Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Mass spectrometric and theoretical study on the formation of uranyl hydride from uranyl carboxylate

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Detailed instrumental parameters used in the ESI and SORI-CID experiments:

ESI mass spectra were acquired in the negative polarity mode with the following instrumental parameters: syringe pump flow rate 2.00 μL/min, capillary 4.5 kV, end plate offset − 0.5 kV, nebulizer 1.5 bar, dry gas 1.5 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, time of flight 0.7 ~ 0.8 ms. The relative abundances of the uranyl carboxylate complexes are highly dependent on the nebulizer/dry gas and time of flight which can be finely tuned. Mass spectra were collected with an acquisition size of 2 M in the range between 100 and 1000 Da. Ions were accumulated in the ICR cell for 0.3 s and 24 scans were averaged for each spectrum. MS/MS analysis was acquired via SORI-CID (sustained off-resonance irradiation collision-induced dissociation) with the following parameters: isolation power 16%, SORI power 0.8%, pulse length 0.2 s, frequency offset − 500 Hz.

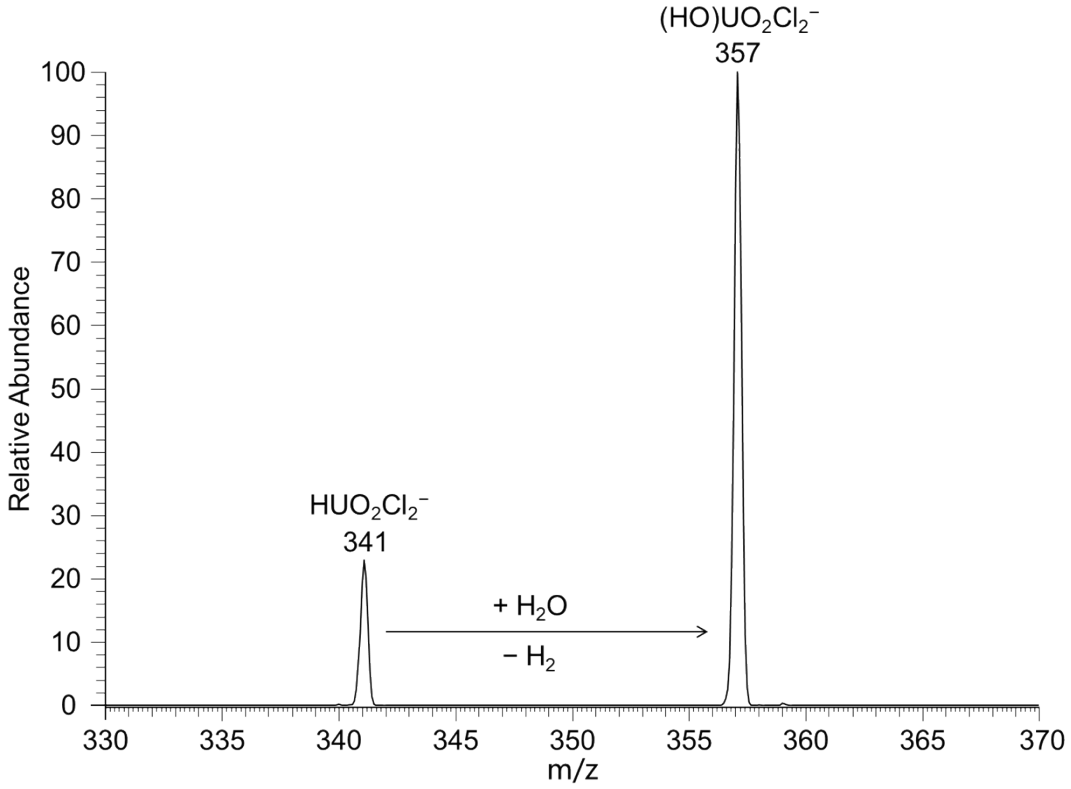

Fig. S1. Mass spectrum of $HUO_2Cl_2^-$ after reaction with H_2O for 5 ms in the ion trap.

$HUO_2Cl_2^-$ is calculated to be more stable than $UO(OH)Cl_2^-$ by 19.3 kcal/mol. The reaction with H_2O (background H_2O residing in the ion trap) was carried out inside a linear ion trap with a background pressure around 7.0×10^{-6} Torr of a ThermoScientific (San Joe, CA) LTQ-XL LIT mass spectrometer equipped with a Heated Ion Max electrospray (ESI) source. The UO_2Cl_2 (ca. 200 μM) and $CH_3CHCHCO_2H$ mixture (metal:ligand = 1:10) in methanol was used as the ESI solution. The $(CH_3CHCHCO_2)UO_2Cl_2^-$ anion was mass selected and subjected to CID, which results in the appearance of the $HUO_2Cl_2^-$ peak. $HUO_2Cl_2^-$ was further isolated and stored in the ion trap for 5 ms to react with background H_2O.

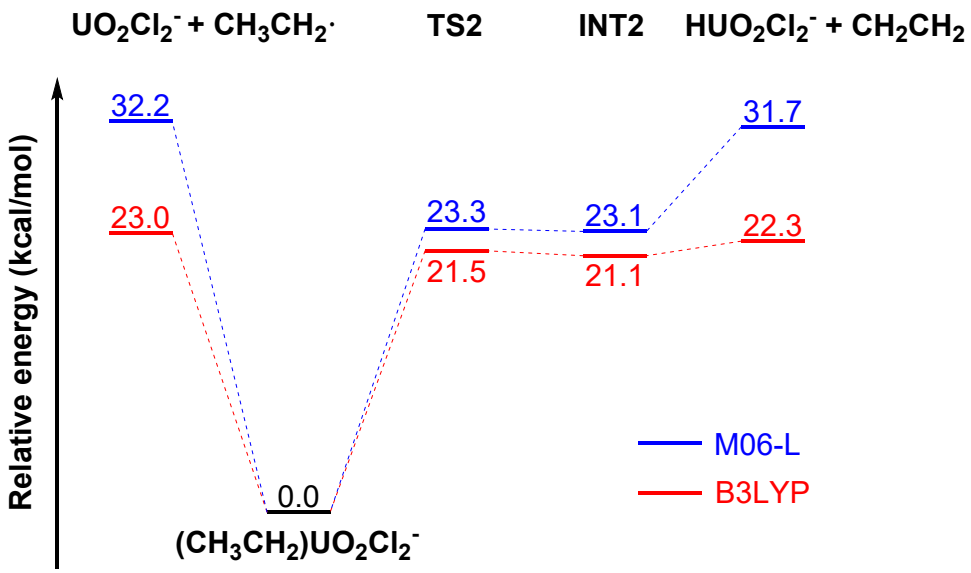

Fig. S2. Potential energy profiles for the formation of $UO_2Cl_2^-$ and $HUO_2Cl_2^-$ from

$(CH_3CH_2)UO_2Cl_2^-$ using the B3LYP and M06-L functionals.

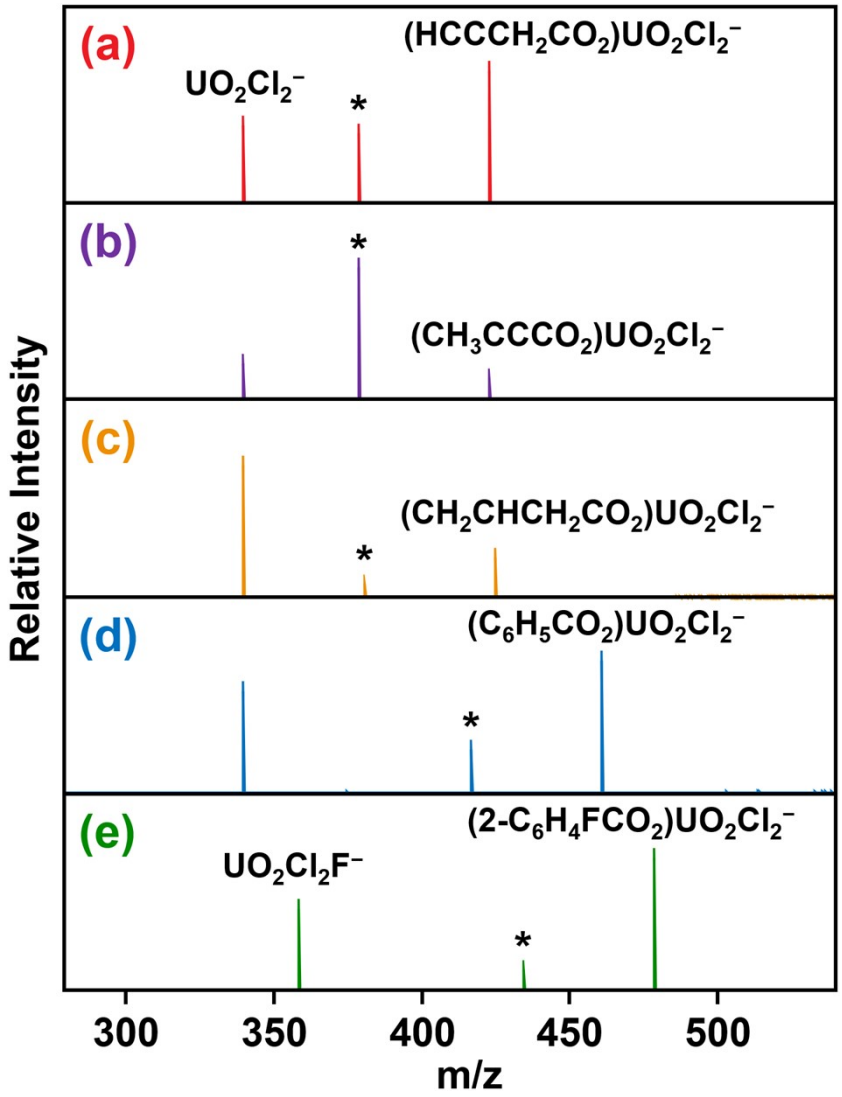

Fig. S3. CID mass spectra of $(RCO_2)UO_2Cl_2^-$. R = (a) $HCCCH_2$, (b) CH_3CC, (c) CH_2CHCH_2, (d) C_6H_5, (e) 2-C_6H_4F. A single isotopomer was mass selected. The asterisks denote the decarboxylation products of $(RCO_2)UO_2Cl_2^-$.

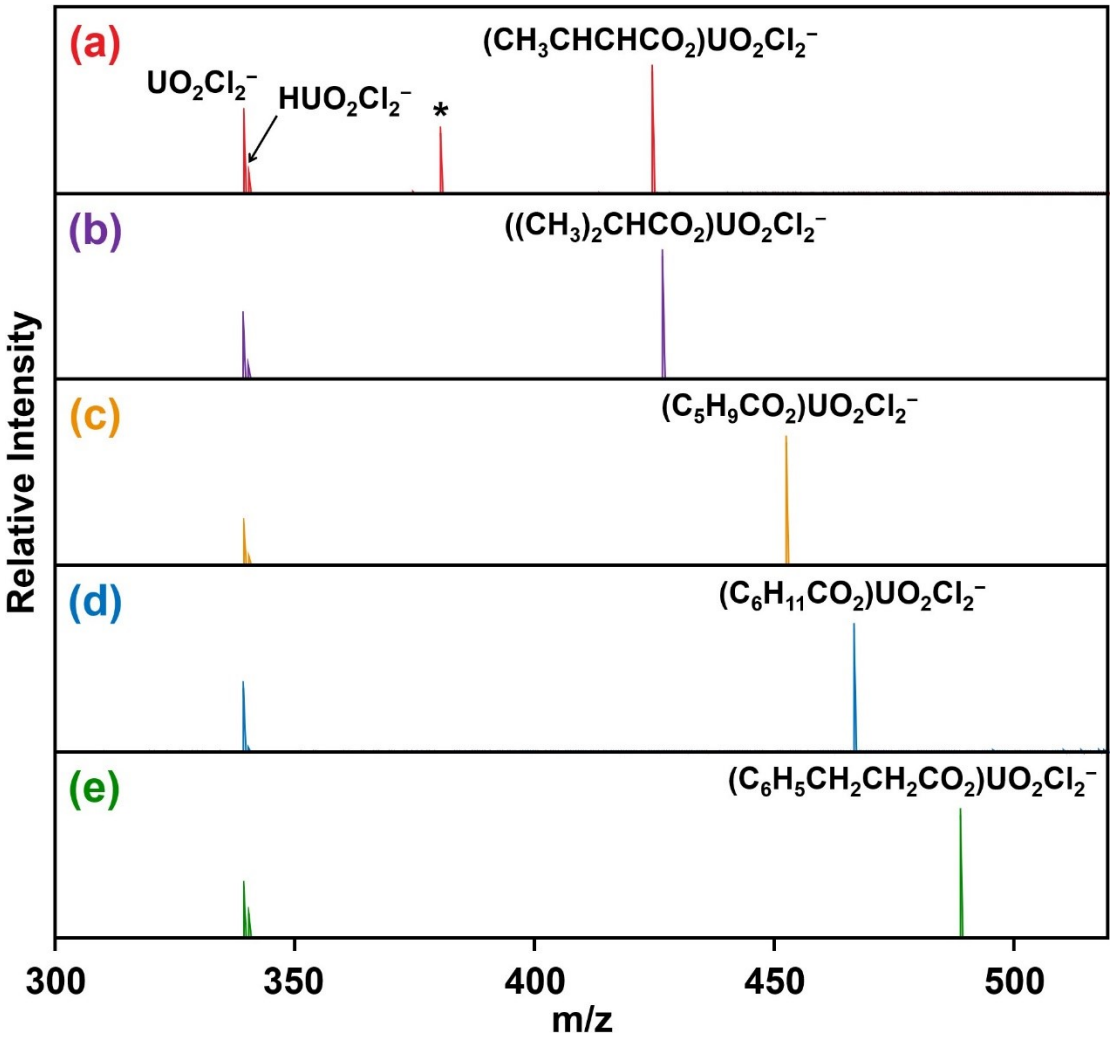

Fig. S4. CID mass spectra of $(RCO_2)UO_2Cl_2^-$, R = (a) CH_3CHCH, (b) $(CH_3)_2CH$, (c) C_5H_9, (d) C_6H_{11}, (e) $C_6H_5CH_2CH_2$. A single isotopomer was mass selected. The asterisk denotes the decarboxylation product of $(CH_3CHCHCO_2)UO_2Cl_2^-$.

Table S1. The energies of R· and R^- losses from $(R)UO_2Cl_2^-$ calculated at the B3LYP/6-311++G(d,p)/SDD level.[a]

R	Energies (kcal/mol)	
	R· loss	**R^- loss**
CH_3CH_2	23.0	105.7
$CH_3CH_2CH_2$	23.6	100.3
CH_3CHCH	38.7	99.2
CH_2CHCH_2	25.5	90.9

[a]The energy of HCO_2^- loss is calculated to be 83.5 kcal/mol while that of HCO_2· loss is 87.7 kcal/mol.

Table S2. Observed and calculated m/z of some uranium containing species.

Species	Observed m/z[a]	Calculated m/z[a]	Error in ppm
$UO_2Cl_2^-$	339.97918	339.97887	-0.92
$HUO_2Cl_2^-$	340.98624	340.986697	-1.34
$(HCO_2)UO_2Cl_2^-$	384.97708	384.97653	-1.43

$(CH_3CO_2)UO_2Cl_2^-$	398.99218	398.99248	-0.75
$(CH_3)UO_2Cl_2^-$	355.00266	355.00235	-0.88
$(CH_3CH_2CO_2)UO_2Cl_2^-$	413.00783	413.00783	0.00
$(CH_3CH_2)UO_2Cl_2^-$	369.01813	369.01800	-0.36
$(CH_3CH_2CH_2CO_2)UO_2Cl_2^-$	427.02373	427.02348	-0.59
$(CH_3CH_2CH_2)UO_2Cl_2^-$	383.03417	383.03365	-1.36
$(CH_3CHCHCO_2)UO_2Cl_2^-$	425.00792	425.00783	-0.23
$(CH_3CHCH)UO_2Cl_2^-$	381.01819	381.01800	-0.5
$(CH_2CHCH_2CO_2)UO_2Cl_2^-$	425.00807	425.00783	-0.57
$(CH_2CHCH_2)UO_2Cl_2^-$	381.01829	381.01800	-0.76

[a] For the most abundant isotopomer of each complex.

Table S3. Selected bond lengths (Å) and angles (degree) of $(R)UO_2Cl_2^-$ shown in Figures 2 and 6. Parameters calculated using the M06-L functional are listed in parentheses.

R	U−O	U−Cl	O−U−O	Cl−U−Cl	O−U−Cl
H	1.775	2.677	175.7	129.5	90.9
	1.775	2.677	(175.7)	(130.8)	(90.9)
	(1.770)	(2.684)			
	(1.770)	(2.684)			
CH_3	1.778	2.686	177.3	132.0	90.7
	1.778	2.688			
CH_3CH_2	1.784	2.709	174.5	120.5	91.9
	1.784	2.686	(173.6)	(121.9)	(92.3)
	(1.779)	(2.711)			
	(1.779)	(2.697)			

$CH_3CH_2CH_2$	1.784	2.708	174.1	120.4	90.7
	1.784	2.685			
CH_2CHCH_2	1.784	2.679	175.1	111.6	91.4
	1.783	2.679			
CH_3CHCH	1.777	2.681	176.1	128.0	90.7
	1.778	2.681			

Table S4. Selected bond lengths (Å) and angles (degree) for the transition states and intermediates shown in Figures 3 and 6. Parameters calculated using the M06-L functional are listed in parentheses.

TS/INT	**U−O**	**U−Cl**	**O−U−O**	**Cl−U−Cl**	**O−U−Cl**
TS1	1.785	2.704	172.2	110.6	92.5
	1.785	2.678			
INT1	1.782	2.710	172.2	110.7	93.1
	1.783	2.658			

TS2	1.783	2.710	172.5	111.0	92.5
	1.783	2.674	(171.4)	(108.8)	(92.0)
	(1.778)	(2.701)			
	(1.778)	(2.679)			
INT2	1.782	2.710	172.5	111.4	92.9
	1.782	2.664	(171.5)	(109.7)	(91.3)
	(1.777)	(2.705)			
	(1.777)	(2.673)			
TS4	1.781	2.720	174.5	113.1	91.7
	1.781	2.683			
INT4	1.779	2.728	173.2	110.8	91.0
	1.779	2.655			
TS5	1.782	2.709	173.0	111.7	91.5
	1.782	2.672			
INT5	1.780	2.713	172.5	112.1	90.8
	1.780	2.654			

Cartesian coordinates of the uranyl complexes and transition states obtained at the B3LYP/6−311++G(d,p)/SDD level of theory. $UO_2Cl_2^-$ possesses a doublet

ground state while all the other species possess singlet ground states.

$(CH_3CH_2CH_2)UO_2Cl_2^-$

U	-0.23242100	-0.02079700	0.03406000
O	0.12410900	-0.17196000	-1.70745700
O	-0.42157300	0.06278600	1.80588300
Cl	-2.68555100	-1.06589500	-0.27651400
Cl	0.14317900	2.65794500	-0.08616900
C	1.52022400	-1.66455500	0.40453100
H	1.66034100	-2.33561700	-0.44540600
H	1.40411200	-2.22908600	1.33041500
C	2.57877000	-0.57675100	0.48188400
H	2.13092600	0.44910700	0.33002100
H	2.99310800	-0.49821600	1.49214700
C	3.70583400	-0.68008500	-0.55371400
H	4.37787600	0.18408400	-0.51289800
H	4.29755400	-1.58490700	-0.38243700
H	3.28992500	-0.73517200	-1.56334100

TS1 ($-318.86\ cm^{-1}$)

U	0.19426600	-0.08389800	0.05761200
O	-0.20244700	-0.36465600	-1.65988300

O	0.36805100	0.10938100	1.82322100
Cl	0.59563800	2.55643300	-0.36711100
Cl	2.49993600	-1.43216900	-0.13750400
C	-2.41736000	0.83573000	0.35825900
H	-2.47061800	1.32205400	-0.61024200
H	-2.15723900	1.45489700	1.20875900
C	-2.79469100	-0.46348500	0.51710800
H	-1.17182100	-1.54341400	0.47001600
H	-2.87345900	-0.85912300	1.52403200
C	-3.48001200	-1.26257100	-0.56144300
H	-3.26639100	-2.32838600	-0.46902000
H	-4.56612900	-1.12073700	-0.48213800
H	-3.16405700	-0.93498400	-1.55353100

INT1

U	0.26672500	-0.12389900	0.07325500
O	-0.13456000	-0.52794600	-1.61597700
O	0.44403100	0.20203400	1.81618600
Cl	0.06428400	2.52497200	-0.45928400
Cl	2.78373200	-0.94133200	-0.17858200
C	-2.73947900	0.71377800	0.50087200
H	-2.84118700	1.30466700	-0.40334000
H	-2.41599700	1.24191100	1.39084400

C	-3.01879100	-0.59597800	0.52377800
H	-0.63768700	-1.87092100	0.59555900
H	-2.89917300	-1.14231400	1.45507900
C	-3.52159700	-1.39067900	-0.64441100
H	-2.86680400	-2.24549400	-0.83009900
H	-4.52541100	-1.78071900	-0.43430600
H	-3.56531300	-0.78578600	-1.55258600

$HUO_2Cl_2^-$

U	0.00000000	0.00000000	0.25006100
H	0.00000000	0.00000000	2.27379600
O	0.00000000	1.77369300	0.31729800
O	0.00000000	-1.77369300	0.31729800
Cl	2.42116900	0.00000000	-0.89282800
Cl	-2.42116900	0.00000000	-0.89282800

$UO_2Cl_2^-$

U	0.00000000	0.00000000	0.28514300
O	0.00000000	1.77947700	0.73164100
O	0.00000000	-1.77947700	0.73164100
Cl	2.31407700	0.00000000	-1.11586600
Cl	-2.31407700	0.00000000	-1.11586600

$(CH_3CH_2)UO_2Cl_2^-$

U	0.05833500	-0.03799600	-0.00000100
O	-0.00049400	-0.09986500	1.78158400
O	-0.00056400	-0.09983500	-1.78158400
Cl	2.74401200	0.01212300	-0.00005300
Cl	-1.35906900	2.27047100	0.00004600
C	-0.91556500	-2.26274300	0.00000100
H	-0.68734700	-2.83777600	0.89796500
H	-0.68737000	-2.83776900	-0.89797400
C	-2.31790500	-1.67455000	0.00002000
H	-2.89847600	-1.93154900	0.88990700
H	-2.32989900	-0.54847600	0.00002800
H	-2.89849600	-1.93153800	-0.88985700

TS2 ($-170.17\ cm^{-1}$)

U	-0.08990900	-0.14283500	0.00002000
O	-0.00674700	-0.22417600	1.77932100
O	-0.00682200	-0.22426200	-1.77928500
Cl	0.73744300	2.43284400	-0.00004900
Cl	-2.75942700	-0.29253600	-0.00003300
C	2.75211500	-0.42958500	-0.00002900
H	2.88655600	0.12185500	0.92325800
H	2.88635100	0.12195900	-0.92328500

C	2.50086800	-1.75999800	-0.00007300
H	2.48265900	-2.33335000	0.91768200
H	0.49791500	-2.09666400	0.00008100
H	2.48253700	-2.33323500	-0.91789700

INT2

U	-0.12911900	-0.16385200	0.00000400
O	-0.03816000	-0.23720300	1.77787600
O	-0.03820400	-0.23725900	-1.77786800
Cl	0.85271600	2.36249800	-0.00004800
Cl	-2.79266700	-0.17062100	0.00003600
C	2.94390700	-0.35620900	-0.00002400
H	3.05409800	0.20492200	0.92088600
H	3.05407900	0.20490400	-0.92094700
C	2.69564000	-1.67325900	-0.00000900
H	2.60600700	-2.23833300	0.91948900
H	0.31155000	-2.14821700	0.00002900
H	2.60598600	-2.23835100	-0.91949300

$(HCO_2)UO_2Cl_2^-$ (bidentate)

U	0.00000000	0.00000000	0.02734300
C	0.00000000	0.00000000	-2.82740500
H	0.00000000	0.00000000	-3.93128000

O	1.77213400	0.00000000	-0.02503000
O	-1.77213400	0.00000000	-0.02503000
Cl	0.00000000	2.13933900	1.59815500
Cl	0.00000000	-2.13933900	1.59815500
O	0.00000000	1.10552600	-2.22229200
O	0.00000000	-1.10552600	-2.22229200

$(HCO_2)UO_2Cl_2^-$ (monodentate)

O	-4.05659100	0.46170100	-0.13629200
C	-3.27724200	-0.45949700	0.00248600
O	-2.00513400	-0.37172800	0.27004500
U	0.18484000	0.00485100	0.02872800
O	0.35754300	0.00968300	1.79185900
O	-0.03841400	0.01594500	-1.72842700
Cl	1.66581400	-2.18664300	-0.14315400
Cl	1.40585700	2.35706800	-0.10130800
H	-3.61944700	-1.51134800	-0.07950600

TS3 ($-39.14\ cm^{-1}$)

O	-4.10864900	-1.64261900	-0.01821500
C	-3.62686300	-0.58562400	0.00920600
O	-3.23472500	0.50864800	0.02805200
U	0.32607200	-0.06250600	0.04001900

O	0.46086600	0.04468800	1.80655200
O	0.02768500	-0.24320000	-1.70043800
Cl	2.64910500	-1.34843400	-0.14024100
Cl	0.16417200	2.60023100	-0.15392300
H	-1.22454900	-1.35634800	0.33621400

INT3

O	-4.27093900	-1.16118000	0.01187300
C	-4.22713400	-0.00030300	0.01575600
O	-4.27084100	1.16055600	0.01186800
U	0.40123300	-0.00001100	0.03880800
O	0.61156900	-0.00000800	1.80028500
O	0.04321100	-0.00003100	-1.69918700
Cl	1.56379800	-2.39625000	-0.14787400
Cl	1.56271400	2.39676500	-0.14784000
H	-1.60537200	-0.00061800	0.36356400

$(CH_3CHCH)UO_2Cl_2^-$

U	0.28497700	0.00000900	0.04569900
O	-0.17016500	-0.00017000	-1.67291000
O	0.62345300	0.00011600	1.79058300
Cl	1.42964600	2.41112600	-0.21209500
Cl	1.43290300	-2.40955000	-0.21229400

C	-4.56410500	-0.00132400	-0.00520500
H	-5.05871200	-0.88054000	-0.43924700
H	-4.74746000	-0.00220800	1.07306800
C	-2.08225600	-0.00128000	0.58509900
H	-2.40361100	-0.00209500	1.63610200
C	-3.08551400	-0.00084000	-0.31097000
H	-2.84751100	-0.00007700	-1.37666200
H	-5.05901200	0.87841000	-0.43784800

TS4 (−429.66 cm^{-1})

U	0.16934000	-0.08411900	0.00003800
O	0.09428200	-0.12476400	-1.77904700
O	0.09465400	-0.12451300	1.77914600
Cl	0.63856700	2.59508000	-0.00020300
Cl	2.41855100	-1.54613200	-0.00009800
C	-2.38573000	0.93074200	0.00020600
H	-2.13188900	1.96619300	0.00027600
C	-2.79030500	-0.22382200	0.00010300
H	-1.35314800	-1.43334200	0.00031800
C	-3.75293700	-1.33437000	-0.00015300
H	-3.61398700	-1.96450700	-0.88135000
H	-3.61423900	-1.96472400	0.88092800
H	-4.77463100	-0.93785100	-0.00025700

INT4

U	0.22465300	-0.13086000	0.00002600
O	0.12359700	-0.16182700	-1.77606900
O	0.12386500	-0.16159100	1.77613800
Cl	0.25568300	2.59671500	-0.00014200
Cl	2.69545100	-1.10331200	-0.00009800
C	-2.75979400	0.92128700	0.00022500
H	-2.37244900	1.91491200	0.00033200
C	-3.16857600	-0.21319100	0.00007600
H	-0.83888900	-1.86578300	0.00022300
C	-3.73406100	-1.55550700	-0.00011100
H	-3.40141900	-2.11023000	-0.87954700
H	-3.40153700	-2.11042800	0.87924300
H	-4.82817000	-1.50535100	-0.00018200

$(CH_2CHCH_2)UO_2Cl_2^-$

U	-0.05113600	-0.00001400	0.00390000
O	0.06094400	0.00011800	-1.77556700
O	-0.01158600	-0.00034900	1.78700700
Cl	-1.55800300	-2.21424700	-0.02926000
Cl	-1.55281300	2.21772600	-0.02932300
C	2.37714200	-1.23792300	0.19793500

H	2.52652800	-2.14752200	-0.37136000
H	2.28721000	-1.34718100	1.27410000
C	2.38005900	1.23314200	0.19898000
H	2.29018800	1.34183700	1.27519600
C	2.68103300	-0.00249500	-0.36914300
H	2.53118500	2.14281700	-0.36973200
H	2.92899500	-0.00232400	-1.42928200

TS5 (−312.34 cm^{-1})

U	-0.17755900	-0.10043000	0.00001000
O	-0.07400900	-0.13533400	1.77841200
O	-0.07390200	-0.13538900	-1.77838300
Cl	-0.47310400	2.59258200	-0.00004500
Cl	-2.53760900	-1.35424900	-0.00003300
C	2.51006600	0.81348300	0.00003300
H	2.36844000	1.35809000	0.92810800
H	2.36839500	1.35810400	-0.92802700
H	1.20118400	-1.58767500	0.00006600
C	3.68718100	-1.51101100	-0.00003000
C	2.91943200	-0.45012700	0.00001100
H	4.76662900	-1.37148900	-0.00006400
H	3.29614400	-2.51740500	-0.00003400

INT5

U	0.25391400	-0.13586700	0.00060700
O	0.13993400	-0.17220500	-1.77530500
O	0.14438400	-0.16278000	1.77694800
Cl	0.07588000	2.57174200	-0.00590900
Cl	2.77345600	-0.96985900	-0.00040800
C	-2.87413500	0.75997100	0.00813600
H	-2.68929800	1.30221800	-0.91388700
H	-2.68851300	1.29133600	0.93631700
H	-0.74922800	-1.90375400	0.00677300
C	-3.79482500	-1.68320900	-0.00512000
C	-3.32548400	-0.46816100	0.00111200
H	-4.86537900	-1.86648400	-0.00554600
H	-3.11432000	-2.52724700	-0.01001400