Supporting Information

The formation mechanism of Uranium and Thorium Hydride Phosphorus: A Systematically Theoretical Study

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Table S1 Comparison of observed values and calculated harmonic frequencies for H_2UPH. [a]SDD for U and aug-cc-pVTZ for H and P atoms. [b]SDD for U and 6-311++G (d, p)[1,2] for H and P atoms. [c]M06-2X-ZORA/def2-TZVPP-SARC level of theory. [d] Observed argon matrix frequencies.[3]

Method	Harmonic frequencies (cm^{-1})								
B3LYP[a]	1990.5	1495.5	1472.6	761.9	471.2	428.6	350.9	268.8	211.5
PW91[a]	1917.4	1518.3	1493.0	949.0	473.9	446.7	366.3	321.7	239.3
TPSS[4][a]	2001.6	1533.9	1498.1	972.0	746.7	509.7	457.9	349.3	274.9
B3PW91[a]	1944.7	1508.6	1482.9	904.7	480.7	440.1	375.7	295.1	263.9
PBE0[5][a]	2020.4	1573.7	1544.7	927.6	503.3	461.7	402.5	325.1	272.4
B3LYP[b]	2052.9	1549.3	1524.4	790.5	487.2	450.8	365.7	282.7	240.0
PW91[b]	1925.9	1522.5	1498.5	937.3	473.5	450.4	366.6	317.3	230.8
TPSS[b]	2096.9	1550.5	1529.8	1164.5	822.6	520.5	461.5	350.3	270.8
B3PW91[b]	2024.6	1566.1	1540.3	920.6	500.5	463.3	393.2	326.0	268.3
PBE0[b]	2029.8	1575.3	1546.5	964.2	504.8	468.1	406.8	336.6	281.7
M06-2X[c]	2031.7	1526.3	1473.0	790.4	494.3	443.8	402.2	357.9	246.5
Expt.[d]		1473.7	1456.5						

Table S2 Comparison of observed values and calculated harmonic frequencies for H_2ThPH. [a]SDD for Th and aug-cc-pVTZ for H and P atoms. [b]SDD for Th and 6-311++G (d, p) for H and P atoms. [c] M06-2X-ZORA/def2-TZVPP-SARC level of theory. [d]Ref. [3], Observed argon matrix frequencies.

Method	Harmonic frequencies (cm^{-1})								
B3LYP[a]	2104.6	1489.9	1448.4	757.0	495.7	438.5	400.3	342.8	236.0
PW91[a]	2018.1	1482.2	1442.3	831.0	489.1	445.9	402.1	352.5	247.9
TPSS[a]	2049.2	1510.8	1460.7	851.5	514.3	446.2	399.7	343.9	260.2
B3PW91[a]	2091.0	1524.2	1474.9	818.7	510.9	444.7	406.0	346.9	261.1
PBE0[a]	2099.4	1533.1	1484.2	843.9	514.2	449.1	409.9	351.2	265.1
B3LYP[b]	2100.6	1493.5	1451.2	752.4	497.1	439.4	400.7	344.8	233.8
PW91[b]	2018.6	1492.5	1443.8	822.8	489.0	447.3	403.4	355.4	251.3
TPSS[b]	2050.8	1513.5	1464.3	842.6	514.1	446.8	400.7	347.9	264.1
B3PW91[b]	2089.6	1528.6	1478.9	811.9	511.0	445.3	407.0	351.2	264.1
PBE0[b]	2100.5	1536.4	1487.7	833.6	513.9	449.6	410.8	355.2	268.3
M06-2X[c]	2065.1	1507.4	1473.4	766.3	479.2	429.7	389.4	346.3	258.0
Expt.[d]		1467.2	1436.6						

Table S3 Comparison of the calculation results of the bond lengths (Å) and relative PW91 energies (kcal/mol) of the complex II and the complex III about $U+PH_3$ obtained in ref. [3] and the calculation results of this paper. [a] Calculations used the SDD for U and aug-cc-pVTZ for H and P atoms. [b] Obtained from ref. [3].

property	B3LYP[a]	PW91[a]	B3PW91[a]	B3LYP[b]	PW91[b]
r(U-P)	2.760	2.661	2.716	2.762	2.662
r(U-H_1)	2.041	2.022	2.033	2.046	2.030
r(P-H_2)	1.444	1.473	1.450	1.436	1.467
r(P-H_3)	1.453	1.481	1.461	1.446	1.477
Energy		0.00			0.00
r(U-P)	2.465	2.446	2.434	2.459	2.444
r(U-H_1)	1.996	1.990	1.984	1.997	1.992
r(U-H_2)	2.011	2.001	1.996	2.010	2.004

r(P-H_3)	1.471	1.496	1.481	1.468	1.491
Energy		6.52			0.10

Table S4 Comparison of the calculation results of the bond lengths (Å) and relative PW91 energies (kcal/mol) of the complex II and the complex III about Th+PH_3 obtained in ref. [3] and the calculation results of this paper. [a] Calculations used the SDD for Th and aug-cc-pVTZ for H and P atoms. [b] Obtained from ref. [3].

property	B3LYP[a]	PW91[a]	B3PW91[a]	B3LYP[b]	PW91[b]	CCSD(T) [b]
			the complex II			
r(Th-P)	2.759	2.665	2.710	2.735	2.660	2.749
r(Th-H_1)	2.064	2.058	2,.062	2.024	2.025	2.037
r(P-H_2)	1.453	1.481	1.462	1.420	1.454	1.421
r(P-H_3)	1.453	1.481	1.462	1.461	1.508	1.464
Energy		22.68			22.80	
			the complex III			
r(Th-P)	2.775	2.741	2.702	2.530	2.512	2.538
r(Th-H_1)	2.068	2.060	2.066	2.056	2.048	2.058
r(Th-H_2)	2.068	2.060	2.066	2.065	2.054	2.068
r(P-H_3)	1.470	1.478	1.470	1.460	1.477	1.467
Energy		0.00			0.00	

Table S5 Relative energies (kcal/mol) of the stationary points on the U+PH_3. [a]Calculations used the SDD for U and aug-cc-pVTZ for H and P atoms. [b] M06-2X-ZORA/def2-TZVPP-SARC level of theory.

	I	TS1	II	TS2a	III	TS2b	IV
B3LYP[a]	30.66	34.80	0.00	16.04	6.52	13.89	12.49
PW91[a]	27.83	31.99	0.00	13.80	11.19	7.05	6.35
B3PW91[a]	30.12	30.38	0.00	15.86	15.67	5.65	5.48
M06-2X[b]	21.49	32.27	0.00	11.44	10.72	6.87	5.29
$<s^2>$	3.04	2.99	2.94	2.71	2.10	2.99	2.97

Table S6 Relative energies (kcal/mol) of the stationary points on the Th+PH_3. [a] Calculations used the SDD for Th and aug-cc-pVTZ for H and P atoms. [b] M06-2X-ZORA/def2-TZVPP-SARC level of theory.

	I	TS1	II	TS2a	III	TS2b	IV
B3LYP[a]	33.04	38.95	0.00	12.16	3.06	14.99	8.76
PW91[a]	34.51	39.23	0.00	13.14	5.85	7.21	3.98
B3PW91[a]	35.59	41.14	0.00	13.54	5.19	11.66	7.32
M06-2X[b]	27.03	34.74	0.00	15.47	6.05	14.86	8.42
$<s^2>$	2.02	2.02	2.00	2.01	2.06	2.00	2.01

Table S7 Mayer bond order analysis for all of the minima and transition states involved in the reaction of U+PH_3 at the M06-2X-ZORA/def2-TZVPP-SARC level of theory.

Species	I	TS1	II	TS2a	III	TS2b	IV
U-P	0.462	0.749	1.011	1.716	2.197	1.559	2.028

P-H1	0.964	0.623						
P-H2	0.926	0.892	0.899	0.241		0.389	0.070	
P-H3	0.926	0.916	0.904	0.826	0.767	0.827	0.794	
U-H1		0.311	0.923	0.934	0.947	0.462	0.107	
U-H2		0.093	0.710		0.948	0.209	0.109	
U-H3		0.088	0.149		0.217	0.174	0.206	
H1-H2						0.425	0.856	

Species	I	TS1'	II'	TS1	II	TS2a	III	TS2b	IV
Th-P	1.207	1.286	1.325	1.431	1.635	1.990	2.154	1.605	2.165
P-H1	0.892	0.875	0.100	0.094					
P-H2	0.874	0.871	0.918	0.923	0.844	0.959	0.801	0.809	0.788
P-H3	0.874	0.871	0.953	0.938	0.844	0.928	0.801	0.809	0.788
Th-H1	0.117	0.142	0.863	0.873	0.934	0.939	0.948	0.512	0.181
Th-H2	0.056	0.052			0.166	0.778	0.947	0.229	0.179
Th-H3	0.056	0.052	0.098	0.030	0.166	0.048	0.196	0.179	0.218
H1-H2			0.164	0.001		0.152		0.402	0.752

Table S8 Mayer bond order analysis for all of the minima and transition states involved in the reaction of Th+PH_3 at the M06-2X-ZORA/def2-TZVPP-SARC level of theory.

Species		$\rho(r)$	$\nabla^2\rho(r)$	$G(r)$	$V(r)$	$H(r)$
I(^{1}A)	Th-P	0.065	0.134	0.050	-0.067	-0.017
	P-H1	0.161	-0.081	0.130	-0.281	-0.150
	P-H2	0.161	-0.081	0.130	-0.281	-0.150
	P-H3	0.154	-0.039	0.130	-0.270	-0.140
TS1'(^{1}A)	Th-P	0.073	0.138	0.056	-0.077	-0.021
	P-H1	0.156	-0.016	0.138	-0.280	-0.142
	P-H2	0.165	-0.046	0.142	-0.298	-0.155
	P-H3	0.163	-0.046	0.143	-0.298	-0.155
II'(^{1}A)	Th-P	0.079	0.077	0.045	-0.080	-0.026
	Th-H1	0.098	0.030	0.048	-0.088	-0.040
	P-H2	0.164	0.001	0.152	-0.304	-0.152
	P-H3	0.159	0.023	0.149	-0.293	-0.144
TS1(^{1}A)	Th-P	0.084	0.050	0.044	-0.080	-0.032
	Th-H1	0.109	-0.020	0.045	-0.095	-0.050

	P-H2	0.162	0.027	0.155	-0.302	-0.148
	P-H3	0.167	0.027	0.162	-0.316	-0.155
II(^{1}A)	Th-P	0.087	0.020	0.037	-0.068	-0.031
	Th-H1	0.097	0.004	0.040	-0.080	-0.040
	P-H2	0.142	-0.007	0.121	-0.244	-0.123
	P-H3	0.142	-0.006	0.121	-0.244	-0.123
TS2a(^{1}A)	Th-P	0.110	0.012	0.054	-0.105	-0.051
	Th-H1	0.083	0.032	0.036	-0.065	-0.028
	Th-H2	0.073	0.088	0.044	-0.065	-0.022
	P-H3	0.163	0.012	0.152	-0.301	-0.149
III(^{1}A)	Th-P	0.099	0.038	0.052	-0.094	-0.042
	Th-H1	0.088	0.029	0.039	-0.071	-0.032
	Th-H2	0.089	0.027	0.040	-0.072	-0.033
	P-H3	0.137	0.064	0.131	-0.246	-0.115
TS2b(^{3}A)	Th-P	0.093	0.041	0.048	-0.086	-0.038
	Th-H1	0.070	0.100	0.043	-0.062	-0.018
	P-H2	0.087	-0.040	0.024	-0.058	-0.034
	P-H3	0.141	0.042	0.131	-0.251	-0.120
	H1-H2	0.133	-0.256	0.028	-0.119	-0.092
IV(^{3}A)	Th-P	0.101	0.031	0.052	-0.097	-0.044
	P-H3	0.136	0.040	0.124	-0.237	-0.114
	H1-H2	0.236	-0.929	0.010	-0.253	-0.242

Table S9 Topological properties of the charge density calculated at the (3, -1) BCPs for all species involved in the reaction of Th+PH_3 at the B3LYP/SDD/aug-cc-pVTZ level of theory. (ρ(bcp) and $\nabla^2\rho$(bcp) in a.u.)

Fig. S1 Comparison of observed values and calculated harmonic frequencies and the corresponding vibration direction for H_2UPH. Expt, Ref. [3], Observed argon matrix frequencies. Harmonic frequency in cm^{-1}.

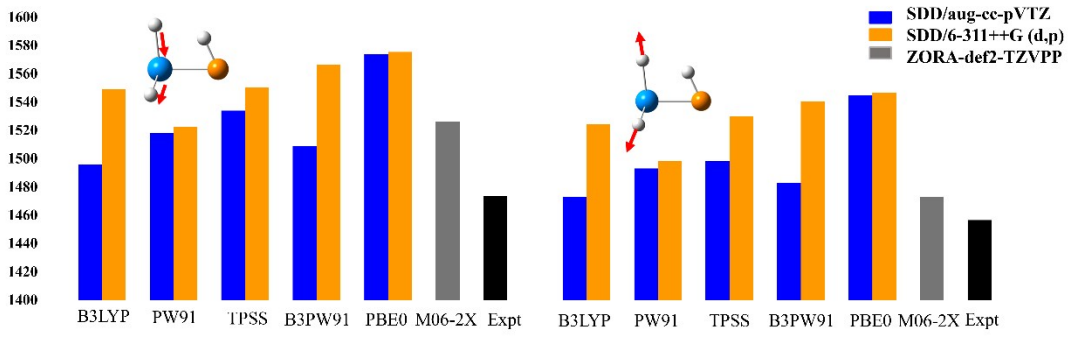


Fig. S2 Comparison of observed values and calculated harmonic frequencies and the corresponding vibration direction for H_2ThPH. Expt, Ref. [3], Observed argon matrix frequencies. Harmonic frequency in cm^{-1}.

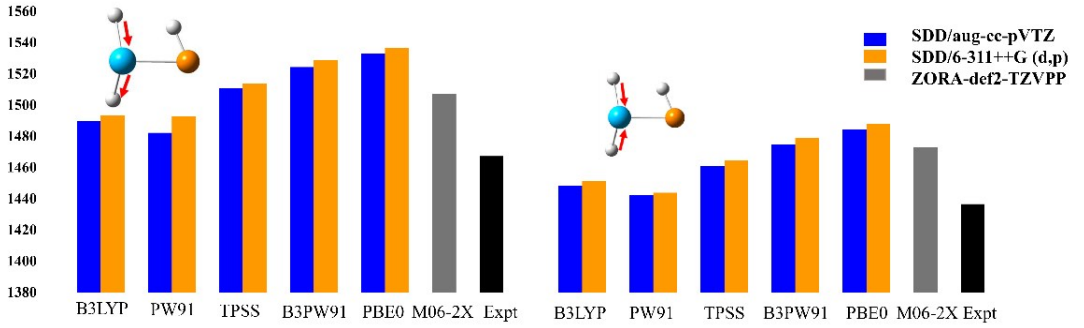
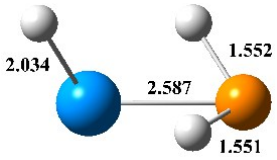
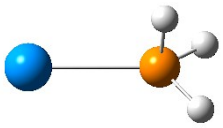


Fig. S3 Structures and selected geometric parameters of MECP (3-5) on the U+PH_3 potential energy surface. Bond distances are Å and angles are in degree.



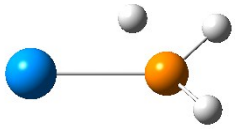
	x	y	z
U	-0.26260631	0.25541025	-0.37188483
P	2.15459492	-0.10208516	0.47776464
H	1.79899885	1.12260690	-0.40676054
H	0.95498950	-0.14922446	1.45976551
H	-1.02488341	1.94840219	0.45869805

Fig. S4 Optimized Cartesian x, y, z coordinates for the reaction of U+PH_3 at the B3LYP/SDD/aug-cc-pVTZ level of theory.



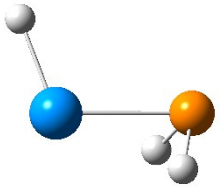
I(^{5}A)

	x	y	z
U	0.49222800	0.00009000	-0.00147800
P	-2.40241800	0.00219400	-0.03606100
H	-2.58441200	-0.09670900	1.36731100
H	-3.33701200	-1.01597400	-0.41829000
H	-3.32729900	1.07152100	-0.27208300



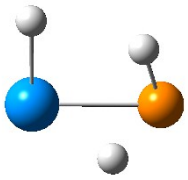
TS1(^{5}A)

	x	y	z
U	-0.46716300	-0.00169800	-0.00107000
P	2.32705500	-0.04266200	-0.08255500
H	1.59638200	0.90029100	0.82841100
H	3.40332700	0.90613400	-0.14885500
H	3.07343000	-1.01024700	0.65719100



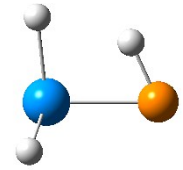
II(^{5}A)

	x	y	z
U	0.41292200	-0.02395400	0.00000800
P	-2.34359000	0.11598300	-0.04884700
H	-1.91725300	-0.18846500	1.30631200
H	-2.03556800	-1.23566700	-0.45320100
H	1.11784200	1.88810900	-0.12118500



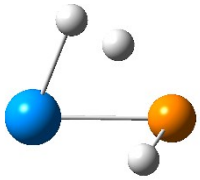
U	-0.37003400	-0.02563000	-0.00949300
P	2.14223100	-0.04619900	-0.05622800
H	1.55517700	1.29208500	0.04521700
H	0.95213600	-0.22340000	1.55655200
H	-0.59764400	1.98226200	0.11500000

TS2a(^{3}A)



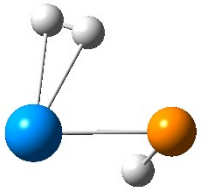
	x	y	z
U	-0.34695300	-0.00977000	-0.02972500
P	2.11719900	-0.06855200	0.00655200
H	-0.53948400	1.82895400	0.72513000
H	-0.83456900	-1.13958600	1.56139100
H	1.53572000	1.23775500	0.34993000

III(^{3}A)



	x	y	z
U	-0.39173800	-0.02120200	-0.00412900
P	2.19214900	-0.07885100	-0.07145900
H	1.64850400	-0.33897100	1.26743400
H	0.31975600	2.00367700	0.12388700
H	1.18940900	1.46862800	0.06047700

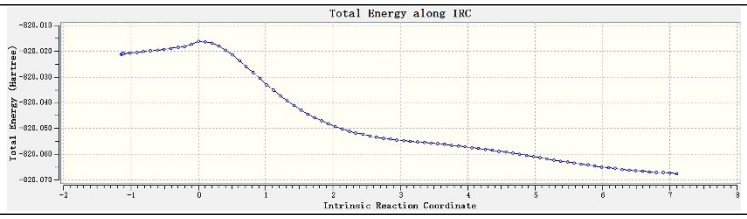
TS2b(^{5}A)



	x	y	z
U	0.37316500	-0.03537300	-0.00317400
P	-2.14156500	-0.07643900	-0.06617200
H	-1.56664500	-0.05250800	1.29409000
H	-0.68906000	2.08536100	-0.01509900
H	0.04796800	2.36806800	0.00558900

IV(^{5}A)

Fig. S5 The IRC curve corresponding to TS imaginary frequency of U+PH_3 at the B3LYP/SDD/aug-cc-pVTZ level of theory.

property	imaginary frequency	intrinsic reaction coordinate image
TS1	-867.9 cm^{-1}	

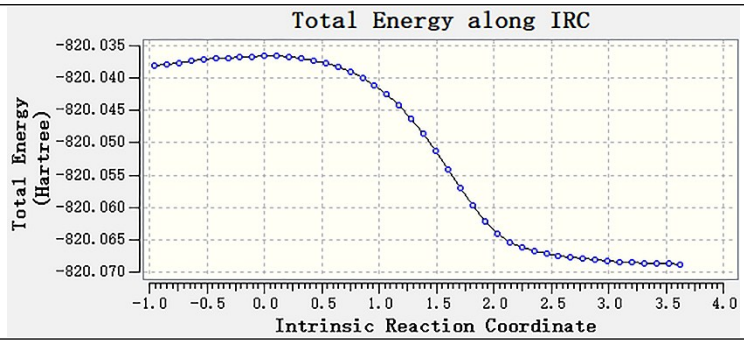
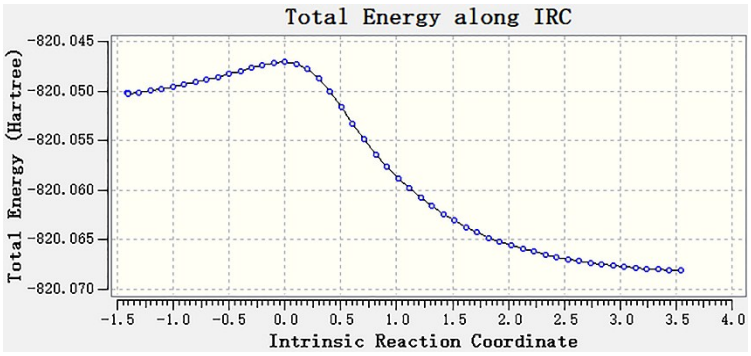
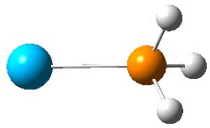
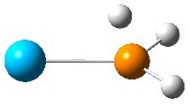
TS2a	-327.7 cm^{-1}	
TS2b	-811.6 cm^{-1}	

Fig. S6 Optimized Cartesian x, y, z coordinates for the reaction of Th+PH_3 at the B3LYP/SDD/aug-cc-pVTZ level.



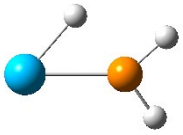
I(^{3}A)

	x	y	z
Th	-0.48734100	-0.00001300	0.00000200
P	2.31352300	-0.00026100	-0.00000400
H	3.05420400	-0.38472700	1.15732600
H	3.04872400	1.19755300	-0.24417700
H	3.05493600	-0.80770400	-0.91329300



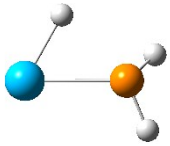
TS1'(^{1}A)

	x	y	z
Th	0.45294500	-0.00134800	-0.00255300
P	-2.18059700	-0.02816800	-0.05829000
H	-3.19211500	0.93947100	-0.40294100
H	-3.15138100	-1.01121900	0.35290300
H	-1.71259500	0.61557100	1.15417300



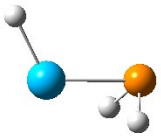
II'(^{1}A)

	x	y	z
Th	-0.43822200	-0.01032900	0.00000600
P	2.17323500	-0.03187900	-0.00011500
H	3.15956700	0.97379600	0.00078800
H	2.99442000	-1.18911800	0.00052900
H	0.68745100	1.62308100	-0.00011600



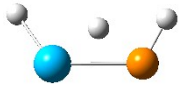
TS1(^{1}A)

	x	y	z
Th	0.44427300	-0.01281600	0.00389200
P	-2.25289900	-0.01453000	-0.09493000
H	-2.90066300	0.87840900	0.79159300
H	-2.78794100	-1.23264600	0.40506700
H	-0.50250500	1.72566100	-0.12299000



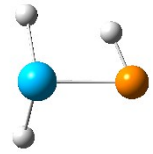
	x	y	z
Th	-0.40555500	-0.01996800	-0.01017500
P	2.30171400	0.13890300	-0.00215000
H	1.84312100	-0.74366400	-1.07635000
H	1.89336300	-0.83637500	1.00291700
H	-1.84600300	1.41576600	-0.12997500

II(^{3}A)



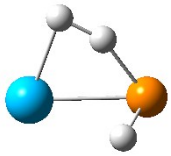
	x	y	z
Th	-0.38643300	-0.02488700	0.00135600
P	2.15518500	-0.06896500	-0.07445600
H	-1.49996900	1.64493500	-0.47505900
H	2.82783300	1.17395900	0.05305800
H	1.12334600	0.45537600	1.41678200

TS2a(^{3}A)



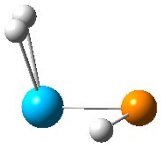
	x	y	z
Th	0.36345000	-0.00607600	-0.03010100
P	-2.16910400	-0.06950200	0.00996300
H	0.79782000	-1.45978500	1.36952400
H	0.65296000	1.78080600	0.94381900
H	-1.62469100	1.26839600	0.24627800

III(^{3}A)



	x	y	z
Th	-0.40186500	-0.02084800	-0.00465500
P	2.19768000	-0.07062700	-0.07337200
H	1.66524500	-0.48031200	1.23155500
H	0.31097600	1.98318000	0.16791300
H	1.22644600	1.43284700	0.12008500

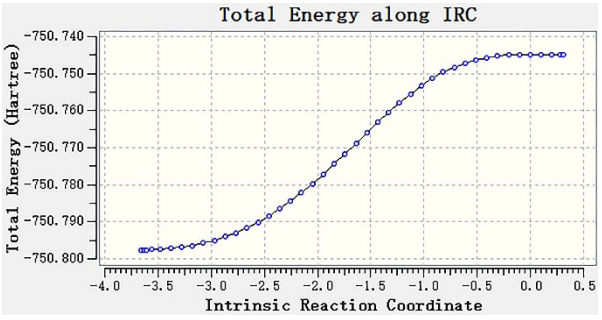
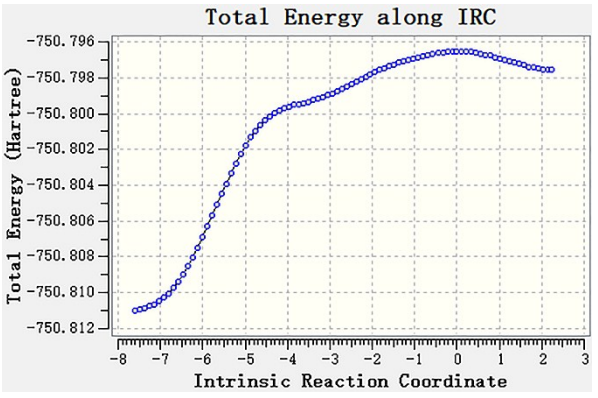
TS2b(^{3}A)

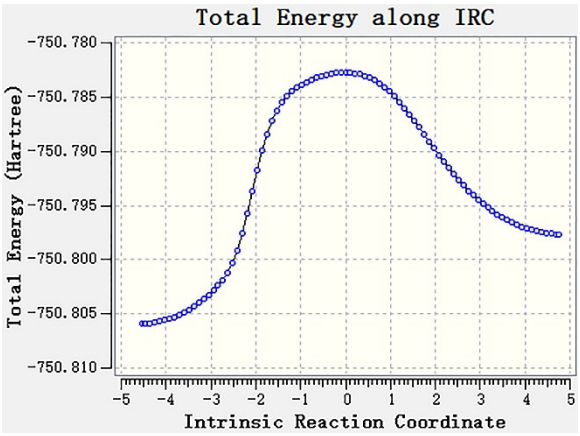
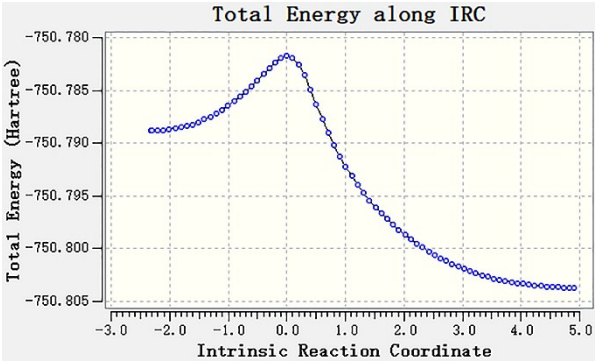


	x	y	z
Th	-0.36126600	-0.05717000	-0.00267400
P	2.15697200	0.03848700	-0.06788800
H	1.59765800	0.07806400	1.29439100
H	-0.69906500	2.24987800	0.38198500
H	-0.73925200	2.24004900	-0.41741500

IV(^{3}A)

Fig. S7 The IRC curve corresponding to TS imaginary frequency of Th+PH_3 at the B3LYP/SDD/aug-cc-pVTZ level of theory.

property	imaginary frequency	intrinsic reaction coordinate image
TS1'	-339.8 cm^{-1}	
TS1	-157.3 cm^{-1}	

TS2a	-863.5 cm^{-1}	
TS2b	-1035.1 cm^{-1}	

References

1 R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys*., 1980., **72**, 650–654.

2 J. P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys*., 1997., **107**, 5016–5021

3 L. Andrews, H. G. Cho, K. S. Thanthiriwatte, D. A. Dixon, *Inorg. Chem*., 2017, **56**, 2949-2957.

4 J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.,* 2003, **91**, 146401.

5 C. Adamo, V. Barone, *J. Chem. Phys*., 1999, **110**, 6158–6170.