Electronic Supplementary Material (ESI) for ChemComm.

Branched tetrasilane substituted phosphines – synthesis and characterisation of $PhSi(Si\textit{i}Pr_2)_3P$ and $\{PhSi(SiMe_2)_3\}_2P_{14}$

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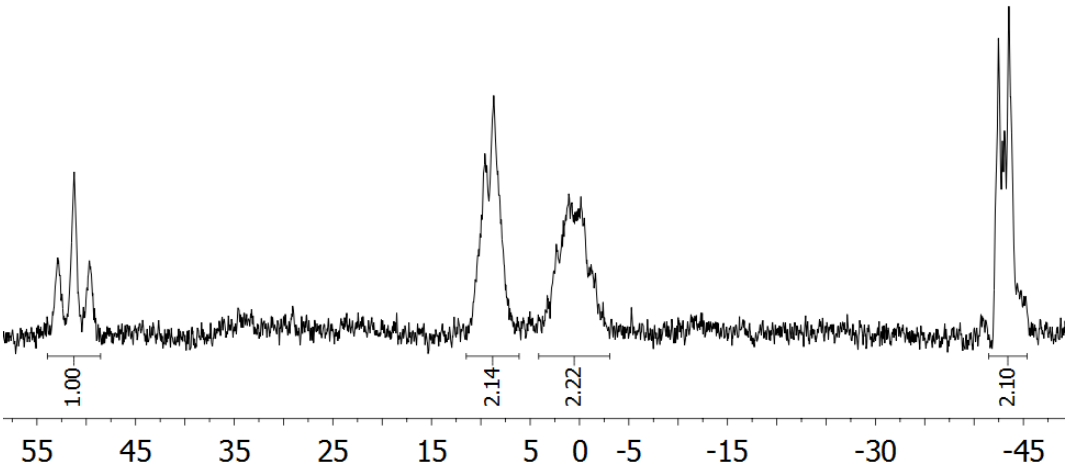
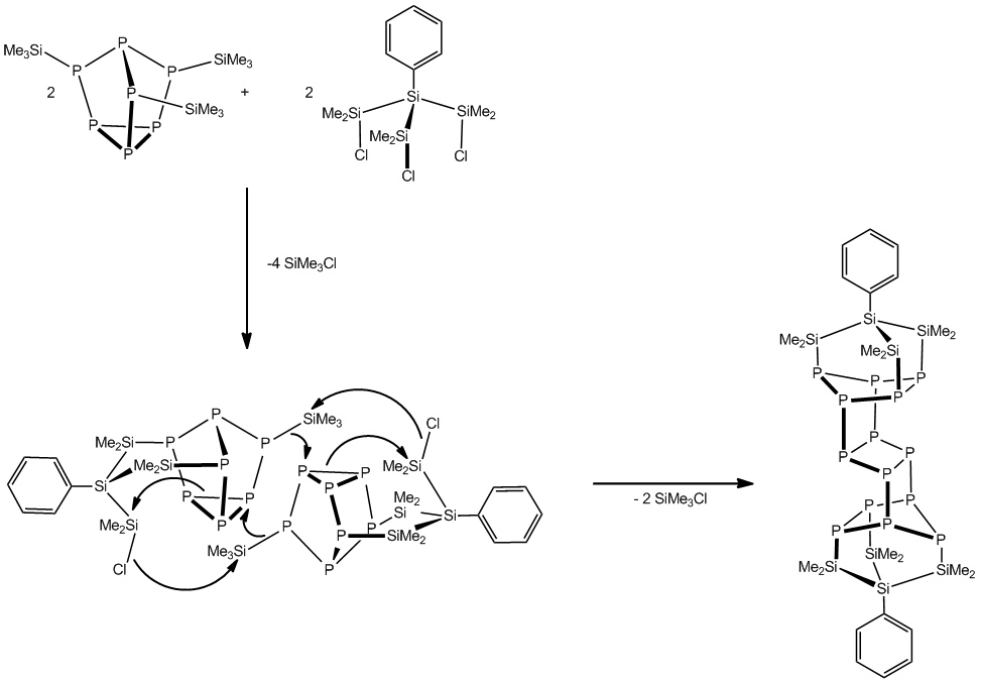
Supplementary information

$^{31}P\{1H\}$ NMR spectrum of compound 1 in THF-d_8

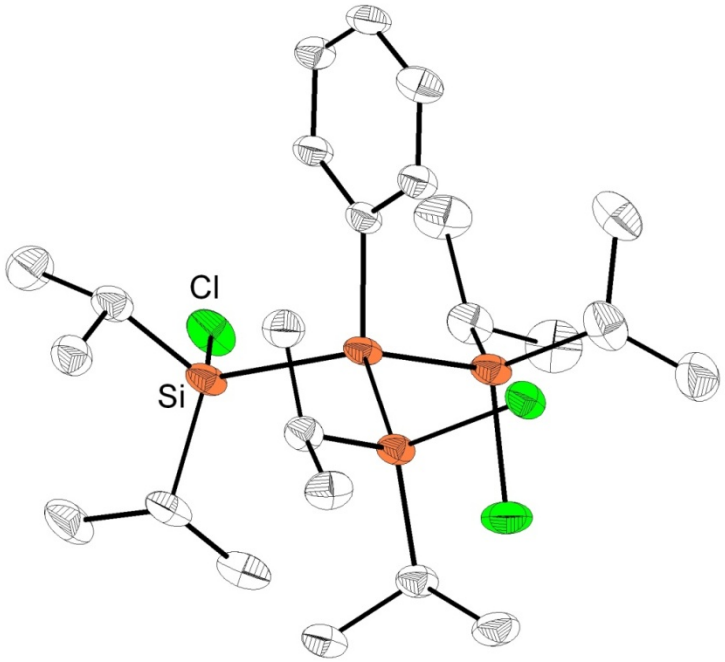


Proposed mechanism for the formation of Compound 1



X-Ray data of the compound PhSi(Si*i*Pr$_2$Cl)$_3$ (2)

Empirical formula	$C_{24}H_{47}Cl_3Si_4$	
Formula weight	554.33 g/mol	
Temperature	100.0(2) K	
Crystal system, space group	triclinic, *P*-1	
Unit cell dimensions	a = 1087.61(4) Å	alpha = 98.653(3) deg.
	b = 1689.32(7) Å	beta = 92.241(3) deg.
	c = 17010.03(7) Å	gamma = 96.040(3) deg.
Volume	3067.8(2) Å^3	
Z, calculated density	4, 1.200 g/m^3	
Absorption coefficient	0.467 mm^{-1}	
F(000)	1192	
Theta range for data collection	1.59 to 26.84 deg.	
Reflections collected / unique	31096 / 12938 (R_{int} = 0.0616)	
Final R indices	R_1 = 0.0489	
	wR_2 = 0.1128 (all data)	



Molecular structure of ***2****; thermal ellipsoids represent a 50% probability level, hydrogen atoms are not shown, selected bond lengths (pm) and angles (°): Si-Si 236.68(12) - 240.20(10), Si-Cl 208.50(10) - 210.12(11); Si-Si-Si 106.54(4) - 114.66(4), Si-Si-Cl 105.82(5) - 107.42(5).*

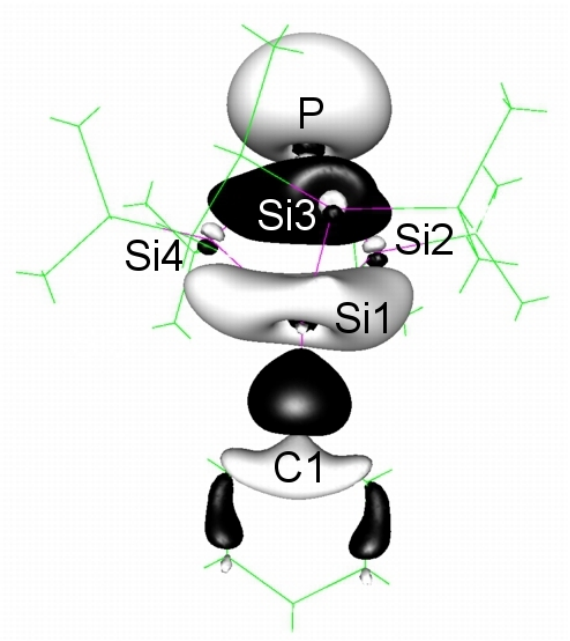
DFT calculations of the compound PhSi(Si*i*Pr$_2$)$_3$P (3)

DFT calculations were done with the program system TURBOMOLE[1] using the RIDFT program[2] and employing the Becke–Perdew 86 (BP86) functional[3] with def2-TZVP bases[4] and respective fitting bases[5] for the evaluation of the Coulomb matrix. Mulliken Population analyses[6] served to evaluate atomic orbital contributions to the molecular orbitals. MO plots were generated using the visualization tool gOpenMol.[7]

Crystal structure geometry and optimized structure of **3** have both been analyzed, yet differences in geometry and electronic situation are negligible. Thus, following values are for calculations based on crystal structure geometry without restriction of symmetry (point group c_1).

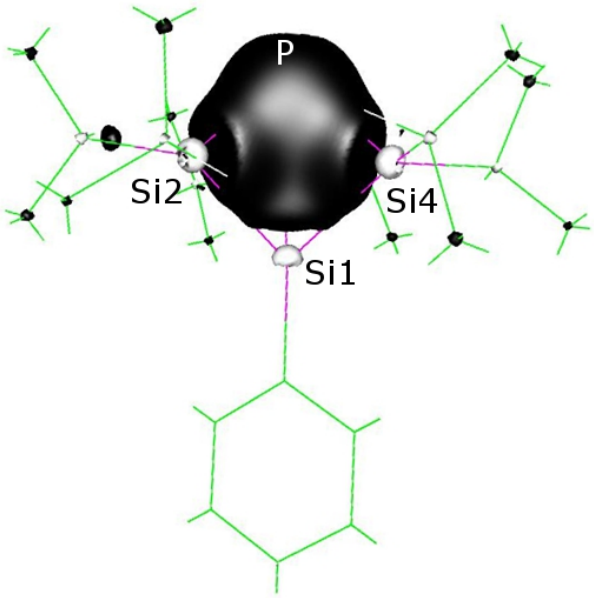
Phosphorous atomic valence orbitals substantially contribute to two molecular orbitals: 65a and 131a. The latter represents the HOMO (E = -5.114 eV) of the molecule with strong lone pair character and high phosphorous p-orbital character, whereas 65a (E = -16.076 eV) is the all symmetric bonding orbital with significant contributions of Si1-Si4 and P atomic s orbitals, explaining the observed large coupling constants in ^{31}P NMR.

Further contributions of phosphorous atomic valence orbitals are scattered on 31 different MO with overall contributions from 0.01 to 0.36.



Atom	Overall contr.	Atomic *s* contr.	Atomic *p* contr.
P	1.056	0.094	0.962
Si1	0.247	0.110	0.076
Si2	0.167	0.004	0.126
Si3	0.085	0.003	0.058
Si4	0.121	0.004	0.087
C1	0.188	0.028	0.158

*Graphical representation and Mulliken orbital contribution of the HOMO (131a) of compound **3**. Contour plot threshold 0.04.*



Atom	Overall contr.	Atomic *s* contr.	Atomic *p* contr.
P	0.506	0.457	0.048
Si1	0.164	0.112	0.050
Si2	0.234	0.212	0.015
Si3	0.225	0.207	0.011
Si4	0.218	0.203	0.009

*Graphical representation and Mulliken orbital contribution of the MO with significant phosphorous atomic s orbital contribution (65a) of compound **3**. Contour plot threshold 0.05.*

[1] TURBOMOLE Version 6.4, (c) TURBOMOLE GmbH 2012. TURBOMOLE is a development of University of Karlsruhe and Forschungszentrum Karlsruhe 1989-2007, TURBOMOLE GmbH since 2007.

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[7] gOpenMol, Leif Laaksonen, Center for Scientific Computing, Espoo, Finland, Version 3.0, 2005: D. L. Bergman, L. Laaksonen, A. Laaksonen, *J. Mol. Graph. Model.* **1997**, *15*, 301-306.