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M_5X_3-Type Rare Earth Silicides and Germanides and Their Ternary Phases with Carbon

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M_5X_3-type rare earth silicides crystallize in Cr_5B_3-type tetragonal (La–Nd) and Mn_5Si_3-type hexagonal structures (Sm–Lu except Eu). The corresponding germanides are all (except Eu and Yb) of the Mn_5Si_3 type. Atomic parameters of the Mn_5Si_3-type structure were determined, and the interatomic distances were calculated. M_5X_3C ternary phases were obtained for the Mn_5Si_3-type compounds with the same hexagonal structure but different lattice size. Geometrical arguments show that carbon occupies the octahedral holes of the hexagonal lattice.

Introduction

The crystal structures of the rare earth silicides and germanides of general formula M_5X_3 (X = Si, Ge) have been reported in a number of works. Except for the La–Nd silicide group,[1,2] which has the Cr_5B_3-type tetragonal structure, all of the other compounds crystallize in the Mn_5Si_3-type hexagonal form.[3-13]

A characteristic of this latter structure is that small metalloids (C, B, N, etc.) can be inserted into it without structural effect. Many transition metal silicides and germanides have been investigated for such phases. Recent studies on Mo_5Si_3[14] have shown a possible stabilizing effect on the hexagonal structure of small amounts of carbon, nitrogen, or boron, these metalloids mainly occupying the octahedral holes formed by the hexagonal structure.

The aims of this work were the preparation of M_5X_3-type rare earth silicides and germanides, determination of the exact atomic parameters of the hexagonal lattice, and study of the effect of the addition of carbon on these compounds.

Experimental Section

Preparation.—Rare earth metal lumps (99.9% purity) were filed to powder in a drybox filled with helium gas. The rare earth powder was thoroughly mixed with silicon or germanium (both of 99.9% purity) and pressed into disks, which were heated in an induction furnace at 1500–1600° until they melted. Heating of the samples was carried out in tantalum boats and was usually complete in 5 min. Before heating started, the reaction site was repeatedly washed with argon in order to ensure a completely inert atmosphere during the reaction. The same procedure was used for preparing ternary phases with carbon.

Following preparation, the products were ground and analyzed by the X-ray diffraction method. The density of the compounds was determined by the pycnometric buoyancy method using water. X-Ray diffraction methods were used in the analysis of all of the reaction products.

X-Ray.—Thin layers of the powdered samples were spread out on microscopic slides coated with petrolatum and analyzed by the X-ray powder diffraction method, using a Philips diffractometer, the radiation being Ni-filtered Cu Kα (λ 1.5418 Å).

The unit cell was computed by a least-squares program[15] using an average of 20 reflections. Good agreement was obtained between observed and calculated $\sin^2 \theta$ values. The maximum error in the lattice constants was ± 0.01 Å.

Values of the experimental structure factors were determined from carefully measured intensities. Intensity data were recorded on a strip chart while scanning the reflections at 0.5° (2θ)/min. Each reflection was scanned twice, in increasing and decreasing angle directions. The areas of the peaks were measured with a planimeter. The structure factors were calculated by a computer program.[16]

Results

Lattice parameters and density values obtained for the M_5X_3-type rare earth and yttrium silicides and germanides are given in Tables I–III. These results show that the La–Nd silicides crystallize in Cr_5B_3-type tetragonal unit cells, while the other silicides (except Eu) and the whole series of germanides (except Eu and Yb) have the Mn_5Si_3-type hexagonal structure.

TABLE I
LATTICE CONSTANTS OF Cr_5B_3-TYPE SILICIDES

M_5Si_3	a, Å	c, Å
La_5Si_3	7.96	14.14
Ce_5Si_3	7.85	13.69
Pr_5Si_3	7.81	13.74
Nd_5Si_3	7.76	13.62

In Figure 1, the values of the lattice constants were plotted against the atomic number of the rare earths. The decrease toward the higher atomic numbers corresponds well with the lanthanide contraction of the rare earth elements.

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(15) M. H. Mueller, L. Heaton, and K. I. Miller, *ibid.*, **13**, 828 (1960).

(16) D. K. Smith, UCRL 7196, a Fortran program for calculating X-ray powder diffraction patterns, 1963.

TABLE II

LATTICE CONSTANTS AND DENSITIES OF Mn_5Si_3-TYPE SILICIDES

M_5Si_3	a, Å	c, Å	d, g/cm³ Obsd	d, g/cm³ Calcd
Sm_5Si_3	8.58	6.48	6.65	6.72
Gd_5Si_3	8.52	6.39	7.06	7.20
Tb_5Si_3	8.43	6.30	7.43	7.44
Dy_5Si_3	8.39	8.28	7.58	7.78
Ho_5Si_3	8.34	6.25	8.05	8.00
Er_5Si_3	8.29	6.22	8.30	8.22
Tm_5Si_3	8.26	8.18	8.46	8.46
Yb_5Si_3	8.25	6.28	8.35	8.52
Lu_5Si_3	8.24	6.13	8.71	8.84
Y_5Si_3	8.42	6.32	4.50	4.52

TABLE III

LATTICE CONSTANTS AND DENSITIES OF Mn_5Si_3-TYPE GERMANIDES

M_5Ge_3	a, Å	c, Å	d, g/cm³ Obsd	d, g/cm³ Calcd
La_5Ge_3	8.95	6.90	6.21	6.34
Ce_5Ge_3	8.84	6.72	6.67	6.70
Pr_5Ge_3	8.79	6.66	6.86	6.86
Nd_5Ge_3	8.74	6.60	7.03	7.14
Sm_5Ge_3	8.64	6.52	7.50	7.62
Gd_5Ge_3	8.57	6.43	7.96	8.16
Tb_5Ge_3	8.49	6.37	8.54	8.46
Dy_5Ge_3	8.44	6.33	8.67	8.76
Ho_5Ge_3	8.37	6.27	8.87	9.10
Er_5Ge_3	8.34	6.25	9.16	9.30
Tm_5Ge_3	8.30	6.22	9.31	9.50
Lu_5Ge_3	8.23	6.16	9.79	10.04
Y_5Ge_3	8.46	6.36	5.41	5.58

Density values of the different Mn_5Si_3-type silicides and germanides given in Tables II and III show good agreement with the calculations from crystal data, assuming the Mn_5Si_3-type structure with two formula units in the unit cell. The Mn_5Si_3-type unit cell has the space group D_{6h}^3-$P6_3/mcm$. In order to determine the x_I and x_{II} values for the $6g_I$ and $6g_{II}$ positions of this space group, intensity measurements were carried out for several compounds. The atomic parameters and their standard deviations were determined by a least-squares refinement program. The best agreement between the observed and calculated values of the intensities in the cases of the silicides and germanides was found for $x_I = 0.24 \pm 0.01$ and $x_{II} = 0.60 \pm 0.03$. In Table IV observed and calculated values of the intensities are listed for Gd_5Si_3, Er_5Si_3, and Lu_5Si_3 and for Ce_5Ge_3, Gd_5Ge_3, Er_5Ge_3, and Lu_5Ge_3.

Ternary phases of the M_5X_3-type compounds with varying amounts of carbon were prepared. The carbon added to the M_5X_3 compounds was in the atomic ratios of 0.5, 1.0, 1.5, and 2.0. In the case of Cr_5B_3-type silicides, addition of carbon caused disappearance of the tetragonal structure and a complex pattern was obtained. An exception was Nd_5Si_3, in which, after the addition of carbon, the Mn_5Si_3-type hexagonal structure was formed. When carbon was added to the Mn_5Si_3-type silicides and germanides, the hexagonal structure remained until the composition of M_5X_3C. At higher carbon content, the hexagonal phase begins to disappear, and at $M_5X_3C_2$ a completely different but undetermined structure was obtained. In Table V lattice constants of the ternary silicides and germanides are given. It should be pointed out that in the cases of the germanides of La, Tb, Lu, and Y, additional phases were obtained even at an $M_5Ge_3C_{0.5}$ composition. In the case of $La_5Ge_3C_{1.5}$, a well-defined single phase was formed with a body-centered cubic lattice.[17]

TABLE IV

RELATIVE INTEGRATED INTENSITIES OF DIFFERENT Mn_5Si_3-TYPE RARE EARTH SILICIDES AND GERMANIDES

	Gd_5Si_3		Er_5Si_3		Lu_5Si_3		Ce_5Ge_3		Gd_5Ge_3		Er_5Ge_3		Lu_5Ge_3	
hkl	I_{obsd}	I_{calcd}	I_{obsd}	I_{calcd}	I_{obsd}	I_{calcd}	I_{obsd}	I_{calcd}	I_{obsd}	I_{calcd}	I_{obsd}	I_{calcd}	I_{obsd}	I_{calcd}
100	[a]	0.0	[a]	0.0	[a]	0.0	[a]	1.0	[a]	0.8	[a]	0.6	[a]	0.6
110	6.0	6.9	6.2	7.3	5.6	7.5	[a]	1.2	[a]	1.7	[a]	2.0	[a]	2.3
200	12.6	17.7	23.3	18.9	18.9	19.0	3.9	5.7	5.6	7.0	5.6	8.4	5.8	8.4
111	17.3	24.4	25.9	25.8	20.8	26.6	2.9	4.4	3.8	6.2	4.5	7.5	5.8	8.4
002	[a]	3.7	[a]	3.5	[a]	3.4	6.4	7.4	6.8	6.7	6.3	6.4	3.7	6.1
102	19.9	28.4	28.2	29.0	23.1	29.1	10.5	16.8	13.5	18.0	18.8	18.9	19.6	19.5
210	23.9	28.5	28.3	28.8	36.6	29.2	22.8	21.8	19.6	22.9	20.4	23.5	21.1	23.9
211 112	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
300	17.3	18.6	13.9	18.5	18.6	18.7	19.6	18.9	14.5	19.0	18.5	19.1	19.3	19.0
202	[a]	0.4	[a]	0.4	[a]	0.3	[a]	2.3	[a]	1.9	[a]	1.7	[a]	1.6
220	[a]	1.3	[a]	1.3	[a]	1.3	[a]	0.8	[a]	0.9	[a]	0.9	[a]	0.9
212	[a]	0.1	[a]	0.1	[a]	0.1	[a]	0.2	[a]	0.2	[a]	0.2	[a]	0.2
310	[a]	0.4	[a]	0.4	[a]	0.4	[a]	1.3	[a]	1.1	[a]	1.1	[a]	1.0
221	[a]	1.3	[a]	1.3	[a]	1.3	[a]	2.5	[a]	2.3	[a]	2.2	[a]	2.1
311	[a]	0.1	[a]	0.0	[a]	0.0	[a]	2.2	[a]	1.7	[a]	1.5	[a]	1.3
302	[a]	2.6	[a]	2.7	[a]	2.8	[a]	0.5	[a]	0.7	[a]	0.8	[a]	0.9
113	[a]	4.5	[a]	4.7	[a]	4.8	[a]	0.9	[a]	1.2	[a]	1.5	[a]	1.6
400	[a]	3.1	[a]	3.1	[a]	3.2	[a]	1.8	[a]	1.9	[a]	2.0	[a]	2.1
222	12.6	15.1	19.0	15.2	17.4	15.3	11.0	11.6	8.5	12.0	11.1	12.2	13.1	12.4
312	6.3	7.7	6.9	7.9	5.6	8.0	[a]	3.0	[a]	3.5	[a]	3.8	[a]	4.1
320					21.2	18.8	[a]	1.1						
	15.3	18.8	15.1						12.8	17.1	15.9	17.1	17.4	17.1
213			9.4	8.2	7.9	8.4	13.1	16.1						
321	11.3	8.2							4.7	6.3	6.1	6.4	4.3	6.5
004			30.4	23.0			18.1	12.2						
402	35.8	35.3			42.7	35.9			26.5	26.4	23.8	26.9	24.5	27.4
							22.0	19.0						
410			11.4	12.5										

[a] Not observed.

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(17) I. Mayer and I. Shidlovsky, *J. Appl. Cryst.*, **1**, 194 (1968).

TABLE V

LATTICE CONSTANTS OF Ln_5Si_3C AND Ln_5Ge_3C COMPOUNDS

Compound	*a*, Å	*c*, Å	Compound	*a*, Å	*c*, Å
Nd_5Si_3C	8.66	6.60	Ce_5Ge_3C	8.84	6.72
Sm_5Si_3C	8.57	6.54	Pr_5Ge_3C	8.79	6.71
Gd_5Si_3C	8.52	6.46	Nd_5Ge_3C	8.74	6.68
Tb_5Si_3C	8.42	6.32	Sm_5Ge_3C	8.64	6.59
Dy_5Si_3C	8.38	6.36	Gd_5Ge_3C	8.57	6.52
Ho_5Si_3C	8.33	6.32	Tb_5Ge_3C	8.49	6.41
Er_5Si_3C	8.29	6.30	Dy_5Ge_3C	8.45	6.42
Tm_5Si_3C	8.26	6.26	Ho_5Ge_3C	8.37	6.38
Yb_5Si_3C	8.25	6.28	Er_5Ge_3C	8.34	6.37
Lu_5Si_3C	8.25	6.15	Tm_5Ge_3C	8.30	6.32
Y_5Si_3C	8.40	6.40	Lu_5Ge_3C	8.23	6.26
			Y_5Ge_3C	8.45	6.45

Discussion

Two types of crystal structure were obtained with the M_5X_3-type compounds: the Cr_5B_3-type tetragonal and the Mn_5Si_3-type hexagonal structures. Of these two structures, the Mn_5Si_3 type is the more densely packed. In this structure, layers containing both metals and nonmetals are present, while in the Cr_5B_3 structure the nonmetals are located between the metallic layers. The formation of one of these structures will therefore depend on the ratio R_M/R_X. When this ratio is larger than 1.37, the Cr_5B_3 structure forms, while at lower values (in our case beginning from Sm_5Si_3) the more densely packed Mn_5Si_3 structure is preferred. The critical importance of the value of R_M/R_X in the formation of one of the above structures was also proved in the case of the transition and alkaline earth silicides and germanides.[1,18]

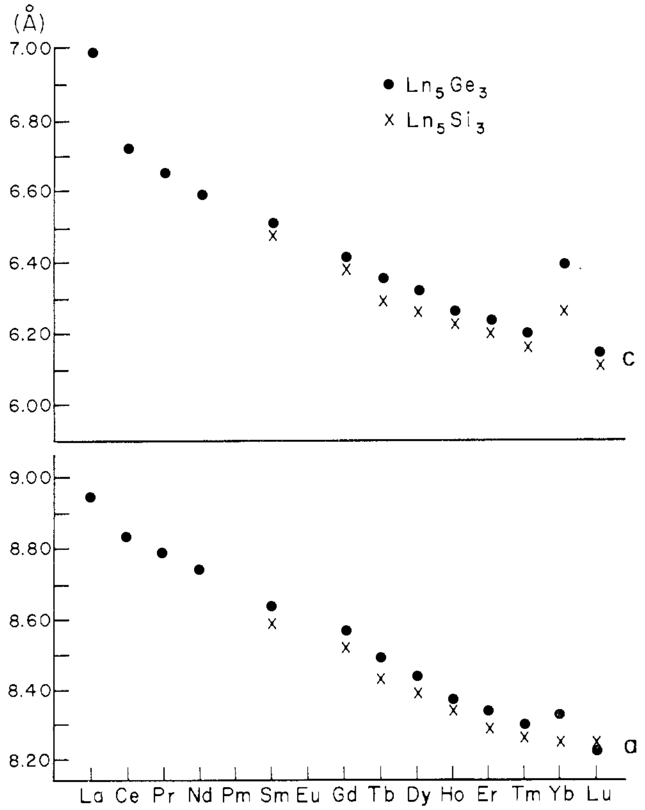

Figure 1.—Variation of the lattice constants *a* and *c* with the atomic number, for Ln_5Si_3 and Ln_5Ge_3 compounds.

TABLE VI

INTERATOMIC DISTANCES IN THE Mn_5Si_3-TYPE SILICIDES AND GERMANIDES (Å)[a]

	M(4d)			M(6g)					X		M(6g)–
Compound	6X	2M(4d)	6M(6g)	2X	1X	2X	2M(6g)	4M(6g)	2X	2X	M(6g)
Sm_5Si_3	3.08	3.24	3.71	2.99	3.1	3.5	3.6	3.84	3.7	4.5	5.2
Gd_5Si_3	3.05	3.19	3.67	2.97	3.1	3.5	3.5	3.79	3.6	4.5	5.2
Tb_5Si_3	3.02	3.15	3.63	2.94	3.0	3.4	3.5	3.75	3.6	4.5	5.1
Dy_5Si_3	3.01	3.14	3.62	2.92	3.0	3.4	3.5	3.73	3.6	4.4	5.1
Ho_5Si_3	2.99	3.12	3.60	2.91	3.0	3.4	3.5	3.71	3.6	4.4	5.1
Er_5Si_3	2.97	3.11	3.58	2.89	3.0	3.4	3.5	3.69	3.6	4.4	5.1
Tm_5Si_3	2.96	3.09	3.56	2.88	3.0	3.4	3.4	3.67	3.5	4.4	5.0
Yb_5Si_3	2.97	3.14	3.57	2.87	3.0	3.4	3.4	3.71	3.6	4.4	5.0
Lu_5Si_3	2.95	3.06	3.55	2.87	3.0	3.4	3.4	3.65	3.5	4.4	5.0
Y_5Si_3	3.02	3.16	3.63	2.94	3.0	3.4	3.5	3.75	3.6	4.5	5.1
La_5Ge_3	3.23	3.45	3.88	3.12	3.2	3.7	3.7	4.06	3.9	4.7	5.5
Ce_5Ge_3	3.18	3.36	3.82	3.08	3.2	3.6	3.7	3.97	3.8	4.7	5.4
Pr_5Ge_3	3.16	3.33	3.80	3.06	3.2	3.6	3.7	3.94	3.8	4.7	5.4
Nd_5Ge_3	3 14	3.30	3.77	4.04	3.2	3.6	3.6	3.91	3.7	4.6	5.3
Sm_5Ge_3	3.10	3.26	3.73	3.01	3.1	3.5	3.6	3.86	3.7	4.6	5.3
Gd_5Ge_3	3.07	3.22	3.70	2.99	3.1	3.5	3.6	3.82	3.6	4.5	5.2
Tb_5Ge_3	3.05	3.19	3.66	2.96	3.1	3.5	3.5	3.78	3.6	4.5	5.2
Dy_5Ge_3	3.03	3.16	3.64	2.94	3.0	3.4	3.5	3.76	3.6	4.5	5.1
Ho_5Ge_3	3.00	3.13	3.61	2.92	3.0	3.4	3.5	3.72	3.6	4.4	5.1
Er_5Ge_3	2.99	3.12	3.60	2.91	3.0	3.4	3.5	3.71	3.5	4.4	5.1
Tm_5Ge_3	2.97	3.11	3.58	2.89	3.0	3.4	3.5	3.69	3.5	4.4	5.1
Lu_5Ge_3	2.95	3.08	3.55	2.87	3.0	3.4	3.4	3.66	3.5	4.4	5.0
Y_5Ge_3	3.03	3.18	3.65	2.95	3.1	3.5	3.5	3.77	3.6	4.5	5.2

[a] Estimated mean deviations (Å): M(4d)–6X, ±0.05; M(4d)–2M(4d), ±0.01; M(4d)–6M(6g), ±0.05; M(6g)–2X, ±0.05; M(6g)–1X, ±0.2; M(6g)–2X, ±0.1; M(6g)–2M(6g), ±0.15; M(6g)–4M(6g), ±0.05; X–2X, ±0.25; X–2X, ±0.15; M(6g)–M(6g), ±0.14.

Attempts to prepare M_5X_3-type europium compounds were unsuccessful, and only Yb_5Si_3 was obtained in the case of ytterbium. A possible reason for these findings might be the divalency of Eu and Yb in the metallic

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(18) W. Jeitschko and E. Parthé, *Acta Cryst.*, **19**, 275 (1965).

state, with metallic radii much too large for the formation of one of the above structures.

In Table VI, bond lengths between the atoms in the Mn_5Si_3-type lattices are listed. The shortest distance between the metals is in the 4d position. Taking half these distances, one gets values equal to the covalent radii of these metals. On the other hand, the bond length between the metals in the 6g position equals the length known in the metallic state. It can therefore be concluded that the metal–metal bond in the lattice is of two different types, covalent in the c direction (4d), and of a metallic character in the layers normal to the c axis (6g).

Carbon atoms occupy the 0, 0, 0 and 0, 0, $^1/_2$ positions in the lattice and so are located in octahedral holes formed by the 6g metals. Table VII lists the diameters of the octahedral holes in the Mn_5Si_3-type lattice for the various binary compounds, as well as for the compounds containing carbon. The third column contains the effective radii of carbon in the ternary phases. The diameter of the octahedral holes (D) was calculated by the expression

$$D = r_{\text{oct}} - r_{\text{M}_{6g}}$$

where r_{oct} is the diagonal length between two metals in neighboring layers ($\sqrt{(1 - 2x_{\text{M}})^2c^2 + (0.5x)^2a^2}$), and $r_{\text{M}_{6g}}$ is the metal–metal distance in the 6g position ($1.732ax_{\text{M}}$).

From the values shown in Table VII it can be seen that the diameter of the octahedral holes decreases toward the heavier rare earth elements and that the effective radii of carbon (actually half the diameter of the octahedral hole) in these compounds have values falling between the values of the covalent radius (0.77 Å[19]) and atomic radius (0.914 Å[20]) of carbon.

These facts explain the increase of cell constant c in the ternary phases toward the heavier elements, this increase being necessary for the existence of octahedral holes with enough space for the location of the carbon atoms. Because of their size, the octahedral holes can accommodate one carbon atom only, in good agreement with our experimental results. According to the values of the estimated effective radii of the carbon, the bonds formed between the metals and carbon are essentially atomic with a slight covalent character.

TABLE VII

DIAMETERS OF THE OCTAHEDRAL HOLES (D) AND RADII OF CARBON (R_C) IN VARIOUS Mn_5Si_3-TYPE LATTICES

	M_5Si_3	M_5Si_3C		M_5Ge_3	M_5Ge_3C	
M	D, Å	D, Å	R_C	D, Å	D, Å	R_C
Ce	...	...	...	1.74	1.74	0.87
Pr	...	...	...	1.73	1.74	0.87
Nd	...	1.70	0.85	1.71	1.73	0.865
Sm	1.65	1.69	0.845	1.68	1.71	0.855
Gd	1.65	1.67	0.835	1.66	1.67	0.835
Tb	1.64	1.63	0.815	1.64	1.66	0.83
Dy	1.62	1.65	0.825	1.63	1.66	0.83
Ho	1.61	1.64	0.82	1.62	1.65	0.825
Er	1.60	1.63	0.185	1.61	1.65	0.825
Tm	1.60	1.62	0.81	1.60	1.64	0.82
Yb	1.62	1.62	0.81	...	...	...
Lu	1.57	1.58	0.79	1.59	1.62	0.81
Y	1.63	1.66	0.83	1.64	1.67	0.835

Stabilization of the hexagonal structure was obtained in the case of Nd_5Si_3 by filling the octahedral holes with carbon. In view of the ratio R_M/R_{Si}, Nd_5Si_3 would not crystallize in the Mn_5Si_3-type structure, but the addition of carbon in the octahedral holes and formation of Nd_6C bonds caused an energy gain, thus stabilizing the hexagonal phase.

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The Chloramination of Some Ditertiary Phosphines and Arsines

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The reactions of various phenyl-substituted ditertiary phosphines and arsines with chloramine have been shown to result in the formation of double-chloramination products in the presence of ammonia. In some cases, monochloramination products could be isolated using ammonia-free chloramine. The new compounds obtained have been characterized by their elemental analyses and infrared and proton magnetic resonance spectra.

Introduction

It has been well established that chloramine reacts with tertiary phosphines or arsines to form aminophosphonium or aminoarsonium chlorides.[1-4] Apart from the simple tertiary phosphines, reactions of chloramine with systems containing more than one phosphorus atom and more than one basic site, *e.g.*, bis(diphenylphosphino)amines[5] and bis(diphenylphosphino)hydrazines,[6,7] have been studied and it has been shown that chloramination always occurs on the phos-

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