Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for:

Elementary kinetics of nitrogen electroreduction to ammonia on late transition metals

Gholamreza Rostamikia,[2] Sharad Maheshwari,[1] and Michael J. Janik[1,*]

1 - The Pennsylvania State University, Department of Chemical Engineering, University Park, PA, U. S. A.
2 – University of North Carolina – Wilmington, Department of Chemistry and Biochemistry, Wilmington, NC, U. S. A.

*corresponding author: mjanik@psu.edu, tel. (814)863-9366, fax. (814)865-7846

Table S1. DFT calculated non-electrochemical barriers for N_2 hydrogenation and NH^* hydrogenation on different surfaces. Transition state barrier for N_2 hydrogenation was referenced to $G_{N2(gas)}+G_{H^*}+G_{H2O}$

Surface	Activation barrier (eV) for $H^* + H_2O + N_2(gas) \rightarrow N2H^* + H2O$	Activation barrier (eV) for $NH^* + H_2O + H^* \rightarrow NH_2^* + H_2O$	U^0
Pt(111)	1.59	0.93	0.25
Ir(111)	1.68	1.19	0.20
Rh(111)	1.51	1.38	0.31
Cu(111)	2.58	0.95	0.03
Ni(111)	1.80	1.26	0.36
Pd(111)	1.68	1.21	0.40
Ru(0001)	1.83	-	0.38
Fe(110)	1.05	1.64	0.48

Table S2. DFT calculated non-electrochemical barriers for water assisted transfer of hydrogen (H*) from one surface site to another. Two sets of calculations were performed where H* was positioned on Atop site or hollow site at the initial state and final state. The transition state corresponding to the lower energy initial state was used to calculate data in table 2.

Surface	H* at FCC hollow site			H* at Atop site		
	Gibbs free energy of initial state (eV)	Gibbs free energy of transition state (eV)	Ga (eV)	Gibbs free energy of initial state (eV)	Gibbs free energy of transition state (eV)	Ga(eV)
Pt(111)	-224.90	-224.25	0.65	-224.92	-224.54	0.38
Ir(111)	-318.47	-317.57	0.89	-318.55	-317.68	0.87
Rh(111)	-263.54	-262.45	1.09	-263.35	-262.48	0.87
Cu (111)	-143.35	-142.20	1.15	-142.80	-142.15	0.65
Ni(111)	-203.05	-201.90	1.15	-202.55	-201.85	0.70
Pd(111)	-195.67	-194.71	0.96	-195.20	-194.85	0.35
Ru(0001)	-328.69	-327.44	1.25	-328.57	-327.34	1.23
Fe(110)	-301.31	-299.99	1.32			

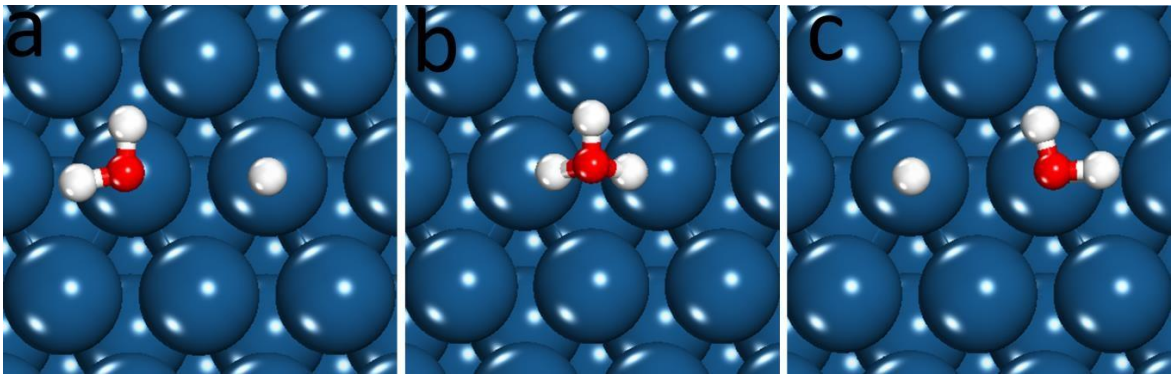

Figure S1. Equilibrium and transition states for water assisted transfer of hydrogen (H*) from one surface site to another on Pt(111), H* was at Atop site at the initial state, (a) initial state, (b) transition state and (c) final state.

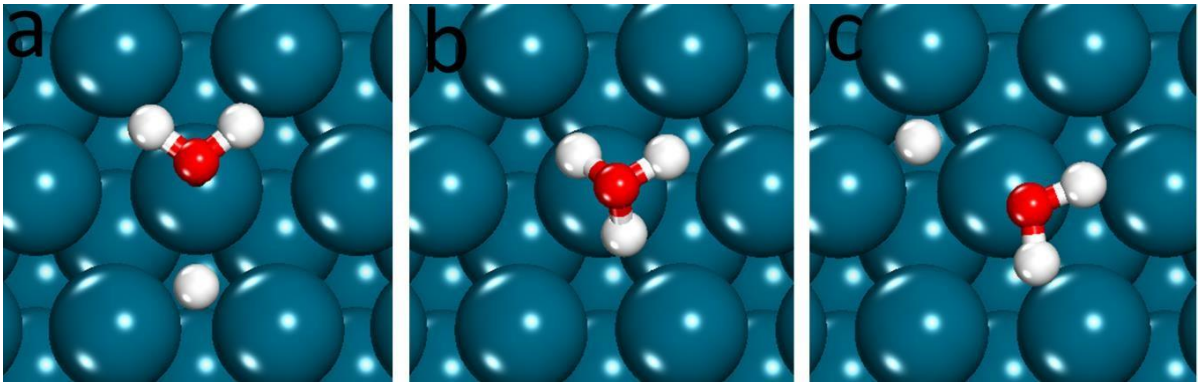

Figure S2. Equilibrium and transition states for water assisted transfer of hydrogen (H*) from one surface site to another on Pd(111), H* was at FCC hollow site at the initial state, (a) initial state, (b) transition state and (c) final state.

Table S3. DFT calculated N_2 dissociation barriers on late transition metal surfaces.

Surface	Referenced Initial state Gibbs free energy, $G^*+G_{N2(gas)}$ (eV)	Gibbs free energy of transition state (eV)	Ga (eV)
Pt(111)	-224.30	-220.42	3.88
Ir(111)	-317.87	-315.05	2.82
Rh(111)	-262.81	-260.41	2.40
Cu (111)	-142.98	-138.63	4.36
Ni(111)	-202.31	-200.27	2.03
Pd(111)	-194.89	-191.30	3.58
Ru(0001)	-327.85	-326.12	1.72
Fe(110)	-300.53	-299.94	0.59

Table S4. DFT calculated hydrogen evolution barriers on late transition metal surfaces. Lowest energy initial state was used for all transition state searches. At the initial state for platinum and iridium, two H* were adsorbed on Atop site and nearby FCC hollow site. At the initial state of all other FCC metals and ruthenium, two H* were adsorbed at the FCC hollow site and nearby HCP hollow site.

Surface	Gibbs free energy of initial state (eV)	Gibbs free energy of transition state (eV)	Ga (eV)
Pt(111)	-214.46	-213.79	0.67
Ir(111)	-307.99	-307.31	0.67
Rh(111)	-253.01	-252.33	0.68
Cu (111)	-132.59	-132.10	0.49
Ni(111)	-192.61	-191.80	0.81
Pd(111)	-185.26	-184.62	0.64
Ru(0001)	-318.12	-317.35	0.77
Fe(110)	-291.30	-290.00	1.30

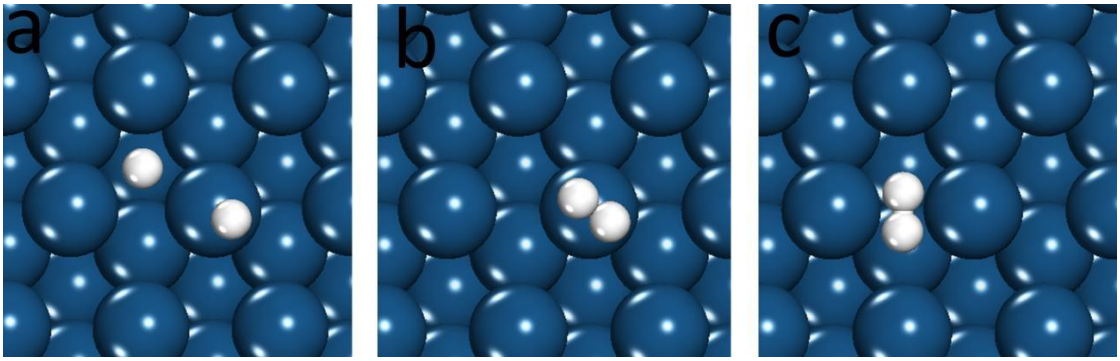

Figure S3. Equilibrium and transition states for hydrogen evolution reaction on Ir(111), (a) initial state, (b) transition state and (c) final state.

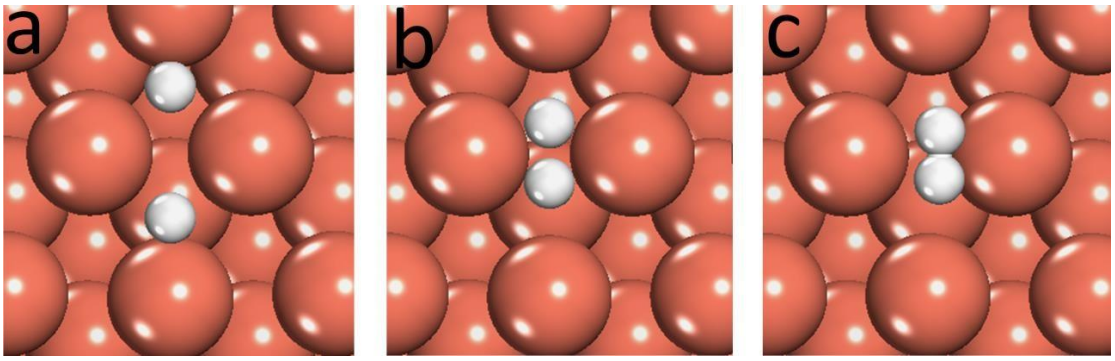

Figure S4. Equilibrium and transition states for hydrogen evolution reaction on Cu(111), (a) initial state, (b) transition state and (c) final state.

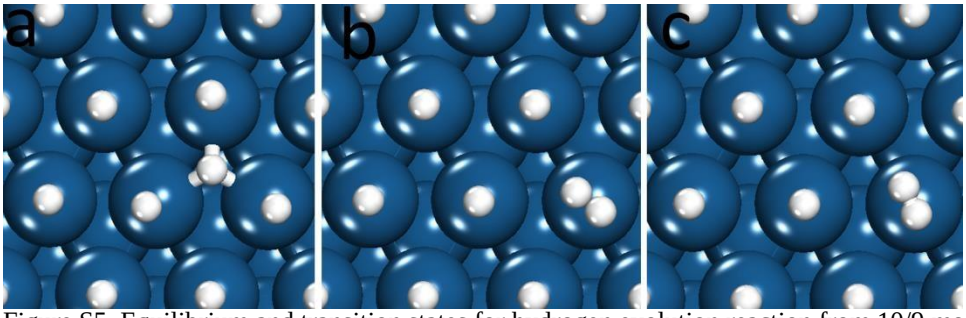

Figure S5. Equilibrium and transition states for hydrogen evolution reaction from 10/9 monolayer hydrogen on Pt(111), (a) initial state, (b) transition state and (c) final state.

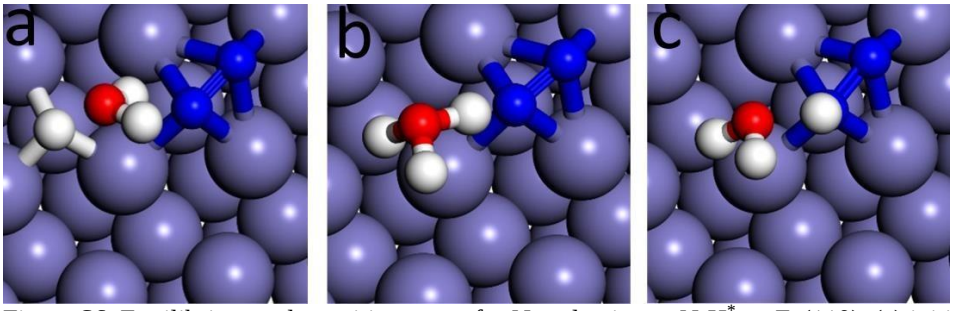

Figure S6. Equilibrium and transition states for N_2 reduction to N_2H^* on Fe(110), (a) initial state, (b) transition state and (c) final state.

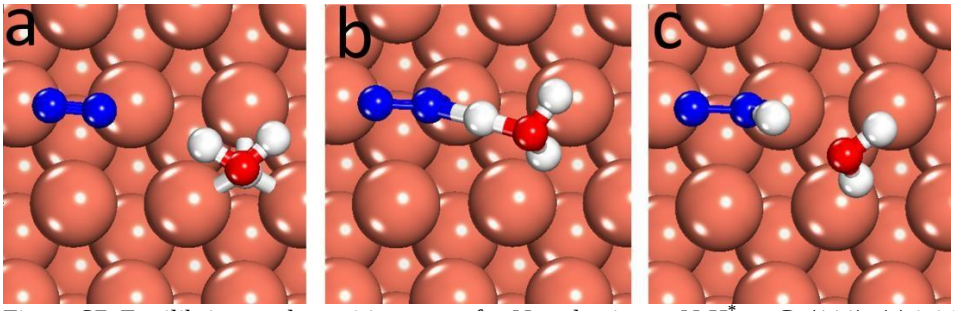

Figure S7. Equilibrium and transition states for N_2 reduction to N_2H^* on Cu(111), (a) initial state, (b) transition state and (c) final state.

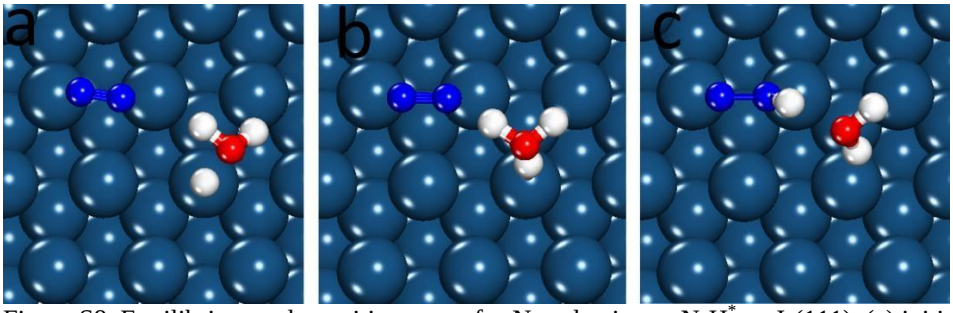

Figure S8. Equilibrium and transition states for N_2 reduction to N_2H^* on Ir(111), (a) initial state, (b) transition state and (c) final state.

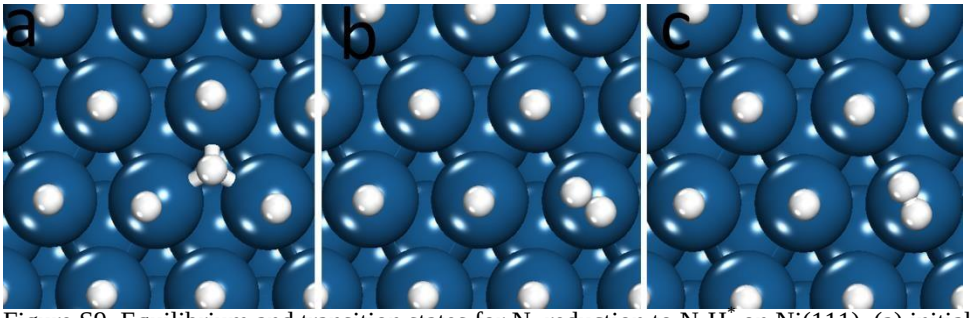

Figure S9. Equilibrium and transition states for N_2 reduction to N_2H^* on Ni(111), (a) initial state, (b) transition state and (c) final state.

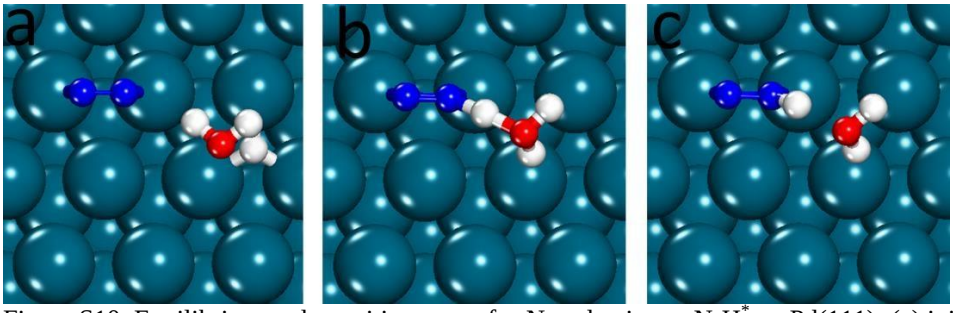

Figure S10. Equilibrium and transition states for N_2 reduction to N_2H^* on Pd(111), (a) initial state, (b) transition state and (c) final state.

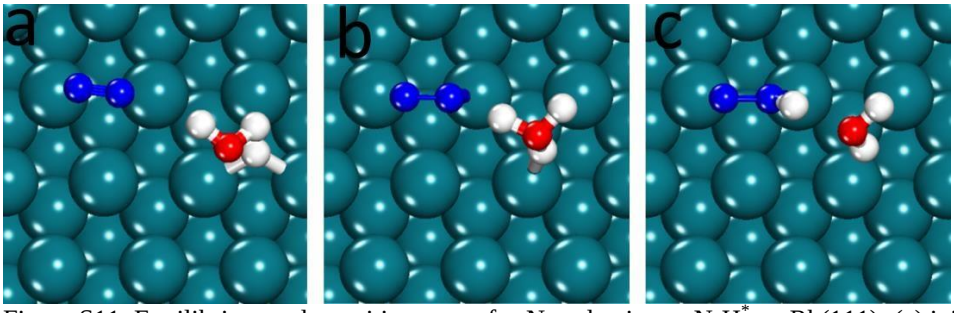

Figure S11. Equilibrium and transition states for N_2 reduction to N_2H^* on Rh(111), (a) initial state, (b) transition state and (c) final state.

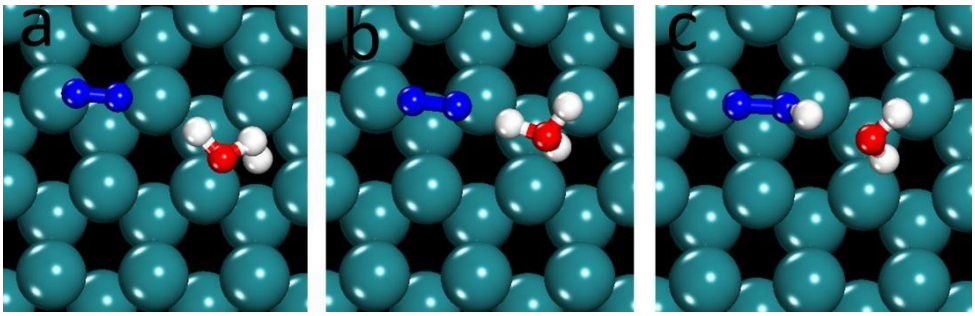

Figure S12. Equilibrium and transition states for N_2 reduction to N_2H^* on Ru(0001), (a) initial state, (b) transition state and (c) final state.

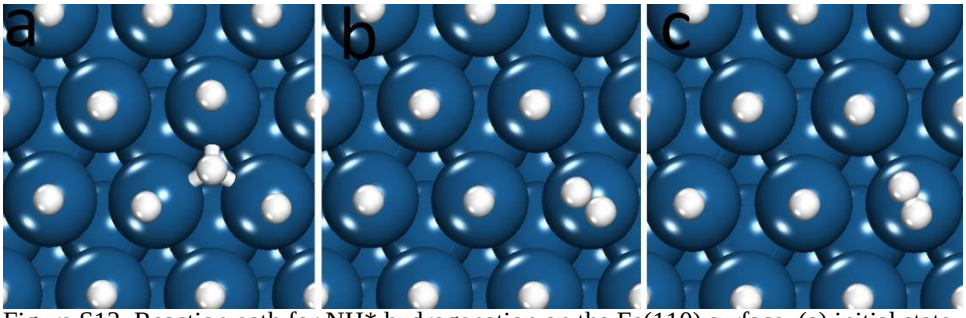

Figure S13. Reaction path for NH* hydrogenation on the Fe(110) surface, (a) initial state, (b) transition state and (c) final state

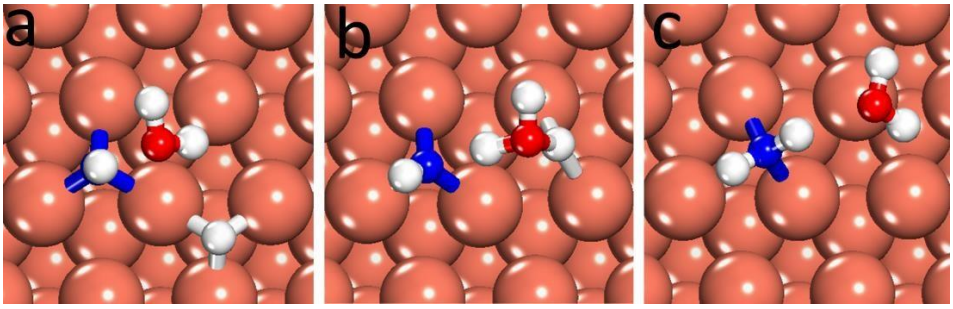

Figure S14. Reaction path for NH* hydrogenation on the Cu(111) surface, (a) initial state, (b) transition state and (c) final state

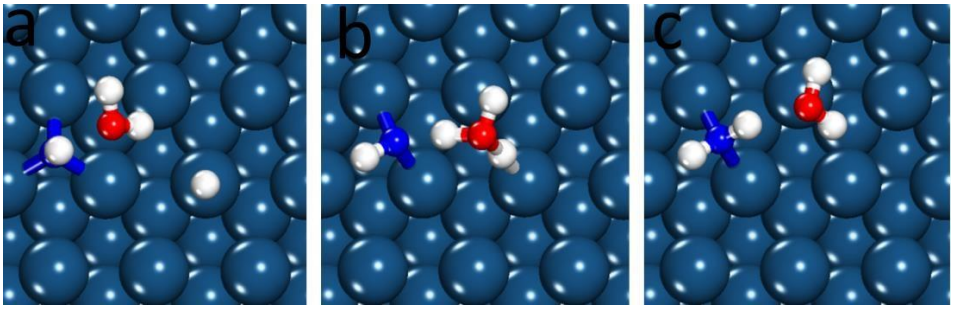

Figure S15. Reaction path for NH* hydrogenation on the Ir(111) surface, (a) initial state, (b) transition state and (c) final state

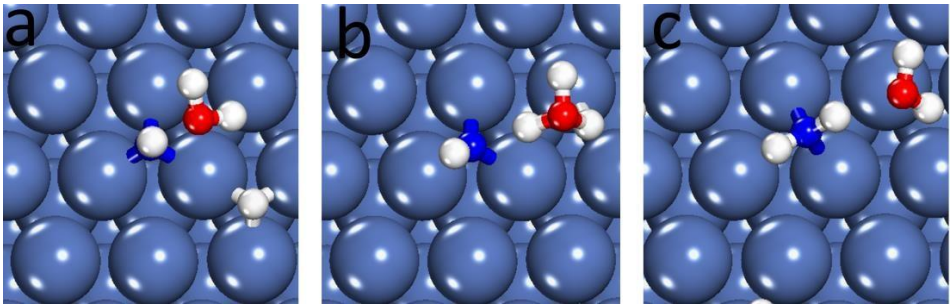

Figure S16. Reaction path for NH* hydrogenation on the Ni(111) surface, (a) initial state, (b) transition state and (c) final state

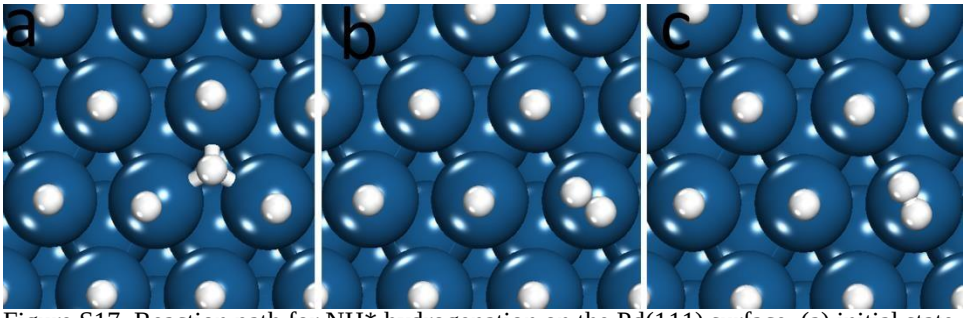

Figure S17. Reaction path for NH* hydrogenation on the Pd(111) surface, (a) initial state, (b) transition state and (c) final state

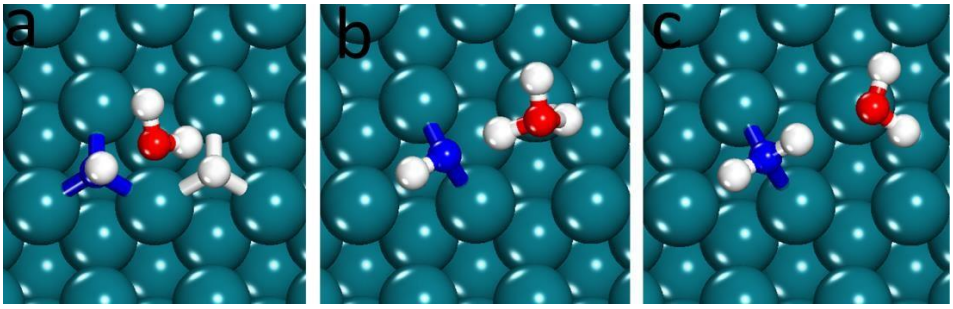

Figure S18. Reaction path for NH* hydrogenation on the Rh(111) surface, (a) initial state, (b) transition state and (c) final state