Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Redox-enhanced hemilability of the tris(*tert*-butoxy)siloxy ligand at cerium

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Contents

1. ^{1}H NMR Spectra

(* solvent)

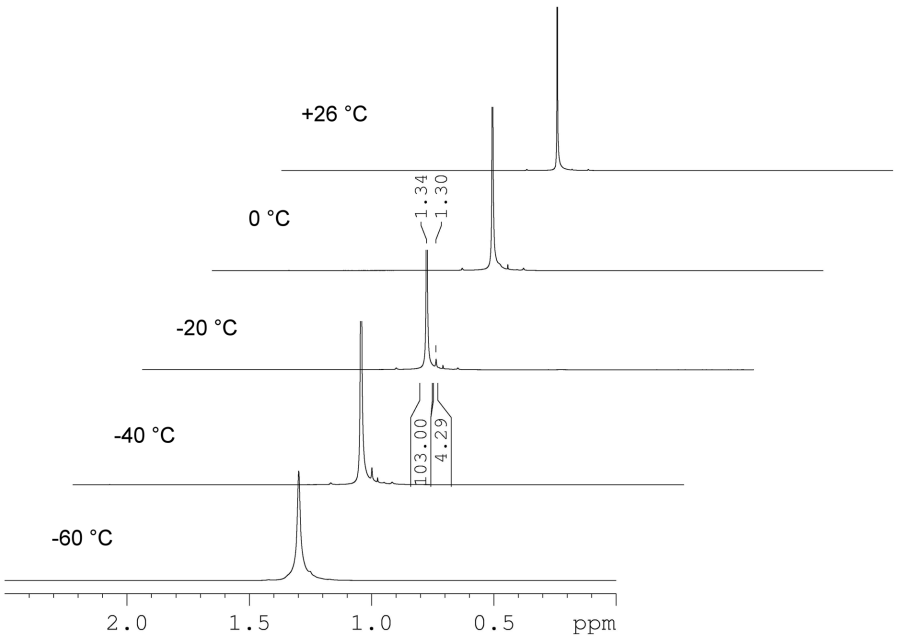

Figure S1. VT NMR spectra (500.13 MHz, CD_2Cl_2, TMS) of $Ce[OSi(O\mathit{t}Bu)_3]_4$ (**1**).

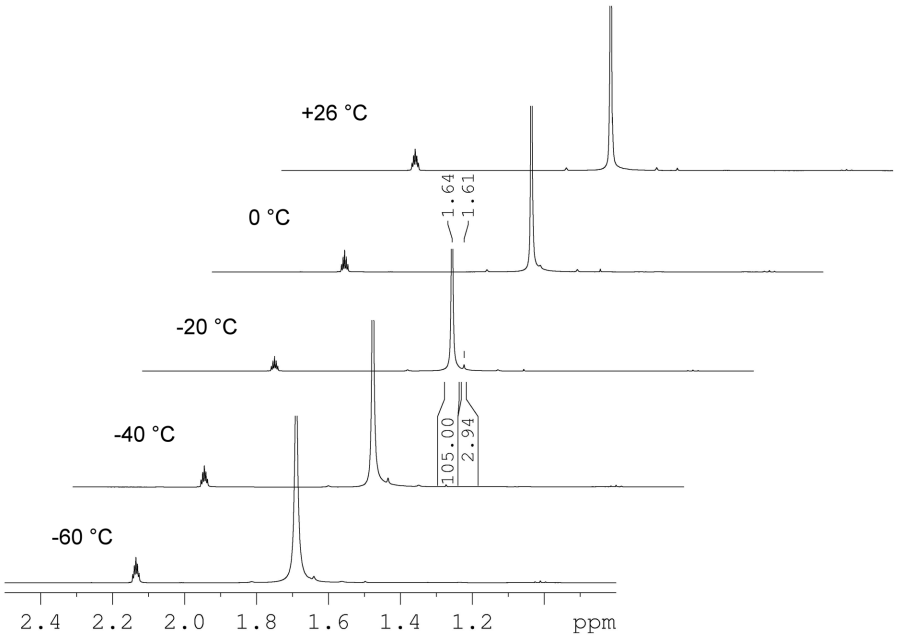

Figure S2. VT NMR spectra (500.13 MHz, [D8]Tol, TMS) of $Ce[OSi(O\mathit{t}Bu)_3]_4$ (**1**).

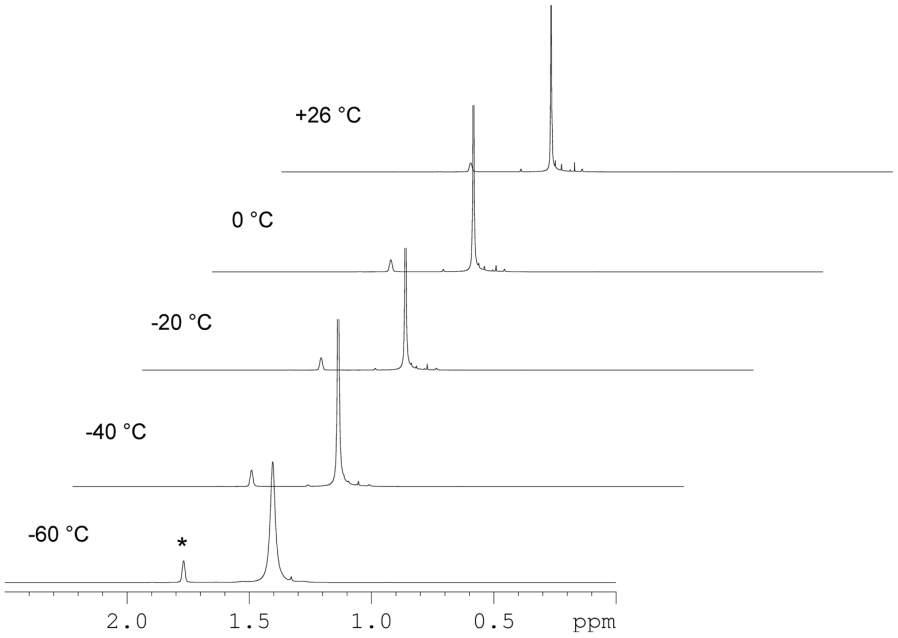

Figure S3. VT NMR spectra (500.13 MHz, [D8]THF, TMS) of Ce[OSi(O*t*Bu)$_3$]$_4$ (**1**).

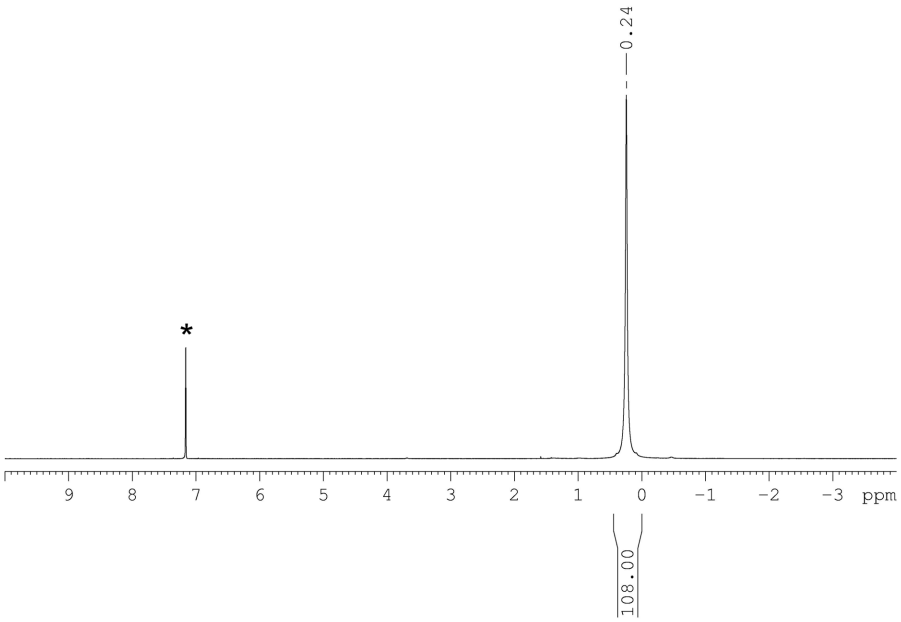

Figure S4. ^{1}H NMR spectrum (400.13 MHz, 26 °C, C_6D_6, TMS) of [Ce{OSi(O*t*Bu)$_3$}$_4$K] (**2**).

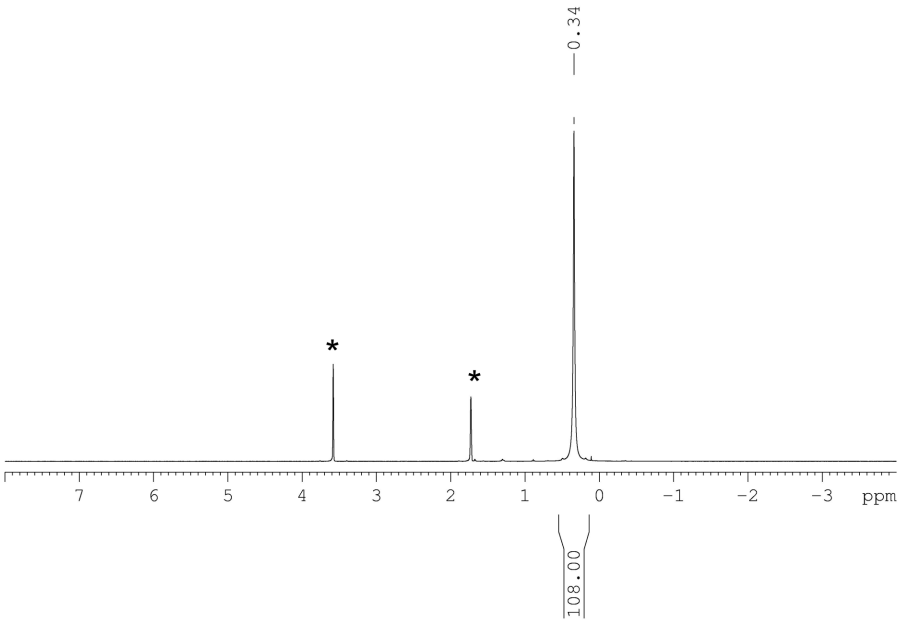

Figure S5. ^{1}H NMR spectrum (400.13 MHz, 26 °C, [D8]THF, TMS) of [Ce{OSi(O*t*Bu)$_3$}$_4$K] (**2**).

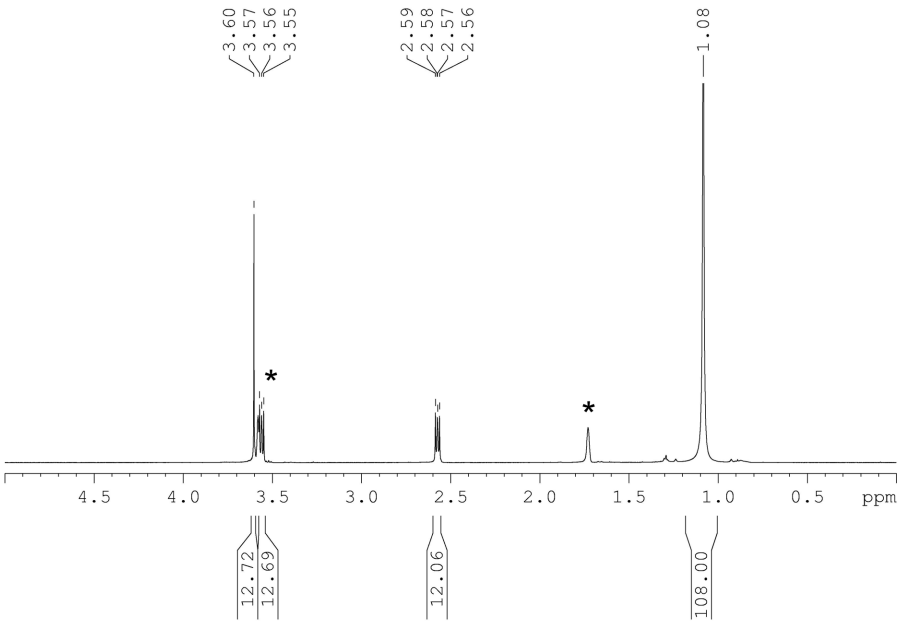

Figure S6. ^{1}H NMR spectrum (400.13 MHz, 26 °C, [D8]THF, TMS) of [Ce{OSi(O*t*Bu)$_3$}$_4$][K(2.2.2-crypt)] (**3**).

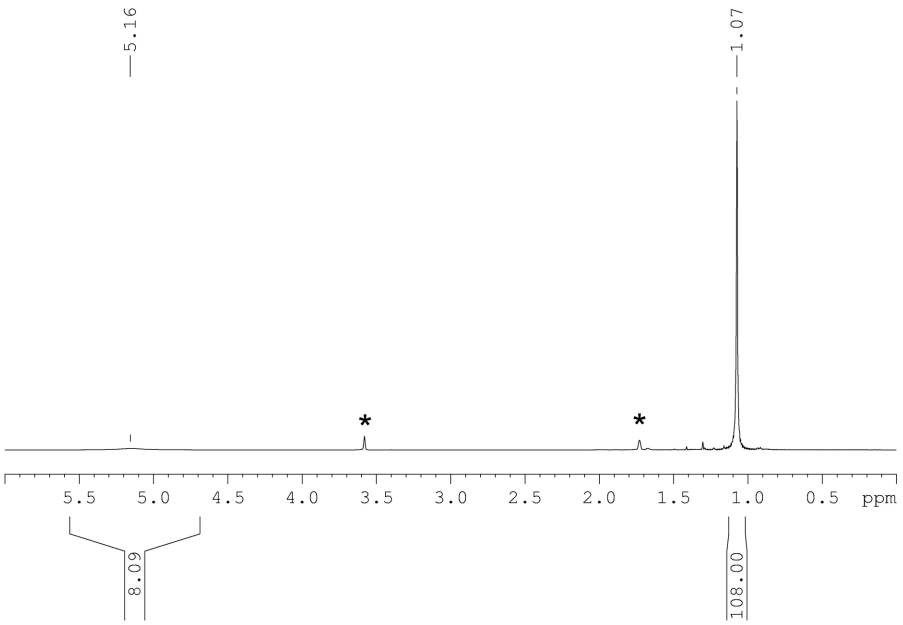

Figure S7. ^{1}H NMR spectrum (400.13 MHz, 26 °C, [D8]THF, TMS) of [Ce{OSi(O*t*Bu)$_3$}$_4$][CoCp$_2$] (**4**). No further resonances were observed in the range of 100 - (-100 ppm).

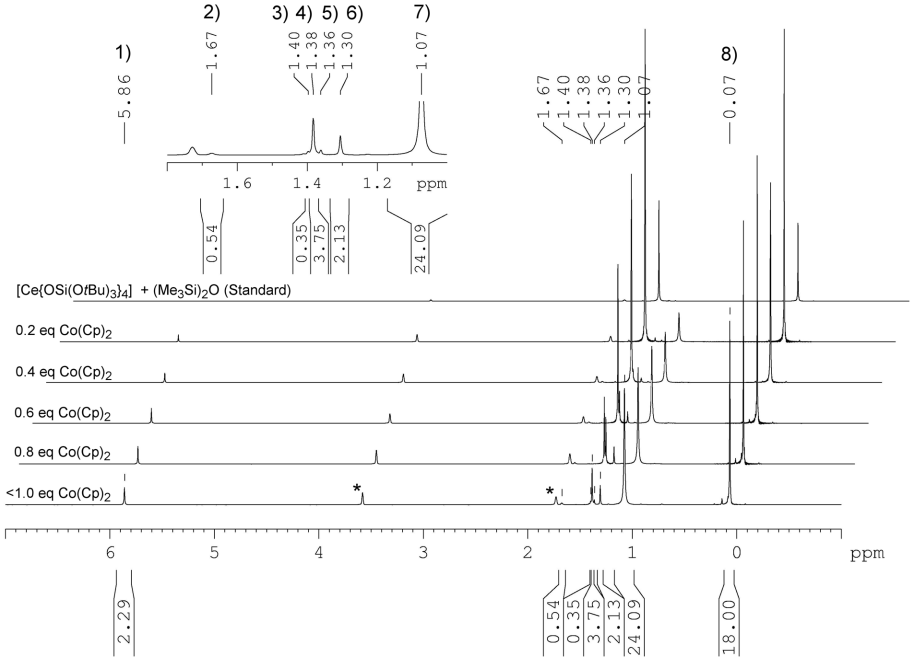

Figure S8. ^{1}H NMR spectra (400.13 MHz, 26 °C, [D8]THF, TMS) monitoring the ambient temperature reaction of [Ce{OSi(O*t*Bu)$_3$}$_4$] (**1**) and increasing equivalents of [CoCp$_2$]. Peak labelling/resonances of compounds: 1) [Co(Cp)$_2$]$^+$; 2) [Ce{OSi(O*t*Bu)$_3$}$_3$]$_2$; 3) Ce[OSi(O*t*Bu)$_3$]$_4$ (**1**); 4) & 5) unclearly assignable reaction product; 6) HOSiO*t*Bu$_3$; 7) [Ce{OSi(O*t*Bu)$_3$}$_4$]$^-$ (**4**$^-$); 8) internal standard (Me$_3$Si)$_2$O.

2. DRIFT Spectra

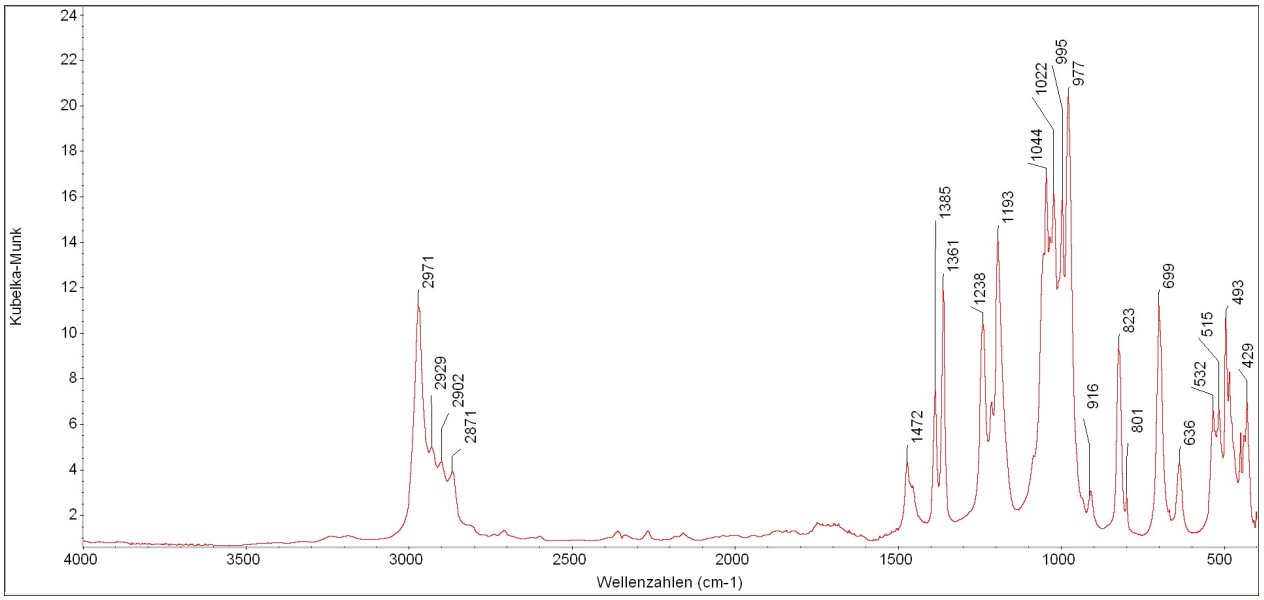

Figure S9. DRIFT spectrum of [Ce{OSi(O*t*Bu)$_3$}$_4$K] (**2**).

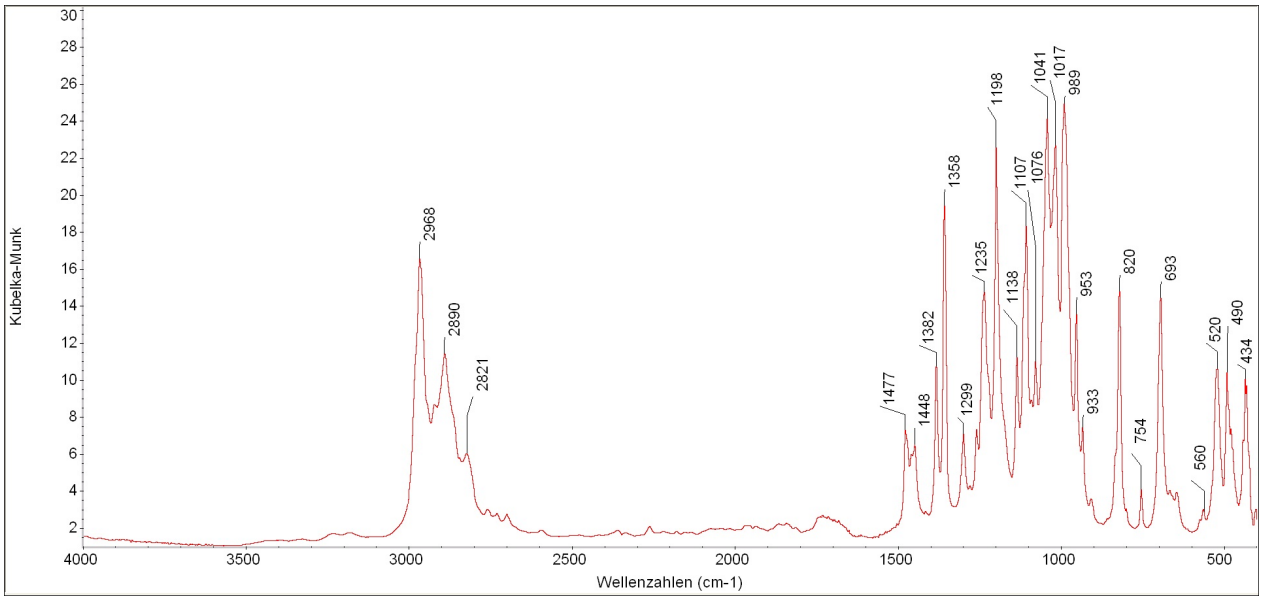

Figure S10. DRIFT spectrum of [Ce{OSi(O*t*Bu)$_3$}$_4$][K(2.2.2-crypt)] (**3**).

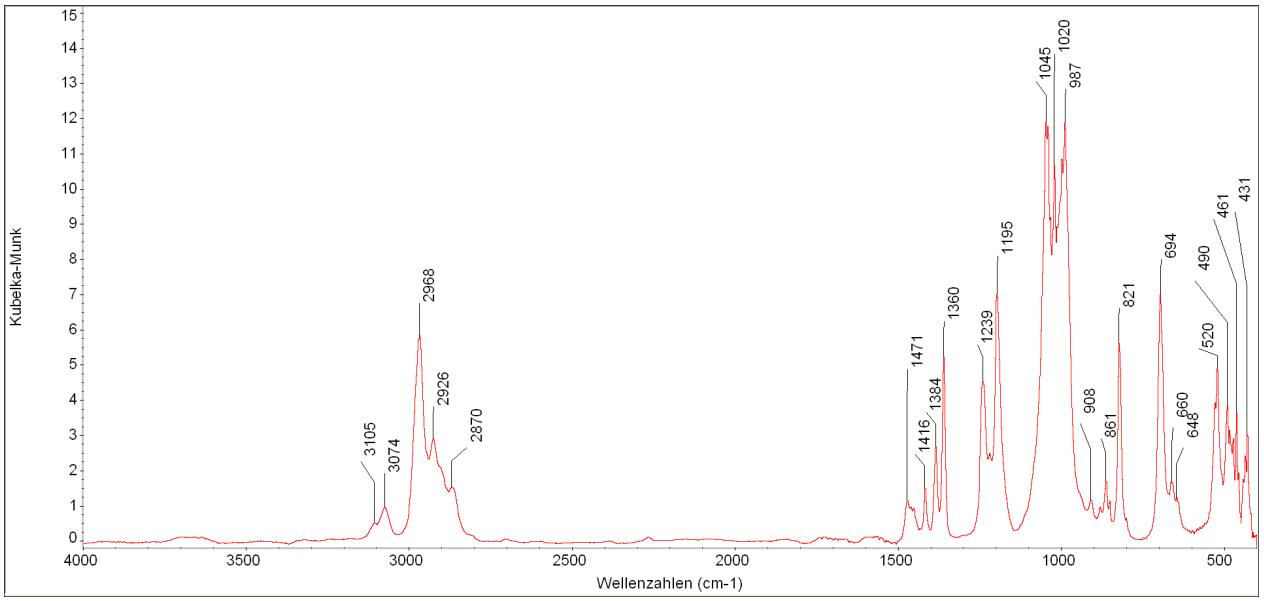

Figure S11. DRIFT spectrum of [Ce{OSi(O*t*Bu)$_3$}$_4$][CoCp$_2$] (**4**).

3. Electrochemical Studies

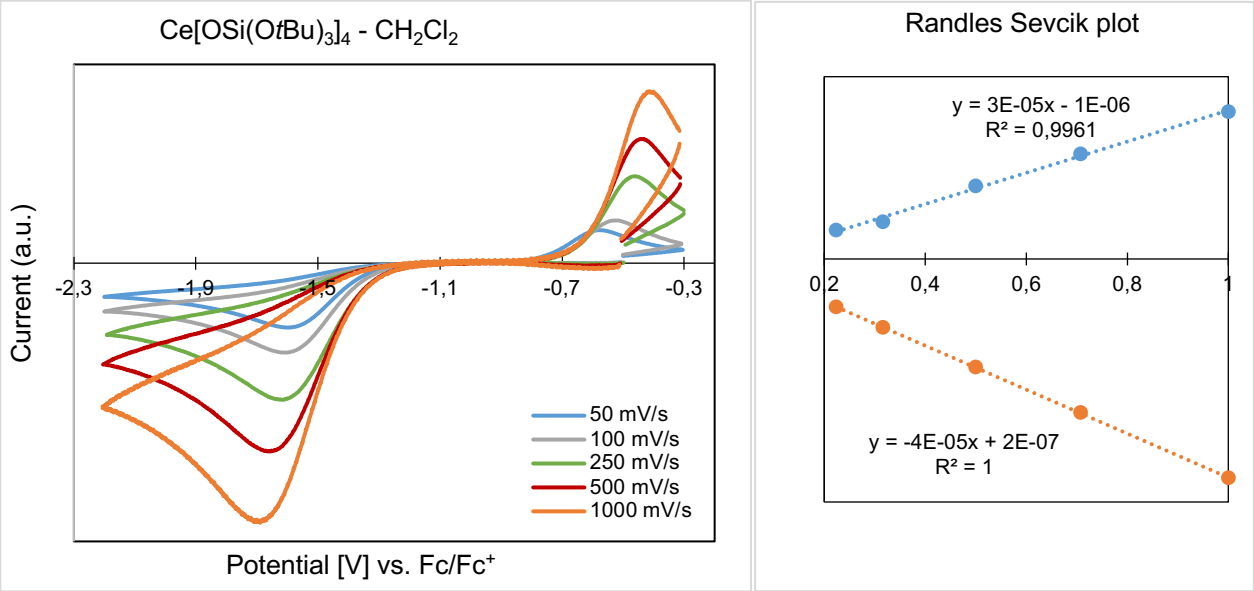

Figure S12. Left: cerium(III/IV) redox couple of complex **1** in CH_2Cl_2 at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S1. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S12) of complex **1** in CH_2Cl_2 at ambient temperature

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pa}/i_{pc}
50	-1.60	-0.58	1.02	0.51
100	-1.61	-0.53	1.08	0.48
250	-1.61	-0.46	1.15	0.63
500	-1.65	-0.43	1.22	0.66
1000	-1.69	-0.41	1.28	0.66

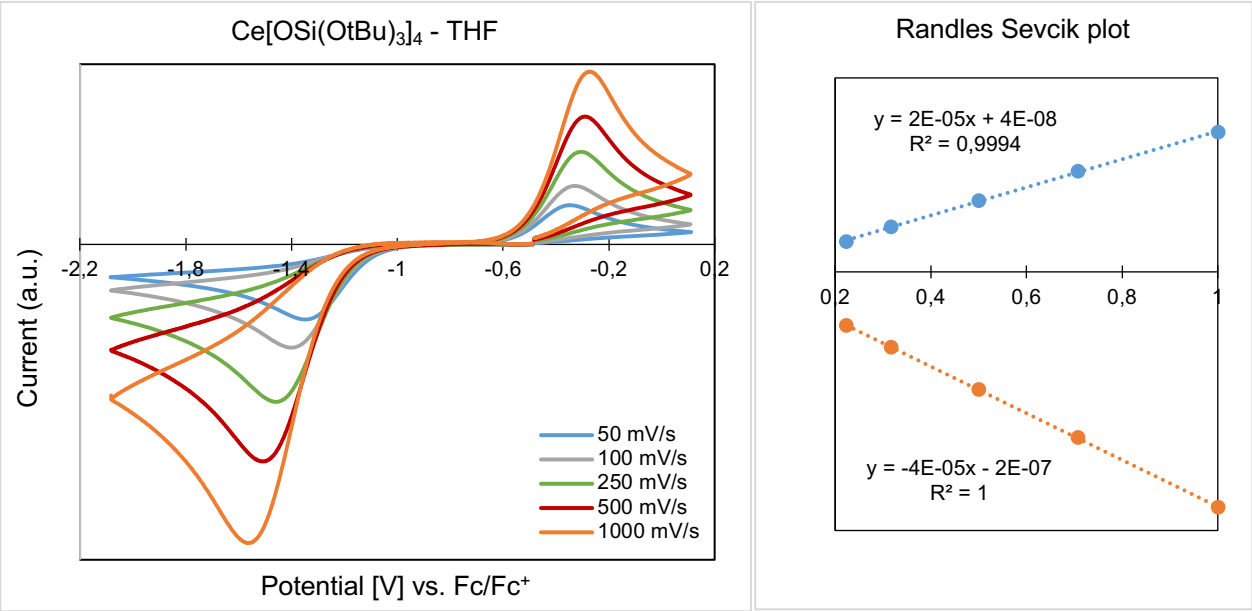

Figure S13. Left: cerium(III/IV) redox couple of complex **1** in THF at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S2. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S13) of complex **1** in THF at ambient temperature

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pa}/i_{pc}
50	-1.35	-0.35	1.00	0.52
100	-1.40	-0.33	1.07	0.56
250	-1.46	-0.31	1.15	0.59
500	-1.51	-0.29	1.22	0.59
1000	-1.57	-0.27	1.23	0.58

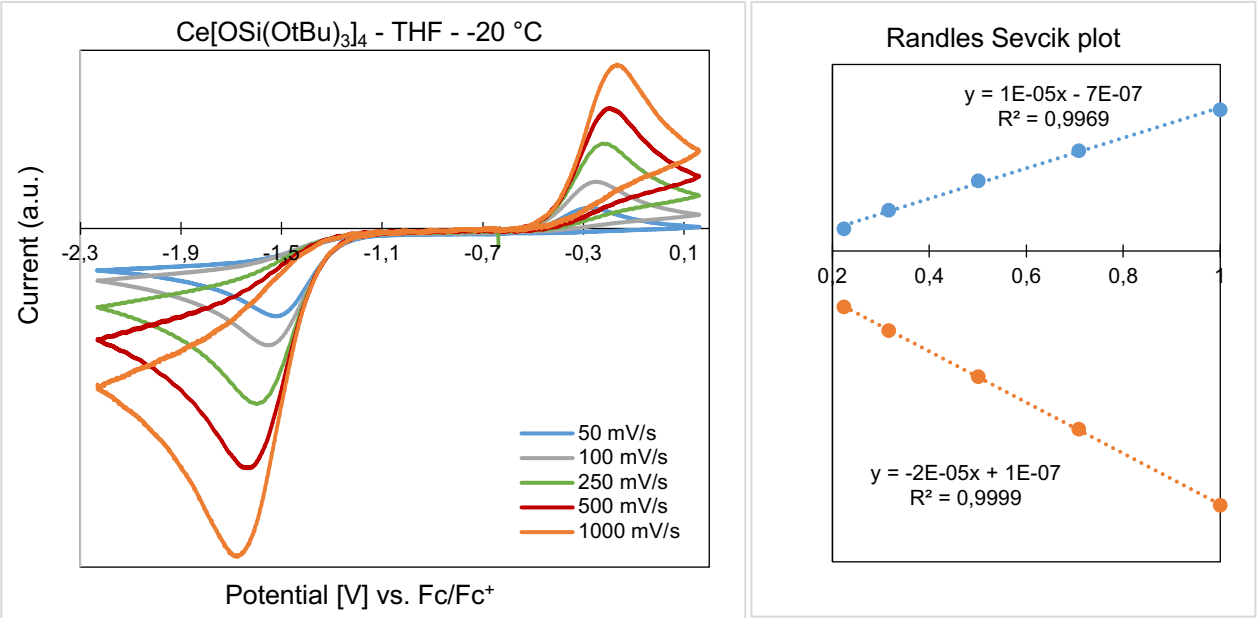

Figure S14. Left: cerium(III/IV) redox couple of complex **1** in THF at -20 °C and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S3. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S14) of complex **1** in THF at -20 °C

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pa}/i_{pc}
50	-1.52	-0.27	1.25	0.24
100	-1.55	-0.25	1.30	0.40
250	-1.60	-0.23	1.37	0.48
500	-1.64	-0.20	1.44	0.50
1000	-1.68	-0.17	1.51	0.50

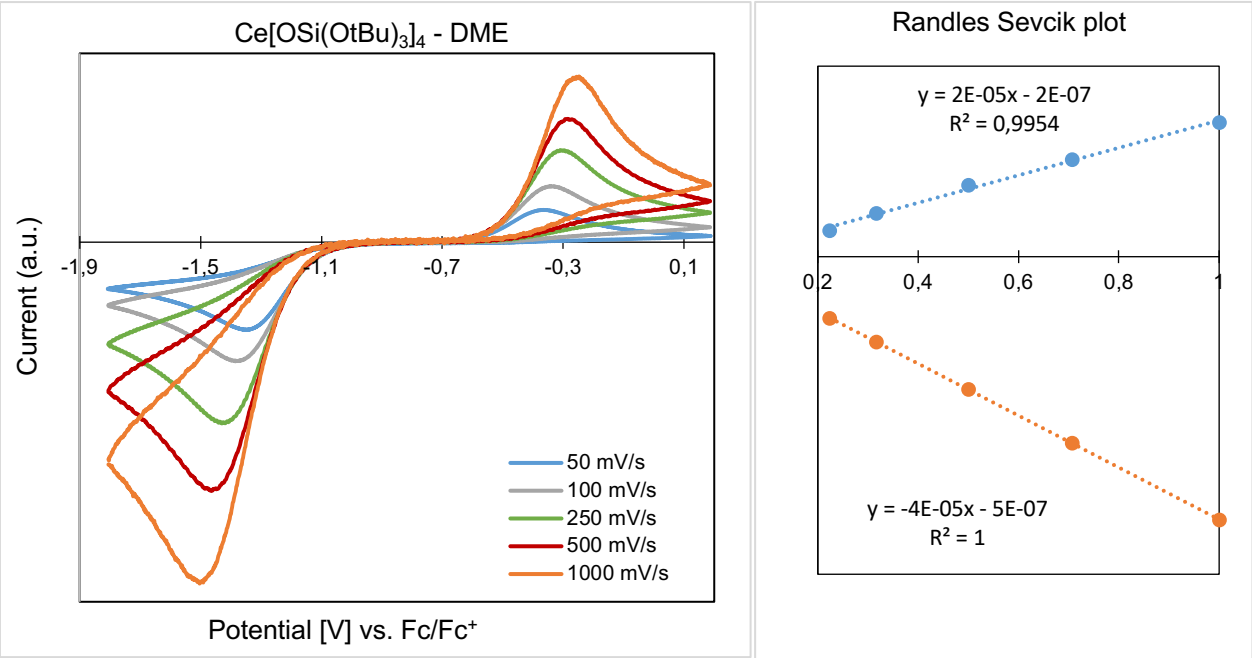

Figure S15. Left: cerium(III/IV) redox couple of complex **1** in DME at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S4. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S15) of complex **1** in DME at ambient temperature

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pa}/i_{pc}
50	-1.35	-0.37	0.99	0.37
100	-1.39	-0.34	1.04	0.47
250	-1.43	-0.31	1.12	0.51
500	-1.46	-0.28	1.18	0.50
1000	-1.50	-0.25	1.26	0.48

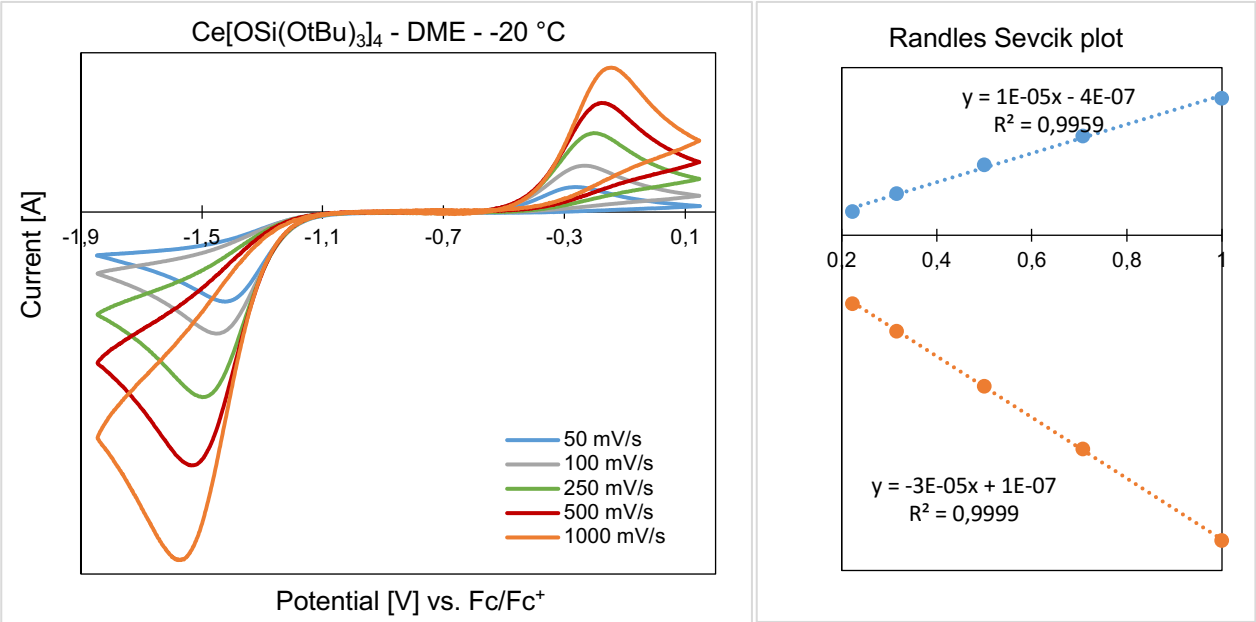

Figure S16. Left: cerium(III/IV) redox couple of complex **1** in DME at -20 °C and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S5. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S16) of complex **1** in DME at -20 °C

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pa}/i_{pc}
50	-1.42	-0.27	1.16	0.28
100	-1.45	-0.24	1.22	0.38
250	-1.50	-0.20	1.30	0.43
500	-1.53	-0.18	1.36	0.43
1000	-1.58	-0.14	1.44	0.42

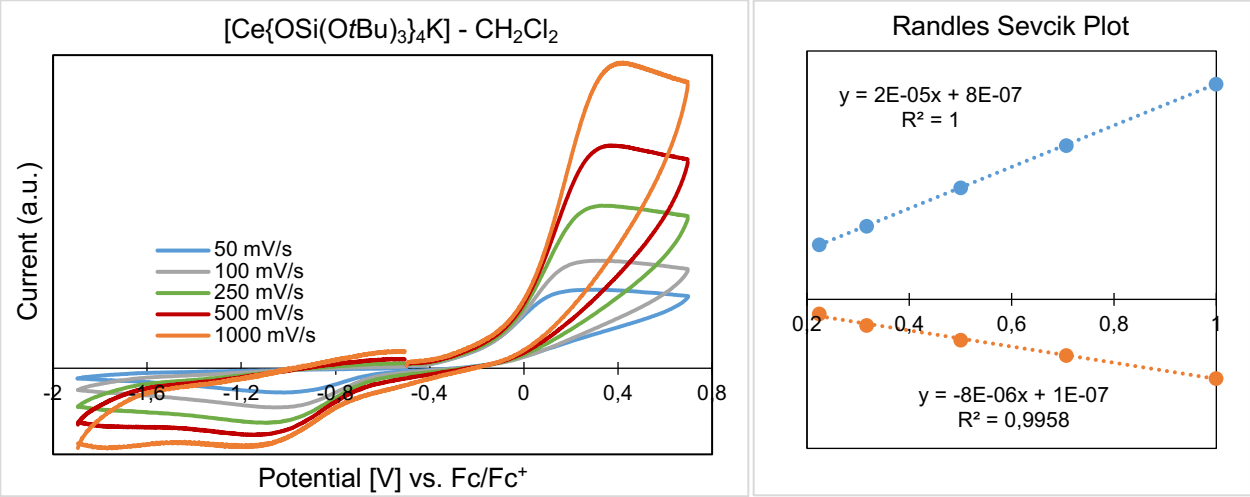

Figure S17. Left: cerium(III/IV) redox couple of complex **2** in CH_2Cl_2 at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S6. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S17) of complex **2** in CH_2Cl_2 at ambient temperature

[mV/s]	E_{pc2} [V]	E_{pc1} [V]	E_{pa} [V]	$\Delta E_{pc1}/E_{pa}$ [V]	$\Delta E_{pc2}/E_{pa}$ [V]	i_{pc1}/i_{pa}
50	-	-1.03	0.28	1.31	-	0.31
100	-	-1.07	0.31	1.38	-	0.36
250	-	-1.09	0.33	1.42	-	0.34
500	-	-1.13	0.37	1.51	-	0.30
1000	-1.77	-1.18	0.42	1.60	2.19	0.26

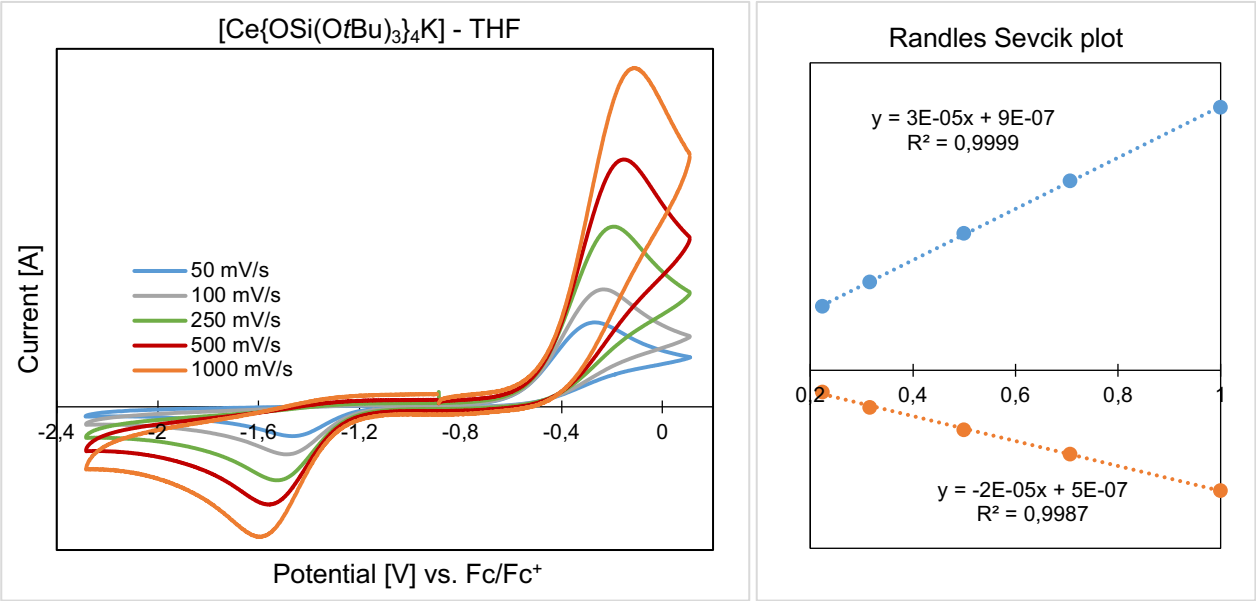

Figure S18. Left: cerium(III/IV) redox couple of complex **2** in THF at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S7. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S18) of complex **2** in THF at ambient temperature

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pc}/i_{pa}
50	-1.47	-0.27	1.20	0.35
100	-1.49	-0.24	1.25	0.40
250	-1.53	-0.20	1.34	0.41
500	-1.55	-0.16	1.40	0.40
1000	-1.59	-0.11	1.48	0.38

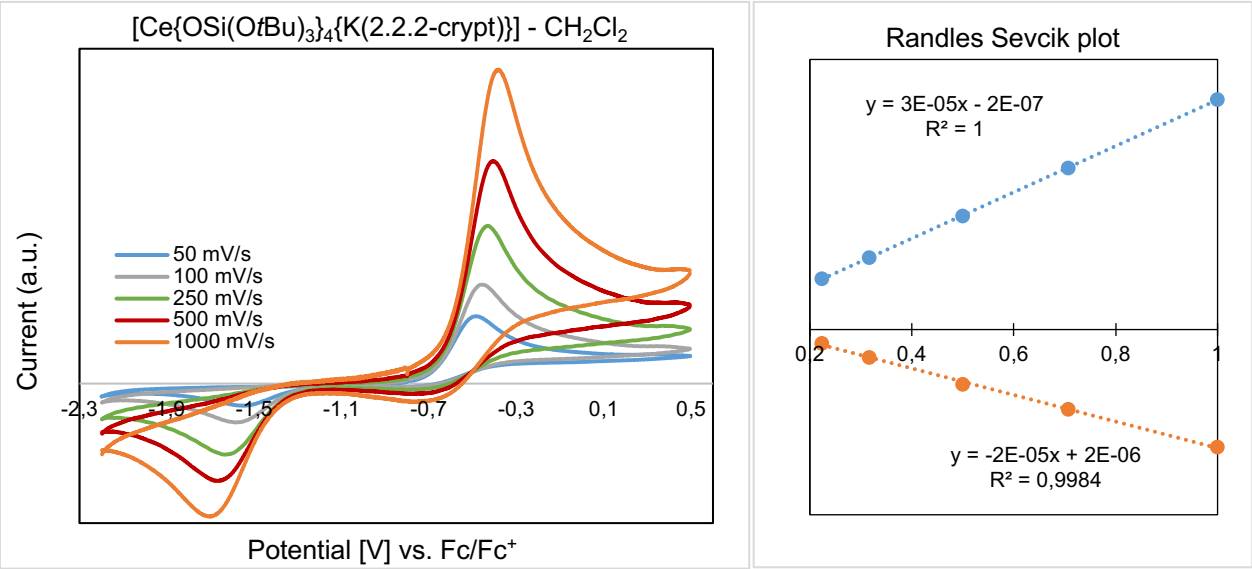

Figure S19. Left: cerium(III/IV) redox couple of complex **3** in CH_2Cl_2 at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S8. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S19) of complex **3** in CH_2Cl_2 at ambient temperature

[mV/s]	E_{pc} [V]	E_{pa1} [V]	E_{pa2} [V]	$\Delta E_{pc}/E_{pa1}$ [V]	$\Delta E_{pc}/E_{pa2}$ [V]	i_{pc}/i_{pa1}
50	-1.55	-0.49	0.31	-1.07	1.86	0.33
100	-1.59	-0.45	0.34	-1.14	1.93	0.39
250	-1.64	-0.43	0.38	-1.20	2.02	0.45
500	-1.68	-0.41	0.42	-1.27	2.10	0.44
1000	-1.70	-0.38	0.46	-1.32	2.16	0.42

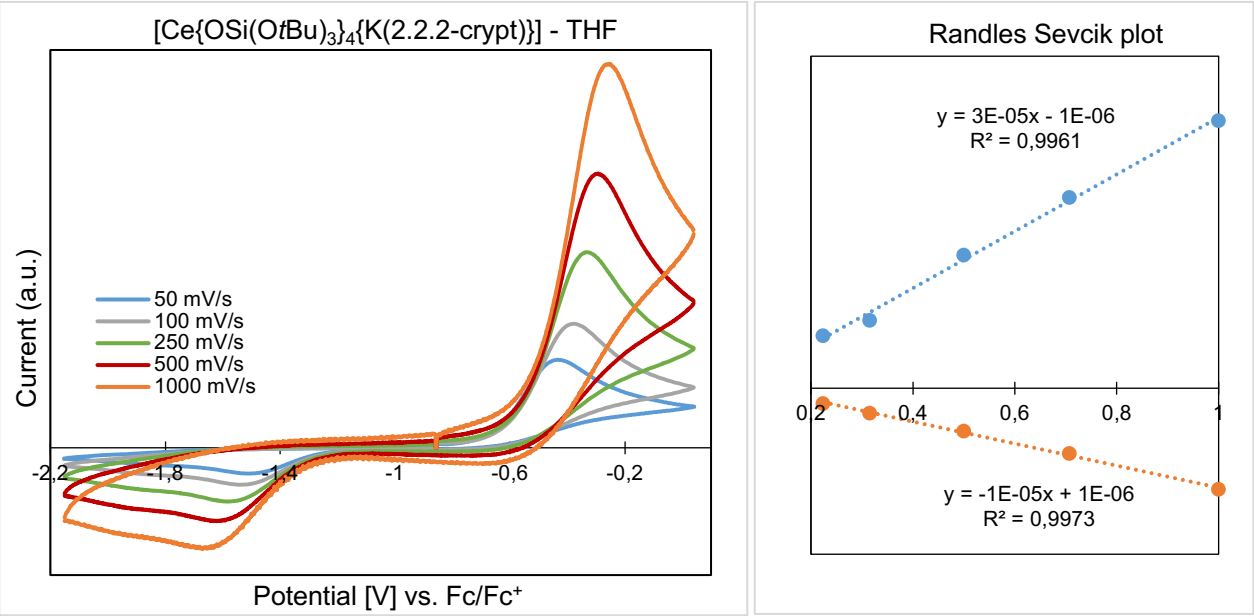

Figure S20. Left: cerium(III/IV) redox couple of complex **3** in THF at ambient temperature and varying scan rates; right: corresponding Randles Sevcik plot of the anodic (blue) and cathodic (orange) redox features.

Table S9. Electrochemical data for the redox couples vs Fc/Fc^+ (Figure S20) of complex **3** in THF at ambient temperature.

[mV/s]	E_{pc} [V]	E_{pa} [V]	$\Delta E_{pc}/E_{pa}$ [V]	i_{pa}/i_{pc}
50	-1.51	-0.43	1.08	0.29
100	-1.54	-0.38	1.16	0.30
250	-1.58	-0.33	1.25	0.28
500	-1.62	-0.29	1.33	0.27
1000	-1.67	-0.25	1.42	0.26

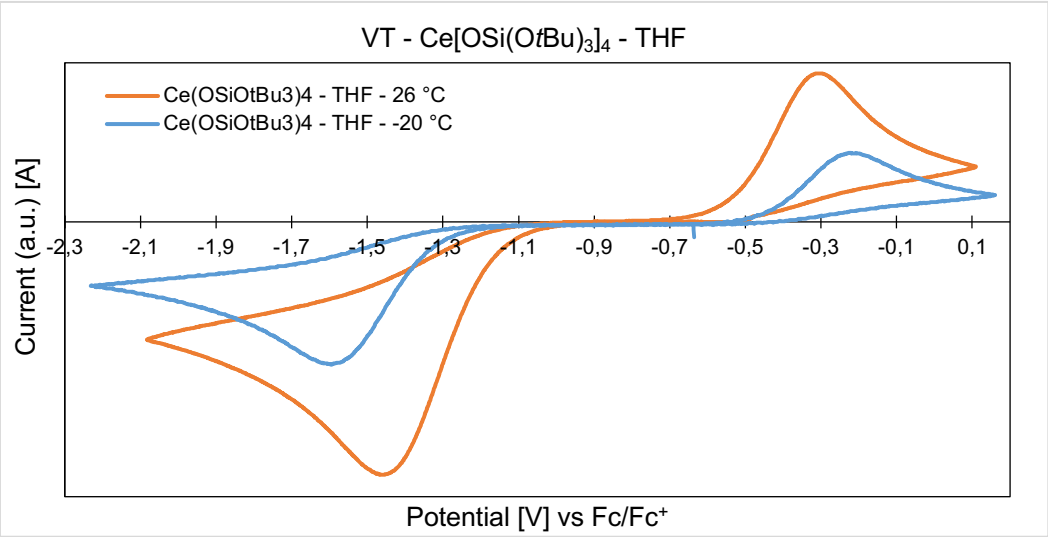

Figure S21. Cerium(III/IV) redox couples (250 mV/s) of complex **1** in THF at 26 °C (orange trace) and -20 °C (blue trace). Arrows indicate the shifts of changing redox features at lower temperature.

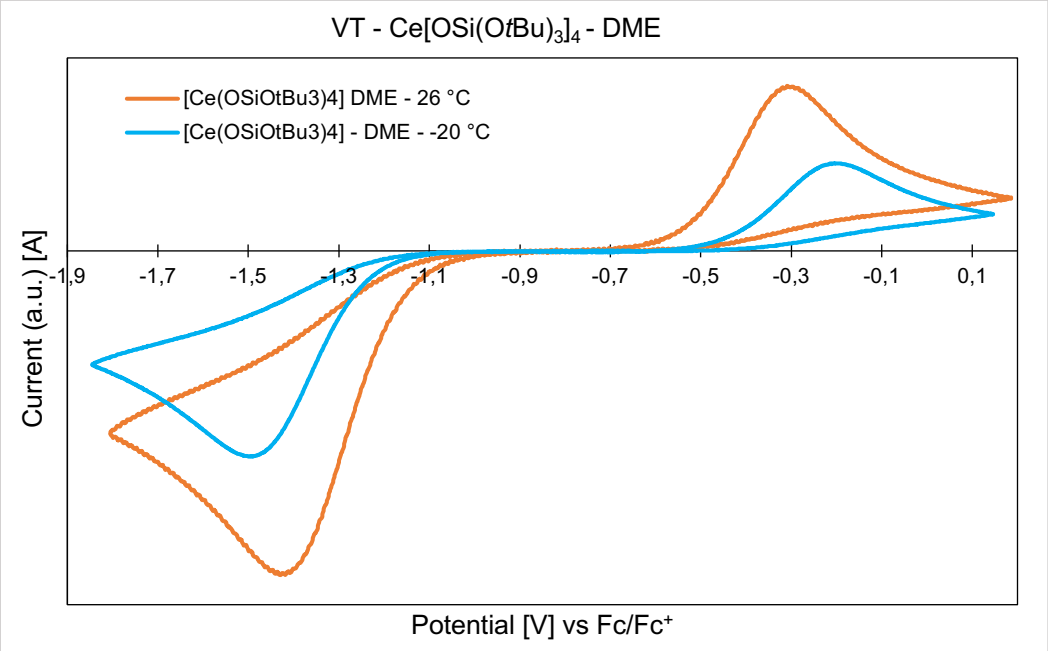

Figure S22. Cerium(III/IV) redox couples (250 mV/s) of complex **1** in DME at 26 °C (orange trace) and -20 °C (blue trace). Arrows indicate the shifts of changing redox features at lower temperature.

4. Drawings of Molecular Structures

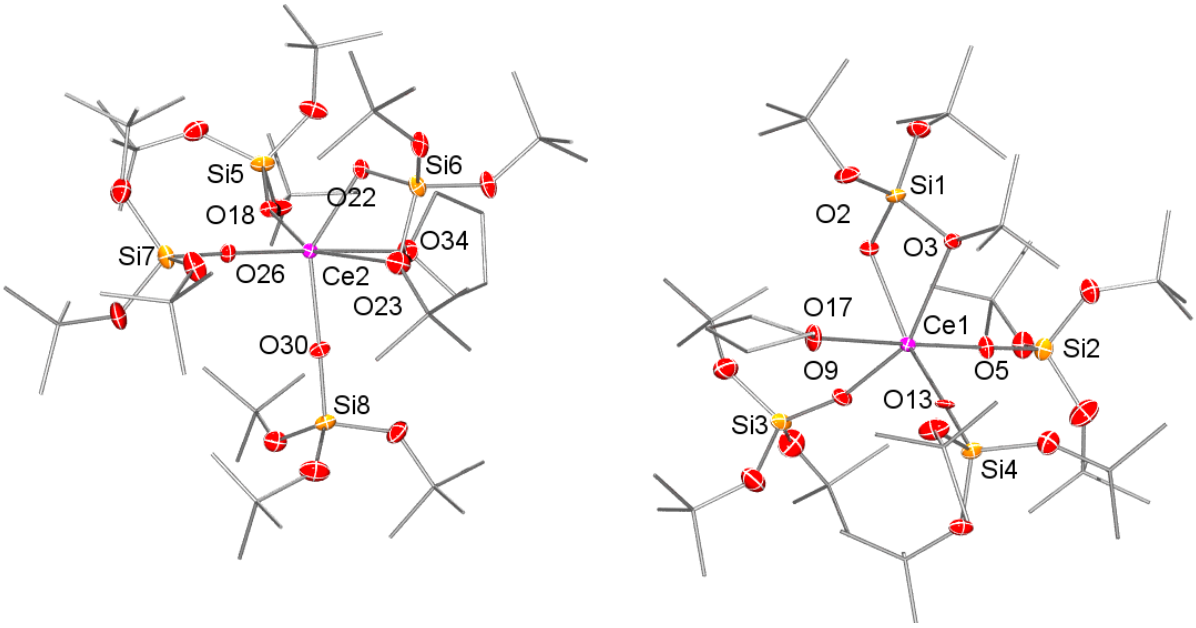

Figure S23. ORTEP representation of the asymmetric unit of Ce[OSi(O*t*Bu)$_3$]$_4$(THF) (**1(THF)**) with thermal ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce1–O2 2.203(8), Ce1–O3 2.681(8), Ce1–O5 2.118(13), Ce1–O9 2.112(8), Ce1–O13 2.146(8), Ce1–O17 2.573(14), O2–Si1 1.581(9), O5–Si2 1.603(13), O9–Si3 1.598(9), O13–Si4 1.605(9), O2–Ce1–O9 99.5(3), O2–Ce1–O13 140.7(3), O3–Ce1–O9 156.4(3), O3–Ce1–O13 88.2(3), O9–Ce1–O13 108.5(3), O5–Ce1–O17 177.7(3), O2–Ce1–O5 102.8(4), O2–Ce1–O17 77.1(3).

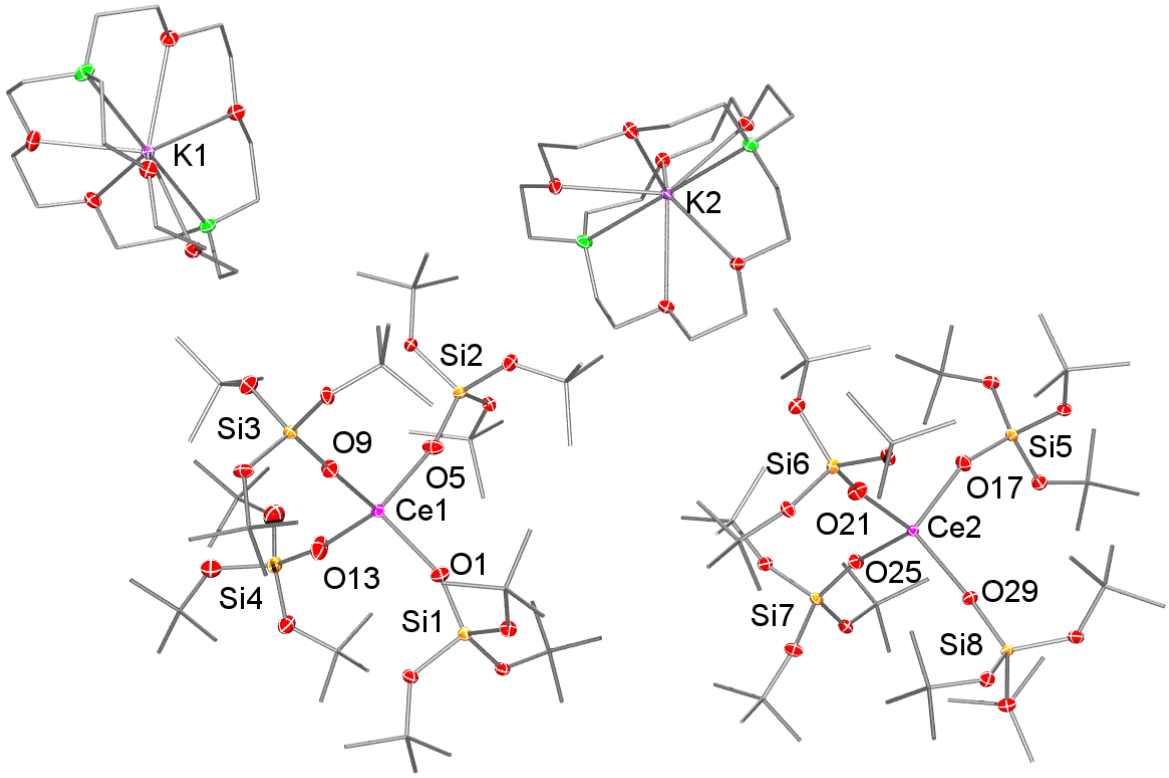

Figure S24. ORTEP representation of the asymmetric unit of [Ce{OSi(O*t*Bu)$_3$}$_4$][K(2.2.2crypt)] (**3**) with thermal ellipsoids set at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce2–O17 2.226(4), Ce2–O21 2.229(4), Ce2–O25 2.238(4), Ce2–O29 2.246(4), O17–Si5 1.584(4), O21–Si6 1.584(4), O25–Si7 1.586(4), O29–Si8 1.582(4), O21–Ce2–O25 106.92(17), O21–Ce2–O29 111.24(16), O17–Ce2–O21 107.89(17), O17–Ce2–O25 106.04(16), O17–Ce2–O29 110.45(15), O25–Ce2–O29 113.98(16).

5. Computational Details

Table S10. Cartesian coordinates of optimized structure for **1** in CH_2Cl_2 solvent field

Sum of electronic and thermal Free Energies = –4730.523906 Hartrees

C	1.995369	4.56767	2.760319	H	-5.48563	-1.41057	1.259128
C	0.851811	5.558556	2.500627	H	-6.77598	-2.21803	0.341644
H	0.830292	5.849896	1.447355	H	-6.80929	-0.45526	0.558517
H	0.97827	6.459036	3.112751	C	-6.29411	-0.99397	-2.09492
H	-0.11214	5.104757	2.75422	H	-6.9678	-0.14307	-1.94309
C	3.348736	5.206244	2.418292	H	-6.90454	-1.89652	-2.21488
H	4.166168	4.495581	2.575612	H	-5.72706	-0.8282	-3.01429
H	3.52342	6.077408	3.059742	O	1.258377	1.591502	0.125791
H	3.377774	5.541055	1.376993	O	1.769214	3.367547	1.980784
C	1.985824	4.112529	4.224937	O	3.618819	2.973528	-0.02199
H	1.030155	3.638105	4.47271	O	1.355649	4.2548	-0.4959
H	2.130068	4.966753	4.895798	O	1.05378	-1.35276	-1.28175
H	2.787819	3.389293	4.408677	O	0.06694	-1.65719	1.668403
C	4.678382	2.008622	0.157487	O	-0.08039	-1.45781	4.423706
C	5.977258	2.821447	0.238286	O	-1.32203	0.212896	2.55404
H	6.10473	3.427252	-0.66549	O	-2.23591	-2.23743	3.085284
H	6.843527	2.157394	0.333562	O	-1.86742	0.146253	-0.93004
H	5.959383	3.493171	1.102981	O	-3.27918	2.346389	-1.1762
C	4.700473	1.091007	-1.07103	O	-3.49686	0.396441	-3.11099
H	3.765583	0.528818	-1.15417	O	-4.60262	0.087918	-0.72629
H	5.526356	0.374333	-1.00636	Si	2.018783	3.022906	0.382081
H	4.831595	1.68339	-1.98345	Si	2.082645	-2.5411	-1.75443
C	4.477209	1.19629	1.443197	Si	-0.85778	-1.34664	2.979182
H	4.412199	1.856145	2.314382	Si	-3.2907	0.724943	-1.50397
H	5.31766	0.509635	1.594632	Ce	-0.00556	-0.12961	0.101877
H	3.559759	0.601975	1.388891	C	2.096037	-2.531	4.354891
C	1.613882	4.760848	-1.82759	H	1.679231	-3.44468	4.792581

C	2.882129	5.625098	-1.80042	H	3.145039	-2.45331	4.662674
H	2.765954	6.447338	-1.08542	H	2.059514	-2.6176	3.264962
H	3.073486	6.056822	-2.78967	C	1.89683	-0.01848	4.227461
H	3.746773	5.025381	-1.50523	H	1.911808	-0.06493	3.1343
C	1.760742	3.606404	-2.82772	H	2.927502	0.119132	4.572632
H	2.628357	2.986216	-2.58367	H	1.316095	0.857318	4.532317
H	1.895783	3.996646	-3.84281	C	-2.78158	-3.26941	5.21464
H	0.866125	2.975183	-2.82129	H	-1.86633	-2.9004	5.685445
C	0.393144	5.617813	-2.18242	H	-3.07777	-4.20212	5.708182
H	-0.51666	5.00863	-2.18124	H	-3.57703	-2.53238	5.371609
H	0.510252	6.064783	-3.17587	C	-3.85937	-3.96955	3.046624
H	0.267776	6.425693	-1.45317	H	-4.6504	-3.22475	3.185196
C	4.204198	-3.69117	-0.26877	H	-4.19768	-4.91659	3.48133
C	3.033777	-1.5794	-4.27144	H	-3.70802	-4.11686	1.971844
C	0.181583	-4.66402	-1.92411	O	2.984104	-2.92644	-0.42367
C	1.306912	-1.3017	4.822059	O	3.153802	-2.05402	-2.91211
C	-2.24788	1.167929	3.165777	O	1.281329	-3.8448	-2.37886
C	-1.9922	2.497668	2.453192	C	5.395892	-2.74376	-0.46029
H	-0.94421	2.794888	2.558957	H	5.389052	-2.32597	-1.4708
H	-2.622	3.28457	2.883448	H	6.342187	-3.27504	-0.30567
H	-2.23	2.417013	1.387216	H	5.343394	-1.91864	0.258199
C	-1.9469	1.293038	4.663561	C	4.175739	-4.23063	1.166676
H	-2.09816	0.342602	5.184397	H	4.100776	-3.40534	1.882802
H	-2.61473	2.036087	5.113003	H	5.088069	-4.79639	1.386206
H	-0.9144	1.616468	4.828898	H	3.315104	-4.89211	1.313476
C	-3.68456	0.689966	2.932671	C	4.279309	-4.8526	-1.27022
H	-3.87866	0.560067	1.863908	H	5.194993	-5.43048	-1.10177
H	-4.39287	1.428443	3.325361	H	4.295653	-4.48146	-2.29941
H	-3.86222	-0.26474	3.43476	C	4.469371	-1.28747	-4.72761
C	-2.5606	-3.50395	3.714864	H	4.931277	-0.5327	-4.08207

C	-4.31739	3.355622	-1.24065	H	4.479055	-0.91447	-5.7577
C	-5.18532	3.265458	0.022101	H	5.076959	-2.19799	-4.68417
H	-5.67713	2.290963	0.077897	C	2.194893	-0.29532	-4.30115
H	-5.95254	4.048359	0.015274	H	1.173673	-0.4866	-3.95952
H	-4.57047	3.395303	0.918573	H	2.146608	0.106264	-5.31975
C	-3.57834	4.698386	-1.28543	H	2.637377	0.466547	-3.65102
H	-2.93039	4.808205	-0.40925	C	2.406996	-2.66208	-5.16037
H	-4.28942	5.531942	-1.29624	H	2.996375	-3.58408	-5.11255
H	-2.95633	4.764455	-2.18467	H	2.37774	-2.32534	-6.20297
C	-5.18304	3.188497	-2.49753	H	1.387552	-2.89261	-4.84015
H	-4.57138	3.235537	-3.40382	C	-1.13253	-3.9863	-2.3299
H	-5.92795	3.990848	-2.54594	H	-1.23508	-3.01605	-1.83568
H	-5.715	2.232229	-2.4885	H	-1.99112	-4.6081	-2.05145
C	-2.63476	0.49635	-4.266	H	-1.1607	-3.82569	-3.41295
C	-1.66484	1.677898	-4.13491	C	0.337264	-6.00381	-2.65599
H	-2.20824	2.619601	-4.01013	H	0.331835	-5.84839	-3.74027
H	-1.04068	1.757094	-5.03181	H	-0.48359	-6.68281	-2.39982
H	-1.00339	1.543524	-3.27282	H	1.282505	-6.48474	-2.38208
C	-3.56663	0.701504	-5.46733	C	0.231604	-4.8773	-0.40535
H	-4.27958	-0.12684	-5.54128	H	1.172896	-5.34963	-0.10778
H	-2.99229	0.747241	-6.39928	H	-0.59101	-5.53165	-0.09441
H	-4.13171	1.633714	-5.36304	H	0.133785	-3.92963	0.134213
C	-1.86637	-0.82335	-4.40581	C	1.28227	-1.22254	6.352473
H	-1.22981	-0.99075	-3.5321	H	0.828729	-2.12585	6.774337
H	-1.23369	-0.81246	-5.30069	H	0.699578	-0.35617	6.683035
H	-2.56567	-1.66251	-4.48913	H	2.299023	-1.12794	6.748947
C	-5.34709	-1.1416	-0.89573	C	-1.44244	-4.52584	3.473877
C	-4.39153	-2.32487	-1.09259	H	-0.50846	-4.20385	3.944505
H	-3.81011	-2.20782	-2.01223	H	-1.26687	-4.66005	2.401231
H	-4.95358	-3.26306	-1.16305	H	-1.71786	-5.49733	3.899335

H	-3.69807	-2.40222	-0.24848	H	3.42444	-5.52616	-1.15719
C	-6.15367	-1.3179	0.39664				

Table S11. Comparison of parameters between X-ray structure and optimized model for **1**

	X-ray structure	**Optimized model**
Average Ce−O (Å)	2.110(2)	2.150
Average O−Ce−O (°)	108.51(7)	108.04

Table S12. Cartesian coordinates of optimized structure for **Int$_1$** in CH_2Cl_2 solvent field

Sum of electronic and thermal Free Energies = –4730.679054 Hartrees

C	1.210249	5.167003	2.466048	H	-5.38114	-1.90865	1.153077
C	-0.12538	5.853907	2.140917	H	-6.30295	-3.16548	0.298497
H	-0.22214	5.998366	1.061748	H	-6.77264	-1.45859	0.145089
H	-0.19159	6.829982	2.636333	C	-5.76284	-2.31399	-2.27725
H	-0.96353	5.237637	2.483707	H	-6.63811	-1.66113	-2.37344
C	2.385475	6.048886	2.017349	H	-6.11018	-3.354	-2.26749
H	3.341857	5.559267	2.225701	H	-5.12257	-2.16167	-3.14947
H	2.363248	7.005012	2.55339	O	1.162161	1.847893	0.147254
H	2.332639	6.256613	0.944821	O	1.239486	3.87364	1.83313
C	1.311727	4.892015	3.973301	O	3.225014	3.654863	-0.05018
H	0.491951	4.241737	4.298255	O	0.796423	4.443643	-0.71284
H	1.259743	5.825355	4.545705	O	1.379936	-1.43133	-1.24437
H	2.258904	4.393932	4.209037	O	0.007631	-1.68393	1.839917
C	4.397395	2.876963	0.25253	O	-0.17844	-1.17842	4.558389
C	5.580853	3.850783	0.1608	O	-1.53747	0.210338	2.57892
H	5.62213	4.307371	-0.83441	O	-2.26688	-2.23462	3.338913
H	6.528828	3.33115	0.341328	O	-1.8908	-0.08898	-1.14433
H	5.478505	4.651029	0.902079	O	-3.67522	1.811236	-1.56633
C	4.543325	1.765984	-0.79736	O	-3.49229	-0.24618	-3.37089
H	3.681812	1.093335	-0.76191	O	-4.60103	-0.60115	-1.00386

H	5.451758	1.178384	-0.62246	Si	1.611296	3.384212	0.283053
H	4.603629	2.199789	-1.8023	Si	2.611712	-2.42934	-1.51034
C	4.317059	2.277414	1.664611	Si	-0.93063	-1.27986	3.076762
H	4.19915	3.066649	2.414638	Si	-3.34683	0.18954	-1.76582
H	5.230763	1.717209	1.89509	Ce	0.037844	-0.15149	0.067758
H	3.466912	1.593184	1.745338	C	2.077208	-2.07658	4.579825
C	0.943981	4.75509	-2.11109	H	1.734008	-2.97383	5.107432
C	2.004795	5.855775	-2.26441	H	3.116411	-1.88499	4.872187
H	1.715331	6.744524	-1.69199	H	2.045462	-2.27144	3.504217
H	2.115768	6.14664	-3.31591	C	1.680369	0.386636	4.209278
H	2.970389	5.502727	-1.89288	H	1.726742	0.22706	3.127829
C	1.336839	3.513948	-2.92589	H	2.686124	0.651707	4.555153
H	2.317456	3.139663	-2.6173	H	1.015941	1.233796	4.40718
H	1.384259	3.75887	-3.9933	C	-2.52946	-3.33908	5.482765
H	0.601123	2.714958	-2.78929	H	-1.61677	-2.88724	5.880214
C	-0.4273	5.269767	-2.56948	H	-2.69312	-4.30187	5.981215
H	-1.18744	4.49013	-2.45026	H	-3.37396	-2.68236	5.721165
H	-0.40068	5.5699	-3.62336	C	-3.72022	-4.11158	3.402263
H	-0.72817	6.137282	-1.97148	H	-4.56248	-3.44595	3.621035
C	4.763602	-3.11253	0.222419	H	-3.93004	-5.09074	3.847576
C	3.646284	-1.52107	-4.00415	H	-3.65125	-4.23254	2.315779
C	1.105018	-4.82808	-1.68014	O	3.458785	-2.58615	-0.08442
C	1.18384	-0.87672	4.925913	O	3.735381	-1.88443	-2.6146
C	-2.54654	1.101581	3.116139	O	2.151877	-3.92671	-2.08574
C	-2.4074	2.407254	2.324705	C	5.790954	-1.97979	0.076021
H	-1.39652	2.815096	2.427258	H	5.805955	-1.61713	-0.95537
H	-3.12236	3.154756	2.688318	H	6.79675	-2.32533	0.343738
H	-2.60602	2.235738	1.260963	H	5.528624	-1.14355	0.733863
C	-2.29764	1.354617	4.609307	C	4.695704	-3.57895	1.683554
H	-2.36212	0.425688	5.183898	H	4.40406	-2.74825	2.335389

H	-3.04555	2.053287	5.001448	H	5.668678	-3.95637	2.018907
H	-1.30538	1.788529	4.77028	H	3.956506	-4.37965	1.797628
C	-3.93831	0.492669	2.897438	C	5.13795	-4.29244	-0.68749
H	-4.10228	0.288649	1.834712	H	6.116122	-4.69414	-0.39829
H	-4.71506	1.187476	3.23832	H	5.191999	-3.97446	-1.73267
H	-4.03943	-0.4459	3.447912	C	5.017147	-0.92814	-4.36001
C	-2.41628	-3.52754	3.962557	H	5.222359	-0.04422	-3.74593
C	-4.88183	2.586204	-1.70392	H	5.053723	-0.63303	-5.41478
C	-5.7033	2.466612	-0.4113	H	5.808727	-1.66385	-4.17888
H	-5.99242	1.425855	-0.24399	C	2.548256	-0.46896	-4.21893
H	-6.61009	3.080839	-0.46835	H	1.563009	-0.87024	-3.96553
H	-5.11284	2.804726	0.447374	H	2.531017	-0.14361	-5.26578
C	-4.42186	4.036894	-1.90562	H	2.730396	0.407617	-3.58808
H	-3.79817	4.359074	-1.06458	C	3.373679	-2.76728	-4.85998
H	-5.28123	4.713533	-1.97776	H	4.159377	-3.51544	-4.70579
H	-3.83242	4.128967	-2.82478	H	3.352359	-2.50503	-5.92432
C	-5.71826	2.130216	-2.90915	H	2.416322	-3.22055	-4.59034
H	-5.13492	2.190176	-3.83329	C	-0.22615	-4.35658	-2.2829
H	-6.60157	2.770644	-3.01657	H	-0.48533	-3.36437	-1.90381
H	-6.05725	1.097974	-2.78151	H	-1.03669	-5.05033	-2.02988
C	-2.59348	-0.10902	-4.48615	H	-0.15132	-4.30035	-3.37492
C	-1.81152	1.21087	-4.41589	C	1.491241	-6.19695	-2.25983
H	-2.49499	2.065878	-4.39157	H	1.597282	-6.13397	-3.34858
H	-1.15826	1.316316	-5.28971	H	0.726905	-6.94823	-2.03037
H	-1.18761	1.241979	-3.51735	H	2.44537	-6.53629	-1.84136
C	-3.47538	-0.13093	-5.74288	C	1.001256	-4.91666	-0.14991
H	-4.05763	-1.05824	-5.78407	H	1.954699	-5.23472	0.284119
H	-2.86363	-0.06696	-6.65008	H	0.235333	-5.64853	0.133541
H	-4.17428	0.71272	-5.73693	H	0.727234	-3.95209	0.289096
C	-1.63287	-1.30673	-4.49295	C	1.158988	-0.64793	6.443306

H	-1.03916	-1.32138	-3.57513	H	0.767596	-1.53363	6.955896
H	-0.95085	-1.26002	-5.35031	H	0.518986	0.205085	6.694196
H	-2.19635	-2.24482	-4.55352	H	2.167204	-0.44681	6.822763
C	-4.99521	-1.98665	-0.98736	C	-1.23692	-4.44816	3.616093
C	-3.77326	-2.90505	-0.83917	H	-0.29676	-4.04479	4.005332
H	-3.10728	-2.81715	-1.70337	H	-1.1417	-4.5633	2.531506
H	-4.0905	-3.95175	-0.76143	H	-1.38757	-5.44086	4.05575
H	-3.20473	-2.64908	0.060897	H	4.398671	-5.09538	-0.60819
C	-5.91949	-2.14114	0.228305				

Table S13. Cartesian coordinates of optimized structure for **3** in CH_2Cl_2 solvent field

Sum of electronic and thermal Free Energies = –4730.685605 Hartrees

C	5.441378	-1.00637	-1.30087	H	-1.6782	-0.80447	-3.49647
C	4.903053	0.26995	-1.96312	H	-2.29951	-0.30983	-5.08954
H	4.242419	0.025367	-2.80029	C	-5.52131	-0.14707	0.631464
H	5.730271	0.877728	-2.34786	C	-5.71852	1.336746	0.973516
H	4.341008	0.872495	-1.242	H	-4.94879	1.670436	1.678111
C	6.361498	-0.63923	-0.12862	H	-6.70071	1.506216	1.429426
H	6.722548	-1.54469	0.371668	H	-5.64607	1.951762	0.069523
H	5.823231	-0.03154	0.606555	C	-6.58273	-0.59666	-0.38351
H	7.229501	-0.0695	-0.47939	H	-6.45298	-1.65138	-0.64268
C	6.204901	-1.86414	-2.3216	H	-6.51678	-0.00575	-1.30246
H	6.591878	-2.76981	-1.84056	H	-7.58646	-0.46795	0.038153
H	7.053729	-1.30854	-2.73781	C	-5.60225	-1.00165	1.90578
H	5.542152	-2.16144	-3.1382	H	-5.42387	-2.05339	1.66658
C	2.994058	-4.68042	-0.01397	H	-6.58772	-0.90836	2.377646
C	1.866115	-5.66944	0.312802	H	-4.84427	-0.67734	2.627769
H	1.225858	-5.26875	1.106253	C	-3.85779	-4.19076	-0.80532
H	2.273396	-6.62961	0.649688	C	-5.09323	-4.39809	-1.69488
H	1.244586	-5.84894	-0.57168	H	-5.08362	-3.6908	-2.52785

C	3.860474	-5.23416	-1.15502	H	-6.00911	-4.23895	-1.11411
H	4.674209	-4.5451	-1.39834	H	-5.11553	-5.41845	-2.09592
H	3.261082	-5.39182	-2.05707	C	-3.9074	-5.1465	0.394396
H	4.300885	-6.19421	-0.86149	H	-3.03125	-5.00341	1.035681
C	3.853272	-4.4217	1.233392	H	-3.9249	-6.1903	0.060711
H	4.627446	-3.68245	1.010966	H	-4.80598	-4.96049	0.993081
H	4.334337	-5.3458	1.575723	C	-2.56937	-4.42341	-1.60798
H	3.231382	-4.03645	2.049149	H	-1.68797	-4.25359	-0.98089
C	2.070406	-2.66174	-3.94752	H	-2.51844	-3.74839	-2.46778
C	1.676958	-1.26913	-4.46131	H	-2.53276	-5.45367	-1.9808
H	2.565458	-0.72626	-4.80373	C	-1.43317	2.019825	4.512407
H	1.205104	-0.68955	-3.66313	C	-2.65657	1.150636	4.184509
H	0.976405	-1.34555	-5.30125	H	-2.52617	0.639107	3.225044
C	0.829575	-3.43332	-3.47488	H	-3.55738	1.771868	4.118059
H	1.110512	-4.41643	-3.0837	H	-2.81163	0.393127	4.958699
H	0.131408	-3.58036	-4.30697	C	-1.64858	2.745395	5.848647
H	0.305535	-2.88484	-2.68623	H	-0.76464	3.340453	6.103669
C	2.790676	-3.44922	-5.05119	H	-1.81872	2.021553	6.653492
H	3.087728	-4.43856	-4.68604	H	-2.51388	3.416056	5.79689
H	3.692852	-2.91678	-5.37245	C	-1.18158	3.037636	3.391061
H	2.139979	-3.58298	-5.92286	H	-0.30897	3.656777	3.626751
C	2.602226	4.818137	0.291547	H	-2.04649	3.698615	3.261518
C	2.607833	5.978753	-0.71429	H	-0.99216	2.524838	2.443183
H	2.982733	5.647216	-1.68769	C	-0.68463	-2.76492	4.26513
H	3.25375	6.787616	-0.35324	C	-1.74929	-2.94105	3.172917
H	1.600093	6.381538	-0.85176	H	-1.44718	-2.42966	2.253702
C	2.042366	5.284339	1.644293	H	-2.70621	-2.52017	3.50109
H	2.046896	4.456203	2.361899	H	-1.90185	-4.00237	2.944461
H	1.013363	5.63421	1.527148	C	-1.13759	-3.45239	5.561517
H	2.648335	6.099445	2.057713	H	-0.38396	-3.32243	6.346308

C	4.025464	4.26947	0.467546	H	-1.29252	-4.52583	5.403849
H	4.023141	3.423023	1.163053	H	-2.0785	-3.01512	5.913771
H	4.696249	5.04025	0.86411	C	0.659852	-3.34674	3.804632
H	4.424881	3.923614	-0.49241	H	1.430217	-3.18461	4.56446
C	1.018881	3.527643	-3.75251	H	0.989851	-2.87481	2.873237
C	1.245268	4.657346	-4.76713	H	0.567142	-4.42436	3.626065
H	1.980093	5.374727	-4.38527	C	3.093834	0.278365	4.245218
H	0.308735	5.193495	-4.95716	C	3.741142	-0.45235	3.060549
H	1.613699	4.258693	-5.7192	H	3.868936	-1.51584	3.291402
C	-0.03227	2.541607	-4.28283	H	4.726518	-0.03031	2.831297
H	-0.21949	1.754992	-3.54686	H	3.110779	-0.36786	2.170366
H	0.304995	2.077261	-5.21706	C	2.920505	1.770894	3.925846
H	-0.97584	3.063258	-4.48002	H	2.415514	2.285958	4.748588
C	2.342624	2.80276	-3.46905	H	2.32455	1.907018	3.017335
H	2.201638	2.006018	-2.73239	H	3.897296	2.242092	3.765874
H	3.093101	3.501079	-3.08424	C	3.950241	0.107659	5.508216
H	2.734454	2.350065	-4.38726	H	3.485967	0.621796	6.357257
C	-1.86655	5.337214	-0.67219	H	4.955128	0.519646	5.360775
C	-1.54861	6.525386	-1.59289	H	4.045616	-0.95424	5.760911
H	-0.90765	7.246452	-1.07263	O	1.75652	-0.96469	-1.00797
H	-2.46839	7.040378	-1.8948	O	2.338922	-3.4537	-0.38838
H	-1.02579	6.180584	-2.4885	O	4.373637	-1.79047	-0.73275
C	-2.77524	4.327362	-1.38775	O	3.028017	-2.51768	-2.88242
H	-2.98641	3.469975	-0.7402	O	-0.12443	2.084587	-0.89635
H	-2.30388	3.961348	-2.30491	O	1.81499	3.708718	-0.1809
H	-3.72839	4.79665	-1.65808	O	0.516041	4.166603	-2.5643
C	-2.5436	5.832623	0.613001	O	-0.63175	4.722388	-0.25455
H	-2.76781	4.99175	1.278068	O	-1.86736	-1.0745	-0.81733
H	-3.4814	6.351699	0.384185	O	-4.08071	-1.374	-2.41848
H	-1.88651	6.527936	1.147093	O	-4.19167	-0.24683	0.088176

C	-3.82983	-0.5166	-3.54742	O	-3.89242	-2.86125	-0.24943
C	-3.79172	0.958272	-3.12245	O	0.255898	-0.05937	2.29834
H	-2.96623	1.144753	-2.429	O	-0.25162	1.222647	4.691888
H	-4.72768	1.243779	-2.63127	O	-0.57401	-1.36899	4.584885
H	-3.65148	1.60414	-3.99698	O	1.835	-0.34721	4.543923
C	-4.99622	-0.75327	-4.51724	Si	2.833663	-2.13033	-1.27085
H	-5.04584	-1.80953	-4.80432	Si	0.365735	3.612939	-0.99714
H	-4.87488	-0.15421	-5.42692	Si	-3.4447	-1.38245	-0.87573
H	-5.94756	-0.48003	-4.04755	Si	0.311426	-0.13331	3.903043
C	-2.50289	-0.92396	-4.20423	Ce	-0.03368	-0.00193	0.018279
H	-2.5408	-1.97399	-4.51625				

Table S14. Comparison of parameters between X-ray structure and optimized model for **3**

	X-ray structure	**Optimized model**
Average Ce−O (Å)	2.222(5)	2.291
Average O−Ce−O (°)	109.4(2)	109.2

Table S15. Cartesian coordinates of optimized structure for **Int$_2$** in CH_2Cl_2 solvent field

Sum of electronic and thermal Free Energies = –4730.536525 Hartrees

C	-3.59972	4.091777	-0.82852	H	1.73919	-0.20271	-3.74815
C	-4.02728	2.839896	-1.6059	H	2.073442	-0.83787	-5.37413
H	-3.44007	2.730173	-2.52309	C	4.270153	-3.3223	0.309032
H	-5.08436	2.909615	-1.8863	C	3.5361	-4.65985	0.465142
H	-3.89345	1.940479	-0.99582	H	2.659227	-4.54058	1.110867
C	-4.42719	4.229532	0.455115	H	4.19409	-5.41323	0.91226
H	-4.09516	5.099535	1.032071	H	3.198465	-5.02974	-0.50921
H	-4.31882	3.338078	1.08173	C	5.469926	-3.48322	-0.63506
H	-5.48892	4.358352	0.217354	H	6.00058	-2.53454	-0.76165
C	-3.74627	5.350728	-1.69422	H	5.147129	-3.83435	-1.62026
H	-3.43841	6.237875	-1.12932	H	6.175292	-4.21438	-0.22432

H	-4.78957	5.486352	-2.00182	C	4.725244	-2.79671	1.677356
H	-3.12327	5.27478	-2.58915	H	5.214079	-1.82461	1.568301
C	0.748006	5.27498	0.266775	H	5.429643	-3.494	2.145458
C	2.271277	5.293798	0.443319	H	3.864243	-2.68004	2.344746
H	2.590808	4.470659	1.091704	C	5.348056	1.085726	-0.66251
H	2.596918	6.236615	0.896686	C	6.548884	0.621519	-1.49793
H	2.772583	5.184125	-0.5245	H	6.209382	0.124162	-2.4103
C	0.309376	6.402349	-0.67816	H	7.161302	-0.08292	-0.92384
H	-0.7764	6.399784	-0.81389	H	7.178235	1.475115	-1.77518
H	0.782518	6.295896	-1.65942	C	5.823552	1.723599	0.648248
H	0.597308	7.37423	-0.26183	H	4.968597	2.041177	1.254796
C	0.048302	5.405384	1.626462	H	6.449349	2.600124	0.446971
H	-1.03694	5.353035	1.502191	H	6.411926	1.006068	1.230541
H	0.302237	6.358778	2.103982	C	4.481362	2.074863	-1.45294
H	0.361271	4.593938	2.292901	H	3.606704	2.377233	-0.86767
C	-0.14939	3.627976	-3.87963	H	4.136752	1.628734	-2.39107
C	-0.7294	2.344474	-4.48863	H	5.057798	2.974408	-1.69682
H	-1.79198	2.479322	-4.71937	C	-0.42226	-2.65744	4.312038
H	-0.63086	1.508681	-3.78988	C	0.537914	-3.12456	3.209506
H	-0.20642	2.086191	-5.41657	H	0.06373	-3.04274	2.225275
C	1.337462	3.449332	-3.54485	H	0.818984	-4.17192	3.367962
H	1.744334	4.356269	-3.0865	H	1.453445	-2.52404	3.209286
H	1.907701	3.240372	-4.45693	C	0.247195	-2.73484	5.691132
H	1.489844	2.613822	-2.85402	H	-0.44271	-2.38471	6.467003
C	-0.33904	4.808709	-4.84023	H	1.144052	-2.1101	5.715743
H	0.054798	5.73044	-4.39844	H	0.531535	-3.76729	5.924822
H	-1.40247	4.957279	-5.05713	C	-1.70655	-3.49418	4.290345
H	0.18419	4.626671	-5.78544	H	-2.40845	-3.13549	5.051149
C	-5.05532	-1.96419	0.198662	H	-1.48486	-4.54738	4.495193
C	-5.76618	-2.92072	-0.76878	H	-2.19336	-3.42687	3.311697

H	-5.84397	-2.47845	-1.76696	C	2.457052	1.029119	4.557384
H	-6.77839	-3.13594	-0.40836	C	3.817195	0.323895	4.61002
H	-5.22665	-3.86935	-0.85068	H	4.067256	-0.10245	3.632577
C	-4.90509	-2.60822	1.583576	H	3.798273	-0.48707	5.346209
H	-4.39422	-1.92228	2.268491	H	4.607016	1.028464	4.893025
H	-4.31908	-3.52884	1.513482	C	2.093112	1.604154	5.933017
H	-5.88688	-2.8482	2.007883	H	1.099206	2.059106	5.903499
C	-5.82755	-0.64331	0.302364	H	2.819798	2.365466	6.239143
H	-5.30248	0.053998	0.964334	H	2.089777	0.809403	6.687295
H	-6.83218	-0.81225	0.705672	C	2.468431	2.13064	3.488632
H	-5.92458	-0.17536	-0.68336	H	1.499301	2.637676	3.440602
C	-2.96468	-2.03836	-3.83406	H	2.691965	1.708698	2.502737
C	-3.87188	-2.80001	-4.80865	H	3.233001	2.879824	3.723105
H	-4.88515	-2.88815	-4.40204	C	-2.19568	1.70219	4.387298
H	-3.48194	-3.80855	-4.98394	C	-2.25366	3.22608	4.543807
H	-3.92936	-2.27974	-5.77114	H	-1.64763	3.544749	5.398931
C	-1.53855	-1.94505	-4.39256	H	-3.28441	3.55911	4.708048
H	-0.87952	-1.43982	-3.68039	H	-1.86869	3.719738	3.645063
H	-1.52717	-1.38493	-5.33463	C	-3.00791	1.260135	3.162444
H	-1.13842	-2.94696	-4.5835	H	-2.96452	0.173309	3.034872
C	-3.53468	-0.6407	-3.55841	H	-2.62455	1.73528	2.253127
H	-2.89784	-0.08477	-2.86286	H	-4.05935	1.545222	3.281759
H	-4.53931	-0.70847	-3.12926	C	-2.70199	1.009829	5.659995
H	-3.59721	-0.06726	-4.49005	H	-2.61825	-0.07586	5.561904
C	-1.81291	-5.18069	-0.63967	H	-3.75085	1.266401	5.848493
C	-2.7933	-5.95857	-1.52843	H	-2.10969	1.327746	6.525294
H	-3.74218	-6.11281	-1.00243	O	-0.73519	1.778415	-1.07355
H	-2.38177	-6.94115	-1.78669	O	0.437246	3.973061	-0.28589
H	-2.99261	-5.40771	-2.45123	O	-2.22247	3.979407	-0.39359
C	-0.48132	-4.94997	-1.36687	O	-0.90891	3.966471	-2.69595

H	0.20938	-4.37562	-0.74056	O	-1.21259	-1.55642	-0.94078
H	-0.63765	-4.40671	-2.30407	O	-3.7393	-1.60654	-0.28743
H	-0.00881	-5.90948	-1.60569	O	-2.93794	-2.83352	-2.62644
C	-1.57702	-5.93067	0.676764	O	-2.42006	-3.91985	-0.26481
H	-0.88802	-5.37338	1.32021	O	1.949765	-0.30606	-1.02296
H	-1.14798	-6.92047	0.485524	O	3.988046	-1.18089	-2.60921
H	-2.52172	-6.06236	1.215465	O	3.291287	-2.40459	-0.23517
C	3.349262	-1.66388	-3.81398	O	4.574944	-0.07395	-0.27051
C	2.453737	-2.8735	-3.51414	O	0.028024	0.138746	1.952977
H	1.639221	-2.60236	-2.83475	O	-0.84262	-1.29318	4.075224
H	3.032272	-3.68194	-3.05603	O	1.496626	0.000262	4.221201
H	2.008419	-3.25263	-4.44074	O	-0.79487	1.38246	4.213346
C	4.493485	-2.06944	-4.75158	Si	-0.86236	3.412261	-1.13929
H	5.150099	-1.2141	-4.94457	Si	-2.56448	-2.47744	-1.0561
H	4.100667	-2.42627	-5.71007	Si	3.443711	-0.98116	-1.06073
H	5.092118	-2.86958	-4.30309	Si	-0.02774	0.058534	3.593599
C	2.53258	-0.52041	-4.43084	Ce	0.017773	0.001318	-0.16483
H	3.178227	0.340752	-4.63579				