Supporting Information

Nitrogen-rich Ce-N compounds under high pressure

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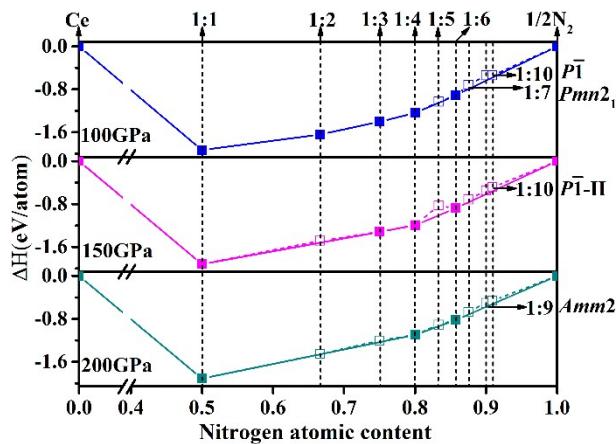
**Fig. S1.** The convex hull diagram of Ce-N system at 100, 150, 200 GPa.
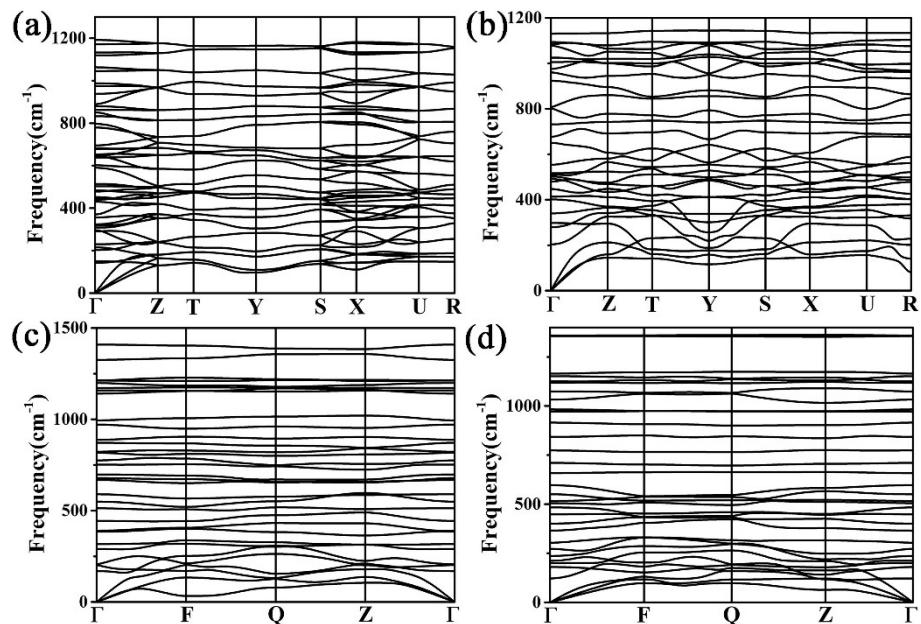
Fig. S2. Phonon dispersion curves for (a) $Pmn2_1$-CeN$_7$ at 50 GPa, (b) $Amm2$-CeN$_9$ at 50 GPa, (c) $P\bar{1}$-CeN$_{10}$ at 50 GPa, and (d) $P\bar{1}$-II-CeN$_{10}$ at 10 GPa.
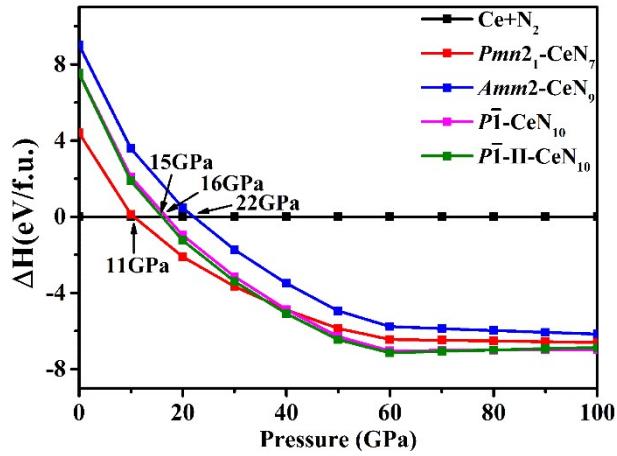
Fig. S3. Enthalpy-pressure diagrams of $Pmn2_1$-CeN$_7$, $Amm2$-CeN$_9$, $P\bar{1}$-CeN$_{10}$, and $P\bar{1}$-II-CeN$_{10}$.
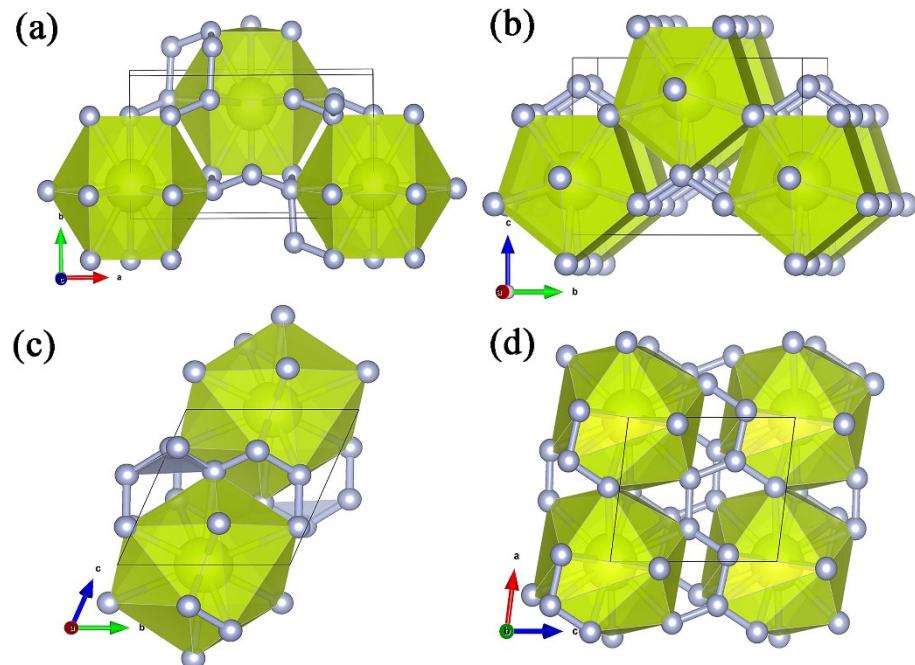

Fig. S4. Polyhedral structures of predicted Ce-N compounds: (a) $C2$-CeN$_7$, (b) $Amm2$-CeN$_9$, (c) $P\bar{1}$-CeN$_{10}$, and (d) $P\bar{1}$-II-CeN$_{10}$.
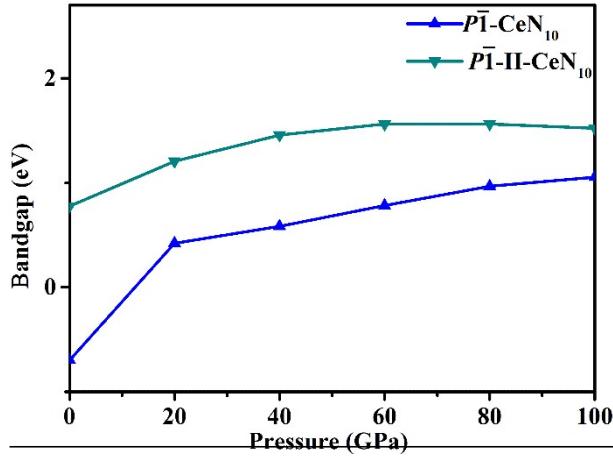
Fig. S5. Band gaps of the $P\bar{1}$-CeN$_{10}$ and $P\bar{1}$-II-CeN$_{10}$ with variable pressure.
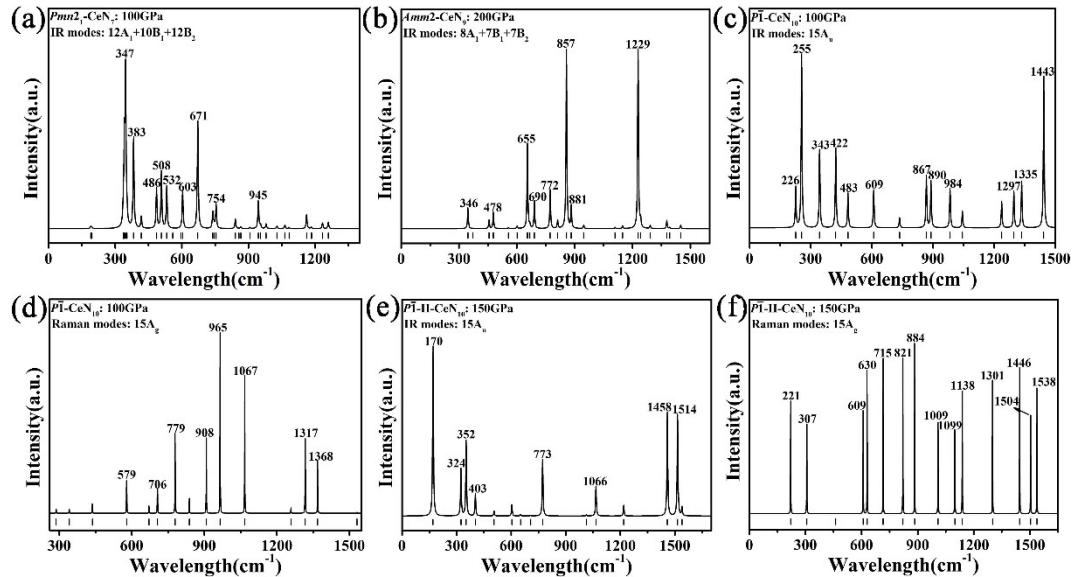
Fig. S6. (a) IR spectra of $Pmn2_1$-CeN$_7$, (b) IR spectra of $Amm2$-CeN$_9$, (c) and (d) IR and Raman spectra of $P\bar{1}$-CeN$_{10}$, (e) and (f) IR and Raman spectra of $P\bar{1}$-II-CeN$_{10}$.
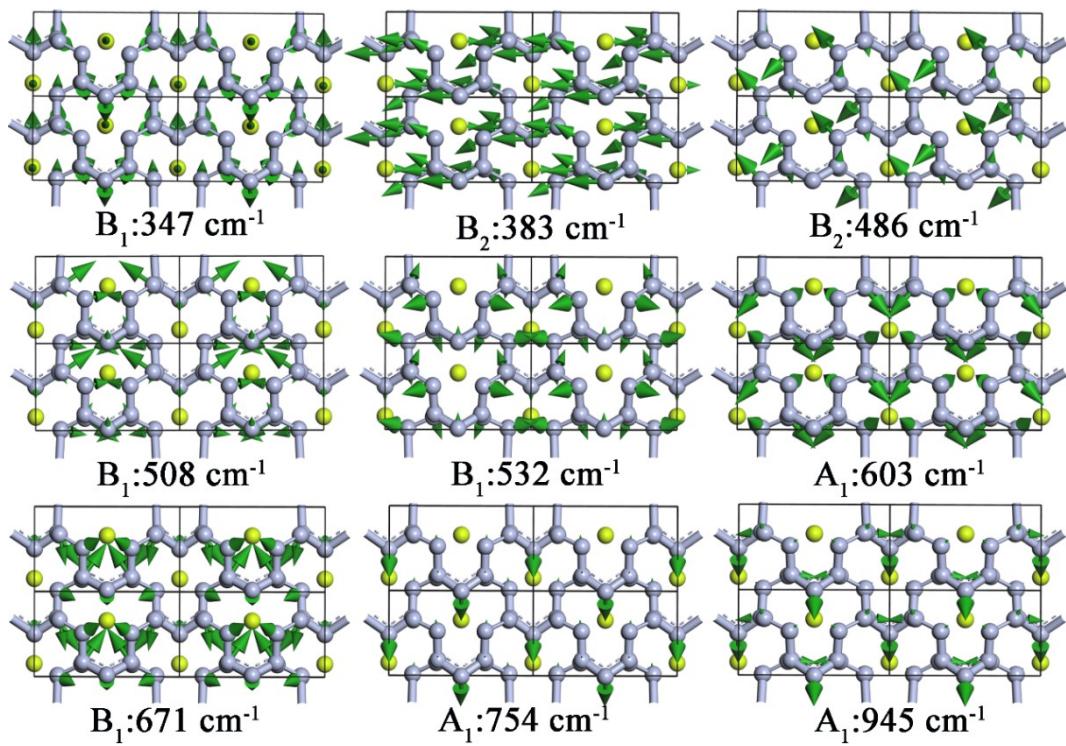
Fig. S7. IR vibrational modes of $Pmn2_1$-CeN$_7$ at 100 GPa.

B$_1$:347 cm^{-1} B$_2$:383 cm^{-1} B$_2$:486 cm^{-1}

B$_1$:508 cm^{-1} B$_1$:532 cm^{-1} A$_1$:603 cm^{-1}

B$_1$:671 cm^{-1} A$_1$:754 cm^{-1} A$_1$:945 cm^{-1}
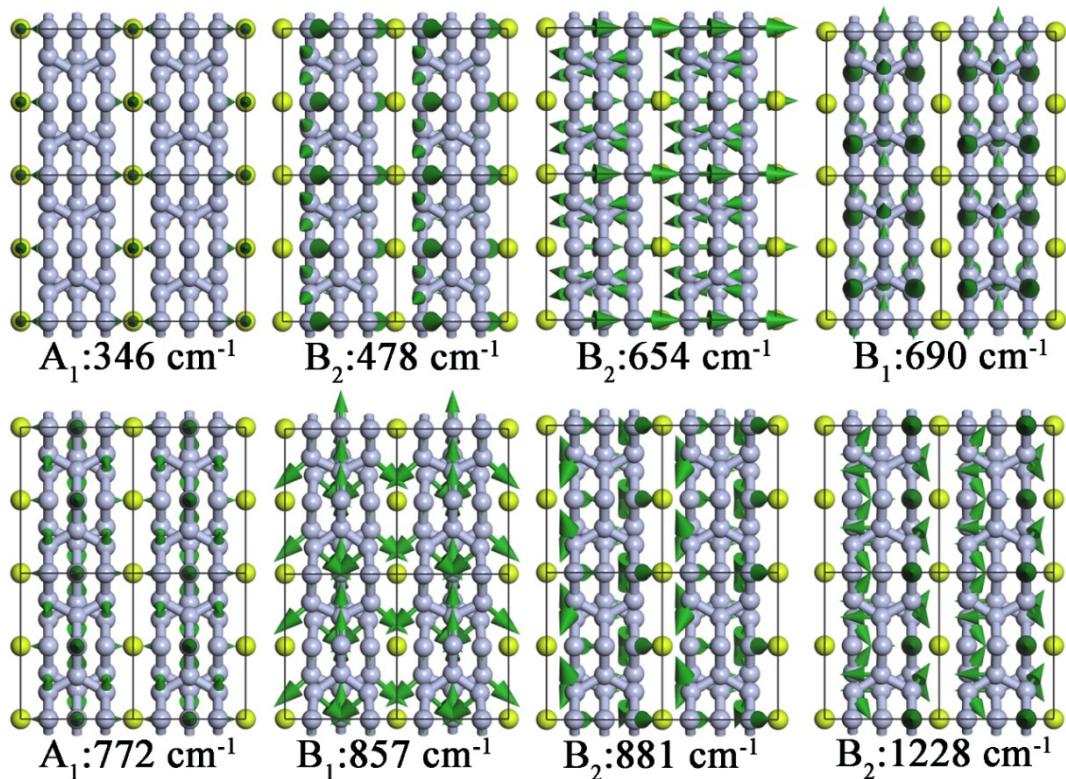
Fig. S8. IR vibrational modes of $Amm2$-CeN$_9$ at 200 GPa.

A$_1$:346 cm^{-1} B$_2$:478 cm^{-1} B$_2$:654 cm^{-1} B$_1$:690 cm^{-1}

A$_1$:772 cm^{-1} B$_1$:857 cm^{-1} B$_2$:881 cm^{-1} B$_2$:1228 cm^{-1}
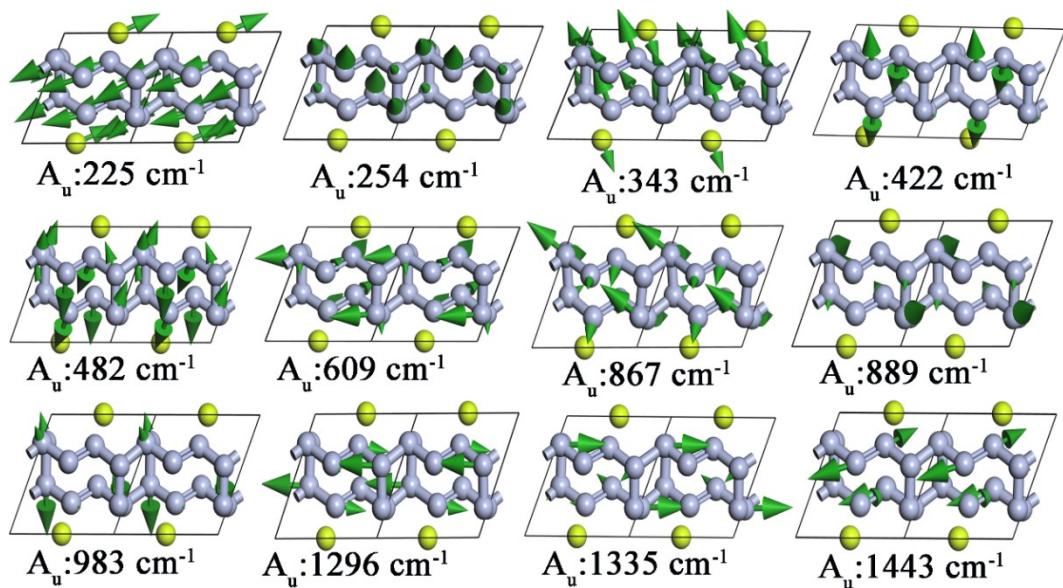
Fig. S9. IR vibrational modes of $P\bar{1}$-CeN$_{10}$ at 100 GPa.
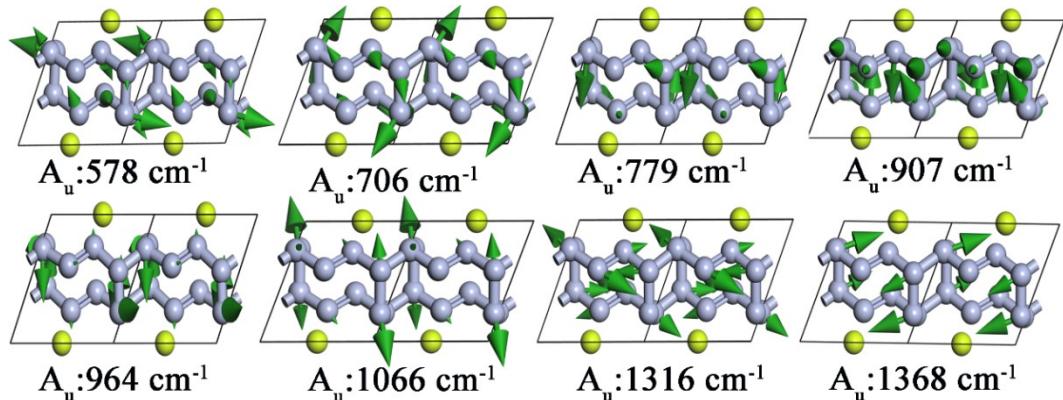
**Fig. S10.** Raman vibrational modes of $P\bar{1}$-CeN$_{10}$ at 100 GPa.
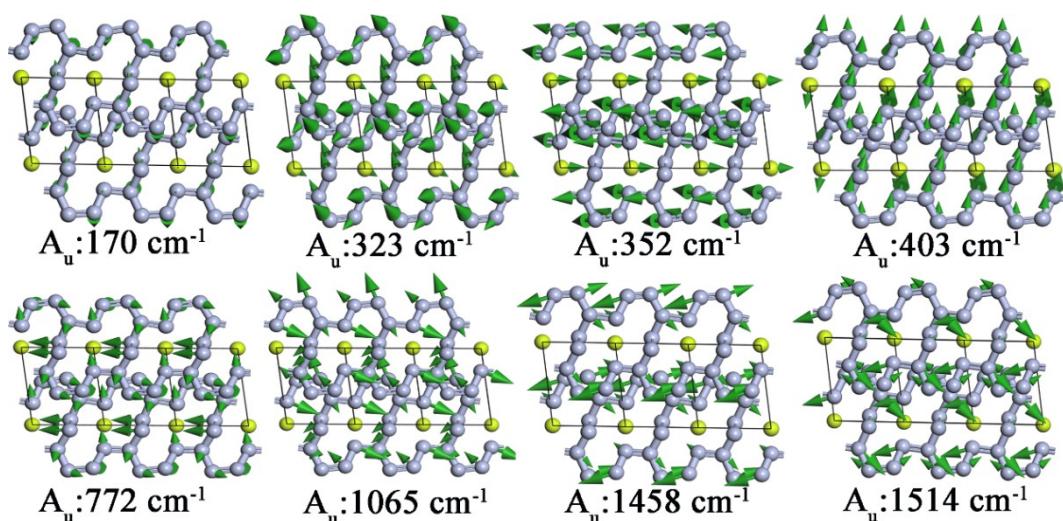
**Fig. S11.** IR vibrational modes of $P\bar{1}$-II-CeN$_{10}$ at 150 GPa.
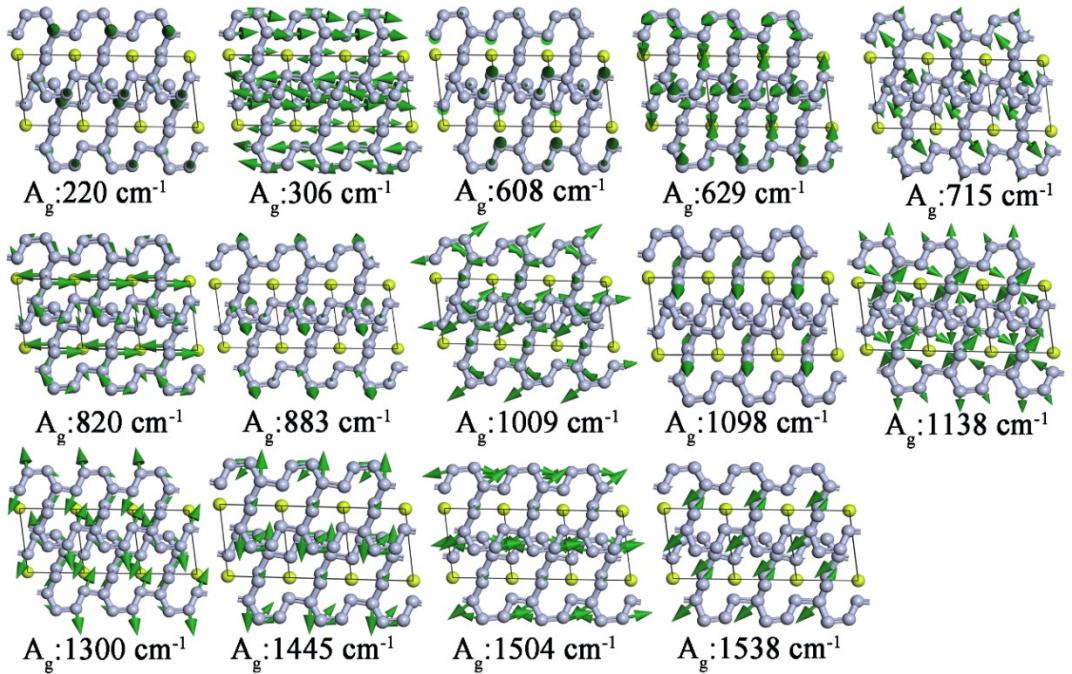
Fig. S12. Raman vibrational modes of $P\bar{1}$-II-CeN$_{10}$ at 150 GPa.

Table S1 Elastic constants (GPa) of the four phases at predict pressures.

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{23}$
$Pmn2_1$-CeN$_7$	660	806	778	154	249	219	229	347	169

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{23}$
$Amm2$-CeN$_9$	1247	1793	1071	422	291	440	444	294	355

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{15}$	C$_{23}$	C$_{25}$	C$_{35}$	C$_{46}$
$P\bar{1}$-CeN$_{10}$	671	1435	722	241	244	215	176	300	-25	164	-95	53	-101

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{15}$	C$_{23}$	C$_{25}$	C$_{35}$	C$_{46}$
$P\bar{1}$-II-CeN$_{10}$	1177	913	1096	116	321	211	216	474	-129	150	-25	-107	-17

For the orthorhombic phase, the mechanical stability criteria are shown as follows:

C$_{11}$ > 0; C$_{44}$ > 0; C$_{55}$ > 0; C$_{66}$ > 0;

C$_{11}$C$_{22}$ > C$_{12}$^{2};

C$_{11}$C$_{22}$C$_{33}$ + 2C$_{12}$C$_{13}$C$_{23}$ - C$_{11}$C$_{23}$^{2} - C$_{22}$C$_{13}$^{2} - C$_{33}$C$_{12}$^{2} > 0.

For the triclinic phase, the mechanical stability criteria are shown as follows:

$C_{11} > 0$; $C_{22} > 0$; $C_{33} > 0$; $C_{44} > 0$; $C_{55} > 0$; $C_{66} > 0$;

$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0$;

$(C_{33}C_{55} - C_{35}C_{35}) > 0$;

$(C_{44}C_{66} - C_{46}C_{46}) > 0$;

$(C_{22} + C_{33} - 2C_{23}) > 0$;

$(C_{22}(C_{33}C_{55}-C_{35}C_{35}) + 2C_{23}C_{25}C_{35}-C_{23}C_{23}C_{55}-C_{25}C_{25}C_{33})>0(2(C_{15}C_{25}(C_{33}C_{12}-C_{13}C_{23})$

$+ C_{15}C_{35}(C_{22}C_{13}-C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23}-C_{12}C_{13})) - (C_{15}C_{15}(C_{23}C_{33}-C_{23}C_{23}) +$

$C_{25}C_{25}(C_{11}C_{33}-C_{13}C_{13}) + C_{35}C_{35}(C_{11}C_{22}-C_{12}C_{12})) + C_{55}g)>0$.

$g=C_{11}C_{22}C_{33} - C_{11}C_{23}C_{23} - C_{22}C_{13}C_{13} - C_{33}C_{12}C_{12} + 2C_{12}C_{13}C_{23}$.

At predict pressure, the orthorhombic $Pmn2_1$-CeN$_7$ and $Amm2$-CeN$_9$, triclinic $P\bar{1}$-CeN$_{10}$ and $P\bar{1}$-II-CeN$_{10}$ are mechanically stable due to that their elastic constants satisfy to the criteria.

Table S2 Structural parameters (Å, °) of the four Ce-N compounds.

Structure	Lattice parameters	Atomic Positions
$Pmn2_1$-CeN$_7$	a =6.934, b =3.856, c =4.006 Å α=β=γ=90°	Ce1 (2a) (0.000, 0.226, -0.155) N1(4b) (0.339, 0.193, -0.177) N2 (4b) (0.828, 0.176, -0.652) N3 (4b) (0.166, 0.716, -0.011) N4 (2a) (0.500, 0.304, -0.020)
$Amm2$-CeN$_9$	a =4.455, b =5.780, c =4.313 Å α=β=γ=90°	Ce1 (2a) (0.000, 0.000, -0.670) N1(4c) (0.757, 0.000, -0.162) N2 (2b) (0.500, 0.000, -0.678) N3 (8f) (0.749, 0.313, -0.827) N4 (4e) (0.500, 0.198, -0.830)
$P\bar{1}$-CeN$_{10}$	a =4.169, b =4.217, c =4.512 Å α=67.004, β=104.702, γ=94.408°	Ce1 (1e) (0.500, 0.500, 0.000) N1(2i) (0.761, 0.824, 0.578) N2 (2i) (0.917, 0.012, 0.753) N3 (2i) (0.252, 0.048, 0.756) N4 (2i) (0.759, 0.320, 0.602) N5 (2i) (0.932, 0.519, 0.734)
$P\bar{1}$-II-CeN$_{10}$	a =3.645, b =4.090, c =4.657 Å α=107.381, β=82.415, γ=91.117°	Ce1 (1e) (0.000, 0.500, 0.000) N1(2i) (0.300, 0.179, 0.327) N2 (2i) (0.230, 0.709, 0.444) N3 (2i) (0.047, 0.879, 0.701) N4 (2i) (0.517, 0.826, 0.932) N5 (2i) (0.578, 0.723, 0.415)

Table S3 Bond lengths and -ICOHP in Ce-N compounds.

phase	N-N bond	bond length	number of bonds	average bond length	-ICOHP
$Pmn2_1$-CeN$_7$	N1-N2	1.43	4	1.37	12.80
	N1-N4	1.35	4		
	N2-N3	1.32	4		
	N1-N3	1.38	4		
$Amm2$-CeN$_9$	N1-N1	1.29	4	1.30	14.56
	N1-N3	1.29	4		
	N1-N4	1.30	4		
	N2-N4	1.32	4		
	N3-N4	1.30	4		
$P\bar{1}$-CeN$_{10}$	N1-N3	1.37	2	1.35	12.93
	N2-N3	1.39	2		
	N1-N2	1.35	2		
	N1-N5	1.35	2		
	N2-N4	1.34	2		
	N4-N5	1.29	2		
$P\bar{1}$-II-CeN$_{10}$	N1-N3	1.30	2	1.29	14.96
	N3-N2	1.29	2		
	N2-N5	1.26	2		
	N5-N1	1.29	2		
	N1-N4	1.29	2		
	N4-N4	1.38	1		

Table S4 Elastic constants (GPa) of the four phases at ambient pressure.

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{23}$
$Pmn2_1$-CeN$_7$	162	254	256	27	61	59	62	75	69

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{23}$
$Amm2$-CeN$_9$	370	689	149	148	51	165	95	57	74

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{15}$	C$_{23}$	C$_{25}$	C$_{35}$	C$_{46}$
$P\bar{1}$-CeN$_{10}$	811	210	194	54	61	57	49	51	-41	48	2	19	-7

phase	C$_{11}$	C$_{22}$	C$_{33}$	C$_{44}$	C$_{55}$	C$_{66}$	C$_{12}$	C$_{13}$	C$_{15}$	C$_{23}$	C$_{25}$	C$_{35}$	C$_{46}$
$P\bar{1}$-II-	467	135	309	38	88	27	2	61	-7.8	28	-6	-19	-5

CeN_{10}												

At ambient pressure, the criteria of mechanical stability are the same as above. The orthorhombic $Pmn2_1$-CeN$_7$ and $Amm2$-CeN$_9$, triclinic $P\bar{1}$-CeN$_{10}$ and $P\bar{1}$-II-CeN$_{10}$ are mechanically stable due to that their elastic constants satisfy to the criteria.