Supporting Information

A First Principles Exploration on the Versatile Configurations at Alkynyl-protected Coinage Metal(111) Interface

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Table S1. Binding energies (BE: eV) and the optimized structures (only the topmost surface layer is shown) of methylethynyl (CH_3-C≡C-) at different adsorption sites on Au (111) with 4 layers of slab in a 4 × 4 lateral cell. The initial angle between the 111 plane and linear methylethynyl is 90°.

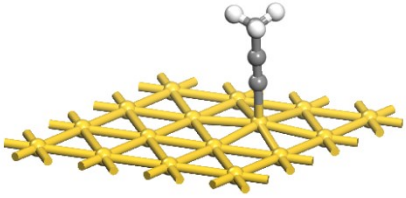
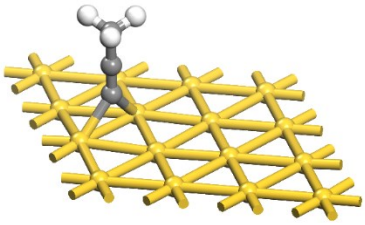
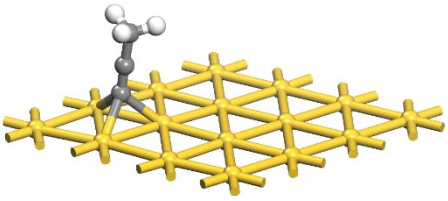
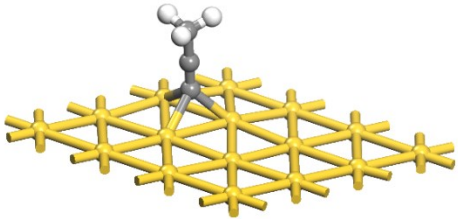
Sites	The optimized structures	BE (eV)
top		-3.06
bridge		-3.34
hcp		-3.40
fcc		-3.45

Table S2. Binding energies (BE: eV) and the optimized structures (only the topmost surface layer is shown) of methylethynyl (CH_3-C≡C-) at different adsorption sites on Ag (111) with 4 layers of slab in a 4 × 4 lateral cell. The initial angle between the 111 plane and linear methylethynyl is 90°.

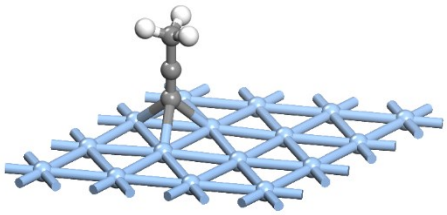
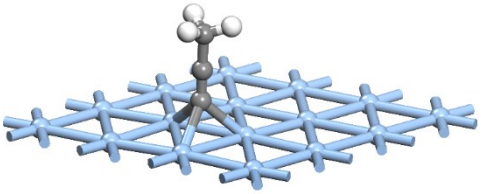
Sites	The optimized structures	BE (eV)
top	Relaxed to hcp	/
bridge	Relaxed to fcc	/
hcp		-3.54
fcc		-3.55

Table S3. Binding energies (BE: eV) and the optimized structures (only the topmost surface layer is shown) of methylethynyl (CH_3-C≡C-) at different adsorption sites on Cu (111) with 4 layers of slab in a 4 × 4 lateral cell. The initial angle between the 111 plane and linear methylethynyl is 90°.

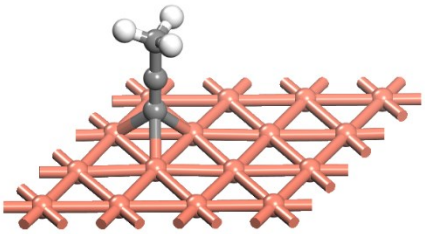
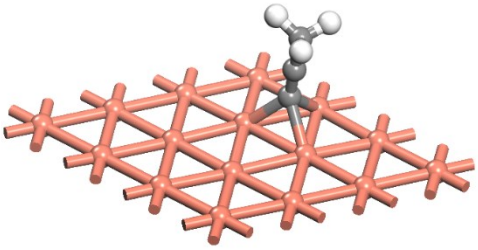
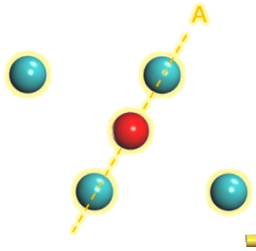
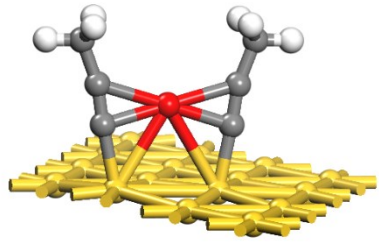
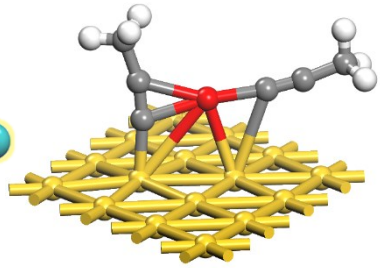
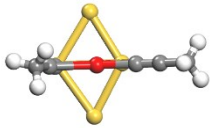
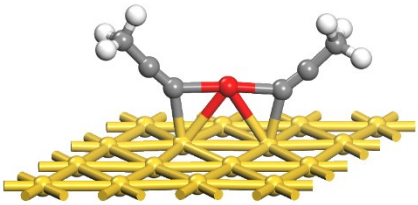
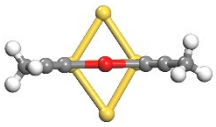
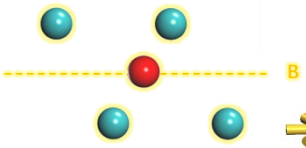
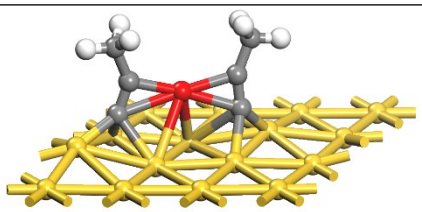
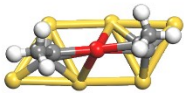
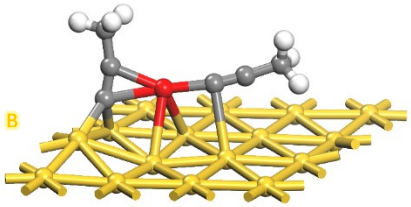
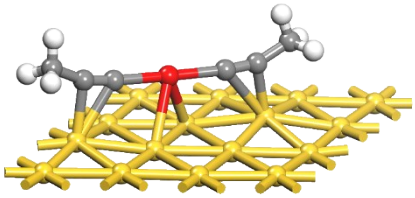
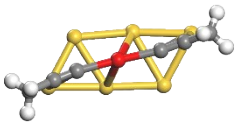
Sites	The optimized structures	BE (eV)
top	Relaxed to hcp	/
bridge	Relaxed to fcc	/
hcp		-4.23
fcc		-4.24

Table S4. The orientation, the optimized geometry structures and binding energies (per ligand) for $CH_3C{\equiv}C\text{-}Au_{adatom}\text{-}C{\equiv}CCH_3$ staple motif at the bridge sites on Au(111). Only the topmost surface layer is shown. Color legend: Au_{adatom}, red; other Au, yellow; C, grey; H, white.

The orientation	The optimized structures	BE (eV)
	 	-3.04
	 	-3.32
	 	-3.28
	 	-3.09
	 	-3.32
	 	-3.44

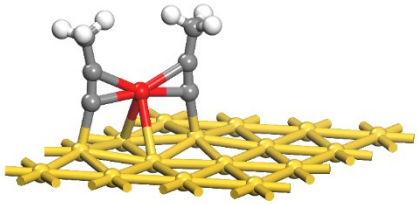
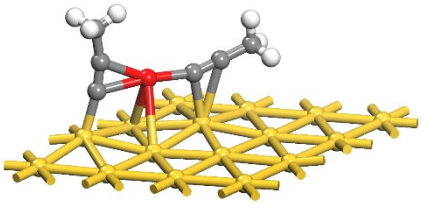
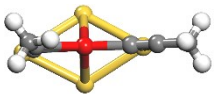
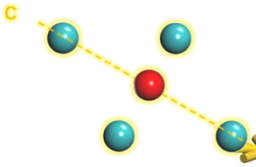
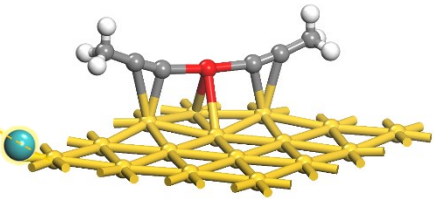
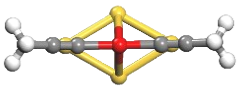
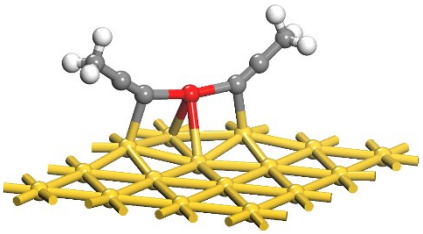
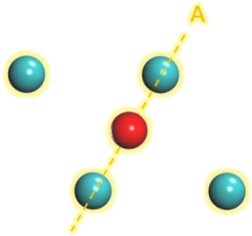
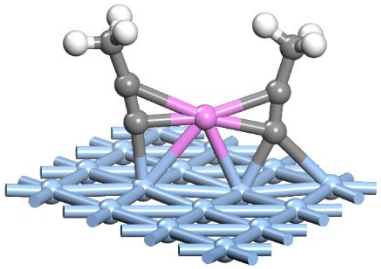
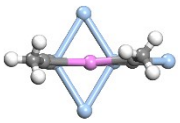
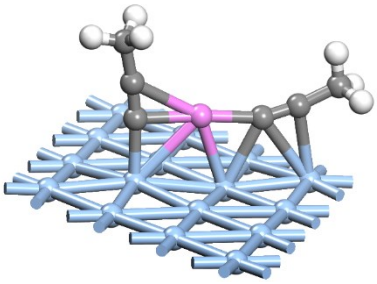
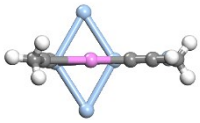
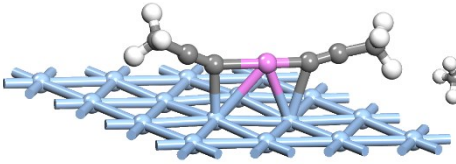
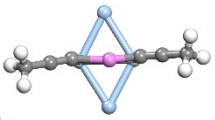
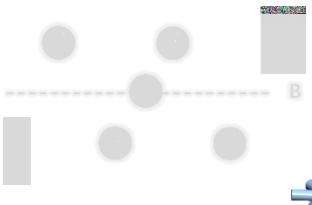
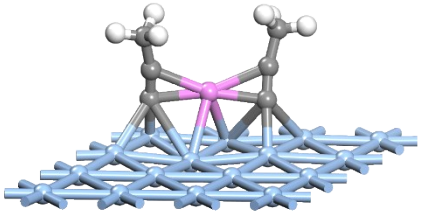
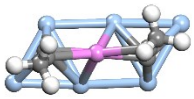
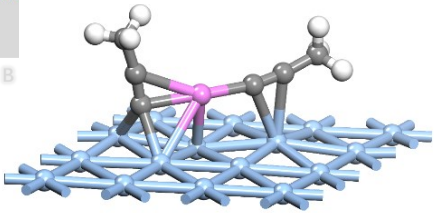
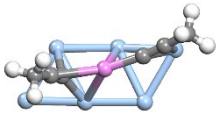
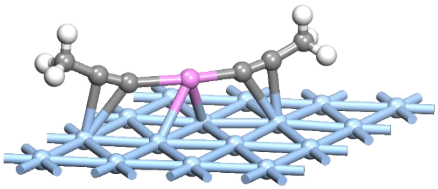
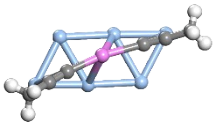
			-3.28
			-3.37
			-3.58
			-3.45

Table S5. The orientation, the optimized geometry structures and binding energies (per ligand) for $CH_3C{\equiv}C\text{-}Ag_{adatom}\text{-}C{\equiv}CCH_3$ staple motif at the bridge sites on Ag(111). Only the topmost surface layer is shown. Color legend: Ag_{adatom}, purple; other Ag, baby blue; C, grey; H, white.

The orientation	The optimized structures	BE (eV)
	 	-3.16
	 	-3.31
	 	-3.35
	 	-3.22
	 	-3.41
	 	-3.47

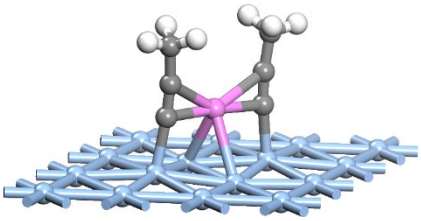
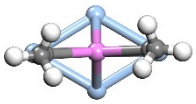
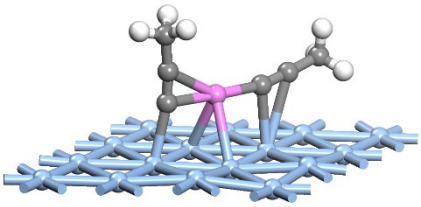
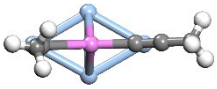
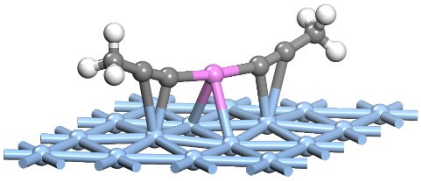
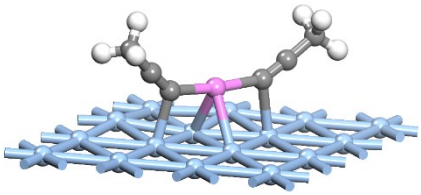
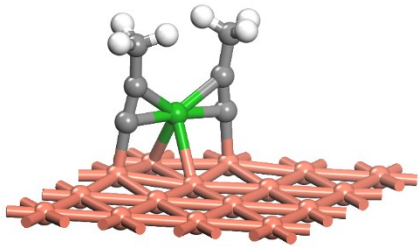
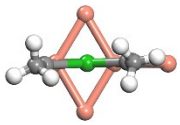
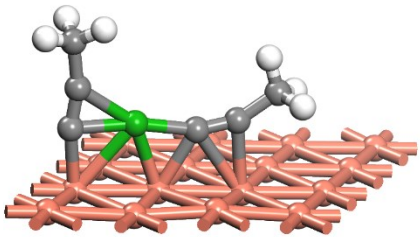
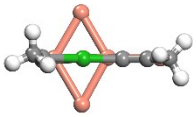
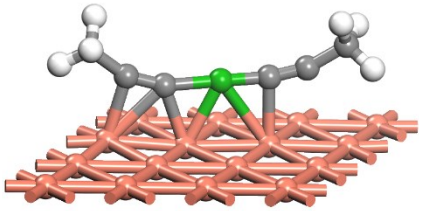
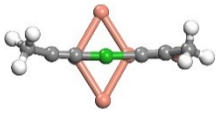
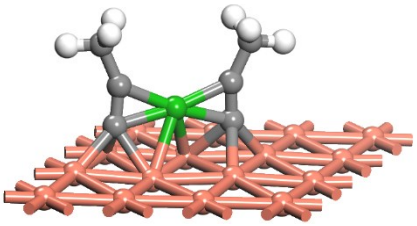
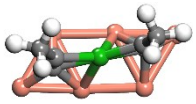
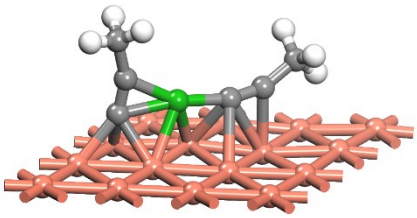
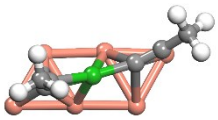
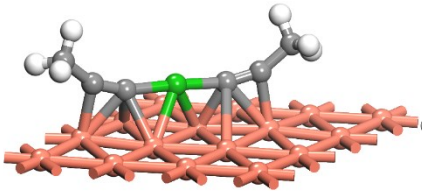
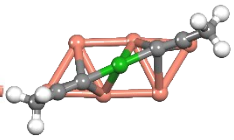
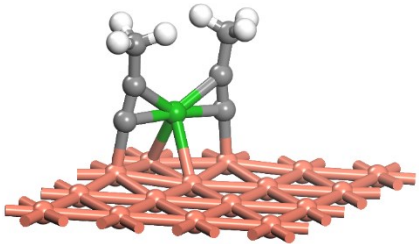
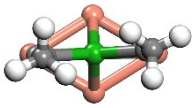
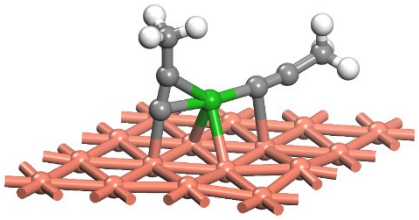
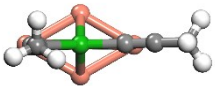
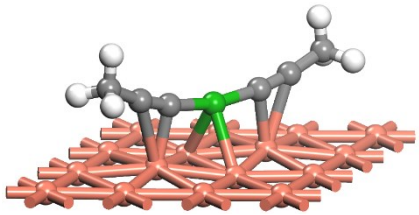
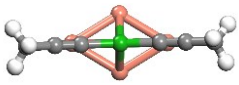
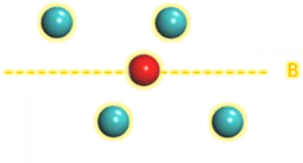
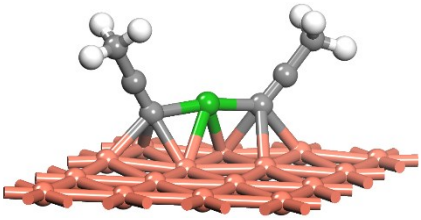
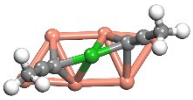
			-3.23
			-3.44
			-3.48
			-3.46

Table S6. The orientation, the optimized geometry structures and binding energies (per ligand) for $CH_3C{\equiv}C\text{-}Cu_{adatom}\text{-}C{\equiv}CCH_3$ staple motif at the bridge sites on Cu(111). Only the topmost surface layer is shown. Color legend: Cu_{adatom}, green; other Cu, brick-red; C, grey; H, white.

The orientation	The optimized structures	BE (eV)
	 	-3.89
	 	-3.96
	 	-3.96
	 	-4.14
	 	-4.13
	 	-4.12

			-3.88
			-3.93
			-3.99
			-4.07

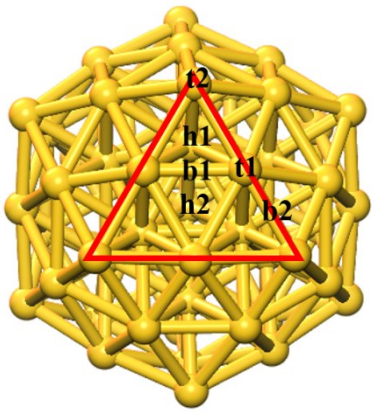


Figure S1. Schematic presentation of adsorption sites of high-symmetry on a triangular face of the Au_{55} nanocluster.

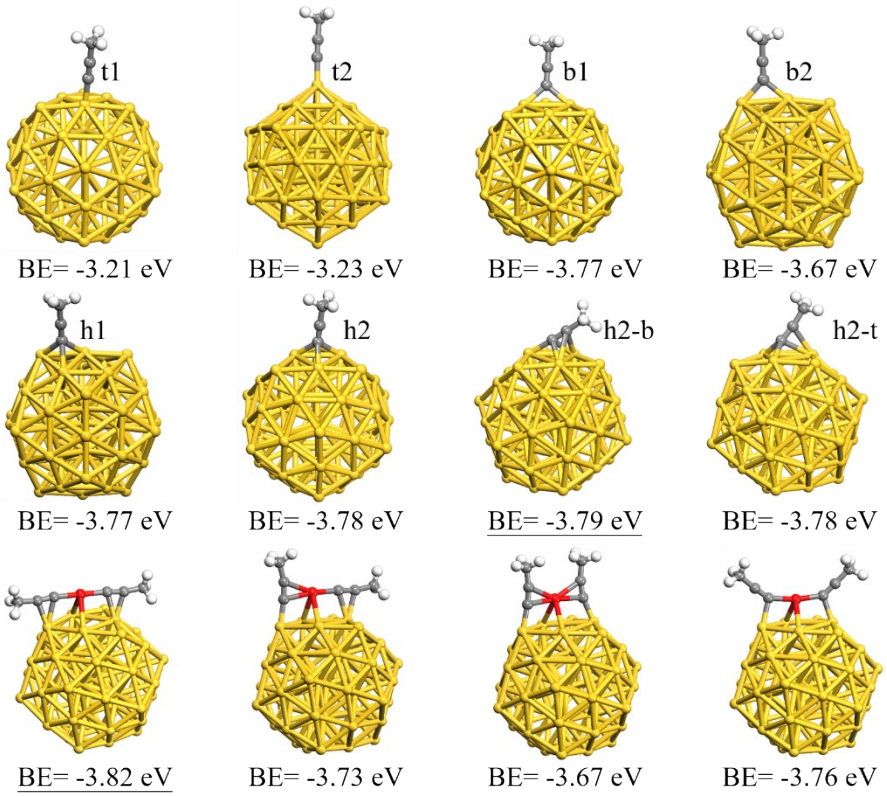


Figure S2. The binding energies and optimized structures of $CH_3C{\equiv}C$ covalently bonded to icosahedral Au_{55} cluster. Color legend: Au_{adatom}, red; other Au, yellow; C, grey; H, white.

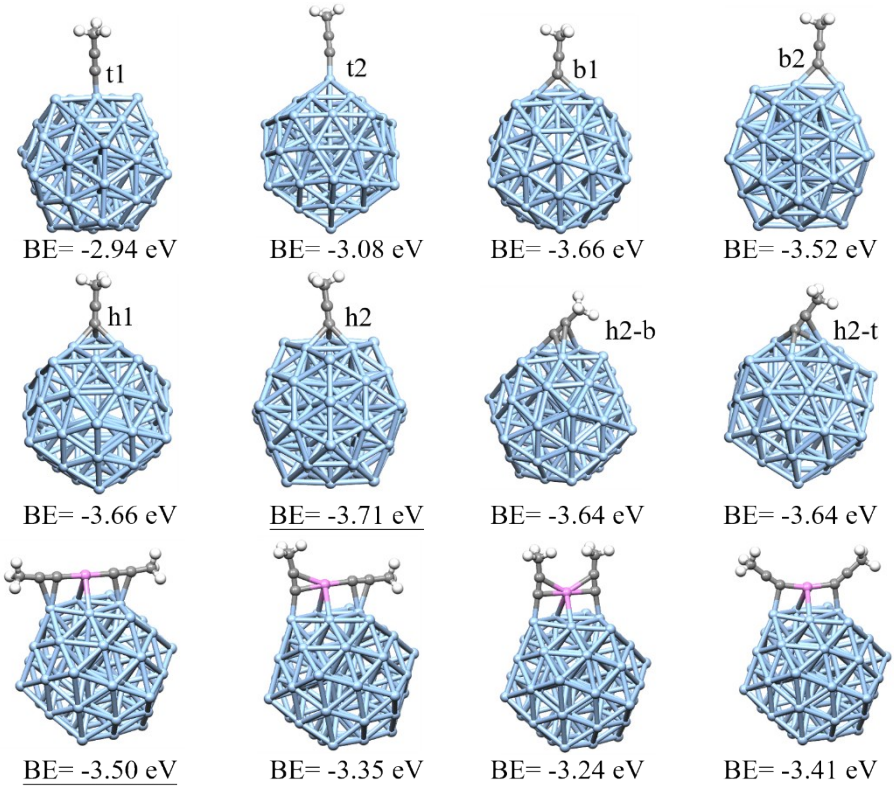


Figure S3. The binding energies and optimized structures of $CH_3C{\equiv}C$ covalently bonded to icosahedral Ag_{55} cluster. Color legend: Ag_{adatom}, purple; other Ag, baby blue; C, grey; H, white.

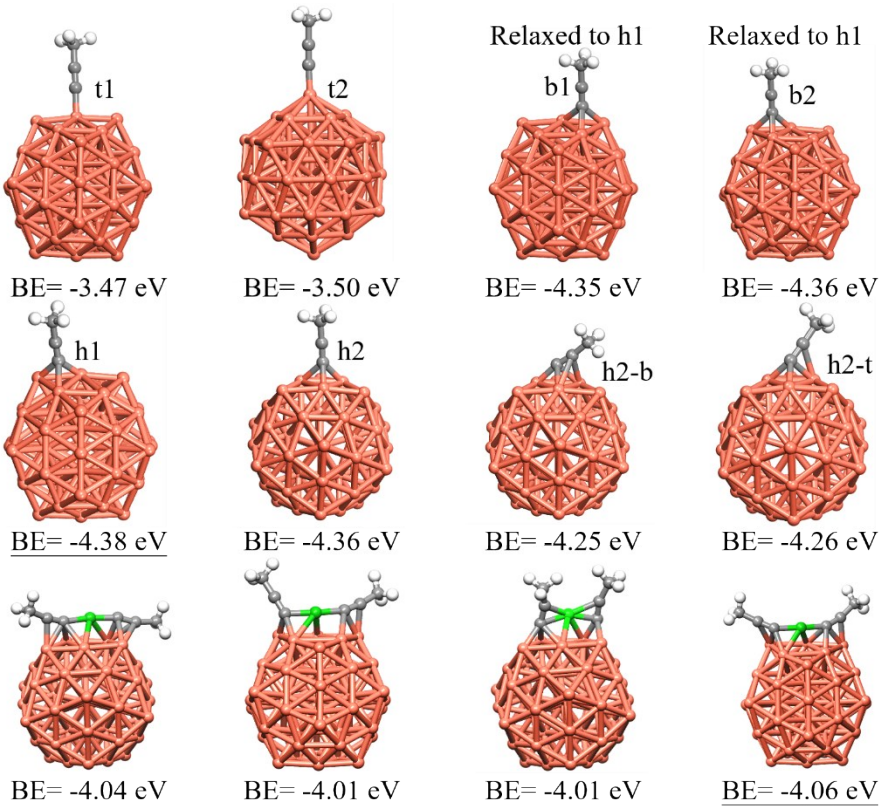


Figure S4. The binding energies and optimized structures of $CH_3C{\equiv}C$ covalently bonded to icosahedral Cu_{55} cluster. Color legend: Cu_{adatom}, green; other Cu, brick-red; C, grey; H, white.

Table S7. Comparison of binding energies per $CH_3C{\equiv}C$- for the most stable mode of the bridge and staple motifs on the three coinage metal(111) surfaces with and without including the D3 approximation.

Category / The most stable Mode		PBE-D3 level	PBE (without vdW correction)
Au(111)	Bridge motif	-3.54 eV	-3.17 eV
	Staple motif	-3.58 eV	-2.87 eV
Ag(111)	Bridge motif	-3.55 eV	-3.29 eV
	Staple motif	-3.48 eV	-2.90 eV
Cu(111)	Bridge motif	-4.26 eV	-3.86 eV

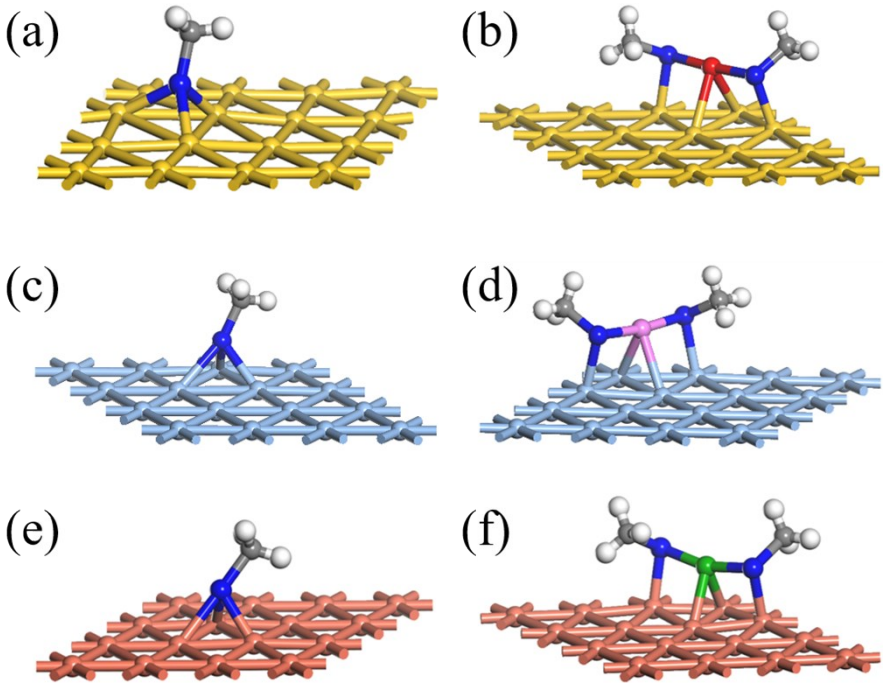


Figure S5. The optimized structures (only the topmost surface layer is shown) of methylthiolate (CH_3S-) for the bridging and staple motifs on (a-b) Au(111), (c-d) Ag(111), and (e-f) Cu(111) with 4 layers of slab in a 4 × 4 lateral cell. The initial angle between the surface normal and S-C bond is 30°. S atom is highlighted in blue.