Hexacoordinated Group-14 Elements with Phosphorus Donor Ligands: Syntheses and Structures of $Cl_2E[C(PMe_2)_2(SiMe_3)]_2$ (E = Si, Ge, Sn)

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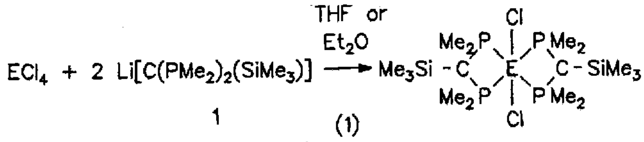
The group-14 tetrahalides ECl_4 (E = Si, Ge, Sn) react with two equivalents of $Li[C(PMe_2)_2(SiMe_3)]$ to give the *trans*-hexacoordinated complexes $Cl_2E[C(PMe_2)_2(SiMe_3)]_2$, which were characterized spectroscopically and by structure determinations in the solid state. The complexes were found to crystallize with or without tetrahydrofuran (THF) molecules, depending on the presence or absence of this solvent. In the case of the silicon complex, the structures of both crystal forms were determined, showing slightly different molecular structures of the complexes in the solid state. Without cocrystallized THF, $Cl_2Si[C(PMe_2)_2(SiMe_3)]_2$ has no crystallographically imposed molecular symmetry, while in the presence of THF its crystallographic symmetry is C_{2h} (2/*m*). The tin and germanium complexes were crystallized either with and without THF molecules, respectively, their crystal structures being isotypic with the respective ones of the silicon complex. In all cases, small amounts of the *cis*-hexacoordinated isomers were also observed in solution, but only in the case of the silicon complex, it was isolated in pure form. It rearranges to the *trans* isomer at ambient temperature. *trans*-$Cl_2Si[C(PMe_2)_3]_3$, *trans*-$Cl_2Si[C(PPh_2)_2(SiMe_3)]_2$ and *cis*-$Me_2Si[C(PMe_2)_2(SiMe_3)]_2$ were likewise obtained.

Higher coordination numbers (CN > 4) for group-14 elements have attracted considerable interest in recent years[1,2], especially in the case of silicon. Hexacoordination is quite common for tin(IV), whereas much less is known about germanium and silicon. It is commonly accepted that the tendency to form hexacoordinated species decreases in the sequence Sn > Ge > Si. This clearly holds for derivatives with polar bonds, and in fact, electronegative substituents (halogens and nitrogen- or oxygen-based ligands) are regarded as a prerequisite for the realization of higher coordination numbers. For tin, a variety of sulfur-based ligands (e.g. dithiocarbamates or -phosphinates) also seem appropriate, but unisobidentate bonding modes are typical[3]. No attempts were made to include phosphorus-based ligands in a comparative structural study[4]. On the other hand, diphosphinomethanide complexes of the group-14 elements in the +2 oxidation state reveal the potential of these ligands for hypervalency and subtle differences in the small polarity of the E−P bonds lead to a reversal of the sequence of high coordination numbers: Sn ≈ Si > Ge[5]. High coordination numbers with diphosphinomethanide ligands are well known for main-group-[6], transition-[7], and lanthanide-[8] metal centers. Therefore high coordination numbers of group-14 elements with diphosphinomethanide ligands in the normal +4 oxidation state may also be anticipated and allow a demonstration of the possibilities and border lines for hexacoordination with ligands of low electronegativity. Some of the results in this paper were documented earlier[9] and some preliminary accounts are given in refs.[10,11].

Results and Discussion

When element group-14 tetrahalides ECl_4 (E = Si, Ge, Sn) are allowed to react with 2 equivalents of $Li[C(PMe_2)_2(SiMe_3)]$ (**1**), in ethereal solvents, colorless crystalline solids **2a−c** are obtained after work-up with pentane [Eq. (1)].



(1)

2a−c

2b was already obtained earlier as a result of a redox reaction in the system Ge^{II}/diphosphinomethanide[10]. NMR data (^1H, ^{13}C, ^{31}P) suggest a chelating binding mode of two diphosphinomethanide ligands to the ECl_2 fragments, resulting in *trans*-hexacoordinated, rigid molecules in all cases. This is at variance with the results obtained by the reaction of $SiCl_4$ with two equivalents of $Li[HC(PMe_2)]_2$, where in the substitution product the diphosphinomethanide ligands are bound to silicon via carbon, exclusively leading to tetracoordinated silicon in this case[12]. Only one single resonance line is observed in the $^{31}P\{^1H\}$-NMR spectra of **2a**− **c** in the temperature range

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from −100 to 80 °C, indicating equivalence of all four phosphorus atoms. The germanium compound **2b** shows the highest coordination shift for the ^{31}P nuclei of the ligand: the chemical shifts range from $\delta = +51.31$ (**2a**) and $+59.93$ (**2c**) to $+76.42$ (**2b**). In no case ^{29}Si- or ^{119}Sn-NMR resonances for the coordination centers were observed. The non-observability of these nuclei when connected to chlorine ligands was found in several related cases[12]. This phenomenon might perhaps be due to the quadrupole influence of the chlorine nuclei, but since it is restricted to only a very limited number of cases, other influences might also contribute. Clearly this point needs further investigations.

The elemental analyses of **2a**−**c** are only in accord with formula **2a**−**c**, if diethyl ether was used as solvent or if the solvent THF was removed rigorously after the reaction was complete. Indeed, two crystal modifications of **2a** were obtained from pentane (or pentane/toluene mixtures), depending on the presence or absence of THF during the synthesis: **2aa** contains THF in the crystal lattice, its crystals being isomorphous to **2c** (space group: (*Cmca*), both being obtained from syntheses in THF. Complex **2ab**, on the other hand, crystallizes without solvent and is isomorphous to **2b** (space group: $P2_1/c$), both complexes being obtained from synthesis in diethyl ether. Thus, two pairs of isotypic crystal structures of three homologous complexes were obtained, which allow a particularly detailed structural study and comparison. The overall molecular structures of all four compunds, **2aa**, **2ab**, **2b**, and **2c** (Figures 1−4), are very similar. Two chelating silyl substituted diphosphinomethanide ligands are coordinated via their phosphorus atoms in the equatorial plane of a slightly distorted octahedron to the group-14 elements E = Si, Ge or Sn, the remaining two coordination sites (*trans* to each other) being occupied by the chlorine substituents forming a nearly linear Cl−E−Cl axis (Table 1). The distortions mainly arise from the double four-membered chelate ring formation at the metalloid centers. With cocrystallized THF molecules (**2aa** and **2c**) the crystal lattice formed is of noticeably higher symmetry than without solvent molecules (**2ab** and **2b**). Apparently, the presence of THF allows a much better packing of the individual molecules of **2a** which should also hold for the corresponding Ge and Sn complexes. As described above, of the Ge complex **2b** only crystals in the absence of THF were structurally investigated, however, while crystals of the Sn complex **2c** were only grown in the presence of THF. The higher symmetry of the THF containing crystal structures extends to the molecular symmetries as well, the molecules of **2aa** and **2c** having crystallographical D_{2h} symmetry in the solid state while **2ab** and **2b** have no crystallographic symmetry. Actually, the molecular symmetry of **2aa** and **2c** even comes close to D_{2d} if the methyl groups at Si are omitted. This requires the four-membered chelate rings and also the substituent geometry at the carbanionoide C atoms (C1/C2) to be essentially planar. In **2ab** and **2b** the lower symmetry of the crystal lattice apparently induces deviations from this highest possible symmetry resulting in minor conformational differences which are clearly seen by comparison between Figures 1 and 4, and Figures 2 and 3. As can be seen from the structural parameters of the two silicon complexes **2aa** and **2ab** listed in Table 1, these conformational differences do

Figure 1. Molecular structure of **2aa** in the crystal (ORTEP; displacement ellipsoids at the 50% level; H atoms omitted for clarity). symmetry code used: Atom': $x, -y, 1-z$; Atom'': $1-x, -y, 1-z$; Atom''': $1-x, y, z$

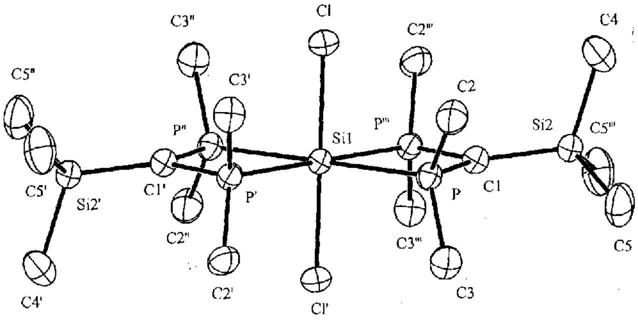


Figure 2. Molecular structure of **2ab** in the crystal

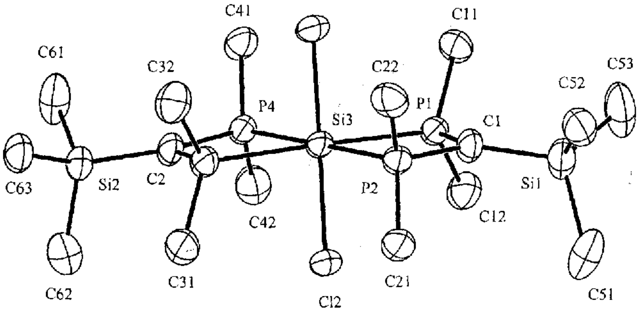


Figure 3. Molecular structure of **2b** in the crystal

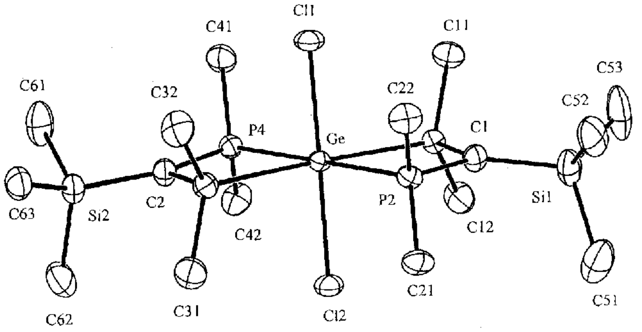
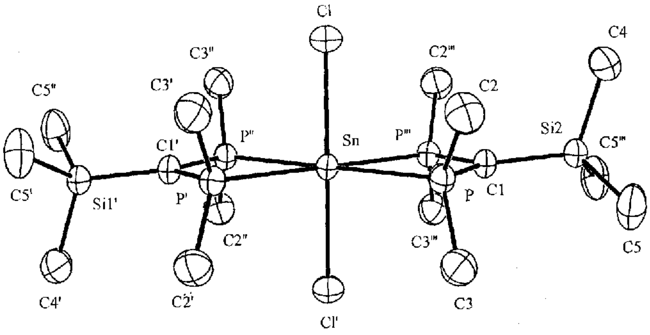


Figure 4. Molecular structure of **2c** in the crystal. (For the symmetry code used see caption of Figure 1)



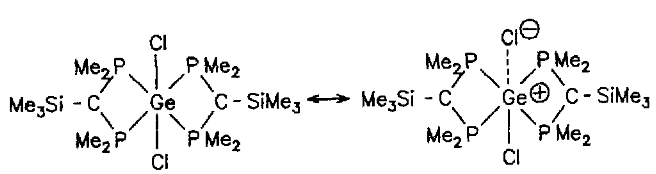
not lead to noticeable differences between bonding parameters (distances and angles), however. Only a few structural parameters of hexacoordinated Si, Ge, and Sn complexes are at hand for comparison with those in complexes **2a**–**2c**: in *trans*-(3,5-$Me_2C_6H_3CH_2PMe_2)_2SiCl_4$ d(Si–P) = 2.359(1) and d(Si–Cl) = 2.205(1)/2.212(1) Å were found[4]. The former value compares well with d(Si–P) in **2aa**/**2ab** and with those of tetracoordinated Si complexes (2.20–2.33 Å)[12–14], whereas the Si–Cl bonds are shorter than in **2aa**/**2ab**.

Table 1. ^{31}P-NMR shifts and some bond lengths [Å] and angles [°] in the molecular structures of **2aa**, **2ab**, **2b**, and **2c** in the crystal (with esd.'s in units of the last significant figure in parentheses)

E	Si **2aa**	Si **2ab**	Ge **2b**	Sn **2c**
$\delta^{31}P$	+51.31	+51.31	+76.42	+59.93
E-P	2.348(1)	2.339(2)/2.345(2) 2.340(2)/2.339(2)	2.410(1)/2.412(1) 2.411(1)/2.415(1)	2.591(1)
E-Cl	2.272(1)	2.286(2)/2.265(2)	2.386(1)/2.434(1)	2.532(1)
P-C[a]	1.739(3)	1.737(5)/1.724(6) 1.721(6)/1.734(5)	1.727(5)/1.725(4) 1.734(4)/1.722(4)	1.736(2)
Cl-E-Cl	180.0	179.5(1)	178.7(1)	180.0
P-E-P (ring)	71.2(1)	71.3(1)	69.9(1)/69.8(1)	66.1(1)
P-C[a]-P	103.6(1)	104.1(3)/104.2(3)	106.3(2)/106.1(2)	109.0(2)
Sum of angles at C1/C2	359.6(2)	359.3(3)/359.6(3)	359.4(3)/359.8(3)	359.8(2)

[a] Ylidic C atom.

Close inspection of the E–Cl bonds in complexes **2a**–**2c** reveals a peculiar trend of germanium to adopt lower coordination numbers than both its homologous counterparts silicon and tin. In relation to normally assumed covalent radii for Si/Ge/Sn and Cl atoms, the E–Cl bonds of the Ge complex **2b** are longer than in the other two cases and, moreover, are found to be noticeably different [2.386(1)/2.434(1) Å]. This must be interpreted as a pronounced tendency of the Ge complex towards a fivefold coordination (formulas **2b**–**A**, **B**). This beginning formation of an ion pair with cationic germanium is paralleled by the ^{31}P-NMR shifts (Table 1). In **2b** the resonance of the phosphorus nucleus is noticeably shifted to lower field, indicating an appreciably stronger cationic character.



2b–A 2b–B

Similar observations, i.e. a sequence Sn ≈ Si > Ge for the tendency to form higher coordination numbers in compounds of group-14 elements involving bonds with low polarity (as, e.g. E–P bonds) were made with the dimethyl derivatives of **2a**–**c**[15] as well as in diphosphinomethanide complexes of group-14 elements in the oxidation state +2[5]. This deviation from expectation was explained by differences in the polarity of the E–P bonds: germanium as the most electronegative element in this series forms the least polar bonds to phosphorus.

Some other structural features deserve further comment:

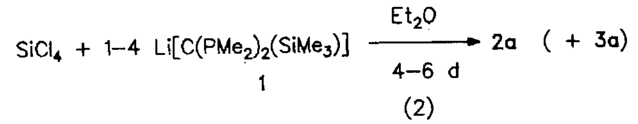
(a) the (ylidic) P–C bond lengths within the chelate rings are essentially equal in all four compounds (ca. 1.73 Å) and reflect the ylidic character of these bonds, as it was found earlier in similar compounds[11].

(b) the angles P–E–P within the chelate rings decrease in the order Si (**2aa**, **2ab**) > Ge (**2b**) > Sn (**2c**), reflecting the increasing E–P bond lengths.

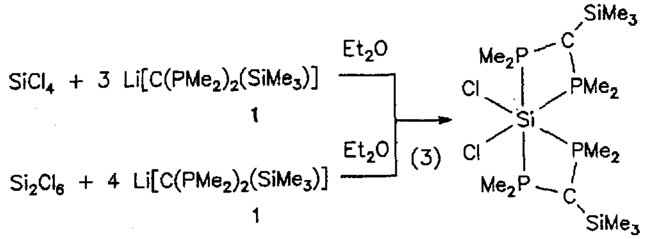
(c) Likewise, the increasing P–C–P angle ("bite angle") from E = Si to Sn reflects the increasing size of E.

Quite remarkable is the trans arrangement of the two chlorine atoms. In most bis-chelate element(IV) dihalide hexacoordinate complexes, the halogen atoms have a *cis* arrangement[1]. Thus, the question arises, whether the compounds described here may also adopt a *cis* arrangement. Indeed, ^{31}P-NMR spectra of **2a**–**c** at room temperature show additional lines of very low intensity, which can be attributed to an AA'BB' spin system expected for the *cis* isomers **3a**–**c** (Si: 4%, Ge: 5%, Sn: 2%, approximately). Upon cooling, the intensity of these signals increases considerably (for Si at −100 °C: **2a**/**3a** ≈ 1:1). It is not clear, however, whether this is due to a true predominance of the *cis* isomers in an equilibrium with the *trans*-species at low temperature, since the latter precipitate on cooling due to their low solubility. As a consequence of the inhomogeneity of these samples, a considerable line broadening of the signals prevents the extraction of reliable NMR parameters from these spectra. An alternative way to prepare *cis* complexes was therefore desirable.

Besides minor amounts of **3a** the disubstitution product **2a** was the only product of the reaction between $SiCl_4$ and $Li[C(PMe_2)_2(SiMe_3)]$ regardless of stoichiometry and after prolonged reaction times (4–7 days).



$$\underset{}{SiCl_4} + 1\text{–}4\ \underset{\mathbf{1}}{Li[C(PMe_2)_2(SiMe_3)]} \xrightarrow[4\text{–}6\ d]{Et_2O} \mathbf{2a}\ \ (+\ \mathbf{3a}) \qquad (2)$$

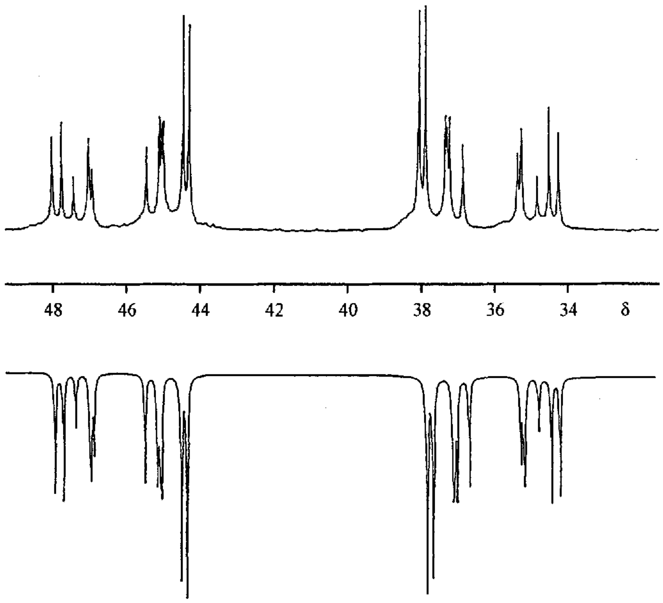


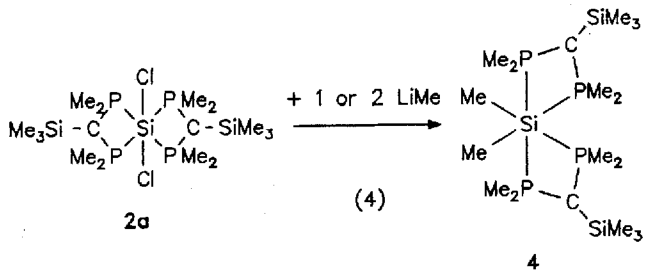
3a

Obviously, the second substitution step is faster than the first, but a third substitution step is not possible due to the low reactivity of **2a**. If a 3:1 reaction is carried out under normal reaction times (10 h) or, alternatively, Si_2Cl_6 is used instead of $SiCl_4$, the only product isolated is the *cis* isomer **3a**, essentially free of **2a**. Compound **3a** forms a yellow crystalline solid (from pentane), but crystals large enough for X-ray crystallography could not be obtained because it rearranges at room temperature within several days to the equilibrium mixture **2a**/**3a** = 95:5, from which only crystals of

2a can be grown[16]. Nevertheless, the ^{31}P-NMR spectrum of pure **3a** can be recorded in this way. The observed AA'BB' spin system may be reproduced computationally (Figure 5) and reveals a remarkably high $^{2}J(P_AP_B)$ coupling constant of 392 Hz. Whereas **3a** may be readily reduced to the silicon(II) derivative $Si[C(PMe_2)_2(SiMe_3)]_2$[5c], **2a** is essentially inert to reduction. Though the latter is also inert to further substitution reactions with lithium diphosphinomethanide **1**, it very slowly reacts at room temperature with methyllithium. Regardless of the stoichiometry, the *cis*-hexacoordinated dimethyl derivative **4** was obtained [Eq. (4)].

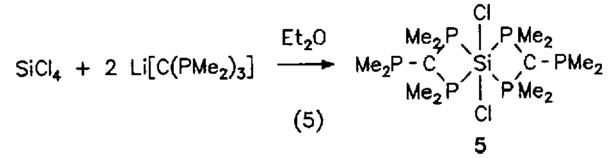
Figure 5. Observed (top) and calculated (bottom) $^{31}P\{^{1}H\}$-NMR spectrum of **3a** in [D$_8$]toluene





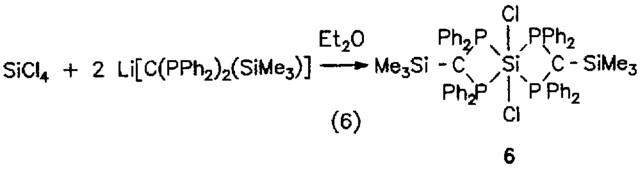
Complex **4** was also isolated on an independent route and is described in a subsequent paper[15]. Nevertheless, all these observations confirm, that the high coordination number in **2a** reduces the Si−Cl reactivity considerably compared to tetracoordinated silicon compounds. This is at variance with observations with other neutral hexaccoordinated silicon(IV) compounds[1] and underlines the importance of these investigations of highly coordinated element group-14 species with element-donor bonds of low polarity.

The single line observed in the ^{31}P-NMR spectrum of **2a** (see above) in principle may be attributed to a rigid *trans*-octahedral structure or to very rapid exchange processes. Though no indication of this kind of fluctuation was observed by temperature variation, an independent confirmation of the structural rigidity was obtained by the synthesis of **5**, which was isolated as a colorless solid [Eq. (5)].



If any dissociative exchange process would occur, the exocyclic phosphino groups should get involved, as often observed in other triphosphinomethanide complexes (see for examples ref.[5a,b]). The ^{31}P-NMR spectrum of **5** at room temperature has the appearance of an $(A_2B)_2$ spin system (one triplet resonance at $\delta P_A = +49.42$, one quintuplet resonance at $\delta P_B = -51.21$, "J" = 16.1 Hz), which excludes any rapid exchange process. Thus, it may be concluded, that the hexacoordination of silicon in compounds **2a** and **5** is preserved in solution.

It might be anticipated, that by decreasing the donor ability of the phosphino groups electronically and by steric hindrance, equilibria between hexa- and tetracoordination might be induced. Therefore, the *P*-phenyl complex **6** was synthesized according to Eq. (6).



The yellow complex **6** obtained shows a single ^{31}P-NMR resonance at $\delta P = +62.31$ (in $C_6D_5CD_3$), which is temperature independent. The difference in coordination shifts of **6** and **2a** ($\Delta\delta = 11.00$) corresponds roughly to that ($\Delta\delta = 18.84$) between $Si[C(PMe_2)_2(SiMe_3)]_2$ ($\delta P = -5.22$)[5c] and $Si[C(PPh_2)_2(SiMe_3)]_2$ ($\delta P = +13.62$)[9b] and allows an assignment of a rigid, hexacoordinated *trans* structure also to **6**.

In conclusion, hexacoordination of group-14 elements Si, Ge, and Sn with up to four phosphorus donor ligands is feasible. These compounds are quite robust, both thermally and chemically. Subtle structural and spectroscopic differences reveal the specific nature of these compounds with bonds of low polarity, which is at variance with "normal" hexacoordinated species of these elements and mirrors, the order of electronegativity Sn ≈ Si < Ge.

Experimental

A. Synthesis of Compounds

All operations were performed under dry nitrogen and with thoroughly dried solvents and glassware. *Caution:* All reagents and products are extremely air sensitive. Standard vacuum-line techniques were used. $Li[C(PMe_2)_2(SiMe_3)]$[17], $Li[C(PMe_2)_3]$[17], and $Li[C(PPh_2)_2(SiMe_3)] \times$ TMEDA[18] were prepared according to literature procedures, all other reagents were purchased from commercial sources. − NMR: JEOL JNM GX 400, 20°C, [D$_6$]benzene unless stated otherwise. Chemical shifts refer to Me_4Si (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). "t", "quint", "sept", "m" denote symmetric multiplets of complex spin systems with a deceptively simple appearance with N = distance between the two outermost lines. – MS: Varian MAT 311A. – Melting points (uncorrected): Measured in sealed capillaries and are uncorrected.

For clarity and consistency, the nomenclature of compounds follows that in numerous previous papers and is at variance with IUPAC nomenclature recommendations of 1990; e.g., the term "phosphinomethanide" is used instead of "phosphanylmethanide" throughout the paper.

trans-Dichlorobis[bis(dimethylphosphino)(trimethylsilyl)methanido-P,P']silane (**2a**). – *a)* **2ab** *(Solvate-Free Compound):* To a solution of 500 mg (2.33 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ in 40 ml of diethyl ether 200 mg (1.17 mmol) of $SiCl_4$ was added by means of a pipette at $-78\,°C$ with stirring. The mixture was allowed to warm up to room temp. and stirred for another 10 h. After removal of the solvent, the residue was extracted four times with each 40 ml of pentane. The combined pentane solutions were reduced to a volume of 60 ml and on slow cooling colorless needles precipitated from the solution. Yield: 570 mg (95%), m.p. 153 °C. – MS (EI, 70 °C); *m/z* (%): 369 (1.5) $[M^+ - 2\,Cl]$, 305 (20) $[M^+ - C(PMe_2)_2(SiMe_3)]$, 147 (18) $[HC(PMe_2)_2(SiMe_3)^+]$, 73 (100) $[SiMe_3^+]$. – ^1H NMR: $\delta = 1.55$ ("quint", $N = 8.0$ Hz, 24 H, PMe_2), 0.38 (s, 18 H, $SiMe_3$); $^{13}C\{^1H\}$ NMR: $\delta = 19.21$ ("quint", $N = 10.7$ Hz, PMe_2), 3.42 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR: $\delta = +51.31$ [s, ^{29}Si sat.: $^1J(SiP) = 89.9$, $^2J(SiP) = 11.5$ Hz]. – $C_{16}H_{42}Cl_2P_4Si_3$ (518.64): calcd. C 37.41, H 8.24, Cl 13.80; found C 37.02, H 8.11, Cl 13.55.

b) **2aa** *(THF Solvate of* **2a***):* The same procedure as for **2ab** was used, but Et_2O was replaced by THF as solvent. Colorless crystals were obtained from pentane/toluene. – $C_{20}H_{50}Cl_2OP_4Si_3$ (590.75): calcd. C 40.66, H 8.53, Cl 12.00; found C 38.82, H 8.79, Cl 10.69.

trans-Dichlorobis[bis(dimethylphosphino)(trimethylsilyl)methanido-P,P']germane (**2b**): The same procedure as for the synthesis of **2ab** was used. Reagents: 560 mg (2.62 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ and 0.28 ml (1.31 mmol) of $GeCl_4$. – Yield: 190 mg (26%) of a yellow solid, m.p.: 173–177 °C. – $^{31}P\{^1H\}$ NMR: $\delta = +76.40$ (s). – $C_{16}H_{42}Cl_2GeP_4Si_2$ (558.07): calcd. C 34.44, H 7.58, Cl 12.71; found C 33.89, H 7.18, Cl 12.97.

trans-Dichlorobis[bis(dimethylphosphino)(trimethylsilyl)methanido-P,P']stannane · THF (**2c**): The same procedure as for the preparation of **2aa** was used. Reagents: 1.12 g (5.25 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ and 0.30 ml of (2.61 mmol) $SnCl_4$. – Yield: 1.08 g (68%) of a yellow solid, m.p.: 187–190 °C. – $^{31}P\{^1H\}$ NMR: $\delta P = +59.92$ (s). – $C_{20}H_{50}Cl_2OP_4Si_2Sn$ (676.28): calcd. C 35.52, H 7.45, Cl 10.48; found C 43.92, H 7.22, Cl 9.75.

cis-Dichlorobis[bis(dimethylphosphino)(trimethylsilyl)methanido-P,P']silane (**3a**). – *a) From $SiCl_4$ and $Li[C(PMe_2)_2(SiMe_3)]$:* To a solution of 660 mg (3.08 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ in 40 ml of diethyl ether 170 mg (1.03 mmol, 0.12 ml) of $SiCl_4$ at $-78\,°C$ with stirring. The further procedure followed that of **2ab**. Small yellow crystals were obtained. Yield: 440 mg (87%). – $^{31}P\{^1H\}$ NMR: AA'BB' spin system, $\delta P_{A/A'} = 45.14$, $\delta P_{B/B'} = +36.15$, $J_{AA'} = 35.1$, $J_{BB'} = 16.3$, $J_{AB} = J_{A'B'} = 392.2$, $J_{AB'} = J_{A'B} = 120.2$ Hz.

b) From Si_2Cl_6 and $Li[C(PMe_2)_2(SiMe_3)]$: To a solution of 1.0 g (4.66 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ in 30 ml of THF 0.20 ml (1.17 mmol) of Si_2Cl_6 was added at $-78\,°C$ with stirring. After warming up the mixture to room temperature, stirring was continued for another 20 h. The solvent was removed in vacuo and the residue extracted twice with 30 ml of pentane each. After removal of the pentane, a yellow solid was obtained (Yield not determined). – $C_{16}H_{42}Cl_2P_4Si_3$ (518.64): calcd. C 37.41, H 8.24, Cl 13.80; found C 37.80, H 8.39, Cl 12.73.

cis-Bis[bis(dimethylphosphino)(trimethylsilyl)methanido-P,P']-dimethylsilane (**4**): To a solution of 600 mg (1.16 mmol) of **2ab** in 40 ml of diethyl ether 1.55 ml (2.32 mmol) of 1.5 N $LiCH_3/Et_2O$ was added at $-78\,°C$ with stirring. The mixture was allowed to warm up to room temp. and stirred for another 10 h. After removal of the solvent, the residue was extracted twice with 20 ml of pentane each. After removal of the pentane a yellow crystalline solid remained. Its NMR are identical with those of an authentic sample[15]. Yield: 470 mg (86%).

trans-Dichlorobis[(dimethylphopshino)methanido-P,P']silane (**5**): To a solution of 500 mg (2.47 mmol) of $Li[C(PMe_2)]_3$ in 40 ml of diethyl ether 0.14 ml (1.24 mmol) of $SiCl_4$ was added at $-78\,°C$ with stirring. The same procedure as for the preparation of **2ab** was used. Thus a white solid was obtained. Yield: 540 mg (89%), m.p. 173 °C. – MS (EI, 70 °C); *m/z* (%) = 488 (11) $[M^+]$, 453 (18) $[M^+ - Cl]$, 293 (40) $[M^+ - C(PMe_2)_3]$. – NMR: ^1H: $\delta = 1.63$ ["sept", $N = 58.4$ Hz, 24 H, PMe_2 (endo)], 1.22 ["m", $N = 28.2$ Hz, 12 H, PMe_2 (exo)]; $^{13}C\{^1H\}$: $\delta = 19.31$ ["m", $N = 70.0$ Hz, PMe_2 (endo)], 13.62 [s, PMe_2 (exo)]; $^{31}P\{^1H\}$: $\delta = +49.42$ ["t", $N = 16.1$ Hz, PMe_2 (endo)], -51.10 ["quint", $N = 16.1$ Hz, PMe_2 (exo)]. – $C_{14}H_{36}P_6SiCl_2$ (489.28): calcd. C 34.37, H 7.42, Cl 14.49; found C 31.87, H 7.20, Cl 15.97.

trans-Dichlorobis[bis(diphenylphosphino)(trimethylsilyl)methanido-P,P']silane (**6**): To a solution of 800 mg (1.38 mmol) of $Li[C(PPh_2)_2(SiMe_3)] \times TMEDA$ in 50 ml of diethyl ether 0.08 ml (0.69 mmol) of $SiCl_4$ was added at $-78\,°C$ with stirring. The same procedure as for the preparation of **2ab** was used and a yellow solid was obtained. Yield: 530 mg (76%). – ^1H NMR: $\delta = 7.2-7.8$ (m, 40 H, PPh_2), 0.32 (s, 18 H, $SiMe_3$); $^{13}C\{^1H\}$ NMR: $\delta = 137.3-141.5$ (m, PPh_2), 5.32 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR: $\delta = +62.30$ (s). – $C_{56}H_{58}P_4Si_3Cl_2$ (1010.14): calcd. C 66.59, H 5.79, Cl 7.02; found C 64.23, H 5.81, Cl 7.98.

B. X-ray Structure Determination

Suitable single crystals were grown from solution (**2aa**, **2c**: pentane/THF; **2ab**, **2b**: pentane) and examined directly with the diffractometer (**2aa**, **2ab**, **2b**: Syntex-P2$_1$; **2c**: Enraf-Nonius CAD4; Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator). Crystal data and numbers pertinent to data collection and structure refinement are collected in Table 2. Crystals containing THF (**2aa**, **2c**) were found to be isomorphous, space group *Cmca* (No. 64). Those crystallized in the absence of THF (**2ab**, **2b**) also were isomorphous, space group $P2_1/c$ (No. 14). The metrical lattice symmetry was checked for higher symmetry by cell reduction programs (DELOS[19], LePAGE[20]). The integrated intensities measured with the diffractometer were corrected for Lorentz and polarization effects, those of **2ab** and **2c** also for intensity decay during data collection (**2ab**: −7%; **2c**: −4.7%). The intensities of **2b** and **2c** were also corrected empirically for absorption by means of ψ-scans in steps of 10° around the diffraction vectors of 4 (**2b**) or 9 (**2c**) reflexions near $\chi = 90°$ which served to evaluate the relative transmissions (**2b**: 0.74–1.00; **2c**: 0.89–1.00). The structures were solved with direct methods (SHELX-86[21], SHELX-76[22]) and completed by Fourier syntheses. Major difficulties arose in the location and refinement of the additional THF molecules present in the crystals of **2aa** and **2c**. They are located around a site with crystallographic $2/m$ symmetry and found to be heavily disordered. They were modelled as 3 C atoms with split occupancy amounting to approximately 1 THF molecule per complex. Calculation of density and absorption coefficient was also based on this composition. Their refinement was performed with isotropic displacement parameters. All other non-H atoms were refined with anisotropically. Hydrogen atoms in **2aa** and **2c** were included as fixed atom contri-

Table 2. Crvstal structure data of **2aa. 2ab. 2b**. and **2c**

	2aa	**2ab**	**2b**	**2c**
Formula	$C_{16}H_{42}Cl_2P_4Si_3\cdot C_4H_8O$	$C_{16}H_{42}Cl_2P_4Si_3$	$C_{16}H_{42}Cl_2GeP_4Si_2$	$C_{16}H_{42}Cl_2P_4Si_3Sn\cdot C_4H_8O$
M_r	585.68	513.572	558.08	676.284
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	*Cmca* (No. 64)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Cmca* (No. 64)
a [Å]	13.821(2)	10.521(1)	10.578(1)	13.816(2)
b [Å]	12.050(2)	11.730(1)	11.723(1)	12.156(2)
c [Å]	19.309(3)	23.666(3)	23.721(3)	19.859(2)
β [°]	90.	95.02(1)	94.97(1)	90.
V [Å^3]	3215.8	2909.4	2930.5	3335.3
Z	4	4	4	4
d_{calcd} [g/cm^3]	1.210	1.172	1.265	1.347
μ(Mo-K_α) [cm^{-1}]	5.2	5.6	15.1	12.0
F(000) [e]	1256	1096	1168	1400
T [°C]	-40	-50	-45	-35
Scan	ω	ω	ω	$\vartheta/2\vartheta$
Scan width (in ω)	0.8	0.8	0.9	$0.9 + 0.35 \tan \vartheta$
$(\sin \vartheta/\lambda)_{max}$ [Å^{-1}]	0.596	0.572	0.572	0.638
hkl range	±16, +14, +22	+12, +13, ±27	+12, +13, ±27	+17, +15, -25 (+ Friedel equiv.)
Refl. (measd./unique)	3222/1489	5075/4556	5117/4542	4086/1897
R_{int}	0.026	0.054	0.046	0.011
Refl. obs. [$F_o \gtrsim 4.0\,\sigma(F_o)$]	1279	3298	3732	1682
H atoms (found/calcd.)	9/2	30/12	34/8	9/2
Parameters ref.	74	268	268	74
R [a]	0.050	0.059	0.040	0.032
wR [b]	0.055	0.056	0.046	0.038
$\Delta\rho_{fin}$(max/min) [e/Å^3]	+0.76/-0.74	+0.65/-0.33	+0.42/-0.48	+0.88/-0.83

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – [b] $wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

butions into structure factor calculations, those in **2ab** and **2b** were refined together with the attached methyl carbon atoms as rigid groups with fixed isotropic displacement parameters. Refinement was carried out on F with all structure factors with $F_o > 4\sigma(F_o)$. The function minimized was: $\Sigma w(|F_o|-|F_c|)^2$ with $w = 1/\sigma^2(F_o)$ (SHELX-76)[22]. Program used for the molecular drawings: ORTEP[23]. Further crystal structure data are available[24].

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[1] [1a] C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371. – [1b] V. E. Shklover, Yn. T. Struchkov, M. G. Voronkov, *Russ. Chem. Rev.* **1989**, *53*, 3.

[2] [2a] D. Kummer, S. G. Chaudry, W. Depmaier, G. Mattern, *Chem. Ber.* **1990**, *123*, 2241 and cited literature. – [2b] R. Tacke, J. Becht, A. Lopez-Mras, J. Sperlich, *J. Organomet. Chem.* **1993**, *446*, 1 and cited literature.

[3] See e.g.: [3a] C. Silvestru, I. Haiduc, *J. Organomet. Chem.* **1989**, *365*, 83 and cited literature; [3b] R. K. Chadha, J. E. Drake, A. B. Sakar, *Inorg. Chim. Acta* **1988**, *143*, 31 and cited literature.

[4] Phosphane coordination to $SiCl_4$ was observed already leading to hexacoordinated *trans* complexes $(R_3P)_2SiCl_4$: K. Issleib, H. Reinhold, *Z. Anorg. Allg. Chem.* **1962**, *314*, 113; G. A. Ozin, *Chem. Commun.* **1969**, 104. d(Si–P) = 2.26(1) Å in *trans*-$(Me_3P)_2SiCl_4$: H. E. Blayden, M. Webster, *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 703. Due to the low quality of the structure determination this value is only of limited reliability. d(Si–P) = 2.359(1) Å, d(Si–Cl) = 2.205(1)/2.212(1) Å in *trans*-(3,5-$Me_2C_6H_3CH_2PMe_2)_2SiCl_4$: G. Müller, M. Waldkircher, unpublished results.

[5] [5a] H. H. Karsch, A. Appelt, G. Müller, *Organometallics* **1986**, *5*, 1664. – [5b] H. H. Karsch, B. Deubelly, G. Hanika, J. Riede, G. Müller, *J. Organomet. Chem.* **1988**, *344*, 153. – [5c] H. H. Karsch, U. Keller, S. Gamper, G. Müller, *Angew. Chem.* **1990**, *102*, 297; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 295.

[6] For example in $Al[(Me_2P)_2C(SiMe_3)]_3$: H. H. Karsch, A. Appelt, J. Riede, G. Müller, *Organometallics* **1987**, *6*, 316.

[7] For example in $CpZr[(Me_2P)_2C(SiMe_3)]_3$: H. H. Karsch, M. Kawecki, A. Schier, not yet published.

[8] For example in $Li[La\{(Me_2P)_2C(SiMe_3)\}_4]$: H. H. Karsch, G. Ferazin, H. Koijman, O. Steigelmann, A. Schier, P. Bissinger, W. Hiller, *J. Organomet. Chem.* **1994**, *482*, 151.

[9] [9a] B. Deubelly, Dissertation TU München **1988**. – [9b] U. Keller, Dissertation TU München **1992**.

[10] H. H. Karsch, B. Deubelly, J. Riede, G. Müller, *Angew. Chem.* **1987**, *99*, 703; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 673.

[11] H. H. Karsch, *Russ. Chem. Bull.* **1993**, *42*, 1937.

[12] See for example: H. H. Karsch, R. Richter, B. Deubelly, A. Schier, M. Paul, M. Heckel, K. Angermaier, W. Hiller, *Z. Naturforsch. B: Chem. Sci.* **1994**, *49*, 1798.

[13] H. H. Karsch, K. Zellner, G. Müller, *Organometallics* **1991**, *10*, 2884.

[14] W. S. Sheldrick, *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport) John Wiley & Sons, **1989**, Chapter 3, p. 260.

[15] H. H. Karsch, U. Keller, B. Deubelly, F. Bienlein, G. Baumgartner, G. Müller, P. Bissinger, M. Heckel, *Chem. Ber.*, submitted.

[16] An excess of lithium diphosphinomethanide in the solution lowers the conversion rate considerably – this is the reason for the stoichiometry in Eq. (2), but the effect is not yet understood.

[17] H. H. Karsch, A. Appelt, B. Deubelly, K. Zellner, J. Riede, G. Müller, *Z. Naturforsch. B: Chem. Sci.* **1988**, *43*, 1416.

[18] H. H. Karsch, G. Grauvogl, P. Mikulcik, P. Bissinger, G. Müller, *J. Organomet. Chem.* **1994**, *465*, 65.

[19] H. Zimmermann, H. Burzlaff, *Z. Kristallogr.* **1985**, *170*, 241.

[20] Y. LePage, *J. Appl. Crystallogr.* **1982**, *15*, 255.

[21] G. M. Sheldrick in *Crystallographic Computing 3*, (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Oxford University Press **1985**, p. 175.

[22] G. M. Sheldrick, *SHELX-76, Program for Crystal Structure Determination*, University of Cambridge, Cambridge, England, **1976**.

[23] C. K. Johnson, *ORTEP-II*, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, **1976**.

[24] Further crystal structure data, including complete tables of atomic parameters and observed and calculated structure factors may be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the depository number CSD-59243, the names of the authors, and the journal citation.

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