Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Continuous and Ultrathin Platinum Films on Graphene using Atomic Layer Deposition: A Combined Computational and Experimental Study

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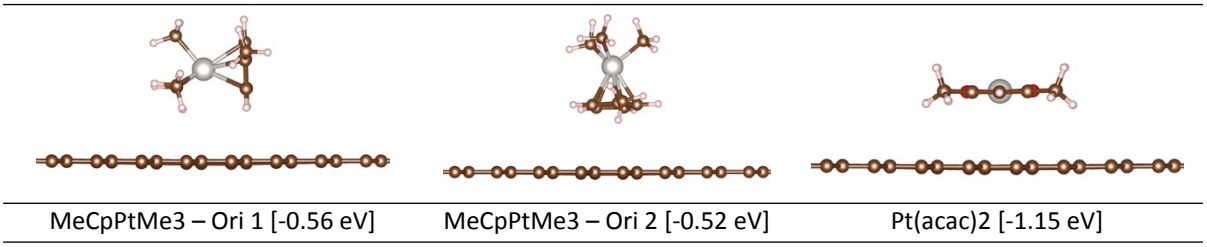
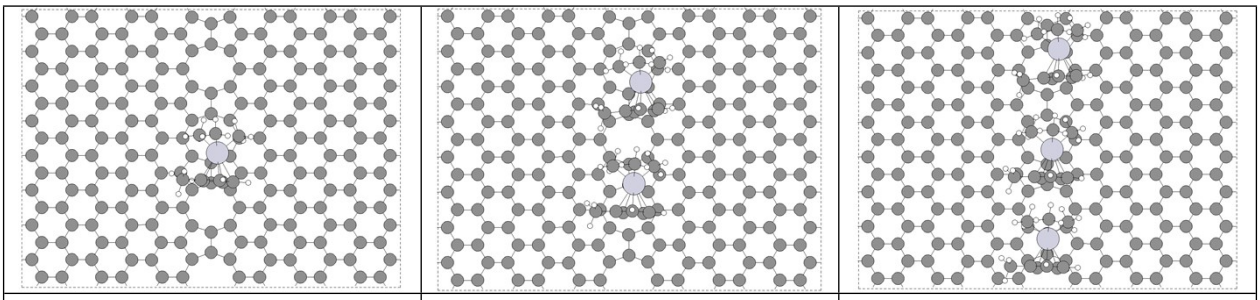
Supporting Figures (Figure S1-S7)



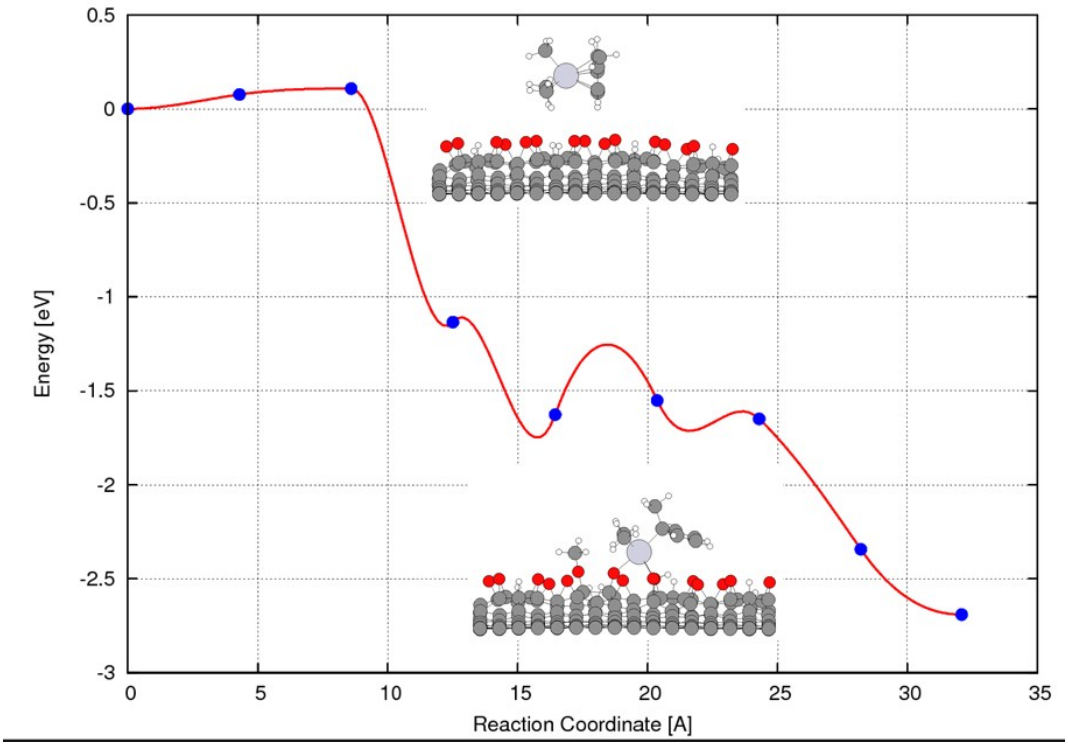
MeCpPtMe3 – Ori 1 [-0.56 eV]	MeCpPtMe3 – Ori 2 [-0.52 eV]	Pt(acac)2 [-1.15 eV]

Figure S1. Different physisorption orientations of $MeCpPtMe_3$ and $Pt(acac)_2$ on pristine graphene [and associated binding energies] as predicted at the PBE-D3 level of theory.



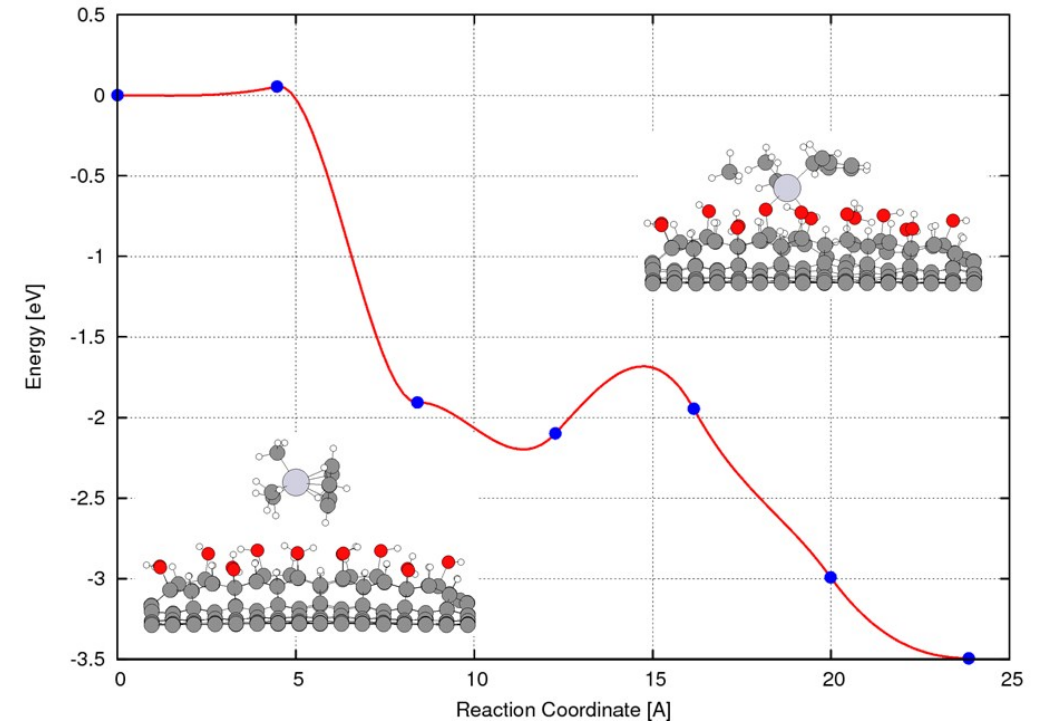
-0.51 eV	-0.62 eV	-0.75eV

Figure S2. Binding of multiple $MeCpPtMe_3$ precursor molecules on graphene with grain boundaries.



$2(C\text{-}O)^* + MeCpPtMe_{3\,(g)} \rightarrow C\text{-}MeCpPtMe_2^* + C\text{-}Me^*$

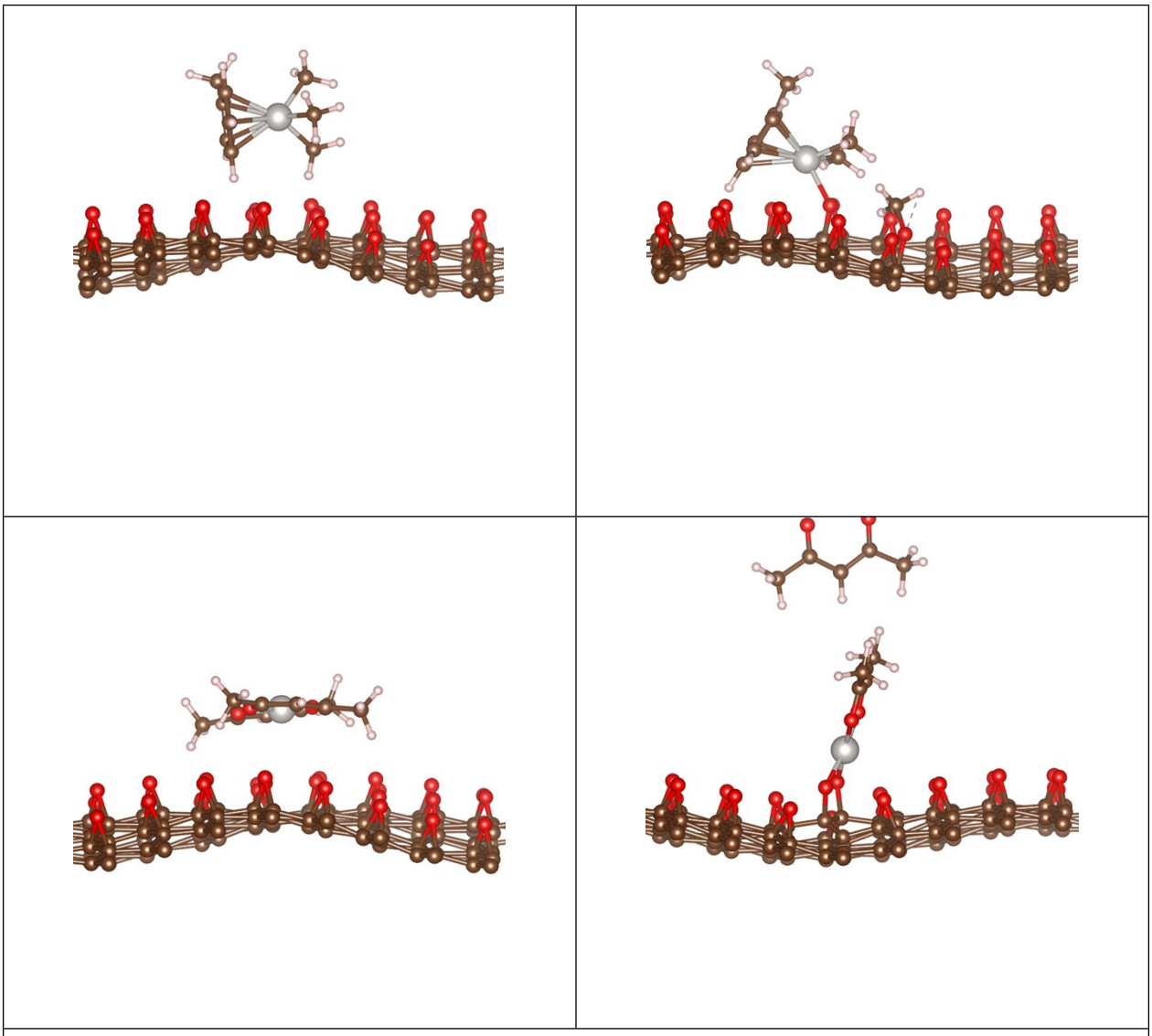
$\Delta Ea=0.15$ eV, $\Delta Er=-2.73$ eV.



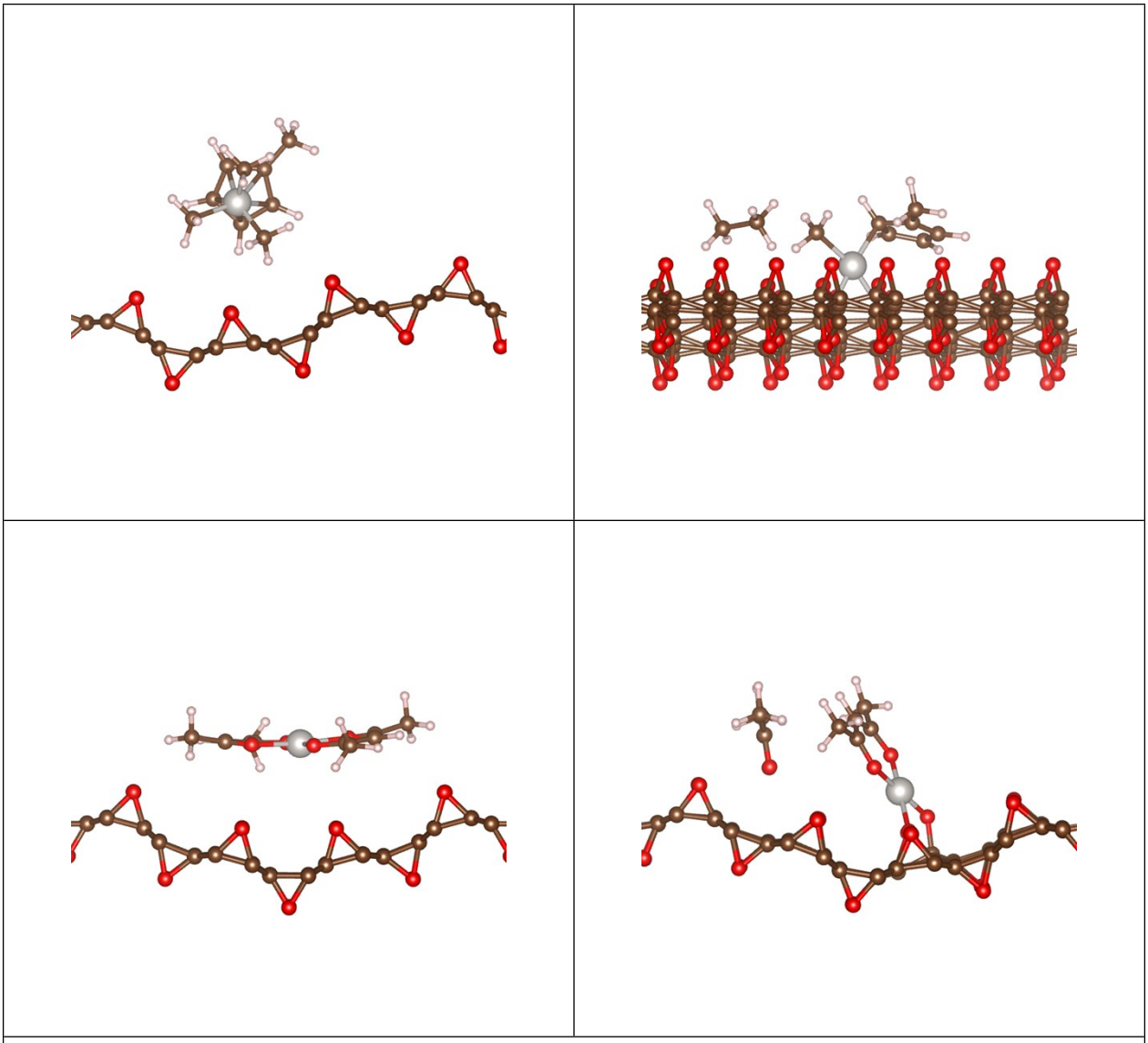
$2(C\text{-}OH)^* + MeCpPtMe_{3\,(g)} \rightarrow C\text{-}MeCpPtMe_2^* + CH_{4\,(g)}$

$\Delta Ea=0.05$ eV, $\Delta Er=--3.42$ eV.

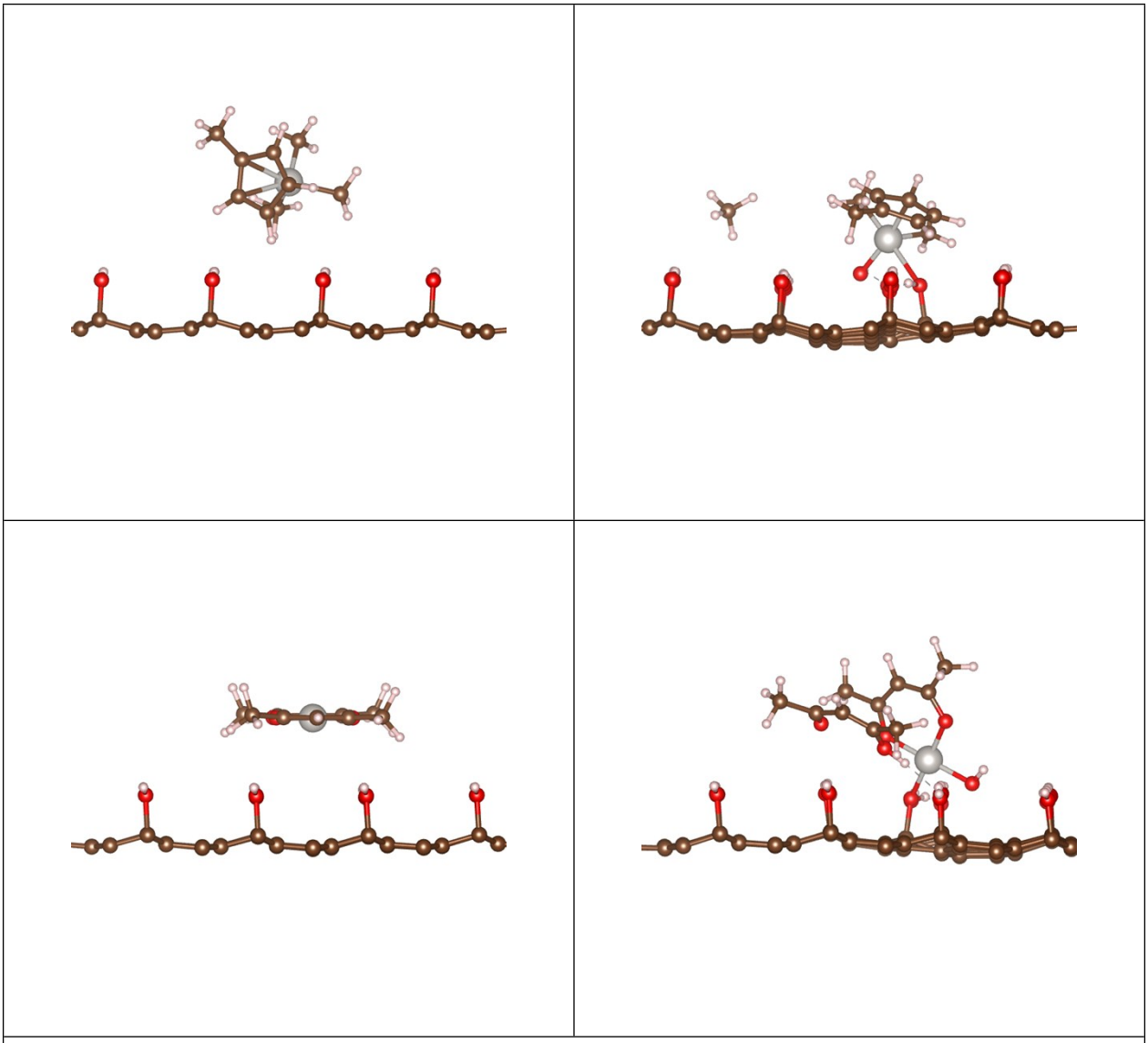
Figure S3. PBE-D3 level energetics (from CI-NEB computations) corresponding to MeCpPtMe3 binding on graphene with (top) epoxydated and (bottom) hydroxylated grain boundaries. Here, the first points (physisorbed species) are (top) -0.40 eV and (bottom) -0.49 eV with respect to the respective separated species (MeCpPtMe3 and graphene).



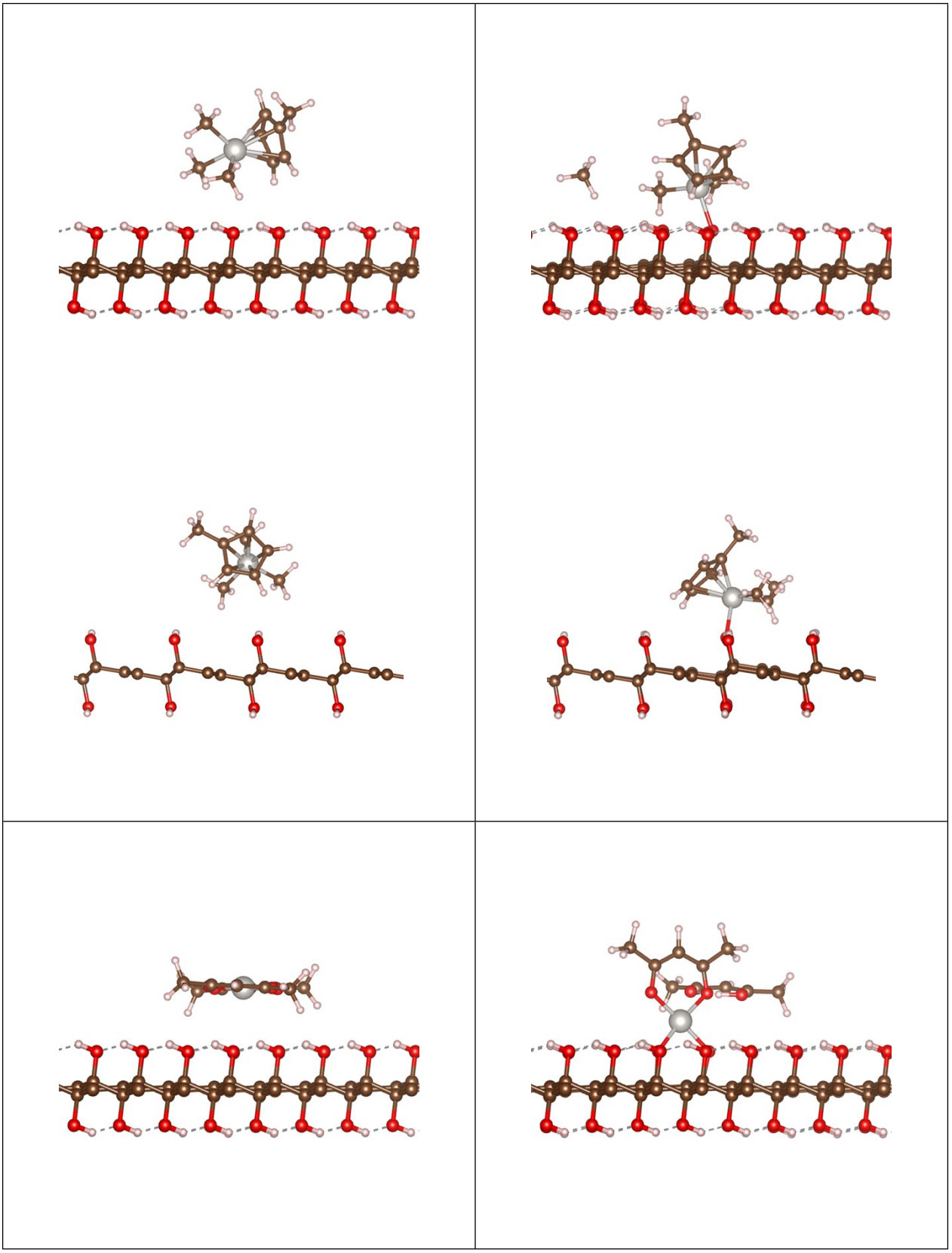
(a) Epoxydated GO (single-sided)

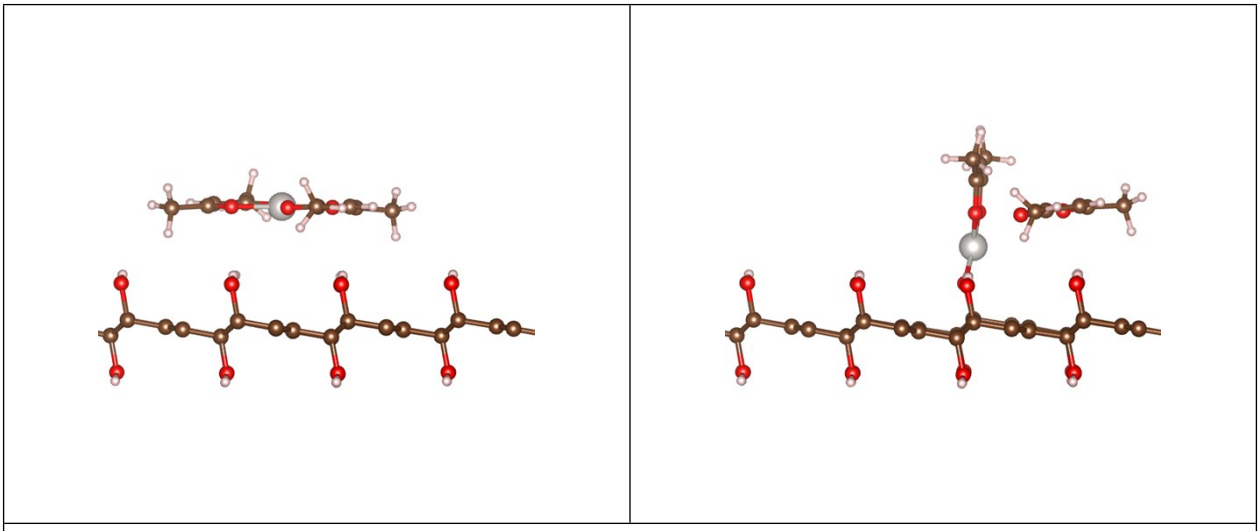


(b) Epoxydated GO (double-sided)

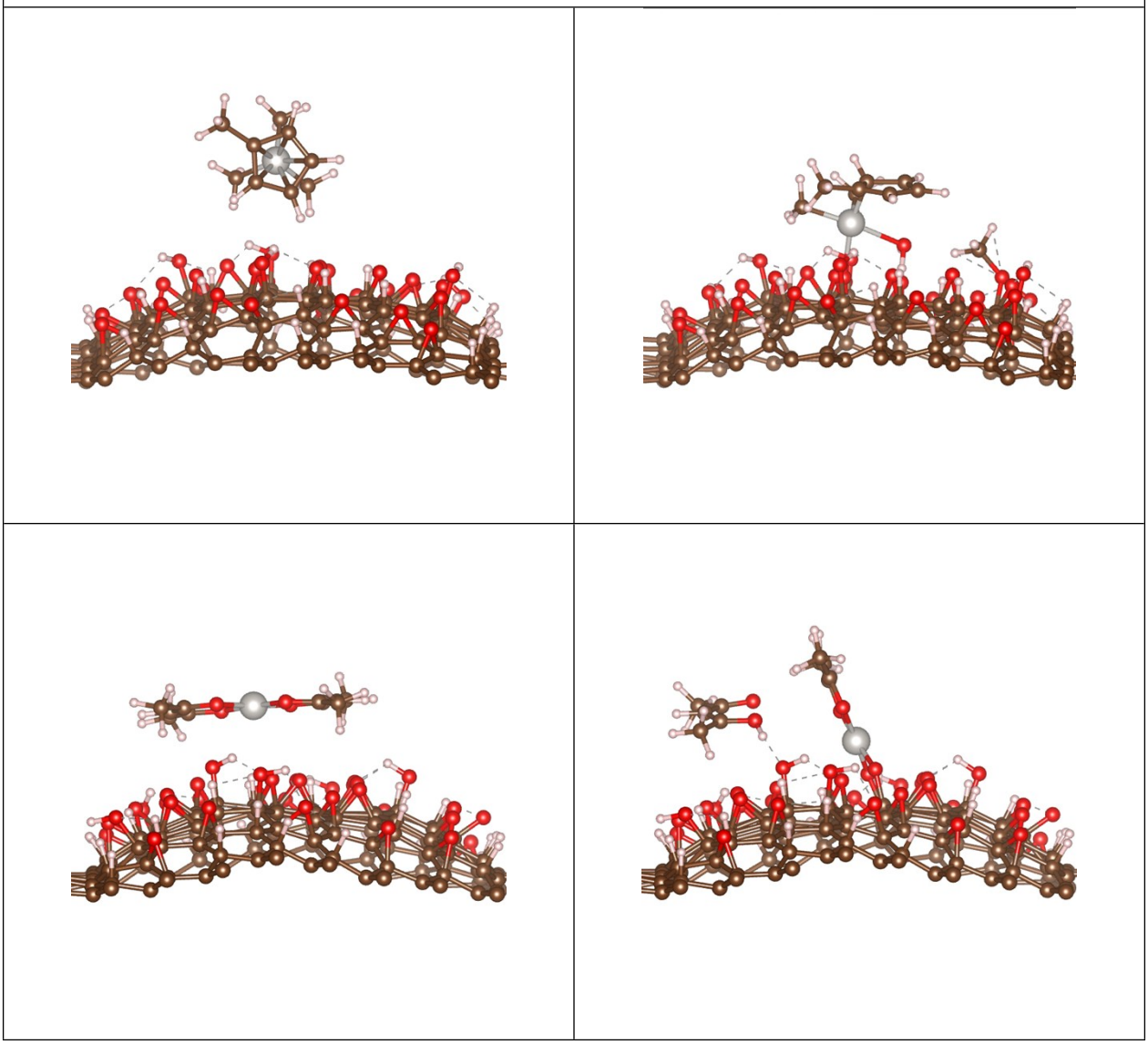


(c) Hydroxylated GO (single-sided)





(d) Hydroxylated GO (double-sided)



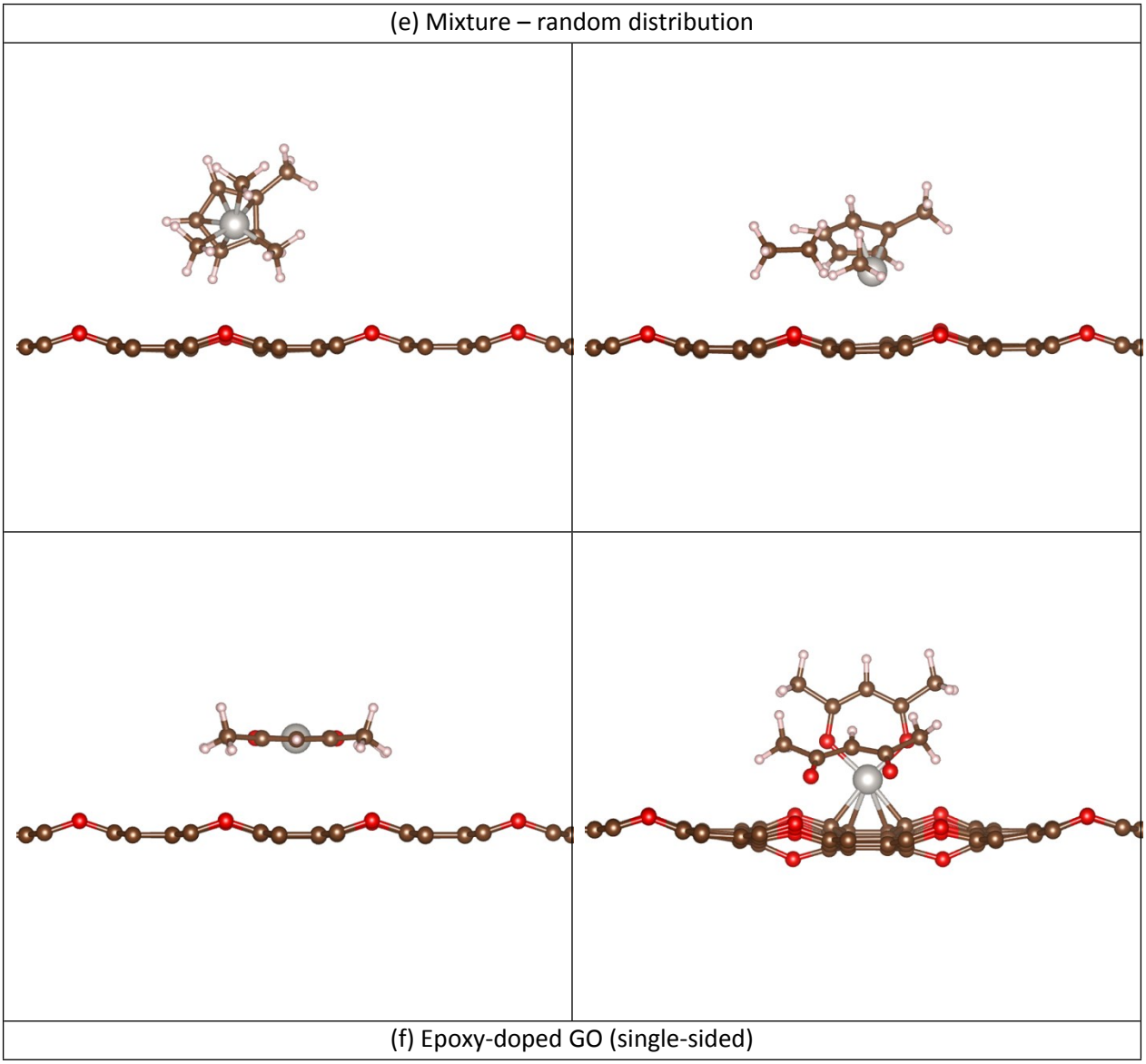
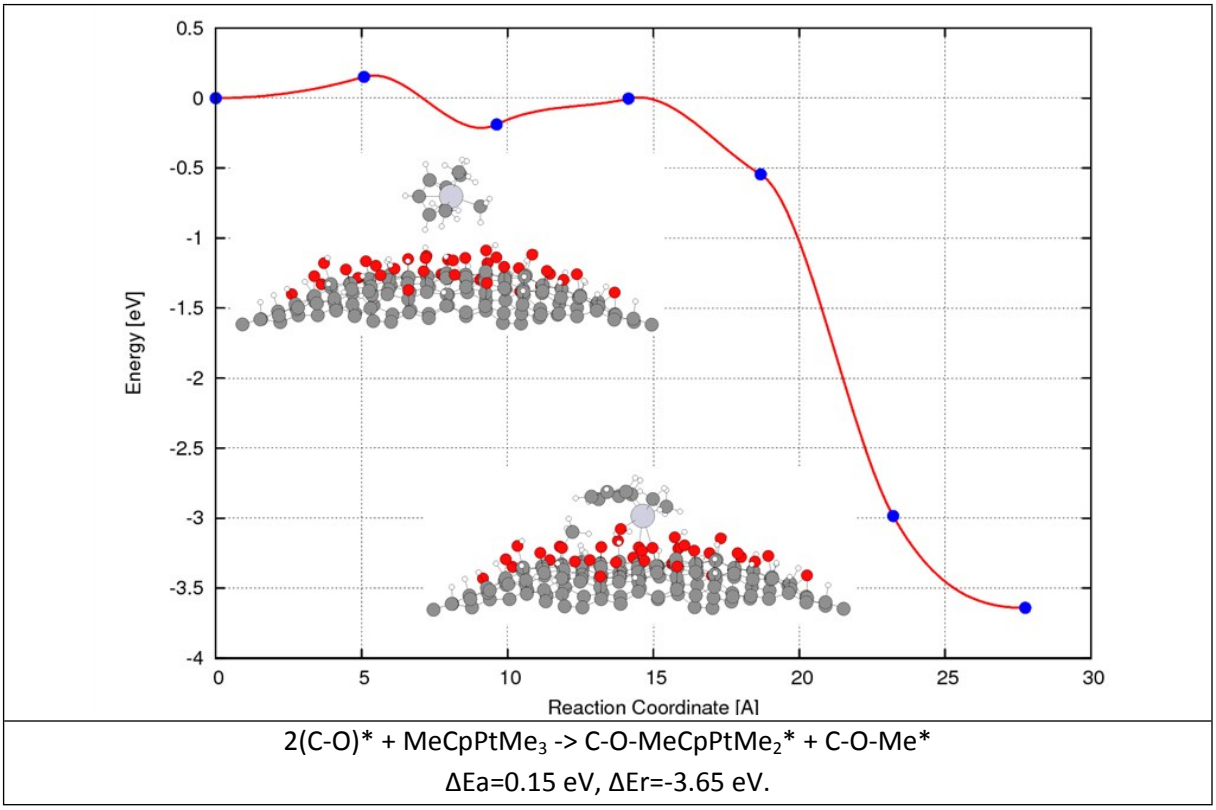


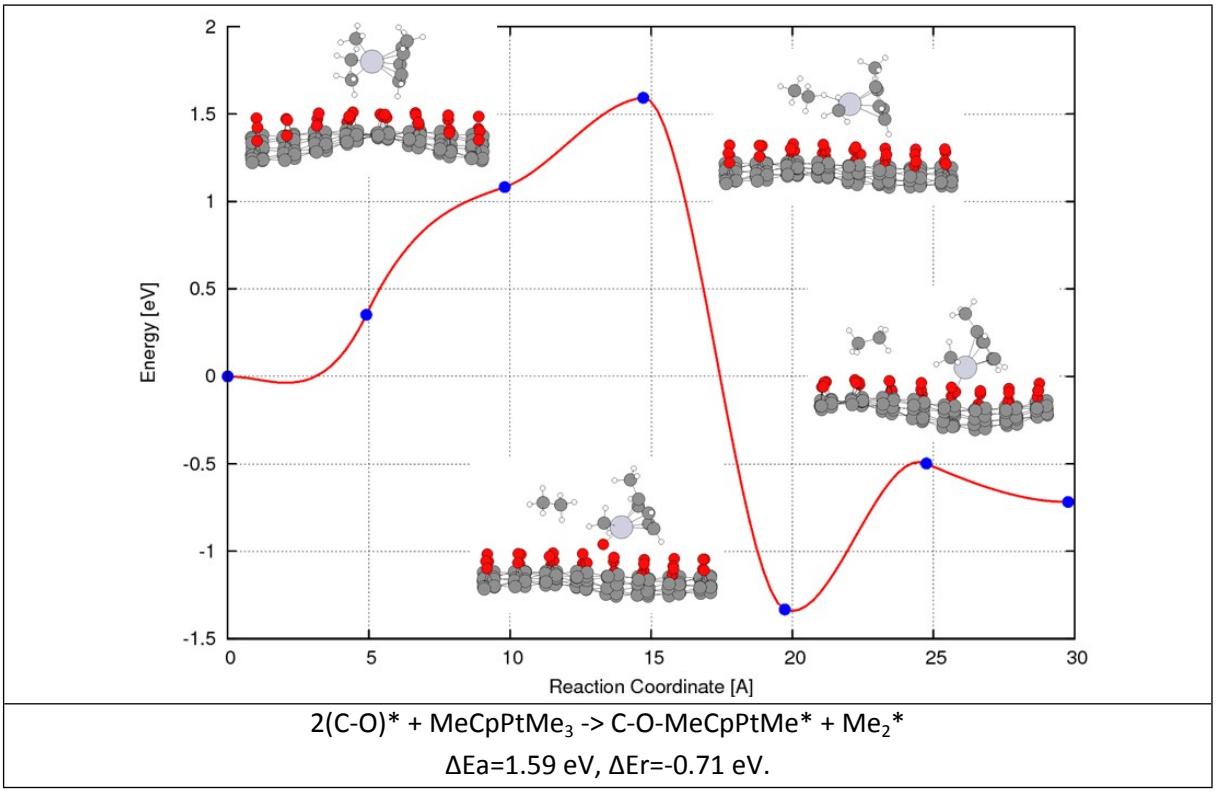
Figure S4. Ball-and-stick representation of the lowest-energy (left) physisorbed and (right) chemisorbed species of MeCpPtMe3 and Pt(acac)2 on selected graphene oxide models considered in current DFT calculations. Relative chemisorption energies are given in brackets. Color code, C: brown; O: red; H: pink-white; Pt: Gray.



2(C-O)* + $MeCpPtMe_3$ -> C-O-$MeCpPtMe_2$* + C-O-Me*

ΔEa=0.15 eV, ΔEr=-3.65 eV.

Figure S5. Minimum energy path of MeCpPtMe3 binding on GO mixture via methyl transfer release mechanism as predicted by PBE-D3 level of theory.



2(C-O)* + $MeCpPtMe_3$ -> C-O-MeCpPtMe* + Me_2*

ΔEa=1.59 eV, ΔEr=-0.71 eV.

Figure S6. Minimum energy path of MeCpPtMe3 binding on GO mixture via Me2 release mechanism as predicted by PBE-D3 level of theory.

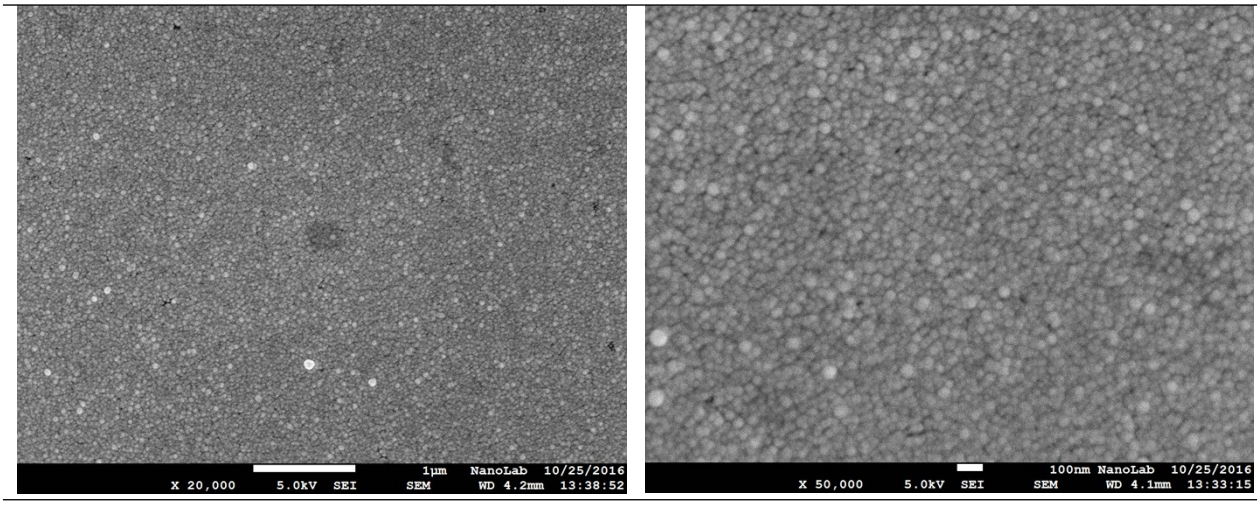


Figure S7. SEM images (with 20k X and 50 k X magnifications) showing the Pt ALD coverage after 1000 ALD cycles using $MeCpPtMe_3$ as the Pt precursor on graphene oxide obtained by a 5-min O_2 plasma treatment.