by photolytic displacement of carbonyl groups to give mono- and disubstituted derivatives[1] or by displacement of diglyme in (diglyme)$Mo(CO)_3$ to give trisubstituted derivatives.[2]

We find that tris-nitrile derivatives are prepared very conveniently by direct reaction. For instance on refluxing $Mo(CO)_6$ in excess acetonitrile under nitrogen, a near quantitive yield of $(CH_3CN)_3Mo(CO)_3$ is obtained with evolution of 3 moles of gas in less than 4 hr. It is identical with the compound prepared by Werner and Coffield *via* a different route.

Similarly $W(CO)_6$ after 40-hr. reflux gives $(CH_3CN)_3W(CO)_3$. It can be crystallized from acetone–hexane to give a yellow solid of somewhat greater air stability. *Anal.* Calcd. for $C_9H_9N_3O_3W$: C, 27.64; H, 2.32; N, 10.75. Found: C, 27.6; H, 2.22; N, 10.55. Three moles of gas are evolved on treatment with iodine in methanol.

The corresponding chromium compound $(CH_3CN)_3Cr(CO)_3$ is a yellow pyrophoric solid. *Anal.* Calcd. for $C_9H_9N_3O_3Cr$: C, 41.71; H, 3.50; N, 16.21. Found: C, 43.00; H, 3.95; N, 13.90. Exact analysis was made difficult because of its extreme sensitivity.

These compounds serve as excellent intermediates in the formation of new compounds not available by other routes.

[1] (a) W. Strohmeier and G. Schönauer, *Chem. Ber.*, **94**, 1346 (1961); (b) W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 622 (1960).

[2] R. P. M. Werner and T. H. Coffield, VIth Intern. Conf. on Coördination Chemistry, Detroit, 1961, Preprint p. 534, Macmillan Co., New York, N. Y.

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Preparation and Properties of Boron Sesquiselenide[1]

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Received September 2, 1961

The reaction of boron with the chalcogenides was investigated by a number of persons prior to 1900,[2-7] but the majority of work was carried out with boron and sulfur and their reaction product, boron sesquisulfide. Although Sabatier[5] and Moissan[6,7] have reported the preparation of a compound believed to be boron sesquiselenide, no characterization was performed to substantiate or refute their beliefs.

As a result of renewed interest in boron chemistry, the reaction of boron and sulfur has been re-examined,[8,9] but not that of boron and selenium. The purpose of this study was to develop a technique for preparing boron sesquiselenide and to determine some of its physical properties.

Experimental

Starting materials consisted of 99% pure electrolytic boron and 99.9% pure selenium powder obtained from the Fairmount Chemical Company, Inc., Newark, New Jersey.

The preparation apparatus was a 25-mm. Vycor heating tube in which a tantalum boat filled with boron was located. The inlet to the tube was connected by a standard taper joint to a round bottom 250-ml. flask adapted with a ring-sealed side arm which extended into the bottom of the flask. To the outlet end of the heating tube a fritted disk and a bubbler filled with carbon disulfide were attached in series with standard taper joints. Dry hydrogen, bubbled through the selenium which was heated to about 250° in the round bottom flask, was swept over the boron which had been heated to between 850 and 950°. The hydrogen flow was maintained between 20 and 30 cc. per min. and the reaction product, minute yellow particles which appeared as smoke, was swept from the reaction zone to the fritted disk collector. The collector was isolated from the system and transferred into an argon-filled drybox equipped with a vacuum entry lock and a recirculating system. Because of the moisture sensitivity of the product, subsequent handling of it was performed in this dry atmosphere.

Analysis and Measurement of Physical Properties.—The product was placed in an erlenmeyer flask equipped with a cork stopper and a tared drying tube containing glass wool saturated with nitric acid. Approximately 20 ml. of a dilute sodium hydroxide solution was added to 0.1 g. of product by injecting the hydroxide solution through the stopper with a hypodermic needle. Two portions of hydrochloric acid then were added to this solution, the second portion of which was saturated with sulfur dioxide to precipitate the red form of selenium.[10] This procedure minimized the escape of hydrogen selenide. The selenium was filtered, washed with alcohol and ether,

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[1] Abstracted in part from the M.S. thesis of W. E. Hutchinson presented to the Graduate College of Michigan State University. Presented at the September, 1960, American Chemical Society National Meeting, New York, N. Y.

[2] (a) J. J. Berzelius, *Pogg. Ann.*, **2**, 113 (1824); (b) F. Wohler and H. St. C. Deville, *Ann. chim. phys.*, **52**, 63 (1858).

[3] P. Sabatier, *Compt. rend.*, **112**, 862 (1891).

[4] H. Moissan, *ibid.*, **115**, 203 (1892).

[5] P. Sabatier, *ibid.*, **112**, 1000 (1891).

[6] H. Moissan, *ibid.*, **114**, 617 (1892).

[7] H. Moissan, *Ann. chim. phys.*, (7) **6**, 296 (1895).

[8] P. B. Zeeman, *Phys. Rev.*, **80**, 902 (1950).

[9] F. T. Greene and J. L. Margrave, *J. Am. Chem. Soc.*, **81**, 5555 (1959).

[10] N. H. Furman, Ed., "Scott's Standard Methods of Chemica Analysis," 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, Vol. 1, p. 784.

dried at temperatures which started at 30° and terminated at 120°, and then weighed. About 3% of the selenide ion escaped as hydrogen selenide gas and was oxidized to selenium in the nitric acid-saturated glass wool of the drying tube, whose weight gain was determined.

The percentage of boron was determined by a standard mannitol titration technique.[11]

Since the decomposition point was higher than could be determined conveniently by conventional methods, the solid product, sealed in an evacuated quartz ampoule, was placed into a tube furnace. The temperature, measured with an iron–constantan thermocouple, was increased slowly so that the sample could be examined at 5° increments to ascertain the decomposition point.

X-Ray powder photographs were obtained using a Norelco 114.59-mm. diameter powder camera and nickel filtered copper Kα radiation (λ_{α_u} = 1.5418 Å.).

Infrared spectral data were obtained by preparing mineral oil mulls of the product and recording the spectra from 2 to 37 μ with a Perkin-Elmer Model 221 spectrometer.

Analytical results of different preparations show the percentages: Se = 90.9, 91.02, 91.87; B = 8.51, 8.77. Percentages calculated for B_2Se_3 are: Se = 91.64, B = 8.36; for $HBSe_2$: Se = 93.03, B = 6.37. The preceding results indicate that the yellow solid is B_2Se_3.

Results and Discussion

When the boron sesquiselenide was heated in a sealed ampoule, it was observed to decompose at 556 ± 10° into a metallic gray portion and a red substance. A positive selenium test was obtained on the red material and the metallic solid was assumed to be either boron or a lower boron selenide.

At a temperature between 195 and 235°, the yellow powder form of boron sesquiselenide changed to a more compact solid formation with a darker color. Infrared spectra and X-ray powder photographs were taken of these two forms in an effort to compare them. The X-ray powder photographs of the unheated yellow powder showed no lines, indicating that it was amorphous, while the heated product produced many lines. The "*d*-values" of the more intense lines of the heated product are listed in Table I.

TABLE I

INTERPLANAR *d*-VALUES OF B_2Se_3

d-Value, Å.	Intensity	*d*-Value, Å.	Intensity
6.53	S	2.82	VW
4.09	MS	2.64	VW
3.90	MS	2.37	M
3.77	MS	2.30	M
3.27	S	2.17	MS
3.10	W	2.111	W
		1.395	M

A comparison of these *d*-values with those of the cubic and hexagonal boric oxide indicates that the specimen is not directly related to either structure, and the lines cannot be indexed on the basis of cubic, tetragonal, or hexagonal symmetry.

Infrared spectra were obtained for both the amorphous and crystalline forms of the product. These are listed in Table II, together with that reported by Greene and Margrave[9] for boron sesquisulfide, and they indicate a similarity between the species.

TABLE II

INFRARED BANDS—AMORPHOUS AND CRYSTALLINE PRODUCTS

Amorphous B_2Se_3 cm.$^{-1}$	Crystalline B_2Se_3 cm.$^{-1}$	B_2S_3[9] cm.$^{-1}$
1372	1300	1322
1250	1150	990
837		919
611		859
580		602

Shifts from 1372 to 1300 cm.$^{-1}$ and from 1250 to 1150 cm.$^{-1}$ are noted when the amorphous form of boron sesquiselenide is converted to the crystalline form, but such shifts frequently are found with polymorphic substances.

Since boron sesquiselenide is extremely moisture-sensitive, it reacted with the water vapor present in a static argon-filled drybox containing phosphorus pentoxide as the desiccant. Only when care was taken to remove the last traces of water from the drybox could the sesquiselenide be handled without decomposition.

That hydrogen selenide and not selenium entered into the reaction was proved by substituting prepurified nitrogen for the hydrogen gas used in the reaction. In experiments of equivalent duration, only a small yield was obtained using the nitrogen, too small a yield to manipulate without complete loss due to hydrolysis.

During this experiment, and another in which the boron was not placed in the tantalum boat, selenium vapor was not observed on the collection assembly. However, in an experiment in which the velocity of the hydrogen gas was increased gradually, the color of the dust collecting on the disk changed from yellow to orange to red. When the velocity of the gas was decreased, small amounts of selenium collected immediately adjacent to the outlet of the furnace, and the product again was bright yellow. From these experiments it was inferred that selenium was not present on

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(11) Reference 10, p. 168.

the disk along with the product if the flow of hydrogen was adjusted properly.

Since large quantities of both boron and selenium were used, and only small amounts of the product could be collected because of the size of the fritted disk, the reaction was never run to completion and a yield could not be calculated. However, when the amorphous boron was used for more than three consecutive runs the yield of boron sesquiselenide obtained as a function of time decreased sharply. Possible reasons for this decrease may have been the partial sintering of the boron into a clinker and subsequent loss of surface area.

Attempts to determine the solubility of boron sesquiselenide in various non-aqueous solvents were inconclusive because of the traces of moisture which could not be removed, but they indicated that the product was insoluble in anhydrous ether and carbon disulfide, as would be expected for an ionic species.

This reaction was considered as a means of preparing boron sesquitelluride, but it failed to proceed, probably because of the absence of sufficient quantities of hydrogen telluride in the gaseous phase since, unlike hydrogen selenide, the equilibrium concentration of the hydrogen telluride decreases as the temperature is increased.[12]

Present work is being directed toward an elucidation of the crystal structure and an investigation of some chemical properties of this molecule.

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(12) L. M. Dennis and R. P. Anderson, *J. Am. Chem. Soc.*, **36**, 882 (1914).

Correspondence

Critical Temperatures of Metals and their Estimates by Gates and Thodos

Sir:

In recent papers[1-3] it was shown that the temperature range of *liquid metals, i.e.*, the range from the melting to the critical point, is far greater than for any other type of substance. It extends, in view of their elementary and atomic nature, far beyond the thermal limits of existence of any other solid or liquid; even the stablest of the latter dissociate into atoms at about 5000-6000°K. In contrast, the refractory metals such as Re, Ta, and W will be liquids up to a critical temperature of about 20,000, 22,000, and 23,000°K., respectively.

It also was shown[1-3] that one can construct a liquid temperature range diagram of metals demonstrating the relationship between liquid (and saturated vapor) density *vs.* temperature over the whole liquid temperature range, from the melting point to the critical point, by using the theorem of corresponding states of van der Waals, the law of rectilinear diameter of Cailletet and Mathias, and experimental data on heats and entropies of vaporization, vapor pressure, and particularly experimental liquid density data over as wide a temperature range as possible.

Subsequently it has come to our attention that Gates and Thodos[4] estimated the critical temperatures of metals, but arrived at values that differed substantially from ours, as the comparison in Table I shows.

TABLE I

COMPARISON OF THE CRITICAL TEMPERATURE OF METALS ESTIMATED BY THE METHOD OF GATES AND THODOS[4] *vs.* THE INSTITUTE'S

	Normal b.p.,[5] °K.	Critical temp., °K.	
		Gates and Thodos	R. I. T. U.
W	5800	11500	23000
Mo	5100	9880	17000
Sn	2960	5809	8700
Pb	2024	3584	5400
Na	1163	2124	2800

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(1) A. V. Grosse, "The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures," Report of the Research Institute of Temple University, September, 1960; see also *Nuclear Sci. Abstr.*, **15**, 4018, 31197 (1961).

(2) A. V. Grosse, American Rocket Society, Space Flight Report to the Nation, New York Coliseum, Oct. 9-15, 1961, Paper No. 2159-61.

(3) A. V. Grosse, *J. Inorg. & Nuclear Chem.*, **22**, 23 (1961).

(4) D. S. Gates and G. Thodos, *A.I.Ch.E. Journal*, **6**, 50 (1960).

(5) All data on normal boiling points and ΔH_{vap} are taken from D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Advances in Chemistry Series No. 18, 1956.