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Associative *vs.* dissociative binding of CO_2 on M_5 transition metal clusters

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Reaction paths were calculated using density functional theory for the reaction of carbon dioxide with a series of transition metal pentamers, M_5 + CO_2, (M = Nb, Mo, Ru, Rh, Pd, Ag, Pt). A stochastic search algorithm was used to identify geometries with intact CO_2, as well as geometries where the CO_2 molecule was partly (O + CO) and fully dissociated (O + C + O). Nb_5 and Mo_5 clusters were found to thermodynamically dissociate CO_2. Pd_5 and Ag_5 were found to leave the CO_2 molecule intact, Ru_5 could partly dissociate CO_2, while for Rh_5 and Pt_5, the fate of the adsorbed CO_2 was dependent on the cluster geometry. The change in the CO_2 π_u orbital energy in the capture species on initial reaction with the M_5 cluster was found to distinguish clusters where CO_2 fully dissociated, but could not distinguish clusters where CO_2 was found to partly dissociate. The charge transfer to the CO_2 molecule at the first transition state, did however, distinguish clusters that fully dissociate CO_2, those that partly dissociate CO_2 to O + CO, and those that leave CO_2 fully intact.

1. Introduction

In recent years, there has been increasing interest in the activation of CO_2. Especially in the context of the environment, the ability to activate captured CO_2 towards further reaction, turns a problem of needing to store the captured CO_2[1] into a solution – a cheap C1 feedstock.[2,3] CO_2 is unfortunately well-known for its thermodynamic and kinetic stability, and it is unreactive in the gas phase,[4] thus requiring activation *via* some catalyst species in order to weaken and/or break the CO bonds. Activation of CO_2 typically proceeds *via* introducing electron density into the antibonding π^* orbitals of CO_2, weakening the C═O bonds and allowing the CO_2 the molecule to bend away from linear, simultaneously creating a dipole and increasing the reactivity of CO_2.[5–7]

Several manufactured materials including foams,[8] $CaCO_3$ microspheres,[9] and novel cements[10] have been proposed and used to capture and store CO_2. More recently, novel materials including, Metal- and Covalent Organic Frameworks,[11–13] carbon nanotubes,[14] MXenes,[15–20] and nanofilms[21] have been proposed to not only capture, but to valorize CO_2 for further use. CO_2 is activated by electron donation into the antibonding π^* orbitals of CO_2, weakening the C═O bonds allowing the CO_2 molecule to bend.[5–7,22,23] In the majority of these materials above, the active site of the catalyst is a metal atom[24] and thus there is considerable interest in the mechanism of CO_2 activation by various metals[25] and there has been a great volume of spectroscopic and theoretical work over decades[26–29] investigating the interaction of CO_2 with single transition metal atoms/ions, $M^{+/0/-}$. A range of CO_2 binding motifs have thus been identified, including η^1 coordination (*via* the C atom), bidentate η^2 binding (*via* C, O), and dissociative addition where binding produces CO and O species. Where multiple CO_2 molecules adsorb, oxalate formation has also been identified.[7,30]

In between single atoms and bulk surfaces, transition metal clusters have long been an avenue for the investigation of gas phase reactions, with a variety of substrates including CO,[22,31] N_2O[32] and notably CO_2.[32,34,35] Size effects are well-known in the cluster regime, with several experimental[36] and computational studies[37] noting properties varying over several orders of magnitude upon single atom addition.

One study from Mackenzie group illustrated these size effects with respect to CO_2 activation, employing small Pt_4^- and Pt_5^- anionic clusters. They showed that while Pt_4^- + CO_2 has a dissociative global minimum (*i.e.* Pt_4^-(CO)O), the spectroscopically observed species possessed intact CO_2 (Pt_4^-OCO), whereas for the one atom larger cluster anion, Pt_5^-, infrared multiphoton dissociation (IR-MPD) spectroscopy showed the computationally predicted global minimum, dissociatively bound Pt_5^-(CO)O exists and in contrast to Pt_4^-, no evidence of molecularly bound CO_2 was seen, despite such a species being predicted within the energy of their cluster source.[38]

Inspired by this work of Mackenzie *et al.*,[38] and following on from our work on M_4 clusters,[39] we report a ''horizontal'' study, investigating the reaction of CO_2 with M_5 neutral transition metal clusters from niobium through silver and additionally including platinum.

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2. Computational method

The computational method employed here is the same as in our previous work, and recapped here.[39] Structures of M_5 clusters, for M = Nb–Ag (excluding Tc) and Pt were generated using the Kick stochastic structure search procedure with five individual M atoms supplied.[40,41] Full searches were undertaken on the lowest possible multiplicity (singlet or doublet) and all minima identified were re-optimized at higher multiplicities. For all metal species, the lowest four multiplicities were calculated, but for ruthenium and rhodium, the search was extended up to the 15-tet and the 12-tet, respectively. No symmetry was imposed at any point in the search, nevertheless, several clusters adopted clear point group symmetry, as evidenced by geometric parameters and frequencies. We chose not to confirm the symmetry by further calculation, as the addition of CO_2 would immediately break symmetry.

The lowest energy structure of each M_5 cluster was then adopted as a fragment in a further stochastic search process. Kick runs were undertaken with the following configurations: $M_5 + CO_2$(linear); $M_5 + CO_2$(bent); $M_5 + CO + O$; $M_5 + C + O + O$. In order to easily identify the transition state where the CO_2 molecule first began to dissociate, a Kick run was also undertaken explicitly searching for transition states, employing the M_5 cluster and the bent CO_2 molecule as fragments. Additional starting geometries were generated by hand (*e.g.* CO_2 bound to different symmetry-distinct metal atoms, end-on/side-on, linear/bent, $\mu^1/\mu^2/\mu^3$-bound). From these calculations, the physisorbed ''capture'' species and the M_5CO_2 global minimum were identified, and the reaction pathway was then filled in and confirmed by a series of Quasi-Synchronous Transit (QST) and Intrinsic Reaction Coordinate (IRC) calculations.

The zero energy for each $M_5 + CO_2$ system is defined as the sum of the energies of the M_5 metal cluster in the lowest possible multiplicity and the CO_2 molecule. Thus structures with a negative relative energy (below the zero energy) are more stable than the separated reactants; structures with a positive relative energy (energy higher than the zero energy) are unstable with respect to the infinitely separated reactants. basis set superposition error (BSSE) was disregarded, as were zero-point energies and entropic contributions, as previous work that the effect of BSSE and ZPE on relative energies is minimal and that adding entropic effects was found to consistently raise relative energies by $\approx$0.5 eV at 298 K.[31] All structure searches were undertaken with the B3P86 density functional[42] and Stuttgart Relativistic Small Core (SRSC) basis set,[43–45] as previous studies[31,46] have shown this to be an accurate and computationally efficient combination. The final pathways were re-optimized at all relevant multiplicities using the TPSS functional[47] with the Def2TZVP basis set[48,49] and employing the D3-BJ empirical dispersion term.[50] This latter combination, while more expensive, has also been shown to reproduce energetic ordering and vibrational data for reactions of small molecules on gas phase transition metal clusters including Rh_n[51] and Pt_n.[52] All calculations were undertaken using the Gaussian 16 software.[53] All structures presented are included in the SI (xyz, zip) and absolute and relative energies for each structure at all multiplicities studied are presented in the SI (xlsx).

3. Results and discussion

3.1. Nb_5

The Nb_5 cluster is an odd-electron species and therefore may be a doublet, quartet,.... The doublet multiplicity was found to be the lowest in energy, in line with previous calculations.[54] In slight contrast to the early calculations of Salahub *et al.* on neutral Nb_5, we identified the minimum energy structure to be of C_{2v} symmetry with equatorial–equatorial bond lengths of 2.63 (2) and 2.87 Å and axial–equatorial bond lengths of 2.49 (2) and 2.61 Å. This cluster was used for the CO_2 pathway without constraint.

Two pathways were identified for the reaction of $Nb_5 + CO_2$, shown in Fig. 1 and 2. Corresponding geometric data is shown in Table S1. Both pathways begin with the CO_2 molecule approaching the equatorial niobium atoms, and the CO_2 molecule bending over one of the triangular faces of the Nb_5 cluster. Structures *I–V* of both pathways are therefore the same. The two pathways diverge with a choice of which CO bond breaks first. In the pathway shown in Fig. 1, the CO bond that is closest to the equatorial plane of the Nb_5 cluster breaks first resulting in a CO molecule bound to an axial niobium atom and the lone oxygen atom attached to an equatorial niobium atom. The second pathway, shown in Fig. 2 breaks the other CO bond, resulting in the CO molecule bound to equatorial niobium atoms and the dissociated oxygen atom bound to an axial niobium atom. Both pathways result in very similar global minima, with the CO_2 molecule completely dissociated, at relative energies of −6.76 and −6.68 eV respectively. These two structures, Fig. 1-IX and 2-XI, may interconvert, *via* a transition state shown on the first pathway, Fig. 1-X.

3.2. Mo_5

The molybdenum atom is and even-electron species and therefore the Mo_5 cluster is also an even-electron species and we investigate the singlet, triplet,... surfaces. Several authors have calculated the structure and properties of the Mo_5 cluster using a variety of density functional methods, basis sets and structure search approaches. Plá and Diez identified a singlet global minimum of a capped out-of-plane rhombus, but with singlet and triplet trigonal bipyramid structures both only 0.03 eV per atom higher in energy.[55] Vega and coworkers predicted a triplet bipyramid with C_{2v} symmetry,[56] while Yin and Chen identified a singlet trigonal bipyramid with C_1 symmetry.[57] Kantorovich and coworkers used the AIRSS approach[58] to identify 9 Mo_5 structures within 1 eV of the global minimum, which they predict to be a C_{2v} singlet trigonal bipyramid.[59] Sumer and Jellinek identified a similar set of low energy structures, but their global minimum had only C_2 symmetry.[60] Lei predicted a singlet trigonal bipyramid structure.[61] In general agreement with these studies, we identified the global minimum to be a

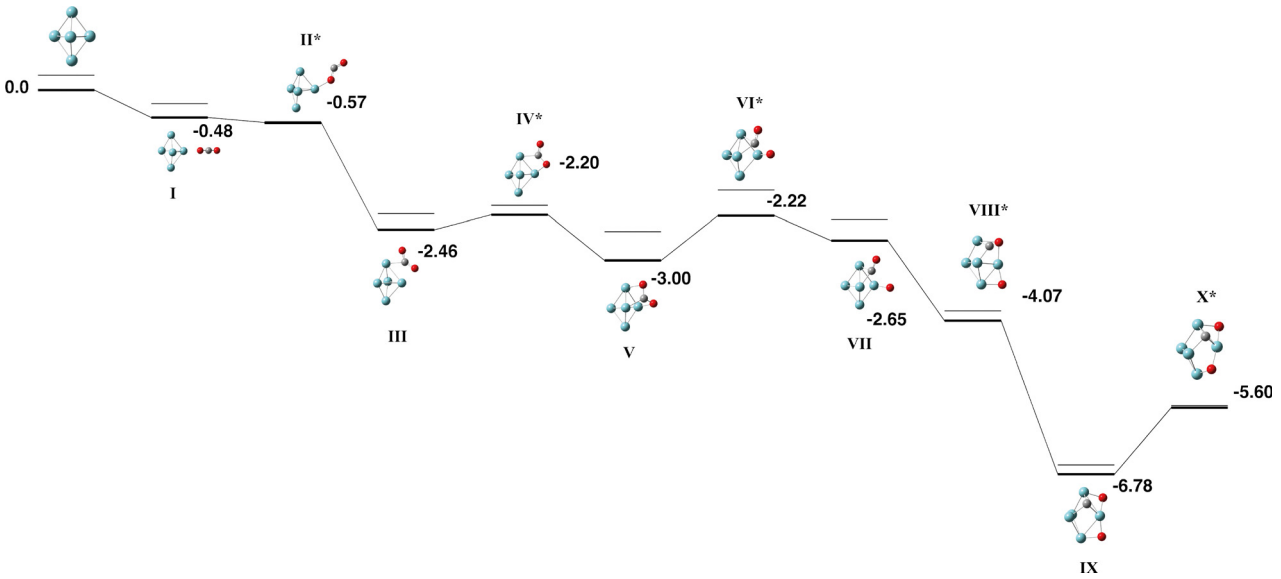

Fig. 1 Stationary points on the Nb_5 + CO_2 potential energy surface. The doublet multiplicity is shown in bold and the quartet multiplicity is shown with thin lines. Relative energies are given in eV. Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

singlet trigonal bipyramid with approximately D_{3h} symmetry and bond lengths of 2.34 Å (axial–equatorial) and 2.83 Å (equatorial–equatorial) and we employed this structure, without symmetry constraint, in our reaction with CO_2.

A single pathway was identified for the reaction of Mo_5 + CO_2, it is shown in Fig. 3 and Table S2. The pathway begins with the CO_2 molecule approaching the axial molybdenum atoms, and the CO_2 molecule breaks over the axial atom of the Mo_5 cluster in the first transition state (structure Fig. 3-II). The remaining CO molecule binds in a μ^3 fashion to a triangular face of the Mo_5 cluster, before twisting, rotating parallel to the face and then dissociating. The Mo_5CO_2 global minimum therefore has the CO_2 molecule fully dissociated with the carbon atom μ^3-bound, and the oxygen atoms μ^2 and μ^1-bound, with a relative binding energy of −4.91 eV with respect to the singlet Mo_5 + CO_2.

3.3. Ru_5

Ruthenium also has an even number of electrons and therefore we consider the singlet, triplet, quintet and septet multiplicities for the Ru_5 cluster. The Ru_5 cluster has been calculated previously by different authors and DFT methods,[62–65] but there is good agreement amongst researchers that the ground state structure of Ru_5 is a square pyramid structure with singlet multiplicity. We similarly identify a square pyramidal singlet

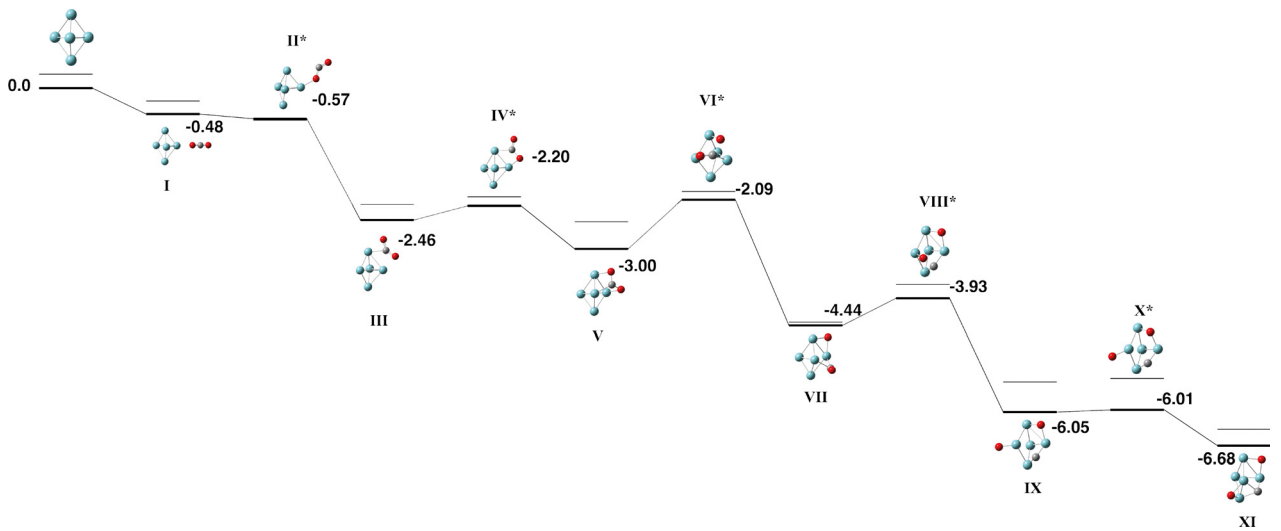

Fig. 2 Second reaction pathway on the Nb_5 + CO_2 potential energy surface. The doublet multiplicity is shown in bold and the quartet and sextet multiplicities are shown with thin lines. Relative energies are given in eV. Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

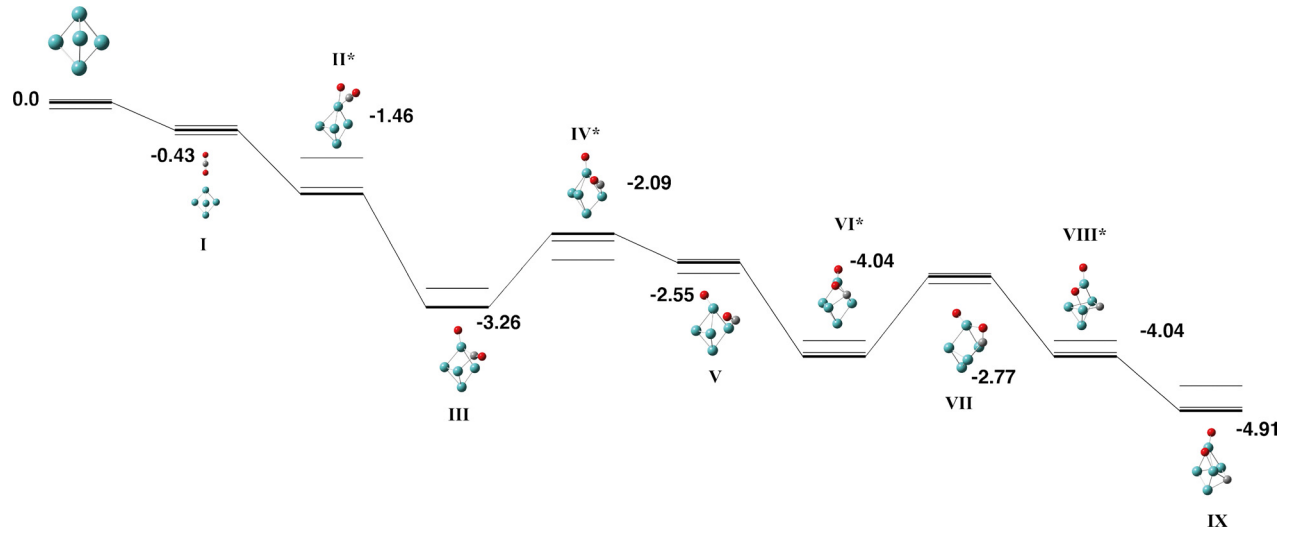

Fig. 3 Reaction pathway of $Mo_5 + CO_2$. The singlet potential energy surface is shown in bold and the triplet and quintet multiplicities are shown with thin lines. Relative energies for the singlet surface are given in eV, energies of higher multiplicities are included in SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

structure with bond distances of 2.28 and 2.49 Å for the base–base and base–apex bonds respectively.

Two pathways were identified for the $Ru_5 + CO_2$ reaction, they are shown in Fig. 4 and 5. Corresponding geometric data is shown in Table S3. The singlet to nonet multiplicities were quite close in energy and so the pathway calculations were extended up to the 15-tet. The CO_2 molecule may approach either the apex ruthenium atom (Fig. 4) or one of the base ruthenium atoms (Fig. 5). In both cases, the first CO bond breaks with a barrier below the zero energy defined by $E[Ru_5(\text{singlet})] + E[CO_2]$, and leaving the CO molecule bound to the apex ruthenium atom. Two candidates for the global minimum Ru_5CO_2 structure are identified: The first structure has the CO molecule bound in a μ^1 geometry to the apex Ru atom and the dissociated oxygen atom μ^1-bound to a base Ru atom and in the Ru_4 plane. The second geometry has the CO molecule μ^2-bound to the Ru(apex)–Ru(base) bond opposite the μ^1-bound oxygen atom. These two geometries are interconvertible by a transition state at −2.15 eV (*i.e.* a 0.49 eV barrier) with an imaginary frequency of $134i$ cm^{-1}. The barrier to dissociating the second CO bond is 0.27 eV above zero energy for the singlet pathway, but below zero energy for the triplet to the 13-tet multiplicities. The lowest energy structure identified with CO_2 completely dissociated has a μ^1 and a μ^2 oxygen atom and a μ^2-bound carbon atom. This structure has an energy of −2.17 eV, 0.47 eV higher in energy than the Ru_5OCO global minima.

3.4. Rh_5

The Rh_5 cluster is an odd-electron species and therefore we consider the doublet – 12-tet multiplicities. Rhodium is of intense interest as a catalyst and many researchers have calculated the Rh_5 cluster. In an early study, Kelin and co-workers chose to model a trigonal bipyramid Rh_5, but did not investigate other geometries due to computational expense.[66] Rubio-Arroyo and coworkers predicted a twisted bowtie structure and two trigonal bipyramidal strucutres.[67] Aguilera-Granja *et al.* predict a square pyramidal Rh_5 cluster.[62] Futschek *et al.* predict three Rh_5 isomers, a C_{4v} square pyramid and both a "tall" and a "flat" trigonal bipyramid structure, both of D_{3h} symmetry.[68] Similarly, Pederson and coworkers present a sextet square pyramid as the ground state, with a trigonal bipyramid being

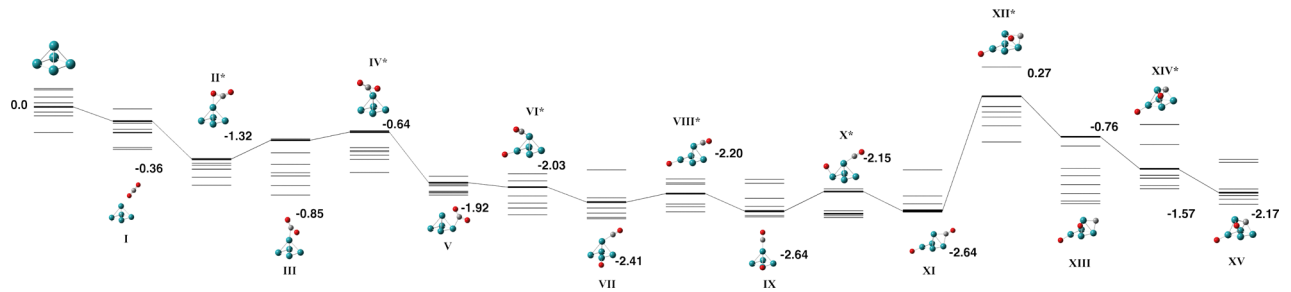

Fig. 4 Stationary points on the $Ru_5 + CO_2$ reaction pathway. The singlet potential energy surface is bolded and the triplet - 15-tet multiplicities are shown with thin lines. Relative energies are given in eV for the singlet multiplicity and included in the SI (xlsx) for all multiplicities. Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

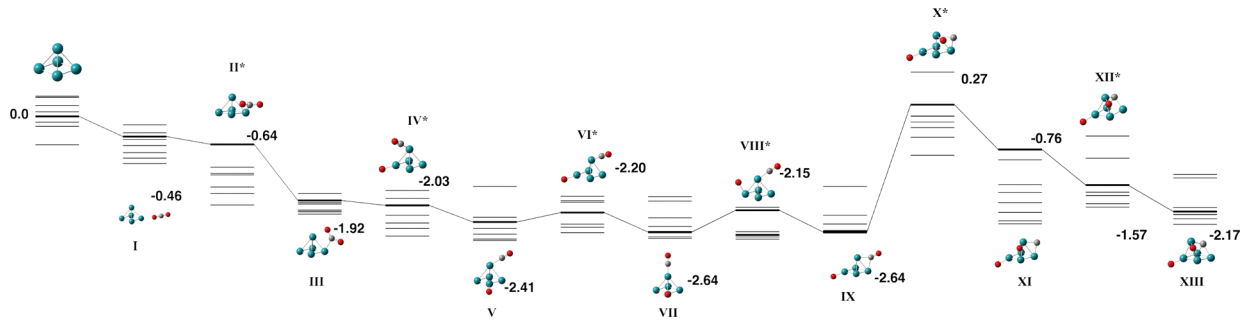

Fig. 5 Alternate reaction path on the Ru_5 + CO_2 potential energy surface. The singlet multiplicity is shown in bold and the triplet - 15-tet multiplicities are shown with thin lines. Relative energies are given in eV. Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

higher in energy at all spin multplicities.[69] Nguyen and Pham[70] and Poulain and coworkers,[32] both employ a square pyramidal Rh_5 structure in their reactivity studies with N_2O.

Our initial search on the doublet surface, yielded a square pyramid ground state, but had a trigonal bipyramid structure only 0.12 eV higher in energy. Re-optimizing these structures at higher multiplicities (up to the 12-tet) showed that the sextet square pyramid was the lowest energy Rh_5 structure and that it is isoenergetic with the sextet and octet trigonal bipyramid structures. Therefore both square pyramid and trigonal bipyramid structures were considered for reaction with CO_2. In the reaction pathways below, pathways for the doublet – decet surfaces are presented as the 12-tet was higher in energy.

3.4.1. Square pyramidal Rh_5. Two pathways are shown for the square pyramid Rh_5 in Fig. 6 and 7 with geometric data in Table S4, it is possible to interconvert between them. The two pathways illustrate two "choices": Firstly, the capture species, when the CO_2 molecule first binds to the Rh_5 cluster, may employ either a base rhodium atom (Fig. 7) or an apex atom (Fig. 6). Either of these capture species leads to a bent CO_2 molecule bound to a Rh(apex)–Rh(base) bond, which is the lowest energy structure (Fig. 7-III and 6-III) at −1.61 eV. From this structure, the CO_2 molecule may break resulting in the CO molecule bound to the base rhodium atom (Fig. 7) with an energy of −1.06 eV, or leave the CO molecule bound to the apex rhodium atom (Fig. 6), where the barrier energy is −0.26 eV. This pathway leads to a structure (Fig. 6-VII), with CO μ^2-bound to an Rh(apex)–Rh(base) bond and the dissociated oxygen atom μ^1-bound to an adjacent Rh(base) atom, this structure is effectively isoenergetic with the bent CO_2 structure, Fig. 6-III. On either pathway, further dissociating the remaining CO molecule faces a high barrier, 1.20 or 1.92 eV above zero energy, indicating that CO_2 dissociation into three separate atoms is unlikely to occur on this cluster.

3.4.2. Trigonal bipyramidal Rh_5. A single pathway is presented for the reaction of trigonal bipyramid Rh_5 + CO_2 in Fig. 8 and Table S5. The features of the pathway are broadly similar to that of the square pyramidal pathways shown in Fig. 6 and 7. The CO_2 molecule approaches an apex rhodium atom, a bent CO_2 molecule lies across a Rh(apex)–Rh(equatorial) bond (Fig. 8-III), the first CO bond breaks leaving the CO molecule bound to an apex rhodium atom, leading to the lowest energy structure, Fig. 8-IX at −1.98 eV, where the oxygen atom is μ^2-bound to a Rh(apex)–Rh(equatorial) bond and the CO molecule is μ^1-bound to an apex rhodium atom. Breaking the second CO bond requires 1.10 eV above zero energy.

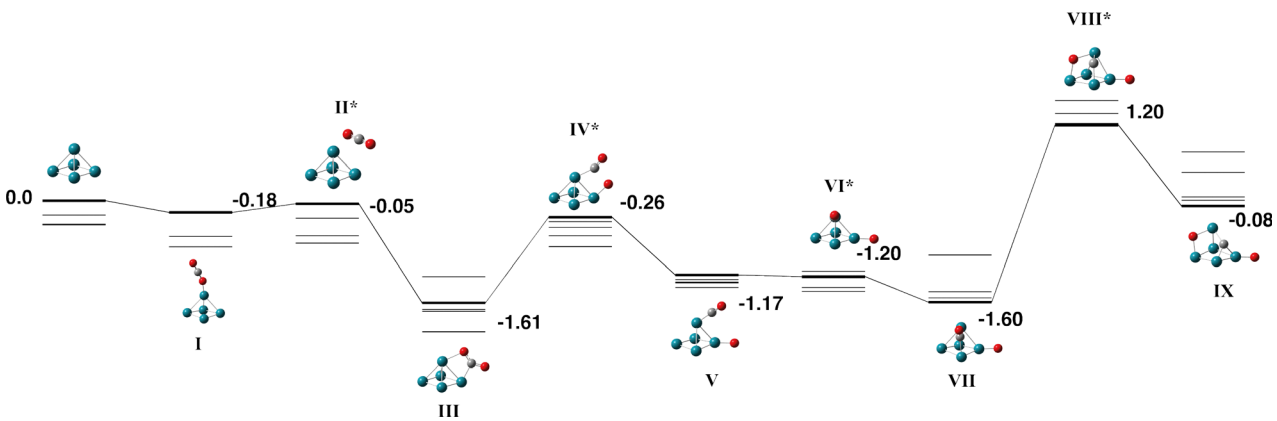

Fig. 6 Stationary points on the Rh_5 + CO_2 potential energy surface for the square pyramidal Rh_5 isomer. Doublet multiplicity is shown in bold and the quartet – decet multiplicities are shown with thin lines. Relative energies of doublet geometries are given in eV and included for all multiplicities in the SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

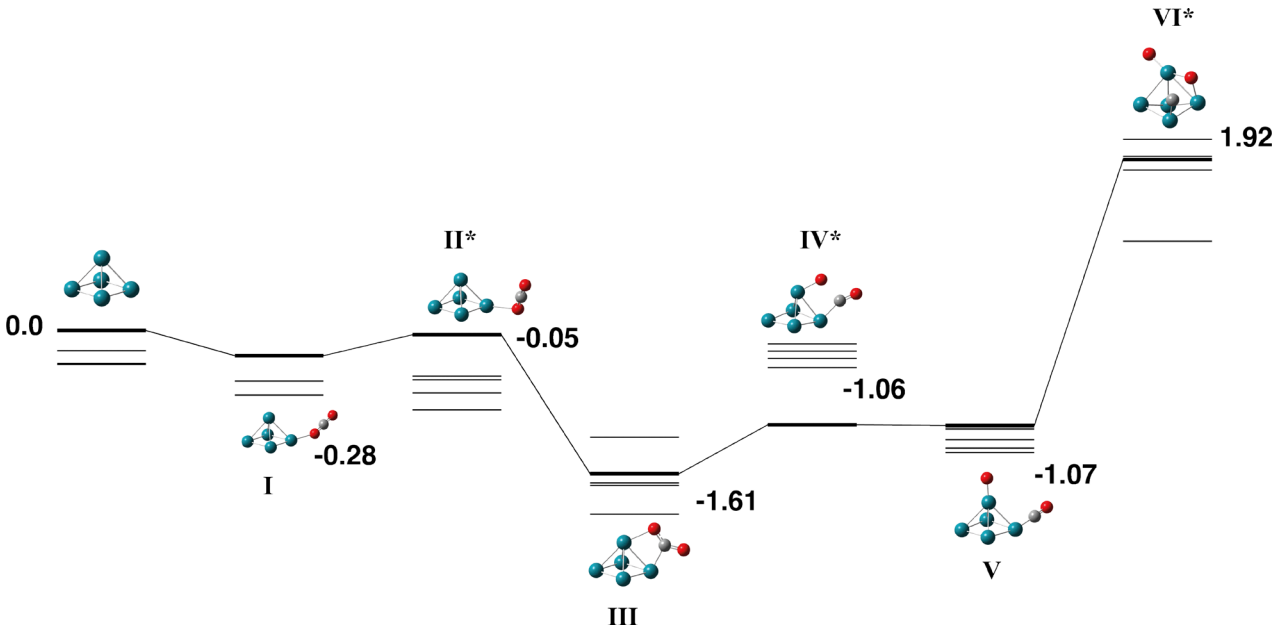

Fig. 7 Alternate pathway on the $Rh_5 + CO_2$ potential energy surface for the square pyramidal Rh_5 isomer. In this pathway, the first CO bond breaking in transition state VI leaves the CO molecule attached to the base Rh atom. The doublet multiplicity is shown in bold and the quartet – decet multiplicities are shown with thin lines. The final transition state leads to the same final structure as Fig. 6 as the CO breaks across the triangular Rh_3 face. Relative energies are given in eV. Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

3.5. Pd_5

The Pd_5 cluster is an even-electron species and therefore we consider the singlet – septet multiplicities. Small Pd clusters have also been calculated by a variety of different methods over many years: Morokuma and coworkers predicted a Pd_5 ground state of a triplet trigonal bipyramid Pd_5 structure with D_{3h} symmetry but noted a C_{2v} trigonal bipyramid only 0.4 kcal mol^{-1} higher in energy, and also a triplet C_{4v} square pyramid only 2.3 kcal mol^{-1} higher in energy.[71] Several other authors predict a triplet trigonal bipyramid structure.[72–76] Our search also identified a triplet trigonal bipyramid as the global minimum, and while we did not constrain symmetry, the structure has C_{2v} symmetry. We did also identify the square pyramidal structure, the triplet was the lowest energy multiplicity for this structure and was 0.11 eV higher than the triplet trigonal bipyramid. While these two structures are sufficiently close in energy such that they are likely to coexist, we choose only the trigonal bipyramid to react with CO_2.

The $Pd_5 + CO_2$ reaction pathway is shown in Fig. 9 and Table S6, the quintet and septet pathways were high in energy and so only the singlet and triplet are shown. The capture species and adjacent transition state (structures Fig. 9-I and II) are shown for both an apex atom approach and an equatorial atom approach. Both approaches result in a bent CO_2 molecule weakly bound to the central Pd(apex)–Pd(equatorial) bond with a binding energy of −1.34 eV relative to the zero energy. This is the global minimum structure for the pathway, breaking the first of the two CO bonds requires +1.08 eV and the barrier to breaking the second CO bond is +4.45 eV.

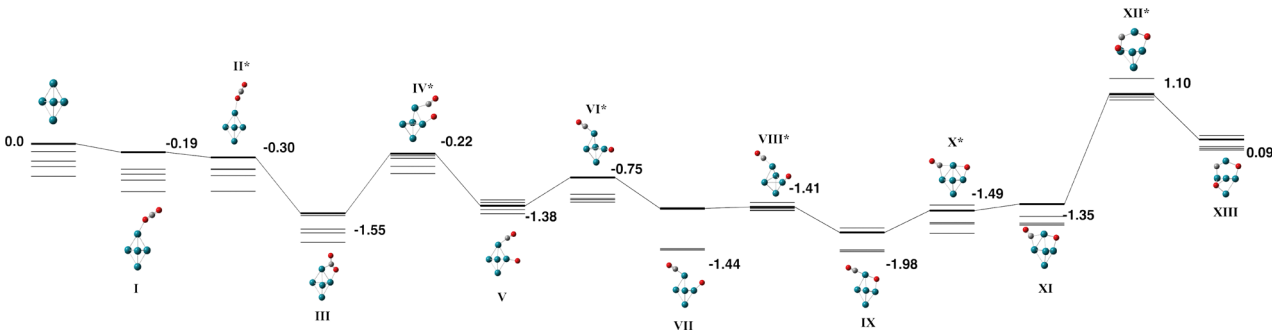

Fig. 8 Reaction pathway for trigonal bipyramidal $Rh_5 + CO_2$. The doublet multiplicity is shown in bold and the quartet – decet multiplicities are shown with thin lines. Relative energies shown are for the doublet surface and are given in eV, relative energies for all multiplicities are included in the SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

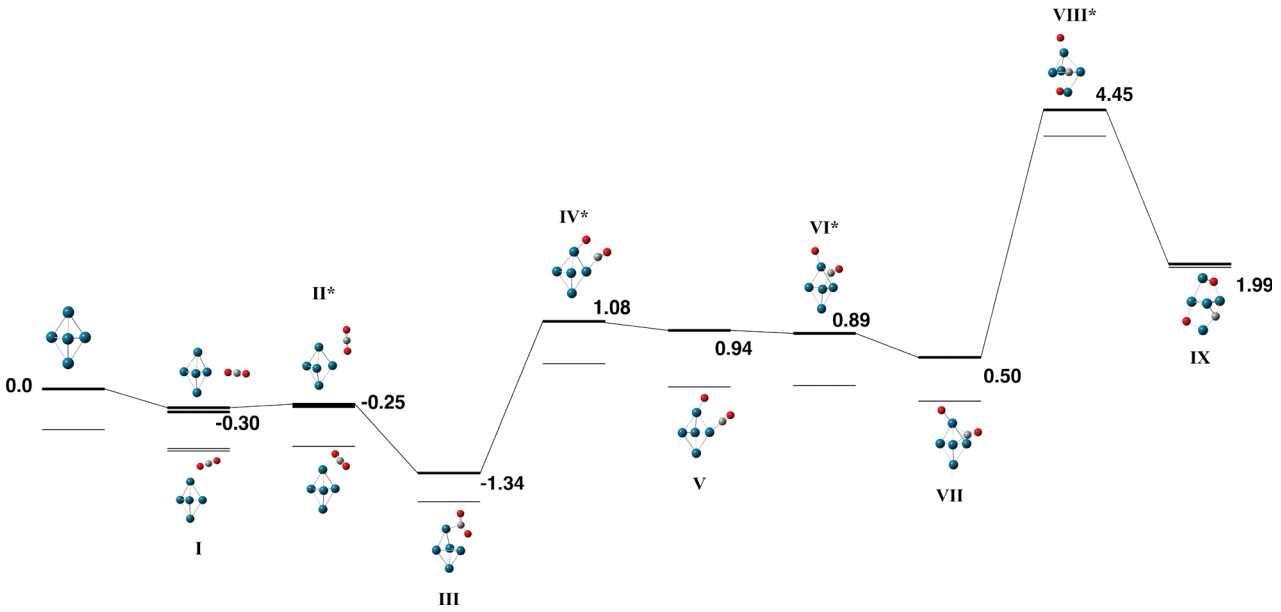

Fig. 9 Stationary points on the $Pd_5 + CO_2$ potential energy surface. The singlet multiplicity is shown in bold and the triplet multiplicity is shown with thin lines. Relative energies corresponding to singlet geometries are given in eV, all relative energies are included in SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

3.6. Pt_5

The 5d transition metal, platinum was also studied due to its intense interest and frequent use as a catalyst. The Pt_5 cluster is studied at the singlet – septet multiplicities. A variety of structures have been obtained for the Pt_5 cluster with significant differences in predicted energetics and several authors debating whether the cluster is planar or three-dimensional.[77] Sumer and Jellinek identified several Pt_5 low-energy isomers, including a planar edge-capped square, trigonal bipyramid, edge-capped tetrahedron, square pyramid, planar trapezoidal and planar bowtie. On inclusion of spin–orbit effects, only the first three structures remained.[60] Kleinman and coworkers also studied the effect of spin–orbit coupling identifying the planar edge-capped square, followed by square pyramid, trigonal bipyramid, trapezoidal and bowtie structures.[78] Wang *et al.* identified a quintet trigonal bipyramid as their gas-phase global minimum.[79] Sebetci predicts a edge-capped tetrahedron global minimum, followed by a distorted rhombus, a trigonal bipyramid, a bowtie and trapezoidal structures.[80] Grönbeck and Andreoni noted that the class of density functional had a strong effect on the predicted isomer, with a planar edge-capped square favoured by BLYP whereas a distorted square pyramid was predicted by LSDA.[81] Singh *et al.* and Kumar and Kawazoe both predict the planar edge-capped square as the global minimum,[82,83] but Cao identified a square pyramidal structure as the basis of their reactivity study.[84] MRSDCI calculations of Majumdar *et al.* identified a distorted tetragonal pyramid.[85]

3.6.1. Trigonal bipyramidal Pt_5. In our search on the singlet surface, we identified bent trapezoidal, twisted bowtie, trigonal bipyramid and square pyramid structures all within 0.05 eV. The trigonal bipyramid and square pyramid structures were chosen to react with CO_2 and are shown in Fig. 10 and 11 respectively. Geometric data for both pathways is tabulated in Tables S7 and S8. Somewhat analogously to the $Pd_5 + CO_2$ reaction, the lowest energy Pt_5CO_2 structure at −1.67 eV has a bent CO_2 molecule bound to a Pt(apex)–Pt(equatorial) bond. This minimum could convert *via* a structure with μ^2-bound CO and a μ^1-bound oxygen atom (structure Fig. 10-V) (−0.77 eV) to a low-energy (−1.50 eV) structure (Fig. 10-VII) with the CO molecule μ^1-bound to an equatorial platinum atom and the dissociated oxygen atom μ^1-bound to an apex platinum atom. From that structure, dissociating the CO molecule has a barrier of +3.85 eV, and the product is also higher than zero energy by +2.67 eV. This is consistent with the IR-MPD + DFT study of Green *et al.*, who did not observe CO_2 frequencies in their $[Pt_5CO_2]^-$, but did observe a band at 1980 cm^{-1}, which they assigned to η^1-bound CO.[52]

3.6.2. Square pyramidal Pt_5. The pathway for the reaction of CO_2 to the square pyramidal isomer of Pt_5 is shown in Fig. 11 and Table S8. The CO_2 molecule approaches the apex platinum atom before twisting over a triangular face of the cluster (structure Fig. 11-III, −0.84 eV). Breaking the first CO bond requires +0.25 and +0.14 eV on the singlet and triplet surfaces, but is exothermic by −0.09 and −0.53 eV for the triplet and septet surfaces respectively. The lowest energy structure, Fig. 11-V, at −0.88 eV, has the CO molecule μ^2-bound across a Pt(apex)–Pt(base) bond and the dissociated oxygen atom μ^1-bound to a platinum atom on the base of the cluster. Attempting to continue the pathway search to break the second CO bond resulted in the Pt_5 cluster deforming to a trigonal bipyramid, applying constraints to the Pt_5 coordinates resulted in structures with multiple imaginary frequencies. The fluxional nature of small transition metal complexes is well known, and it is not unexpected that these two Pt_5 clusters may interconvert.

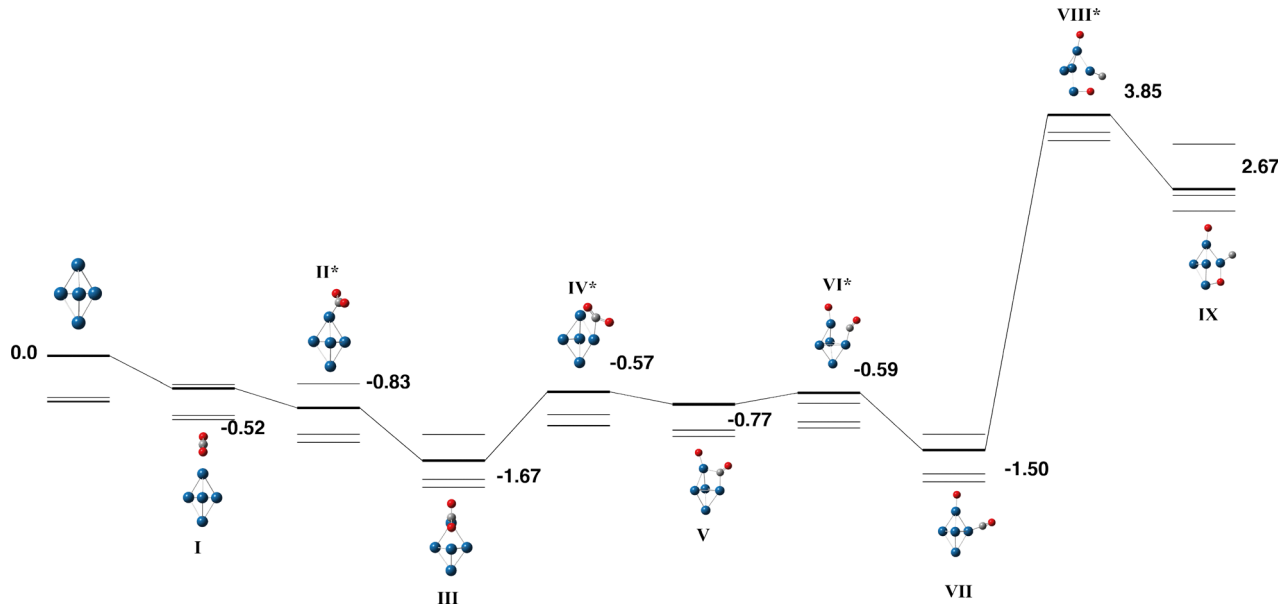

Fig. 10 Stationary points on the $Pt_5 + CO_2$ potential energy surface beginning with the trigonal bipyramidal Pt_5 isomer. The singlet multiplicity is shown in bold and the triplet – septet multiplicities are shown with thin lines. Relative energies for the singlet surface are given in eV, relative energies for all multiplicities are included in SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

3.7. Ag_5

The Ag_5 cluster is an odd-electron species and we consider the doublet – octet multiplicities. Atolabi *et al.* conducted one of several studies into the gas-phase Ag_5 structure and predicted that the doublet planar trapezoidal structure was 0.49 eV lower in energy than the doublet trigonal bipyramid structure.[86] The B3PW91 calculations of Hisayoshi and coworkers predicted a similar energy difference of 0.53 eV.[87] Fournier,[88] Wang and coworkers,[89] and Koutecký and coworkers all predict a C_{2v} doublet trapezoidal structure.[90] Fazli and coworkers also employed a trapezoidal Ag_5 cluster in their DFT study. Recent synthetic advances have produced a ligand-free trigonal bipyramid Ag_5 cluster,[91] which has been tested as an anti-tumour agent.[92] The same cluster was employed by Atolaibi *et al.* in their DFT-study with CO_2, CH_4, and H_2O molecules. While these authors considered the trapezoidal Ag_5 isomer for reaction with CH_4 and indicated that the trapezoidal isomer was more stable, they only calculated the trigonal bipyramid for their calculations with CO_2, showing weak interaction of the CO_2 molecule with both the apex and equatorial silver atoms.[93]

The trapezoidal Ag_5 structure was chosen as the basis for the reaction path search, and the resulting pathway for the reaction of $Ag_5 + CO_2$ is shown in Fig. 12 with geometric data tabulated in Table S9. The doublet surface only is presented as all higher

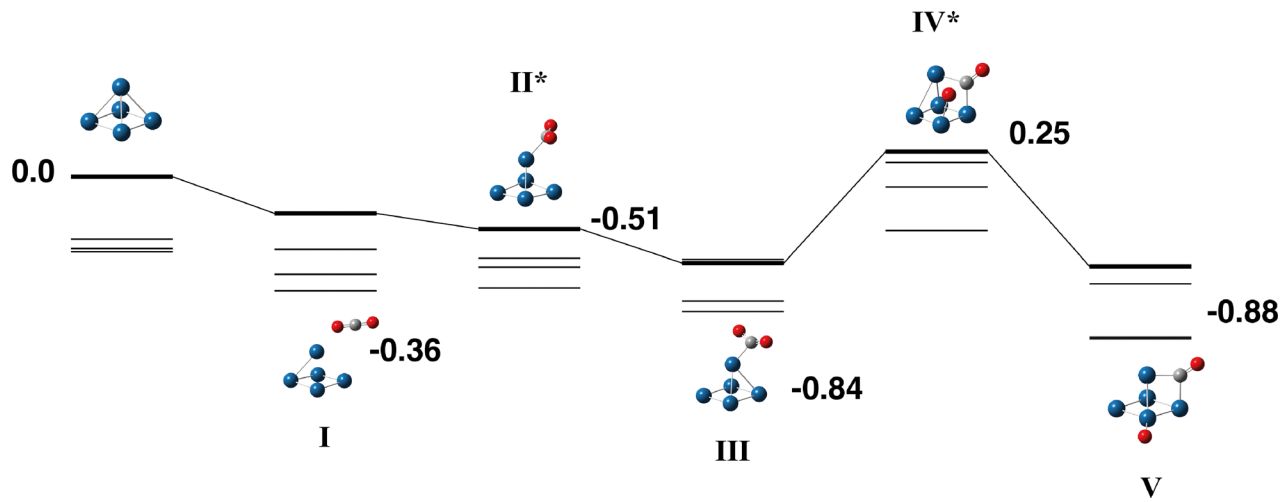

Fig. 11 Stationary points on the $Pt_5 + CO_2$ potential energy surface for the square pyramidal Pt_5 isomer. The singlet multiplicity is shown in bold and the triplet – septet multiplicities are shown with thin lines. Singlet relative energies are given in eV, other multiplicities are included in SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

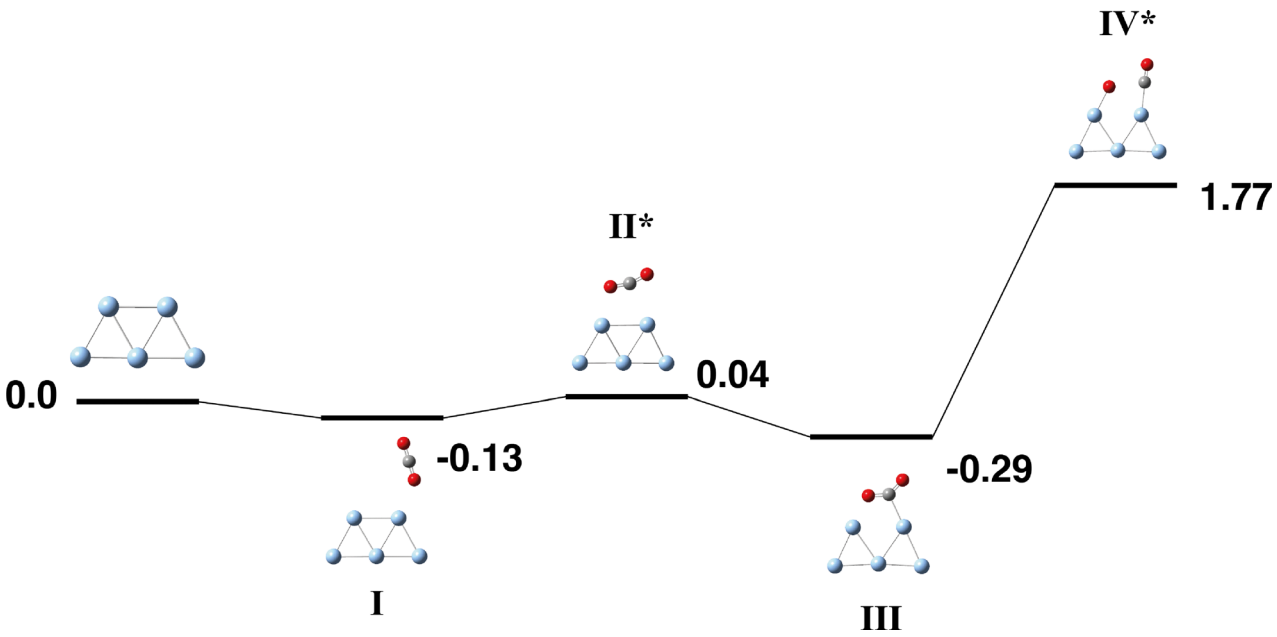

Fig. 12 Reaction pathway for the Ag_5 + CO_2 doublet potential energy surface. Other multiplicities are high in energy and are not shown. Relative energies are given in eV, and are included for higher multiplicities in the SI (xlsx). Metal atoms are shown in blue/green, oxygen atoms are shown in red and the carbon atom is shown in grey.

multiplicities were more than 1 eV higher in energy. CO_2 interacts only very weakly with the Ag_5 cluster, the capture species has the CO_2 molecule interacting with one of the atoms on the short edge of the trapezoid and is only −0.13 eV below zero energy. Only one other structure, Fig. 12-III was below zero energy, with an energy of −0.29 eV. Attempting to break the first CO_2 bond requires +1.77 eV. Searches were made for structures with the CO_2 molecule dissociated (*e.g.* CO + O, C + 2(O)), and an IRC was started from the transition state Fig. 12-IV, but in all these calculations the Ag_5 cluster did not remain intact and therefore we did not continue the reaction path.

3.8. Periodic trends

A previous computational study on the reaction of carbon monoxide, CO, with second-row transition metal timers showed that capture species were very similar in energy across the periodic table, with the exception of silver clusters, which bound CO only weakly.[31] This was observed similarly here for the M_5 clusters with CO_2, and is shown in Fig. 13. The consistent energy of the capture species can be rationalized in both cases that the capture species is defined as the first interaction of the two species and represents physisorption, where the chemical/electronic structure of the two species is barely perturbed. This is also consistent with the axial and equatorial, or apex and base capture species having similar interaction energies, where both were identified for the one M_5 cluster.

In the previous study of the interaction of M_3 + CO, there were only two other species of interest, the associative and dissociatively bound species.[31] In the case of CO_2 as a reactant, there are now three species of interest: the lowest energy bound OCO, the lowest energy O + CO and the lowest energy fully dissociated 2(O) + C structure. The energies of the associatively bound OCO species are relatively similar across the periodic

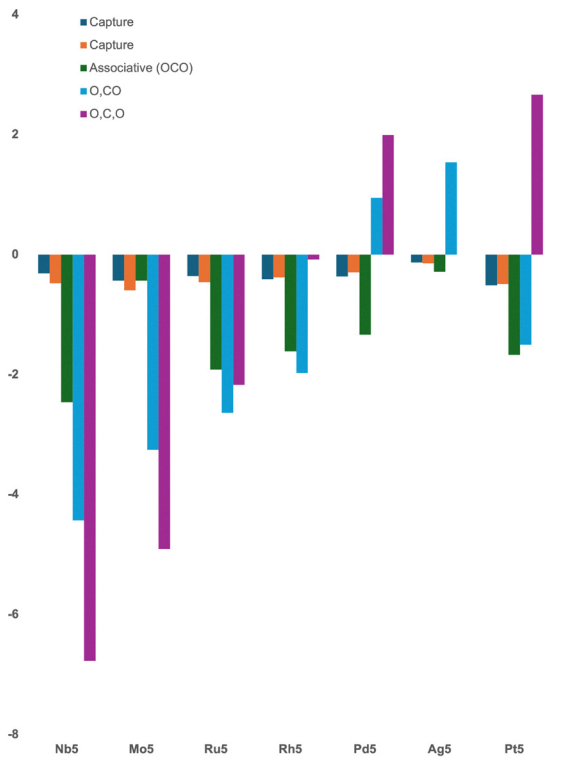

Fig. 13 Plot of the relative energies of capture, lowest energy associative (OCO), lowest energy partly dissociated (O,CO) and fully dissociative (O,C,O) structures of M_5 metal clusters in the lowest possible multiplicity.

table, ranging from −2.463 eV (Nb_5) to −1.340 eV (Pd_5), the two exceptions were Ag_5, which binds weakly, with a $Ag_5\cdots OCO$ binding energy of only −0.289 eV, and Mo_5, where CO_2 molecule dissociates *via* interaction with the axial atom of the cluster only. In structure Fig. 3-II, the C···O distance is 1.80 Å and the θ_{OCO} angle is 122°. The lowest energy associative structure for Mo_5CO_2 is therefore the capture species.

Similar trends are observed for the energies of the partly dissociative (O + CO) and fully dissociative (2(O) + C) structures. Both energies rise moving left to right across the second row of transition metals (Nb–Ag). The M_5O + CO energies become disfavourable (positive) for Pd_5, while the fully dissociated structures are disfavoured to the right of Rh_5 inclusive. The lone third row pentamer in this study, Pt_5, favourably dissociates CO_2 to CO + O, but the fully dissociative structure is disfavoured with respect to the zero energy, Pt_5 + CO_2.

Table 1 shows the calculated vibrational frequencies of CO_2 in the capture species for each M_5 cluster. The two bending frequencies, now non-degenerate, are red-shifted by ≈60 cm^{-1}, but no trend was observed for this reduction. The frequencies of the symmetric and asymmetric CO_2 stretches do not change significantly on interaction with the M_5 cluster. To attempt a diagnostic for the fate of CO_2, the energy of the CO_2 π_u orbital and the ΔE, with respect to the calculated value for free CO_2 (−0.03280 a.u.) is also shown in Table 1. For Nb_5 and Mo_5, a strong reduction in the orbital energy of ≈0.05 a.u. is observed. Both of these clusters dissociate CO_2 fully. All other M_5 clusters lowered the CO_2 π_u orbital energy by ≈0.02 a.u. and no distinction between clusters that possess a fully intact CO_2 in their minimum energy structure *vs.* clusters that partly dissociate CO_2 to O + CO was observed. Nevertheless, the orbital energy does indicate those clusters that fully dissociate CO_2 into atoms.

Table 2 shows the Hirshfeld charges on CO_2 molecule in the capture species and the first transition state for each of the reaction pathways. The q(CO_2) for the physisorbed capture species, as in the previously presented M_4 clusters,[39] is consistent and positive (≈0.1) for all M_5 clusters, except Ru_5 with CO_2 bound to the apex atom, suggesting that this species is actually a chemisorbed species. Considering the charge transfer observed in the first transition state, the same diagnostic holds for M_5 clusters also as the M_4 clusters; For the left-most three clusters, full CO_2 dissociation is thermodynamically possible, though for Ru_5, this would require surmounting a +0.27 eV barrier on the singlet surface, but a below zero energy barrier on higher multiplicity surfaces (see SI spreadsheet for details) having $q(CO_2) < -0.35\ e^-$. Right-most clusters, Pd_5 and Ag_5, do not dissociate either CO_2 bond and have low back-donation to CO_2, $< 0.2e^-$, and clusters that likely activate CO_2 without fully dissociating it, Rh_4, Pt_4, have intermediate $q(CO_2)$ values.

Table 2 Hirshfeld charge on CO_2 in capture species and first transition state for M_5CO_2 reaction pathways

System	Capture species $q(CO_2)$	TS 1 $q(CO_2)$
Nb_5	0.142	−0.418
Mo_5	0.118	−0.494
Ru_5 apex	−0.381	−0.3747
Ru_5 base	0.098	−0.434
Rh_5 sq. py.	0.094	−0.336
Rh_5 tri. bipy.	0.106	−0.314
Pd_5 a	0.086	0.037
Pd_5 b	0.088	0.008
Ag_5	0.043	−0.112
Pt_5 tri. bipy.	0.121	−0.247
Pt_5 sq. py.	0.095	−0.332

Fig. 14 shows the barrier heights (transition state energies) for two key transition states in each pathway, corresponding to the breaking of the first and second CO bond. The trends seen are broadly similar to the equivalent M_4 clusters.[39] The left-right divide previously seen for both barriers between Ru/Rh, is slightly less clear for the M_5 clusters, with both Ru_5 and Rh_5 being likely to break the first CO bond, but not the second. The softer barriers for Pt_5 compared to Pd_5 also suggest that the first CO bond would break on this cluster, leading to O + CO products on the cluster surface in this case also. Han and coworkers studied a range of mono and bimetallic metal surfaces and made similar conclusions, that activation energies for CO_2 dissociation increase left to right across the periodic table, with Au, Ag, and Pd based alloys having CO_2 dissociation barriers >1.50 eV.[18]

Table 1 CO_2 vibrational frequencies (ν_{CO_2}), key orbital energies and adsorption and interaction energies for M_5CO_2 capture species. Absolute energy of the CO_2 π_u orbital is −0.893 eV (−0.03280 a.u)

System	Bend 1	Bend 2	Symm stretch	Asym stretch	$E(M_{5,HOMO})$	$E(M_{5,LUMO})$	$E(\pi_u)$	$\Delta E(\pi_u)$	E_{ads}	E_{int}
			(cm^{-1})				(eV)			
CO_2	622	622	1283	2319			−0.893	0.0		
Nb_5	554	577	1277	2341	−4.332	−2.730	−2.351	−1.458	−0.483	−0.484
Mo_5	560	560	1279	2340	−4.388	−2.406	−2.383	−1.491	−0.438	−0.439
Ru_5 apex	521	557	1259	2323	−5.655	−2.817	−1.394	−0.502	−0.361	−0.370
Ru_5 base	462	585	1254	2326	−4.637	−2.808	−1.476	−0.583	−0.462	−0.466
Rh_5 sq. py.	546	571	1268	2325	−4.970	−3.471	−1.455	−0.563	−0.282	−0.452
Rh_5 tri. bipy.	528	571	1266	2328	−5.028	−3.226	−1.446	−0.554	−0.188	−0.499
Pd_5 a	583	587	1281	2326	−5.304	−4.239	−1.512	−0.620	−0.301	−0.346
Pd_5 b	581	587	1278	2325	−5.373	−4.252	−1.609	−0.716	−0.368	−0.369
Ag_5	593	605	1281	2314	−5.074	−2.813	−1.379	−0.487	−0.133	−0.133
Pt_5 tri. bipy.	552	564	1277	2336	−5.606	−4.416	−1.742	−0.849	−0.516	−0.547
Pt_5 sq. py.	551	570	1261	2310	−5.466	−4.272	−1.536	−0.643	−0.360	−0.377

Fig. 14 Plot of the relative energies of barriers to dissociation of the first (blue) and second (orange) C···O bonds for M_5CO_2 reaction pathways on the lowest multiplicity (singlet or doublet) surface.

3.9. M_4 *vs.* M_5 clusters

Each reaction path presented here and for the equivalent M_4 clusters[39] may be distilled into a profile containing six species; the capture species, lowest energy M_nCO_2, $TS_{O\cdots CO}$, lowest energy $M_nO{\cdot}CO$, $TS_{C\cdots O}$ and lowest energy $M_nO{\cdot}C{\cdot}O$. These abbreviated reaction profiles are shown in Fig. S1–S7. Reactions on M_5 surfaces are typically more exothermic than the equivalent M_4 clusters. Excluding palladium, increasing the cluster size lowers the energy of the first barrier by $\approx$0.5 eV. This is consistent with the B3LYP results for Zr_4 and Zr_5 clusters computed by Ghanty and coworkers.[33] The height of the second barrier on adding the fifth metal atom is less consistent, lowering for Nb, Mo and Rh, but rising for the other metals. This is consistent with the left hand metals (Nb, Mo) dissociating CO_2 fully, right side metals (Pd, Ag, Pt) keeping CO_2 intact, and central metals (Ru, Rh) showing intermediate behaviour, which is therefore the most tunable by alteration of the cluster size.

4. Conclusions

We have explored the chemistry of CO_2 reaction on a series of M_5 transition metal clusters, by deriving reaction pathways using Density Functional Theory. Rh_5 and Pt_5 clusters had multiple competitive ground state geometries, and reaction paths were derived for each, noting that the trigonal bipyramid and square pyramidal geometries may interconvert.

Moving from left to right across the M_5 series, the energies of the capture species remained relatively constant as expected for the minimally interacting, physisorbed species. The energies of the lowest energy associatively-bound species with CO_2 fully intact also fell within a narrow range of −2.463 to −1.340 eV, generally rising from Nb_5 to Ag_5. The energetics of the partly (O + CO), and fully (O + C + O) dissociated species define the outcome of the reaction, with both rising strongly as one moves to the right of the periodic table. The partly dissociated species was found to be disfavoured with respect to the separated M_5 +CO_2 reactants for Pd_5, Ag_5 and Pt_5, while the fully dissociated species was disfavoured from Rh_5 and could not be located for Ag_5.

The energy of the CO_2 π_u orbital was found to distinguish those structures that dissociate CO_2 fully (Nb_5 and Mo_5) from those that do not, but could not resolve clusters that partly dissociate CO_2 from those that leave CO_2 fully intact. The magnitude of charge transfer to the CO_2 fragment was found to be diagnostic with strong (>0.35e), weak (<0.2e) and intermediate values indicating full CO_2 dissociation, no dissociation, and activation respectively.

Author contributions

NTTY, AN, YR, MR, IN: investigation, writing – original draft MAA: conceptualization of this study, methodology, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: geometric parameters (pdf), structures (xyz) and energies, vibrational data (xlsx) for all pathways. See DOI: https://doi.org/10.1039/d5cp03418c.

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