N(1), N(2)) are greater than 3.6 Å. The distance between Cl(3) and N(3) is 3.535 (8) Å. This is a longer distance than expected for hydrogen bonding, but the P(3)–N(3)–Cl(3) and P(4)–N(3)–Cl(3) angles of 119 and 111° suggest that the geometry is suitable for hydrogen-bond formation. The next closest intermolecular contacts for ring II are Cl(3)–N(4), 3.710 (7) Å, and Pt(2)–N(3), 3.796 (6) Å.

The three main conclusions derived from this work are as follows. (1) The formation of a transannular chelation bridge between the cyclophosphazene ring and platinum in compound **1** appears to be favored by the square-planar characteristics of platinum and the potential for π bonding between the phosphazene ring and the metal. (2) The cyclotetraphosphazene ring is exceedingly flexible and can accommodate a wide range of different puckered structures according to the demands of coordination or crystal-packing forces. (3) Coordination by a ring nitrogen atom to a proton or the metal causes a lengthening of the P–N bonds that flank the coordination site. This latter factor now appears to be a general characteristic of a wide range of cyclophosphazenes.[2,8–12,15,17–19]

Acknowledgment. We thank the Army Research Office for the support of this work. We are also indebted to Drs. D. K. Smith, M. Y. Bernheim, and R. A. Arcus for their helpful suggestions.

Registry No. **1**, 70368-91-1; **2**, 61735-18-0.

Supplementary Material Available: Tables III and VIII listing structure factor amplitudes for $[N_4P_4(CH_3)_8]Pt^{II}Cl_2{\cdot}CH_3CN$ and $[H_2N_4P_4(CH_3)_8]^{2+}PtCl_4^{2-}$ (22 pages). Ordering information is given on any current masthead page.

References and Notes

(1) H. R. Allcock, R. W. Allen, and J. P. O'Brien, *J. Am. Chem. Soc.*, **99**, 3984 (1977).
(2) R. W. Allen, J. P. O'Brien, and H. R. Allcock, *J. Am. Chem. Soc.*, **99**, 3987 (1977).
(3) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974, Table 2.3.1.
(4) D. T. Cromer, "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974, Table 2.2B.
(5) G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1609 (1966).
(6) J. Iball, M. MacDougall, and S. Scrimgeour, *Acta Crystallogr., Sect. B*, **31**, 1672 (1975).
(7) M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Am. Chem. Soc.*, **79**, 3017 (1957).
(8) A. L. MacDonald and J. Trotter, *Can. J. Chem.*, **52**, 734 (1974).
(9) H. P. Calhoun, R. T. Oakley, N. L. Paddock, and J. Trotter, *Can. J. Chem.*, **53**, 2413 (1975).
(10) J. Trotter and S. H. Whitlow, *J. Chem. Soc. A*, 455 (1970).
(11) H. P. Calhoun and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 382 (1974).
(12) H. R. Allcock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, **12**, 2963 (1973).
(13) M. W. Dougill, *J. Chem. Soc.*, 5471 (1961).
(14) H. T. Searle, J. Dyson, T. N. Ranganathan, and N. L. Paddock, *J. Chem. Soc., Dalton Trans.*, 203 (1975).
(15) H. P. Calhoun, N. L. Paddock, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2708 (1973).
(16) W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 61 (1973).
(17) W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 1482 (1971).
(18) W. Harrison, N. L. Paddock, J. Trotter, and J. N. Wingfield, *J. Chem. Soc., Chem. Commun.*, 23 (1972).
(19) F. A. Cotton, G. A. Rusholm, and A. Shaver, *J. Coord. Chem.*, **3**, 99 (1973).

Contribution from the Department of Molecular Science, University of Warwick, Coventry CV4 7AL, United Kingdom,
the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071,
and I.B.M. Research Laboratory, San Jose, California 91193

Synthesis and Structure of 3,7-Diphenyl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1,5*-S^{IV})tetrazadiarsocine and 3,7-Dimesityl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1,5*-S^{IV})tetrazadiarsocine, $As_2S_2N_4C_{12}H_{10}$ and $As_2S_2N_4C_{18}H_{22}$

N. W. ALCOCK,[1a] E. M. HOLT,*[1b] J. KUYPER,[1c] J. J. MAYERLE,[1c] and G. B. STREET[1c]

Received November 9, 1978

The crystal data for the title compounds are as follows. $As_2S_2N_4C_{18}H_{22}$: triclinic, $P\bar{1}$, at −100 °C; $a = 7.390$ (2), $b = 8.089$ (2), $c = 18.235$ (5) Å; $\alpha = 86.63$ (2), $\beta = 106.16$ (2), $\gamma = 98.89$ (2)°; $V = 1034.1$ (5) Å^3; $Z = 2$; $D_c = 1.63$ g cm^{-3}; μ(Mo Kα) 36.15 cm^{-1}; $R = 6.3\%$ for 2764 reflections. $As_2S_2N_4C_{12}H_{10}$: orthorhombic, *Pnma*, at −100 °C; $a = 21.288$ (4), $b = 28.581$ (6), $c = 7.532$ (1) Å; $V = 4582.8$ (4) Å^3; $Z = 12$; $D_c = 1.84$ g cm^{-3}; μ(Mo Kα) 48.68 cm^{-1}; $R = 5.7\%$ for 2718 reflections. In each material, the $As_2S_2N_4$ group exists as a boat-shaped ring with arsenic atoms at prow and helm, joined by two –N–S–N chains. The four nitrogen atoms are coplanar. Each arsenic is also bonded to a phenyl or mesityl group. While the ring is conformationally similar to the S_4N_4 cage, cross-ring As–As or S–S interactions may be considered minimal. Attempts to prepare polymers analogous to $(SN)_x$, either by thermal splitting of the title compounds or by reaction of arylarsenic dichloride with sulfur diimides, have been unsuccessful.

Introduction

The solid-state polymerization of S_2N_2 by thermal splitting of S_4N_4 leads to the superconducting polymer $(SN)_x$.[2] Bromination of $(SN)_x$ has been shown to give rise to $SNBr_{0.4}$, an intercalation compound of $(SN)_x$.[3] This same compound can be prepared by the direct polymerization of solid S_4N_4 in the presence of bromine vapor. Similar polymers can be envisaged in which sulfurs are replaced by isoelectronic aryl arsenic groups.

In this paper, we report the preparation and single-crystal X-ray structures of two possible precursors to $(RAsNSN)_x$: 3,7-diphenyl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1,5*-S^{IV})tetrazadiarsocine and 3,7-dimesityl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1,5*-S^{IV})tetrazadiarsocine.

Experimental Section

General Methods. Phenylarsenic dichloride was obtained commercially and the mesitylarsenic dichloride was prepared by reaction of mesitylmagnesium bromide with $AsCl_3$ in ether. Vacuum distillation of the resulting mixed mesitylarsenic chloride and bromide followed by hydrolysis gave the corresponding dihydroxide, which was then treated with concentrated HCl to give mesitylarsenic dichloride, which was purified by vacuum distillation. ^1H NMR spectra (Table I) were

0020-1669/79/1318-2235$01.00/0

Table I. ^{1}H NMR Data in CH_2Cl_2 Solution (ppm from CH_2Cl_2)

compd	ring protons	ortho CH_3	para CH_3	Me_3Si
$Me_3SiNSNSiMe_3$				−5.08
$Me_3SiNSNSNSNSiMe_3$				−5.03
$PhAsCl_2$	2.57, 2.23			
$PhAsCl(\text{-}NSNSiMe_3)$[a]	2.48, 2.15			−5.09
$Ph_2As_2S_2N_4$	2.54, 2.20			
$PhAsCl(\text{-}NSNSNSNSiMe_3)$[a]	2.44, 2.18			−5.04
$mesAsCl_2$	1.61	−2.62	−3.02	
$mesAsCl(\text{-}NSNSiMe_3)$[a]	1.55	−2.69	−3.06	−5.20
$mesAs(\text{-}NSNSiMe_3)_2$[a]	1.46	−2.76	−3.10	−5.23
$(mes)_2As_2S_2N_4$	1.605	−2.82	−3.03	
$mesAsCl(\text{-}NSNSNSNSiMe_3)$[a]	1.59	−2.68	−3.03	−5.04
$PhAsS_3N_4$[a]	2.04			
$mesAsS_3N_4$[a]	1.67	−2.88	−3.05	

[a] Compounds formed in solution. Structure assigned on the basis of experimental data (see text).

recorded on a Varian HA 100 NMR spectrometer. Elemental analyses were performed by Childers Laboratories, Milford, NJ. All solvents were dried before use.

Preparation of 3,7-Dimesityl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1*,*5*-S^{IV})tetrazadiarsocine (A). Equivalent amounts (10 mmol) of mesitylarsenic dichloride and bis(trimethylsilyl)sulfur diimine[4] were added to a 50/50 mixture of hexane and CH_2Cl_2 (20 mL). The mixture was then set aside at ambient temperature and the crystalline orange precipitate removed every 24 h, until no further crystallization was observed (3–5 days). An additional yield could be obtained by further crystallization in a refrigerator. Total yield was about 70%. The phenyl derivative (B) was obtained similarly, although the reaction proceeded somewhat faster. Both compounds were recrystallized from CH_2Cl_2/hexane or from benzene. Anal. Calcd for A: C, 42.26; H, 4.34; N, 10.90; S, 12.29. Found: C, 42.52; H, 4.36; N, 11.02; S, 12.61. Calcd for B: C, 34.22; H, 2.42; N, 14.81; S, 12.90. Found: C, 33.97; H, 2.38; N, 15.12; S, 13.21.

Reaction of $Me_3SiNSNSNSNSiMe_3$ with $ArAsCl_2$ (Ar = Phenyl, Mesityl). Equimolar amounts of $Me_3SiNSNSNSNSiMe_3$ and $PhAsCl_2$ (4 mmol) were dissolved in CH_2Cl_2 (20 mL). The mixture was filtered after 2 days and the solvent removed under vacuum. The residue was then extracted with pentane, and the extracts were set aside at −20 °C. After 2 weeks, an orange-yellow precipitate was isolated which was shown to have ^{1}H NMR and mass spectra identical with those of $Ph_2As_2S_2N_4$. In the course of handling the reaction mixture, the walls of the apparatus became coated with a blue film of conducting $(SN)_x$. The analogous reaction with $mesAsCl_2$ (mes = mesitylene) gave $(mes)_2As_2S_2N_4$ identified by its ^{1}H NMR spectrum and by chemical analysis (C, H, S).

^{1}H NMR Studies. The reactions between $ArAsCl_2$ (Ar = phenyl, mesityl) and both $Me_3SiNSNSiMe_3$ (C) and $Me_3SiNSNSNSNSiMe_3$ (D) were followed by ^{1}H NMR with dichloromethane as solvent. The concentrations of both reactants were varied independently between 0.1 and 1 M for C and between 0.3 and 0.6 M for D. In benzene the reaction proceeded similarly, but the rates were much slower. ^{1}H NMR data for all compounds isolated or observed in solution are summarized in Table I.

X-ray Experimental Studies. Data were collected on a Syntex $P2_1$ diffractometer with graphite monochromatized Mo Kα radiation (λ 0.710 69 Å) to a $2\theta_{max}$ of 55° at scan rates between 1.0 and 29.3° min^{-1} depending on the intensity of a 2-s prescan. The crystal was held at −100 °C with a Syntex L-T 1 attachment. Three standard reflections were measured after every 97 reflections, and these showed no significant change in intensity during data collection. After correction for Lorentz, polarization, and absorption effects[5] (mesityl crystal size 0.15 × 0.20 × 0.44 mm, transmission coefficients 0.60–0.82; phenyl crystal size 0.12 × 0.22 × 0.38 mm, transmission coefficients 0.68–0.75), 2764 reflections for the mesityl modification and 2718 reflections for the phenyl modification were considered observed and were used in refinement.

Table II. Positional Parameters for $As_2S_2N_4C_{18}H_{22}$

atom	*x*	*y*	*z*
As(1)	0.5554 (2)	−0.2022 (2)	0.3092 (1)
As(2)	0.3772 (2)	0.0170 (2)	0.1425 (1)
S(1)	0.7715 (4)	0.1127 (4)	0.2519 (2)
S(2)	0.2481 (4)	0.0349 (4)	0.2848 (2)
N(1)	0.6123 (14)	0.1528 (13)	0.1830 (5)
N(2)	0.7607 (14)	−0.0273 (14)	0.3078 (6)
N(3)	0.3818 (14)	−0.0804 (13)	0.3330 (6)
N(4)	0.2380 (14)	0.0940 (13)	0.2033 (6)
C(11)	0.6585 (15)	−0.2920 (13)	0.4115 (6)
C(12)	0.7349 (15)	−0.1950 (13)	0.4779 (6)
C(13)	0.8099 (16)	−0.2744 (14)	0.5469 (7)
C(14)	0.8106 (16)	−0.4474 (15)	0.5523 (7)
C(15)	0.7320 (16)	−0.5419 (14)	0.4868 (7)
C(16)	0.6557 (16)	−0.4650 (13)	0.4162 (7)
C(17)	0.7409 (18)	−0.0052 (14)	0.4775 (7)
C(18)	0.8940 (20)	−0.5316 (17)	0.6286 (8)
C(19)	0.5749 (21)	−0.5791 (15)	0.3474 (8)
C(21)	0.2889 (15)	0.1510 (14)	0.0496 (6)
C(22)	0.2283 (15)	0.0559 (13)	−0.0169 (6)
C(23)	0.1656 (16)	0.1385 (15)	−0.0875 (6)
C(24)	0.1656 (17)	0.3108 (16)	−0.0915 (7)
C(25)	0.2264 (19)	0.4011 (15)	−0.0248 (7)
C(26)	0.2890 (18)	0.3242 (14)	0.0468 (7)
C(27)	0.2239 (18)	−0.1323 (14)	0.0177 (7)
C(28)	0.0976 (25)	0.3971 (20)	−0.1699 (8)
C(29)	0.3488 (23)	0.4325 (16)	0.1179 (8)

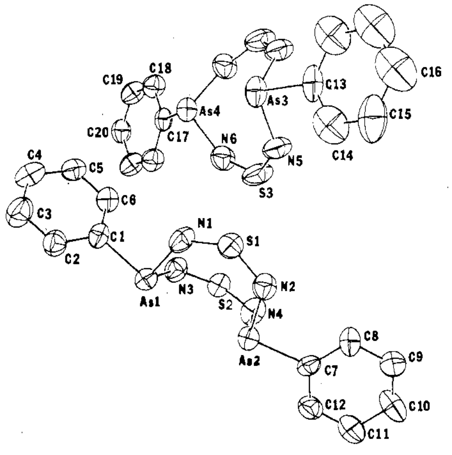

Figure 1. Projection of the structure $As_2S_2N_4C_{12}H_{10}$.

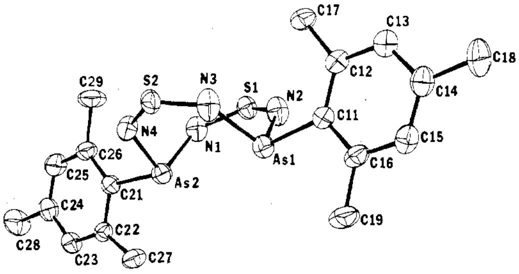

Figure 2. Projection of the structure $As_2S_2N_4C_{18}H_{22}$.

A Patterson synthesis allowed location of the arsenic atoms in each case. In the phenyl structure, $Z = 12$ required location of 1.5 independent molecules, one complete molecule and one on a crystallographic mirror plane. Successive least-squares difference Fourier cycles located the other atoms. Hydrogen positions were not included. At the conclusion of full-matrix refinement of positional parameters, anisotropic thermal parameters, and the scale factor, the agreement parameters *R* were equal to 6.3% (mesityl) and 5.7% (phenyl), where $R = (\|F_o| - |F_c\|/|F_o|) \times 100$ and the maximum shift/error ratio was 0.16. Unit weights were used throughout. Anomalous dispersion corrections were made for As.[6] Scattering factors were taken from Cromer and Mann.[7] All calculations were performed on an XDS Sigma 7 by using X-RAY 76.[8] Final positional parameters are shown in Tables II and III and the derived bond angles and distances in Tables IV and V. Projection views of the structures appear in Figures 1 and 2.

Results and Discussion

Motivated by the desire to prepare compounds analogous to $(SN)_x$ and its precursors S_4N_4 and S_2N_2, we have inves-

Table III. Positional Parameters for $As_2S_2N_4C_{12}H_{10}$

atom	x	y	z
As(1)	−0.07036 (6)	0.06373 (4)	0.25607 (17)
As(2)	0.07129 (6)	0.00510 (4)	0.31371 (16)
S(1)	0.0384 (2)	0.0952 (1)	0.5025 (4)
S(2)	0.0376 (1)	0.0625 (1)	−0.0163 (4)
N(1)	−0.0245 (5)	0.1017 (4)	0.4091 (13)
N(2)	0.0859 (4)	0.0562 (4)	0.4626 (13)
N(3)	−0.0267 (4)	0.0776 (4)	0.0478 (14)
N(4)	0.0846 (5)	0.0339 (4)	0.0912 (13)
C(1)	−0.1371 (5)	0.1083 (4)	0.2168 (15)
C(2)	−0.1957 (6)	0.0981 (5)	0.2839 (17)
C(3)	−0.2454 (6)	0.1293 (6)	0.2533 (23)
C(4)	−0.2352 (7)	0.1713 (5)	0.1596 (19)
C(5)	−0.1761 (6)	0.1801 (5)	0.0905 (20)
C(6)	−0.1266 (6)	0.1488 (5)	0.1113 (18)
C(7)	0.1543 (5)	−0.0217 (4)	0.3273 (15)
C(8)	0.2065 (5)	0.0034 (5)	0.3917 (16)
C(9)	0.2661 (6)	−0.0183 (5)	0.3883 (16)
C(10)	0.2730 (6)	−0.0618 (6)	0.3145 (19)
C(11)	0.2205 (7)	−0.0872 (5)	0.2479 (20)
C(12)	0.1615 (6)	−0.0654 (4)	0.2543 (18)
As(3)	0.07014 (8)	0.2500	0.44601 (24)
As(4)	−0.01532 (8)	0.2500	0.04202 (22)
S(3)	0.0851 (2)	0.1788 (1)	0.1413 (6)
N(5)	0.1049 (5)	0.1998 (4)	0.3178 (14)
N(6)	0.0391 (5)	0.2000 (4)	0.0136 (14)
C(13)	0.1366 (7)	0.2500	0.6263 (22)
C(14)	0.1575 (8)	0.2076 (6)	0.6906 (20)
C(15)	0.2006 (9)	0.2076 (7)	0.8359 (22)
C(16)	0.2236 (10)	0.2500	0.8997 (31)
C(17)	−0.0466 (7)	0.2500	0.8024 (20)
C(18)	−0.0617 (6)	0.2924 (5)	0.7176 (16)
C(19)	−0.0940 (6)	0.2924 (5)	0.5538 (17)
C(20)	−0.1111 (8)	0.2500	0.4770 (24)

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $As_2S_2N_4C_{18}H_{22}$

As(1)–N(2)	1.91 (1)	C(14)–C(18)	1.52 (2)
As(1)–N(3)	1.88 (1)	C(16)–C(19)	1.53 (2)
As(2)–N(1)	1.89 (1)	C(21)–C(22)	1.40 (2)
As(2)–N(4)	1.89 (1)	C(22)–C(23)	1.41 (1)
S(1)–N(1)	1.52 (1)	C(23)–C(24)	1.39 (2)
S(1)–N(2)	1.48 (1)	C(24)–C(25)	1.38 (2)
S(2)–N(3)	1.52 (1)	C(25)–C(26)	1.40 (2)
S(2)–N(4)	1.52 (1)	C(26)–C(21)	1.40 (2)
As(1)–C(11)	1.95 (1)	C(22)–C(27)	1.52 (2)
As(2)–C(21)	1.96 (1)	C(24)–C(28)	1.54 (2)
C(11)–C(12)	1.41 (2)	C(26)–C(29)	1.53 (2)
C(12)–C(13)	1.39 (2)	As(1)–As(2)	3.461 (2)
C(13)–C(14)	1.40 (2)	S(1)–S(2)	4.027 (5)
C(14)–C(15)	1.39 (2)	As(1)–S(1)	3.080 (3)
C(15)–C(16)	1.40 (2)	As(1)–S(2)	3.117 (4)
C(16)–C(11)	1.39 (2)	As(2)–S(1)	3.053 (3)
C(12)–C(17)	1.53 (2)	As(2)–S(2)	3.022 (4)
N(2)–As(1)–N(3)	100.7 (5)	C(18)–C(14)–C(13)	121 (1)
N(1)–As(2)–N(4)	98.1 (4)	C(18)–C(14)–C(15)	120 (1)
N(2)–As(1)–C(11)	98.4 (4)	C(19)–C(16)–C(15)	117 (1)
N(3)–As(1)–C(11)	97.5 (5)	C(19)–C(16)–C(11)	123 (1)
N(1)–As(2)–C(21)	97.5 (4)	C(26)–C(21)–C(22)	121 (1)
N(4)–As(2)–C(21)	98.8 (5)	C(21)–C(22)–C(23)	118 (1)
As(1)–N(2)–S(1)	129.6 (6)	C(22)–C(23)–C(24)	121 (1)
As(1)–N(3)–S(2)	131.9 (7)	C(23)–C(24)–C(25)	119 (1)
As(2)–N(1)–S(1)	126.8 (6)	C(24)–C(25)–C(26)	122 (1)
As(2)–N(4)–S(2)	124.2 (6)	C(25)–C(26)–C(21)	118 (1)
N(1)–S(1)–N(2)	126.6 (6)	C(27)–C(22)–C(21)	124 (1)
N(3)–S(2)–N(4)	126.4 (6)	C(27)–C(22)–C(23)	117 (1)
C(16)–C(11)–C(12)	120 (1)	C(28)–C(24)–C(23)	119 (1)
C(11)–C(12)–C(13)	119 (1)	C(28)–C(24)–C(25)	121 (1)
C(12)–C(13)–C(14)	122 (1)	C(29)–C(26)–C(25)	118 (1)
C(13)–C(14)–C(15)	119 (1)	C(29)–C(26)–C(21)	123 (1)
C(14)–C(15)–C(16)	121 (1)	As(1)–C(11)–C(12)	124.8 (8)
C(15)–C(16)–C(11)	120 (1)	As(1)–C(11)–C(16)	115.2 (8)
C(17)–C(12)–C(11)	123 (1)	As(2)–C(21)–C(22)	113.0 (8)
C(17)–C(12)–C(13)	118 (1)	As(2)–C(21)–C(26)	125.4 (8)

Table V. Selected Bond Lengths (Å) and Angles (deg) for $As_2S_2N_4C_{12}H_{10}$

As(1)–N(1)	1.86 (1)	C(7)–C(8)	1.41 (2)
As(1)–N(3)	1.86 (1)	C(8)–C(9)	1.41 (2)
As(2)–N(2)	1.87 (1)	C(9)–C(10)	1.37 (2)
As(2)–N(4)	1.89 (1)	C(10)–C(11)	1.42 (2)
As(3)–N(5)	1.88 (1)	C(11)–C(12)	1.40 (2)
As(4)–N(6)	1.85 (1)	C(12)–C(7)	1.37 (2)
S(1)–N(1)	1.52 (1)	C(13)–C(14)	1.38 (2)
S(1)–N(2)	1.53 (1)	C(14)–C(15)	1.43 (2)
S(2)–N(3)	1.51 (1)	C(15)–C(16)	1.39 (2)
S(2)–N(4)	1.52 (1)	C(17)–C(18)	1.41 (1)
S(3)–N(5)	1.52 (1)	C(18)–C(19)	1.41 (2)
S(3)–N(6)	1.50 (1)	C(19)–C(20)	1.39 (2)
As(1)–C(1)	1.93 (1)	As(1)–As(2)	3.477 (2)
As(2)–C(7)	1.93 (1)	As(3)–As(4)	3.545 (2)
As(3)–C(13)	1.96 (2)	S(1)–S(2)	4.018 (4)
As(4)–C(17)	1.92 (1)	S(3)–S(3)′	4.070 (6)
C(1)–C(2)	1.38 (2)	As(1)–S(1)	3.101 (4)
C(2)–C(3)	1.40 (2)	As(1)–S(2)	3.080 (3)
C(3)–C(4)	1.41 (2)	As(2)–S(1)	3.024 (4)
C(4)–C(5)	1.38 (2)	As(2)–S(2)	3.064 (3)
C(5)–C(6)	1.39 (2)	As(3)–S(3)	3.084 (4)
C(6)–C(1)	1.42 (2)	As(4)–S(3)	3.045 (4)
N(1)–As(1)–N(3)	97.8 (4)	C(4)–C(5)–C(6)	122 (1)
N(2)–As(2)–N(4)	99.6 (5)	C(5)–C(6)–C(1)	118 (1)
N(5)–As(3)–N(5)′	99.4 (5)	C(12)–C(7)–C(8)	121 (1)
N(6)–As(4)–N(6)′	101.0 (5)	C(7)–C(8)–C(9)	118 (1)
N(1)–As(1)–C(1)	95.5 (5)	C(8)–C(9)–C(10)	120 (1)
N(3)–As(1)–C(1)	95.6 (4)	C(9)–C(10)–C(11)	121 (1)
N(2)–As(2)–C(7)	97.3 (4)	C(10)–C(11)–C(12)	118 (1)
N(4)–As(2)–C(7)	94.8 (5)	C(11)–C(12)–C(7)	121 (1)
N(5)–As(3)–C(13)	94.1 (4)	C(14)–C(13)–C(14)′	123 (1)
N(6)–As(4)–C(17)	96.2 (4)	C(13)–C(14)–C(15)	118 (2)
As(1)–N(1)–S(1)	132.5 (7)	C(14)–C(15)–C(16)	119 (2)
As(2)–N(2)–S(1)	125.2 (6)	C(15)–C(16)–C(15)′	121 (2)
As(1)–N(3)–S(2)	131.1 (6)	C(18)–C(17)–C(18)′	119 (1)
As(2)–N(4)–S(2)	127.3 (6)	C(17)–C(18)–C(19)	120 (1)
As(3)–N(5)–S(3)	130.0 (7)	C(18)–C(19)–C(20)	119 (1)
As(4)–N(6)–S(3)	130 2 (7)	C(19)–C(20)–C(19)′	121 (1)
N(1)–S(1)–N(2)	125.2 (6)	As(1)–C(1)–C(2)	118.0 (9)
N(3)–S(2)–N(4)	125.2 (6)	As(1)–C(1)–C(6)	120.4 (8)
N(5)–S(3)–N(6)	125.6 (6)	As(2)–C(7)–C(8)	122.5 (9)
C(6)–C(1)–C(2)	121 (1)	As(2)–C(7)–C(12)	116.3 (8)
C(1)–C(2)–C(3)	119 (1)	As(3)–C(13)–C(14)	118.5 (9)
C(2)–C(3)–C(4)	120 (1)	As(4)–C(17)–C(18)	120.3 (7)
C(3)–C(4)–C(5)	119 (1)		

tigated the reactions between arylarsenic dichloride (aryl = phenyl, mesityl) and bis(trimethylsilyl)sulfur diimines. The analogous reactions with arylsulfenyl chlorides were reported previously.[4] Attempts to prepare the most simple product from this reaction, $ArAsSN_2$, which would be an interesting analogue of S_2N_2, were unsuccessful, and only the S_4N_4 analogue 3,7-diaryl-3*H*,7*H*-1,5,2,4,6,8,3,7-dithia(*1,5-S*^{IV})-tetrazadiarsocine was isolated from reaction 1. In order to

$$2ArAsCl_2 + 2Me_3SiNSNSiMe_3 \rightarrow Ar_2As_2S_2N_4 + 4MeSiCl \quad (1)$$

identify the reaction intermediates, this reaction was followed by ^1H NMR. The presence of a large excess of $ArAsCl_2$ resulted in a relatively fast reaction (2). On the other hand,

$$ArAsCl_2(excess) + Me_3SiNSNSiMe_3 \rightarrow ArAs(Cl)NSNSiMe_3 + Me_3SiCl \quad (2)$$

in the presence of a large excess of $Me_3SiNSNSiMe_3$ the product of reaction 2, $ArAs(Cl)NSNSiMe_3$, rapidly underwent further reaction according to reaction 3. Reaction 3 could

$$ArAs(Cl)NSNSiMe_3 + Me_3SiNSNSiMe_3 \rightarrow ArAs(NSNSiMe_3)_2 + Me_3SiCl \quad (3)$$

only be studied effectively when Ar = mesityl, when the resonances of the aryl protons could be observed separately. Both reactions 2 and 3 were followed by a much slower reaction to give the final product $Ar_2As_2S_2N_4$. Although the products of reactions 2 and 3 were too unstable to be isolated from the excess of reactants used, both reactions went to 80–90% completion, and so by integration of the ^{1}H NMR spectra, it was possible to show that the expected amount of Me_3SiCl was formed in each case. The changes in the chemical shifts of the mesityl protons are also consistent with the compositions of the products in reactions 2 and 3. The chemical shift of the mesityl protons of $mesAsCl_2$ shows a constant upfield shift as successive chlorines are replaced by $-NSNSiMe_3$. Furthermore, integration of the peaks corresponding to the aryl and trimethylsilyl protons gave the appropriate ratios; although no evidence could be obtained for the presence of $ArAsSN_2$, its formation as an intermediate cannot be excluded.

In an attempt to make the S_4N_4 analogue $ArAsS_3N_4$, the reaction of $ArAsCl_2$ with $Me_3SiNSNSNSNSNSiMe_3$ was investigated. The only isolatable product was $Ar_2As_2S_2N_4$ which was obtained in moderate yield. Following this reaction by ^{1}H NMR in CH_2Cl_2 solution showed that the first step was a fairly rapid reaction (4). For Ar = phenyl this reaction was

$$ArAsCl_2 + Me_3SiNSNSNSNSiMe_3 \rightarrow ArAs(Cl)NSNSNSNSiMe_3 + Me_3SiCl \quad (4)$$

complete in about 15 min; the corresponding mesityl compound reacted more slowly. Although the resonance of the Me_3Si group in this arsine-substituted product was barely resolved from the starting material, integration of the spectrum gave approximately the correct ratio for the Me_3SiCl and the other Me_3Si proton resonances. Due to a further reaction of the $ArAs(Cl)NSNSNSNSiMe_3$ leading to formation of Me_3SiCl, the ratio was slightly high. This further reaction involved the formation of several other products, but the most intense resonances were those of $Ar_2As_2S_2N_4$. An appreciable amount (10–20%) of a second product, which could not be isolated, was observed. Since $ArAs(Cl)NSNSNSNSiMe_3$ might be expected to cyclize with elimination of Me_3SiCl, we suggest that this product is $ArAsS_3N_4$.

The formation of the principal product, $Ar_2As_2S_2N_4$, probably results from the disproportionation of two molecules of $ArAs(Cl)NSNSNSNSiMe_3$. Some fragmentation of this molecule also takes place since a small amount of $ArAs(Cl)NSNSiMe_3$ was detected. The appearance of a blue film of $(SN)_x$ on the walls of the reaction flasks indicates the presence of S_2N_2 which would be expected as the other product of fragmentation of $ArAs(Cl)NSNSNSNSiMe_3$.

Discussion of X-ray Reults

The eight-membered $As_2S_2N_4$ system exists as a boat-shaped ring with the arsenic atoms at prow and helm positions. The four nitrogen atoms are coplanar within experimental limits (maximum deviation from the plane is 0.02 Å for both structures), with two arsenic atoms on one side of the plane and two sulfur atoms on the other side. Thus the general conformation of the ring is reminiscent of the S_4N_4 cage which shows the same coplanarity of four nitrogen atoms and alternate up and down configuration of the sulfur atoms.[9] However, whereas S_4N_4 shows very short cross-ring sulfur–sulfur distances of 2.586 (8)–2.576 (8) Å, the cross-ring sulfur–sulfur distances here average 4.038 Å, longer than the van der Waals contact distances of 3.60–3.66 Å.[10] The cross-ring As–As average distance of 3.49 Å is shorter than the reported van der Waals diameter of arsenic (3.7 Å) and could signify weak secondary As–As interaction. The cage structure of As_4S_4,[11] where the planar sulfur atoms are bridged by alternate up and down arsenic atoms, shows considerably shorter arsenic–arsenic distances of 2.54 Å. It seems clear that cross-ring interactions are not important in the conformation of the $As_2S_2N_4$ ring.

The arsenic–mesityl carbon bond lengths are 1.95 (1) and 1.96 (1) Å, and the arsenic–phenyl carbon bond lengths are 1.92 (1), 1.93 (1), 1.96 (2), and 1.93 (1) Å as compared to the arsenic–phenyl carbon bond lengths of 1.924 (8) and 1.932 (9) Å observed in (triphenylarsino)trisulfur tetranitride.[12] Angles between the bonds around the arsenic atoms range from 94.1 (4) to 101.0 (5)°, consistent with formulation of the arsenic hybridization as sp^3 with an unshared pair of electrons occupying the fourth orbital. The arsenic–nitrogen bonds are 1.85 (1)–1.91 (1) Å in length as compared to the 1.837 (2) Å in (triphenylarsino)trisulfur tetranitride and the 1.87 Å reported by Weiss and Eisenhuth[13] for $As_4(NCH_3)_6$.

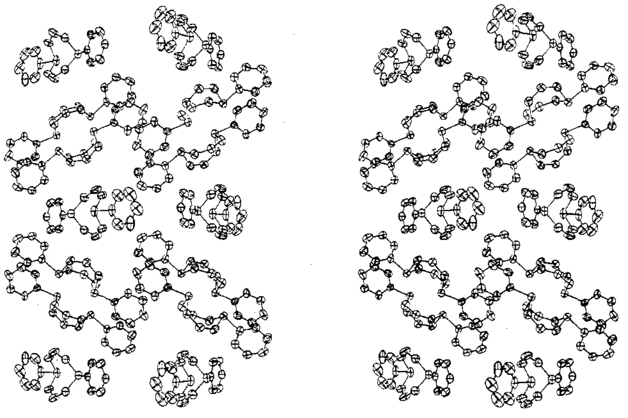

Figure 3. Packing of $As_2S_2N_4C_{12}H_{10}$.

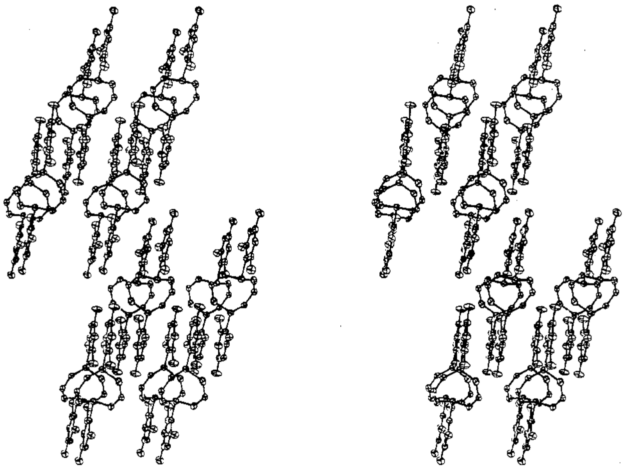

Figure 4. Packing of $As_2S_2N_4C_{18}H_{22}$.

The sulfur–nitrogen bond lengths (1.48 (1)–1.53 (1) Å) are among the shortest observed. The nearest comparable values are 1.453 Å in $S_5N_5^+AlCl_4^-$[14] and 1.493 Å in $S_4N_3^+NO_3^-$.[15] The bond angles observed at sulfur (125.2 (6)–126.6 (6)°) are among the largest observed in these systems: 124.1° in $(p\text{-}ClC_6H_5)_2S_3N_2$,[16] 124.2° in $Ph_2C(NS)_3NCPh_2$,[17] and 124.6° in $(S_5N_5)(Cl_3POSnCl_5)$.[18] This observation is consistent with earlier correlations of the SN bond length and the angle subtended at sulfur.[19] The sulfur–nitrogen bonds are not as short as the 1.446 (10) Å observed in NSF[20] and the 1.416Å in NSF_3,[21] materials in which the SN bond order is three. The –N–S–N– linkages in $As_2S_2N_4C_{12}H_{10}$ and $As_2S_2N_4C_{18}H_{22}$ are probably best seen as involving four delocalized electrons, one contributed by each nitrogen and two by the sulfur. This view is consistent with the bond lengths and the angles subtended at sulfur and nitrogen.

The packing of molecules into the cell shows considerable variation upon substitution of the phenyl for the mesityl group. The mesityl material shows the aromatic rings nearly perpendicular to the plane of the four nitrogen atoms (dihedral angles 87.0 and 89.2°), whereas the phenyl material shows one molecule of the asymmetric unit having the planes of the aromatic rings skewed at dihedral angles of 69.4 and 54.6°

to the plane of the four nitrogen atoms and the other molecule having these planes nearly parallel (dihedral angles 2.2 and 13.9°). The packing of the mesityl-substituted $As_2S_2N_4$ rings shows parallel planes of mesityl rings, whereas the phenyl substituted material shows no such regularity of orientation of the aromatic rings (Figures 3 and 4).

Acknowledgment. N.W.A. and E.M.H. gratefully acknowledge the assistance of a grant from NATO.

Registry No. $As_2S_2N_4C_{18}H_{22}$, 70369-31-2; $As_2S_2N_4C_{12}H_{10}$, 70369-32-3; $Me_3SiNSNSNSNSiMe_3$, 53380-71-5; $PhAsCl_2$, 696-28-6; $MeSAsCl_2$, 70369-33-4; $Me_3SiNSNSiMe_3$, 18156-25-7; PhAsCl(-$NSNSiMe_3$), 70369-34-5; PhAsCl(-$NSNSNSNSiMe_3$), 70369-35-6; MeSAsCl(-$NSNSiMe_3$), 70369-36-7; MeSAs(-$NSNSiMe_3)_2$, 70369-37-8; MeSAsCl(-$NSNSNSNSiMe_3$), 70369-38-9; $PhAsS_3N_4$, 70369-39-0; $MeSAsS_3N_4$, 70369-40-3.

Supplementary Material Available: Observed and calculated structure amplitudes and anisotropic thermal parameters (31 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Warwick. (b) To whom correspondence should be addressed at the Department of Biochemistry, University of Georgia, Athens, GA 30602. (c) I.B.M. Research Laboratory.

(2) Greene, R. L.; Street, G. B.; Suter, L. *J. Phys. Rev. Lett.* **1975**, *34*, 577.

(3) Street, G. B.; Gill, W. D.; Geiss, R. H.; Greene, R. L.; Mayerle, J. J. *J. Chem. Soc., Chem. Commun.* **1977**, 407.

(4) Kuyper, J.; Street, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 7848.

(5) Alcock, N. W. "Crystallographic Computing", Ahmed, F., Ed.; Munksgaard: Copenhagen, 1970; p 271.

(6) "International Tables for Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(7) Cromer, D.; Mann, J. *Acta Crystallogr., Sect. A*, **1968**, *24*, 321.

(8) Stewart, J. M. "The X-Ray System, Technical Report TR-446 of the Computer Science Center"; University of Maryland, College Park, MD, 1976.

(9) Sharma, B. D.; Donohue, J. *Acta Crystallogr.*, **1963**, *16*, 891.

(10) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(11) Tobelko, K. I.; Zvonkova, Z. V.; Zhdanov, G. S. *Dokl. Akad. Nauk SSSR* **1954**, *96*, 749.

(12) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Chem. Commun.*, **1977**, 514.

(13) Weiss, J.; Eisenhuth, W. *Z. Anorg. Allg. Chem.* **1977**, *350*, 9.

(14) Hazell, A. C.; Hazell, R. G. *Acta Chem. Scand.* **1972**, *26*, 1987.

(15) Cordes, A. W.; Kruh, R.; Gordon, E. K. *Inorg. Chem.* **1965**, *4*, 681.

(16) Olsen, F. B.; Barrick, J. C. *Inorg. Chem.* **1973**, *12*, 1353.

(17) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1357.

(18) Roesky, H. W.; Bowing, W. G.; Rayment, I.; Shearer, H. M. M. *J. Chem. Soc., Chem. Commun.* **1975**, 735.

(19) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc.* **1974**, 1990.

(20) Kirchhoff, W. H.; Wilson, E. B., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1726.

(21) Kirchhoff, W. H.; Wilson, E. B., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 334.

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60201,
and Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560

Cationic Binuclear Trihydride Complexes of Platinum. A Fluxional Behavior for Bridging and Terminal Hydrido Ligands. Crystal and Molecular Structure of $[Pt_2H_3\{(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2\}_2][B(C_6H_5)_4]$

T. H. TULIP,[1a] T. YAMAGATA,[1b] T. YOSHIDA,[1b] R. D. WILSON,[1a] JAMES A. IBERS,*[1a] and SEI OTSUKA*[1b]

Received November 27, 1978

A series of complexes of bis(diphosphine)trihydridodiplatinum(II) cations have been prepared from the corresponding mononuclear *cis*-(diphosphine)dihydridoplatinum(II) or dimeric bis(diphosphine)diplatinum(0) compexes. These complexes are very stable. While their IR spectra are consistent with the presence of both terminal and bridging hydrido ligands, the NMR spectra are consistent with only one form of hydride coordination and show equivalence within the sets of H, P, and Pt atoms. These results suggest a rapid exchange of bridging and terminal hydrido ligands. The static molecular structure is proposed to involve one bridging and two terminal hydrido ligands. The complex $[Pt_2H_3\{(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2\}_2][B(C_6H_5)_4]$ crystallizes in space group C_{2h}^5-$P2_1/c$ with four formula units in a cell of dimensions a = 19.41 (1) Å, b = 18.03 (1) Å, c = 21.51 (1) Å, and β = 120.57 (3)°. The complex is sensitive to X radiation as evidenced by its progressive decomposition during data collection. Three data subsets on different crystals were acquired and merged to yield a total of 3468 unique reflections having $F_o^2 > 3\sigma(F_o^2)$. Least-squares refinement, including anisotropic thermal parameters for Pt and P atoms but isotropic parameters for the other nonhydrogen atoms, led to final conventional agreement indices (on F) of R = 0.081 and R_w = 0.101. The hydrido ligands were not located, but their positions are inferred from the coordination geometries of the Pt atoms. The Pt–Pt separation is 2.768 (2) Å and the dihedral angle between the two P–Pt–P coordination planes is 89°. The spectral and structural details, as well as those of the fluxional process, are discussed and related to those of similar mono- and binuclear platinum complexes.

Interest in hydride complexes of the transition metals has grown steadily since the first report by Hieber and Leutert in 1931.[2-4] The synthetic, analytical (spectroscopic[5] and diffraction[6]), and theoretical challenges posed by these complexes, augmented by the recognition of their intimate involvement in many aspects of homogeneous catalysis,[7] have drawn ever-increasing attention during the past two decades. Most recently much of this interest has turned to polyhydride complexes, both mono- and polymetallic. Although a wide variety of monohydride complexes of Pt(II) are well-known,[8-10] dihydride species were not reported until recently.[11-17] Thermally and kinetically stable *trans*-dihydride complexes, *trans*-PtH_2L_2, have been prepared in which the auxiliary ligands, L, are sterically demanding tertiary phosphines.[11-15] We have previously described the synthesis of an analogous series of novel *cis*-dihydride complexes of Pt(II).[17] Their isolation was made possible by constraining the two phosphorus donor atoms to cis positions by their incorporation into a chelating diphosphine incapable of spanning trans coordination sites and by including bulky phosphine substituents which kinetically stabilize the *cis*-dihydride coordination.

Although polynuclear complexes incorporating bridging hydrido ligands are known for many of the transition metals, few examples have been reported for platinum, e.g., $Pt_2Y_2(\mu\text{-}H)_2L_2$ [L = PCy_3 (Cy = cyclohexyl); Y = H, MR (M = Si, Ge; R = alkyl)].[18,19] In our continuing investigations into the chemistry of *cis*-dihydridoplatinum(II) and related dimeric Pt(0) complexes, we have discovered an interesting series of cationic trihydridodiplatinum complexes, $[Pt_2H_3(diphos)_2]X$ [(diphos) = $R_1R_2P(CH_2)_nPR_1R_2$ (n = 2, 3, $R_1 = R_2 = t$-Bu; n = 2, R_1 = Ph, R_2 = t-Bu); X = Cl, OMe, BPh_4], which could be prepared by a number of routes. The IR spectra of these complexes are consistent with the presence of both bridging and terminal hydrido ligands. However, ^1H and ^{31}P NMR

0020-1669/79/1318-2239$01.00/0 © 1979 American Chemical Society