

## **Supplementary Materials**

**Formic Acid Generation from CO<sub>2</sub> Reduction by MOF-253 Coordinated Transition Metal Complexes: A Computational Chemistry Perspective**

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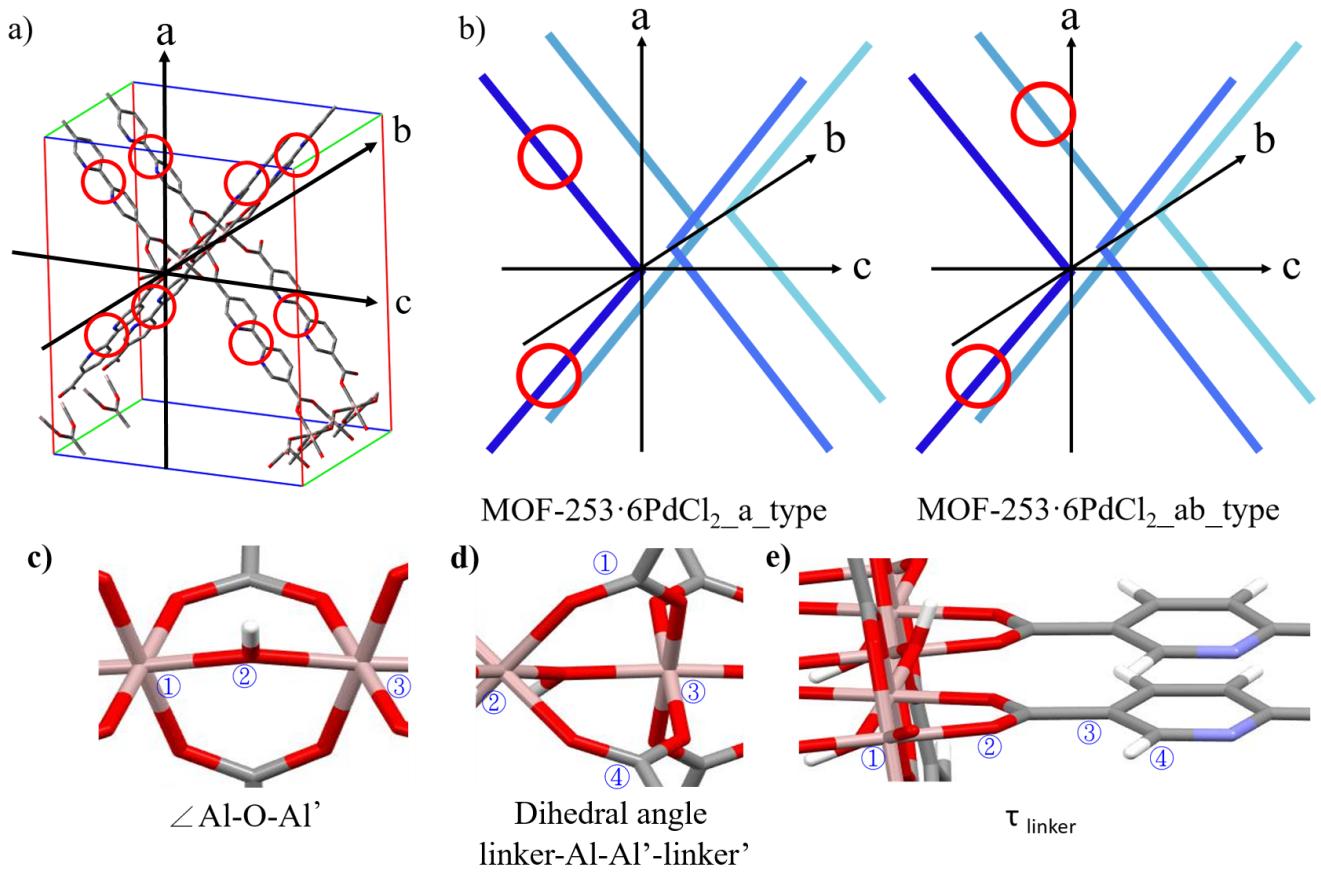


Figure S1. (a) Optimized MOF-253 using experimental lattice constants. (b) The schematic diagram of MOF-253·6PdCl<sub>2</sub> with the different empty sites. The red circles are the free coordination site on the linkers. (c) Al–O–Al bending angle, (d) dihedral angle of linker-Al-Al'-linker', and (e) the rotation angle of bpy fragment ( $\tau_{\text{linker}}$ ) are the structure information of the MOF-253 model.

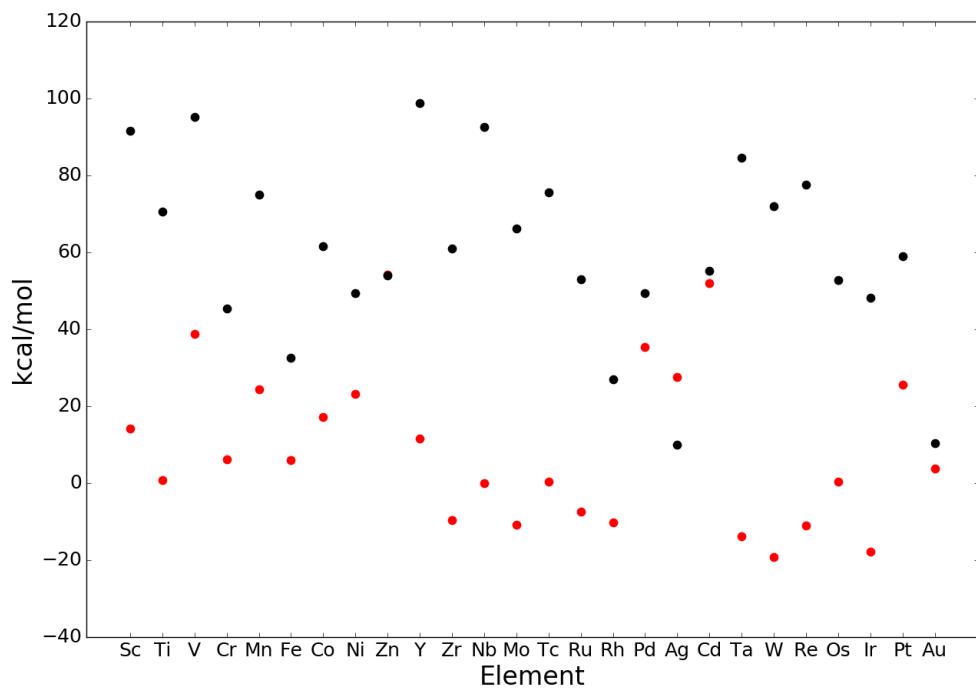


Figure S2. Energetic comparison between H atom transfer (red dot) and Cl atom transfer (black dot) from low-spin  $\text{LMH}_2\text{Cl}_2$  complexes

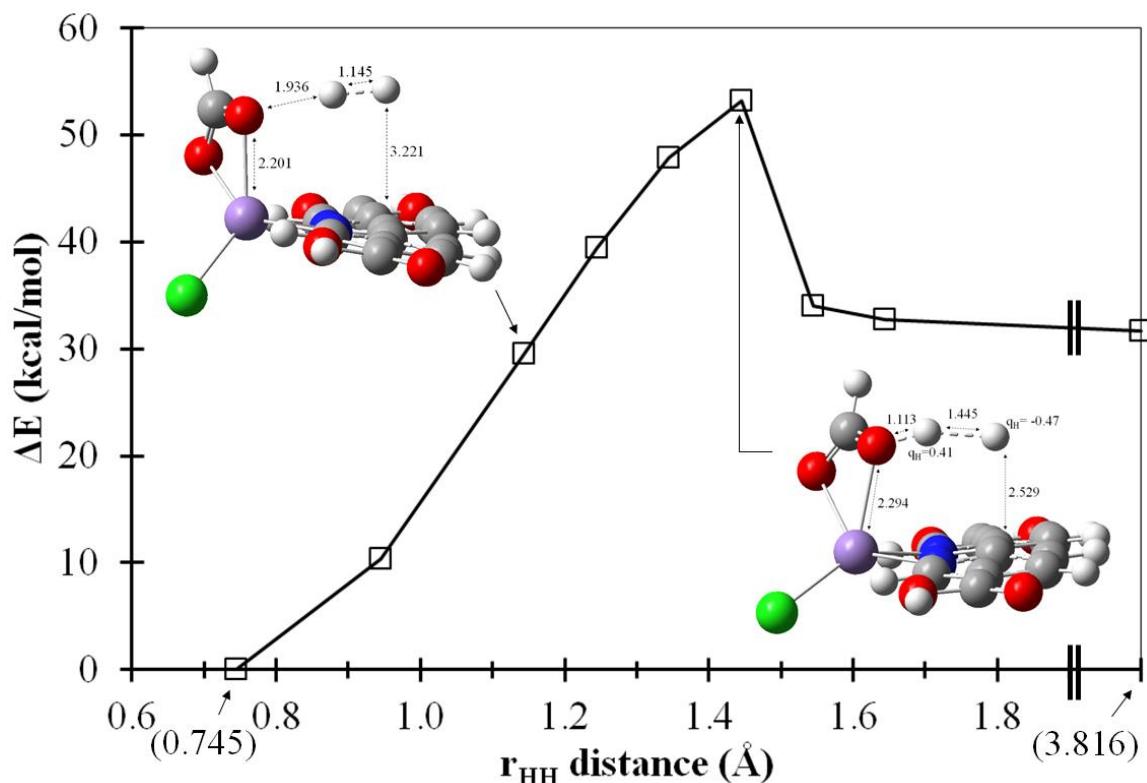


Figure S3. The calculated energetics of constrained optimization along H–H interatomic distance of LMnCl(HCO<sub>2</sub>)(H<sub>2</sub>) complex. The qH notation represents the atomic charge predicted by Natural Population Analysis.

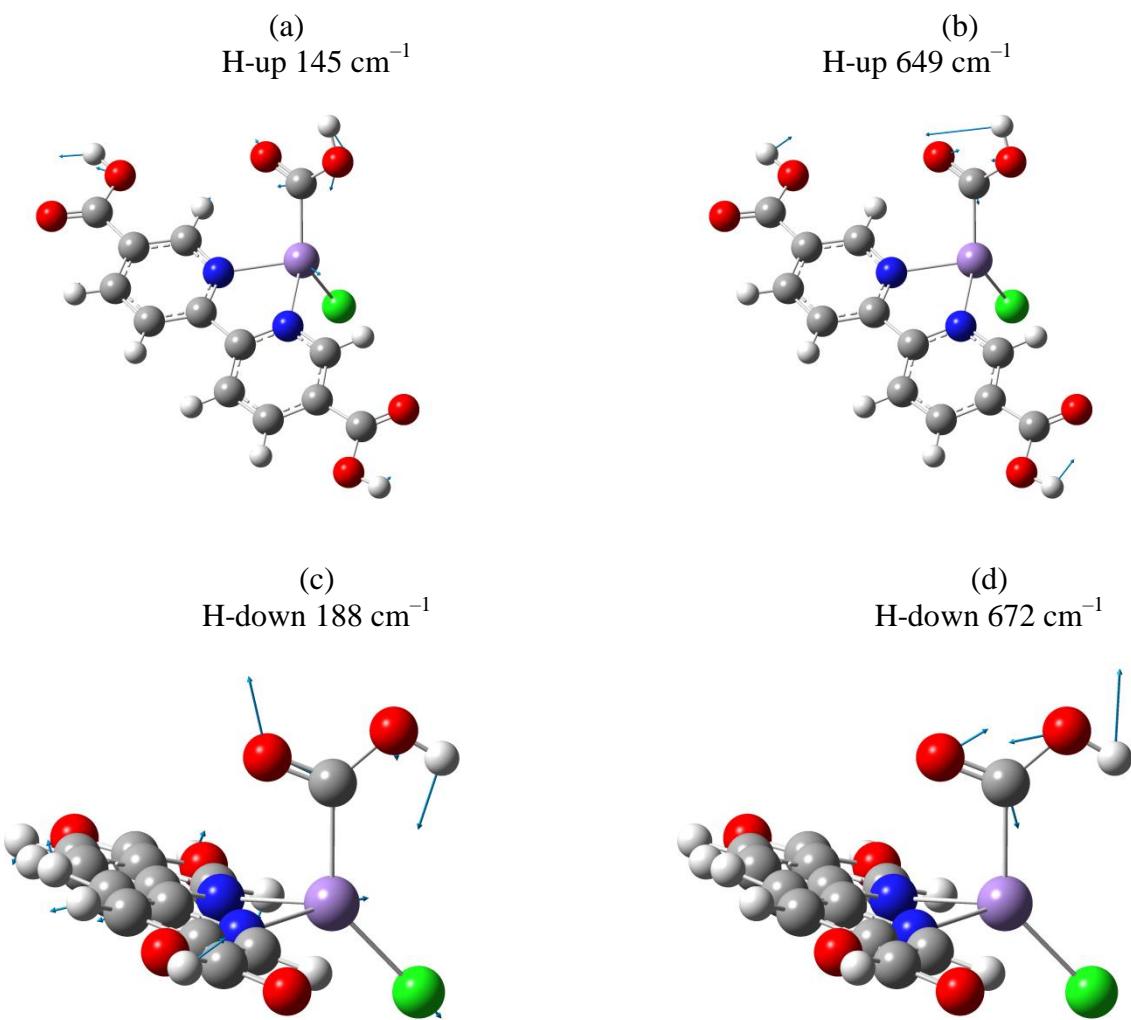


Figure S4. The identified vibrational modes of  $\text{LMnCl}(\text{COOH})$  minimum structures (H-up and H-down) weaken the interactions between Mn and COOH. The arrows denote the qualitative atomic displacements. The H-up minimum is predicted to be 2.6 kcal/mol lower in energy than H-down case.

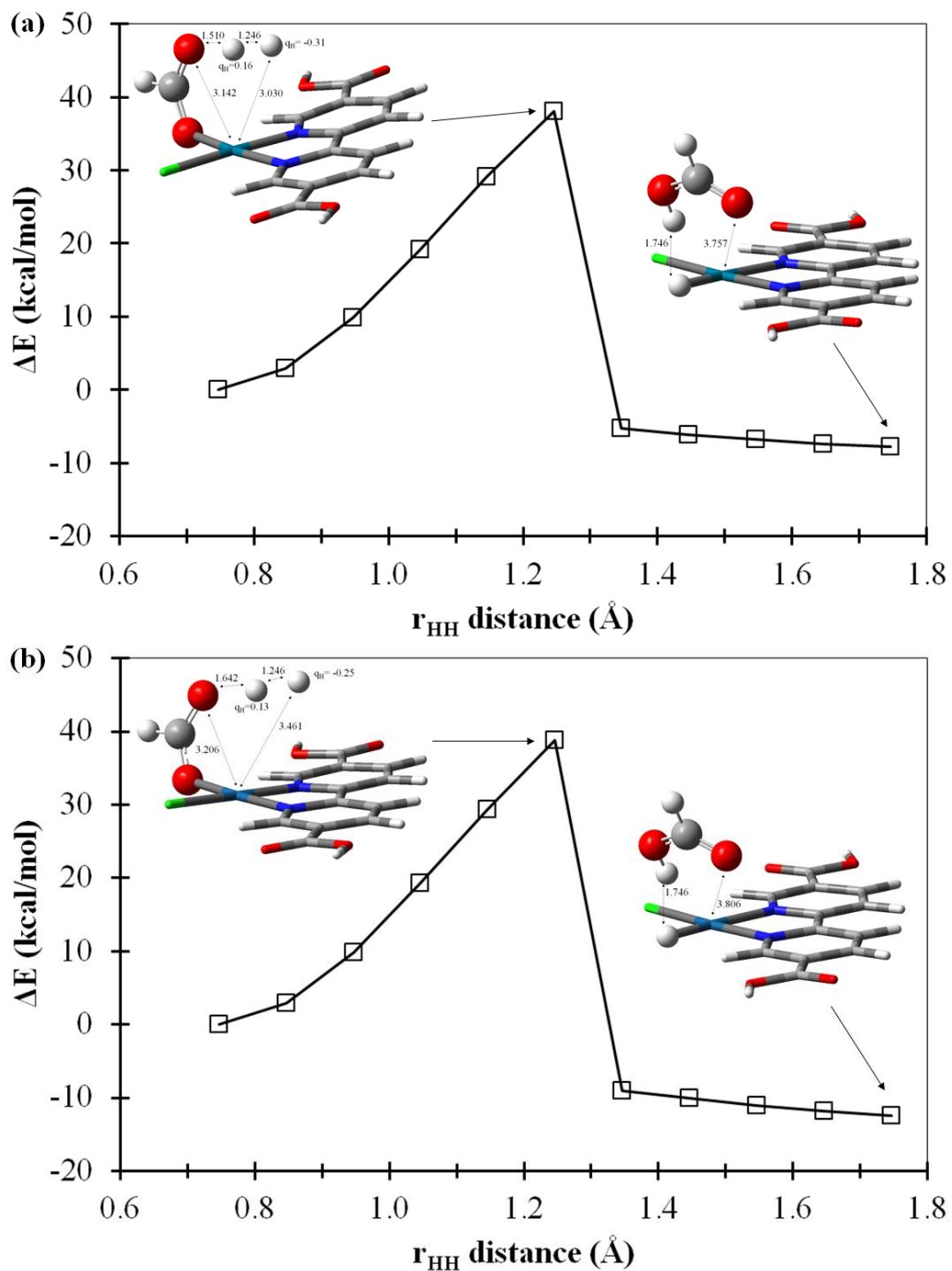


Figure S5. The calculated energetics of constrained optimization along H–H interatomic distance of (a) LPdCl( $\text{HCO}_2$ )( $\text{H}_2$ ) and (b) LPPtCl( $\text{HCO}_2$ )( $\text{H}_2$ ) complexes. The qH notation represents the atomic charge predicted by Natural Population Analysis.

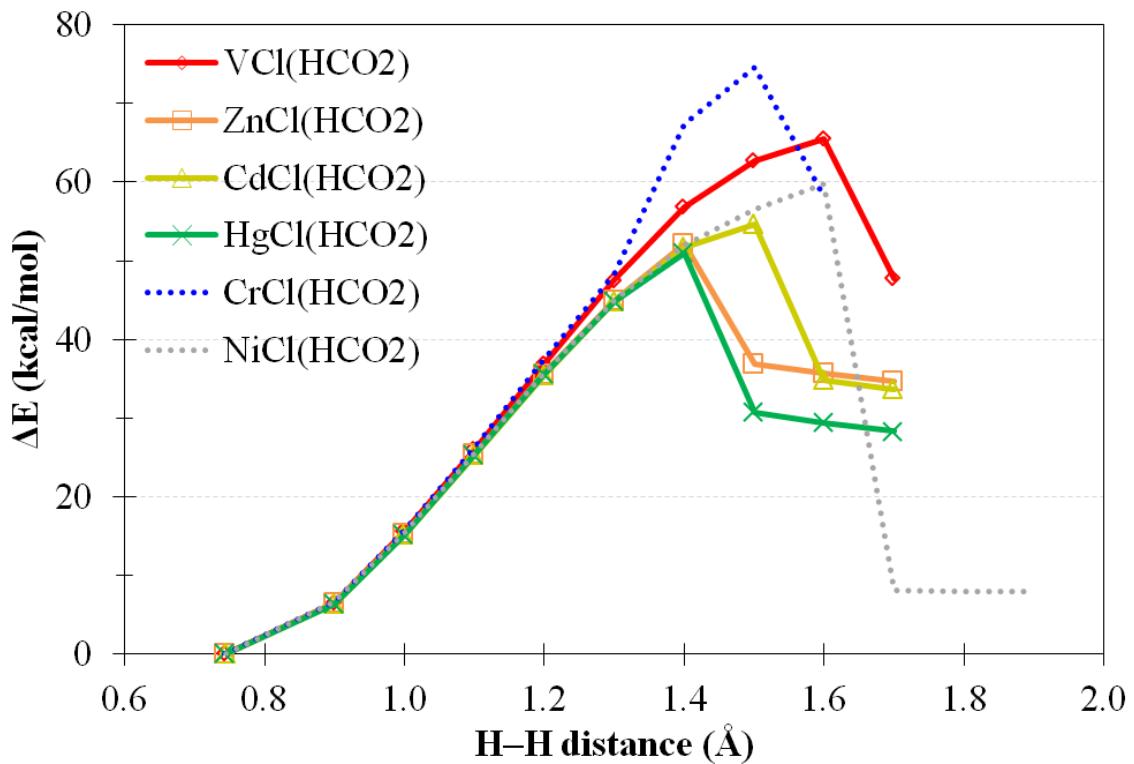


Figure S6. The schematic representation of H<sub>2</sub> activation by MCl(HCO<sub>2</sub>), M = V, Zn, Cd, and Hg complexes. The solid lines denote the heterolytic H<sub>2</sub> activation pathways leading to the formation of HCOOH and Hbpy ligand as the H–H distances increase. The dotted lines denote non-physical reaction profiles for M = Cr (s=2/2) and Ni (s=0) cases.

Table S1. Various  $\text{MCl}_2$ ,  $\text{M} = \text{Pd}$  and  $\text{Sc}$ , formation energetics (in eV) in MOF-253<sup>1,2</sup>

Entry	Coordination	E_DFT	E <sub>tot</sub>	E <sub>avg</sub>
(1)	Pristine	-1555.74482		-
(2)	8PdCl <sub>2</sub>	-1648.67757	-30.8042	-3.85
(3)	7PdCl <sub>2</sub>	-1636.96451	-26.8572	-3.84
(4)	6PdCl <sub>2</sub> _aa	-1625.20293	-22.8617	-3.81
(5)	6PdCl <sub>2</sub> _ab	-1625.32115	-22.9799	-3.83
(6)	6PdCl <sub>2</sub> _ac	-1625.22135	-22.8801	-3.81
(7)	6PdCl <sub>2</sub> _bb	-1625.39509	-23.0538	-3.84
(8)	6PdCl <sub>2</sub> _cc	-1625.29802	-22.9568	-3.83
(9)	8ScCl <sub>2</sub>	-1688.77110	-29.8151	-3.73
(10)	7ScCl <sub>2</sub>	-1672.07770	-26.1225	-3.73
(11)	4ScCl <sub>2</sub>	-1672.17710	-14.8299	-3.71

1.  $E_{\text{tot}}$  denotes the total binding energy of  $n^*\text{MCl}_2$  in MOF-253, being expressed  $E_{\text{tot}} = E_{\text{MOF-}n\text{M}} - E_{\text{MOF}} - n^*E_{\text{MCl}_2}$  where  $E_{\text{MOF-}n\text{M}}$  and  $E_{\text{MOF}}$  represent the energy of MOF with or without the adsorbates, respectively.
2.  $E_{\text{avg}}$  denotes the average adsorption energy of  $\text{MCl}_2$  in MOF-253 as  $E_{\text{ads}} = E_{\text{tot}} / n - E_{\text{MCl}_2}$  where  $E_{\text{MCl}_2}$  represents the single gaseous molecule.  $E_{\text{PdCl}_2}$  is -7.76607 eV and  $E_{\text{ScCl}_2}$  is -12.90140 eV.

Table S2. Calculated structural information of MOF-253 upon PdCl<sub>2</sub> coordination<sup>1</sup>

Adsorbates	$\angle \text{Al-O-Al}'$	$\phi(\text{Pd})$	$\phi(\text{w/o Pd})$	$\tau_{\text{linker}}$ (w/o PdCl <sub>2</sub> )	$\tau_{\text{linker}}$ (with PdCl <sub>2</sub> )
Pristine	131.80		97.16	7.27	
8PdCl <sub>2</sub>	132.16	97.30			23.84
7PdCl <sub>2</sub>	132.00	97.15	98.23	11.62	24.46
6PdCl <sub>2</sub> _aa	132.01	96.98	97.92	8.45	26.06
6PdCl <sub>2</sub> _ab	131.97	97.32	96.92	2.69	26.06
6PdCl <sub>2</sub> _ac	131.99	96.38	98.18	12.15	24.54
6PdCl <sub>2</sub> _bb	131.77	97.53	97.22	12.14	26.15
6PdCl <sub>2</sub> _cc	131.88	96.86	97.27	4.37	25.97

1. The dihedral angles of linker-Al-Al'-linker' shown in Figure 1d are labelled as  $\phi(\text{Pd})$  and  $\phi(\text{w/o Pd})$  for the cases with or without PdCl<sub>2</sub> coordination, respectively.

Table S3. The labels of the spin states of  $\text{LMCl}_2(\text{H}_2)$  intermediates<sup>1</sup>

spins	Low Spin (LS)	High Spin (HS)	Medium Spin (MS)
$\text{LScCl}_2(\text{H}_2)$	1/2	X	X
$\text{LTiCl}_2(\text{H}_2)$	0	1	X
$\text{LVCl}_2(\text{H}_2)$	1/2	3/2	X
$\text{LCrCl}_2(\text{H}_2)$	0	2	1
$\text{LMnCl}_2(\text{H}_2)$	1/2	5/2	3/2
$\text{LFeCl}_2(\text{H}_2)$	0	2	1
$\text{LCoCl}_2(\text{H}_2)$	1/2	3/2	X
$\text{LNiCl}_2(\text{H}_2)$	0	1	X
$\text{LCuCl}_2(\text{H}_2)$	1/2	X	X
$\text{LZnCl}_2(\text{H}_2)$	0	X	X
$\text{LYCl}_2(\text{H}_2)$	1/2	X	X
$\text{LZrCl}_2(\text{H}_2)$	0	1	X
$\text{LNbCl}_2(\text{H}_2)$	1/2	3/2	X
$\text{LMoCl}_2(\text{H}_2)$	0	2	1
$\text{LTcCl}_2(\text{H}_2)$	1/2	5/2	3/2
$\text{LRuCl}_2(\text{H}_2)$	0	2	1
$\text{LRhCl}_2(\text{H}_2)$	1/2	3/2	X
$\text{LPdCl}_2(\text{H}_2)$	0	1	X
$\text{LAGCl}_2(\text{H}_2)$	1/2	X	X
$\text{LCdCl}_2(\text{H}_2)$	0	X	X
$\text{LTaCl}_2(\text{H}_2)$	1/2	3/2	X
$\text{LWCl}_2(\text{H}_2)$	0	2	1
$\text{LReCl}_2(\text{H}_2)$	1/2	5/2	3/2
$\text{LOsCl}_2(\text{H}_2)$	0	2	1
$\text{LIrCl}_2(\text{H}_2)$	1/2	3/2	X
$\text{LPtCl}_2(\text{H}_2)$	0	1	X
$\text{LAuCl}_2(\text{H}_2)$	1/2	X	X
$\text{LHgCl}_2(\text{H}_2)$	0	X	X

<sup>1</sup> X denotes the corresponding spin state is not taken into account in this study.

Table S4. The H–H bond lengths ( $\text{\AA}$ ) of the optimized 6-coordinated  $\text{LMCl}_2(\text{H})_2$  intermediates <sup>1</sup>

spins	LS	HS	MS
$\text{LScCl}_2(\text{H})_2$	1.869		
$\text{LTiCl}_2(\text{H})_2$			
$\text{LVCl}_2(\text{H})_2$			
$\text{LCrCl}_2(\text{H})_2$			
$\text{LMnCl}_2(\text{H})_2$		1.835	1.820
$\text{LFeCl}_2(\text{H})_2$	0.775		
$\text{LCoCl}_2(\text{H})_2$			
$\text{LNiCl}_2(\text{H})_2$	1.787		
$\text{LCuCl}_2(\text{H})_2$			
$\text{LZnCl}_2(\text{H})_2$			
$\text{LYCl}_2(\text{H})_2$			
$\text{LZrCl}_2(\text{H})_2$	2.552		
$\text{LNbCl}_2(\text{H})_2$	2.839		
$\text{LMoCl}_2(\text{H})_2$	2.024		1.683
$\text{LTcCl}_2(\text{H})_2$	1.558	1.945	2.042
$\text{LRuCl}_2(\text{H})_2$	0.820	1.819	1.720
$\text{LRhCl}_2(\text{H})_2$	0.804	1.532	
$\text{LPdCl}_2(\text{H})_2$	0.780	1.806	
$\text{LAgCl}_2(\text{H})_2$			
$\text{LCdCl}_2(\text{H})_2$			
$\text{LTaCl}_2(\text{H})_2$	2.761	0.780	
$\text{LWCl}_2(\text{H})_2$	2.647	0.771	1.896
$\text{LReCl}_2(\text{H})_2$	1.765	2.168	2.195
$\text{LOsCl}_2(\text{H})_2$	1.739	1.994	1.920
$\text{LIrCl}_2(\text{H})_2$	1.950	1.862	
$\text{LPtCl}_2(\text{H})_2$	2.099	2.064	
$\text{LAuCl}_2(\text{H})_2$			
$\text{LHgCl}_2(\text{H})_2$			

<sup>1</sup> The blank cells represent that the stable dihydrido intermediates cannot be identified where the criteria of inter-hydrogen distance is greater than 0.75 $\text{\AA}$ .

Table S5. The H–H bond lengths ( $\text{\AA}$ ) of the optimized 5-coordinated  $\text{LMCl}(\text{H})_2$  intermediates <sup>1</sup>

spins	LS	HS	MS
$\text{LScCl}(\text{H})_2$	2.949		
$\text{LTiCl}(\text{H})_2$	2.157		
$\text{LVCl}(\text{H})_2$	1.801	1.844	
$\text{LCrCl}(\text{H})_2$	2.678	3.342	
$\text{LMnCl}(\text{H})_2$	0.814		0.784
$\text{LFeCl}(\text{H})_2$		0.777	
$\text{LCoCl}(\text{H})_2$	1.857		
$\text{LNiCl}(\text{H})_2$			
$\text{LCuCl}(\text{H})_2$			
$\text{LZnCl}(\text{H})_2$	1.900		
$\text{LYCl}(\text{H})_2$	3.338		
$\text{LZrCl}(\text{H})_2$	3.090		
$\text{LNbCl}(\text{H})_2$	2.232	2.162	
$\text{LMoCl}(\text{H})_2$	1.808	1.879	
$\text{LTcCl}(\text{H})_2$	2.742	1.752	2.692
$\text{LRuCl}(\text{H})_2$	2.126	1.985	
$\text{LRhCl}(\text{H})_2$	1.960	0.807	
$\text{LPdCl}(\text{H})_2$	1.757		
$\text{LAgCl}(\text{H})_2$			
$\text{LCdCl}(\text{H})_2$	2.101		
$\text{LTaCl}(\text{H})_2$	2.969	2.971	
$\text{LWCl}(\text{H})_2$	2.872	2.859	
$\text{LReCl}(\text{H})_2$	1.813	2.007	1.935
$\text{LOsCl}(\text{H})_2$	2.172	1.913	
$\text{LIrCl}(\text{H})_2$	2.048	1.564	
$\text{LPtCl}(\text{H})_2$	1.624		
$\text{LAuCl}(\text{H})_2$	2.045		
$\text{LHgCl}(\text{H})_2$	2.618		

<sup>1</sup> The blank cells represent that the stable dihydrido intermediates cannot be identified where the criteria of inter-hydrogen distance is greater than 0.75 $\text{\AA}$ .