

**Supporting Information**  
**for**  
**Switch in relative stability between *cis* and *trans* 2-butene on Pt(111)**  
**as a function of experimental conditions: A DFT study.**

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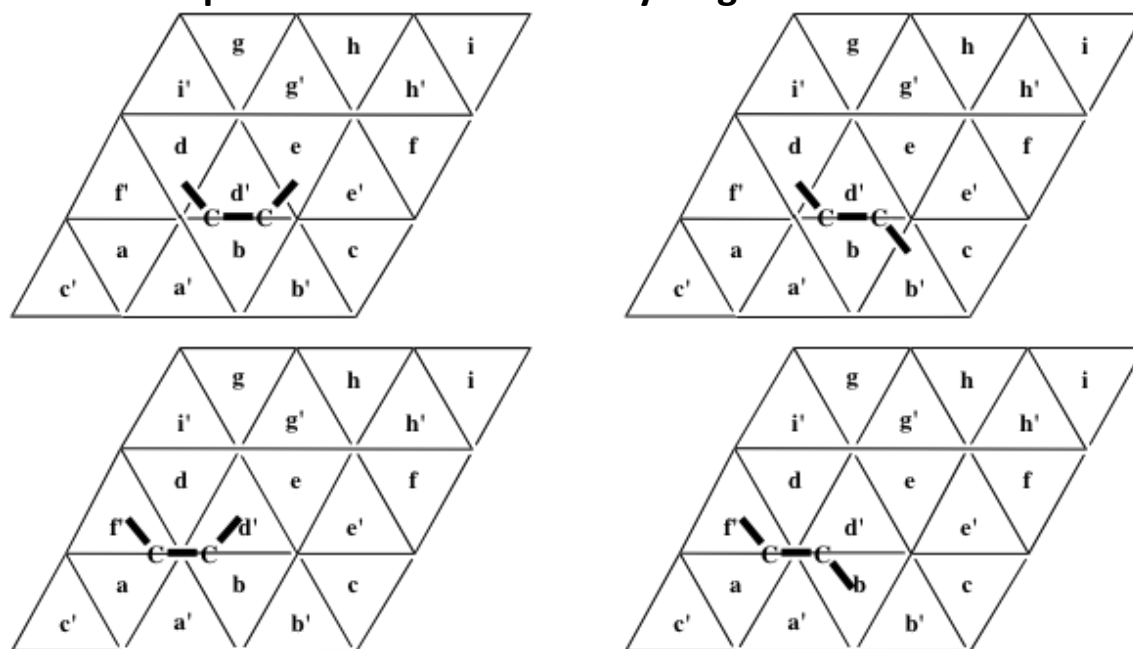
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## I. Coadsorption of 2-butene with hydrogen atoms.



**Figure S1:** Schematic representation of the different positions of the hydrogen atom around 2-butene: top, *cis* and *trans* di- $\sigma$  geometry; bottom, *cis* and *trans*  $\pi$  geometry.

### A. With the PW91 functional

#### 1. Coadsorption with one H and nine H atoms

Co-adsorption of *cis* and *trans* 2-butene with one or nine H atoms has already been studied in our previous work.<sup>1</sup> Only main results are summarized here to provide a general view to readers.

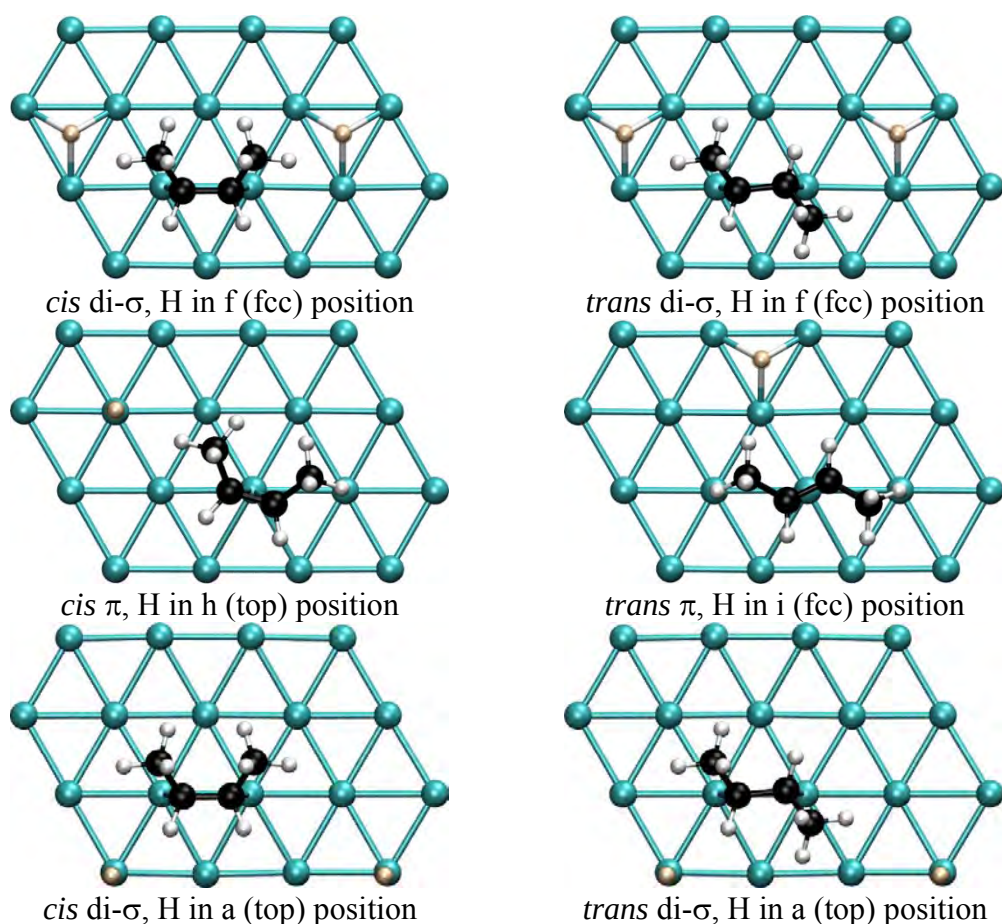
##### a) Coadsorption with one H atom

One H atom has been adsorbed at the 9 possible fcc sites (a to i), at the 9 possible hcp sites (a' to i') and at the top sites not occupied by a carbon atom (called xtop, x being the letter referring to the fcc site just above), in the cases of *cis* and *trans* di- $\sigma$  and  $\pi$  2-butene adsorption modes. The results are given in Table S1 and the structures are shown in Figure S2. For some H positions close to 2-butene, there is a migration between neighboring sites. In the case of the *cis* geometry, either di- $\sigma$  or  $\pi$ , some positions are symmetrically equivalent.

For the di- $\sigma$  2-butene geometries, the best site is fcc (f) but for the  $\pi$  geometry, some top sites are of identical stability and even more stable. The hcp sites are a little farther, which is in line with the relative adsorption energy of hydrogen at the three types of sites on Pt(111) (fcc > top ~ hcp).

**Table S1:** Relative energies (in eV) of the coadsorption states of 2-butene, di- $\sigma$  and  $\pi$ , with one hydrogen atom on Pt(111). The d top site does not exist. The letters into parentheses correspond to a migration to another site. Calculations were done with the PW91 functional. Table taken from Ref. 1 (also Ref. 46 in the main text).

| H position | <i>cis</i> di- $\sigma$ | <i>trans</i> di- $\sigma$ | <i>cis</i> $\pi$ | <i>trans</i> $\pi$ |
|------------|-------------------------|---------------------------|------------------|--------------------|
| a          | 0.03                    | 0.03                      | 0.28             | 0.22               |
| b          | 0.62                    | 0.58                      | 0.09 (b')        | 0.18               |
| c          | 0.03                    | 0.05                      | 0.02             | 0.02               |
| d          | 0.13                    | 0.14                      | 0.12             | 0.07               |
| e          | 0.13                    | 0.07 (g')                 | 0.05             | 0.02               |
| f          | <b>0.0</b>              | <b>0.0</b>                | 0.05             | 0.07               |
| g          | 0.02                    | 0.03                      | 0.01             | <b>0.0</b>         |
| h          | 0.02                    | 0.02                      | 0.01             | 0.02               |
| i          | 0.02                    | 0.04                      | 0.02             | <b>0.0</b>         |
| a'         | 0.02 (h)                | 0.02 (h)                  | 0.02 (h)         | 0.01 (h)           |
| b'         | 0.02 (i)                | 0.04 (i)                  | 0.08             | 0.14               |
| c'         | 0.03                    | 0.05                      | 0.09             | 0.07               |
| d'         | 0.13 (d)                | 0.14 (d)                  | 0.17             | 0.02 (e)           |
| e'         | 0.09                    | 0.15                      | 0.09             | 0.07               |
| f'         | 0.09                    | 0.15                      | 0.18             | 0.31               |
| g'         | 0.08                    | 0.07                      | 0.05             | 0.05               |
| h'         | 0.07                    | 0.08                      | 0.07             | 0.05               |
| i'         | 0.08                    | 0.09                      | 0.07             | 0.06               |
| a top      | 0.01                    | 0.01                      | 0.03             | 0.05               |
| b top      | 0.08                    | 0.11                      | 0.03             | 0.03               |
| c top      | 0.01                    | 0.06                      | <b>0.0</b>       | 0.02               |
| e top      | -                       | -                         | 0.11             | 0.07               |
| f top      | 0.01                    | 0.02                      | 0.11             | 0.06               |
| g top      | 0.13                    | 0.12                      | 0.04             | 0.04               |
| h top      | 0.05                    | 0.02                      | <b>0.0</b>       | <b>0.0</b>         |
| i top      | 0.05                    | 0.06                      | 0.04             | 0.03               |



**Figure S2:** Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed with 1 H atom in the (3×3) unit cell used in the calculations ( $\theta_{\text{H}} = 0.11$  ML) (di- $\sigma$  and  $\pi$  geometries). The most stable structures with the H atom in top are also shown. Calculations were done with the PW91 functional.

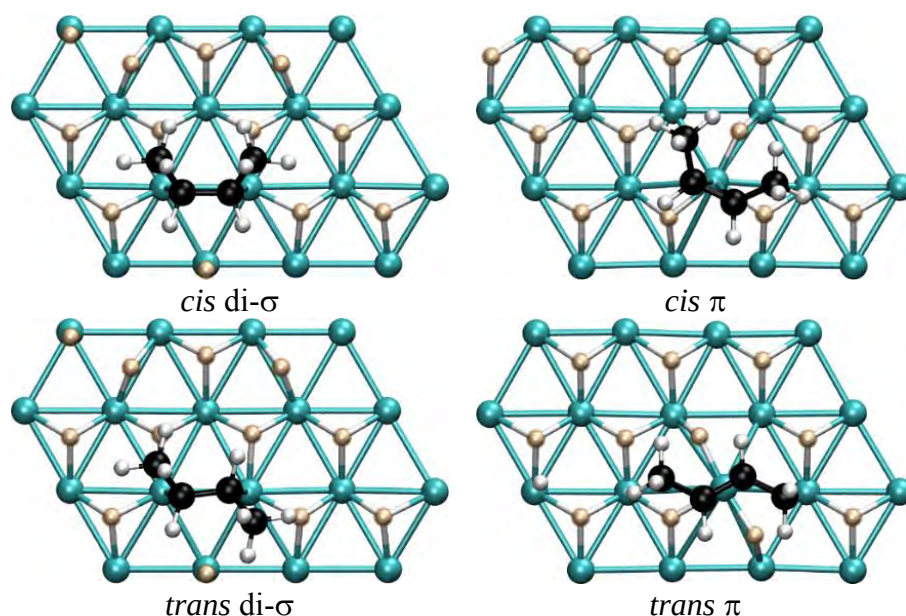
#### b) Coadsorption with nine H atoms

In the case of nine H atoms ( $\theta_{\text{H}} = 1.00$  ML) coadsorbed with the 2-butenes, several configurations have been considered starting from the all-fcc sites and by taking into account the results obtained with one H atom. The H atoms in fcc positions leading to the most energetically disfavored systems have been displaced to on-top or bridge positions. In this study, the most stable systems for the di- $\sigma$  geometries were found to correspond to those where  $\text{H}_{\text{b}}$  is displaced to a on-top position and  $\text{H}_{\text{h}}$  and  $\text{H}_{\text{i}}$  moved to bridges sites, as illustrated in **Figure S3** and **Figure S4**. For the  $\pi$  geometries, one and two H atoms end up in bridge positions for the cases of the *cis* and *trans* isomers, respectively. Additional AIMD simulations were performed (see text) and led to the same isomers.

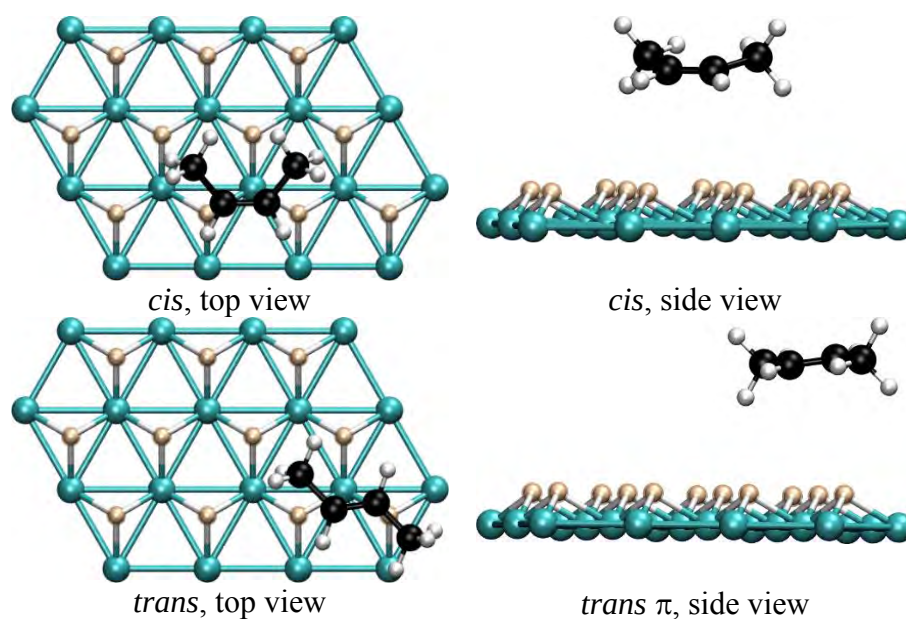
When the surface is saturated with hydrogen, our previous calculations have demonstrated that the  $\pi$  adsorption geometry is more stable than the di- $\sigma$  one, in agreement with the experimental data, which show that the adsorption of alkenes becomes  $\pi$  when coadsorbates saturate the surface.<sup>2</sup> With all dispersion functionals mentioned in our previous work, except BEEF, the inverse order was

found. Hence, the use of these functionals for introducing the dispersion improves the adsorption energy but might give incorrect adsorption geometries or sites.

As the most stable configuration correspond to a physisorbed 2-butene on top of a fully hydrogenated platinum surface (**Figure S4**), the correct ordering between the chemisorbed  $\sigma$  and  $\pi$  geometry does not matter in the thermodynamic stability of *cis/trans* butene and will not be discussed further.



**Figure S3:** Most stable structures of the *cis* and *trans* isomers of 2-butene **coadsorbed** with 9 H atoms in the (3×3) unit cell used in the calculations ( $\theta_{\text{H}} = 1.00$  ML) (di- $\sigma$  and  $\pi$  geometries). Calculations were done with the PW91 functional.

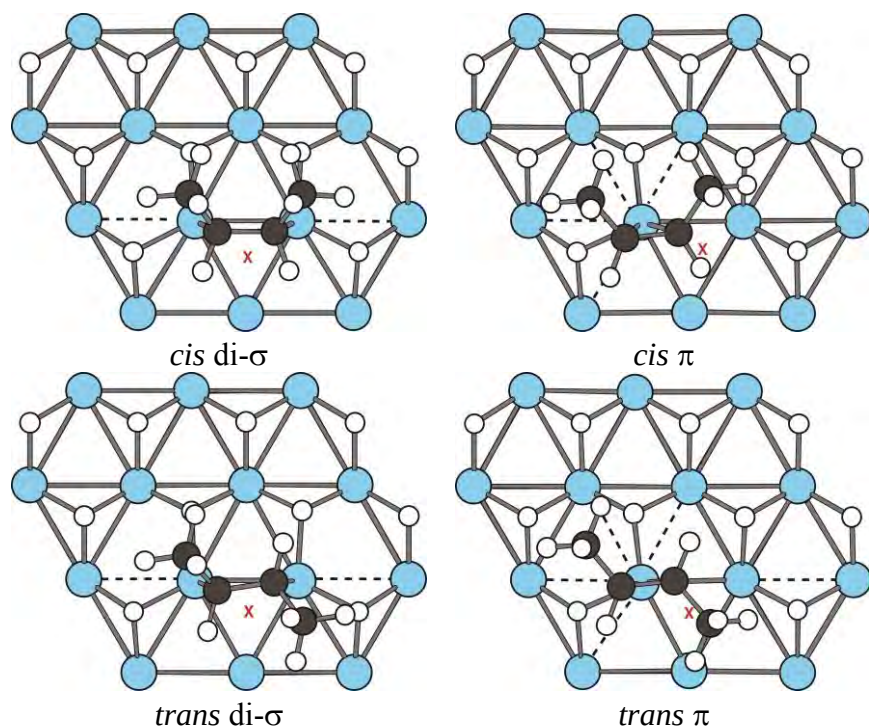


**Figure S4:** Most stable structures of the *cis* and *trans* isomers of 2-butene **physisorbed** with 9 H atoms in the (3×3) unit cell used in the calculations ( $\theta_{\text{H}} = 1.00$  ML) (di- $\sigma$  and  $\pi$  geometries). Calculations were done with the PW91 functional.



## 2. Coadsorption with eight H atoms

To obtain the coadsorption configurations with eight H atoms, one H needs to be removed from the system containing nine H atoms (the hydrogen-saturated surface). There are nine possibilities for this, but some of those are equivalent by symmetry for the *cis* isomer. All the appropriate configurations were considered in our calculations and their energies compared (see Table S2). The stability order was found to exhibit the opposite trend to that is seen in the case with one coadsorbed H atom (Table S1). Specifically, for the *cis* di- $\sigma$  geometry, the least stable structure with one coadsorbed hydrogen atom corresponds to that where the H is in position b, followed by those with the H in positions d and e. By contrast, for the 8 H coadsorbed structures, the most stable configuration is the one where position b is empty, and those where positions d or e are empty and H<sub>b</sub> is in an on-top position are 0.23 eV less stable. However, the configurations where positions h or i are empty, always with H<sub>b</sub> in the on-top position, are even more stable. For the *trans* di- $\sigma$  geometry, the same trend is observed, namely, the system where site b is vacant being the most stable. In the case of the  $\pi$  geometries, leaving site a or b vacant also leads to the most stable but with only small differences in energy with the other sites, which shows that these forms have less constraints on the surface. The most stable structures for the four 2-butene structures in the presence of eight H atoms in the unit cell are shown on **Figure S5**.



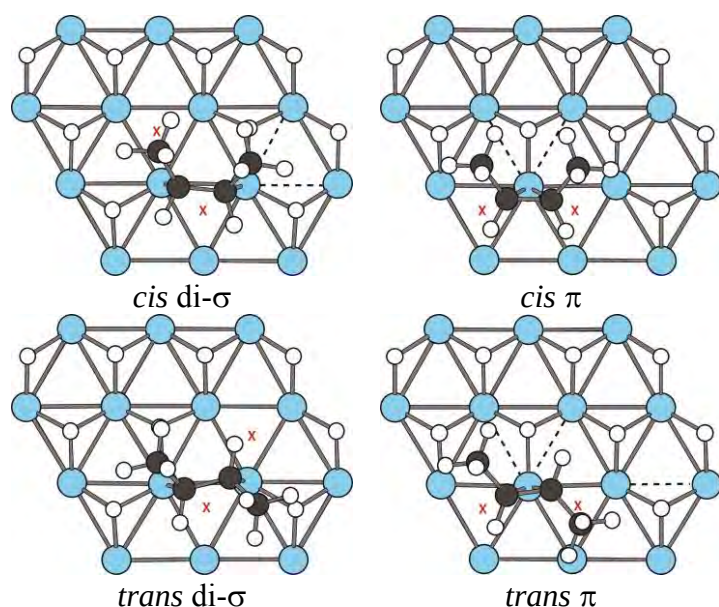
**Figure S5:** Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed with 8 H atoms in the (3 $\times$ 3) unit cell used in the calculations ( $\theta_{\text{H}} = 0.89$  ML) (di- $\sigma$  and  $\pi$  geometries). The red cross indicates the vacant site. Calculations were done with the PW91 functional.

**Table S2:** Relative energies (in eV) of the coadsorption states of 2-butene, di- $\sigma$  and  $\pi$ , with eight hydrogen atoms on Pt(111). The letters correspond to the vacant site, following Figure 1. For all di- $\sigma$  systems, except b, H<sub>b</sub> is in the on-top position. a) H<sub>i</sub> moves from bridge to its initial fcc position. b) H<sub>h</sub> moves from bridge to its initial fcc position. Calculations were done with the PW91 functional.

| H position | <i>cis</i> di- $\sigma$ | <i>trans</i> di- $\sigma$ | <i>cis</i> $\pi$ | <i>trans</i> $\pi$ |
|------------|-------------------------|---------------------------|------------------|--------------------|
| a          | 0.38                    | 0.38                      | <b>0.0</b>       | 0.01               |
| b          | <b>0.0</b>              | <b>0.0</b>                | <b>0.0</b>       | <b>0.0</b>         |
| c          | 0.38                    | 0.39                      | 0.13             | 0.07               |
| d          | 0.24                    | 0.24                      | 0.06             | 0.02               |
| e          | 0.24                    | 0.18                      | 0.05             | 0.04               |
| f          | 0.47                    | 0.47                      | 0.11             | 0.04               |
| g          | 0.33                    | 0.33                      | 0.13             | 0.06               |
| h          | 0.19 <sup>a)</sup>      | 0.19 <sup>a)</sup>        | 0.15             | 0.02               |
| i          | 0.19 <sup>b)</sup>      | 0.18 <sup>b)</sup>        | 0.13             | 0.09               |

### 3. Coadsorption with seven H atoms

Removing another H from the (3x3) Pt(111) unit cell used in our calculations leads to a system where the olefin is coadsorbed with seven H atoms. There are 36 combinations for this coverage, but we have here considered only the 15 most probable configurations based on the results obtained for 8 H atoms. The relative energies calculated for those are given in Table S3. As expected, the best configurations correspond to those where two vacant sites are created at the least stable positions for the coadsorption of one H atom, namely, position b and position d or e for the di- $\sigma$  geometries and positions a and b for the  $\pi$  geometries. In the case of the di- $\sigma$  geometries, all the configurations where position b is vacant are close in energy of each other (within 0.14 and 0.19 eV for the *cis* and *trans* isomers, respectively). In the case of the  $\pi$  geometries, the range of the coadsorption energies is smaller than in the case of the di- $\sigma$  geometries (within 0.33 eV compared to 0.55-0.61 eV), as already observed in the case of the coadsorption of the alkene with 8H. The best coadsorption structures of 2-butene in the presence of seven H are shown in **Figure S6**.



**Figure S6:** Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed with 7 H atoms in the (3×3) unit cell used in the calculations ( $\theta_{\text{H}} = 0.78$  ML) (di- $\sigma$  and  $\pi$  geometries). The red crosses indicate the vacant sites. Calculations were done with the PW91 functional.

**Table S3:** Relative energies (in eV) of the coadsorption states of 2-butene, di- $\sigma$  and  $\pi$ , with seven hydrogen atoms on Pt(111). The letters correspond to the vacant sites, following Figure 1. a) In this configuration, 2-butene has rotated and a structure similar to (a, b) is obtained. Calculations were done with the PW91 functional.

| H position | <i>cis</i> di- $\sigma$ | <i>trans</i> di- $\sigma$ | <i>cis</i> $\pi$ | <i>trans</i> $\pi$ |
|------------|-------------------------|---------------------------|------------------|--------------------|
| a, b       | 0.08                    | 0.12                      | <b>0.0</b>       | <b>0.0</b>         |
| a, c       | 0.55                    | 0.50                      | 0.19             | 0.13               |
| a, d       | 0.30                    | 0.34                      | a)               | 0.04               |
| a, e       | 0.33                    | 0.32                      | 0.21             | 0.17               |
| a, f       | 0.55                    | 0.59                      | 0.13             | 0.09               |
| b, c       | 0.08                    | 0.13                      | 0.19             | 0.11               |
| b, d       | <b>0.0</b>              | 0.05                      | 0.17             | 0.07               |
| b, e       | <b>0.0</b>              | <b>0.0</b>                | 0.13             | 0.10               |
| b, f       | 0.14                    | 0.19                      | 0.21             | 0.13               |
| c, d       | 0.33                    | 0.38                      | 0.33             | 0.16               |
| c, e       | 0.30                    | 0.27                      | 0.25             | 0.23               |
| c, f       | 0.55                    | 0.61                      | 0.34             | 0.22               |
| d, e       | 0.15                    | 0.13                      | 0.28             | 0.09               |
| d, f       | 0.40                    | 0.43                      | 0.26             | 0.12               |
| e, f       | 0.40                    | 0.37                      | 0.33             | 0.23               |



#### 4. Coadsorption with six, five, four, three and two H atoms

To study the further removal of one, two or three H atoms from the last structures, to yield surfaces with ~~the~~ butene coadsorbed with 6, 5 or 4 H atoms, only selected configurations were considered based on the observation that the most stable configurations for 8 H and 7 H are obtained by making the vacant sites at the less stable positions for the coadsorption of one H atom. Moreover, the results reported in Table S4 show that the  $\pi$  geometries are never the most stable except in the case of 9 H atoms. Hence, only the di- $\sigma$  geometries were considered here. In the case of 6 H atoms, the vacant sites for the most stable configurations were found to be at positions b, d, and e for both *cis* and *trans* isomers. With 5 H atoms, two possibilities were tested, with vacancies at either the b, d, e, and a or the b, d, e, and c positions. For the *cis* isomer those are symmetrical and for the *trans*, their energies were estimated to differ by only 0.02 eV. For 4 H atoms, only configurations b, d, e, a, and c were considered.

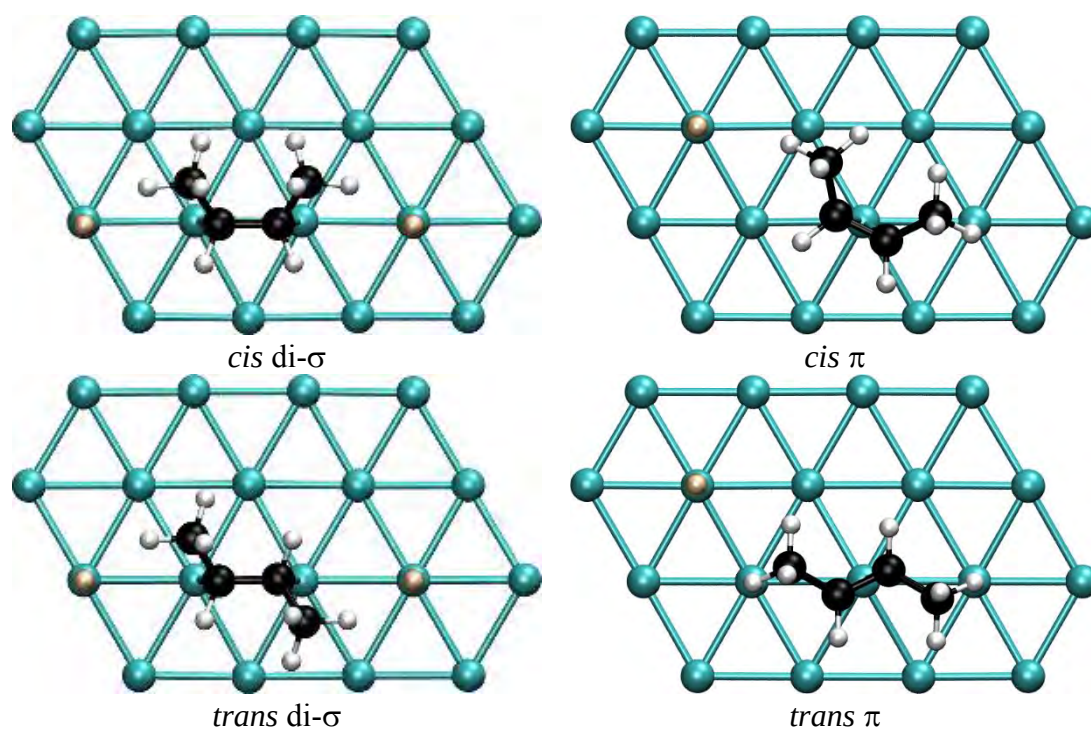
In the cases of 2 H atoms, the systems were constructed by adding one H atom to the most stable configuration found for the coadsorption of 2-butene and one H atom using the relative energies listed in Table S1 as a reference. Coadsorption with 3 H atoms was constructed by adding one H atom to most stable configurations found with 2 H atoms. In the cases of 2 H and 3 H atoms, the optimal systems were found where one hydrogen occupied an on-top position. The H atoms are eventually at positions f, i and an on-top for the 3 H system and at positions f and h for the 2H system. The optimized adsorption structures are shown in Figure 1 in the main text.

## B. With PBE-TS

The same procedures were followed for the PBE-TS functional. Only the main results are reported here.

**Table S4:** Relative energies (in eV) of the coadsorption states of 2-butene, di- $\sigma$  and  $\pi$ , with one hydrogen atom on Pt(111). Calculations were done with the PBE-TS functional. The d top site does not exist. The letters into parentheses correspond to a migration to another site; br x-y means the bridge site between sites x and y.

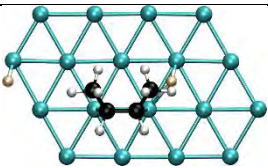
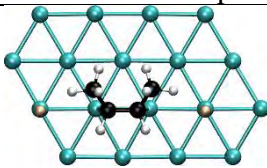
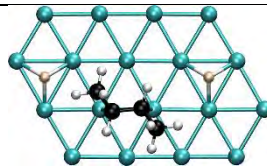
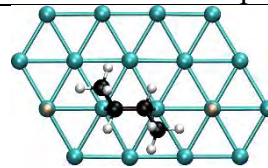
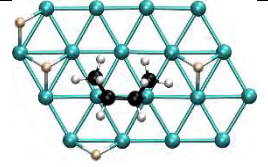
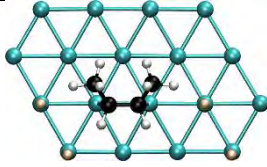
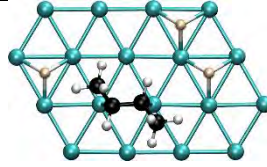
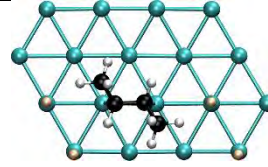
| H position | <i>cis</i> di- $\sigma$ | <i>trans</i> di- $\sigma$ | <i>cis</i> $\pi$ | <i>trans</i> $\pi$ |
|------------|-------------------------|---------------------------|------------------|--------------------|
| a          | 0.06                    | 0.06                      | 0.14 (c')        | 0.03 (g)           |
| b          | 0.70                    | 0.05 (i)                  | 0.13 (b')        | 0.08 (i)           |
| c          | 0.06                    | 0.08                      | 0.06             | 0.03               |
| d          | 0.10 (i')               | 0.14 (br d-i')            | 0.12 (i')        | 0.09 (i')          |
| e          | 0.10 (g')               | 0.09 (g')                 | 0.11             | 0.08               |
| f          | 0.02                    | 0.02                      | 0.11             | 0.09               |
| g          | 0.04                    | 0.05                      | 0.04             | 0.03               |
| h          | 0.04                    | 0.03                      | 0.06             | 0.02               |
| i          | 0.04                    | 0.05                      | 0.06             | 0.04               |
| a'         | 0.04 (h)                | 0.04 (h)                  | 0.06 (h)         | 0.05 (h)           |
| b'         | 0.04 (i)                | 0.05 (i)                  | 0.14             | 0.04 (i)           |
| c'         | 0.05                    | 0.06                      | 0.14             | 0.14               |
| d'         | 0.10 (d)                | 0.11 (i')                 | 0.24             | 0.07 (e)           |
| e'         | 0.02 (f)                | 0.02 (f)                  | 0.14             | 0.08               |
| f'         | 0.02 (f)                | 0.02 (f)                  | 0.24             | 0.09 (f)           |
| g'         | 0.10                    | 0.09                      | 0.07             | 0.08               |
| h'         | 0.10                    | 0.10                      | 0.11             | 0.09               |
| i'         | 0.10                    | 0.11                      | 0.13             | 0.09               |
| a top      | 0.01                    | 0.01                      | 0.03             | 0.12               |
| b top      | 0.09                    | 0.11                      | 0.04             | 0.06               |
| c top      | 0.01                    | 0.06                      | 0.02             | 0.01               |
| e top      | -                       | -                         | 0.12             | 0.09               |
| f top      | <b>0.0</b>              | <b>0.0</b>                | 0.12             | 0.08               |
| g top      | 0.13                    | 0.12                      | 0.06             | 0.11               |
| h top      | 0.06                    | 0.01                      | <b>0.0</b>       | <b>0.0</b>         |
| i top      | 0.07                    | 0.06                      | 0.06             | 0.06               |

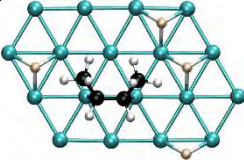
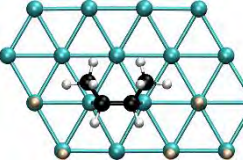
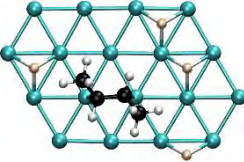
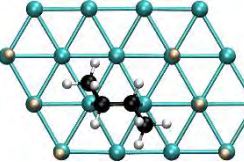
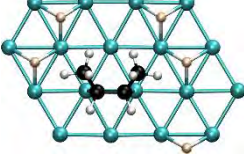
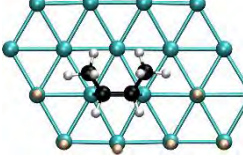
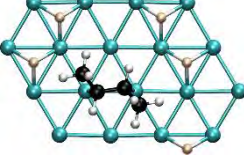
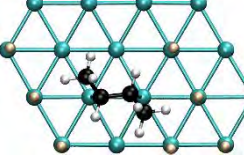
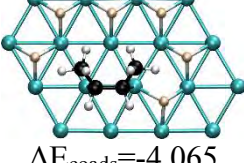
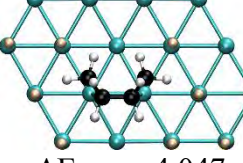
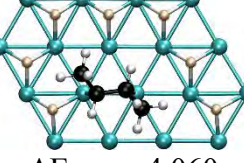
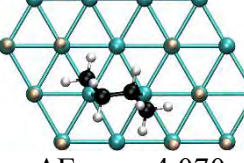
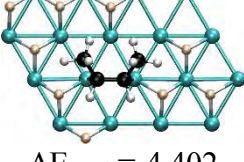
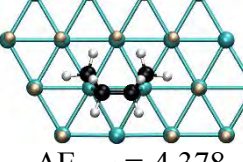
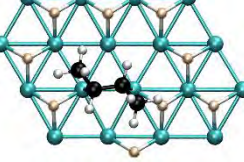
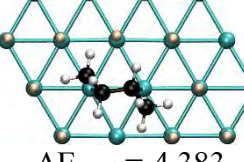
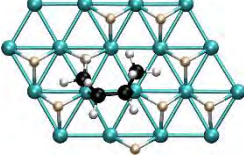
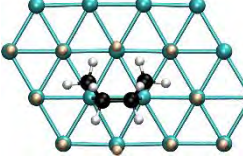
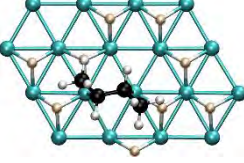
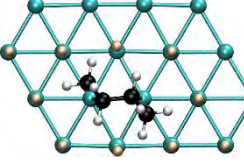
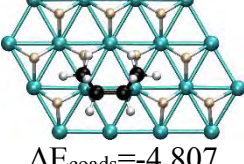
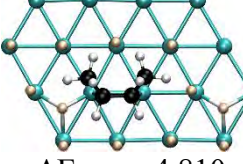
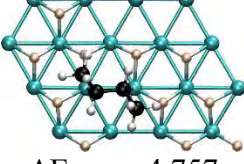
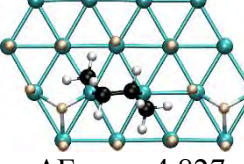
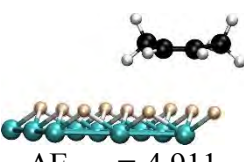
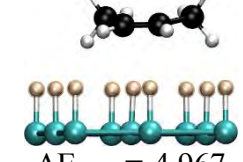
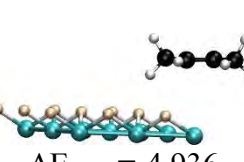
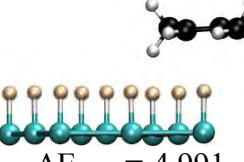


**Figure S7:** Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed with 1 H atom with the PBE-TS functional in the (3×3) unit cell used in the calculations ( $\theta_{\text{H}} = 0.11$  ML) (di- $\sigma$  and  $\pi$  geometries).

The most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed with 1 to 9 H atoms are shown in

**Figure S8.** For all configurations, the coadsorption energies ( $\Delta E_{\text{coads}}$ ) and free energies ( $\Delta G_{\text{coads}}$ ) (at  $P=10^{-7}$  torr,  $T=80\text{K}$  and for a  $P_{\text{H}_2}/P_{\text{butene}}$  ratio of 25) are given in eV. It is worth emphasizing the configurations in which all H atoms are coadsorbed on top sites are the most stable at 0K (except for  $n=5$  and  $n=6$ ), they become less stable when temperature effects are included. This is mostly due to the fact that the Pt-H vibration is much harder when the H atom is on a top site than on a fcc site.

| n | <i>Cis di-σ</i>                                                                                                                                             | <i>Cis di-σ</i> 'all top'                                                                                                                                   | <i>Trans di-σ</i>                                                                                                                                            | <i>Trans di-σ</i> 'all top'                                                                                                                                   |
|---|-------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | <br>$\Delta E_{\text{coads}}=-2.257$<br>$\Delta G_{\text{coads}}=-1.769$ | <br>$\Delta E_{\text{coads}}=-2.278$<br>$\Delta G_{\text{coads}}=-1.740$ | <br>$\Delta E_{\text{coads}}=-2.277$<br>$\Delta G_{\text{coads}}=-1.790$ | <br>$\Delta E_{\text{coads}}=-2.291$<br>$\Delta G_{\text{coads}}=-1.751$ |
| 2 | <br>$\Delta E_{\text{coads}}=-2.744$<br>$\Delta G_{\text{coads}}=-2.151$ | <br>$\Delta E_{\text{coads}}=-2.788$<br>$\Delta G_{\text{coads}}=-2.097$ | <br>$\Delta E_{\text{coads}}=-2.763$<br>$\Delta G_{\text{coads}}=-2.171$ | <br>$\Delta E_{\text{coads}}=-2.808$<br>$\Delta G_{\text{coads}}=-2.115$ |

|   |                                                                                                                                                                 |                                                                                                                                                                 |                                                                                                                                                                  |                                                                                                                                                                   |
|---|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 3 | <br>$\Delta E_{\text{coads}} = -3.206$<br>$\Delta G_{\text{coads}} = -2.507$   | <br>$\Delta E_{\text{coads}} = -3.279$<br>$\Delta G_{\text{coads}} = -2.427$   | <br>$\Delta E_{\text{coads}} = -3.222$<br>$\Delta G_{\text{coads}} = -2.522$   | <br>$\Delta E_{\text{coads}} = -3.297$<br>$\Delta G_{\text{coads}} = -2.444$   |
| 4 | <br>$\Delta E_{\text{coads}} = -3.658$<br>$\Delta G_{\text{coads}} = -2.872$   | <br>$\Delta E_{\text{coads}} = -3.696$<br>$\Delta G_{\text{coads}} = -2.682$   | <br>$\Delta E_{\text{coads}} = -3.666$<br>$\Delta G_{\text{coads}} = -2.864$   | <br>$\Delta E_{\text{coads}} = -3.701$<br>$\Delta G_{\text{coads}} = -2.678$   |
| 5 | <br>$\Delta E_{\text{coads}} = -4.065$<br>$\Delta G_{\text{coads}} = -3.102$   | <br>$\Delta E_{\text{coads}} = -4.047$<br>$\Delta G_{\text{coads}} = -2.852$   | <br>$\Delta E_{\text{coads}} = -4.060$<br>$\Delta G_{\text{coads}} = -3.100$   | <br>$\Delta E_{\text{coads}} = -4.070$<br>$\Delta G_{\text{coads}} = -2.876$   |
| 6 | <br>$\Delta E_{\text{coads}} = -4.402$<br>$\Delta G_{\text{coads}} = -3.285$  | <br>$\Delta E_{\text{coads}} = -4.378$<br>$\Delta G_{\text{coads}} = -3.006$  | <br>$\Delta E_{\text{coads}} = -4.394$<br>$\Delta G_{\text{coads}} = -3.274$  | <br>$\Delta E_{\text{coads}} = -4.383$<br>$\Delta G_{\text{coads}} = -3.011$  |
| 7 | <br>$\Delta E_{\text{coads}} = -4.606$<br>$\Delta G_{\text{coads}} = -3.334$ | <br>$\Delta E_{\text{coads}} = -4.644$<br>$\Delta G_{\text{coads}} = -3.082$ | <br>$\Delta E_{\text{coads}} = -4.594$<br>$\Delta G_{\text{coads}} = -3.320$ | <br>$\Delta E_{\text{coads}} = -4.657$<br>$\Delta G_{\text{coads}} = -3.088$ |
| 8 | <br>$\Delta E_{\text{coads}} = -4.807$<br>$\Delta G_{\text{coads}} = -3.367$ | <br>$\Delta E_{\text{coads}} = -4.810$<br>$\Delta G_{\text{coads}} = -3.075$ | <br>$\Delta E_{\text{coads}} = -4.757$<br>$\Delta G_{\text{coads}} = -3.316$ | <br>$\Delta E_{\text{coads}} = -4.827$<br>$\Delta G_{\text{coads}} = -3.091$ |
| 9 | <br>$\Delta E_{\text{coads}} = -4.911$<br>$\Delta G_{\text{coads}} = -3.450$ | <br>$\Delta E_{\text{coads}} = -4.967$<br>$\Delta G_{\text{coads}} = -3.137$ | <br>$\Delta E_{\text{coads}} = -4.936$<br>$\Delta G_{\text{coads}} = -3.466$ | <br>$\Delta E_{\text{coads}} = -4.991$<br>$\Delta G_{\text{coads}} = -3.156$ |

**Figure S8:** Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed in di- $\sigma$  geometry with  $n$  H atoms ( $n=1$  to 9) in the  $(3 \times 3)$  unit cell used in the calculations ( $\theta_{\text{H}} = 0.11$  to 1 ML). For all configurations, the coadsorption energies and free energies (at  $P=10^{-7}$  torr,  $T=80\text{K}$ , and for a  $P_{\text{H}_2}/P_{\text{butene}}$  ratio of 25) are given. Calculations were done with the PBE-TS functional.



### C. With optPBE

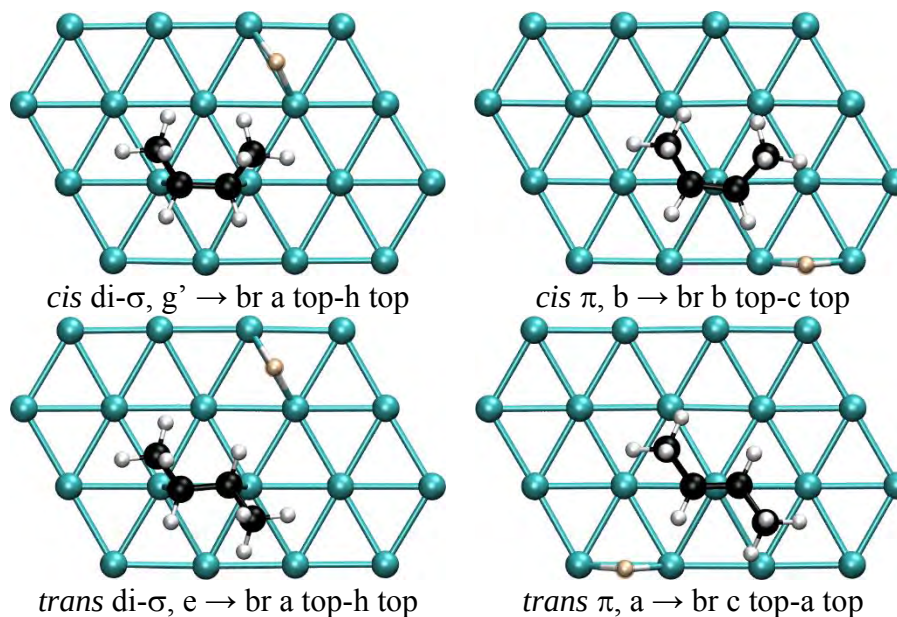
The same procedures were followed for the optPBE functional. Only the main results are reported here. All configurations were examined for the coadsorption of one H atom and 2-butene on Pt(111). Energies are collected in Table S5. Some configurations with H atoms in bridge positions are depicted in

**Figure S9.**

**Table S5:** Relative energies (in eV) of the coadsorption states of 2-butene, di- $\sigma$  and  $\pi$ , with one hydrogen atom on Pt(111). The calculations were done with the optPBE functional. The d top site does not exist. The letters into parentheses correspond to a migration to another site; br x-y means the bridge site between sites x and y.

| H position | <i>cis</i> di- $\sigma$  | <i>trans</i> di- $\sigma$ | <i>cis</i> $\pi$         | <i>trans</i> $\pi$       |
|------------|--------------------------|---------------------------|--------------------------|--------------------------|
| a          | 0.13                     | 0.13                      | 0.20 (c')                | 0.11<br>(br c top-a top) |
| b          | 0.72                     | 0.14 (i)                  | 0.13<br>(br b top-c top) | 0.28                     |
| c          | 0.13                     | 0.16                      | 0.13                     | 0.12                     |
| d          | 0.24                     | 0.25                      | 0.24                     | 0.17 (i')                |
| e          | 0.24                     | 0.11<br>(br a top-h top)  | 0.16                     | 0.13                     |
| f          | 0.10                     | 0.10                      | 0.16                     | 0.17                     |
| g          | 0.12                     | 0.13                      | 0.12                     | 0.11                     |
| h          | 0.12                     | 0.12                      | 0.12                     | 0.12                     |
| i          | 0.12                     | 0.14                      | 0.13                     | 0.11                     |
| a'         | 0.12 (h)                 | 0.11 (h)                  | 0.10 (h)                 | 0.12 (h)                 |
| b'         | 0.11 (i)                 | 0.14 (i)                  | -                        | 0.24                     |
| c'         | 0.13                     | 0.15                      | 0.20                     | 0.18                     |
| d'         | 0.24 (d)                 | 0.25 (d)                  | 0.29                     | 0.13 (e)                 |
| e'         | 0.10 (f)                 | 0.11<br>(br a top-i top)  | 0.21                     | 0.17                     |
| f'         | 0.10 (f)                 | 0.10 (f)                  | 0.29                     | 0.16 (f)                 |
| g'         | 0.12<br>(br a top-h top) | 0.11<br>(br a top-i top)  | 0.17                     | 0.16                     |
| h'         | 0.18                     | 0.18                      | 0.19                     | 0.16                     |
| i'         | 0.12 (i)                 | 0.20                      | 0.19                     | 0.17                     |
| a top      | <b>0.0</b>               | <b>0.0</b>                | 0.03                     | 0.05                     |
| b top      | 0.07                     | 0.11                      | 0.03                     | 0.03                     |
| c top      | <b>0.0</b>               | 0.06                      | <b>0.0</b>               | 0.01                     |
| e top      | -                        | -                         | 0.11                     | 0.07                     |
| f top      | <b>0.0</b>               | <b>0.0</b>                | 0.11                     | 0.06                     |
| g top      | 0.14                     | 0.12                      | 0.05                     | 0.04                     |

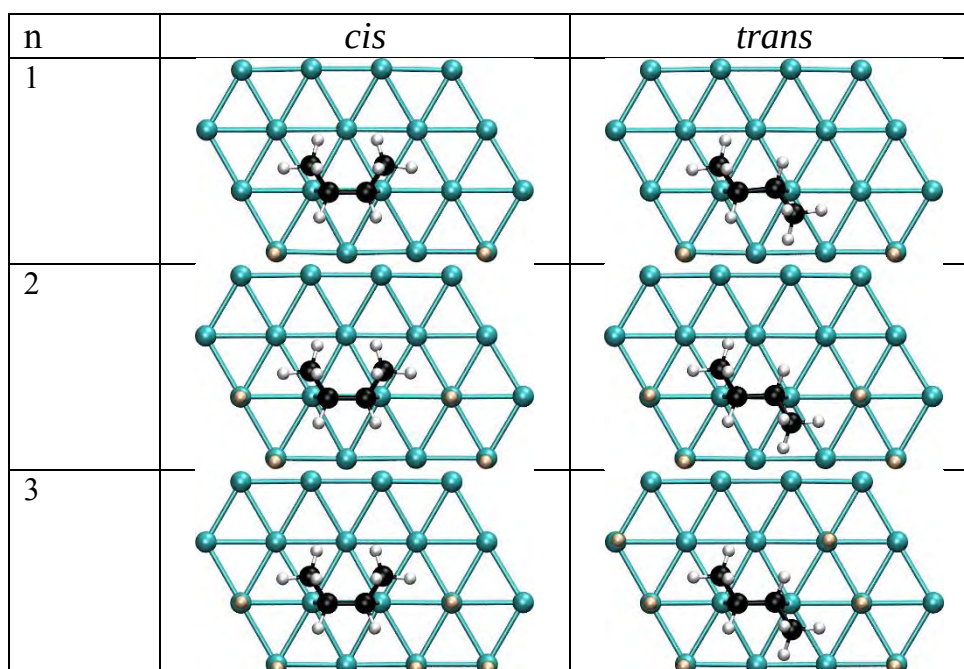
|       |      |            |            |            |
|-------|------|------------|------------|------------|
| h top | 0.06 | <b>0.0</b> | <b>0.0</b> | <b>0.0</b> |
| i top | 0.06 | 0.07       | 0.06       | 0.03       |



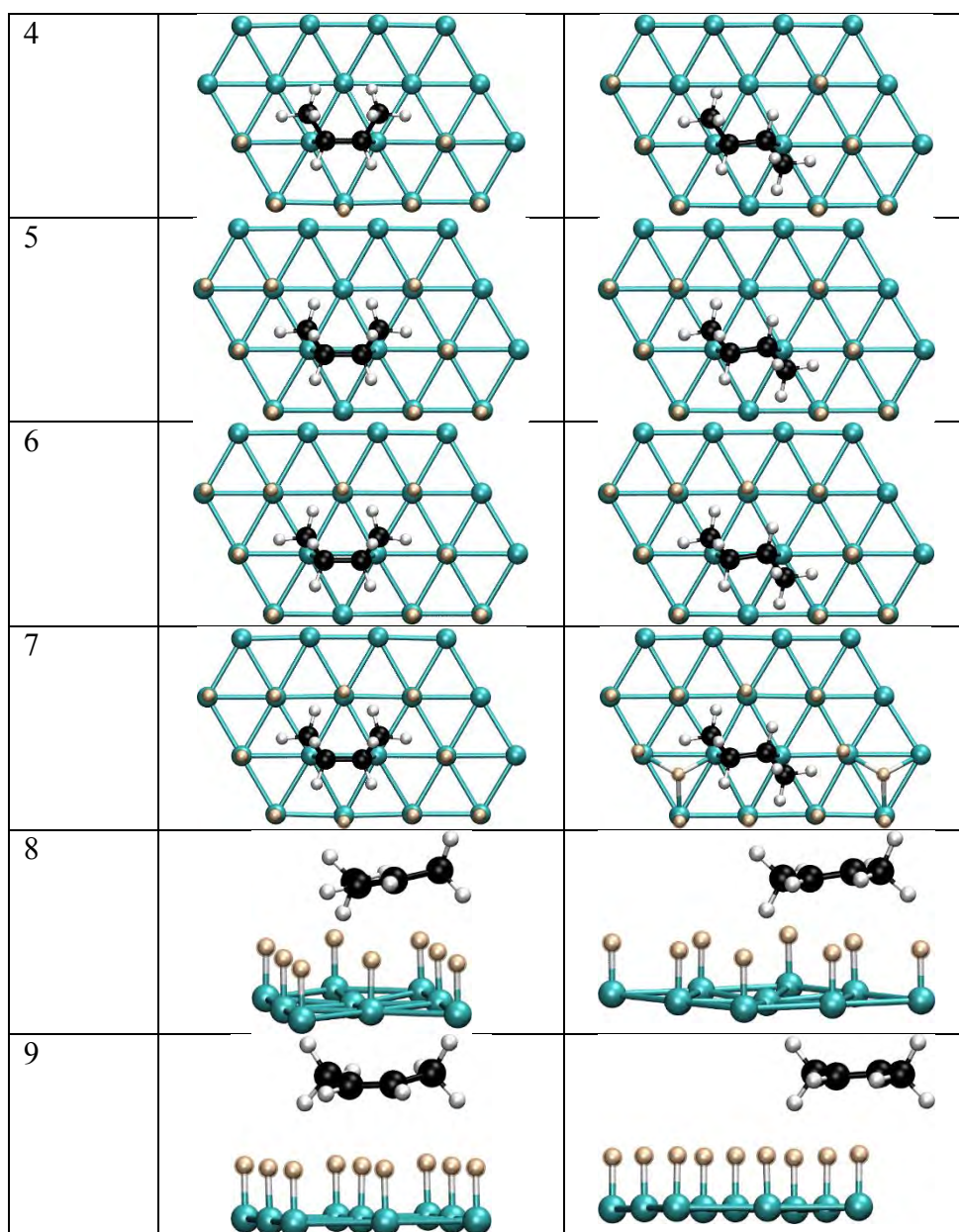
**Figure S9:** Structures of the *cis* and *trans* isomers of 2-butene **coadsorbed** with 1 H atom in the (3 $\times$ 3) unit cell used in the calculations ( $\theta_H = 0.11$  ML). Di- $\sigma$  and  $\pi$  geometries with the H atom in bridge position. The calculations were done with the optPBE functional.

Our calculations have shown that optPBE favors greatly configurations where all H atoms are on top sites. Therefore, only those configurations are shown in

**Figure S10.**



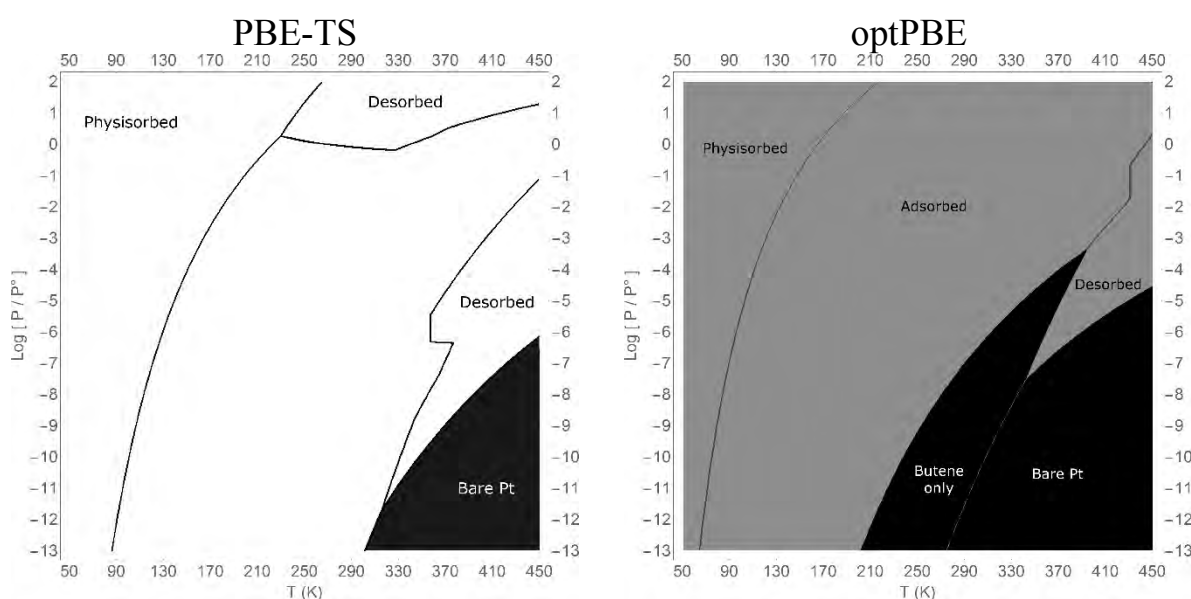




**Figure S10:** Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed in di- $\sigma$  geometry with  $n$  H atoms ( $n=1$  to 9) in the  $(3\times 3)$  unit cell used in the calculations ( $\theta_{\text{H}} = 0.11$  to 1 ML). The calculations were done with the optPBE functional.

### D. Fcc or top sites?

Both PBE+TS and optPBE functionals favor the adsorption of H atoms in top position at 0K in disagreement with experiments. However, when thermal effects are included, the PBE+TS functional favors configurations in which most atoms are in fcc positions. The favored adsorption sites are illustrated in **Figure S11** as a function of the total pressure and temperature with a  $P_{\text{H}_2}/P_{\text{Butene}}$  pressure ratio of 25. In both cases, at least two configurations were considered for each hydrogen coverage: one in which most of the H atoms are in fcc sites, and one in which most of the H atoms are in top sites.



**Figure S11:** Thermodynamic stability of coadsorbed hydrogen with 2-butene on platinum, with a  $P_{\text{H}_2}/P_{\text{Butene}}$  pressure ratio of 25. Black: bare platinum or 2-butene adsorbed alone; Grey: H adsorption favored on top sites; White: H adsorption favored on fcc sites.

## II. Energetics

### A. Test of the density functional

The adsorption energies of *trans* 2-butene on Pt(111) computed with different functionals are given in Table S6, together with the interatomic Pt-Pt distance and the relative energies of one H atom on the fcc, hcp and top site of the Pt(111) surface.

**Table S6:** Adsorption energy  $\Delta E_{\text{ads}}(\text{but})$  of *trans* 2-butene on Pt(111) (in eV) computed with different functionals, Pt-Pt distance ( $d_{\text{Pt-Pt}}$  in Å) and relative adsorption energy (in meV) of one H atom on bare Pt(111) on fcc, hcp and top sites.

| Functional | $\Delta E_{\text{ads}}(\text{but})$<br>(eV) | $d_{\text{Pt-Pt}}$ (Å) | $\Delta E_{\text{ads}}(\text{H})$ |     |     |
|------------|---------------------------------------------|------------------------|-----------------------------------|-----|-----|
|            |                                             |                        | fcc                               | hcp | top |
| PW91       | -0.959                                      | 2.820                  | 0                                 | 51  | 39  |
| PBE        | -0.934                                      | 2.809                  | 0                                 | 50  | 19  |
| revPBE     | -0.437                                      | 2.826                  | -                                 | -   | -   |
| optPBE     | -1.533                                      | 2.821                  | 54                                | 110 | 0   |
| optB86b    | -1.857                                      | 2.793                  | 14                                | 67  | 0   |
| optB88     | -1.678                                      | 2.813                  | 45                                | 100 | 0   |
| PBE-TS     | -1.773                                      | 2.785                  | 0                                 | 53  | 31  |
| BEEF       | -1.063                                      | 2.826                  | 41                                | 96  | 0   |

### B. Electronic energies

The coadsorption energies of the most stable configurations can be computed following Equation (1).

$$\Delta E_{\text{coads}}(\text{nH}+\text{But}) = E_{\text{Tot}} - E_{\text{but(g)}} - n/2E_{\text{H2(g)}} - E_{\text{Pt}} \quad (1)$$

An alternative way to express the energetics of the adsorption is with respect to the platinum surface already pre-dosed with the hydrogen, by using Equation (2) below.

$$\Delta E_{\text{ads}}(\text{But}) = E_{\text{Tot}} - E_{\text{but(g)}} - E_{\text{nH@Pt}} \quad (2)$$

In this case, the reported energy only comes from the contribution of the butene; the changes due to hydrogen pre-adsorption are already included in the  $E_{\text{nH@Pt}}$  term (the energy of the Pt slab covered with n adsorbed hydrogen atoms). This reflects more accurately what is measured in TPD experiments.

#### 1. PW91

Coadsorption energies computed with the PW91 functional are reported in Table S7 following equation (1) and (2). As expected, 2-butene is destabilized by the presence of adsorbed hydrogen atoms, and becomes unstable with 9 H. However, the overall coadsorption of 2-butene and 9 H is still generally favored, that is, the system still favors the coadsorption of all these species even if each of individual molecule lose some stability if coadsorption is not considered.

Coadsorption free energies computed with the PW91 functional are reported in Table S8.

**Table S7:** Coadsorption energies ( $\Delta E_{\text{coads}}(\text{nH}+\text{But})$ , eV,  $n=0$  to 9) of *cis*- and *trans*-2-butene coadsorbed with  $n$  H atoms on the Pt(111) surface (equation 1) and adsorption energies ( $\Delta E_{\text{ads}}(\text{But})$ , eV) for the most stable geometries of *cis*- and *trans*-2-butene adsorbed on a hydrogen-precovered Pt(111) surface (equation 2). The calculations were done by using a five-layer slab with a  $5\times 5\times 1$  K-point mesh and the PW91 functional. The dipole correction is included. The last line corresponds to physisorbed butene.

| n               | $\Delta E_{\text{coads}}(\text{nH}+\text{But})$ |                         |                    |                  | $\Delta E_{\text{ads}}(\text{But})$ on $\text{nH}@\text{Pt}(111)$ |                         |
|-----------------|-------------------------------------------------|-------------------------|--------------------|------------------|-------------------------------------------------------------------|-------------------------|
|                 | <i>trans</i> di- $\sigma$                       | <i>cis</i> di- $\sigma$ | <i>trans</i> $\pi$ | <i>cis</i> $\pi$ | <i>trans</i> di- $\sigma$                                         | <i>cis</i> di- $\sigma$ |
| 0               | -0.94                                           | -0.94                   | -0.57              | -0.67            | -0.94                                                             | -0.94                   |
| 1               | -1.41                                           | -1.39                   | -1.03              | -1.13            | -0.91                                                             | -0.90                   |
| 2               | -1.84                                           | -1.83                   |                    |                  | -0.91                                                             | -0.89                   |
| 3               | -2.24                                           | -2.24                   |                    |                  | -0.86                                                             | -0.86                   |
| 4               | -2.61                                           | -2.61                   |                    |                  | -0.74                                                             | -0.74                   |
| 5               | -2.96                                           | -2.96                   |                    |                  | -0.67                                                             | -0.67                   |
| 6               | -3.26                                           | -3.26                   |                    |                  | -0.56                                                             | -0.57                   |
| 7               | -3.43                                           | -3.44                   | -3.09              | -3.25            | -0.32                                                             | -0.33                   |
| 8               | -3.57                                           | -3.63                   | -3.32              | -3.40            | -0.08                                                             | -0.14                   |
| 9               | -3.44                                           | -3.50                   | -3.59              | -3.63            | 0.26                                                              | 0.22                    |
| 9 (physisorbed) | -3.77                                           | -3.78                   |                    |                  |                                                                   |                         |

**Table S8:** Coadsorption Gibbs free energy ( $\Delta G_{\text{coads}}$ , eV, equation 1) for *cis*- and *trans*-2-butene with  $n$  H atoms on the Pt(111) surface and *cis*- and *trans*-2-butene adsorption Gibbs free energy ( $\Delta G_{\text{ads}}$ , eV, equation 2) on a hydrogen pre-covered Pt(111) surface (with  $n$  H atoms). Only the most stable structures were considered. The calculations were done by using a five-layer slab with a  $5\times 5\times 1$  K-point mesh and the PW91 functional, under high-vacuum pressure ( $10^{-7}$  Torr), at 80K and for a  $P_{\text{H}_2}/P_{\text{butene}}$  ratio of 25. The dipole correction is included.

| n | $\Delta G_{\text{coads}}$ on Pt(111) |            | $\Delta G_{\text{ads}}$ on $\text{nH}@\text{Pt}(111)$ |            |
|---|--------------------------------------|------------|-------------------------------------------------------|------------|
|   | <i>trans</i>                         | <i>cis</i> | <i>trans</i>                                          | <i>cis</i> |
| 1 | -0.97                                | -0.96      | -0.53                                                 | -0.52      |
| 2 | -1.25                                | -1.23      | -0.45                                                 | -0.43      |
| 3 | -1.53                                | -1.52      | -0.39                                                 | -0.39      |
| 4 | -1.81                                | -1.82      | -0.35                                                 | -0.35      |
| 5 | -2.02                                | -2.01      | -0.26                                                 | -0.25      |
| 6 | -2.15                                | -2.16      | -0.12                                                 | -0.13      |
| 7 | -2.16                                | -2.17      | 0.13                                                  | 0.12       |
| 8 | -2.13                                | -2.19      | 0.38                                                  | 0.32       |
| 9 | -2.05                                | -2.09      | 0.65                                                  | 0.61       |

From the results summarized in Tables S7 and S8, it can be seen that the coadsorption energy referred to the free gas-phase butene and hydrogen molecules increases with hydrogen coverage. However, it is also seen that energy already reaches a plateau when eight hydrogen atoms have been coadsorbed. Indeed the final coadsorption energies for the most stable configurations of the two alkenes are almost identical with 8 versus 9 coadsorbed hydrogen atoms once the changes in the preferred adsorption geometry (from di- $\sigma$  to  $\pi$ ) are taken into consideration. In fact, when 9 hydrogen atoms are present on the surface, the 2-butene molecule is only physisorbed.

## 2. PBE-TS

**Table S9:** Coadsorption energies ( $\Delta E_{\text{coads}}(\text{nH+But})$ , eV,  $n=0$  to 9) of *cis*- and *trans*-2-butene coadsorbed with  $n$  H atoms on the Pt(111) surface (equation 1) for the most stable geometries of *cis*- and *trans*-2-butene adsorbed on a hydrogen-precovered Pt(111) surface (equation 2). The calculations were done by using a five-layer slab with a  $5 \times 5 \times 1$  K-point mesh and the PBE-TS functional. The dipole correction is included. The last line corresponds to physisorbed butene. The values for the systems where the H are on-top Pt are given in parentheses.

| n               | $\Delta E_{\text{coads}}(\text{nH+But})$ |                         |
|-----------------|------------------------------------------|-------------------------|
|                 | <i>trans</i> di- $\sigma$                | <i>cis</i> di- $\sigma$ |
| 0               |                                          |                         |
| 1               | -2.28 (-2.29)                            | -2.26 (-2.28)           |
| 2               | -2.76 (-2.81)                            | -2.74 (-2.79)           |
| 3               | -3.22 (-3.30)                            | -3.21 (-3.28)           |
| 4               | -3.67 (-3.70)                            | -3.66 (-3.70)           |
| 5               | -4.06 (-4.07)                            | -4.06 (-4.05)           |
| 6               | -4.39 (-4.38)                            | -4.40 (-4.38)           |
| 7               | -4.59 (-4.66)                            | -4.61 (-4.64)           |
| 8               | -4.76 (-4.83)                            | -4.81 (-4.81)           |
| 9 (physisorbed) | -4.94 (-4.99)                            | -4.91 (-4.97)           |

## 3. OptPBE

**Table S10:** Coadsorption energies ( $\Delta E_{\text{coads}}(\text{nH+But})$ , eV,  $n=0$  to 9) of *cis*- and *trans*-2-butene coadsorbed with  $n$  H atoms on the Pt(111) surface (equation 1) for the most stable geometries of *cis*- and *trans*-2-butene adsorbed on a hydrogen-precovered Pt(111) surface (equation 2). The calculations were done by using a five-layer slab with a  $5 \times 5 \times 1$  K-point mesh and the optPBE functional. The dipole correction is included. For 7, 8 and 9 H, physisorbed butene has also been considered. The values for the systems where the H are on-top Pt are given in parentheses.

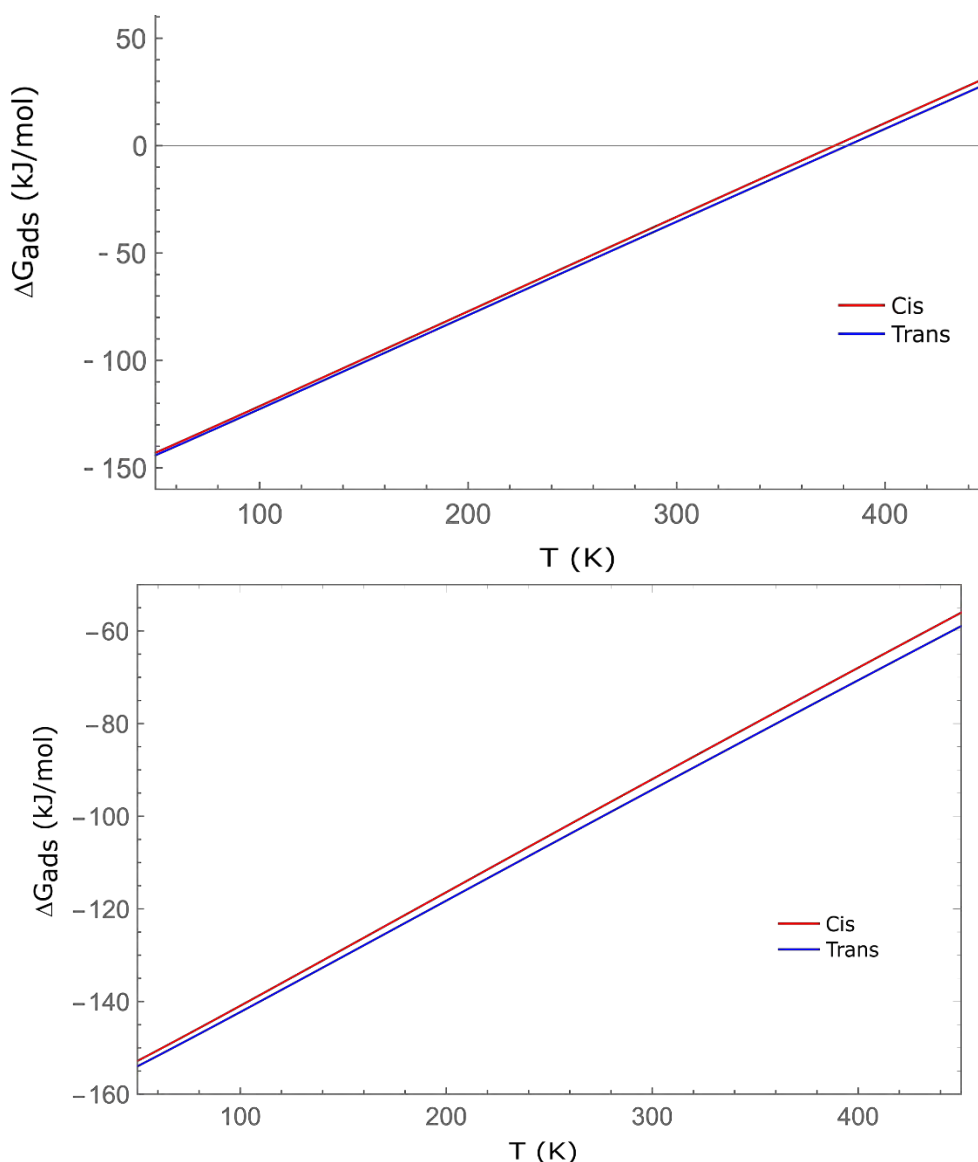
| n               | $\Delta E_{\text{coads}}(\text{nH+But})$ |                         |
|-----------------|------------------------------------------|-------------------------|
|                 | <i>trans</i> di- $\sigma$                | <i>cis</i> di- $\sigma$ |
| 0               | -1.51                                    | -1.50                   |
| 1               | -1.84 (-1.93)                            | -1.82 (-1.92)           |
| 2               | -2.14 (-2.34)                            | -2.11 (-2.32)           |
| 3               | -2.51 (-2.70)                            | -2.38 (-2.75)           |
| 4               | -2.69 (-3.01)                            | -2.69 (-3.01)           |
| 5               | -2.87 (-3.27)                            | -2.86 (-3.25)           |
| 6               | -3.03 (-3.48)                            | -3.04 (-3.47)           |
| 7               | -3.15 (-3.64)                            | -3.13 (-3.62)           |
| 7 (physisorbed) | (-3.32)                                  | (-3.31)                 |
| 8               | -3.10 (-3.67)                            | -3.11 (-3.65)           |
| 8 (physisorbed) | (-3.72)                                  | (-3.65)                 |
| 9 (physisorbed) | -3.16 (-3.96)                            | -3.11 (-3.92)           |



## C. Free energy diagrams

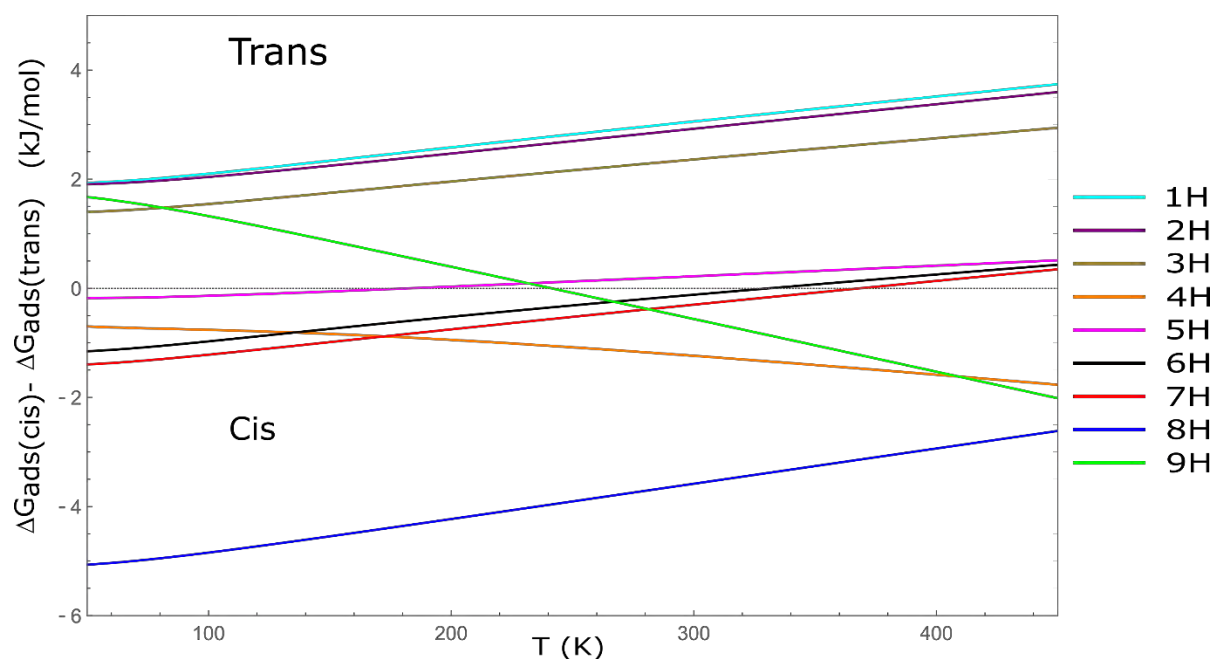
### 1. PBE-TS

The PBE-TS free energy profile for the adsorption of *cis* and *trans* 2-butene on bare Pt(111) are shown Figure S12 for  $P=10^{-7}$  torr and  $P=1$  bar to illustrate the importance of H coverage: on the bare Pt(111) the *trans* conformer is always the more stable isomer.



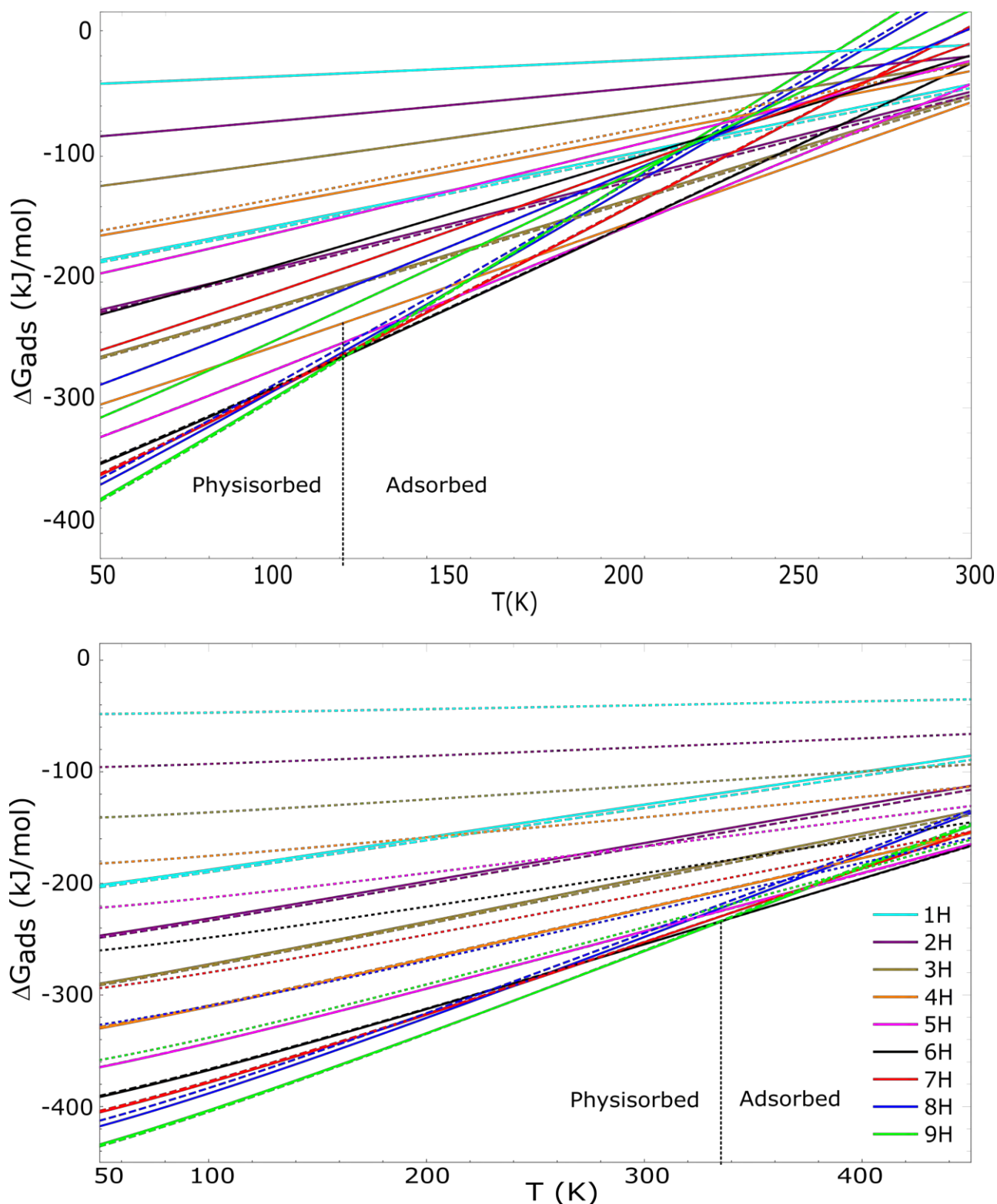
**Figure S12:** PBE-TS Gibbs free adsorption energy diagrams of 2-butene on bare Pt as a function of temperature at a pressure of  $10^{-7}$  Torr with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 25 (top), and at a pressure of 1 bar with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 10 (bottom).

To further confirm the importance of H coverage, the difference of adsorption free energy between the *cis* and *trans* 2-butene isomers is shown on **Figure S13**. A positive value indicates that the *trans* isomer is the most stable, while a negative value indicates that the *cis* isomer is the most stable.

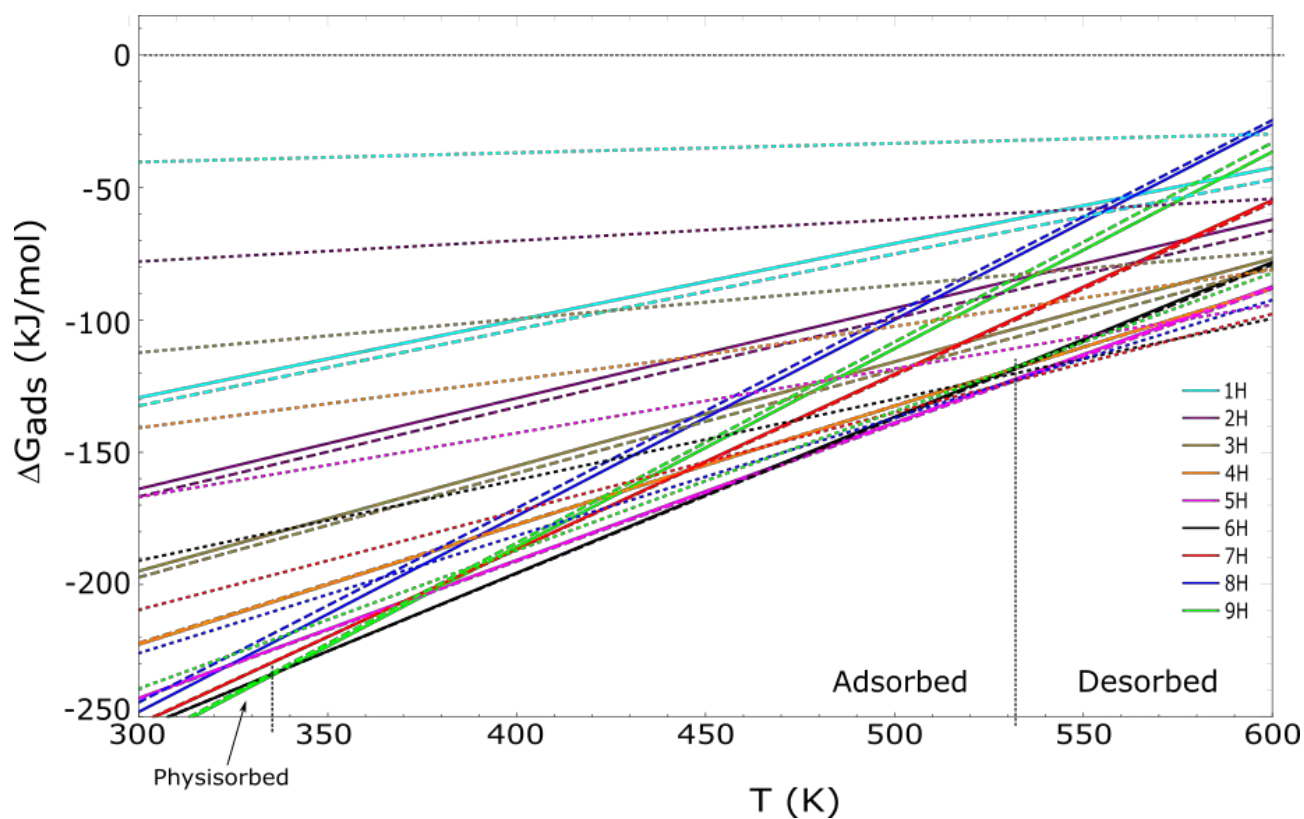


**Figure S13:** Coadsorption free energy difference for the *cis* and *trans* isomers of 2-butene coadsorbed with *n* H atoms as a function of temperature.

The free energy curves for the coadsorption of 2-butene and *n* H atoms evaluated with the PBE-TS functional are shown in **Figure S14** for  $P=10^{-7}$  Torr (top) and  $P=1$  bar (bottom) and in **Figure S15** for  $P=1$  bar and  $T=300$  to  $600$  K to illustrate the desorption of 2-butene, arising for  $T \approx 532$  K. This temperature corresponds to a desorbed *trans* 2-butene with a platinum surface covered by 7 hydrogen atoms.



**Figure S14:** PBE-TS Gibbs free coadsorption energy diagrams of 2-butene coadsorbed with  $n$  H atoms as a function of the temperature at a pressure of  $10^{-7}$  Torr with a constant pressure ratio  $P_{\text{H}_2}/P_{\text{butene}}$  of 25 (top), and at a pressure of 1 bar with a constant pressure ratio  $P_{\text{H}_2}/P_{\text{butene}}$  of 10 (bottom). The solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, dotted lines correspond to the desorbed *trans* isomer.

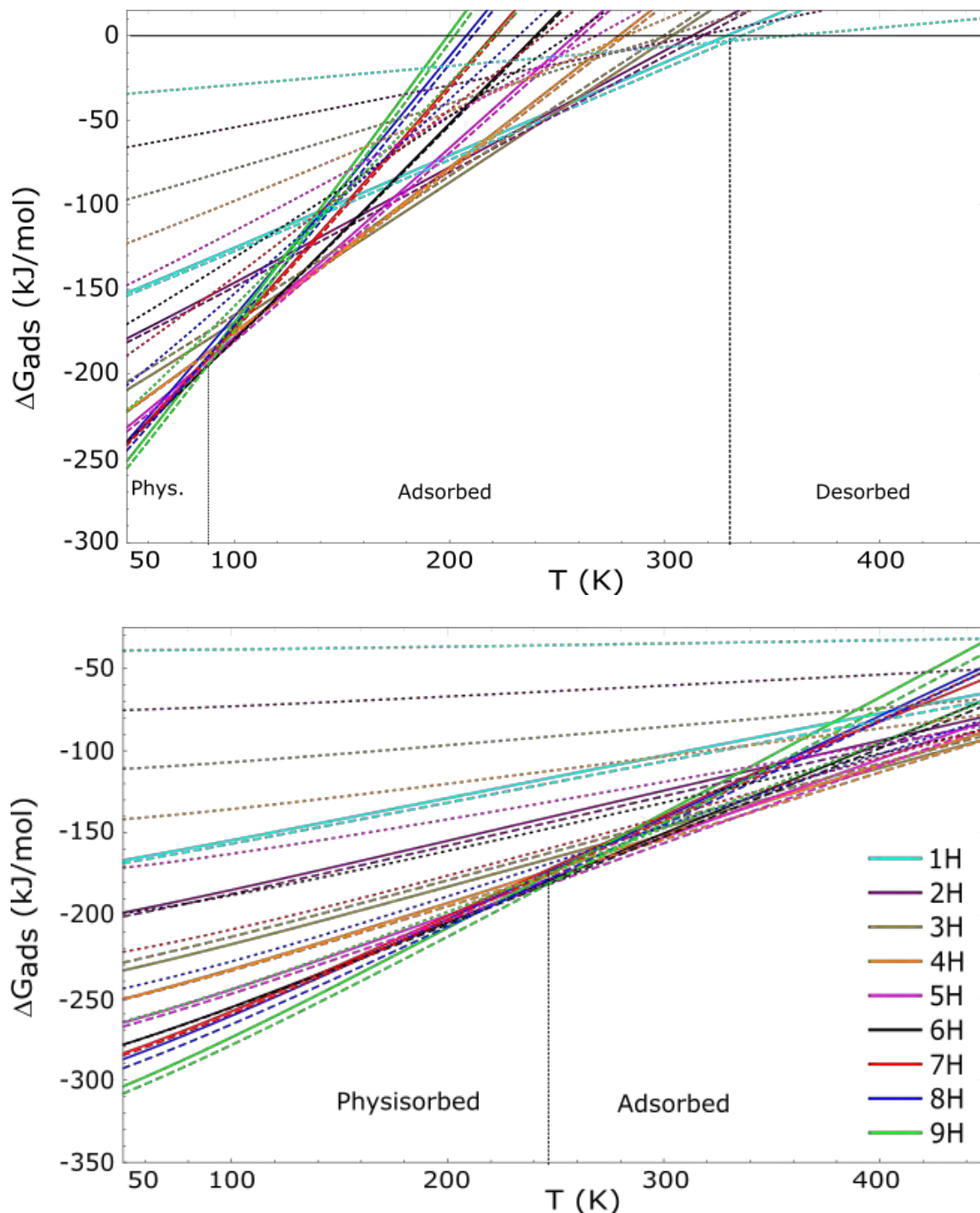


**Figure S15:** Gibbs free coadsorption energy diagrams (with the PBE-TS functional) of 2-butene coadsorbed with  $n$  H atoms as a function of the temperature, at a pressure of 1 bar with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 10 for  $T=300$  to  $600$  K. Solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, dotted lines correspond to the desorbed *trans* isomer.

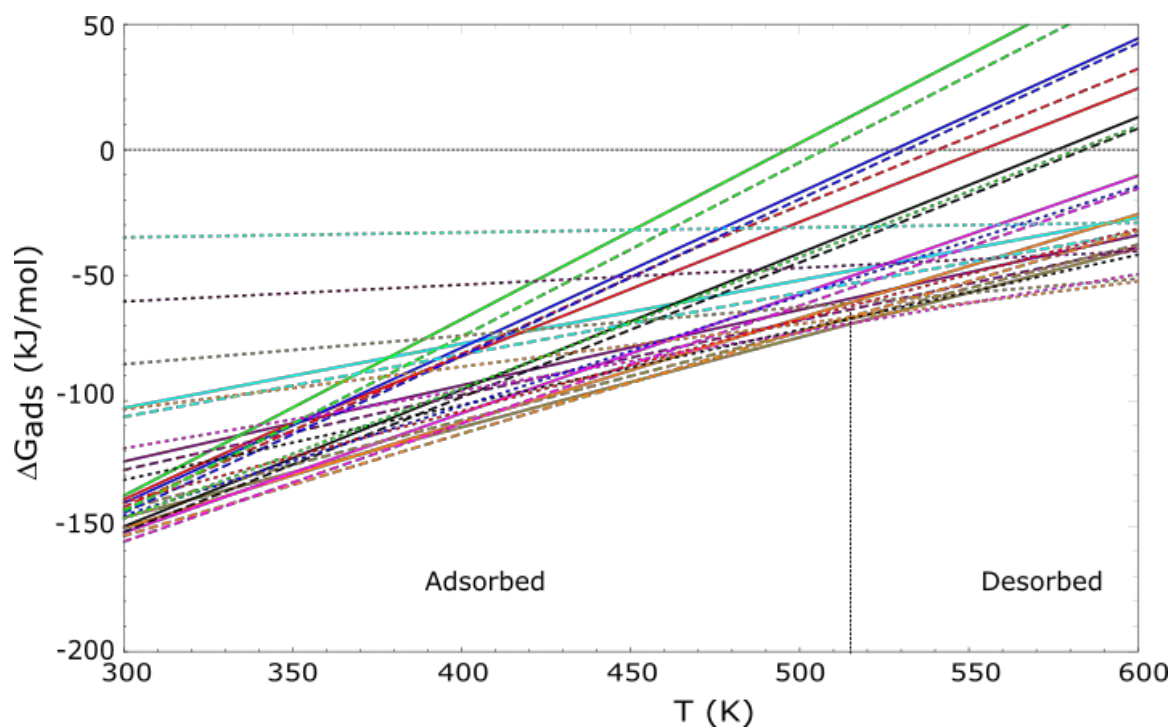
## 2. optPBE

The free energy curves for the coadsorption of 2-butene and  $n$  H atoms evaluated with the optPBE functional are shown

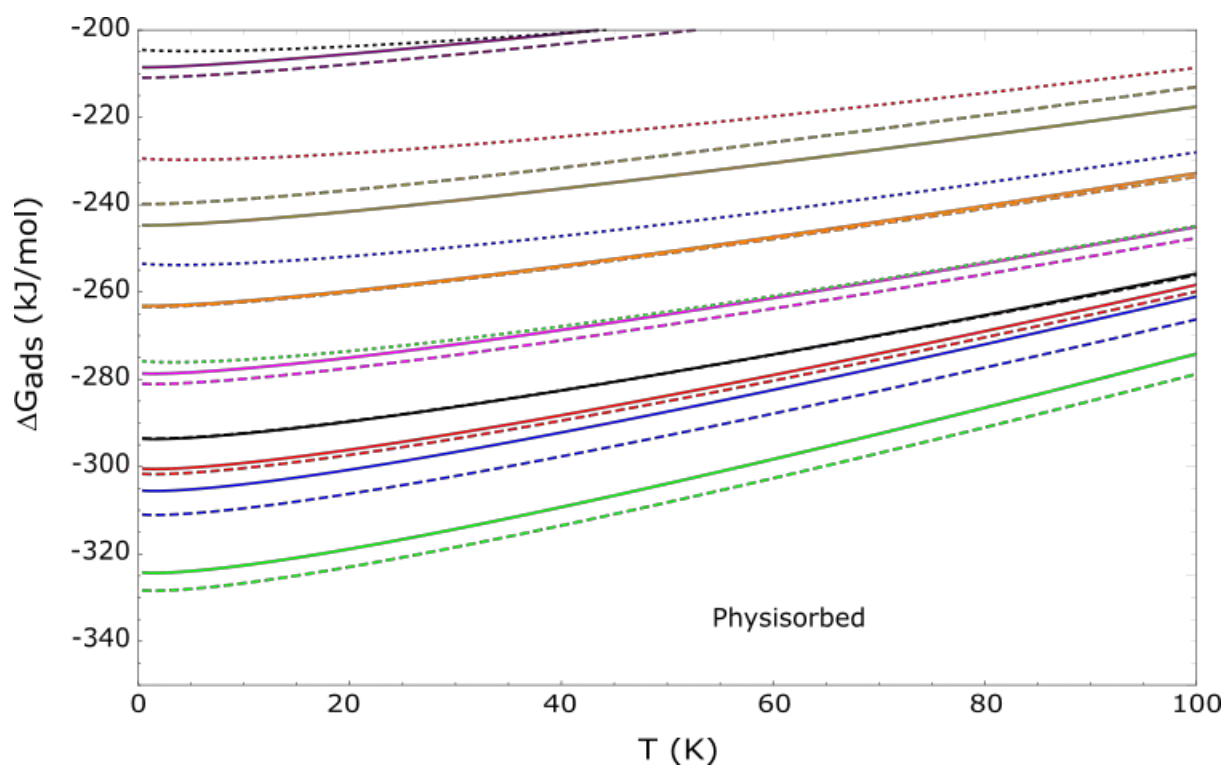
**Figure S16** for  $T=50$  to  $450$  K. The desorption of 2-butene arises for  $T \approx 315$  K at  $P=1$  bar and is shown on **Figure S17**. The non linear evolution of the Gibbs free energy at low temperatures (below  $50$  K) is shown on **Figure S18**.



**Figure S16:** Gibbs free coadsorption energy diagrams (with the optPBE functional) of 2-butene coadsorbed with  $n$  H atoms as a function of the temperature, at a pressure of  $10^{-7}$  Torr with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 25 (top), and at a pressure of 1 bar with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 10 (bottom). Solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, dotted lines correspond to the desorbed *trans* isomer.



**Figure S17:** Gibbs free coadsorption energy diagrams (with the optPBE functional) of 2-butene coadsorbed with  $n$  H atoms as a function of the temperature, at a pressure of 1 bar with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 10 for  $T=300$  to 600K. Solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, dotted lines correspond to the desorbed *trans* isomer.

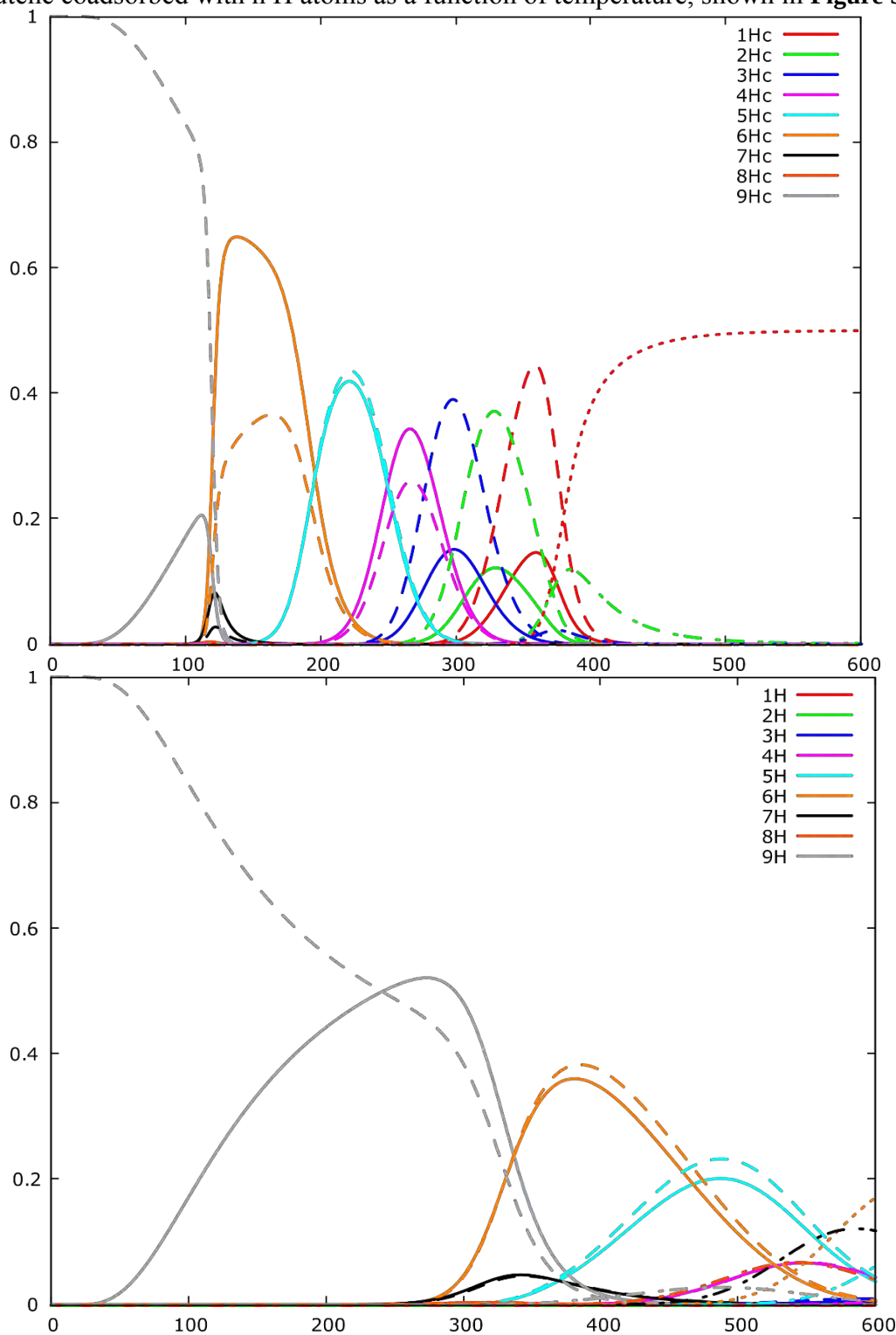


**Figure S18:** Gibbs free coadsorption energy diagrams (with the optPBE functional) of 2-butene coadsorbed with  $n$  H atoms as a function of the temperature, at a pressure of 1 bar with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 10 for  $T=0$  to 100K. Solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, dotted lines correspond to the desorbed *trans* isomer.



### D. Isomer proportion

In order to give a detailed view of the surface state, we also computed the proportion of the *cis* and *trans* 2-butene coadsorbed with  $n$  H atoms as a function of temperature, shown in **Figure S19**.



**Figure S19:** Proportion of the *cis* and *trans* 2-butene coadsorbed with  $n$  H atoms as a function of temperature at a pressure of  $10^{-7}$  Torr with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 25 (top), and at a pressure of 1 bar with a constant pressure ratio  $P_{H_2}/P_{butene}$  of 10 (bottom). The solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, and dotted lines to the desorbed *trans* isomer.

## E. References

- 1) Li, J.; Fleurat-Lessard, P.; Delbecq, F. Mechanistic investigation of the cis/trans isomerization of 2-butene on Pt(1 1 1): DFT study of the influence of the hydrogen coverage *J. Catal.* **2014**, *311*, 190-198.
- 2) a) Cassuto, A.; Mane, M.; Hugenschmidt, M.; Dolle, P.; Jupille, J. The effect of K, Cs and O atoms on ethylene adsorption on the Pt(111) surface *Surf. Sci.* **1990**, *237*, 63-71; b) Kubota, J.; Ohtani, T.; Kondo, J. N.; Hirose, C.; Domen, K. IRAS study of  $\pi$ -bonded ethylene on a Pt(111) surface in the presence of gaseous ethylene and hydrogen *Appl. Surf. Sci.* **1997**, *121/122*, 548-541; c) Yin, J.; Trenary, M.; Meyer, R. Site Switching from Di- $\sigma$  Ethylene to  $\pi$ -Bonded Ethylene in the Presence of Coadsorbed Nitrogen on Pt(111) *J. Phys. Chem. C* **2010**, *114*, 12230-12233.