of 60 mesh 5 Å. molecular sieve operated at room temperature. For the hydrogen detection experiments all coulometric and kinetic work was carried out under an atmosphere of argon which also served as the carrier gas in the chromatographic system. By calibrating the system with hydrogen-saturated solvent, we were clearly able to show (on the basis of retention times at constant flow rate and temperature) that hydrogen gas is a product of the ruthenium(II) oxidation. No other gaseous products were detected. Attempts were also made to measure the amount of hydrogen produced using a comparison of peak heights with chromatograms obtained from known samples of hydrogen gas. For a solution having an initial ruthenium(II) concentration of 9.7×10^{-3} *M*, the final hydrogen concentration was determined as approximately 4×10^{-3} *M*. These results are consistent with the observed conversion of ruthenium(II) to (III) but should be viewed with caution because the hydrogen determination is semiquantitative, at best.

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Lewis Acid Adducts of Group IV-A Azides[1]

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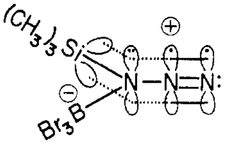
The isolation of complexes having the formula $(C_6H_5)_3MN_3 \cdot P(C_6H_5)_3$[3–5] and the lability of $(CH_3)_3SiN_3$ in the presence of $AlCl_3$[6,7] suggested that group IV-A azides might act as Lewis bases. We find that the Lewis acids $SnCl_4$, BBr_3, and $SbCl_5$ form stable 1:1 adducts with azides of Si, Ge, and Sn. During our investigation, Goubeau, *et al.*, prepared $CH_3N_3 \cdot SbCl_5$[8] and Wiberg and Schmid reported the reaction of silyl azides with $SbCl_5$.[9,9a]

All of the complexes isolated, except for $CH_3(C_6H_5)_2SiN_3 \cdot BBr_3$, were white solids that decomposed without melting. They dissolve without appreciable dissociation in dichloromethane, chloroform, carbon tetrachloride, and benzene; contact with water, alcohols, or acetone causes immediate decomposition.

Wiberg and Schmid report that $(C_6H_5)_3SiN_3$ or $(CH_3)_3SiN_3$ reacts with antimony pentachloride to give the chlorosilane and $(SbCl_4N_3)_2$ directly.[9] We found that $SbCl_5$ adducts are indeed unstable, but that $(CH_3)_3SiN_3 \cdot SbCl_5$ could be isolated from dilute carbon tetrachloride solution. Under the same conditions, $CH_3(C_6H_5)_2SiN_3$ and $SbCl_5$ reacted violently to give off large quantities of gas and leave an unidentified black residue. In contrast, complexes of silyl azides with tin tetrachloride or boron tribromide are quite stable. $CH_3(C_6H_5)_2SiN_3 \cdot BBr_3$, when heated for 2 hr. at 200° and 0.5 mm., distilled unchanged into a cold trap, leaving only traces of tars. Under similar conditions, $(CH_3)_3SiN_3 \cdot BBr_3$ dissociated and recombined on cooler surfaces, forming white crystals identical with the starting material. $(CH_3)_3SiN_3 \cdot SnCl_4$, heated at 190° and 0.5 mm. for 3 hr., remained unaffected, except for formation of traces of a black tar. This great thermal stability is in marked contrast to the compounds $(CH_3)_3SiCN \cdot BX_3$ (X = halogen), which decompose rapidly below room temperature.[10]

Azide band positions in the complexes differ markedly from those of the free azides[3,11]; they are listed in Table I. In addition, all silyl azide complexes show a strong band at about 980 cm.$^{-1}$ not present in other complexes. This may be due to the Si–N–A stretching mode, which appears in the 900–1000 cm.$^{-1}$ region in silazanes and related compounds.[12]

There are two possible sites where electron donation might occur: the nitrogen bonded to the organometallic group (the α nitrogen) or the terminal nitrogen. The azide band shifts and the new band at 980 cm.$^{-1}$ for silyl compounds are more compatible with the α-bonded structure shown below, which has also been proposed for $(C_6H_5)_3SiN_3 \cdot P(C_6H_5)_3$,[3] $CH_3N_3 \cdot SbCl_5$,[8] and the reaction intermediate of R_3SiN_3 with $SbCl_5$.[9]



Experimental

Reagents.—Azides were prepared by the general methods described previously.[3,11] Boron tribromide was obtained from American Potash and Chemical Co. Antimony pentachloride was purchased from J. T. Baker Chemicals Co., and tin tetrachloride from Matheson Coleman and Bell. All solvents used were spectral grade. Benzene was distilled from sodium before use.

Spectra.—Infrared spectra were run on a Perkin-Elmer Model 237 double-beam recording spectrophotometer linear in wave number. Sodium chloride plates were used for solid mulls and liquid films, while matched 0.05 and 0.2 mm. cells were used for solutions. Polystyrene peaks at 2850, 1603, and 906 cm.$^{-1}$ were used for calibration. All frequencies are accurate to ±5 cm.$^{-1}$. Carbon tetrachloride was the solvent of choice for solution spectra, although dichloromethane and chloroform were also used. Concentrations of the complex ranged from 0.01 to 0.1 *M*; excess Lewis acid was often, though not invariably, added. Solution spectra were not noticeably different from the spectra of the free complex.

Azide–Lewis Acid Complexes.—Samples of purified azides were dissolved in a suitable solvent, usually carbon tetrachloride,

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TABLE I
AZIDE–LEWIS ACID COMPLEXES

Compound	Color	Azide ν asym.	$\Delta\nu$ from free azide[a]	Azide ν sym.	$\Delta\nu$ from free azide[a]
$(C_6H_5)_3SiN_3\cdot BBr_3$	Pale yellow	2208	+59	1190	−118
$(C_6H_5)_3GeN_3\cdot BBr_3$	Pale yellow	2208	+108	1220	−50
$(C_6H_5)_3SnN_3\cdot BBr_3$	S.o.[b]	2211	+118	. . .	. . .
$(CH_3)_3SiN_3\cdot BBr_3$	White	2208	+67	1190	−142
$(CH_3)_3SnN_3\cdot BBr_3$	S.o.[b]	2210	+122	. . .	. . .
$CH_3(C_6H_5)_2SiN_3\cdot BBr_3$	Red liq.	2210	+65	1195	−120
$(C_6H_5)_3SiN_3\cdot SnCl_4$	S.o.[b]	2116	−33	1326	+18
$(C_6H_5)_3GeN_3\cdot SnCl_4$	White	2131	+31	1308	+38
$(C_6H_5)_3SnN_3\cdot SnCl_4$	White	2208	+115	1185	−80
$(CH_3)_3SiN_3\cdot SnCl_4$	White	2110	−21	1347	+15
$CH_3N_3\cdot SbCl_5$[8]	Green-yellow	2160	+54	1225	−146
$(CH_3)_3SiN_3\cdot SbCl_5$	Pale yellow	2210	+69	1200	−132
$(C_6H_5)_3SiN_3\cdot P(C_6H_5)_3$[3]	White	2018	−131	*ca.* 1260	−48

[a] See ref. 3 and 11 for infrared bands of free azides. [b] Complex studied in solution only and not isolated.

and mixed with solutions of the Lewis acid in the same solvent in a drybox under nitrogen. After mixing, a portion of the solution was removed for infrared study; the remainder was attached to a vacuum distillation apparatus and the solvent removed. The adduct was then dried *in vacuo* for several hours. Due to their great sensitivity to moisture, these adducts generally were not characterized by elemental analysis but rather by infrared spectroscopy and by hydrolysis and titration to the phenolphthalein end point.[13] The data are given in Table II. Certain of the complexes proved to be intractable and were studied only in solution.

Azidotrimethylsilane–Tin Tetrachloride.—A solution of 0.98 g. (8.5 mmoles) of $(CH_3)_3SiN_3$ in 25 ml. of CCl_4 was treated with 2.0 ml. (17.1 mmoles) of $SnCl_4$ in 5 ml. of CCl_4. After a few minutes, the solution turned opaque and a finely divided solid formed. When the solid had settled, the supernatant liquid was decanted. The white product was washed with 2 ml. of CCl_4 and dried *in vacuo*, yielding 1.22 g. (38%) of $(CH_3)_3SiN_3\cdot SnCl_4$.

TABLE II
ANALYSES OF AZIDE–LEWIS ACID ADDUCTS

Compound	Equivalent weight	
	Calcd.[a]	Found
$(CH_3)_3SiN_3\cdot SnCl_4$	55.2	51.1, 58.6
$(CH_3)_3SiN_3\cdot SbCl_5$	69.0	66.0, 68.2
$(CH_3)_3SiN_3\cdot BBr_3$	91.4	96.8
$CH_3(C_6H_5)_2SiN_3\cdot BBr_3$	122	120
$(C_6H_5)_3GeN_3\cdot BBr_3$	149	150

[a] Calculated on the basis of complete hydrolysis, *e.g.*, $2(CH_3)_3SiN_3\cdot SnCl_4 + 5H_2O \rightarrow (CH_3)_6Si_2O + 2HN_3 + 2SnO_2 + 8H^+ + 8Cl^-$. Equiv. wt. = (mol. wt.)/5.

Anal. Calcd. for $C_3H_9N_3Cl_4SnSi$: C, 9.59; H, 2.41; Cl, 37.7; equiv. wt., 55.2. Found: C, 9.36; H, 2.18; Cl, 35.0; equiv. wt., 58.6.

Azidotrimethylsilane–Antimony Pentachloride.—A solution of 0.375 g. (3.2 mmoles) of $(CH_3)_3SiN_3$ in 15 ml. of CCl_4 was treated with 2 ml. (15.6 mmoles) of $SbCl_5$. The solution immediately turned pale yellow. Evaporation of solvent *in vacuo* gave very pale yellow crystals, which were washed with 0.5 ml. of cold pentane–carbon tetrachloride solution and dried *in vacuo* to give 0.85 g. (64.5%) of $(CH_3)_3SiN_3\cdot SbCl_5$.

Anal. Calcd. for $C_3H_9N_3Cl_5SbSi$: C, 8.91; H, 2.24; Cl, 41.4; equiv. wt., 69.0. Found: C, 8.86; H, 2.11; Cl, 39.9; equiv. wt., 68.2.

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Some Observations on Uranium-Nitrogen Compounds

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Although in the past few years a number of studies have been made of the uranium nitrides, some structures and stoichiometry ranges remain in doubt. Prior to a note[1] of Didchenko and Gortsema (D and G), the work and conclusions of Rundle, *et al.*,[2] had been generally accepted. Rundle found that: (a) three nitrides exist, UN (NaCl structure), U_2N_3 (Mn_2O_3 structure), and UN_2 (CaF_2 structure); (b) solid solutions are very limited in the U–UN and UN–$U_2N_2N_3$ regions but nitrides between U_2N_3 and UN_2 exist as a single phase of intermediate structure; (c) on passing N_2 or NH_3 over U or UH_3 at elevated temperatures, a product of about $UN_{1.75}$ is obtained which at temperatures above 1000° will lose N_2 giving U_2N_3 then UN. To produce UN_2 an excess pressure of 1800 p.s.i. is needed.

Several later workers[3–8] have obtained N:U ratios <1.8, from the same general preparative technique, and (when reported) have found the same structures,

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