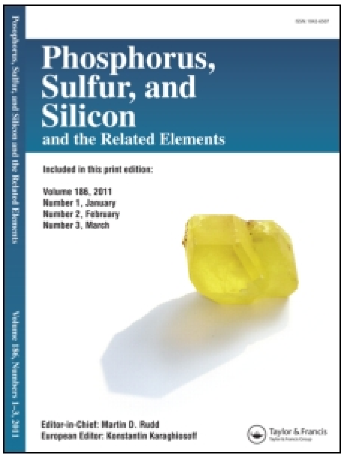

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Bicyclic Arsino Sulfur Diimides

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To cite this Article Herberhold, Max , Distler, Berthold and Schamel, Klaus(1993) 'Bicyclic Arsino Sulfur Diimides', Phosphorus, Sulfur, and Silicon and the Related Elements, 75: 1, 249 — 252
To link to this Article: DOI: 10.1080/10426509308037399
URL: http://dx.doi.org/10.1080/10426509308037399

Phosphorus, Sulfur, and Silicon, 1992, Vol. 73, pp. 249–252
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Communication

BICYCLIC ARSINO SULFUR DIIMIDES

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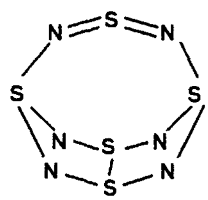
(Received September 15, 1992; in final form September 29, 1992)

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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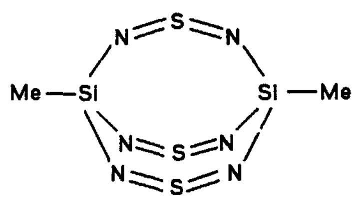
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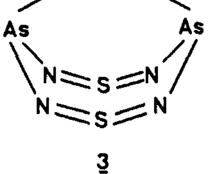
Two arsino sulfur diimide cages, 3 and 4, have been obtained using the salt dipotassium sulfur diimide, K_2SN_2, as a source for sulfur diimide bridges.[6,7] While 3 is formed in the straightforward reaction between bis(dichloroarsinyl)methane derivatives $RCH(AsCl_2)_2$ (R = H, CH_3) and K_2SN_2 (1:2),[6] 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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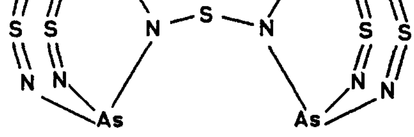
(R = H, Me)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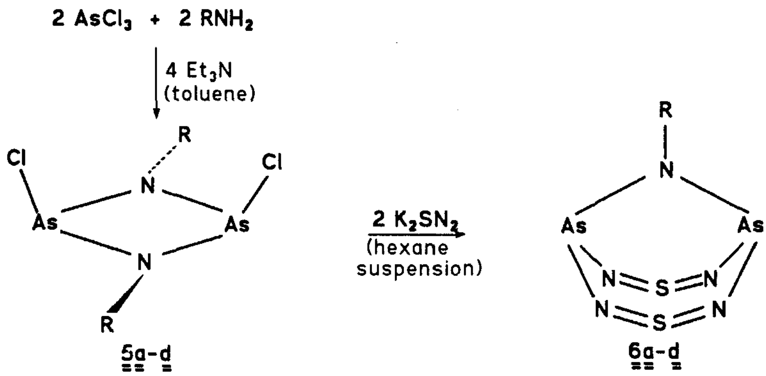
We now describe the synthesis and characterization of arsino sulfur diimide cages which contain an organylimido bridge.

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).

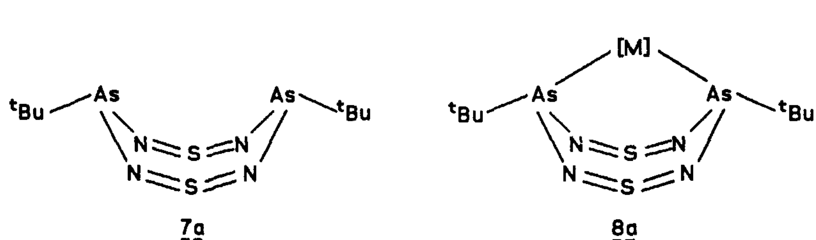


(a, R = *tert*.butyl; b, R = 1,1,3,3-tetramethylbutyl; c, R = phenyl; d, R = 1-adamantyl)

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.



([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^tBu 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).

ACKNOWLEDGEMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

REFERENCES

1. T. Chivers and J. Proctor, *J. C. S. Chem. Commun.*, 642 (1978); *Can. J. Chem.*, **57,** 1286 (1979).
2. H. W. Roesky, M. N. S. Rao, T. Nakajima and W. S. Sheldrick, *Chem. Ber.*, **112,** 3531 (1979).
3. W. S. Sheldrick, M. N. S. Rao and H. W. Roesky, *Inorg. Chem.*, **19,** 538 (1980).
4. H. W. Roesky and H. Wiezer, *Angew. Chem.*, **86,** 130 (1974); *Angew. Chem. Int. Ed. Engl.*, **13,** 146 (1974).
5. H. W. Roesky, M. Witt, B. Krebs, G. Henkel and H.-J. Korte, *Chem. Ber.*, **114,** 201 (1981).
6. M. Herberhold and K. Guldner, *Z. Naturforsch.*, **42b,** 118 (1987).
7. M. Herberhold, K. Guldner, A. Gieren, C. Ruiz-Pérez and T. Hübner, *Angew. Chem.*, **99,** 81 (1987); *Angew. Chem. Int. Ed. Engl.*, **26,** 82 (1987).
8. G. A. Olah and A. A. Oswald, *Can. J. Chem.*, **38,** 1428 (1960).
9. H.-J. Vetter, H. Strametz and H. Nöth, *Angew. Chem.*, **75,** 417 (1963).
10. R. Bohra, H.-W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Acta Cryst.*, **C40,** 1150 (1984).
11. A. Gieren, H. Betz, T. Hübner, V. Lamm, M. Herberhold and K. Guldner, *Z. Anorg. Allg. Chem.*, **513,** 160 (1984).
12. M. Herberhold and K. Schamel, *J. Organomet. Chem.*, **346,** 13 (1988); cf. M. Herberhold, K. Schamel, A. Gieren and T. Hübner, *Phosphorus, Sulfur and Silicon*, **41,** 355 (1989).
13. A. Gieren, T. Hübner, M. Herberhold, K. Guldner and G. Süß-Fink, *Z. Anorg. Allg. Chem.*, **544,** 137 (1987).
14. M. Herberhold and W. Ehrenreich, *Angew. Chem.*, **94,** 637 (1982); *Angew. Chem. Int. Ed. Engl.*, **21,** 633 (1982); *Angew. Chem. Suppl.*, **1982,** 1346.