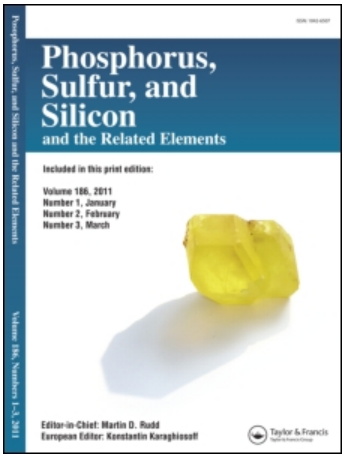

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BICYCLIC ARSINO SULFUR DIIMIDES

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Communication

BICYCLIC ARSINO SULFUR DIIMIDES

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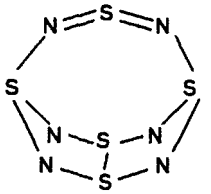
The reaction of cyclodiarsazanes, $[(R)NAsCl]_2$ (R = *tert.* butyl, 1,1,3,3-tetramethylbutyl, phenyl, 1-adamantyl) with the salt K_2SN_2 in hexane suspension leads to cage compounds in which two arsenic atoms are triply bridged by an organylimido and two sulfur diimide units.

Key words: Bicyclic sulfur diimides; cyclodiarsazanes; arsino sulfur diimide cages.

INTRODUCTION

Cages containing defined sulfur diimide units are rare, two prominent examples being the sulfur nitride basket S_5N_6 (1) with a sulfur diimide handle[1–3] and the bis(methylsilicon) compound $MeSi(NSN)_3SiMe$ (2) with three sulfur diimide bridges.[4,5] The sulfur diimide unit can be introduced by either $S(NSiMe_3)_2$ or $S(NSnMe_3)_2$ which may react with suitable chlorides such as $S_4N_4Cl_2$[3] and $MeSiCl_3$,[4] respectively.



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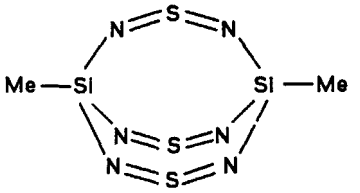

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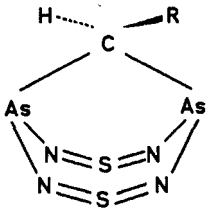
Two arsino sulfur diimide cages, 3 and 4, have been obtained using the salt dipotassium sulfur diimide, K_2SN_2, as a source for sulfur diimide bridges.[6,7] While 3 is formed in the straightforward reaction between bis(dichloroarsinyl)methane derivatives $RCH(AsCl_2)_2$ (R = H, CH_3) and K_2SN_2 (1:2),[6] the double-cage $As_4S_5N_{10}$ (4) is the product of a redox reaction between $AsBr_3$ and K_2SN_2 (2:3).[7]



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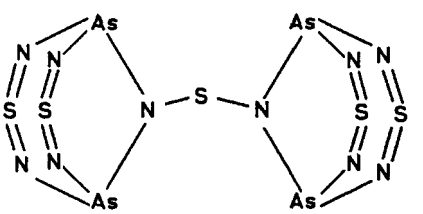
(R = H, Me)



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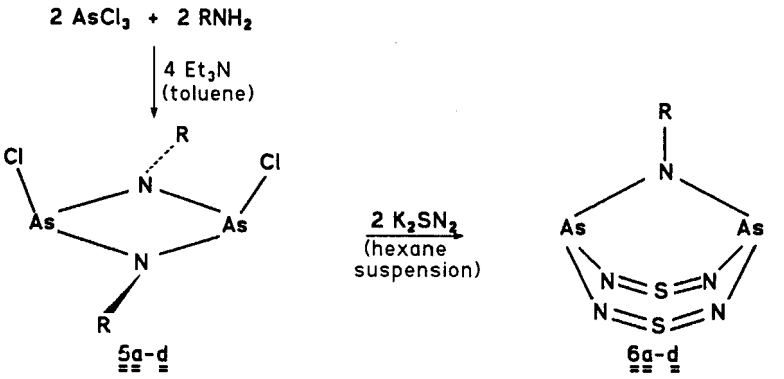
We now describe the synthesis and characterization of arsino sulfur diimide cages which contain an organylimido bridge.

RESULTS AND DISCUSSION

1,3-Diorganyl-2,4-dichloro-1,3,2,4-diazadiarsetidines (cyclodiarsazanes), $[(R)NAsCl]_2$ (5), were prepared from $AsCl_3$ and appropriate amines, RNH_2, in the presence of two equivalents of triethylamine (cf. Reference 8).



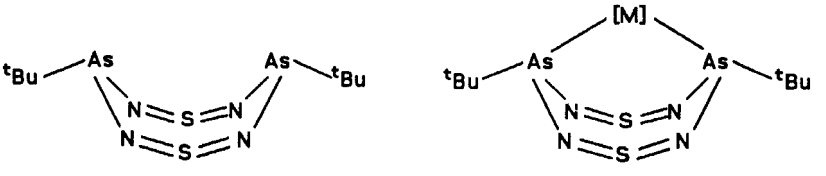
5a–d 6a–d

(a, R = *tert*.butyl; b, R = 1,1,3,3-tetramethylbutyl; c, R = phenyl; d, R = 1-adamantyl)

The cyclodiarsazanes 5a–d are colourless solids. The *tert.* butyl derivative $[(^tBu)NAsCl]_2$ (5a) had been described before[8–10]; according to an X-ray structure analysis,[10] the two chloro substituents lie on the same side of the four-membered ring, and the coordination about the N atoms is approximately planar.

The cyclodiarsazanes 5a–d react with the salt K_2SN_2 in hexane suspension to give the bicyclic arsino sulfur diimides 6a–d. The preparation of cages of type 6 apparently requires large substituents R; attempts to obtain the corresponding cages with R = methyl or isopropyl were not successful.

In contrast to the boat-shaped eight-membered heterocycle $^tBuAs(NSN)_2As^tBu$ (7a), the arsino sulfur diimide cage 6a does not behave as a monodentate ligand in photo-induced reactions with carbonylmetal complexes, $M(CO)_6$ (M = Cr, Mo, W) and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$. Both 6a and 7a are reluctant to add sulfur.



7a 8a

([M] = $Cr(CO)_4$, $Mo(CO)_4$, $W(CO)_4$, $Ni(CO)_2$)

The electron-impact mass spectra of the arsino sulfur diimide cages 6a–d always contain the molecular ion; in the case of 6c (R = Ph) it is the base peak (100%). Characteristic fragments include m/e = 224 ($As_2N_3S^+$), 210 ($As_2N_2S^+$) and 211 ($As_2N_2SH^+$), 167 ($AsN_2S_2^+$), 135 (AsN_2S^+) and 121 ($AsNS^+$). Analogous fragments have been observed in the mass spectra of the arsino sulfur diimide cages 3 and 4. The infrared spectra of 6a–d consistently show strong absorptions in the ranges of 1150–1100 and of 1050–1000 cm^{-1}, which can be assigned to the asymmetric and the symmetric NSN stretching vibrations, respectively. A similar pattern of two absorptions, separated by about 100 cm^{-1} and split into doublets in most cases, appears to be characteristic of all rings and cages which contain two sulfur diimide units, e.g. 7a,[11] 8a,[12,13] 3[6] and 4.[7]

EXPERIMENTAL

All reactions were carried out under argon in rigorously dried solvents. The salt K_2SN_2 was synthesized from $S(NSiMe_3)$ and KO^{t}Bu in dimethoxyethane, as described.[14]

1,3-Diorganyl-2,4-dichloro-1,3,2,4-diazadiarsetidines (5a–d). The procedure used by Olah and Oswald[8] was modified as follows: The amine RNH_2 (10 mmole) was added dropwise to a solution containing $AsCl_3$ (1.81 g, 10 mmole) and triethylamine, NEt_3 (2.02 g, 20 mmole) in 30 mL toluene at 0°C. The reaction mixture was stirred 2 hours at room temperature and then filtered over a frit to remove $[NEt_3H]Cl$ which was washed repeatedly with small portions of toluene. The combined toluene filtrates were concentrated to a volume of 5 mL and the cyclodiarsazane (5a–d) precipitated by addition of 30–40 mL hexane. Additional product was formed upon standing overnight at −25°C. The compounds 5a–d were used for the reactions with K_2SN_2 without further purification.

9-Organyl-3λ⁴,7λ⁴-dithia-2,4,6,8,9-pentaaza-1,5-diarsa-bicyclo-[3.3.1]nonanes (6a–d). General procedure: A suspension of 5a–d (ca 2 mmole) in ca 20 mL hexane was slowly added to a light-yellow suspension of K_2SN_2 (ca 4 mmole) in 30 mL hexane at −40 to −50°C. After 1 hour at −40°C, the cooling was discontinued and the suspension was stirred one additional hour at room temperature. The intensely yellow solution was removed via syringe and brought to dryness.

6a (R = *tert.* butyl): Yellow crystals, m.p. 69–71°C, yield 40% (270 mg). IR (KBr): ν_{as}(NSN) 1142vs/1112s, ν_s(NSN) 1052s/1028s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.21(s). ^{13}C NMR ($CDCl_3$): δ 32.7 ($C(\underline{C}H_3)_3$), 58.1 ($\underline{C}(CH_3)_3$). EI-MS: m/e (%) 341 (M^+, 16), 326 (M^+—CH_3, 100), 266 ($As_2(NSN)NCMe_2^+$, 4), 225 ($As_2N_3SH^+$, 7), 224 ($As_2N_3S^+$, 17), 211 ($As_2N_2SH^+$, 7), 167 ($AsN_2S_2^+$, 6), 135 (AsN_2S^+, 13), 131 (33), 121 ($AsNS^+$, 6), 57 ($C_4H_9^+$, 80).

$As_2C_4H_9N_5S_2$ (340.873)
Calcd. As 43.93 C 14.08 H 2.66 N 20.53
Found As 43.60 C 14.95 H 2.65 N 20.30

6b (R = 1,1,3,3-tetramethylbutyl): Yellow crystals, m.p. ca 35°C, yield 31% (246 mg). IR (KBr): ν_{as}(NSN) 1139vs,br, ν_s(NSN) 1027m cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86s, ($C(CH_3)_3$), 1.26s ($C(CH_3)_2$), 1.45s (CH_2). ^{13}C NMR ($CDCl_3$): δ 31.5 ($C(\underline{C}H_3)_3$), 31.6 ($C(\underline{C}H_3)_2$), 32.9 (CH_2), 56.3/62.0 ($\underline{C}(CH_3)_n$). EI-MS: m/e (%) 397 (M^+, 5), 382 (M^+—CH_3, 8), 351 (M^+—NS, 10), 326 (M^+—C_5H_{11}, 100), 266 ($As_2(NSN)NCMe_2^+$, 4), 225 ($As_2N_3SH^+$, 4), 224 ($As_2N_3S^+$, 20), 211 ($As_2N_2SH^+$, 7), 167 ($AsN_2S_2^+$, 11), 135 (AsN_2S^+, 11), 131 (17), 121 ($AsNS^+$, 6), 58 ($C_3H_7N^+$, 78), 57 ($C_4H_9^+$, 43).

6c (R = phenyl): Yellow crystals, m.p. 58°C, yield 46% (332 mg). IR (KBr); ν_{as}(NSN) 1134vs,br, ν_s(NSN) 1052s/1027s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.25(m). ^{13}C NMR ($CDCl_3$): 115.1 (C^2/C^6), 123.2 (C^4). 128.9 (C^3/C^5), 145.4 (C^1). EI-MS: m/e (%) 361 (M^+, 100), 301 (M^+—NSN, 3), 226 ($As(NSN)NPh^+$, 12), 225 ($As_2N_3SH^+$, 4), 224 ($As_2N_3S^+$, 13), 211 ($As_2N_2SH^+$, 2), 210 ($As_2N_2S^+$, 3), 167 ($AsN_2S_2^+$, 12), 166 ($AsNPh^+$, 100), 135 (AsN_2S^+, 11), 123 ($SNPh^+$, 14), 121 ($AsNS^+$, 6), 77 ($C_6H_5^+$, 82).

6d (R = 1-adamantyl): Yellow crystals, m.p. 123°C, yield 60% (500 mg). IR (KBr): ν_{as}(NSN) 1131s/1093m, ν_s(NSN) 1044w/1014m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.59br. ^{13}C NMR ($CDCl_3$): 29.8, 36.3 and 46.3 (equal intensity). EI-MS: m/e (%) 419 (M^+, 9), 373 (M^+—NS, 2), 362 (12), 225 ($As_2N_3SH^+$, 2), 224 ($As_2N_3S^+$, 12), 211 ($As_2N_2SH^+$, 6), 167 ($AsN_2S_2^+$, 3), 135 (AsN_2S^+, 37), 94 ($C_7H_{10}^+$, 100).

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