ESI

An unprecedented 1,4-diphospha-2,3-disila butadiene (-P=Si-Si=P-) derivative and a 1,3-diphospha-2-silaallyl anion each stabilized by the amidinate ligand

Subrata Kundu, Chandrajeet Mohapatra, Prinson P. Samuel, Johannes Kretsch, M. G. Walawalkar, Regine Herbst-Irmer, Dietmar Stalke*, Sriman De, Debasis Koley*, Herbert W. Roesky*

Content:

(S1) Synthesis

Experimental Section

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box where the O_2 and H_2O levels were kept below 1 ppm. Heteroleptic chlorosilylene LSiCl (**1**)[15] and $TripPCl_2$[16] were prepared according to literature methods. Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent THF-d^8 and C_6D_6 were dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum. EI-MS spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

[(TripP=Si-L)$_2$] (2): The mixture of LSiCl (**1**) (0.20g; 0.67 mmol), TripPCl$_2$ (0.21g; 0.67 mmol) and KC_8 (0.28g; 2.03 mmol) was taken into a 100 mL Schlenk flask and 40 mL of THF was added at -78 °C. Stirring was continued till the solution came to room temperature and stirring proceeded for one additional hour. THF was removed under reduced pressure and n-hexane (50 mL) was added to the residue to extract **2**. The solution was then filtered over a G4 frit. The volume of n-hexane was reduced to 20 mL and the solution was cooled to −35 °C while 0.21 g (58%) of dark yellow colored crystals were formed which were suitable for X-ray diffraction.

^{1}H NMR (500 MHz, 298 K, C_6D_6, ppm) δ: 7.38 (2H, Ar), 7.20-7.26 (6H, Ar), 6.85-7.05 (6H, Ar), 4.69 (m, 4H), 2.96 (m, 2H), 1.56 (d, 24H), 1.38 (d, 12H), 1.35 (s, 36H). ^{13}C NMR (126 MHz, 298 K, C_6D_6, ppm) δ 152.8, 145.2, 132.2, 131.6, 130.2, 127.8, 127.58, 127.54, 127.05, 120.1, 55.3, 34.7, 33.96, 31.9, 24.57. ^{31}P NMR (202 MHz, 298 K, C_6D_6) δ -133; ^{29}Si NMR (99 MHz, 298 K, C_6D_6, ppm) δ 23.3 ppm (dd, $^1J_{Sip}$ = 231 Hz, $^2J_{Sip}$ = 44 Hz). Elemental analysis for $C_{63.50}H_{96}N_4P_2Si_2$: Calc. C, 73.79%; H, 9.36%; N, 5.42%. Found C 73.91%, H 9.29%, N 5.37%. MP. 210 °C (decomp.).

[{(TripP)$_2$SiL}$^-${K(18 crown 6)·THF}$^+$] (3): The mixture of LSiCl (1) (0.20g, 0.67 mmol), TripPCl$_2$ (0.42g, 1.36 mmol), 18-crown-6 ether (0.18g; 0.67 mmol) and KC_8 (551 mg; 4.08 mmol) was placed in a 100 mL Schlenk flask and 40 mL of THF were added at -78 °C. Stirring was continued till the solution came to room temperature and stirring was continued for one hour at room temperature. THF was removed under reduced pressure and toluene (50 mL) was added to the residue to extract **3**. The solution was then filtered over a G4 frit. The volume of toluene was reduced to 15 mL and 1 mL of THF was added to the toluene solution. The latter was cooled to −35 °C. Finally 0.34 g (45%) of dark yellow colored crystals were formed which were suitable for X-ray diffraction.

^{1}H NMR (500 MHz, 298 K, THF-d^{8}, ppm) δ 6.69-7.54 (m, 9H, Ar), 4.87 (m, 4H), 3.62 (s, 24H, crown ether), 3.60 (m, 8H, coordinated THF), 2.70 (m, 2H), 1.77 (m, 8H, coordinated THF), 1.24 (d, 24H); 1.17 (d, 12H); 0.94 (s, 18H). ^{13}C NMR (126 MHz, 298 K, THF-d^{8}, ppm), δ 167.8, 154.8, 142.2, 135.3, 130.3, 127.8, 118.7, 71.3, 54.1, 35.4, 33.6, 29.3, 26.3, 25.7, 25.6, 23.9. ^{31}P NMR (202 MHz, 298 K, C_6D_6) δ -161.5 ppm; ^{29}Si NMR (99 MHz, 298 K, THF-d^{8}, ppm), δ 43.35 ppm (t, $^{1}J_{Sip}$ = 181 Hz). Elemental analysis for $C_{61}H_{101}KN_2O_7P_2Si$: Calc. C, 66.39%; H, 9.22%; N, 2.54%; Found C 66.45%, H 9.25%, N 2.50%. M.P.: 138 °C.

(S2) Theoretical Calculations

Computational Details: All computational calculations are performed by density functional theory (DFT) methods using Gaussian 09[1] (G09) and ADF2013.01[2] program packages. Geometries of all the complexes are optimized with the global-hybrid meta-GGA to the DFT functional, R/U-M062X[3] with SVP[4] basis sets for all atoms without symmetry constraints. Single point solvent calculations are performed at R/U-M06-2X/def2-TZVP//M06-2X/def2-SVP using the SMD continuum solvation model[5] implemented in Gaussian 09. All energy values reported in the manuscript are at R/U-M06-2X/def2-TZVP/SMD//R/U-M06-2X/def2-SVP level of theory. Within ADF2013.01, Natural bond orbital (NBO) analysis is performed by using the NBO 6.0[6] program at the BP86[7] level in combination with a triple-ζ-quality basis set using uncontracted slater-type orbital (STO)[8] augmented with two set of polarization functions for all atoms without any frozen core approximation. Scalar relativistic effects are treated with zeroth-order regular (ZORA) approximation[9]. QTAIM[10] analysis in the AIMALL program is also performed in the wave function generated file at R/U-M06-2X/def2-TZVP//R/U-M06-2X/def2-SVP level of theory. Any bonded pair of atoms has a bond path, *i.e.* a connecting line with maximum electron density. The bond critical point (BCP) is a point on this line where the gradient $\nabla\rho(r)$ of the density is equal to zero. The magnitude of the electron density, $\rho(r)$ and its Laplacian, $\nabla^2\rho(r)$ at the BCP provide information about the strength and type of bond. The Laplacian indicates whether the density is locally concentrated ($\nabla^2\rho<0$) or depleted ($\nabla^2\rho>0$). Ellipticities at BCP represent the deviations of the bonding density from cylindrical symmetry. It is quantitatively expressed as $\varepsilon_{BCP} = \lambda2/\lambda1-1$, where

λ1 and λ2 are eigen values of the Hessian of ρ(r) at BCP. NMR parameters are calculated using zeroth-order regular approximation (ZORA) in the PBE0[11] functional with double polarized valance triple-zeta basis set TZ2P. The resulting chemical shifts are carried out using the formula $\delta = \sigma_{ref} - \sigma$ for ^{29}Si and $\delta = \sigma_{ref} - \sigma - 266.1$[12] for ^{31}P, where σ_{ref} = nuclear shielding constant of reference compound and σ = nuclear shielding constant of **2** and **3**. For ^{29}Si, TMS was taken as standard, whereas for ^{31}P, PH_3 was used. For NBO analysis of **3**, we have truncated K(18-crown-6)ether cation from the optimized geometry. Figures are generated using the CYLview[13] and ADF-GUI visualization program. Figures in the main text are made from Chemcraft[14] visualization program.

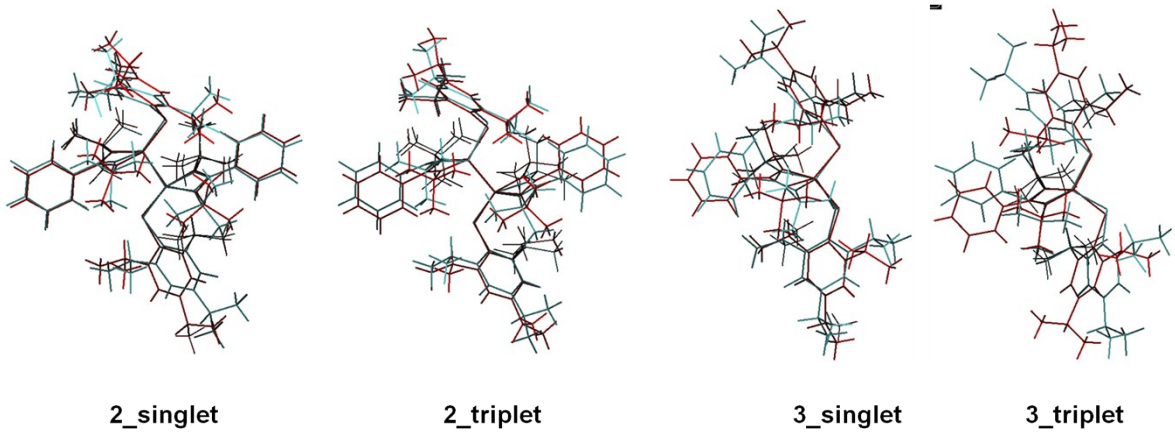

Figure S1. Superposition of crystal structure of **2** and **3** with optimized geometries of different spin states at R/U-M06-2X/def2-SVP level.

Table S1. Calculated geometrical parameters [distances (d) are in Å and angles (A) are in degree (°)] of compound **2** and **3** (in singlet and triplet electronic states).

2	Crystal Structure	R/U-M06-2X/def2-SVP	
		Singlet	Triplet
d(Si1-Si2)	2.382	2.375	2.368
d(Si1-P1)	2.120	2.133	2.294
d(Si2-P2)	2.126	2.125	2.143
d(P1-C1)	1.859	1.868	1.854
d(P2-C2)	1.838	1.877	1.873

d(Si1-N1)	1.834	1.861	1.986
d(Si1-N2)	1.877	1.890	1.889
d(Si2-N3)	1.837	1.856	1.874
d(Si2-N4)	1.879	1.903	1.923
A(P1-Si1-Si2)	110.8	114.4	111.9
A(P2-Si2-Si1)	111.3	114.4	109.3
A(Si1-P1-C1)	107.6	101.5	98.2
A(Si2-P2-C2)	111.0	102.5	103.0
A(N1-Si1-P1)	123.3	123.9	115.9
A(N2-Si1-P1)	129.7	127.8	107.7
A(N3-Si2-P2)	124.3	124.3	123.2
A(N4-Si2-P2)	129.8	129.4	126.8

3	Crystal Structure	R/U-M06-2X/def2-SVP	
		Singlet	Triplet
d(Si1-P1)	2.166	2.146	2.288
d(Si1-P2)	2.168	2.166	2.169
d(P1-C1)	1.873	1.880	1.861
d(P2-C2)	1.875	1.872	1.867
d(Si1-N1)	1.887	1.906	1.791
d(Si1-N2)	1.883	1.925	1.784
A(P1-Si1-P2)	103.1	108.5	92.2
A(C1-P1-Si1)	106.9	104.1	106.4
A(C2-P2-Si1)	120.0	107.1	109.4
A(N1-Si1-P1)	115.6	115.3	118.1
A(N1-Si1-P2)	125.6	121.9	128.3
A(N2-Si1-P1)	122.8	123.7	122.8
A(N2-Si1-P2)	119.2	115.5	124.2

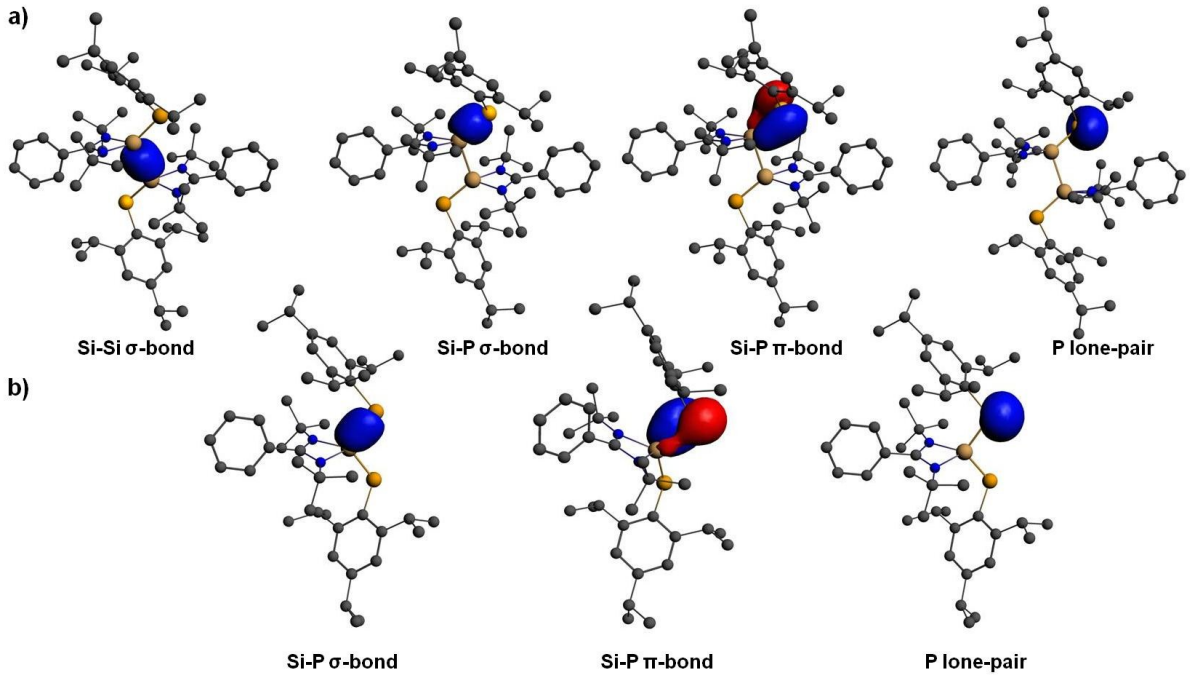

Figure S2. Selected NBOs of a) complex **2** and b) complex **3** (isosurface = 0.06 a.u.). H atoms are omitted for clarity.

Table S2. NBO results of **2** and **3** at BP86/TZ2P level of theory.

	Bond	Occupancy	Polarization	WBI
2	Si–Si	1.878	Si(49.6%)–Si(50.4%)	0.85
	Si–P	1.940	Si(42.6%)–P(57.4%)	1.40
	Si–P	1.847	Si(20.2%)–P(79.8%)	
	LP P	1.886	(63.6% s; 36.4% p)	

	Bond	Occupancy	Polarization	WBI
3	Si–P	1.891	Si(40.9%)–P(59.1%)	1.30
	Si–P	1.828	Si(18.6%)–P(81.4%)	
	LP P	1.885	(66.1% s; 33.8% p)	

Table S3. Partial charges(q) of **2** and **3**.

	Fragments	Partial Charges(q)		Fragments	Partial Charges(q)
2	LSi	0.76	**3**	LSi	0.77
	TripP	-0.76		TripP	-0.88

Table S4. BCP parameters of **2** and **3**

Entry	Bond	ρ(e/Å^3)	$\nabla^2\rho$(e/Å^5)	ε_{BCP}
2	Si–Si	0.092	-0.155	0.075
	Si–P	0.111	-0.059	0.335
	Si–P	0.111	-0.044	0.351

Entry	Bond	ρ(e/Å^3)	$\nabla^2\rho$(e/Å^5)	ε_{BCP}
3	Si–P	0.108	-0.044	0.334
	Si–P	0.106	-0.059	0.268

Table S5. Calculated chemical shifts values (in ppm) of selected atoms for **2** and **3** at PBE0/TZ2P level of theory.

2	Si1	Si2	P1	P2
	30.0	38.9	-141.5	-156.6
3	Si1	P1	P2	
	42.4	-177.8	-141.1	

Table S6: Formal Charges

	Atom	Formal Charge(q)		Atom	Formal Charge(q)
2	Si	1.08	**3**	Si	1.06
	N1	-0.70		N1	-0.67
	N2	-0.71		N2	-0.66
	P	-0.37		P1	-0.38
				P2	-0.39

Table S7: Natural Bond Order (total/covalent/ionic):

Entry	NBO	Total	Covalent	Ionic
2	Si1–N1	0.6873	0.1388 (20%)	0.5485 (80%)
	Si1–N2	0.5551	0.1780 (32%)	0.3770 (68%)
3	Si1–N1	0.8466	0.3193 (38%)	0.5273 (62%)
	Si1–N2	0.5896	0.1020 (18%)	0.4877 (82%)

Table S8: Natural Atom Valences

Entry	Atom	Co-valence
2	Si	3.8
3	Si	3.7

Table S9: 3-center, 4-electron (Hyper Bond)

Entry	Hyper Bond(A-B-C)	%A-B/%B-C	Occupancy
2	N1–C1–N2	47.5/52.5	3.981
3	N1–C1–N2	50.4/49.6	3.990

Table S10. The Cartesian coordinates (in Å) of optimized geometries of **2** and **3** at R/U-M062X/def2-SVP level of theory.

2_singlet			
Si	-1.22968	0.11597	0.83364
P	2.09571	1.91690	0.70025
N	-1.86492	1.41687	-0.33585
N	-1.53363	1.73134	1.76612
N	1.59724	-1.38999	-0.40227
N	1.54360	-1.52735	1.74852
C	-1.82481	2.34653	0.62838
C	-2.06534	1.57469	-1.78950
C	-0.86847	2.30946	-2.40332
H	-0.84058	3.35847	-2.07422
H	-0.93504	2.29652	-3.50148
H	0.07011	1.83410	-2.09392
C	-3.36328	2.33238	-2.09411
H	-3.29719	3.39736	-1.83932
H	-4.20432	1.86793	-1.55590
H	-3.56912	2.25754	-3.17225
C	-2.68267	3.13284	3.46702
H	-2.74555	3.27877	4.55496
H	-3.62643	2.68109	3.12515
H	-2.56735	4.12032	3.00328
C	-0.18232	2.92175	3.46128
H	-0.08138	3.82837	2.84715
H	0.68050	2.27639	3.24254
H	-0.15251	3.21568	4.52124
C	-1.63525	0.95405	4.02988
H	-1.60188	1.23023	5.09317
H	-0.81309	0.25344	3.83331
H	-2.57816	0.42636	3.82017
C	-1.50133	2.20572	3.15998
C	-2.22186	0.16567	-2.37509
H	-1.50079	-0.54766	-1.94649
H	-2.07870	0.19817	-3.46479
H	-3.22775	-0.22191	-2.16483
C	-1.97729	3.81830	0.45608
C	-0.81623	4.58260	0.30049

H	0.15721	4.08042	0.28514
C	-0.91846	5.96675	0.16273
H	-0.01309	6.56276	0.03927
C	-3.32442	5.81642	0.34545
H	-4.30291	6.29777	0.36758
C	-2.16889	6.58305	0.18558
H	-2.24499	7.66634	0.08016
C	1.69526	-2.23154	0.63407
C	-3.23170	4.43384	0.48033
H	-4.12947	3.82797	0.61416
C	1.08023	-2.80635	-2.38507
H	1.44437	-3.77195	-2.00968
H	1.16658	-2.81738	-3.48149
H	0.01577	-2.70485	-2.12320
C	1.88257	-1.62307	-1.83188
C	1.47572	-0.35699	-2.58013
H	0.39258	-0.20216	-2.51717
H	1.74712	-0.45256	-3.64114
H	1.99214	0.51973	-2.16386
C	3.38746	-1.83604	-2.03396
H	3.95092	-0.96878	-1.65751
H	3.60128	-1.95247	-3.10687
H	3.73618	-2.74398	-1.52387
C	1.56845	-1.94393	3.16412
C	2.67281	-2.97552	3.42913
H	3.61571	-2.66913	2.95348
H	2.40101	-3.97694	3.07245
H	2.83885	-3.03972	4.51442
C	0.22025	-2.52789	3.59254
H	0.27125	-2.83430	4.64823

H	-0.03810	-3.40754	2.98624
H	-0.59455	-1.80127	3.47557
C	1.87989	-0.68603	3.98201
H	1.74731	-0.89851	5.05226
H	1.21605	0.14595	3.71000
H	2.91337	-0.34998	3.81732
C	1.83975	-3.71132	0.54635
C	3.09289	-4.32160	0.45392
H	3.99766	-3.71154	0.45917
C	3.18213	-5.70998	0.38015
H	4.16076	-6.18640	0.30925
C	2.02356	-6.48660	0.40245
H	2.09557	-7.57378	0.34614
C	0.77367	-5.87468	0.50104
H	-0.13298	-6.48122	0.52385
C	0.67422	-4.48616	0.57279
H	-0.29945	-3.98914	0.64812
C	-3.78554	-2.51541	-1.04029
C	-3.68200	-1.61548	0.05204
C	-4.87686	-2.42712	-1.91227
H	-4.94436	-3.10972	-2.76211
C	-5.87081	-1.46558	-1.75762
C	-5.77466	-0.60321	-0.66342
H	-6.55873	0.14322	-0.52339
C	-4.72035	-0.66788	0.25195
C	-2.93970	-4.79434	-0.40647
H	-2.93043	-4.51154	0.65678
H	-2.15290	-5.54672	-0.57624
H	-3.91233	-5.26164	-0.62707
C	-2.59131	-3.99340	-2.76531

H	-2.49530	-3.12193	-3.43076
H	-3.45399	-4.58809	-3.10328
H	-1.69581	-4.62092	-2.89141
C	-2.71973	-3.57091	-1.30262
H	-1.76158	-3.11695	-1.00301
C	-7.00817	-1.33957	-2.75278
H	-6.87200	-2.13829	-3.50042
C	-8.37333	-1.54424	-2.09065
H	-9.18030	-1.50128	-2.83750
C	-6.94927	0.00375	-3.48686
H	-7.73869	0.07223	-4.25052
H	-7.08959	0.83822	-2.78189
H	-5.97537	0.14114	-3.97898
H	-8.42367	-2.51562	-1.57895
H	-8.56752	-0.75970	-1.34308
C	-4.75257	0.24699	1.47237
H	-3.73262	0.62151	1.64320
C	-5.66536	1.46290	1.31453
H	-5.53155	2.15282	2.16149
H	-6.72787	1.17585	1.30483
H	-5.45948	2.01175	0.38245
C	-5.15497	-0.54943	2.71990
H	-5.15867	0.09859	3.61118
H	-4.45407	-1.37740	2.89420
H	-6.16647	-0.96566	2.59383
P	-2.17446	-1.77084	1.14437
Si	1.14018	0.01904	0.71553
C	4.96131	1.32743	2.74778
H	4.23633	2.14515	2.63530
H	5.97444	1.73359	2.60206

C	3.69288	1.56021	-0.21829
C	3.87256	2.15864	-1.49303
C	5.04401	1.91142	-2.21873
H	5.16631	2.35612	-3.20894
C	6.06837	1.11086	-1.72221
C	5.90620	0.57001	-0.44555
H	6.70933	-0.04382	-0.03423
C	4.75336	0.78104	0.31471
C	2.83648	3.11292	-2.07192
H	1.85379	2.75907	-1.73018
C	2.80609	3.17009	-3.59822
H	1.92934	3.74600	-3.93081
H	2.74275	2.16421	-4.04007
H	3.69619	3.66865	-4.01163
C	3.02913	4.51571	-1.48222
H	2.97898	4.48948	-0.38357
H	2.25099	5.20295	-1.85105
H	4.01175	4.92106	-1.77038
C	4.69175	0.21563	1.72660
H	3.66513	-0.14314	1.88326
H	4.89375	0.94165	3.77754
C	5.62913	-0.96398	1.97816
H	6.68747	-0.66282	1.95131
H	5.48641	-1.76494	1.23561
H	5.44454	-1.38070	2.97978
H	7.20801	1.37836	-3.48876
C	7.31533	0.83020	-2.53824
C	8.57788	1.34419	-1.84165
H	9.46526	1.18125	-2.47164
H	8.49905	2.41833	-1.62284

H	8.74274	0.81808	-0.88865
C	7.43656	-0.66029	-2.86926
H	6.53981	-1.02133	-3.39315
H	8.31295	-0.85232	-3.50657
H	7.55171	-1.25553	-1.94981
2_triplet			
Si	1.14907	-0.12307	0.53546
P	-2.05743	-1.90148	0.87170
N	2.25932	-1.47843	-0.40076
N	1.59487	-1.57845	1.65373
N	-1.72510	1.41203	-0.31841
N	-1.81503	1.59892	1.82604
C	2.10858	-2.28477	0.63738
C	2.44159	-1.78415	-1.82867
C	1.17197	-2.42474	-2.40042
H	0.95026	-3.38036	-1.90092
H	1.29684	-2.61753	-3.47678
H	0.31156	-1.75576	-2.26181
C	3.64905	-2.69362	-2.08082
H	3.47151	-3.72614	-1.75651
H	4.54017	-2.29760	-1.57065
H	3.85860	-2.71151	-3.16060
C	2.73464	-2.80448	3.50481
H	2.81585	-2.79780	4.60131
H	3.68347	-2.42953	3.08915
H	2.59325	-3.84466	3.18650
C	0.24498	-2.56942	3.48777
H	0.11342	-3.51770	2.94797
H	-0.61859	-1.93430	3.24733
H	0.24279	-2.78033	4.56794
C	1.71877	-0.57642	3.85417
H	1.60383	-0.75093	4.93379
H	0.95593	0.14768	3.53881
H	2.70906	-0.12878	3.67559
C	1.56421	-1.89959	3.09613
C	2.71392	-0.44540	-2.52230
H	1.91212	0.27834	-2.31380
H	2.77690	-0.59425	-3.61024
H	3.66106	-0.01511	-2.16539
C	2.27708	-3.76487	0.65369
C	1.10562	-4.53076	0.62321
H	0.13437	-4.02317	0.58543
C	1.19347	-5.92284	0.63276
H	0.28090	-6.52012	0.60121
C	3.60543	-5.77698	0.72643
H	4.58040	-6.26384	0.77467
C	2.43993	-6.54520	0.68903
H	2.50559	-7.63416	0.70430
C	-1.97812	2.25609	0.68920
C	3.52701	-4.38721	0.70170
H	4.43338	-3.78024	0.73020
C	-1.40596	2.87098	-2.31996
H	-1.97869	3.75811	-2.01875
H	-1.41704	2.82233	-3.41883
H	-0.36354	2.99319	-1.99278
C	-1.99190	1.56812	-1.76098
C	-1.31832	0.39222	-2.46618
H	-0.22712	0.45391	-2.35213
H	-1.56415	0.41370	-3.53777
H	-1.66813	-0.56194	-2.04406

C	-3.50029	1.51083	-2.02663
H	-3.91410	0.54174	-1.71492
H	-3.69145	1.64391	-3.10221
H	-4.02602	2.31378	-1.48860
C	-1.87815	2.04150	3.22518
C	-3.11105	2.91720	3.47688
H	-4.01131	2.43923	3.06382
H	-3.00579	3.91704	3.03653
H	-3.25007	3.04081	4.56085
C	-0.60840	2.80567	3.61442
H	-0.64309	3.07299	4.68119
H	-0.51344	3.73317	3.03185
H	0.28854	2.19660	3.43500
C	-1.99749	0.77055	4.07192
H	-2.03491	1.03444	5.13830
H	-1.13531	0.10887	3.91077
H	-2.90422	0.20476	3.81125
C	-2.22803	3.71645	0.54239
C	-3.51024	4.24968	0.39669
H	-4.37950	3.59059	0.42554
C	-3.67097	5.62433	0.23024
H	-4.67214	6.04197	0.11558
C	-2.55727	6.46407	0.21381
H	-2.68791	7.53930	0.08364
C	-1.27714	5.93069	0.36965
H	-0.40500	6.58641	0.36379
C	-1.10970	4.55772	0.53271
H	-0.11065	4.12463	0.64377
C	3.58285	2.58852	-1.05869
C	3.64145	1.74194	0.06787

C	4.64660	2.58589	-1.96780
H	4.60417	3.22649	-2.85076
C	5.76167	1.76803	-1.79739
C	5.80137	0.93593	-0.67562
H	6.66299	0.28053	-0.53637
C	4.76699	0.90675	0.26086
C	2.50438	4.76569	-0.42120
H	2.59032	4.52196	0.64816
H	1.62625	5.41486	-0.56322
H	3.39994	5.33557	-0.71307
C	2.15401	3.87965	-2.74341
H	2.09955	2.99002	-3.38854
H	2.95455	4.53252	-3.12224
H	1.21040	4.43596	-2.84211
C	2.38447	3.50153	-1.28162
H	1.49228	2.94003	-0.94613
C	6.87138	1.73344	-2.83024
H	6.66250	2.53602	-3.55636
C	8.24532	2.00546	-2.21350
H	9.01990	2.04213	-2.99377
C	6.86013	0.40103	-3.58727
H	7.63093	0.38692	-4.37240
H	7.06062	-0.43557	-2.89947
H	5.88153	0.22234	-4.05589
H	8.25473	2.96048	-1.66962
H	8.52507	1.21052	-1.50535
C	4.87576	0.00658	1.48524
H	3.86106	-0.36216	1.70969
C	5.75669	-1.22157	1.26605
H	5.67479	-1.90726	2.12311

H	6.81968	-0.95164	1.17466
H	5.46173	-1.76250	0.35464
C	5.36439	0.79958	2.70408
H	5.38912	0.15884	3.59950
H	4.71070	1.65829	2.91438
H	6.38166	1.18077	2.52551
P	2.26828	1.72234	1.31403
Si	-1.18960	0.05789	0.86096
C	-5.11328	-1.46144	2.67550
H	-4.32224	-2.22344	2.65783
H	-6.08017	-1.95113	2.47967
C	-3.58297	-1.69282	-0.19406
C	-3.59881	-2.32217	-1.46656
C	-4.73086	-2.21524	-2.28335
H	-4.72792	-2.68425	-3.26990
C	-5.87103	-1.52551	-1.88167
C	-5.86309	-0.94298	-0.61315
H	-6.75448	-0.40558	-0.28337
C	-4.75361	-1.01110	0.23454
C	-2.42045	-3.15707	-1.94904
H	-1.51686	-2.69739	-1.52222
C	-2.25691	-3.20614	-3.46721
H	-1.30189	-3.68968	-3.72305
H	-2.25922	-2.19713	-3.90708
H	-3.05443	-3.79021	-3.95217
C	-2.50438	-4.57401	-1.36891
H	-2.54973	-4.54217	-0.27024
H	-1.62442	-5.16842	-1.66450
H	-3.40694	-5.08797	-1.73567
C	-4.84684	-0.38263	1.61938
H	-3.86445	0.06195	1.83814
H	-5.15166	-1.02082	3.68479
C	-5.88743	0.73076	1.73198
H	-6.91451	0.34459	1.64795
H	-5.75048	1.49724	0.95267
H	-5.81288	1.21617	2.71673
H	-6.84588	-1.96658	-3.71058
C	-7.07086	-1.38823	-2.79933
C	-8.34060	-1.97218	-2.17480
H	-9.18527	-1.91190	-2.87756
H	-8.19513	-3.02481	-1.89442
H	-8.62129	-1.41727	-1.26646
C	-7.28227	0.07196	-3.21147
H	-6.37711	0.48284	-3.68125
H	-8.11772	0.16572	-3.92185
H	-7.51488	0.69270	-2.33196
	3_singlet		
K	-5.92917	1.51553	0.59345
C	-4.71464	4.52351	-1.09802
H	-4.45578	5.59826	-1.10540
H	-5.18443	4.27840	-2.06950
O	-5.61215	4.24421	-0.04633
C	-6.80125	4.98165	-0.13415
H	-7.36705	4.70059	-1.04303
C	-7.63936	4.71056	1.08800
H	-7.07105	4.98126	1.99748
O	-7.98712	3.34771	1.11675
C	-8.88087	3.03211	2.15377
H	-9.81154	3.62157	2.05668
H	-8.42925	3.26389	3.13668

C	-9.21392	1.56433	2.08917
O	-8.04545	0.82184	2.32344
H	-3.06156	-2.05042	0.71661
H	-4.57136	-1.99988	-0.23580
O	-6.43193	0.17560	-1.62978
C	-6.84909	-1.16242	-1.82800
H	-7.89457	-1.18281	-2.19191
H	-6.80023	-1.67404	-0.85657
C	-5.89407	-1.71403	-2.88758
H	-6.34653	-2.52386	-3.47384
H	-4.98550	-2.11291	-2.41308
C	-5.55651	-0.47119	-3.73804
H	-4.47455	-0.39120	-3.90969
H	-6.04302	-0.50576	-4.72143
C	-6.09143	0.70960	-2.90129
H	-5.34871	1.50178	-2.73259
H	-6.99060	1.14969	-3.36910
O	-3.84028	-0.16036	0.36680
C	-3.14586	0.06348	-0.84398
H	-3.81259	-0.16061	-1.69811
H	-2.26872	-0.59793	-0.90397
C	-2.67810	1.48879	-0.90599
H	-2.04069	1.71261	-0.03255
H	-2.05067	1.63023	-1.80327
O	-3.81133	2.34749	-0.93644
C	-3.46415	3.70435	-0.91256
H	-2.74962	3.94416	-1.72100
H	-2.98085	3.96514	0.04786
H	-6.58693	6.06530	-0.18874
H	-8.54781	5.33992	1.05198

H	-9.98030	1.33591	2.85298
H	-9.63684	1.32029	1.09602
C	-8.27962	-0.56142	2.43824
H	-8.69405	-0.96059	1.49313
H	-9.00887	-0.76177	3.24479
C	-6.97819	-1.25268	2.75291
H	-6.54568	-0.82214	3.67623
H	-7.17017	-2.32621	2.93788
O	-6.10672	-1.08009	1.67042
C	-4.84208	-1.68224	1.86669
H	-4.96251	-2.75446	2.10516
H	-4.31921	-1.19519	2.71077
C	-4.03154	-1.53014	0.60934
P	3.33279	1.22177	-2.16722
P	0.34771	-0.13417	-0.94152
Si	2.49554	-0.06449	-0.66659
N	3.28507	0.09128	1.06116
N	3.31393	-1.71565	-0.11077
C	3.76033	-1.14818	1.00534
C	4.74088	-1.74341	1.95674
C	4.39227	-2.73953	2.87124
H	3.35352	-3.06012	2.95101
C	5.37142	-3.31074	3.68314
H	5.09531	-4.08765	4.39758
C	6.69866	-2.89569	3.57832
H	7.46429	-3.35176	4.20797
C	7.04502	-1.89136	2.67380
H	8.08080	-1.55753	2.59215
C	6.06796	-1.30951	1.86961
H	6.32114	-0.51517	1.16238

C	3.57279	-3.03225	-0.70996
C	3.21343	-2.89539	-2.19273
H	2.16129	-2.58918	-2.29242
H	3.35241	-3.85904	-2.70443
H	3.83187	-2.12718	-2.68141
C	2.66922	-4.09527	-0.07197
H	1.60839	-3.83897	-0.19791
H	2.88821	-4.19462	1.00223
H	2.85353	-5.07199	-0.54551
C	3.33524	1.09963	2.12741
C	5.03656	-3.47586	-0.57863
H	5.20571	-4.33882	-1.23962
H	5.28986	-3.78454	0.44479
H	5.72066	-2.67294	-0.87914
C	4.75743	1.63332	2.35083
H	5.24653	1.83593	1.38753
H	5.36981	0.92533	2.92647
H	4.71229	2.57474	2.92063
C	2.77927	0.53083	3.43838
H	2.81566	1.30528	4.21944
H	3.36998	-0.32877	3.78736
H	1.73300	0.21817	3.30700
C	2.43095	2.24289	1.66188
H	2.83470	2.68781	0.74260
H	2.37201	3.01722	2.44124
H	1.42040	1.86468	1.44131
C	4.89203	1.90276	-1.36708
C	4.91360	3.25227	-0.92472
C	6.05504	3.77757	-0.30169
H	6.03649	4.81060	0.04803

C	7.20158	3.01472	-0.10224
C	7.21063	1.71726	-0.62130
H	8.13030	1.13484	-0.52107
C	6.10547	1.16225	-1.27322
C	3.73423	4.18155	-1.18451
H	2.82576	3.56264	-1.13413
C	3.81498	4.71952	-2.61827
H	2.95836	5.37614	-2.83934
H	3.80754	3.88886	-3.33828
H	4.74152	5.29877	-2.76010
C	3.60160	5.33200	-0.18707
H	4.39532	6.08497	-0.31562
H	3.63883	4.97445	0.85330
H	2.64138	5.84833	-0.33809
C	8.40069	3.51189	0.68479
H	9.29775	3.07515	0.21297
C	8.33337	2.98805	2.12531
H	7.44226	3.39246	2.63065
H	9.22385	3.28410	2.70191
H	8.25479	1.89084	2.14341
C	8.56089	5.03043	0.67533
H	8.55748	5.42794	-0.34969
H	9.50586	5.32000	1.15836
H	7.74579	5.51889	1.23101
C	6.25527	-0.18580	-1.97220
H	5.35325	-0.77176	-1.73196
C	6.28427	0.01751	-3.49425
H	5.38055	0.53525	-3.83903
H	6.34533	-0.95384	-4.01067
H	7.16827	0.61260	-3.77441

C	7.49582	-0.98548	-1.57170
H	7.48545	-1.96247	-2.07739
H	7.56187	-1.16992	-0.48933
H	8.41758	-0.47132	-1.88472
C	-0.19494	-1.89095	-0.59160
C	-0.35666	-2.41429	0.72016
C	-0.97796	-3.65088	0.91919
H	-1.09537	-4.03841	1.93580
C	-1.46118	-4.42182	-0.14019
C	-1.27048	-3.92901	-1.42964
H	-1.60591	-4.52512	-2.28090
C	-0.64096	-2.70030	-1.67530
C	0.10693	-1.63498	1.93981
H	0.93062	-0.98651	1.60639
C	-1.01656	-0.72091	2.43947
H	-1.38967	-0.08703	1.62153
H	-0.66820	-0.06764	3.25621
H	-1.85180	-1.33016	2.82738
C	0.61647	-2.52973	3.07071
H	-0.20615	-3.03493	3.60155
H	1.16672	-1.93592	3.81633
H	1.28432	-3.31156	2.67894
C	-2.20132	-5.71797	0.13656
H	-1.82338	-6.10253	1.09887
C	-3.70084	-5.44350	0.30457
H	-4.11520	-5.03015	-0.62925
H	-3.87406	-4.70947	1.10604
H	-4.25496	-6.36273	0.55061
C	-1.96768	-6.79651	-0.92082
H	-2.42226	-7.74829	-0.60786
H	-0.89425	-6.96193	-1.08936
H	-2.42193	-6.51716	-1.88364
C	-0.45226	-2.26868	-3.12574
H	0.40538	-1.57839	-3.13224
C	-0.15171	-3.43314	-4.07212
H	0.18510	-3.04513	-5.04487
H	-1.03962	-4.05736	-4.26224
H	0.63971	-4.08293	-3.67041
C	-1.65400	-1.46641	-3.63677
H	-1.73720	-0.51604	-3.08977
H	-2.58837	-2.04179	-3.51317
H	-1.53557	-1.23004	-4.70591
	3_triplet		
K	-5.73870	-1.68274	-0.50166
C	-4.21818	-4.52600	1.21720
H	-3.86703	-5.57404	1.23929
H	-4.67092	-4.29581	2.20033
O	-5.17559	-4.35299	0.19597
C	-6.30142	-5.17224	0.36235
H	-6.84697	-4.89951	1.28601
C	-7.21074	-5.01127	-0.82778
H	-6.66198	-5.26818	-1.75319
O	-7.66864	-3.68229	-0.88395
C	-8.61386	-3.47145	-1.90207
H	-9.48593	-4.13755	-1.76494
H	-8.16977	-3.68799	-2.89187
C	-9.07242	-2.03714	-1.86102
O	-7.97858	-1.20296	-2.14280
H	-3.19518	2.11773	-0.79401
H	-4.66323	1.97581	0.21312

O	-6.28899	-0.39866	1.74437
C	-6.85787	0.89109	1.87205
H	-7.89374	0.81063	2.25464
H	-6.88093	1.34569	0.87140
C	-5.96222	1.61474	2.87897
H	-6.50328	2.39354	3.43128
H	-5.11839	2.09720	2.36444
C	-5.45780	0.47329	3.78736
H	-4.36994	0.53116	3.92750
H	-5.91912	0.50918	4.78274
C	-5.86891	-0.81060	3.03667
H	-5.04613	-1.52553	2.89824
H	-6.70443	-1.31772	3.55204
O	-3.80169	0.18225	-0.35754
C	-3.07522	0.04833	0.84695
H	-3.75116	0.22062	1.70570
H	-2.26435	0.79073	0.88535
C	-2.47293	-1.32533	0.92473
H	-1.82509	-1.50053	0.04715
H	-1.82674	-1.39215	1.81738
O	-3.51929	-2.28479	0.98035
C	-3.05260	-3.60540	0.96576
H	-2.28976	-3.76442	1.74970
H	-2.58487	-3.84272	-0.00848
H	-6.00399	-6.23440	0.44423
H	-8.06273	-5.70913	-0.73005
H	-9.87345	-1.89385	-2.60970
H	-9.49086	-1.80662	-0.86283
C	-8.33117	0.15301	-2.27530
H	-8.74155	0.53878	-1.32274

H	-9.10413	0.27555	-3.05637
C	-7.10388	0.93994	-2.65671
H	-6.67800	0.52877	-3.59175
H	-7.38846	1.99147	-2.84860
O	-6.17495	0.85702	-1.61135
C	-4.97593	1.56390	-1.86777
H	-5.19971	2.61366	-2.12953
H	-4.43911	1.10066	-2.71636
C	-4.11430	1.52307	-0.63543
P	2.96726	-1.19299	1.81219
P	0.41080	0.56342	0.97919
Si	2.44643	0.39570	0.25011
N	3.00477	0.13939	-1.43201
N	3.50446	1.78790	-0.10124
C	3.71978	1.35956	-1.44146
C	5.09349	1.44309	-2.03490
C	5.35167	2.09760	-3.24078
H	4.52072	2.57787	-3.76442
C	6.64885	2.14856	-3.75879
H	6.83809	2.66422	-4.70217
C	7.70118	1.54980	-3.06909
H	8.71487	1.59337	-3.47158
C	7.45284	0.89573	-1.85791
H	8.27065	0.41835	-1.31172
C	6.15993	0.84474	-1.34872
H	5.94735	0.32139	-0.41375
C	3.65119	3.16084	0.37553
C	3.11883	3.21889	1.80980
H	2.04363	2.98915	1.83083
H	3.27354	4.22379	2.23058

H	3.63773	2.48775	2.45052
C	2.85056	4.13292	-0.50072
H	1.78370	3.86344	-0.49342
H	3.21641	4.09542	-1.53832
H	2.95477	5.16440	-0.12953
C	2.94480	-0.88159	-2.46465
C	5.12680	3.58672	0.37189
H	5.23286	4.58694	0.82027
H	5.53189	3.62535	-0.64893
H	5.73192	2.87508	0.95040
C	4.27687	-1.63676	-2.62221
H	4.63908	-1.97781	-1.64026
H	5.05097	-0.99905	-3.07166
H	4.13929	-2.51321	-3.27669
C	2.55525	-0.26426	-3.81308
H	2.56514	-1.03287	-4.60124
H	3.25787	0.53197	-4.09718
H	1.54452	0.16293	-3.75323
C	1.85328	-1.87102	-2.04799
H	2.12999	-2.36852	-1.10759
H	1.71496	-2.64078	-2.82261
H	0.90120	-1.34371	-1.87875
C	4.65956	-1.82793	1.37015
C	4.76506	-3.11659	0.78947
C	6.01650	-3.60278	0.40440
H	6.08306	-4.58179	-0.07650
C	7.18415	-2.86550	0.59976
C	7.07748	-1.63440	1.24526
H	7.99261	-1.06723	1.42628
C	5.84551	-1.10410	1.64376

C	3.54401	-4.01558	0.64004
H	2.66518	-3.36425	0.52348
C	3.33422	-4.81096	1.93380
H	2.43439	-5.44253	1.86618
H	3.21757	-4.13012	2.78949
H	4.20074	-5.46273	2.12688
C	3.59156	-4.94153	-0.57482
H	4.34116	-5.73837	-0.45226
H	3.82975	-4.38436	-1.49284
H	2.61620	-5.43246	-0.71206
C	8.52345	-3.36861	0.09681
H	9.28650	-2.65127	0.44212
C	8.55190	-3.38490	-1.43533
H	7.81019	-4.09897	-1.82626
H	9.54279	-3.68522	-1.80937
H	8.30612	-2.39462	-1.84511
C	8.88002	-4.74272	0.66822
H	8.86637	-4.73106	1.76722
H	9.88101	-5.05665	0.33533
H	8.16273	-5.50630	0.33004
C	5.79045	0.22754	2.38285
H	4.98403	0.81214	1.90637
C	5.43220	0.01645	3.86074
H	4.49453	-0.54310	3.97988
H	5.31771	0.98574	4.37028
H	6.23489	-0.54472	4.36478
C	7.07561	1.04917	2.29302
H	6.92163	2.03089	2.76473
H	7.38867	1.21962	1.25205
H	7.90311	0.55610	2.82688

C	-0.28950	2.22304	0.48759
C	-0.49512	2.67235	-0.84537
C	-1.21016	3.84957	-1.08567
H	-1.35889	4.18121	-2.11738
C	-1.74941	4.62580	-0.05879
C	-1.51354	4.20695	1.24867
H	-1.88821	4.81176	2.07665
C	-0.78636	3.04542	1.54032
C	-0.00194	1.88352	-2.04858
H	0.83506	1.25382	-1.71741
C	-1.11495	0.95305	-2.54523
H	-1.50121	0.32657	-1.72548
H	-0.75373	0.29040	-3.34828
H	-1.95184	1.54888	-2.95115
C	0.51758	2.77007	-3.18283
H	-0.29207	3.32504	-3.68330
H	1.01124	2.15702	-3.94976
H	1.25523	3.49301	-2.80716
C	-2.58643	5.84830	-0.39006
H	-2.20838	6.24319	-1.34800
C	-4.05100	5.44564	-0.60214
H	-4.46169	5.01456	0.32544
H	-4.13516	4.68792	-1.39567
H	-4.67005	6.31190	-0.88333
C	-2.48119	6.96435	0.64809
H	-2.99797	7.86914	0.29556
H	-1.43177	7.21929	0.85204
H	-2.94882	6.66978	1.60007
C	-0.54998	2.70266	3.00848
H	0.35858	2.08190	3.04039
C	-0.31740	3.93145	3.88976
H	0.04621	3.61665	4.87922
H	-1.24010	4.51046	4.05397
H	0.43182	4.60345	3.44636
C	-1.68673	1.84449	3.57478
H	-1.72017	0.86856	3.06806
H	-2.65794	2.35254	3.44315
H	-1.53811	1.65999	4.65037

(S3) Crystal data of **2** and **3**

Suitable crystals for single crystal X-ray diffraction analysis of compounds **2** and **3** were selected under argon atmosphere and transferred in perfluorated oil on a microscope slide.[17] An appropriate crystal was selected using a polarizer microscope, mounted to the tip of a MiTeGen©MicroMount, fixed to a goniometer head and shock cooled by the crystal cooling device.

The data of **2** and **3** were collected from shock-cooled crystals at 100(2) K on a BRUKER D8 three circle diffractometer equipped with either an INCOATEC Mo or Ag Microsource with mirror optics (MoK_α λ = 0.71073 Å; AgK_α λ = 0.56086 Å) and SMART APEX II detector.

The diffraction data of **2** and **3** was integrated with SAINT[18] and an empirical absorption correction (SADABS)[19] was applied. The structures were solved by direct methods (SHELXT)[20] and refined by full-matrix least-squares methods against F^2 (SHELXL).[21] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using distance restraints and restraints for the anisotropic displacement parameters. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC(**2**): 1507708; CCDC(**3**): 1507709). Crystal data, experimental details for the X-ray measurements and copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/ data_request/cif.

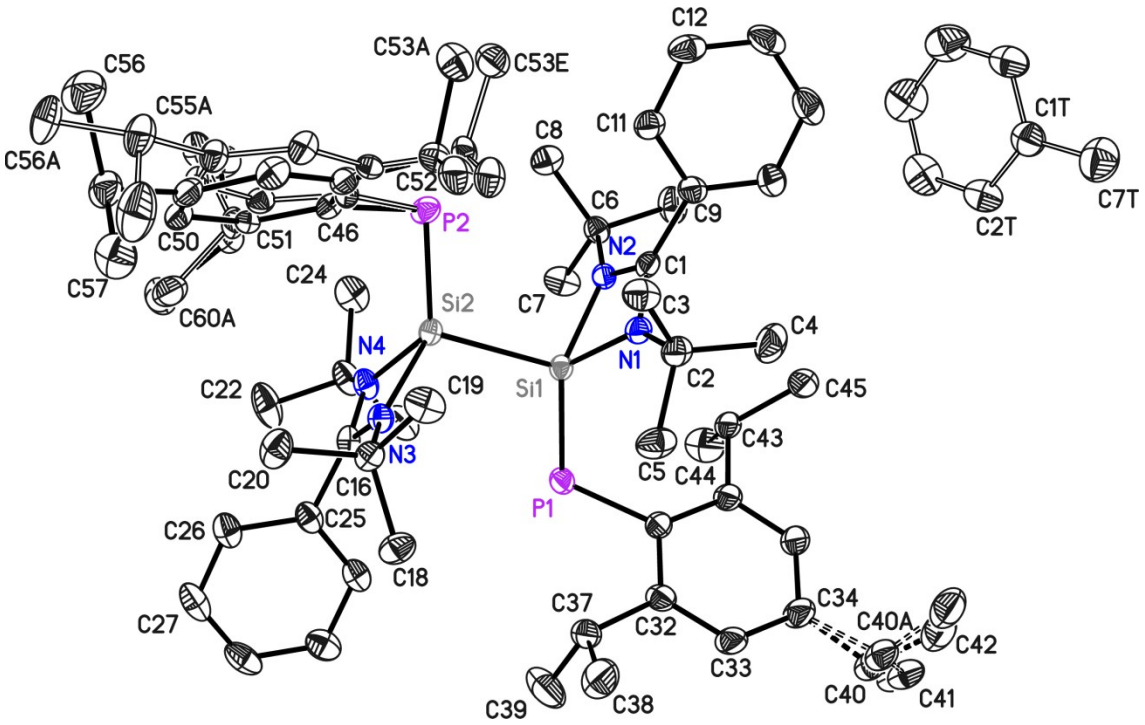

Figure S3: Molecular structure of **2**.

Table S11. Crystal data and structure refinement for **2**.

Identification code	Compound **2**	
Empirical formula	$C_{63.50}H_{96}N_4P_2Si_2$	
Formula weight	1033.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.044(5) Å	α= 81.95(2)°.
	b = 14.466(6) Å	β= 77.12(2)°.
	c = 19.396(8) Å	γ = 69.98(2)°.
Volume	3088(2) $Å^3$	
Z	2	
Density (calculated)	1.112 Mg/m^3	
Absorption coefficient	0.150 mm^{-1}	
F(000)	1126	
Crystal size	0.490 x 0.200 x 0.150 mm^3	

Theta range for data collection	1.788 to 25.433°.
Index ranges	-14<=h<=14, -17<=k<=17, -23<=l<=23
Reflections collected	130813
Independent reflections	11414 [R(int) = 0.0565]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9705 and 0.9268
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11414 / 546 / 847
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0912
R indices (all data)	R1 = 0.0580, wR2 = 0.1043
Extinction coefficient	n/a
Largest diff. peak and hole	0.299 and -0.244 e.Å^{-3}

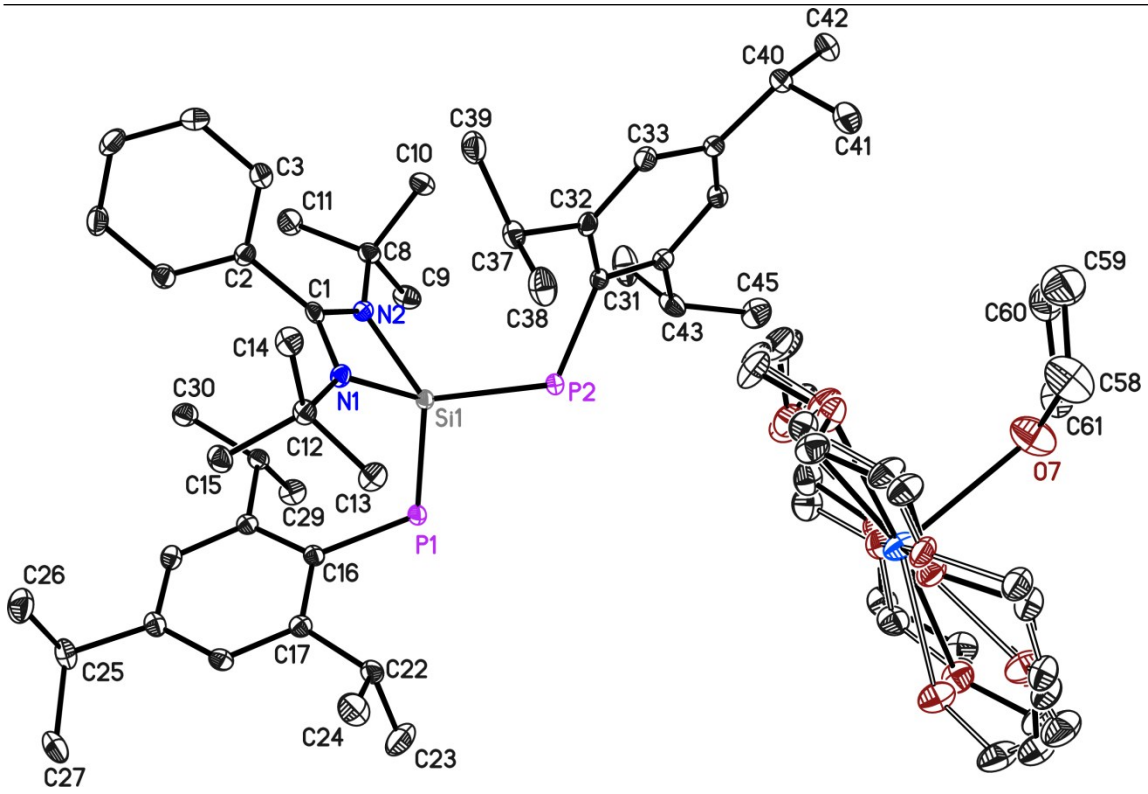

Figure S4: Molecular structure of compound **3**.

Table S12. Crystal data and structure refinement for compound **4**.

Identification code	compound **4**
Empirical formula	$C_{61}H_{101}KN_2O_7P_2Si$

Formula weight	1103.56	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.771(3) Å	α= 101.050(10)°.
	b = 13.848(3) Å	β= 103.860(10)°.
	c = 22.433(5) Å	γ = 100.660(10)°.
Volume	3093.4(13) Å^3	
Z	2	
Density (calculated)	1.185 Mg/m^3	
Absorption coefficient	0.114 mm^{-1}	
F(000)	1200	
Crystal size	0.424 x 0.279 x 0.152 mm^3	
Theta range for data collection	1.523 to 20.289°.	
Index ranges	-13<=h<=13, -17<=k<=17, -27<=l<=27	
Reflections collected	127873	
Independent reflections	12250 [R(int) = 0.0419]	
Completeness to theta = 19.665°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7445 and 0.7138	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12250 / 1901 / 848	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0764	
R indices (all data)	R1 = 0.0416, wR2 = 0.0813	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.471 and -0.247 e.Å^{-3}	

(S4) NMR spectra

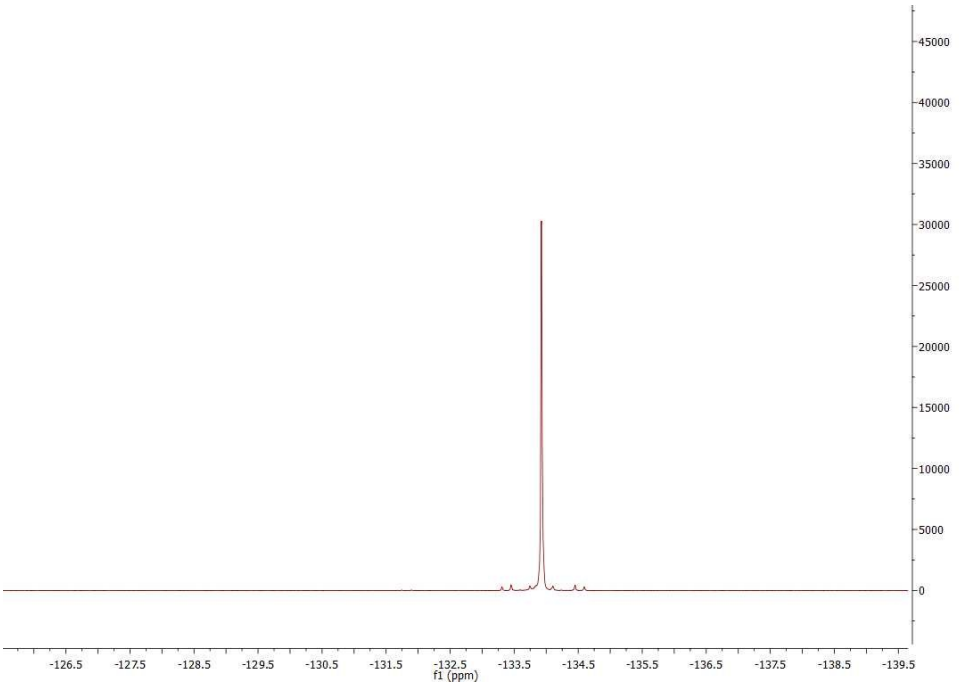

Figure S5: ^{31}P NMR of complex **2**.

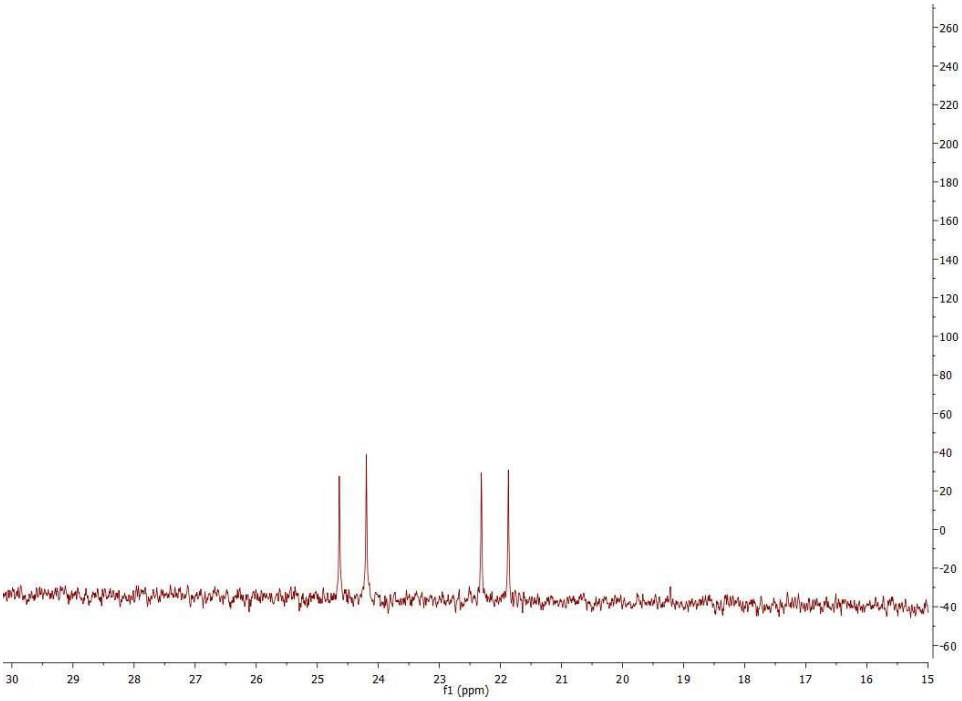

Figure S6: ^{29}Si NMR of complex **2**.

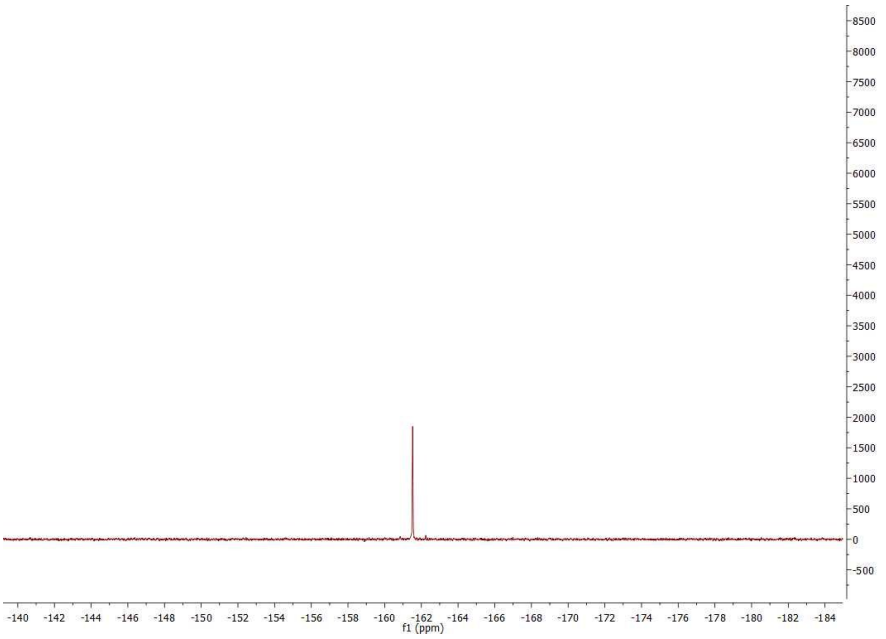

Figure S7: ^{31}P NMR of complex **3**.

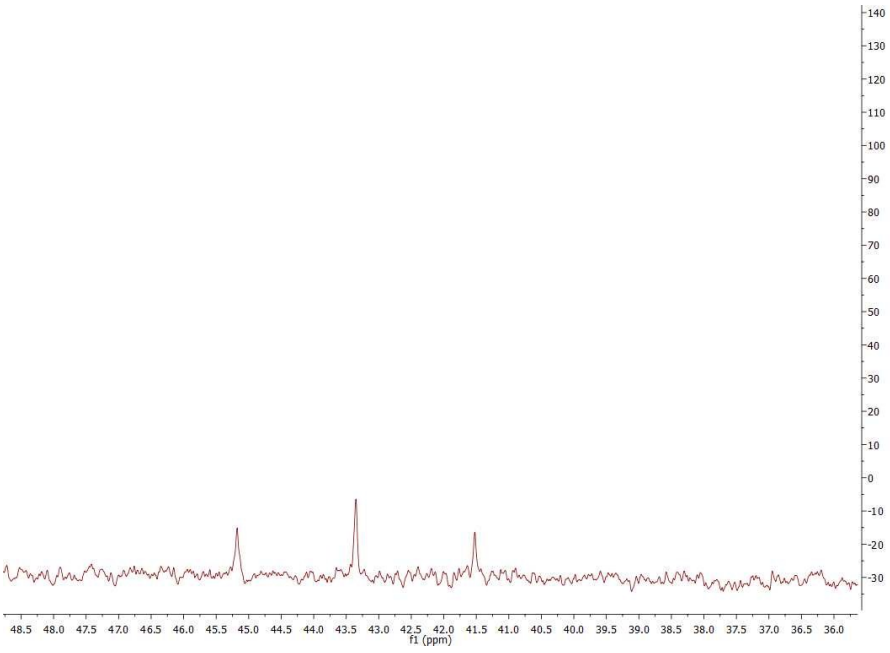

Figure S8: ^{29}Si NMR of complex **3**.

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