Stepwise synthesis of a stable diphosphasilirane and its unexpected dimerization

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Supplementary information

Experimental Section

General: All working procedures were conducted under rigorous exclusion of oxygen and moisture using a Schlenk line and argon atmosphere. Solvents were dried and freshly distilled before use. NMR spectra were recorded with BRUKERAVANCE 300 or with BRUKERDRX 400. The structural analyses were carried out with appropriate single crystals on an automatic diffractometer (STOE-IPDS-2T, STOE-IPDS-2 or BRUKER D8-QUEST). The structures were solved and refined with SHELX.[1] The presentation of crystal structures was effected by DIAMOND3.2.[2] IR vibrational spectra were gathered with the BRUKER ALPHA ATR-FT-IR. The starting materials $[M\{N(SiMe_3)_2\}_2(thf)_2]$ (M = Sr, Ba)[3,4] and $O(Si\textit{i}Pr_2PH_2)_2$[5] were prepared by reported methods.

$O(Si\textit{i}Pr_2PH)_2Si\textit{i}Pr_2$ (1): To 0.92 mL (2.7 mmol, 1 eq.) of $O(Si\textit{i}Pr_2PH_2)_2$ in 25 mL THF were added 2.14 mL (2.6 M in hexane, 5.4 mmol, 2 eq.) of *n*-BuLi slowly at -50 °C. The reaction mixture was warmed to room temperature and stirred for 18 h. Subsequently, the mixture was again cooled to -50 °C and 0.5 mL (2.7 mmol, 1 eq.) of $Si\textit{i}Pr_2Cl_2$ were added. The cooling bath was removed and the reaction was stirred for another 18 h. The solvent was removed under reduced pressure and the remaining residue was extracted with 25 mL *n*-pentane. The solvent was removed in vacuo and at -25 °C colourless crystals of **1** were obtained and purified by removal of the supernatant liquid; yield: 0.85 g (2.0 mmol, 75.3%).

^{1}H NMR (C_6D_6): δ = 1.3 (m, *i*Pr, 14H), 1.2 (m, *i*Pr, 28H), 0.8 (d, $^1J_{PH}$ = 190.0 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.5 (d, $^2J_{CP}$ = 12.9 Hz, *C*H), 17.7 (d, $^3J_{CP}$ = 3.7 Hz, *C*H_3), 17.7 (t, $^2J_{CP}$ = 11.7 Hz, *C*H), 17.8 (d, $^3J_{CP}$ = 4.1 Hz, *C*H_3), 19.0 (t, $^3J_{CP}$ = 4.3 Hz, *C*H_3) ppm; ^{31}P NMR

(C_6D_6): δ = -271.1 (br d, $^1J_{PH} \approx$ 190.0 Hz, P*H*) ppm; $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 16.9 (d, $^1J_{SiP}$ = 42.0 Hz), 19.1 (t, $^1J_{SiP}$ = 49.2 Hz) ppm; MS (-p APCI, 3.8 kV): *m/z* (%) = 421.2 $[M]^-$ (100); IR: = 2942 (m), 2889 (m), 2864 (m), 2286 (w, P-H), 1461 (m), 1385 (w), 1365 (w), 1259 (m), 1068 (s), 1013 (vs), 919 (m), 878 (s), 795 (s), 678 (s), 608 (s), 569 (s), 507 (s), 460 (s) cm^{-1}.

[Sr{O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$}(dme)$_2$] (2): At room temperature, 0.45 g (1.1 mmol, 1 eq.) of O(Si*i*Pr$_2$PH)$_2$Si*i*Pr$_2$ (**1**) and 0.88 g (1.6 mmol, 1.5 eq.) of [Sr{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] were combined in 25 mL of DME. After stirring for 1 h, the reaction mixture was concentrated under reduced pressure. After 14 d at -25 °C, colourless rhombic crystals of **2** were obtained; yield: 0.22 g (0.4 mmol, 36.4%).

Elemental analysis [%] found (calc. for $C_{26}H_{62}Sr_1O_5P_2Si_3$): C 45.21 (45.35), H 8.81 (9.08). ^{31}P NMR (C_6D_6/DME): δ = -266.5 (s, $^1J_{SiP}$ = 39.3 Hz) ppm; MS (-p APCI, 3.8 kV): *m/z* (%) = 421.2 $[M\text{-}Sr+H]^-$ (100).

[Ba{O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$}(dme)$_3$] (3): At room temperature, 0.45 g (1.1 mmol, 1 eq.) of O(Si*i*Pr$_2$PH)$_2$Si*i*Pr$_2$ (**1**) and 0.96 g (1.6 mmol, 1.5 eq.) of [Ba{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] were combined in 25 mL of DME. After stirring for 1 h, the reaction mixture was concentrated under reduced pressure. After 14 d at -25 °C, colourless rhombic crystals of **3** were obtained; yield: 0.35 g (0.6 mmol, 54.5%). **3** shows insufficient solubility in DME/C_6D_6 mixtures. Only a solution in THF-d_8 gives exploitable results, however dme/thf exchange can not be excluded.

Elemental analysis [%] found (calc. for. $C_{30}H_{72}Ba_1O_7P_2Si_3$): C 42.77 (43.49), H 8.09 (8.76). ^1H NMR (THF-d_8): δ = 1.11 (m, *i*Pr, 28H, 1.25 (m, *i*Pr, 14H), 3.27 (s, DME), 3.42 (s, DME) ppm; ^{31}P NMR (THF-d_8): δ = -261.9 (br s) ppm; MS (-p APCI, 3.8 kV): *m/z* (%) = 573.2 $[M]^+$ (100).

O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$ (4): A suspension of 0.99 g (1.2 mmol, 1 eq.) [Ba{O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$}(dme)$_3$] (**3**) and 0.16 mL (1.8 mmol, 1.5 eq.) of 1,2-dibromoethane in 100 mL of benzene were stirred for 18 h at room temperature. The solvent was removed in vacuo and the remaining residue was extracted with 100 mL of *n*-pentane. The solvent was

removed and the resulting colourless oil was distilled to afford compound **4** (96 °C, $1 \cdot 10^{-3}$ mbar) as a white solid with a yield of 0.45 g (1.1 mmol, 89.1%).

Elemental analysis [%] found (calcd.): C 50.14 (51.39), H 10.01 (10.06); ^{1}H NMR (toluene-d_8): δ = 1.2 (m, CH_3, 36H), 2.12 (m, CH, 6H) ppm; ^{13}C NMR (toluene-d_8): δ = 11.7 (t, $^{2}J_{CP}$ = 10.9 Hz, CH), 17.07 (s, CH), 18.4 (br, CH_3), 18.7 (br, CH_3), 18.9 (s, CH_3), 19.2 (br, CH), 19.4 (t, $^{2}J_{CP}$= 10.4 Hz, CH), 21.4 (t, $^{3}J_{CP}$ = 4.4 Hz, CH_3), 21.7 (s, CH_3) ppm; ^{31}P NMR (toluene-d_8): δ = -310.0 (s) ppm; ^{29}Si{^{1}H} NMR (toluene-d_8): δ = -20.6 (t, $^{1}J_{SiP}$ = 70.9 Hz), 37.1 (m) ppm; MS (+p APCI, 3.8 kV): *m/z* (%) = 421.2 $[M+H]^+$ (15), 307.2 $[M\text{-Si}i\text{Pr}_2+H]^+$ (83).

$[O(Si i Pr_2P)_2Si i Pr_2]_2$ (5): 10 mL of toluene were added to 0.21 g (0.5 mmol, 1 eq.) of the non-purified compound **4**. After 7 d at -25 °C, colourless crystals of **5** were obtained; yield: 0.09 g (0.2 mmol, 43.1%).

Elemental analysis [%] found (calcd.): C 49.74 (51.39), H 9.38 (10.06); ^{1}H NMR (toluene-d_8): δ = 1.15-1.60 (m, 72H) ppm; ^{13}C NMR (toluene-d_8): δ = 16.8 (s, CH), 16.9 (s, CH), 17.4 (br, CH), 17.6 (s, CH_3), 17.8-18.9 (m, CH_3), 17.8 (s, CH), 17.9 (s, CH), 18.0 (s, CH), 18.9 (br, CH), 19.3 (d, $^{2}J_{CP}$= 7.8 Hz, CH), 19.3 (br, CH), 20.3 (t, $^{2}J_{CP}$= 19.3 Hz, CH), 21.0 (br, CH), 21.3(d, $^{2}J_{CP}$= 26.2 Hz, CH) ppm; ^{31}P NMR (toluene-d_8): δ = -266.3 (br), -214.3 (br), -213.3 (br), -161.0 (br) ppm; ^{29}Si{^{1}H} NMR (toluene-d_8): δ = 11.6 (br, SiP$_2$), 12.1 (br, SiP$_2$), 26.9 (br, OSiP), 27.0 (br, OSiP), 27.5 (br, OSiP), 27.5 (br, OSiP) ppm; MS (+p APCI, 3.8 kV): *m/z* (%) = 841.4 $[M]^+$ (100).

X-Ray data

[Sr{O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$}(dme)$_2$] (2)

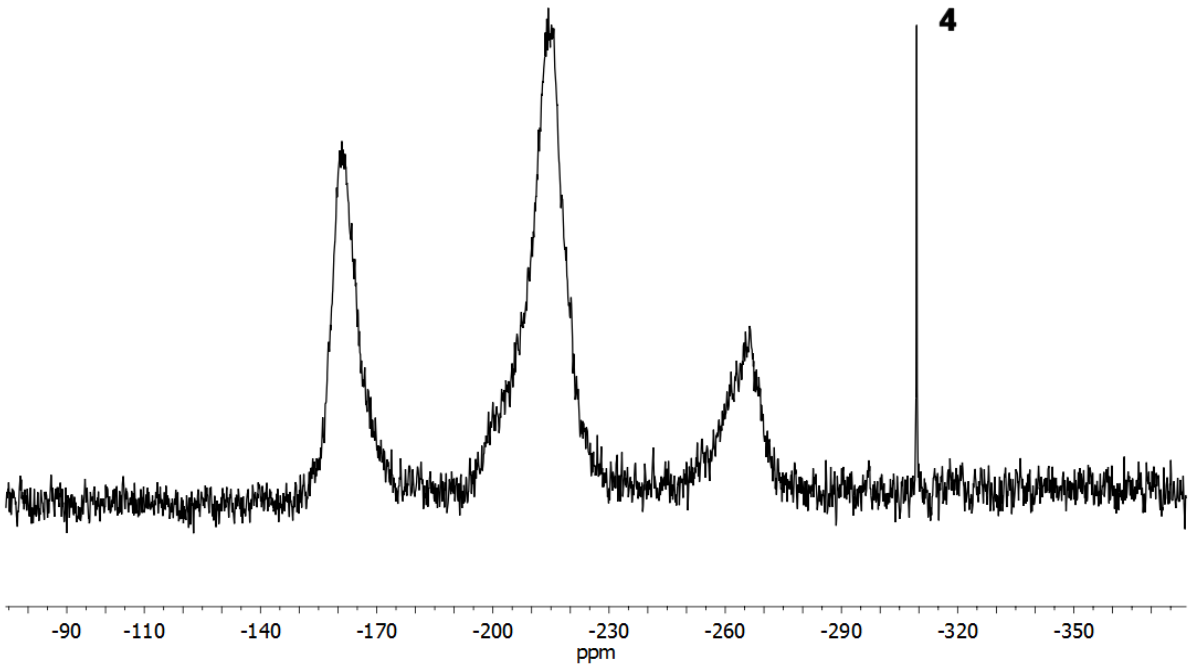
Empirical Formula	$C_{26}H_{62}Sr_1O_5P_2Si_3$	
Formula weight	688.60 g/mol	
Temperature	100.0(2) K	
Crystal system, space group	orthorhombic, *Pbca*	
Unit cell dimensions	a = 14.051(3) Å	alpha = 90 deg.
	b = 16.095(3) Å	beta = 90 deg.
	c = 33.152(7) Å	gamma = 90 deg.
Volume	7.4970(6) Å^3	
Z, calculated density	8, 1.220 g/m^3	
Absorption coefficient	1.649 mm^{-1}	
Crystal size	0.29 · 0.27 · 0.26 mm	
Theta range for data collection	1.22 to 22.50 deg.	
Reflections collected / unique	47121 / 4900	
Final R indices	R_1 = 0.0366	
	wR_2 = 0.0763 (all data)	

[Ba{O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$}(dme)$_3$] (3)

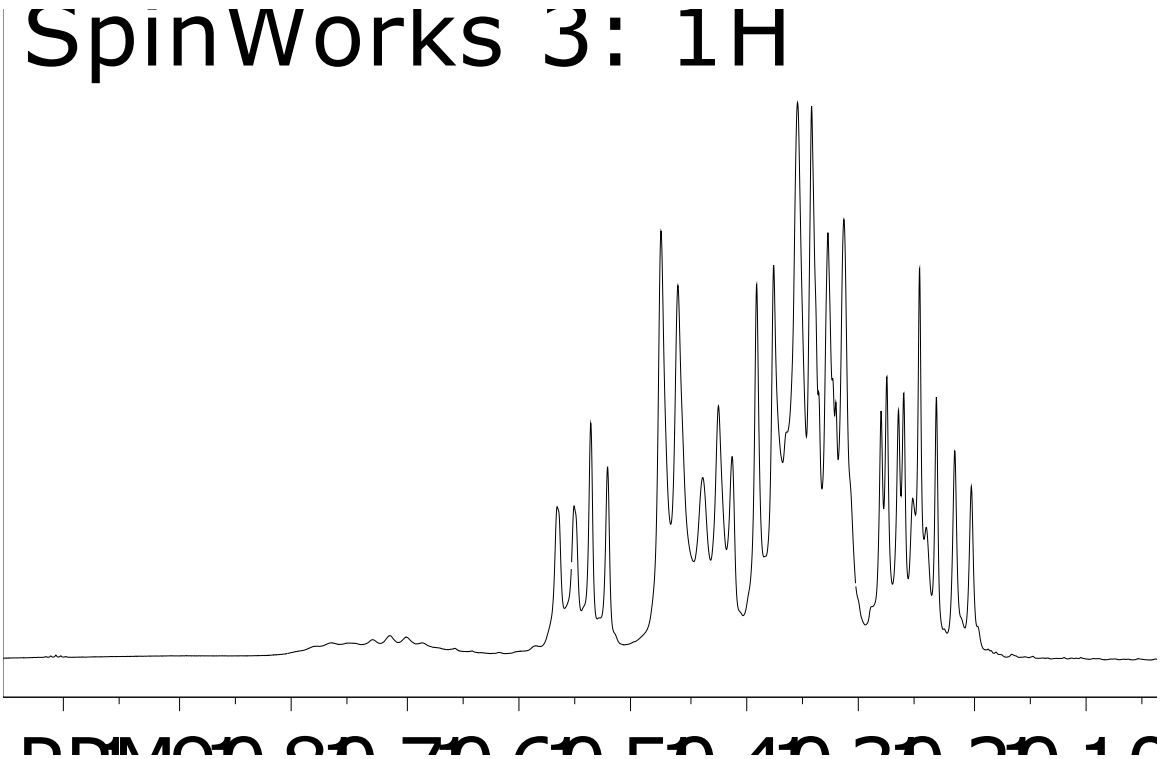
Empirical Formula	$C_{34}H_{82}Ba_1O_9P_2Si_3$	
Formula weight	918.55g/mol	
Temperature	100.0(2) K	
Crystal system, space group	orthorhombic, $P2_12_12_1$	
Flack parameter	0.026(16)	
Unit cell dimensions	a = 12.266(3) Å	alpha = 90 deg.
	b = 16.570(3) Å	beta = 90 deg.
	c = 28.821(5) Å	gamma = 90 deg.
Volume	4841.6(17) Å^3	
Z, calculated density	4, 1.260 g/m^3	
Absorption coefficient	1.003 mm^{-1}	
Crystal size	0.22 · 0.16 · 0.13 mm	
Theta range for data collection	1.87 to 27.18 deg.	
Reflections collected / unique	24870 / 10184	
Final R indices	R_1 = 0.0367	
	wR_2 = 0.1143 (all data)	

[O(Si*i*Pr$_2$P)$_2$Si*i*Pr$_2$]$_2$ (5)

Empirical Formula	$C_{36}H_{84}O_2P_4Si_6$	
Formula weight	841.45	
Temperature	100.0(2) K	
Crystal system, space group	monoclinic, $P2_1/n$	
Unit cell dimensions	a = 13.621(1) Å	alpha = 90 deg.
	b = 25.435(1) Å	beta = 101.199(5) deg.
	c = 14.457(1) Å	gamma = 90 deg.
Volume	4.9133(5) Å^3	
Z, calculated density	4, 1.138 g/m^3	
Absorption coefficient	0.328 mm^{-1}	
Crystal size	0.31 · 0.28 · 0.05 mm	
Theta range for data collection	1.60 to 26.73 deg.	
Reflections collected / unique	57887/ 10374	
Final R indices	R_1 = 0.0318	
	wR_2 = 0.0710 (all data)	



^{31}P NMR spectrum of compound **5** in toluene-d_8



^{1}H NMR spectrum of compound **5** in toluene-d_8

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