$SiCl_2$ with acetylene evolved no volatiles on pumping at room temperature or slightly above. On acid or base hydrolysis, this polymer evolved acetylene and no other volatile product except hydrogen.

Discussion

The reactions of $SiCl_2$ form an interesting comparison with those of SiF_2. The former inserts readily into M–Cl bonds, and this provides a new synthetic route from M–Cl to $M–SiCl_3$. Reactions of this type are rare with SiF_2, which most frequently forms compounds containing at least two silicon atoms. It has been postulated that the initial step in the reaction of SiF_2 with another compound at -196° is the formation of a diradical $\cdot Si_2F_4\cdot$ which then reacts with other molecules. This accounts for the observed reactions with boron trifluoride to give $SiF_3SiF_2BF_2$,[7] with benzene to give $C_6H_6Si_2F_4$,[10] and with acetylene to give $HC\equiv CSiF_2SiF_2CH=CH_2$.

The molecules $C_6H_6Si_2F_4$ and $HC\equiv CSiF_2SiF_2CH=CH_2$, or the polymers from which they had been pumped, were readily hydrolyzed to 1,4-cyclohexadiene and acetylene, respectively. As 1,4-cyclohexadiene and acetylene were also obtained on hydrolysis of the corresponding $SiCl_2$ reaction product, this suggests that in nonchlorinated systems, where insertion into a bond is not favored, $SiCl_2$ may, like SiF_2, polymerize *via* reactive diradicals.

Experimental Section

Silicon dichloride was prepared in the same type of apparatus described by Timms[11] for the preparation of boron monofluoride. In this case, silicon tetrachloride vapor was passed at the rate of about 50 mg/min through an inductively heated graphite container containing about 8 g of 99.9% pure silicon in pea-sized lumps. The maximum temperature in the container was kept below 1380° to prevent sintering of the silicon. The pressure in the container dropped from 5 mm at the top to about 0.2 mm near the nozzle. The silicon dichloride, mixed with unchanged silicon tetrachloride, sprayed out through the nozzle into a liquid nitrogen cooled evacuated flask in which the pressure of permanent gas was below 2×10^{-6} mm. Slight blocking of the nozzle occurred, limiting running time to about 30 min.

When the dichloride was cocondensed with other chlorides, these were added through a Pyrex nozzle mounted below the nozzle from the graphite container. The rate of addition was controlled so that roughly equimolar quantities of silicon dichloride and the other chloride were condensed together.

At the end of a run, the furnace was cooled, and the condensate was warmed to room temperature. Volatiles liberated were pumped into a trap from which they could be transferred to a standard vacuum line. The volatiles were separated by distillation on a low-pressure, low-temperature distillation column. This was capable of giving a clean separation between mixtures of $SiCl_3BCl_2$ and Si_2Cl_6 and of $SiCl_3PCl_2$ and Si_2Cl_6 although these separations were not possible by trap to trap distillation.

$SiCl_3PCl_2$ and $SiCl_3BCl_2$.—The mass spectra of these compounds were taken with a Bendix Model 1400 time-of-flight mass spectrometer equipped with an all-glass direct inlet system allowing evaporation directly from the condensed phase into the ion source of the spectrometer. The spectra showed the compounds to be free of admixed Si_2Cl_6.

The compounds were analyzed for chlorine content by dissolving them in 5% NaOH, acidifying with HNO_3, adding a little $NaNO_2$ to oxidize any lower boron or phosphorus compounds to the +3 or +5 state, respectively, removing oxides of nitrogen, and determining the chloride by the Volhard method. *Anal.* Calcd for $SiCl_3BCl_2$: Cl, 82.1. Found: Cl, 82.7. Calcd for $SiCl_3PCl_2$: Cl, 74.8. Found: Cl, 73.8.

The melting points were obtained by the Stock ring method, using a calibrated pentane thermometer for temperature measurement.

Infrared spectra were taken in a 10-cm glass gas cell with silver chloride windows, using a Perkin-Elmer 211 spectrophotometer.

Polymeric residues left in the flask on the furnace system after volatiles had been pumped off could not be removed efficiently. They were treated with aqueous reagents added to the flask, and the volatiles formed were carried into a trap in a stream of helium. The silanes liberated from $(SiCl_2)_x$ on treatment with 10% HF were separated by gas chromatography at room temperature on a 6-ft column packed with 10% Silicone 702 on Chromosorb P. They were identified by their known relative retention times, with benzene as internal standard, and their relative abundances were estimated from the peak areas using a thermal conductivity detector. The C_6 hydrocarbons obtained by the action of acid or base on the benzene–$SiCl_2$ polymer were separated on a 6-ft column packed with 10% tritolyl phosphate on Chromosorb P. Individual peaks were collected and identified by their mass spectra and infrared spectra. Acetylene liberated from the $SiCl_2$–acetylene polymer was purified on a vacuum line and identified by its infrared spectrum.

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[10] P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Am. Chem. Soc.*, **88**, 940 (1966).

[11] P. L. Timms, *ibid.*, **89**, 1629 (1967).

CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH
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The Synthesis of Iridium Disulfide and Nickel Diarsenide Having the Pyrite Structure

BY RONALD A. MUNSON[1]

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The pyrite structure (space group $T_h{}^6$[Pa3]) is in general a densely packed arrangement and, therefore, tends to be favored when synthesis is attempted between the transition metals and groups Va and VIa elements at high pressure. The preference of copper disulfide for the pyrite structure when synthesized under pressure allows the realization of the 1:2 cation to anion stoichiometry, which cannot be obtained at all if the synthesis is attempted below 15 kbars pressure.[2] The two syntheses which we wish to report here were performed in the "belt" superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. Both syntheses were carried out at 60 kbars pressure. Pressure and temperature calibration have been described.[2] Compositions have been determined by thermogravimetric analysis.

At 1 atm iridium is known to combine with sulfur to

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[2] R. A. Munson, *Inorg. Chem.*, **5**, 1296 (1966).

[3] H. T. Hall, *Rev. Sci. Instr.*, **31**, 125 (1960).

form iridium disulfide having the orthorhombic crystal structure of iridium diselenide,[4,5] in which part of the iridium may be considered to have the +3 oxidation state. If the ratio of sulfur to iridium is increased to nearly 3:1, then a pyrite structure is formed[6] in which the +3 iridium is balanced with cation vacancies. At 60 kbars, a mixture of sulfur and iridium (3:1 mole ratio) will react at 1500° to form the same pyrite structure ($IrS_{2.9}$) observed by Biltz, *et al.*[6] (a = 5.62 Å). If, however, sulfur and iridium in a 2:1 mole ratio react at 60 kbars and 1500°, then a new pyrite phase is found ($IrS_{1.9}$) with a = 5.68 Å. Powder diffraction patterns obtained from samples having an initial composition with a mole ratio between 2 and 3 which were allowed to react under the same conditions showed the presence of both pyrite phases.

Nickel diarsenide crystallizes in an "anomalous" marcasite structure[7] which differs from the Jahn–Teller marcasite structure by having minimal angular distortion about the cation octahedra. In this sense the "anomalous" marcasites are like the pyrites; however, they differ from the pyrites in that the marcasite structure is a less dense packing arrangement. These factors suggest that materials having the "anomalous" marcasite structure might be induced to form the pyrite structure when synthesized under pressure. An intimate mixture of powdered nickel and arsenic in a 1:2.2 mole ratio after reaction at 60 kbars and 1400° was cooled at pressure to room temperature over a period of 0.5 hr. After the release of the pressure a metallic gray material was obtained which gave the X-ray reflections (Table I) of the cubic pyrite structure, a = 5.77 Å. The calculated density, 7.21 g cm^{-3}, may be compared with the pycnometric density of 7.15 ± 0.10 g cm^{-3}. These results suggest that other materials possessing the "anomalous" marcasite structure may also be synthesized in the pyrite arrangement under pressure.

Table I

Spacing and Indexing of the Reflections of Cubic Nickel Diarsenide[a]

d	hkl	Intensity	d	hkl	Intensity
2.86	200	W	1.070	432	M
2.56	210	S	1.051	521	M
2.34	211	S	1.019	440	M
2.03	220	W	0.961	600	W
1.98	221	VW	0.949	610	W
1.73	311	VS	0.936	611	M
1.66	222	W	0.911	620	VW
1.59	230	M	0.880	533	M
1.54	321	S	0.870	622	VW
1.435	400	W	0.860	630	M
1.285	420	W	0.851	631	M
1.255	421	M	0.832	444	VW
1.225	332	W	0.800	640	W
1.174	422	W	0.792	641	S
1.109	511	M	0.785	552	S

[a] Copper Kα_1 nickel-filtered radiation employed with a Norelco camera of diameter 114.6 mm.

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[4] L. B. Barricelli, *Acta Cryst.*, **11**, 75 (1958).

[5] F. Hulliger, *Nature*, **204**, 644 (1964).

[6] W. Biltz, J. Laar, P. Ehrlich, and K. Meisel, *Z. Anorg. Allgem. Chem.*, **233**, 263 (1937).

[7] F. Hulliger and E. Mooser, "Progress in Solid State Chemistry," Vol. 2, H. Reiss, Ed., Pergamon Press Inc., New York, N. Y., 1965, pp 330–377.

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The Formation of the Skutterudite Phase in the Cobalt–Phosphorus System

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Relatively few compounds occur in the skutterudite structure (space group $T_h^5(Im3)$), but the existence of IrP_3 and RhP_3 as well as $CoSb_3$ and $CoAs_3$ in this structure strongly suggests that CoP_3 ought to have this arrangement also. Biltz and Heimbrecht,[2] however, were unsuccessful in preparing cobalt triphosphide with the skutterudite structure at low pressures.

We have been able to prepare the skutterudite phase of cobalt phosphide by allowing powdered cobalt to react with phosphorus in a 3:1 mole ratio at a pressure of 60 kbars and 1400°. However, this product also contained another unidentified compound of cobalt and phosphorus. The pure skutterudite phase could be obtained only when the ratio of phosphorus to cobalt was in the vicinity of 4. Chemical analysis of the pure skutterudite phase established the empirical formula $CoP_{3.90}$ (32.8% cobalt). X-Ray reflections using cobalt Kα iron-filtered radiation indicated the body-centered-cubic structure, a = 7.711 Å. The calculated density based on CoP_4 is 3.97 g cm^{-3} which may be compared with the pycnometric density of 4.04 ± 0.10 g cm^{-3}. Initial structure factor calculations indicate agreement between the intensities listed in Table I and the assumption of random distribution of six cobalt atoms among the eight 8e skutterudite positions.

Table I

Spacing and Indexing of the Reflections of Cubic Cobalt Phosphide

d	hkl	Intensity	d	hkl	Intensity
5.4	101	MW	1.190	541	VW
3.83	200	M	1.162	622	MW
3.12	211	W	1.136	631	MW
2.71	220	M	1.113	444	MW
2.43	310	S	1.090	710	W
2.23	222	MW	1.069	640	M
2.06	321	M	1.049	721	W
1.92	400	W	1.030	642	W
1.81	330	W	1.013	730	M
1.72	420	S	0.980	732	M
1.64	332	W	0.964	800	M
1.57	422	MS	0.950	741	W
1.51	510	M	0.935	820	S
1.32	530	W	0.921	653	W
1.285	600	VW	0.909	822	S
1.219	620	MW	0.896	831	S

These preparations were carried out in the "belt"

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[2] W. Biltz and M. Heimbrecht, *Z. Anorg. Allgem. Chem.*, **241**, 349 (1939).