The Role of Water, CO_2, and Non-Innocent Ligands in the CO_2 Hydrogenation to Formate by Ir(III) PNP Pincer Catalyst Evaluated by Static-DFT and Ab-initio Molecular Dynamics at Reaction Conditions (Supplimentary Informations)

[1]

C.S. Praveen,[*,†,‡] Aleix Comas-Vives,[‡] Christophe Copéret,[‡] and J. VandeVondele[†]

†*Nanoscale Simulations, Dept. of Materials, ETH Zurich Wolfgang-Pauli-Str. 27, 8093 Zurich,Switzerland*

‡*Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir Prelog Weg 1-5, 8093 Zurich, Switzerland*

E-mail: praveen.chandramathy@mat.ethz.ch

1 Dispersion correction on B3LYP using Grimme's DFT-D3

The following table show the electronic energies of different structures and transition states described in Cycle 1, Cycle 2, and Cycle 3 described in the text for B3LYP (gas phase and solvent) and dispersion corrected B3LYP (B3LYP+D3) in gas phase. From the table it is clear that inclusion of dispersion does not bring any considerable change neither in the electronic energies nor in the reaction profiles.

Electronic energies for the structures described in Cycle 1

Table 1: Cycle 1

Structure	B3LYP$_{Gas}$	B3LYP$_{Solvent}$	B3LYP+D3$_{Gas}$
	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
2	0	0	
TS2/3	7.8	4.6	4.8
3	7.6	1.9	4.6
TS3/4	22.14	11.81	20.3
4	-6.7	-8.6	-9.3
5	100.6	4.7	107
6	-42.4	-29.4	-41.6
TS6/7	-27.4	-12	-25.4
7	-35.2	-20.2	-33.3
8	-26.4	-15.4	-18.2
9	-39.6	-28.9	-34.8
TS9/1	-8	2.9	-2.8
1	-53	-44.3	-48.3

Table 2: Cycle 2

Structure	B3LYP$_{Gas}$	B3LYP$_{Solvent}$	B3LYP+D3$_{Gas}$
	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
2	0	0	
TS2/3	7.8	4.6	4.8
3	7.6	1.9	4.6
TS3/4	22.14	11.81	20.3
4	-6.7	-8.6	-9.3
5	100.6	4.7	107
10	83.8	-11.5	87.2
11	-45.4	-30.4	-45.4
TS11/12	-26	-12.9	-27
12	-60	-47.1	-60
1	-53	-44.3	-48.3

Table 3: Cycle 3

Structure	B3LYP$_{Gas}$	B3LYP$_{Solvent}$	B3LYP+D3$_{Gas}$
	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
2	0	0	0
TS2/3	7.8	4.6	4.8
3	7.6	1.9	4.6
TS3/4	22.14	11.81	20.3
4	-6.7	-8.6	-9.3
5	100.6	4.7	107
10	83.8	-11.5	87.2
13	-59.6	-47.5	-58.5
1	-53	-44.3	-48.3

2 Gibbs free energy for the inclusion of water molecules into structure 9 for cleavage

The following table show the Gibbs free energies for the inclusion of additional water molecules in the H_2 cleavage machanism of structure **9**. FNS, INS, and TRS corresponds to the initial final and transition states of the structures given in Fig. 6. The results show that the most feasible transition-state indeed corresponds to the structure when only one water molecule is assistance since the assistance of two and three water molecules have a high entropic cost.

Table 4: Gibb's free energies for the structures in Fig. 6

Structure	E_{Gas}	E_{Sol}	$G_{Correction}$	G_{Gas}	G_{Sol}
	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
Fig 6a FNS	-58.4	-44.4	17.1	-41.3	-27.4
Fig 6a INS	-46.0	-30.3	18.4	-27.6	-11.9
Fig 6a TNS	-25.1	-11.1	21.2	-3.9	10.1
Fig 6b FNS	-66.3	-47.2	29.1	-37.1	-18.1
Fig 6b INS	-53.1	-32.4	31.2	-21.9	-1.2
Fig 6b TNS	-33.0	-16.9	31.2	-1.8	14.3
Fig 6c FNS	-62.9	-45.9	29.1	-33.8	-16.8
Fig 6c INS	-51.4	-31.2	29.5	-22.0	-1.7
Fig 6c TNS	-34.6	-17.9	31.9	-2.7	13.9
Fig 6d FNS	-58.2	-38.3	41.7	-16.5	3.4
Fig 6d INS	-46.7	-24.8	38.7	-8.0	13.9
Fig 6d TNS	-26.0	-4.1	42.5	16.6	38.4

3 Reaction profiles including Gibbs free energy correction

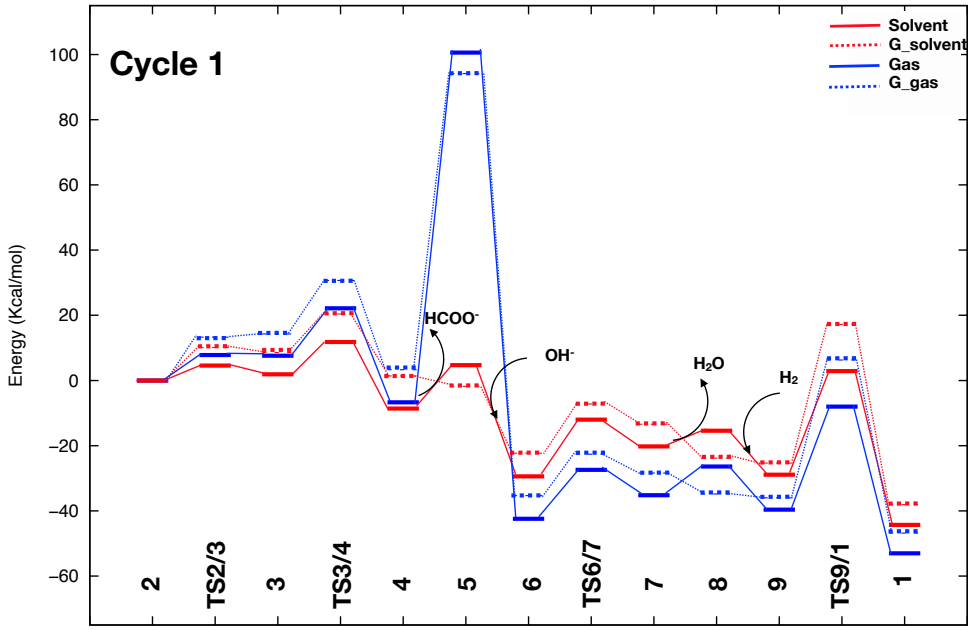

Figure 1: Reaction profile for Cycle 1. Solid red and blue lines indicate the solvent corrected and gas phase electronic energies. The red and blue dashed lines indicate the corresponding Gibb's free energies calculated using Gaussian09

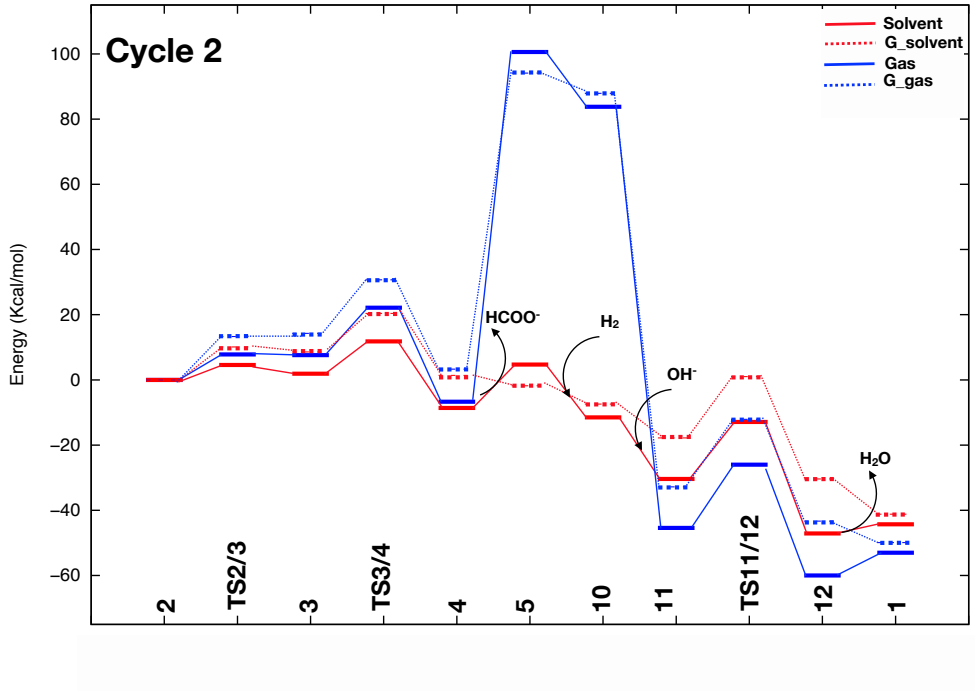

Figure 2: Reaction profile for Cycle 2. Solid red and blue lines indicate the solvent corrected and gas phase electronic energies. The red and blue dashed lines indicate the corresponding Gibb's free energies calculated using Gaussian09

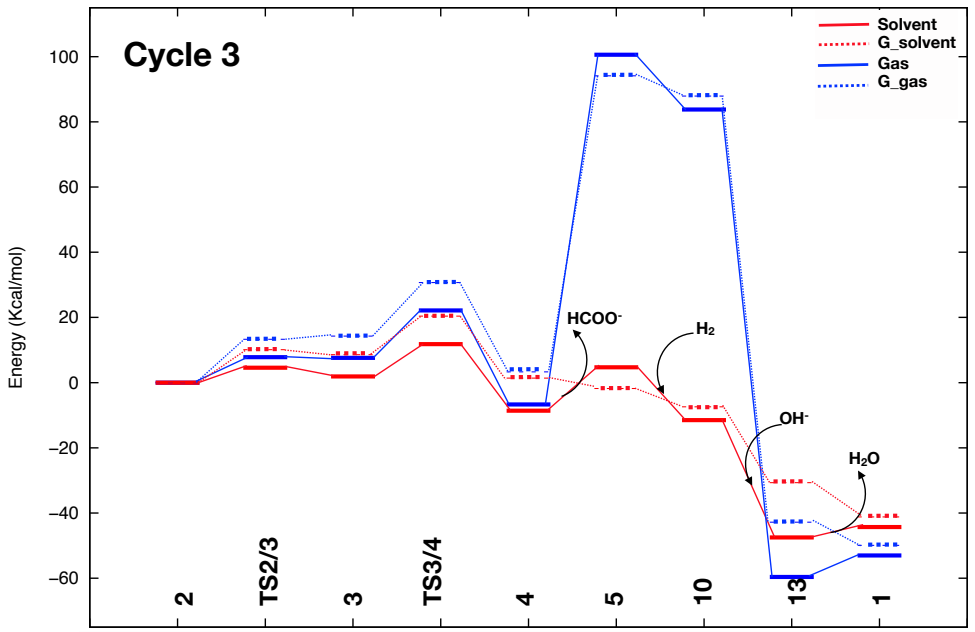

Figure 3: Reaction profile for Cycle 3. Solid red and blue lines indicate the solvent corrected and gas phase electronic energies. The red and blue dashed lines indicate the corresponding Gibb's free energies calculated using Gaussian09

4 Additional figures for the AIMD calculations

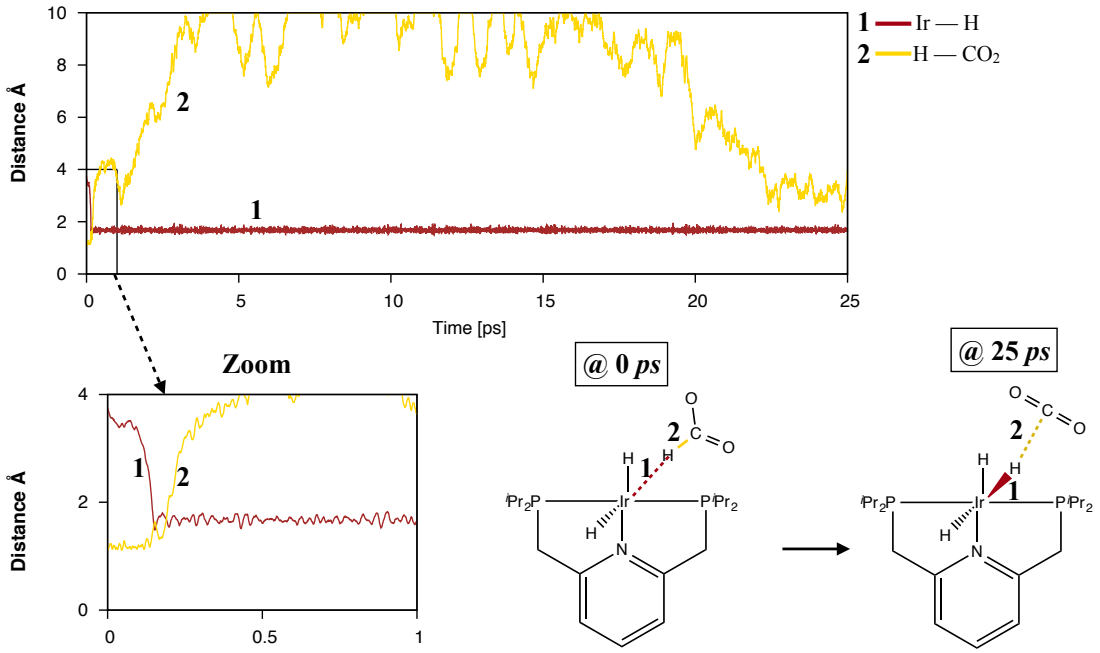

Figure 4: Time evolution of (in ps) selected bond distances (in Å) in the AIMD simulation showing the destabilization of the formate and the regeneration of the linear CO_2 molecule (top panel). A scheme showing the mechanism is displayed in the bottom right panel. The corresponding distances in the graph are color coded and numbered at the schematic representation. Note that solid and dashed lines indicate a bonding and non-bonding situation.

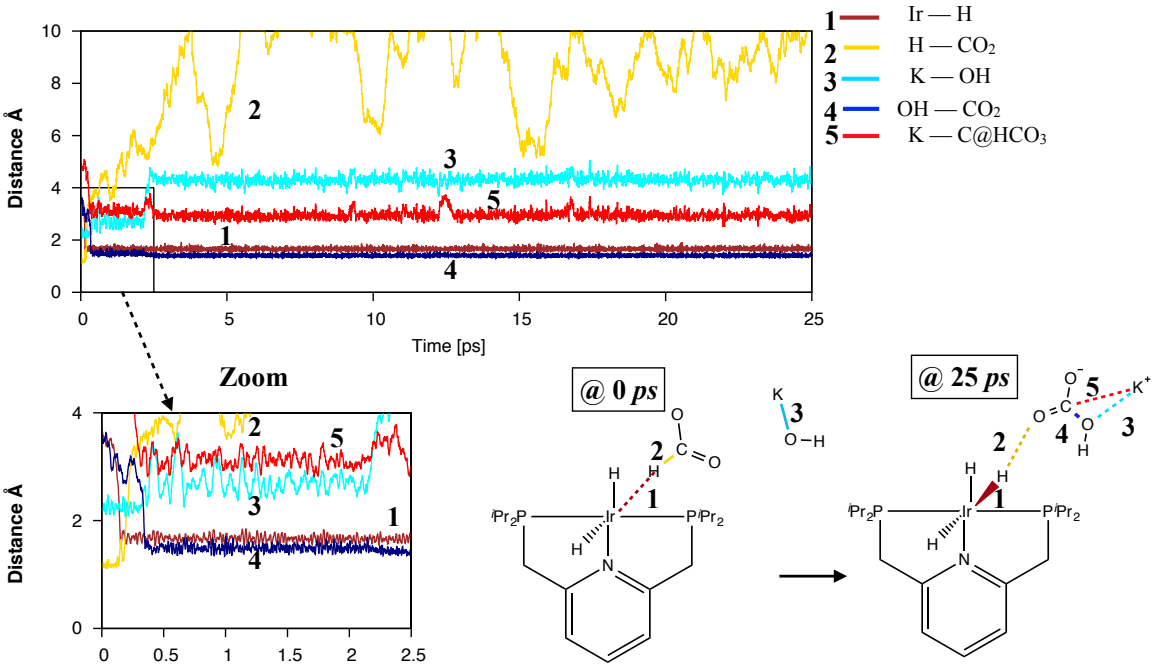

Figure 5: Time evolution of (in ps) selected bond distances (in Å) in the AIMD simulation showing the destabilization of the formate and the subsequent conversion of CO2 to potassium bicarbonate due to the interaction with KOH base(top panel). A zoom of the relevant transformation windows is shown in the bottom left panel. The corresponding distances in the graph are color coded and numbered at the schematic representation.

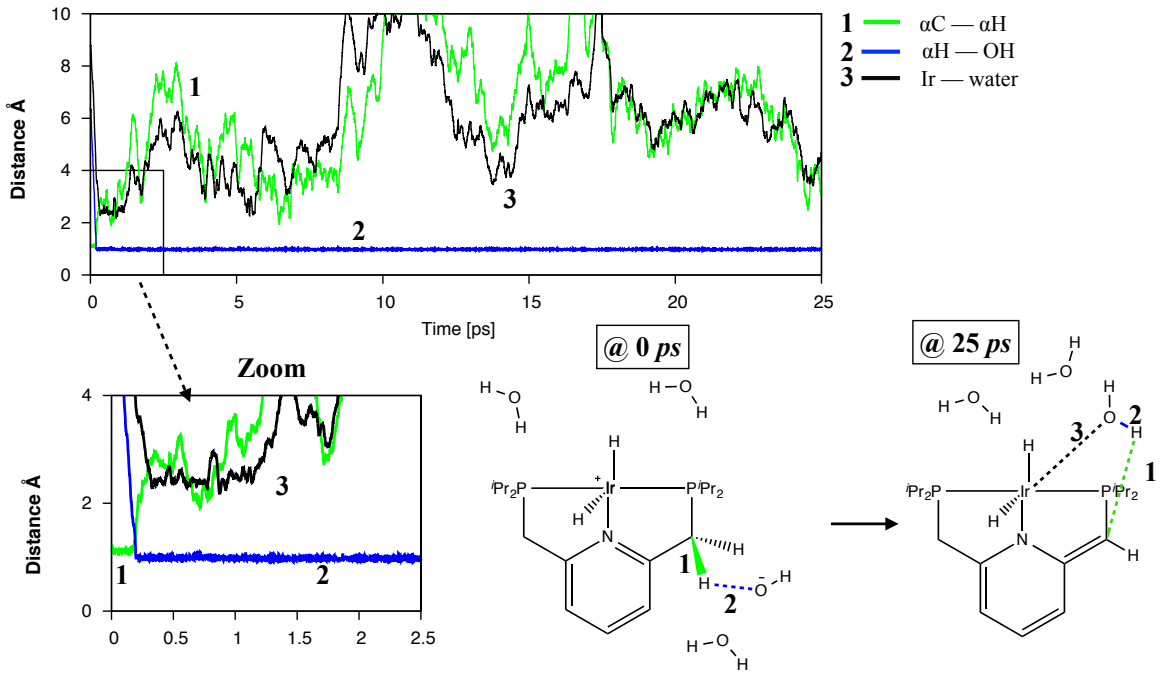

Figure 6: Time evolution of (in ps) selected bond distances (in Å) in the AIMD simulation showing the formation of water at the pyridine ring due to a proton transfer from the alpha carbon to the hydroxyl ion(top panel). The water thus produced, binds very weakly to the metal atom at the beginning and then desorbs. A zoom of the relevant transformation windows is shown in the bottom left panel. The corresponding mechanism is schematically represented in the bottom right panels. The plotted distances in the graph are colour coded and numbered within the schematic representation.

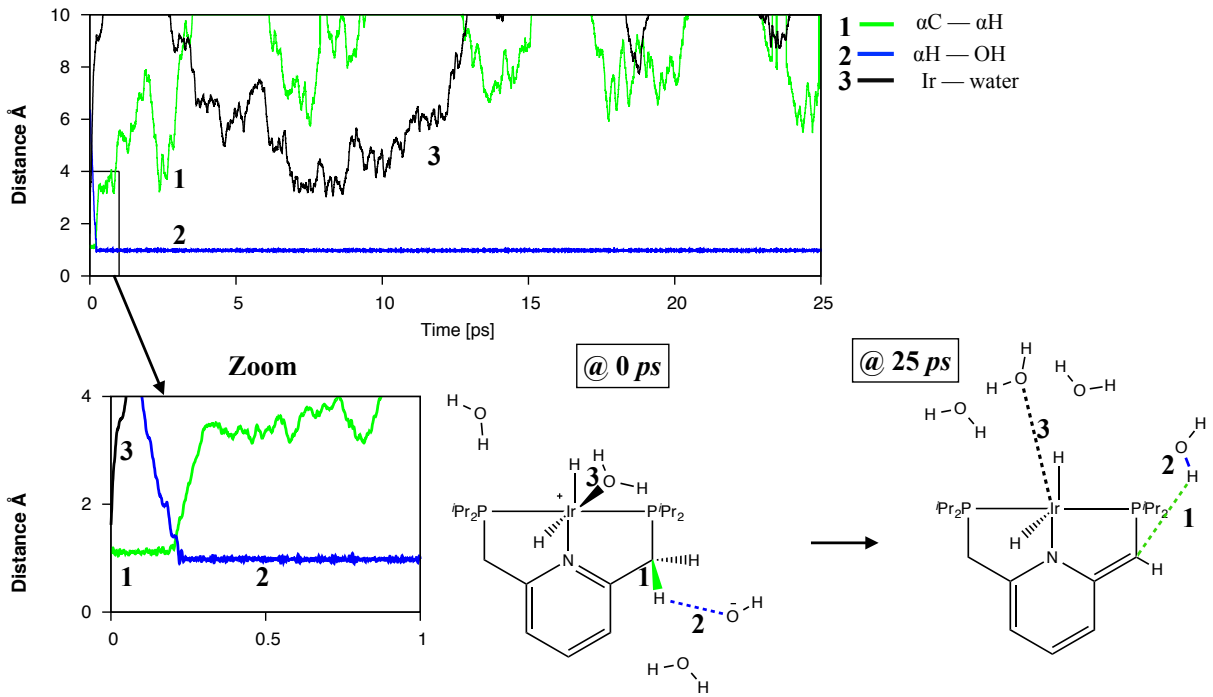

Figure 7: Time evolution of (in ps) selected bond distances (in Å) in the AIMD simulation showing the desorption of a water molecule initially bound to the Ir(III) centre and the subsequent formation of water at the pyridine ring due to a proton transfer from the alpha carbon to the hydroxyl ion(top panel). A zoom of the relevant transformation windows is shown in the bottom left panel. A scheme showing the mechanism is displayed in the bottom right panel. The corresponding distances in the graph are color coded and numbered at the schematic representation.

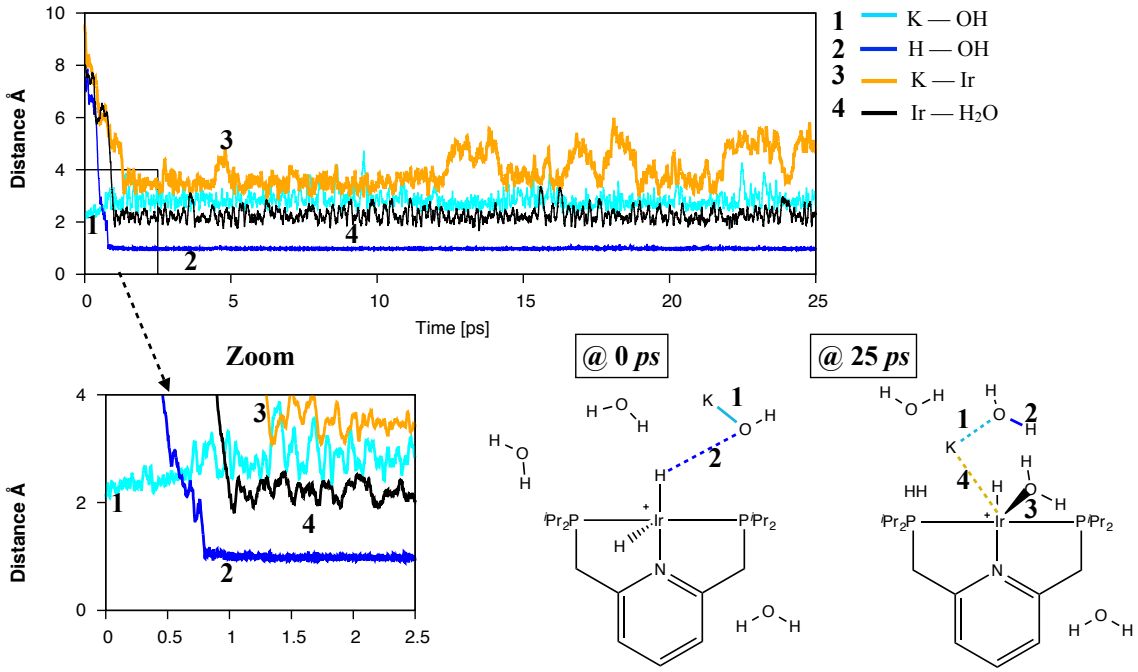

Figure 8: Time evolution of (in ps) selected bond distances (in Å) in the AIMD simulation showing the formation of water molecule at the Ir(III) by the interaction of KOH with one of the two hydrides at the metal centre(top panel). The water thus produced desorbs and the metal centre is saturated by the K ion and a second water molecule. A zoom of the relevant transformation windows is shown in the bottom left panel. A scheme showing the mechanism is displayed in the bottom right panel. The corresponding distances in the graph are color coded and numbered at the schematic representation.

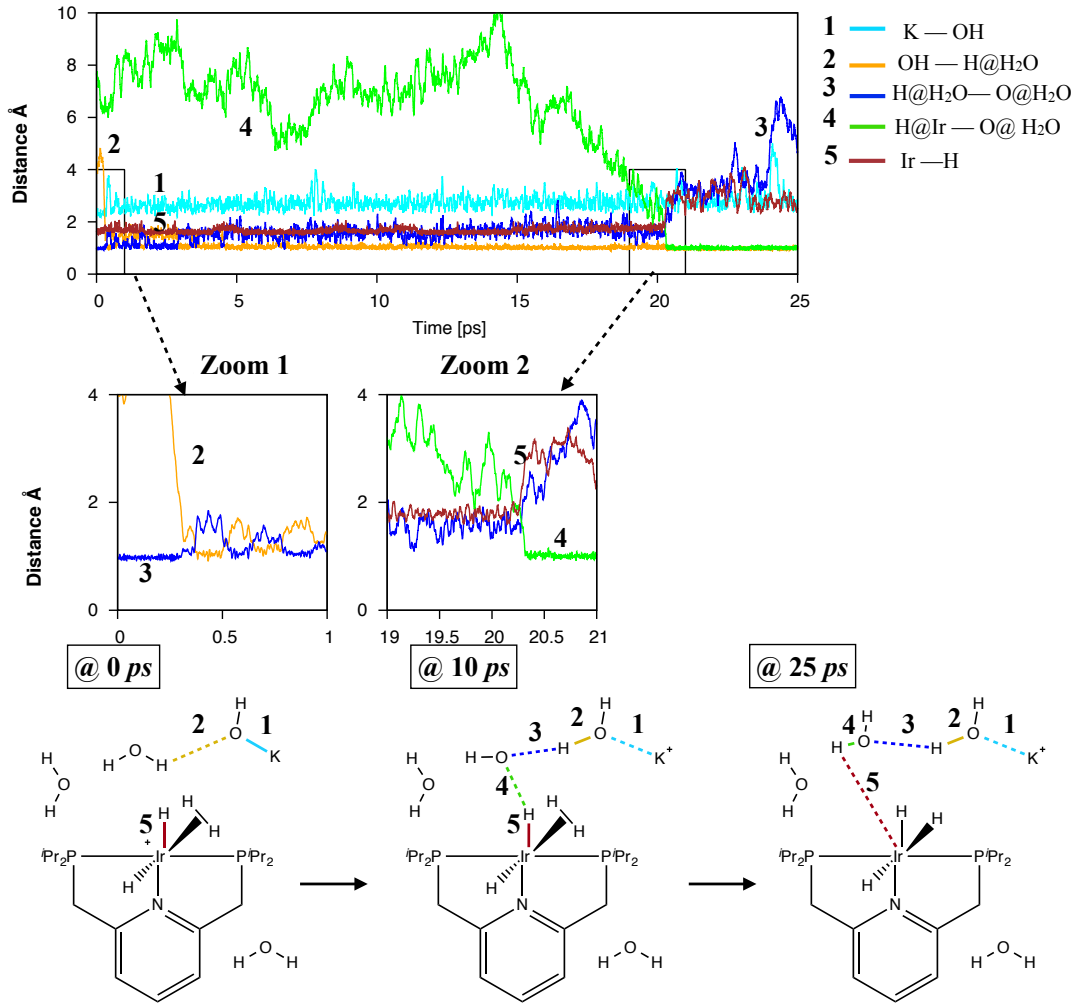

Figure 9: Time evolution of (in ps) selected bond distances (in Å) in the AIMD simulation showing the cyclic proton transfer initiated by the water molecule and KOH and the subsequent splitting of H_2 at the metal centre(top panel). A zoom of the relevant transformation windows are shown in the middle panel. A scheme showing the mechanism is displayed in the bottom panels. The corresponding distances in the graph are color coded and numbered at the schematic representation.