chemical shift of SbH_3 in CCl_4 at −23° with the chemical shifts of the methylstibines in C_6H_6 at +27°, it is interesting that the variation in chemical shift of HSb<, as methyl groups replace protons, parallels the variations observed for other series of compounds, such as $(CH_3)_nGeH_{4-n}$.[13,14] At present, this variation is little understood. In the case of antimony, which possesses a lone pair of electrons and low-lying empty d and f orbitals, the paramagnetic anisotropy of the antimony may play a significant role in determining the actual magnitude of the shielding of the proton directly bonded to the antimony. On the other hand, the amount of s character in the Sb–H bond may have increased in going from SbH_3 to CH_3SbH_2. In this case, not only will the paramagnetic anisotropy be different, but also, owing to the greater penetration of the s orbital into the core, the protons in methylstibine will be more affected by the electron-withdrawing power of the antimony, and so the chemical shift of CH_3SbH_2 may reasonably be expected to be at lower field than the SbH_3 signal.

TABLE II

^1H NMR SPECTRA OF $(CH_3)_nSbH_{3-n}$, n = 0–3

	Chem shift, τ			
Compound	H_3C–Sb	H–Sb	J(H–H), Hz	Ref
SbH_3	...	8.622	...	*a*
CH_3SbH_2	9.52 (triplet)	8.31 (quartet)	6.32	*b*
$(CH_3)_2SbH$	9.38 (doublet)	7.86 (septet)	5.98	*b*
$(CH_3)_3Sb$	9.33	...	...	*b*

[a] *Cf.* ref 2; at −23° in CCl_4, extrapolated to infinite dilution.
[b] This work; at +27° in C_6H_6, extrapolated to infinite dilution.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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The Disproportionation of Digermane in Liquid Ammonia

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While attempting to measure the acid dissociation constant of digermane in liquid ammonia, we have observed that digermane decomposes in liquid ammonia solution to give germane and a solid germanium hydride of variable composition. Similar base-catalyzed decompositions of digermane have been observed by Bornhorst and Ring,[1] but these workers did not investigate the nature of the solid hydride formed. In view of Glarum and Kraus's earlier report[2] of the formation of GeH_2 by the reaction of bromobenzene with sodium germyl in ammonia, we decided to determine if the same substance can be prepared by the ammonia-catalyzed disproportionation of digermane.

Experimental Section

Standard greaseless vacuum-line techniques were employed. Digermane was prepared according to the method of Jolly and Drake.[3] The digermane was shown to be pure by its vapor pressure (235 mm at 0°, invariant with vapor volume, compared with the literature[4] value of 243 mm), its infrared spectrum (which only showed bands due to digermane[5]), and its mass spectrum (which showed only trace contamination by air). Too little germane was formed in the reactions to permit identification by vapor pressure determination, but its purity was shown by its infrared spectrum[6] and mass spectrum, neither of which showed even trace contamination by NH_3 or Ge_2H_6. The spectra were obtained with a Perkin-Elmer Model 137 Infracord spectrometer and a Consolidated Engineering Corp. mass spectrometer, Model 21-620. Ammonia was dried over sodium before its use.

Reactions were carried out in a vessel equipped with two break-seals. A measured amount of digermane and approximately 0.5 ml of liquid ammonia were distilled into the vessel at liquid nitrogen temperature. The vessel was then sealed and placed in a bath of appropriate temperature. When a low-temperature bath was used, care was taken to keep the entire vessel below the level of the bath.

After reaction had proceeded, the vessel was attached to the vacuum line, and one of the seals was opened, keeping the vessel in the low-temperature bath. The volatile contents were then Toepler-pumped through a liquid nitrogen trap until all volatiles had distilled over. A trace of hydrogen could usually be measured in the buret of the Toepler pump. The vessel was then sealed off again and temporarily set aside. The volatiles were then separated. In runs in which all of the digermane had decomposed, it was possible to separate germane and ammonia by means of a −160° trap. However, when digermane was present, the ammonia could not be separated by trap-to-trap distillation; it was removed by distilling the ternary mixture very slowly through a trap of anhydrous magnesium perchlorate at 0°. The germane and digermane were then separated by fractional condensation in traps at −112 and −196°; the amount of each was determined by pressure–volume techniques.

The solid residue in the reaction vessel was then pyrolyzed at 400° for 2 hr. The hydrogen (identified by mass spectrometry) was then Toepler-pumped through the second break-seal and through a −196° trap to remove any ammonia that might have adhered to the solid. The hydrogen was measured and the germanium mirror was either discarded or dissolved in basic hydrogen peroxide and titrated with a pH meter according to the method of Tchakirian.[7]

Results

The results are presented in Table I. The adequacy of the quantitative measurements is attested by the

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TABLE I

QUANTITATIVE DATA FOR Ge_2H_6 DISPROPORTIONATIONS (ALL QUANTITIES IN MMOLES)

					D		Calcd values of *x*	
Temp, °C	Time, hr	*A* Ge_2H_6 in	*B* Ge_2H_6 out	*C* GeH_4 formed	H_2 from GeH_x pyrolysis	*E* Ge in GeH_x	$2D/E$	$2D/[2(A-B)-C]$
−63	96	0.668	0.273	0.481	0.253	0.264	1.92	1.64[a]
−63	96	0.553	0.323	0.260	0.149	0.180	1.66	1.49[a]
−63	25	0.383	0.308	0.064	0.077	0.077	2.00	1.79[a]
−63	25	0.536	0.479	0.0696	0.0695	0.069	2.01	3.16[a]
−45	37	0.200	0	0.220	0.169	...	...	1.88
23[b]	24	0.188	0	0.244	0.0746	...	...	1.13
23	20	0.244	0	0.334	0.0676	...	...	0.88
23[c]	14	0.218	0	0.291	0.0789	...	...	1.09
23	13	0.247	0	0.321	0.0800	...	...	0.92
23	0.25	0.152	0.114	0.0417	0.0316	...	...	1.86[a]

[a] These values are relatively inaccurate because they require the difficult determination of the unreacted Ge_2H_6 (*B*). [b] Ammonia solution 1 *M* in NH_4NO_3. [c] $NH_3:Ge_2H_6$ = 1:1.

fact that the hydrogen in the germane produced and that formed in the pyrolysis of the GeH_x account for the hydrogen in the consumed digermane with an average discrepancy of ±1.2%. In the four experiments where a germanium balance could be calculated, the average discrepancy was ±3.5%.

In the −63° experiments, the solution was initially colorless, but, on standing, the solution turned yellow and a yellow precipitate formed. In the −45° experiment, a yellow precipitate formed quickly. In the room-temperature experiments, a blood red precipitate formed immediately.

Discussion

The results indicate that, in liquid ammonia solution, digermane disproportionates as: $Ge_2H_6 \rightarrow GeH_4 + GeH_2$. At temperatures above −63° (and even at that temperature on standing), the GeH_2 decomposes to germane and a yellow or red precipitate of GeH_x ($x < 2$). The higher the temperature, the more rapidly the GeH_2 decomposes, the lower the value of *x*, and the darker the color of the precipitated GeH_x. Although Glarum and Kraus[2] reported similar properties for GeH_2 prepared from bromobenzene and sodium germyl, their substance was more stable inasmuch as its solution in ammonia did not become colored on standing for 24 hr, and it could be isolated for a short time as a white solid at −33°.

In the hope that the solution at −63° contained a soluble GeH_2 species, the proton magnetic resonance spectrum of a 0.5 *M* Ge_2H_6 solution was obtained. The spectrum showed peaks corresponding to germane, digermane, and a series of three smaller peaks from 8 to 25 cycles upfield from germane, perhaps corresponding to a lower hydride. As the solution decomposed, the digermane peak decreased in amplitude, the germane peak increased, and the little peaks began to merge and broaden. By the time the digermane peak had disappeared, the little peaks were gone. Attempts to get better resolution by increasing the digermane concentration were unsuccessful, probably because of limited solubility of the lower hydride.

Efforts to effect reaction between GeH_2 and acetylene or diphenylacetylene at −63°, in analogy with the high-temperature reactions of GeI_2,[8] were unsuccessful.

We have observed that no reaction occurs when both the digermane and the ammonia are completely in the gas phase; however, reaction proceeds in the presence of even traces of liquid ammonia. The basic catalyst is ammonia itself and not the amide ion because the reaction goes without noticeable change in 1 *M* ammonium nitrate–liquid ammonia solution. Apparently, relatively weak bases cause the disproportionation of digermane. In addition to ammonia and those bases shown to be effective by Bornhorst and Ring,[1] aqueous sodium hydroxide causes the disproportionation.[4,9]

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(9) R. Dreyfuss, unreported observations.

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Kinetic Studies of Amine Substitution in Aminopentacarbonyltungsten(0) Complexes

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Kinetic and mechanistic studies of CO substitution in metal carbonyl complexes have been conducted on numerous systems.[1] Yet relatively little effort has gone into studies involving the substitution of other groups which might also be present in the complex. It was the purpose of the present investigation to examine the rates and mechanisms of amine displacement from $(Am)W(CO)_5$ according to

$$(Am)W(CO)_5 + L \longrightarrow (L)W(CO)_5 + Am \qquad (1)$$

The rate of this reaction was investigated as a function of the basicity of the primary, secondary, and tertiary amines and also of the nucleophilicity of the phosphine or phosphite, L.

Experimental Section

Preparation and Purification of Materials.—The ligands, L, and solvents were purified as given elsewhere.[2] The $(Am)W(CO)_5$ complexes were prepared by the method of ultraviolet irradiation of a tetrahydrofuran solution of $W(CO)_6$ and the desired amine. Most of the complexes had been prepared previously[3] and were identified by their infrared spectra. In addition, satisfactory C, H, and N analyses were obtained for the complexes $((CH_2)_5NH)W(CO)_5$, $((CH_3)_3N)W(CO)_5$, and $(O(CH_2CH_2)_2NH)W(CO)_5$. The products, $(L)W(CO)_5$, of reaction 1 were identified by their uv–visible and infrared spectra which were identical with those of $(L)W(CO)_5$ complexes prepared and

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(1) For a recent review, see R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

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