

Supporting Information

The Role of Modifier Structure in Heterogeneous Enantioselective Hydrogenation: One-to-one Interactions of 1-Phenyl-1,2-propanedione and Methyl Pyruvate with Modifiers on the Pt(111) Surface

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A more detailed analysis of the geometries and energies of the 1-phenyl-1,2-propanedione–modifier and methyl pyruvate–modifier complexes considered in this study is presented here. Justification for the use of $S = 3$ for the Pt_{38} cluster is provided in Section 4. Please note this document has its own list of references.

1. DFT calculations on isolated 1-phenyl-1,2-propanedione–modifier and methyl pyruvate–modifier complexes

When interacting with a modifier, 1-phenyl-1,2-propanedione (PPD) can adopt either one of the two possible conformations depending on whether the torsion angle of the $\text{O}=\text{C}-\text{C}=\text{O}$ moiety, $\text{D}(\text{O}=\text{C}-\text{C}=\text{O})$, gets a negative or a positive value. The complexation energy and the stabilization of the keto carbonyl π and π^* orbitals may depend on the conformation of PPD. The values in parentheses in Tables S2 and S4 refer to the less stable complexes. Only the most stable complexes have been discussed in this paper. Figures 3 and 4 and Table S2 show that in every DFT optimized complex, PPD adopts an *s-cis* like conformation with $\text{D}(\text{O}=\text{C}-\text{C}=\text{O})$ varying between -74 and $+70^\circ$. On the contrary, isolated PPD adopts an *s-trans* type of conformation [$\text{D}(\text{O}=\text{C}-\text{C}=\text{O}) = -140$ or $+140^\circ$] calculated at the same level of theory (B3LYP/T(ON)DZP).

Deviation from planarity is most notable in the cyclic pro-(*R*) and pro-(*S*) complexes (Table S2).

Figures S3 and S4 show that in every DFT optimized complex between methyl pyruvate (MP) and a modifier, MP is almost planar and adopts an *s-cis* conformation [i.e., $D(O=C-C=O) \approx 0^\circ$]. On the contrary, isolated MP adopts an *s-trans* conformation [i.e., $D(O=C-C=O) \approx 180^\circ$]. Deviation from planarity is most notable in the cyclic pro-(*R*) and pro-(*S*) complexes where protonated cinchonidine (CdH^+) adopts the Open(5) conformation (Table S3).

1.1. Bifurcated PPD–modifier complexes. Substitution of the C(9) hydroxyl group with a methoxy group in the Open(3) conformation of CdH^+ does not have any notable effect on the geometries of the bifurcated PPD–modifier complexes (Figures 3 and 4 and Table S2); the hydrogen bond distances between PPD’s carbonyl oxygens and the proton attached to the modifier’s quinuclidine nitrogen are 189–257 pm in the PPD– CdH^+ (Open3) complexes and 188–261 pm in the PPD– $MeOCdH^+$ (Open3) complexes ($MeOCd$ = 9-methoxycinchonidine). The complexation energies are also almost equal, varying between -72 and -75 kJ mol^{-1} , irrespective of the modifier (Table S4). This is reasonable since the C(9) position of the Open(3) conformation is far from the region where the intermolecular interaction takes place. The bifurcated pro-(*R*) complex is more stable than the bifurcated pro-(*S*) complex by 0.9 and 2.4 kJ mol^{-1} in the case of CdH^+ and $MeOCdH^+$, respectively. Interestingly, the relative stabilization of the keto carbonyl orbitals of PPD depends considerably on the modifier. The orbitals are 52 kJ mol^{-1} more stabilized in the pro-(*R*) than in the pro-(*S*) complex when the modifier is CdH^+ but this stability difference reduces to 6 kJ mol^{-1} when the modifier is $MeOCdH^+$. Qualitatively similar results as reported here were found for PPD– CdH^+ (Open3) complexes in our previous calculations at the HF/6-31G* level.¹

The Open(5) conformation of CdH^+ and $MeOCdH^+$ forms 14–16 kJ mol^{-1} less stable bifurcated complexes with PPD than the Open(3) conformation; the complexation energies are around -57 kJ mol^{-1} for the PPD– CdH^+ (Open5) complexes and ca -52 kJ mol^{-1} for the PPD– $MeOCdH^+$ (Open5) complexes (Table S4). Consequently, the intermolecular interaction becomes weaker by 5 kJ mol^{-1} when the C(9) hydroxyl group of CdH^+ is replaced with a methoxy group, probably due to increasing repulsive steric

interactions between the reactant and the modifier. Therefore, the functional group at the C(9) position of the modifier has more effect on the strength of the bifurcated PPD–modifier interaction if the modifier adopts the Open(5) rather than the Open(3) conformation. The hydrogen bond distances between PPD’s carbonyl oxygens and the proton attached to the modifier’s quinuclidine nitrogen are 182–297 pm in the PPD–CdH⁺(Open5) complexes and 193–279 pm in the PPD–MeOCdH⁺(Open5) complexes (Table S2). The bifurcated pro-(*S*) PPD–modifier(Open5) complexes are 0–1 kJ mol^{−1} more stable than the corresponding pro-(*R*) complexes and PPD’s keto carbonyl orbitals lie 0–7 kJ mol^{−1} lower in energy in the pro-(*S*) complexes (Table S4). The stabilization of PPD’s keto carbonyl orbitals depends substantially on the modifier’s conformation; the orbitals are up to 130 kJ mol^{−1} less stable in the PPD–modifier(Open5) complex than in the corresponding PPD–modifier(Open3) complex.

1.2. Bifurcated MP–modifier complexes. Substitution of the C(9) hydroxyl group with a methoxy group in the Open(3) conformation of CdH⁺ does not have any notable effect on the geometries of the bifurcated MP–modifier complexes as can be seen from Figures S3 and S4 and Table S3. For example, the hydrogen bond distances between MP’s carbonyl oxygens and the proton attached to the modifier’s quinuclidine nitrogen are 195–252 pm in the MP–CdH⁺ complexes and 194–255 pm in the MP–MeOCdH⁺ complexes. The complexation energies are almost equal, varying between −85 and −87 kJ mol^{−1} irrespective of the modifier (Table S5). This is reasonable since the C(9) position of the Open(3) conformation is far from the region where intermolecular interactions take place. The bifurcated pro-(*R*) complexes are more stable than the bifurcated pro-(*S*) complexes by ca 1 kJ mol^{−1} and the keto carbonyl orbitals of MP are 32–33 kJ mol^{−1} more stable in the pro-(*R*) complexes. Qualitatively similar results were found for MP–CdH⁺(Open3) complexes in our previous calculations at the HF/6-31G* level.²

The Open(5) conformation of CdH⁺ and MeOCdH⁺ forms 14–17 kJ mol^{−1} less stable bifurcated complexes with MP than the Open(3) conformation; the complexation energies are between −67 and −68 kJ mol^{−1} for the MP–CdH⁺(Open5) complexes and ca −65 kJ mol^{−1} for the MP–MeOCdH⁺(Open5) complexes. The intermolecular interaction becomes ca 3 kJ mol^{−1} weaker when the C(9) hydroxyl group of CdH⁺ is replaced with a

methoxy group, probably due to increasing repulsive steric interactions between the reactant and the modifier. Thus, the functional group at the modifier's C(9) position has more effect on the strength of the bifurcated MP–modifier interaction if the modifier adopts the Open(5) rather than the Open(3) conformation. The hydrogen bond distances between MP's carbonyl oxygens and the proton attached to the modifier's quinuclidine nitrogen are 203–248 pm in the MP–CdH⁺(Open5) complexes and 211–243 pm in the MP–MeOCdH⁺(Open5) complexes. The pro-(*S*) complexes are slightly (< 1 kJ mol^{−1}) more stable than the corresponding pro-(*R*) complexes and MP's keto carbonyl orbitals lie 12–21 kJ mol^{−1} lower in energy in the pro-(*S*) complexes. The stabilization of MP's keto carbonyl orbitals depends substantially on the conformation of the modifier; the orbitals are up to 114 kJ mol^{−1} less stable in the MP–modifier(Open5) complex than in the corresponding MP–modifier(Open3) complex.

1.3. Cyclic PPD–modifier complexes. Cyclic complexes can exist between PPD and the CdH⁺ modifier (Figure 3). When CdH⁺ adopts the Open(3) conformation, the distance between the proton attached to Cd's quinuclidine N and PPD's carbonyl oxygen closer to that proton is 184–186 pm, that is, slightly shorter than the distance between PPD's other carbonyl oxygen and the hydrogen of the C(9) hydroxyl group (201–202 pm, Table S2). In contrast, when CdH⁺ adopts the Open(5) conformation, the C=O[⋯]⁺HN distances are longer (207–212 pm) than the C=O[⋯]HO distances (180–184 pm).

The complexation energies are around −76 kJ mol^{−1} for the PPD–CdH⁺(Open3) complexes and between −62 and −64 kJ mol^{−1} for the PPD–CdH⁺(Open5) complexes (Table S4). Thus, the cyclic complexes are 0–7 kJ mol^{−1} more stable than the corresponding bifurcated complexes. In addition, the keto carbonyl orbitals of PPD are generally more stabilized in the cyclic than in the bifurcated PPD–CdH⁺ complexes (Table S4). If CdH⁺ adopts the Open(3) conformation, the cyclic pro-(*S*) complex is thermodynamically slightly more stable than the cyclic pro-(*R*) complex but the keto carbonyl orbitals are 28 kJ mol^{−1} more stabilized in the latter complex. In contrast, if CdH⁺ adopts the Open(5) conformation, the cyclic pro-(*R*) complex is thermodynamically preferred over cyclic pro-(*S*) but the keto carbonyl orbitals are 5 kJ mol^{−1} more stabilized in the latter complex.

1.4. Cyclic MP–modifier complexes. Cyclic complexes can exist between MP and CdH^+ (Figure S3). When CdH^+ adopts the Open(3) conformation, the distance between the proton attached to Cd's quinuclidine nitrogen and MP's carbonyl oxygen closer to that proton is 187–188 pm, that is, shorter than the distance between MP's other carbonyl oxygen and the hydrogen of the C(9) hydroxyl group (205–234 pm, Table S3). In contrast, when CdH^+ adopts the Open(5) conformation, the $\text{C}=\text{O}\cdots^+\text{HN}$ distances are longer (210–214 pm) than the $\text{C}=\text{O}\cdots\text{HO}$ distances (184 pm).

The complexation energies are around $-80.5 \text{ kJ mol}^{-1}$ for the cyclic MP– $\text{CdH}^+(\text{Open3})$ complexes and between -65 and -68 kJ mol^{-1} for the cyclic MP– $\text{CdH}^+(\text{Open5})$ complexes (Table S5). Thus, the cyclic complexes are 0–6 kJ mol^{-1} less stable than the corresponding bifurcated complexes. Interestingly, MP's keto carbonyl orbitals are generally more stabilized in the cyclic than in the corresponding bifurcated complexes (Table S5). As CdH^+ adopts the Open(3) conformation, the cyclic pro-(*S*) complex is thermodynamically as stable as the corresponding pro-(*R*) complex but MP's keto carbonyl orbitals are notably (by 41 kJ mol^{-1}) more stabilized in the pro-(*R*) complex. As CdH^+ adopts the Open(5) conformation, the cyclic pro-(*S*) complex is more stable than the cyclic pro-(*R*) complex by 2.4 kJ mol^{-1} and the keto carbonyl orbitals are 9 kJ mol^{-1} more stabilized in the pro-(*S*) complex.

2. MM calculations on isolated 1-phenyl-1,2-propanedione–modifier and methyl pyruvate–modifier complexes

2.1. PPD–modifier complexes. Generally, the force field optimized intermolecular distances of the isolated PPD–modifier complexes are fairly close to those obtained at the DFT level (Table S2). The most striking deviation from the DFT optimized geometries is that according to the MM calculations the $\text{O}=\text{C}-\text{C}=\text{O}$ moiety of PPD is essentially planar in the complexes.

The complexes where CdH^+ and MeOCdH^+ adopt the Open(5) conformation are $15\text{--}26 \text{ kJ mol}^{-1}$ less stable than the corresponding PPD–modifier(Open3) complexes (Table S4). These results are in quite good agreement with the results from the DFT calculations. The cyclic PPD– CdH^+ complexes are more stable than the corresponding bifurcated ones by $18\text{--}28 \text{ kJ mol}^{-1}$. Thus, the MM calculations overestimate the stability

difference between the cyclic and bifurcated complexes compared to the DFT results. The MM calculations give the same order for the relative stability of the corresponding pro-(*R*) and pro-(*S*) complexes as DFT except for the bifurcated PPD–CdH⁺(Open5) and bifurcated PPD–MeOCdH⁺(Open3) complexes. For example, according to the MM calculations the bifurcated pro-(*R*) PPD–MeOCdH⁺(Open3) complex has 6 kJ mol^{−1} higher energy than the corresponding pro-(*S*) complex but the DFT calculations predict that the pro-(*S*) complex is less stable than the pro-(*R*) complex.

2.2. MP–modifier complexes. Generally, the force field optimized structures of the isolated MP–CdH⁺ complexes are quite close to those obtained at the DFT level; the hydrogen bond distances in the MP–CdH⁺ complexes seem to vary randomly from the corresponding DFT values (Table S3). The geometries of the MP–MeOCdH⁺ complexes deviate more; the DFT calculations predict clear bifurcated hydrogen-bonded complexes with both C=O⋯⁺HN distances of 194–255 pm while according to the MM calculations, one C=O⋯⁺HN distance is 202–223 pm and the other 314–408 pm (Table S3).

The complexes where CdH⁺ and MeOCdH⁺ adopt the Open(5) conformation are 10–23 kJ mol^{−1} less stable than the corresponding MP–modifier(Open3) complexes (Table S5). If the modifiers adopt the Open(3) conformation, the pro-(*R*) complexes are 3–5 kJ mol^{−1} more stable than the corresponding pro-(*S*) complexes. The pro-(*S*) complexes are thermodynamically preferred over the pro-(*R*) complexes by 4–7 kJ mol^{−1} if the modifiers adopt the Open(5) conformation except in the case of cyclic MP–CdH⁺(Open5) complexes where the pro-(*R*) complex is 2 kJ mol^{−1} more stable than the pro-(*S*) complex. These results are in agreement with the results from the DFT calculations. However, contrary to the DFT calculations the MM calculations indicate that the cyclic MP–CdH⁺ complexes are more stable than the bifurcated ones (by ca 20–30 kJ mol^{−1}). One possible reason for the slight disagreements between the MM and DFT results may originate from the fact that weak intermolecular interactions due to dispersion (van der Waals type interactions) are inappropriately described by DFT^{3–5} but more properly by force fields (see, e.g., ref. 6 and references therein). On the other hand, the hydrogen bonding interactions under study are strong and hydrogen bonding is mainly electrostatic, which is reasonably well accounted for by DFT.⁴ It should be

noted that today there exist approaches to improving DFT for dispersion interactions.⁷ Despite the fact that MM and DFT do not give exactly the same relative energies for various complexes, the important observation is that all DFT optimized structures are also stable at the MM level.

3. MM calculations on 1-phenyl-1,2-propanedione–modifier and methyl pyruvate–modifier complexes on the Pt(111) surface

The MM calculations suggest that PPD, MP, CdH^+ , and MeOCdH^+ adsorb parallel to the Pt(111) surface (i.e., flat adsorption, Figures 5, 6, S5, and S6). According to the DFT calculations^{8–11}, the hybridization of the carbon atoms in the carbonyl, phenyl and quinoline moieties changes from sp^2 towards sp^3 upon adsorption parallel to the Pt(111) surface (see also Figure 2). On the contrary, MM methods cannot model rehybridization and, consequently, PPD’s phenyl ring, the $\text{O}=\text{C}-\text{C}=\text{O}$ moiety of both reactants, and the modifiers’ quinoline ring remain essentially planar on the surface.

3.1. Bifurcated PPD–modifier complexes. Substitution of the C(9) hydroxyl group of $\text{CdH}^+(\text{Open3})$ with a methoxy group has a notable effect on the geometry of the modifier on Pt(111), since the steric interaction between the bulkier methoxy group and the surface causes rotation of the quinuclidine moiety around the $\text{C}(4')-\text{C}(9)$ bond (Figure 1). As a result, the quinuclidine $\text{N}-\text{H}^+$ bond in $\text{MeOCdH}^+(\text{Open3})$ points almost perpendicular to the surface (Figure 6) and, therefore, the NH^+ moiety is more shielded and less capable of forming hydrogen bonds with PPD. This is seen in the $\text{C}=\text{O}\cdots^+\text{HN}$ distances of the bifurcated complexes (Table S2): in the $\text{PPD}-\text{CdH}^+(\text{Open3})$ complexes, these distances are 194–357 pm, but in the $\text{PPD}-\text{MeOCdH}^+(\text{Open3})$ complexes, the distances are much longer, 375–438 pm.

The $\text{C}=\text{O}\cdots^+\text{HN}$ distances are 280–316 pm in the bifurcated $\text{PPD}-\text{CdH}^+(\text{Open5})$ complexes and 333–406 pm in the bifurcated $\text{PPD}-\text{MeOCdH}^+(\text{Open5})$ complexes. Also other kinds of $\text{PPD}-\text{MeOCdH}^+(\text{Open5})$ complexes on the Pt(111) surface than shown in Figure 6 could be realized. However, assuming that the $\text{C}=\text{O}\cdots^+\text{HN}$ interaction is essential for the enantiodifferentiation, these complexes cannot be relevant species in the enantioselective hydrogenation since the $\text{N}-\text{H}^+$ bond of the modifier’s quinuclidine

moiety points upwards (i.e., away from the surface) in these structures, thus not being capable of interacting with PPD adsorbed on the surface.

On the Pt(111) surface, the bifurcated complexes where CdH^+ and MeOCdH^+ adopt the Open(3) conformation are more stable than the corresponding PPD–modifier(Open5) complexes by 107–118 kJ mol^{-1} (Table S4). For the isolated complexes this difference in stability is substantially smaller, 15–26 kJ mol^{-1} , by the MM calculations. The notable effect of the surface on the relative stabilities of the aforementioned complexes is correlated with the relative stabilities of the Open(3) and Open(5) conformations of CdH^+ and MeOCdH^+ ; the Open(3) conformation is 83–86 kJ mol^{-1} more stable than the Open(5) conformation on the Pt(111) surface but without the effect of the surface the energy difference between these conformations reduces to 19–27 kJ mol^{-1} (Table S1).

The bifurcated pro-(*S*) complexes are 4–10 kJ mol^{-1} more stable than the bifurcated pro-(*R*) complexes if the modifiers adopt the Open(3) conformation. On the contrary, the pro-(*S*) complexes are 1–3 kJ mol^{-1} less stable than the pro-(*R*) complexes if the modifiers adopt the Open(5) conformation.

3.2. Bifurcated MP–modifier complexes. As noted above, substitution of the C(9) hydroxyl group of CdH^+ (Open3) with a methoxy group has a notable effect on the geometry of the modifier on the Pt surface: the NH^+ moiety of MeOCdH^+ (Open3) is more shielded and thus less capable of forming hydrogen bonds with MP. This is seen in the $\text{C}=\text{O}\cdots^+\text{HN}$ distances of the bifurcated complexes (Table S3): in the MP– CdH^+ (Open3) complexes, these distances are 197–367 pm, but in the MP– MeOCdH^+ (Open3) complexes the distances are much longer, 393–455 pm.

The proton attached to the modifiers' quinuclidine nitrogen can get closer to MP's carbonyl oxygens if the modifiers adopt the Open(5) conformation rather than the Open(3) conformation. This is indicated by slightly shorter $\text{C}=\text{O}\cdots^+\text{HN}$ distances on average, which are 278–328 pm in the MP– CdH^+ (Open5) complexes and 352–435 pm in the MP– MeOCdH^+ (Open5) complexes (Table S3). Also other kinds of MP– MeOCdH^+ (Open5) complexes on the Pt(111) surface than shown in Figure S6 could be realized. However, as explained in Section 3.1., these complexes cannot be relevant species in the enantioselective hydrogenation.

On the Pt(111) surface, the bifurcated complexes where CdH^+ and MeOCdH^+ adopt the Open(3) conformation are 97–120 kJ mol^{-1} more stable than the corresponding MP–modifier(Open5) complexes (Table S5). Without the impact of the surface this difference in stability is substantially smaller, 10–23 kJ mol^{-1} , by the MM calculations. The surface has therefore a significant effect on the relative stabilities of the complexes. The bifurcated pro-(*R*) complexes are 9–10 kJ mol^{-1} more stable than the bifurcated pro-(*S*) complexes if the modifiers adopt the Open(3) conformation. On the contrary, the pro-(*R*) complexes are 4 kJ mol^{-1} less stable than the pro-(*S*) complexes as the modifiers adopt the Open(5) conformation. These results are in qualitative agreement with the DFT results on isolated complexes.

3.3. Cyclic PPD–modifier complexes. Considering now the geometries of the cyclic complexes, it is first noticed that the cyclic hydrogen-bonded PPD– CdH^+ (Open3) complexes are unstable on the Pt(111) surface due to the steric constraints. Instead, the Open5 conformation of CdH^+ can form certain kinds of hydrogen-bonded cyclic complexes with PPD on the surface (Figure 5). In these complexes, the $\text{C}=\text{O}\cdots\text{HO}-\text{C}(9)$ and $\text{C}=\text{O}\cdots^+\text{HN}$ distances are 220–322 and 263–299 pm, respectively. The cyclic PPD– CdH^+ (Open5) complexes are 78–92 kJ mol^{-1} less stable than the bifurcated PPD– CdH^+ (Open3) complexes but ca 30 kJ mol^{-1} more stable than the bifurcated PPD– CdH^+ (Open5) complexes (Table S4).

3.4. Cyclic MP–modifier complexes. The cyclic hydrogen-bonded MP– CdH^+ (Open3) complexes are not stable on the Pt(111) surface. Instead, the Open(5) conformation of CdH^+ can form certain kinds of cyclic complexes with MP on the surface (Figure S5). In these complexes, both carbonyl oxygens of MP are closer to the modifier’s hydroxyl group hydrogen than the proton attached to the quinuclidine nitrogen: the $\text{C}=\text{O}\cdots\text{HO}-\text{C}(9)$ distances are 186–294 pm while the $\text{C}=\text{O}\cdots^+\text{HN}$ distances are 316–341 pm. Thus, MP interacts via a bifurcated hydrogen bond with the modifier’s OH group. The cyclic MP– CdH^+ (Open5) are 70–80 kJ mol^{-1} less stable than the bifurcated Open(3) complexes but ca 40 kJ mol^{-1} more stable than the bifurcated MP– CdH^+ (Open5) complexes (Table S5).

3.5. Novel PPD–modifier complexes. In addition to the reactant–modifier interaction geometries studied so far, complexes where the modifiers adopt so-called Quinuclidine Adsorbed-Open (QA-Open) conformations were found. The QA-Open conformations are adsorbed on the surface via their quinoline ring and the quinuclidine moiety including the C(10)=C(11) double bond (Figures 5 and 6). The QA-Open(3) and QA-Open(4) conformations can be generated from the adsorbed Open(3) and Open(4) conformations, respectively, by rotating around the C(4')–C(9) bond (Figure 1). Isolated PPD–modifier(QA-Open) complexes are not stable according to the MM and DFT calculations. Instead, the MM calculations show that they are very stable on the Pt(111) surface (Table S4).

In the PPD–CdH⁺(QA-Open) complexes, there is a bifurcated hydrogen bond between PPD's carbonyl oxygens and the modifier's quinuclidine NH⁺. One of the carbonyl oxygens of PPD is also close to the C(9)-OH hydrogen of CdH⁺. In the PPD–CdH⁺(QA-Open3) complexes the C=O[⋯]⁺HN and C=O[⋯]HO distances are 224–266 and 219–236 pm, respectively. In the PPD–CdH⁺(QA-Open4) complexes these distances are slightly longer, 275–342 and 238–321 pm, respectively. The PPD–CdH⁺(QA-Open4) complexes are the most stable complexes on Pt(111) while the PPD–CdH⁺(QA-Open3) and PPD–CdH⁺(Open3) complexes are less stable by ca 30 and 80 kJ mol^{−1}, respectively.

Substitution of the OH group of CdH⁺ with OMe increases the C=O[⋯]⁺HN distances in the PPD–modifier complexes by a few dozens of picometers to 284–366 pm (Table S2). The aforementioned substitution has also a notable effect on the relative stabilities of the complexes. The PPD–MeOCdH⁺(QA-Open4) complexes are the most stable whereas the complexes with MeOCdH⁺ adopting the QA-Open(3) and Open(3) conformation are less stable by ca 20 kJ mol^{−1} (Table S4). The pro-(*R*) PPD–modifier(QA-Open) complexes are 2–6 kJ mol^{−1} more stable than the corresponding pro-(*S*) complexes except in the case of PPD–CdH⁺(QA-Open4) complexes where pro-(*S*) is 6 kJ mol^{−1} more stable than pro-(*R*).

3.6. Novel MP–modifier complexes. Similar novel complexes as described above were also found to exist between MP and the modifiers studied. In the MP–CdH⁺(QA-Open3) complexes the C=O[⋯]⁺HN and C=O[⋯]HO distances are 234–283 and

219–243 pm, respectively (Table S3). In the MP–CdH⁺(QA-Open4) complexes these distances are 39–61 and 87 pm longer, respectively. The MP–CdH⁺(QA-Open4) complexes are ca 40 kJ mol^{−1} more stable than the MP–CdH⁺(QA-Open3) complexes, which in turn are 39–48 kJ mol^{−1} more stable than the MP–CdH⁺(Open3) complexes on the Pt(111) surface (Table S5).

Substitution of the OH group of CdH⁺ with OMe increases the C=O...⁺HN distances in the complexes by a few dozens of picometers to 294–377 pm (Table S3). The aforementioned substitution has also an effect on the relative stabilities of the complexes (Table S5). The MP–MeOCdH⁺(QA-Open4) complexes are the most stable ones while the complexes where MeOCdH⁺ adopts the QA-Open(3) and Open(3) conformation are less stable by 23–36 kJ mol^{−1}. The pro-(*S*) MP–modifier(QA-Open) complexes are 0–5 kJ mol^{−1} more stable than the corresponding pro-(*R*) complexes.

The C(10)=C(11) vinyl moiety of the modifiers is saturated to C(10)–C(11) ethyl moiety during the hydrogenation reaction.^{12–14} The MM calculations suggest that this does not have a large effect on the adsorption geometries (the saturated C(10)–C(11) moiety stays adsorbed on the Pt(111) surface) or the relative energies of various complexes. This result implies that using dihydro-modifiers (i.e., modifiers with a saturated vinyl moiety) instead of Cd and MeOCd does not alter the catalytic behaviour, thus being in line with experiments.¹⁵

4. Justification for the use of $S = 3$ for the Pt₃₈ cluster

A net spin S around 10 was reported by Jacob et al.¹⁶ for the Pt_{9,10,9} and Pt_{12,12,12} clusters. However, these were three-layer clusters with the distance between the Pt atoms fixed to 277.5 pm, that is, rigid clusters. According to Vargas et al.¹⁷, the minimum energy spin state of a two-layer rigid Pt₃₈ cluster was $S = 5$. Recently, $S = 3$ was shown to be the minimum energy net spin for a two-layer Pt₃₁ cluster with seven middle atoms on the top layer relaxed.¹⁸ For a rigid Pt₃₁ cluster with all distances between the Pt atoms fixed to the bulk value of 277.5 pm, the minimum energy spin state was found to be $S = 8$ between the states $S = 0$ and $S = 10$.¹⁸ This shows that relaxation of some Pt atoms in a cluster may change its optimum total spin. Even if the lowest-energy net spin of the Pt₃₈ cluster was not $S = 3$ (as is for the Pt₃₁ cluster), in this study, this choice for the cluster as well as for the cluster plus cinchonidine is justified

since a) a low-spin state should be chosen to represent the electronic structure of a nonmagnetic metal cluster/surface as Pt as well as the cluster plus its corresponding adsorbate,¹⁹ b) for example, the adsorption energy of benzene on Pt₃₁ cluster has been shown to depend only slightly on the spin state,¹⁸ and c) we are interested in *relative* adsorption energies, that is, relative stabilities of Open(3) and QA-Open(4) conformations of cinchona on the Pt(111) surface, which thus will depend even more slightly on the choice of net spin than the absolute adsorption energies.

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Tables and Figures

TABLE S1: Relative energies (kJ mol^{-1}) of stable conformations of protonated and unprotonated cinchonidine (Cd) and 9-methoxycinchonidine (MeOCd) on the Pt(111) surface calculated using the COMPASS force field. Relative energies of the isolated modifiers are given in the parentheses.

species	QA-Open(4)	QA-Open(3)	Open(3)	Open(5)
Cd	0 (0)	16 (— ^a)	71 (5)	137 (12)
CdH ⁺	0 (0)	19 (27)	81 (17)	167 (44)
MeOCd	0 (— ^a)	11 (— ^a)	37 (0)	117 (6)
MeOCdH ⁺	0 (— ^a)	10 (— ^a)	31 (0)	114 (19)

^a Not stable.

TABLE S2: Selected geometrical parameters in 1:1 complexes between 1-phenyl-1,2-propanedione and protonated modifiers. The isolated complexes were optimized with B3LYP/T(ON)DZP (DFT) and the COMPASS force field (MM). The complexes on the Pt(111) slab were optimized with the latter method (MM on Pt). Numbering of carbonyl oxygens is shown in Figure 1.

complex	distance [pm]												
	D(O=C–C=O) [degrees]			O(1)⋯ ⁺ HN			O(2)⋯ ⁺ HN			O(?)⋯HO–C(9)			
	DFT	MM	MM on Pt	DFT	MM	MM on Pt	DFT	MM	MM on Pt	DFT	MM	MM on Pt	O(?) ^a
CdH⁺ in Open(3)													
bifurcated pro-(<i>R</i>)	–39.4 (41.1)	3.8	–0.1	189 (187)	206	236	257 (262)	253	342				
bifurcated pro-(<i>S</i>)	43.2 (–32.1)	–4.3	–3.1	257 (217)	252	357	191 (214)	205	194				
cyclic pro-(<i>R</i>) ^b	–69.2 (67.8)	4.4	—	184 (185)	204	—	344 (342)	312	—	202 (218)	205	—	O(2)
cyclic pro-(<i>S</i>) ^b	–73.6 (65.5)	4.5	—	354 (343)	315	—	186 (187)	204	—	201 (206)	206	—	O(1)
CdH⁺ in Open(5)													
bifurcated pro-(<i>R</i>)	58.4 (–55.3)	3.8	2.7	196 (284)	201	312	286 (187)	327	301				
bifurcated pro-(<i>S</i>)	–60.0 (34.8)	–5.6	–3.2	182 (212)	197	280	297 (236)	329	316				
cyclic pro-(<i>R</i>)	70.0 (–54.7)	3.8	4.4	354 (289)	298	299	212 (203)	194	285	180 (207)	193	220	O(1)
cyclic pro-(<i>S</i>)	70.0 (–60.3)	–4.0	–1.5	207 (200)	195	263	346 (290)	301	280	184 (210)	195	247	O(2)
CdH⁺ in QA-Open(3)													
pro-(<i>R</i>) ^c	—	—	–4.4	—	—	255	—	—	224	—	—	219	O(2)
pro-(<i>S</i>) ^c	—	—	–1.2	—	—	240	—	—	266	—	—	236	O(1)
CdH⁺ in QA-Open(4)													
pro-(<i>R</i>) ^c	—	—	3.2	—	—	342	—	—	299	—	—	238	O(2)
pro-(<i>S</i>) ^c	—	—	–0.6	—	—	275	—	—	314	—	—	321	O(1)
MeOCdH⁺ in Open(3)													
bifurcated pro-(<i>R</i>)	–40.4 (41.5)	–4.3	–6.3	188 (187)	215	395	261 (263)	245	438				
bifurcated pro-(<i>S</i>)	32.2 (–34.1)	4.2	5.9	198 (220)	275	437	236 (214)	203	375				
MeOCdH⁺ in Open(5)													
bifurcated pro-(<i>R</i>)	–48.6 (40.6)	–5.3	3.5	278 (203)	333	406	193 (261)	195	333				
bifurcated pro-(<i>S</i>)	–50.5 (37.4)	3.6	–3.3	193 (215)	197	337	279 (240)	346	399				
MeOCdH⁺ in QA-Open(3)													
pro-(<i>R</i>) ^c	—	—	1.6	—	—	339	—	—	284				
pro-(<i>S</i>) ^c	—	—	–2.0	—	—	296	—	—	366				
MeOCdH⁺ in QA-Open(4)													
pro-(<i>R</i>) ^c	—	—	0.5	—	—	362	—	—	335				
pro-(<i>S</i>) ^c	—	—	–1.4	—	—	351	—	—	343				

^a This indicates to which carbonyl oxygen the distance from the OH hydrogen is measured.

^b The MM optimized structure on Pt does not resemble the DFT optimized structure.

^c No stable isolated structure was found with DFT or MM.

TABLE S3: Selected geometrical parameters in 1:1 complexes between methyl pyruvate and protonated modifiers. The isolated complexes were optimized with B3LYP/T(ON)DZP (DFT) and the COMPASS force field (MM). The complexes on the Pt(111) slab were optimized with the latter method (MM on Pt). Numbering of carbonyl oxygens is shown in Figure 1.

complex	D(O=C–C=O) [degrees]			distance [pm]									
				O(1)··· ⁺ HN			O(2)··· ⁺ HN			O(?)···HO–C(9)			
	DFT	MM	MM on Pt	DFT	MM	MM on Pt	DFT	MM	MM on Pt	DFT	MM	MM on Pt	O(?) ^a
CdH⁺ in Open(3)													
bifurcated pro-(<i>R</i>)	1.1	–0.1	0.4	195	203	197	252	267	367				
bifurcated pro-(<i>S</i>)	0.1	–0.3	–0.2	250	250	332	195	221	280				
cyclic pro-(<i>R</i>) ^b	–1.8	0.3	—	188	204	—	321	326	—	205	205	—	O(2)
cyclic pro-(<i>S</i>) ^b	–4.1	0.3	—	303	323	—	187	209	—	234	201	—	O(1)
CdH⁺ in Open(5)													
bifurcated pro-(<i>R</i>)	–3.3	–1.2	0.2	239	345	316	210	208	297				
bifurcated pro-(<i>S</i>)	–3.6	–0.3	0.0	203	200	278	248	352	328				
cyclic pro-(<i>R</i>)	15.1	–0.1	0.3	347	310	336	214	199	341	184	200	199	O(1)
cyclic pro-(<i>S</i>)	11.3	0.3	0.1	210	193	317	341	315	316	184	217	186	O(2)
CdH⁺ in QA-Open(3)													
pro-(<i>R</i>) ^c	—	—	1.2	—	—	269	—	—	234	—	—	219	O(2)
pro-(<i>S</i>) ^c	—	—	0.3	—	—	236	—	—	283	—	—	243	O(1)
CdH⁺ in QA-Open(4)													
pro-(<i>R</i>) ^c	—	—	0.5	—	—	330	—	—	273	—	—	306	O(2)
pro-(<i>S</i>) ^c	—	—	–0.3	—	—	279	—	—	339	—	—	330	O(1)
MeOCdH⁺ in Open(3)													
bifurcated pro-(<i>R</i>)	1.0	0.0	0.5	194	202	393	255	314	448				
bifurcated pro-(<i>S</i>)	0.1	0.3	–0.3	254	202	455	195	408	450				
MeOCdH⁺ in Open(5)													
bifurcated pro-(<i>R</i>)	0.6	–0.1	0.4	220	359	401	234	223	352				
bifurcated pro-(<i>S</i>)	–1.3	–1.3	0.0	211	204	435	243	352	435				
MeOCdH⁺ in QA-Open(3)													
pro-(<i>R</i>) ^c	—	—	–0.5	—	—	333	—	—	294				
pro-(<i>S</i>) ^c	—	—	–1.2	—	—	298	—	—	340				
MeOCdH⁺ in QA-Open(4)													
pro-(<i>R</i>) ^c	—	—	0.6	—	—	352	—	—	327				
pro-(<i>S</i>) ^c	—	—	–0.4	—	—	325	—	—	377				

^a This indicates to which carbonyl oxygen the distance from the OH hydrogen is measured.

^b The MM optimized structure on Pt does not resemble the DFT optimized structure.

^c No stable isolated structure was found with DFT or MM.

TABLE S4: Absolute complexation energies ($E_{\text{complexation}} = E_{\text{complex}} - E_{\text{reactant}} - E_{\text{modifier}}$), relative energies of the complexes ($\Delta E_{\text{complex}} = E_{\text{complex1}} - E_{\text{complex2}}$), and relative stabilization of the keto carbonyl orbitals ($\Delta E_{\text{orbital}}$) in 1:1 complexes between 1-phenyl-1,2-propanedione and protonated modifiers calculated at the B3LYP/T(ON)DZP level (in kJ mol^{-1}). Relative energies of the isolated complexes (ΔE_{MM}) and the complexes on the Pt(111) surface (ΔE_{MM} on Pt) optimized by the COMPASS force field are also given (in kJ mol^{-1}). The names of the complexes refer to the DFT optimized structures.

complex	$E_{\text{complexation}}$	$\Delta E_{\text{complex}}$	$\Delta E_{\text{orbital}}$	ΔE_{MM}	ΔE_{MM} on Pt	contributions to ΔE_{MM} on Pt	
						valence energy	non-bond energy
CDH⁺ in Open(3)							
bifurcated pro-(<i>R</i>)	−75.1 (−75.0)	1 (1)	0 (2)	20	85	1	84
bifurcated pro-(<i>S</i>)	−74.2 (−72.4)	2 (4)	52 (20)	22	75	5	70
cyclic pro-(<i>R</i>) ^{<i>a</i>}	−75.5 (−73.1)	1 (3)	10 (27)	2	—	—	—
cyclic pro-(<i>S</i>) ^{<i>a</i>}	−76.2 (−72.8)	0 (3)	38 (40)	0	—	—	—
CDH⁺ in Open(5)							
bifurcated pro-(<i>R</i>)	−56.9 (−55.9)	17 (18)	130 (145)	45	192	15	177
bifurcated pro-(<i>S</i>)	−57.7 (−54.1)	16 (20)	130 (105)	46	193	13	180
cyclic pro-(<i>R</i>)	−63.5 (−52.5)	10 (21)	104 (81)	17	163	14	149
cyclic pro-(<i>S</i>)	−61.9 (−53.7)	12 (20)	99 (89)	18	167	13	154
CDH⁺ in QA-Open(3)							
pro-(<i>R</i>) ^{<i>b</i>}	—	—	—	—	31	26	5
pro-(<i>S</i>) ^{<i>b</i>}	—	—	—	—	33	25	8
CDH⁺ in QA-Open(4)							
pro-(<i>R</i>) ^{<i>b</i>}	—	—	—	—	6	1	5
pro-(<i>S</i>) ^{<i>b</i>}	—	—	—	—	0	0	0
MeOCdH⁺ in Open(3)							
bifurcated pro-(<i>R</i>)	−74.5 (−74.4)	0 (0)	0 (1)	6	25	14	11
bifurcated pro-(<i>S</i>)	−72.1 (−71.8)	2 (3)	6 (16)	0	21	13	8
MeOCdH⁺ in Open(5)							
bifurcated pro-(<i>R</i>)	−52.4 (−52.1)	16 (17)	127 (112)	26	133	5	129
bifurcated pro-(<i>S</i>)	−52.4 (−51.2)	16 (17)	120 (109)	26	136	5	131
MeOCdH⁺ in QA-Open(3)							
pro-(<i>R</i>) ^{<i>b</i>}	—	—	—	—	20	18	2
pro-(<i>S</i>) ^{<i>b</i>}	—	—	—	—	26	18	7
MeOCdH⁺ in QA-Open(4)							
pro-(<i>R</i>) ^{<i>b</i>}	—	—	—	—	0	0	0
pro-(<i>S</i>) ^{<i>b</i>}	—	—	—	—	3	−1	4

The numerical value of ' ΔE_{MM} on Pt' may deviate from the sum of valence and non-bond energies since ' ΔE_{MM} on Pt' is calculated from the accurate values.

^a The MM optimized structure on Pt does not resemble the DFT optimized structure.

^b No stable isolated structure was found with DFT or MM.

TABLE S5: Absolute complexation energies ($E_{\text{complexation}} = E_{\text{complex}} - E_{\text{reactant}} - E_{\text{modifier}}$) and relative energies of complexes ($\Delta E_{\text{complex}} = E_{\text{complex1}} - E_{\text{complex2}}$) as well as relative stabilization of the keto carbonyl orbitals ($\Delta E_{\text{orbital}}$) in different 1:1 complexes between methyl pyruvate and protonated modifier molecule calculated at the B3LYP/T(ON)DZP level (in kJ mol⁻¹). Also the relative energies of the isolated complexes (ΔE_{MM}) and complexes on the Pt(111) surface (ΔE_{MM} on Pt) optimized with COMPASS force field are given (in kJ mol⁻¹). The names of the complexes refer to the DFT optimized structures.

complex	$E_{\text{complexation}}$	$\Delta E_{\text{complex}}$	$\Delta E_{\text{orbital}}$	ΔE_{MM}	ΔE_{MM} on Pt	contributions to ΔE_{MM} on Pt	
						valence energy	non-bond energy
CdH⁺ in Open(3)							
bifurcated pro-(<i>R</i>)	−86.6	0	26	19	80	8	73
bifurcated pro-(<i>S</i>)	−85.7	1	58	23	89	−2	91
cyclic pro-(<i>R</i>) ^a	−80.6	6	0	0	—	—	—
cyclic pro-(<i>S</i>) ^a	−80.4	6	41	5	—	—	—
CdH⁺ in Open(5)							
bifurcated pro-(<i>R</i>)	−67.3	17	140	42	200	12	188
bifurcated pro-(<i>S</i>)	−68.0	16	119	38	196	14	182
cyclic pro-(<i>R</i>)	−65.1	19	74	13	158	10	148
cyclic pro-(<i>S</i>)	−67.5	17	65	15	158	12	146
CdH⁺ in QA-Open(3)							
pro-(<i>R</i>) ^b	—	—	—	—	41	27	13
pro-(<i>S</i>) ^b	—	—	—	—	41	24	17
CdH⁺ in QA-Open(4)							
pro-(<i>R</i>) ^b	—	—	—	—	3	1	2
pro-(<i>S</i>) ^b	—	—	—	—	0	0	0
MeOCdH⁺ in Open(3)							
bifurcated pro-(<i>R</i>)	−85.9	0	0	0	26	13	13
bifurcated pro-(<i>S</i>)	−85.1	1	33	3	36	14	22
MeOH⁺ in Open(5)							
bifurcated pro-(<i>R</i>)	−64.6	15	112	23	137	6	131
bifurcated pro-(<i>S</i>)	−64.8	15	100	16	133	8	125
MeOCdH⁺ in QA-Open(3)							
pro-(<i>R</i>) ^b	—	—	—	—	28	19	9
pro-(<i>S</i>) ^b	—	—	—	—	23	19	4
MeOCdH⁺ in QA-Open(4)							
pro-(<i>R</i>) ^b	—	—	—	—	2	−1	3
pro-(<i>S</i>) ^b	—	—	—	—	0	0	0

The numerical value of ' ΔE_{MM} on Pt' may deviate from the sum of valence and non-bond energies since ' ΔE_{MM} on Pt' is calculated from the accurate values.

^a The MM optimized structure on Pt does not resemble the DFT optimized structure.

^b No stable isolated structure was found with DFT or MM.

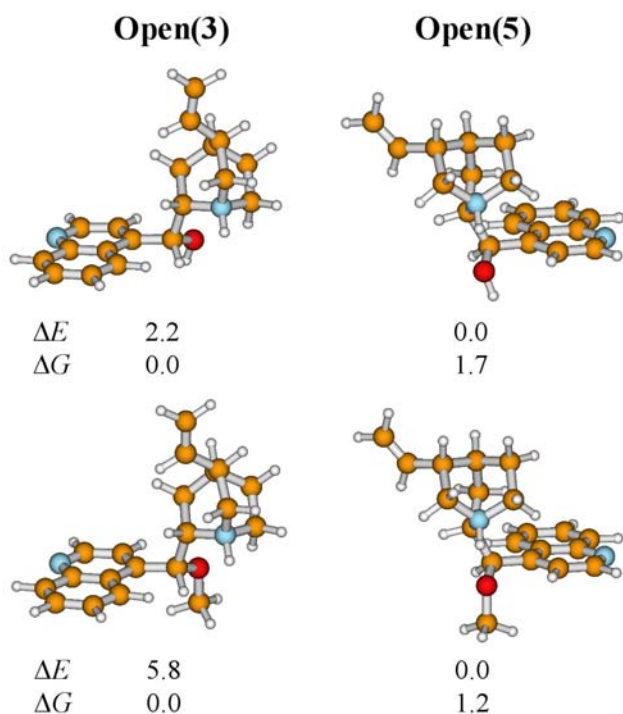


Figure S1. Relative electronic and Gibbs energies (ΔE and ΔG , respectively) of the B3LYP/T(ON)DZP optimized Open(3) and Open(5) conformers of protonated cinchonidine (above) and 9-methoxycinchonidine (below) in kJ mol^{-1} . The conformer with energy = 0.0 kJ mol^{-1} is the more stable one.

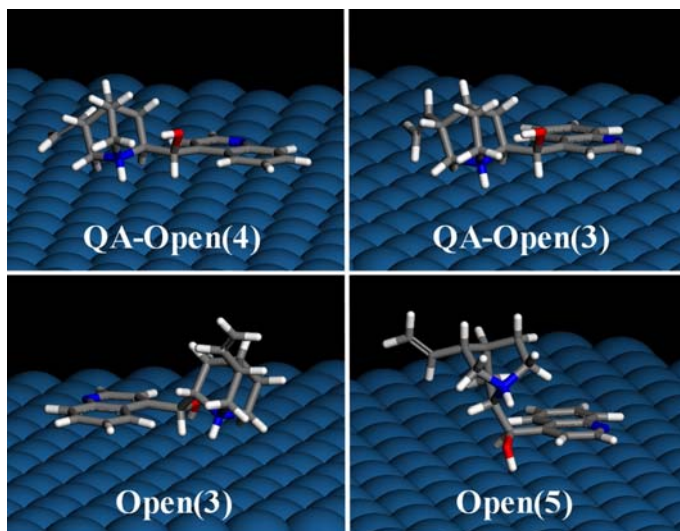


Figure S2. The COMPASS force field optimized stable conformations of CdH⁺ on the Pt(111) surface.

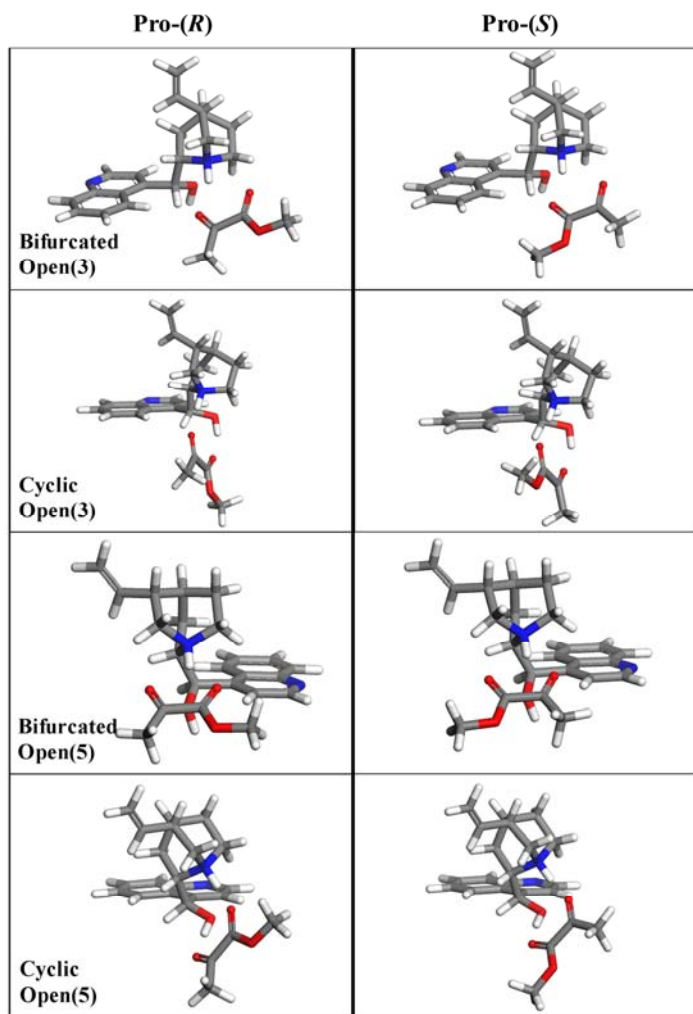


Figure S3. The B3LYP/T(ON)DZP optimized geometries of the MP–CdH⁺ complexes.

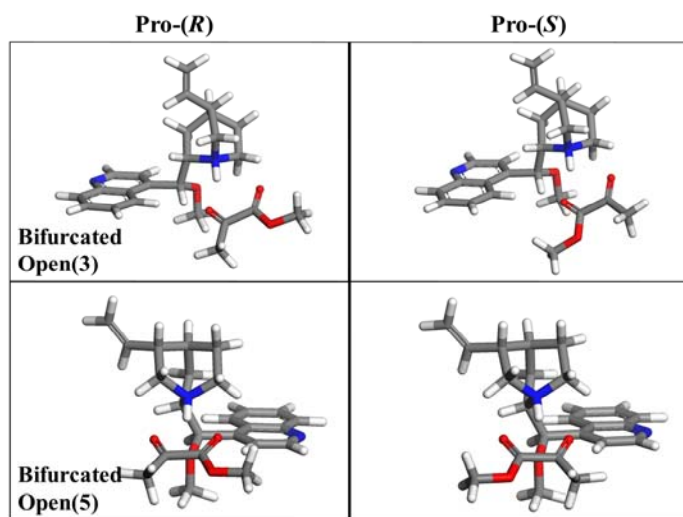


Figure S4. B3LYP/T(ON)DZP optimized geometries of the MP–MeOCdH⁺ complexes.

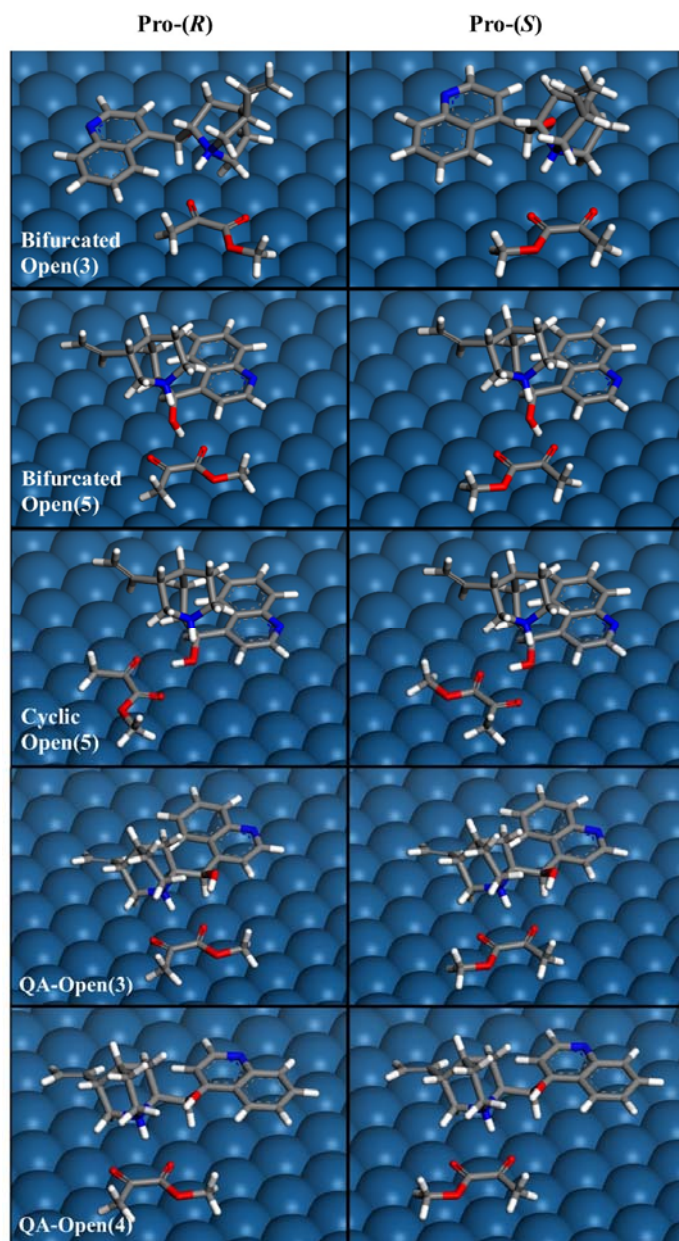


Figure S5. The COMPASS force field optimized MP-CdH⁺ complexes on the Pt(111) surface.

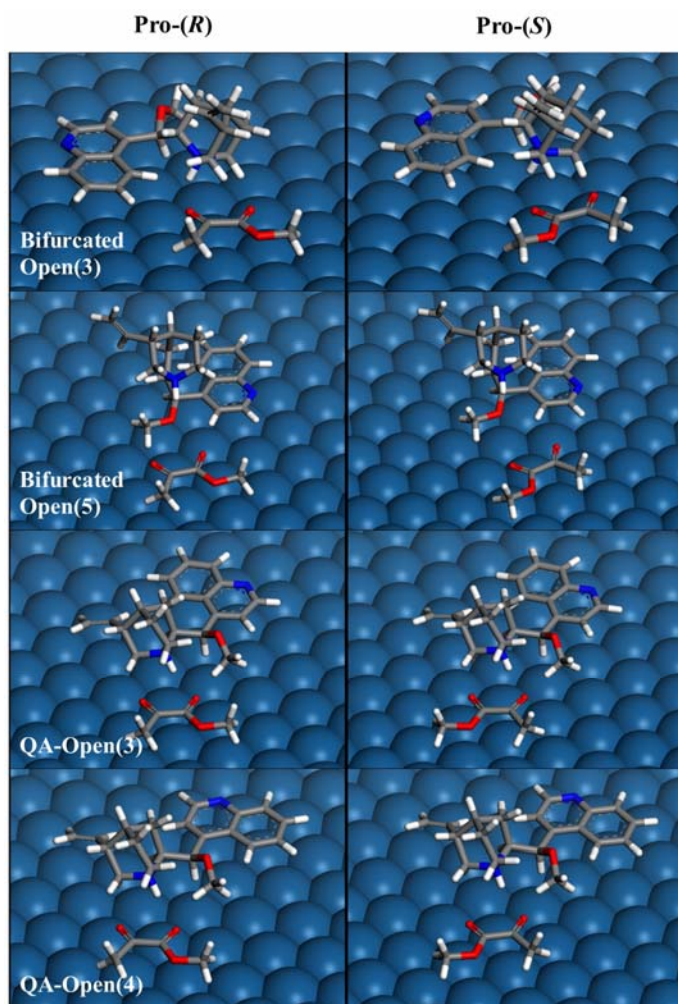


Figure S6. The COMPASS force field optimized MP–MeOCdH⁺ complexes on the Pt(111) surface.

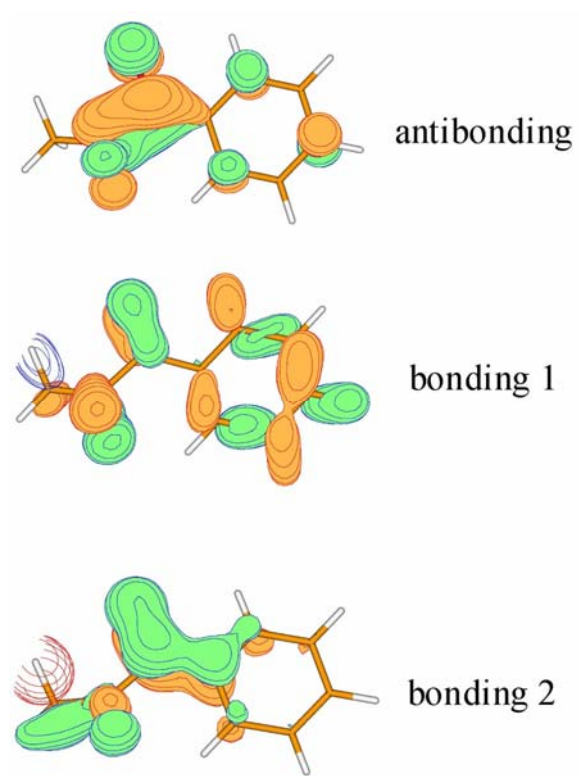


Figure S7. Keto carbonyl antibonding and bonding orbitals of 1-phenyl-1,2-propanedione. The bonding π orbital of the keto carbonyl moiety is split into two molecular orbitals, bonding 1 and bonding 2.

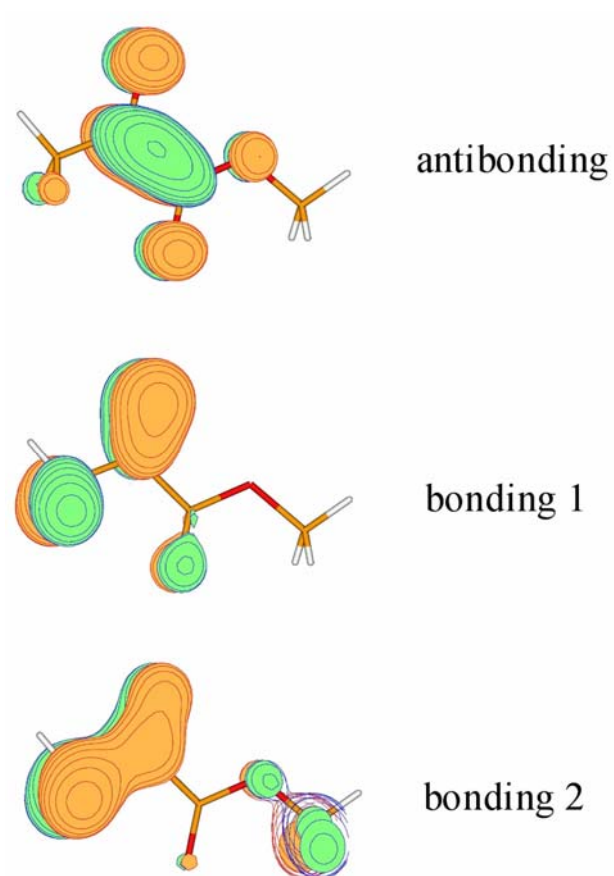


Figure S8. Keto carbonyl antibonding and bonding orbitals of methyl pyruvate. The bonding π orbital of the keto carbonyl moiety is split into two molecular orbitals, bonding 1 and bonding 2.

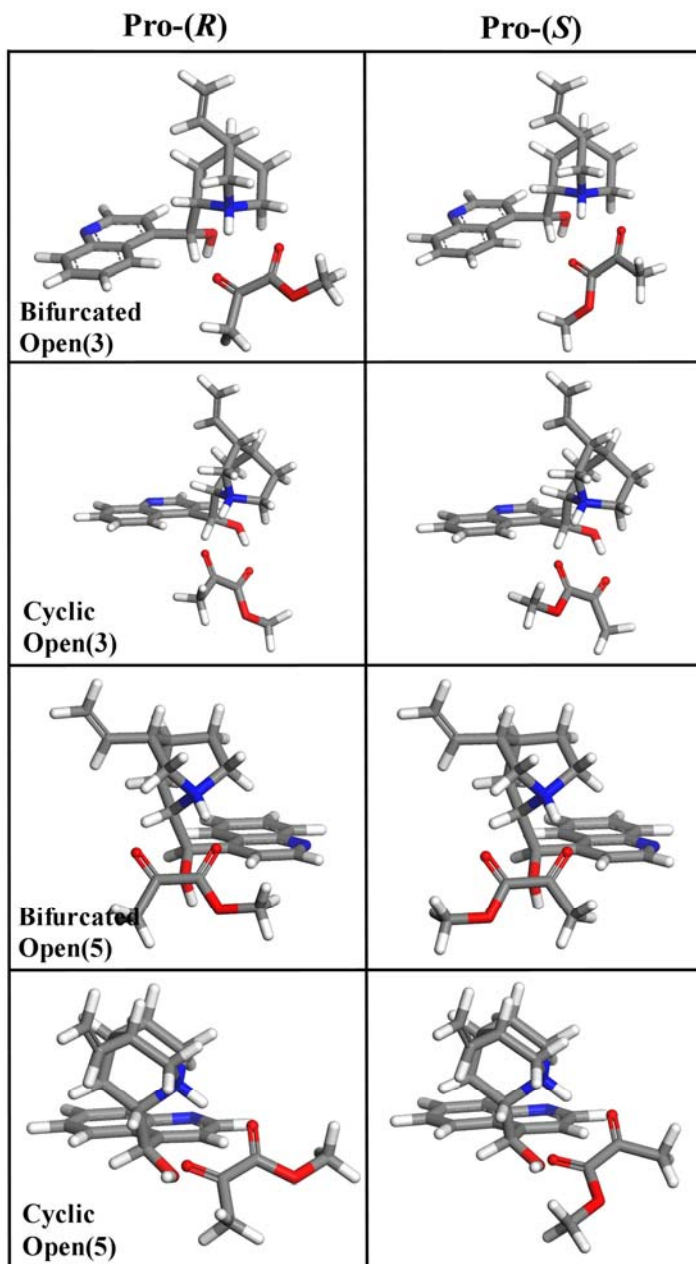


Figure S9. The COMPASS force field optimized geometries of the MP-CdH⁺ complexes.