Supplementary Material (ESI) for Dalton Transactions

Electronic Supporting Information

CF_4 Defluorination by Cp_2Ln-H: a DFT Study

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Table S1 DFT(B3PW91) optimized geometries for Cp_2Ln-H **4**,[4] and Cp_2Ln-F, **5** (Figure 1). The distances are in Å and the angles in degrees. X is the Cp centroïd. All complexes are neutral (Ln^{III}) with the exception of $[Cp_2CeX]^+$ and $[Cp_2EuX]^-$ and $[Cp_2YbX]^-$ for which the oxidation state of the metal are respectively IV and II and II

Ln	Cp_2Ln-H		Cp_2Ln-F		
	M-H	X-Ln-X	M-F	M-X	X-Ln-X
La	2.142	134.3	2.178	2.578	131.4
$Ce^{(IV)}$	1.959	130.0	2.098	2.407	129.8
Pr	2.112	136.9	2.148	2.548	131.6
Nd	2.099	137.9	2.128	2.518	132.1
Pm	2.088	138.9	2.098	2.488	132.5
Sm	2.078	139.6	2.088	2.458	132.9
$Eu^{(II)}$	2.331	131.3	2.278	2.608	131.3
Gd	2.059	141.1	2.077	2.435	133.2
Tb	2.045	140.9	2.063	2.418	133.3
Dy	2.031	140.7	2.051	2.401	133.5
Ho	2.018	140.6	2.038	2.385	133.6
Er	2.005	140.4	2.026	2.369	133.8
Tm	1.994	140.2	2.016	2.355	134.0
$Yb^{(II)}$	2.225	131.6	2.169	2.586	131.3
Lu	1.972	140.1	2.002	2.327	134.5

Table S2 DFT(B3PW91) optimized geometries for the CF_4 adduct, **7**, Cp_2Ln-H(F-CF_3) (Figure 5). The distances are in Å and the angles in degrees. The C-F bonds of CF_3 are equal to 1.311 Å with F-C-F angles equal to 108° for all Ln elements. The C-F^{α} distance is 1.350Å for all lanthanides. X is the Cp centroïd. All complexes are neutral (Ln^{III}) with the exception of $[Cp_2CeX]^+$ and $[Cp_2EuX]^-$ and $[Cp_2YbX]^-$ for which the oxidation state of the metal are respectively IV and II and II.

Ln	Ln-H	Ln-F_{α}	Ln-C	H…F^{α}	Ln-H-F^{α}	H-F^{α}-C	X-Ln-X
La	2.148	2.870	4.059	3.951	45.0	132.6	134.8
$Ce^{(IV)}$	1.961	2.457	3.504	3.025	45.6	132.4	133.9
Pr	2.116	2.805	3.985	3.744	47.8	127.6	136.3
Nd	2.102	2.777	3.951	3.649	49.2	124.5	136.8
Pm	2.089	2.753	3.924	3.567	50.3	122.5	137.2
Sm	2.076	2.730	3.899	3.498	51.2	121.2	137.5
$Eu^{(II)}$	2.331	3.159	4.892	4.102	41.8	137.0	133.0
Gd	2.053	2.694	3.859	3.385	52.7	118.9	137.9
Tb	2.039	2.682	3.846	3.343	53.3	118.0	137.9
Dy	2.029	2.677	3.839	3.332	53.7	116.9	137.9
Ho	2.021	2.662	3.827	3.319	54.6	116.1	137.9
Er	2.003	2.658	3.816	3.311	55.3	115.2	137.9
Tm	1.991	2.642	3.808	3.303	56.1	114.0	138.3
$Yb^{(II)}$	2.223	2.694	4.351	3.990	42.7	134.9	134.9
Lu	1.968	2.637	3.799	3.298	57.3	113.0	139.9

Table S3 DFT(B3PW91) optimized geometries for HCF_3 adduct to Cp_2Ln-F, Cp_2Ln-F^{α}($F^{\alpha'}$-CHF_2) **8** (Figure 5). C-$F^{\alpha'}$ = 1.380 Å, C-H = 1.092 Å, C…F^{α} = 2.860 Å, H...F^{α} = 2.023 Å F^{α}-C-$F^{\alpha'}$ = 106° and H-C-$F^{\alpha'}$ = 108°, Ln-$F^{\alpha'}$-C = 123° for all Ln elements. The distances are in Å and the angles in degrees. X is the Cp centroïd. All complexes are neutral (Ln^{III}) with the exception of $[Cp_2CeX]^+$ and $[Cp_2EuX]^-$ and $[Cp_2YbX]^-$ for which the oxidation state of the metal are respectively IV and II and II.

Ln	Ln-F^{α}	Ln-$F^{\alpha'}$	Ln-C	Ln-$F^{\alpha'}$-F^{α}	X-Ln-X
La	2.219	2.745	3.679	64.0	131.5
$Ce^{(IV)}$	1.995	2.421	3.315	64.2	131.0
Pr	2.184	2.698	3.637	63.3	131.9
Nd	2.169	2.677	3.618	63.0	132.1
Pm	2.153	2.657	3.599	62.7	132.3
Sm	2.139	2.636	3.582	62.4	132.4
$Eu^{(II)}$	2.317	2.854	3.891	62.0	133.0
Gd	2.114	2.601	3.549	61.8	132.9
Tb	2.100	2.586	3.536	61.7	133.0
Dy	2.091	2.578	3.527	61.6	133.2
Ho	2.084	2.566	3.516	61.4	133.4
Er	2.075	2.553	3.502	61.1	133.8
Tm	2.061	2.548	3.496	60.9	134.8
$Yb^{(II)}$	2.291	2.718	3.672	60.6	134.9
Lu	2.054	2.537	3.488	60.2	135.4

Table S4 Energy of reactions (ΔE_A, ΔE_B) and energy barriers ($\Delta E_A^{\ddagger}$,$\Delta E_B^{\ddagger}$) in kcal.mol^{-1} for H/F exchange (eqn. 1) and alkylation (eqn. 2). Results shown in Figure 4.

Ln	ΔE_A	ΔE_B	$\Delta E_A^{\ddagger}$	$\Delta E_B^{\ddagger}$
La	--61.85	-16.89	32.93	47.64
$Ce^{(IV)}$	-41.86	-2.92	43.49	62.53
Pr	-62.19	-17.16	32.65	49.52
Nd	-62.31	-17.26	32.55	47.54
Pm	-62.35	-17.31	32.43	47.62
Sm	-62.43	-17.36	32.36	47.70
$Eu^{(II)}$	-61.57	-25.29	38.98	38.98
Gd	-62.30	-17.19	32.54	48.27
Tb	-62.17	-17.05	32.64	48.64
Dy	-62.07	-16.96	32.74	48.99
Ho	-62.01	-16.85	32.86	49.36
Er	-61.96	-16.74	32.98	49.76
Tm	-61.84	-16.59	33.13	50.15
$Yb^{(II)}$	-60.97	-24.88	40.12	40.12
Lu	-61.30	-16.19	33.57	51.17