Hexacoordinated Group-14 Elements with Phosphorus Donor Ligands: Syntheses and Structures of $Me_2E[C(PMe_2)_2(SiMe_3)]_2$ (E = Si, Ge, Sn)

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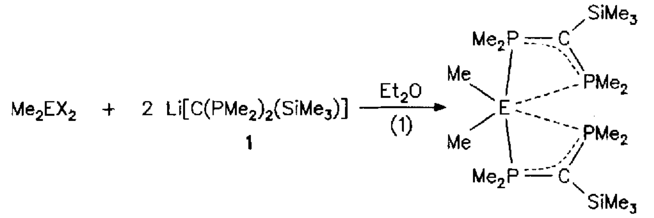
The dimethyl group-14 element dihalides Me_2EX_2 (E = Si, Ge, Sn; X = Cl or Br) react with two equivalents of $Li[C(PMe_2)_2(SiMe_3)]$ to give the *cis*-hexacoordinated complexes $Me_2E[C(PMe_2)_2(SiMe_3)]_2$ (E = Si: **2a**, E = Ge: **2b**, E = Sn: **2c**), which were characterized spectroscopically and by means of X-ray structure determinations. Whereas **2a** and **2b** are isotypic and crystallize in the space group $P2_1/c$, **2c** crystallizes in the space group $C2/c$ with crystallographic $C_2(2)$ molecular symmetry. In all cases the diphosphanylmethanide ligands bind in an unisobidentate fashion. For compound **2c**, this still can be attributed to the *trans* influence of the methyl group, but in **2a** and **2b** clearly borderline cases between hexa- and tetracoordination are found. Compound **2b** (E = Ge) is much more on the side of tetracoordination than **2a**, thus underlining the importance of small polarity differences for the actual coordination number achieved in compounds with relatively unpolar bonds.

In a previous paper it was demonstrated that hexacoordination of group-14 elements is not restricted to compounds with very electronegative substituents: up to four phosphorus donors constitute the planar part of a *trans*-octahedral environment in compounds of the type $Cl_2E[C(PMe_2)_2(SiMe_3)]_2$ (E = Si, Ge, Sn)[1]. It was also demonstrated that the tendency for hexacoordination follows the sequence Sn ~ Si > Ge in these compounds, quite different from the usually accepted one: Sn > Ge > Si. This deviation was attributed to the low polarity of the E−P bonds, which is least with E = Ge, thus rendering these bonds particularly weak with the respective consequences for the actual coordination number achieved. It was obvious that essentially unpolar bonds are most sensitive to slight changes in polarity, and the tendency to form high coordination numbers increases with bond polarity. It seemed highly challenging to extend these studies on main group elements with high coordination numbers to compounds with no substituents of high electronegativity at all, i.e., to replace the chlorine atoms by methyl substituents in the aforementioned compounds. Some of the results of this approach to the frontiers of hexacooordination were documented earlier[2], and some preliminary accounts are given in ref.[3].

Syntheses and Spectroscopic Characterization

Reaction of Me_2ECl_2 (E = Si, Ge, Sn) with lithium diphosphanylmethanide $Li[C(PMe_2)_2(SiMe_3)]$ (**1**) in an ethereal solvent affords the disubstitution products as colorless (**2a**, **b**) or as faintly yellow (**2c**) crystalline solids in high yield [eq. (1)].



2a: E = Si, X = Cl
2b: E = Ge, X = Cl
2c: E = Sn, X = Br

No monosubstitution product could be isolated. Moreover, starting from $MeSiCl_3$ we likewise obtained **2a** along with $SiCl_4$. Thus, **2a**−**c** seem to display a higher stability, although they are extremely sensitive to oxygen and moisture. Compound **2a** was also synthesized from LiMe and $Cl_2Si[C(PMe_2)_2(SiMe_3)]_2$[1], whereas attempts to prepare **2b** from $Cl_2Ge[C(PMe_2)_2(SiMe_3)]_2$ and LiMe did not yield **2b** in pure form, because reduction also took place[2c]. Although **2a** is obviously more stable than the monosubstitution product, in solution its stability is drastically reduced. When dissolved in an unpolar solvent (pentane, benzene), it rearranges completely within several days at room temperature (within hours at 60 °C) to give products, which were not fully characterized as yet. Initiated by a change of P to C coordination of the phosphanylmethanide ligands,

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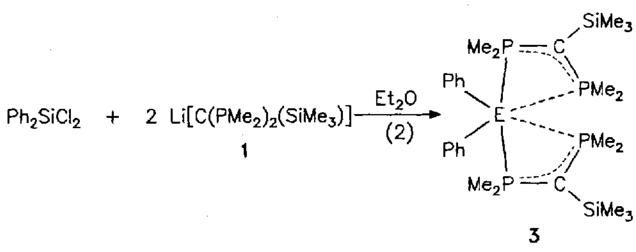
this process apparently involves several steps which are currently under intense investigation[4]. Furthermore, the phosphanylmethanide ligands of **2a** may be easily transferred to a transition metal center with concomitant reduction of silicon in **2a** to a Si(II) derivative[3].

Similarly to eq. (1), *cis*-$Ph_2Si[C(PMe_2)_2(SiMe_3)]_2$ (**3**) was obtained from Ph_2SiCl_2 and two equivalents of **1** [eq. (2)] as yellow crystals, but $t$$Bu_2SiCl_2$ turned out to be unreactive toward **1** even under more forcing conditions.



3

Only one single resonance line in the $^{31}P\{^1H\}$-NMR spectra of **2a**−**c** and **3** at room temperature [$\delta = +27.00$ (**2a**), -3.74 (**2b**), $+31.70$ (**2c**), $+22.73$ (**3**)] indicates rapid equilibration processes in solution which are in full accordance with the ^1H- and $^{13}C\{^1H\}$-NMR spectra. At −100°C AA′BB′-type spectra are obtained for **2a**, **2c** and **3**, whereas for **2b** only line broadening is observed. Only a minor temperature shift of the balanced resonances between −100 and +60°C is observed which is highest for **2b** [$\Delta\delta P = +0.21$ (**2b**)]. The chemical shifts for both P_A and P_B indicate coordination to the central element (**2a**: $\delta P_A = +31.72$, $\delta P_B = +22.31$; **2c**: $\delta P_A = +29.64$, $\delta P_B = +28.79$; **3**: $\delta P_A = +27.22$, $\delta P_B = +17.12$), the difference for $\delta P_A/\delta P_B$ being smallest for **2c**. This suggests that in **2c** the coordination of both types of phosphorus are more similar than in the other three complexes, which is in line with the structures found in the solid state (see below). From these observations hexacoordination with rapid equilibration of axial and equatorial sites within a *cis*-octahedral molecular skeleton and without an appreciable contribution of dissiociative processes can be deduced. Only for **3** the spin system could be resolved, however, because in the other cases the low-temperature limit is not reached at −100°C. Hexacoordination is also indicated by the shift to high field of the resonance for the central ^{29}Si nucleus in **2a** [$\delta^{29}Si = -81.75$ quin, $^1J(SiP) = 44.1$ Hz] and of the ^{119}Sn nucleus in **2c** [$\delta^{119}Sn = -245.22$ quin, $^1J(SnP) = 27.1$ Hz]. The latter data for **2c** are to be compared to the much higher values for other hexacoordinated tin complexes with phosphane donor ligands, i.e. $(R_3P)_2SnCl_4$ [e.g. R = Et: $\delta^{119}Sn = -572$; $^1J(SnP) = -2391$ Hz], all of which exhibit a *trans* configuration. There is one remarkable exception, however: in $(Me_2PhP)_2SnCl_3Me$ [$\delta^{119}Sn = -462$, $^1J(SnP) = -1046/-2973$ Hz] the phosphane ligands are in a *cis* arrangement to each other[5]. Small positive coupling constants (+50 to +430 Hz) and chemical shifts around $\delta^{119}Sn = 0$ are typical of tetrahedral tin compounds with Sn−P bonds[5]. Although we did not determine the sign of the coupling constant in **2c**, one is tempted to conclude from this comparison that in solution **2c** is intermediate between tetrahedral and octahedral coordination, the observed value of $^1J(SnP)$ representing a superposition of the respective coupling constants having positive and negative signs, respectively. The result of the ^{31}P-NMR measurements and the only small temperature dependence of the chemical shift (−80°C: $\delta^{119}Sn = -248$) make this assumption unlikely, however. Therefore, the observed ^{119}Sn-NMR spectrum should indicate that the quite different and novel nature of **2c** is preserved in solution. In particular, the deviations from an undistorted octahedral geometry (see structural results) in **2c** may play a decisive role. Furthermore, it should be noted here that in octahedral tin(IV) complexes the nature of the groups *cis* to phosphorus exert a dominant effect on $^1J(SnP)$[5a]. CP/MAS-NMR spectra of solid **2c** confirm this assumption: though the spectra do not allow an evaluation of the coupling constants, the chemical shifts ($\delta^{119}Sn$: -272.39; $\delta^{31}P$: $+32.08$; $\delta^{29}Si$: -6.43) in the solid state are close to those in solution. Therefore, the solid state structure of **2c** as deduced from an X-ray analysis (see below) is retained also in solution as in the other three cases. The slightly different behavior of **2b** compared to the other compounds may be attributed to a somewhat weaker coordination of the phosphanylmethanide ligands to the central atom than in **2a** and **2c**. Again, this is in line with the X-ray results and emphasizes once again the special role of germanium in phosphorus bonding (cf. refs.[1,3]).

NMR measurements revealed that **2a**, **2c**, and **3** are *cis*-hexacoordinated species in solution with rapid internal exchange of axial and equatorial positions of the phosphorus donor atoms (non-dissociative). For **2b**, a weaker coordination of the phosphanylmethanide ligands was established by the high-field shift of the ^{31}P-NMR resonance, and dissociative pathways to the phosphorus donor atom exchange cannot be ruled out.

Structural Results

The sum of the ligand electronegativities in compounds **2a**−**c** is by far the lowest value of hexacoordinated group-14 element compounds known as yet. Their structural investigation, in particular a comparison of the isotypic crystals of **2a** and **2b**, therefore offers a unique possibility of evaluating the specific influences of polarity effects in hypervalent compounds. From pentane needle-shaped (**2a**, **b**, space group $P2_1/c$) or from toluene rhombic (**2c**, space group $C2/c$) crystals were obtained.

The molecular structures of all three compounds (Figure 1−3, Table 1) are very similar. In the distorted *cis*-octahedral coordination geometries two methyl groups and two Me_2P groups constitute the equatorial plane, leaving the axial positions to the two remaining PMe_2 groups. The molecular symmetry of **2a** and **2b** closely approaches $C_2(2)$ in the solid state. For **2c** this molecular symmetry is determined crystallographically. Thus, molecules of **2a**−**c** are chiral, but in the crystal molecules of each handedness are present in equal amounts. The carbanionoide C atoms within the four-membered chelate rings thus formed are essentially planar, as are the chelate rings themselves.

Figure 1. Molecular Structure of **2a** in the crystal and crystallographic numbering scheme used (SHELXTL-PC; displacement allipsoids at the 50% level; H atoms omitted for clarity)

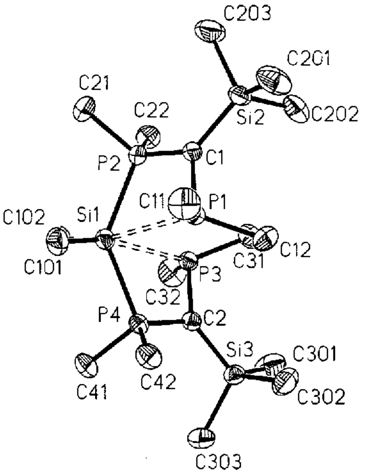


Figure 2. Molecular Structure of **2b** in the crystal (SHELXTL-PC)

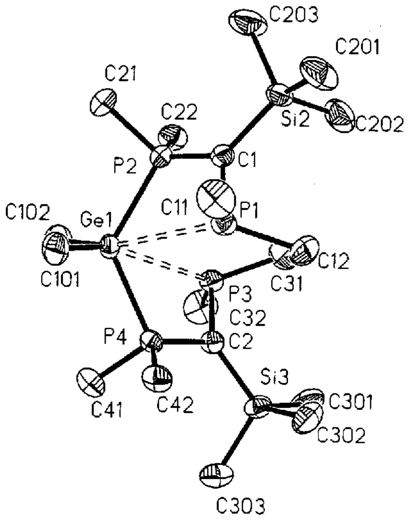


Figure 3. Molecular Structure of **2c** in the crystal (ORTEP-II; atoms denoted with a prime are related to those without a prime by the symmetry operation $-x$, y, $0.5 - z$)

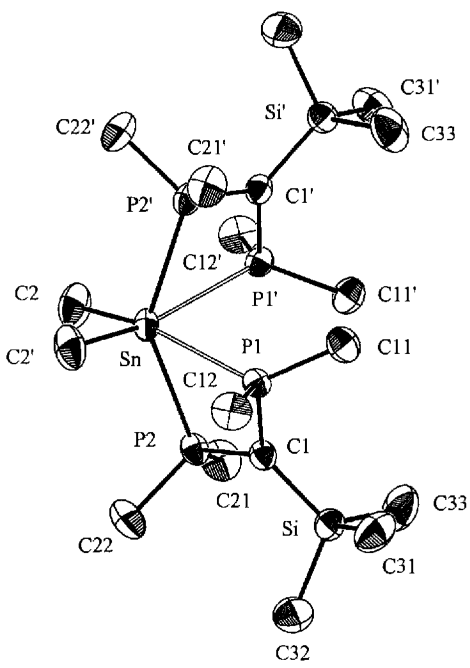
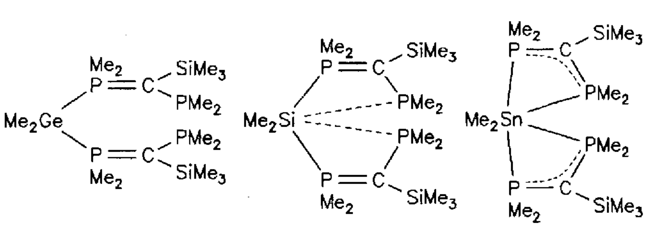


Table 1. Selected bond lengths [Å] and angles [°] in the molecular structures of **2a**–**c**. Standard deviations in units of the last significant figure are given in parentheses; chemically equivalent parameters are grouped together; see captions to Figures 1–3 for atom numbering

	2a (E = Si)	**2b** (E = Ge)	**2c** (E = Sn)
E-P1/P3 (eq)	2.868(2)/2.962(3)	3.211(1)/3.339(1)	2.841(1)
E-P2/P4 (ax)	2.306(1)/2.300(1)	2.338(1)/2.336(1)	2.608(1)
E-C101/C102	1.898(2)/1.902(2)	1.960(2)/1.966(2)	---
Sn-C2	---	---	2.188(3)
P1(eq)-C1/P3(eq)-C2	1.761(2)/1.760(2)	1.772(2)/1.770(2)	1.753(3)
P2(ax)-C1/P4(ax)-C2	1.715(2)/1.715(2)	1.700(2)/1.700(2)	1.729(3)
C1-Si2/C2-Si3	1.829(2)/1.831(2)	1.834(2)/1.842(2)	1.836(3)
P1-E-P3 (eq)	84.1(1)	82.0(1)	---
P1-Sn-P1' (eq)	---	---	82.7(1)
P2-E-P4 (ax)	137.1(1)	125.6(1)	---
P2-Sn-P2' (ax)	---	---	141.8(1)
C101-E-C102	101.5(1)	105.3(1)	---
C2-Sn-C2'	---	---	100.1(2)
P1-E-P2/P3-E-P4)	63.7(1)/61.8(1)	59.1(1)/56.2(1)	61.8(1)
P1-C1-P2/P3-C2-P4)	105.7(1)/105.2(1)	109.8(1)/108.4(1)	107.3(2)

The $E-P_{ax}$ bonds are only slightly longer than single bond values derived from standard covalent radii, whereas the $E-C_{Methyl}$ bonds are within the normal range for single bonds. These methyl groups exert a pronounced *trans* influence on the respective $E-P_{eq}$ bonds in the equatorial plane by lengthening this bond considerably. The amount of this elongation marks the decisive difference between the structures of **2a**–**c**. In **2c**, an 8.9% lengthening of the $Sn-P_{eq}$ bond [2.841(1) Å] compared to the $Sn-P_{ax}$ bond [2.608(1) Å] is within the expected range, whereas in **2a** this bond lengthening amounts to (mean) 26.6% and in **2b** to 40.1%. These quite dramatic differences illustrate that the overall bonding situation is quite different in **2a**, **2b** and **2c**. In the latter case, undoubtedly a "normal" hexacoordinate species is present. Although in **2a** and **2b** the orientation of the Me_2P_{eq} groups (the E–P vector roughly bisecting the Me–P–Me angle) clearly indicates coordination to the central atom, the long $Si-P_{eq}$ distance in **2a** is only attributable to a weak interaction (weak unisobidentate). Thus, **2a** can be regarded as a "frozen intermediate" between hexa- and tetracoordination. In **2b** this interaction is even considerably weaker as judged from the Ge–P bond lengths, so that the germanium derivative certainly is more on the side of a tetracoordinated rather than a hexacoordinated species. This interpretation was confirmed by the variation of the angles C–E–C, which increase from 100.1(2) (**2c**) to 101.7(1) (**2a**) and 105.3(1)° (**2b**), and $P_{ax}-E-P_{ax}$ decreasing from 141.8(1) (**2c**) to 137.1(1) (**2a**) and only 125.6(1)° in **2b**. In other words, geometries ranging from distorted octahedral to distorted tetrahedral have to be inferred from the structural data. The variation of unisobidentate bonding in **2a**–**c** also can be derived from the difference of the phosphorus (P_{ax} and P_{eq}) to carbanion bond lengths Δd(P−C). In **2c**, Δd(P−C) is only 0.024 Å, whereas in **2a** the mean Δd(P−C) value amounts to 0.044 and in **2b** to 0.071 Å. As has often been observed, coordination of phosphanylmethanides via the phosphorus atom leads to an ylidic character of the phosphorus-carbanion bond[1,3a,6]. With diphosphanylmethanides, chelating (bidentate) coordination leads to small Δd(P−C) values (0−0.02 Å), whereas unidentate phosphorus coordination leads to Δd(P−C) values arround 0.08 Å. It emerges that Δd(P−C) gives a reliable measure of iso-/unisobidentate bonding, as it is the case for **2a−c**. An idealized representation of **2a−c** in the solid state, based on the structural data, is given in Figure 4.

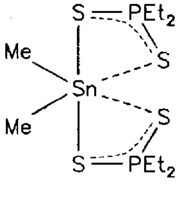
Figure 4. Idealized representations of **2a−c** based on the structural data



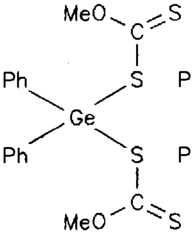
2b **2a** **2c**

Conclusion

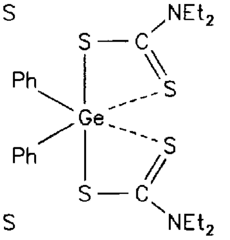
The tendency towards hexacoordination in diphosphanylmethanide *cis*-octahedral complexes follows the sequence Sn > Si > Ge. This is essentially the same trend as observed with the similar *trans*-dichloro complexes[1]. Again we attribute this to the small polarity differences of the element-phosphorus bonds and, in particular, to the especially unpolar nature of the Ge−P bond. Or in other words: the less polar the bonds, the more important are small polarity differences. This conclusion corresponds to similar findings in the series $E[C(PMe_2)_2(SiMe_3)]_2$[7] and is corroborated by a comparison of the structures of **2a−c** with the known structures of **I**[8], **II**[9], and **III**[10].



I



II



III

Within these and related systems also borderline cases between tetra- and hexacoordination were found, but with **2a−c** the first examples of a series ranging from silicon to tin with an identical set of ligands and with a low sum of electronegativities[11] were structurally characterized.

Finally, the decrease in coordination number (CN) from 6 to close to 4 (**2a, 2b**) in going from the solution to the solid state (comparable to $Ge[C(PMe_2)_3]_2$: CN 4 → close to 3)[7] seems puzzling and needs a comment[13]. In principle, one could ascribe this behavior to a solvent effect: the tetracoordinated species should be more polar and thus might be disfavored in unpolar solvents (benzene, toluene), but this effect should apply very similarly to **2a** and **2b**. Packing forces, in principle, might play a role as well but are not relevant to the isotypic structures of **2a** and **2b**.

Most probably, tetra- and hexacoordinated forms of these compounds are very close in energy. Within a 3c4e bonding model, a distortion from a geometry with two equal and moderate weak bonds to a geometry with one stronger and one much weaker (or almost nonbonding) interaction is likely to occur in going from polar to unpolar bonds. If the distorted form is considered the ground state, only small geometrical changes, induced by thermal vibrations, might favor two equal interactions and, thus, the effective coordination number increases (in **2a**, **2b** this model has to be modified due to the different ligands CH_3 and PMe_2 involved). In fact, replacement of the Me_2Si moiety of **2a** by a silacyclobutane moiety, i.e. in $C_3H_6Si[C(PMe_2)_2(SiMe_2Ph)]_2$, leading to geometrical constraints which are more suitable for hexacoordination, gives rise to a decrease of the Si−P_{eq} bond length to a normal value (2.46 Å) as expected for a Si−P single bond *trans* to an alkyl group. Thus, in this case "true" hexacoordination was also observed in the solid state[12].

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Experimental

For general remarks, reagents and instrumentation see ref.[1]. − CP/MAS NMR: Bruker MSL 100 (^{119}Sn, ^{31}P) and MSL 300 (^{29}Si). − For nomenclature see ref.[1].

cis-Bis[(dimethylphosphanyl)(trimethylsilyl)methanido-P,P′]-dimethylsilane (**2a**): To a solution of 0.55 g (2.57 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ in 40 ml of diethyl ether 0.16 ml (0.17 g, 1.28 mmol) of Me_2SiCl_2 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 with two portions of 30 ml of pentane. From the combined pentane solutions the solvent was removed slowly, whereby colorless needles were obtained. Yield: 0.55 g (91%), m.p. 83 °C. − ^{1}H NMR: δ = 1.24 (s, br, 24H, PMe_2), 0.36 ("quint", N = 3.6 Hz, 6H, $SiMe_3$), 0.30 (s, 18H, $SiMe_2$). − $^{13}C\{^1H\}$ NMR: δ = 20.31 ("quint", N = 33.0 Hz, PMe_2), 4.85 [t, ^2J(PC) = 24.8 Hz, $SiMe_2$], 4.75 (s, $SiMe_3$). − $^{29}Si\{^1H\}$ NMR: δ = −7.42 (s, $SiMe_3$), −81.73 [quint, ^1J(PSi) = 44.1 Hz, $Si_{central}$]. − $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): +27.00 (s). − $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, −110 °C): AA′BB′ not completely resolved, δ = +31.72 ($P_{A/A'}$), +22.31 ($P_{B/B'}$). − $C_{18}H_{48}P_4Si_3$ (472.7): calcd. C 45.73, H 10.23, Si 17.82; found C 44.58, H 10.08, Si 17.67.

cis-Bis[bis(dimethylphopshanyl)(trimethylsilyl)methanido-P,P′]-dimethylgermane (**2b**): The procedure is very similar to that for **2a**, but the solvent was THF. 2.92 g (13.63 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ and 1.18 g (0.75 ml, 6.82 mmol) of Me_2GeCl_2 were used. Yield: 3.30 g (94%) of colorless crystals, m.p. 92 °C. − MS (CI,

^{74}Ge), *m*/*z* (%): 457 (13) [$M^+ - PMe_2$], 311 (61) [$M^+ - C(PMe_2)_2(SiMe_3)$], 207 (100) [$C(PMe_2)_2(SiMe_3)^+$]. – ^{1}H NMR: δ = 1.32 (s, br, 24H, PMe_2), 0.52 [quint, $^3J(PH)$ = 2.9 Hz, 6H, $GeMe_2$], 0.30 (s, 18H, $SiMe_3$). – $^{13}C\{^1H\}$ NMR: δ = 19.86 ("t", *N* = 33.0 Hz, PMe_2), 6.16 (s, $SiMe_3$), 0.22 [quint, $^2J(PC)$ = 12.1 Hz, $GeMe_2$]. – $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 25°C): δ = −3.74 (s). – $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, −100°C): δ = 0.21 (s, br). – $C_{18}H_{38}GeP_4Si_2$ (517.2): calcd. C 41.80, H 9.35; found C 39.88, H 9.01.

cis-Bis[bis(dimethylphopshanyl)(trimethylsilyl)methanido-P,P′]-dimethylstannane (**2c**): The procedure is very similar to that for **2a**. 2.08 g (9.71 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ and 1.40 g (4.54 mmol) of Me_2SnBr_2 were used. The product was recrystallized from toluene: colorless crystals, yield 1.90 g (75%), m.p. 83°C. – ^{1}H NMR: δ = 1.48 [s, ^{119}Sn satellites: $^3J(SnH)$ = 7.8 Hz, 24H, PMe_2], 0.48 (m, br, 6H, $SiMe_2$), 0.45 (s, 18H, $SiMe_3$). – $^{13}C\{^1H\}$ NMR: δ = 20.57 ("quint", *N* = 30.2 Hz, PMe_2), 4.69 (s, $SiMe_3$), −0.46 [quint, $^2J(PC)$ = 24.8 Hz, $SnMe_2$]. – $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, +25°C): δ = +30.06 [s, ^{119}Sn satellites: $^1J(SnP)$ = 27.1 Hz). – $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, −100°C): AA′BB′ spin system, not fully resolved, δ = +29.64 ($P_{A/A'}$), +28.79 ($P_{B/B'}$). – $^{119}Sn\{^1H\}$ NMR ($C_6D_5CD_3$, +25°C): δ = −245.22 [quint, $^1J(SnP)$ = 27.1 Hz]. – $^{119}Sn\{^1H\}$ NMR ($C_6D_5CD_3$, −80°C): δ = −248 (broad, unresolved signal). – $C_{18}H_{48}P_4Si_2Sn$ (563.3): calcd. C 38.38, H 8.59; found C 37.53, H 8.42.

cis-Bis[bis(dimethylphosphanyl)(trimethylsilyl)methanido-P,P′]-diphenylsilane (**3**): The procedure is very similar to that for **2a**. 0.54 g (2.52 mmol) of $Li[C(PMe_2)_2(SiMe_3)]$ and 0.32 g (0.27 ml, 1.26 mmol) of Ph_2SiCl_2 were used. Slightly yellowish crystals were obtained from pentane, yield 0.66 g (88%), m.p. 56°C. – ^{1}H NMR: δ = 7.71/7.16 (br, 10H, Ph), 1.37 (br, 24H, PMe_2), 0.31 (s, 18H, $SiMe_3$). – $^{13}C\{^1H\}$ NMR: δ = 142.39 [quint, $^2J(PC)$ = 21.1 Hz, C-1 Aryl], 137.54 [quint, $^3J(PC)$ = 2.2 Hz, C-2,6 Aryl), 128.52 (s, C-4 Aryl), 127.05 (s, C-3,5 Aryl), 21.87 ("t", *N* = 34.7 Hz, PMe_2), 5.09 (s, $SiMe_3$). – $^{31}P\{^1H\}$ NMR (C_6D_6, 20°C): δ = +22.72 (s). – $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, −100°C): AA′BB′ spin system, δ = +27.23 ($P_{A/A'}$), 17.18 ($P_{B/B'}$), $J(AA')$ = 127.2, $J(BB')$ = 43.8, $J(AB')$ = $J(A'B)$ = 130.0, $J(AB)$ = 503.5 Hz. – $^{29}Si\{^1H\}$ NMR: δ = −7.58 (s, $SiMe_3$), −66.57 [quint, $^1J(PSi)$ = 42.3 Hz]. – MS (EI), *m*/*z* (%): 389 (100) [$M^+ - C(PMe_2)_2(SiMe_3)$]. – $C_{28}H_{52}Si_3P_4$ (596.9): calcd. C 56.34, H 8.78, Cl 0; found C 55.49, H 8.57, Cl 0.

Crystal Structure Determinations of **2a–c**: Suitable single crystals were grown from solution (**2a**, **b**: pentane; **2c**: toluene), mounted in argon-filled glass capillaries and examined directly with the diffractometer (Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator). Table 2 compiles the crystal data and important numbers pertinent to data collection and structure refinement. The unit cells found were checked for higher symmetry by cell reduction (DELOS[14], LEPAGE[15]). The integrated intensities measured on the diffractometer were corrected for Lorentz and polarization effects, those of **2b** and **2c** also for absorption (**2b**: DIFABS[16]; **2c**: ψ scans in steps of 10° around the diffraction vectors of 10 reflexions near Θ = 90° which served to evaluate the relative transmission). The structures were solved with direct methods or automated Patterson methods (SHELXS-86[17]) and completed by Fourier syntheses. Refinement was performed with SHELXL-93[18] (**2a**, **b**) or with SHELX-76[19] (**2c**). Molecular drawings were performed with SHELXTL-PC[20] and ORTEP-II[21]. Complete crystal structure data are available[22].

Table 2. Crystal structure data of **2a–c**

	2a	**2b**	**2c**
Formula	$C_{18}H_{48}P_4Si_3$	$C_{18}H_{48}GeP_4Si_2$	$C_{18}H_{48}P_4Si_2Sn$
M_r	472.711	517.211	563.34
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a [Å]	12.927(1)	12.806(1)	23.166(2)
b [Å]	14.765(1)	14.985(1)	9.109(1)
c [Å]	16.349(1)	16.459(2)	15.115(2)
β [°]	111.83(2)	112.67(1)	111.06(1)
V [Å^3]	2896.7	2914.4	2976.5
Z	4	4	4
d_{calcd} [g/cm^3]	1.084	1.179	1.257
μ(Mo-K_α) [cm^{-1}]	3.9	13.6	11.6
F(000) [e]	1032	1104	1176
T [°C]	20	-71	-40
Diffractometer	Syntex-$P2_1$	Enraf-Nonius CAD4	Syntex-$P2_1$
Scan	ω	ω/ϑ	ω
Scan width (° in ω)	1	0.85	0.8
$(\sin \vartheta/\lambda)_{max}$ [Å^{-1}]	0.592	0.638	0.572
hkl range	±15, +17, +19	±16, +19, +20	+26, ±10, ±17
Refl. (measd./unique)	5241/5045	7030/6322	4498/2341
R_{int}	0.026	0.023	0.03
Refl. obs. [$I \geq 2.0\ \sigma(I)$]	4455	4977	2142
Absorption correction	---	DIFABS	empirical (ψ scans)
Relative transmission	---	0.837 - 1.09	0.70 - 1.00
H atoms (found/calcd.)	-/48	-/48	14/10
H atom refinement	riding model	riding model	CH_3 rigid groups, U_{iso} = 0.08 Å^2
parameters ref.	242 on all unique F^2	243 on all unique F^2	138 on all observed *F*
GOF (F^2)	0.947	1.035	---
R [a]	0.038	0.049	0.028
wR [b]	---	---	0.031
*wR*2 [c]	0.093	0.065	---
Extinction coefficient	---	0.0011(2)	---
$\Delta\rho_{fin}$(max/min) [e/Å^3]	0.29/-0.42	0.31/-0.29	0.39/-0.55

[a] $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – [b] $wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. – [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (kP)^2 + mP]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$; k/m = 0.0445/1.21 for **2a**, 0.028/1.06 for **2b**.

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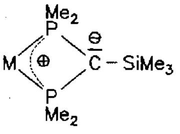
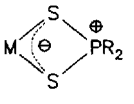
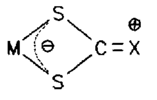

IV


V


VI

(X = OMe, NMe$_2$)

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[13] This situation clearly differs from cases, where a hexacoordinated *transition state* was observed in solution, whereas in the solid state a pentacoordinated species was found as it was deduced for e.g. [o-C$_6$H$_4$(NMe$_2$)]$_2$SiCl$_2$ from ^{1}H-NMR spectra. In these cases, the ^{29}Si-NMR resonance is highly temperature-dependent: H. Handwerker, C. Leis, R. Probst, P. Bissinger, A. Grohmann, P. Kiprof, E. Herdtweck, J. Blümel, N. Auner, C. Zybill, *Organometallics* **1993**, *12*, 2162.

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[96032]