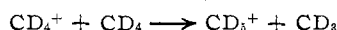


sion orifice size. In parallel experiments with  $\text{IrF}_6$ , the orifice was varied from 0.012 to 0.100 cm without effect. Neither of the cracking patterns from this study given in the tables has been corrected for decreasing ion transmission through the quadrupole mass filter with increasing mass<sup>8-10</sup> (*i.e.*, increasing resolution since the mass filter scans in the constant  $\Delta M$  mode), which under-represents the abundances of higher mass ions.

A comparison of the spectrum for  $\text{BiF}_5$  by Lawless<sup>1</sup> and that obtained in this study shows that there are some differences in the monomer cracking patterns, but the dimer cracking patterns are quite similar. We also observed two ions due to trimeric  $\text{BiF}_5$ , *viz.*,  $\text{Bi}_3\text{F}_{12}^+$  and  $\text{Bi}_3\text{F}_{14}^+$ . Making an approximate correction for the quadrupole transmission efficiency, the abundances of the associated ions relative to the monomeric ions for  $\text{BiF}_5$  vapor are monomer:dimer:trimer::1:0.45:0.005.

Two alternate mechanisms by which the higher mass ions might have arisen may be considered: ion-molecule reactions in the ion source and condensation occurring by isentropic expansion at the beam source. With a typical neutral number density of  $6 \times 10^9 \text{ cm}^{-3}$  and a path length in the ion source of 0.4 cm, and assuming an ionization cross section of  $15 \text{ \AA}^2$  and an ion-molecule reaction cross section of  $100 \text{ \AA}^2$ , the ratio of secondary (dimer) ions to primary (monomer) ions would be  $2 \times 10^{-5}$ . The ion-molecule reaction



known to have a large cross section, was not observed<sup>7</sup> in the present source configuration with a sensitivity of 1 part in  $10^5$ . Termolecular ion-molecule reactions to yield trimer from monomer have very low probability since molecules in the neutral beam have directed rather than random velocities. Upper limit calculations for sequential ion-molecule reactions to yield trimers from monomers predict a ratio of trimer ions to monomer ions of  $1 \times 10^{-9}$ . Similarly, the ratio of trimer to dimer ions resulting from ion-molecule reactions of dimer ions with monomer or dimer neutrals would be expected to be no greater than  $10^{-4}$ .

Free-jet expansion would produce increasing concentrations of associated species as the pressure behind the orifice is increased.<sup>11</sup> In the case of  $\text{BiF}_5$ , the temperature of the oven was varied from 341 to 448°K, corresponding to a pressure increase from 1.2 to 100 Torr. The monomer ion signal increased by a factor of 11 (scattering losses in the vapor cloud immediately after the source aperture are responsible for the non-linear behavior of beam intensity with source pressure),<sup>12</sup> while the dimer ion signal dropped to zero. If either free-jet expansion or ion-molecule reactions were responsible for the associated species observed in this study, one would certainly expect a substantial increase in dimer ion concentration with an 83-fold increase in oven pressure, or an 11-fold increase in number density in the ion source.

In the case of  $\text{SbF}_5$ , significant differences are found in the abundance of dimeric ions between the spectra obtained from our molecular beam source and those ob-

tained from conventional inlets. The spectra reported in Table II for this study include the trimeric species  $\text{Sb}_3\text{F}_{14}^+$ ; tetramer and pentamer ions were also found as well as trace amounts of  $\text{Sb}_2\text{F}_8^+$ ,  $\text{Sb}_2\text{F}_7^+$ ,  $\text{Sb}_2\text{F}_6^+$ , and  $\text{Sb}_2\text{F}_5^+$ . For  $\text{SbF}_5$ , the corrected relative abundances are monomer:dimer:trimer:tetramer:pentamer::1:0.5:0.09:10<sup>-4</sup>:ca. 10<sup>-6</sup>. The small concentration of tetramer ions is indicative that the tetrameric bridged ring structure known for crystalline<sup>13</sup>  $\text{SbF}_5$  does not persist into the vapor phase.

The comparisons in mass spectra for  $\text{SbF}_5$  and  $\text{BiF}_5$  demonstrate the advantage of using a molecular beam source for the mass spectrometric study of reactive species and the necessity of considering the degree of vapor saturation for the detection of associated species. Although  $(\text{SbF}_5)_2$  and  $(\text{BiF}_5)_2$  may indeed be doubly fluorine bridged species, this conclusion should not be drawn from available mass spectrometric data. It should furthermore be stressed that in mass spectrometric studies one observes only ionic species. These do not necessarily arise *in toto* from the corresponding neutral agglomerates; an alternate possibility is that they might come from higher associated clusters as fragment ions from electron impact. Hence, the degree of association may well be underestimated due to the fragmentation of neutral clusters.

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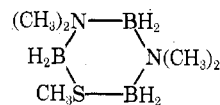
## A Dative-Bonded Sulfur-Boron-Nitrogen Heterocycle

BY ANTON B. BURG

Received March 13, 1972

The dative-bonded dimer  $[(\text{CH}_3)_2\text{NBH}_2]_2$  is known to exist in equilibrium with the monomer<sup>1</sup> or can be converted irreversibly to the cyclohexane-like dative-bonded trimer  $[(\text{CH}_3)_2\text{NBH}_2]_3$  by the action of a transient catalyst derived from pentaborane(9).<sup>2</sup> This trimer has three axial methyl groups in close mutual contact, as proved by the infrared spectrum<sup>2</sup> and the crystallographically determined molecular parameters.<sup>3</sup> Such steric interference is the obvious reason that the trimer is not formed spontaneously from the monomer or dimer.

It now is found that omission of one methyl group from the trimer structure—by allowing a  $\text{CH}_3\text{SBH}_2$  unit to take the place of one of the three  $(\text{CH}_3)_2\text{NBH}_2$  units—so relieves the steric effect that the six-atom ring is easily formed. The resulting new white crystalline cotrimer



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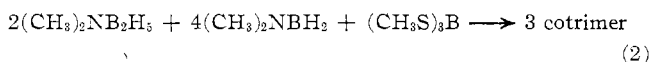
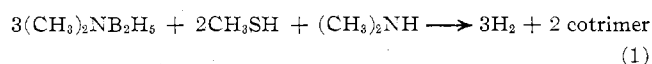
(1) A. B. Burg and C. L. Randolph, Jr., *J. Amer. Chem. Soc.*, **73**, 953 (1951), and preceding references.

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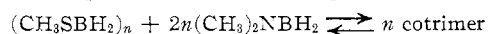
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is fairly stable and reaction resistant even at 100°, in contrast to the decidedly labile  $(\text{CH}_3\text{SBH}_2)_n$  oligomers.<sup>4</sup> For example, whereas  $(\text{CH}_3\text{SBH}_2)_n$  reacts rapidly with  $\text{N}(\text{CH}_3)_3$  to form  $\text{CH}_3\text{SBH}_2 \cdot \text{N}(\text{CH}_3)_3$ ,<sup>4</sup> the cotrimer reacts only slowly at 100° to form  $\text{CH}_3\text{SBH}_2 \cdot \text{N}(\text{CH}_3)_3$ ,  $(\text{CH}_3)_2\text{NBH}_2$ , and the disproportionation products of both. However, the cotrimer is far more labile than the trimer  $[(\text{CH}_3)_2\text{NBH}_2]_3$ ; for, unlike this stable compound, it reacts with diborane at 80–100° to form  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ . In sum, then, the cotrimer  $\text{CH}_3\text{SBH}_2 \cdot [(\text{CH}_3)_2\text{NBH}_2]_2$  offers more stable dative polymer bonding for its component units than occurs in  $(\text{CH}_3\text{SBH}_2)_n$  or  $[(\text{CH}_3)_2\text{NBH}_2]_2$ , but is more labile than the very well-bonded  $[(\text{CH}_3)_2\text{NBH}_2]_3$ .

**Synthesis of the Cotrimer.**—The two experiments for the synthesis of the cotrimer  $\text{CH}_3\text{SBH}_2 \cdot [(\text{CH}_3)_2\text{NBH}_2]_2$  were planned according to the expected processes



For process 1 the plan was to make 6.38 mmol of the cotrimer from reactants measured accurately according to the equation and heated together in a sealed tube for 25 hr at 100–110°. However, after removal of 19.43 mmol of  $\text{H}_2$  (calcd, 19.13), the readily volatile components were isolated (by the usual Stock high-vacuum methods) and measured (in mmol) as 1.31  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ , 6.577  $(\text{CH}_3)_2\text{NBH}_2$ , and 0.56  $[(\text{CH}_3)_2\text{N}]_2\text{BH}$ , meaning that the yield of the cotrimer could not represent more than 65% of the nitrogen and boron. In fact, the <sup>11</sup>B nmr spectrum of the slightly volatile main product (in benzene) could be interpreted as that of a mixture containing only the cotrimer and  $(\text{CH}_3\text{SBH}_2)_n$ . With all amino groups assigned to the cotrimer, the empirical formula of the by-product is calculated as  $(\text{CH}_3\text{SBH}_2)_4(\text{CH}_3\text{S})_2\text{BH}$ . Presumably the small sulfur-rich part was too diffuse for nmr observation. After removal of much of the cotrimer, the remaining viscous liquid was repeatedly heated with more  $(\text{CH}_3)_2\text{NBH}_2$ , bringing the final recovered yield of the cotrimer to 85%, based upon  $\text{CH}_3\text{SH}$ . The equilibrium



was indicated, apparently favoring the cotrimer.

Process 2 was done with 2.661 mmol of  $(\text{CH}_3\text{S})_3\text{B}$ , 6.742 mmol of  $(\text{CH}_3)_2\text{NBH}_2$ , and 6.25 mmol of  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ , heated in a sealed tube for 2.5 days at 105–125°. The readily volatile components now were determined (in mmol) as 0.20  $\text{H}_2$ , 1.470  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ , 0.13  $[(\text{CH}_3)_2\text{N}]_2\text{BH}$ , and 2.601  $(\text{CH}_3)_2\text{NBH}_2$ . Thus only 67% of the original  $(\text{CH}_3)_2\text{N}$  groups could be present as cotrimer. After losses due to exploration of ways to isolate it, the recovered yield of cotrimer was 76% of the predicted 67%.

**Isolation of the Cotrimer.**—Much of the cotrimer from either process could be distilled from the crude mixture at 40–50°, but in the process there was conversion of the by-product into a slightly volatile liquid, distilling with the cotrimer and, if present in quantity, tending to crystallize with it from ether or isohexanes at –78°. More effective, then, was methanolysis of

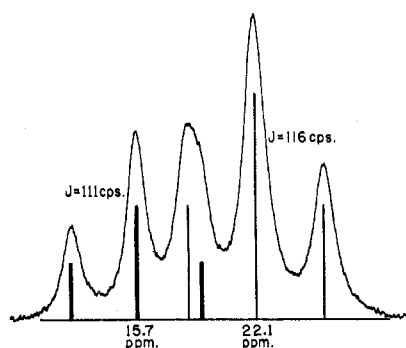


Figure 1.—The <sup>11</sup>B nmr spectrum (32.1 Mc) of a 30% solution of the cotrimer in benzene at 35°. The chemical-shift reference is methyl borate. The pure-liquid cotrimer at 35° showed the upfield triplet badly distorted and poorly resolved and the downfield triplet only as poorly detectable shoulders.

the by-product during a series of 12-hr heatings at 40–50°. Conservation of the cotrimer was demonstrated by the near absence of  $(\text{CH}_3)_2\text{NH}$  (less than 1%) in the resulting  $\text{CH}_3\text{SH}$ . The volatile methanolysis products (hydrogen, mercaptan, and methyl borate) were measured to confirm the empirical formula of the process 2 by-product as  $(\text{CH}_3\text{S})_9\text{B}_8\text{H}_{15}$ .

The methanolysis left almost pure cotrimer, but since the destruction of the last trace of the by-product was tedious, the final purification was by crystallization from ether at –78°.

**Characterization and Analysis.**—The pure cotrimer melted in the range 33.3–33.5° under 20 mm pressure of nitrogen. Its volatility is well expressed by the equation  $\log P = 9.468 - 3014/T$  for the solid (e.g., 0.29 mm at 28°) and for the liquid by  $\log P = 6.185 + 1.75 \log T - 0.004T - 2974/T$  (e.g., 0.88 mm at 45°, 5.0 mm at 75.1°, or 27.1 mm at 111.2°). The latter equation would give the normal boiling point as 218.6° and the Trouton constant as 22.0 eu. The vapor-phase molecular weight at 119° and 26 mm was 173.5; calcd, 173.7.

The analysis of a 27.0-mg sample of the cotrimer by HCl hydrolysis in a sealed tube above 100° was difficult to complete, despite repeated heatings. However, at each point the ratio of  $\text{H}_2$  to  $\text{CH}_3\text{SH}$  was very close to 6.00, meaning that each attacked molecule of the cotrimer was fully destroyed. At 91% completion, the remainder of the initially measured HCl was titrated, showing 1.98  $(\text{CH}_3)_2\text{N}$  per  $\text{CH}_3\text{SH}$ ; also there was 5.95  $\text{H}_2$  per  $\text{CH}_3\text{SH}$ . Boron ran inaccurately high, on account of slight dissolving from the Pyrex glass.

**Nmr Spectra.**—The suggested structural formula for the cotrimer is strongly supported by its nmr spectra. Good resolution is possible only for solutions (benzene). The <sup>11</sup>B spectrum (Figure 1) shows a downfield triplet for the  $\text{N}(\text{BH}_2)\text{N}$  situation and an upfield triplet twice as intense for the two  $\text{BH}_2$  groups between N and S. The crude original-synthesis product showed also a triplet at  $\delta$  31.9 ppm ( $J = 123$  cps), almost exactly matching the <sup>11</sup>B spectrum for  $(\text{C}_2\text{H}_5\text{SBH}_2)_3$  (by Muetterties, *et al.*<sup>4</sup>); assignment to  $(\text{CH}_3\text{SBH}_2)_n$  is obvious.

The proton nmr spectrum of the cotrimer (taken with benzene as an internal standard, at  $\tau$  2.76) shows a sharp singlet for  $\text{CH}_3\text{S}$  at  $\tau$  8.18. The  $(\text{CH}_3)_2\text{N}$  peak (4 times as intense) at  $\tau$  7.68 is decidedly broader, with some evidence of unresolved complexity attributable

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to either H-C-N coupling or a small difference between axial and equatorial methyl groups, or both. The BH protons gave no observable signals.

**Infrared Spectrum.**—The vapor-phase infrared spectrum of the cotrimer was recorded by means of the Beckman IR7 instrument, with the cell in an asbestos-board box heated to known temperatures by a heater-blower, all within the cell chamber. The frequencies of the peaks ( $\text{cm}^{-1}$ ) are listed with relative intensities in parentheses, as follows: 3027 (3.7), 3023 sh (2.8), 2991 (6.0), 2947 (7.6), 2897 (1.6), 2854 (1.0), 2555 (0.7), 2545 (1.0), 2453 (1.6), 2393 (1.4), 2337 (4.6), 2322 (4.6), 2278 (1.4), 1471 (3.5), 1452 (3.1), 1435 (4.9), 1406 (0.8), 1326 (0.2), 1224 (11), 1173 (13), 1126 (12), 1108 (11), 1078 (6), 1038 (3.0), 963 (3.6), 944 (4.4), 914 (3.0), 883 (1.2), 862 (1.8), 824 (2.4), 804 (1.8), 732 (0.6), 640 (0.7). Most of these peaks can be assigned in the same manner as for  $[(\text{CH}_3)_2\text{NBH}_2]_3$ ,<sup>2</sup> with the difference that the multiplicity of modes, such as  $\text{CH}_2$  stretching, deformation, rocking, and wagging, or similar effects with  $\text{BH}_2$ , would be due to the different situations of these groups rather than to steric splitting of axial groups or atoms. Neither these results nor the proton nmr spectrum would suggest any steric effects in the cotrimer.

**The Trimethylamine Reaction.**—A mixture of 0.1075 mmol each of  $(\text{CH}_3)_3\text{N}$  and the cotrimer, heated for 15 min at  $100^\circ$ , showed no reaction, suggesting that a tertiary amine could be used to remove the  $\text{CH}_3\text{SBH}_2$  by-product. However, after 29 hr in a sealed tube at  $100^\circ$ , 59% of the  $(\text{CH}_3)_2\text{NBH}_2$  units had been liberated as the monomer and dimer, while 57% of the  $\text{CH}_3\text{SBH}_2$  units appeared as the  $(\text{CH}_3)_3\text{N}$  complex.<sup>4</sup> A 34% disproportionation of  $(\text{CH}_3)_2\text{NBH}_2$  groups was represented by a 0.036-mmol yield of  $[(\text{CH}_3)_2\text{N}]_2\text{BH}$ , while somewhat more  $(\text{CH}_3)_3\text{NBH}_3$  could be ascribed to this disproportionation and that of the complex  $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_3$ .

**The Diborane Reaction.**—Diborane also was not readily reactive toward the cotrimer. Nearly equimolar portions of diborane and the cotrimer (0.24 mmol each) were placed in a vertical stopcocked reaction tube attached to the vacuum line. The lower half of the tube was repeatedly heated for hours at  $80$ – $100^\circ$ , eventually yielding 0.32 mmol of  $(\text{CH}_3)_2\text{NB}_2\text{H}_5$ , at the cost of 0.205 mmol of diborane.

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## Effects of Chelate Ring Substituents on the Polarographic Redox Potentials of Tris( $\beta$ -diketonato)ruthenium(II,III) Complexes

BY GEORGE S. PATTERSON<sup>1</sup> AND R. H. HOLM\*

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The effect of substituent variation on the polaro-

graphic half-wave potentials for oxidation and reduction of certain general types of organic molecules has been extensively investigated in recent years.<sup>2</sup> In a number of cases these potentials have been linearly correlated with Hammett or Taft substituent parameters. Related studies of coordination and organometallic complexes are considerably less numerous. However, in some instances correlation between various properties of these complexes, such as ligand substituent parameters or basicities and half-wave or half-cell potentials have been found.<sup>3–6</sup> The present study was initiated as a consequence of the somewhat unexpected finding that  $\text{Ru}(\text{tfac})_3$ <sup>7</sup> was readily reduced chemically to  $\text{Ru}(\text{tfac})_3^-$  and that the corresponding electrochemical process was characterized by a half-wave potential very near 0 V *vs.* sce.<sup>8</sup> The anion could be isolated in the form of a moderately air-sensitive salt. In contrast, the half-wave potential for reduction of  $\text{Ru}(\text{acac})_3$  was *ca.* 0.8 V more cathodic and well-characterized salts of  $\text{Ru}(\text{acac})_3^-$  could not be obtained. These results indicated a decided effect of substituents on redox potentials of ruthenium(II,III) tris( $\beta$ -diketonates), a matter which is explored more fully in this report. Coincident with our recent<sup>8</sup> and present work has been the demonstration that  $\text{M}(\text{SacSac})_3$  complexes [ $\text{M} = \text{Fe}(\text{III}), \text{Ru}(\text{III}), \text{Os}(\text{III})$ ] also undergo electrochemical reductions to the corresponding monoanions.<sup>9</sup>

### Experimental Section

**Preparation of Compounds.**— $\text{Ru}(\text{dbm})_3$ ,<sup>10</sup>  $\text{Ru}(\text{SacSac})_3$ ,<sup>9</sup>  $\text{Ru}(\text{bipy})_3(\text{ClO}_4)_2$ ,<sup>11</sup>  $\text{Os}(\text{acac})_3$ ,<sup>12</sup>  $\text{Os}(\text{SacSac})_3$ ,<sup>9</sup> and  $\text{Os}(\text{bipy})_3(\text{ClO}_4)_2$ <sup>13</sup> were prepared by published methods. *cis*- and *trans*- $\text{Ru}(\text{tfac})_3$  and  $-\text{Ru}(\text{bzac})_3$  were available from previous work,<sup>8</sup> and the general procedure used to prepare these complexes was applied to the synthesis of  $\text{Ru}(\text{tfbzac})_3$  and  $\text{Ru}(\text{dpm})_3$ . Benzoyltrifluoroacetone<sup>14</sup> and dipivaloylmethane<sup>15</sup> were obtained by literature methods.  $\text{Ru}(\text{tfbzac})_3$  appeared as red crystals, mp  $171$ – $173^\circ$ . *Anal.* Calcd for  $\text{C}_{30}\text{H}_{18}\text{F}_9\text{O}_6\text{Ru}$ : C, 48.27; H, 2.43; F, 22.90. Found: C, 47.55; H, 2.46; F, 22.30.  $\text{Ru}(\text{dpm})_3$  appeared as solid crystals (sublimed), mp  $220$ – $223^\circ$ . *Anal.* Calcd for  $\text{C}_{33}\text{H}_{57}\text{O}_6\text{Ru}$ : C, 60.90; H, 8.83. Found: C, 61.10; H, 8.79. **(Ph<sub>3</sub>As)[Ru(hfac)<sub>3</sub>].**— $\text{K}_2[\text{RuCl}_3(\text{H}_2\text{O})]$  (0.52 g, 1.38 mmol) and 0.48 g (4.1 mmol) of potassium bicarbonate were refluxed in 5.0 ml of hexafluoroacetylacetone for 3 days. Chloroform (15 ml) was added, the mixture was refluxed for another day, and the

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(7) The following ligand abbreviations are employed: acac, acetylacetonate; dpm, dipivaloylmethanide; bzac, benzoylacetonate; tfac, trifluoroacetylacetonate; hfac, hexafluoroacetylacetonate; tfbzac, benzoyltrifluoroacetonate; dbm, dibenzoylmethanide; SacSac, dithioacetylacetonate.

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