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Pyrolysis of Methylgermane and Methylsilane

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It has been demonstrated that the pyrolysis of disilane in a flow system with low-temperature trapping generates trisilane in at least a 90% yield according to[1]

$$2Si_2H_6 \longrightarrow SiH_4 + Si_3H_8 \qquad (1)$$

Similarly, good yields of tetrasilane[1] and trigermane[2] were also obtained from the pyrolysis of trisilane and digermane, respectively. If the silicon–carbon and germanium–carbon bonds are more inert to pyrolysis than the corresponding bonds to hydrogen, the pyrolysis of alkylsilanes or -germanes could lead to useful syntheses.

In Table I, we list a typical result from the pyrolysis of methylgermane and methylsilane in flow systems with low-temperature (−112°) trapping. These results demonstrate that in methylsilane the silicon–carbon bond is thermally more inert than the silicon–hydrogen bonds. However in methylgermane, the germanium–carbon bond is at least as labile as the germanium–hydrogen bonds.

TABLE I
PYROLYSIS OF CH_3EH_3 (E = Si, Ge)

				Amt of products, mmol				
E	Temp, °C	Time, hr	Amt of reactant consumed, mmol	H_2	CH_4	$(CH_3)_2$-EH_2	$(CH_3)_3EH$	1,2-$(CH_3)_2$-E_2H_4
Ge	420	24	1.27	1.24	0.59	0.23	0.02	0.10
Si	520	15	1.37	0.84	0.02	0.16	0	0.53

The two reactions were also very different with respect to the amount of metalloid lost to the walls. In the methylsilane pyrolysis, only 11% of the silicon was deposited in the form of polymeric solids. However in the methylgermane pyrolysis, 65% of the germanium was deposited in polymeric solids while all of the methyl groups were still present in volatile products. Thus it appears that the main decomposition of methylgermane yielded methyl and germyl radicals. Since digermane and methyldigermane were not produced, the germyl (or germene from germyl decomposition) radicals probably decomposed before they could react to form digermanes. Note that the ratio of hydrogen produced to germanium lost to the walls was 1.51. Both methylsilane and methylgermane were found considerably more stable toward pyrolysis than silane[3] or germane.[4]

Experimental Section

All experiments were carried out in Pyrex vacuum systems. Separations were made by trap to trap distillations. Methylgermane was prepared from the reaction of potassium germyl with methyl chloride[5] while methylsilane was prepared by the lithium aluminum hydride reduction of methyltrichlorosilane. The compounds were identified by mass spectra which consisted only of peaks due to the ions CEH_{6-x}^+, EH_{3-x}^+, and CH_{3-x}^+ (E = Ge and Si). The infrared spectra of our samples were identical with those reported[6,7] and the absence of the very strong bands from silane[8] or germane[9] demonstrated the absence of these compounds.

The pyrolysis of methylgermane was carried out in a Toepler pumped flow system[1] containing a cold trap cooled to −112°. The pyrolysis of methylsilane was carried out in a Vycor reactor tube of 5-cm³ volume connected to an automatic Toepler pump with two cold traps (at −112°) following the heated zone. The Vycor reactor was placed in the center of a 30-mm hole drilled through an 80-mm diameter brass bar (16 cm long). A thermometer was placed in contact with the Vycor reactor. The ends of the brass bar ovens were sealed with glass wool and asbestos. The inner walls of both reactors were coated with germanium or silicon from previous decomposition reactions. Under these conditions, methylsilane did not decompose at 500° and methylgermane did not decompose at 325°.

The product fractions which passed a −196° cold bath were Toepler pumped into a calibrated volume to determine their quantities while their hydrogen to methane ratios were obtained from mass spectra. The compounds of the form $(CH_3)_xEH_{4-x}$ (E = Si or Ge) were identified by mass spectra which contained the ion expected but did not contain ions with more methyl groups or ions with two silicon or two germanium atoms. Infrared spectra confirmed the identifications and demonstrated that molecules of lower molecular weight were absent since very strong infrared bands were absent.

The product fraction from the methylgermane pyrolysis which did not pass a −95° trap was analyzed as follows. Infrared spectra demonstrated that methyl- and dimethylgermane were absent.[6] The mass spectra of these samples contained the $(CH_3)_3Ge^+$ and $(CH_3)_2Ge_2H_{4-x}^+$ ions and other ions expected from trimethylgermane and dimethyldigermane. A typical proton nmr spectrum consisted of a poorly defined triplet centered at −0.49 ppm (TMS = 0.0 external standard) and a quartet centered at −3.56 ppm. A small additional absorption occurred at −3.57 ppm. The relative integrated intensity of the C–H resonance compared to that of the Ge–H resonance was 1.78. The nmr spectrum demonstrated that CH_3GeH_5 was not present.[10] The absorption at −3.57 ppm and part of the triplet distortion can be assigned to trimethylgermane.[11] The rest of the spectrum is that expected for 1,2-dimethyldigermane. The GeH_2 absorption in $CH_3Ge_2H_5$ was observed at −3.58 ppm.[10] The relative ratio of the C–H to Ge–H intensities was used to calculate the relative quantities of trimethylgermane and 1,2-dimethyldigermane.

The 1,2-dimethyldisilane was identified by an infrared spectrum,[12] by a mass spectrum from which the low intensity at *m/e* 76 suggested that methyldisilane was absent,[13] and by a neat nmr spectrum. A typical proton nmr spectrum consisted of a triplet centered at −0.21 ppm and a quartet centered at −3.50 ppm. The relative intensities were 1.51:1, respectively. In addition, very weak resonances were observed at −3.55 and −3.12 ppm.

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Thus the nmr spectrum is that expected for 1,2-dimethyldisilane and the spectrum demonstrates that methyldisilane was absent.[13] The very weak resonances observed probably were due to 1,1-dimethyldisilane.[14] From the integrated intensities one can estimate that the ratio of 1,2-dimethyldisilane to 1,1-dimethyldisilane was about 60:1.

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Preparation and Nuclear Magnetic Resonance Spectrum of *cis*-Dichlorobis(bipyridyl)iridium(III) Hexafluorophosphate

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During our investigations of the nmr contact shifts of several paramagnetic tris-bipyridyl complexes it was necessary for us to prepare the tris(bipyridyl)iridium(III) ion for use as a diamagnetic reference. Following the literature method of preparation,[1] we encountered a product which upon further investigation turned out to be *cis*-dichlorobis(bipyridyl)iridium(III) hexafluorophosphate, a previously unreported compound, and not the tris(bipyridyl)iridium(III) complex as expected. We wish to report the results of our nmr investigations of this complex.

The tris(bipyridyl)iridium(III) ion has been previously reported to be the sole product of the reaction of $IrCl_6^{3-}$ and bipyridyl.[1] It was first reported to be bright orange, but later was shown to be canary yellow[2] upon recrystallization from aqueous solution containing activated charcoal. The orange color was assumed by these authors to be due to contamination with small amounts of *trans*-dichlorobis(bipyridyl)iridium(III) in analogy with the colors noted for the similar phenanthroline complexes.[2] Our preparation yielded only a small amount of orange precipitate and a yellow solution from which the *cis* complex was isolated upon cooling and addition of KPF_6.

Examination of the nmr spectrum (Figure 1), indicated immediately that the complex did not contain the desired tris(bipyridyl)iridium(III) ion. In contrast with the usual spectrum of a tris-bipyridyl complex (as illustrated by $Os(bipy)_3^{2+}$ in Figure 2), many more peaks were present than would be expected. In order to interpret the spectrum and to determine which protons belong to equivalent rings of the bipyridyl molecule (in C_{2v} symmetry, both rings of bipyridyl are no longer equivalent), decoupling experiments were carried out and spectra were also recorded at 100°. Room-temperature and 100° spectra were virtually identical except for slight sharpening of the very small couplings. It was assumed, therefore, that the molecule is very stable and does not undergo rearrangement.

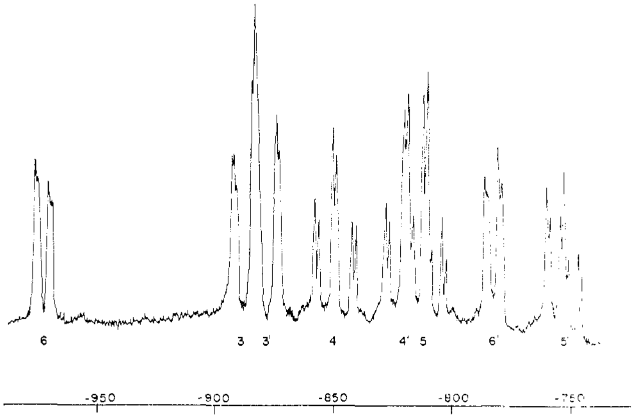

Figure 1.—*cis*-Dichlorobis(bipyridyl)iridium(III) hexaflurophosphate in DMSO at 100 MHz.

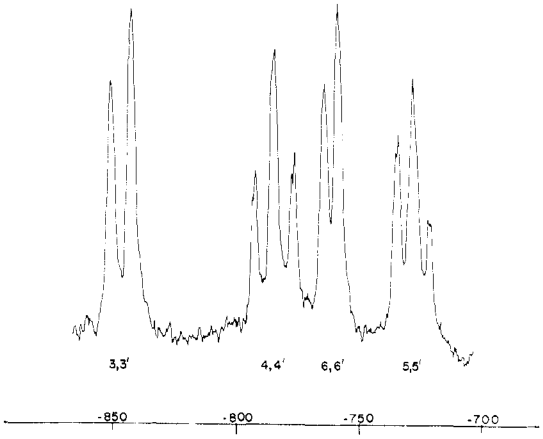

Figure 2.—Tris(bipyridyl)osmium(II) hexafluorophosphate in CD_3CN at 100 MHz.

In general, what is observed for a tris complex is a spectrum consisting of two doublets from the 3 and 6 protons and two triplets from the 4 and 5 protons (see Figure 3 for the numbering system). The triplets result from overlap of two doublets due to spin–spin splittings of comparable magnitudes from two adjacent protons. Since the 3 and 6 protons experience large couplings to only one other proton, doublets result. Inter-ring coupling is not observed. The spectrum of the iridium complex, while appearing complicated, can be reduced to a series of doublets and triplets indicating eight nonequivalent protons. The results of our analysis are presented in Table I, and a brief summation of the method used to interpret the decoupled spectra follows.

The decoupling experiment provides an easy way to separate the resonances belonging to atoms on the same

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