Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Zwitterionic Si-C-Si-P and Si-P-Si-P Four-Membered Rings with Two-Coordinate Phosphorus Atoms**

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Content:

(S1). Syntheses of 3 and 4

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 usually kept below 1 ppm. Adamantyl phosphalkyne was purchased from Aldrich and used as received. White phosphorus was sublimized prior to use. Compounds **1** and **2** were prepared according to literature methods.[S1, S2] 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 solvents C_6D_6, and D_8-[THF] were dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. 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.

3: To the mixture of **1** (0.29 g, 1.00 mmol) and 1-adamantyl phosphaalkyne (0.07 g, 0.38 mmol) at –20 °C toluene (25 mL) was added and the color of the solution immediately changed from colorless to red. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure and the crude product was extracted with toluene (10 mL). Concentration and storing at 0 °C in a freezer afforded reddish yellow crystals of **3** (0.15 g, 68.22%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): *d* 1.21 (s, 4H, Ad), 1.26 (s, 36 H, *t*Bu), 1.72 (s, 12H, Ad), 6.90-7.10 (m, 10 H, Ph) ppm; ^{13}C NMR (125.75 MHz, C_6D_6, 25 °C): *d* 32.8 (C*Me*$_3$), 40.2, 41.6, 50.9, 51.6 (adamantyl), 56.9 (*C*Me$_3$), 129.4, 130.6, 132.2, 133.2 (*Ph*), 136.2 (Si-*C*-Ad), 171.23 (N*C*N) ppm; ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C) –243 ppm; ^{29}Si{^{1}H} NMR (99.36 MHz, C_6D_6, 25 °C): *d* –5.1 ppm ($^{1}J_{\mathrm{Si\text{-}P}}$ = 75.45 Hz); EI-MS: *m/z*: 696 (100%). Elemental analysis for $C_{41}H_{61}N_4PSi_2$: calcd C, 70.64; H, 8.82; N, 8.04; found C, 71.16; H, 9.12; N, 8.10.

Alternate synthesis of 3: To the mixture of **2** (0.10 g, 0.19 mmol) and 1-adamantyl phosphaalkyne (0.03 g, 0.19 mmol) at –20 °C toluene (25 mL) was added and the color of the solution immediately changed from dark red to pale red. The reaction mixture was stirred overnight. Concentration and storing at room temperature afforded reddish yellow crystals of **3** (0.06 g, 44.78%).

4: To the mixture of **1** (0.29 g, 1.00 mmol) and white phosphorus (0.124 g, 1.00 mmol) at room temperature toluene (25 mL) was added and the color of the solution immediately changed from colorless to dark yellow with the formation of a yellow solid. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure, the solid was washed with toluene (10 mL) to remove PhC(N*t*Bu)$_2$SiCl$_3$ and then extracted with THF (25 mL). Concentration and storing at –32 °C in a freezer afforded yellow crystals of **4** (0.17 g, 60%). Mp 168-175°C. ^{1}H NMR (500 MHz, [D$_8$]-THF, 25 °C): *d* 1.36 (s, 36 H, *t*Bu), 6.61-6.98 (m, 10 H, Ph) ppm; ^{13}C{^{1}H} NMR (125.75 MHz, [D$_8$]-THF, 25 °C): *d* 33.1(C*Me*$_3$), 53.5 (*C*Me$_3$), 125.6, 127.6, 129.3, 135.9 (*Ph*), 171.23 (N*C*N) ppm; ^{31}P NMR (121.5 MHz, [D$_8$]-

THF, 25 °C): *d* –166.02 ppm; $^{29}Si\{^1H\}$ NMR (99.36 MHz, [D$_8$]-THF, 25 °C): *d* 25.6 ppm ($^1J_{Si\text{-}P}$ = 109.02 Hz). EI-MS: *m/z*: 580 [M$^+$] (100%). Elemental analysis for $C_{30}H_{46}N_4P_2Si_2$: calcd C, 62.04; H, 7.98; N, 9.65; found C, 62.29; H, 8.08; N, 9.72.

Alternate synthesis of 4: THF (25 mL) was charged to the mixture of white phosphorus (0.03 g, 0.21 mmol) and **2** (0.11 g, 0.21 mmol) at room temperature. The color of the solution changed immediately from deep red to faint red. The reaction mixture was stirred for 2 h and all volatiles were removed in vacuum. The residue was treated with THF (10 mL) and filtered through celite. The solution was concentrated and stored at – 32 °C to yield yellow crystals of **4** (0.12 g, 50%).

(S2). Crystal data for 3 and 4

Shock cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP2.[S3] The data of **3** was measured on a Bruker TXS-Mo rotating anode with Helios mirror optics; **4** was measured on an INCOATEC Mo Microsource with Quazar mirror optics. Both had a APEX II detector on a D8 goniometer. The diffractometers where equipped with a low-temperature device and used MoK$_a$ radiation, ? = 0.71073 Å. The data sets were integrated with SAINT[S4] and an empirical absorption (SADABS) was applied.[S5] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[S6] 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 bond lengths restraints and isotropic displacement parameters restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic

Data Center. The crystal data are available from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	3·3toluene	**4·2thf**
CCDC number	793275	793276
Empirical formula	$C_{62}H_{85}N_4PSi_2$	$C_{38}H_{62}N_4O_2P_2Si_2$
Formula weight	973.49	725.04
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$
Unit cell dimensions [Å], [°]	a = 13.540(2)	a = 13.7643(15)
	b = 18.636(3)	b = 23.392(3) b = 104.973(2)
	c = 22.541(4)	c = 13.0870(14)
Volume [Å^3]	5687.8(17)	4070.6(8)
Z	4	4
Density (calculated) [Mg/m]	1.137	1.183
Absorption coefficient [mm^{-1}]	0.132	0.202
F(000)	2112	1568
Crystal size [mm^3]	0.256 x 0.138 x 0.10	0.12 x 0.1 x 0.08
Theta range for data collection [°]	1.42 to 27.13	1.74 to 27.69
Index ranges	$-17<=h<=17$, $-23<=k<=23$,	$-17<=h<=17$, $-30<=k<=30$,
	$-28<=l<=28$	$-17<=l<=17$
Reflections collected	84501	52804
Independent reflections	12583 [R(int) = 0.0341]	4761 [R(int) = 0.0510]
Completeness to theta = 27.13°	99.9 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.98279 and 0.91086	0.9828 and 0.8726
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12583 / 228 / 720	4761 / 0 / 227
Goodness-of-fit on F^2	1.086	1.065
Final R indices [I>2sigma(I)]	$R1$ = 0.0467, $wR2$ = 0.1240	$R1$ = 0.0451, $wR2$ = 0.1134
R indices (all data)	$R1$ = 0.0505, $wR2$ = 0.1267	$R1$ = 0.0580, $wR2$ = 0.1223
Largest diff. peak and hole [eÅ^{-3}]	0.686 and -0.271	0.902 and -0.232

(S3). Theoretical Calculations for 3 and 4

All theoretical calculations were performed with Gaussian 09 (Rev. A.02) on the B3LYP/6-311G* level of theory.[S7]

Coordinates of the optimized geometry of **3**

N1	-2.829836	-0.776811	-1.047294
N2	-2.824241	-0.647476	1.105392
N3	2.806978	-0.662134	1.114555
N4	2.808124	-0.826327	-1.034851
P1	-0.023152	-2.599586	0.148800
SI1	-1.259368	-0.767081	0.029421
SI2	1.239878	-0.786597	0.037128
C1	5.090299	-0.829485	0.041074
C2	5.825480	0.358985	-0.016939
H2	5.306829	1.310472	-0.058519
C3	7.217273	0.323837	-0.038795
H3	7.777119	1.252028	-0.086641
C4	7.887312	-0.897450	-0.004110
H4	8.971837	-0.924290	-0.022826
C5	7.159601	-2.084164	0.055653
H5	7.674755	-3.038574	0.086167
C6	5.767280	-2.052343	0.079074
H6	5.205819	-2.977910	0.137157
C7	3.110374	-1.150439	-2.450830
C8	4.281231	-0.321133	-3.005695
H8A	5.239339	-0.597317	-2.567072
H8B	4.117486	0.746056	-2.836019
H8C	4.355599	-0.481025	-4.084884
C9	3.397229	-2.657454	-2.595692
H9A	2.573377	-3.242526	-2.181305
H9B	4.319227	-2.940220	-2.083932
H9C	3.510728	-2.923124	-3.650953
C10	1.845855	-0.809575	-3.250926
H10A	1.604871	0.252021	-3.174986
H10B	0.993762	-1.380819	-2.883515
H10C	1.995650	-1.055829	-4.305248
C11	3.598247	-0.779351	0.042890
C12	3.134279	-0.570742	2.559048
C13	1.797752	-0.628982	3.311343
H13A	1.284056	-1.571382	3.114193
H13B	1.137591	0.184196	3.007893
H13C	1.972102	-0.547184	4.387222
C14	3.835790	0.761481	2.880994
H14A	3.232147	1.606950	2.542544
H14B	4.818895	0.827874	2.412744
H14C	3.977308	0.859080	3.961211
C15	3.999714	-1.758140	3.020568
H15A	5.005744	-1.727869	2.602391
H15B	3.531737	-2.704434	2.738726
H15C	4.095609	-1.741595	4.109825
C16	-3.617911	-0.745188	0.030960
C17	-5.110592	-0.792899	0.041314
C18	-5.790447	-2.014308	0.070705
H18	-5.230834	-2.942748	0.073474
C19	-7.183179	-2.042418	0.090771
H19	-7.699721	-2.996244	0.114830
C20	-7.908688	-0.853283	0.078104

H20	-8.993343	-0.877061	0.092690
C21	-7.236112	0.366844	0.046332
H21	-7.794121	1.297309	0.036686
C22	-5.844359	0.398040	0.029878
H22	-5.323848	1.349263	0.013481
C23	-3.160000	-0.865331	-2.491767
C24	-1.820502	-0.887114	-3.240242
H24A	-1.238441	-1.765965	-2.957533
H24B	-1.226909	-0.000971	-3.013588
H24C	-1.996231	-0.921422	-4.318410
C25	-3.912485	-2.170708	-2.812093
H25A	-4.917169	-2.183054	-2.389274
H25B	-3.360110	-3.032497	-2.430252
H25C	-4.010106	-2.284773	-3.895498
C26	-3.977339	0.354356	-2.954144
H26A	-3.457548	1.283260	-2.709859
H26B	-4.967534	0.381348	-2.497685
H26C	-4.115334	0.319374	-4.038571
C27	-3.128425	-0.822121	2.548471
C28	-4.212346	0.157340	3.031315
H28A	-5.194878	-0.065745	2.616478
H28B	-3.951106	1.185492	2.767545
H28C	-4.294346	0.101007	4.120392
C29	-3.544315	-2.277120	2.838682
H29A	-2.780915	-2.969500	2.477225
H29B	-4.497118	-2.526575	2.368673
H29C	-3.659272	-2.428892	3.916024
C30	-1.825595	-0.526602	3.302793
H30A	-1.493012	0.497610	3.128826
H30B	-1.034186	-1.204409	2.981444
H30C	-1.979096	-0.661596	4.376456
C31	0.001327	0.506179	-0.072972
C32	0.020513	2.024450	-0.119977
C33	1.337702	2.555426	-0.747021
H33A	2.191387	2.185210	-0.165349
H33B	1.447759	2.145354	-1.757060
C34	-1.149173	2.586816	-0.971583
H34A	-1.082297	2.176567	-1.985245
H34B	-2.101147	2.237254	-0.552786
C35	-0.103861	2.653518	1.297944
H35A	0.711241	2.280225	1.928038
H35B	-1.036071	2.306675	1.757757
C36	-0.078746	4.194444	1.254703
H36	-0.166088	4.592415	2.273678
C37	1.247177	4.665254	0.627166
H37A	1.289935	5.761498	0.603261
H37B	2.093162	4.331076	1.240855
C38	1.368829	4.095677	-0.798478
H38	2.314361	4.426534	-1.246897
C39	0.190319	4.602292	-1.651978
H39A	0.278427	4.224909	-2.678259
H39B	0.210333	5.697514	-1.716107
C40	-1.134922	4.127902	-1.025415
H40	-1.976250	4.479780	-1.636068
C41	-1.256963	4.698270	0.400011
H41A	-1.265948	5.795195	0.370541
H41B	-2.207991	4.387998	0.850804

Coordinates of the optimized geometry of **4**

N1	2.854412	1.077265	0.051541
N2	-2.854399	1.077278	-0.051519
P3	0.000000	-0.000493	-1.772599
SI1	1.300291	-0.000005	-0.000002
SI2	-1.300255	-0.000003	-0.000002
C1	3.147983	2.485359	0.421462
C2	4.317534	3.067206	-0.390612
H2A	5.275854	2.619072	-0.131146
H2B	4.392158	4.140150	-0.193742
H2C	4.150666	2.934482	-1.462399
C3	3.436916	2.581262	1.931285
H3A	2.611163	2.157588	2.506964
H3B	3.559931	3.626724	2.228989
H3C	4.355212	2.052381	2.196066
C4	1.880877	3.289742	0.097584
H4A	1.629233	3.213704	-0.962026
H4B	2.037306	4.343290	0.342538
H4C	1.032561	2.927771	0.679681
C5	3.646736	0.000000	-0.000001
C6	5.138198	-0.000001	-0.000003
C7	5.842873	-0.121136	1.201567
H7	5.301769	-0.228530	2.135128
C8	7.235346	-0.117749	1.199888
H8	7.773545	-0.211594	2.137278
C9	7.934236	-0.000006	-0.000005
H9	9.019236	-0.000008	-0.000006
C10	-3.147983	2.485335	-0.421619
C11	-1.880765	3.289729	-0.098182
H11A	-1.628767	3.213717	0.961344
H11B	-2.037288	4.343274	-0.343099
H11C	-1.032624	2.927783	-0.680551
C12	-4.317278	3.067317	0.390722
H12A	-5.275642	2.618977	0.131800
H12B	-4.392130	4.140186	0.193522
H12C	-4.149925	2.934947	1.462474
C13	-3.437290	2.581038	-1.931367
H13A	-2.611784	2.157053	-2.507186
H13B	-3.560092	3.626479	-2.229233
H13C	-4.355786	2.052367	-2.195844
C14	-3.646724	0.000006	-0.000005
C15	-5.138191	0.000002	-0.000011
C16	-5.842864	-0.121265	-1.201568
H16	-5.301769	-0.228785	-2.135119
C17	-7.235338	-0.117879	-1.199893
H17	-7.773528	-0.211817	-2.137279
C18	-7.934236	-0.000013	-0.000017
H18	-9.019237	-0.000019	-0.000019
N1A	2.854416	-1.077269	-0.051538
N2A	-2.854407	-1.077269	0.051527
P3A	-0.000001	0.000480	1.772595
C1A	3.147997	-2.485361	-0.421458
C2A	4.317558	-3.067192	0.390611
H2AA	5.275871	-2.619043	0.131144
H2BA	4.392197	-4.140135	0.193740
H2CA	4.150692	-2.934473	1.462400
C3A	3.436926	-2.581264	-1.931282
H3AA	2.611167	-2.157600	-2.506959
H3BA	3.559954	-3.626724	-2.228984
H3CA	4.355216	-2.052371	-2.196066

C4A	1.880902	-3.289759	-0.097575
H4AA	1.629258	-3.213722	0.962035
H4BA	2.037343	-4.343306	-0.342528
H4CA	1.032581	-2.927800	-0.679672
C7A	5.842872	0.121130	-1.201574
H7A	5.301767	0.228526	-2.135133
C8A	7.235344	0.117738	-1.199896
H8A	7.773542	0.211582	-2.137288
C10A	-3.148015	-2.485316	0.421638
C11A	-1.880829	-3.289751	0.098177
H11D	-1.628847	-3.213750	-0.961353
H11E	-2.037382	-4.343291	0.343099
H11F	-1.032667	-2.927833	0.680532
C12A	-4.317347	-3.067252	-0.390681
H12D	-5.275687	-2.618865	-0.131748
H12E	-4.392245	-4.140117	-0.193471
H12F	-4.150006	-2.934898	-1.462436
C13A	-3.437300	-2.581007	1.931391
H13D	-2.611769	-2.157055	2.507197
H13E	-3.560138	-3.626444	2.229259
H13F	-4.355772	-2.052301	2.195883
C16A	-5.842871	0.121255	1.201545
H16A	-5.301780	0.228779	2.135098
C17A	-7.235345	0.117857	1.199863
H17A	-7.773540	0.211789	2.137247

(S4). Solid-state NMR

Solid-state NMR spectra were recorded at temperatures of 5–10 °C on a 9.4 T (400 MHz ^{1}H Larmor frequency) wide-bore instrument. **3** and **4** were prepared in micro-crystalline form and packed under inert atmosphere into 2.5-mm and 4.0-mm MAS rotors. ^{1}H–^{29}Si and ^{1}H–^{13}C cross-polarization (CP) spectra were recorded on 4.0-mm rotors, with MAS frequencies of 1675 Hz, 2860 Hz and 7000 Hz for ^{29}Si, and 11000 Hz for ^{13}C. ^{1}H–^{31}P CP spectra were recorded on 2.5-mm rotors at MAS frequencies of 5700 Hz, 7000 Hz and 20000 Hz. For **4**, the 7 kHz ^{1}H–^{31}P spectra were recorded on a 4.0-mm rotor.

The swept-frequency TPPM sequence was used for proton decoupling during acquisition, with an RF field amplitude of 83.3 kHz, sweep window of 0.32 and phase angle of 12.5°.[S8] Chemical shifts were calibrated using external references: TMS for ^{29}Si, 1M H_3PO_4 for ^{31}P, adamantane for ^{13}C (corresponding to DSS at 0 ppm).

The chemical shift anisotropies of ^{29}Si and ^{31}P were extracted by comparison of spinning sideband intensities with the sideband pattern of simulated spectra (Figure S4.2). Simulated spectra were generated within the numerical simulation routine GAMMA[S9] over a large range of possible anisotropy and asymmetry values. The ^{29}Si or ^{31}P anisotropic chemical shift was considered as the relevant internal system Hamiltonian, and powder averaging involved 1154 crystallite orientations. Values which minimized the peak intensity residual sum of squares were used to produce the back-calculated spectra (Table S4.1).

Table S4.1. Chemical shift tensor parameters and optimum CP contact times

Compound	Nucleus	τ_{CP} (ms)	δ_{iso} (ppm)	δ_{xx} (ppm)	δ_{yy} (ppm)	δ_{zz} (ppm)	η_{asym}	δ_{aniso} (ppm)
3 (exp.)	^{31}P	5.6	-326.1	-367.7	-367.7	-242.9	0	83.2
3 (theo.)	^{31}P		-341.1	-405.6	-389.9	-227.9	0.139	113.2
4 (exp.)	^{31}P	11.6	-166.4	-49.6	-63.4	-386.2	0.063	-219.8
4 (theo.)	^{31}P		-132.0	39.7	-43.0	-392.8	0.317	-260.8
3	^{29}Si	5.1	-8.4	43.8	3.4	-72.4	0.631	-64.0
4	^{29}Si	7.8	24.0	-46.2	-21.8	140.0	0.210	116.0

The following convention is employed:

The principal components of the CSA tensor are δ_{xx}, δ_{yy} and δ_{zz}, with $\left|\delta_{zz} - \delta_{iso}\right| \geq \left|\delta_{xx} - \delta_{iso}\right| \geq \left|\delta_{yy} - \delta_{iso}\right|$

Isotropic chemical shift: $\delta_{iso} = \tfrac{1}{3}\left(\delta_{xx} + \delta_{yy} + \delta_{zz}\right)$

Anisotropy: $\delta_{aniso} = \delta_{zz} - \delta_{iso}$

Asymmetry: $\eta_{asym} = \dfrac{\delta_{yy} - \delta_{xx}}{\delta_{aniso}}$, where $\eta_{asym} = 0$ is axially symmetric;

τ_{CP} is the cross-polarization contact time yielding maximum intensity.

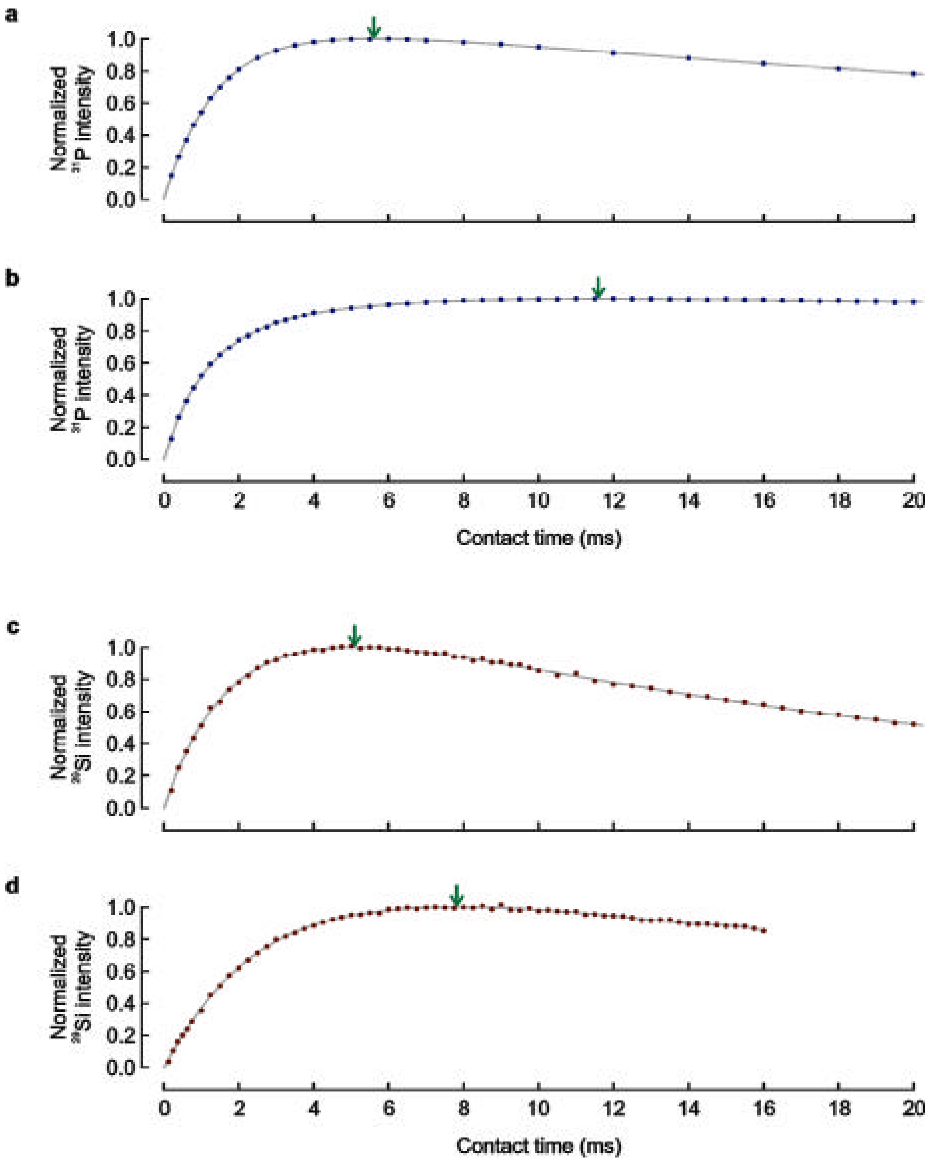


Figure S4.1. Cross-polarization profiles. The build-up of magnetization for compounds **3** (a,c) and **4** (b,d) was monitored by incrementing the contact time between ^{1}H and ^{31}P (a,b; 20 kHz MAS), or ^{1}H and ^{29}Si (c,d; 7 kHz MAS). Arrows indicate the point of maximal intensity.

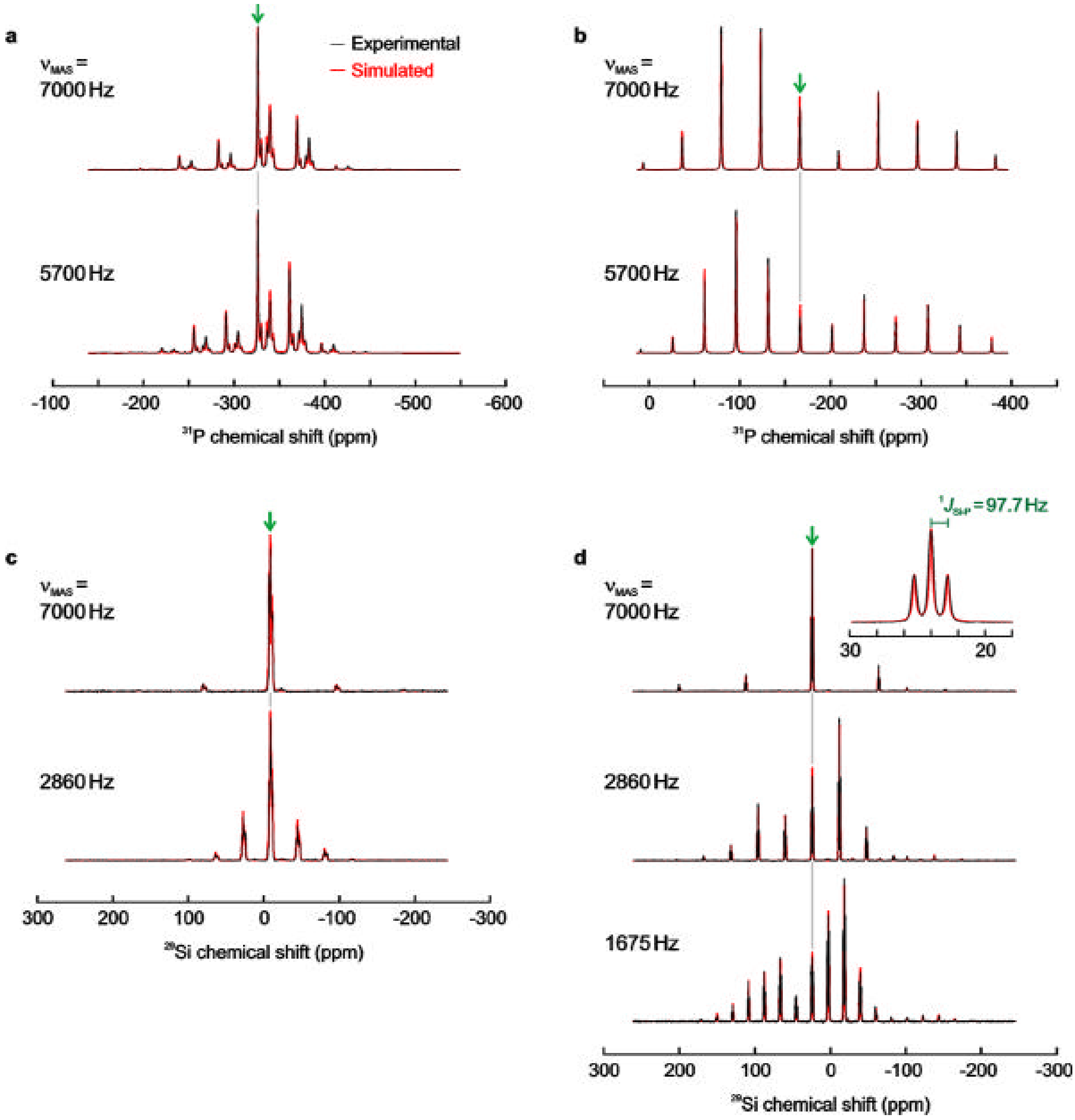
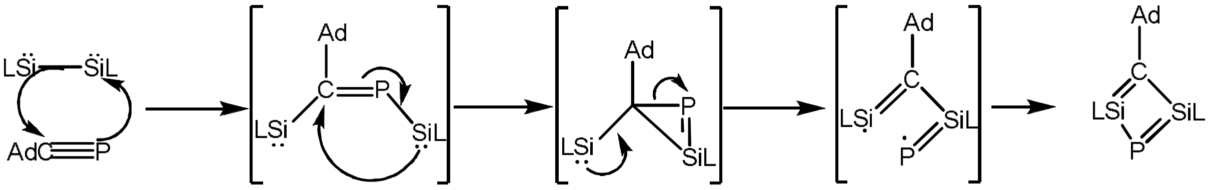
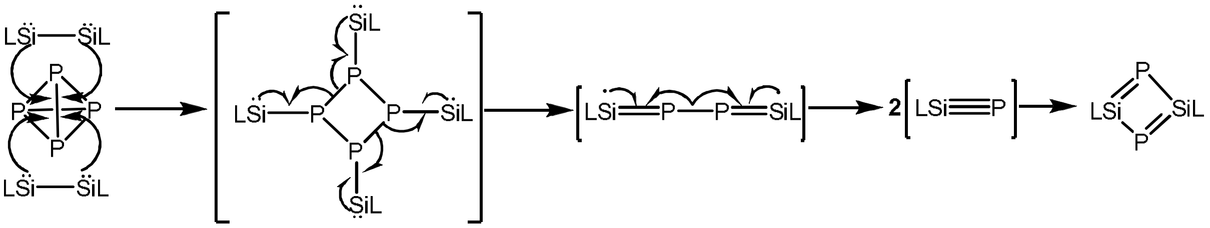


Figure S4.2. Experimental (black) and simulated (red) spinning sideband patterns for compounds **3** (a,c) and **4** (b,d). Cross-polarization spectra were recorded on ^{31}P (a,b) and ^{29}Si (c,d) at multiple magic-angle spinning frequencies (ν_{MAS}). The isotropic peaks are indicated by arrows. The excerpt in (d) presents the multiplet structure of the ^{29}Si resonance of **4** due to silicon-phosphorus *J* coupling.

(S5). Tentative mechanism for the formation of 3 and 4 from 2.



Mechanism for the formation of **3**



Mechanism for the formation of **4**

(S6). References

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