Electronic Supporting Information

White phosphorus activation by a Th(III) complex†

Alasdair Formanuik,[a] Fabrizio Ortu,[a] Reece Beekmeyer,[b] Andrew Kerridge,[c] Ralph W. Adams[a] and David P. Mills[a,*]

[a]School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

[b]Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, U.K.

[c]Department of Chemistry, Faraday Building, Lancaster University, Lancaster, LA1 4YB, U.K

Contents

1. Experimental Procedures

Caution – White phosphorus is spontaneously flammable in air, highly toxic and reacts violently with oxidants, therefore extreme care should be taken during manipulations. Thorium-232 is a weak α-emitter ($t_{1/2}$ 1.41 x 10^{10} years), therefore all manipulations should be performed in suitable laboratories that have been designated for radiochemical use, and α-counting equipment should be available. All manipulations were performed using standard Schlenk techniques or in an Inert Purelab HE 2GB glovebox. Toluene was dried by refluxing over potassium and stored over a potassium mirror, and was degassed before use. [Th(Cp″)$_3$)][1] was prepared according to published procedures. White phosphorus (obtained from a chemical amnesty) was dried *in vacuo* for 4 hours and sublimed before use. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 400.2, 100.6, 79.5 and 162.0 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (^{1}H, ^{13}C and ^{29}Si) or external H_3PO_4 (^{31}P). The FTIR spectrum was recorded as a Nujol mull in KBr discs on a Shimadzu IRAffinity-1S spectrometer and the UV/Vis spectrum was recorded on a Shimadzu UV-2600 spectrometer. Elemental microanalysis was carried out by Mrs Anne Davies and Mr Martin Jennings at the Microanalysis Service, School of Chemistry, The University of Manchester, UK.

[{Th(Cp″)$_3$}$_2$(μ-η^1:η^1-P$_4$)] (1): Toluene (20 ml) was added to a pre-cooled mixture of [Th(Cp″)$_3$] (0.569 g, 0.66 mmol) and P_4 (0.041 g, 0.33 mmol). The reaction mixture was allowed to warm to room temperature slowly and stirred for 72 hours. The dark orange reaction mixture was filtered, reduced in volume to *ca*. 2 ml and stored at –25 °C for 16 hours to give **1·C$_7$H$_8$** as orange crystals, which were isolated and dried *in vacuo* (0.115 g, 19 %). Anal calcd for $C_{73}H_{134}P_4Si_{12}Th_2$, **1·C$_7H_8$**: C, 45.30 %; H, 6.97 %. Found: C, 45.02 %; H, 6.98 %. ^{1}H NMR (298 K, d_6-benzene, 400.2 MHz) δ: 0.58 (s, 54 H, $SiMe_3$), 0.60 (s, 54 H, $SiMe_3$), 7.02 (m, 6 H, Cp-*H*), 7.16 (m, 12 H, Cp-*H*). ^{13}C{^{1}H} NMR (298 K, d_6-benzene, 100.6 MHz) δ: 2.66 ($SiMe_3$), 2.86 ($SiMe_3$), 131.40 (Cp-*C*H), 132.33 (Cp-*C*H), 132.53 (Cp-*C*), 137.96 (Cp-*C*H), 138.23 (Cp-*C*). ^{29}Si{^{1}H} NMR (298 K, d_6-benzene, 79.5 MHz) δ: –8.02 ($SiMe_3$). ^{31}P{^{1}H} NMR (298 K, d_6-benzene, 162.0 MHz) δ: –246.55 (br m, $\Delta_\nu \approx 2000$ Hz), 10.35 (br m, $\Delta_\nu \approx 2000$ Hz), 227.59 (t, $^{1}J_{PP} \approx 400$ Hz), 328.86 (t, $^{1}J_{PP} \approx 400$ Hz). ^{31}P{^{1}H} NMR (193 K, d_6-benzene, 162.0 MHz) δ: –244.85-258.48 (m), –7.17-16.43 (m), 216 (t, $^{1}J_{PP}$ = 411 Hz), 220 (t, $^{1}J_{PP}$ = 411 Hz), 317 (t, $^{1}J_{PP}$ = 411 Hz), 323 (t, $^{1}J_{PP}$ = 411 Hz). UV/Vis (λ, nm; ε, M^{-1} cm^{-1}): 285 (30,400) 425 (9,000), 477 (11,200). FTIR ν/ cm^{-1} (Nujol): 1317 (w), 1200 (m), 918 (s), 822 (w), 754 (m), 692 (m), 638 (m), 615 (w).

2. $^{31}P\{^{1}H\}$ NMR spectra of 1

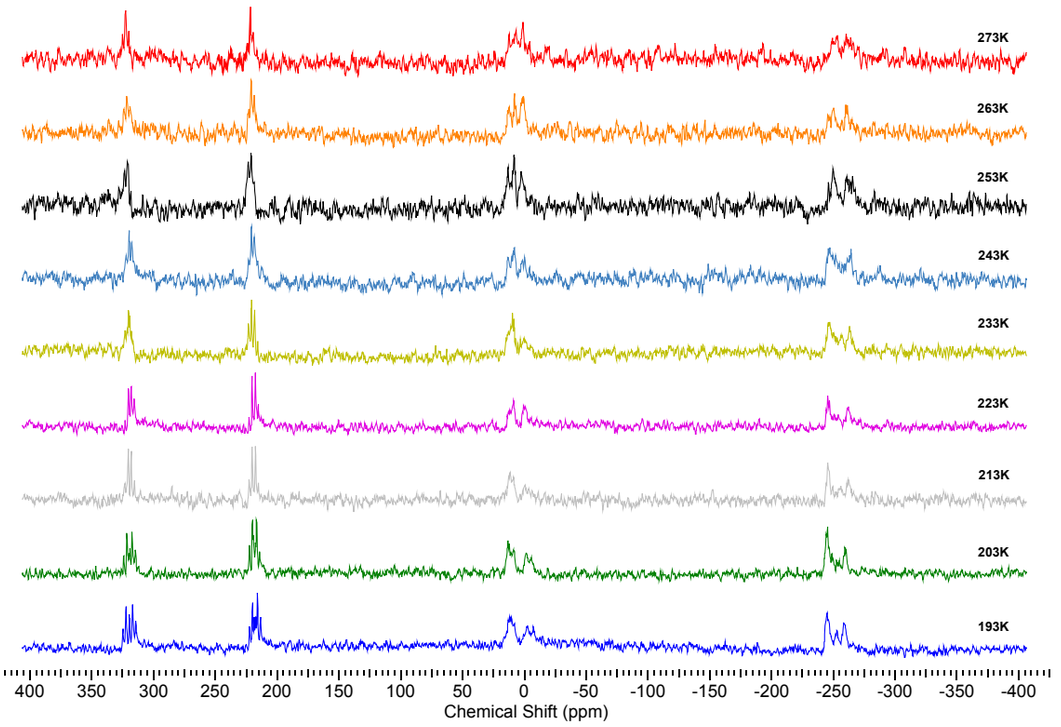

Figure S1. VT $^{31}P\{^{1}H\}$ NMR spectra of **1** from 198-273 K (toluene/d_8-toluene).

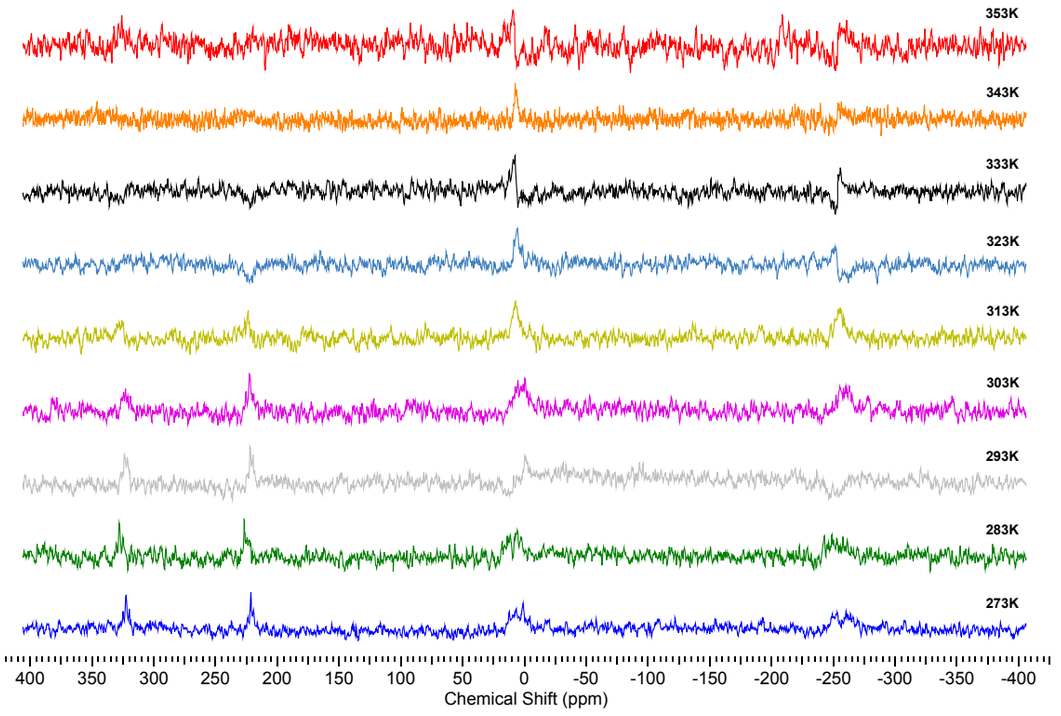

Figure S2. VT $^{31}P\{^{1}H\}$ NMR spectra of **1** from 273-353 K (toluene/d_8-toluene).

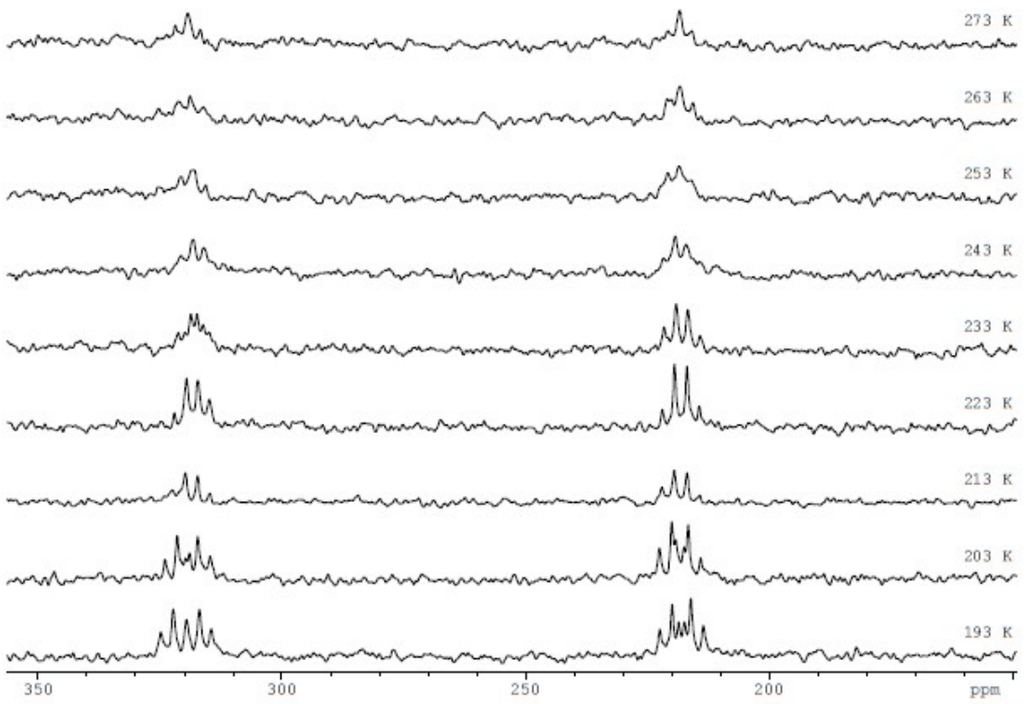

Figure S3. VT $^{31}P\{^{1}H\}$ NMR spectra of **1** from 193-273 K, low field resonances only (toluene/d_8-toluene).

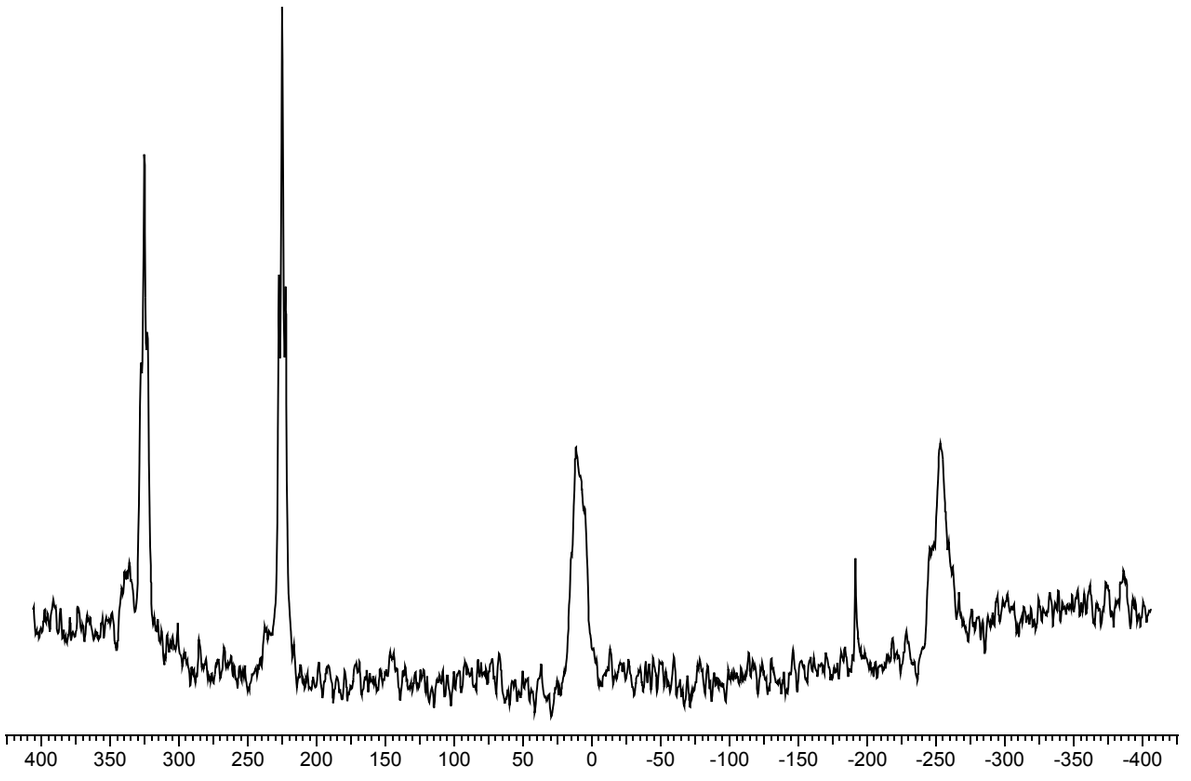

Figure S4. $^{31}P\{^{1}H\}$NMR spectrum of **1** at 298 K (THF/d_8-THF).

3. ^{1}H NMR spectrum of 1

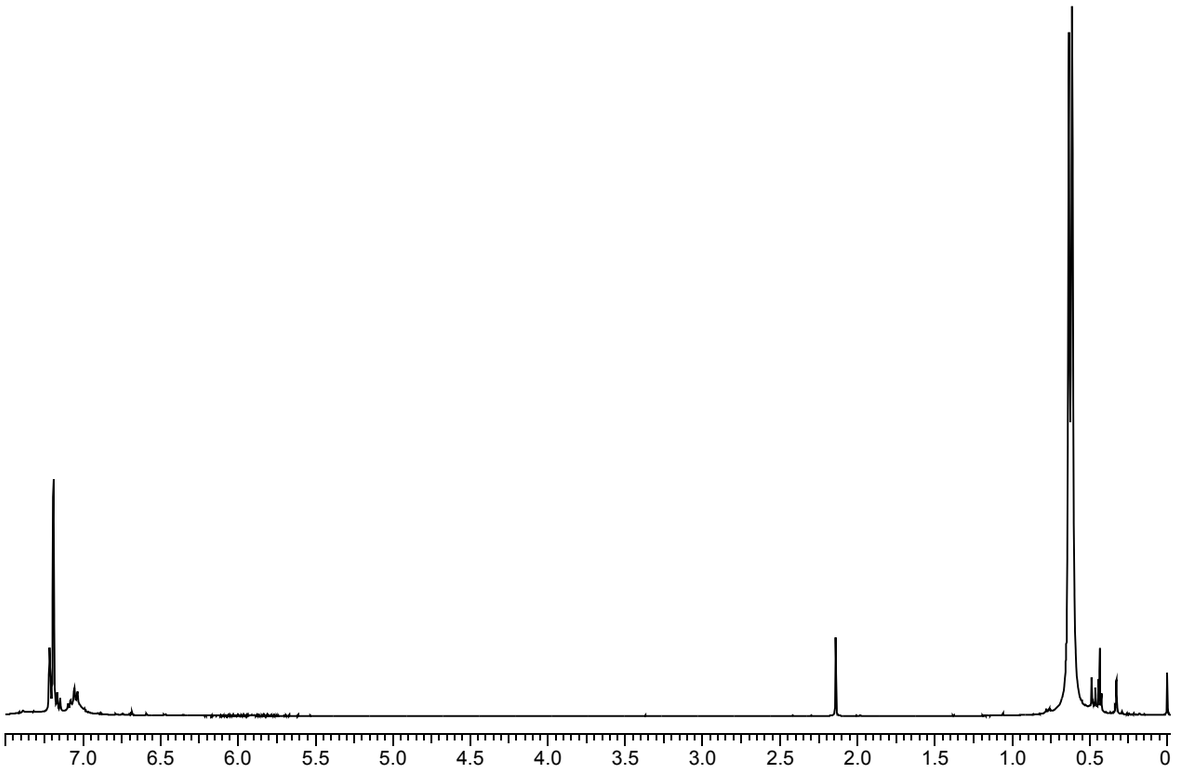

Figure S5. ^{1}H NMR spectrum of **1** at 298 K (d_6-benzene).

4. UV/Vis spectrum of 1

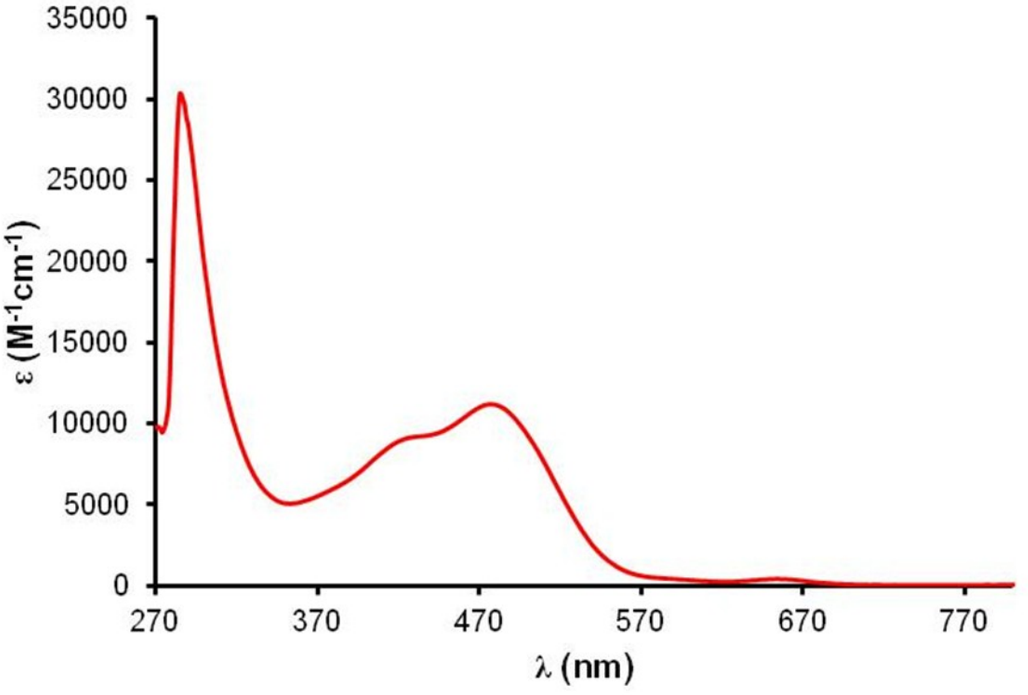

Figure S6. UV/Vis spectrum of **1** (0.1 mM in toluene).

5. Crystallographic details

The crystal data for **1** is compiled in Table S1. The crystal was examined on a Rigaku Oxford Diffraction SuperNova CCD area detector diffractometer using mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on 1° frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed absorption correction with a beam profile correction was applied. The structure was solved by direct methods and were refined by full-matrix least-squares on all unique F^2 values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; U_{iso}(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro[2] was used for control and integration, SHELXTL[3] and OLEX2[4] were employed for structure solution and refinement and POVRAY[5] was used for molecular graphics. CCDC 1426081 contains the supplementary crystal data for this article. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for **1·C$_7$H$_8$**.

	1·C$_7$H$_8$
Formula	$C_{73}H_{134}P_4Si_{12}Th_2$
Fw	1936.80
cryst size, mm	0.4156 x 0.3631 x 0.2902
cryst syst	Cubic
space group	*Pa*–3
a, Å	21.10705(17)
b, Å	21.10705(17)
c, Å	21.10705(17)
α, °	90
β, °	90
γ, °	90
V, Å^3	9403.3(2)
Z	4
ρ_{calcd}, g cm^{-3}	1.368
μ, mm^{-1}	3.145
no. of reflections measd	52308
no. of unique reflns, R_{int}	2868, 0.0600
no. of reflns with $F^2 > 2\sigma(F^2)$	2024
transmn coeff range	0.294 – 1.000
R, R_w[a] ($F^2 > 2\sigma(F^2)$)	0.0537, 0.1542
R, R_w[a] (all data)	0.0794, 0.1755
S[a]	1.050
Parameters	249
max., min. diff map, e Å^{-3}	1.261, –0.600

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

6. Computational details

Geometry optimisations were performed using version 6.6 of the TURBOMOLE software package[6] at the density functional level of theory, using the PBE0 hybrid-GGA exchange correlation functional.[7] The size of the system (210 atoms, 930 electrons) necessitated the use of only the def2-SVP (Th: def-SVP) basis set[8] for geometry optimisation of the complex. Simplified systems were optimised using both SVP and TZVP basis sets and comparison of geometrical parameters revealed only small variations. Analytical vibrational frequency analysis was performed and confirmed the structure to be an energetic minimum. Subsequent single point energy calculations were performed using the def2-TZVP basis set except for the Th ion, for which the SARC all-electron basis set,[9] of TZVP quality, was applied: in these all electron calculations, relativistic effects were included via application of the 2nd order Douglas-Kroll-Hess (DKH) Hamiltonian. Densities obtained from these calculations were analysed with the AIMAll[10] and Multiwfn[11] codes.

Gas-phase geometry optimisation using Ahlrich's def2-SVP (P, Si, C, H) and def-SVP (Th) basis sets, the latter incorporating an effective core potential replacing 60 core electrons on the thorium atom.

PBE0/SVP optimised gas-phase optimised structure, E = –8237.833108115 a.u.

Th	0.0364883	0.2300893	4.3616369	H	-5.8801722	2.6509877	4.1216512
P	0.0644837	0.3675549	1.4009777	H	-5.5763993	1.2089882	5.1226608
Si	-2.2137092	-2.2158224	7.2927777	C	-5.0696566	0.2554487	2.0230110
C	-2.5726092	-0.0138083	5.3832128	H	-5.5111816	-0.5967860	2.5627015
H	-2.9060845	0.7071028	6.1305774	H	-5.8890789	0.8536556	1.5926666
C	-1.9567633	-1.2645269	5.6838206	H	-4.4652561	-0.1373806	1.1896507
Si	-4.0109825	1.3118675	3.1657424	C	-3.3112737	2.7503786	2.1713048
C	-1.7632143	-1.9025311	4.4195013	H	-2.5543925	2.4117188	1.4461074
H	-1.3446249	-2.8978077	4.2731471	H	-4.1341287	3.2076466	1.5972724
C	-2.2527317	-1.0694663	3.3979505	H	-2.8704071	3.5388336	2.7985730
H	-2.2585671	-1.3055973	2.3333934	P	-1.5504380	0.2401457	0.0063760
C	-2.7691992	0.1298765	3.9823216	C	-1.1195014	-3.7455099	7.4101503
C	-5.0895509	2.0131025	4.5488298	H	-0.0598211	-3.5019891	7.5753891
H	-4.5166104	2.6320665	5.2575728	H	-1.4518845	-4.3635622	8.2598786

H	-1.1903968	-4.3688410	6.5052594
C	-1.9887409	-1.1539465	8.8288226
H	-2.5842710	-0.2296302	8.7799431
H	-2.3214607	-1.7145304	9.7172953
H	-0.9361117	-0.8798762	8.9845265
C	-4.0096642	-2.7931232	7.2327043
H	-4.1897082	-3.4236417	6.3478247
H	-4.2699980	-3.3788590	8.1294001
H	-4.6968488	-1.9343166	7.1744725
P	-0.0591496	-0.3632265	-1.4014512
P	1.5560539	-0.2359547	-0.0069208
Si	-0.6958318	3.0926110	7.6912452
C	1.2059111	2.5331130	5.5171855
H	2.0702709	2.4090491	6.1707711
C	-0.1479811	2.5653851	5.9646389
Si	2.8178914	3.3752084	3.1826669
C	-0.9242980	2.8273574	4.7940671
H	-2.0056081	2.9545175	4.7744522
C	-0.0690583	2.9453741	3.6856013
H	-0.3806597	3.1587495	2.6634524
C	1.2827335	2.7668386	4.1180215
C	4.0412380	3.9706327	4.4926619
H	4.3958132	3.1462537	5.1323575
H	4.9268094	4.4161496	4.0114303
H	3.5895773	4.7329523	5.1466458
C	2.2420860	4.8343066	2.1389897
H	1.7176541	5.5858814	2.7491985
H	3.1001722	5.3238343	1.6508236
H	1.5564605	4.4960770	1.3456363
C	3.7055743	2.1717968	2.0431739
H	3.0234664	1.7395339	1.2934611
H	4.4871377	2.7283132	1.4992807
H	4.2025387	1.3471853	2.5747126
C	-2.5621531	2.9493489	7.9136464
H	-2.9087677	1.9067374	7.9670099
H	-2.8529088	3.4408065	8.8562391
H	-3.1096042	3.4520520	7.1011463
C	0.1744738	2.1766909	9.0842378
H	1.2688136	2.1951371	8.9705605
H	-0.0658702	2.6575162	10.0462526
H	-0.1497515	1.1286797	9.1472909
C	-0.2363908	4.9194164	7.8123959
H	-0.7280991	5.5010972	7.0168552
H	-0.5395813	5.3428211	8.7838518
H	0.8506791	5.0599254	7.7036932
Si	3.0991243	-0.8530062	7.3871207
C	1.5135780	-2.0135227	5.1874273
H	1.0132449	-2.7640536	5.8005848
C	2.2471481	-0.9013260	5.7042733
Si	1.2224243	-3.5666281	2.6844454
C	2.7849151	-0.2420101	4.5575899
H	3.4331219	0.6331421	4.5818509
C	2.3831046	-0.9244096	3.3970791
H	2.6743730	-0.6720466	2.3758294
C	1.5827556	-2.0509459	3.7709489
C	0.9448013	-5.0243580	3.8561906
H	0.0376291	-4.9086423	4.4705555
H	0.8273405	-5.9528771	3.2742987
H	1.7983335	-5.1603526	4.5388848
C	2.7985264	-3.8675011	1.6996568
H	3.6705637	-3.9685498	2.3645379
H	2.7137898	-4.7864585	1.0973153
H	2.9830063	-3.0282280	1.0108595
C	-0.2301416	-3.4755502	1.4937495

H	-0.1754764	-2.5830413	0.8503224
H	-0.1947385	-4.3693464	0.8482780
H	-1.2046719	-3.4785004	2.0034402
C	3.9032468	0.8205729	7.7147310
H	3.1700091	1.6163557	7.9121254
H	4.5528408	0.7442582	8.6016677
H	4.5370981	1.1392774	6.8723276
C	1.9807587	-1.3139746	8.8269614
H	1.4705232	-2.2743543	8.6587842
H	2.5849628	-1.4173144	9.7427391
H	1.2188417	-0.5455998	9.0167741
C	4.4715608	-2.1436855	7.2749387
H	5.1607326	-1.9127077	6.4474548
H	5.0573866	-2.1845925	8.2076943
H	4.0543520	-3.1461308	7.0899618
Th	-0.0354528	-0.2288854	-4.3623281
Si	2.2201253	2.2042395	-7.2988702
C	2.5731669	0.0030159	-5.3871344
H	2.9025528	-0.7201165	-6.1341617
C	1.9620980	1.2559635	-5.6882861
Si	4.0083939	-1.3262324	-3.1695523
C	1.7728124	1.8961421	-4.4244715
H	1.3585052	2.8933012	-4.2786456
C	2.2601902	1.0622097	-3.4026069
H	2.2684339	1.2995691	-2.3383127
C	2.7708906	-0.1399301	-3.9863145
C	5.0826824	-2.0335553	-4.5527911
H	4.5062662	-2.6509562	-5.2600840
H	5.8712598	-2.6741976	-4.1259784
H	5.5720586	-1.2320388	-5.1281064
C	5.0725311	-0.2730569	-2.0287965
H	5.5174468	0.5766189	-2.5697432
H	5.8896097	-0.8744716	-1.5984572
H	4.4706023	0.1234631	-1.1953867
C	3.3034239	-2.7603717	-2.1724744
H	2.5489166	-2.4174551	-1.4467862
H	4.1251174	-3.2203788	-1.5989602
H	2.8582962	-3.5477527	-2.7980883
C	1.1321783	3.7384123	-7.4159625
H	0.0711519	3.4991925	-7.5788162
H	1.4654759	4.3540323	-8.2670973
H	1.2074907	4.3625424	-6.5119739
C	1.9876312	1.1413767	-8.8331133
H	2.5822075	0.2163718	-8.7857019
H	2.3175811	1.7007175	-9.7233997
H	0.9340825	0.8684350	-8.9844100
C	4.0186045	2.7740254	-7.2432050
H	4.2030862	3.4051976	-6.3597066
H	4.2795787	3.3572362	-8.1413597
H	4.7022814	1.9124235	-7.1849901
Si	0.6803378	-3.0982651	-7.6897073
C	-1.2160454	-2.5283971	-5.5134367
H	-2.0809275	-2.4015749	-6.1658016
C	0.1369625	-2.5665303	-5.9630646
Si	-2.8270211	-3.3622612	-3.1747703
C	0.9141667	-2.8303287	-4.7934778
H	1.9949850	-2.9618731	-4.7753685
C	0.0602738	-2.9438754	-3.6835308
H	0.3726131	-3.1575509	-2.6616754
C	-1.2915177	-2.7603597	-4.1138938
C	-4.0496854	-3.9656311	-4.4818103
H	-4.4035374	-3.1450927	-5.1268405
H	-4.9357206	-4.4081157	-3.9986349
H	-3.5974774	-4.7319528	-5.1307305

C	-2.2520632	-4.8144133	-2.1211238
H	-1.7271039	-5.5700174	-2.7258755
H	-3.1106114	-5.3007357	-1.6305761
H	-1.5672466	-4.4708790	-1.3293441
C	-3.7157627	-2.1519095	-2.0434159
H	-3.0348943	-1.7170335	-1.2940733
H	-4.4988546	-2.7054311	-1.4986341
H	-4.2110374	-1.3293363	-2.5796322
C	2.5465081	-2.9595970	-7.9163144
H	2.8949077	-1.9178438	-7.9744576
H	2.8343684	-3.4552941	-8.8575744
H	3.0947319	-3.4601291	-7.1030017
C	-0.1908720	-2.1831023	-9.0826494
H	-1.2849992	-2.1988709	-8.9665412
H	0.0462850	-2.6663549	-10.0442367
H	0.1355630	-1.1359398	-9.1485136
C	0.2166618	-4.9242817	-7.8062117
H	0.7092551	-5.5054894	-7.0108728
H	0.5163947	-5.3501624	-8.7776594
H	-0.8704115	-5.0622660	-7.6943343
Si	-3.0969920	0.8646531	-7.3855444
C	-1.5041034	2.0203060	-5.1880325
H	-1.0012644	2.7686293	-5.8018214
C	-2.2425169	0.9108459	-5.7038946
Si	-1.2047121	3.5731355	-2.6858124
C	-2.7821034	0.2542257	-4.5565374
H	-3.4338610	-0.6182965	-4.5799948
C	-2.3767116	0.9354186	-3.3965967
H	-2.6681697	0.6846251	-2.3750164
C	-1.5720969	2.0585570	-3.7715044
C	-0.9224178	5.0292708	-3.8584356
H	-0.0164624	4.9096003	-4.4738518
H	-0.8003935	5.9574688	-3.2769690
H	-1.7761701	5.1686066	-4.5401791
C	-2.7784136	3.8806879	-1.6992665
H	-3.6510579	3.9841602	-2.3629698
H	-2.6895035	4.8000383	-1.0981244
H	-2.9649508	3.0428772	-1.0092348
C	0.2485654	3.4766562	-1.4964745
H	0.1902213	2.5853436	-0.8517115
H	0.2184125	4.3715409	-0.8522427
H	1.2225778	3.4739397	-2.0071539
C	-3.9093728	-0.8057045	-7.7092962
H	-3.1799523	-1.6050957	-7.9062535
H	-4.5597368	-0.7280049	-8.5955453
H	-4.5435597	-1.1200795	-6.8655131
C	-1.9790902	1.3182564	-8.8280967
H	-1.4629416	2.2757924	-8.6617834
H	-2.5847807	1.4244079	-9.7425712
H	-1.2220451	0.5453832	-9.0191629
C	-4.4630938	2.1620027	-7.2730479
H	-5.1518892	1.9356647	-6.4439714
H	-5.0503465	2.2041647	-8.2048499
H	-4.0408099	3.1627604	-7.0904671

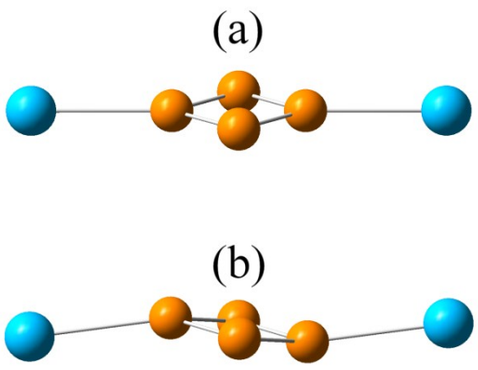

Figure S7. Comparison of (a) experimental and (b) PBE0/SVP optimised structures, demonstrating, the non-linearity of the Th–P_4–Th unit in the latter. Coordinating Cp″ ligands omitted for clarity.

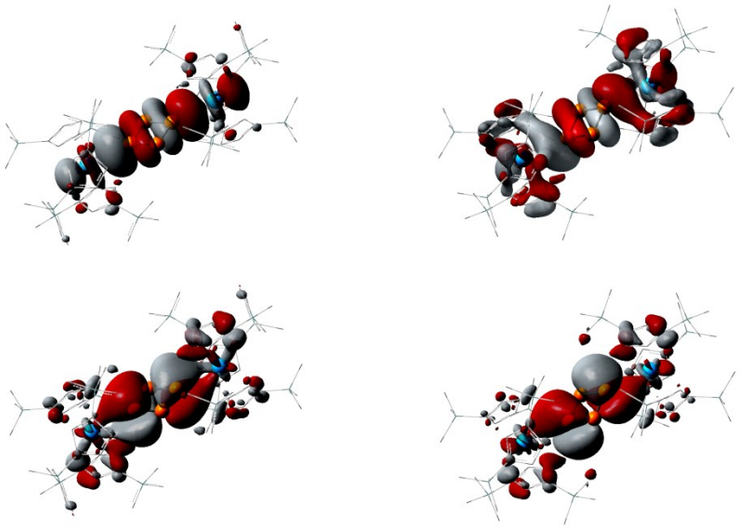

Figure S8. σ- and π-bonding orbitals at the experimental (left) and PBE0/SVP-optimised (right) geometries. Isosurfaces rendered at a value of 0.015 a.u.

System	ρ_{BCP}(Th,P)	*H*	δ(Th,P)	*Q*(Th)
PBE0/SVP	0.0503	-0.011	0.439	+2.30
Exp.	0.0473	-0.010	0.464	+2.28

Table S2. QTAIM derived parameters associated with Th–P bonds. Values averaged over multiple bonds/centres. All values are in a.u.

System	ρ_{BCP}(P,P)	*H*	δ(P,P)	*Q*(P_4)
PBE0/SVP	0.125	-0.075	1.29	-1.21
Exp.	0.148	-0.112	1.33	-1.27
P_4^{2-}	0.120	-0.068	1.45	-2.00

Table S3. QTAIM derived parameters associated with P–P bonds. Values averaged over multiple bonds/centres. All values are in a.u.

7. References

1. P. C. Blake, M. F. Lappert, J. L. Atwood and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1986, 1148.

2. *CrysAlis PRO*, Agilent Technologies: Yarnton, England, 2010.

3. (a) G. M. Sheldrick, *Acta Cryst., Sect. C.*, 2015, **71**, 3; (b) G. M. Sheldrick, *Acta Cryst., Sect. A*, 2008, **64**, 112.

4. Olex2: O. V., Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

5. P. o. V. P. Ltd., in http://www.povray.org/, Persistence of Vision Pty. Ltd., Williamstown, Victoria, Australia, 2004.

6. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.

7. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

8. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

9. D. A. Pantazis and F. Neese, *J. Chem. Theory Comput.*, 2011, **7**, 677.

10. T. A. Keith, *AIMAll (Version 14.11.23), TK Gristmill Software, Overl. Park KS, USA*, 2014.

11. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580.