Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
ARTICLE

DOI: 10.1002/zaac.201400492

The Electrophilic Character of Bunsen's Cacodyl Disulfide, $Me_2As(S)$-S-$AsMe_2$, Towards Some Nucleophiles of Groups 15 and 16

Panayiotis V. Ioannou*[a] and Dimitris G. Vachliotis[a]

Keywords: Dimethylarsino dimethyldithioarsinate; Amines; Phosphines; Phenol; Thiophenol; Methoxide; Phenoxide; Thiophenoxide

Abstract. The reactivity of Bunsen's cacodyl disulfide, $Me_2As(S)$-S-$AsMe_2$, towards nitrogen, phosphorus(III), oxygen and sulfur(II) nucleophiles was evaluated with the aim at identifying its electrophilic atom. The nitrogen nucleophiles either did not react or bind or split the disulfide. All phosphorus(III) nucleophiles desulfurized it. Water, methanol and phenol did not react but thiophenol reacted giving an equilibrated system. The anions MeO^-, PhO^- and PhS^- split the disulfide. From the results obtained it seems that the arsenic and sulfur of the As = S group are the most likely electrophilic atoms depending on the nature of the nucleophile, the As^{III} being much less reactive in the presence of As=S.

Introduction

The great experimental chemist *Robert Bunsen*[1] in 1843 prepared a compound $Me_4As_2S_2$ which he named cacodyl disulfide by reducing cacodylic acid, Me_2AsO_2H, with hydrogen sulfide.[2] Its structure was not the expected As^{III}/As^{III} bis(dimethylarsenic)disulfide (**2**) but the As^{V}/As^{III} dimethylarsino dimethyldithioarsinate[3,4]] and mechanisms of its formation have been proposed.[4,5]

Bunsen's cacodyl disulfide (**1**) is a remarkable chemical chameleon. When dissolved in non-basic solvents it equilibrates with **2** to the extent of approx. 10 %, thus showing an internal redox property.[6]

Bunsen, apart from studying the behavior of his disulfide towards heat, HCl, H_2SO_4 and HNO_3, he found that it reacted with metal salts of the non-reducible metals Pb^{II}, Sb^{III} and Bi^{III} giving the complexes $(Me_2AsS_2)_xM$ (= L_xM)[2] and we extended the list by preparing complexes with Zn^{II}, Cd^{II} and Ag^{I} under conditions that afforded pure products.[7]

With compounds of lighter metals like $AlCl_3$, compound **1** was isomerized to **2**, $GaCl_3$ and $InCl_3$ bound to **1**, while $Tl(AcO)_3$ was reduced giving LTl.[8] *Bunsen* himself also found that the reducible Au^{III} and Cu^{II} gave the complexes LAu and LCu[2] and we[7] verified the production of LCu identifying some by-products. Pd^{II} also produced L_2Pd that was unstable and decomposed to unknown compounds,[9] but Hg^{II} was not reduced.[7] It was proposed[7,8] that the electron for the reduction came from the bound $Me_2AsS_2^-$ group and reasonable mechanisms for the reduction of Cu^{II} and Tl^{III} have been proposed later on.[10] In all cases, **1** attacked the cation with either sulfur atoms acting as nucleophiles.[7]

Because the reaction of *Bunsen*'s disulfide (**1**) with metal cations produces L_xM and $xMe_2As:^+$ that is wasted, the salt $Me_2AsS_2Na{\cdot}2H_2O$ (**3b**) was prepared[9,11,12] and used for the preparation of many complexes although it too, has the limitation that, after protonation to **3a**, compound **1** is produced.[10]

Another aspect of the behavior of **1** is its electrophilic property reacting with Lewis bases first encountered by *Zingaro* et al.[6] by dissolving **1** in pyridine and aniline and recording the ^1H NMR spectra that remained unexplained until we studied the reaction of **1** with group 15 nucleophiles: Ph_3N, Et_3N and DMAP (4-dimethylaminopyridine), Ph_3P, $(MeO)_3P$, $(EtO)_3P$, $(PhO)_3P$ and $(PhS)_3P$, Ph_3As and $(PhS)_3As$ which gave fission or desulfurization products that depended on the nature of the nucleophile.[5] The results were best interpreted by the initial attack of the nucleophile on the electrophilic As=S sulfur and cations like Me_2As-S-NEt_3^+ [5] and Me_2As-S-$NC_5H_5^+$ [6] and the anion Me_2As-S^- were present, as the ^1H NMR spectra indicated.

From group 16 nucleophiles, H_2O in CD_3OD slowly isomerized **1** to **2** and two singlets appeared attributable to $Me_2As(S)$-OH and $Me_2As(S)$-OCD_3,[5] but when **1** was dissolved in acetate buffer pH 4.6 and chromatographed it decomposed giving cacodylic acid (Me_2AsO_2H), dimethylarsinous acid (Me_2As-OH), dimethylthioarsinic acid ($Me_2As(S)$-OH) and the unstable[5] dimethyldithioarsinic acid (**3a**).[4] The reaction of **1** with Me_3COOH gave two novel As^{V}/As^{V} compounds: $Me_2As(S)$-S-$As(O)Me_2$ and $Me_2As(S)$-O-$As(S)Me_2$.[13] Bubbling H_2S for 5 min to a solution of **1**+**2** very slowly (12 days) resulted in the disappearance of **2** but the reaction was not studied further.[5] With a strong nucleophile, triethylamine-activated octasulfur, **1** reacted slowly reaching an equilibrium containing **1** and the ions

* Prof. Dr. P. V. Ioannou
Fax: +30-2610-997118
E-mail: ioannou@chemistry.upatras.gr
[a] Department of Chemistry
University of Patras
26504 Patras, Greece

Me_2As-S-NEt_3^+ and $Me_2As(S)$-S^-.[14] With an even stronger nucleophile, S^{2-} + $1/8S_8$, the disulfide **1** gave the salt $Me_2AsS_2Na{\cdot}2H_2O$ (**3b**).[9,11]

In this paper we report on the reaction of **1**, sometimes equilibrated with **2**,[6] with some more nucleophiles (molecules and salts) of groups 15 and 16 of the Periodic Table. Some molecules have hydrogen atoms connected to the nucleophilic center that can protonate the incipient anions. We looked at the possibility of obtaining a salt of Me_2As-SH (**5a**) useful for the introduction of the Me_2As-S- group into various molecules.[15] Finally, we tried to find the most probable electrophilic center of **1** in its reactions with group 16 nucleophiles.

Results and Discussion

Reaction Conditions and Identification of the Products

For some NMR experiments the reactants were added in the tube followed by the solvent thus not allowing **1** to equilibrate[6] with **2**. In other experiments **1** was equilibrated with **2** in order to explore the electrophilic reactivity of **2** as well.

The identification of the products was based on the ^{1}H NMR shifts[5,7] shown under the formulae (Figure 1) although not all singlet signals in various experiments could be assigned.

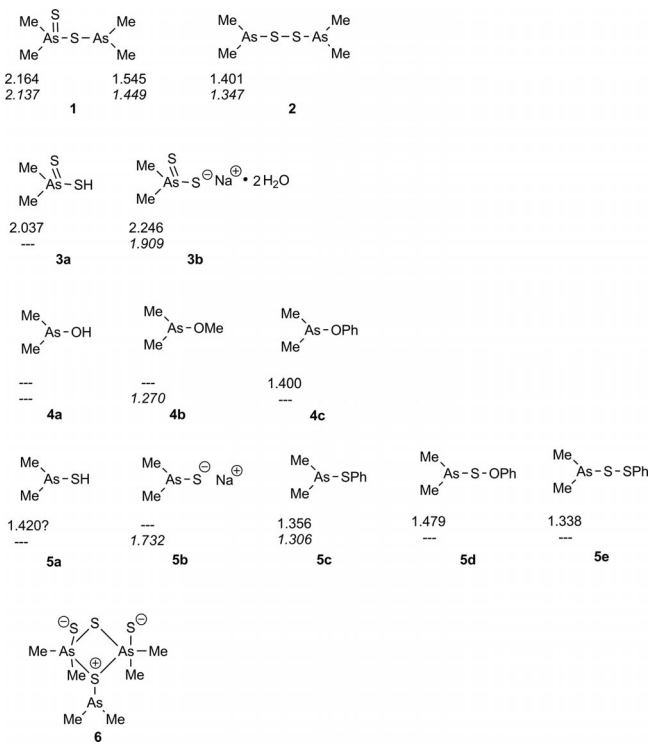

Figure 1. Formulae of the compounds encountered in this work showing the *Me*$_2$As proton shifts in $CDCl_3$ and in CD_3OD (italics).

Reaction of 1 with Group 15 Lewis Bases

Adding one equivalent of **1** to solutions of pyridine and aniline in $CDCl_3$ we observed binding of the base to **1** as the shifting of the aromatic protons indicated and at the same time isomerization to equilibrium quantity of **2**. Addition of bases in excess (10x) did not produced any new singlet signals. These data can be understood as being due to the weak basicity of pyridine and aniline (pK_b 8.96 and 9.38[16]) that caused only binding and isomerization but not splitting. For the latter to take place neat bases are obviously required.[6] The same behavior was observed with diphenylamine. In this case the pK_b is 13.2[16] and the crystal structure of the base showed that the lone pair on nitrogen is not on a sp^3 hybrid orbital.[17] $(Me_2N)_3P$ desulfurized **1** giving $(Me_2N)_3P$ = S (δ =81.71 ppm; lit.[18] –77.5 ppm).

Reaction of 1 with Oxygen and Sulfur(II) Nucleophiles

Bunsen's disulfide (**1**) is stable in methanol.[6] Phenol is more acidic (pK_a 9.9) than methanol and water[16] and it is expected that the phenolate anion will slowly react with **1**. However, equimolar quantities of **1** and phenol in $CDCl_3$ showed only binding and isomerization to the equilibrium quantity of **2**.

Contrary to the non-reactivity of phenol, when one equivalent of thiophenol was added to equilibrated **1**+**2** in $CDCl_3$ (Figure 2A) immediate reactions took place (Figure 2B) that seems to have reach an equilibrium in approx. 24 h (Figure 2C) thus indicating thiophilicity of **1**. Free thiophenol (-S*H* at ap-

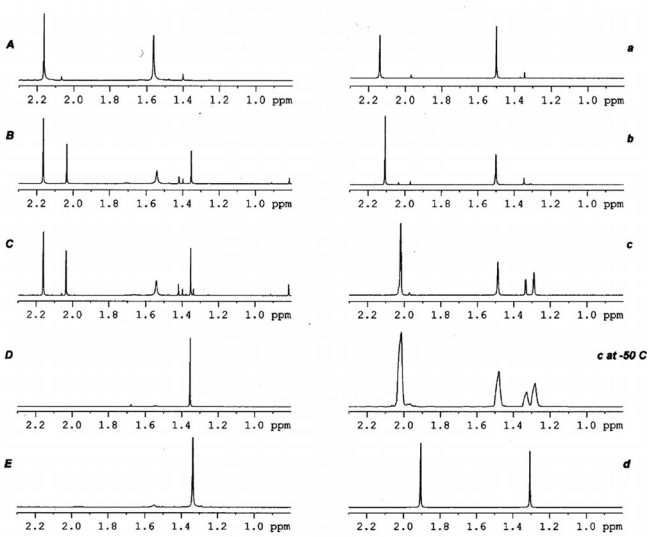

Figure 2. Addition of equimolar quantity of PhSH to equilibrated **1**+**2** (**A**), in 5 min produced Me_2AsS_2H (**3a**) (at 2.037 ppm) and Me_2As-SPh (**5c**) (at 1.354 ppm) (**B**). The system reached an equilibrium (**C**) having PhS*H* (at 3.45 ppm), **1**, **2**, **3a**, **5c**, and **5e**. The small singlets at 0.816 and 1.420 ppm are tentatively assigned to Me_2As-H and Me_2As-SH (**5a**), respectively, while the singlet at 0.914 ppm could not be assigned. Isolated Me_2As-SPh **5c** resonates at 1.356 ppm (**D**), while in the presence of an equimolar quantity of PhSSPh resonates at 1.337 ppm[5] (**E**). Spectra (**A**)–(**E**) in $CDCl_3$. The reaction of equilibrated **1**+**2** (**a**) with $PhSNa{\cdot}2H_2O$ under 1:0.1 stoichiometry produced Me_2As-SPh (**5c**) (at 1.311 ppm) and shifted the *Me*$_2$As(S) protons (**b**), while under 1:0.5 stoichiometry more **5c** was produced (**c**, run at –25 °C). The singlets did not split but broadened at –50 °C (**c at –50 °C**). Under 1:1 stoichiometry the products **3b** and **5c** resonated at 1.909[9] and 1.308 ppm, respectively, at 25 °C (**d**). Spectra (**a**)–(**d**) in CD_3OD.

prox. 3.5 ppm), **1** and **2** were always present. The concentration of **2** was initially less but thereafter greater than its equilibrium concentration. The singlet for *Me*$_2$As protons of **1** was always broad and its integration was less than expected. The main products that appeared at once were Me_2AsS_2H (**3a**) and Me_2As-SPh (**5c**). Then, a new singlet signal for Me_2As-SSPh (**5e**) appeared (Figure 2C). Thus, the production of **3a/5c** implies involvement of either As or S of As = S and the production of **5e** indicates attack at As=S sulfur. These alternatives indicate that thiophenol prefers the As = S sulfur and, from a common intermediate, **3a/5c** and **5e** can arise (see Figure 3). The chemical shifts of **5c** and **5e** in $CDCl_3$ (Figure 2) are the opposite of those reported[5] due to a more concentrated solution of a mixture of **5c** + PhSSPh then used as standard (Figure 2E). The other two singlet signals at 1.420 and 0.816 ppm (Figure 2B and Figure 2C) can tentatively be assigned to Me_2As-SH **5a** and Me_2As-H, respectively, based on mechanistic considerations although a detailed picture cannot be offered for the following reasons.

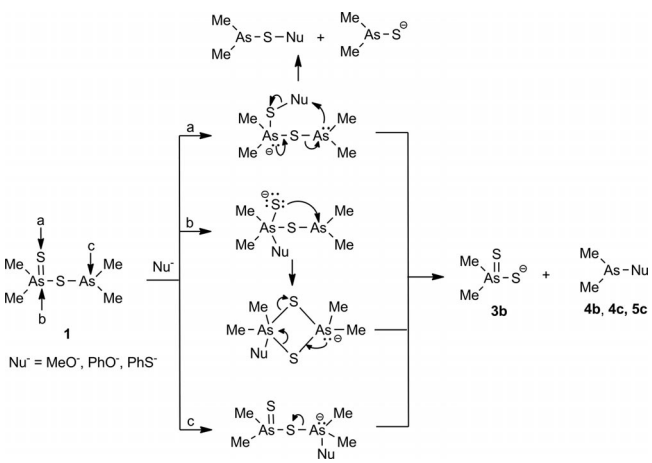

Figure 3. Probable intermediates from the attack of a strong Lewis base on *Bunsen*'s disulfide (**1**).

The known dimethyldithioarsinic acid (**3a**) is an intermediate in the synthesis of **1** (from cacodylic acid and H_2S[4,5]) by dimerization and expulsion of H_2S and S_8. The molecule Me_2As-SH (**5a**), found in the literature[19] but mistaken for $Me_2As(S)$-OH,[20] should be reactive and can be autoxidized to either cacodylic acid Me_2AsO_2H[21] (not detected at 1.956 ppm in $CDCl_3$) or $Me_2As(S)$-OH[22] (which in D_2O resonated at 2.11[23] or 2.12[24] ppm) that seems to be absent in our system. Finally, **5a** can conceivably disproportionate to **3a**, cacodyl (Me_2As-$AsMe_2$), and H_2S. Cacodyl (resonating at δ = 1.11 ppm in $CDCl_3$[25] and at δ = 1.04 ppm in benzene[26]) was absent in our system probably because it reacted with H_2S (by analogy with HCl[27]) to give **5a** and dimethylarsine Me_2As-H. The singlet signal at 0.816 ppm can be attributed to this arsine because in benzene resonates at δ = 0.79 ppm.[26]

In an attempt to get a better understanding on the reaction of **1** with PhSH, we studied the reaction of **1** with PhONa in chloroform and in dry ether and of MeONa, PhSNa, and PhSNa·$2H_2O$ in methanol.

Although $CDCl_3$ is not a good solvent, we did the reaction of **1** and PhONa in it in order to identify the initial products. Thus, in 30 min a little amount of **3b** was detected at 2.246 ppm[5] and **2** plus Me_2As-OPh (**4c**) resonating at 1.401 ppm. A small singlet signal at 1.478 ppm was due to Me_2As-S-OPh (**5d**) (obtained from the reaction of Me_2As-S-I with PhONa; P.V.I. unpublished). In 8 h some **1** remained, the main singlet signals corresponded to **4c** and **3b**. The other singlet signals could not be assigned. Running the reaction of **1** and PhONa in dry ether for 24 h, the salt **3b**[9] contaminated by Me_2As-SNa (**5b**) and the very readily hydrolyzed, volatile (b.p. 101 °C/12 Torr[28]) Me_2As-OPh (**4c**) contaminated by Me_2As-S-OPh (**5d**) were isolated. Thus, the phenolate attacked **1** at As=S arsenic(V) *and* sulfur.

Addition of MeONa in MeOH to a solution of equilibrated **1**+**2** in CD_3OD under a 0.5:1 molar ratio gave a yellowish solution whose ^{1}H NMR spectrum after 5 min clearly showed **1** that had not reacted. The "product" Me_2AsS_2Na (**3b**) resonated at 2.012 ppm while Me_2As-OMe (**4b**)[28] at 1.269 ppm. The interaction created more Me_2As-SS-$AsMe_2$ (**2**) than the equilibrium value and a new singlet at 1.971 ppm having the 1/5 intensity of the "product" appeared. Thus, under these conditions MeO^- partly isomerized **1** to **2** and split **1** to **4b** and **3b**, the latter interacting with the $Me_2As(S)$-group of **1**. Under 1:1 stoichiometry, apart from **3b** and **4b**, small singlet signals at 1.553, 1.731 and 1.970 ppm appeared that could not be assigned. The important point is that MeO^- reacted with **2**, probably at As^{III} giving **4b** and Me_2As-S-S^- that rearranged to **3b**[5] or **2** that rearranged to **1** which then reacted. Both compounds had reacted when the NMR tube was left open for 7 days giving four products that were not identified. Summarizing, these results tend to indicate that MeO^- can attack **1** at As^V and certainly at As=S sulfur and to a lesser degree at As^{III}.

A preparative run of **1** with PhSNa·$2H_2O$ under 1:1 molar ratio in methanol gave the known[9] Me_2AsS_2Na·$2H_2O$ (**3b**) and Me_2As-SPh (**5c**) (known in the literature[29,30] but no data have been reported). We used the chemical shifts of **5c** in $CDCl_3$ and in CD_3OD to distinguish between **5c** and **5e** in runs with PhSH and PhSNa·$2H_2O$/PhSNa. The reaction of **1** with PhSNa·$2H_2O$ in CD_3OD differed from that of **1** with PhSH in $CDCl_3$ in that in the titration experiments (Figure 2a–d) the PhSNa had always totally reacted as the pattern of the aromatic protons revealed. Under 1:0.1→0.8 molar ratios of **1** to PhSNa·$2H_2O$, **2** was produced in quantities more than the equilibrium one. The absence of the singlet signals due to *Me*$_2$As(S) protons of **1** and of the product **3b** and the appearance of only one singlet between 2.137 and 1.909 ppm signifies a very fast exchange probably via a complex of **1** and $Me_2AsS_2^-$ in which the Me_2As^{III} group also participates, e.g. **6** (Figure 1). The broadness of the *Me*$_2$As-SPh protons at approx. 1.30 ppm, too, may be due to its complexation with $Me_2AsS_2^-$. The difference in the spectra of **1** with MeO^- and PhS^- at 1:0.5 molar ratios should be attributed to the greater thiophilicity of **1**. Under 1:1 stoichiometry, **2** had reacted as in the case of MeO^- and the spectrum showed only two sharp singlet signals due to **3b** and **5c** (Figure 2d). The reaction of **1** with anhydrous PhSNa (1:0.5 molar ratio) gave the same spec-

trum as in Figure 2c implying that the waters do not affect the mechanism. Thus, PhS^- behaved as MeO^- and not as PhO^- or PhSH.

Summarizing, the results on the reaction of **1** with MeO^-, PhO^- and PhS^- can be understood by attack of the nucleophile on As^{III}, As^V, or As = S sulfur but not on the As-S-As sulfur (Figure 3). It seems that attack at As^{III} of **1** is not preferred in the presence of the As=S group (because **2** reacted when all **1** had reacted (Figure 2c vs. 2d) despite the fact that mechanistically can give the products in one step. Thus, there is a choice between As^V and As=S sulfur as targets of these anionic nucleophiles. Probably attack at As^V is favored because it may be in the form As^+-S^- having a vacant orbital ready to accept the electron pair of an anionic nucleophile.

Conclusions

The interaction of *Bunsen*'s cacodyl disulfide (**1**) in solution with nitrogen nucleophiles examined in this paper and in the literature[18] fall into three groups: non-reactive (Ph_3N), binding and equilibrating (Ph_2NH, $PhNH_2$, pyridine), splitting to a cation and an anion (Et_3N, 4-dimethylaminopyridine). All phosphorus(III) compounds examined[5] desulfurized **1** as did $(Me_2N)_3P$. Desulfurization was also observed with Ph_3As, while with $(PhS)_3As$ the reaction was more complicated.[5] Therefore, with group 15 nucleophiles, the electrophile was the As=S sulfur of **1**.

While water, methanol and phenol were inert towards **1**, thiophenol was reactive, indicating thiophilicity of **1** at the As=S sulfur, but gave an equilibrium mixture of **1**, **2**, PhSH and products. With strong Lewis bases such as PhO^-, **1** gave two sets of products **3b/4c** and **5b/5d**, while with MeO^- and PhS^-, **1** was neatly split to $Me_2AsS_2^-$ (**3b**) and **4b** and **5c**, respectively, but these reactions do not offer greater advantages over the existing methods of preparation of **3b**[9,11,12] or **4b**,[28] **4c**,[28] and **5c**[29] the latter three prepared from Me_2As-*X*. Therefore, with group 16 anionic nucleophiles no definite conclusion can be reached because the electrophilic atom in **1** can be either the arsenic(V) or sulfur of the As=S group, the As^{III} having a low reactivity in the presence of As = S.

Experimental Section

Bunsen's cacodyl disulfide **1** was prepared according to *Zingaro* et al.[5,6] Aniline (Penta, Prague), diphenylamine (BDH), crystalline phenol and sodium methoxide 0.5 M in methanol (Aldrich), tris(dimethylamino)phosphine and sodium phenoxide 98% (Alfa Aesar), and thiophenol (Merck) were used as received. Pyridine was distilled over KOH and kept over 4 Å molecular sieves. Silica gel 60 H (Merck) was used for thin layer chromatography, TLC.

TLCs were run on microslides and visualization was effected by iodine vapors. IR spectra were obtained on a Perkin–Elmer, model 16PC, FT-IR spectrometer, while ^{1}H NMR spectra (400 MHz) and ^{31}P NMR spectra (162 MHz) were recorded with a Bruker DPX Avance spectrometer with internal TMS (0.000 ppm) as standard. Elemental analyses were obtained through the Centre of Instrumental Analyses, University of Patras, Patras, Greece.

Preparation of Sodium Thiophenolate Dihydrate

In a 10 mL round-bottomed flask thiophenol (875 mg, 7.87 mmol) was diluted with methanol (3 mL), solid sodium hydroxide (286 mg, 7.16 mmol) was added and stirred at room temperature for 1 h. The clear, colorless solution was evaporated and dried in vacuo to give a white solid (1.0340 g). To the solid, diethyl ether (10 mL) was added, stirred at room temp. for 30 min, transferred to a centrifuge tube and centrifuged. The solid was washed with diethyl ether (10 mL) by stirring at room temp. for 30 min. Centrifugation and drying in vacuo gave the product as the dihydrate (871 mg, 72%) as a white solid. M.p.: approx. 130 °C some shrinking and "sweats", 170 °C more shrinking, 185 °C water droplets on the wall, 220 °C the water droplets evaporated, no melting up to 300 °C. Calculated for $C_6H_5SNa{\cdot}2H_2O$ (M_r 168.18): C 42.85, H 5.39, S 19.06%; found C 42.78, H 4.80, S 20.44%. **IR** (KBr): 3274 vs, broad, 1650 s, 1626 s, 1592 m, 1572 s, 1458 s, 1428 m, 1258 w, 1172 w, 1084 s, 1064 m, 1020 m, 746 vs, 700 vs, 560 s. **^{1}H NMR** (CD_3OD, TMS): δ = 6.73 (apparent triplet, 1 H, *para*-H), 6.89 (apparent triplet, 2 H, *meta*-H), 7.35 (apparent doublet, 2 H, *ortho*-H).

Preparation of Anhydrous Sodium Thiophenolate

Modified procedure of *Kornblum* et al.[31] In a 5 mL oven-dried round-bottomed flask containing thiophenol (61 mg, 0.55 mmol) was added sodium methoxide 0.5 M in methanol (1.00 mL, 0.50 mmol), the solution was evaporated (Rotary, 45 °C) and dried in vacuo for 1 h. Addition of dry ether (3 mL) and stirring for 30 min gave a white powder that was transferred to an oven-dried centrifuge tube and centrifuged. After drying in vacuo at room temp. for 1 h the product (64 mg, 97%) was obtained as a white very hygroscopic powder, infusible up to 300 °C. Calculated for C_6H_5SNa (M_r 132.15): C 54.53, H 3.81, S 24.26%; found C 54.17, H 4.64, S 24.65%. **IR** (KBr): absorbs water from KBr; exactly the same as that of $PhSNa{\cdot}2H_2O$. **^{1}H NMR** (CD_3OD, TMS): similar to that of $PhSNa{\cdot}2H_2O$.

Reaction of Bunsen's Disulfide (1) with Some Lewis Bases of Groups 15 and 16

In a NMR tube **1** (0.05–0.10 mmol) was dissolved in $CDCl_3$ or CD_3OD (0.5–0.75 mL), an equimolar quantity of the nucleophile was added and the progress of the reaction was followed by ^{1}H NMR spectroscopy. For mechanistic studies, **1** was titrated with various amounts of the nucleophile and the progress of the reactions was followed by ^{1}H NMR spectroscopy.

Reaction of Bunsen's Disulfide (1) with PhONa

To a solution of **1** (137 mg, 0.5 mmol) in dry ether (5 mL) in an oven-dried centrifuge tube was added sodium phenolate (58 mg, 0.5 mmol) and the suspension stirred at room temp. for 24 h. Centrifugation, washing with diethyl ether (2 × 2 mL) by stirring at room temp. for 10 min each time, gave a white solid (112.5 mg, expected $Me_2AsS_2Na{\cdot}2H_2O$ (**3b**) 114 mg).**^{1}H NMR** (CD_3OD, TMS): δ = 1.906 (s, 6 H, CH_3 of **3b**), 1.732 (s, 1.83 H, CH_3 attributed to Me_2As-S^-Na^+ **5b**) and small singlets at 1.552 and 1.971 ppm.

From the ether supernatants, after evaporation only (Rotary, 18 °C), a colorless mobile liquid (106.5 mg, expected Me_2As-OPh (**4c**) 99.0 mg) was obtained. TLC (Et_2O/petroleum ether 1:1) showed spots at R_f 0.96 (strongest), 0.74 (PhOH), and 0.03. **IR** (neat): 3364 s, broad, 3044 m, 2978 m, 2906 m, 1604 s, 1594 vs, 1500 vs, 1483 vs, 1472 vs, 1406

m, 1364 m, 1234 vs, 1166 s, 1152 m, 1070 m, 1024 m, 1000 w, 892 m, 828 m, 812 s, 754 vs, 692 vs, 578 m, 506 m. **^{1}H NMR** ($CDCl_3$, TMS): δ = 1.400 (s, 6 H, CH_3 of **4c**), 1.479 (s, 3 H, CH_3 attributable (P.V.I. unpublished) to Me_2As-S-OPh (**5d**)), small singlets at 1.311 and 1.344 ppm and traces of ether. In the aromatic region PhOH was detected.

Reaction of Bunsen's Disulfide (1) with PhSNa·2H$_2$O: Preparation of Me$_2$As-SPh (5c) and Me$_2$AsS$_2$Na·2H$_2$O (3b)

To a mixture of **1** (137 mg, 0.5 mmol) and sodium thiophenolate dihydrate (84 mg, 0.5 mmol) in a 10 mL round-bottomed flask was added methanol (4 mL) and the solution stirred at room temp. for 2 h. Evaporation and drying in vacuo gave a white solid that was extracted with dichloromethane (3 × 2 mL) by stirring at room temp. for 15 min each time. Drying the solid in vacuo gave $Me_2AsS_2Na{\cdot}2H_2O$ **3b** (107 mg, 94%) as a white solid soluble in methanol and water and insoluble in dichloromethane, ether and acetone. M.p.: at approx. 170 °C sinters, at approx. 185 °C shrinks and turns light orange and at 200–203 °C melts to an opalescent orange oil. Calculated for $C_2H_6AsS_2Na{\cdot}2H_2O$ (M_r 228.13): C 10.53, H 4.42, S 28.11%; found C 10.95, H 4.07, S 27.97%. **IR** (KBr): same as $Me_2AsS_2Na{\cdot}2H_2O$ (**3b**).[9] **^{1}H NMR** (CD_3OD, TMS): δ = 1.906 (s). It resonates exactly at the same position as $Me_2AsS_2Na{\cdot}2H_2O$ (**3b**).[9]

The dichloromethane extracts were evaporated and dried in vacuo for a short time to give Me_2As-SPh (**5c**) (95 mg, 88%) as a colorless mobile liquid having a faint smell, soluble in chloroform, ether and methanol. TLC (ether/petroleum ether 1:5, R_f 0.75). Calculated for $C_8H_{11}AsS$ (M_r 214.15): C 44.87, H 5.18, S 14.97%; found C 44.40, H 4.90, S 14.65%. **IR** (neat): 3070 m, 3056 m, 2990 m, 2906 m, 1580 s, 1476 s, 1436 s, 1416 m, 1302 w, 1254 m, 1084 m, 1066 m, 1024 s, 1000 w, 896 s, 836 s, 740 vs, 690 vs, 578 m. **^{1}H NMR** ($CDCl_3$, TMS): δ = 1.356 (s, 6 H, Me_2), 7.25 (m, 3 H, *m* and *p*–Ph–*H*), 7.43 (m, 2 H, *o*–Ph–*H*). **^{1}H NMR** (CD_3OD, TMS): δ = 1.306 (s, 6 H, Me_2), 7.25 (m, 3 H, *m* and *p*–Ph–*H*), 7.40 (m, 2 H, *o*–Ph–*H*).

Acknowledgments

The authors acknowledge Professor *D. Papaioannou* of this Department for useful comments on the mechanisms reported herein.

References

[1] D. Seyferth, *Organometallics* **2001**, *20*, 1488–1498.
[2] R. Bunsen, *Justus Liebigs Ann. Chem.* **1843**, *46*, 1–48.
[3] N. Cameron, J. Trotter, *J. Chem. Soc.* **1964**, 219–227.
[4] M. W. Fricke, M. Zeller, H. Sun, V. W.-M. Lai, W. R. Cullen, J. A. Shoemaker, M. R. Witkowski, J. T. Creed, *Chem. Res. Toxicol.* **2005**, *18*, 1821–1829.
[5] P. V. Ioannou, D. G. Vachliotis, T. D. Sideris, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2077–2084.
[6] R. A. Zingaro, K. J. Irgolic, D. H. O'Brien, L. J. Edmonson Jr., *J. Am. Chem. Soc.* **1971**, *93*, 5677–5681.
[7] P. V. Ioannou, D. G. Vachliotis, T. D. Sideris, *Z. Anorg. Allg. Chem.* **2009**, *635*, 329–336.
[8] P. V. Ioannou, G. M. Tsivgoulis, D. G. Vachliotis, *Main Group Chem.* **2009**, *8*, 151–161.
[9] P. V. Ioannou, D. G. Vachliotis, V. Nastopoulos, A. J. Tasiopoulos, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2203–2209.
[10] P. V. Ioannou, *Main Group Chem.* **2014**, *13*, 243–250.
[11] A. T. Casey, N. S. Ham, D. J. Mackey, R. L. Martin, *Aust. J. Chem.* **1970**, *23*, 1117–1123.
[12] M. Förster, H. Hertel, W. Kuchen, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 811.
[13] L. Silaghi-Dumitrescu, S. Pascu, I. Silaghi-Dumitrescu, I. Haiduc, M. N. Gibbons, D. B. Sowerby, *J. Organomet. Chem.* **1997**, *549*, 187–192.
[14] T. D. Sideris, G. M. Tsivgoulis, D. G. Vachliotis, P. V. Ioannou, *Main Group Chem.* **2009**, *8*, 163–176.
[15] K. Tani, S. Hanabusa, S. Kato, S. Mutoh, S. Suzuki, M. Ishida, *J. Chem. Soc., Dalton Trans.* **2001**, 518–527.
[16] P. Sykes, *A Guide Book to Mechanism in Organic Chemistry*, 2nd Ed, Longmans, London, **1965**.
[17] M. A. Rodriguez, S. D. Bunge, *Acta Crystallogr., Sect. E* **2003**, *59*, o1123–o1125.
[18] E. Fluck, H. Binder, *Z. Anorg. Allg. Chem.* **1967**, *354*, 139–148.
[19] K. T. Suzuki, B. K. Mandal, A. Katagiri, Y. Sakuma, A. Kawakami, Y. Ogra, K. Yamaguchi, Y. Sei, K. Yamanaka, K. Anzai, M. Ohmichi, H. Takayama, N. Aimi, *Chem. Res. Toxicol.* **2004**, *17*, 914–921.
[20] H. Naranmandura, N. Suzuki, K. T. Suzuki, *Chem. Res. Toxicol.* **2006**, *19*, 1010–1018.
[21] G. C. Chen, R. A. Zingaro, C. R. Thompson, *Carbohydr. Res.* **1975**, *39*, 61–66.
[22] H. R. Hansen, A. Raab, M. Jaspars, B. F. Milne, J. Feldmann, *Chem. Res. Toxicol.* **2004**, *17*, 1086–1091.
[23] M. Fricke, M. Zeller, W. Cullen, M. Witkowski, J. Creed, *Anal. Chim. Acta* **2007**, *583*, 78–83.
[24] M. Bartel, F. Ebert, L. Leffers, U. Karst, T. Schwerdtle, *J. Toxicol.* **2011**; DOI:10.1155/2011/373141.
[25] R. K. Harris, R. G. Hayter, *Can. J. Chem.* **1964**, *42*, 2282–2291.
[26] A. L. Rheingold, E. J. Pleau, W. T. Ferrar, *Inorg. Chim. Acta* **1977**, *22*, 215–218.
[27] W. R. Cullen, *Can. J. Chem.* **1963**, *41*, 322–328.
[28] J. M. F. Braddock, G. E. Coates, *J. Chem. Soc.* **1961**, 3208–3211.
[29] G. Conole, J. E. Davies, J. D. King, M. J. Mays, M. McPartlin, H. R. Powell, P. R. Raithby, *J. Organomet. Chem.* **1999**, *585*, 141–149.
[30] G. C. Pappalardo, K. J. Irgolic, R. A. Pyles, E. Montoneri, *Spectrochim. Acta* **1982**, *38A*, 363–366.
[31] N. Kornblum, L. Cheng, R. C. Kerber, M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith, P. A. Wade, *J. Org. Chem.* **1976**, *41*, 1560–1564.

Received: October 26, 2014
Published Online: January 20, 2015

