Electronic Supplementary Information

Synthesis and Structures of $[S=(H)P(\mu\text{-}NR)]_2$, Potential Building Blocks for Inorganic Phosphorus-Sulfur Macrocycles

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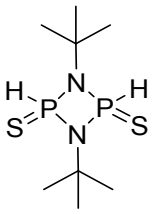
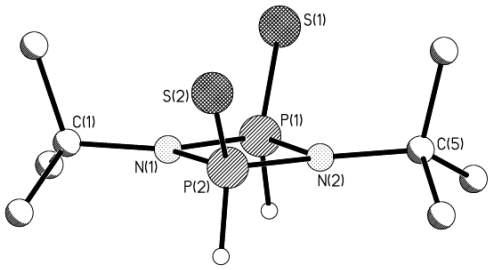
Compound **IIIa**





Full details of the synthesis and characterisation are in the text of the paper.

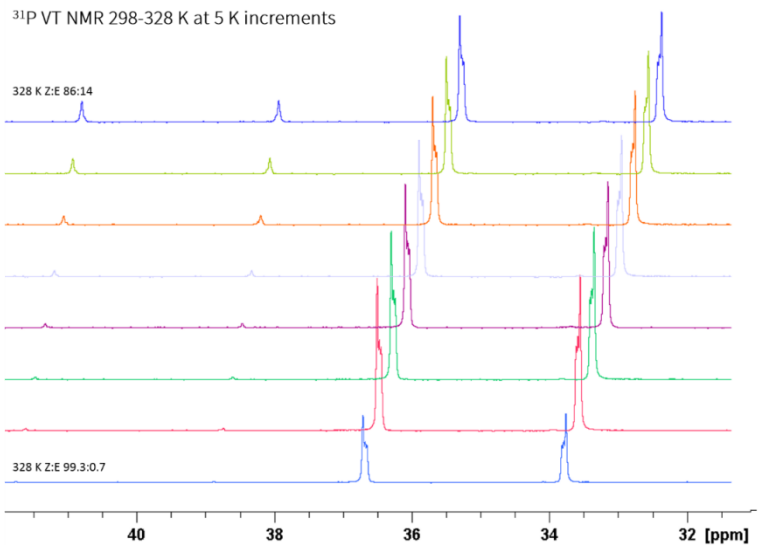
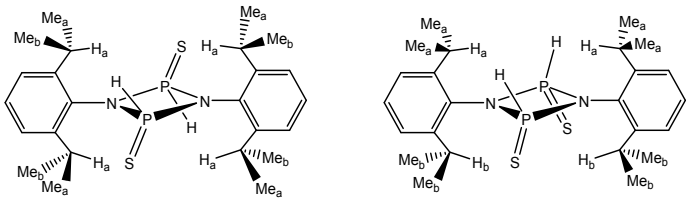


Fig S1: ^{31}P VT NMR (202.5 MHz, d_8-Tol) study of IIIa showing conversion to *trans* isomer.

Compound **IIIb**



trans-**IIIb** *cis*-**IIIb**

Synthesis: A solution of LiSH was made by bubbling SH_2 through a solution of nBuLi (0.52ml, 1.6M, 1.45 mmol) in THF (25ml). The solvent was removed by half to as to remove excess SH_2 and topped up to 25ml. A solution of $[P(\mu\text{-NDipp})Cl]_2$ (200mg) in THF (25 ml) was added dropwise at -78 ^oC and the solution left to stir to room temp. Removal of the solvent and extraction with pentane (filt. Celite) followed by recrystallization from hexane/thf at -16 ^oC yielded the products as crystals and white powder (30mg, 15%).

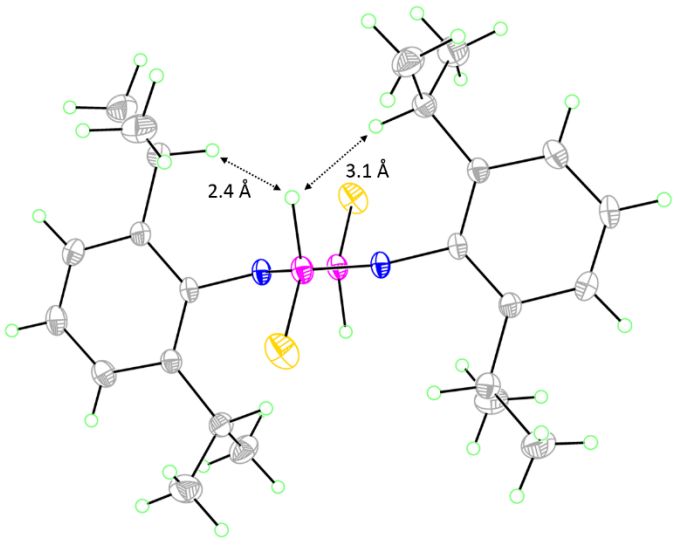


Fig S2: Solid-state structure of **IIIb**.

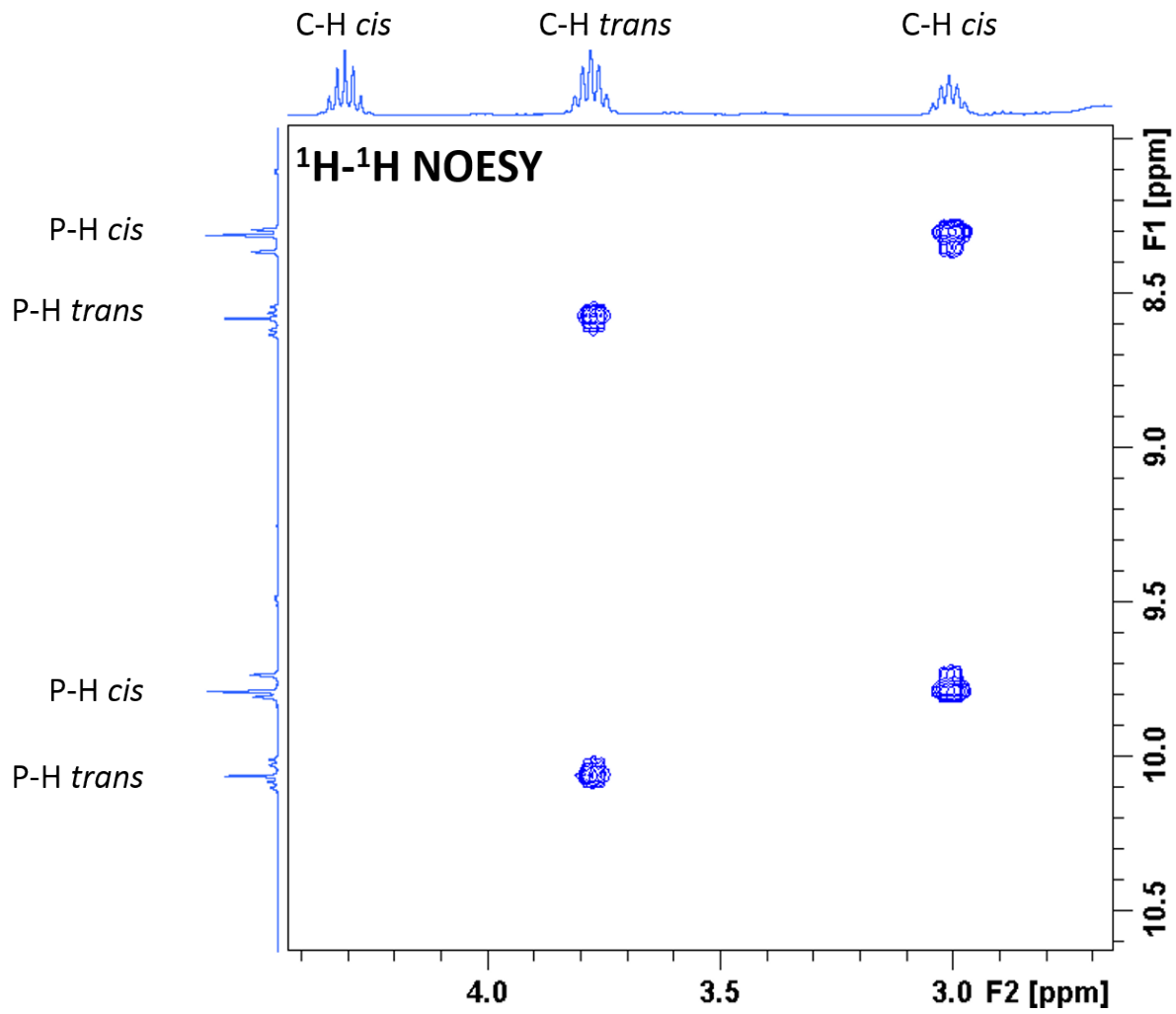


Fig S3: Room-temperature (400 MHz, d_8-toluene) ^{1}H-^{1}H NOESY spectrum (mixing time = 1000 ms) of **IIIb** expanded to show through-space correlation between P-H *cis* and P-H *trans* in the *trans* species with the corresponding CH groups of the ^{i}Pr groups.

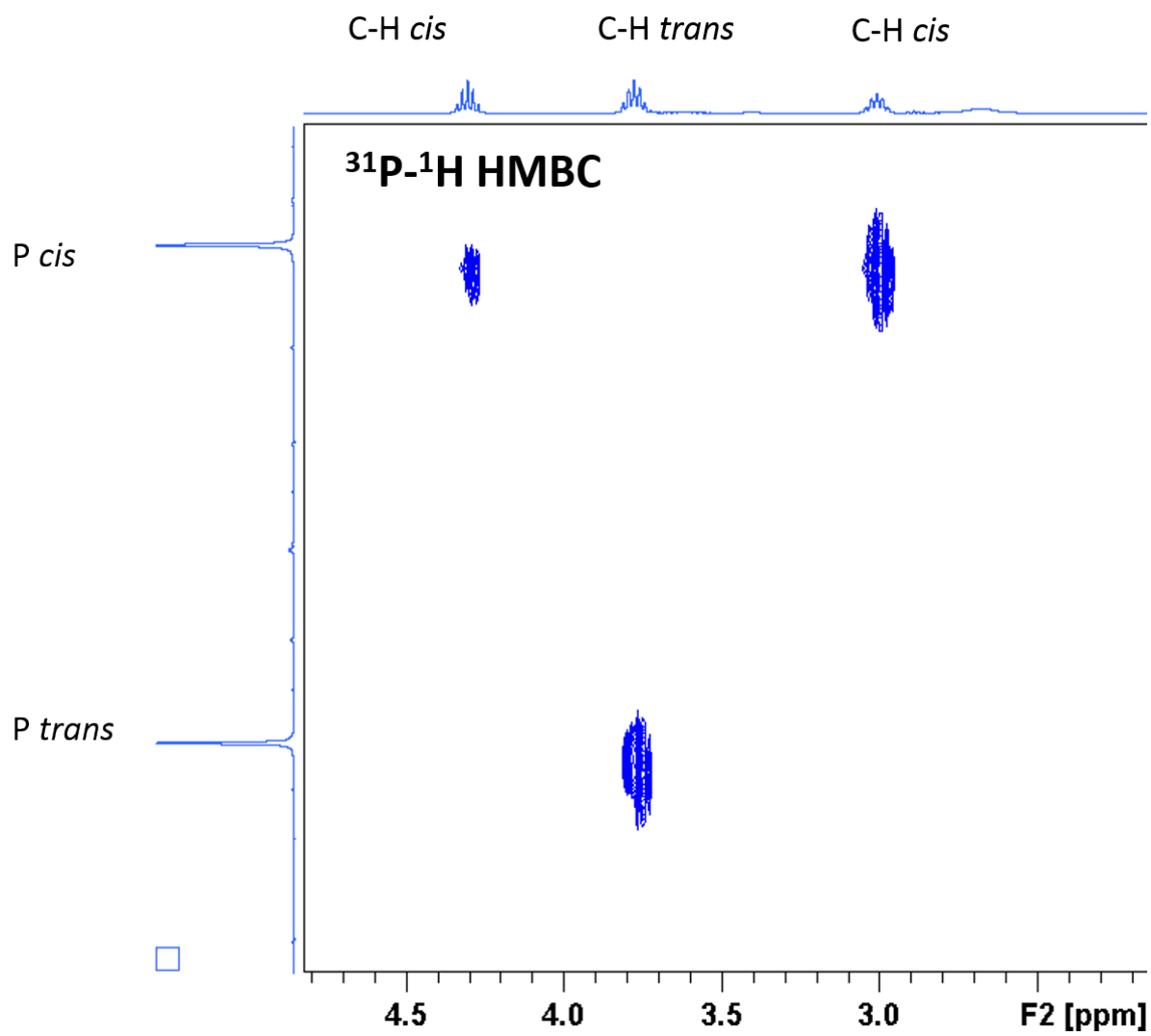


Fig S4: Room-temperature (d_8-toluene) ^{1}H-^{31}P HMBC spectrum of **IIIb** expanded to show coupling between inequivalent Ha and Hb in the *cis* species and Ha *trans* with their respective ^{31}P resonance.

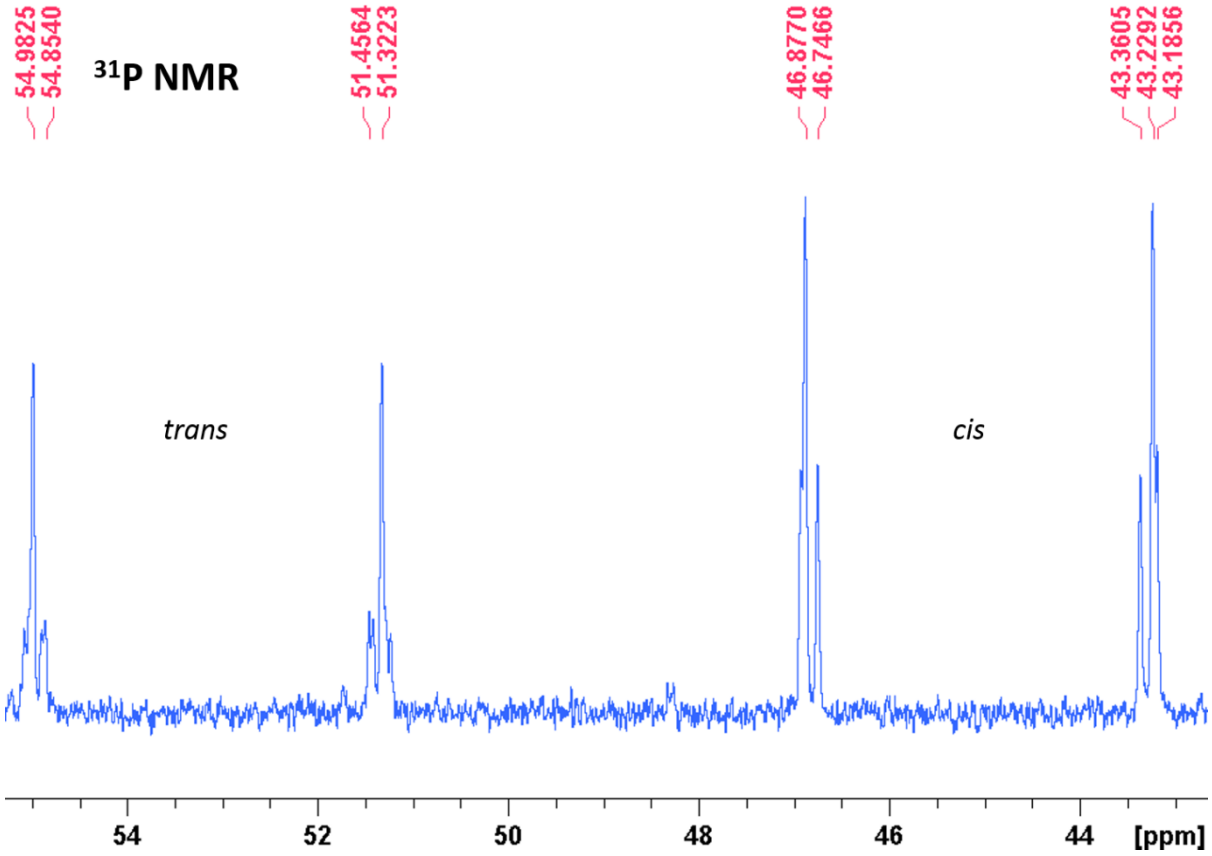
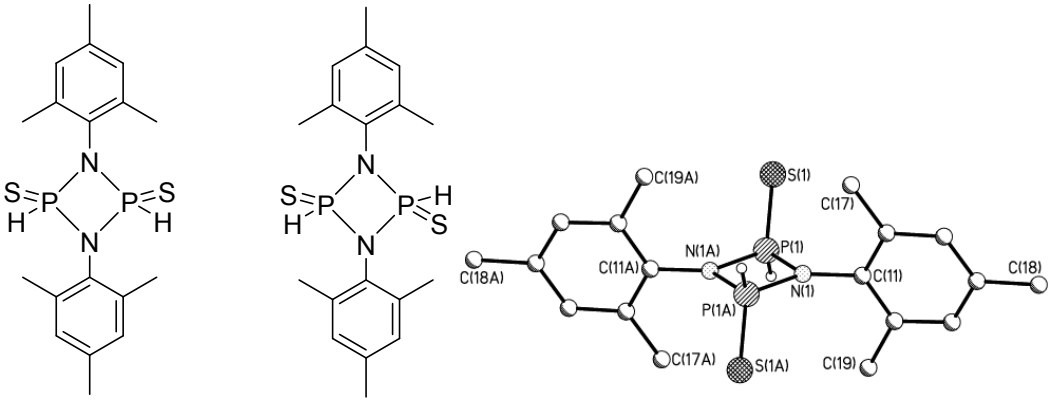


Fig S5: ^{31}P spectrum of **IIIb** (161.7 MHz, d_6-Benzene, +25^{o}C) expanded to show AA´XX´ nature of the phosphorus signals for the *cis* and *trans* species.

Compound **IIIc**



Synthesis: A solution of LiSH was made by bubbling SH_2 through a solution of nBuLi (0.52ml, 1.6M, 1.45 mmol) in THF (25ml). The solvent was removed by half to as to remove excess SH_2 and topped up to 25ml. A solution of $[PN(u\text{-}Mes)Cl]_2$ (200mg) in THF (25 ml) was added dropwise at -78 ^oC and the solution left to stir to room temp. Removal of the solvent and extraction with toluene (filt. Celite) yielded the product as a white powder (144 mg, 73%).

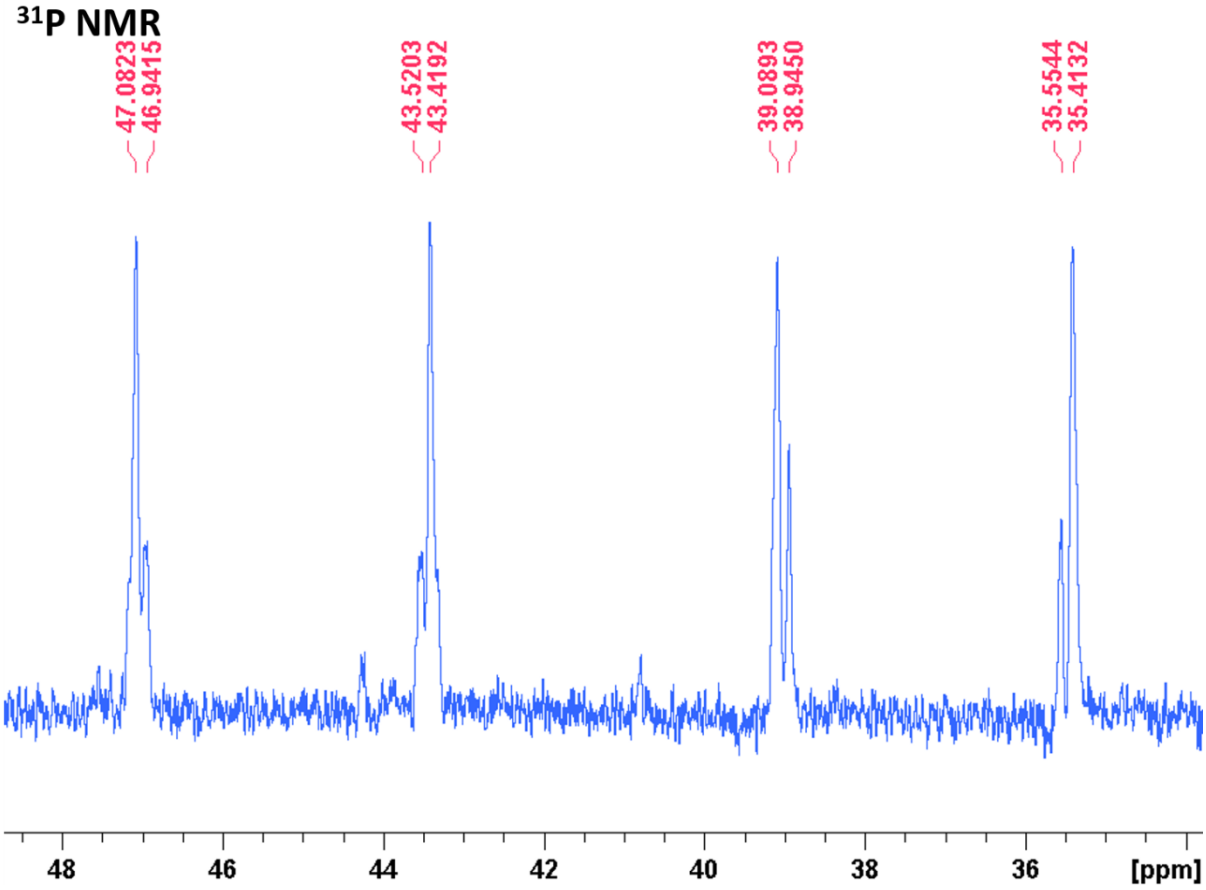


Fig S6: ^{31}P spectrum of **IIIc** (161.7 MHz, d_6-Benzene, +25^oC) expanded to show AA'XX' nature of the phosphorous signals for the *cis* and *trans* species.

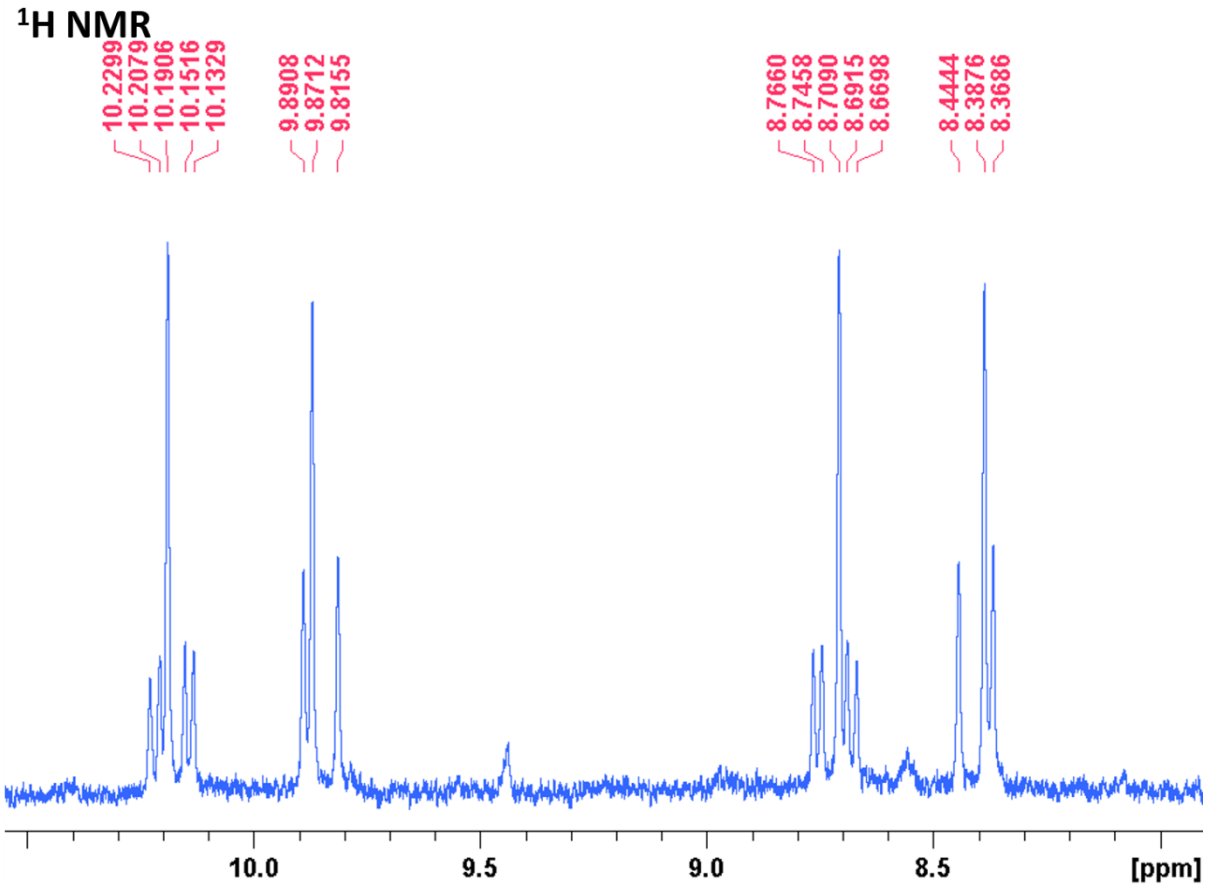


Fig S7: ^{1}H spectrum of IIIc (400 MHz, d_6-benzene, +25^{o}C) expanded to show AA'XX' nature of the P-H hydrogens in the *cis* and *trans* species.

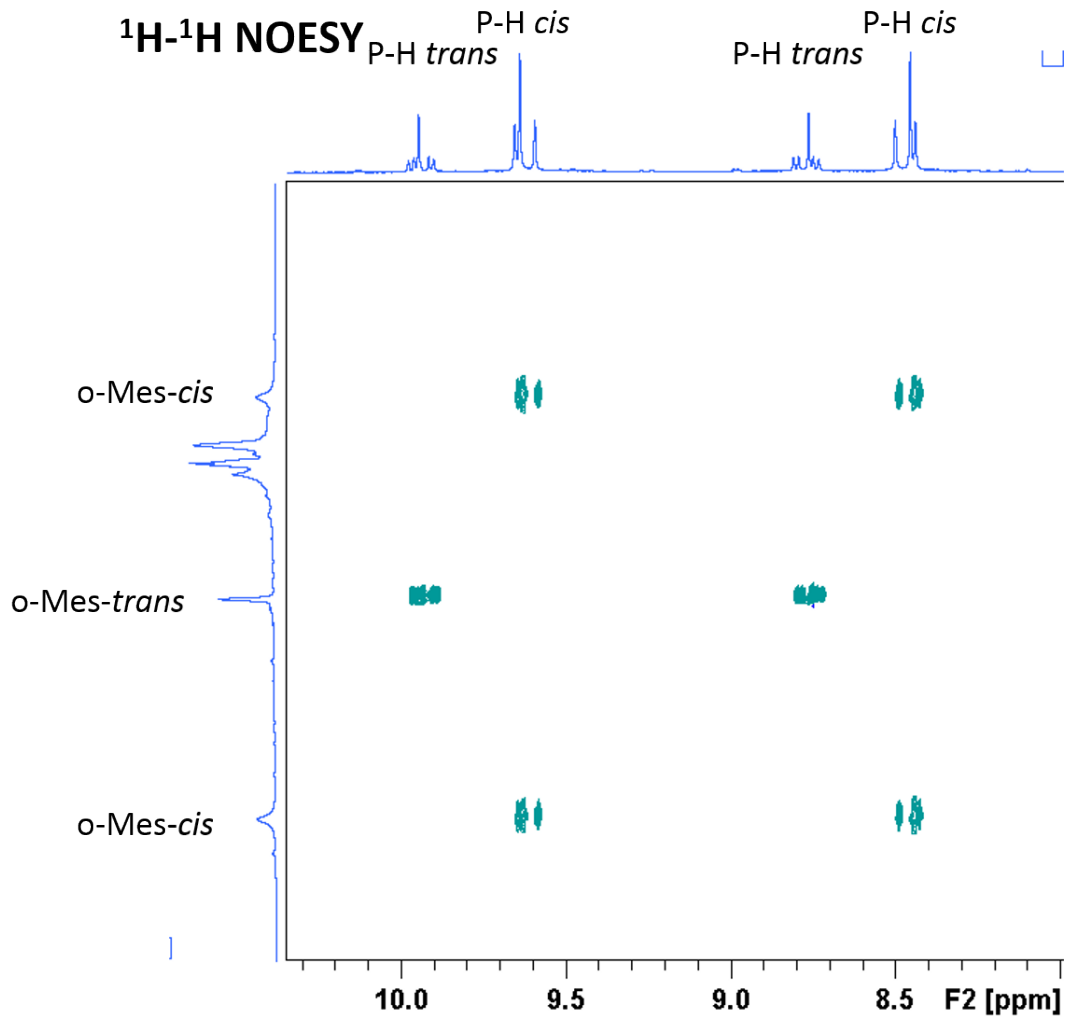
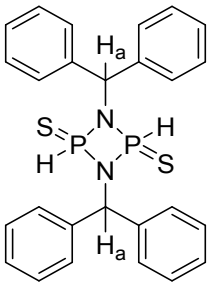


Fig S8: ^{1}H-^{1}H NOESY spectrum of IIIc (400 MHz, d_6-Benzene, +25°C, mixing time 1000ms) expanded to show spatial proximity of *o*-Mes groups with the P-H protons. (while one resonance is observed for the *o*-CH_3 group of the *trans* isomer, two magnetically inequivalent *o*-CH_3 groups are observed for the *cis* isomer arising from restricted rotation of the C-N bond. These groups interconvert slowly at room temperature on the NMR time scale.

Compound **IIId**



Synthesis: A solution of LiSH was made by bubbling SH_2 through a solution of nBuLi (0.5ml, 1.6M, 0.8 mmol) in THF (25ml). The solvent was removed by half to as to remove excess SH_2 and topped up to 25 ml. A solution of $[P(\mu\text{-NBenz})Cl]_2$ (200mg, 0.4mmol) in THF (25 ml)

was added dropwise at -78 °C and the solution stirred to room temp followed by immediate removal of the solvent. Extraction with toluene (filtered Celite) yielded the product as a white powder (109 mg, 55%).

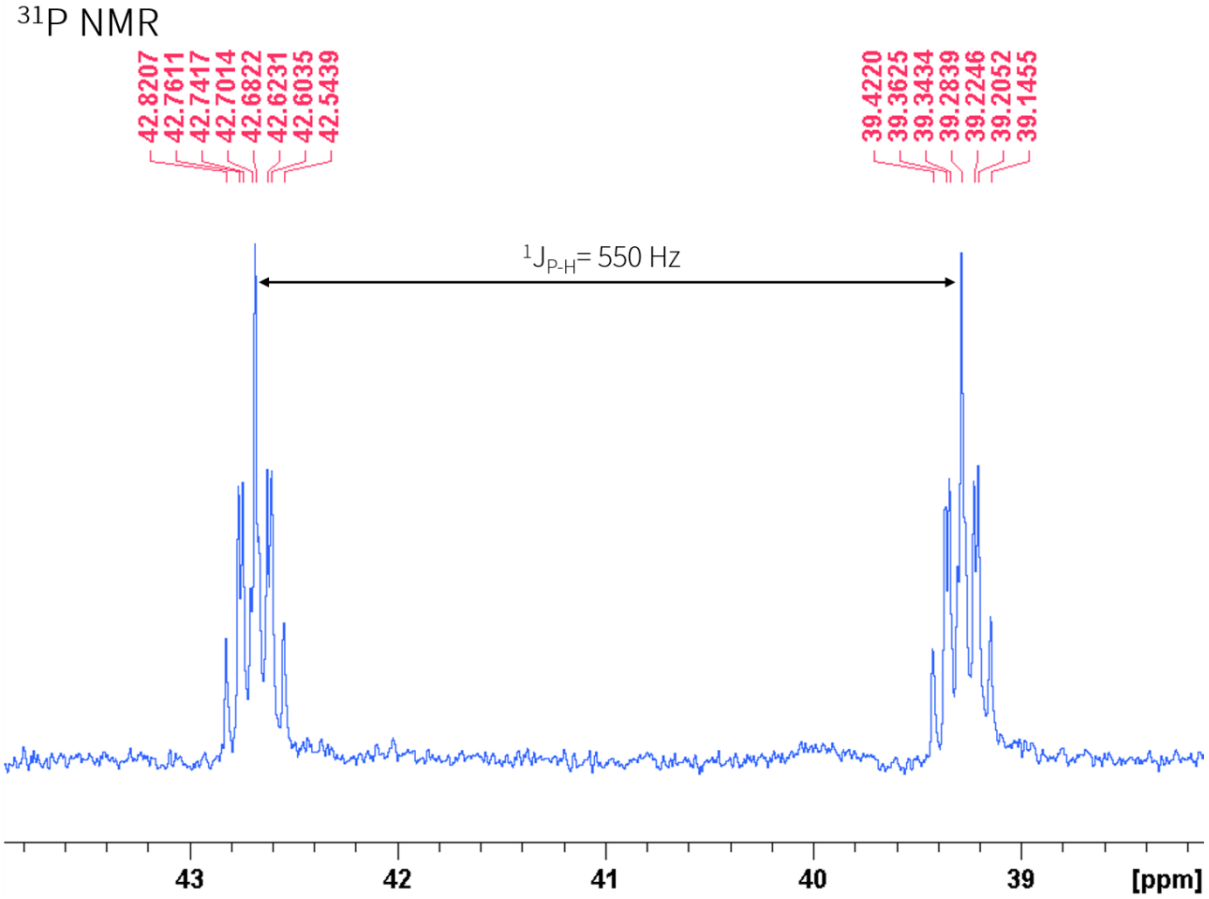
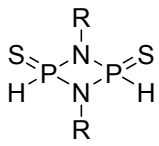


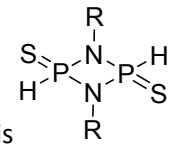
Fig S9: ^{31}P spectrum of **IIId** (500 MHz, d_6-benzene, +25°C) expanded to show AA'XX' nature of the phosphorus signal.

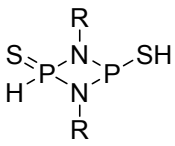
Computational Section

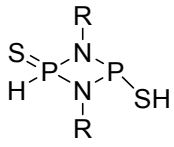
General Information

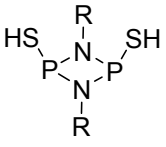
Computational studies of the four different derivatives (R = ^{t}Bu, DIPP, Mes, Benzhydryl) were performed employing Gaussian 09 Rev. B.01 software package.[1] All structures were optimized at the B3LYP/cc-pVTZ (PCM = THF) level of theoy.[2,3] Frequency calculations were performed to ensure that all found geometries correspond to energetic minima on the PES. Coordinates of optimized structures can be found in a separate geometry file. The following nomenclature has been used in this file:

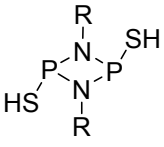

R_phn_s_cis


R_phn_s_trans


R_phn_sh_cis


R_phn_sh_trans


R_pn_sh_cis


R_pn_sh_trans

Thermodynamic Data

Unless stated otherwise all energies are provided in atomic units.

R = tBu	phn_s_cis	phn_s_trans	phn_sh_cis	phn_sh_trans	pn_sh_cis	sh_trans
E0	-1905,8641	-1905,8609	-1905,8576	-1905,8544	-1905,8478	-1905,8415
EZPE	0,2809	0,2809	0,2782	0,2781	0,2758	0,2756
Etot	0,2993	0,2993	0,2976	0,2975	0,2960	0,2958
Hcorr	0,3002	0,3002	0,2985	0,2984	0,2970	0,2968
Gcorr	0,2350	0,2352	0,2311	0,2306	0,2274	0,2275
E0+EZPE	-1905,5832	-1905,5800	-1905,5794	-1905,5763	-1905,5720	-1905,5659
E0+Etot	-1905,5648	-1905,5616	-1905,5600	-1905,5569	-1905,5518	-1905,5456
E0+Hcorr	-1905,5639	-1905,5607	-1905,5591	-1905,5560	-1905,5508	-1905,5447
E0+Gcorr	-1905,6291	-1905,6257	-1905,6265	-1905,6238	-1905,6204	-1905,6140
ΔE	0,0000	0,0032	0,0066	0,0097	0,0163	0,0227
ΔE kJ/mol	0,00	8,52	17,20	25,56	42,85	59,50
ΔH	0,0000	0,0032	0,0048	0,0079	0,0131	0,0192

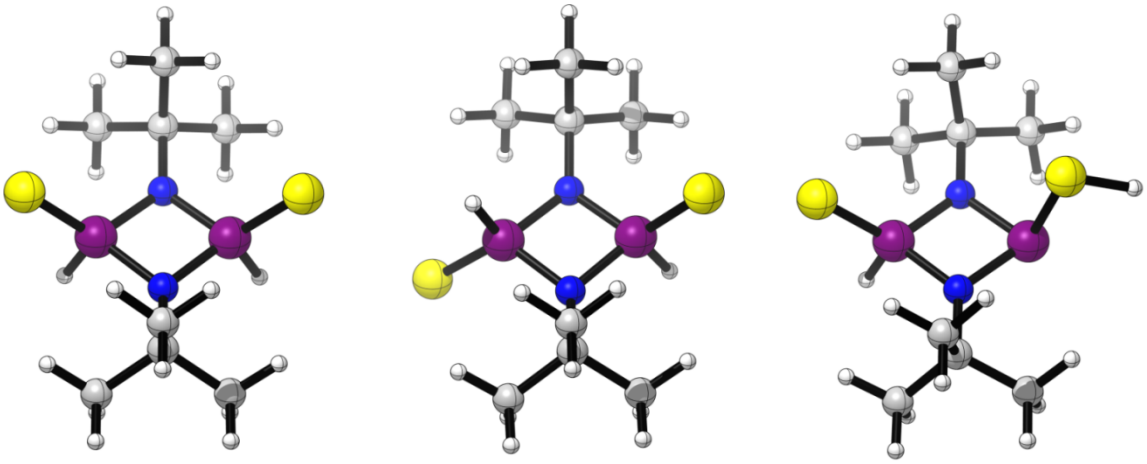
ΔH kJ/mol	0,00	8,42	12,62	20,72	34,28	50,40
ΔG	0,0000	0,0034	0,0026	0,0053	0,0087	0,0152
ΔG kJ/mol	0,00	9,04	6,91	14,01	22,85	39,82
R = DIPP	phn_s_cis	phn_s_trans	phn_sh_cis	phn_sh_trans	pn_sh_cis	sh_trans
E0	-2525,4231	-2525,4233	-2525,4166	-2525,4169	-2525,4069	-2525,4054
EZPE	0,5551	0,5548	0,5524	0,5523	0,5501	0,5494
Etot	0,5889	0,5887	0,5871	0,5871	0,5856	0,5853
Hcorr	0,5898	0,5897	0,5881	0,5881	0,5865	0,5863
Gcorr	0,4896	0,4882	0,4845	0,4851	0,4824	0,4792
E0+EZPE	-2524,8680	-2524,8685	-2524,8642	-2524,8646	-2524,8568	-2524,8561
E0+Etot	-2524,8342	-2524,8346	-2524,8295	-2524,8298	-2524,8213	-2524,8201
E0+Hcorr	-2524,8333	-2524,8337	-2524,8286	-2524,8289	-2524,8203	-2524,8191
E0+Gcorr	-2524,9335	-2524,9351	-2524,9321	-2524,9318	-2524,9244	-2524,9262
ΔE	0,0000	-0,0002	0,0065	0,0062	0,0162	0,0177
ΔE kJ/mol	0,00	-0,58	17,03	16,25	42,64	46,44
ΔH	0,0000	-0,0004	0,0047	0,0044	0,0129	0,0141
ΔH kJ/mol	0,00	-1,03	12,38	11,58	33,97	37,10
ΔG	0,0000	-0,0016	0,0014	0,0017	0,0091	0,0073
ΔG kJ/mol	0,00	-4,22	3,69	4,35	23,82	19,08

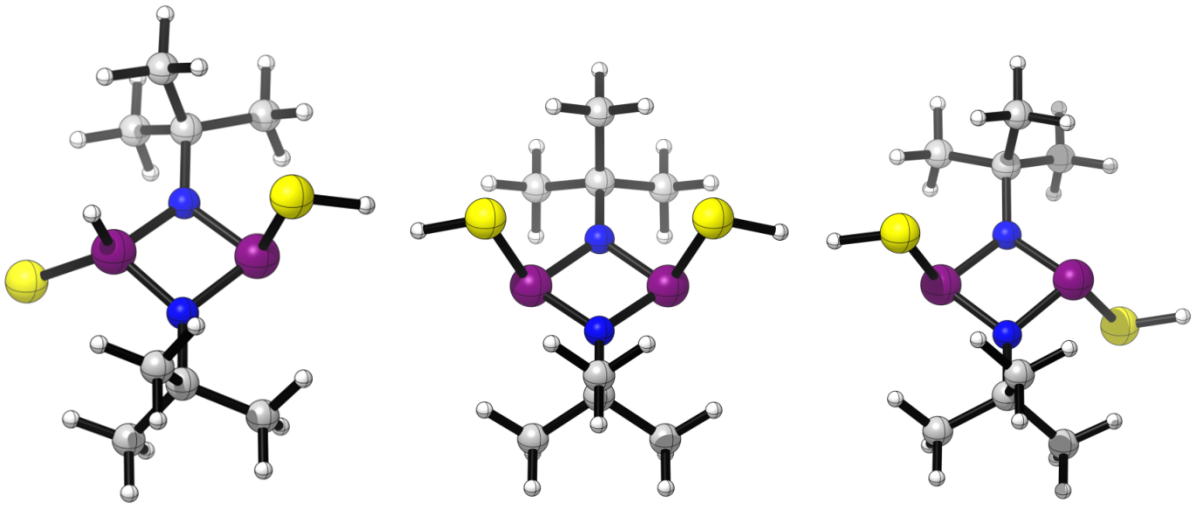
R = Mes	**phn_s_cis**	**phn_s_trans**	**phn_sh_cis**	**phn_sh_trans**	**pn_sh_cis**	**sh_trans**
E0	-2289,5382	-2289,5382	-2289,5325	-2289,5331	-2289,5236	-2289,5227
EZPE	0,3828	0,3832	0,3805	0,3804	0,3781	0,3778
Etot	0,4100	0,4101	0,4084	0,4083	0,4068	0,4067
Hcorr	0,4109	0,4111	0,4094	0,4093	0,4078	0,4076
Gcorr	0,3231	0,3240	0,3199	0,3201	0,3168	0,3164
E0+EZPE	-2289,0956	-2289,0957	-2289,0914	-2289,0924	-2289,0842	-2289,0835
E0+Etot	-2289,0685	-2289,0688	-2289,0635	-2289,0645	-2289,0555	-2289,0546
E0+Hcorr	-2289,0675	-2289,0678	-2289,0626	-2289,0636	-2289,0545	-2289,0537
E0+Gcorr	-2289,1553	-2289,1549	-2289,1520	-2289,1527	-2289,1455	-2289,1449
ΔE	0,0000	0,0000	0,0056	0,0050	0,0145	0,0155
ΔE kJ/mol	0,00	-0,05	14,72	13,17	38,13	40,57
ΔH	0,0000	-0,0003	0,0050	0,0039	0,0130	0,0138
ΔH kJ/mol	0,00	-0,88	13,00	10,28	34,11	36,29
ΔG	0,0000	0,0004	0,0033	0,0026	0,0098	0,0105
ΔG kJ/mol	0,00	1,00	8,64	6,84	25,71	27,45

R = Benzhyd.	phn_s_cis	phn_s_trans	phn_sh_cis	phn_sh_trans	pn_sh_cis	sh_trans
E0	-2594,4608	-2594,4647	-2594,4581	-2594,4586	-2594,4528	-2594,4481
EZPE	0,4378	0,4373	0,4354	0,4349	0,4326	0,4324
Etot	0,4663	0,4660	0,4647	0,4645	0,4630	0,4628
Hcorr	0,4672	0,4670	0,4656	0,4654	0,4639	0,4638
Gcorr	0,3733	0,3704	0,3702	0,3683	0,3647	0,3641
E0+EZPE	-2593,9586	-2593,9606	-2593,9575	-2593,9571	-2593,9524	-2593,9475
E0+Etot	-2593,9300	-2593,9318	-2593,9282	-2593,9275	-2593,9220	-2593,9171
E0+Hcorr	-2593,9291	-2593,9309	-2593,9273	-2593,9265	-2593,9210	-2593,9161
E0+Gcorr	-2594,0230	-2594,0275	-2594,0227	-2594,0237	-2594,0202	-2594,0158
ΔE	0,0000	-0,0039	0,0027	0,0022	0,0080	0,0127
ΔE kJ/mol	0,00	-10,31	7,20	5,87	21,03	33,24
ΔH	0,0000	-0,0018	0,0018	0,0026	0,0081	0,0130
ΔH kJ/mol	0,00	-4,61	4,81	6,71	21,21	34,07
ΔG	0,0000	-0,0044	0,0004	-0,0006	0,0028	0,0073
ΔG kJ/mol	0,00	-11,60	0,94	-1,62	7,39	19,06

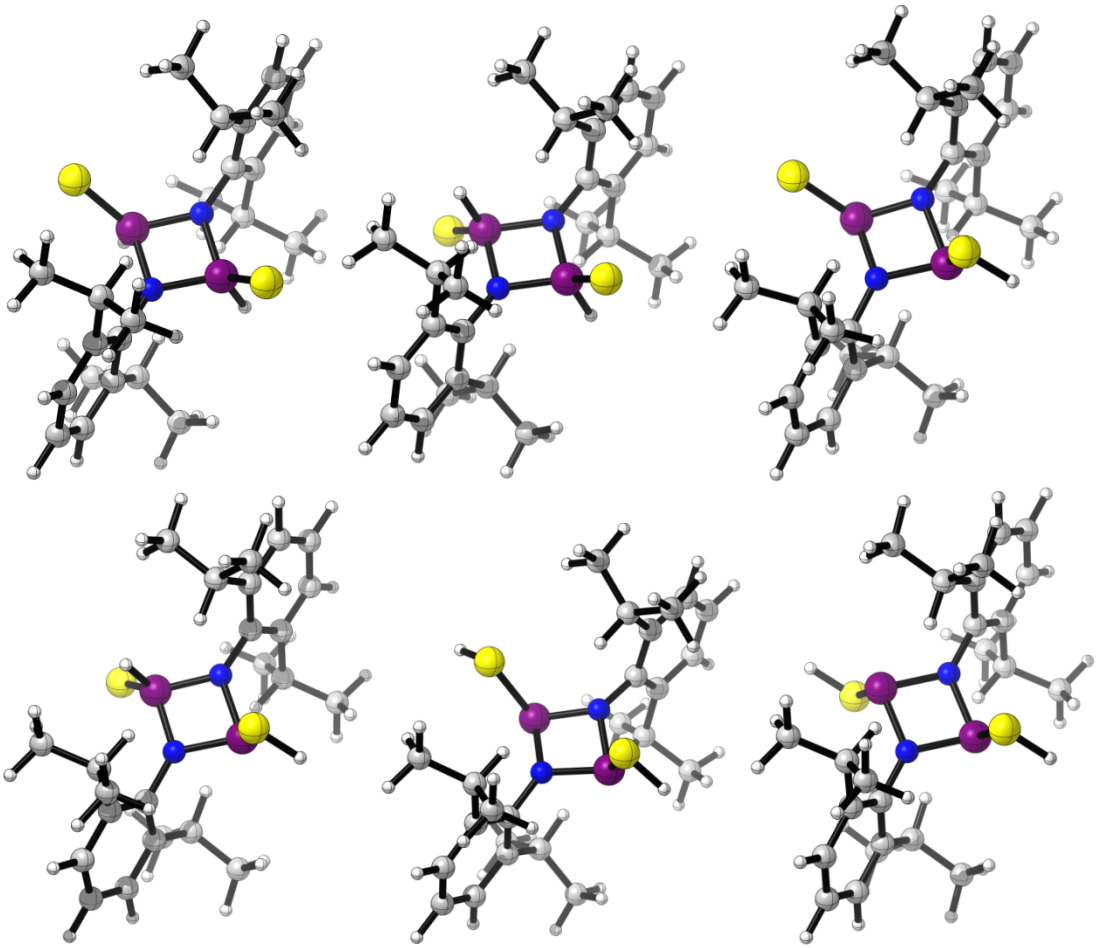
Geometries

R = tBu

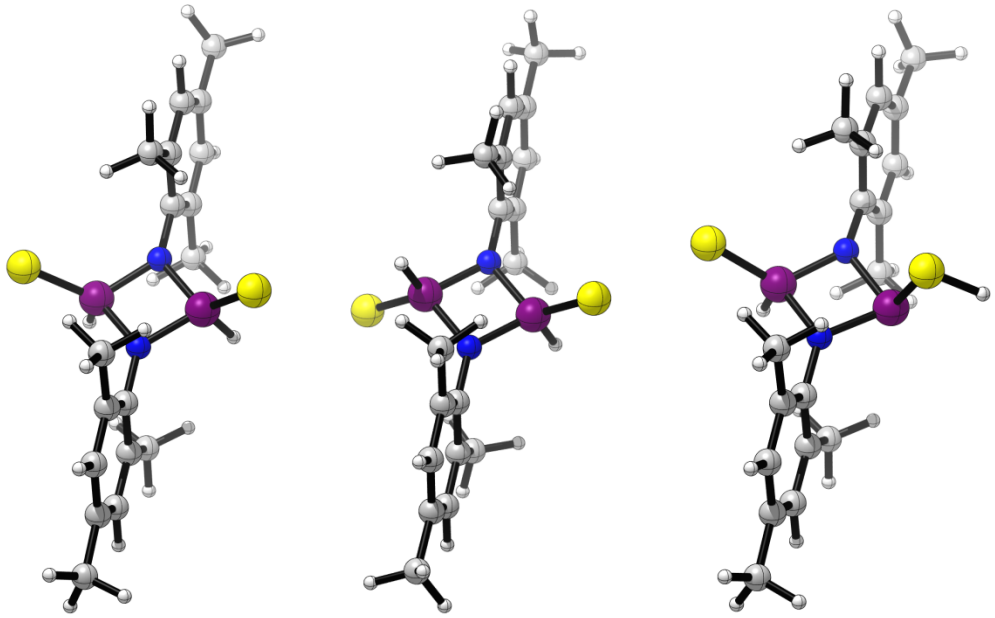


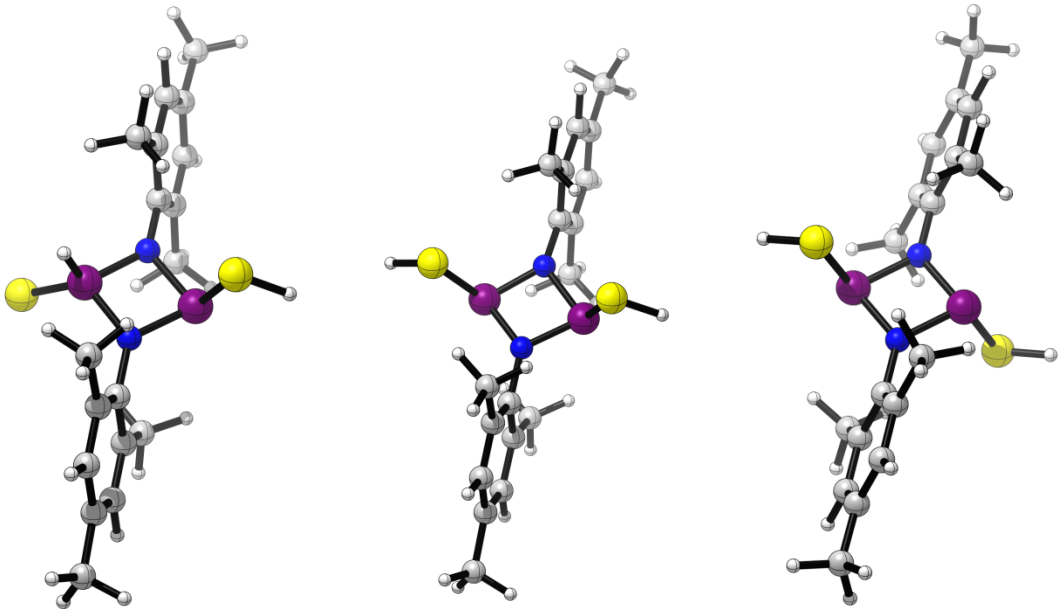


R = DIPP

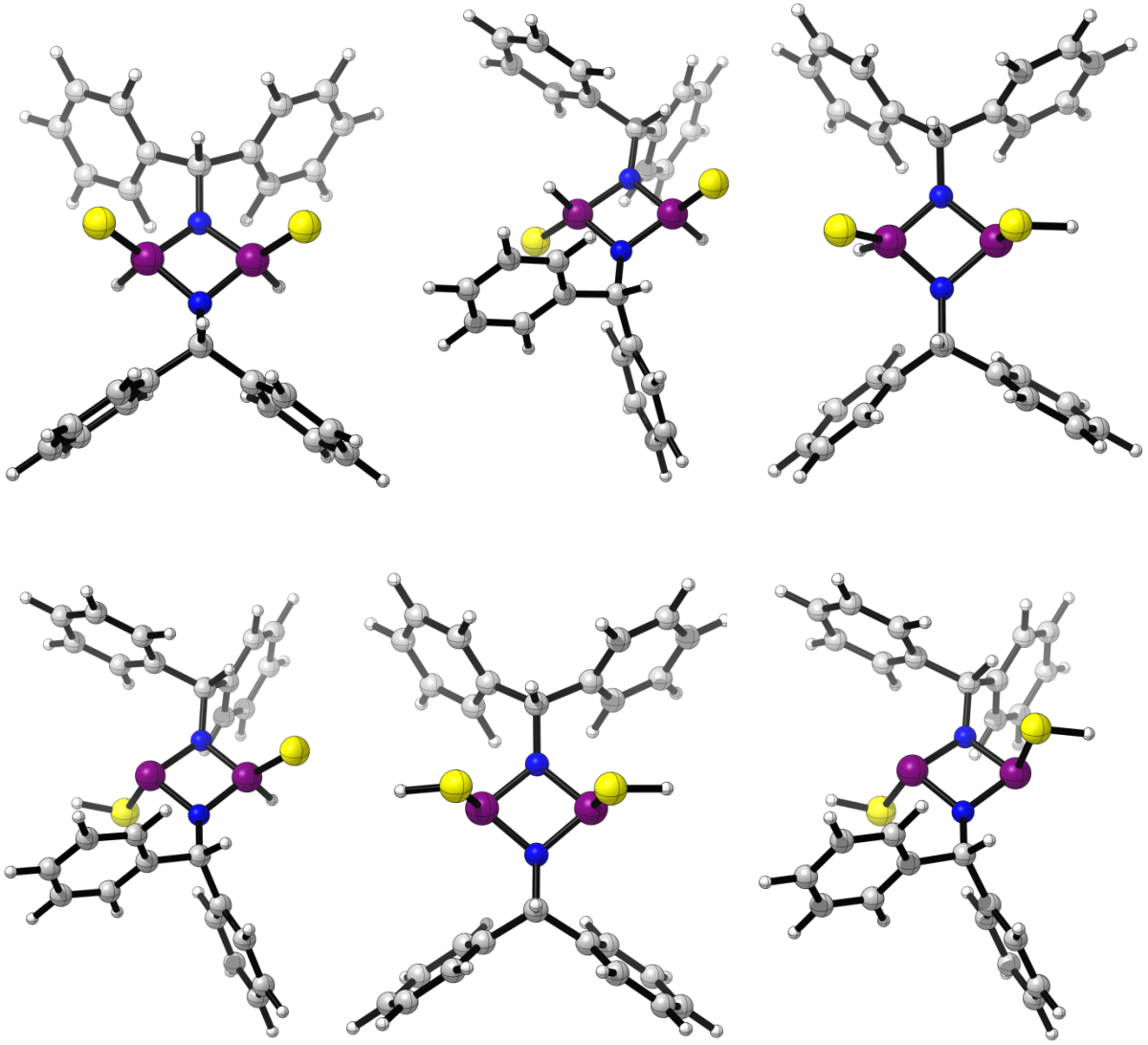


R = Mes





R = Benzhydryl



Activation Barriers

Calculations have been performed for the isomer bearing a tBu substituent. The same basis set, functional and solvent as for the previous calculations has been used. The following intramolecular inversion mechanisms have been considered: (i) direct inversion of the tetrahedral phosphorus center (marked in red, *via* TS1) and (ii) proton shift from P to S (*via* TS2) followed by lone-pair inversion at the P center (*via* TS3, vertex inversion). Transition states have been optimized and their nature has been confirmed by frequency calculations giving one imaginary frequency.

	TS1	TS2	TS3
E0	-1905,7748	-1905,7950	-1905,7843
EZPE	0,2793	0,2771	0,2754
Etot	0,2973	0,2960	0,2943
Hcorr	0,2983	0,2969	0,2952
Gcorr	0,2341	0,2309	0,2288
E0+EZPE	-1905,4955	-1905,5178	-1905,5089
E0+Etot	-1905,4775	-1905,4990	-1905,4900
E0+Hcorr	-1905,4765	-1905,4980	-1905,4891
E0+Gcorr	-1905,5407	-1905,5641	-1905,5554
ΔE	0,0893	0,0692	0,0798
ΔE kJ/mol	234,49	181,58	209,62
ΔH	0,0874	0,0658	0,0748
ΔH kJ/mol	229,34	172,88	196,47
ΔG	0,0884	0,0651	0,0737
ΔG kJ/mol	232,17	170,89	193,52

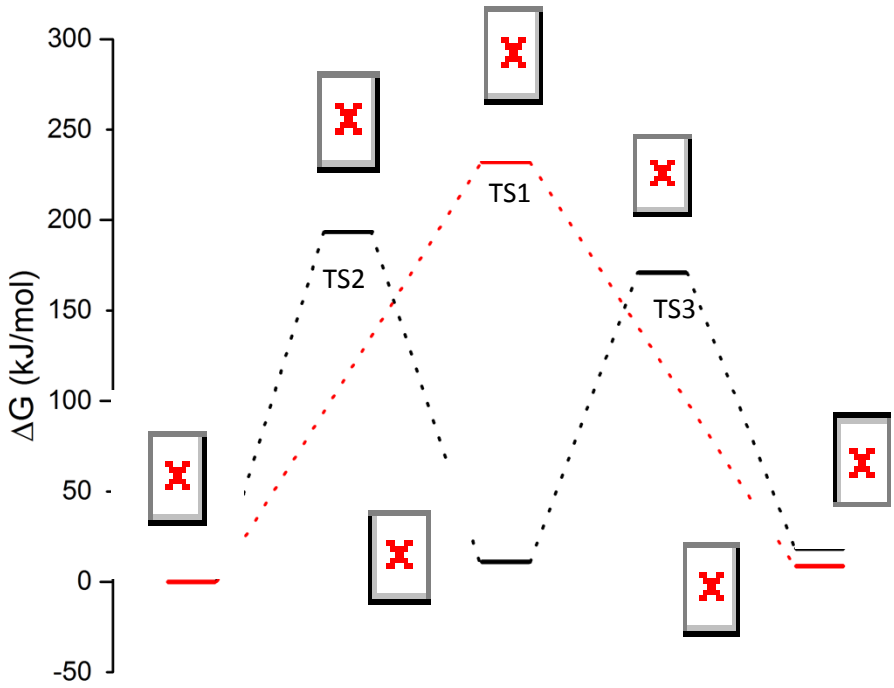


Fig. S10 Transition state calculations- (i) a concerted pathway in which *cis*-**IIIa** is converted into *trans*-**IIIa** directly *via* rotation of one P(H)=S fragment (red); (ii) a stepwise pathway involving P(H)=S/P-SH tautomerism and phosphorus lone pair inversion (black).

References

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