Phosphine Ligands-coated Cu Nanoparticle Catalyzed Selective Semihydrogenation of Alkynes: Electronic or Hindrance Effects of Ligand?

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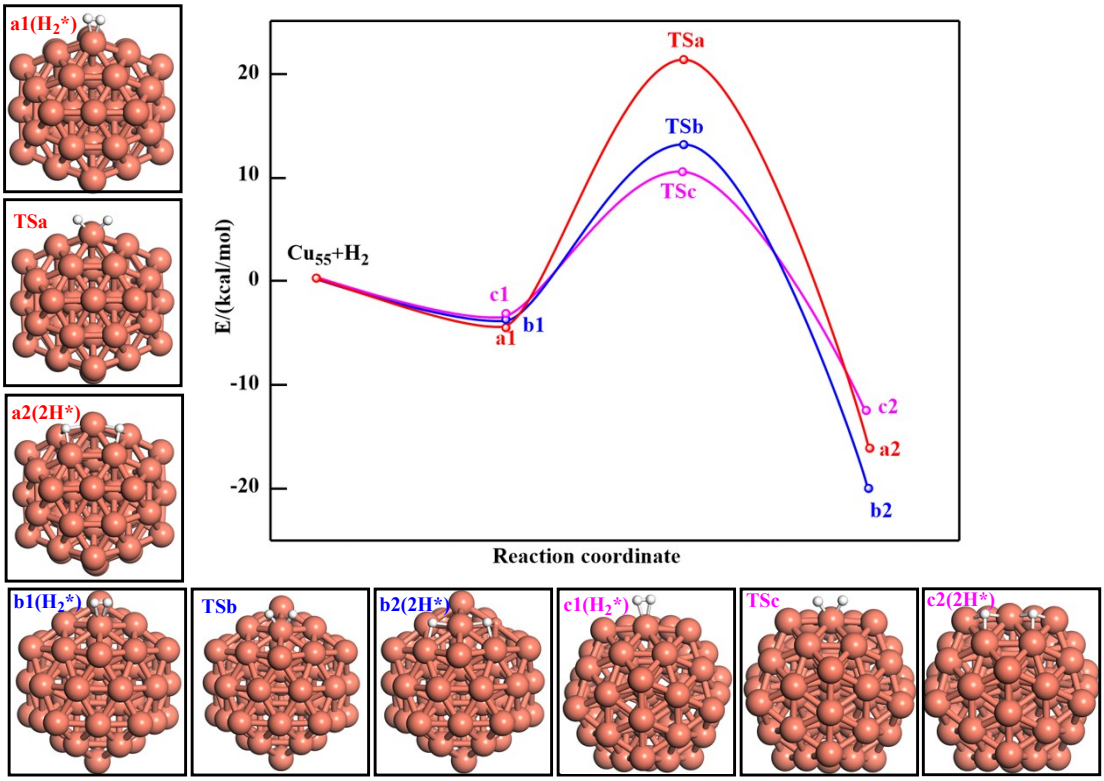


Figure S1. The representative pathways of H_2 dissociation at the top and edge sites of the Cu_{55}. The * represents the adsorption state.

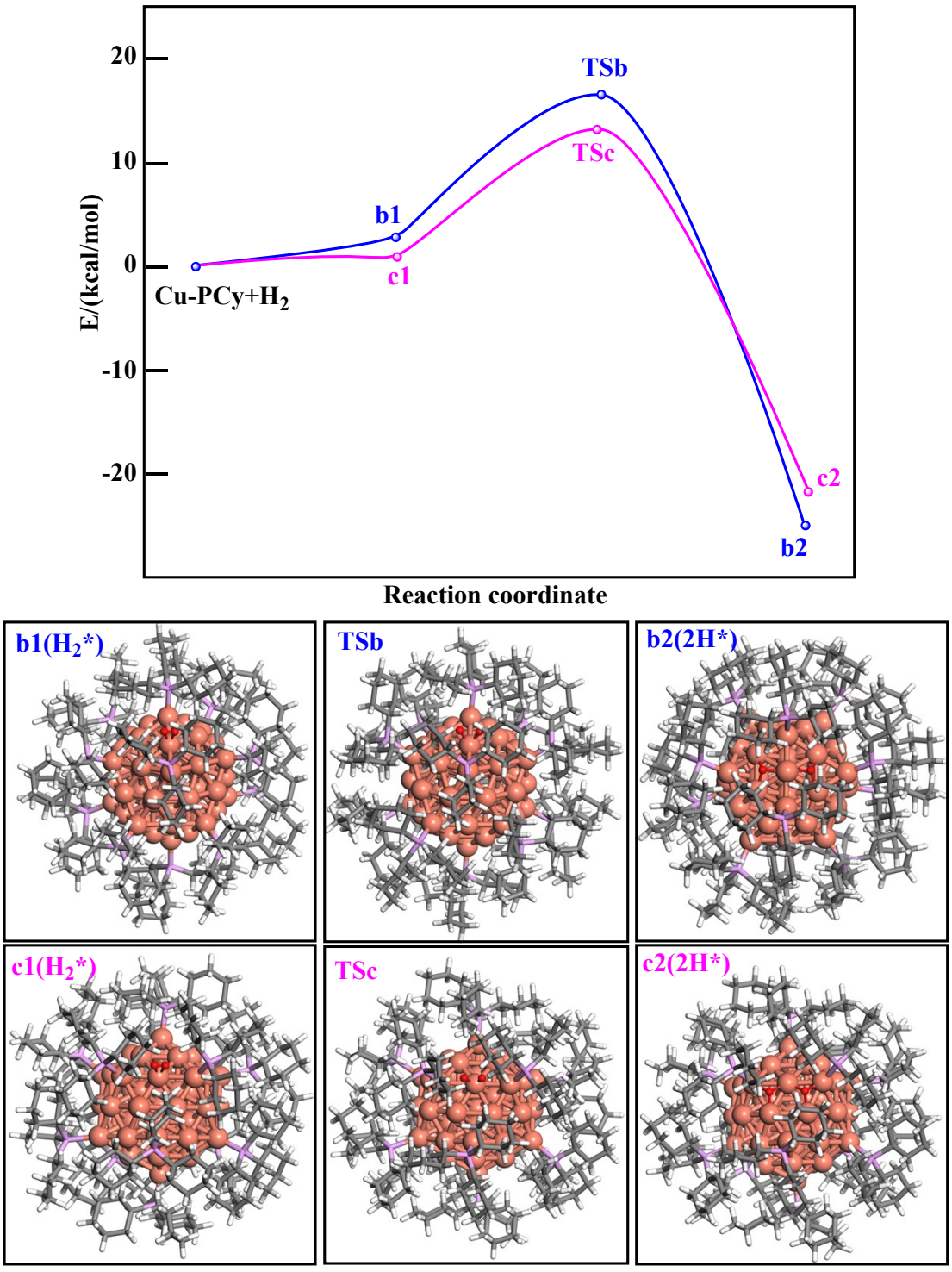


Figure S2. The representative pathways of H_2 dissociation at the top and edge sites of the Cu-PCy. (The * represents the adsorption state. The H is labeled as red.)

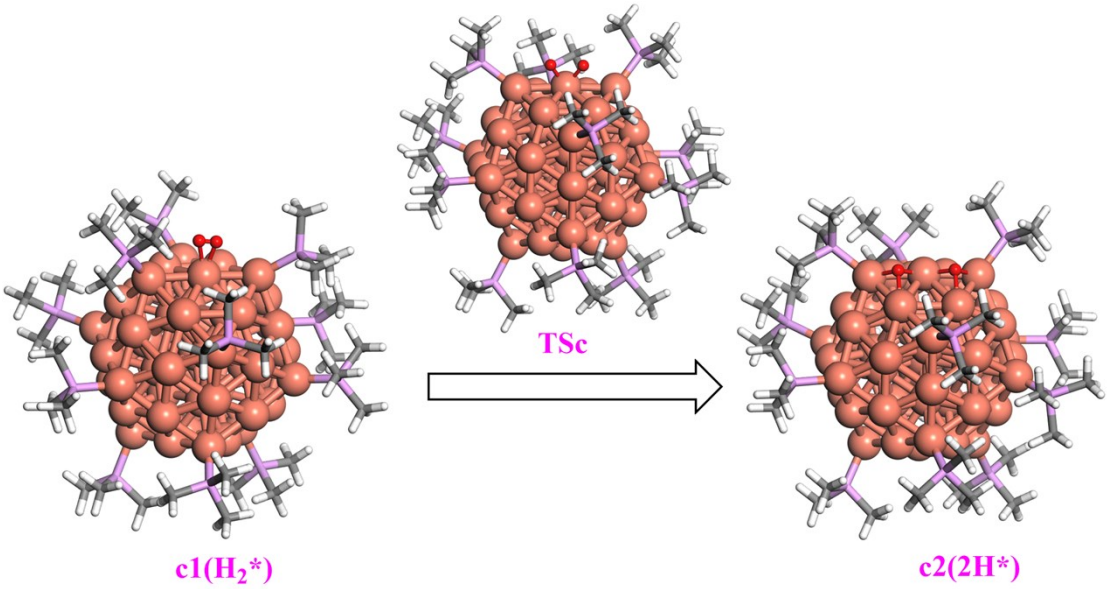


Figure S3. The representative pathways of H_2 dissociation at the top and edge sites of the Cu-PMe. (The * represents the adsorption state. The H is labeled as red.)

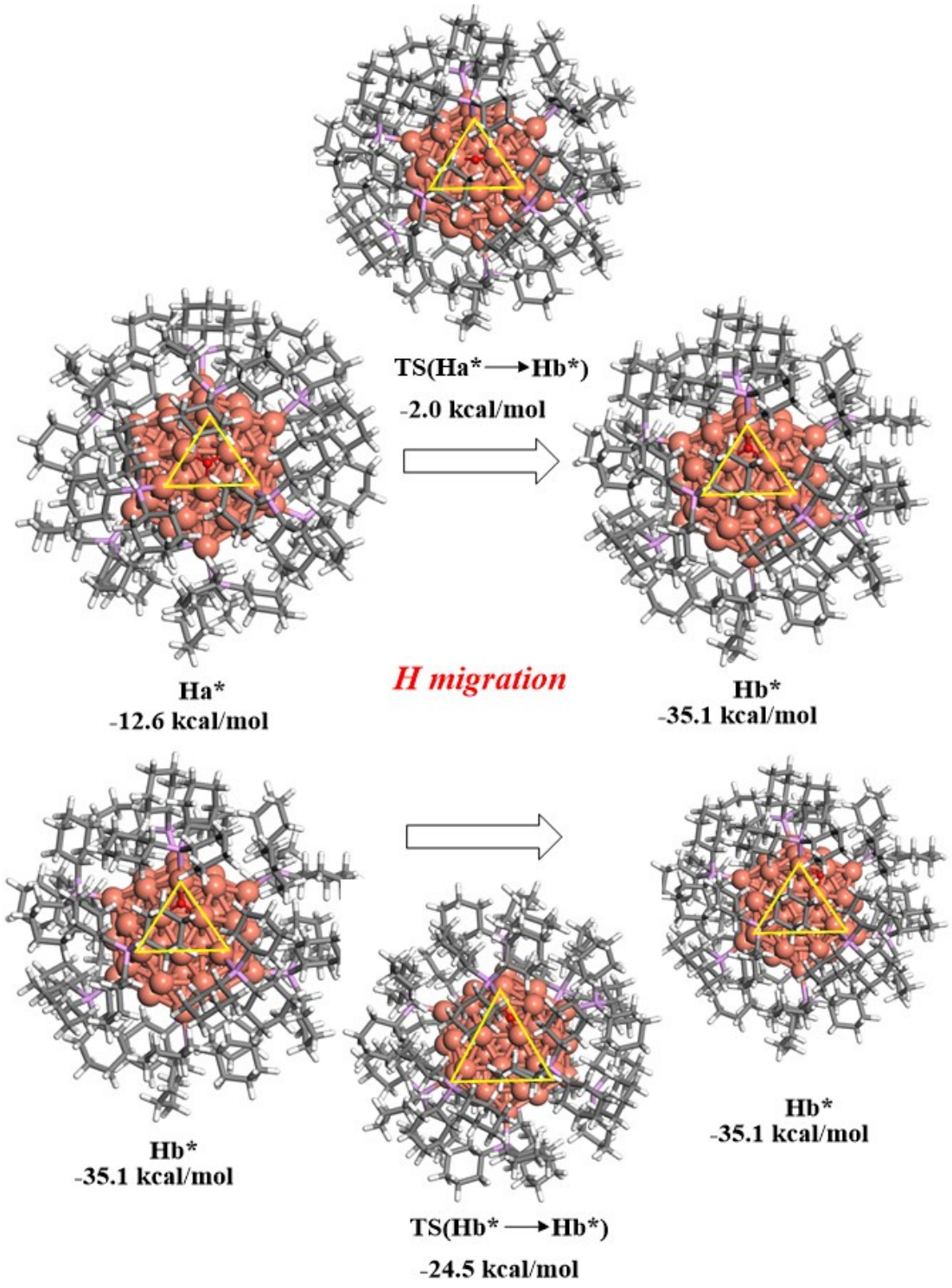


Figure S4. The representative pathways of diffusion of a H atom on the Cu-PCy. (The * represents the adsorption state. The H is labeled as red.)

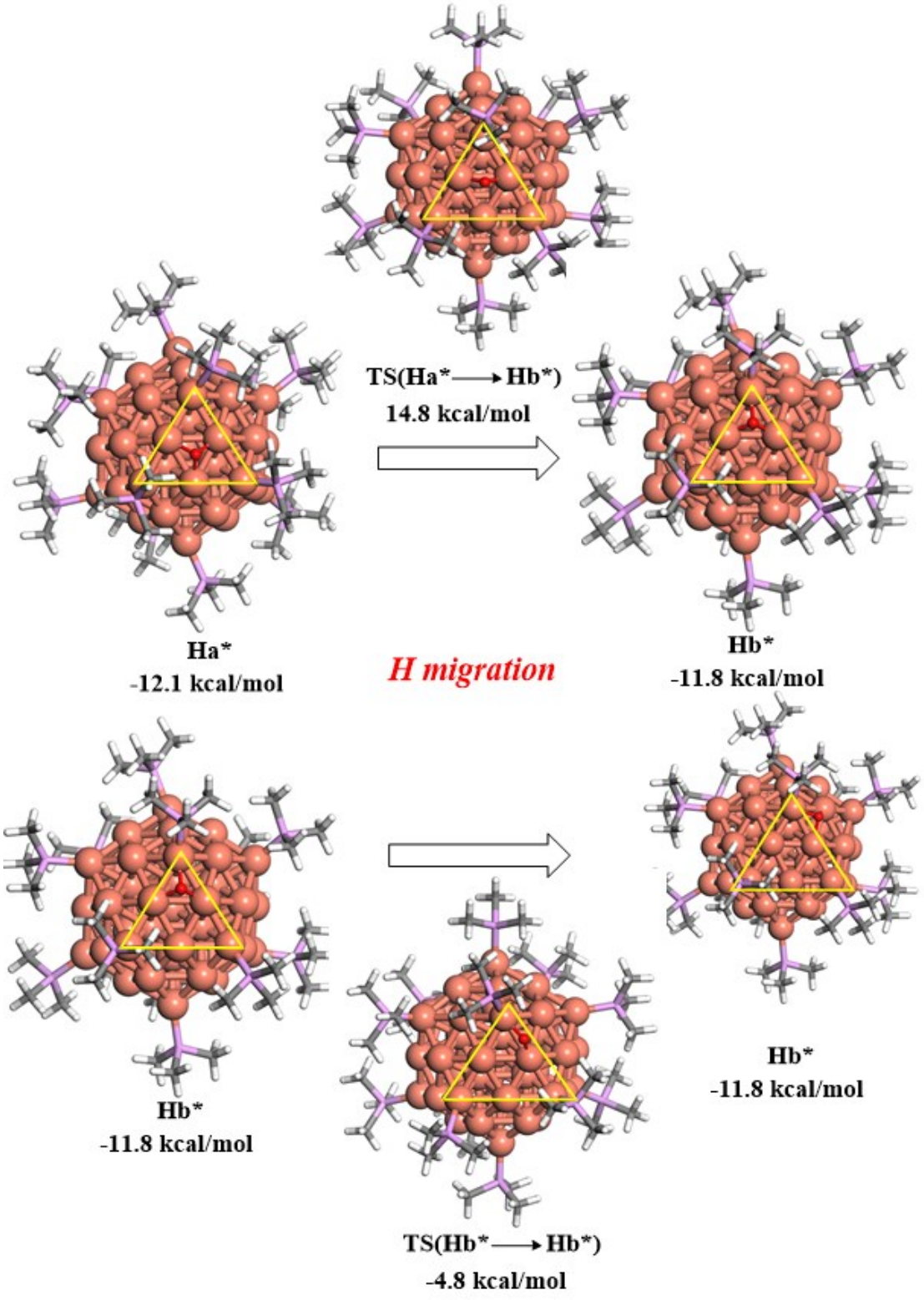


Figure S5. The representative pathways of diffusion of a H atom on the Cu-PMe. (The * represents the adsorption state. The H is labeled as red.)

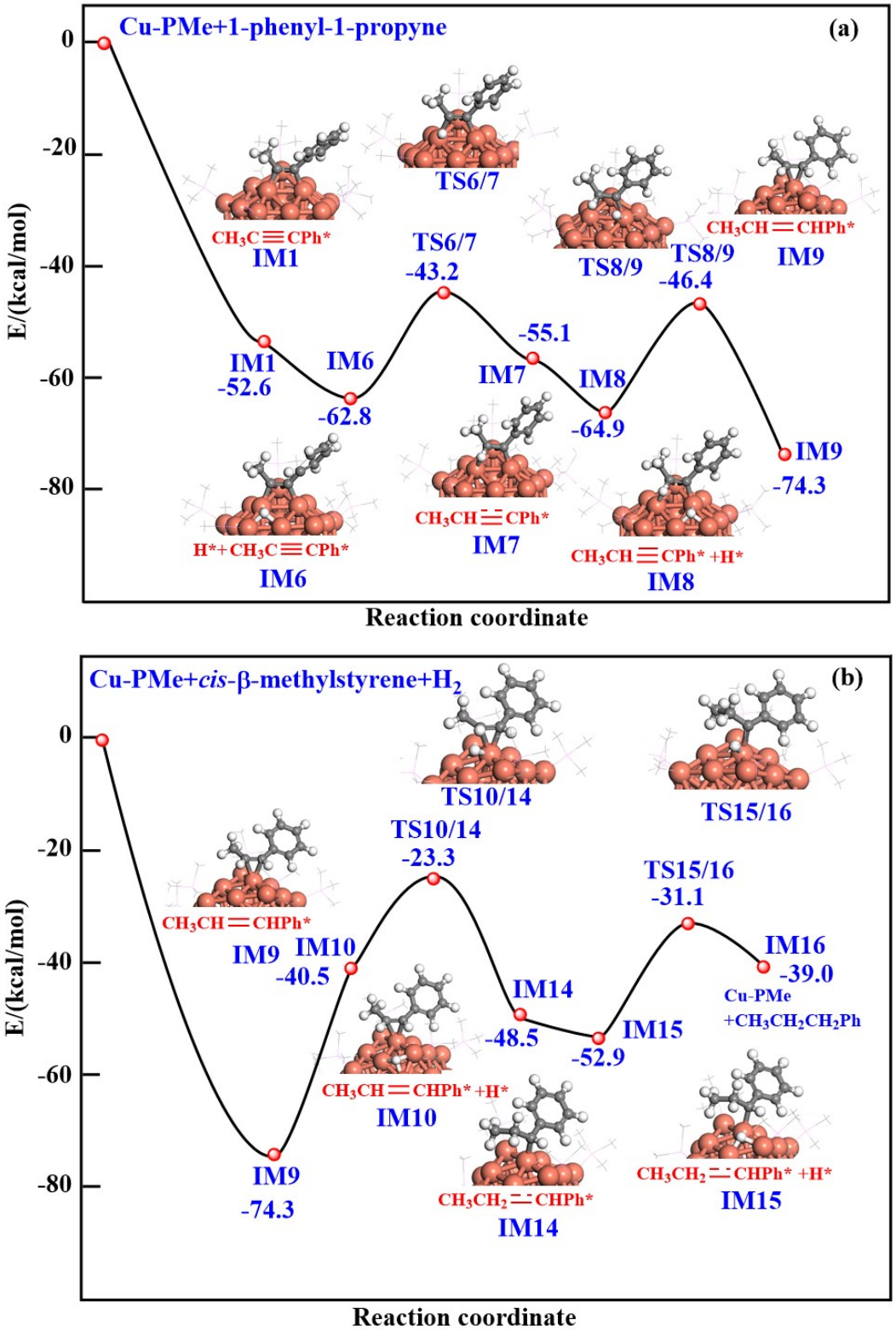


Figure S6. The potential energy profiles of the hydrogenation mechanism of the 1-phenyl-1-propyne (a) and *cis*-β-methylstyrene (b) catalyzed by the Cu-PMe. The * represents the adsorption state.

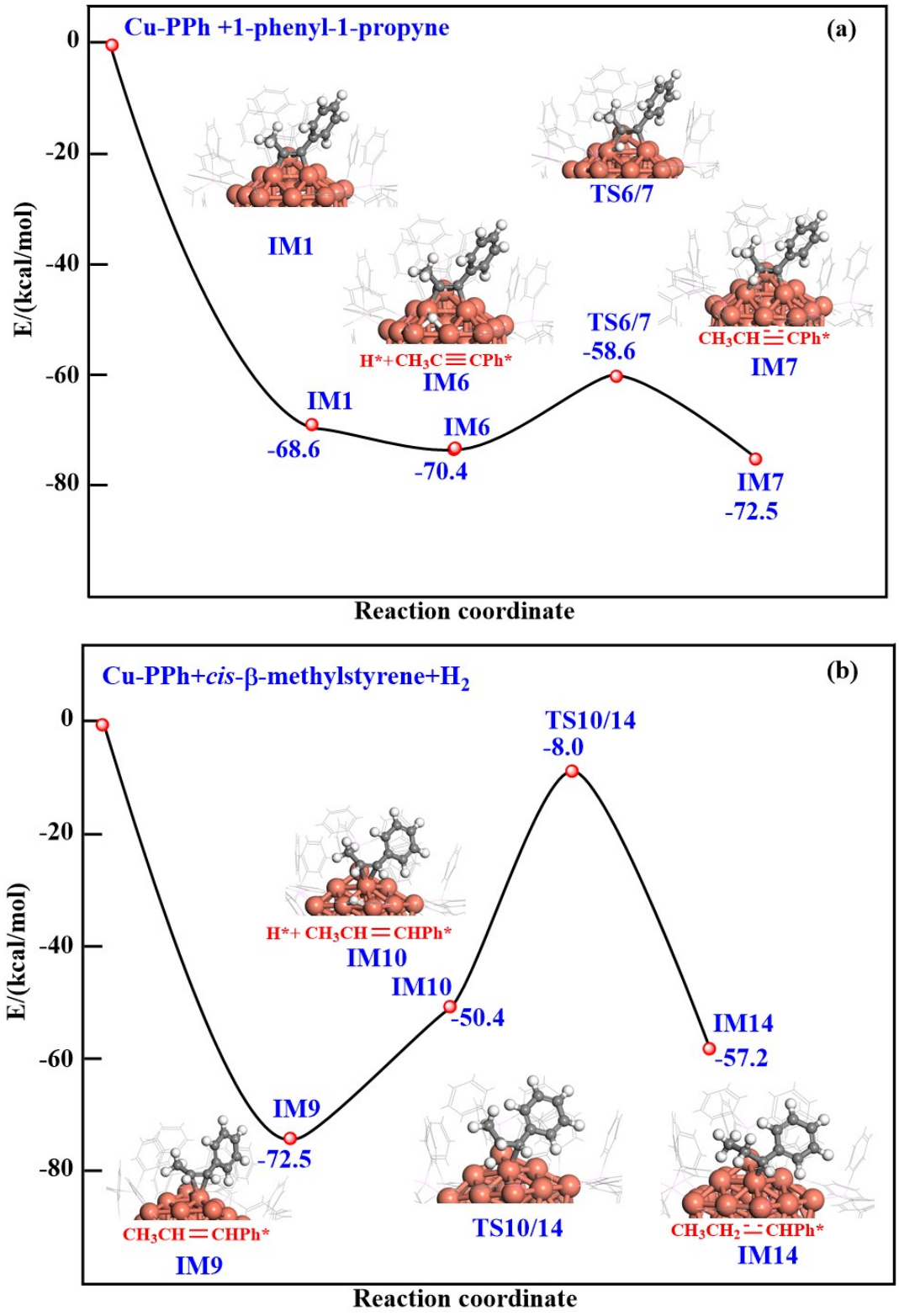
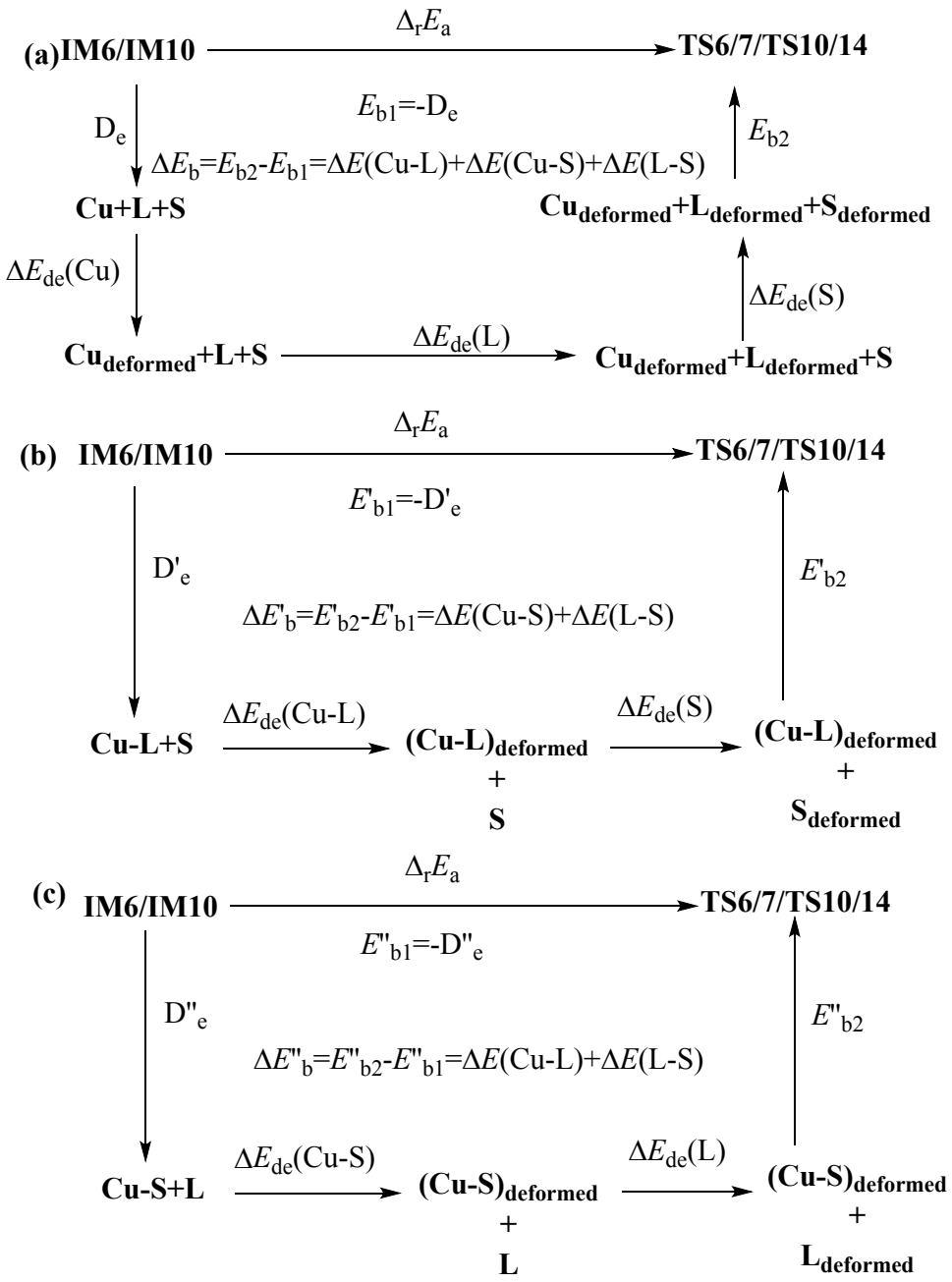


Figure S7. The potential energy profiles of the hydrogenation mechanism of the 1-phenyl-1-propyne (a) and *cis*-β-methylstyrene (b) catalyzed by the Cu-PPh. The * represents the adsorption state.

Details for Energy Decomposition Analysis



$$\Delta_r E_a = \Delta E_{de}(Cu) + \Delta E_{de}(L) + \Delta E_{de}(S) + \Delta E(Cu\text{-}L) + \Delta E(Cu\text{-}S) + \Delta E(L\text{-}S)$$

Cu is on behalf of Cu_{55} fragment.

S is the substrate fragment.

L refers to the ligand fragment.

Scheme S1. Framework of energy decomposition analysis "**IM6/IM10 → TS6/7/TS10/14"**.

In Scheme 1, De represented the energy required to dissociate the **IM6/IM10** into

Cu, L and S fragments. D'e represented the energy required to dissociate the **IM6/IM10** into Cu-L and S fragments. D"e represented the energy required to dissociate the **IM6/IM10** into Cu-S and L fragments. ΔE_{de}(L), ΔE_{de}(Cu), ΔE_{de}(S), ΔE_{de}(Cu-L) and ΔE_{de}(Cu-S) referred to the energy needed to deform the L, Cu, S, Cu-L and Cu-S fragments to the geometries they have in **TS6/7/TS10/14**, respectively. The interaction energies between the Cu and L fragments, between the Cu and S fragments and between the S and L fragments in the reactants and transition states were represented by ΔE_{b1}, $\Delta E'_{b1}$ and $\Delta E''_{b1}$ (ΔE_{b1}, $\Delta E'_{b1}$ and $\Delta E''_{b1}$= $-D_e$, $-D'_e$ and $-D''_e$) and ΔE_{b2}, $\Delta E'_{b2}$ and $\Delta E''_{b2}$. Based on the ΔE_{b1}, $\Delta E'_{b1}$ and $\Delta E''_{b}$ shown in Scheme 1, the interaction energies between the Cu and L fragments, between the Cu and S fragments and between the S and L fragments in the reactants and transition states can be achieved.

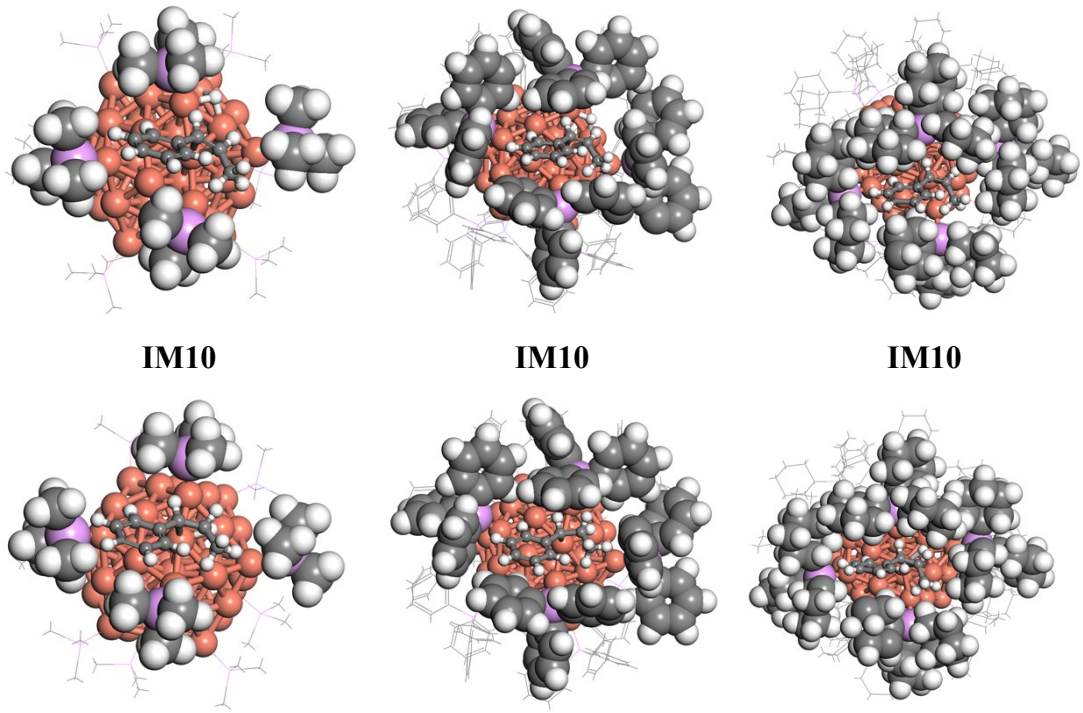


Figure S8. The optimized geometries of the **IM10** and **TS10/14**.

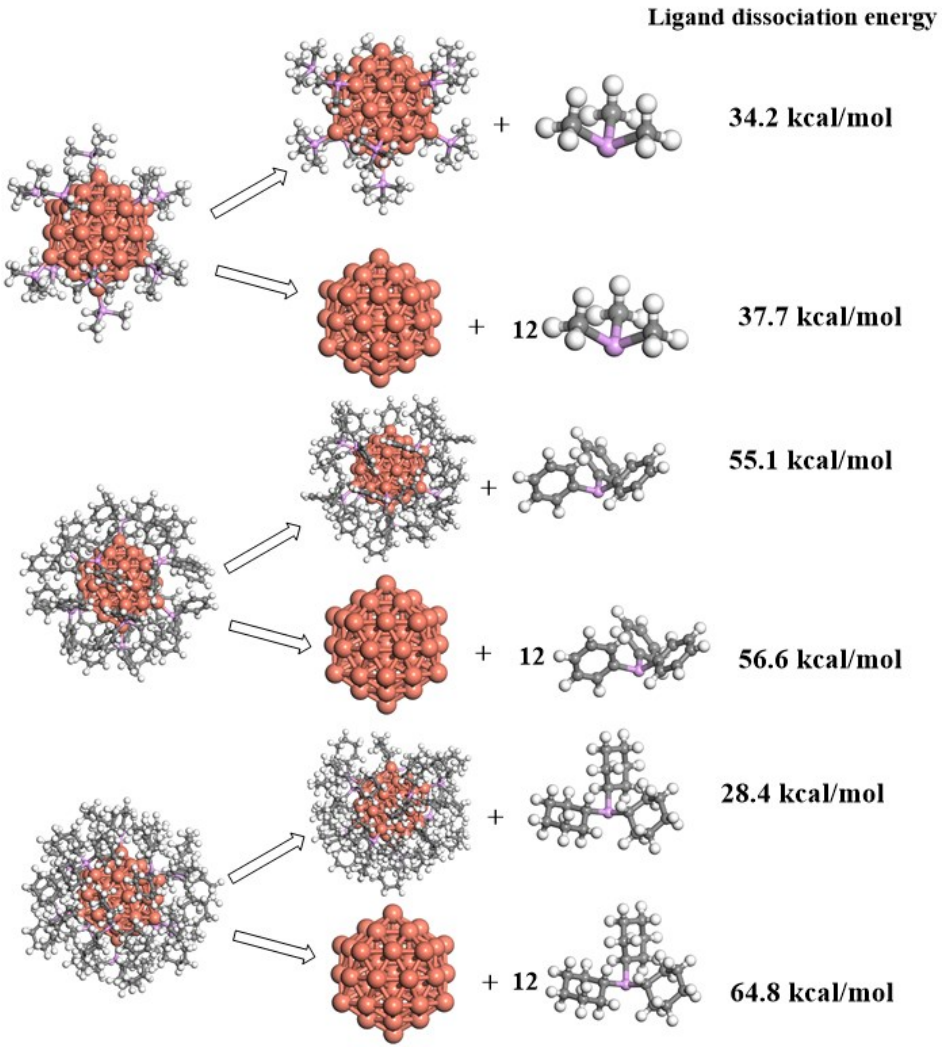


Figure S9. The ligand dissociation energies for the Cu-PMe, Cu-PPh and Cu-PCy.