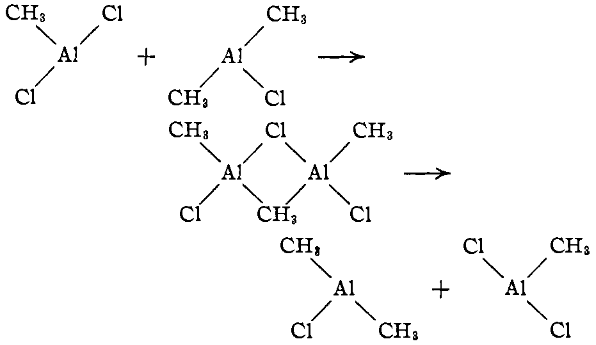
shifts were 1.75, 1.75 and 1.45 p.p.m., respectively, to higher fields than the resonance due to the solvent protons. Cooling the solutions to their freezing point, approximately 0°, produced no line splitting. Therefore in dimethylaluminum chloride also, exchange between bridging and nonbridging groups probably occurs readily.

In addition to methyl exchange within the dimer, halogens and methyl groups may exchange between molecules in the mixed methylaluminum halides. Trimethylaluminum, aluminum iodide and the intermediate iodomethyl compounds were shown to be in rapid equilibrium.[4,5] A solution of methylaluminum chloride (25%) in dimethylaluminum chloride (75%) shows only a single sharp proton resonance signal both at room temperature and at −60°. Since the chemical shift between the two compounds is 12 cycles at a frequency of 40 Mc. one can estimate[3] that the maximum energy for intermolecular methyl exchange is 12 kcal. mole^{-1}. This is similar to that reported, 6–14 kcal. mole^{-1}, for the methyl groups in trimethylaluminum.[2] In this case, however, it is difficult to envision a mechanism for intermolecular methyl group exchange which does not involve dissociation to monomers. One possible mechanism for the exchange is shown.



---

[4] A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

[5] K. S. Pitzer and H. S. Gutowsky, This Journal, **68**, 220 (1946).

Baker Chemical Laboratory
Cornell University S. Brownstein
Ithaca, New York, and B. C. Smith
Division of Applied Chemistry
National Research Council G. Erlich
Ottawa, Canada A. W. Laubengayer

Received December 16, 1959

LINKAGE ISOMERISM: SYNTHESIS AND ISOMERIZATION OF NITRITOPENTAMMINE COMPLEXES OF RHODIUM(III) AND IRIDIUM(III)[1]

Sir:

The only reported example of linkage isomerism for metal complexes is that of nitro (Co-NO_2) and nitrito (Co-ONO) ammines of cobalt(III).[2] We wish to report the successful synthesis of Rh$(NH_3)_5ONO^{2+}$ and Ir$(NH_3)_5ONO^{2+}$ salts and their isomerization to the corresponding stable nitropentammine complexes. Some question had been raised as to the existence of nitritoammine cobalt(III) complexes[3] so that the isolation of such rhodium(III) and iridium(III) compounds is further proof of this type of isomerism, if additional proof is needed. The preparation of these compounds serves as a good example of the usefulness of reaction mechanism studies in the carrying out of preparative work.

On the basis of kinetic studies[4] it had been proposed that the formation of Co$(NH_3)_5ONO^{2+}$ takes place by an attack of N_2O_3 or NO^+ on the oxygen of Co$(NH_3)_5OH^{2+}$. That there is no Co–O bond cleavage in this reaction was substantiated by oxygen-18 experiments.[5] It would therefore appear that a similar low energy reaction path should be available to analogous metal complexes. Then if rearrangement to the stable nitro compound is sufficiently slow, reaction at mild conditions may yield the kinetic nitrito product. This communication reports just such an observation.

At elevated temperatures the reactions of Rh$(NH_3)_5OH^{2+}$ and Ir$(NH_3)_5OH^{2+}$ with NO_2^- are reported[6] to produce salts of Rh$(NH_3)_5NO_2^{2+}$ and Ir$(NH_3)_5NO_2^{2+}$. However, at ice-bath temperatures similar reaction mixtures yield instead salts of Rh$(NH_3)_5ONO^{2+}$ and Ir$(NH_3)_5ONO^{2+}$. For example, to an ice cold solution containing 0.67 g. of [Ir$(NH_3)_5H_2O$]Cl_3 in 20 cc. of water was added 0.96 g. of solid $NaNO_2$. Once the solid had dissolved 1 cc. of 6*M* HCl was added and a crystalline material separated immediately. This salt was collected and washed with dilute ice cold HCl and acetone, then air dried (yield 0.54 g. or 83%.)

Anal. Calcd. for [Ir$(NH_3)_5$ONO]Cl_2: N, 21.3; H, 3.8; Cl, 18.0. Found: N, 21.2; H, 3.7; Cl, 17.6.

Under similar conditions a good yield of [Rh$(NH_3)_5$ONO]Cl_2 was obtained.

Anal. Calcd. for [Rh$(NH_3)_5$ONO]Cl_2: N, 27.3; H, 4.9; Cl, 23.3. Found: N, 27.9; H, 4.7; Cl, 22.7.

The presence of M–ONO linkage was verified and its rate of isomerization to M–NO_2 followed by an examination of the infrared spectra of the solid compounds. Using KBr disks of the solids, absorption peaks at 1460 and 1060 cm.$^{-1}$ are found which decrease in intensity and simultaneously two new bands appear at 1420 and 830 cm.$^{-1}$. These bands have been shown to be due to M-ONO and M–NO_2, respectively, for cobalt(III) complexes.[7]

The isomerizations of solid [M$[NH_3]_5$ONO]Cl_2 in KBr disks have half-lives of 6 hr. at 48°, 3.5 hr. at 22° and 2.5 hr. at 57° for M = Co(III), Rh(III) and Ir(III), respectively. Work is now in progress on the kinetics and mechanism of forma-

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-315. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] S. M. Jørgensen, *Z. anorg. Chem.*, **5**, 169 (1893).

[3] R. Duval, C. Duval and J. Lecomte, *Bull. soc. chim.*, [5] **14**, 1048 (1947).

[4] R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, This Journal, **76**, 5920 (1954).

[5] R. K. Murmann and H. Taube, This Journal, **78**, 4886 (1956).

[6] S. M. Jørgensen, *J. prakt. Chem.*, [2] **34**, 414 (1886); A. Werner and O. deVries, *Ann.*, **364**, 103 (1909).

[7] R. B. Penland, T. J. Lane and J. V. Quagliano, This Journal, **78**, 887 (1956).

tion and rearrangement of these nitritoammine complexes. Other metal systems are also being investigated to see whether additional examples of linkage isomerism can be obtained.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY FRED BASOLO
EVANSTON, ILLINOIS G. S. HAMMAKER

RECEIVED DECEMBER 28, 1959

PREPARATION OF TETRABORON SILICIDE, B_4Si

Sir:

Much effort is being expended today in the search for high temperature, oxidation resistant materials. In this respect, we wish to report for the first time the preparation in large quantities of a new silicide of boron, tetraboron silicide, B_4Si.[1]

The question of compound formation in the system boron–silicon has been reviewed recently by Cline[2] in his paper on investigations of B_6Si. We have not observed any evidence to date for the existence of B_3Si as first reported by Moissan and Stock[3] and more recently by Samsonov and Latysheva.[4] Only the presently reported B_4Si[5] and the known B_6Si have been found.

B_4Si is prepared by heating the elements in an inert atmosphere at temperatures not exceeding 1370°. Above this temperature, B_4Si is thermally unstable; and the interesting phase transformation $B_4Si \rightarrow B_6Si$ is now being studied.

Amorphous boron of 83 to 95% purity has been used, each material giving the identical product. Crystalline silicon of 98% purity was used. An intimate mixture of 500 g. of 86.6% boron[6] (40 moles) and 574 g. of 98% silicon,[7] +200 mesh, (20 moles) was placed in a large metallurgical fire clay crucible of the sillimanite type[8] and heated in an electrical resistance-type furnace in argon atmosphere to 1370° over 4–5 hours, soaked at 1370° for 2–3 hours, and furnace cooled.

The product consisted of a glassy, slag-like top and an inner, black friable core. The latter was powdered readily and sieved through a 325 mesh screen, the fine portion being shown by X-ray powder diffraction patterns to be B_4Si plus traces of B_6Si. Tetraboron silicide is readily distinguishable from hexaboron silicide by its X-ray powder pattern,[5] the six strongest lines (*d* Å.) and respective intensities being: 4.15, 30; 2.75, 90; 2.67, 100; 1.606, 50: 1.582, 30; 1.510, 30. Chemical analysis of the fine fraction showed B, 60.6%; Si, 36.8%, and Mg, 0.65%. The B/Si molar ratio is 4.28, slightly larger due to the presence of traces of B_6Si than the expected value of 4.00 required for B_4Si. Yields of B_4Si of 50–80%, based on boron, have been achieved by proper choice of reaction conditions. It seems very likely that B_4Si completely free of B_6Si can be prepared by the reaction of the elements in inert atmosphere for periods longer than 2–3 hours at temperatures below 1370° and above about 1200°. Such studies are now in progress.

B_4Si is highly oxidation resistant due to the formation of a protective boron–silicon–oxygen coating which first forms upon exposure of the material to air at elevated temperatures. Shapes fabricated from B_4Si by powder metallurgical techniques have withstood oxidation in air for over 100 hours at 1370° and showed excellent thermal shock resistance, no cracks being observed when pieces were removed from 1370° to room temperature numerous times. The ceramic properties of B_4Si are now being investigated.

RESEARCH DIVISION
ALLIS-CHALMERS MFG. CO. ERVIN COLTON
MILWAUKEE 1, WIS.

RECEIVED DECEMBER 30, 1959

---

[1] The writer prefers the nomenclature "tetraboron silicide" in contrast to "silicon tetraboride" in consistency with the boron–carbon system in which B_4C is called "boron carbide."

[2] C. F. Cline, *J. Electrochem. Soc.*, **106**, 322 (1959).

[3] H. Moissan and A. Stock, *Compt. rend.*, **131**, 139 (1900).

[4] G. V. Samsonov and V. P. Latysheva, *Doklady Akad. Nauk S.S.S.R.*, **105**, 499 (1955), *Chem. Abstr.*, **50**, 7639h (1956).

[5] V. I. Matkovich, *Acta. Cryst.* (1959). The complete crystal structure of B_4Si has been submitted for publication.

[6] From F. W. Berk and Co., Wood-Ridge, N. J., and Metalsalts Corp., Hawthorne, N. J.

[7] Union Carbide Metals Co.

[8] Denver Fire Clay Co., Denver, Colo.

REARRANGEMENT AND FRAGMENTATION REACTIONS IN CARBENOID DECOMPOSITION OF DIAZO HYDROCARBONS

Sir:

Tosylhydrazones of aliphatic aldehydes and ketones react with bases in aprotic solvents to give diazo compounds.[1,2] The diazo compounds undergo thermal carbenoid decomposition[1,2] with loss of nitrogen to yield olefins derived from hydrogen-migration and cyclopropanes by intramolecular-insertion.[1] Carbon-skeleton rearrangement did not occur appreciably even in systems involving *tert*-butylcarbenes. Rearrangement in carbenoid decomposition of diazo ketones is quite common, however.[3]

It is now reported that cyclopropanecarboxaldehyde tosylhydrazone[4] reacts with sodium methoxide in diethyl Carbitol or N-methylpyrrolidone at 180°[5a] to yield (Equations 1–2) cyclobutene (60, 67%)[5b] by *ring-expansion*, ethylene (13, 10%) and acetylene (13, 10%) by *carbon-skeleton fragmentation*, and 1,3-butadiene (4.5, 7%) by *ring-rupture*.[6a,b] Methylenecyclopropane was not detected.[6b] Formation of cyclobutene is thus a prime example of extensive carbon-skeleton rearrangement in a simple carbenoid system.[7] De-

---

[1] L. Friedman and H. Shechter, THIS JOURNAL, **81**, 5512 (1959); L. Friedman, Ph.D. Dissertation, The Ohio State University, 1959.

[2] Similar conclusions have been reached by J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

[3] W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, Chapter 2, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

[4] All tosylhydrazones gave satisfactory analyses.

[5] (a) The tosylhydrazones and sodium methoxide were added to the solvent at 25°, allowed to stand for a few minutes and then heated at 180°. Decomposition is complete in less than 5 min. (b) The tosylhydrazones decompose to hydrocarbons in excellent yields; the percentages reported herein are actual product compositions.

[6] (a) The hydrocarbons were analyzed, separated, and identified by gas-chromatographic and subsequent infrared methods; comparisons were made with authentic samples. (b) Minor amounts of other hydrocarbons also were obtained.

[7] (a) L. Hellerman and R. L. Garner, THIS JOURNAL, **57**, 139 (1935), report that thermal decomposition of 1-diazo-2,2,2-triphenylethane gives triphenylethylene. It is thus apparent that phenyl migration occurs in triphenylmethylcarbene systems. (b) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958), raise the question that reaction of 1,1-dibromocyclopropanes with magnesium or sodium to give allenes may involve carbenoid processes.