

Supporting Information for

A Versatile Access to Very Short P=P Double Bonds in Mixed-Valent $1\lambda^5$ -Diphosphenes via 1,3-Silyl Migration

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1) Preparative Procedures

Procedure of NMR kinetic experiment reacting MesP(Li)TIPS (1a**) with diphenylphosphinic acid chloride, formation of **2a**, 1,3 trihydrysilyl migration to **3a**, and degradation to **4a** and **6a**:** 2.5 mL of a 0.2 M (0.5 mmol) solution of **1a**/THF/*n*-hexane were cooled to -78 °C. 0.5 mL of a 1 M (0.5 mmol) solution of diphenylphosphinic acid chloride in THF were added rapidly. An NMR sample was prepared by taking a 0.4 mL aliquot and addition of 0.1 mL of C₆D₆. The sample was kept at -78 °C before the NMR kinetic study started at 24 °C/297 K. For 3 h a ³¹P{¹H}-NMR spectrum was measured every 6 min. All integrals were normalized to the integral of the signal at 34.7 ppm in the 1st spectrum after 6 min.

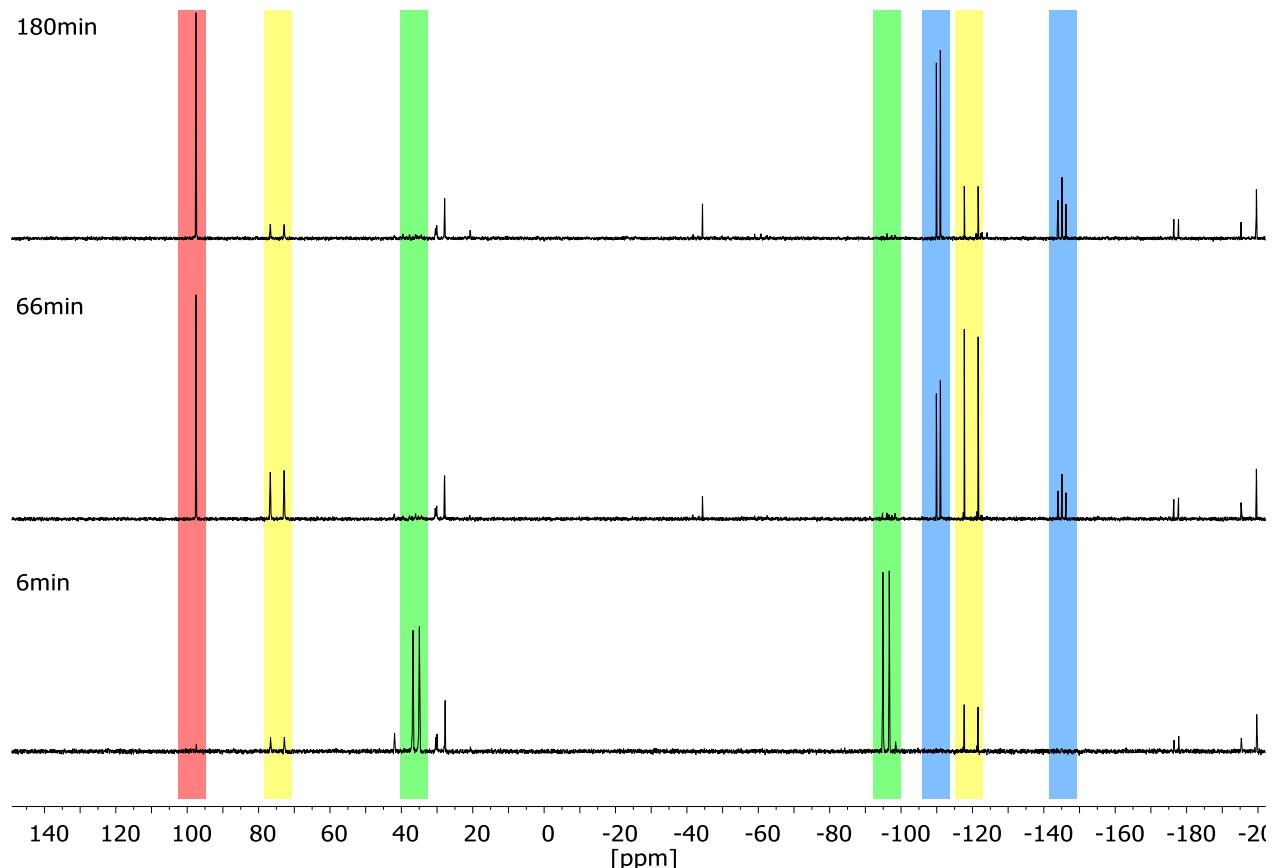


Figure S1: ³¹P{¹H} NMR spectra 161.98 MHz, [D₆]benzene, 295.2 K) of NMR-kinetic experiments after 6 min, 66 min and 180 min showing signals of **2a** (green), **3a** (yellow), **4a** (red), and **6a** (blue).

2) NMR Spectra

a) Lithium 2,4,6-trimethylphenyl-(triisopropylsilyl)phosphanide (**1a**)

$^{31}\text{P}\{^1\text{H}\}$

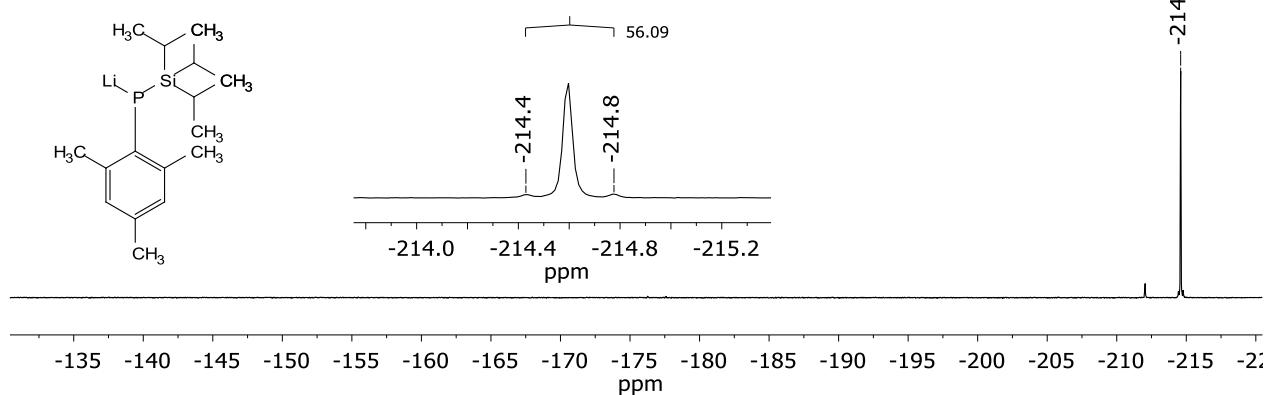


Figure S2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of lithium 2,4,6-trimethylphenyl-(triisopropylsilyl)phosphanide (**1b**) (400.13 MHz, C_6D_6 , 297 K).

b) Lithium 2,4,6-triisopropylphenyl-(triphenylsilyl)phosphanide (**1b**)

TippP(Li)SiPh₃, 1H-29Si-DEPT

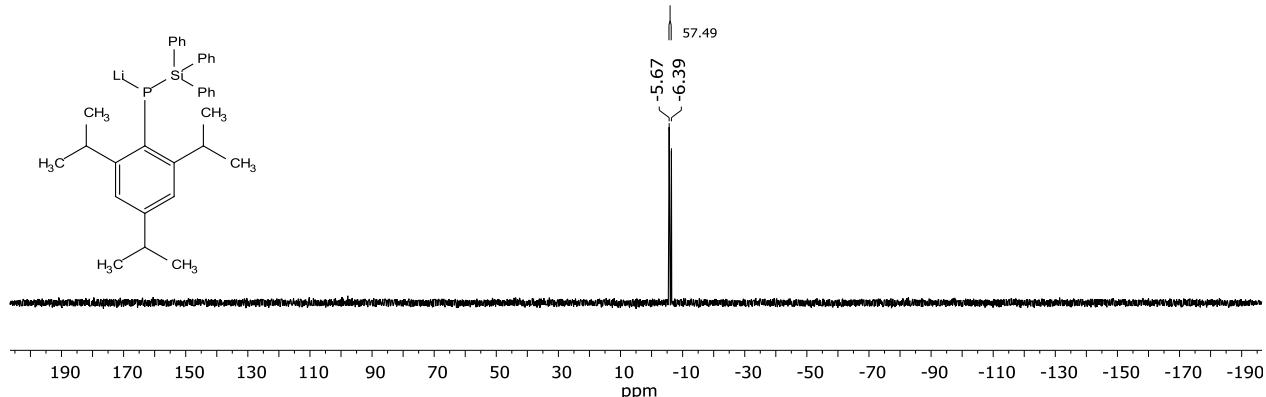


Figure S3: $^{1}\text{H}-^{29}\text{Si}$ -DEPT NMR spectrum of lithium 2,4,6-triisopropylphenyl-(triphenylsilyl)phosphanide (**1b**) (79.46 MHz, C_6D_6 , 297 K).

TippP(Li)SiPh₃, 31P

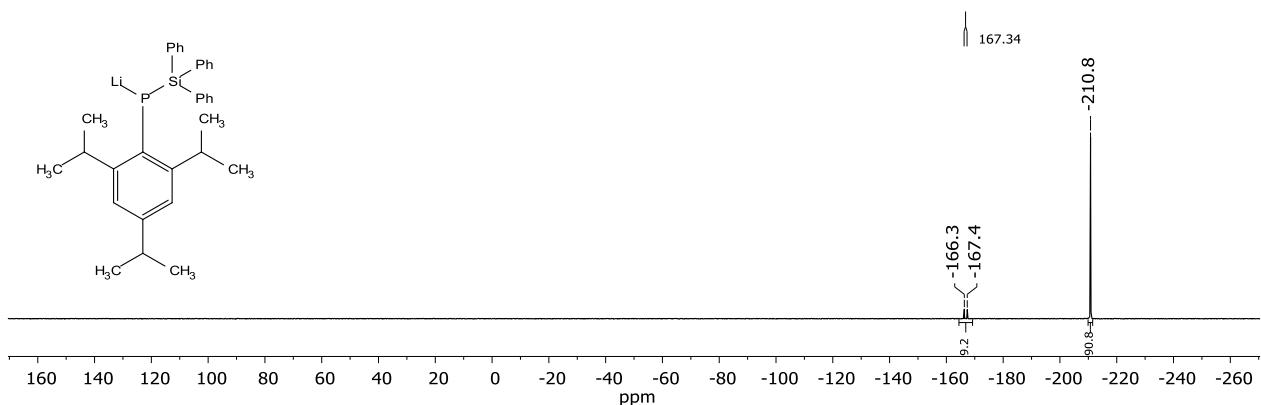


Figure S4: ³¹P NMR spectrum of lithium 2,4,6-triisopropylphenyl-(triphenylsilyl)phosphanide (**1b**) (161.97 MHz, C₆D₆, 297 K).

c) (diphenyl)[(2,4,6-triisopropylphenyl)phosphinidenyl](triphenylsiloxy)phosphane
(3b)

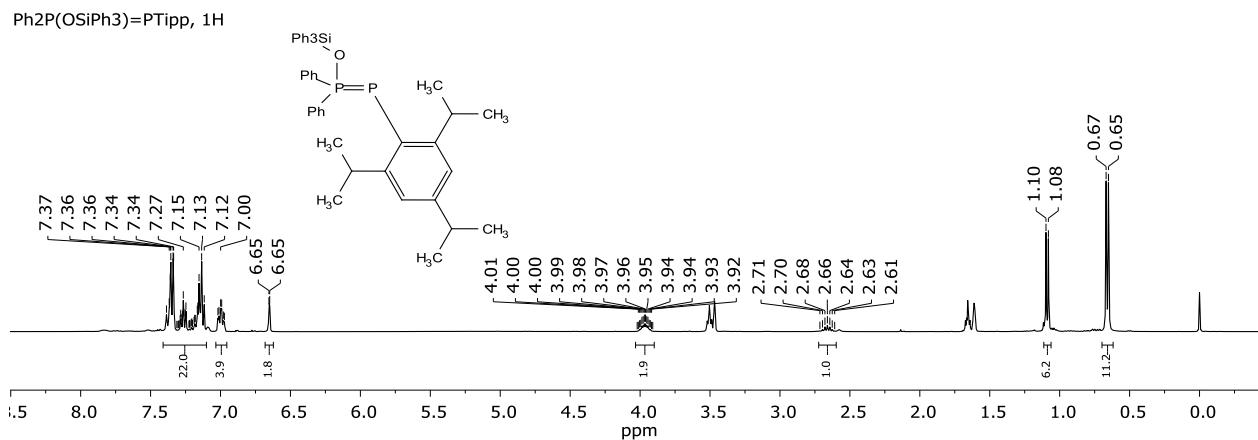


Figure S5: ¹H NMR spectrum of (diphenyl)[(2,4,6-triisopropylphenyl)phosphinidenyl](triphenylsiloxy)phosphane (**3b**) (400.13 MHz, [D₈]THF, 297 K).

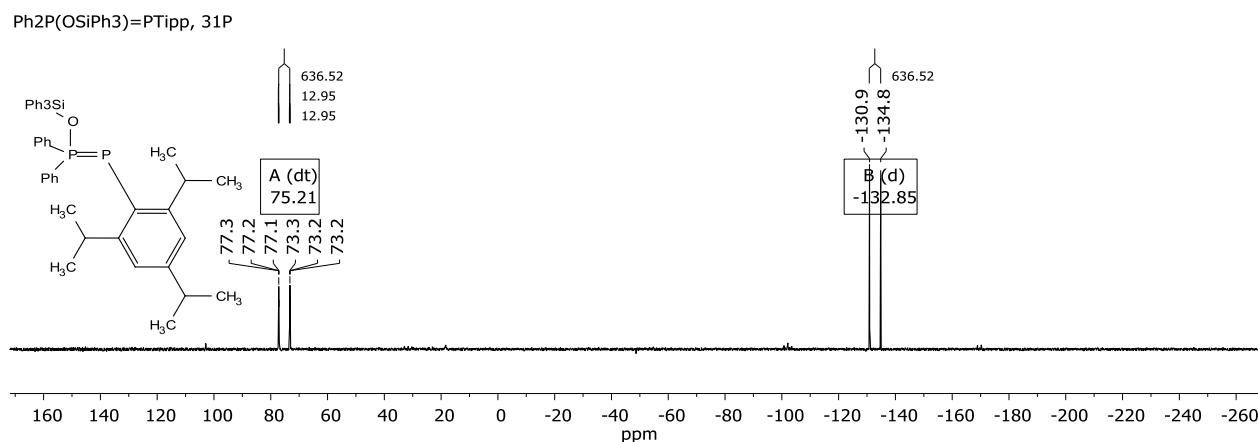


Figure S6: ³¹P NMR spectrum of (diphenyl)[(2,4,6-triisopropylphenyl)phosphinidenyl](triphenylsiloxy)phosphane (**3b**) (161.97 MHz, [D₈]THF, 297 K).

Ph₂P(OSiPh₃)=PTipp, ¹³C{¹H}

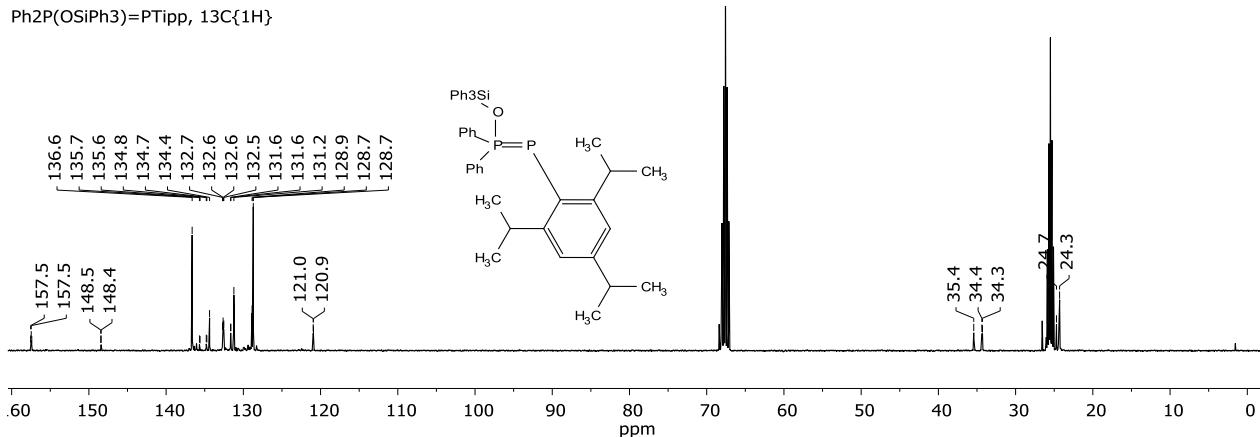


Figure S7: ¹³C{¹H} NMR spectrum of (diphenyl)[(2,4,6-triisopropylphenyl)phosphinidenyl](triphenylsiloxy)phosphane (**3b**) (100.62 MHz, [D₈]THF, 297 K).

Ph₂P(OSiPh₃)=PTipp, 1H-²⁹Si-DEPT

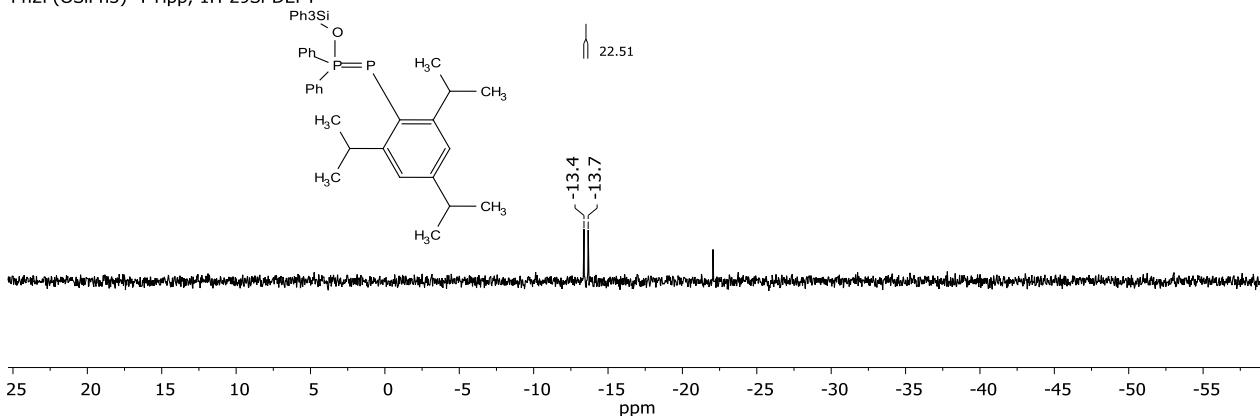


Figure S8: ¹H-²⁹Si-DEPT NMR spectrum of (diphenyl)[(2,4,6-triisopropylphenyl)phosphinidenyl](triphenylsiloxy)phosphane (**3b**) (79.49 MHz, [D₈]THF, 297 K).

d) Reaction monitoring

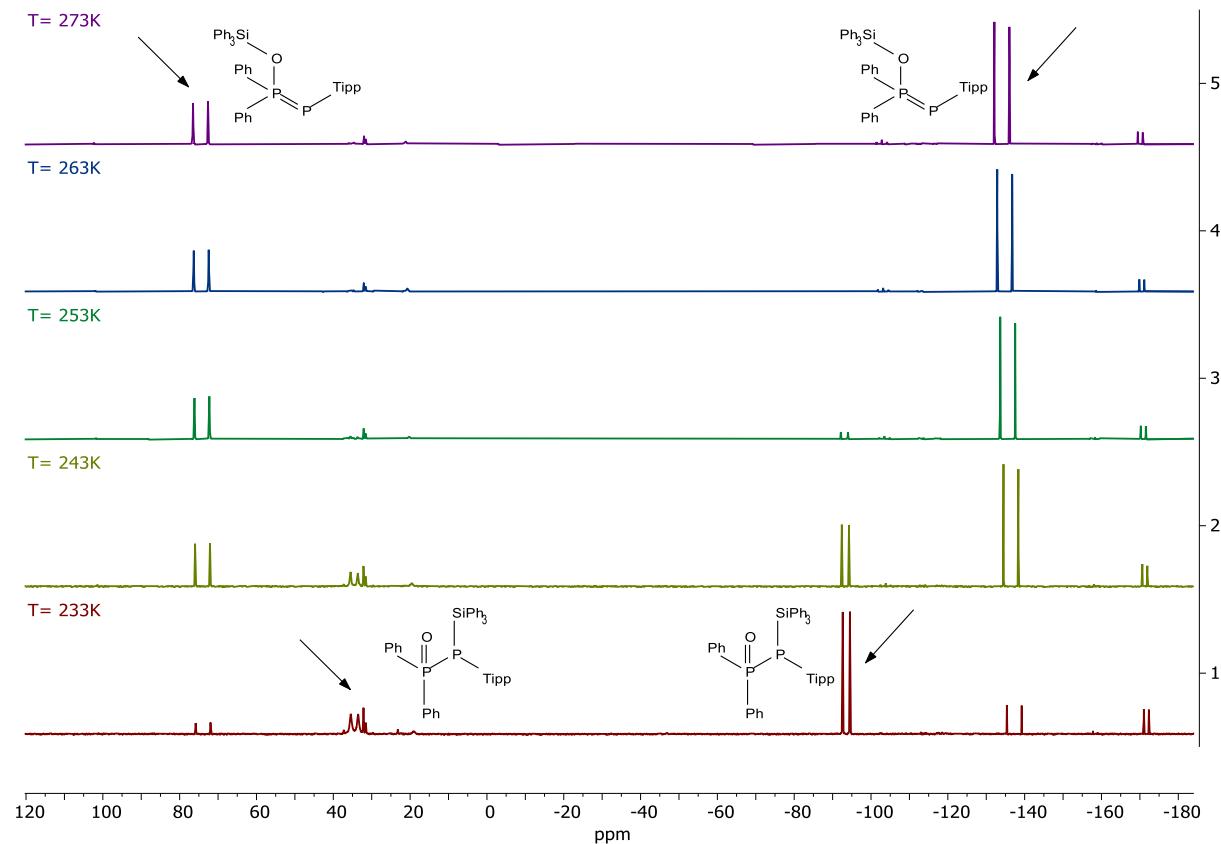


Figure S9: Immediate ^{31}P NMR measurement after mixing of diphenylphosphinic chloride and lithium 2,4,6-triisopropylphenyl-(triphenylsilyl)phosphanide (**1b**) at different temperatures. (161.97 MHz, C_6D_6).

3) IR spectrum of **3b**

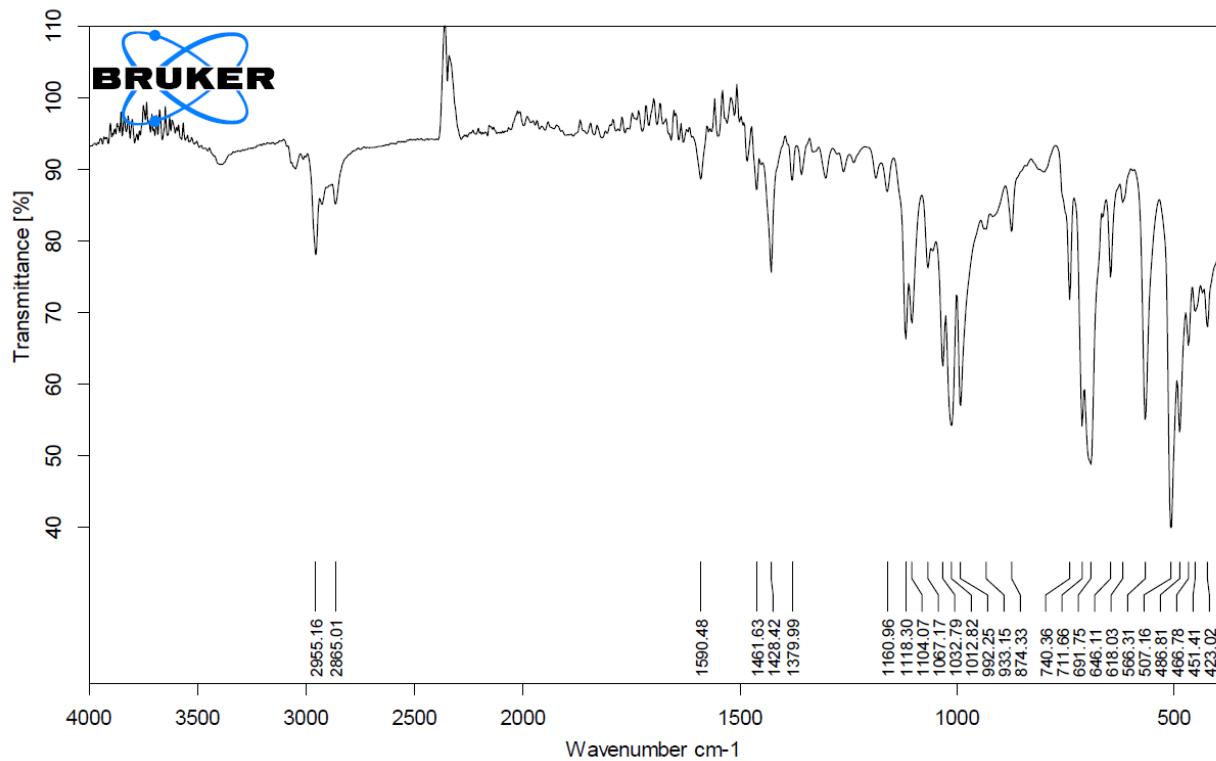


Figure S10: IR spectrum of (diphenyl)[(2,4,6-triisopropylphenyl)phosphinidenyl](triphenylsiloxy)phosphane (**3b**) (Listing: IR, solid (cm⁻¹): 2955 m, 2865 w, 1590 w, 1462 w, 1428 m, 1380 w, 1161 m, 1118 m, 1104 m, 1067 s, 1033 s, 1013 s, 933 m, 874 m, 740 m, 712 s, 691 s, 646 m, 618 w, 566 s, 507 s, 487 s, 467 m, 451 s, 451 m, 423 m).

4) Structure Determination of **3b**

The intensity data for compound **3b** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans^[1-3]. The structures were solved by direct methods (SHELXT^[4]) and refined by full-matrix least squares techniques against F_o² (SHELXL-2018^[5]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystal of **3b** contains large voids, filled with disordered solvent molecules. The size of the voids is 297 Å³/unit cell. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON^[6] resulting in 86 electrons/unit cell. All non-hydrogen atoms were refined anisotropically^[5]. XP^[7] and POV-Ray^[8] were used for structure representations.

*Crystal Data for **3b*** ([*] derived parameters do not contain the contribution of the disordered solvent): C₄₉H₅₆O₂P₂Si [*], M = 766.96 g mol⁻¹ [*], colorless prism, size 0.110 x 0.092 x 0.090 mm³, triclinic, space group P $\bar{1}$, a = 11.9281(2), b = 13.5118(3), c = 16.5193(3) Å, α = 100.152(1), β = 99.979(1), γ = 112.453(1) $^\circ$, V = 2335.81(8) Å³, T = -140 °C, Z = 2, $\rho_{\text{calcd.}}$ = 1.090 g cm⁻³ [*], $\mu(\text{Mo-K}\alpha)$ = 1.54 cm⁻¹ [*], multi-scan, trans_{min}: 0.7033, trans_{max}: 0.7456, F(000) = 820, 27420 reflections in h(-15/15), k(-17/17), l(-20/21), measured in the range 1.299° $\leq \Theta \leq$ 27.484°, completeness $\Theta_{\text{max}} = 99.5\%$, 10650 independent reflections, R_{int} = 0.0300, 9089 reflections with F_o > 4σ(F_o), 488 parameters, 0 restraints, R_{1obs} = 0.0501, wR²_{obs} = 0.1225, R_{1all} = 0.0598, wR²_{all} = 0.1296, GOOF = 1.037, largest difference peak and hole: 1.214 / -0.386 e Å⁻³.

Supporting Information available: Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2048033 for **3b**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

- [1] COLLECT, Data Collection Software; Nonius B.V., Netherlands, **1998**.
- [2] „Processing of X-Ray Diffraction Data Collected in Oscillation Mode“: Otwinowski, Z.; Minor, W. in Carter, C. W.; Sweet, R. M. (eds.): *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, pp. 307-326, Academic Press **1997**.
- [3] SADABS 2.10, Bruker-AXS inc., 2002, Madison, WI, U.S.A
- [4] Sheldrick, G. M. *Acta Cryst.* (2015). **A71**, 3-8.
- [5] Sheldrick, G. M. *Acta Cryst.* (2015). **C71**, 3-8.
- [6] Spek, A. L. (2015). *Acta Cryst.* **C71**, 9-18.
- [7] Siemens (1994). XP. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- [8] POV-Ray, Persistence of Vision Raytracer: Victoria, Australia, **2007**.

5) Quantum chemical calculations

While searching for the transition state TS we reduced the substituents to be all phenyl groups (path d). The following numbering scheme is in accordance with the main text:

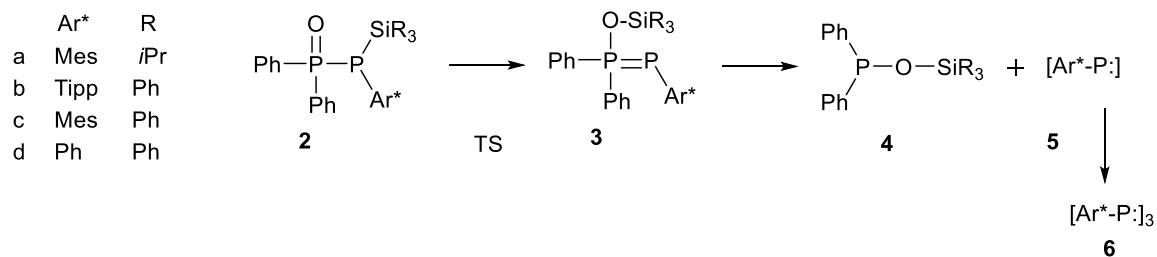


Figure S11. Overview on the compounds (numbering underneath the molecule drawings) that have been studied theoretically (aryl groups Ar* are characterized by a letter following the compound number).

First, we studied the involved species **2** and **3** as well as the expected degradation products **4** - **6**. For each system we modeled a couple of possible input structures, mainly rotamers around the P-P-bond. All obtained (local) minima are summarized together with key geometry parameters in the following table. All listed items were optimized with default settings and verified to be minima by frequency calculations (if not otherwise stated). Given is **the Total Electronic Energy (EE)**, **the Zero-Point-Energy (ZPE)** and **the Enthalpy (H)** calculated from the EE and the correction to the Enthalpy from the output file). All stable molecules were calculated as restricted singlets RM062X/6-311+G(d,p) (method 1) while the PAr*-fragments were calculated as unrestricted singlets or triplets with UM062X/6-311+G(d,p) (method 2).

a) Energy and Structure Parameter Summary

Table S1. List of calculated energy and structure parameters.

#	Comment	m	EE [au]	ZPE [au]	H [au] / dH[kJ/mol]	r(P1-P2) [Å]	r(P1-O) [Å]	r(P2-Si) [Å]	r(O-Si) [Å]	a(P1-P2-C13) [°]	a(P2-P1-O) [°]	a(O-P1-C1) [°]	d(O-P1-P2-C13) [°]	d(O-P1-P2-Si) [°]
2a1		1	-2215.718	0.651	-2215.027	2.215	1.502	2.310	3.873	104.545	120.608	111.553	93.295	25.923
2a2		1	-2215.713	0.652	+15.3	2.196	1.498	2.302	5.118	98.490	107.516	115.745	65.518	168.755
2b1		1	-2790.867	0.813	-2790.005	2.208	1.502	2.281	3.957	113.052	122.158	111.809	72.185	42.080
2b2		1	-2790.849	0.815	+49.6	2.216	1.497	2.284	5.012	105.485	107.799	115.203	64.754	165.765
2b3	iPr pointing towards P	1	-2790.838	-no freq -										
2c1		1	-2555.041	0.642	-2554.358	2.208	1.502	2.281	3.840	112.042	122.316	111.756	79.193	34.492
2c2		1	-2555.035	0.643	+16.4	2.217	1.497	2.291	4.991	97.338	107.436	115.716	66.709	171.014
2c3		1	-2555.033	0.642	+20.9	2.228	1.496	2.279	4.850	106.155	112.564	113.886	13.215	124.990
2d		1	-2437.124	0.558		2.211	1.504	2.298	3.600	100.063	119.141	110.854	69.828	35.722
TSa		1	-2215.693	0.652	-2215.002	2.132	1.561	2.726	1.974	100.038	102.301	108.289	154.830	0.913
TSb		1	-2790.831	0.813	-2789.971	2.145	1.566	2.547	1.956	104.357	98.944	110.956	117.582	1.978
TSb2	Si deviated from PPO plane	1	-2790.828	0.813	+9.0	2.145	1.566	2.547	1.899	104.774	98.944	107.222	102.395	17.804
TSc		1	-2555.010	0.641	-2554.329	2.145	1.566	2.547	1.956	109.145	98.944	111.376	104.529	1.978
TSd		1	-2437.095	0.557	-2436.502	2.142	1.561	2.552	2.001	99.879	100.671	109.172	81.395	11.826
TSd2	Ph groups rotated differently	1	-2437.093	0.558	+7.0	2.161	1.562	2.517	1.982	97.872	97.982	109.642	102.550	0.390
3a1		1	-2215.741	0.651	-2215.051	2.104	1.617	4.406	1.699	95.331	117.172	101.892	121.927	19.997
3a2	based on IRC endpoint	1	-2215.638	-no freq -		2.098	1.627	4.238	1.698	98.290	121.397	100.232	99.793	11.391
3b1	= „A“ in Table 1	1	-2790.883	0.814	-2790.021	2.075	1.620	4.653	1.670	91.702	115.019	99.966	54.196	15.692
3b2	= „B“ in Table 1	1	-2790.878	0.813	+11.9	2.095	1.639	4.084	1.685	96.547	119.045	99.687	106.302	20.726
3b3	= „C“ in Table 1	1	-2790.873	0.814	+26.6	2.094	1.613	4.201	1.686	104.711	118.674	98.941	28.819	17.518
3b4		1	-2790.861	-no freq -		2.099	1.640	4.050	1.686	98.964	117.458	100.289	115.664	19.378

#	Comment	m	EE [au]	ZPE [au]	E[au] / dE[kJ/mol]	r(P1-P2) [Å]	r(P1-O) [Å]	r(P2-Si) [Å]	r(O-Si) [Å]	a(P1-P2-C13) [°]	a(P2-P1-O) [°]	a(O-P1-C1) [°]	d(O-P1-P2-C13) [°]	d(O-P1-P2-Si) [°]
3c1	based on RSA for 3b	1	-2555.057	0.642	-2554.374	2.079	1.628	4.825	1.679	92.659	115.608	100.355	60.995	0.709
3c2		1	-2555.054	0.642	+8.3	2.098	1.607	4.295	1.680	102.495	118.231	98.855	27.208	15.778
3c3		1	-2555.053	0.641	+8.9	2.091	1.641	4.153	1.686	97.285	120.840	99.323	99.356	21.073
3d		1	-2437.137	0.558		2.081	1.631	4.245	1.681	90.420	118.762	98.253	68.428	22.957
4b-d1		1	-1864.184	0.464	-1863.690		1.666		1.668			96.997		
4b-d2		1	-1864.184	0.464	+0.1		1.666		1.668			96.968		
4b-d3		1	-1864.184	0.464	+1.1		1.659		1.663			102.465		
4a		1	-1524.876	0.473	-1524.374		1.652		1.682			97.900		
5b1	Triplet	2	-926.627	0.345	-926.262									
5b2	Triplet	2	-926.621	0.345	+14.7									
5b3	Singlet	1	-926.589	0.344	+95.2	one methyl group points towards the P, one H displaced towards P								
5b4	Triplet	2	-926.589	0.345	+100.2									
5a1,5c1	Triplet	2	-690.805	0.174	-690.619									
5a2,5c2	Singlet	1	-690.757	0.173	124.6									
6b	Ring, started as eea conformation, optimizes to aaa	1	-2780.077	1.043	-2778.976	1.872	1.859	2.196	2.264	60.181		107.019	93.340	
6a,6c		1	-2072.618	0.529	-2072.055	1.857	1.859	2.242	2.240	59.054		89.786	105.786	
6d1	optimizes to aaa	1	-1718.871	0.279	-1718.572	1.840	1.846	2.208	2.213	61.509		97.670	99.173	
6d2	open chain, Ph on both sides	1	-1718.823	0.279	+124.9	1.831	1.810	2.064	2.064	142.332		11.441	11.446	
6d3	open chain, started with eae	1	-1718.817	0.278	+141.5	1.843	1.816	2.056	2.056	120.926		153.318	153.305	

Table S2. The enthalpy differences plotted in Figure 4 (main text).

ΔH [kJ/mol]	a (green)	b (red)	c (blue)
2	0,00	0,00	0,00
Δ	64,76	90,13	76,40
TS	64,76	90,13	76,40
Δ	-127,93	-132,93	-119,79
3	-63,18	-42,80	-43,39
Δ	150,88	179,95	169,26
4 + 5	87,71	137,15	125,87
Δ	-173,01	-165,87	-173,01
4 + 1/3 6	-85,30	-28,71	-47,14

To give a comprehensive overview of the species involved, the next pages contain visual representations of the optimized coordinates in a standard orientation: either the view along the P-P-bond and the oxygen straight up or a 90° rotation of that. Color code: P orange, O red, and Si turquoise; H atoms omitted for clarity reasons.

b) Visual Comparison of calculated molecules

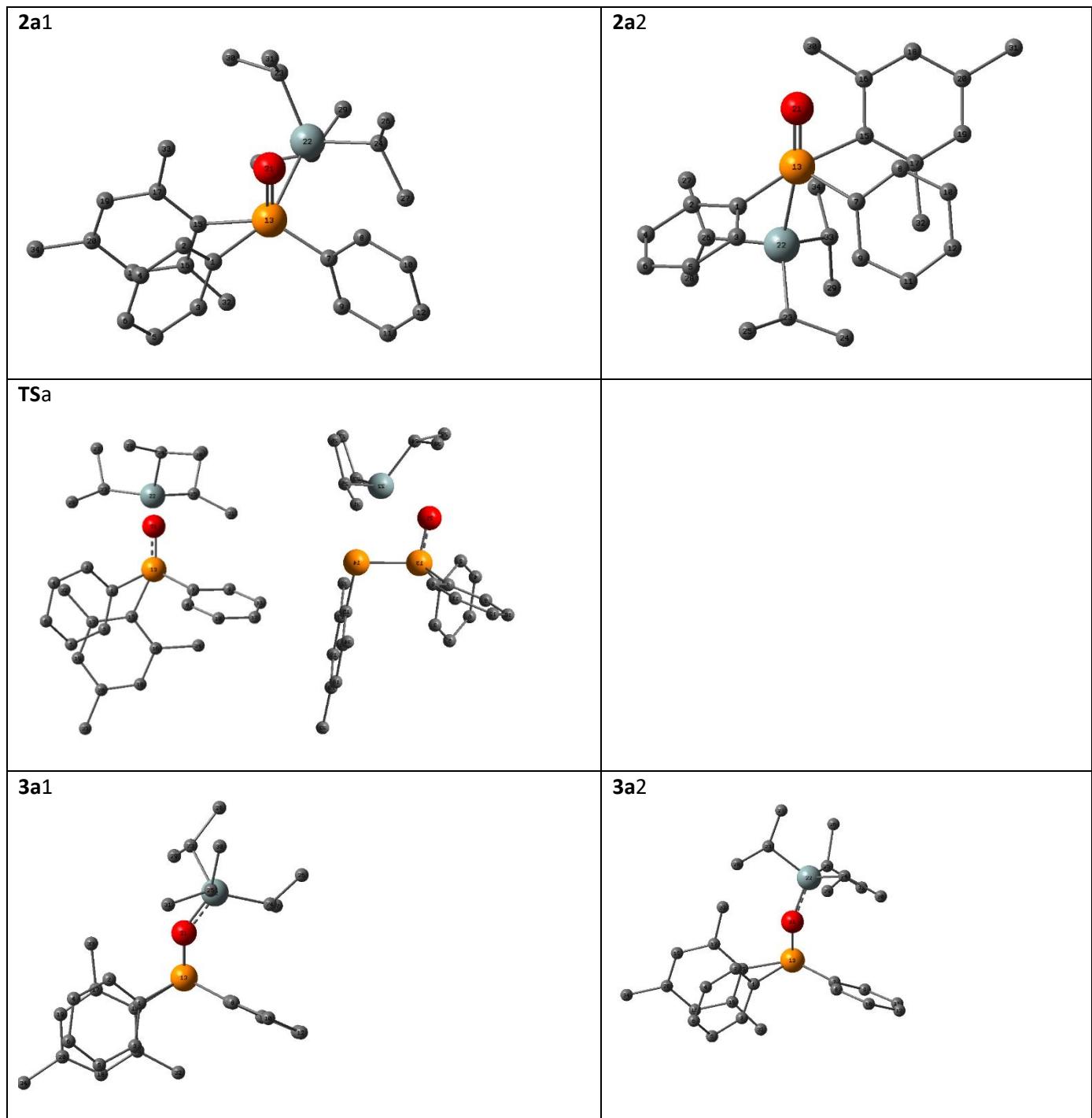


Figure S12. Calculated molecular structures of **2a**, **TSa** and **3a**, H atoms are omitted for clarity reasons.

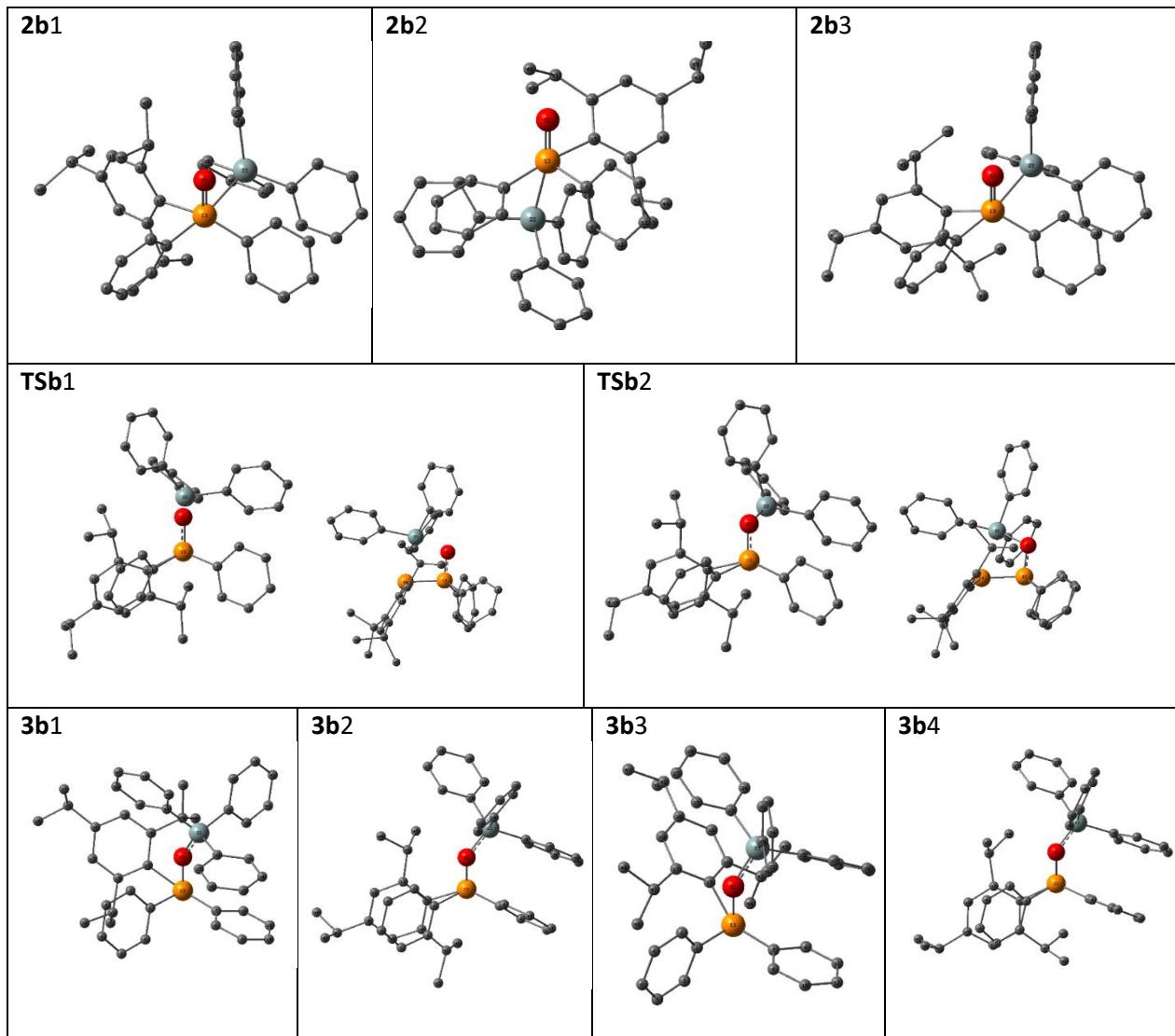


Figure S13. Calculated molecular structures of **2b**, **TSb** and **3b**. H atoms are omitted for clarity reasons.

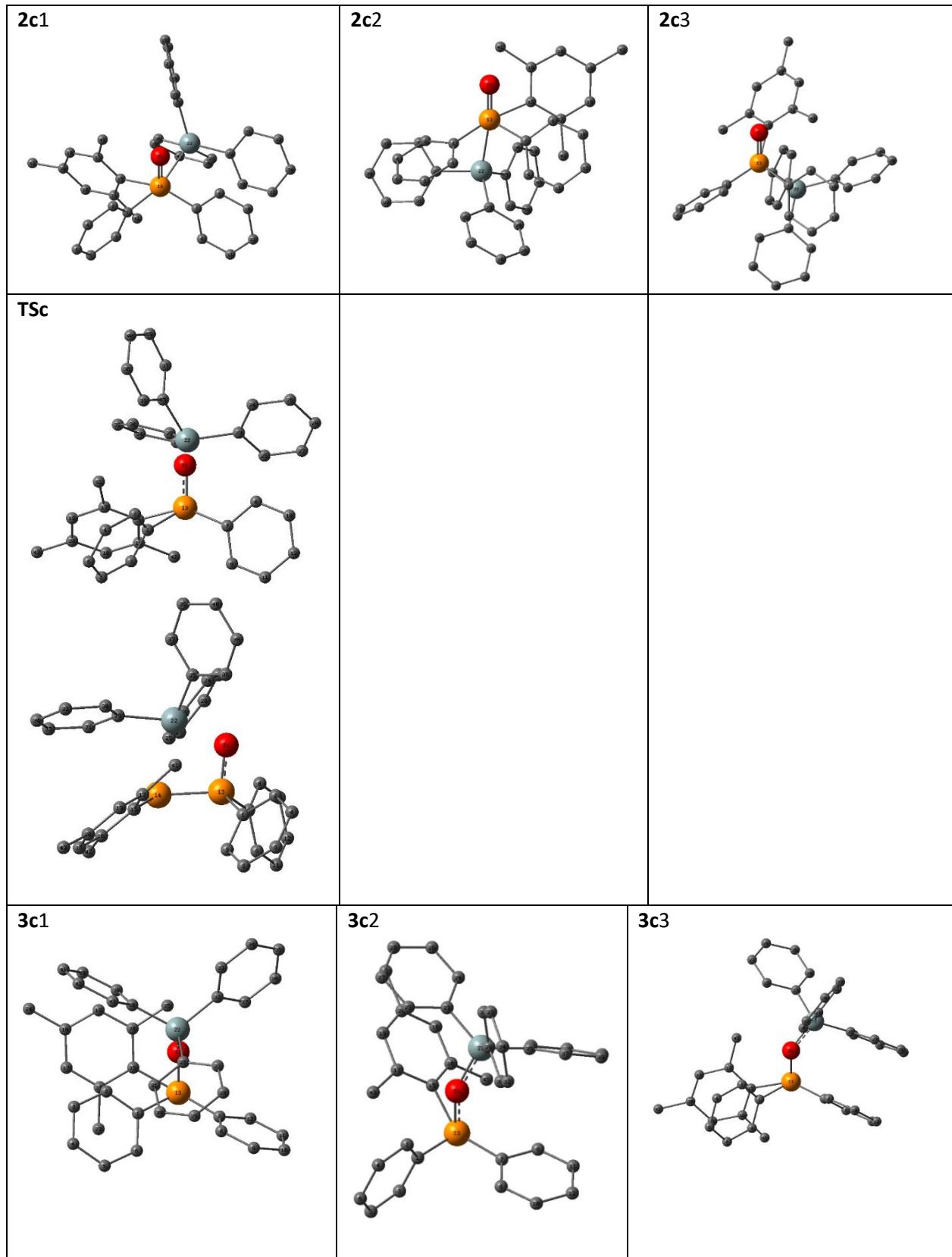


Figure S14. Calculated molecular structures of **2c**, **TSc** and **3c**, H atoms are omitted for clarity reasons.

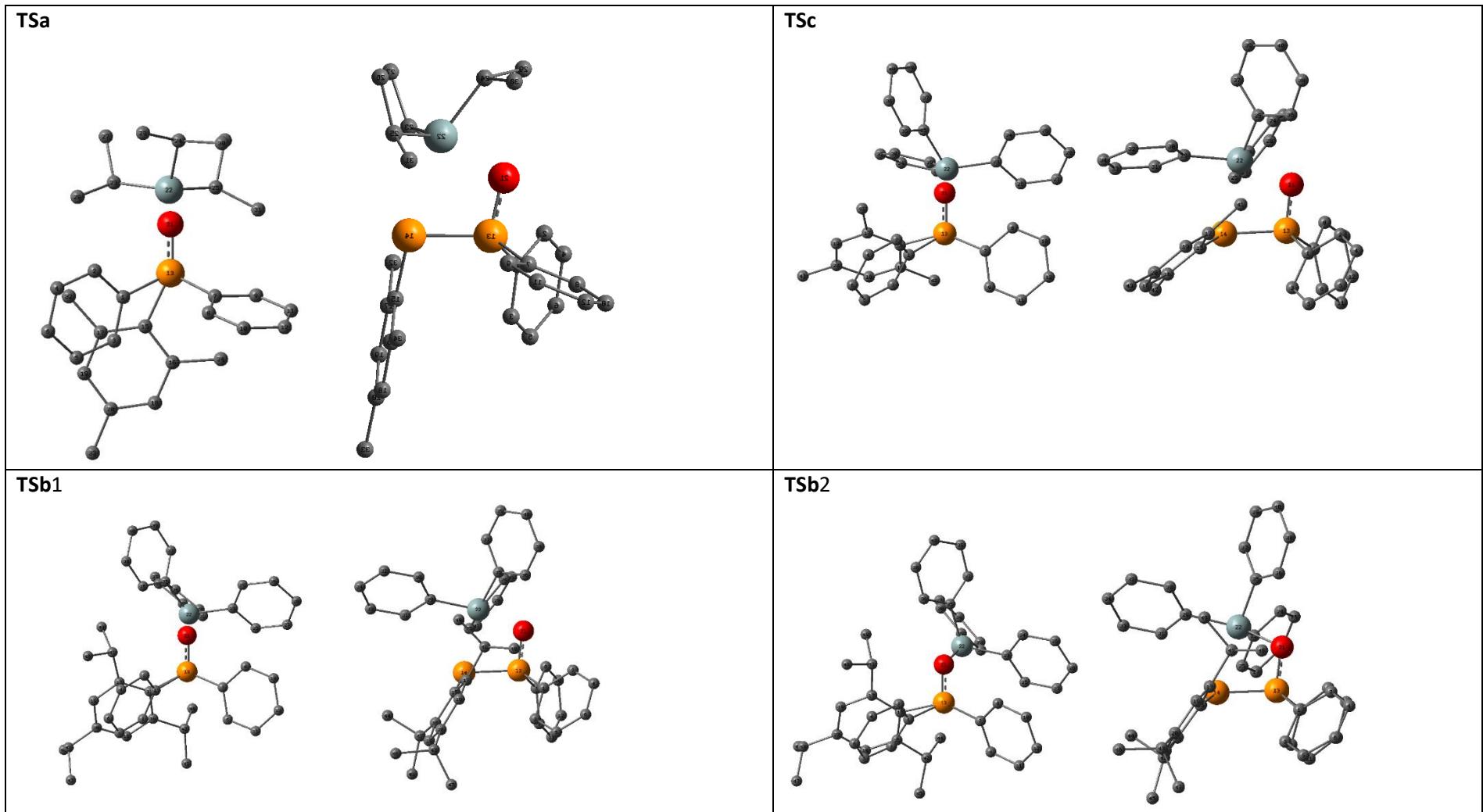


Figure S15. Representation of the transition states **TS** (In order to make the rotamers comparable, the views are along the P-P-axis with the O straight up. The second view is rotated by about 90°.)