Supporting information to accompany, Uranium(VI) Bis(imido) Bis(Sulfonamide) and Dihalide Complexes: Synthesis and Density Functional Theory Analysis

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Table 1S. Crystal data and structure refinement for $U(N^tBu)_2(\eta^1\text{-}N(Me)SO_2Ar')(\eta^3\text{-}N(Me)(SO_2Ar')(Me_2bpy)\text{-}CH_2Cl_2$ (**4**).

Identification code	apx880s	
Empirical formula	$C_{36}\ H_{40}\ N_6\ O_4\ S_2\ U$ - CH_2Cl_2	
Formula weight	826.46	
Temperature	140(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 11.8477(19) Å	α= 90°.
	b = 13.585(2) Å	β= 91.082(2)°.
	c = 26.019(4) Å	γ = 90°.
Volume	4187.1(12) $Å^3$	
Z	6	
Density (calculated)	1.967 Mg/m^3	
Absorption coefficient	6.072 mm^{-1}	
F(000)	2444	
Crystal size	0.18 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.90 to 25.49°.	
Index ranges	-14<=h<=14, -16<=k<=16, -31<=l<=31	
Reflections collected	37901	
Independent reflections	7770 [R(int) = 0.1462]	
Completeness to theta = 25.00°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7770 / 0 / 454	
Goodness-of-fit on F^2	0.929	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1174	
R indices (all data)	R1 = 0.0999, wR2 = 0.1304	
Largest diff. peak and hole	1.780 and -0.871 e.$Å^{-3}$	

Table 2S. Crystal data and structure refinement for *trans*-$U(N^tBu)_2(Cl)_2(OPPh_3)_2$ (**8**).

Identification code	apx574	
Empirical formula	C_{42} H_{48} Cl_2 N_2 O_2 P_2 U	
Formula weight	983.69	
Temperature	141(1) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.478(2) Å	α= 86.106(3)°.
	b = 10.914(3) Å	β= 75.756(3)°.
	c = 11.358(3) Å	γ = 69.243(2)°.
Volume	1064.6(5) $Å^3$	
Z	1	
Density (calculated)	1.534 Mg/m^3	
Absorption coefficient	4.048 mm^{-1}	
F(000)	486	
Crystal size	0.20 x 0.11 x 0.09 mm^3	
Theta range for data collection	2.00 to 28.13°.	
Index ranges	-12<=h<=12, -14<=k<=13, -15<=l<=14	
Reflections collected	11805	
Independent reflections	4773 [R(int) = 0.0423]	
Completeness to theta = 25.00°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4773 / 0 / 244	
Goodness-of-fit on F^2	0.679	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0980	
R indices (all data)	R1 = 0.0393, wR2 = 0.0997	
Largest diff. peak and hole	2.025 and -1.027 $e.Å^{-3}$	

Table 3S. Crystal data and structure refinement for *trans*-$U(N^tBu)_2(Br)_2(OPPh_3)_2$ (**9**).

Identification code	apx486a	
Empirical formula	$C_{44}\ H_{48}\ Br_2\ N_2\ O_2\ P_2\ U$	
Formula weight	1096.63	
Temperature	120(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 11.355(4) Å	α= 90°.
	b = 11.018(4) Å	β= 108.18°.
	c = 18.192(6) Å	γ = 90°.
Volume	2162.2(13) $Å^3$	
Z	2	
Density (calculated)	1.684 Mg/m^3	
Absorption coefficient	5.713 mm^{-1}	
F(000)	1068	
Crystal size	0.20 x 0.14 x 0.10 mm^3	
Theta range for data collection	2.19 to 28.29°.	
Index ranges	-14<=h<=14, -13<=k<=14, -24<=l<=23	
Reflections collected	23463	
Independent reflections	5047 [R(int) = 0.0648]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5989 and 0.3946	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5047 / 5 / 231	
Goodness-of-fit on F^2	2.436	
Final R indices [I>2sigma(I)]	R1 = 0.0858, wR2 = 0.1885	
R indices (all data)	R1 = 0.1035, wR2 = 0.1909	
Largest diff. peak and hole	2.309 and -4.044 $e.Å^{-3}$	

Table 4S. Crystal data and structure refinement for $[U(N^tBu)_2(Cl)(\mu\text{-}Cl)(Me_2bpy)]_2\text{-}CH_2Cl_2$ (**10**).

Identification code	apx576s	
Empirical formula	$C_{42}\ H_{64}\ Cl_8\ N_8\ U_2$ - CH_2Cl_2	
Formula weight	1440.67	
Temperature	141(1) K	
Wavelength	0.71073 Å	
Crystal system	trigonal	
Space group	P $\bar{3}$1c	
Unit cell dimensions	a = 22.3732(16) Å	α= 90°.
	b = 22.3732(16) Å	β= 90°.
	c = 40.327(6) Å	γ = 120°.
Volume	17482(3) $Å^3$	
Z	12	
Density (calculated)	1.642 Mg/m^3	
Absorption coefficient	5.952 mm^{-1}	
F(000)	8304	
Crystal size	0.18 x 0.14 x 0.14 mm^3	
Theta range for data collection	1.82 to 25.26°.	
Index ranges	-26<=h<=26, -26<=k<=26, -48<=l<=48	
Reflections collected	165193	
Independent reflections	10550 [R(int) = 0.1201]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.4896 and 0.4138	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10550 / 0 / 503	
Goodness-of-fit on F^2	1.184	
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1034	
R indices (all data)	R1 = 0.0740, wR2 = 0.1109	
Largest diff. peak and hole	0.993 and -5.440 $e.Å^{-3}$	

Table 5S. Crystal data and structure refinement for $U(N^tBu)_2(Br)_2(Me_2bpy)_2$ (**11**).

Identification code	apx975	
Empirical formula	$C_{20}\ H_{30}\ Br_2\ N_4\ U$	
Formula weight	724.33	
Temperature	141(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 16.7594(17) Å	α= 90°.
	b = 9.4974(9) Å	β= 112.1060(10)°.
	c = 16.9780(17) Å	γ = 90°.
Volume	2503.7(4) $Å^3$	
Z	4	
Density (calculated)	1.922 Mg/m^3	
Absorption coefficient	9.686 mm^{-1}	
F(000)	1360	
Crystal size	0.30 x 0.12 x 0.10 mm^3	
Theta range for data collection	2.42 to 28.42°.	
Index ranges	-21<=h<=21, -12<=k<=12, -22<=l<=21	
Reflections collected	27617	
Independent reflections	5975 [R(int) = 0.0872]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.4442 and 0.1592	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5975 / 0 / 252	
Goodness-of-fit on F^2	0.754	
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0606	
R indices (all data)	R1 = 0.0357, wR2 = 0.0636	
Largest diff. peak and hole	1.843 and -1.093 $e.Å^{-3}$	

Table 6S. Geometry Optimization for $U(N^tBu)_2(F)_2(OPPh_3)_2$.

U	0.000003	0.000020	-0.000091
F	0.032764	-0.101557	2.195033
P	3.801331	-0.088487	-0.006901
O	2.366188	-0.603948	-0.049714
N	0.395080	1.834963	0.037557
C	0.258596	3.286288	-0.087092
C	-0.379254	3.840447	1.203060
H	-1.365491	3.391722	1.363584
H	-0.495707	4.930995	1.144805
H	0.243376	3.601779	2.071488
C	-0.630663	3.615174	-1.303504
H	-0.202635	3.187374	-2.215813
H	-0.724082	4.701660	-1.434106
H	-1.631888	3.192426	-1.172507
C	1.655415	3.908288	-0.282046
H	2.302883	3.679996	0.570282
H	1.581602	4.999597	-0.378608
H	2.129137	3.515079	-1.188026
C	4.030836	1.206086	1.252086
C	3.163319	1.210297	2.356820
H	2.345444	0.498390	2.425090
C	3.326315	2.170433	3.356866
H	2.645857	2.176239	4.203348
C	4.344407	3.121884	3.264006
H	4.463576	3.868697	4.044587
C	5.202015	3.124332	2.161086
H	5.984850	3.873240	2.077812
C	5.044184	2.171777	1.153874
H	5.696196	2.195937	0.285744
C	4.314870	0.546623	-1.634957
C	3.317516	0.914881	-2.552538
H	2.266102	0.795675	-2.306665
C	3.683773	1.410976	-3.805669
H	2.908480	1.687424	-4.514306
C	5.030687	1.542335	-4.148005
H	5.308366	1.928910	-5.125080
C	6.024033	1.163037	-3.241305
H	7.073032	1.247432	-3.511791
C	5.668937	0.659107	-1.990348
H	6.446225	0.336211	-1.302606
C	4.939294	-1.453776	0.407468
C	4.677781	-2.716351	-0.149716
H	3.807279	-2.855257	-0.783927
C	5.521756	-3.790700	0.126980

H	5.310117	-4.766300	-0.301495
C	6.632631	-3.614030	0.956424
H	7.288342	-4.453358	1.172005
C	6.895408	-2.362323	1.514794
H	7.752282	-2.224785	2.168557
C	6.050097	-1.283791	1.245400
H	6.248601	-0.317546	1.699090
F	-0.033003	0.101661	-2.195195
P	-3.801333	0.088465	0.006959
O	-2.366194	0.603962	0.049507
N	-0.394942	-1.834943	-0.037726
C	-0.258514	-3.286282	0.086774
C	0.379537	-3.840314	-1.203332
H	1.365805	-3.391584	-1.363650
H	0.495969	-4.930869	-1.145171
H	-0.242951	-3.601550	-2.071835
C	0.630543	-3.615309	1.303298
H	0.202364	-3.187602	2.215581
H	0.723929	-4.701809	1.433803
H	1.631793	-3.192558	1.172510
C	-1.655375	-3.908278	0.281441
H	-2.302700	-3.679892	-0.570969
H	-1.581593	-4.999597	0.377908
H	-2.129234	-3.515147	1.187383
C	-4.030998	-1.206030	-1.252081
C	-3.163604	-1.210145	-2.356914
H	-2.345740	-0.498227	-2.425206
C	-3.326702	-2.170202	-3.357018
H	-2.646339	-2.175936	-4.203577
C	-4.344776	-3.121670	-3.264120
H	-4.464026	-3.868421	-4.044749
C	-5.202256	-3.124218	-2.161101
H	-5.985071	-3.873143	-2.077796
C	-5.044322	-2.171741	-1.153829
H	-5.696230	-2.195986	-0.285625
C	-4.314628	-0.546744	1.635055
C	-3.317165	-0.914890	2.552560
H	-2.265778	-0.795537	2.306638
C	-3.683279	-1.411056	3.805707
H	-2.907901	-1.687416	4.514285
C	-5.030152	-1.542594	4.148133
H	-5.307716	-1.929224	5.125219
C	-6.023608	-1.163398	3.241509
H	-7.072578	-1.247927	3.512065
C	-5.668659	-0.659399	1.990540
H	-6.446035	-0.336578	1.302864

C	-4.939389	1.453757	-0.407152
C	-4.677718	2.716342	0.149935
H	-3.807051	2.855252	0.783917
C	-5.521755	3.790693	-0.126569
H	-5.309994	4.766300	0.301829
C	-6.632846	3.614016	-0.955721
H	-7.288603	4.453347	-1.171152
C	-6.895780	2.362298	-1.513995
H	-7.752823	2.224754	-2.167536
C	-6.050409	1.283765	-1.244795
H	-6.249038	0.317513	-1.698417

Table 7S. Geometry Optimization for $UO_2F_2(OPPh_3)_2$.

U	-0.00000200	0.00001300	-0.00001400
F	-0.06438000	2.16723100	-0.04170400
P	-3.78117400	-0.01075900	-0.05577800
O	-2.33854100	-0.05154400	-0.56137500
C	-3.99805800	1.15741000	1.32020200
C	-3.16194800	2.28489200	1.37350000
H	-2.37084000	2.42544300	0.64254600
C	-3.32311200	3.21401300	2.40149500
H	-2.66485800	4.07653500	2.44702800
C	-4.31182100	3.02993900	3.37039800
H	-4.43004500	3.75586800	4.17050400
C	-5.13988900	1.90634500	3.32228000
H	-5.89915600	1.75280700	4.08418000
C	-4.98162700	0.96694000	2.30296900
H	-5.60912300	0.08057000	2.28571700
C	-4.32587900	-1.66127800	0.48320500
C	-3.35749600	-2.55779500	0.96390500
H	-2.30777300	-2.28200300	0.98083600
C	-3.74621300	-3.82584400	1.39810800
H	-2.99217300	-4.51778500	1.76151400
C	-5.08973900	-4.20403500	1.35897400
H	-5.38580400	-5.19341800	1.69741100
C	-6.05360000	-3.31644900	0.87447900
H	-7.09784000	-3.61337400	0.82991200
C	-5.67408000	-2.04925100	0.43158700
H	-6.42427500	-1.37324700	0.03077400
C	-4.87297400	0.52057500	-1.41354600
C	-4.48760700	0.20314900	-2.72561800
H	-3.54880200	-0.31413300	-2.89886300
C	-5.29868800	0.57482500	-3.79749200
H	-4.99358200	0.33397400	-4.81187100
C	-6.49445000	1.26000900	-3.56812000
H	-7.12305500	1.55026900	-4.40567100
C	-6.87779800	1.58278700	-2.26472600
H	-7.80059400	2.12762900	-2.08571300
C	-6.06796600	1.21894800	-1.18764600
H	-6.35772700	1.49460100	-0.17771700
F	0.06437600	-2.16720500	0.04167400
P	3.78117200	0.01075500	0.05577800
O	2.33853400	0.05155700	0.56135800
C	3.99805900	-1.15740000	-1.32021200
C	3.16194600	-2.28487900	-1.37352400
H	2.37083500	-2.42543500	-0.64257600
C	3.32311200	-3.21399100	-2.40152700

H	2.66485700	-4.07651000	-2.44707100
C	4.31182700	-3.02991100	-3.37042400
H	4.43005300	-3.75583300	-4.17053600
C	5.13989700	-1.90631900	-3.32229100
H	5.89916900	-1.75277600	-4.08418600
C	4.98163300	-0.96692400	-2.30297200
H	5.60913300	-0.08055600	-2.28570800
C	4.32590600	1.66127400	-0.48317800
C	3.35754100	2.55781100	-0.96387300
H	2.30781400	2.28203500	-0.98081500
C	3.74628000	3.82586100	-1.39805500
H	2.99225300	4.51781800	-1.76145700
C	5.08981100	4.20403100	-1.35890500
H	5.38589300	5.19341500	-1.69732600
C	6.05365400	3.31642500	-0.87441500
H	7.09789900	3.61333400	-0.82983500
C	5.67411300	2.04922600	-0.43154400
H	6.42429400	1.37320500	-0.03073500
C	4.87294800	-0.52060800	1.41355400
C	4.48757300	-0.20318200	2.72562400
H	3.54877700	0.31411600	2.89886300
C	5.29863700	-0.57488100	3.79750400
H	4.99352600	-0.33402900	4.81188200
C	6.49438800	-1.26008500	3.56814000
H	7.12298000	-1.55036300	4.40569600
C	6.87774300	-1.58286400	2.26474800
H	7.80053100	-2.12772100	2.08574100
C	6.06792900	-1.21900300	1.18766200
H	6.35769400	-1.49465500	0.17773500
O	-0.45675100	0.00470000	1.73380500
O	0.45674600	-0.00467600	-1.73383100

Table 8S. Geometry Optimization for $U(N^tBu)_2(Cl)_2(OPPh_3)_2$.

U	0.000067	-0.000237	0.000448
Cl	-0.074540	0.090569	2.750195
P	-3.877376	0.044749	-0.015407
O	-2.387922	0.368525	-0.088659
N	-0.236411	-1.832735	0.012889
C	-0.207328	-3.295125	-0.093621
C	0.268844	-3.875082	1.251465
H	1.276639	-3.517982	1.488320
H	0.287356	-4.971916	1.211880
H	-0.395540	-3.563077	2.063041
C	0.753284	-3.699071	-1.228285
H	0.446235	-3.238972	-2.172176
H	0.760668	-4.790045	-1.350162
H	1.773507	-3.368539	-1.009155
C	-1.628598	-3.798556	-0.410182
H	-2.326653	-3.517172	0.384208
H	-1.633471	-4.892067	-0.503365
H	-1.986094	-3.372249	-1.353475
C	-4.230318	-1.278112	1.183337
C	-3.463570	-1.306332	2.360840
H	-2.665831	-0.586211	2.523059
C	-3.698763	-2.296155	3.315621
H	-3.092949	-2.318269	4.216746
C	-4.693518	-3.254333	3.106832
H	-4.871004	-4.025265	3.852094
C	-5.453799	-3.230374	1.935283
H	-6.219429	-3.982217	1.764520
C	-5.222676	-2.247514	0.971772
H	-5.802028	-2.249066	0.053796
C	-4.521659	-0.424538	-1.650289
C	-3.611897	-0.794592	-2.652214
H	-2.542317	-0.767866	-2.465565
C	-4.085966	-1.159786	-3.914200
H	-3.374941	-1.433940	-4.688031
C	-5.455940	-1.160743	-4.180028
H	-5.819060	-1.446053	-5.163867
C	-6.363213	-0.779662	-3.186974
H	-7.429114	-0.762586	-3.397189
C	-5.899091	-0.403853	-1.927102
H	-6.606930	-0.078530	-1.169073
C	-4.825604	1.511854	0.509047
C	-4.516827	2.744926	-0.089484
H	-3.718372	2.804238	-0.823362
C	-5.224168	3.891384	0.267367

H	-4.976596	4.843051	-0.194230
C	-6.245611	3.816601	1.218902
H	-6.794735	4.712146	1.496912
C	-6.556800	2.594397	1.815730
H	-7.345336	2.535333	2.560809
C	-5.848140	1.442932	1.464988
H	-6.085260	0.497122	1.942113
Cl	0.075879	-0.091565	-2.749245
P	3.877393	-0.044407	0.015113
O	2.388065	-0.368338	0.090234
N	0.235854	1.832314	-0.011963
C	0.206590	3.294559	0.096478
C	-0.266199	3.876189	-1.249080
H	-1.273357	3.519300	-1.488915
H	-0.284894	4.972975	-1.208195
H	0.400312	3.565243	-2.059323
C	-0.756913	3.697047	1.229205
H	-0.452075	3.235951	2.173330
H	-0.764785	4.787883	1.352288
H	-1.776531	3.366600	1.007137
C	1.627061	3.797514	0.417294
H	2.327070	3.517351	-0.375804
H	1.631678	4.890883	0.512134
H	1.982185	3.369746	1.360812
C	4.228872	1.280358	-1.181943
C	3.463272	1.308118	-2.360224
H	2.667273	0.586423	-2.524009
C	3.697194	2.299491	-3.313689
H	3.092252	2.321231	-4.215409
C	4.689561	3.259704	-3.102834
H	4.866059	4.031840	-3.847083
C	5.448699	3.236192	-1.930552
H	6.212457	3.989573	-1.758200
C	5.218826	2.251763	-0.968327
H	5.797292	2.253592	-0.049799
C	4.523756	0.422287	1.649913
C	3.615134	0.789724	2.653837
H	2.545313	0.762780	2.468535
C	4.090743	1.152770	3.915869
H	3.380640	1.425002	4.691226
C	5.461090	1.154135	4.179768
H	5.825403	1.437763	5.163653
C	6.367230	0.775664	3.184680
H	7.433439	0.758942	3.393355
C	5.901591	0.402033	1.924724
H	6.608587	0.078767	1.165028

C	4.824884	-1.510597	-0.513140
C	4.514615	-2.745332	0.081119
H	3.715161	-2.806409	0.813748
C	5.221763	-3.891084	-0.278412
H	4.973017	-4.844053	0.179853
C	6.244498	-3.813907	-1.228351
H	6.793458	-4.708894	-1.508471
C	6.557206	-2.590003	-1.820913
H	7.346757	-2.529067	-2.564765
C	5.848740	-1.439245	-1.467501
H	6.086974	-0.492086	-1.941399

Table 9S. Geometry Optimization for $UO_2Cl_2(OPPh_3)_2$.

U	-0.00018200	-0.00007800	-0.00058400
Cl	-0.19018700	2.68646700	0.02891300
P	-3.84585200	-0.03152800	-0.02656900
O	-2.33564200	-0.13880500	-0.24571700
O	-0.17546700	-0.02683000	1.76709600
C	-4.24588300	0.67056200	1.59995900
C	-3.45373700	1.73178500	2.07215200
H	-2.61092300	2.09637700	1.49086300
C	-3.73953000	2.30790700	3.30927600
H	-3.11879400	3.12064200	3.67463600
C	-4.80987000	1.83832800	4.07476300
H	-5.02668700	2.29002800	5.03908300
C	-5.59617900	0.78317700	3.60820300
H	-6.42183300	0.40922900	4.20726100
C	-5.31433800	0.19450900	2.37449200
H	-5.91515400	-0.63987800	2.02540900
C	-4.59680900	-1.68071300	-0.16474500
C	-3.78424100	-2.79637300	0.09435000
H	-2.73387300	-2.66570700	0.33782500
C	-4.32614600	-4.07948500	0.00840800
H	-3.69163700	-4.93949800	0.20131800
C	-5.66912300	-4.25510200	-0.33119000
H	-6.08562400	-5.25653400	-0.39896800
C	-6.47674100	-3.14627200	-0.59676300
H	-7.51826500	-3.28210000	-0.87461200
C	-5.94291600	-1.85991200	-0.51998900
H	-6.56938100	-1.00367100	-0.75390500
C	-4.56754800	1.05099700	-1.29461800
C	-3.87967400	1.19795800	-2.50910300
H	-2.92554500	0.70037200	-2.65332700
C	-4.41377000	2.00586100	-3.51311600
H	-3.87419800	2.12705800	-4.44785900
C	-5.63022200	2.66253100	-3.31360400
H	-6.04156500	3.29252600	-4.09761100
C	-6.31303200	2.52321000	-2.10293300
H	-7.25105900	3.04692900	-1.94134000
C	-5.78176700	1.72393600	-1.09054800
H	-6.29986700	1.64309300	-0.13883600
Cl	0.18974500	-2.68666000	-0.03010500
P	3.84583100	0.03138300	0.02648600
O	2.33539900	0.13827700	0.24409600
O	0.17504100	0.02689200	-1.76825200
C	4.24734000	-0.67180300	-1.59923600
C	3.45455500	-1.73209600	-2.07234400

H	2.61036100	-2.09541500	-1.49226800
C	3.74159300	-2.30905900	-3.30881200
H	3.12035700	-3.12109900	-3.67486600
C	4.81379200	-1.84119300	-4.07272500
H	5.03157800	-2.29352200	-5.03653200
C	5.60074200	-0.78690500	-3.60525300
H	6.42786600	-0.41426600	-4.20310000
C	5.31767100	-0.19741500	-2.37222600
H	5.91897100	0.63637200	-2.02255100
C	4.59640000	1.68083900	0.16387300
C	3.78420200	2.79619400	-0.09775200
H	2.73417200	2.66537200	-0.34259200
C	4.32598200	4.07940000	-0.01257500
H	3.69176200	4.93918400	-0.20744300
C	5.66846600	4.25545400	0.32878100
H	6.08485400	5.25697400	0.39594500
C	6.47567900	3.14696300	0.59690600
H	7.51678300	3.28312000	0.87616700
C	5.94196000	1.86050100	0.52091500
H	6.56808300	1.00456700	0.75683900
C	4.56674900	-1.04984300	1.29607700
C	3.87776700	-1.19612000	2.51000500
H	2.92331600	-0.69878700	2.65295100
C	4.41124600	-2.00302100	3.51516600
H	3.87083500	-2.12369400	4.44949300
C	5.62814500	-2.65935300	3.31732800
H	6.03900600	-3.28855400	4.10222400
C	6.31205600	-2.52072200	2.10718800
H	7.25044300	-3.04420400	1.94692400
C	5.78143800	-1.72245700	1.09367900
H	6.30038100	-1.64217800	0.14238000

Table 10S. Geometry Optimization for $U(N^tBu)_2(Br)_2(OPPh_3)_2$.

U	-0.000020	-0.000270	0.001721
Br	0.023257	0.876398	-2.802973
N	-0.000015	-1.760888	-0.544588
C	-1.523360	-3.599079	-1.095154
H	-2.001849	-3.017033	-1.891403
H	-2.085442	-3.443037	-0.168112
H	-1.585757	-4.661676	-1.362620
C	-0.050858	-3.178723	-0.919739
C	0.603729	-4.018356	0.195253
H	1.659587	-3.748253	0.308672
H	0.545877	-5.086814	-0.050054
H	0.104434	-3.847859	1.154703
P	3.926608	0.033712	0.013545
O	2.402915	0.020216	0.014784
C	4.154851	0.400429	4.073251
H	3.457753	0.608484	4.879615
C	4.530611	1.481710	-0.912274
C	5.923509	-0.201385	1.994174
H	6.609093	-0.473830	1.195904
C	3.686620	0.359078	2.758536
H	2.631682	0.510206	2.553228
C	4.573563	0.068725	1.711750
C	5.501802	0.159598	4.347478
H	5.862178	0.192373	5.372315
C	5.747219	2.117595	-0.620280
H	6.362690	1.776729	0.206344
C	6.161793	3.211299	-1.379766
H	7.101152	3.704389	-1.144732
C	6.385794	-0.144679	3.308109
H	7.430645	-0.352734	3.521973
C	3.731028	1.956551	-1.964996
H	2.773124	1.491756	-2.184257
C	4.154218	3.051292	-2.721019
H	3.525405	3.414222	-3.528968
C	4.634199	-1.453759	-0.769040
C	4.543396	-2.681219	-0.090107
H	4.093821	-2.724157	0.898114
C	5.027396	-3.846590	-0.681725
H	4.951719	-4.791981	-0.151874
C	5.214965	-1.412304	-2.044988
H	5.285930	-0.470596	-2.579752
C	5.606522	-3.797292	-1.952762
H	5.984861	-4.706712	-2.411983
C	5.698280	-2.582170	-2.633142

H	6.144573	-2.542531	-3.622954
C	5.367695	3.677275	-2.430627
H	5.691747	4.533256	-3.016850
C	0.713061	-3.362191	-2.245695
H	0.251903	-2.773081	-3.045842
H	0.712247	-4.419224	-2.543323
H	1.752331	-3.033319	-2.139073
Br	-0.023383	-0.876874	2.806799
N	-0.000288	1.760063	0.548796
C	1.521994	3.602831	1.086802
H	2.009924	3.021292	1.877713
H	2.075853	3.449972	0.154332
H	1.583307	4.665289	1.355091
C	0.049332	3.177717	0.924750
C	-0.618735	4.016250	-0.183033
H	-1.674646	3.742526	-0.286772
H	-0.562354	5.084626	0.062967
H	-0.127876	3.848592	-1.147340
P	-3.926512	-0.033510	-0.014435
O	-2.402807	-0.020270	-0.013209
C	-4.144498	-0.459572	-4.068819
H	-3.445240	-0.678840	-4.870328
C	-4.532604	-1.467534	0.931509
C	-5.918828	0.171477	-2.003266
H	-6.606626	0.455168	-1.210841
C	-3.679692	-0.398683	-2.753654
H	-2.625182	-0.545766	-2.543326
C	-4.569491	-0.093780	-1.713447
C	-5.490902	-0.223710	-4.349963
H	-5.848625	-0.271675	-5.375129
C	-5.748768	-2.107409	0.646470
H	-6.362537	-1.778501	-0.186241
C	-6.165035	-3.189790	1.421087
H	-7.104068	-3.686071	1.191524
C	-6.377706	0.095234	-3.317417
H	-7.422117	0.299521	-3.536982
C	-3.735040	-1.927132	1.992458
H	-2.777263	-1.459652	2.206454
C	-4.159826	-3.010707	2.763508
H	-3.532445	-3.362064	3.577661
C	-4.635472	1.465812	0.743997
C	-4.542437	2.682860	0.046849
H	-4.090288	2.710749	-0.940738
C	-5.027423	3.857221	0.619570
H	-4.950004	4.794463	0.075681
C	-5.219442	1.443863	2.018974

H	-5.292203	0.510365	2.567706
C	-5.609769	3.827357	1.889731
H	-5.988887	4.743751	2.334207
C	-5.703734	2.622683	2.588159
H	-6.152545	2.598175	3.577322
C	-5.372943	-3.640561	2.480076
H	-5.698230	-4.487890	3.078068
C	-0.702588	3.357188	2.258084
H	-0.231900	2.768770	3.053167
H	-0.702488	4.413896	2.556860
H	-1.741722	3.024952	2.160907

Table 11S. Geometry Optimization for $UO_2Br_2(OPPh_3)_2$.

U	0.00005200	-0.00216700	0.00048700
Br	0.28393600	2.87201000	-0.06749400
P	3.85127500	-0.06744100	0.00490000
O	2.32999900	-0.23585400	0.02979300
C	4.41555800	-4.09948800	0.23608300
H	3.80525900	-4.96222000	0.48624600
C	4.43840100	0.82596600	1.47308600
C	5.96817400	-1.87574700	-0.44443400
H	6.56826000	-1.01824400	-0.73675400
C	3.84818800	-2.82465400	0.27700400
H	2.80229200	-2.70122200	0.54234300
C	4.62836900	-1.70760200	-0.05900100
C	5.75194600	-4.26343300	-0.13226000
H	6.18855600	-5.25806800	-0.16382800
C	5.48570000	0.35261600	2.27655000
H	5.98127400	-0.58270000	2.03610000
C	5.88520800	1.08092200	3.39865600
H	6.69494700	0.71001500	4.02083100
C	6.52808700	-3.15216900	-0.47386800
H	7.56429000	-3.28030700	-0.77422400
C	3.78694400	2.02790400	1.80386000
H	2.96085200	2.39325700	1.19832700
C	4.18916800	2.74403000	2.92976400
H	3.67714600	3.66663500	3.18684500
C	4.36352100	0.87768000	-1.45834600
C	3.55432400	0.82542100	-2.60440100
H	2.62292300	0.26768300	-2.59053000
C	3.93695800	1.51981900	-3.75194500
H	3.30257300	1.48815500	-4.63284800
C	5.54643500	1.63239800	-1.46863800
H	6.15932800	1.70316800	-0.57426600
C	5.12123000	2.26013700	-3.76425500
H	5.41285100	2.80220400	-4.65976200
C	5.92496000	2.31755100	-2.62338400
H	6.83851400	2.90553300	-2.62705700
C	5.23821200	2.27399800	3.72474400
H	5.54732700	2.83544200	4.60238100
Br	-0.28223300	-2.87654000	0.06865400
P	-3.85155600	0.06822100	-0.00561500
O	-2.32983800	0.23222600	-0.03087400
C	-4.40704300	4.10046300	-0.25362100
H	-3.79540500	4.96064200	-0.50923300
C	-4.43982200	-0.82840800	-1.47138000
C	-5.96297900	1.88348000	0.44136800

H	-6.56411300	1.02873400	0.73951400
C	-3.84279900	2.82414200	-0.29032100
H	-2.79793800	2.69695700	-0.55790800
C	-4.62466300	1.71047100	0.05296300
C	-5.74204800	4.26919500	0.11762300
H	-6.17622400	5.26499400	0.14590200
C	-5.49420400	-0.36201700	-2.26961600
H	-5.99389600	0.57070200	-2.02750600
C	-5.89518900	-1.09365200	-3.38902700
H	-6.71036200	-0.72814600	-4.00729400
C	-6.51984300	3.16134900	0.46643000
H	-7.55489900	3.29331600	0.76907300
C	-3.78267500	-2.02651600	-1.80470600
H	-2.95108700	-2.38607300	-1.20323800
C	-4.18648800	-2.74598700	-2.92791600
H	-3.67016700	-3.66562300	-3.18702100
C	-4.36685300	-0.87083300	1.46050500
C	-3.55870600	-0.81579700	2.60719100
H	-2.62648100	-0.25945600	2.59235300
C	-3.94341700	-1.50577500	3.75669500
H	-3.30988700	-1.47197000	4.63813500
C	-5.55071000	-1.62403100	1.47212600
H	-6.16271600	-1.69713700	0.57734000
C	-5.12870900	-2.24446000	3.77032700
H	-5.42194900	-2.78307900	4.66738400
C	-5.93132400	-2.30473200	2.62883200
H	-6.84562100	-2.89155200	2.63354600
C	-5.24264900	-2.28304600	-3.71759800
H	-5.55298900	-2.84704400	-4.59316500
O	0.04323300	-0.04670300	-1.77371900
O	-0.04344100	0.04238800	1.77468000

Table 12S. Geometry Optimization for $U(N^tBu)_2(I)_2(OPPh_3)_2$.

U	0.000100	0.002426	-0.001113
I	0.038033	-3.167681	-0.159204
P	-3.923485	-0.010831	-0.049313
O	-2.397955	0.002546	-0.105908
C	-4.590575	1.294917	-1.129512
C	-4.556344	0.293869	1.633067
C	-4.561888	-0.754517	2.569636
H	-4.251573	-1.752003	2.272876
C	-4.592721	-1.616537	-0.574188
C	-5.366404	0.762478	4.272540
H	-5.680578	0.944511	5.296688
C	-5.912644	-1.999934	-0.279215
H	-6.553308	-1.354403	0.315290
C	-4.957411	1.577675	2.032066
H	-4.952889	2.395829	1.318975
C	-3.797341	2.431580	-1.356728
H	-2.803893	2.506714	-0.921919
C	-4.255598	-3.710446	-1.743263
H	-3.599787	-4.381099	-2.290177
C	-5.553090	3.377093	-2.730254
H	-5.927212	4.184861	-3.353638
C	-5.863295	1.203984	-1.714241
H	-6.475992	0.320508	-1.564310
C	-3.763759	-2.479964	-1.304466
H	-2.731167	-2.209135	-1.495571
C	-5.571623	-4.080511	-1.463542
H	-5.950896	-5.039731	-1.805539
C	-4.967008	-0.518649	3.882613
H	-4.968117	-1.333849	4.600554
C	-4.284404	3.468590	-2.154755
H	-3.663938	4.343625	-2.325154
C	-6.399904	-3.226056	-0.729940
H	-7.419792	-3.519727	-0.497466
C	-5.359670	1.808597	3.348378
H	-5.666484	2.806082	3.649644
C	-6.340517	2.243708	-2.511675
H	-7.323548	2.165042	-2.967745
N	-0.054578	-0.071462	1.836379
C	-0.055815	-0.152006	3.304292
C	-0.675788	-1.496785	3.725977
H	-0.135878	-2.333829	3.273503
H	-1.720563	-1.555171	3.405093
H	-0.643138	-1.601003	4.818057
C	1.398143	-0.062131	3.804516

H	2.001644	-0.877164	3.393096
H	1.428223	-0.126742	4.899440
H	1.851647	0.888463	3.505003
C	-0.881776	1.020879	3.862888
H	-0.900659	0.979672	4.959554
H	-1.912367	0.976069	3.496967
H	-0.452963	1.979260	3.554659
I	-0.037131	3.172567	0.156935
P	3.923711	0.008212	0.049920
O	2.398032	-0.001304	0.104391
C	4.586147	-1.288660	1.143598
C	4.558297	-0.314192	-1.628461
C	4.569766	0.725555	-2.574526
H	4.263387	1.727037	-2.287328
C	4.595723	1.617348	0.560567
C	5.370266	-0.810277	-4.262349
H	5.685182	-1.002971	-5.284316
C	5.916879	1.995216	0.263894
H	6.557060	1.342847	-0.323623
C	4.954437	-1.603300	-2.015172
H	4.945284	-2.414945	-1.294739
C	3.790452	-2.421868	1.379496
H	2.797808	-2.499307	0.943194
C	4.261472	3.722600	1.709919
H	3.606351	4.399595	2.249798
C	5.541818	-3.357954	2.765044
H	5.913287	-4.160701	3.396448
C	5.857864	-1.194680	1.730005
H	6.472439	-0.313693	1.573275
C	3.767634	2.489163	1.281823
H	2.734254	2.222236	1.474175
C	5.578639	4.087323	1.428545
H	5.959484	5.048853	1.762206
C	4.975844	0.476038	-3.884687
H	4.981573	1.284677	-4.609985
C	4.274136	-3.452467	2.187824
H	3.651873	-4.324924	2.364761
C	6.406099	3.224416	0.703972
H	7.426924	3.513792	0.470222
C	5.357642	-1.847904	-3.328718
H	5.660589	-2.849400	-3.620433
C	6.331654	-2.227953	2.537803
H	7.313911	-2.146865	2.995114
N	0.054034	0.076142	-1.838648
C	0.054239	0.158631	-3.306467
C	0.705107	1.488993	-3.727345

H	0.186440	2.337721	-3.271682
H	1.751831	1.521553	-3.409257
H	0.672097	1.596217	-4.819117
C	-1.402441	0.104262	-3.803922
H	-1.985319	0.933373	-3.390906
H	-1.432996	0.170256	-4.898752
H	-1.878419	-0.835197	-3.504093
C	0.851132	-1.032579	-3.868482
H	0.868879	-0.989962	-4.965117
H	1.883192	-1.012680	-3.504459
H	0.400651	-1.981162	-3.560992

Table 13S. Geometry Optimization for $UO_2I_2(OPPh_3)_2$.

U	-0.00009100	0.00149000	0.00004500
I	0.02719500	-3.10478100	-0.02076300
P	-3.85600400	-0.00755500	-0.02294800
O	-2.33380000	-0.00564400	-0.20941000
C	-4.62367900	1.14789400	-1.19603600
C	-4.32016200	0.49077900	1.66072100
C	-3.50758900	0.07493100	2.72889200
H	-2.60358900	-0.49546300	2.54181300
C	-4.52613800	-1.66693900	-0.32629200
C	-4.99660400	1.18261300	4.28275700
H	-5.25669200	1.45542200	5.30192800
C	-5.69564700	-2.11470100	0.30822800
H	-6.20349200	-1.48302400	1.03141900
C	-5.46704300	1.25909900	1.91215100
H	-6.08689500	1.60359500	1.08973100
C	-3.91696500	2.31191200	-1.54109700
H	-2.92624100	2.49508700	-1.13411500
C	-4.36071900	-3.77606100	-1.50233600
H	-3.82936400	-4.42687900	-2.19015200
C	-5.75053300	2.99062800	-2.96852000
H	-6.18736600	3.70562400	-3.66055800
C	-5.89199400	0.90821600	-1.74707100
H	-6.43281200	-0.00152300	-1.50318800
C	-3.85633500	-2.50420500	-1.23203600
H	-2.93493700	-2.17463700	-1.70036700
C	-5.53135500	-4.21423300	-0.87978900
H	-5.91867500	-5.20731300	-1.09082800
C	-3.84902600	0.42562100	4.03456100
H	-3.21206300	0.11184300	4.85626700
C	-4.48438400	3.22676500	-2.42784500
H	-3.93109800	4.12165700	-2.69713900
C	-6.19823700	-3.38479100	0.02495000
H	-7.10134700	-3.72999000	0.52041300
C	-5.80464300	1.59875000	3.22288600
H	-6.69098300	2.19752400	3.41291800
C	-6.45351100	1.83247800	-2.62876500
H	-7.43334500	1.64172100	-3.05763000
I	-0.02692600	3.10792600	0.02140000
P	3.85583900	0.00659800	0.02268200
O	2.33359100	0.00734100	0.20893200
C	4.62219400	-1.14369700	1.20168100
C	4.31952600	-0.50091500	-1.65835100
C	3.50571100	-0.09234500	-2.72838900
H	2.60086900	0.47758900	-2.54401100

C	4.52784000	1.66676400	0.31756700
C	4.99576400	-1.20627600	-4.27681400
H	5.25577900	-1.48433000	-5.29458600
C	5.69719700	2.11052600	-0.32006600
H	6.20392200	1.47505200	-1.04070300
C	5.46745300	-1.26887000	-1.90605900
H	6.08817700	-1.60794700	-1.08202900
C	3.91540300	-2.30637900	1.55111200
H	2.92530000	-2.49206900	1.14373300
C	4.36508900	3.78168900	1.48356200
H	3.83478600	4.43622600	2.16865400
C	5.74756500	-2.97818700	2.98368700
H	6.18376900	-3.68997600	3.67941900
C	5.88984100	-0.90127700	1.75306700
H	6.43067900	0.00749800	1.50569000
C	3.85945400	2.50895700	1.21978400
H	2.93810300	2.18247700	1.69035300
C	5.53556200	4.21590700	0.85796200
H	5.92386100	5.20967600	1.06390200
C	3.84709800	-0.44975800	-4.03224800
H	3.20924600	-0.14160200	-4.85539200
C	4.48210700	-3.21707200	2.44259300
H	3.92881400	-4.11095100	2.71522800
C	6.20101700	3.38157000	-0.04332800
H	7.10398300	3.72365700	-0.54120700
C	5.80495600	-1.61528900	-3.21504900
H	6.69211300	-2.21376500	-3.40218300
C	6.45063600	-1.82141500	2.63953000
H	7.42994500	-1.62847500	3.06861200
O	-0.16887400	-0.01951600	1.76577400
O	0.16872000	0.02253800	-1.76573600

Table 14S. Comparison of selected experimental and theoretical U-X (X = halide) metrical parameters in complexes UO_2^{2+} complexes.

	Optimized Geometry					Experimental Geometry			
	F	Cl	Br	I		F	Cl	Br	I
U=O	1.792	1.776	1.775	1.773		1.772[a]	1.764	1.766[b]	1.760
U-X	2.168	2.693	2.889	3.106		2.338[a]	2.645	2.839[b]	3.0476
U-O(PPh_3)	2.405	2.352	2.341	2.343		2.375[a]	2.300	2.249[b]	2.298

[a] values obtained from $[\{UO_2(\mu\text{-}F)(OPPh_3)_3\}_2][BF_4]_2$

[b] values obtained from $UO_2Br_2(OAsPh_3)_2$

Table 15S. Comparison of selected experimental and theoretical U-X (X = halide) metrical parameters in complexes $U(N^tBu)_2^{2+}$ complexes.

	Optimized Geometry					Experimental Geometry			
	F	Cl	Br	I		F	Cl	Br	I
U=N	1.877	1.84	1.843	1.839		[c]	1.848	1.828	1.840
U-X	2.197	2.752	2.938	3.174		[c]	2.747	2.867	3.0880
U-O(PPh_3)	2.442	2.417	2.402	2.400		[c]	2.344	2.335	2.338

[c] experimental structure was not determined