Supplemental Information

Evaluating the Electronic Structure of Formal Ln^{II} Ions in $Ln^{II}(C_5H_4SiMe_3)_3^{1-}$ Using XANES Spectroscopy and DFT Calculations

Megan E. Fieser,[1,a] Maryline G. Ferrier,[2,a] Jing Su,[2,a] Enrique Batista,[2]* Samantha K. Cary,[2] Jonathan W. Engle,[2,3] William J. Evans,[1]* Juan S. Lezama Pacheco,[4] Stosh A. Kozimor,[2]* Angela C. Olson,[2] Austin J. Ryan,[1] Benjamin W. Stein,[2] Gregory L. Wagner,[2] David H. Woen,[1] Tonya Vitova,[5] and Ping Yang[2]*

[1] *University of California, Irvine CA 92697*

[2] *Los Alamos National Laboratory, Los Alamos, NM 87545*

[3] *University of Wisconsin, Madison, Wisconsin 53711*

[4] *Stanford University, Palo Alto, CA 94305*

[5] *Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany*

[a] M. E. Fieser, M. G. Ferrier, J. Su contributed equally to this work.

* To whom correspondence should be addressed, stosh@lanl.gov; wevans@uci.edu; erb@lanl.gov; pyang@lanl.gov

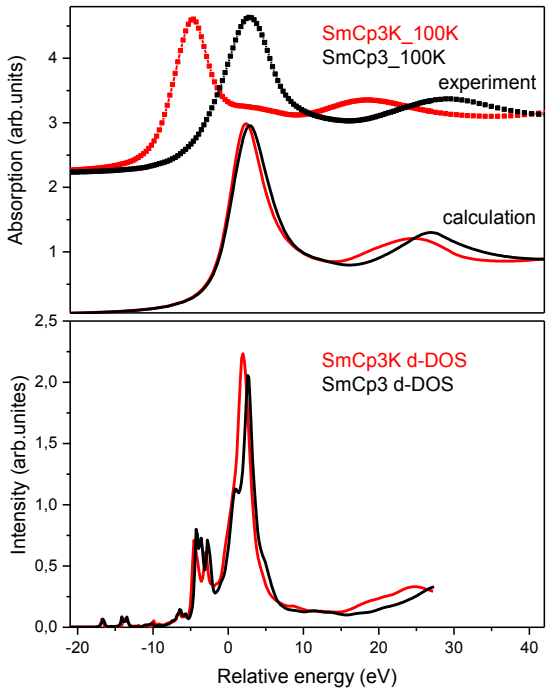

Figure S1: *Top*-The experimental and calculated (FEFF9.6 code) Sm L_3-edge XANES spectra from $Sm(C_3H_4SiMe_3)_3^{x-}$ (x = 0, 1). *Bottom*-The calculated d-DOS (bottom) from $Sm(C_3H_4SiMe_3)_3^{x-}$ (x = 0, black trace; x = 1 red trace).

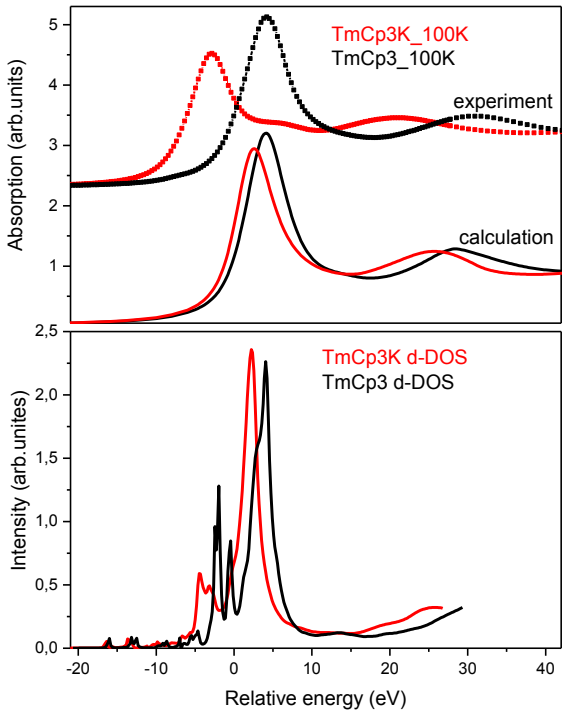

Figure S2: *Top*-The experimental and calculated (FEFF9.6 code) Tm L_3-edge XANES spectra from $Tm(C_3H_4SiMe_3)_3^{x-}$ (x = 0, 1). *Bottom*-The calculated d-DOS (bottom) from $Tm(C_3H_4SiMe_3)_3^{x-}$ (x = 0, black trace; x = 1 red trace).

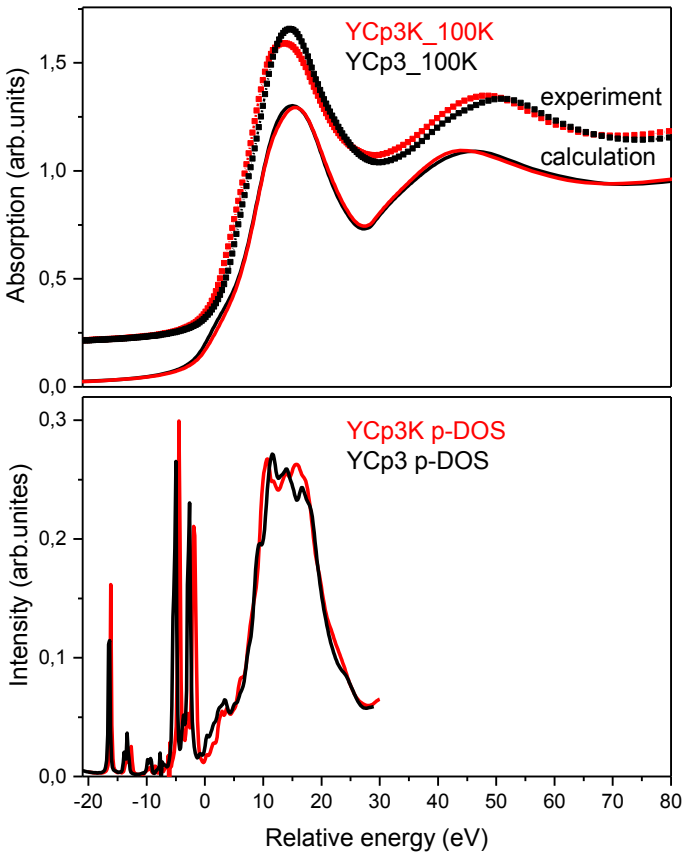

Figure S3: *Top*-The experimental and calculated (FEFF9.6 code) Y K-edge XANES spectra from $Y(C_3H_4SiMe_3)_3^{x-}$ (x = 0, 1). *Bottom*-The calculated d-DOS (bottom) from $Y(C_3H_4SiMe_3)_3^{x-}$ (x = 0, black trace; x = 1 red trace).

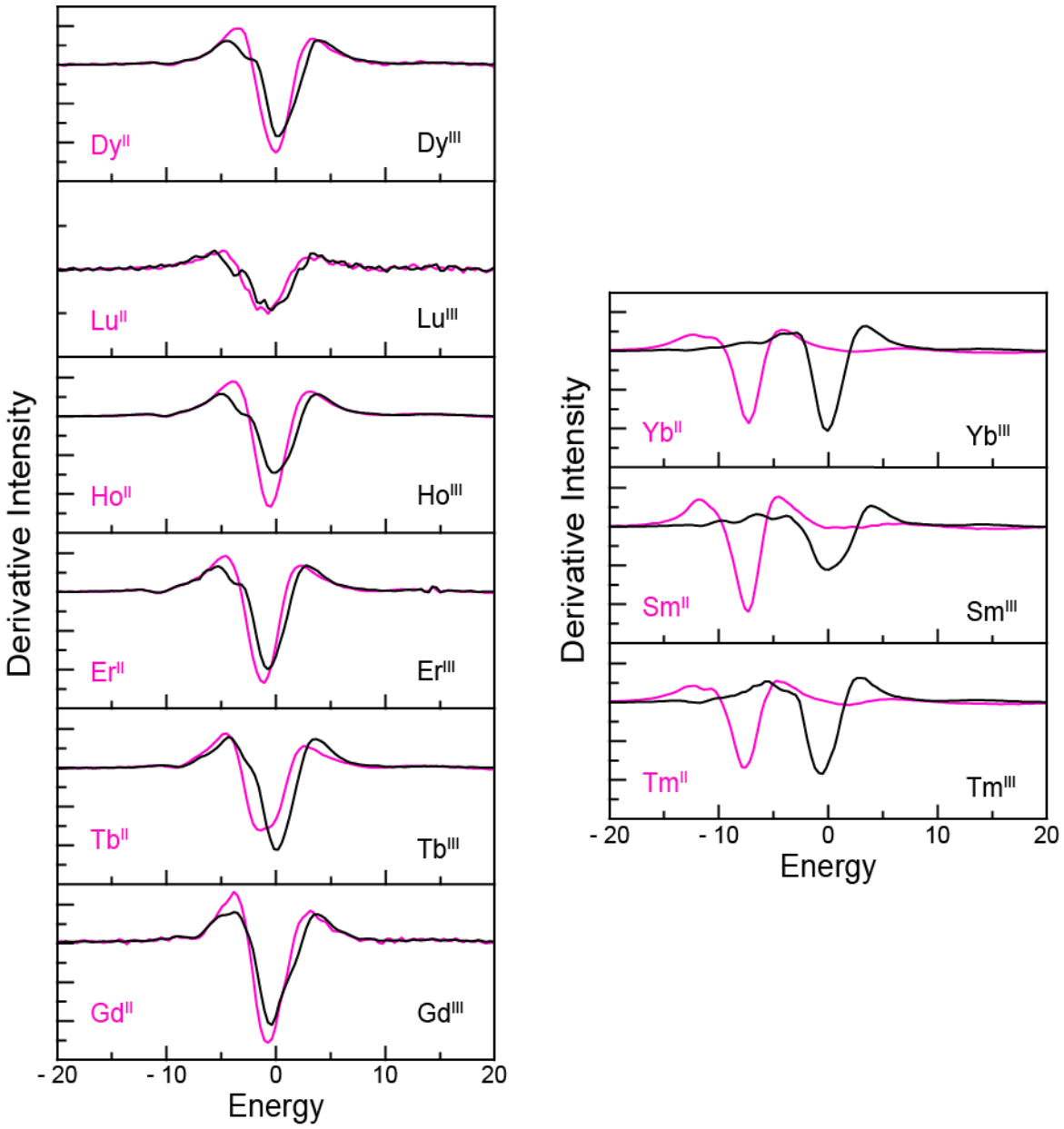

Figure S4. Second derivatives of the L_3-edge XANES measurements obtained from $Ln^{III}(C_5H_4SiMe_3)_3$ (black traces) and $[K(2.2.2\text{-cryptand})][Ln^{II}(C_5H_4SiMe_3)_3]$ (pink trace) for Ln = Dy, Lu, Ho, Er, Tb, Gd on the left and Yb, Sm, Tm on the right. Note, even though the $Lu(C_5H_4SiMe_3)_3^{x-}$ (x = 0, 1) data is quite noisy, the second derivatives indicate that a pre-edge feature is well resolved from the rising edge.

Branching ratios were determined as described previously using a graphical approach based on the integration of the second-derivative of the data as defined by $A_5/(A_5+A_4)$. Here, A_5 and A_4 are the total areas under the second derivative of the L_3 and L_2-edge peaks, respectively. The branching ratio performed on all lanthanide compounds gave similar results 0.62 – 0.66, see Table S1.

Table S1. Branching ratio for $Ln^{III}(C_5H_4SiMe_3)$, $[K(2.2.2\text{-cryptand})][Ln^{II}(C_5H_4SiMe_3)]$ for Ln = Sm, Tb, Ho, Tm, $Sm^{II}(C_5Me_5)_2(THF)_2$, $TmI_2(THF)_3$, and $TmI_3(THF)_{3.5}$.

Compound	Branching Ratio	STDEV	STDEV (%)
$Sm^{II}(C_5H_4SiMe_3)_3^{1-}$	0.655	0.00073	0.11
$Sm^{III}(C_5H_4SiMe_3)_3$	0.626	0.00017	0.03
$Sm^{II}(C_5Me_5)_2THF_2$	0.647	0.00076	0.12
$Tb^{II}(C_5H_4SiMe_3)_3^{1-}$	0.639	0.0008	0.13
$Tb^{III}(C_5H_4SiMe_3)_3$	0.656	0.0004	0.06
$Ho^{II}(C_5H_4SiMe_3)_3^{1-}$	0.611	0.0044	0.72
$Ho^{III}(C_5H_4SiMe_3)_3$	0.639	0.003	0.05
$Tm^{II}(C_5H_4SiMe_3)_3^{1-}$	0.647	0.00847	1.31
$Tm^{III}(C_5H_4SiMe_3)_3$	0.641	0.00112	0.17
$Tm^{II}I_2(THF)_3$	0.620	0.0024	0.39
$Tm^{III}I_3(THF)_{3.5}$	0.642	0.00147	0.23

Table S2. The DFT-PBE//TZP optimized ground-state geometrical coordinates (in Å) and DFT-XC//TZ2P (XC=PBE, BLYP, B3LYP, BHandHLYP) single-point calculated total bonding energies (*E*, in kcal/mol) of $Ln(C_5H_4SiMe_3)_3^{x-}$ (Ln = Sm, Ho; x = 0, 1).

$Sm(C_5H_4SiMe_3)_3$ ($4f^5 5d^0$, sextet state) *E(PBE)*=-8935.82; *E(BLYP)*= -8485.47 *E(B3LYP)*= -10154.16; *E(BHandHLYP)*= -12489.41	$Sm(C_5H_4SiMe_3)_3^-$ ($4f^6 5d^0$, septet state) *E(PBE)*= -8971.53; *E(BLYP)*= -8520.87 *E(B3LYP)*= -10191.16; *E(BHandHLYP)*= -12515.81
1.Sm 0.588630 6.013376 3.465276	1.Sm 0.491007 5.987784 3.468516
2.Si 2.095627 8.909309 0.888513	2.Si 2.288933 8.802001 0.896949
3.Si -2.198432 9.156150 4.382272	3.Si -2.260108 9.204081 4.383259
4.Si 2.009055 2.651269 5.329473	4.Si 2.272345 2.728553 5.296229
5.C 0.835056 6.222294 0.682105	5.C 0.808983 6.266185 0.632215
6.H -0.038290 6.556995 0.126100	6.H -0.043787 6.698079 0.110766
7.C 1.141731 4.873379 0.991244	7.C 0.999507 4.889700 0.890383
8.H 0.552803 4.001555 0.708795	8.H 0.332162 4.082491 0.588258
9.C 2.376805 4.859275 1.690104	9.C 2.234146 4.743005 1.586753
10.H 2.905759 3.974881 2.041347	10.H 2.682177 3.801881 1.903158
11.C 2.818989 6.200032 1.814616	11.C 2.792366 6.030521 1.755992
12.H 3.750888 6.513957 2.281957	12.H 3.742824 6.247410 2.242034
13.C 1.864635 7.068794 1.197908	13.C 1.911830 7.003583 1.173603
14.C 3.727013 9.170631 -0.033349	14.C 3.860034 8.985939 -0.165734
15.H 3.723587 8.632314 -0.992553	15.H 3.728549 8.483935 -1.136400
16.H 4.578502 8.797330 0.555166	16.H 4.722507 8.518193 0.333697
17.H 3.900593 10.238214 -0.238719	17.H 4.105561 10.043935 -0.352042
18.C 0.665975 9.559967 -0.163503	18.C 0.863890 9.639681 -0.036443
19.H -0.307524 9.425158 0.329929	19.H -0.078286 9.578162 0.527064
20.H 0.629402 9.042352 -1.133733	20.H 0.706928 9.158738 -1.014050
21.H 0.792284 10.635029 -0.362639	21.H 1.083577 10.704271 -0.213064
22.C 2.190192 9.862932 2.527612	22.C 2.620106 9.749099 2.512678
23.H 1.265745 9.775097 3.118853	23.H 1.738299 9.738820 3.171540
24.H 2.361979 10.935160 2.345295	24.H 2.888493 10.799690 2.312809
25.H 3.023292 9.495571 3.146193	25.H 3.450202 9.286217 3.068743
26.C -1.928040 6.227477 4.696173	26.C -2.108116 6.283096 4.681453
27.H -1.958783 6.243498 5.784156	27.H -2.111811 6.285639 5.770857
28.C -1.977665 5.060884 3.894927	28.C -2.188634 5.129683 3.867846
29.H -2.050948 4.036288 4.258386	29.H -2.276767 4.101144 4.220650
30.C -1.956501 5.466686 2.535110	30.C -2.158849 5.550244 2.507337
31.H -2.006139 4.810604 1.668016	31.H -2.204731 4.901111 1.633739
32.C -1.888274 6.883425 2.508961	32.C -2.049144 6.958781 2.492797
33.H -1.891728 7.497079 1.609796	33.H -2.013050 7.580223 1.598657
34.C -1.864624 7.380175 3.850660	34.C -2.009521 7.442303 3.845884
35.C -3.972381 9.245775 5.038102	35.C -4.105699 9.514367 4.751693
36.H -4.689016 8.922077 4.268870	36.H -4.715765 9.302065 3.860417
37.H -4.231678 10.272652 5.339055	37.H -4.293314 10.556007 5.059290

38.H -4.104800 8.591699 5.912913	38.H -4.455554 8.849895 5.556658
39.C -1.035326 9.741490 5.759407	39.C -1.309440 9.645718 5.967543
40.H 0.020115 9.734950 5.448974	40.H -0.222770 9.564389 5.817877
41.H -1.129940 9.113472 6.658147	41.H -1.584297 8.974998 6.796230
42.H -1.291005 10.772109 6.051024	42.H -1.539144 10.677081 6.280754
43.C -2.041910 10.317025 2.896505	43.C -1.758829 10.426409 3.019745
44.H -1.021646 10.341705 2.487632	44.H -0.683705 10.367375 2.796875
45.H -2.304095 11.343859 3.194073	45.H -1.985719 11.459910 3.326787
46.H -2.726357 10.022317 2.086909	46.H -2.308448 10.225909 2.087122
47.C 2.860338 5.478962 5.009670	47.C 2.808956 5.629720 5.148046
48.H 3.781489 5.241470 4.481891	48.H 3.757775 5.532842 4.623075
49.C 2.446011 6.777616 5.394485	49.C 2.239386 6.841002 5.600259
50.H 2.994107 7.703363 5.223004	50.H 2.676077 7.834450 5.495916
51.C 1.214800 6.651304 6.089974	51.C 1.005860 6.531421 6.241396
52.H 0.649053 7.462784 6.542544	52.H 0.329463 7.247439 6.704221
53.C 0.876405 5.275428 6.123186	53.C 0.818962 5.133592 6.173939
54.H -0.000362 4.854871 6.612606	54.H -0.030851 4.589898 6.587141
55.C 1.886116 4.525527 5.441913	55.C 1.933511 4.545714 5.482696
56.C 3.778210 2.169981 4.865650	56.C 3.988061 2.440310 4.533910
57.H 3.879623 1.074928 4.821191	57.H 4.184247 1.363847 4.408612
58.H 4.497437 2.546864 5.607701	58.H 4.774349 2.856267 5.182106
59.H 4.068195 2.569232 3.882093	59.H 4.079096 2.918827 3.547921
60.C 1.555276 1.902539 7.006064	60.C 2.244568 1.866862 6.994470
61.H 0.522159 2.154902 7.288926	61.H 1.266426 1.998139 7.482292
62.H 2.220418 2.277507 7.797603	62.H 3.006355 2.300648 7.659928
63.H 1.636236 0.804964 6.980203	63.H 2.437732 0.785730 6.903096
64.C 0.817767 1.943234 4.029830	64.C 0.968336 1.846434 4.224962
65.H -0.229235 2.184983 4.268612	65.H -0.040914 1.997756 4.639101
66.H 0.900947 0.845694 3.992783	66.H 1.154020 0.760933 4.178853
67.H 1.033944 2.323218 3.019520	67.H 0.967757 2.235875 3.195281
$Ho(C_5H_4SiMe_3)_3$ ($4f^{10}5d^0$, quintet state)	$Ho(C_5H_4SiMe_3)_3^-$ ($4f^{10}5d^1$, sextet state)
E(PBE)=-8854.32; *E(BLYP)*=-8406.99	*E(PBE)*=-8868.29; *E(BLYP)*=-8417.36
E(B3LYP)=-10049.08;*E(BHandHLYP)*=-12349.56	*E(B3LYP)*=-10063.06; *E(BHandHLYP)*= -12359.95
1.Ho 0.587092 6.052398 3.479993	1.Ho 0.621110 6.020346 3.421939
2.Si 2.066086 8.874173 0.892095	2.Si 2.158731 9.024863 1.014691
3.Si -2.163198 9.153958 4.366358	3.Si -2.240234 8.991296 4.320680
4.Si 2.020467 2.645229 5.278073	4.Si 1.820920 2.661707 5.468456
5.C 0.793492 6.185649 0.751886	5.C 0.937327 6.352483 0.715244
6.H -0.078669 6.507602 0.187625	6.H 0.059593 6.694985 0.171639
7.C 1.097480 4.845736 1.095859	7.C 1.280308 4.999452 0.948372
8.H 0.510842 3.966948 0.832471	8.H 0.717094 4.125742 0.624398
9.C 2.333880 4.847452 1.794800	9.C 2.502152 4.980133 1.672077
10.H 2.860656 3.970973 2.166399	10.H 3.027961 4.089793 2.010396
11.C 2.776041 6.189040 1.888816	11.C 2.903853 6.317426 1.885652
12.H 3.706731 6.515331 2.349035	12.H 3.802992 6.627402 2.416345
13.C 1.818513 7.045259 1.256252	13.C 1.928852 7.204859 1.317705
14.C 3.696574 9.087403 -0.043546	14.C 3.703265 9.293156 -0.073428
15.H 3.682299 8.521933 -0.986870	15.H 3.602863 8.750502 -1.025974

16.H	4.545500	8.719995	0.552324	16.H	4.604324	8.911069	0.430867
17.H	3.883283	10.146325	-0.279973	17.H	3.865322	10.360007	-0.297400
18.C	0.639756	9.507725	-0.174025	18.C	0.676609	9.717454	0.051156
19.H	-0.333982	9.393071	0.323786	19.H	-0.266316	9.579345	0.598204
20.H	0.598416	8.965095	-1.130279	20.H	0.583677	9.208715	-0.920901
21.H	0.773737	10.576254	-0.401271	21.H	0.802682	10.794521	-0.140929
22.C	2.180631	9.872643	2.502725	22.C	2.442679	10.043019	2.592413
23.H	1.260258	9.807631	3.102897	23.H	1.583199	9.960376	3.273686
24.H	2.360202	10.938034	2.290400	24.H	2.612616	11.106759	2.355576
25.H	3.015422	9.514949	3.124820	25.H	3.326504	9.671152	3.134131
26.C	-1.861348	6.235932	4.714409	26.C	-1.880652	6.087230	4.568860
27.H	-1.888254	6.268245	5.801573	27.H	-1.922207	6.077596	5.655931
28.C	-1.894842	5.057046	3.930883	28.C	-1.878609	4.938696	3.736327
29.H	-1.958322	4.037287	4.308462	29.H	-1.915692	3.902812	4.067676
30.C	-1.887539	5.444435	2.564250	30.C	-1.865667	5.386836	2.388170
31.H	-1.934341	4.774851	1.708056	31.H	-1.844022	4.749637	1.505453
32.C	-1.833754	6.859494	2.517162	32.C	-1.839555	6.798730	2.394545
33.H	-1.845660	7.461371	1.610638	33.H	-1.818093	7.433694	1.510399
34.C	-1.805362	7.376445	3.853383	34.C	-1.828207	7.268669	3.752030
35.C	-3.936969	9.223156	5.024438	35.C	-4.094814	9.068340	4.766125
36.H	-4.650213	8.883273	4.259004	36.H	-4.711390	8.800082	3.894375
37.H	-4.210524	10.248569	5.317668	37.H	-4.393380	10.073829	5.104483
38.H	-4.058627	8.574207	5.904585	38.H	-4.330402	8.352403	5.568782
39.C	-1.006106	9.768759	5.735672	39.C	-1.295936	9.539550	5.873847
40.H	0.050422	9.760458	5.429046	40.H	-0.218838	9.622976	5.668392
41.H	-1.101150	9.157687	6.645982	41.H	-1.429169	8.821755	6.697796
42.H	-1.266654	10.803544	6.007556	42.H	-1.662466	10.520186	6.218834
43.C	-2.028107	10.303118	2.869650	43.C	-1.951970	10.282107	2.960935
44.H	-1.008515	10.345034	2.460955	44.H	-0.885763	10.374602	2.712101
45.H	-2.311322	11.327032	3.157913	45.H	-2.311289	11.268682	3.294712
46.H	-2.706230	9.987246	2.062701	46.H	-2.496510	10.021541	2.040387
47.C	2.821327	5.490930	4.977881	47.C	2.805247	5.401232	4.948568
48.H	3.751449	5.273945	4.458242	48.H	3.695131	5.099103	4.400319
49.C	2.385461	6.776825	5.377174	49.C	2.480453	6.729428	5.314182
50.H	2.924408	7.712457	5.231698	50.H	3.065556	7.620813	5.093036
51.C	1.147511	6.621266	6.059876	51.C	1.248900	6.698372	6.020623
52.H	0.567056	7.417995	6.519433	52.H	0.728345	7.559701	6.432556
53.C	0.827287	5.242527	6.062933	53.C	0.818092	5.353628	6.082430
54.H	-0.048244	4.800538	6.534164	54.H	-0.090977	5.003420	6.566637
55.C	1.850851	4.517987	5.373710	55.C	1.759924	4.517378	5.388461
56.C	3.802487	2.206371	4.818593	56.C	2.696196	1.880333	3.976026
57.H	3.933087	1.113800	4.791774	57.H	2.796846	0.791816	4.116101
58.H	4.510823	2.613573	5.555243	58.H	3.707271	2.295742	3.844086
59.H	4.084101	2.596738	3.829144	59.H	2.130242	2.062636	3.051169
60.C	1.602060	1.912687	6.971568	60.C	2.801364	2.117768	7.013998
61.H	0.563196	2.136917	7.257197	61.H	2.331053	2.512109	7.928058
62.H	2.259757	2.323142	7.751693	62.H	3.829325	2.510714	6.976408
63.H	1.718046	0.817955	6.964892	63.H	2.856132	1.020409	7.100618
64.C	0.843975	1.877084	4.002111	64.C	0.086608	1.905272	5.626786
65.H	-0.207319	2.097676	4.241767	65.H	-0.464683	2.345068	6.472028

66.H 0.957283 0.781743 3.990408 67.H 1.043419 2.243436 2.984082	66.H 0.152341 0.818521 5.796231 67.H -0.499126 2.079889 4.712851
$Ho(C_5H_4SiMe_3)_3^-$ ($4f^{11}5d^0$, quartet state) *E(PBE)*=-8883.41; *E(BLYP)*=-8436.21 *E(B3LYP)*=-10064.88; *E(BHandHLYP)*=12332.83	
1.Ho 0.560913 6.029876 3.471738 2.Si 2.191469 8.840747 0.902511 3.Si -2.257497 9.114345 4.405883 4.Si 2.070488 2.718803 5.290380 5.C 0.823075 6.232947 0.668127 6.H -0.046906 6.612968 0.135765 7.C 1.080538 4.874384 0.953740 8.H 0.453408 4.029228 0.670398 9.C 2.317437 4.800183 1.656290 10.H 2.803469 3.888916 2.002153 11.C 2.810691 6.114720 1.808013 12.H 3.746738 6.387445 2.292835 13.C 1.882169 7.033598 1.212541 14.C 3.748238 9.059939 -0.172515 15.H 3.627284 8.539870 -1.135070 16.H 4.627944 8.627491 0.328478 17.H 3.958065 10.122526 -0.375362 18.C 0.731583 9.611530 -0.033350 19.H -0.201901 9.538148 0.542926 20.H 0.577781 9.100074 -0.995971 21.H 0.918117 10.676908 -0.240639 22.C 2.498401 9.815880 2.505920 23.H 1.629865 9.765240 3.180887 24.H 2.708187 10.877392 2.295358 25.H 3.361241 9.401684 3.050372 26.C -1.962532 6.212974 4.716675 27.H -1.973009 6.224732 5.805444 28.C -1.999469 5.052231 3.910342 29.H -2.053917 4.023658 4.268208 30.C -1.980477 5.463820 2.547301 31.H -2.001872 4.807199 1.678834 32.C -1.915790 6.875475 2.523070 33.H -1.900590 7.491775 1.624973 34.C -1.894108 7.370974 3.874034 35.C -4.123038 9.301047 4.758528 36.H -4.710137 9.050685 3.861581 37.H -4.382486 10.326872 5.066777 38.H -4.434456 8.612237 5.558917 39.C -1.355343 9.621726 5.998900 40.H -0.265936 9.646870 5.849761 41.H -1.565975 8.915472 6.816887 42.H -1.683035 10.622125 6.325466 43.C -1.831734 10.369344 3.045828	

44.H -0.754414 10.385093 2.826812 45.H -2.129683 11.384234 3.354342 46.H -2.363647 10.134392 2.110848 47.C 2.865265 5.547056 5.029899 48.H 3.790138 5.340963 4.494925 49.C 2.416916 6.822231 5.434225 50.H 2.940302 7.765797 5.277337 51.C 1.170098 6.661346 6.104695 52.H 0.577656 7.454757 6.555297 53.C 0.852050 5.283773 6.097361 54.H -0.031508 4.836673 6.550706 55.C 1.892221 4.564118 5.412065 56.C 3.818590 2.264969 4.698357 57.H 3.941192 1.171593 4.647554 58.H 4.578511 2.663404 5.387592 59.H 4.026036 2.673928 3.698288 60.C 1.809060 1.920527 6.999863 61.H 0.802986 2.147794 7.385199 62.H 2.537366 2.311993 7.726173 63.H 1.915589 0.824620 6.955566 64.C 0.818301 1.891283 4.119718 65.H -0.214377 2.107133 4.434433 66.H 0.948330 0.795986 4.112408 67.H 0.932791 2.257829 3.088561	

Table S3. Relative single-point energy difference in kcal/mol between $f^{10}d^{1}$ and $f^{11}d^{0}$ in $Ho^{II}(C_5H_4SiMe_3)_3^{1-}$ from different functional results at the PBE//TZP optimized ground-state geometries.

Compound	Δ*E*(PBE)	Δ*E*(B3LYP)	Δ*E*(BHandHLYP)
$f^{10}d^{1}$	0	0	0
$f^{11}d^{0}$	-15.1	-1.8	27.1