TABLE I

MAJOR INFRARED ABSORPTIONS OF TETRAMETHYLENE SULFOXIDE COMPLEXES (CM.$^{-1}$)

Compound	Solvent or mull	Assignments									
		CH stretch	CH_2 deformations						S=O[a]		C—S
C_4H_8SO	CCl_4 (15%)	2930, 2860	1447	1411	1303	1271	1147	1097	1035	875	730
$PdCl_2\cdot 2TMSO$	KBr	2930	1446	1398	1307	1260	...	1074	1119	875	...
$[Co(TMSO)_6]I_2$	Nujol	2930, 2860	1445	1406	1307	...	1146	1102	947	...	717
$[Co(TMSO)_6][CoCl_4]$	Nujol–HCBD		1445	1408	1304	...	1140	1095	937	...	717
$3CuBr_2\cdot 4TMSO$	KBr	2980, 2910	1445	1408	1302	1250	...	1104	937	875	...
$CuBr_2\cdot TMSO$	Nujol–HCBD		1426	1393	1300	...	...	...	925	870	715
$3CuCl_2\cdot 4TMSO$	Nujol–HCBD		1448	1409	1302	...	...	1107	933	...	714
$CuCl_2\cdot TMSO$	KBr		1445	1407	1303	1250	...	1104	941	876	...

[a] This band is by far the most intense one of the entire spectrum in each case.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA

Compound	$\chi_M \times 10^6$, c.g.s. units	T, °K.	μ_{eff}, B.M.
$CuCl_2\cdot TMSO$[a]	1409	325.5	1.90[c]
	1560	297.8	
	1742	273.8	
	2624	194.7	
	8416	80.7	
$3CuCl_2\cdot 4TMSO$[b]	4302	298.0	1.90[c]
	7100	195.5	
	20,347	80	

[a] The diamagnetic correction is 120 × 10^{-6} c.g.s. unit. [b] The diamagnetic correction is 421 × 10^{-6} c.g.s. unit. [c] Average magnetic moment per copper ion.

the magnitude of the infrared frequency shift. The ligand field *Dq* values for these two ligands are identical for Co(II), Ni(II), and Cr(III).[8] Such a correlation of the shift of the S–O vibration in dimethyl sulfoxide is complicated by coupling with the methyl rocking frequency

The reactions which occur when the compounds of general formula $3CuX_2\cdot 4TMSO$ are heated in ethanol and acetone are interesting and have not been observed when the DMSO complexes are treated under similar conditions. New compounds of general formula $CuX_2\cdot TMSO$ are formed from this reaction. The infrared spectra of both types of TMSO complexes are quite similar. This similarity in the S–O vibrational region indicates that the sulfoxide is not acting as a bridging ligand in the $CuX_2\cdot TMSO$ complex.

The complexes $3CuX_2\cdot 4TMSO$ are probably best formulated as $[Cu(TMSO)_4][Cu_2Cl_6]$ since TMSO is not removed at 80° under high vacuum, whereas the $CuX_2\cdot TMSO$ complexes are probably dimers with a symmetrical $\mathrm{Cu}{<}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}{>}\mathrm{Cu}$ bridge. The latter formulation is analogous to the structure[9] of $Cu_2Cl_4(CH_3CN)_2$, which exhibits the halo-bridging linkage, and the organic molecules are bonded to the copper atoms in positions which are *trans* for the entire molecule. However, the TMSO complexes do not exhibit the unusual magnetic properties of the $LiCuCl_3\cdot 2H_2O$,[10] but are similar to those of $CsCuCl_3$.[11] Both $3CuCl_2\cdot 4TMSO$ and $CuCl_2\cdot TMSO$ exhibited normal magnetic behavior over the temperature range studied (Table II).

The interesting deoxygenation of the sulfoxide in the sulfur-bonded Pd(II) complex is currently under investigation.

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Formation of $B_{10}H_{15}^-$ as an Intermediate in Borohydride Attack on Decaborane-14[1]

BY RILEY SCHAEFFER AND FRED TEBBE

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The reaction of decaborane-14 with borohydride salts has been studied by at least two groups of workers[2,3] and has been shown to proceed by the over-all reaction (in the case of the sodium salt)

$$2NaBH_4 + 2B_{10}H_{14} \rightarrow 2NaB_{10}H_{13} + 2H_2 + B_2H_6 \quad (1)$$

Aftandilian, *et al.*, have confirmed this observation and shown that at higher temperatures further reaction occurs to produce $B_{11}H_{14}^-$ salts,[4] and in aqueous solution, Muetterties has shown that $B_{10}H_{14}^{-2}$ salts are the principal products.[5] By monitoring the reaction with ^{11}B n.m.r. spectra at invervals we have now been able to demonstrate that in ethereal solvents the reaction largely proceeds in two stages with preliminary hydride transfer to form $B_{10}H_{15}^-$ salts and subsequent hydrogen elimination to form the previously observed $B_{10}H_{13}^-$ derivatives.

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$$NaBH_4 + B_{10}H_{14} \rightarrow NaB_{10}H_{15} + {}^1/_2B_2H_6 \qquad (2)$$

$$NaB_{10}H_{15} \rightarrow NaB_{10}H_{13} + H_2 \qquad (3)$$

Experimental

A Varian Model 4300B spectrometer operating at 19.3 Mc./sec. was used to obtain ^{11}B n.m.r. spectra. Mass spectra were obtained with a Consolidated Engineering Corporation Model 21-620A spectrometer. Isotopic analyses were made by comparison of the *m/e* 20 and *m/e* 21 peaks with those of diborane of known isotopic content.[6] The source of boron for the diborane and sodium borohydride of known isotopic content was $CaF_2 \cdot BF_3$ enriched to 96 ± 1% ^{10}B, supplied by the Oak Ridge National Laboratories. A value of 96.4 ± 0.2% ^{10}B best fit the observed mass spectrum of the standard diborane. A value of 20.0 ± 0.2% ^{10}B gave the best fit for the spectrum of isotopically normal diborane, in agreement with observations of previous workers.[6] It was assumed that the isotopically normal decaborane also contained 20.0% ^{10}B.

Isotopically normal sodium borohydride and tricaprylmethylammonium borohydride were obtained from Metal Hydrides, Inc. Decaborane (sublimed before use) and lithium borohydride were from laboratory stock. Ethylene glycol dimethyl ether (Ansul Ether 121) was distilled under vacuum from lithium aluminum hydride.

Room temperature reactions of borohydride with decaborane of normal isotopic content were initiated in 5-mm. n.m.r. tubes by addition of solvent to a mixture of the dry solids or by mixing solutions of the materials. During the initial, vigorous reactions (complete within a few seconds when solutions were mixed) diborane and small quantities of hydrogen were formed. The major boron-containing product in solution was identified as $B_{10}H_{15}^-$ by the n.m.r. spectrum. Chemical shifts for the lithium salt in diethyl ether (relative to the diethyl etherate of boron trifluoride) with estimated errors of less than 1 p.p.m. were +10.9, +17.6, and +24.2 p.p.m. compared to reported values for the $B_{10}H_{15}^-$ ion[7] of +9.5, +16.8, and +25.1 p.p.m. Salts of $B_{10}H_{15}^-$ identified by the ^{11}B n.m.r. spectrum formed at room temperature from decaborane with sodium borohydride in ethylene glycol dimethyl ether solution, with lithium borohydride in diethyl ether solution, or with tricaprylmethylammonium borohydride in benzene solution. When aqueous tetramethylammonium hydroxide was added to an ethylene glycol dimethyl ether solution of $NaB_{10}H_{15}$, the ^{11}B n.m.r. spectrum of the resulting aqueous solution closely resembled that of $B_{10}H_{14}^{2-}$,[5,8] the basic form of $B_{10}H_{15}^-$, providing additional confirmation of the identity of the latter.

Production of hydrogen in the above experiments clearly suggests that the over-all reaction (1) occurs to some extent although perhaps only as a result of steps 2 and 3. An estimate of the yield of $NaB_{10}H_{13}$ was obtained by measuring the hydrogen and diborane evolved in the reaction of 4.58 mmoles of decaborane with 5.22 mmoles of sodium borohydride. About 5 ml. of ethylene glycol dimethyl ether was condensed into an evacuated flask containing the dry solids at −196°. When the contents of the sealed flask reached the melting temperature of the ether, an intensely colored purple solution was formed which rapidly turned yellow at slightly higher temperature. The solution was allowed to warm to room temperature within a 10-min. period and was agitated at room temperature for an additional 5 min. Hydrogen, 0.81 mmole, was recovered and measured in a calibrated Toepler system. Using the hydrogen evolved as evidence for formation of an equal amount of $NaB_{10}H_{13}$, one may calculate that 17.6% of the decaborane was converted to this salt. The diborane–ether mixture was removed from the reaction vessel and condensed into a flask containing water in excess of that needed for hydrolysis. The hydrogen produced, 13.52 mmoles, is equivalent to that expected from 98.6% of the diborane required by either eq. 1 or 2. The essentially quantitative recovery of diborane and confirming n.m.r. evidence shows that 82.4% of the decaborane was converted to $NaB_{10}H_{15}$.

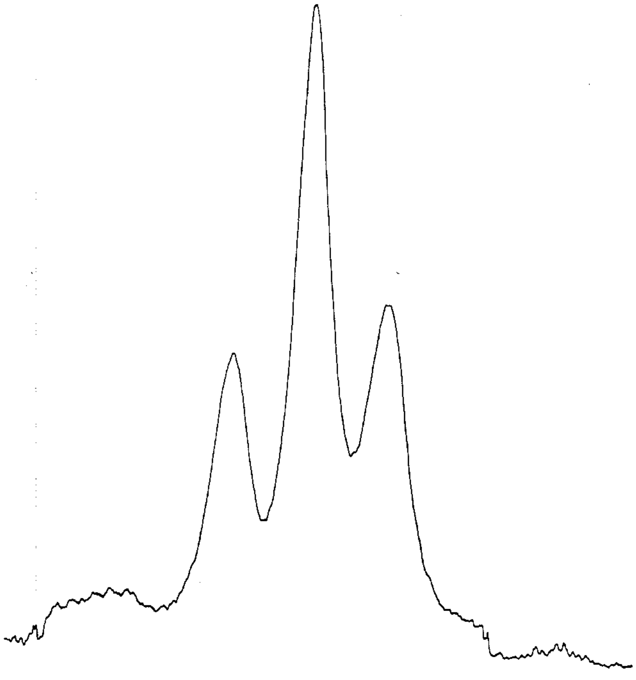

Fig. 1.—^{11}B n.m.r. spectrum of $NaB_{10}H_{15}$ formed from reaction of decaborane with sodium borohydride in ethylene glycol dimethyl ether solution.

The decomposition of $NaB_{10}H_{15}$ at room temperature was followed by frequent observations of the ^{11}B n.m.r. spectra of the ethylene glycol dimethyl ether solution. The three-line spectrum of the $B_{10}H_{15}^-$ ion (Fig. 1) decreased in intensity as a spectrum characteristic of $NaB_{10}H_{13}$[9] appeared, but $NaB_{10}H_{15}$ persisted for more than 3.5 hr. After 12 hr. the spectrum showed that $B_{10}H_{15}^-$ was absent and that the solution contained primarily $NaB_{10}H_{13}$ in the presence of a small amount of other material with approximately the spectral characteristics of $NaB_{11}H_{14}$. The spectrum taken again after the yellow solution had remained at room temperature for several weeks consisted solely of a doublet (δ +15.9 ± 0.5 p.p.m., J = 140 ± 3 c.p.s.) which may be ascribed to $NaB_{11}H_{14}$ (lit.[4] J = 140 c.p.s.; determined with an authentic sample,[10] δ +16.1 p.p.m., J = 139 c.p.s.). This result is, of course, the one expected on consideration of the results of earlier studies.[4]

The reaction of 0.635 mmole of isotopically normal decaborane with 0.697 mmole of 96.4% ^{10}B sodium borohydride was carried out at 0° in ethylene glycol dimethyl ether solution. In order to make the *m/e* 20 and *m/e* 21 peaks more easily read in the mass spectrum of the diborane, 3.12 mmoles of $^{10}B_2H_6$ was added as an isotopic dilutant. The initially vigorous reaction subsided after about 7 min., and it was assumed that conversion to $NaB_{10}H_{15}$ was essentially complete. After 2.75 hr. the diborane isotopic content was measured to be 80.2% ^{10}B, which corresponds to exchange of the diborane with 27% of the decaborane boron. Approximately one-fifth of the hydrogen according to eq. 3 had evolved at this time. The exchange approached completion only after 25 hr. at 0°. *Anal.* Calcd.: ^{10}B, 59.8. Found (at 25 hr.): ^{10}B, 61.2.

Discussion

The generation of the $B_{10}H_{15}^-$ ion in these experi-

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ments strongly suggests hydride ion transfer from the borohydride to decaborane, probably in a single step. It is possible that the reaction occurs by the formation of diborohydride-like BHB linkage[11] between the borohydride and the most positive[12] 6(9) decaborane atom, followed by loss of a borane group and possible rearrangement to the as yet undetermined $B_{10}H_{15}^-$ structure. The initial attack of borohydride ion would thus occur in a manner similar to the first step of a proposed mechanism[13,14] for reaction of acetonitrile with decaborane and would resemble the many other known examples of nucleophilic attack on decaborane. The formation of $NaB_{10}H_{13}$ in 18% yield (as judged by hydrogen evolution) during the early stages of the reaction between sodium borohydride and decaborane allows the possibility that a competing mechanism may operate to produce $NaB_{10}H_{13}$ directly by reaction 1 previously proposed.[3] The majority of the $B_{10}H_{13}^-$, however, was produced by the decomposition $B_{10}H_{15}^-$ according to eq. 3. The subsequent appearance of $NaB_{11}H_{14}$ in solution indicates that the over-all reaction of sodium borohydride with decaborane in ethylene glycol dimethyl ether solution is similar to the synthesis of $NaB_{11}H_{14}$ in dioxane solution.

Isotope studies of the decaborane–sodium borohydride system were concerned primarily with the exchange reaction of diborane with $NaB_{10}H_{13}$ after hydrogen evolution according to eq. 3 had taken place. An analysis of the diborane in the early stages of the exchange, however, indicated that after 2.5 hr. at 0° only 27% of the decaborane boron had exchanged with the diborane. In an experiment previously described in the literature,[15] diborane was mixed with preformed $NaB_{10}H_{13}$ and exchange of diborane with all ten boron atoms of the decaborane cage had reached completion within 1 hr. It is apparent that B_2H_6–$NaB_{10}H_{15}$ exchange and $NaB_{10}H_{15}$–$NaB_{10}H_{13}$ exchange either do not take place or are slow with respect to the diborane–$NaB_{10}H_{13}$ reaction. A more detailed study of isotope exchange in this system would be of interest.

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On the Nature of $SeCl_4 \cdot 2C_5H_5N$

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Present knowledge of the stereochemistry of selenium in its IV oxidation state reveals an interesting and rather unique situation concerning the role of the lone pair of electrons on selenium. The tetrahalides appear to be either molecular substances with structures based on a trigonal bipyramid shape $(:SeX_4)$[1,2] or ionic materials $(:SeX_3^+ + X^-)$ with pyramidal trihalide cations.[3] In each of these situations the lone pair of electrons appears to play a significant role in the geometry of the molecule or ion. In contrast to this, the hexahaloselenate ions (SeX_6^{-2}) are reported to be octahedral, and the lone pair of electrons is considered "stereochemically inert."[4]

The reported addition product of selenium tetrachloride with two molecules of pyridine is of interest with respect to this situation concerning the role of the lone-pair electrons. Several reports of this material have appeared in the literature,[5–7] and speculation as to the nature of the substance has included a molecular compound $SeCl_4 \cdot 2py$ isoelectronic with the hexahaloselenates, and a pyridine adduct of a chloroselenium cation such as $(SeCl_3py_2)^+$ or $(SeCl_2py_2)^{+2}$. In this communication we wish to report an investigation of this addition product which indicates the material is, in solution, a pyridine derivative of a trichloroselenium cation.

Experimental

Materials.—Anhydrous selenium tetrachloride was prepared by reaction of powdered black selenium and gaseous chlorine according to the method described in *Inorganic Syntheses*.[8]

Fisher reagent grade pyridine was distilled once through a 40-cm. Vigreux column. The acetonitrile used as the solvent for the dissociation study was purchased from Matheson Coleman and Bell.

General Experimental Procedures.—All of the selenium compounds investigated in this study decompose immediately when exposed to air of average humidity; therefore all of the work was performed in a plastic bag[9] filled with dry nitrogen.

Analytical Methods.—The selenium analysis was obtained by dissolving the sample in dilute sulfuric acid, adding starch indicator and sodium thiosulfate solution, and back-titrating the excess thiosulfate with iodine solution. Nitrogen analyses were obtained by the Kjeldahl method using a Pregl type microapparatus.[10] For the chlorine and bromine analysis the standard Volhard method was used; an acid solution of the sample was titrated with thiocyanate solution after the addition of excess standard silver nitrate.

X-Ray Powder Patterns.—Because the samples decomposed readily in air they were sealed in 0.3-mm. o.d. capillary tubing, and diffraction patterns were recorded photographically on a General Electric camera of radius 7.2 cm., using Cu Kα radiation obtained from a standard Norelco unit. The intensities were estimated visually.

Preparation and Characteristic of $SeCl_4 \cdot 2py$.—Newly prepared selenium tetrachloride was added gradually to freshly distilled

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