Supporting Information for:

Elucidating Cation Effects in Homogeneously Catalyzed Formic Acid Dehydrogenation

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S1. The reorientation step in methanol solvent without cation

Selected snapshots of the reactant and product states for the reorientation step in methanol solvent without cation along with important distances is shown in Figure S1.

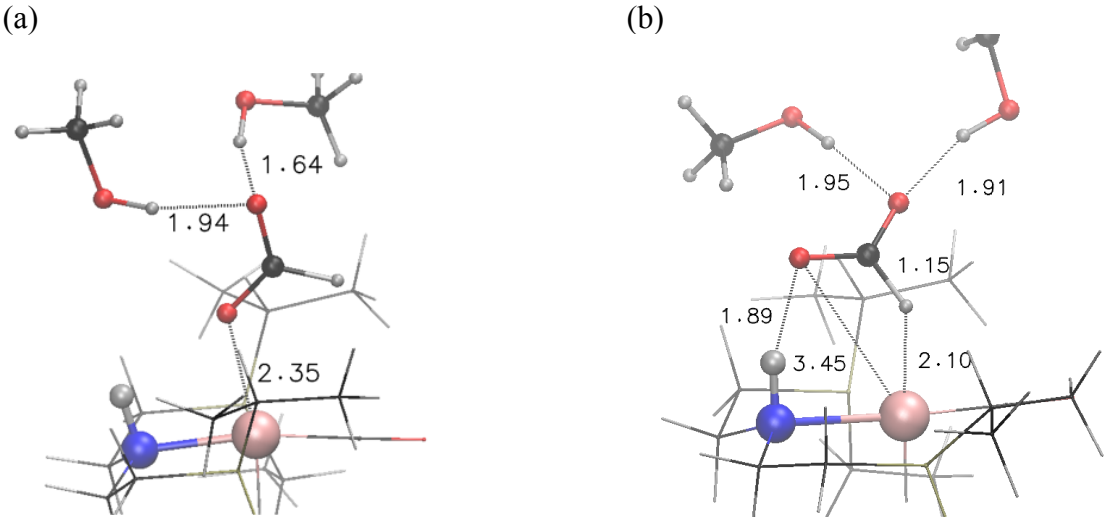

Figure S1. Representative snapshots from the constrained dynamics simulations along with important distances in Å of (a) the reactant with Q = 2.35 Å, and (b) product with Q = 3.45 Å. Solvent molecules are omitted for clarity. Color coding: hydrogen (light grey), carbon (dark grey), oxygen (red), nitrogen (blue), phosphorus (yellow), ruthenium (pink).

S2. The reorientation step in methanol solvent with cation

Selected snapshots of the reactant and product states for the reorientation step in methanol solvent with Li+ cation along with important distances is shown in Figure S2.

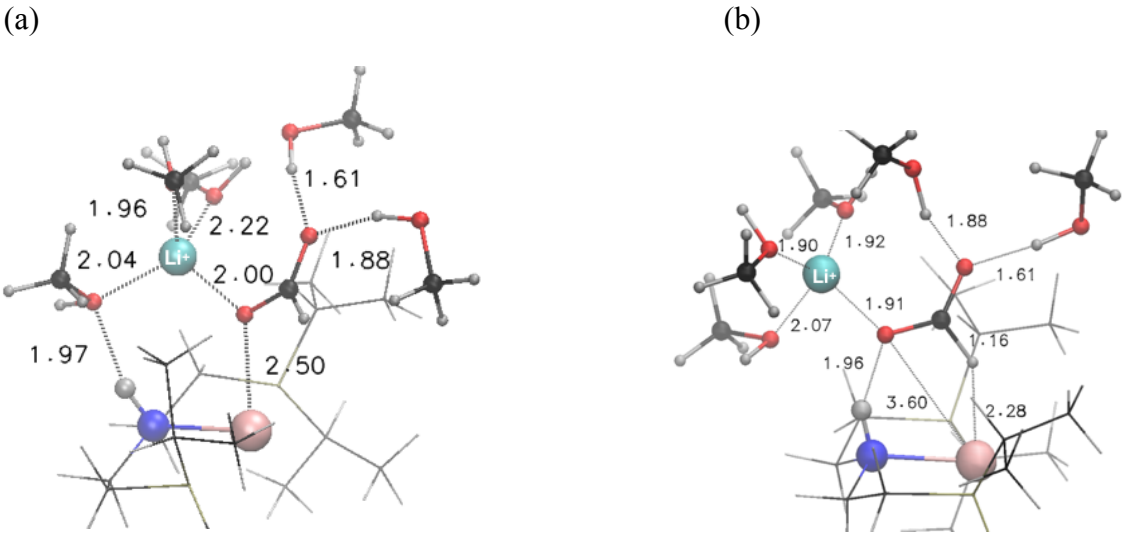

Figure S2. Representative snapshots from the constrained dynamics simulations along with important distances in Å of (a) the reactant with Q = 2.50 Å, and (b) product with Q = 3.60 Å. Solvent molecules are omitted for clarity. Color coding: hydrogen (light grey), carbon (dark grey), oxygen (red), nitrogen (blue), phosphorus (yellow), ruthenium (pink).

S3. Hydride transfer in methanol solvent without cation

Selected snapshots of the reactant state for the hydride transfer in methanol solvent without cation along with important distances is shown in Figure S3.

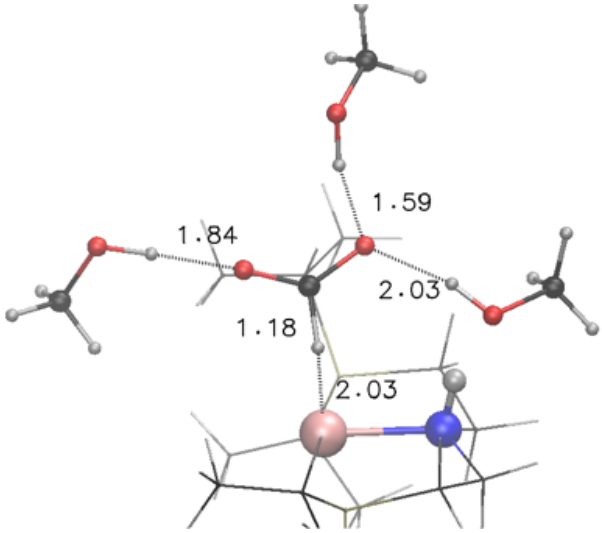

Figure S3. Representative snapshot from the constrained dynamics simulations along with important distances in Å of the reactant with Q = -0.85 Å. Solvent molecules are omitted for clarity. Color coding: hydrogen (light grey), carbon (dark grey), oxygen (red), nitrogen (blue), phosphorus (yellow), ruthenium (pink).

S4. Hydride transfer in methanol solvent with cation

Selected snapshots of the reactant and product states for the hydride transfer in methanol solvent with Li+ cation along with important distances is shown in Figure S4.

(a) (b)

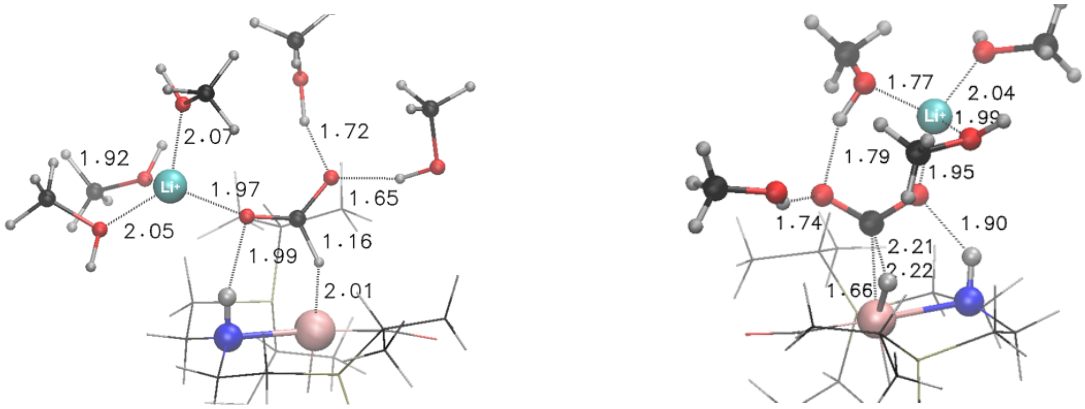

Figure S4. Representative snapshots from the constrained dynamics simulations along with important distances in Å of (a) the reactant with Q = -0.85 Å and (b) product with Q = 0.55 Å. Solvent molecules are omitted for clarity. Color coding: hydrogen (light grey), carbon (dark grey), oxygen (red), nitrogen (blue), phosphorus (yellow), ruthenium (pink).

S5. Wannier function center Analysis

Wannier function centers (WFCs) of the two electron pairs involved in the hydride transfer step for the product states obtained in methanol solution without and with cation along with important distances is shown in Figure S5.

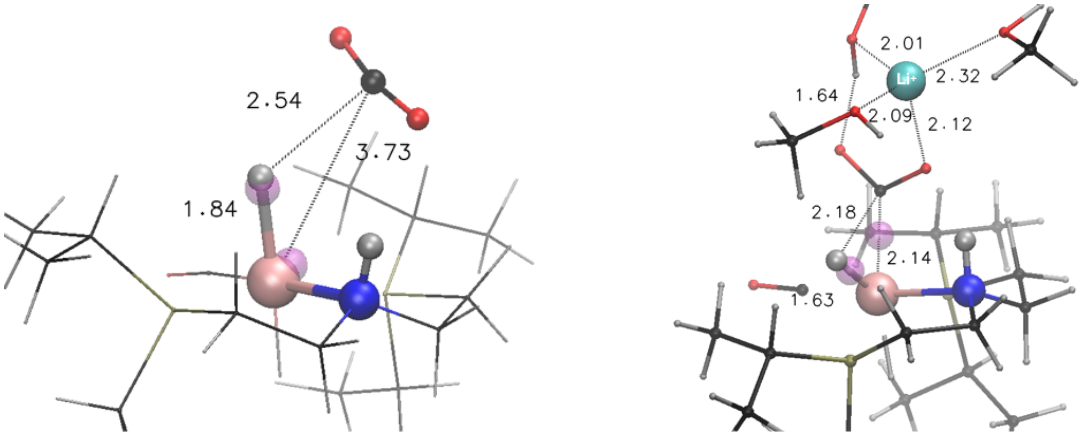

Figure S5. Wannier function centers (WFCs) of the two electron pairs involved in hydride transfer step shown in purple for the product state along with important distances in Å in (a) methanol solution without cation and (b) methanol solution in the presence of Li+ cation. Solvent molecules are omitted for clarity. Color coding: hydrogen (light grey), carbon (dark grey), oxygen (red), nitrogen (blue), phosphorus (yellow), ruthenium (pink).