Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Catalysis at the Sub-Nanoscale: Complex CO Oxidation Chemistry on a Few Au Atoms

Nima Nikbin[a], Natalie Austin[b], Dionisios G. Vlachos[a], Michail Stamatakis[c] and Giannis Mpourmpakis[b]

[a] Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, USA

[b] Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, USA

[c] Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

Supporting Information

KMC Methodology Details

The Graph-Theoretical KMC framework was employed[1,2] as implemented in the software package *Zacros*.[3] The simulation requires a lattice structure, an energetics model and a reaction mechanism as input. These components are outlined below for each of the Au nanoclusters considered.

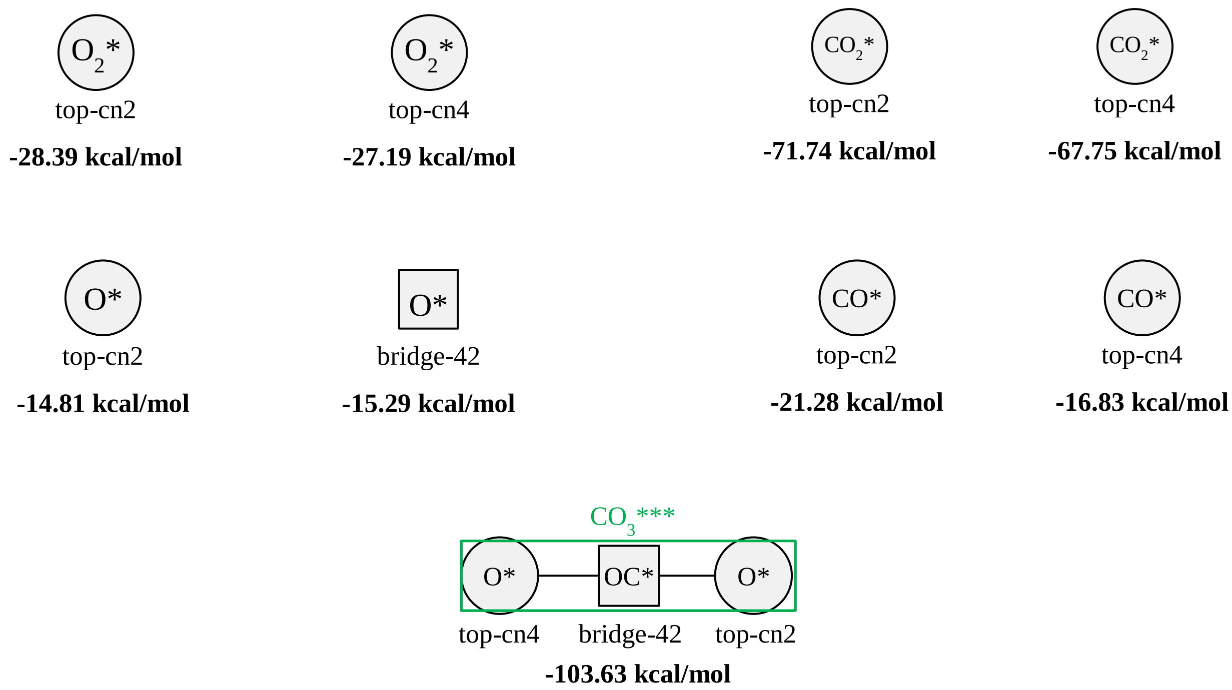
Au_6^- Nanocluster

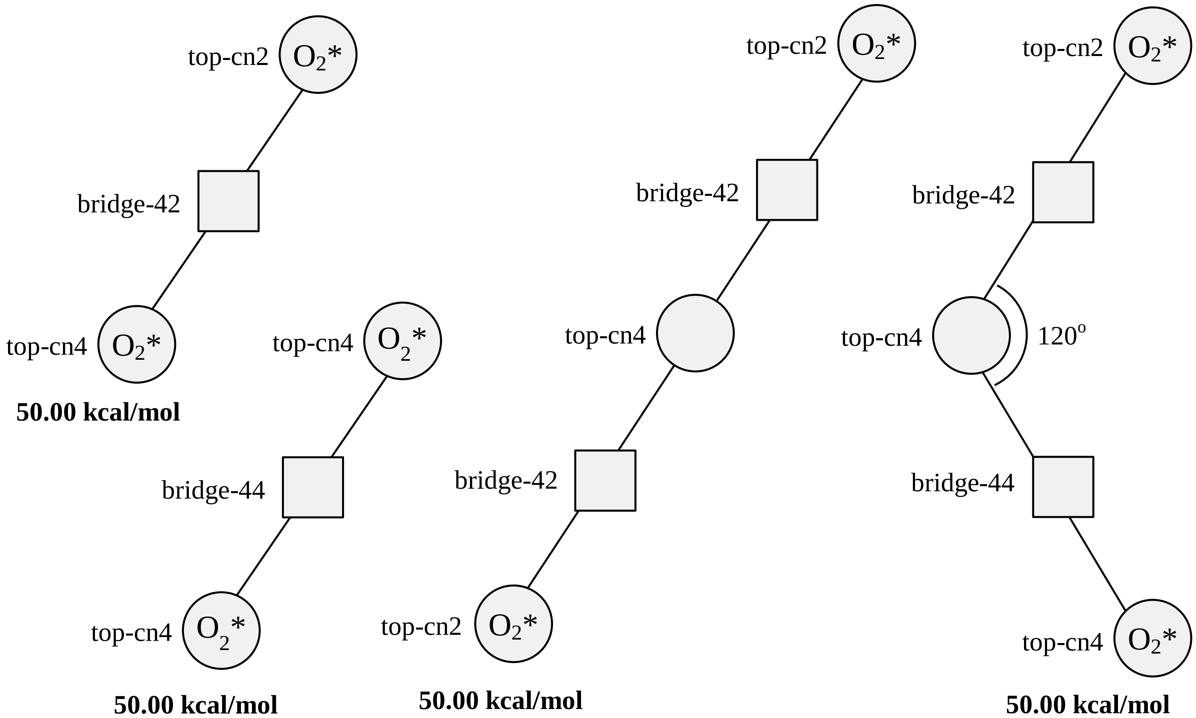
Lattice Structure

For Au_6^- both bridge and top sites are considered (Figure 1a in main manuscript). The different types of these sites are shown in the figure on the right. Thus, the corner top sites have coordination number 2 (top-cn2) whereas the edge top sites have coordination number 4 (top-cn4). There are two different types of bridge sites as well, connecting two top-cn4 sites (bridge-44), or a top-cn2 with a top-cn4 site (bridge-42). The former are only included for completeness as the molecular species investigated do not bind therein.

Lattice Energetics Model

Single- and two-body contributions to the total energy of the lattice were taken into account. The corresponding patterns are shown below. The *ab-initio* calculations showed that if an O_2 molecule is bound to the nanocluster, a second O_2 molecule cannot bind. This behavior was modelled by including the four pairwise patterns in the bottom of the figure whose energetic contributions were arbitrarily set to a high value (50 kcal/mol).

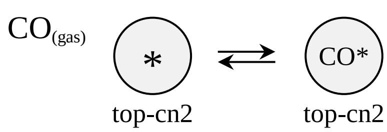




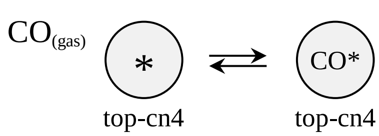
Reaction Mechanism

The reaction mechanism consists of 12 reversible steps (24 elementary steps total) which are shown below. Reported are also the kinetic parameters: prefactor of the forward step, ratio of the forward versus reverse prefactors, as well as activation energy and reaction energy at the zero coverage limit. The latter is computed from the lattice energetics model.

<u>CO adsorption</u>

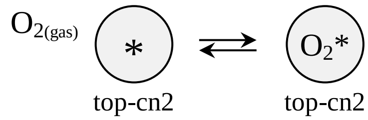


$\mathbf{A_{fwd} = 7.872{\cdot}10^{7}\ bar^{-1}{\cdot}s^{-1},\ A_{fwd}/A_{rev} = 7.361{\cdot}10^{-8}\ bar^{-1},\ E^{0}_{a,fwd} = 0.00\ kcal/mol,\ \Delta E^{0}_{rxn} = -21.28\ kcal/mol}$

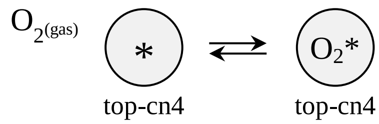


$\mathbf{A_{fwd} = 7.872{\cdot}10^{7}\ bar^{-1}{\cdot}s^{-1},\ A_{fwd}/A_{rev} = 6.606{\cdot}10^{-8}\ bar^{-1},\ E^{0}_{a,fwd} = 0.00\ kcal/mol,\ \Delta E^{0}_{rxn} = -16.83\ kcal/mol}$

O_2 adsorption

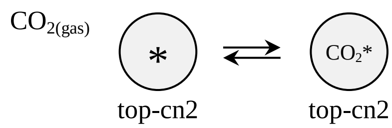


A_{fwd} = 7.365·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 7.361·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -28.39 kcal/mol

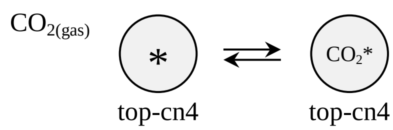


A_{fwd} = 5.597·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.715·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -27.19 kcal/mol

CO_2 adsorption

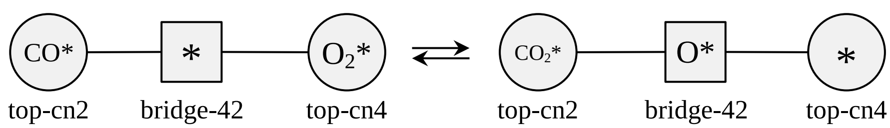


A_{fwd} = 6.280·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 1.256·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -15.01 kcal/mol



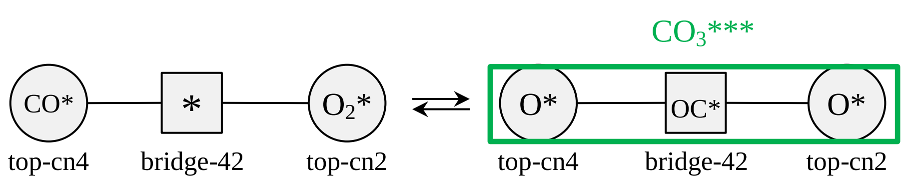
A_{fwd} = 6.280·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 1.994·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -11.02 kcal/mol

CO oxidation by O_2



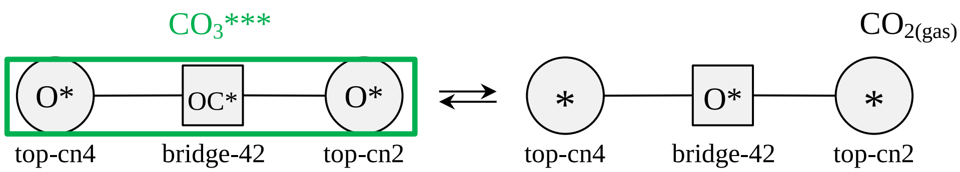
A_{fwd} = 3.458·10^{10} s^{-1}, A_{fwd}/A_{rev} = 2.294·10^{-4}, $E^0_{a,fwd}$ = 11.40 kcal/mol, ΔE^0_{rxn} = -38.57 kcal/mol

CO_3 formation



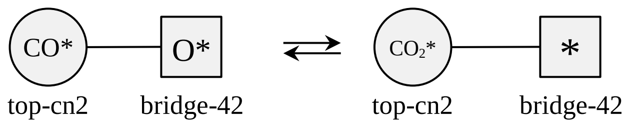
$A_{fwd} = 1.612 \cdot 10^{10}$ s^{-1}, $A_{fwd}/A_{rev} = 1.054 \cdot 10^{-4}$, $E^0_{a,fwd} = 16.50$ kcal/mol, $\Delta E^0_{rxn} = -58.41$ kcal/mol

CO$_3$ decomposition

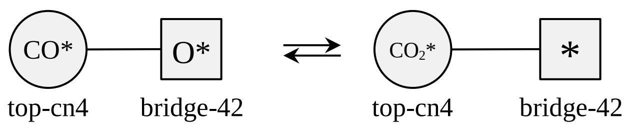


$A_{fwd} = 9.891 \cdot 10^{13}$ s^{-1}, $A_{fwd}/A_{rev} = 9.854 \cdot 10^{+8}$ bar, $E^0_{a,fwd} = 32.76$ kcal/mol, $\Delta E^0_{rxn} = 32.09$ kcal/mol

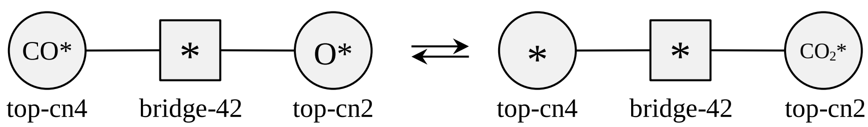
CO oxidation by O



$A_{fwd} = 5.830 \cdot 10^{7}$ s^{-1}, $A_{fwd}/A_{rev} = 8.603 \cdot 10^{-8}$, $E^0_{a,fwd} = 18.27$ kcal/mol, $\Delta E^0_{rxn} = -35.17$ kcal/mol



$A_{fwd} = 1.318 \cdot 10^{12}$ s^{-1}, $A_{fwd}/A_{rev} = 1.521 \cdot 10^{-2}$, $E^0_{a,fwd} = 12.35$ kcal/mol, $\Delta E^0_{rxn} = -35.63$ kcal/mol



$A_{fwd} = 2.412 \cdot 10^{11}$ s^{-1}, $A_{fwd}/A_{rev} = 2.784 \cdot 10^{-3}$, $E^0_{a,fwd} = 11.86$ kcal/mol, $\Delta E^0_{rxn} = -36.11$ kcal/mol

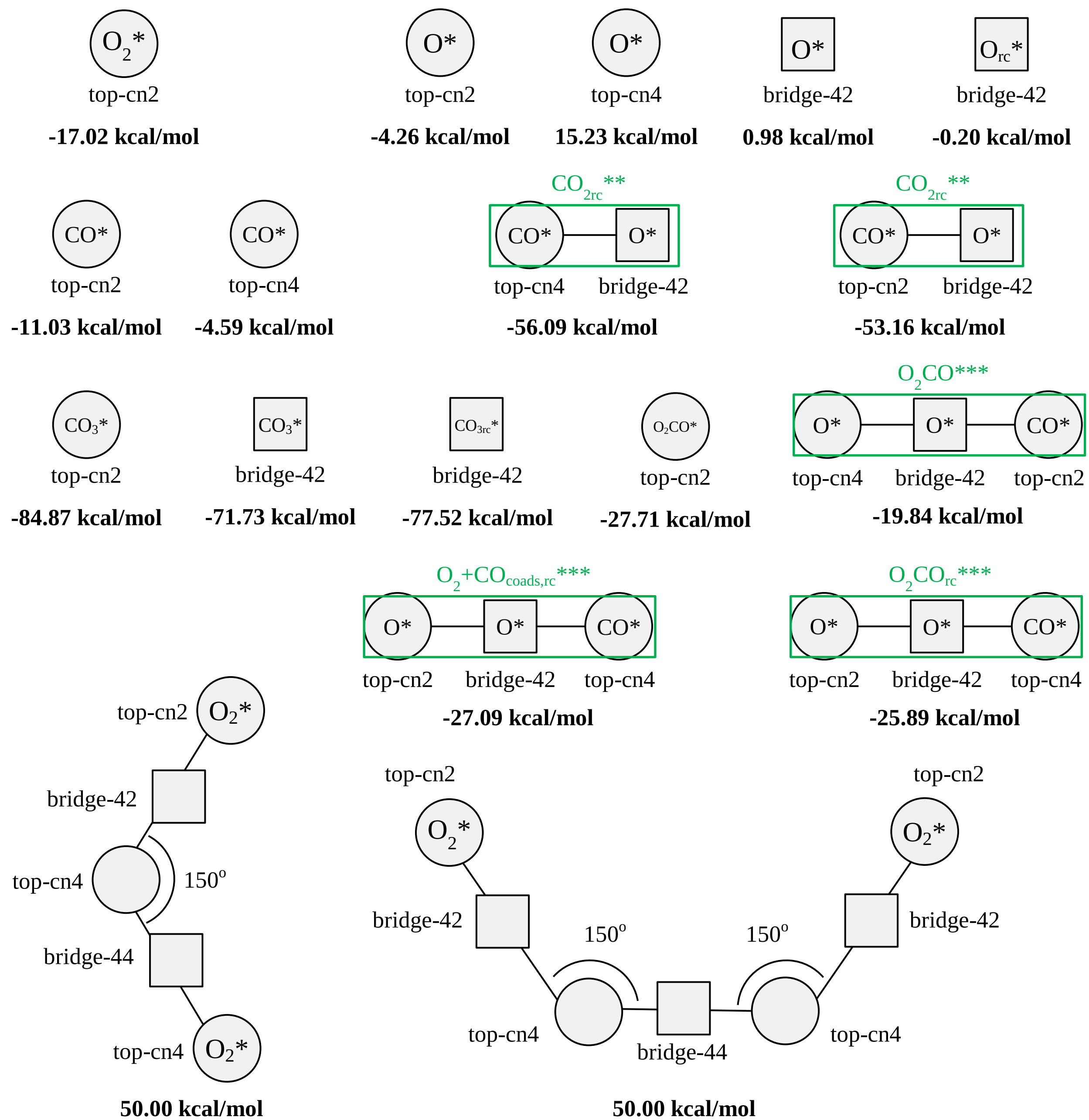
Au_8^- Nanocluster

Lattice Structure

Similarly to the case of Au_6^-, Au_8^- has four different site types (Figure 1b in main manuscript), two top and two bridge as shown in the figure on the right. Thus, there are top sites with coordination numbers 2 (top-cn2) and 4 (top-cn4), and bridge that connect two top-cn4 sites (bridge-44), or a top-cn2 with a top-cn4 site (bridge-42). The former are only included for completeness as the molecular species investigated do not bind therein.

Lattice Energetics Model

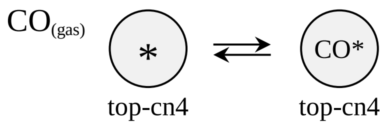
Single- and two-body contributions to the total energy of the lattice were taken into account. The corresponding patterns are shown below. The *ab-initio* calculations showed that if an O_2 molecule is bound to the nanocluster, a second O_2 molecule cannot bind. This behavior was modelled by including the pairwise additive O_2-O_2 patterns whose energetic contributions were arbitrarily set to a high value (50 kcal/mol). Moreover, this cluster exhibits reconstruction for specific reaction pathways, which is implicitly taken into account in the binding energies of species. Thus, the subscript "rc" denotes species bound on the reconstructed structure. Finally, the gas species energies are 2.90 kcal/mol for CO, 2.07 kcal/mol for O_2 and -58.99 kcal/mol for CO_2. All energies incorporate zero point energy corrections.



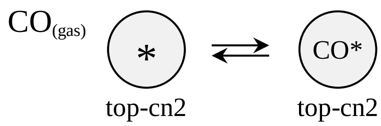
Reaction Mechanism

The reaction mechanism consists of 22 reversible steps (44 elementary steps total) which are shown below. Reported are also the kinetic parameters: prefactor of the forward step, ratio of the forward versus reverse prefactors, as well as activation energy and reaction energy at the zero coverage limit. The latter is computed from the lattice energetics model.

CO adsorption

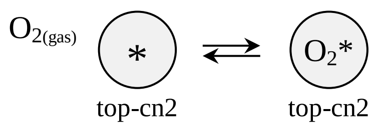


A_{fwd} = 7.871·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 4.028·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -7.49 kcal/mol



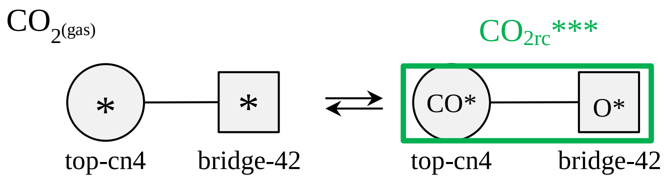
A_{fwd} = 7.871·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.404·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -13.93 kcal/mol

O_2 adsorption

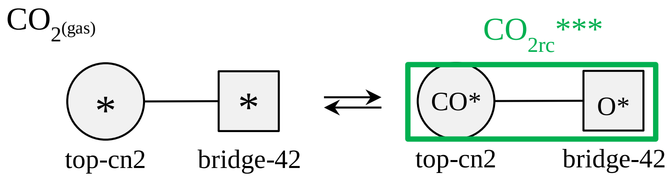


A_{fwd} = 7.365·10^7 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 6.286·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -19.08 kcal/mol

CO_2 adsorption

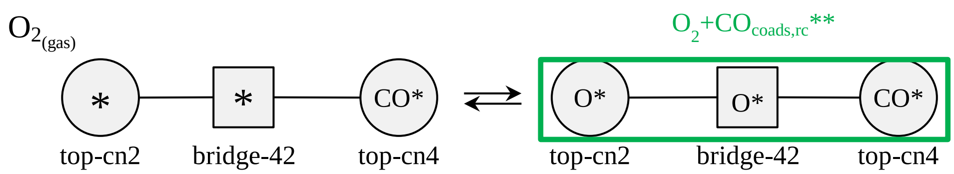


A_{fwd} = 1.947·10^6 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.368·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 7.30 kcal/mol, ΔE^0_{rxn} = 2.90 kcal/mol

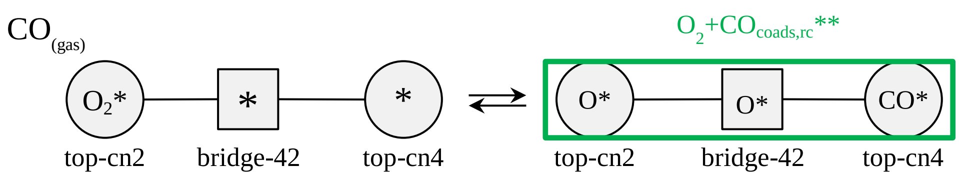


$A_{fwd} = 3.243 \cdot 10^5$ bar$^{-1} \cdot$s^{-1}, $A_{fwd}/A_{rev} = 2.869 \cdot 10^{-8}$ bar^{-1}, $E^0_{a,fwd} = 14.41$ kcal/mol, $\Delta E^0_{rxn} = 5.83$ kcal/mol

$CO+O_2$ coadsorption & reconstruction

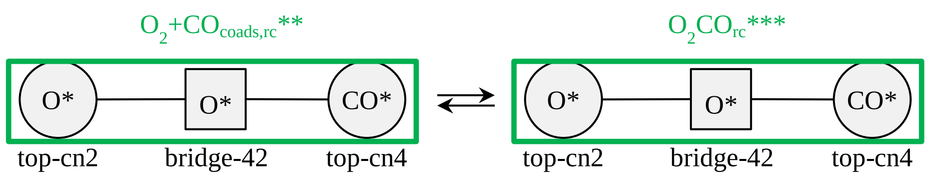


$A_{fwd} = 2.033 \cdot 10^8$ bar$^{-1} \cdot$s^{-1}, $A_{fwd}/A_{rev} = 3.912 \cdot 10^{-9}$ bar^{-1}, $E^0_{a,fwd} = 0.00$ kcal/mol, $\Delta E^0_{rxn} = -24.57$ kcal/mol



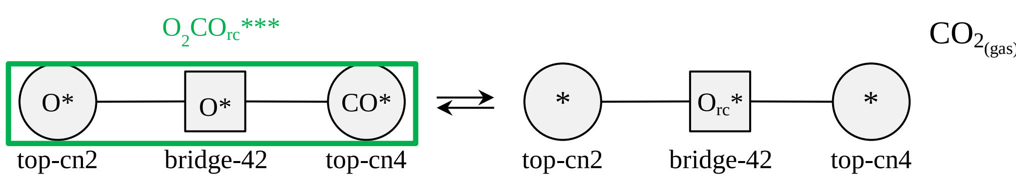
$A_{fwd} = 2.173 \cdot 10^8$ bar$^{-1} \cdot$s^{-1}, $A_{fwd}/A_{rev} = 9.269 \cdot 10^{-9}$ bar^{-1}, $E^0_{a,fwd} = 0.00$ kcal/mol, $\Delta E^0_{rxn} = -12.97$ kcal/mol

O_2CO formation (reconstructed)



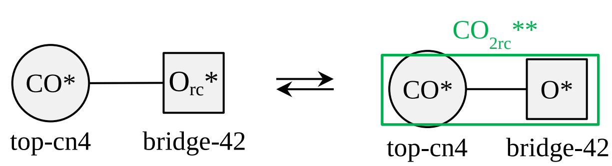
$A_{fwd} = 3.338 \cdot 10^8$ s^{-1}, $A_{fwd}/A_{rev} = 1.000$, $E^0_{a,fwd} = 2.63$ kcal/mol, $\Delta E^0_{rxn} = 1.20$ kcal/mol

O_2CO decomposition (reconstructed)

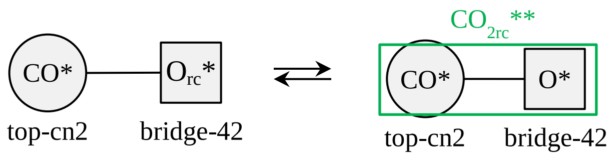


$A_{fwd} = 5.403 \cdot 10^{12}$ s^{-1}, $A_{fwd}/A_{rev} = 2.055 \cdot 10^7$ bar, $E^0_{a,fwd} = 11.35$ kcal/mol, $\Delta E^0_{rxn} = -33.30$ kcal/mol

CO oxidation by O

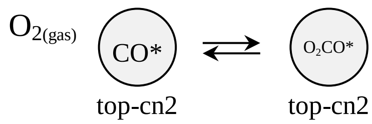


$A_{fwd} = 5.209 \cdot 10^{12}$ s^{-1}, $A_{fwd}/A_{rev} = 1.901 \cdot 10^{-1}$, $E^0_{a,fwd} = 0.00$ kcal/mol, $\Delta E^0_{rxn} = -51.30$ kcal/mol



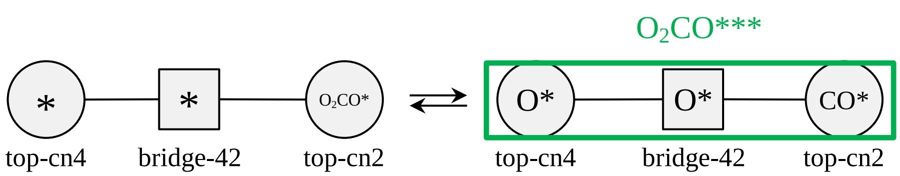
A_{fwd} = 5.209·10^{12} s^{-1}, A_{fwd}/A_{rev} = 1.917·10^{-1}, $E^{0}_{a,fwd}$ = 0.00 kcal/mol, ΔE^{0}_{rxn} = -41.93 kcal/mol

O_2CO formation



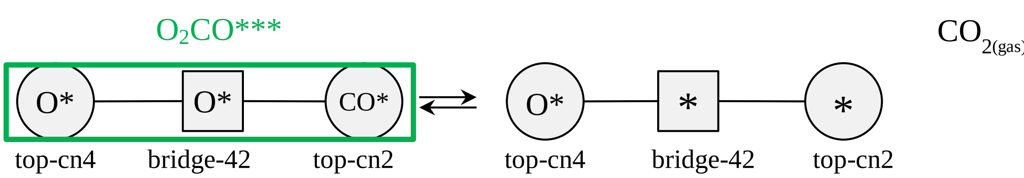
A_{fwd} = 7.365·10^{7} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 1.448·10^{-7} bar^{-1}, $E^{0}_{a,fwd}$ = 0.00 kcal/mol, ΔE^{0}_{rxn} = -18.74 kcal/mol

O_2CO tilting

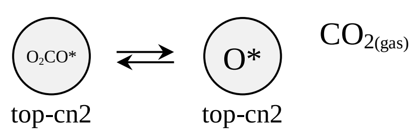


A_{fwd} = 1.405·10^{11} s^{-1}, A_{fwd}/A_{rev} = 2.701·10^{-2}, $E^{0}_{a,fwd}$ = 9.67 kcal/mol, ΔE^{0}_{rxn} = 7.87 kcal/mol

O_2CO decomposition

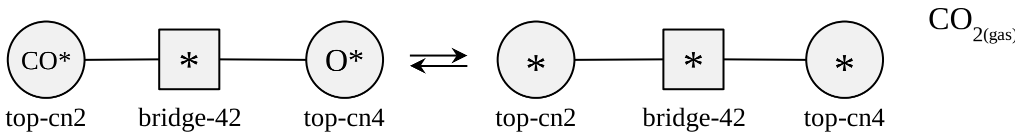


A_{fwd} = 8.468·10^{12} s^{-1}, A_{fwd}/A_{rev} = 4.799·10^{7} bar, $E^{0}_{a,fwd}$ = 9.45 kcal/mol, ΔE^{0}_{rxn} = -23.92 kcal/mol

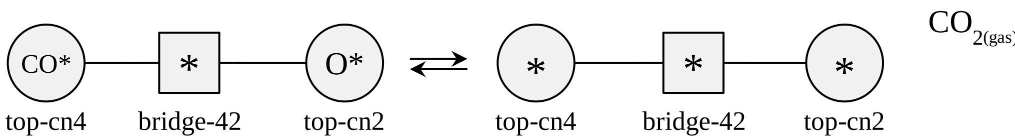


A_{fwd} = 1.400·10^{12} s^{-1}, A_{fwd}/A_{rev} = 1.495·10^{6} bar, $E^{0}_{a,fwd}$ = 14.81 kcal/mol, ΔE^{0}_{rxn} = -35.54 kcal/mol

CO oxidation by O

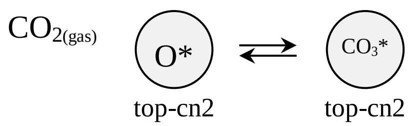


$A_{fwd} = 7.159 \cdot 10^{10}\ s^{-1}$, $A_{fwd}/A_{rev} = 2.861 \cdot 10^{6}$ bar, $E^{0}_{a,fwd} = 3.92$ kcal/mol, $\Delta E^{0}_{rxn} = -63.19$ kcal/mol

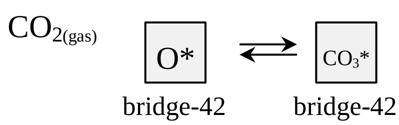


$A_{fwd} = 6.397 \cdot 10^{11}\ s^{-1}$, $A_{fwd}/A_{rev} = 2.096 \cdot 10^{6}$ bar, $E^{0}_{a,fwd} = 10.06$ kcal/mol, $\Delta E^{0}_{rxn} = -50.14$ kcal/mol

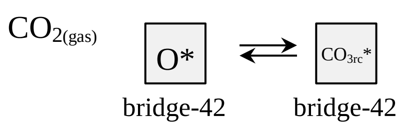
CO_3 formation



$A_{fwd} = 3.180 \cdot 10^{6}\ bar^{-1} \cdot s^{-1}$, $A_{fwd}/A_{rev} = 2.659 \cdot 10^{-6}\ bar^{-1}$, $E^{0}_{a,fwd} = 0.08$ kcal/mol, $\Delta E^{0}_{rxn} = -21.62$ kcal/mol



$A_{fwd} = 1.433 \cdot 10^{6}\ bar^{-1} \cdot s^{-1}$, $A_{fwd}/A_{rev} = 3.621 \cdot 10^{-8}\ bar^{-1}$, $E^{0}_{a,fwd} = 0.36$ kcal/mol, $\Delta E^{0}_{rxn} = -13.72$ kcal/mol



$A_{fwd} = 1.266 \cdot 10^{6}\ bar^{-1} \cdot s^{-1}$, $A_{fwd}/A_{rev} = 7.080 \cdot 10^{-7}\ bar^{-1}$, $E^{0}_{a,fwd} = 1.54$ kcal/mol, $\Delta E^{0}_{rxn} = -18.33$ kcal/mol

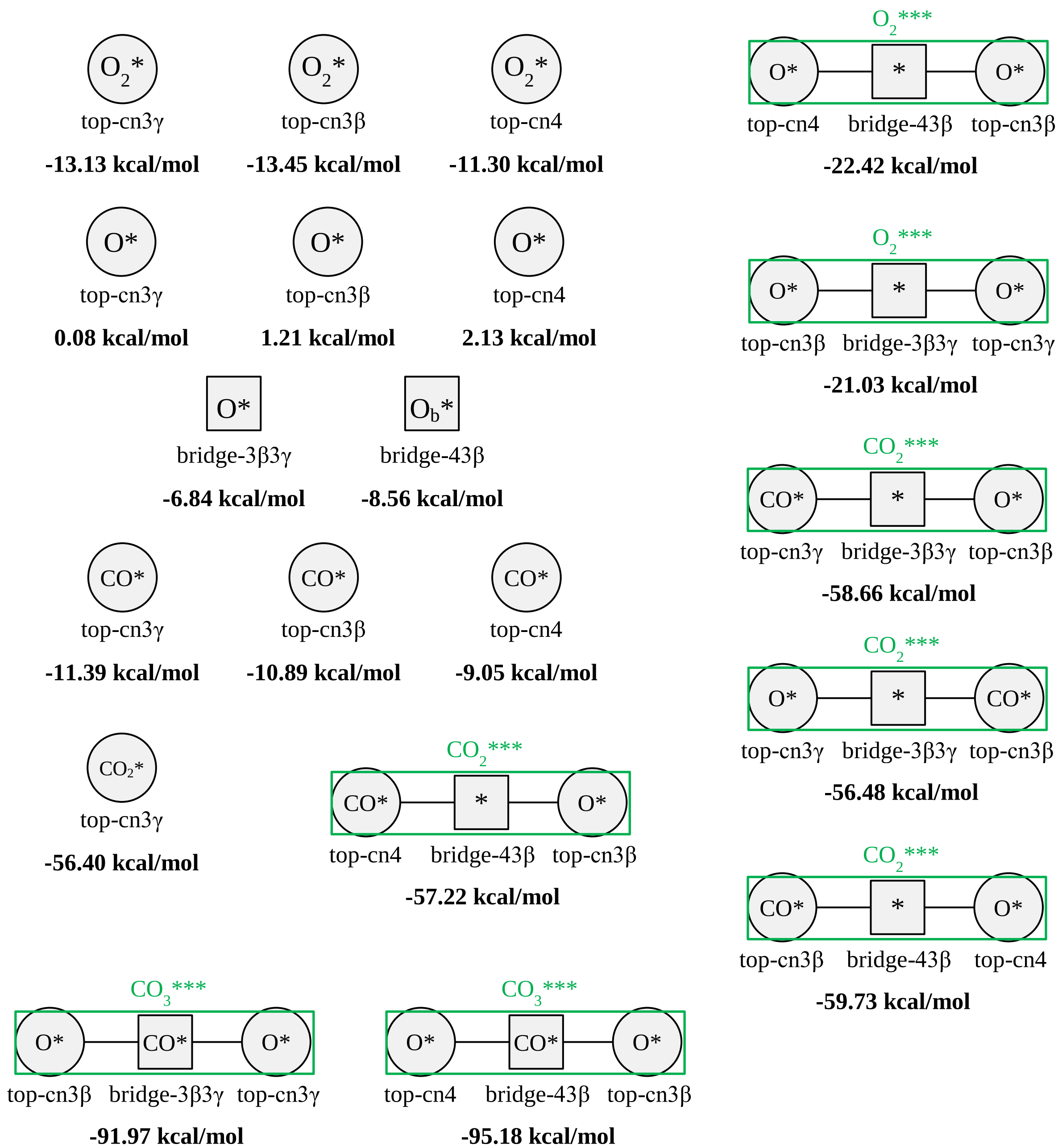
Au_{10}^{-} Nanocluster

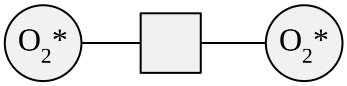
Lattice Structure

The Au_{10}^{-} cluster (Figure 1c, in main manuscript) has 4 different top site types: one with coordination number 4 (top-cn4), two with coordination numbers equal to 3 (top-cn3β, top-cn3γ), and one with coordination number 6 (top-cn6). Moreover, there are 6 bridge site types (bridge-43β, bridge-46, bridge-3β3γ, bridge-3β6, bridge-3γ6, bridge-66). The internal sites (top-cn6, bridge-46, bridge-3β6, bridge-3γ6, bridge-66) are only included for completeness as the molecular species investigated do not bind therein.

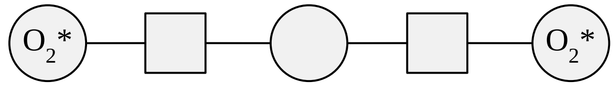
Lattice Energetics Model

Single- and two-body contributions to the total energy of the lattice were taken into account. The corresponding patterns are shown below. The *ab-initio* calculations showed that if an O_2 molecule is bound to the nanocluster, a second O_2 molecule cannot bind. This behavior was modelled by including the pairwise additive O_2-O_2 patterns whose energetic contributions were arbitrarily set to a high value (50 kcal/mol). Finally, the gas species energies are 2.90 kcal/mol for CO, 2.07 kcal/mol for O_2 and -56.97 kcal/mol for CO_2. All energies incorporate zero point energy corrections.

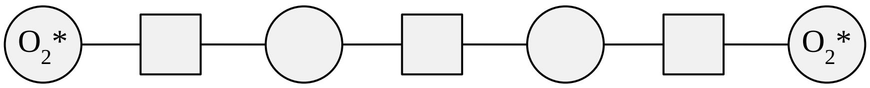




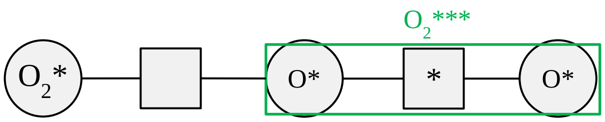
50.00 kcal/mol



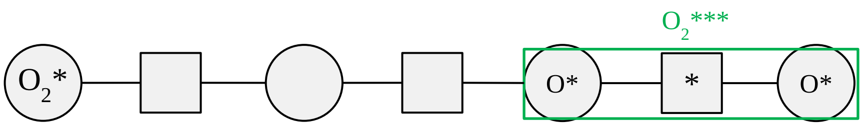
50.00 kcal/mol



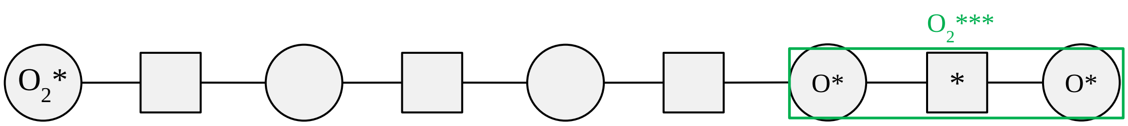
50.00 kcal/mol



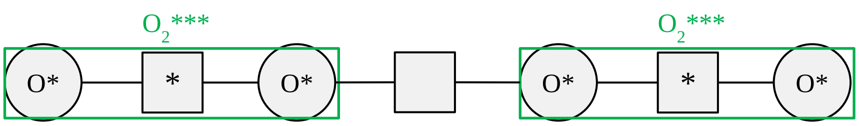
50.00 kcal/mol



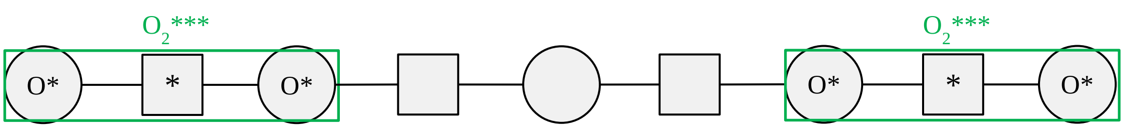
50.00 kcal/mol



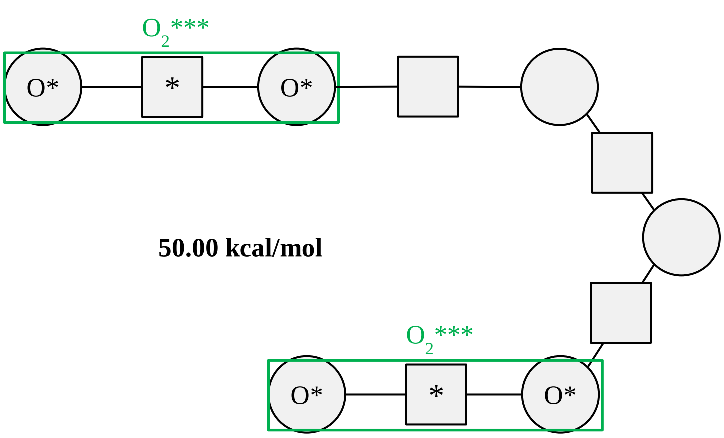
50.00 kcal/mol



50.00 kcal/mol



50.00 kcal/mol

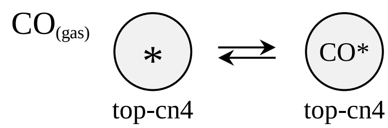


50.00 kcal/mol

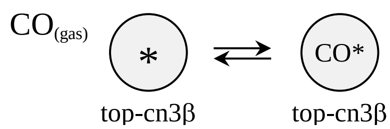
Reaction Mechanism

The reaction mechanism consists of 45 reversible steps (90 elementary steps total) which are shown below. Reported are also the kinetic parameters: prefactor of the forward step, ratio of the forward versus reverse prefactors, as well as activation energy and reaction energy at the zero coverage limit. The latter is computed from the lattice energetics model.

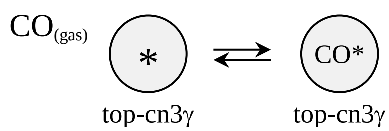
CO adsorption



$\mathbf{A_{fwd} = 7.871 \cdot 10^{7}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 2.181 \cdot 10^{-7}\ bar^{-1},\ E^{0}_{a,fwd} = 0.00\ kcal/mol,\ \Delta E^{0}_{rxn} = -11.95\ kcal/mol}$

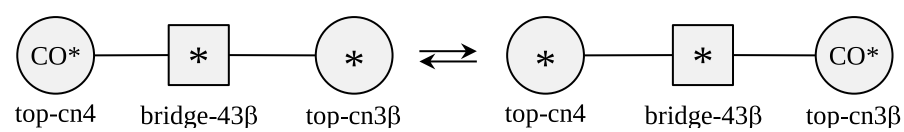


$\mathbf{A_{fwd} = 7.871 \cdot 10^{7}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 3.081 \cdot 10^{-7}\ bar^{-1},\ E^{0}_{a,fwd} = 0.00\ kcal/mol,\ \Delta E^{0}_{rxn} = -13.79\ kcal/mol}$

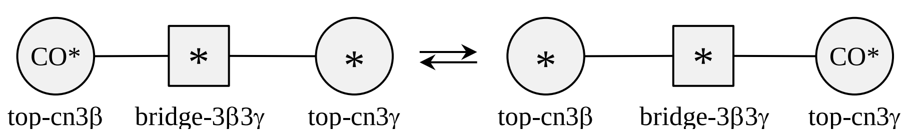


$\mathbf{A_{fwd} = 7.871 \cdot 10^{7}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 6.832 \cdot 10^{-7}\ bar^{-1},\ E^{0}_{a,fwd} = 0.00\ kcal/mol,\ \Delta E^{0}_{rxn} = -14.29\ kcal/mol}$

CO diffusion

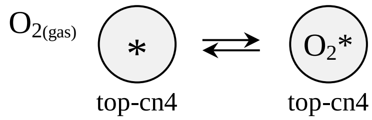


$\mathbf{A_{fwd} = 1.282 \cdot 10^{12}\ s^{-1},\ A_{fwd}/A_{rev} = 1.413,\ E^{0}_{a,fwd} = 6.19\ kcal/mol,\ \Delta E^{0}_{rxn} = -1.84\ kcal/mol}$

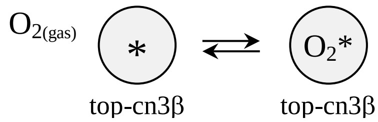


$\mathbf{A_{fwd} = 9.496 \cdot 10^{11}\ s^{-1},\ A_{fwd}/A_{rev} = 2.217,\ E^{0}_{a,fwd} = 2.13\ kcal/mol,\ \Delta E^{0}_{rxn} = -0.50\ kcal/mol}$

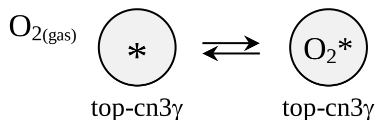
O_2 adsorption



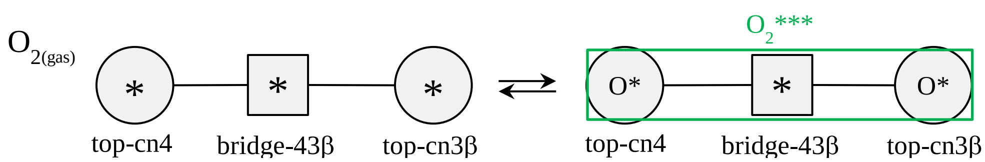
A_{fwd} = 7.365·10^{7} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 5.689·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -13.37 kcal/mol



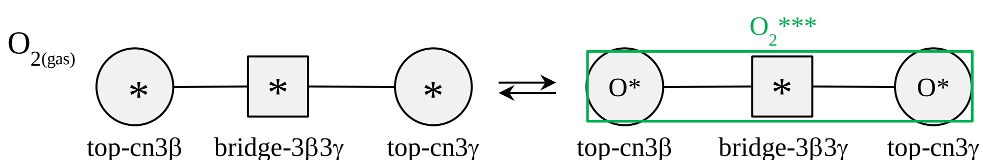
A_{fwd} = 7.365·10^{7} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 1.425·10^{-6} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -15.52 kcal/mol



A_{fwd} = 7.365·10^{7} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 6.029·10^{-7} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -15.20 kcal/mol

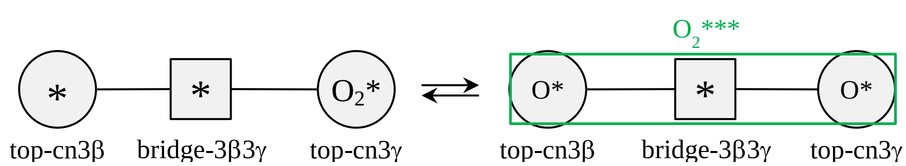


A_{fwd} = 2.033·10^{8} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 5.152·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -24.49 kcal/mol

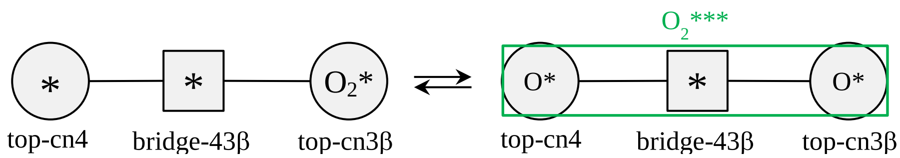


A_{fwd} = 2.033·10^{8} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 5.637·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -23.10 kcal/mol

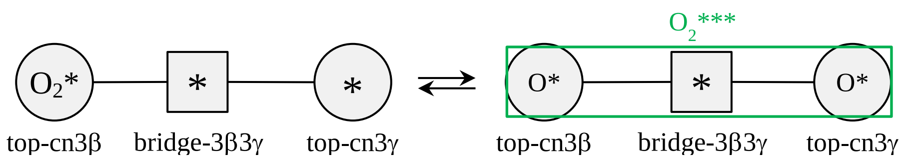
O_2 tilting



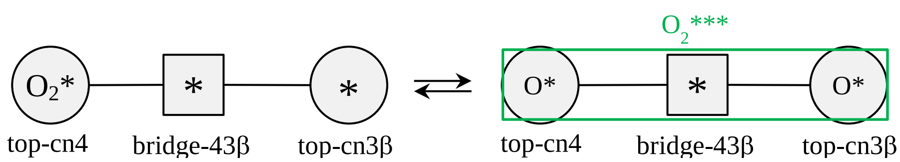
A_{fwd} = 2.145·10^{12} s^{-1}, A_{fwd}/A_{rev} = 9.349·10^{-2}, $E^0_{a,fwd}$ = 0.04 kcal/mol, ΔE^0_{rxn} = -7.90 kcal/mol



A_{fwd} = 3.565·10^{11} s^{-1}, A_{fwd}/A_{rev} = 3.616·10^{-2}, $E^0_{a,fwd}$ = 0.62 kcal/mol, ΔE^0_{rxn} = -8.97 kcal/mol

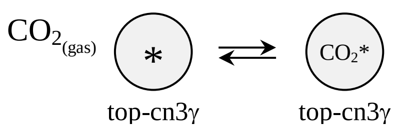


A_{fwd} = 4.699·10^{11} s^{-1}, A_{fwd}/A_{rev} = 3.957·10^{-2}, $E^0_{a,fwd}$ = 0.48 kcal/mol, ΔE^0_{rxn} = -7.58 kcal/mol

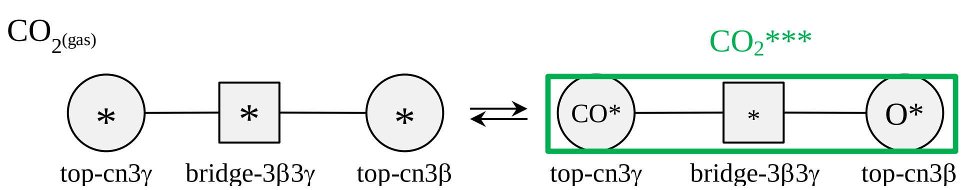


A_{fwd} = 1.006·10^{12} s^{-1}, A_{fwd}/A_{rev} = 9.056·10^{-2}, $E^0_{a,fwd}$ = 0.20 kcal/mol, ΔE^0_{rxn} = -11.12 kcal/mol

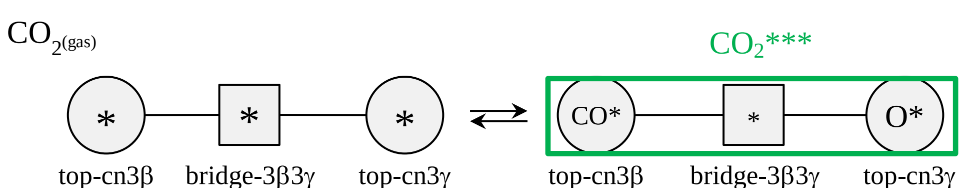
<u>CO_2 adsorption</u>



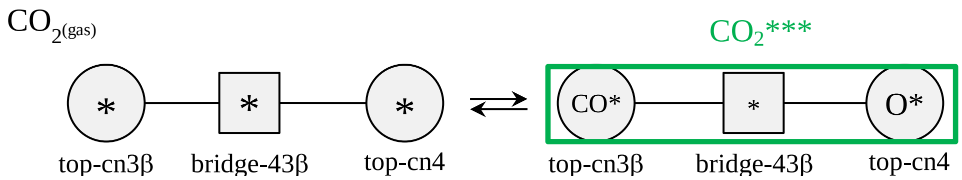
A_{fwd} = 6.280·10^{7} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.063·10^{-6} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = 0.57 kcal/mol



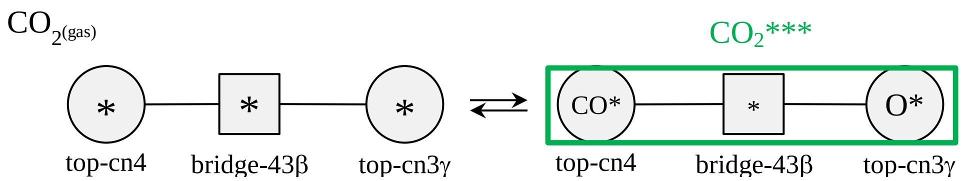
A_{fwd} = 1.733·10^{8} bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.303·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -1.69 kcal/mol



A_{fwd} = 1.733·10^8 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.554·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = 0.48 kcal/mol

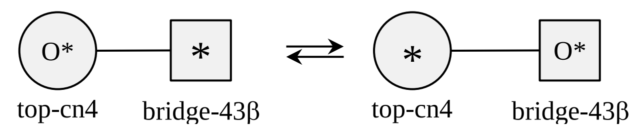


A_{fwd} = 1.733·10^8 s^{-1}, A_{fwd}/A_{rev} = 2.782·10^{-8}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -2.77 kcal/mol

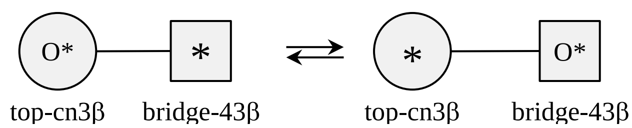


A_{fwd} = 1.733·10^8 bar^{-1}·s^{-1}, A_{fwd}/A_{rev} = 3.132·10^{-8} bar^{-1}, $E^0_{a,fwd}$ = 0.00 kcal/mol, ΔE^0_{rxn} = -0.25 kcal/mol

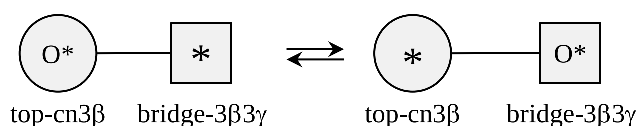
<u>O diffusion</u>



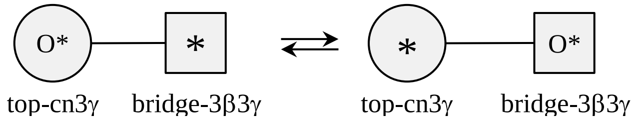
A_{fwd} = 5.209·10^{12} s^{-1}, A_{fwd}/A_{rev} = 2.641·10^{-1}, $E^0_{a,fwd}$ = 0.38 kcal/mol, ΔE^0_{rxn} = -10.68 kcal/mol



A_{fwd} = 5.209·10^{12} s^{-1}, A_{fwd}/A_{rev} = 3.958·10^{-1}, $E^0_{a,fwd}$ = 14.91 kcal/mol, ΔE^0_{rxn} = -9.77 kcal/mol

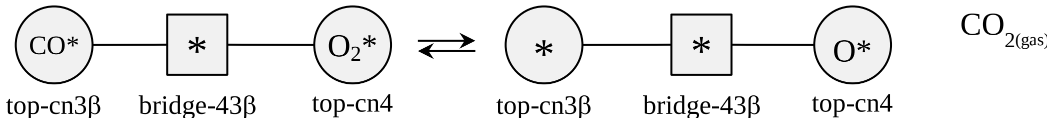


A_{fwd} = 5.209·10^{12} s^{-1}, A_{fwd}/A_{rev} = 3.993·10^{-1}, $E^0_{a,fwd}$ = 3.86 kcal/mol, ΔE^0_{rxn} = -8.05 kcal/mol

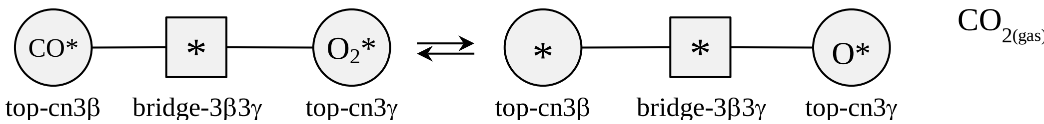


A_{fwd} = 5.209·10^{12} s^{-1}, A_{fwd}/A_{rev} = 4.716·10^{-1}, $E^0_{a,fwd}$ = 19.61 kcal/mol, ΔE^0_{rxn} = -6.93 kcal/mol

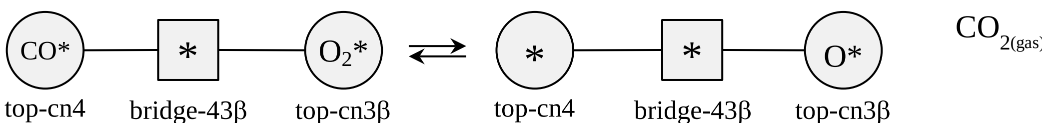
CO oxidation by O_2



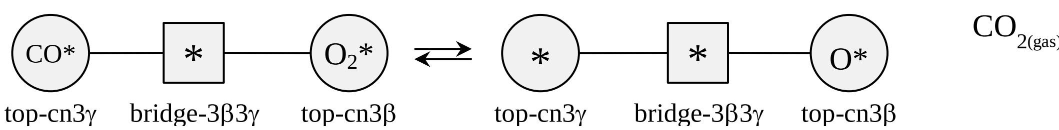
A_{fwd} = 1.123·10^{11} s^{-1}, A_{fwd}/A_{rev} = 8.811·10^{5} bar, $E^0_{a,fwd}$ = 9.54 kcal/mol, ΔE^0_{rxn} = -32.65 kcal/mol



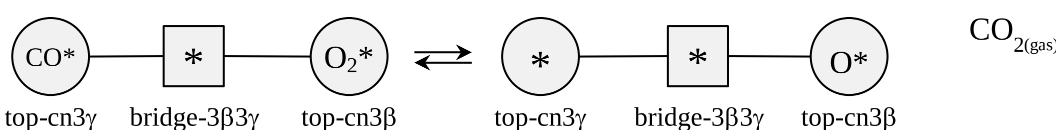
A_{fwd} = 8.760·10^{10} s^{-1}, A_{fwd}/A_{rev} = 4.697·10^{5} bar, $E^0_{a,fwd}$ = 12.11 kcal/mol, ΔE^0_{rxn} = -32.86 kcal/mol



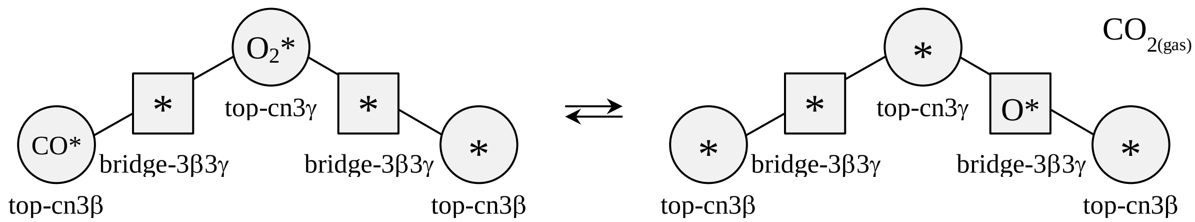
A_{fwd} = 3.559·10^{10} s^{-1}, A_{fwd}/A_{rev} = 3.316·10^{5} bar, $E^0_{a,fwd}$ = 10.50 kcal/mol, ΔE^0_{rxn} = -33.25 kcal/mol



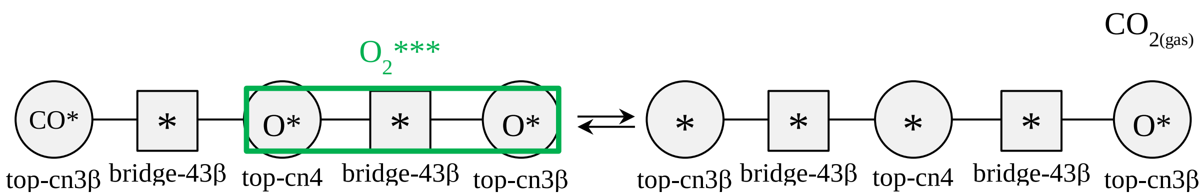
A_{fwd} = 1.051·10^{10} s^{-1}, A_{fwd}/A_{rev} = 1.059·10^{5} bar, $E^0_{a,fwd}$ = 11.80 kcal/mol, ΔE^0_{rxn} = -30.92 kcal/mol



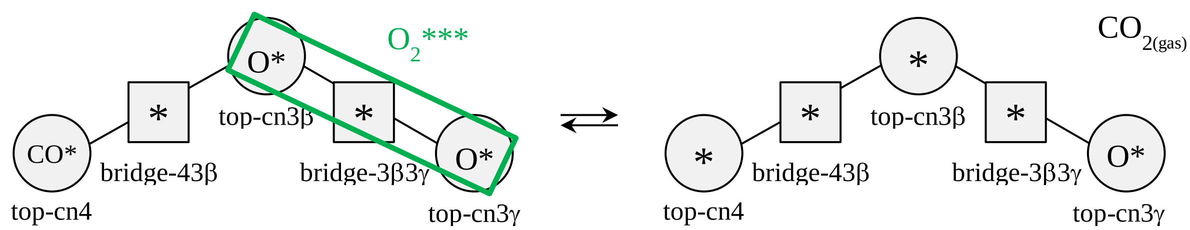
A_{fwd} = 7.536·10^{10} s^{-1}, A_{fwd}/A_{rev} = 1.059·10^{5} bar, $E^0_{a,fwd}$ = 51.15 kcal/mol, ΔE^0_{rxn} = -30.92 kcal/mol



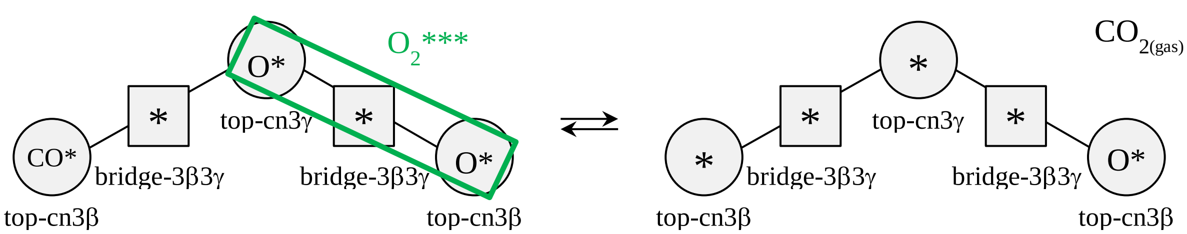
A_{fwd} = 6.469·10^{11} s^{-1}, A_{fwd}/A_{rev} = 4.697·10^{5} bar, $E^{0}_{a,fwd}$ = 52.59 kcal/mol, ΔE^{0}_{rxn} = -32.86 kcal/mol



A_{fwd} = 2.488·10^{12} s^{-1}, A_{fwd}/A_{rev} = 6.491·10^{6} bar, $E^{0}_{a,fwd}$ = 47.25 kcal/mol, ΔE^{0}_{rxn} = -22.45 kcal/mol

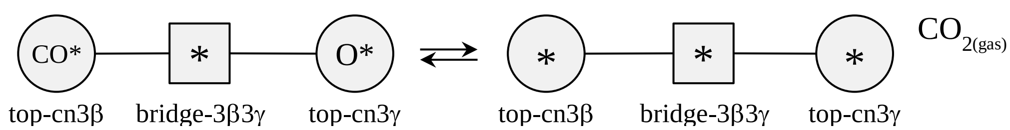


A_{fwd} = 9.992·10^{12} s^{-1}, A_{fwd}/A_{rev} = 7.097·10^{6} bar, $E^{0}_{a,fwd}$ = 46.75 kcal/mol, ΔE^{0}_{rxn} = -26.80 kcal/mol

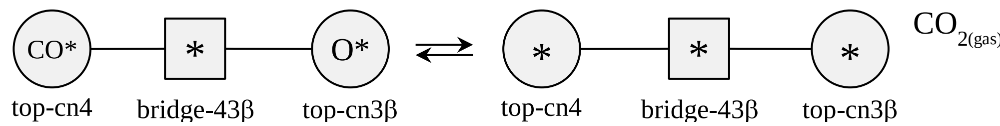


A_{fwd} = 2.835·10^{12} s^{-1}, A_{fwd}/A_{rev} = 5.933·10^{6} bar, $E^{0}_{a,fwd}$ = 53.67 kcal/mol, ΔE^{0}_{rxn} = -23.84 kcal/mol

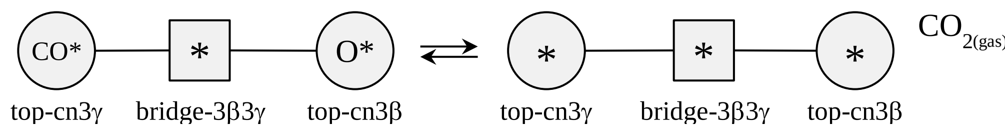
CO oxidation by O



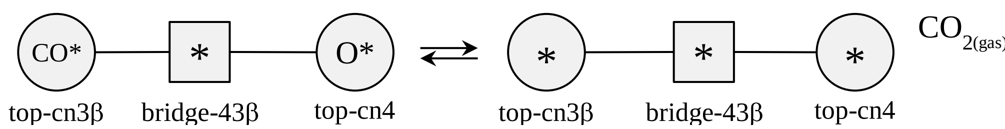
A_{fwd} = 1.246·10^{12} s^{-1}, A_{fwd}/A_{rev} = 3.488·10^{6} bar, $E^{0}_{a,fwd}$ = 2.98 kcal/mol, ΔE^{0}_{rxn} = -46.16 kcal/mol



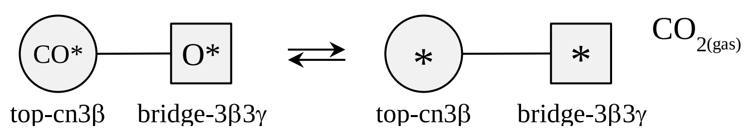
$\mathbf{A_{fwd} = 5.056 \cdot 10^{12}\ s^{-1},\ A_{fwd}/A_{rev} = 4.172 \cdot 10^{6}\ bar,\ E^{0}_{a,fwd} = 3.90\ kcal/mol,\ \Delta E^{0}_{rxn} = -49.13\ kcal/mol}$



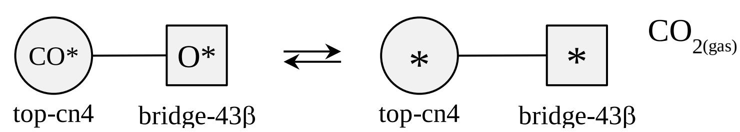
$\mathbf{A_{fwd} = 4.488 \cdot 10^{12}\ s^{-1},\ A_{fwd}/A_{rev} = 1.332 \cdot 10^{6}\ bar,\ E^{0}_{a,fwd} = 4.70\ kcal/mol,\ \Delta E^{0}_{rxn} = -46.79\ kcal/mol}$



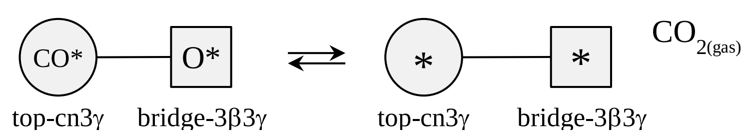
$\mathbf{A_{fwd} = 1.498 \cdot 10^{12}\ s^{-1},\ A_{fwd}/A_{rev} = 1.971 \cdot 10^{6}\ bar,\ E^{0}_{a,fwd} = 4.95\ kcal/mol,\ \Delta E^{0}_{rxn} = -48.21\ kcal/mol}$



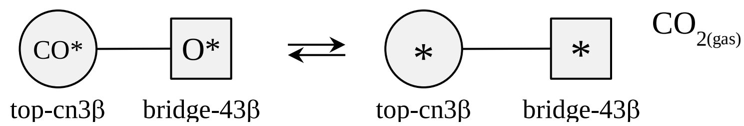
$\mathbf{A_{fwd} = 2.643 \cdot 10^{12}\ s^{-1},\ A_{fwd}/A_{rev} = 7.396 \cdot 10^{6}\ bar,\ E^{0}_{a,fwd} = 2.63\ kcal/mol,\ \Delta E^{0}_{rxn} = -39.24\ kcal/mol}$



$\mathbf{A_{fwd} = 1.278 \cdot 10^{13}\ s^{-1},\ A_{fwd}/A_{rev} = 1.054 \cdot 10^{7}\ bar,\ E^{0}_{a,fwd} = 3.43\ kcal/mol,\ \Delta E^{0}_{rxn} = -39.36\ kcal/mol}$

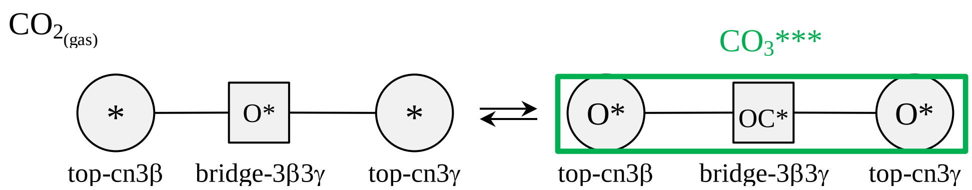


$\mathbf{A_{fwd} = 1.124 \cdot 10^{13}\ s^{-1},\ A_{fwd}/A_{rev} = 3.336 \cdot 10^{6}\ bar,\ E^{0}_{a,fwd} = 4.31 kcal/mol,\ \Delta E^{0}_{rxn} = -38.74\ kcal/mol}$

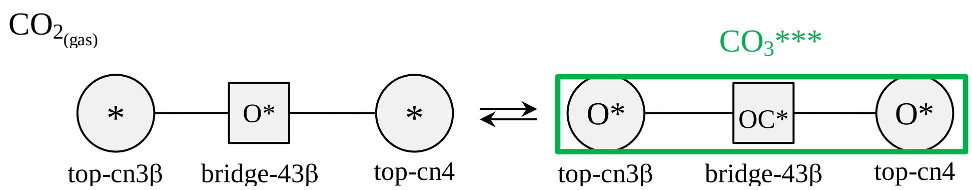


$\mathbf{A_{fwd} = 5.675 \cdot 10^{12}\ s^{-1},\ A_{fwd}/A_{rev} = 7.463 \cdot 10^{6}\ bar,\ E^{0}_{a,fwd} = 4.42\ kcal/mol,\ \Delta E^{0}_{rxn} = -37.52\ kcal/mol}$

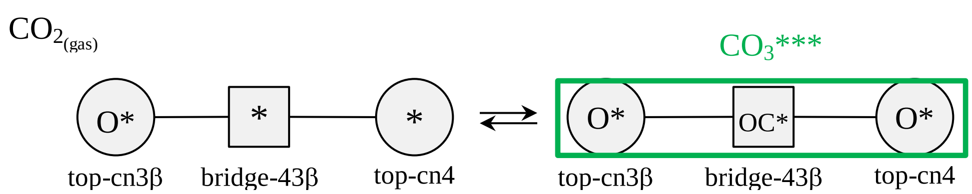
<u>CO_3 formation</u>



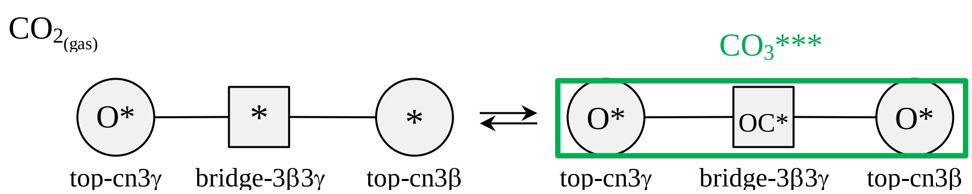
$\mathbf{A_{fwd} = 7.027 \cdot 10^{6}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 8.241 \cdot 10^{-8}\ bar^{-1},\ E^{0}_{a,fwd} = 0.03\ kcal/mol,\ \Delta E^{0}_{rxn} = -28.16\ kcal/mol}$



$\mathbf{A_{fwd} = 2.343 \cdot 10^{6}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 5.869 \cdot 10^{-8}\ bar^{-1},\ E^{0}_{a,fwd} = 0.29\ kcal/mol,\ \Delta E^{0}_{rxn} = -29.65\ kcal/mol}$



$\mathbf{A_{fwd} = 1.839 \cdot 10^{6}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 2.323 \cdot 10^{-8}\ bar^{-1},\ E^{0}_{a,fwd} = 0.42\ kcal/mol,\ \Delta E^{0}_{rxn} = -39.42\ kcal/mol}$



$\mathbf{A_{fwd} = 2.914 \cdot 10^{7}\ bar^{-1} \cdot s^{-1},\ A_{fwd}/A_{rev} = 3.886 \cdot 10^{-8}\ bar^{-1},\ E^{0}_{a,fwd} = 0.00\ kcal/mol,\ \Delta E^{0}_{rxn} = -35.08\ kcal/mol}$

References

1 Stamatakis, M. & Vlachos, D. G. A Graph-Theoretical Kinetic Monte Carlo Framework for on-Lattice Chemical Kinetics. *J. Chem. Phys.* **134**, 214115, doi:10.1063/1.3596751 (2011).

2 Nielsen, J., d'Avezac, M., Hetherington, J. & Stamatakis, M. Parallel Kinetic Monte Carlo Simulation Framework Incorporating Accurate Models of Adsorbate Lateral Interactions. *J. Chem. Phys.* **139**, 224706, doi:10.1063/1.4840395 (2013).

3 Stamatakis, M. *Zacros: Advanced Lattice-KMC simulation Made Easy*, <http://tinyurl.com/zacroskmc> (2013).

4 Stamatakis, M., Christiansen, M., Vlachos, D. G. & Mpourmpakis, G. Multiscale Modeling Reveals Poisoning Mechanisms of MgO-Supported Au Clusters in CO Oxidation. *Nano Lett.* **12**, 3621-3626, doi:10.1021/nl301318b (2012).