Electronic Supplementary Material (ESI) for Chemical Communications.

Gas-Phase Synthesis and Structure of Thorium Benzyne Complexes

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1) Experimental section

Reagents. Benzoic acid, 2,6-dimethylbenzoic acid, 2-, 3- and 4-methylbenzoic acids, 2-, 3- and 4-cyanobenzoic acids, 2-, 3- and 4-halobenzoic acids (F, Cl and Br) were purchased from Macklin and used without further purification. The $ThCl_4$ stock solutions was prepared by dissolving $ThCl_4$ powder in boiling concentrated hydrochloric acid and then diluting by Milli-Q ultrapure water at ambient temperature. The thorium isotope employed was ^{232}Th which undergoes α-decay with a half-life of 1.4×10^{10} years, and its handling requires proper shielding, waste disposal and personal protective gear.

Mass spectrometry. The experiments were performed on either a Bruker Daltonics (Bremen, Germany) SolariX XR 7.0T Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) or a ThermoFisher Scientific LTQ XL Linear ion trap mass spectrometer (LIT-MS). Both instruments are equipped with a heated electrospray ionization (ESI) source. The acetonitrile solutions of 0.1 mM $ThCl_4$ and 0.3 mM benzoic acid or substituted benzoic acid mixtures were prepared for negative ion mode ESI experiments to generate suitable thorium chloride benzoate ions with the general formula of $ThCl_{5-x}L_x^-$ (L = benzoate or substituted benzoate ligands). The first isotope of $ThCl_4L^-$ was selected as the precursor for further CID experiments. These anions were readily identified via the isotopic patterns mainly arising from 75.77% ^{35}Cl and 24.23% ^{37}Cl as well as 50.69% ^{79}Br and 49.31% ^{81}Br in some cases.

The detailed instrumental parameters for FTICR-MS. Syringe pump flow rate 4.00 μL/min, capillary 4.0 kV, end plate offset -0.5 kV, nebulizer 2 bar, dry gas 0.5 bar, dry temperature 200 °C, capillary exit 220.0 V, deflector plate 2 V, funnel 1 150.0 V, skimmer 1 15 V, funnel RF amplitude 150.0 Vpp, collision voltage 2.5 V, DC extract bias -0.5 V, the time of flight was finely tuned (0.6~0.8 ms) to optimized the signals of thorium chloride benzoate anions. High purity nitrogen gas for nebulization and drying in the ESI source was supplied from the boil-off of a liquid nitrogen Dewar.

The pressure inside the ICR cell is about 5.00×10^{-10}~1×10^{-9} mbar. MS/MS analyses were acquired via SORI-CID (sustained off-resonance irradiation collision-induced dissociation) with the following parameters: isolation power 14%, SORI power 0.9~1.0%, pulse length 0.3 s, frequency offset -500 Hz. Mass spectra were collected with an acquisition size of 2M (mass resolving power more than 250000 at m/z 500) in the range between 21.5 and 1000 Da. Ions were accumulated in the ICR cell for 0.3 s and 36 scans were averaged for each spectrum.

The detailed instrumental parameters for LIT-MS. Solution flow rate 4.00 μL/min, source voltage 3.50 kV, source current 2.98 μA, source temperature 44.28 °C, sheath gas flow rate 4.99 arb, capillary voltage -30.80 V, capillary temperature 275.00 °C, tube lens voltage -102.77 V, multipole 00/0/1 offset 5.94/6.35/13.18 V, lens 0 and 1 5.82 and 33.03 V, gate/front/back lens 47.95/6.28/-0.37 V, front/center/back section 9.08/12.03/7.12 V, multipole RF amplitude 396.16 Vpp. High purity nitrogen gas for nebulization/drying in the ESI source and helium buffer gas were supplied from the nitrogen and helium cylinders. The pressure inside the LIT is about 7.0×10^{-6} Torr. The abundance of precursor ion strongly depends on the voltages of capillary and tube lens. MS/MS analyses were acquired via CID with the following parameters: normalized collision energy (NCE) 15~20%, activation Q value 0.250, activation time 30 ms.

2) Computational methods

DFT calculations on the related species in this work were performed with the Gaussian 09 package using the hybrid B3LYP density functional.[1-3] The 60-electron core pseudopotential basis set was used for Th,[4] and the 6-311++G(d,p) basis set was used for all the remaining atoms (C, H, O and Cl).[5,6] All the geometrical parameters were fully optimized, and zero point energy corrections were included in the self-consistent field energy of the two thorium aryl complexes. Gibbs energies (298.15 K) were employed in the potential energy surface. Vibrational frequencies were calculated for all optimized structures to check that they

correspond to ground-state structures (no imaginary frequency) or transition-state structures (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition states and local minima.[7,8] Natural localized molecular orbital (NLMO) analysis was performed on the optimized geometries using the NBO6 program.[9]

3) References

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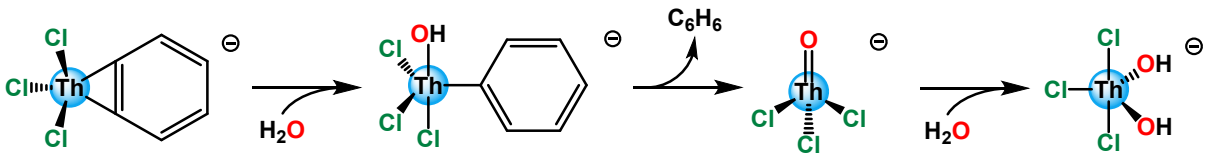
4) Additional figures and tables



Scheme S1. The reaction route of (η^2-C_6H_4)$ThCl_3^-$ with H_2O.

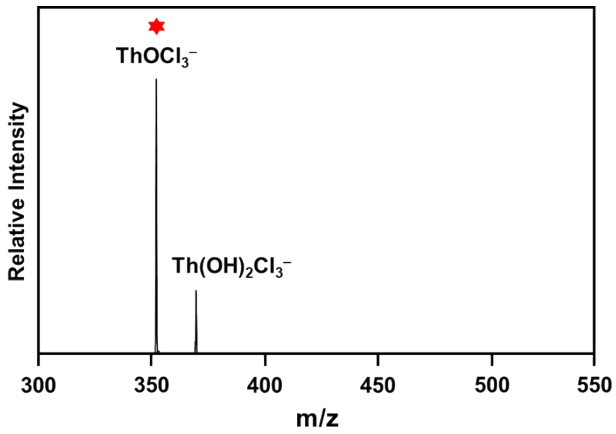


Figure S1. Mass spectrum of $ThOCl_3^-$ (*) when a single isotopomer was mass selected without applying CID energy by using LIT-MS.

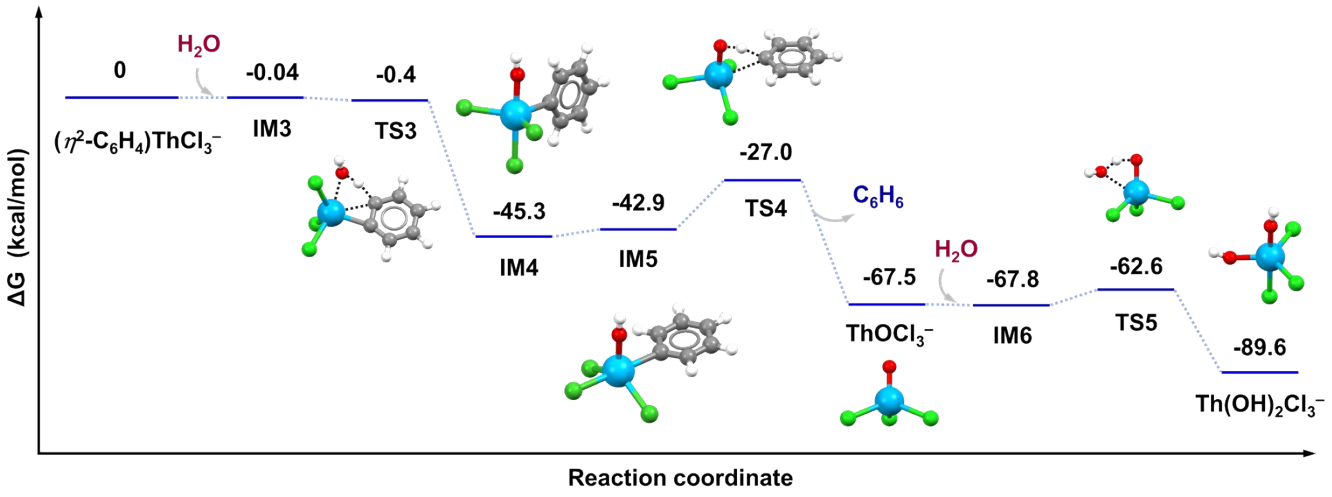


Figure S2. Potential energy surface for the reaction of (η^2-C_6H_4)$ThCl_3^-$ and H_2O (Th: cyan; C: gray; H: white; O: red; Cl: green). The isomerization between IM4 and IM5 was not explored. TS3 is 1.4 kcal/mol higher than IM3 (self-consistent field energy), but 0.9 kcal/mol lower than IM3 when the zero point energy correction is included.

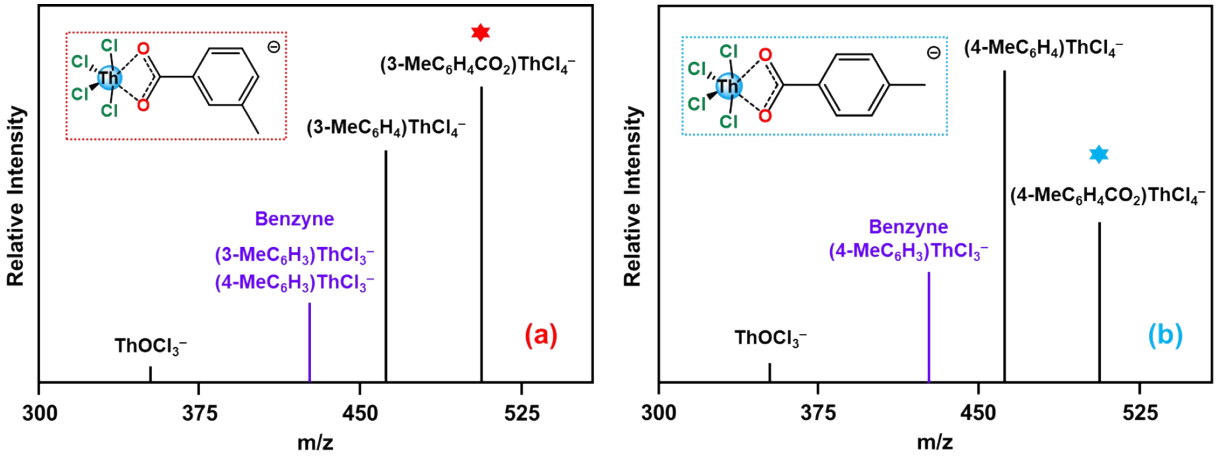


Figure S3. CID mass spectra of a single isotopomer of (a) $(3\text{-MeC}_6\text{H}_4\text{CO}_2)\text{ThCl}_4^-$ (*) and (b) $(4\text{-MeC}_6\text{H}_4\text{CO}_2)\text{ThCl}_4^-$ (*) using FTICR-MS (SORI power 1.0%). The structures of the carboxylate precursors are shown in the insets. $(3\text{-MeC}_6\text{H}_3)\text{ThCl}_3^-$ and $(4\text{-MeC}_6\text{H}_3)\text{ThCl}_3^-$ denote two isomers of the thorium benzyne complexes.

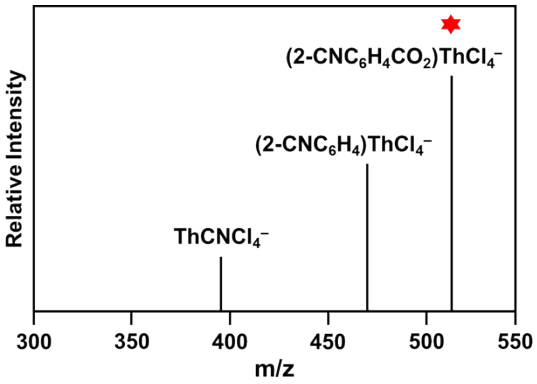


Figure S4. CID mass spectrum of $(2\text{-CNC}_6\text{H}_4\text{CO}_2)\text{ThCl}_4^-$ (*) using FTICR-MS. A single isotopomer was mass selected (SORI power 0.9%).

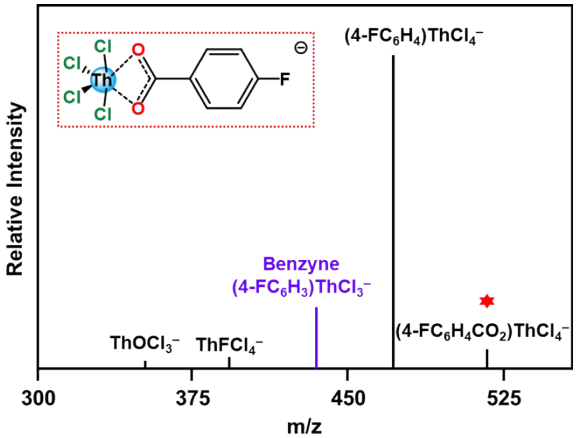


Figure S5. CID mass spectrum of $(4\text{-FC}_6\text{H}_4\text{CO}_2)\text{ThCl}_4^-$ (*) using FTICR-MS. A single isotopomer was mass selected (SORI power 1.0%). The structure of the carboxylate precursor is shown in the inset.

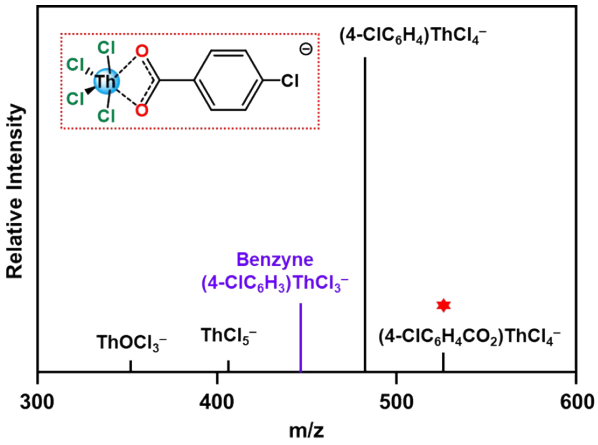


Figure S6. CID mass spectrum of $(4\text{-}ClC_6H_4CO_2)ThCl_4^-$ (*) using FTICR-MS. A single isotopomer was mass selected (SORI power 1.0%). The structure of the carboxylate precursor is shown in the inset.

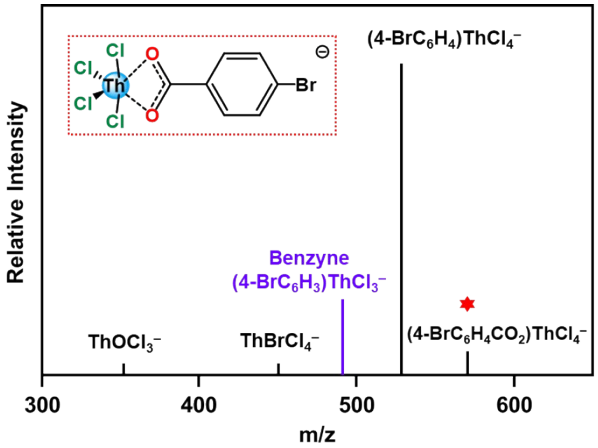


Figure S7. CID mass spectrum of $(4\text{-}BrC_6H_4CO_2)ThCl_4^-$ (*) using FTICR-MS. A single isotopomer was mass selected (SORI power 1.0%). The structure of the carboxylate precursor is shown in the inset.

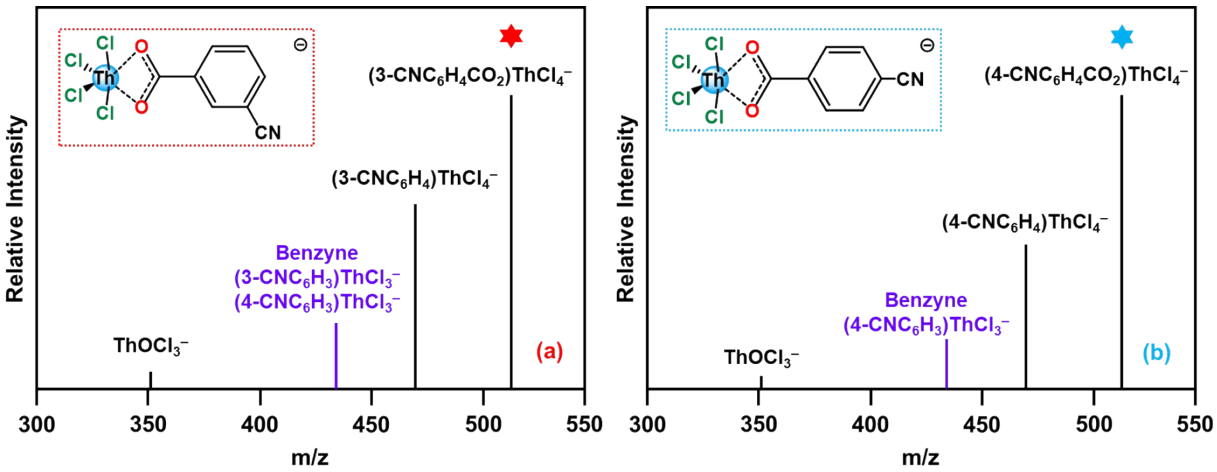


Figure S8. CID mass spectra of a single isotopomer of (a) $(3\text{-}CNC_6H_4CO_2)ThCl_4^-$ (*) and (b) $(4\text{-}CNC_6H_4CO_2)ThCl_4^-$ (*) using FTICR-MS (SORI power 0.9%). The structures of the carboxylate precursors are shown in the insets. $(3\text{-}CNC_6H_3)ThCl_3^-$ and $(4\text{-}CNC_6H_3)ThCl_3^-$ denote two isomers of the thorium benzyne complexes.

Table S1. Experimental and calculated mass-to-charge ratios (m/z) of related species.

Species	Exp. m/z	Cal. m/z	Error
$(C_6H_5CO_2)ThCl_4^-$	492.94133	492.94297	0.82 ppm
$(C_6H_5)ThCl_4^-$	448.95167	448.95314	0.74 ppm
$(C_6H_4)ThCl_3^-$	412.97512	412.97646	0.67 ppm
$(MeC_6H_4CO_2)ThCl_4^-$	506.95866	506.95862	-0.02 ppm
$(MeC_6H_4)ThCl_4^-$	462.96904	462.96879	-0.20 ppm
$(MeC_6H_3)ThCl_3^-$	426.99233	426.99211	-0.13 ppm
$(2,6\text{-}Me_2C_6H_3CO_2)ThCl_4^-$	520.97401	520.97427	0.14 ppm
$(2,6\text{-}Me_2C_6H_3)ThCl_4^-$	476.98401	476.98444	0.21 ppm
$(FC_6H_4CO_2)ThCl_4^-$	510.93285	510.93355	0.36 ppm
$(FC_6H_4)ThCl_4^-$	466.94299	466.94372	0.38 ppm
$(FC_6H_3)ThCl_3^-$	430.96641	430.96704	0.60 ppm
$(ClC_6H_4CO_2)ThCl_4^-$	526.90474	526.90400	-0.64 ppm
$(ClC_6H_4)ThCl_4^-$	482.91373	482.91307	-0.76 ppm
$(ClC_6H_3)ThCl_3^-$	446.93803	446.93749	-0.59 ppm
$(BrC_6H_4CO_2)ThCl_4^-$	570.85424	570.85348	-0.76 ppm
$(BrC_6H_4)ThCl_4^-$	526.86339	526.86256	-0.83 ppm
$(BrC_6H_3)ThCl_3^-$	490.88741	490.88698	-0.60 ppm
$(CNC_6H_4CO_2)ThCl_4^-$	517.93806	517.93822	0.30 ppm
$(CNC_6H_4)ThCl_4^-$	473.94855	473.94839	-0.33 ppm
$(CNC_6H_3)ThCl_3^-$	437.97215	437.97171	-0.69 ppm
$ThCNCl_4^-$	397.91675	397.91709	0.69 ppm
$ThOCl_3^-$	352.93894	352.94008	0.63 ppm
$ThCl_4^-$	371.91427	371.91402	-0.20 ppm

5) Cartesian coordinates, free energies (Hartree) and frequencies of related species obtained at the B3LYP/SDD/6-311++G(d,p) level of theory.

CO_2

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16080000
O	0.00000000	0.00000000	-1.16080000

EE + Thermal Free Energy Correction = -188.655921

HCl

Cl	0.00000000	0.00000000	0.07148800
H	0.00000000	0.00000000	-1.21530200

EE + Thermal Free Energy Correction = -460.845238

$(C_6H_5CO_2)ThCl_4^-$

Th	1.11548900	-0.00000700	-0.00059200
Cl	0.85542100	2.66849700	-0.01258900
Cl	2.66965700	0.00019000	2.15888700
Cl	2.72572900	-0.00029900	-2.12012900
Cl	0.85509700	-2.66848800	-0.01224000
O	-1.12032100	-0.00002700	-1.10425600
O	-1.12222500	0.00007800	1.10014500
C	-1.75460300	0.00003000	-0.00248100
C	-3.24609200	0.00003600	-0.00322400
C	-3.94552200	0.00009900	-1.21362100
C	-3.94575400	-0.00002200	1.20707500
C	-5.33746300	0.00010600	-1.21237000
H	-3.38251700	0.00014400	-2.13866000
C	-5.33766200	-0.00002400	1.20569200
H	-3.38279600	-0.00007500	2.13213700
C	-6.03453800	0.00005300	-0.00339000
H	-5.87951400	0.00016500	-2.15180700
H	-5.87976800	-0.00008300	2.14510100
H	-7.11959000	0.00005900	-0.00346100

EE + Thermal Free Energy Correction = -2669.452226

IM1

Th	1.18330200	0.03013500	-0.00295200
Cl	1.06369100	-0.49194600	-2.62338400
Cl	1.56238900	2.62929600	-0.37161400
Cl	3.42440800	-1.38657200	0.22197500
Cl	1.01552300	0.26556300	2.65656000
O	-2.05899000	-2.43303800	0.27360100
O	-0.97563700	-0.48815400	0.05360300
C	-2.06891300	-1.22436400	0.13651400
C	-3.35943500	-0.45077100	0.04927500
C	-3.38142400	0.93974200	-0.09346000
C	-4.56782800	-1.15301600	0.11582200
C	-4.59603200	1.61873500	-0.16732500
H	-2.44621100	1.48145200	-0.14522100
C	-5.78053400	-0.47505900	0.04107600
C	-5.79694900	0.91366100	-0.10042200
H	-4.60360900	2.69774700	-0.27681100
H	-6.71329900	-1.02669200	0.09313100
H	-6.74219300	1.44339200	-0.15821900
H	-4.53033300	-2.22990500	0.22615200

EE + Thermal Free Energy Correction = -2669.441867

TS1 (-233 cm^{-1})

Th	0.73887000	-0.12736900	-0.01748300
Cl	0.60491500	-0.29598100	2.65858300
Cl	1.04154900	-2.72416800	-0.44943800
Cl	3.20508100	0.85908200	0.14900100
Cl	0.60341600	0.57571800	-2.60536300
O	-2.24238600	2.93350500	0.36636400
O	-0.01015300	2.33684500	0.37567500
C	-1.20359000	2.40316000	0.33557700
C	-1.89652000	0.16245600	0.02288500
C	-2.58088700	-0.28775700	1.17436600
C	-2.58460700	0.01902600	-1.20313500
C	-3.85266200	-0.85817500	1.10827600
H	-2.10865400	-0.19769400	2.14691500
C	-3.85559900	-0.55135000	-1.27982900
C	-4.49487800	-0.99191200	-0.12174300
H	-4.34214600	-1.19637600	2.01697500
H	-4.34777600	-0.64926400	-2.24311200
H	-5.48483900	-1.43431100	-0.17731600
H	-2.11643800	0.35625300	-2.12197700

EE + Thermal Free Energy Correction = -2669.369924

$(C_6H_5)ThCl_4^-$ isomer (a)

Th	-0.63128200	-0.00000500	0.00002800
Cl	-0.62699000	-2.65937900	-0.36092500
Cl	-0.62705400	2.65941200	0.36065900
Cl	-1.79226500	0.32700900	-2.37772800
Cl	-1.79129900	-0.32711500	2.37820600
C	1.88596500	0.00001400	-0.00002700
C	2.63838700	-1.18809100	0.13904800
C	2.63832000	1.18815900	-0.13915700
C	4.03501500	-1.19405000	0.14440300
H	2.12446000	-2.13941400	0.23948400

C	4.03494400	1.19413700	-0.14492200
H	2.12433700	2.13946400	-0.23947600
C	4.73994200	0.00007100	-0.00024000
H	4.57233200	-2.13177700	0.25743400
H	4.57221000	2.13191300	-0.25786300
H	5.82591000	0.00008900	-0.00036100

EE + Thermal Free Energy Correction = -2480.739061

$(C_6H_5)ThCl_4^-$ isomer (b)

Th	0.00000000	0.00000000	0.63832600
Cl	0.00000000	2.67521200	0.54245200
Cl	-2.40323300	-0.00003000	1.80494100
Cl	2.40323300	0.00003000	1.80494100
Cl	0.00000000	-2.67521200	0.54245200
C	0.00000000	0.00000000	-1.85128800
C	1.19574500	0.00064700	-2.59370800
C	-1.19574500	-0.00064700	-2.59370800
C	1.20510000	0.00064500	-3.98973400
H	2.15629300	0.00118500	-2.07930000
C	-1.20510000	-0.00064500	-3.98973400
H	-2.15629300	-0.00118500	-2.07930000
C	0.00000000	0.00000000	-4.69241000
H	2.14750000	0.00115700	-4.52997400
H	-2.14750000	-0.00115700	-4.52997400
H	0.00000000	0.00000000	-5.77868600

EE + Thermal Free Energy Correction = -2480.736521

TS2 (-185 cm^{-1})

Th	0.74603300	-0.08368500	0.04111400
Cl	2.93209200	0.84966700	-1.24235800
Cl	-3.47324500	-2.59424900	-0.03061900
Cl	0.16484600	-2.29792100	-1.37421900
Cl	1.47141600	-0.42994900	2.60566500
C	-0.64720100	1.78145100	-0.29357600
C	-1.14409500	3.07479600	-0.53842300
C	-1.50857400	0.75691200	0.17135900
C	-2.48590000	3.35525500	-0.30903800
H	-0.48887900	3.86385500	-0.90421100
C	-2.86681800	1.06299100	0.39691300
H	-2.45270100	-1.81637600	-0.24667500
C	-3.34523200	2.34787200	0.16345200
H	-2.87787600	4.35329200	-0.48955100
H	-3.56163100	0.30674700	0.75674100
H	-4.39178500	2.58016100	0.34536200

EE + Thermal Free Energy Correction = -2480.640434

IM2

Th	0.37796700	-0.62165600	0.00943200
Cl	1.32362000	-1.90770500	-2.15084300
Cl	-5.15152700	1.25533300	0.02181100
Cl	-2.34876100	-0.84392600	-0.30662000
Cl	0.82471300	-1.76529900	2.39837600
C	1.77994600	1.29199400	0.06876400
C	2.82430100	2.23592200	0.11589600
C	0.44374000	1.73792300	-0.05015900
C	2.53574700	3.59411600	0.04495200
H	3.86298700	1.92046800	0.20632300
C	0.16235800	3.11561600	-0.11885700
H	-4.07392100	0.51123600	-0.09603100
C	1.20428300	4.03475400	-0.07205000
H	3.33872800	4.32668900	0.07882700
H	-0.86132000	3.47503600	-0.20932100
H	0.99749500	5.10084100	-0.12627900

EE + Thermal Free Energy Correction = -2480.647039

$(C_6H_4)ThCl_3^-$

Th	-0.51814100	-0.05097300	0.00005500
Cl	-1.72267600	2.37668000	-0.00004500
Cl	-1.38197800	-1.17208800	2.29381000
Cl	-1.38240500	-1.17260300	-2.29329200
C	1.78436900	-0.67669100	-0.00003700
C	3.04419700	-1.30702900	-0.00008900
C	4.20616200	-0.54271500	-0.00036000
C	4.13369700	0.86251800	-0.00058000
C	2.89772800	1.50003500	-0.00052900
C	1.71565400	0.73556800	-0.00026400
H	3.12833300	-2.39344000	0.00008300
H	5.05209200	1.44513600	-0.00079100
H	2.86119600	2.58878500	-0.00070100
H	5.18022600	-1.02680500	-0.00040700

EE + Thermal Free Energy Correction = -2019.801686

IM3

Th	0.52359700	-0.00150800	0.04500800
Cl	1.33204900	-0.43986700	2.57302900
Cl	1.40658000	1.68803300	-1.93321500
Cl	1.72842600	-2.15670100	-1.04629500
C	-1.69907900	-0.74500200	-0.26508700
C	-2.80959400	-1.55583500	-0.55973100
C	-4.09630100	-1.04898600	-0.41249800
C	-4.28589200	0.27109100	0.02987800
C	-3.19108000	1.07913700	0.32205400
C	-1.87745500	0.58319800	0.17880400
H	-2.67542600	-2.58005200	-0.90346100
H	-5.29591800	0.65791700	0.14338000
H	-3.37909300	2.09750300	0.66440100

H	-4.96103500	-1.66881700	-0.63707200
O	0.16645800	2.54414600	0.88026900
H	-0.74569100	2.18566400	0.70440800
H	0.41823000	3.03380200	0.08511900

EE + Thermal Free Energy Correction = -2096.256631

TS3 (-704 cm^{-1})

Th	0.53741100	0.03820700	0.05188000
Cl	1.39218100	-0.60180800	2.51823500
Cl	1.42814200	1.75120000	-1.86709900
Cl	1.77282200	-2.05376200	-1.11539400
C	-1.69086400	-0.68679600	-0.32959100
C	-2.75736200	-1.51664300	-0.71943300
C	-4.07126900	-1.10152200	-0.53061000
C	-4.33691600	0.14864500	0.05102300
C	-3.28993300	0.97865700	0.43884600
C	-1.95217100	0.57364800	0.25265000
H	-2.56399800	-2.48839600	-1.16927000
H	-5.36682000	0.46434500	0.19791200
H	-3.52409600	1.94254700	0.88944900
H	-4.89817900	-1.74105000	-0.82929100
O	-0.07610900	2.32693400	1.00976000
H	0.09456300	3.02641000	0.36902100
H	-0.99189600	1.74041300	0.70994800

EE + Thermal Free Energy Correction = -2096.257248

IM4

Th	0.65078000	-0.15054500	0.00008200
Cl	1.85916400	-0.24171500	-2.41686400
Cl	1.85882100	-0.24197900	2.41716400
Cl	0.76768500	2.56884500	-0.00004900
C	-1.89148500	-0.03700300	0.00002900
C	-2.62301100	1.17202900	-0.00024500
C	-4.01985300	1.20417500	-0.00032600
C	-4.74803400	0.01472200	-0.00009100
C	-4.06505400	-1.20110700	0.00021100
C	-2.66795100	-1.21713700	0.00026400
H	-2.08927000	2.11808200	-0.00040800
H	-5.83399500	0.03518100	-0.00014100
H	-4.62081200	-2.13546200	0.00041300
H	-4.54031500	2.15837800	-0.00056900
O	0.49127000	-2.28401000	-0.00092900
H	0.58447900	-3.23655200	-0.00307300
H	-2.16448700	-2.18015300	0.00049600

EE + Thermal Free Energy Correction = -2096.328792

IM5

Th	0.64526400	0.00007000	0.12207200
Cl	0.63154500	-2.39156200	-1.12456400
Cl	3.37888800	-0.00023700	0.25869300
Cl	0.63153200	2.39230600	-1.12348800
C	-1.93277600	0.00035900	-0.00677200
C	-2.68969400	1.19196400	0.01583000
C	-2.68900900	-1.19170900	0.01584400
C	-4.08655900	1.20204200	0.06414700
H	-2.17803300	2.15155300	-0.01833500
C	-4.08588000	-1.20252100	0.06412400
H	-2.17684400	-2.15100800	-0.01834300
C	-4.79296600	-0.00043500	0.08976500
H	-4.62425100	2.14709400	0.07550900
H	-4.62305300	-2.14787000	0.07539300
H	-5.87870600	-0.00071800	0.12312500
O	0.47104200	-0.00127600	2.24281800
H	0.38669200	-0.00191700	3.19508800

EE + Thermal Free Energy Correction = -2096.324994

TS4 (-1230 cm^{-1})

Th	0.75716700	0.00000000	0.11370500
Cl	0.50263100	-2.34697500	-1.20928000
Cl	3.43786400	-0.00001900	0.38760800
Cl	0.50265100	2.34700100	-1.20924000
C	-2.05653200	-0.00000100	0.53490600
C	-2.77642200	1.19542800	0.34906300
C	-2.77643100	-1.19542800	0.34908800
C	-4.12594200	1.20459000	-0.00977300
H	-2.27162100	2.14960400	0.47832400
C	-4.12595100	-1.20458700	-0.00974600
H	-2.27163600	-2.14960500	0.47836800
C	-4.80539300	0.00000200	-0.19162800
H	-4.64642700	2.14791700	-0.15077900
H	-4.64644400	-2.14791400	-0.15073000
H	-5.85385400	0.00000300	-0.47464400
O	0.12027300	-0.00002000	2.05117700
H	-0.95073400	-0.00000600	1.57063600

EE + Thermal Free Energy Correction = -2096.299606

$ThOCl_3^-$

Th	-0.00091700	-0.00033800	0.21727400
O	-0.00014700	-0.00066800	2.12039700
Cl	-2.56121800	-0.26709300	-0.71732100
Cl	1.51551900	-2.07982400	-0.71585500
Cl	1.05062100	2.34901900	-0.71493100

EE + Thermal Free Energy Correction = -1864.125449

IM6

Th	0.06058300	0.01163300	0.15499800

O	-0.38118100	0.09591200	2.03034500
H	-2.24487000	0.68377900	1.49807600
Cl	2.44436500	-1.30238000	-0.02425500
Cl	0.61228500	2.43771200	-0.98932700
Cl	-1.69027000	-1.71396600	-1.14616100
O	-2.54538300	0.90149400	0.59441300
H	-3.02354100	0.12676400	0.26969800

EE + Thermal Free Energy Correction = -1940.580840

TS5 (-1245 cm^{-1})

Th	-0.00986500	0.02836900	0.13989500
O	-0.49959900	0.14464000	2.10072700
H	-1.58653800	0.60985400	1.73681900
Cl	2.32237700	-1.34706600	0.22795500
Cl	0.80554100	2.28106400	-1.13910100
Cl	-1.50827400	-1.70354000	-1.33377000
O	-2.24931800	1.02577700	0.80095300
H	-3.06822300	0.55580600	0.62275500

EE + Thermal Free Energy Correction = -1940.572612

$Th(OH)_2Cl_3^-$

Th	0.00246700	-0.14457800	0.16594300
O	0.00018800	0.04241000	2.31516500
H	0.00244200	-0.27510800	3.21726100
Cl	-0.03924600	2.58905600	-0.04006300
Cl	-2.38354400	-0.31038200	-1.14327300
Cl	2.39233500	-0.24813100	-1.14315800
O	0.02902600	-2.29094800	0.32792600
H	0.05957800	-3.24377400	0.25350700

EE + Thermal Free Energy Correction = -1940.615537

H_2O

O	0.00000000	0.00000000	0.11704100
H	0.00000000	0.76348700	-0.46816500
H	0.00000000	-0.76348700	-0.46816500

EE + Thermal Free Energy Correction = -76.454884

C_6H_6

C	0.99420700	-0.97758800	-0.00000300
C	-0.34966400	-1.34965500	-0.00005700
C	-1.34378000	-0.37218800	0.00005200
C	-0.99412200	0.97767700	-0.00000600
C	0.34954700	1.34968300	-0.00005300
C	1.34381300	0.37207200	0.00004700
H	1.76716900	-1.73798400	0.00006300
H	-0.62136200	-2.39937400	-0.00008100
H	-2.38874200	-0.66150700	0.00011900
H	-1.76727300	1.73787200	-0.00002200
H	0.62149400	2.39933300	0.00000300
H	2.38871000	0.66164900	0.00003700

EE + Thermal Free Energy Correction = -232.238681