Theoretical exploration of the origin of selectivity for oxidative carbonylation reaction catalyzed by Pd single atom embedded on graphene

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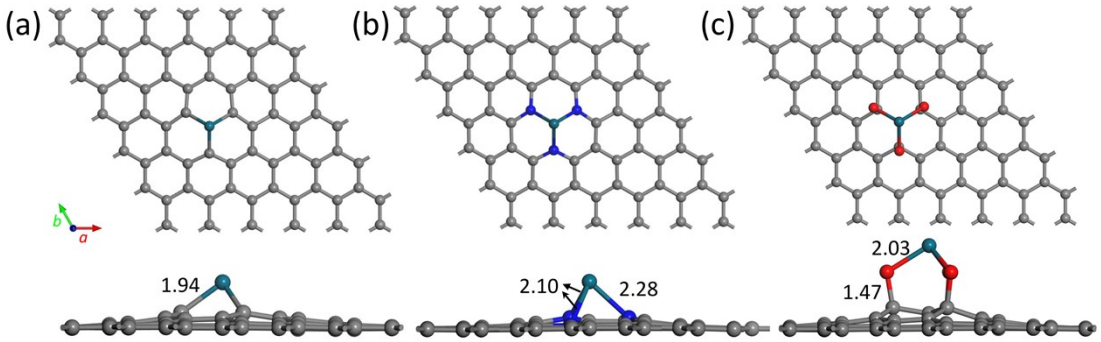

Figure S1. (a-c) Optimization structures and (d-f) charge different density for $Pd_1@C_3$-Gr, $Pd_1@N_3$-Gr, and $Pd_1@O_3$-Gr, respectively. The bond distances are given in angstrom.

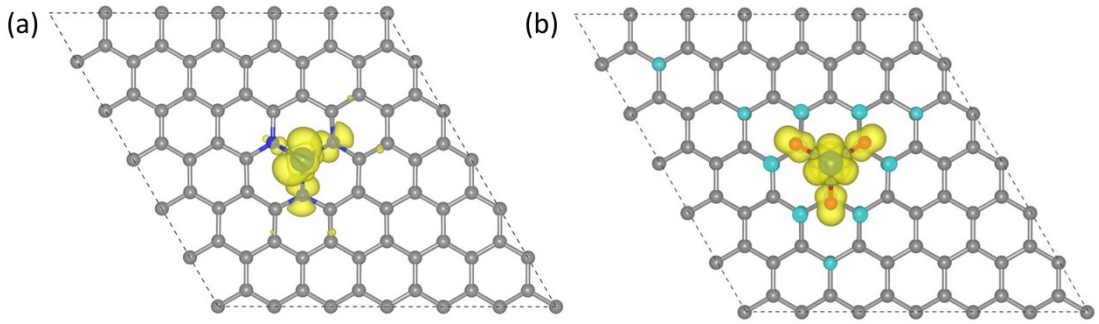

Figure S2. The spin density map for $Pd_1@N_3$-Gr and $Pd_1@O_3$-Gr. (isosurface = 0.03)

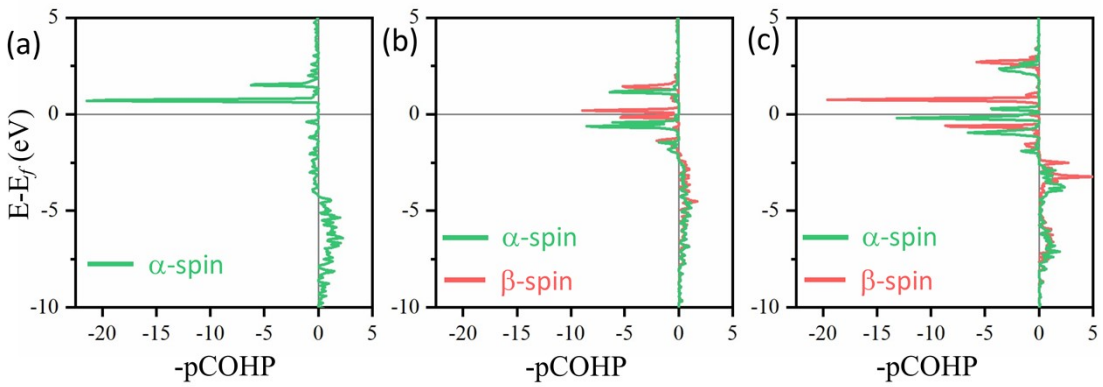

Figure S3. The IPDOS for Pd-4*d* orbitals of $Pd_1@X_3$-Gr (X = C/N/O). The integral of COHP up to Fermi level for $Pd_1@X_3$-Gr (X=C/N/O) species are calculated to be 4.58, 2.03, and 3.13, suggesting the interaction between Pd single atom and the supports is in the order of $Pd_1@C_3$-Gr > $Pd_1@O_3$-Gr > $Pd_1@N_3$-Gr.

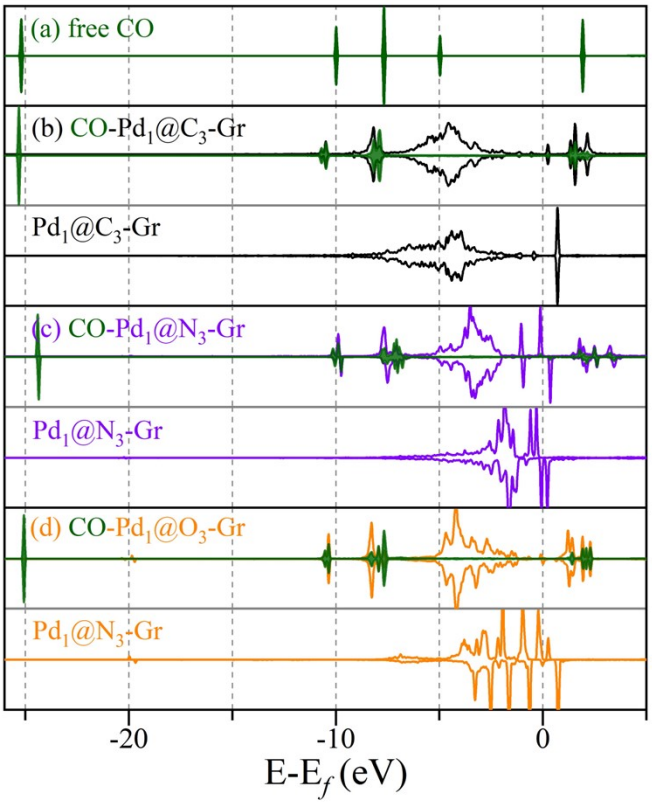

Figure S4. (a) The *s*, *p*-PDOS for free CO molecule before being adsorption, (b-d) The *s*, *p*-PDOS for adsorbed CO and Pd-*d* PDOS for CO-$Pd_1@X_3$-Gr, together with the Pd-*d* PDOS of $Pd_1@X_3$-Gr before adsorption, for X = C, N, O, respectively. The bonding state of d-orbital in Pd1@C3 are farthest way from the Fermi level resulting to the weakest π back donation with CO.

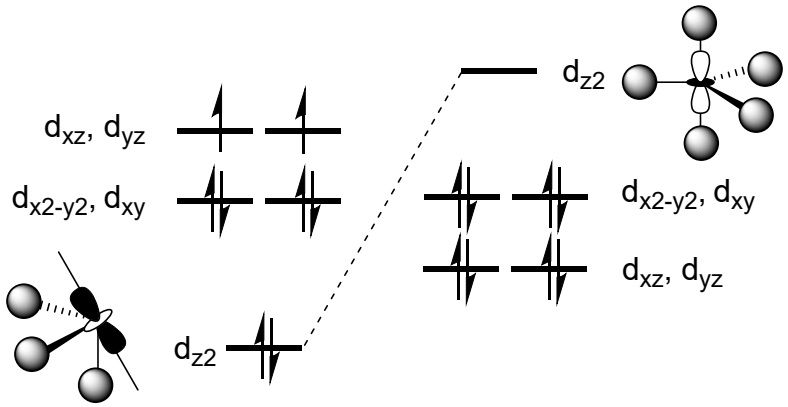

Figure S5. The shcemeatic diagram of the transformation energy levels of d-orbitals for 3-coordination $Pd_1@X_3$ to 5-coodination $Pd_1@X_3$ with two adsorbates. The stabilization of dz2 for $Pd_1@O_3$ makes it hard to transform into 5-coordinated trigonal bipyrimidal structure.

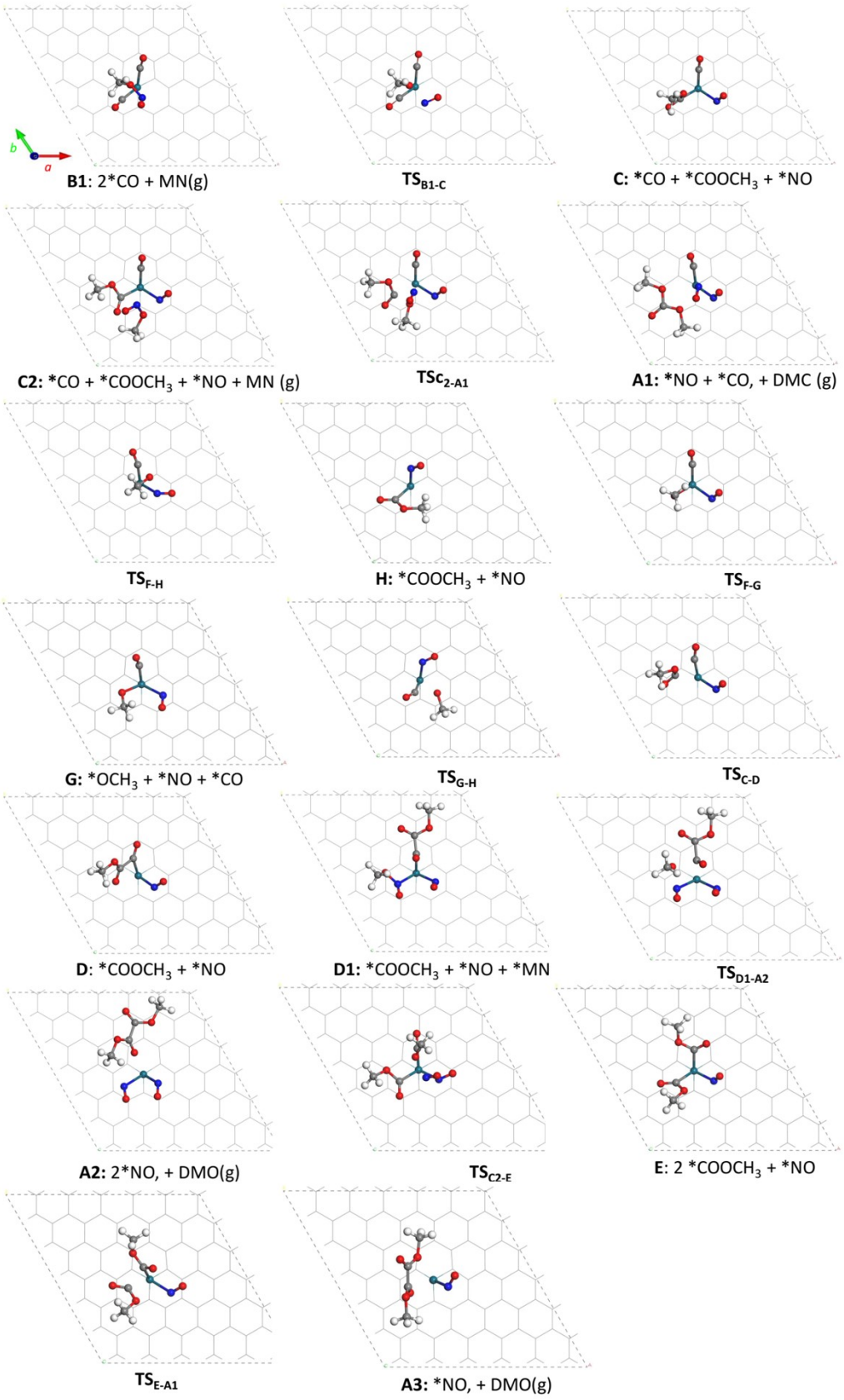

Figure S6. The corresponding top view for optimized structures of the intermediates and transition states shown in Figure 4.

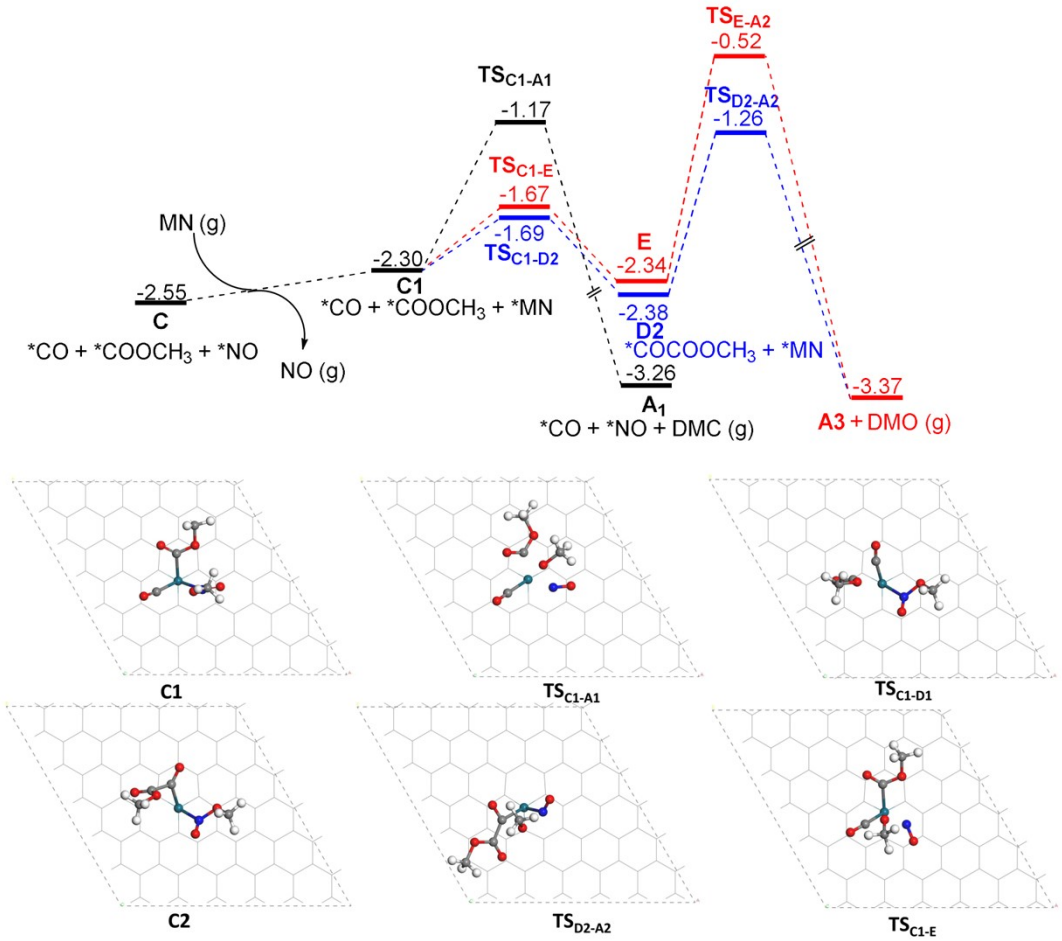

Figure S7. The calculated energy profiles for the **P1**, **P2** and **P3** through **C1** intermediate. (The energies are given in eV.) And the top view of the optimization structures of intermediates and transition states shown in energy profiles.

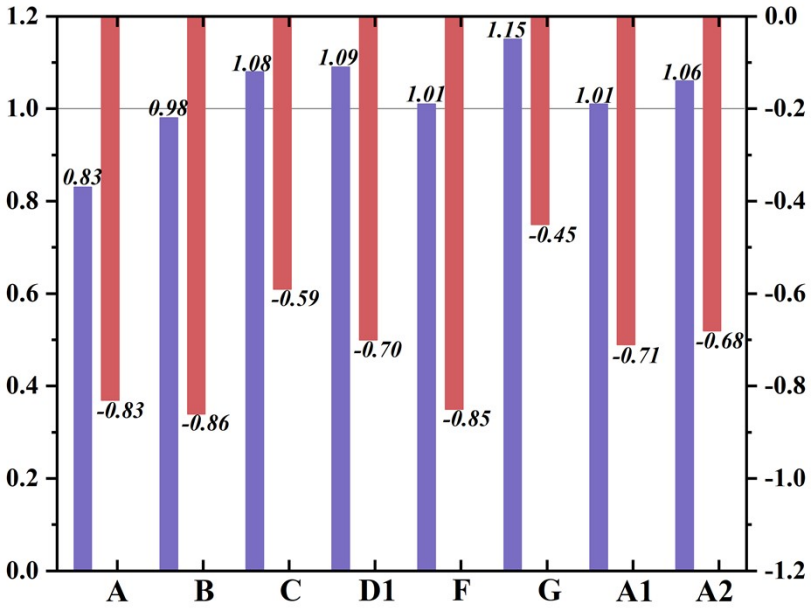

Figure S8. The calculated atomic Mülliken charges for Pd (in purple) and C atoms of supported graphene (in read).

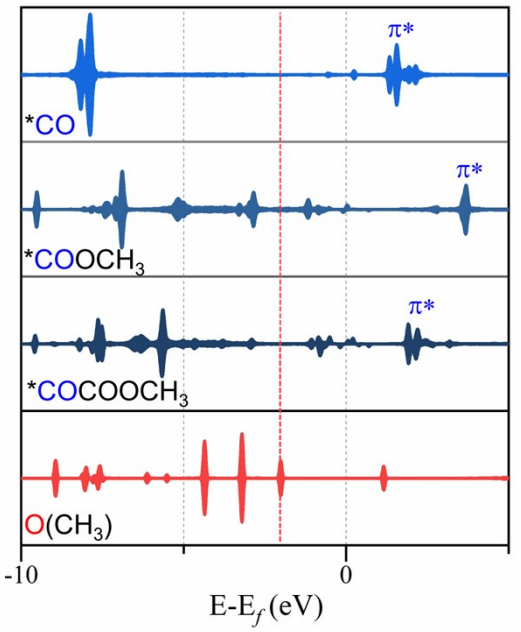

Figure S9. PDOS diagrams of *s*, *p*-orbitals of *CO, *$COOCH_3$ and *$COCOOCH_3$ units in **C**, respectively, together with the O atom in methoxyl unit.

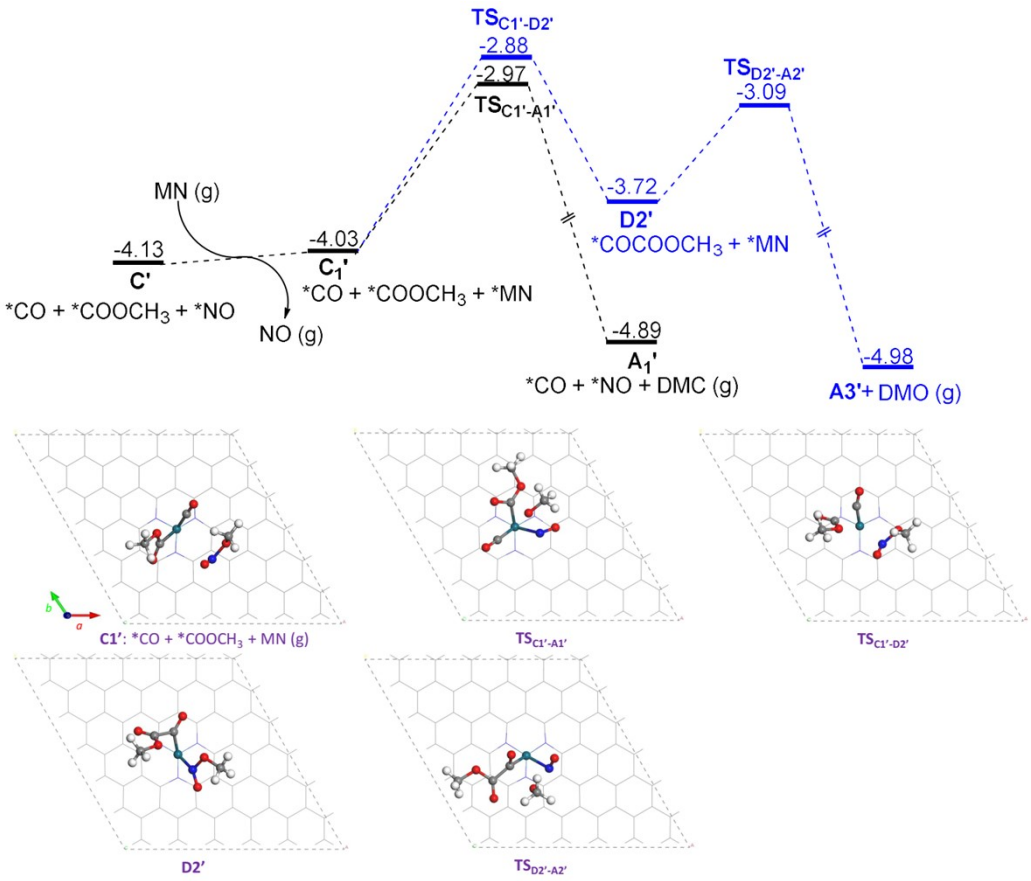

Figure S10. The calculated energy profiles for the **P1** and **P2** *via* **C1'** intermediate for $Pd_1@N_3$-Gr. The energies are given in eV. And the top view of the optimization structures of intermediates and transition states shown in energy profiles.

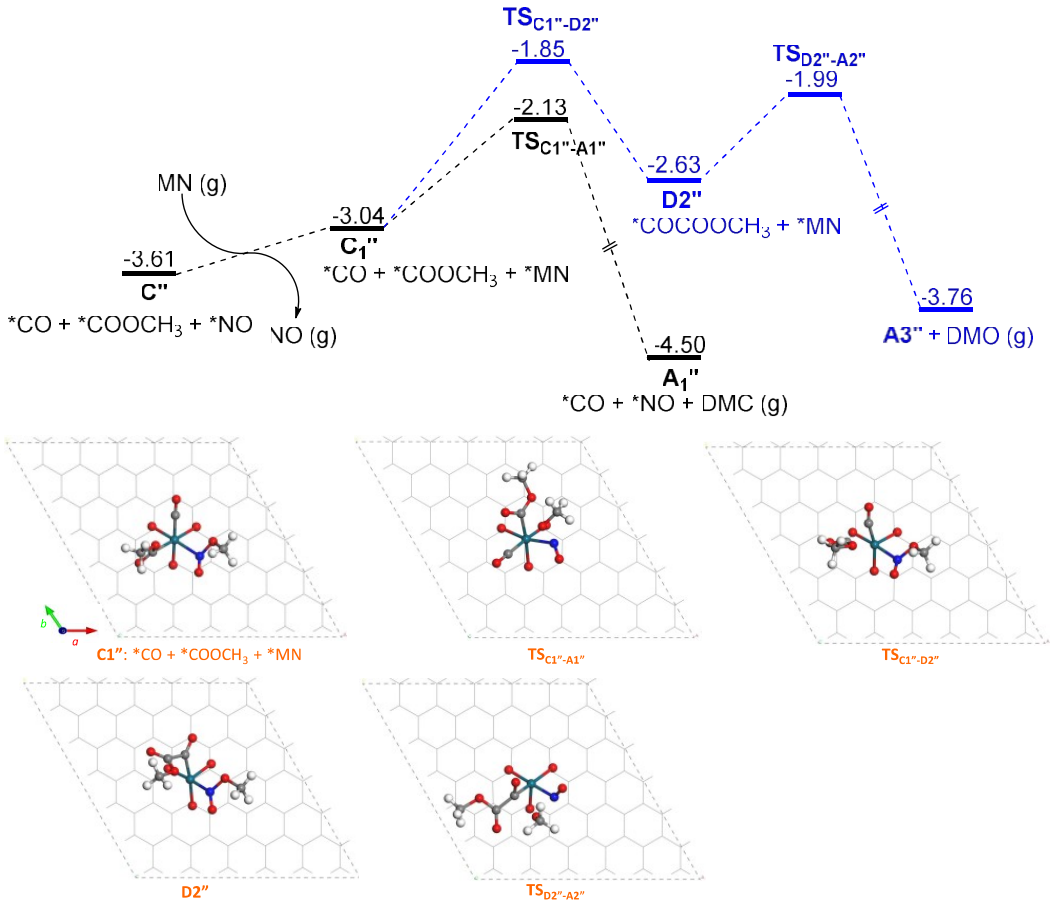

Figure S11. The calculated energy profiles for the **P1** and **P2** *via* **C1"** intermediate for $Pd_1@O_3$-Gr. The energies are given in eV. And the top view of the optimization structures of intermediates and transition states shown in energy profiles.

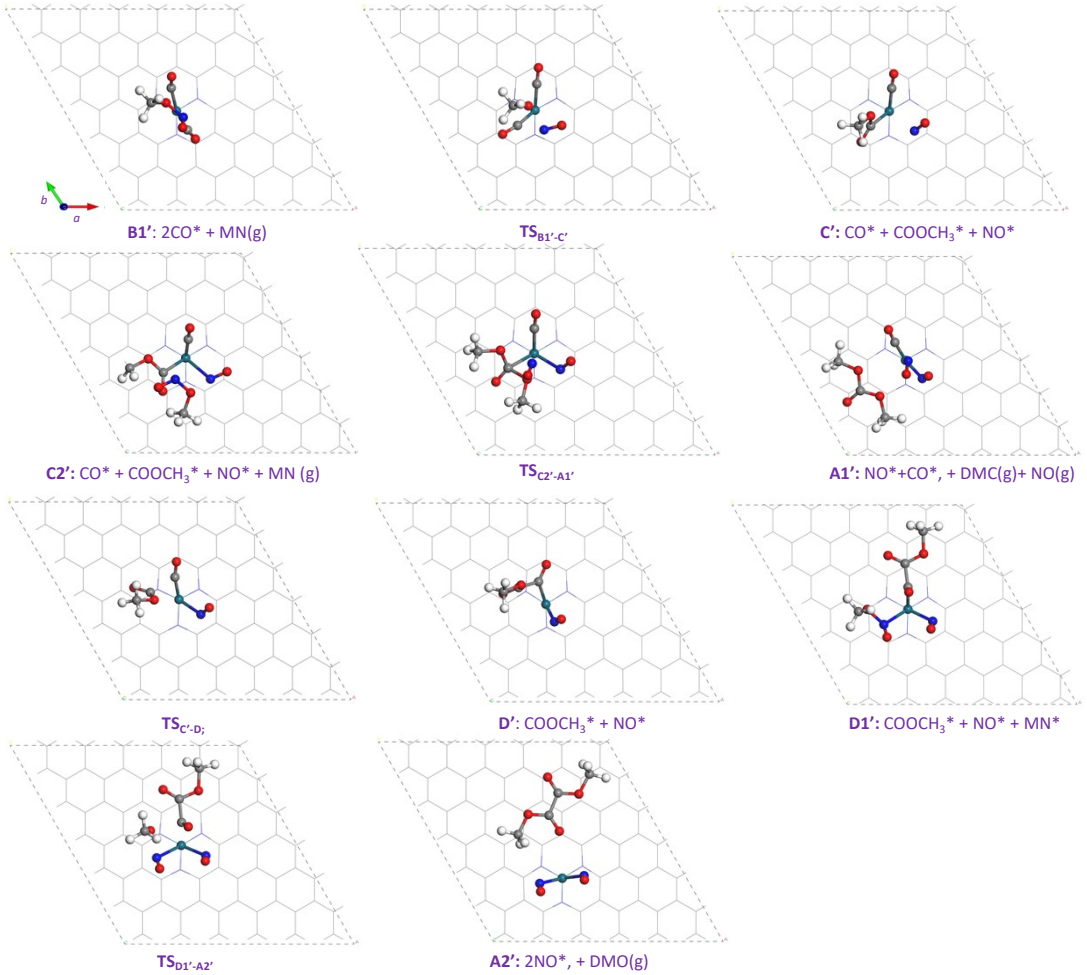

Figure S12. The top view of the optimization structures of intermediates and transition states for $Pd_1@N_3$-Gr shown in Figure 7.

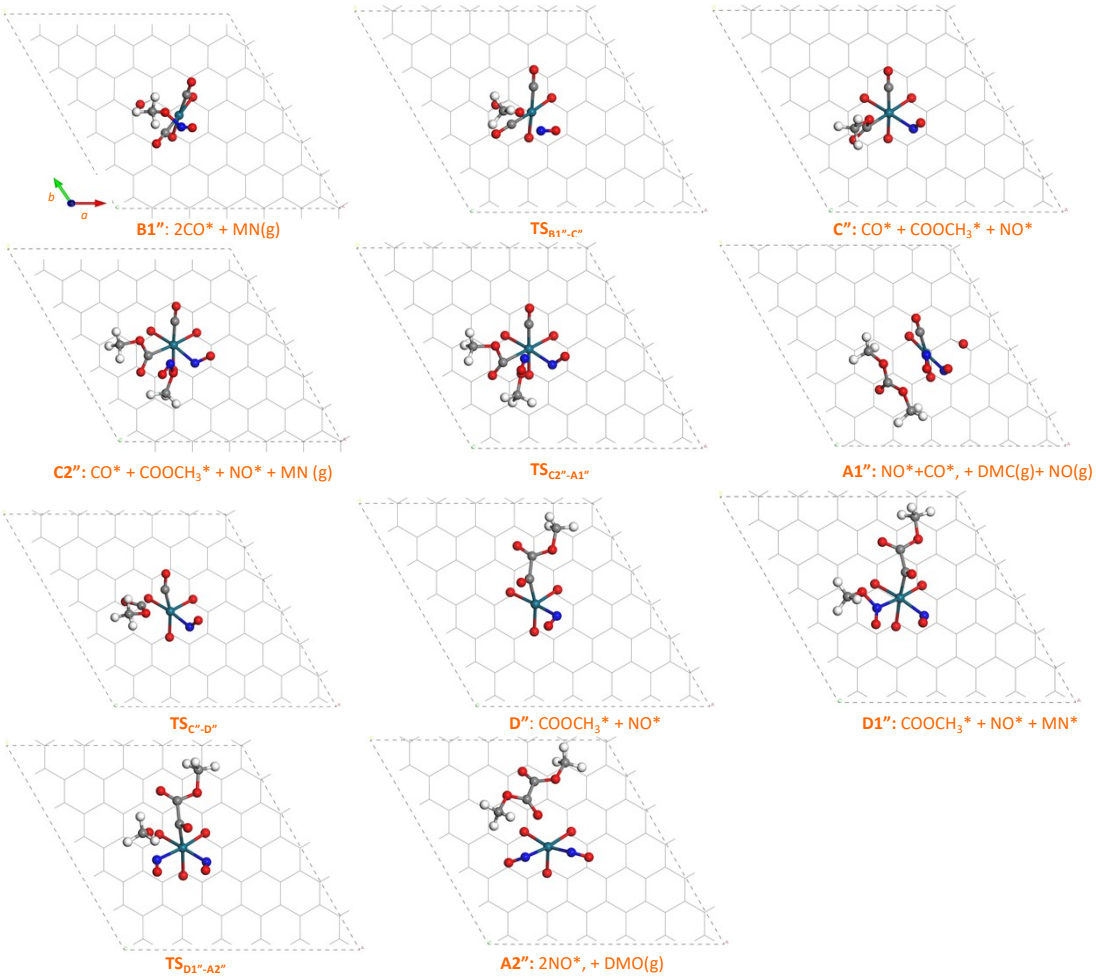

Figure S13. The top view of the optimization structures of intermediates and transition states for $Pd_1@O_3$-Gr shown in Figure 7.

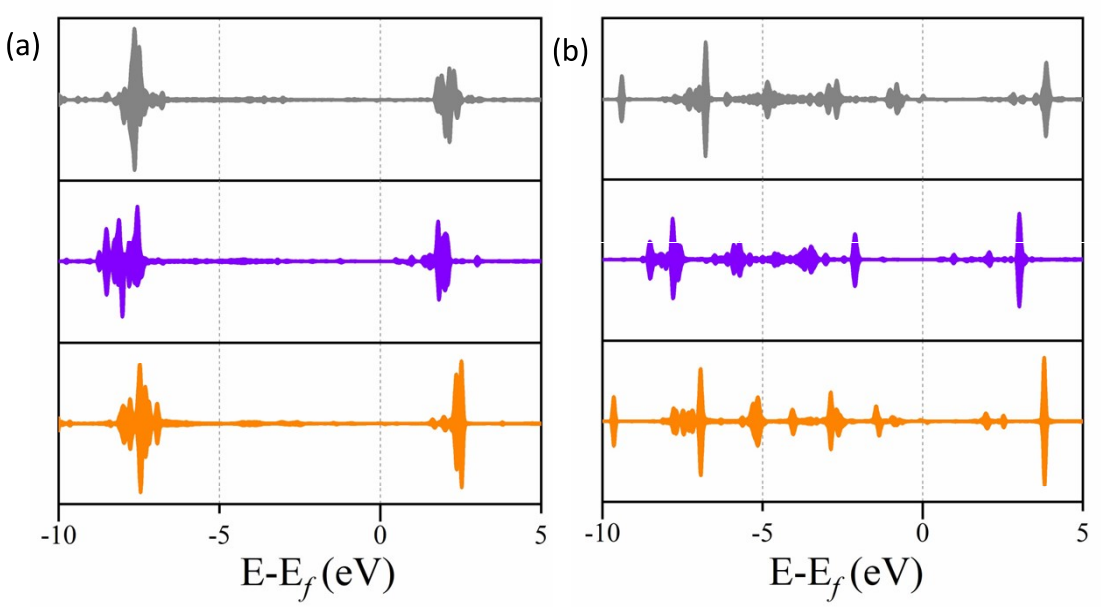

Figure S14. The PDOS of *s,p*-orbitals of (a) *CO and (b) *$COOCH_3$ units in intermediate for $Pd_1@X_3$-Gr, from top to bottom corresponds to X = C/N/O, respectively.

Table S1. Calculated adsorption electronic energies ($\mathbf{E}_{ads}$), Gibbs free energies at 0K and 400K ($\mathbf{G}_{ads}$) for the CO+NO and 2NO adsorbed on the supported Pd single atom catalysts (corresponding to **A1** and **A2** intermediates in the context), together with the differences in energy with the initial adsorption intermediate (**B**/**F**). All energy values are given in eV.

adsorbates	catalysts	$\mathbf{E}_{ads}$	$\mathbf{G}_{ads}$ (0K)	$\mathbf{G}_{ads}$ (400K)	$\mathbf{\Delta G}$ (400K) [a]
CO + NO	$Pd_1@C_3$-Gr	-2.30	-1.86	-1.94	0.19 [b]
(**A1**)	$Pd_1@N_3$-Gr	-4.18	-3.71	-3.76	0.73 [c]
	$Pd_1@O_3$-Gr	-3.79	-3.32	-3.37	0.11 [d]
2 NO	$Pd_1@C_3$-Gr	-2.82	-2.03	-2.06	0.31 [b]
(**A2**)	$Pd_1@N_3$-Gr	-4.57	-3.75	-3.75	0.72 [c]
	$Pd_1@O_3$-Gr	-4.13	-3.01	-3.03	-0.23 [d]

[a] $\mathbf{\Delta G}$ (400K) = G_{ads} (**F**/**B**, 400K) – G_{ads} (**A1**/**A2**, 400K).

[b] The differences in energy with **F**.

[c] The differences in energy with **B'**.

[d] The differences in energy with **B"**.