$(Et_4N)_2[Fe_2S_2I_4]$, 65045-63-8; $(Et_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, 62873-87-4; $(n\text{-}Bu_4N)_2[Fe_4S_4Cl_4]$, 65103-98-2; $(Me_4N)_2[Fe_4S_4Cl_4]$, 65103-99-3; $(Et_4N)_2[Fe_4S_4Cl_4]$, 62758-02-5; $(Et_4N)_2[Fe_4S_4Br_4]$, 65208-04-0; $(Et_4N)_2[Fe_4S_4I_4]$, 65208-05-1; **5**, 65045-40-1; *o*-xylene-α,α'-dithiol, 41383-84-0; PhCOCl, 98-88-4; $(Me_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, 52678-92-9; $[Fe_4S_{s4}(SPh)_4]^{2-}$, 52325-39-0; $[Fe_2S_2(SPh)_4]^{2-}$, 55939-69-0; $(Et_4N)_2[Fe_2S_2Cl_4]$, 62682-81-9; $(Ph_4As)_2[Fe_2S_2Cl_4]$, 65045-64-9.

References and Notes

(1) For a review of this research cf. R. H. Holm and J. A. Ibers in "Iron-Sulfur Proteins", Vol. III, W. Lovenberg, Ed., Academic Press, New York, N.Y., 1977, Chapter 7; R. H. Holm, *Acc. Chem. Res.*, in press.

(2) Symbols and abbreviations: A, bridging ligand; L, terminal ligand; S_2-*o*-xyl, *o*-xylyl-α,α'-dithiolate; tfd, $(CF_3)_2C_2S_2$.

(3) R. W. Lane, J. A. Ibers, R. B. Frankel, G. C. Papaefthymiou, and R. H. Holm, *J. Am. Chem. Soc.*, **99**, 84 (1977).

(4) (a) R. W. Lane, A. G. Wedd, W. O. Gillum, E. J. Laskowski, R. H. Holm, R. B. Frankel, and G. C. Papaefthymiou, *J. Am. Chem. Soc.*, **99**, 2350 (1977); (b) J. Cambray, R. W. Lane, A. G. Wedd, R. W. Johnson, and R. H. Holm, *Inorg. Chem.*, **16**, 2565 (1977).

(5) For a partial listing cf. R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976).

(6) J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 1032 (1975).

(7) B.-K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, **14**, 3103 (1975).

(8) C.-H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1, 493 (1965).

(9) For an extensive list of references to structures containing this unit cf. B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, **15**, 2467 (1976).

(10) H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, **14**, 322 (1975).

(11) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966); C.-H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966).

(12) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 402 (1977).

(13) Trinh-Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 408 (1977).

(14) R. S. Gall, C. T.-W. Chu, and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 4019 (1974).

(15) I. Bernal, B. R. Davis, M. L. Good, and S. Chandra, *J. Coord. Chem.*, **2**, 61 (1972).

(16) (a) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973); (b) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *ibid.*, **96**, 4168 (1974).

(17) E. J. Laskowski, R. B. Frankel, W. O. Gillum, G. C. Papaefthymiou, J. Renaud, J. A. Ibers and R. H. Holm, results submitted for publication.

(18) A. L. Balch, *J. Am. Chem. Soc.*, **91**, 6962 (1969).

(19) G. R. Dukes and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 528 (1975).

(20) (a) E. E. van Tamelen, private communication and results presented at the 1st International Symposium on Nitrogen Fixation, Washington State University, Pullman, Wash., June 1974; (b) A. Schwartz and E. E. van Tamelen, *J. Am. Chem. Soc.*, **99**, 3189 (1977).

(21) M. A. Bobrik, K. O. Hodgson, and R. H. Holm, *Inorg. Chem.*, **16**, 1851 (1977).

(22) E. Fromm and A. Forster, *Justus Liebigs Ann. Chem.*, **394**, 338 (1912).

(23) B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 4159 (1974).

(24) R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle, and T. Herskovitz, *J. Am. Chem. Soc.*, **96**, 2109 (1974).

(25) D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, **10**, 1559 (1971).

(26) P. C. Healy, A. H. White, and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1369 (1972).

(27) S. Koch, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **97**, 6714 (1975).

(28) N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, **8**, 534 (1969).

(29) (a) P. Sōhar and J. Kuszmann, *J. Mol. Struct.*, **3**, 359 (1969); (b) J. L. Ryan, *Inorg. Synth.*, **15**, 225 (1974); (c) J. L. Ryan, *Inorg. Chem.*, **8**, 2058 (1969).

(30) L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969); M. Akbar Ali and S. E. Livingstone, *ibid.*, **13**, 101 (1974).

(31) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

(32) C. L. Green, R. P. Houghton, and D. A. Phipps, *J. Chem. Soc., Perkin Trans. 1*, 2623 (1974).

(33) R. C. Job and T. C. Bruice, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2478 (1975).

(34) W. O. Gillum, R. B. Frankel, S. Foner, and R. H. Holm, *Inorg. Chem.*, **15**, 1095 (1976).

(35) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2437 (1972).

(36) W. E. Hatfield in "Theory and Applications of Molecular Paramagnetism", E. A. Boudreaux and L. N. Mulay, Ed., Wiley-Interscience, New York, N.Y., 1976, Chapter 7.

(37) Extension of this treatment to four coupled centers (2Fe(II) + 2Fe(III)) yielded a $\chi^t(T)$ expression which failed to account for the magnetic properties of $[Fe_4S_4Cl_4]^{2-}$. While data at $T > 200$ K appear to coincide with theory for $-J \simeq 220$ cm^{-1}, those at lower temperatures deviate (Figure 5). The validity of a spin Hamiltonian formalism with quantized coupled spins $\tilde{S}_i, \tilde{S}_j, \ldots$, and a single J value for a cluster of this type is questionable. Similar results are obtained in attempting to fit data for $[Fe_4S_4(SR)_4]^{2-}$. This problem will be addressed in a subsequent publication.

(38) The relatively low $[Fe_4S_4X_4]^{2-,3-}$ potentials suggested that the trianions should be accessible by chemical reduction and less oxidatively unstable than $[Fe_4S_4(SR)_4]^{3-}$. However, the reductive method which affords thiolate trianions in good yield[4] when applied to $[Fe_4S_4Cl_4]^{2-}$ gave only a black intractable solid.

(39) The only *empirical* regularity we have detected in potential shifts within halide and thiolate dimer and tetramer series is monotonic negative displacement with decreasing HX[40] and thiol[41] solution acidities.

(40) R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, New York, N.Y., 1973, Chapter 6.

(41) J. P. Danehy and K. N. Parameswaran, *J. Chem. Eng. Data*, **13**, 386 (1968).

(42) For examples cf. P. Zuman, "Substituent Effects in Organic Polarography", Plenum Press, New York, N.Y., 1967.

(43) C. K. Jørgensen, *Prog. Inorg. Chem.*, **12**, 101 (1970).

(44) A. Müller, E. Diemann, and C. K. Jørgensen, *Struct. Bonding (Berlin)*, **14**, 23 (1973); H. H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, **71**, 1138 (1967).

(45) J. V. Pivnichny and H. H. Brintzinger, *Inorg. Chem.*, **12**, 2839 (1973).

(46) P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

(47) B. D. Bird and P. Day, *J. Chem. Phys.*, **49**, 392 (1968).

(48) M. T. Vala, Jr., and P. J. McCarthy, *Spectrochim. Acta, Part A*, **26**, 2183 (1970); M. Vala, Jr., P. Mongan, and P. J. McCarthy, *J. Chem. Soc., Dalton Trans.*, 1870 (1972).

Contribution from the Department of Chemistry,
The University of Mississippi, University, Mississippi 38677

Group 5 Boranes. 3. Transition-Metal Complexes of Arsaboranes[1,2]

J. L. LITTLE* and S. S. PAO

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In aqueous sodium hydroxide, cobalt chloride and nickel chloride react with $B_{10}H_{12}As^-$ to give $Co(B_{10}H_{10}As)_2^{3-}$ and $Ni(B_{10}H_{10}As)_2^{2-}$, respectively. Reacting $B_{10}H_{12}AsCH_3$, C_5H_6, $CoCl_2$, and excess KOH in anhydrous ethyl alcohol gives $(C_5H_5)Co(B_{10}H_{10}As)^-$. The piperidinium salt of $B_9H_{10}As_2^-$ treated in aqueous sodium hydroxide with cobalt chloride gives $Co(B_9H_9As_2)_2^-$, while $(C_5H_5)Co(B_9H_9As_2)$ is produced by reacting the piperidinium salt of $B_9H_{10}As_2^-$ with $CoCl_2$, C_5H_6, and triethylamine in THF. Alternatively, $(C_5H_5)Co(B_9H_9As_2)$ may be produced by reacting 1,2-$B_{10}H_{10}As_2$, C_5H_6, and $CoCl_2$ in piperidine.

Transition-metal complexes of 11-particle icosahedral fragments containing one[3-5] or two carbon atoms,[6] one sulfur,[7] selenium,[8] tellurium,[8] or phosphorus atom,[2] and both C and P[9] or C and As[10] are known.

We now report complexes of this cage fragment containing one or two arsenic atoms. Preparation of the ligands themselves has already been reported.[11]

Experimental Section

Preparations of III and V were carried out in a nitrogen atmosphere. Salts of $B_{10}H_{12}As^-$ and $B_9H_{10}As_2^-$ plus 1,2-$B_{10}H_{10}As_2$ and $B_{10}H_{12}AsCH_3$ were prepared according to literature methods.[11] Hydrous

Table I. Analytical Data

No.	Compd	% calcd C	% calcd H	% calcd Metal	% found C	% found H	% found Metal
I	$[(CH_3)_4N]_3[Co(B_{10}H_{10}As)_2]\cdot H_2O$	21.01	8.51	8.59	20.77	8.44	8.54
II	$[(CH_3)_4N]_2[Ni(B_{10}H_{10}As)_2]$	16.19	7.47	9.89	15.85	7.46	10.16
III	$(CH_3)_4N[C_5H_5Co(B_{10}H_{10}As)]$	27.65	6.95	15.06	27.25	7.23	15.50
IV	$(CH_3)_4N[Co(B_9H_9As_2)_2]$	7.44	4.68	9.13	7.52	4.89	9.23
V	$C_5H_5CoB_9H_9As_2$[a]	15.79	3.71	15.50	15.90	3.70	14.86

[a] Mp 289–291 °C.

Table II. Infrared Spectra (KBr Pellets) (cm^{-1})

I	3602 w, 3020 w, 2490 vs, 1484 m, 1448 w, 1284 w, 1015 s, 948 m, 895 m, 760 w, 730 w, 698 w, 451 w
II	3030 w, 2510 vs, 1483 s, 1409 w, 1290 w, 1007 s, 948 m, 897 m, 765 w, 735 m
III	3095 w, 3020 w, 2490 vs, 1484 m, 1415 m, 1288 w, 1063 w, 1019 s, 946 s, 893 w, 850 w, 824 s, 763 w, 730 m, 692 w, 412 w
IV	3020 w, 2520 vs, 2444 w, 1482 m, 1415 w, 996 s, 944 m, 926 w, 880 w, 864 w, 757 m, 726 w, 495 w
V	3106 w, 2510 vs, 1416 m, 1060 w, 999 s, 978 m, 920 w, 872 w, 845 s, 752 w, 728 w, 717 w, 581 w, 440 w, 405 w

Table III. Proton NMR Data[a]

No.	Resonance	Rel intens	Assign
I[b]	6.60		$(CH_3)_4N^+$
II[c]	6.58		$(CH_3)_4N^+$
III[c]	6.60	12.0	$(CH_3)_4N^+$
	5.02	4.9	C_5H_5
IV[c]	6.59		$(CH_3)_4N^+$
V[c]	4.17		C_5H_5

[a] Relative to $(CH_3)_4Si = 10.0$. [b] Dimethyl-d_6 sulfoxide solution. [c] Acetone-d_6 solution.

cobalt and nickel chlorides were used as received from Fisher and J. T. Baker Chemical Companies, respectively. Anhydrous cobalt chloride was prepared from the hexahydrate by heating it at 10^{-1} Torr and 100 °C for 2 days. Tetrahydrofuran (THF) was refluxed over $LiAlH_4$ overnight and then distilled just prior to use. Melting points were taken in sealed, evacuated capillaries and are uncorrected.

Analytical data are reported in Table I. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Infrared spectra (Table II) were obtained with a Perkin-Elmer 621 instrument and are reported as very strong (vs), strong (s), medium (m), or weak (w). Proton NMR spectra (Table III) were obtained with a Varian EM-360 spectrometer, and boron (^{11}B) NMR spectra (Table IV) were obtained at 70.6 MHz with a Varian HR-220 spectrometer and are externally referenced to $(C_2H_5)_2O\cdot BF_3$. UV–visible spectra (Table V) were obtained with a Cary 17 instrument.

$[(CH_3)_4N]_3[Co(B_{10}H_{10}As)_2]\cdot H_2O$ (I) and $[(CH_3)_4N]_2[Ni(B_{10}H_{10}As)_2]$ (II). To 50 mL of 33% sodium hydroxide solution in a round-bottomed flask was added 1.00 g of $CsB_{10}H_{12}As$. Then 3.0 g of $CoCl_2\cdot 6H_2O$ or $NiCl_2\cdot 6H_2O$ dissolved in a minimum of warm water was added with stirring. The resulting slurry was stirred and maintained at 55 °C for 33 h for the cobalt reaction or 50 °C for 10 h for the nickel reaction. The reaction mixture was then filtered on a fritted glass funnel, and the solids were washed with hot water until the filtrate became colorless. Air was bubbled through the combined filtrate and washings from the nickel reaction until a yellow color appeared. Precipitation with tetramethylammonium chloride solution gave crude solids which were recrystallized from hot water (I) or a small volume of acetonitrile (II) to give 0.973 g (93% yield) of I and 0.468 g (52% yield) of II.

$(CH_3)_4N(C_5H_5)Co(B_{10}H_{10}As)$ (III). This salt was prepared in the same manner as $(CH_3)_4N(C_5H_5)Co(B_{10}H_{10}P)$.[11] The quantities of reagents used were 1.96 g of $B_{10}H_{10}AsCH_3$, 4.4 mL of C_5H_6, and 3.2 g of $CoCl_2$. The initial quantity of KOH was 6.8 g, and the final quantity was 4.1 g. The air-dried crude tetramethylammonium salt was extracted twice with 10-mL portions of hot ethylene dichloride. The remaining solid was then extracted with several fractions of boiling methanol, and the methanol solution was filtered while hot. Reducing the volume of methanol and allowing the solution to cool gave 1.57 g (43% yield) of orange-brown crystals of III.

Table IV. Boron (^{11}B) NMR Spectra at 70.6 MHz

No.	Rel intens	Chem shifts, δ^a (J_{BH}, Hz)
I[b]	1:2:2:1:2:2	6.2 (130), 4.3 (130), 1.7 (~120), 0.0 (120), −11.9 (125), ~−13.4 (~125)
II[c]	1:4:1:2:2	20.9 (130), 12.5 (140), 8.3 (145), −4.3 (130), −6.1 (~130)
III[d]	2:1:1:2:2:2	8.0 (125), ~6.7 (~120), 5.0 (120), 3.2 (140), −7.3 (135), −12.7 (145)
IV[d]	1:1:2:2:1:2	20.6 (145), ~16.1 (~140), 12.3 (115), 11.5 (130), ~−1.7 (~140), −2.6 (145)
V[d]	1:5:2:1	17.1 (145), 12.3 (145), −4.7 (155), −8.8 (165)

[a] Relative to $(C_2H_5)_2O\cdot BF_3 = 0$. [b] As a trisodium salt in water. [c] Dimethylformamide solution. [d] Acetone solution.

Table V. Electronic Spectra[a]

No.	λ_{max}, mμ (ε)	No.	λ_{max}, mμ (ε)
I	451 (384)	IV	473 (260)
	309 (28 700)		348 (14 900)
	210[b] (24 800)		283 (8400)
II	332 (21 400)		231 (15 400)
	305 (20 600)	V	443 (326)
III	431 (305)		341[b] (1710)
	313[b] (1850)		311 (10 700)
	266 (18 700)		266 (10 400)
	201[b] (15 500)		239 (15 500)

[a] Acetonitrile solution. [b] Shoulder

$(CH_3)_4N[Co(B_9H_9As_2)_2]$ (IV). To 1.00 g of 1,2-$B_{10}H_{10}As_2$ under a nitrogen blanket in a 50-mL three-necked flask was added 20 mL of piperidine, and the solution was stirred magnetically for 22 h. Excess piperidine was removed by rotary evaporation, and the crude solid dried several hours at 10^{-2} Torr and 110 °C. Fifty milliliters of 33% NaOH solution was placed in a 125-mL Erlenmeyer flask, and 2.0 g of $CoCl_2\cdot 6H_2O$ dissolved in a minimum of warm water was added with stirring. Then the crude piperidinium salt of $B_9H_{10}As_2^-$ from above was added and the slurry stirred for 24 h. The slurry was filtered, and the filtrate washed several times with distilled water. The remaining solid was then extracted with several small portions of acetone until there was very little color in the extract. Water and $(CH_3)_4NCl$ solution were added to the acetone solution and then more water was added until precipitation of the crude brown salt was complete. After air-drying, the crude salt was dissolved in acetone and chromatographed on a 6-in. neutral alumina column using acetone. The orange band was collected and the solvent removed by rotary evaporation. Recrystallization was effected by dissolving in acetone, adding absolute ethanol, and slowly rotary evaporating to give small dark red needles of IV (0.562 g, 46% yield).

$(C_5H_5)Co(B_9H_9As_2)$ (V). Method A. In a three-necked 50-mL flask under a nitrogen blanket was stirred 0.50 g of 1,2-$B_{10}H_{10}As_2$ in 20 mL of piperidine for 22 h. Excess piperidine was removed in vacuo and the resulting solids were dried at 10^{-1} Torr and 110 °C for several hours. The flask was fitted with a reflux condenser and gas inlet, and a nitrogen blanket was once again established. To the flask was added 50 mL of dry THF, 10 mL of dry $(C_2H_5)_3N$, 3.0 mL of freshly cracked C_5H_6, and 2.0 g of anhydrous $CoCl_2$ in that order. Stirring was carried out for 17 h, and then the mixture was refluxed for 1 h. After the mixture was cooled, a stream of O_2 was bubbled through it for 1 h, and the THF removed in vacuo. The solid residues were extracted with several portions of methylene chloride, silica gel was added, and the solvent was removed on a rotary evaporator. Chromatography of the solids on a silica-gel column with 25% methylene chloride–75% hexane gave a yellow band. Removal of the solvent and crystallization of the solid from ethylene dichloride–heptane gave 0.33 g (46% yield) of orange plates of V.

Method B. To 0.50 g of 1,2-$B_{10}H_{10}As_2$ under a nitrogen blanket in a 50-mL two-necked flask fitted with a reflux condenser and nitrogen inlet was added 25 mL of piperidine. Then 3.0 mL of C_5H_6 and 2.0 g of anhydrous $CoCl_2$ were added, and the mixture was stirred at room temperature for 10 h and refluxed for 12 h. Excess piperidine was removed in vacuo, and the residues were chromatographed[12] as in method A to give 0.24 g of V (33% yield).

Results and Discussion

The complexes $Co(B_{10}H_{10}As)_2^{3-}$ and $Ni(B_{10}H_{10}As)_2^{2-}$ are obtained when a strong aqueous solution of sodium hydroxide reacts with $CsB_{10}H_{12}As$ and cobalt chloride or nickel chloride. Salts of several large cations may be prepared, although the tetramethylammonium salts are most conveniently prepared and purified. Precipitation of the cobalt complex anion with tetramethylammonium chloride solution and recrystallization from hot water give $[(CH_3)_4N]_3[Co(B_{10}H_{10}As)_2]\cdot H_2O$ (I) in very high yield. The water of crystallization is seen both in the elemental analysis (Table I) and in the infrared spectrum (Table II, 3602 cm^{-1}). Waters of crystallization have been observed for Cs^+ salts of the analogous "carbollide" complexes $M(B_{10}H_{10}CH)_2^{3-}$, where M = Cr, Fe, or Co.[4] The boron (^{11}B) NMR spectrum at 70.6 MHz was obtained using a trisodium salt (eluted from the sodium form of a strongly acidic ion-exchange resin with hot water) because of the insolubility of the tetramethylammonium salt in most solvents. Doublets in the 70.6-MHz boron NMR spectrum (Table IV) overlap badly, but the 1:2:2:1:2:2 pattern corresponds to the expected C_s cage symmetry.

Precipitation of $Ni(B_{10}H_{10}As)_2^{2-}$ with tetramethylammonium chloride solution and recrystallization from a small quantity of acetonitrile give a moderate yield of $[(CH_3)_4N]_2[Ni(B_{10}H_{10}As)_2]$ (II) as large reddish orange crystals. The boron NMR spectrum shows a 1:4:1:2:2 pattern, which corresponds to C_s cage symmetry except for the accidental degeneracy of two doublets of area 2 each. As has been observed[4,6] for $B_{10}H_{10}CH^{3-}$ and $B_9C_2H_{11}^{2-}$ complexes of nickel, $B_{10}H_{10}As^{3-}$ stabilizes the Ni^{IV} oxidation state.

Attempts to synthesize $(C_5H_5)Co(B_{10}H_{10}As)^-$ from salts of $B_{10}H_{12}As^-$ gave no product, even though the complex ion $(C_5H_5)Co(B_{10}H_{10}CH)^-$ had been successfully prepared[5] from a salt of $B_{10}H_{12}CH^-$. Thus, as in the case of the phosphaborane[2] $(C_5H_5)Co(B_{10}H_{10}P)^-$, we started with a cage having an alkyl substituent on the heteroatom. Reacting $B_{10}H_{12}AsCH_3$, C_5H_6, and $CoCl_2$ in a KOH solution of ethyl alcohol gave after precipitation with $(CH_3)_4NCl$ solution a moderate yield of $(CH_3)_4N(C_5H_5)Co(B_{10}H_{10}As)$ (III). None of the expected $(C_5H_5)Co(B_{10}H_{10}AsCH_3)$ was found.

When attempts were made to methylate the arsenic on III with methyl iodide in THF, cage disruption was the result (similar results were found with ethyl iodide). This is in contrast to the analogous phosphaborane complex, in which the phosphorus is alkylated smoothly in high yield by a variety of alkyl iodides.[2]

Complex III had the only integrable proton NMR spectrum (Table III) of any of the arsaborane complexes: the resonance at τ 6.60 (relative area 12.0) is assigned to the $(CH_3)_4N^+$ ion and the resonance at τ 5.02 is assigned to the cyclopentadienyl protons. The boron-11 NMR spectrum was completely resolved into doublets of relative areas 2:1:1:2:2:2, as expected for C_s cage symmetry.

Synthesis of complexes of 7,8-$B_9H_9As_2^{2-}$ proved to be a difficult task. Many different salts of the $B_9H_{10}As_2^-$, transition-metal ions, and reaction conditions were tried before the first complex was successfully synthesized. Cobalt is the only metal of which complexes have yet been made, and the only salt of $B_9H_{10}As_2^-$ found to be synthetically useful is the piperidinium salt. Thus reacting $C_5H_{10}NH_2B_9H_{10}As_2$ and cobalt chloride in strong aqueous sodium hydroxide solution followed by precipitation with $(CH_3)_4NCl$ solution gives a moderate yield of $(CH_3)_4NCo(B_9H_9As_2)_2$ (IV). The Co^{II} complex initially formed is evidently oxidized to a Co^{III} complex by air during the reaction.

The boron-11 NMR spectrum of IV is in a 1:1:2:2:1:2 pattern of doublets (the upfield set of doublets is very poorly resolved), readily interpretable in terms of C_s cage symmetry.

Reacting the piperidinium salt of $B_9H_{10}As_2^-$, freshly cracked cyclopentadiene, triethylamine, and $CoCl_2$ in THF produces $(C_5H_5)Co(B_9H_9As_2)$ (V) in moderate yield. An alternate route starting with 1,2-$B_{10}H_{10}As_2$ in piperidine gives a lower yield of V, the only neutral arsaborane complex thus far synthesized.

The boron-11 NMR spectrum of V is in a 1:5:2:1 pattern, interpretable as C_s cage symmetry with two doublets of area 2 each and one doublet of area 1 accidentally degenerate. The cyclopentadienyl protons are found at τ 4.17 in the proton NMR spectrum (Table III), which is close to the values of the resonances for the complexes $C_5H_5Co(B_{10}H_{10}PR)$.[2] An absorption at 3106 cm^{-1} in the infrared spectrum is attributable to C_5H_5.

The low-resolution mass spectrum of V cuts off at m/e 382, corresponding to the $^{11}B_9{}^1H_{14}{}^{12}C_5{}^{75}As_2{}^{59}Co^+$ parent ion.

Electronic spectra of the complexes are presented in Table V and are quite similar to spectra of analogous complexes of 11-particle fragments containing C, P, S, Se, or Te.

Attempts were made to synthesize a complex of the formula $Fe(B_{10}H_{10}As)_2^{3-}$ using $CsB_{10}H_{12}As$ and ferrous ammonium sulfate in an aqueous base solution under a nitrogen blanket. A burgandy color developed (the color of the $Fe(B_{10}H_{10}CH)_2^{3-}$ ion), and iron metal was deposited. However, rapid decomposition took place when the solution was exposed to air.

Attempts to synthesize the neutral molecule $(C_5H_5)Ni(B_{10}H_{10}As)$ using $CsB_{10}H_{12}As$, sodium amalgam, and $(C_5H_5)_2Ni$ in acetonitrile solution gave about 1% yield of a volatile dark orange complex showing a cutoff in the low-resolution mass spectrum at m/e 319, corresponding to the molecular ion $^{11}B_{10}{}^1H_{15}{}^{12}C_5{}^{75}As^{59}Ni^+$. Hawthorne and coworkers had successfully synthesized $(C_5H_5)Ni(B_{11}H_{11})^-$ from $B_{11}H_{13}^{2-}$ by a similar route.[13] Because of the very low yield, we did not investigate this material further.

Attempts at alkylating the nonbonding pairs of electrons on arsenic atoms for the complexes I–IV resulted in cage degradation.

Thus the chemistry of arsaborane–transition-metal complexes, as well as the number of complexes that can be made, is very limited. This is in direct contrast to the rich chemistry associated with most other heteroborane ligands.[6] We have observed that when very heavy members of a given family are substituted into a borane cage, both the percent yields of the products and the number of readily accessible compounds drop dramatically. Our studies of stibaboranes bear this out.[14]

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References and Notes

(1) Presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977.

(2) Part 2: J. L. Little, *Inorg. Chem.*, **15**, 114 (1976).

(3) P. A. Wegner, L. J. Guggenberger, and E. L. Muetterties, *J. Am. Chem. Soc.*, **92**, 3473 (1970).
(4) W. H. Knoth, *Inorg. Chem.*, **10**, 598 (1971).
(5) R. R. Rietz, D. F. Dustin, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1580 (1974).
(6) G. B. Dunks and M. F. Hawthorne in "Boron Hydride Chemistry", E. L. Muetterties, Ed., Academic Press, New York, N.Y., 1975, p 383, and references therein.
(7) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).
(8) J. L. Little, G. D. Friesen, and L. J. Todd, *Inorg. Chem.*, **16**, 869 (1977).
(9) J. L. Little, P. S. Welcker, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, **9**, 63 (1970); L. I. Zakharkin and A. I. L'Vov, *Zh. Obshch. Khim.*, **41**, 1880 (1971); P. S. Welcker and L. J. Todd, *Inorg. Chem.*, **9**, 286 (1970); D. C. Beer and L. J. Todd, *J. Organomet. Chem.*, **36**, 77 (1972); **55**, 363 (1973).
(10) A. R. Burke, Ph. D. Thesis, University of Illinois, 1969; L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, **9**, 2175 (1970); L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *J. Am. Chem. Soc.*, **91**, 3376 (1969); D. C. Beer and L. J. Todd, *J. Organomet, Chem.*, **36**, 77 (1972).
(11) J. L. Little, S. S. Pao, and K. K. Sugathan, *Inorg. Chem.*, **13**, 1752 (1974).
(12) Sometimes there is an impurity eluted from the column with the product which can be removed by boiling the eluate, removing the solvent, and rechromatographing the solids.
(13) B. P. Sullivan, R. N. Leyden, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 455 (1975).
(14) J. L. Little, to be submitted for publication.

Contribution from Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138,
and the Department of Chemistry, The City College, City University of New York, New York, New York 10031

The Question of Fluxional Behavior in $B_3H_8^-$ and B_5H_{11}

I. M. PEPPERBERG, D. A. DIXON, W. N. LIPSCOMB,* and T. A. HALGREN

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The structures of $B_3H_8^-$ and B_5H_{11} have been examined by molecular orbital techniques to study whether they exhibit fluxional behavior. The PRDDO (partial retention of diatomic differential overlap) method was employed in this study, and the negative ion $B_3H_8^-$ was also examined by ab initio extended-basis 4-31G calculations. The pseudorotation process, which involves conversion of the equilibrium geometry double-bridge structure to a single-bridge structure, followed by rotation of the BH_3 group, was found to afford a low-energy pathway. The calculated 4-31G barrier to hydrogen exchange is about 1 kcal/mol (in the gas phase) and is consistent with fluxional behavior for $B_3H_8^-$. The bonding in $B_3H_8^-$ is examined in terms of localized molecular orbitals, vacant-orbital topology theory, and donor/acceptor interactions of the molecular subunits. Geometry optimization of B_5H_{11} was performed in C_s symmetry starting from a set of crystal coordinates. A recently reported asymmetric crystal structure of C_1 symmetry was also examined. After substantial optimization, this C_1 structure was less stable than the C_s structure, but only by about 1 kcal/mol. An identical energy increase was obtained for the C_s structure by displacing the unique terminal hydrogen on the apical boron by 10°. Thus, B_5H_{11} appears to have C_s symmetry and not to be fluxional. A low-lying vibration involving substantial displacement of the unique hydrogen on the apex is indicated, however.

Fluxional behavior in the boron hydrides has been observed in a number of instances.[1] Two systems that have been postulated to be fluxional (i.e., to be comprised of two or more structures which interconvert rapidly on the NMR time scale) are $B_3H_8^-$ and B_5H_{11}. Observation of the former in solution by NMR shows that all protons and borons remain equivalent on the NMR time scale even down to 137 K.[2] Thus, a rapid intramolecular tautomerization occurs, the activation energy for which has been estimated to be no greater than 8 kcal/mol.[2] In the solid state, only one structural study of the ion, an x-ray diffraction study of $((NH_3)_2BH_2^+)(B_3H_8^-)$,[3] has been reported for other than transition-metal complexes. This study indicates that the anion has C_{2v} symmetry, as shown in Figure 1a, and has two hydrogen bridges and three BH_2 groups. Solid-state NMR results have also been obtained for KB_3H_8 and for $(CH_3)_4NB_3H_8$. At room temperature, the proton and ^{11}B spectra indicate equivalent borons and protons on the NMR time scale.[4]

The pseudorotation process proposed by Lipscomb for $B_3H_8^-$ (Figure 2) involves transformations between a one-bridge and a two-bridge structure.[5] The two distinct phases of this mechanism are (1) an exchange of bridge and terminal hydrogens, which corresponds to the interconversion of the double- and single-bridge structures, and (2) a subsequent rotation of the BH_3 group in the single-bridge structure. Since the single-bridge structure can reclose to either of the two equivalent two-bridge structures, all borons and all hydrogens can exchange. A theoretical study employing the NEMO method in conjunction with unoptimized geometries yielded barriers of 4.4 and 2.5 kcal/mol, respectively, for the successive bridge–terminal exchange and BH_3-rotation steps.[6]

An unambiguous experimental determination of the molecular structure of B_5H_{11} has proven to be difficult to obtain.[7] The initial crystal structure of Lavine and Lipscomb (LL) suggests that the molecule has C_s symmetry.[7] NMR studies have also been reported[8] but do not establish whether B_5H_{11} has C_s symmetry or has two equivalent interconverting forms of C_1 (no) symmetry. This perplexing question has not been resolved, despite the new crystal structure determination by Huffman and Schaeffer,[9] who reported a C_1 structure. If the ground state of the molecule in fact lacks symmetry, then, as noted, it must have a fluxional structure.

Theoretical studies of systems such as these may have predictive value, even though such studies strictly apply only to processes occurring in the gas phase, where solvation effects are absent. The NEMO studies on $B_3H_8^-$ are subject to this limitation and are further suspect because of the sizable approximations to ab initio theory employed in the method. Ab initio SCF and localized-orbital studies have been reported for B_5H_{11}.[10] However, these studies employed geometries based on the C_s crystal structure of Lavine and Lipscomb and thus do not answer the question of the symmetry of the molecule.

In this study, we have examined various structures for $B_3H_8^-$ using both PRDDO[11] and 4-31G[12] calculations. PRDDO is an efficient approximate method which employs minimum basis sets of Slater atomic orbitals and which accurately reproduces the results of ab initio calculations using minimum-basis sets. The ab initio 4-31G calculations are much more expensive but employ more flexible basis sets which circumvent some of the special difficulties which arise in minimum-basis-set calculations on negative ions; the larger basis sets allow for the necessary expansion of the charge distribution in regions of excess electron density. For B_5H_{11}, several structures have been examined at the PRDDO level, and a characterization of the bonding in terms of the localized

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