method used for the chromium analog; yield 32%, m.p. 183.4–184° dec.

Anal. Calcd. for $C_{16}H_{19}O_{11}N_2Co$: C, 40.52; H, 4.04; N, 5.91. Found: C, 41.11; H, 4.08; N, 5.63.

Bromination of the Formyl Cobalt Chelate (XVIa).—To a solution of the monoformyl cobalt chelate (1.0 g., 0.0026 mole) in 20 ml. of chloroform was added N-bromosuccinimide (1.01 g., 0.0057 mole). The green solution was stirred at room temperature for 90 min., after which it was extracted with 25 ml. of aqueous 5% $NaHSO_3$ solution and then with 25 ml. of water. The organic layer was separated and dried, and the solvent was removed. The green residue was purified by chromatography on Florisil using 1:1 benzene–methylene chloride as an eluent. The second band was collected and recrystallized from benzene–ethanol. The bis-(3-bromo-2,4-pentanediono)-(3-formyl-2,4-pentanediono)-cobalt(III) was isolated as green crystals, m.p. 162–165° dec., yield 0.234 g. The infrared spectrum of this chelate exhibits the same bands as the tribromo and the monoformyl cobalt chelates except that there is no band at 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{19}O_7BrCo$: C, 35.45; H, 3.53; Br, 29.48. Found: C, 35.34; H, 3.47; Br, 30.36.

Attempted Catalytic Hydrogenation of Tris-(3-nitro-2,4-pentanediono)-chromium(III) (IV).—A solution of 0.20 g. of the nitro chelate (IV) in 25 ml. of glacial acetic acid was treated with 60 p.s.i. of hydrogen over 0.025 g. of PtO_2 for 2 hr. at room temperature. The solution was filtered and decomposed with 10 ml. of ice water. The red-brown precipitate was collected and found to be the pure nitro chelate (IV). Attempted reduction of the rhodium nitro chelate (VI) gave the same results.

Attempted Catalytic Hydrogenation of Tris-(3-nitro-2,4-pentanediono)-cobalt(III) (V).—When the nitro cobalt chelate was treated in the above manner, the acetic acid solution became pink and no product could be isolated from the reaction mixture.

Attempted Chemical Reductions of Tris-(3-nitro-2,4-pentanediono)-rhodium(III) (VI).—(A) Gaseous hydrogen chloride was bubbled into a suspension of 5.0 g. of stannous chloride dihydrate in 100 ml. of glacial acetic acid until the mixture became a homogeneous solution. The solution was chilled in an ice bath to the point where it was semi-solid and 0.40 g. of the nitro rhodium chelate (VI) was added while the solution was stirred vigorously. The ice bath was removed and the mixture was stirred for 45 min. The solution was decomposed with 500 g. of ice-water. The yellow precipitate was collected and dried; yield 0.21 g. An infrared spectrum of this product showed that it was the nitro rhodium chelate (VI).

The acidic filtrate was neutralized with 6 *N* sodium hydroxide and then extracted three times with methylene chloride. The extracts were colorless and left no residue upon evaporation of the solvent.

(B) A mixture of 0.10 g. of the rhodium nitro chelate (VI), 1.0 g. of zinc dust, and 100 ml. of glacial acetic acid was heated quickly to the boiling point and then allowed to cool to room temperature. The total reaction time was 30 min. The usual workup afforded a small amount of the nitro chelate (VI). The majority of the starting material seemed to have been destroyed during the reaction.

Notes

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Borazine Derivatives. II. A Carbon-Bridged Bisborazine Compound[1]

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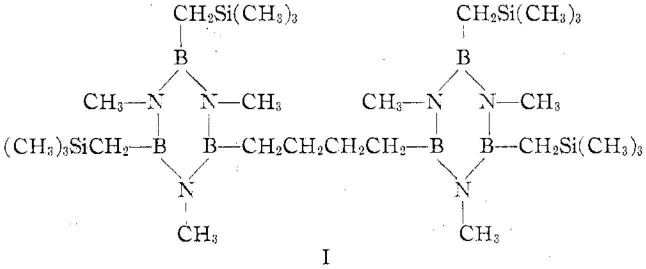
In a previous paper[1] we described the preparation of B-tris-(trimethylsilylmethyl)-N-trimethylborazine and related compounds by the Grignard procedure. These compounds exhibited high thermal stability and were stable toward basic hydrolysis and oxidation. For some possible applications it was desirable to have similar compounds, but of higher molecular weight. One approach to this goal examined by us involved the linking of borazine rings through difunctional organic groups. We report here the synthesis of B-chloro-B-bis-(trimethylsilylmethyl)-N-trimethylborazine and its reaction with the di-Grignard reagent of 1,4-dichlorobutane to give the carbon-bridged borazine I. This compound was not



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[1] Part I. D. Seyferth and H. P. Kögler, *J. Inorg. Nucl. Chem.*, **15**, 99 (1960).

stable toward hydrolysis, nor was B-*n*-butyl-B-bis-(trimethylsilylmethyl)-N-trimethylborazine. Apparently the hydrolytic stability of B-tris-(trimethylsilylmethyl)-N-trimethylborazine is a result of the steric hindrance due to the three bulky, branched neopentyl-type substituents on boron. A decrease in the steric shielding of just one of the three boron atoms of the borazine ring apparently provides a site for solvolytic attack, and the borazine is hydrolyzed.

The recent report on the thermal stability of selected borazines[2] made it of interest to study more thoroughly the thermal stability of silyl-substituted borazines. The bridged borazine I and B-tris-(trimethylsilylmethyl)-N-trimethylborazine were heated for 3-hr. periods in sealed, evacuated ampoules, with the test temperature being increased from 300 to 500° in 50° increments. The bridged bisborazine appeared to be completely decomposed at the lowest temperature to a yellowish oil which no longer could be crystallized. On the other hand, B-tris-(trimethylsilylmethyl)-N-trimethylborazine showed appreciable stability (>70% recovery of pure material by recrystallization after the heating period at temperatures up to 400°). This compound was, however, converted to a non-crystallizable, brown oil by heating at 500° for 3 hr. It may be noted that hexamethylborazine was recovered unchanged after *ca.* 3 hr. at 500°.[2]

Experimental[3]

Preparation of B-Chloro-B-bis-(trimethylsilylmethyl)-N-trimethylborazine.—The Grignard reagent was prepared from 28.8 g. (1.2 g.-atoms) of magnesium turnings and 147.2 g. (1.2 moles) of chloromethyltrimethylsilane in 1 l. of ether. This solution was added slowly during 2.5 hr. with rapid stirring to a suspension of 113 g. (0.5 mole) of B-trichloro-N-trimethylborazine in 500 ml. of ether. The mixture was refluxed for 4 hr., allowed to stand overnight, and filtered. The ether was distilled from the filtrate. The residue was fractionally distilled at 1 mm., and the fraction distilling between 130 and 160° was collected. Redistillation of the latter gave: (1) 77.4 g., b.p. 115–119° at 0.5 mm.; (2) *ca.* 4 ml. at 120–128° at 0.45 mm.; and (3) 10.0 g., b.p. 128–129° at 0.45 mm. Fraction 3 crystallized on standing. Recrystallization from methanol gave B-tris-(trimethylsilylmethyl)-N-trimethylborazine; white needles, m.p. 59–60°.

Anal. Calcd. for $C_{15}H_{42}N_3B_3Si_3$: C, 47.25; H, 11.1; N, 11.02. Found: C, 47.36; H, 11.13; N, 11.25.

Fraction 1 appeared to be reasonably pure B-chloro-B-bis-(trimethylsilylmethyl)-N-trimethylborazine.

Anal. Calcd. for $C_{11}H_{31}ClN_3B_3Si_2$: C, 40.09; H, 9.48; N, 12.75; B, 9.43. Found: C, 39.93; H, 9.06.

Redistillation of fraction 1 resulted in: (1a) less than 1 ml., b.p. 85–95° at 0.03 mm.; (1b) 8 ml., b.p. 95–105° at 0.03 mm.; and (1c) 50 g., b.p. 105–108° at 0.03 mm. Fraction 1c was the pure liquid monochloro compound.

Anal. Found: C, 40.36; H, 9.73; N, 13.01; B, 9.43. This product was readily hydrolyzed by atmospheric moisture.

Further reactions carried out to accumulate more product showed that higher dilution was beneficial, giving much improved yields. Thus a reaction of 0.79 mole of trimethylsilylmethylmagnesium chloride with 0.33 mole of B-trichloro-N-trimethylborazine using 2 l. of ether gave a 49% yield of the desired monochloro derivative.

Reaction of B-Chloro-B-bis-(trimethylsilylmethyl)-N-trimethylborazine with the Grignard Reagent from 1,4-Dichlorobutane.—To a tetrahydrofuran solution containing about 7.7 mmoles of $ClMg(CH_2)_4MgCl$ was added 4.9 g. (15 mmoles) of B-chloro-B-bis-(trimethylsilylmethyl)-N-trimethylborazine in 50 ml. of tetrahydrofuran. The mixture was kept at room temperature for 2 days, refluxed for 6 hr., and subsequently evaporated under reduced pressure. The solid residue was extracted with 150 ml. of warm diethyl ether. Evaporation of the extracts left a non-distillable oil. The latter was triturated with methanol and kept in the refrigerator until it had solidified. The solid was recrystallized from ether–methanol at −25° to give white needles, m.p. 93–94°, 2.8 g. (58%).

Anal. Calcd. for $C_{26}H_{70}N_6B_6Si_4$: C, 48.47; H, 10.95; N, 13.05. Found: C, 48.27; H, 10.78; N, 12.76.

The molecular weight, determined cryoscopically in benzene, was 675 (calcd. 644). The infrared spectrum of the compound showed absorption due to the trimethylsilyl groups at 1250 cm.$^{-1}$ and at 840 and 755 cm.$^{-1}$, as well as bands due to the borazine ring system at 1390 cm.$^{-1}$ (strong) and 1410 cm.$^{-1}$ (broad).

Thermal Stability Experiments.—Small samples of the compounds were sealed in evacuated Pyrex ampoules and heated for 3 hr. at the temperatures listed. The observations made with B-tris-(trimethylsilylmethyl)-N-trimethylborazine are given in Table I.

TABLE I

THERMAL STABILITY OF $[(CH_3)_3SiCH_2BNCH_3]_3$

Temp.	Appearance and m.p. after heating	Recovery of pure material, m.p. 59–60° (%)
300	White crystals, 54–56°	>90
350	White crystals, 47–56°	>90
400	White crystals, 43–52°	>70
450	White solid suspended in yellowish oil	*ca.* 40
500	Brown oil	0

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(2) H. C. Newson, W. D. English, A. L. McCloskey, and W. G. Woods, *J. Am. Chem. Soc.*, **83**, 4134 (1961).

(3) All reactions were carried out under an atmosphere of prepurified nitrogen. Analyses by Alfred Bernhardt, Mülheim, Ruhr, Germany.