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Reactions of Ruthenium Cyclopentadienyl Precursor in the Metal Precursor Pulse of Ru Atomic Layer Deposition

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Table S1. The calculated reaction energy for hydrogen transfer step and reaction barriers on Ru (001) and (100) surfaces with NH_x terminations corresponding to zero-K condition. If the reaction energies of hydrogen transfer step are positive, the barriers are not calculated.

	$A: H^* + RuCp_2 \rightarrow RuCp^* + HCp$			$B: H^* + RuCp \rightarrow Ru^* + HCp$		
	$E_{adsorption}$	$E_{hydrogen}{}^{I}$	$E_{barrier}$	$E^{Des}{}_{CpH}{}^{I}$	$E_{hydrogen}{}^{II}$	$E_{barrier}$
Ru(001)	-1.47	-0.17	1.33	-0.34	-0.04	0.98
Ru(100)	-0.62	0.48	2.67	3.20	2.46	Not calculated

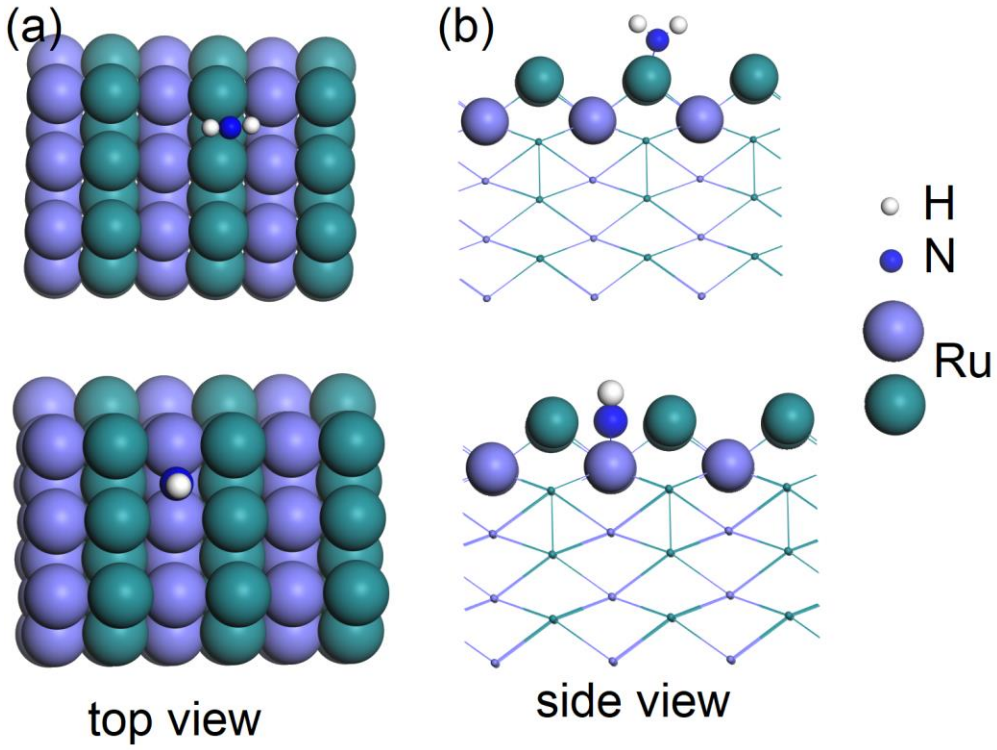

Figure S1. The configurations of the (a) top view and (b) side view of single NH and NH_2 adsorbed on Ru(100) surface. NH prefers channel bridge and NH_2 prefers surface bridge site.

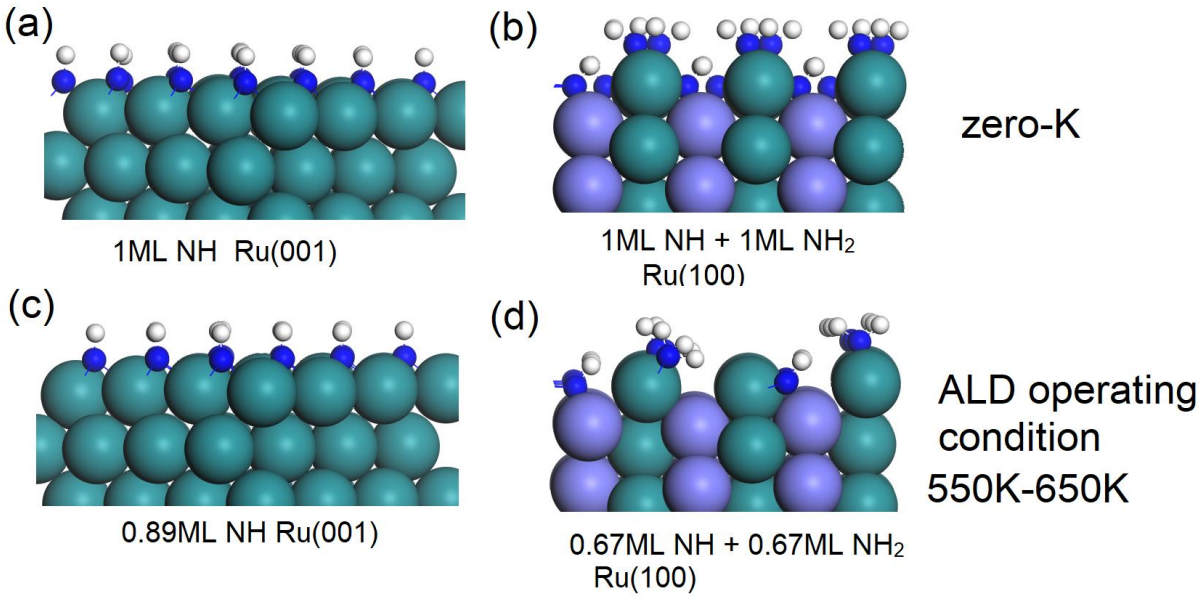

Figure S2. The side view of NH_x-terminated Ru surface at zero-K or high coverage condition including (a) Ru(001), and (b) Ru(100) and at ALD operating condition, with lower coverage including (c) Ru(001), and (d) Ru(100). Ru atoms are represented by green colour for surface terminating atoms and purple colour for the channel atoms in the (100) surface; N atom and H atom are represented by dark blue and white atom, respectively.

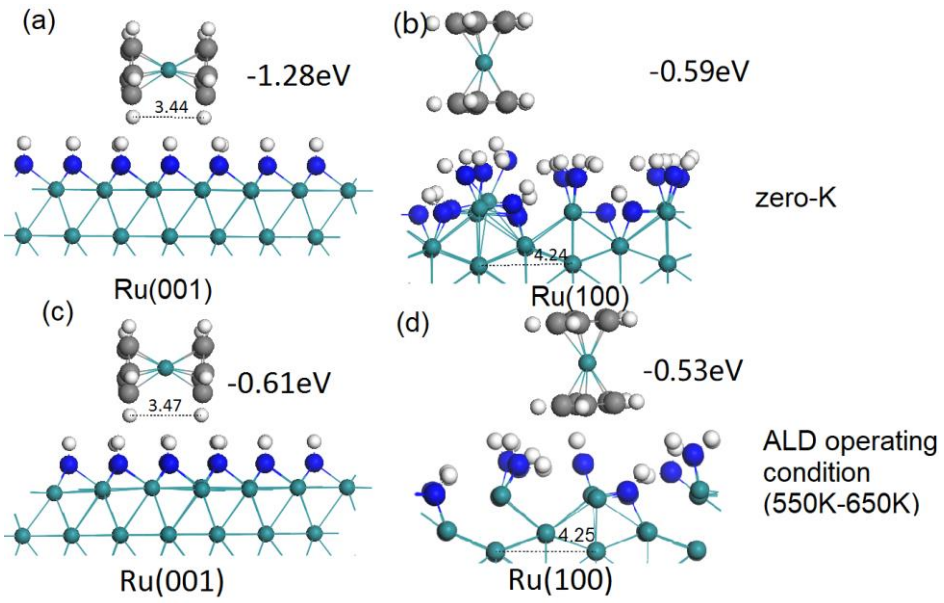

Figure S3. The configurations of the less stable adsorption mode of precursor $RuCp_2$ on (a) Ru(001) surface, and (b) Ru(100) surface at zero-K and on (c) Ru(001) surface, and (d) Ru(100) surface at ALD operating condition. Ru atoms are represented by green colour. N atom and H atom are represented by dark blue and white atom, respectively.

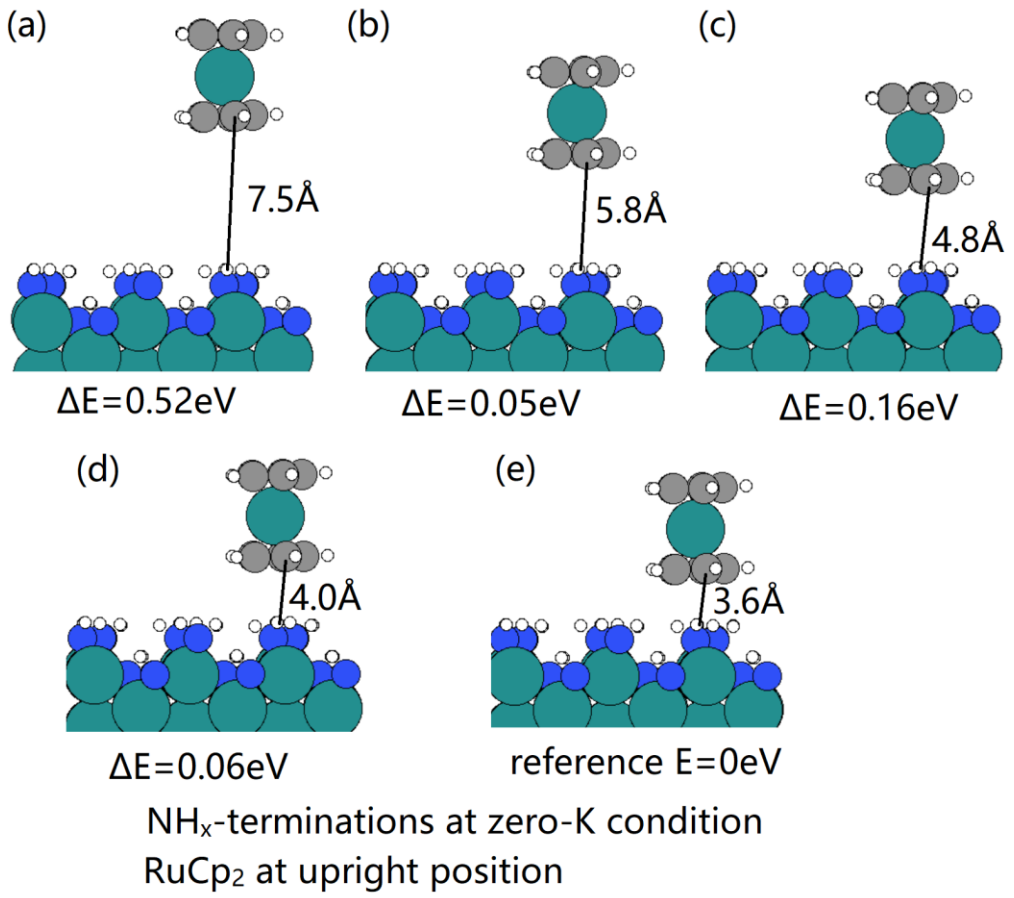

Figure S4. The computed energies for metal precursor $RuCp_2$ at upright position on Ru(100) surface with NH_x terminations at zero-K condition.

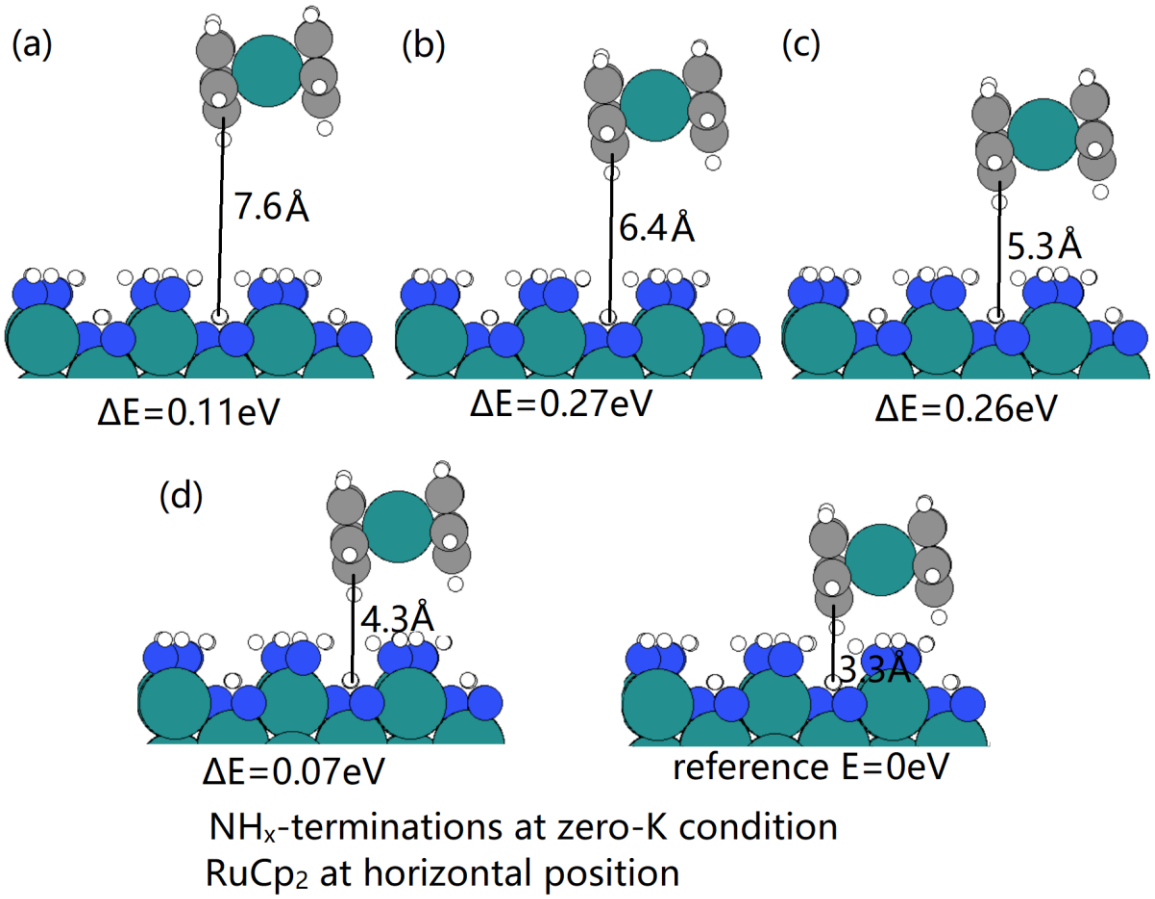

Figure S5. The computed energies for metal precursor RuCp2 at horizontal position on Ru(100) surface with NH_x terminations at zero-K condition.

The adsorption energy of precursor A at the metal surface is computed from

$$E_{ad} = E_{tot} - E_{\frac{NHx}{Metal}} - E_A$$

where E_{tot}, $E_{NHx/Metal}$, and E_A are the energy of the NH_x-terminated metal slab with the precursor $RuCp_2$ adsorbed, the slab model for the NH_x-terminated metal surface, and isolated precursor $RuCp_2$, respectively. A negative adsorption energy corresponds to exothermic adsorption. All the energies are computed with the van der Waals correction included. For the values of $E_{NHx/Metal}$, we have performed the calculations with surface bounded $RuCp_2$ removed to exclude any effect of surface NH_x rearrangement after the adsorption of $RuCp_2$.

Here, $RuCp_2$ can be placed in **upright** position with only one Cp ring interacting with substrate and **horizontal** position with two Cp rings interacting with substrate. At each binding mode, $RuCp_2$ is moved from far away from substrate NH_x-terminated Ru surface (C-H distance around 8Å) to close to substrate NHx-terminated Ru surface (C-H distance around 3Å). The results are shown in Figure S4 (upright position) and Figure S5 (horizontal position). The energies are with reference to the structure with the lowest energy, which is the structure of surface bounded $RuCp_2$ with shortest C-H distance. The adsorption energies are then computed with reference to the values of the two structure of surface bounded $RuCp_2$ with shortest C-H distance, which are -0.59eV for upright position and -0.62eV for horizontal position.

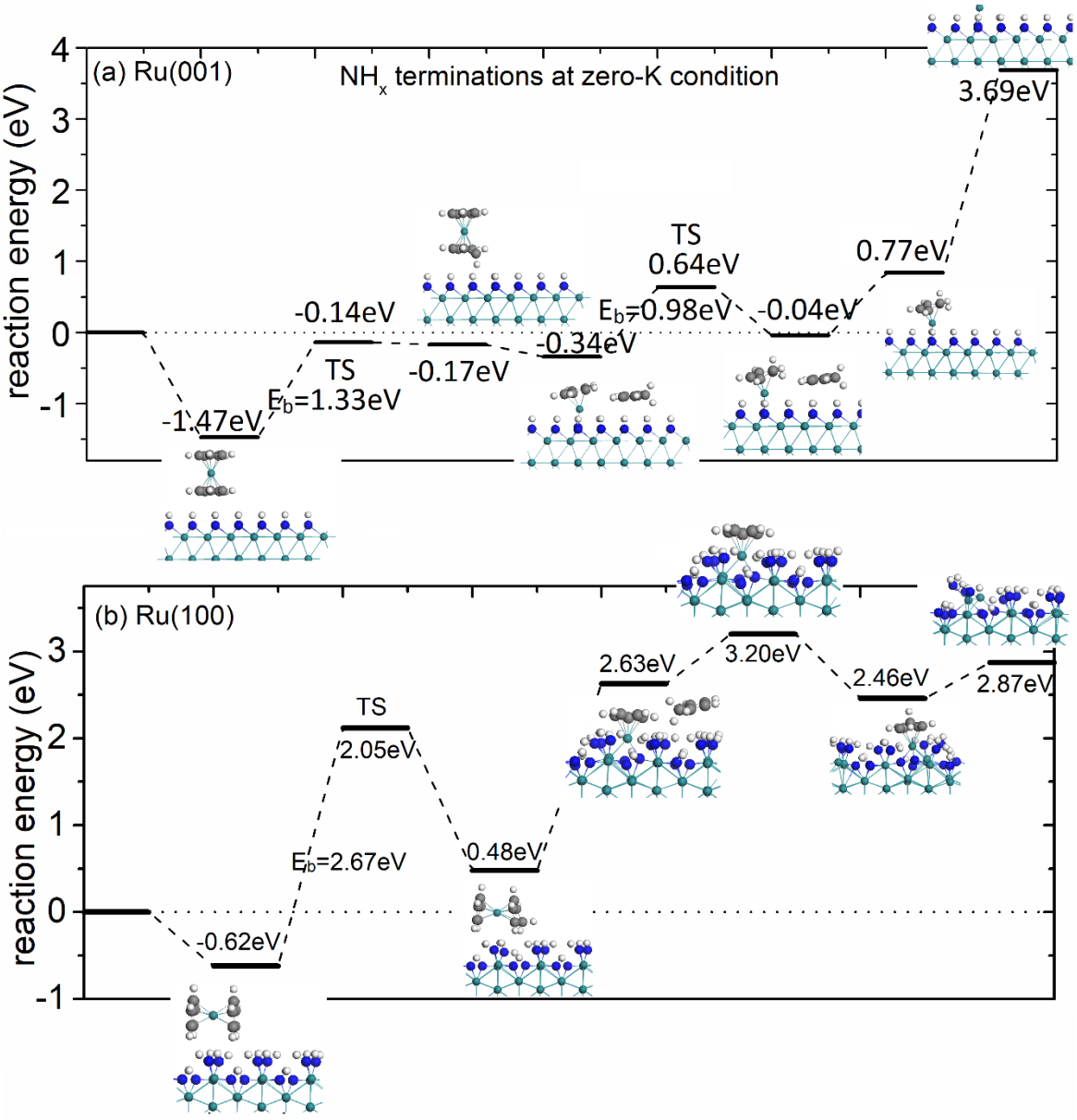

Figure S6. The plotted metal precursor reaction pathway on (a) Ru(001) surface and (b) Ru(100) surface with NH_x terminations at zero-K condition. The Cp ligand is eliminated via hydrogen transfer. The substrate Ru atoms are represented by green spheres. Carbon, nitrogen and hydrogen atoms are represented by grey, blue and white colour, respectively.

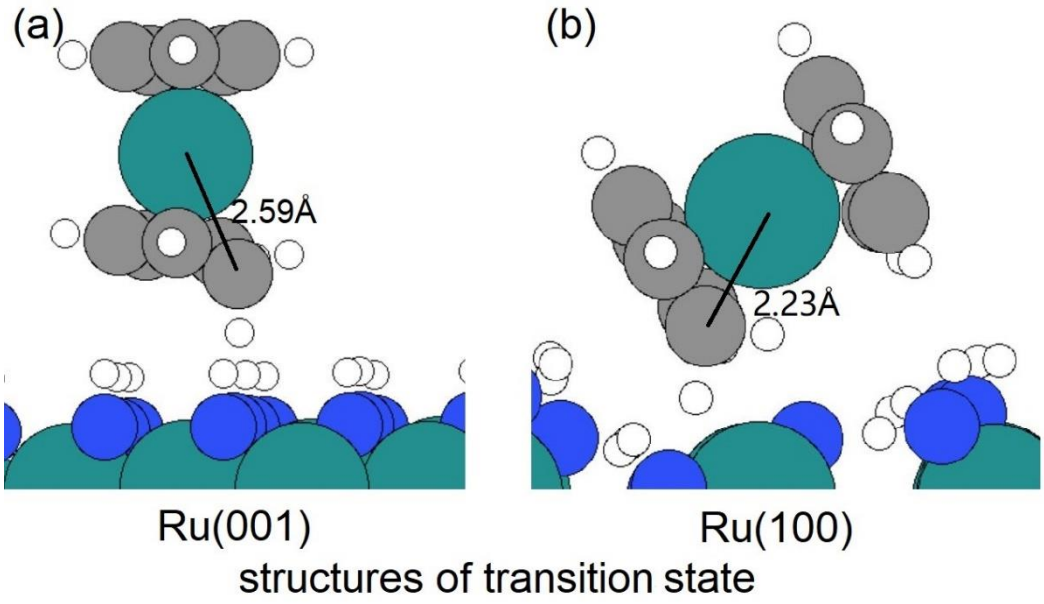

Figure S7. The structures of transition state for hydrogen transfer on NH_x-terminated (a) Ru(001) surface and (b) Ru(100) surface.