

X-ray powder diffraction characterization of the elusive tetraphosphine $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ silane

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X-ray powder diffraction data for the tetraphosphinic $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ silane are reported. Its crystal and molecular structures were determined by simulated annealing and full-profile Rietveld refinement methods. $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ was found to have tetragonal symmetry with $P-42_1c$ space group. The lattice parameters were determined to be $a=17.211(2)$ Å, $c=7.553(1)$ Å, $V=2237.5(5)$ Å³. The crystal structure was found to contain isolated $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ molecules. In each $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ molecule, the central Si atom was fixed at the -4 symmetric position bearing four CH_2PPh_2 branches. This environment was confirmed by ³¹P CP/MAS NMR measurements. Thermo-diffractometric measurements in the 20–120 °C range were also used to estimate the linear and volumetric thermal expansion coefficients ($\partial \ln V / \partial T = 1.8 \times 10^{-4} \text{ K}^{-1}$), typical for very “soft” materials. © 2007 International Centre for Diffraction Data. [DOI: 10.1154/1.2424476]

Key words: powder diffraction, silane, phosphine, Rietveld refinement

I. INTRODUCTION

Chelating phosphines incorporating ethoxysilane groups are used successfully as linkers for immobilizing catalysts on oxide supports in order to improve their recyclability and lifetime. During the preparation of several phosphines of the type $(\text{EtO})_x\text{Si}(\text{CH}_2\text{PPh}_2)_{4-x}$ [$x=1-3$, $\text{Ph}=\text{C}_6\text{H}_5$ (Bogza *et al.*, 2005)], we also synthesized the tetraphosphine $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ in high yields from cheap starting materials. $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ has the potential to act as a multidentate bridging ligand for different metals, allowing the preparation of organometallic polymers or dendrimers incorporating metal complexes, as shown for the analogue $\text{Si}(\text{CH}_2\text{CH}_2\text{PPh}_2)_4$ (Hendriksen *et al.*, 1989; Ropartz *et al.*, 2002). While the ethoxy derivatives could eventually be prepared as single crystals and were characterized by conventional X-ray diffraction structure methods (Bogza *et al.*, 2005), $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ was only obtained as a colorless polycrystalline material. In this paper, $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ was characterized by *ab initio* X-ray powder diffraction (XRPD) methods (Masciocchi *et al.*, 2005) and multinuclear NMR spectroscopy in solution (¹H, ¹³C, ²⁹Si, and ³¹P), ³¹P CP/MAS NMR in the solid state, and high-resolution (FAB) mass spectrometry.

II. EXPERIMENTAL

$\text{Ph}_2\text{PCH}_2\text{Li}\cdot(\text{TMEDA})$ (1.76 g, 5.44 mmol) was dissolved in a mixture of pentane (10 ml) and THF (5 ml), and then treated with SiCl_4 (0.23 g, 1.36 mmol). Stirring the reaction mixture for 2 h at RT caused the precipitation of a colorless material, which was filtered, washed with pentane, and dried *in vacuo*. Yield: 0.74 g, 0.89 mmol, 64.5%. Relevant spectral data can be found in Bogza *et al.* (2005).

Diffraction data were recorded on a Bruker AXS D8 Advance diffractometer operating in the θ : θ mode, equipped with a secondary beam graphite monochromator, a Na(Tl)I scintillation counter, and pulse-height amplifier discrimination. $\text{CuK}\alpha$ radiation ($\lambda=1.5418$ Å) was used. The X-ray generator and diffractometer settings were 40 kV, 40 mA, DS 0.5°, AS 0.5°, and RS 0.1 mm. Carefully ground powders were deposited on a quartz zero-background plate. Experimental conditions were step scan mode, with $5 < 2\theta < 105^\circ$, $\Delta 2\theta=0.02^\circ$, and $t=30$ s step^{-1} . Silicon NBS 640b was used as an external standard. The recorded pattern (shown in Figure 1) could not be matched with any of the phases reported in the Powder Diffraction File (ICDD, 2005).

Peak search methods and indexing of the first 16 lines ($2\theta < 27^\circ$) by TOPAS-R (Bruker AXS, 2005) allowed the determination of a primitive tetragonal cell with approximate lattice parameters $a=17.20$, $c=7.54$ Å, $V=2231$ Å³, and $\text{GoF}=53.1$. A survey of the 2006 version of the Cambridge Structural Database showed no match of any compound with these lattice metrics (or one derived therefrom by standard cell-reduction programs). We therefore decided to solve the structure by *ab initio* XRPD methods using the experimental data shown above and the assigned *hkl* indices are reported in Table I.

Systematic absences, density, and geometrical considerations indicated $Z=2$ and (among others) space group $P-42_1c$, later confirmed by successful structure solution and refinement. The structural model employed in the final whole-pattern Rietveld refinement was determined *ab initio* by the simulated annealing technique implemented in TOPAS-R; the silicon atom was fixed at the cell origin and (partially flexible) rigid bodies for the phosphine branches were used, helping convergence and stability, with three refinable conformational parameters: the C-P-C-Si and two C-C-P-C torsional angles. The background contribution was

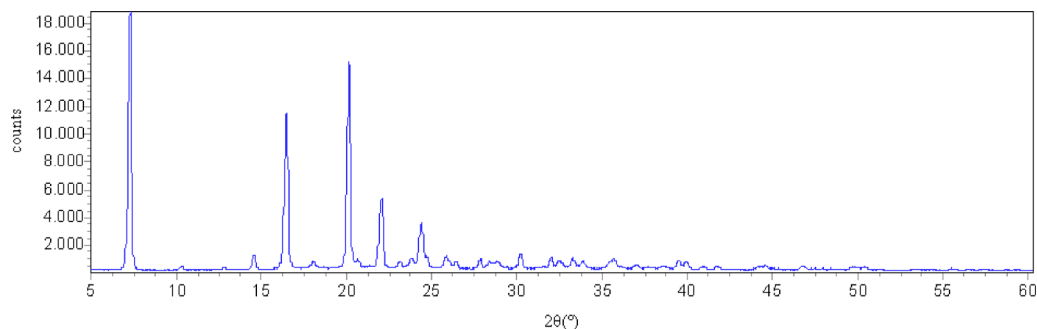


Figure 1. Raw diffraction data for $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ in the $5 < 2\theta < 60^\circ$ range.

modelled by a polynomial function, no preferred orientation correction was found to be necessary, and a single isotropic B_M value was refined. Peak shapes were described by the fundamental parameters approach with anisotropic peak broadening. The final Rietveld refinement plot and a sketch of the crystal and molecular structures are shown in Figures 2 and 3, respectively. Table II contains the relevant crystal data and data analysis parameters, and Table III contains the final fractional atomic coordinates.

TABLE I. X-ray powder diffraction data for $\text{Si}(\text{CH}_2\text{PPh}_2)_4$.

$2\theta_{\text{obs}}$ (deg)	I/I ₀	<i>h</i>	<i>k</i>	<i>l</i>	d_{obs} (Å)	d_{cal} (Å)
7.263	100.0	1	1	0	12.1615	12.1544
10.286	1.3	0	2	0	8.5930	8.5945
12.827	1.1	0	1	1	6.8959	6.9093
14.559	5.8	2	2	0	6.0793	6.0772
16.452	62.0	2	1	1	5.3837	5.3850
18.600	1.0	3	2	0	4.7666	4.7674
20.126	82.0	3	1	1	4.4086	4.4105
20.660	4.1	0	4	0	4.2957	4.2972
21.316	1.8	4	1	0	4.1650	4.1689
22.037	28.0	3	2	1	4.0304	4.0304
23.138	3.2	4	2	0	3.8410	3.8436
23.809	4.5	0	4	1	3.7342	3.7342
24.379	18.0	4	1	1	3.6482	3.6491
24.699	5.4	1	1	2	3.6017	3.6033
25.862	5.3	0	2	2	3.4423	3.4547
26.042	4.1	4	2	1	3.4189	3.4249
26.388	3.4	5	1	0	3.3749	3.3710
27.837	4.2	2	2	2	3.2024	3.2054
28.803	3.5	3	1	2	3.0971	3.0994
30.204	6.0	3	2	2	2.9566	2.9585
31.995	4.7	4	1	2	2.7951	2.7974
32.511	3.7	5	3	1	2.7518	2.7458
		6	2	0		
33.303	4.7	4	2	2	2.6882	2.6925
33.880	3.6	6	1	1	2.6438	2.6464
35.455	3.5	5	4	1	2.5298	2.5292
35.681	4.6	5	1	2	2.5143	2.5138
36.089	2.1	0	1	3	2.4868	2.4888
37.008	2.2	6	3	1	2.4271	2.4263
37.711	1.2	6	4	0	2.3835	2.3837
38.580	1.5	0	7	1	2.3318	2.3350

Thermodiffractometric experiments were performed in air in the 10–120 °C range using a custom-made sample heater with nominal ± 0.1 °C stability, assembled by Officina Elettrotecnica di Tenno, Ponte Arche, Italy.

III. DISCUSSION

The crystals of $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ contain isolated molecules, and each $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ molecule has one central Si atom located at the -4 symmetric position, the origin of the unit cell of the acentric $P-42_1c$ space group (see Figure 3). This feature is also shared by the $\text{Si}(\text{CH}_2X)_4$ [$X=\text{Cl}$ (Daiss *et al.*, 2004) and Br (Ilg *et al.*, 2006)] and SiAr_4 species [Ar = Phenyl (Claborn *et al.*, 2002), Pyrrol-1-yl (Frenzel *et al.*, 1995), 2-Furan-2-yl (Neugebauer *et al.*, 2000)]. At variance, $\text{Si}(\text{CH}_2\text{OH})_4$ (Ilg *et al.*, 2006) and $\text{C}(\text{CH}_2\text{OH})_4$ (Semmingsen, 1988), but not $\text{C}(\text{CH}_2\text{Br})_4$, $P2_1/c$ (Klaeboe *et al.*, 1986), crystallize in different tetragonal space groups, although maintaining crystallographically imposed S_4 symmetry. Consistently, all four CH_2PPh_2 branches share identical environments, so that in the ^{31}P CP/MAS NMR spectrum only one sharp singlet appears at $\delta -29.6$ ppm (versus 85% H_3PO_4), i.e., at slightly higher field than the $(\text{EtO})_x\text{Si}(\text{CH}_2\text{PPh}_2)_{4-x}$ ($x=1,2$) derivatives (Bogza *et al.*, 2005). Despite the typical low accuracy suffered by the individual geometrical parameters (bond distances and angles) derived from XRPD data, the observed coordination at the central atom is rather well defined [$\text{Si}-\text{C}(1)$ 1.848(3) Å, $\text{C}(1)-\text{Si}-\text{C}(1)$ 108.0(2)–110.2(1)°], matching single crystal data results of the tetrahedral species cited above.

As for other nearly globular species, the crystal packing, dictated by weak(er), mostly $\text{H}\cdots\text{H}$ intermolecular contacts, reflects archetypic structures, which in this case, can be retraced to the body-centered cubic one. Worthy of note, the crystal structure of the title compound, determined by the relative arrangement of the different molecules and by the ordered disposition of their four branches, is acentric, but neither polar nor chiral (and reflects the S_4 symmetry of the isolated molecule).

On measuring the powder pattern of $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ at different temperatures (10–120 °C) with 10 °C steps, we did not observe any discontinuity in the cell volume (nor in the a and c cell parameters), which would be necessary if a dehydration process were active; thus, there is no manifestation of water in the lattice cavities located near $0,0,\frac{1}{4}$ [which

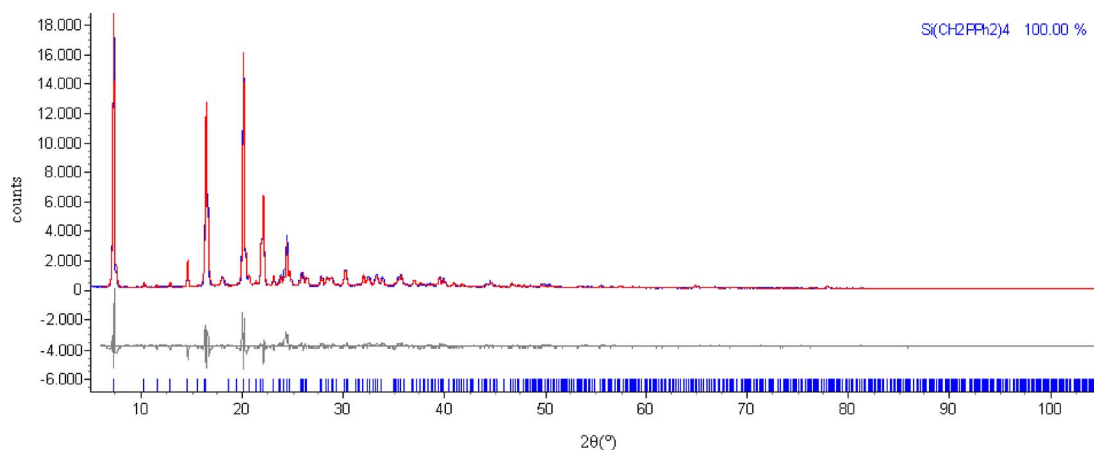


Figure 2. Final Rietveld refinement plot with peak markers and difference plot at the bottom.

PLATON (Spek, 2005) estimated as $4 \times 15 \text{ \AA}^3$, with shortest interactions of 3.45 \AA —H atoms excluded]. A nearly ideal linear behavior for this temperature dependence is shown in Figure 4. From the cell parameters thus obtained, the linear and volumetric thermal expansion coefficients could be derived ($\partial \ln a / \partial T = 4.3 \times 10^{-5} \text{ K}^{-1}$, $\partial \ln c / \partial T = 9.9 \times 10^{-5} \text{ K}^{-1}$, and $\partial \ln V / \partial T = 1.8 \times 10^{-4} \text{ K}^{-1}$), showing values typical for very “soft” materials. For comparison, near RT, $\partial \ln V / \partial T = 1.8 \times 10^{-4} \text{ K}^{-1}$ for (liquid) mercury, $2.2 \times 10^{-4} \text{ K}^{-1}$ for (solid) sulphur, and $4.8 \times 10^{-4} \text{ K}^{-1}$ for glycerine (Perry *et al.*, 1998).

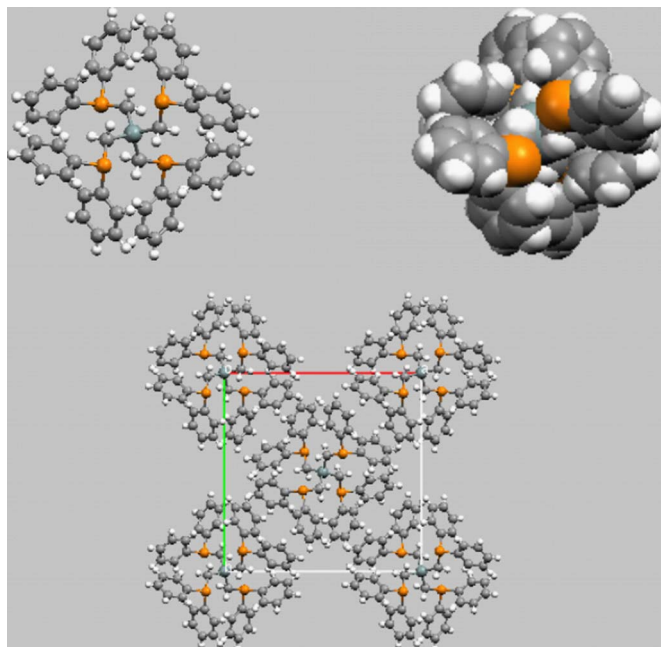


Figure 3. Schematic drawing of $\text{Si}(\text{CH}_2\text{PPh}_2)_4$, viewed down [001]. In each molecule, the Si atom is the unique central atom bearing four CH_2PPh_2 branches, and P atoms are those connected to a methylene and two phenyl groups. Hydrogen atoms are shown as white spheres. Top: the molecular structure (left, ball and sticks; right, space filling models); bottom: the crystal packing. Relevant geometrical parameters: Si–C(1) $1.848(3) \text{ \AA}$, C(1)–Si–C(1) $108.0(2)$ – $110.2(1)^\circ$, Si–C(1)–P–C(2) $179.4(5)$, Si–C(1)–P–C(8) $67.4(4)^\circ$.

IV. CONCLUSIONS

In the absence of single crystals, the structure of $\text{Si}(\text{CH}_2\text{PPh}_2)_4$, a recently published member of the polysubstituted $\text{Si}(\text{CH}_2\text{X})_4$ class, was determined by employing *uniquely* conventional laboratory X-ray powder diffraction data and state-of-the-art *ab initio* techniques. The final model was eventually refined, in $P-42_1c$, by the Rietveld method, using rigid groups with flexible conformational freedom (one C–P–C–Si and two C–C–P–C torsion angles). This work completes the structural characterization of the $(\text{EtO})_x\text{Si}(\text{CH}_2\text{PPh}_2)_{4-x}$ series and allows a detailed comparison with simpler tetrasubstituted $E(\text{CH}_2\text{X})_4$ ($E = \text{C}, \text{Si}$) derivatives.

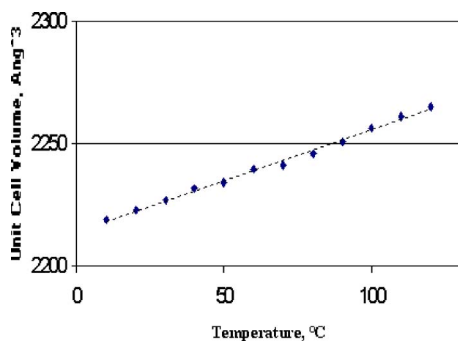
Moreover, with the aid of a custom made sample heater, the temperature dependence of the lattice parameters was also determined, which indicated a 2% increase in volume upon heating from 10°C up to 120°C . This large value, typical for nonrigid molecular solids, is likely related to a dynamic process involving large variations of the intra- and intermolecular contacts, eventually leading to reorientation of the globular molecules well before melting. Work can be anticipated in the direction of studying the thermal behavior of $\text{Si}(\text{CH}_2\text{PPh}_2)_4$ at higher temperatures, coupling TG and DSC observations to HT diffraction data.

TABLE II. Crystal data and data analysis parameters for $\text{Si}(\text{CH}_2\text{PPh}_2)_4$.

Formula	$\text{C}_{52}\text{H}_{48}\text{P}_4\text{Si}$
fw, g mol ⁻¹	824.87
System	Tetragonal
Space group	$P-42_1c$
a , Å	17.211(2)
c , Å	7.553(1)
V , Å^3	2237.5(5)
Z	2
ρ , g cm ⁻³	1.224
$F(000)$	868
2θ range	5–105
R_p , R_{wp}	0.114, 0.146
R_{Bragg}	0.056
GoF	3.06

TABLE III. Fractional atomic coordinates for Si(CH₂PPh₂)₄.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Si	0	0	0
P	0.102 06	0.093 23	0.293 64
C (1)	0.019 40	0.084 71	0.143 76
C (2)	0.090 51	0.188 63	0.396 33
C (3)	0.130 69	0.212 74	0.544 71
C (4)	0.120 75	0.287 60	0.608 92
C (5)	0.069 72	0.337 36	0.528 34
C (6)	0.028 08	0.313 65	0.384 78
C (7)	0.038 02	0.239 19	0.317 57
C (8)	0.191 94	0.100 18	0.168 23
C (9)	0.197 83	0.155 09	0.037 47
C (10)	0.264 77	0.161 01	-0.062 57
C (11)	0.325 36	0.112 23	-0.035 75
C (12)	0.320 51	0.056 98	0.092 06
C (13)	0.254 44	0.051 35	0.195 79
H (1A)	0.009 38	0.132 35	0.082 56
H (1B)	-0.025 38	0.073 59	0.211 00
H (3)	0.160 83	0.180 64	0.590 29
H (4)	0.147 51	0.298 29	0.724 52
H (5)	0.067 02	0.387 46	0.572 07
H (6)	-0.007 21	0.349 14	0.331 18
H (7)	0.010 77	0.221 21	0.204 54
H (9)	0.155 93	0.190 51	0.018 02
H (10)	0.266 93	0.198 14	-0.135 36
H (11)	0.372 70	0.116 93	-0.098 59
H (12)	0.366 66	0.022 63	0.111 41
H (13)	0.245 90	0.009 84	0.282 23

Figure 4. Temperature dependence of the unit cell volume of Si(CH₂PPh₂)₄, in the 10–120 °C range.

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