Electronic Supplementary Information (ESI)

Gold catalyzed hydrogenations of small imines and nitriles: Enhanced reactivity of Au surface toward H_2 via collaboration with a Lewis base

Gang Lu,[a,b] *Peng Zhang,*[a] *Dongqing Sun,*[a] *Lei Wang,*[a] *Kebin Zhou,*[a] *Zhi-Xiang Wang,**[a] *and Guo-Cong Guo**[b]

[a]College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

[b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

Corresponding Authors: zxwang@ucas.ac.cn; gcguo@fjirsm.ac.cn

Fig. S1: Geometric (the key bond lengths in Å) and energetic (kcal mol^{-1}, relative to Au(111) + H_2) results for the H_2 activation on Au(111).

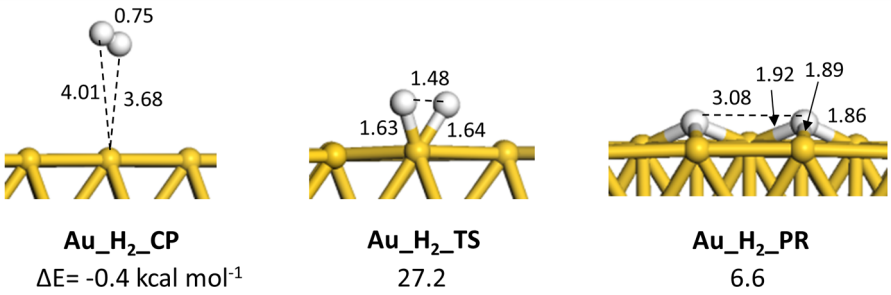


Fig. S2: The PDOS of H_2 and Au d_{xy}, d_{yz}, d_{xz}, d_{x2-y2} states in the transition state of **Au_H$_2$_NH$_3$_TS**. The Fermi level was set at 0. There are almost not obvious state mixing between these four kinds of *d* states and the H_2 state.

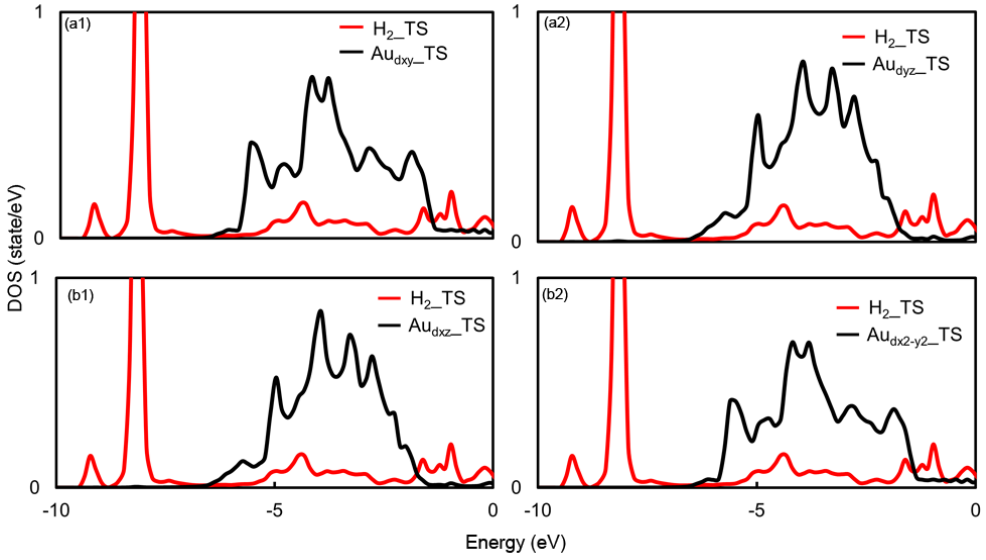
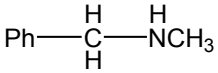
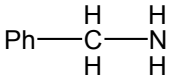


Fig. S3: Spectroscopic data for the synthesized amines.



N-Benzylmethylamine: light yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.75 (s, 2H), 7.25-7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 36.1, 56.2, 127.1, 128.3, 128.5, 140.2; MS (EI) m/z 121 (M^+, 55%), 120 (100%), 91 (54%), 44 (40%).



Benzylamine: colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 2H), 7.21-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 46.6, 126.9, 127.2, 128.6, 143.5; MS (EI) m/z 107 (M^+, 58%), 106 (100%).

Fig. S4: TEM images of the gold powder before (a) and after (b) reactions.

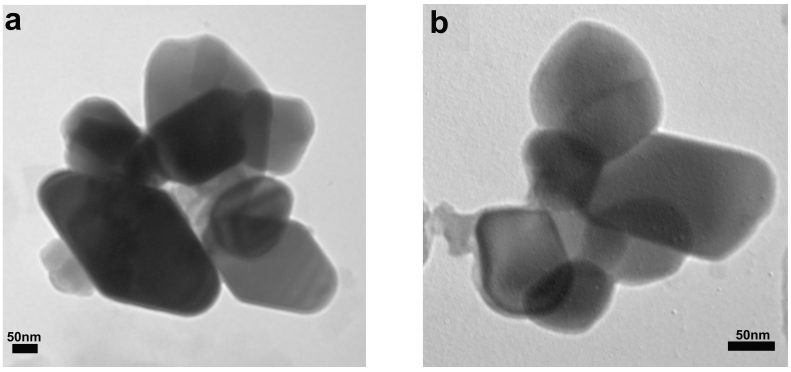


Fig. S5: Geometric (the key bond lengths in Å) and energetic (kcal mol^{-1}) results for the activations of N-H bonds of Me_2C=NH and Me_2CHNH_2 and O-H bond of Me_2CHOH on Au(111). The binding energies of **IMa**, **IMb** and **IMc** are 5.1, 7.4 and 1.4 kcal mol^{-1} relative to clean surface and free molecules, respectively. Obviously, these bond activations are unfavorable both kinetically and thermodynamically.