Mass-analyzed threshold ionization spectroscopy of lanthanide imide LnNH (Ln= La and Ce) radicals from N-H bond activation of ammonia

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Table S1: Bond lengths (Å), bond angles (°), and relative energies (E_{rel}, cm^{-1}) of the different spin states of the LnNH and NLnH (Ln = Na and Ce) molecules from DFT/B3LYP calculations.

	State	E_{rel}	N-H	Ln-H	Ln-N	Ln-N-H	N-Ln-H
^{2}LaNH	$^2\Sigma^+$	0	1.016		1.923	180.0	
^{4}LaNH	$^4\Delta$	21004	1.019		2.216	180.0	
^{1}LaNH$^+$	$^1\Sigma^+$	41747	1.019		1.877	180.0	
^{3}LaNH$^+$	$^3\Sigma^+$	62586	1.021		2.144	180.0	
^{2}NLaH	^{2}A′	14346		2.213	1.887		143.7
^{4}NLaH	^{4}A′	30615		2.084	2.175		123.4
^{1}NLaH$^+$	$^1\Sigma^+$	75873		1.993	1.814		180.0
^{3}NLaH$^+$	^{3}A′	76249		2.028	2.076		121.1
^{1}CeNH	$^1\Sigma^+$	9170	1.016		1.879	180.0	
^{3}CeNH	$^3\Phi$	0/0	1.018/1.017		1.904/1.917	180.0/180.0	
^{2}CeNH$^+$	$^2\Phi$	42649/41237	1.021/1.019		1.857/1.876	180.0/180.0	
^{4}CeNH$^+$	$^4\Pi$ or $^4\Phi$	63079	1.023		2.129	180.0	
^{1}NCeH	^{1}A′	7437		2.120	1.703		133.1
^{3}NCeH	^{3}A′	15374		2.201	1.848		164.2
^{2}NCeH$^+$	$^2\Phi$	69342		1.931	1.720		180.0
^{4}NCeH$^+$	^{4}A′	78710		2.010	2.037		122.9

Table S2: DFT/B3LYP calculated relative energies (E_{rel}, kcal mol^{-1}) with and without vibrational zero-point energy (ZPE) corrections of the intermediates (IMn) and transition states (TSn) and imaginary frequencies (IMG, cm^{-1}) for the formation of LaNH ($^2\Sigma^+$) and CeNH ($^3\Phi$) from Ln + NH_3 (Ln = La and Ce) reactions.

Species	IMG	E_{rel}	
		wo/ ZPE	w/ ZPE
La+NH_3		0.0	0.0
IM1		-15.5	-14.5
IM2		-49.4	-54.0
IM3		-35.3	-42.1
TS1	1412i	1.8	-2.7
TS2	1292i	-24.2	-30.1
LaNH + H_2		-35.1	-42.7
Ce+NH_3		0.0	0.0
IM1		-17.9	-16.9
IM2		-45.5	-50.2
IM3		-32.8	-39.5
TS1	1408i	2.6	-1.9
TS2	1280i	-21.0	-26.9
CeNH + H_2		-32.2	-39.8