▌ **Structure Determination** |*Hot Paper*|

Ionic Dissociation of SiCl$_4$: Formation of [SiL$_6$]Cl$_4$ with L=Dimethylphosphinic Acid

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Abstract: Reactions of SiCl$_4$ with R$_2$PO(OH) (R=Me, Cl) yield compounds with six-fold coordinated silicon atoms. Whereas R=Me afforded the hexacoordinated tetra-cationic silicon complex [Si(Me$_2$PO(OH))$_6$]$^{4+}$ with chloride counter-ions, R=Cl caused release of HCl with formation of a cyclic dimeric silicon complex [Si(Cl$_2$PO(OH))(Cl$_2$PO$_2$)$_3$(μ-Cl$_2$PO$_2$)]$_2$ with bridging bidentate dichlorophosphates.

Design of hypercoordinated silicon compounds is of particular interest in organic chemistry, where they may play roles as catalysts and reagents.[1,2] As heavier congener of carbon, silicon and its higher coordination number compounds are of particular academic interest as well. Thus, various neutral, anionic and cationic silicon complexes have been reported.[3,4] A more specific topic are hexacoordinated silicon compounds with [SiO$_6$] skeletons. In naturally occurring low-pressure silicates[5] and silicophosphate minerals[6] the silicon atom is present in fourfold coordination. Only several high-pressure silicates, for example, stishovite or MgSiO$_3$[5] and synthesized (at atmospheric pressure) crystalline silicophosphate compounds, for example, SiP$_2$O$_7$[7] or Si$_5$O(PO$_4$)$_6$[8] contain hexacoordinated silicon atoms. Molecular silicon compounds with [SiO$_6$] skeletons include besides anionic species, like the dianions of [Si^{VI}(PO$_4$)$_6$(Si^{IV}(OEt)$_2$)$_6$],[9] [Si^{VI}(S$_2$O$_7$)$_3$][10,11] or [Si^{VI}(P$_3$O$_9$)$_2$],[12] also neutral complexes[13] and cationic complexes. The latter include mainly monocationic species[14] while some tetracationic complexes are known in literature only for systems with very soft

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.202000435.

("silicophobic") counter-ions, for example, hexa(pyridine-N-oxide)silicon tetraiodide ([Si(pyO)$_6$]I$_4$)[15] or hexakis(N,N-dimethylformamide)silicon tetraiodide ([Si(DMF)$_6$]I$_4$).[16] As to neutral O-donor ligands, hypercoordinated adducts of SiF$_4$ with phosphine oxides, trans-[SiF$_4$(OPPh$_3$)$_2$],[17] and of SiCl$_4$ with phosphoric amides, for example, [Cl$_3$Si(OP(NMe$_2$))$_3$]-cation,[18] are also known, while OH-functionalized P=O-compounds tend to act as anionic ligands.

In this regard, dichlorophosphates ([Cl$_2$PO$_2$]$^-$) are described as bridging bidentate ligands through the coordination of both oxygens to metal atoms. Additionally, dichlorophosphate can operate as monofunctional and also as trifunctional group.[19] In trimethylsilyl dichlorophosphate, Cl$_2$PO$_2$SiMe$_3$, only one oxygen is coordinated to silicon because of the poor hypercoordination tendency of SiMe$_3$ groups.[19,20] Dimethylphosphinate groups ([Me$_2$PO$_2$]$^-$) were also handled as bridging bidentate ligands.[21–23] Here, we report the crystal structures of the two different six-fold coordinated silicon compounds **SiPCl** and **SiPMe** (Scheme 1), which enhance the portfolio of coordination motifs. The complexes were prepared by reaction of SiCl$_4$ with dichlorophosphoric acid in benzene (**SiPCl**) and dimethylphosphinic acid in chloroform (**SiPMe**) (see Supporting Information for details).

Figure 1 shows the molecular structure of **SiPCl** in the crystal (triclinic, space group P-1). A compound of this formal composition "H[Si(O$_2$PCl$_2$)$_5$]" has been reported in literature (also obtained by the reaction of dichlorophosphoric acid and SiCl$_4$ in benzene),[24] but its structure has not been elucidated so far. Compound **SiPCl** is a cyclic dimer, which is located about a center of inversion. Two bridging Cl$_2$PO$_2$ ligands between two silicon atoms furnish a Si$_2$O$_4$P$_2$ eight-membered ring. The remaining four coordination sites at each of the octahedrally coordinated Si atoms host monodentate O-donor ligands, that is,

Scheme 1. Preparation of the hexacoordinated silicon compounds **SiPMe** and **SiPCl** ([SiO$_6$]-structural units are bold indicated for clarity).

Chemistry–A European Journal

Communication
doi.org/10.1002/chem.202000435

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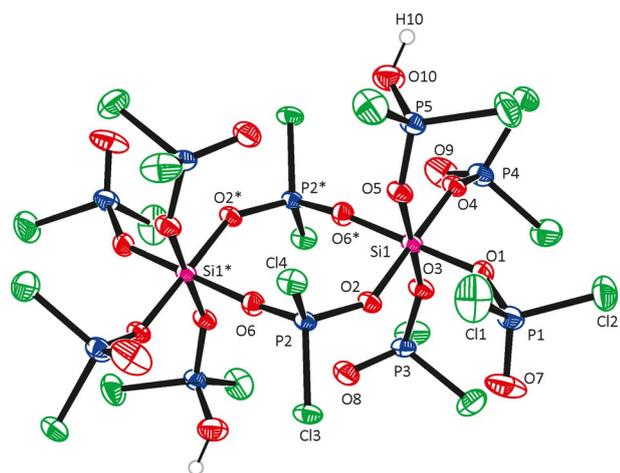
Figure 1. Molecular structure of **SiPCl** in the crystal. (ORTEP representation with 50% probability ellipsoids). The P1O7Cl1Cl2 group was disordered and refined in two positions (site occupancy ratio 0.81(2):0.19(2)). Selected bond lengths and angles are provided in Table 1.

Figure 2. ^{31}P DQ-SQ-MAS-NMR spectrum of **SiPCl**.

three $Cl_2PO_2^-$ anions and one $(HO)OPCl_2$ molecule. Thus, the molecule bears five crystallographically non-equivalent dichlorophosphate groups. The silicon coordination spheres are slightly distorted octahedra with bond lengths and *trans*-O-Si-O angle ranges of 1.73–1.79 Å and 175.6–178.4°, respectively. The Si—O bond lengths increase in the order monodentate anionic < bridging anionic < mono-dentate neutral ligand (O1 and O5 share roles of anionic and neutral ligand as their Cl_2PO_2 moieties are intermolecularly connected by hydrogen bridges (i.e., O10—H10 is directed toward O7* of an adjacent molecule, O7* generated from O7 by symmetry operation *x*-1, *y*, *z*)). The intermolecular separation O10—O7* (2.48 Å) is in accord with a highly attractive hydrogen bridge, but disorder of the P1O7Cl1Cl2 group hampers any detailed discussion of this hydrogen bridge. The P—O distances range from 1.45 Å (normal double bond lengths) to 1.53 Å and the angles about phosphorus span a range of 105–114° with angles increasing in the order Cl-P-Cl < Cl-P-O < O-P-O (in accordance with VSEPR). P—Cl and P—O distances in **SiPCl** do not differ significantly from corresponding distances in $POCl_3$ (P—Cl: 1.98 Å, P=O: 1.45 Å)[25] or other related compounds with Cl_2PO_2 ligands, for example, $[(Cl_3SnOPCl_3)^+(PO_2Cl_2)^-]_2$ (P—Cl: 1.98 Å, P—O: 1.50 Å).[26]

^{29}Si and ^{31}P solid-state NMR spectroscopy points out few impurities from dichlorophosphoric acid and its (silylated) condensation products in the bulk solid material. Nevertheless, we were able to assign the ^{29}Si chemical shift (−214.5 ppm) to the $[Si(OP)_6]$ octahedra and the ^{31}P NMR signals to the phosphorous atoms of the crystal structure **SiPCl** ($\delta(^{31}P) =$ 1.8 ppm (P1), −21.5 ppm (P2), 4.5 ppm (P3), −10.4 ppm (P4), 15.1 ppm (P5)). The combination of ^{31}P single pulse (SP), cross polarization (CP) and ^{31}P double quantum (DQ)/single quantum (SQ) MAS NMR spectra allows the complete assignment of the ^{31}P chemical shifts. The latter spectrum is given in Figure 2. We observe one diagonal DQ peak at −21.5 ppm (for the spatially closest chemically equivalent atoms P2) and furthermore, two
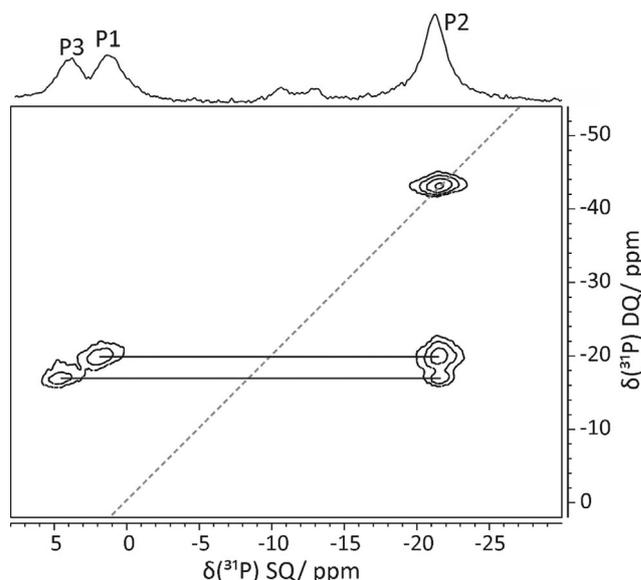
DQ peak pairs at 1.8 ppm and −21.5 ppm (P1-P2) as well as at 4.5 ppm and −21.5 ppm (P3−P2). A detailed explanation of the NMR analysis and the assignment is given in Supporting Information.

Following our studies, we changed the phosphorus compound from dichlorophosphoric acid to dimethylphosphinic acid. Dimethylphosphinate groups $[(Me_2PO_2]^-)$ were also reported as bridging bidentate ligands.[21–23] Known structures with dimethylphosphinate groups, for example, $Et_2Sn(O_2PMe_2)_2$,[21] $Me_3SnO_2PMe_2$[22] and $Et_2ClSnO_2PMe_2$[23] are polymeric, whereas $Ph_2Sn(O_2PMe_2)_2$ has a polymeric ring-chain structure. The Me_2PO_2 ligands functioning as double bridges, like in **SiPCl**, between tin atoms to give eight-membered $Sn_2O_4P_2$ rings.[21] Here, we can report a new crystalline product based on dimethylphosphinic acid as a neutral oxygen-donor ligand, which was obtained by the reaction of tetrachlorosilane with dimethylphosphinic acid in chloroform.

Contrary to our expectation (i.e., substitution with release of HCl), a novel tetra-cationic silicon complex was created by ionic dissociation of $SiCl_4$, because the dimethylphosphinic acid (pK = 3.1)[27] is a weaker acid than for example, methylphosphonic acid (pK = 2.3)[27] or methylphosphoric acid (pK = 1.5).[25] In contrast the dichlorophosphoric acid is described as a strong acid, which forces weaker acids out of its salts, for example, HCl from $CaCl_2$.[28] The formula composition in the crystal structure of compound **SiPMe** (monoclinic, space group C2/c, Figure 3) comprises a $[Si(Me_2PO(OH))_6]^{4+}$ cation, four chloride ions and one chloroform molecule. The Si atom is located on a crystallographic center of inversion, thus the asymmetric unit contains a half cation, two Cl anions and half a molecule $CHCl_3$. The silicon atom of **SiPMe** is surrounded by the dimethylphosphinic acid molecules as neutral ligands in a nearly regular octahedral geometry with an average Si—O bond length of 1.76 Å (Table 1). The P—O distances range from 1.52 to 1.55 Å and are in good agreement with normal single

Chemistry–A European Journal   Communication
doi.org/10.1002/chem.202000435

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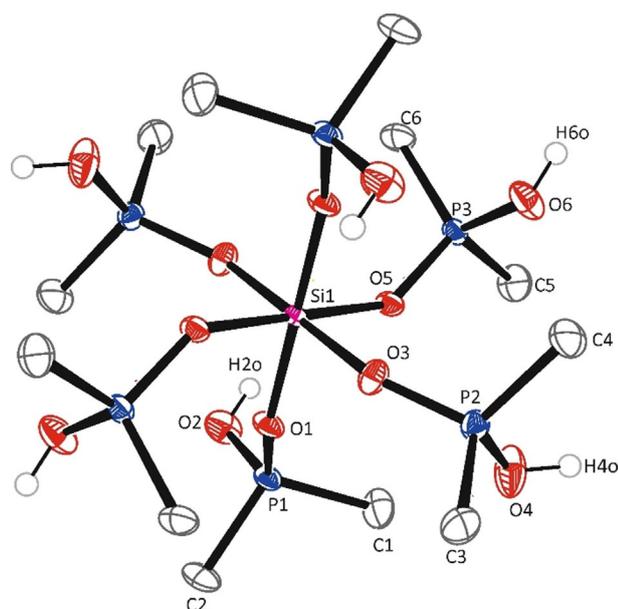
Figure 3. Molecular structure of **SiPMe**. (ORTEP representation with 50% probability ellipsoids; C-bonded hydrogen atoms omitted for clarity). The crystal structure is built up from [Si(Me$_2$PO(OH))$_6$]$^{4+}$-cations with four chloride ions and one molecule chloroform. Selected bond lengths and angles are summarized in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for SiPCl and SiPMe.			
Bond lengths [Å]		**Angles [°]**	
SiPCl			
Si1–O1	1.770(2)	O3-Si1-O5	178.42(10)
Si1–O2	1.763(2)	O4-Si1-O2	175.64(10)
Si1–O3	1.730(2)	O2-Si1-O5	87.87(9)
Si1–O4	1.736(2)	O6-P2-O2	114.06(11)
Si1–O5	1.790(2)	O2-P2-Cl4	108.57(8)
Si1–O6	1.773(2)	Cl3-P2-Cl4	105.98(4)
SiPMe			
Si1–O1	1.7505(11)	O1-Si1-O3	89.14(6)
Si1–O3	1.7648(11)	O1-Si1-O5	89.77(5)
Si1–O5	1.7710(11)	O3-Si1-O5	90.97(5)
P3–O5	1.5230(11)	O5-P3-O6	107.99(7)
P3–O6	1.5543(13)	O5-P3-C6	113.32(8)
		O6-P3-C6	110.10(9)
		O5-P3-C5	107.65(8)
		O6-P3-C5	108.79(9)
		C6-P3-C5	108.88(9)

bond lengths. One of the Cl anions in the asymmetric unit is hydrogen bonded to the OH groups of two neighboring cations. The other one is hydrogen bonded to only one cation. The H···Cl separations of these hydrogen bonds are around 2.1 Å. Additionally, Cl$_3$CH···Cl (2.7 Å) and PCH$_3$···Cl (2.9 Å) contacts were also found. Only a few other tetra-cationic silicon compounds with neutral ligands were reported in literature, for example, hexa(pyridine-N-oxide)silicon tetraiodide, [Si(pyO)$_6$]I$_4$,[15] hexakis(N,N-dimethylformamide)silicon tetraiodide, [Si(DMF)$_6$]I$_4$,[16] hexakis(N,N-dimethylformamide)-silicon tris(tribromide) chloride, [Si(DMF)$_6$][Br$_3$]$_3$Cl[29] and complexes

with six N-donor atoms.[30,31] The compound **SiPMe** is insoluble in organic solvents, so the ^{29}Si and ^{31}P NMR chemical shifts ($\delta(^{29}$Si) = −204.2 ppm; $\delta(^{31}$P) = 56.88 ppm) were obtained from solid state NMR experiments.

In order to probe whether the weaker Si–Br bond dissociates in a related manner, SiBr$_4$ was treated with dimethylphosphinic acid, too. In fact, the corresponding bromide salt **SiP-Me^{Br}** formed, which shows very similar ^{29}Si and ^{31}P NMR signals and crystallizes as an isomorph of **SiPMe** (with longer unit cell axes because of the larger halide anion). Thus, a comparison of the corresponding data of **SiPMe** and **SiPMe^{Br}** is given in the Supporting Information. The chemistry related to compound **SiPMe** is subject of ongoing investigations, because **SiPMe** is the first example of a structurally characterized tetra-cationic hexacoordinated silicon tetrachloride. Many further structures of such tetra-cationic silicon complexes may be accessible based on reactions of SiCl$_4$ and SiBr$_4$ with other phosphinic acid derivatives.

Furthermore, the activation of SiCl$_4$ with chiral bisphosphoramides is known in literature[32] and leads to cationic silicon species, which are employed as catalysts, for example, for the enantioselective allylation of aldehydes.[32–35] Also, phosphoric amides proved highly active as Lewis base catalysts for the disproportionation of methylchlorodisilanes.[36] This activation of the weak Lewis acid SiCl$_4$ and other chlorosilanes by that special kind of very polar Lewis base (which has an inherent negative connotation because of the toxicity of phosphoric amides) may be transferred to the chlorosilane/phosphinic acid derivatives system, which would represent a non-toxic alternative to chlorosilane/phosphoramide systems. In addition to the donor qualities, dialkylphosphinic acids offer tools for including chiral information or linkers to solid supports (or both) by their alkyl backbone, rendering OP(OH)(alkyl)$_2$ a fundamental motif worthwhile being studied in this regard.

CCDC 1967458 (**SiPCl**), 1967459 (**SiPMe**) and 1987161 (**SiP-Me^{Br}**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Conflict of interest

The authors declare no conflict of interest.

[1] S. Rendler, M. Oestreich, *Synthesis* **2005**, *11*, 1727–1747.
[2] J.-i. Tateiwa, A. Hosomi, *Eur. J. Org. Chem.* **2001**, 1445–1448.
[3] R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927–950.
[4] J. Wagler, U. Böhme, E. Kroke, *Higher-Coordinates Molecular Silicon Compounds in Functional Molecular Silicon Compounds I.* 155 (Ed.: D.

Scheschkewitz), Springer, Heidelberg, New York, Dordrecht, London, **2014**, pp. 29–105.

[5] L. W. Finger, R. M. Hazen, *Acta Crystallogr. Sect. B* **1991**, *47*, 561–580.

[6] "The Crystal Chemistry of Phosphate Minerals": D. M. C. Huminicki, F. C. Hawthorne in *Phosphates, Vol. 48* (Ed.: M. J. Kohn, J. Rakovan, J. M. Hughes), De Gruyter, Inc., Boston, **2019**, pp. 123–254.

[7] D. M. Poojary, R. B. Borade, F. L. Campbell III, A. Clearfield, *J. Solid State Chem.* **1994**, *112*, 106–112.

[8] H. Mayer, *Monatsh. Chem.* **1974**, *105*, 46–54.

[9] S. Jähnigen, E. Brendler, U. Böhme, E. Kroke, *Chem. Commun.* **2012**, *48*, 7675–7677.

[10] C. Logemann, T. Kluner, M. S. Wickleder, *Chem. Eur. J.* **2011**, *17*, 758–760.

[11] C. Logemann, J. Witt, D. Gunzelmann, J. Senker, M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2012**, *638*, 2053–2061.

[12] M. B. Geeson, P. Ríos, W. J. Transue, C. C. Cummins, *J. Am. Chem. Soc.* **2019**, *141*, 6375–6384.

[13] O. Seiler, C. Burschka, T. Fenske, D. Troegel, R. Tacke, *Inorg. Chem.* **2007**, *46*, 5419–5424.

[14] M. Kira, L. C. Zhang, C. Kabuto, H. Sakurai, *Organometallics* **1998**, *17*, 887–892.

[15] D. Kummer, T. Seshadri, *Z. Anorg. Allg. Chem.* **1977**, *432*, 147–152.

[16] B. Deppisch, B. Gladrow, D. Kummer, *Z. Anorg. Allg. Chem.* **1984**, *519*, 42–52.

[17] K. George, A. L. Hector, W. Levason, G. Reid, G. Sanderson, M. Webster, W. Zhang, *Dalton Trans.* **2011**, *40*, 1584–1593.

[18] S. E. Denmark, B. M. Eklov, *Chem. Eur. J.* **2008**, *14*, 234–239.

[19] A.-F. S. K. Dehnicke, *Struct. Bonding* **1976**, *28*, 51–82.

[20] A. F. Shihada, Z. S. Salih, *Z. Anorg. Allg. Chem.* **1980**, *469*, 159–163.

[21] A.-F. Shihada, F. Weller, *Z. Naturforsch. B* **1997**, *52*, 587–592.

[22] F. Weller, A.-F. Shihada, *J. Organomet. Chem.* **1987**, *322*, 185–192.

[23] A.-F. Shihada, F. Weller, *Z. Naturforsch. B* **1998**, *53*, 699–703.

[24] M. Meisel, H. Grunze, *Z. Anorg. Allg. Chem.* **1973**, *400*, 128–136.

[25] D. E. C. Corbridge, *Phosphorus: Chemistry, Biochemistry and Technology, 6th ed.*, Taylor&Francis, **2013**.

[26] D. Moras, A. Mitschler, R. Weiss, *Chem. Commun. (London)* **1968**, 26a.

[27] P. C. Crofts, G. M. Kosolapoff, *J. Am. Chem. Soc.* **1953**, *75*, 3379–3383.

[28] H. Grunze, *Z. Chem.* **1966**, *6*, 266–267.

[29] A. Bekaert, P. Lemoine, J. D. Brion, B. Viossat, *Z. Kristallogr.* **2005**, *220*, 425–426.

[30] D. Kummer, H. Köster, *Z. Anorg. Allg. Chem.* **1973**, *402*, 297–304.

[31] D. Kummer, K. E. Gaisser, J. Seifert, R. Wagner, *Z. Anorg. Allg. Chem.* **1979**, *459*, 145–156.

[32] S. E. Denmark, S. M. Pham, *Org. Lett.* **2001**, *3*, 2201–2204.

[33] S. E. Denmark, G. L. Beutner, T. Wynn, M. D. Eastgate, *J. Am. Chem. Soc.* **2005**, *127*, 3774–3789.

[34] S. E. Denmark, B. M. Eklov, P. J. Yao, M. D. Eastgate, *J. Am. Chem. Soc.* **2009**, *131*, 11770–11787.

[35] S. E. Denmark, T. Wynn, G. L. Beutner, *J. Am. Chem. Soc.* **2002**, *124*, 13405–13407.

[36] U. Herzog, R. Richter, E. Brendler, G. Roewer, *J. Organomet. Chem.* **1996**, *507*, 221–228.