Supporting Information

Table 1. Calculated bond length for HXN and XN at DFT/6-311++G(3df,3pd)/SDD level of theory. X=Ti, Zr, Hf, Ce, Th.

Molecular	BP86		B3LYP		B3PW91	
	BL [a]	Freq [b]	BL	Freq	BL	Freq
HCe≡N	1.724	957.6	1.704	1008.4	1.694	1028.7
Ce≡N	1.771	915.4	1.764	940.5	1.753	959.8
HTi≡N	1.583	1091.2	1.565	1138.5	1.556	1151.8
Ti≡N	1.577	1104.2	1.558	1146.6	1.551	1162.3
HZr≡N	1.732	981.5	1.721	1011.1	1.708	1029.5
Zr≡N	1.725	999.8	1.710	1032.1	1.703	1045.4
HHf≡N	1.763	921.2	1.752	947.3	1.739	971.0
Hf≡N	1.759	918.3	1.744	950.0	1.734	982.9
HTh≡N	1.822	942.5	1.821	964.6	1.805	987.5
Th≡N	1.811	973.1	1.808	991.8	1.795	1014.8

[a] BL = Bond Length (in Å).
[b] Freq = Frequencies (in cm^{-1}).

Table 2. ADF energies of some low-lying Ce≡N MOs at SR-ZORA/GGA PBE level using Slater TZ2P basis functions. [a]

E_{MO} / eV	MO [b]	Contributions of AOs			
-5.386 (2) [c]	1π (2)	60% N2pπ	28% Ce5dπ	11% Ce4fπ	-
-4.660	1σ	45% N2pσ	19% Ce5dσ	17% Ce4fσ	8% Ce6pσ
-3.108	2σ	79% Ce6sσ	6% Ce6dσ	2% Ce4fσ	11% Ce6pσ

[a] The equilibrium B3LYP geometry (R_{Ce-N} = 1.764 Å) has been used. Contributions of AOs below 3% are not presented.

[b] The order of MOs are followed from the energy level diagram in figure 5.

[c] The number 2 in parentheses stands for second degenerate component.

Table 3. ADF energies of some low-lying HCe≡N MOs at SR-ZORA/GGA PBE level using Slater TZ2P basis functions. [a]

E_{MO} / eV	MO [b]	Contributions of AOs				
-6.316	1A'	37% N2pπ	30% Ce5dπ	-	-	22% H1sσ
-5.984	1A"	61% N2pπ	25% Ce5dπ	12% Ce4fπ	-	-
-5.381	2A'	37% N2pσ	6% Ce5dσ	15% Ce4fσ	-	22% H1sσ
-4.725	3A'	23% N2pσ	13% Ce5dσ	22% Ce4fσ	10% Ce6sσ	17% H1sσ

[a] The equilibrium B3LYP geometry (R_{Ce-N}= 1.704 Å & R_{H-Ce} = 2.113 Å for H-Ce) has been used. Contributions of AOs below 3% are not presented.

[b] The order of MOs are followed from the energy level diagram in figure 5.

Table 4. ADF energies of some low-lying HCe MOs at SR-ZORA/GGA PBE level using Slater TZ2P basis functions. [a]

E_{MO} / eV	MO [b]	Contributions of AOs			
-5.573	1A'	14% Ce6sσ	22% Ce5dσ	-	59% H1sσ
-3.348	1A"	70% Ce6sσ	25% Ce5dπ	-	-
-2.566	2A'	-	7% Ce5dσ	92% Ce4fσ	-
-2.513	3A'	-	79% Ce5dσ	20% Ce4fσ	-

[a] The equilibrium B3LYP geometry ($R_{H\text{-}Ce}$ = 2.113 Å) has been used. Contributions of AOs below 3% are not presented.

[b] The order of MOs are followed from the energy level diagram in figure 5.