est ligands bonded to the Co^{2+} cation. This was clarified to some extent based on a magnetic susceptibility study of complex III. Magnetic susceptibility of III was measured at 297, 78, and 4.2°K. The observed gram-atom susceptibility χ_M independent of magnetic field from 3000 to 8000 Oe was found to obey the Curie–Weiss relationship, $\chi_{Co} = C/(T - \theta)$, between 78 and 300°K. A Curie constant (C) of 2.86 ± 0.03 and a Weiss constant (θ) of -12 ± 2°K was obtained at 8000 Oe. The average magnetic moment per cobalt atom in complex III, $\bar{\mu}$, calculated from the equation $\bar{\mu} = \sqrt{3KC/N\beta^2}$ is equal to 4.78 ± 0.03 BM. The magnetic moment for the $CoCl_4^{2-}$ moiety based on the reported measurement[4] of Cs_2CoCl_4 is $\mu = 4.46$ BM. The moment for the moiety $[II \cdot Co^{2+}]$ can be calculated *via* the relationship $\bar{\mu}^2 = (\mu_1^2 + \mu_2^2)/2$ and was found to be 5.04 ± 0.04 BM. This value is very close to the value of 5.2 BM which is the moment exhibited by Co^{2+} in a high-spin octahedral complex ($^4T_{1g}$) with a spin–orbit coupling constant of $\lambda = 170$ cm^{-1}.[5]

The fact that the above-calculated value of 5.04 BM is slightly lower than the expected value is not unreasonable for a complex such as $[II \cdot Co^{2+}]$ which is expected to depart at least to some extent from pure octahedral symmetry. Lowering of the moment toward the spin-only moment value is not uncommon for complexes in which the ligand field departs from perfect symmetry.

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Tributyltin Hydride Reduction of Chloroboranes

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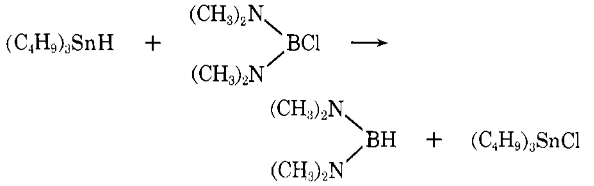
The majority of reductions by organotin hydrides proceed by free-radical mechanisms.[1] However, polar reactions have recently been established for the addition of organotin hydrides to phenyl and hexyl isocyanates,[2] for the cleavage of tin–nitrogen bonds by triphenyltin hydrides,[3] and for addition of tin hydrides to substituted acetylenes.[4] We wish to report convenient laboratory syntheses for bis(dimethylamino)borane (**1**) and 1,3,2-benzodioxaborole (**2**) by reduction of the corresponding B-chloro compound with tributyltin hydride and an investigation of the reaction mechanism.

Tributyltin hydride was found to react smoothly (neat) with bis(dimethylamino)chloroborane at 90° to give bis(dimethylamino)borane (**1**) in 73% yield. 2-Chloro-1,3,2-benzodioxaborole gave the corresponding hydride (**2**) in 42% yield. Infrared spectra suggested that tributyltin chloride also was produced in these reactions, in addition to other unidentified byproducts.



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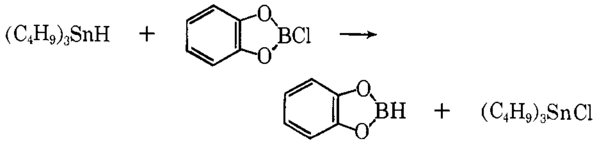
(1)



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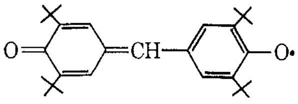
(2)

Reduction of alkyl halides by organotin hydrides has been demonstrated[1] to follow a free-radical path. More pertinent to reaction 1 is the fact that acid chlorides also react with organotin hydrides by a radical mechanism.[1] The electronic similarity between a chloroborane and an acid chloride might suggest a radical-chain mechanism for reaction 1 also.

If such a process did occur, the rate of the reaction should be enhanced by free-radical initiators and depressed by inhibitors. A polar mechanism should show no rate effect from these additives and should proceed faster in a polar solvent than in a nonpolar solvent. The reaction was carried out neat, with added α,α'-azobis(isobutyronitrile) (AIBN), with added galvinoxyl (**3**), and in hexane and chlorobenzene solvents. Relative rates were obtained by measuring the increasing ratio of the B–H/Sn–H infrared absorptions periodically and plotting the ratio against time.



3

The results, listed in Table I, ruled out a radical-chain process and are consistent with a polar mechanism. The reaction was not catalyzed by added AIBN and was not inhibited by galvinoxyl. The effect of solvent was as expected for a bimolecular heterolytic reaction. In the nonpolar hexane (ϵ 1.87), the rate was greatly reduced by a dilution effect. In chlorobenzene (ϵ 5.9), dilution of reacting species again tended to reduce the rate but significant solvation stabilization of the polar transition state operated to increase the rate, with a net result of a rate close to that of the neat reactants. The moderate rate increase with added **3** could be due to its polarity.

The reaction appears to represent a fourth example of an organotin hydride reduction by a heterolytic mechanism, but the exact nature of the transition state is only speculative at this point. A four-centered

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TABLE I

RELATIVE RATES FOR TRIBUTYLTIN HYDRIDE–BIS(DIMETHYLAMINO)CHLOROBORANE REACTION

Conditions	Relative rate[a]	Std dev
Neat reactants	1.00	0.2
Added AIBN[b]	0.96	0.3
Added galvinoxyl[b]	1.56	0.2
Chlorobenzene solvent[c]	0.67	0.1
Hexane solvent[c]	0.04	0.01

[a] Slope of least-squares straight line for plot of B–H/Sn–H ratio *vs.* time, normalized to 1.00 for the neat reactants. [b] Additive at 10 mole % level. [c] Solvent: solute mole ratio = 20:1.

intermediate or transition state has been demonstrated for the reduction of trichloroborane with an optically active silicon hydride.[5] A similar configuration, with some charge separation to explain solvent effects, seems likely here. However, a direct displacement mechanism cannot be ruled out by the data at hand.

Experimental Section

Bis(dimethylamino)borane (1).—A mixture of freshly distilled bis(dimethylamino)chloroborane (6.15 g, 0.0457 mol) and 13.30 g (0.0457 mol) of tributyltin hydride was heated 0.5 hr at 90°. The pot temperature then was raised and 0.7 g of distillate was removed, bp 69–71°. After standing over the weekend, distillation was continued to give a second fraction, 3.35 g, bp 68° (52 mm). The product, obtained in 73% yield, was identified as bis(dimethylamino)borane by comparison of boiling point (lit.[6] bp 70° at 52 mm, extrapolated) and by an identical infrared spectrum with that of an authentic sample. The residue showed infrared peaks characteristic of tributyltin chloride plus additional absorptions at 1525, 1510, 1350 (w), 1220, 1190 (w), 1110, 905 (w), and 807 (w) cm^{-1}.

Relative Rates.—Bis(dimethylamino)chloroborane (2.0 g, 0.0149 mol) was dissolved in 3.8 ml (4.0 g, 0.0149 mol) of tributyltin hydride in a three-necked flask with a rubber septum and a reflux condenser topped with a nitrogen by-pass. At time zero, the flask was immersed in a bath at 60.5 ± 0.5°. At noted intervals, samples were removed by a hypodermic needle through the rubber septum and their infrared spectra were recorded. Extent of reaction was followed by the increasing ratio of B–H absorption at 2480 cm^{-1} to Sn–H absorption at 1820 cm^{-1}. Separate runs were made with the above quantities of reactants in the presence of the following additives: (A) α,α'-azobis(isobutyronitrile), 0.049 g, 0.0015 mol; (B) galvinoxyl, 0.124 g, 0.0015 mol; (C) hexane, 25.6 g, 0.298 mol; (D) chlorobenzene, 33.5 g, 0.298 mol. Relative rates were obtained by comparing the slopes of plots of B–H/Sn–H ratios *vs.* time.

1,3,2-Benzodioxaborolane (2).—A solution of 2-chloro-1,3,2-benzodioxaborole (4.9 g, 0.0318 mol) and tributyltin hydride (8.06 g, 0.0318 mol) was heated at 90° 2 hr and allowed to stand at room temperature overnight. Distillation of the reaction mixture provided 1.59 g (42% yield) of 2 at 88° (156 mm); infrared $\nu_{\max}^{\text{B-H}}$ 2680 cm^{-1}.

Anal. Calcd for $C_6H_5BO_2$: C, 60.07; H, 4.21; B, 9.03. Found: C, 59.89; H, 4.18; B, 8.99.

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The Absolute Configurations of Bis-Bidentate Chelate Compounds. The Case of the *cis*-Bis(pyridine)bis(*o*-phenanthroline)-ruthenium(II) ion

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The present methods of determining the absolute configurations of dissymmetric metal complexes by means of their circular dichroism spectra are of two kinds, namely, the empirical and nonempirical. In the former, the absolute configurations of a series of related complexes are determined by a knowledge of the absolute configuration of one complex[1,2] or that of the ligand[3,4] together with the sign of the circular dichroism exhibited by equivalent[2,4] spectroscopic transitions. The nonempirical method, however, requires only a knowledge of the polarization directions of particular electronic transitions of the molecule and, in principle, gives the absolute configuration of the molecule without reference to or a knowledge of the independently determined absolute configuration of a related molecule. This latter method was first proposed classically by Kuhn,[5] set in a quantum mechanical framework by Moffitt,[6] and applied to and developed for inorganic complexes by Mason.[7–9] The predictions of the nonempirical method have been recently confirmed by the X-ray diffraction determination[10] of the absolute configuration of the (−)-tris(*o*-phenanthroline)iron(II) ion, (−)-$[Fe(phen)_3]^{2+}$. In this note we wish to outline the method for determining the absolute configurations of *cis*-bis-bidentate complexes containing conjugated bidentate ligands. For this purpose we have chosen the recently resolved[11] *cis*-bis(pyridine)bis(*o*-phenanthroline)ruthenium(II) ion, *cis*-$[Ru(phen)_2(py)_2]^{2+}$, which may serve as a representative example of this class of complexes.

The $\pi \rightarrow \pi^*$ transitions of the *o*-phenanthroline molecule are either short-axis (z) or long-axis (x) polarized (see Figure 1(a)). These transitions, however, have not been rigorously identified, although molecular orbital calculations, together with the polarized crystal

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