the two cleavage mechanisms can then generate the ten dimeric complexes. No new mechanism is required to account for the formation of $\text{(base)MS}_4\text{C}_4\text{(CF}_3)_2\text{(CN)}_2^-$ upon addition of base once $\text{MS}_4\text{C}_4\text{(CF}_3)_2\text{(CN)}_2^-$ or the dimers D–J are formed.

Dithiolene exchange in the case of the base adducts appears to involve dissociation with exchange occurring *via* the mechanism already proposed for the bis-dithiolene dimers. Accordingly, the addition of base should suppress dissociation and slow ligand exchange as is observed. The fact that triphenylphosphine inhibits exchange more effectively than does triphenylarsine accords well with the greater stability (toward dissociation) of the phosphine adduct.[4] An alternate means for exchange could involve, initially, dimerization of base adducts by formation of extraplanar M–S bonds. Such dimerization has been proposed to explain the solid-state properties of the neutral complex $\text{(C}_6\text{H}_5\text{O)}_3\text{PCoS}_4\text{C}_4\text{(CF}_3)_4$.[4] Base inhibition of this mechanism could be ascribed to the formation of six-coordinate bis adducts which could not undergo dimerization. However this mechanism is unlikely because no evidence has been found for bis adducts $\text{(base)}_2\text{MS}_4\text{C}_4\text{R}_4^-$ in these systems.

Finally some comments on mixed-metal dimers are in order. Clearly our results indicate that, in solution, a dimer of the type $\text{CoFeS}_4\text{C}_4\text{R}_4^{2-}$ will be in rapid equilibrium with $\text{Co}_2\text{S}_8\text{C}_8\text{R}_8^{2-}$ and $\text{Fe}_2\text{S}_8\text{C}_8\text{R}_8^{2-}$; consequently attempts to isolate mixed-metal, dianionic dimers will probably be fruitless. Attempts to detect mixed-metal dimers polarographically with a single type of dithiolene ligand have been unsuccessful because the polarography of these complexes is only very slightly dependent on the metal. Direct polarographic observation of the dimer $\text{CoS}_4\text{C}_4\text{(CF}_3)_4\text{FeS}_4\text{C}_4\text{(CN)}_4^{2-}$ with structure B has been possible; the half-wave potential for its oxidation is +0.76 V. Similar attempts at detecting $\text{CoS}_4\text{C}_4\text{(CN)}_4\text{FeS}_4\text{C}_4\text{(CF}_3)_4^{2-}$ were thwarted by the rapid onset of the second reorganization reaction. These exchange reactions require both a dimeric species and rapid dimer–monomer equilibrium. Since the extent and kinetics of disproportionation or dissociation of the oxidized dimers $\text{M}_2\text{S}_8\text{C}_8\text{R}_8^{-1,0}$ have not been determined, these factors may allow for the isolation of mixed-metal species in these oxidation states.

Experimental Section

The ligand-exchange reactions were followed by the polarographic technique developed by Davison, *et al.*[2] Dichloromethane solutions for exchange studies were prepared so that the initial concentration of each of the exchanging species was 1.00 m*M*. Periodically aliquots of these solutions were withdrawn, mixed with the supporting electrolyte, and diluted with dichloromethane for polarographic measurements. For a typical exchange reaction only the waves (for a particular redox step) due to the parent complexes $\text{MS}_4\text{C}_4\text{(CF}_3)_4^-$ and $\text{MS}_4\text{C}_4\text{(CN)}_4^-$ were observed initially, but slowly the height of those waves decreased as the height of a new wave, positioned between the initial waves, increased. There was, however, no change in the total wave height due to all species and consequently no loss of electroactive species. These observations are similar to those reported by Davison, *et al.*[2] The new wave is ascribed to the mixed-ligand species $\text{MS}_4\text{C}_4\text{(CF}_3)_2\text{(CN)}_2^-$.

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3-Trimethylamino-3-beryl-1,2-dicarba-*closo*-dodecaborane(12) and Related Species

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The reconstruction of the 1,2-dicarba-*closo*-dodecaborane(12) icosahedron from the reaction of the (3)-1,2-dicarbollide ion [(3)-1,2-$\text{B}_9\text{C}_2\text{H}_{11}^{2-}$] with phenylboron dichloride

$$\text{(3)-1,2-B}_9\text{C}_2\text{H}_{11}^{2-} + \text{C}_6\text{H}_5\text{BCl}_2 \longrightarrow \text{3-C}_6\text{H}_5\text{-1,2-B}_{10}\text{C}_2\text{H}_{11} + 2\text{Cl}^-$$

has been described.[2,3] The similar reaction of BeCl_2 with the (3)-1,2-dicarbollide ion

$$\text{(3)-1,2-B}_9\text{C}_2\text{H}_{11}^{2-} + \text{BeCl}_2 \longrightarrow \text{3-BeCl-1,2-B}_9\text{C}_2\text{H}_{11}^- + \text{Cl}^-$$

in the presence and absence of donor solvents failed to insert a Be atom into the open face of the (3)-1,2-dicarbollide ion under all conditions attempted. However, since the expected 3-BeCl-1,2-$\text{B}_9\text{C}_2\text{H}_{11}^-$ icosahedral species would be isoelectronic with the known $\text{B}_{11}\text{CH}_{12}^-$ ion,[4] due to the isoelectronic relationship of B–B and Be–C atomic pairs,[5] further work was successfully undertaken and briefly reported elsewhere.[5] This note describes these initial results in greater detail.

Results and Discussion

Earlier work[6] had illustrated the existence of a highly acidic $\text{B}_9\text{C}_2\text{H}_{13}$ species which resulted from the protonation of the (3)-1,2-$\text{B}_9\text{C}_2\text{H}_{12}^-$ ion. This species may be formally considered to be a diprotonated (3)-1,2-dicarbollide ion, and, as such, one might expect (3)-1,2-$\text{B}_9\text{C}_2\text{H}_{13}$ to react with metal alkyls to produce 2 mol of alkane through protolysis of metal–alkyl bonds with insertion of the metal into the open face of the icosahedral fragment. In the case of beryllium alkyls, the intervention of a donor solvent, :L, would probably be required to stabilize the product. Thus, dialkylberyllium etherates appeared to be the reagents of choice with which to test the proposed reaction sequence

$$\text{(3)-1,2-B}_9\text{C}_2\text{H}_{13} + \text{BeR}_2\cdot 2(\text{O(C}_2\text{H}_5)_2) \xrightarrow{\text{C}_6\text{H}_6\text{–(C}_2\text{H}_5)_2\text{O}} 2\text{RH} + \text{3-BeO(C}_2\text{H}_5)_2\text{-1,2-B}_9\text{C}_2\text{H}_{11} + (\text{C}_2\text{H}_5)_2\text{O}$$

Accordingly, diethyl- and dimethylberyllium diethyl etherates were allowed to react with (3)-1,2-$\text{B}_9\text{C}_2\text{H}_{13}$ in benzene solution containing added diethyl ether. One mole of alkane was rapidly produced upon mixing the reagents at room temperature and additional alkane was evolved upon the removal of solvent at 50°. The resulting white crystalline product (mp 120–121°) was

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[2] M. F. Hawthorne and P. A. Wegner, *J. Amer. Chem. Soc.*, **87**, 4392 (1965).

[3] M. F. Hawthorne and P. A. Wegner, *ibid.*, **90**, 896 (1968).

[4] W. H. Knoth, *ibid.*, **89**, 1274 (1967).

[5] G. Popp and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968).

[6] R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, **86**, 1642 (1964).

characterized[5] by elemental analysis and the ^{1}H nmr spectrum as $B_9BeC_2H_{11} \cdot O(C_2H_5)_2$ (I), Figure 1.

The ^{1}H nmr spectrum contained a quartet (area 4) and triplet (area 6) characteristic of two equivalent ethyl groups as well as a broad singlet (area 2) at δ 2.75. The latter resonance was assigned to the two equivalent protons attached to the carborane carbon atoms. I was very sensitive to moist air and readily hydrolyzed to produce the (3)-1,2-$B_9C_2H_{12}^-$ ion which was identified by its characteristic infrared spectrum.

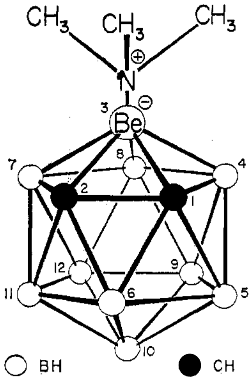

Figure 1.—Proposed structure of (3)-$BeN(CH_3)_3$-1,2-$B_9C_2H_{11}$ (III). The diethyl etherate (I) presumably has the same gross structure with $(C_2H_5)_2O$ replacing $N(CH_3)_3$.

In contrast to the above results, it was subsequently found that the reaction of diethylberyllium containing only $^1/_3$ mol of complexed diethyl ether per mole of dialkylberyllium with (3)-1,2-$B_9C_2H_{13}$ in benzene solution produced 2 mol of ethane and a white benzene-insoluble product (II) which was isolated by filtration. The filtrate afforded the diethyl ether complex I. The isolated white solid was extremely sensitive to air and hygroscopic. These properties prevented the acquisition of meaningful elemental analyses although infrared spectra were obtained. Nmr data could not be collected due to the insolubility of II in nonreactive solvents. The infrared spectrum of II contained the usual terminal B–H stretching absorption plus an unusual absorption at 2150 cm^{-1}, a region in which Be–H–B or B–H–B bridge units could possibly absorb. Since the insolubility of II suggests a high molecular weight and the 2150-cm^{-1} infrared band suggests the presence of a bridge system, we tentatively suggest that II is composed of repeating units of icosahedral geometry [3-Be-1,2-$B_9C_2H_{11}$]$_n$ having Be–H–B bridge linkages between repeating units. In this way a terminal B–H unit of one repeating unit (perhaps in the 10 position, Figure 1) could satisfy the electron deficiency of the Be atom present in a neighboring icosahedron by sharing its electron pair in a Be–H–B bridge. It should be mentioned that 2150 cm^{-1} is a higher frequency than that usually observed in B–H–B bridge systems and we have no adequate model for characteristic Be–H–B frequencies.

The reaction of dimethylberyllium containing excess diethyl ether with (3)-1,2-$B_9C_2H_{13}$ in benzene solution produced crude I which was further treated with $(CH_3)_3N$. The product of the trimethylamine reaction (III), mp 221–223° dec, was characterized as (3)-[$BeN(CH_3)_3$]-1,2-$B_9C_2H_{11}$ (Figure 1) by elemental analysis and ^{1}H nmr spectra. Complex III was also obtained from II by treatment with $(CH_3)_3N$. The ^{1}H nmr spectrum of III in CH_2Cl_2 solution contained a broad singlet associated with carborane C–H protons at δ 2.55 (area 2) and a sharp singlet at δ 2.90 (area 9) associated with the methyl group protons of the $N(CH_3)_3$ ligand.

While III was considerably more stable toward air than I, degradation with ethanolic KOH produced the (3)-1,2-$B_9C_2H_{12}^-$ ion in 79% yield.

Attempts were made to prepare derivatives which contained NH_3 and $(C_2H_5)_2S$ ligands without complete success. In these cases the reaction was complicated by incomplete displacement of diethyl ether from I by $(C_2H_5)_2S$ and by the instability of the NH_3 complex. Attempts to use $(C_2H_5)_2S$ as the reaction solvent were to no avail since the stronger diethyl ether ligand was present in the beryllium alkyl starting material.

Experimental Section

Materials.—The (3)-1,2-$B_9C_2H_{13}$ starting material was prepared as previously described[6] and sublimed before use. Dimethyl- and diethylberyllium were supplied through the courtesy of Professor G. E. Coates and used without further purification. All solvents were rigorously dried, degassed under high vacuum, and stored under nitrogen. All manipulations were carried out in a nitrogen-filled glove box or utilized vacuum-line techniques. Infrared spectra were obtained with Perkin-Elmer Models 137 and 621 spectrophotometers. The ^{1}H nmr spectra were determined with a Varian A-60 spectrometer. Boron-11 nmr spectra were obtained with a Varian HA-100 spectrometer operating at 32.1 MHz and are not reported due to their uninformative nature. Gases (CH_4, C_2H_6) were identified by their characteristic vpc retention times using a Carle 100 instrument. All operations were conducted under nitrogen.

Preparation of (3)-$BeO(C_2H_5)_2$-1,2-$B_9C_2H_{11}$ (I).—The reaction vessel was a 100-ml three-necked round-bottomed flask, equipped with a pressure-equalized addition funnel, a magnetic stirring bar, and a reflux condenser. The round-bottomed flask contained a solution of 7.04 g (52.5 mmol) of (3)-1,2-$B_9C_2H_{13}$ in 40 ml of dry, oxygen-free benzene and 15 ml of dry, oxygen-free diethyl ether. In the addition funnel was placed 6.0 ml of diethylberyllium etherate which contained 49.5 mmol of diethylberyllium. The apparatus was connected to a reflux condenser and gas buret. The solution was maintained at 35° and with stirring the diethylberyllium was added dropwise. Gas evolution occurred which stopped when the addition of diethylberyllium was completed. The evolved gas was identified as ethane by its characteristic vpc retention time; its volume was 1385 ml (1202 ml expected for 1 molar equiv). The solvent was removed on the vacuum line and upon heating to 50° further gas evolution occurred. The gas was trapped with liquid nitrogen and identified as ethane. After the gas evolution had stopped (12 hr), a white solid remained which was dissolved in CH_2Cl_2. The solid was crystallized from this solution by dropwise addition of hexane and slow evaporation of this solvent mixture by passing dry, oxygen-free nitrogen over the surface. This procedure was repeated three times. The white solid product, mp 120–121°, was obtained in 55% yield. The product is very air sensitive (liquefies if it is exposed to air) and it is decomposed by water. Degradation with ethanolic KOH gave (3)-1,2-$B_9C_2H_{12}^-$ which was isolated as the white tetramethylammonium salt in 84% yield and identified by its infrared spectrum. *Anal.* Calcd for $BeB_9C_8H_{21}O$: Be, 4.18; B, 45.16; C, 33.42; H, 9.82. Found: Be, 3.87; B, 44.74; C, 33.26; H, 9.97.

Reaction of Diethylberyllium with $B_9C_2H_{13}$. Preparation of II.—The reaction vessel was a 100-ml three-necked round-bottomed flask, equipped with a pressure-equalized 10-ml addition funnel, a magnetic stirring bar, and a reflux condenser bearing a gas buret.

The round-bottomed flask contained a solution of 7.72 g (57 mmol) of (3)-1,2-$B_9C_2H_{13}$ in 50 ml of dry, oxygen-free benzene. In the addition funnel was 7 ml of diethylberyllium etherate which contained 57.8 mmol of diethylberyllium and 21.2 mmol of diethyl ether. The solution was maintained at room temperature and the diethylberyllium was added dropwise with stirring. Gas evolution occurred immediately and after about 1 ml of diethylberyllium was added a white solid precipitated. The evolved gas was identified as ethane by its characteristic vpc retention time; its volume was 2500 ml after the addition was completed (2800 ml expected).

The white precipitate was separated by filtration, washed three times with 10 ml of benzene, and dried under high vacuum at 50°. The yield was 2.15 g. From the filtrate $B_9C_2H_{11}Be \cdot O(C_2H_5)_2$ (I) was obtained as described earlier. The white solid did not melt below 350° and was not soluble in common organic solvents such as benzene, pentane, dichloromethane, acetone, tetrahydrofuran, or chloroform.

If treated for about 5 hr with liquid trimethylamine, $B_9C_2H_{11}Be \cdot N(CH_3)_3$ could be isolated in a 67% yield.

The infrared spectrum in a Nujol mull exhibits five distinct absorptions in the B–H region: 2550 (sh), 2850 (sh) 2590, 2610, and 2640 cm^{-1} (sh). It possesses a bridge-type hydrogen which absorbs at 2150 cm^{-1}. The absorptions between 700 and 1200 cm^{-1} which can be ascribed to cage absorptions have the same pattern as those of $B_9C_2H_{11}Be \cdot O(C_2H_5)_2$ and $B_9C_2H_{11}Be \cdot N(CH_3)_3$ but are shifted about 15 cm^{-1} to lower frequencies.

Preparation of (3)-$BeN(CH_3)_3$-1,2-$B_9C_2H_{11}$ (III).—The reaction vessel was a 100-ml three-necked round-bottomed flask, equipped with a pressure-equalized addition funnel, a magnetic stirring bar, and a reflux condenser. The round-bottomed flask contained a solution of 6.44 g (48 mmol) of (3)-1,2-$B_9C_2H_{13}$, dissolved in 50 ml of dry oxygen-free benzene. In the addition funnel was 1.87 g (48 mmol) of dimethylberyllium, dissolved in 8 ml of dry diethyl ether. The solution was maintained at room temperature and the dimethylberyllium solution was added dropwise with stirring. Gas evolution occurred immediately which stopped when the addition of dimethylberyllium was completed. The evolved gas was identified as methane from its characteristic vpc retention time.

After the reaction was completed, a yellow oil layer had separated on the bottom of the flask. The upper colorless benzene layer was decanted, and the remaining oil was washed three times with 40 ml of dry benzene and dried under high vacuum at room temperature. The remaining semisolid was dissolved in 30 ml of dry dichloromethane and filtered, and dry trimethylamine was passed through the solution. A white material precipitated which was separated by filtration, washed with benzene, and dried under high vacuum. This white solid was recrystallized from a dichloromethane–hexane mixture by passing dry oxygen-free nitrogen over the surface of the solution. The white solid product (mp 221–223° dec) was obtained in a 51% overall yield. The product was less air sensitive than the analogous etherate and was decomposed by water.

Degradation with ethanolic KOH gave (3)-1,2-$B_9C_2H_{12}^-$ which was isolated as the white tetramethylammonium salt in 79% yield and identified by its infrared spectrum. *Anal.* Calcd for $BeB_9C_5H_{20}N$: Be, 4.50; B, 48.54; C, 29.93; H, 10.05; N, 6.98. Found: Be, 3.79; B, 47.45; C, 28.46; H, 9.67; N, 7.19.

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The Photochemistry of $(en)_2Co(NH_2)(O_2)Co(en)_2^{4+}$

BY JOAN S. VALENTINE AND DONALD VALENTINE, JR.*

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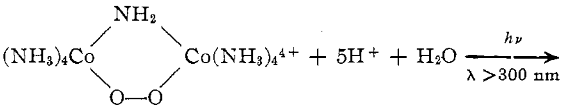
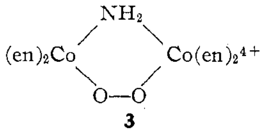
Irradiation of the O_2^- to Co^{III} electron absorption bands of **1** and **2** led in acidic, aqueous solutions to reactions 1 and 2.[1] These reactions were found to be molecular processes in which the photoreactive excited states of the μ-superoxo complexes collapsed to give fragments such as $Co(NH_3)_5(O_2)^{3+}$ and a short-lived cobalt(II)–ammine which decayed subsequently to Co^{2+}.[1] The apparent simplicity of this mechanism and the absence of side reactions led us to believe that reactions such as (1) and (2) might prove general for μ-superoxo-dicobalt ammines. We have now studied the photochemistry of **3** and **4** which are, respectively, analogs of **2** and **1** with coordinated ammonia replaced by chelating organic amines.

$$\underset{\mathbf{1}}{(NH_3)_5CoO_2Co(NH_3)_5^{5+}} + 5H^+ + H_2O \xrightarrow[\lambda > 300\text{ nm}]{h\nu} Co(NH_3)_5(H_2O)^{3+} + Co^{2+} + 5NH_4^+ + O_2 \quad (1)$$



2

$$Co(NH_3)_5(H_2O)^{3+} + Co^{2+} + 5NH_4^+ + O_2 \quad (2)$$



3

$(tetren)CoO_2Co(tetren)^{5+}$
4

Results and Discussion

Samples of **3** prepared following Werner[2] (reaction 3a) were found to be contaminated with as much as 20% of $(en)_2Co(NH_2)(NO_2)Co(en)_2^{4+}$, **5**, which could be isolated by destroying **3** photochemically and separating **5** from the photochemical decomposition products (*vide infra*) by ion-exchange chromatography. Elution of the fraction containing **5** with 4 *M* HCl gave a solution which upon flash evaporation afforded the chloride salt of **5**, identical with an authentic sample.[3] Formation

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[1] J. S. Valentine and D. Valentine, Jr., *J. Amer. Chem. Soc.*, in press. Preliminary reports of this work appeared in: (a) D. Valentine, Jr., and J. Valentine, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. L-19; (b) J. Valentine and D. Valentine, Jr., in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, pp 72–74; (c) D. Valentine, Jr., J. Valentine, and B. Sarver, "Proceedings of the Symposium on Electronically Excited States," Los Angeles, Calif., Oct 1969, in press.

[2] A. Werner, *Justus Liebig's Ann. Chem.*, **375**, 1 (1910).

[3] A. Werner, *Chem. Ber.*, **46**, 3674 (1913). Complex **5** forms a nitrate salt isostructural with the nitrate of **3**: *cf.* G. L. Goodman, H. G. Hecht, and J. A. Weil, *Advan. Chem. Ser.*, **36**, 90 (1962), and references therein. We had no success in purifying **3** contaminated with **5**. Recent work with **3** and the related $(pn)_2Co(NH_2)(O_2)Co(pn)_2^{4+}$ (pn = 1,2-diaminopropane), including both circular dichroism studies and the products of reaction of **3** with iodide ion, should probably be reexamined. See ref 4 and also Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 146 (1969).