hline R_3P(SEt)]^+(SEt)^- + [MeSCu(PR_3)] \\ \hline \end{tabular}$$

Scheme 4 Competing desulfurization and reductive Cu-mediated disulfide cleavage of Me_2S_2 (R = Et, Ph).

The presented work showed that As-chalcogenides can be converted into unusual anions. Desulfurization and reductive cleavage both occurred in reactivity studies of the disulfides $[(PhAs)_2(\mu-S_2)(\mu-S)]$ and Me_2S_2 with mixtures of Cu(I) thiolates and tertiary phosphines.

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Notes and references

[‡] All structures were solved by direct methods and refined using SHELXTL with anisotropic thermal parameters for heavy atoms (Table 1).³¹ Disordered components were refined with isotropic thermal parameters.

§ *Crystal data for* 1: C₄₈H₈₀As₄Cu₄P₄S₄, M = 1463.08, triclinic, a = 11.8503(9), b = 12.4641(9), c = 12.6238(10) Å, a = 63.637(6), β = 64.437(6), $γ = 77.138(6)°, <math>U = 1506.0(2) Å^3$, T = 100(2) K, space group $P\overline{1}$ (no. 2), Z = 1, μ (Mo-Ka) = 3.849 mm⁻¹, 13441 reflections measured, 6856 unique ($R_{int} = 0.0594$) which were used in all calculations. wR_2 (all data) = 0.0.1454, $R_1 = 0.0525 \{I > 2\sigma(I)\}$.

Crystal data for 2: $C_{108}\dot{H}_{105}As_4\dot{C}u_4O_3P_4S_6$ M = 2321.00, monoclinic, a = 26.626(2), b = 19.8281(9), c = 19.0953(10) Å, $\beta = 99.870(5)^\circ$, U = 9931.9(10) Å³, T = 100(2) K, space group $P2_1/c$ (no. 14), $Z = 4, \mu$ (Mo-Ka) = 2.410 mm⁻¹, 31368 reflections measured, 20179 unique ($R_{int} = 0.0670$) which were used in all calculations. wR_2 (all data) = 0.1174, $R_1 = 0.0516$ { $I > 2\sigma(I)$ }.

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All operations were carried out in an atmosphere of purified dinitrogen. All solvents were dried over the appropriate drying agent and freshly distilled prior to use. Cu(1) thiolates were synthesized according to a published procedure.³² PhAs(O)(OH)₂ was obtained from Strem Chemicals. [(PhAs)₂(µ-S₂)(µ-S)]: The published synthesis for [(PhAs)₂(µ-S₂)(µ-S)) (µ-S)] was modified as follows.^{23,24} 9.7 g (48.0 mmol) of PhAs(O)(OH)₂ was dissolved in a mixture of 50 mL H₂O and 100 mL concentrated hydrochloric acid. The solution was stirred and cooled in an ice bath. H₂S (g) was passed through the cold reaction mixture for 90 min. A pale yellow precipitate formed which was recrystallised from DME (DME = 1,2-dimethoxyethane) to give [(PhAs)₂(µ-S)]; 8.2 g, yield 85%, mp 142 °C. Found: C, 35.98; H, 2.48. C₁₂H₁₀As₂S₃ requires C, 36.01; H, 2.52%. The identity of the compound was confirmed by repeated unit cell determination of crystals.

1: A mixture of [(PhAs)₂(µ-S₂)(µ-S)] 200 mg (0.50 mmol) and CuSCy 179 mg (1.00 mmol) was dissolved in 10 mL THF. The reaction mixture was stirred for 1 day. A brown precipitate formed together with a yellow solution. Upon addition of 0.3 mL PEt₃ (2.00 mmol) a yellow solution was obtained. The reaction mixture was filtered and concentrated under reduced pressure to a volume of *ca*. 2 mL and layered with 15 mL hexane. After three days yellow crystals of 1 were obtained; 107 mg, yield 29%, mp 120 °C (decomp.). Found: C, 39.50; H, 5.55. C48H80As4Cu4P4S4 requires C, 39.40; H, 5.51%; v_{max}/cm⁻¹ (KBr) 3039 w (C-H, ar.), 2956 s, 2927 m, 2872 m, 1454 m, 1433 m (C-H, alkyl), 1576 w, 1474 m, 734 s, 689 s (C=C), 1413 m (P–C), 1328 w (As–C); $\delta_{\rm H}$ (400 MHz; CDCl₃; 23 °C) 1.24, 1.88 (m, PCH₂CH₃), 7.08–7.49 (m, 20H, ArH); $\delta_{\rm C}$ (100 MHz; CDCl₃; 25 °C) 6.5 (d, ${}^{2}J_{PC} = 4.5$ Hz, CH₃), 23.0 (d, ${}^{1}J_{PC} = 51.6$ Hz, P–CH₂); δ_{P} (162 MHz; CDCl₃; 23 °C; 65% H₃PO₄) 54.9, 52.4 (s, S=PEt₃), -11.5 (br., CuPEt₃). 2: A mixture of [(PhAs)₂(µ-S₂)(µ-S)] 200 mg (0.50 mmol) and CuSEt 124 mg (1.00 mmol) was dissolved in 10 mL THF. The yellow solution was stirred for 15 h at room temperature. 524 mg (2.00 mmol) PPh₃ were dissolved in 5 mL THF and added to the reaction mixture. The reaction was then filtered and layered with hexane. After one day yellow crystals of 2 were obtained; 105 mg, yield 20%, mp 167 °C. Found: C, 54.84; H, 3.92. $C_{108}H_{105}As_4Cu_4O_3P_4S_6$ (-3 thf) requires C, 54.78; H, 3.88%; v_{max}/cm^{-1} (KBr) 3040 m (C-H), 1574 w, 1479 m, 739 s, 695 s (C=C), 1429 s (P-C), 1308 w (As-C); δ_H (400 MHz; CDCl₃; 23 °C) 6.9–7.3 (m, 80 H, ArH); δ_C (100 MHz; CDCl₃; 23 °C) 127.8–134.3 (ArC); δ_P (162 MHz; CDCl₃; 23 °C; 65% H₃PO₄) -3.6 (s, CuPPh₃). The mother liquor was evaporated and the solid residue analysed. δ_P (162 MHz; CDCl₃; 23 °C; 65% H₃PO₄) 43 (s,

S=PPh₃), 29 (s, [Ph₃PSEt]⁺[EtS]⁻), -5.1 (s, PPh₃); m/z (MALDI-TOF, 2,6-dihydroxyacetophenone) 322.8 (100%) (C₂₀H₂₀PS, [Ph₃PSEt]⁺ requires 323.1), 323.8 (25), 324.8 (8).

Reactions of Cu(1) thiolates/tertiary phosphines with Me_2S_2 : δ_P (162 MHz; CDCl₃; 23 °C; 65% H₃PO₄) 54.9, 52.4 (s, S=PEt₃), 40.2 [s, Et₃P(SEt)⁺], -11.5 (br., CuPEt₃) and 43.4 (s, S=PPh₃), 29.2 [s, Ph₃P(SEt)⁺], -5.1 (s, PPh₃).

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