Supporting Information

Huang et al. 10.1073/pnas.1017430108

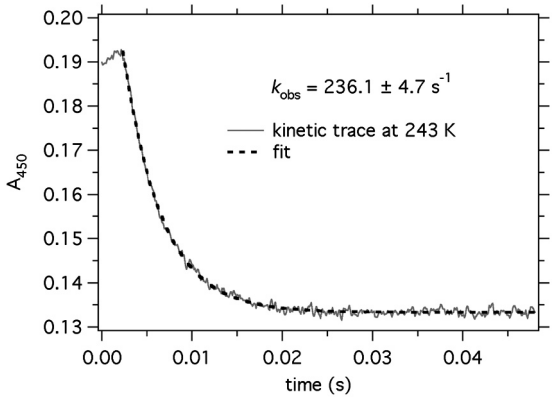

Fig. S1. Kinetic trace and single exponential fit of the data at 243 K. Values of k_{obs} in Figs. S1–S6 are the mean of eight determinations for each figure.

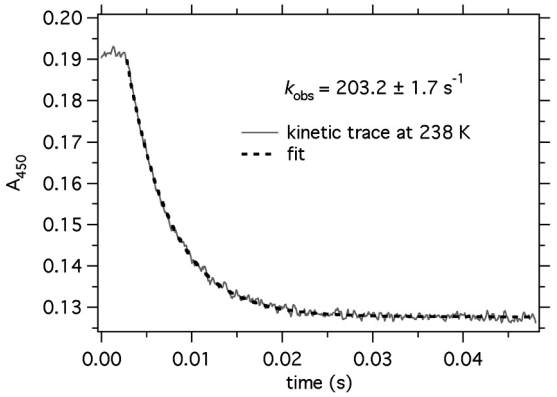

Fig. S2. Kinetic trace and single exponential fit of the data at 238 K.

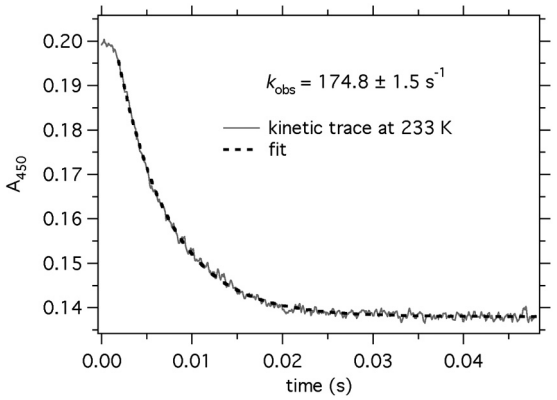

Fig. S3. Kinetic trace and single exponential fit of the data at 233 K.

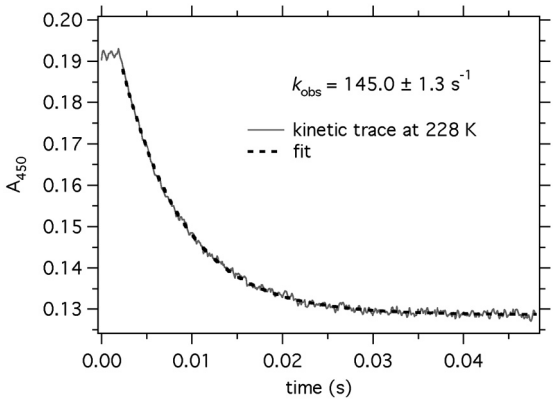

Fig. S4. Kinetic trace and single exponential fit of the data at 228 K.

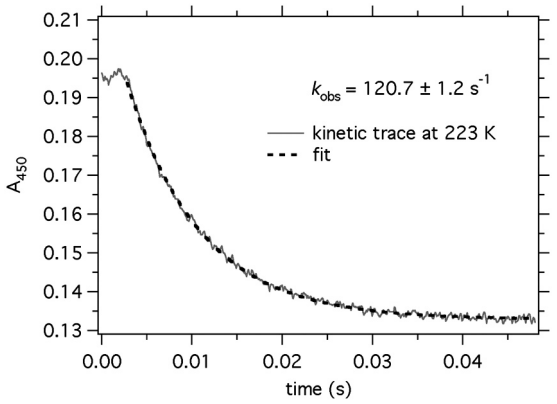

Fig. S5. Kinetic trace and single exponential fit of the data at 223 K.

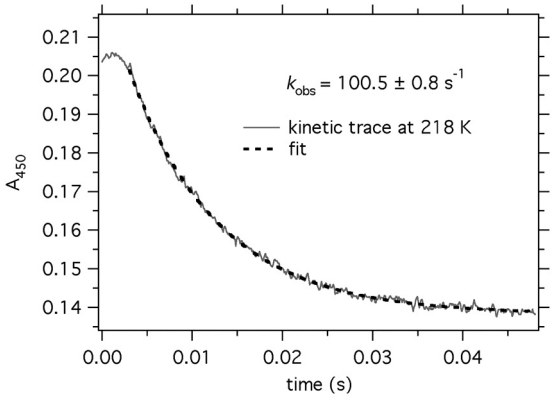

Fig. S6. Kinetic trace and single exponential fit of the data at 218 K.

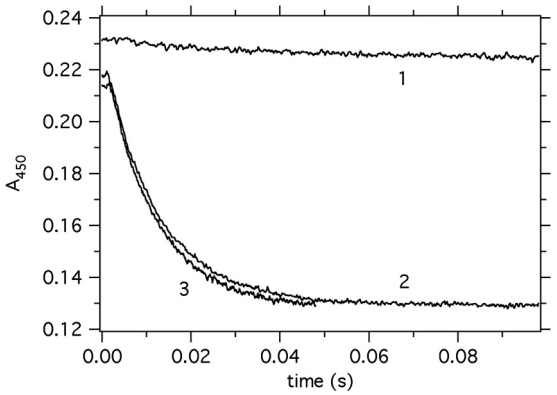

Fig. S7. Kinetics traces acquired at 450 nm, 218 K, $\{[Ni(py{N_2}^{Me2})(OH)]^{1-}\} = 0.1$ mM and $[CO_2] = 1$ mM in DMF. Trace **1**—no CO_2, 800 equiv of water; trace **2**—800 equiv water; trace **3**—no water.

Table S1. Observed (s^{-1}) and second-order ($M^{-1}{\cdot}s^{-1}$) rate constants at temperatures

T, °C		k_{obs} (at $[CO_2] = 1$ mM)							Average
−30	232.5	234.1	243	236.9	243.5	233.5	233.2	231.8	236.1
−35	202.7	201.6	202	203.1	205.2	203.2	206.2	201.7	203.2
−40	175	176.2	174.2	172.6	175.5	172.7	175.7	176.5	174.8
−45	144.1	142.2	145.9	145.8	144.8	146	145	145.9	145.0
−50	120.7	120.8	118.9	121.5	119.1	121	120.9	122.5	120.7
−55	100.3	101	100.6	99.25	101.1	99.72	101.7	100.7	100.5

T, °C	T, K	k	$k_2 = k/CO_2$	k_2/T	$\ln(k_2/T)$	$1/T$
−30	243	236.1	236,100	971.60	6.88	0.0041
−35	238	203.2	203,200	853.78	6.75	0.0042
−40	233	174.8	174,800	750.21	6.62	0.0043
−45	228	145.0	145,000	635.96	6.46	0.0044
−50	223	120.7	120,700	541.26	6.29	0.0045
−55	218	100.5	100,500	461.01	6.13	0.0046

T, °C		$[CO_2]$, M						
		0.00025	0.0005	0.00075	0.001	0.0015	0.002	0.0025
−30	k_{obs}, s^{-1}	125.2	203.4	231.3	272.8			
		121.9	203.0	237.4	279.1			
		123.0	203.0	236.1	298.2			
		120.3	207.0	240.2	285.1			
	Average	122.6	204.1	236.3	283.8			
−38	k_{obs}, s^{-1}		132.0	183.6	204.2	269.0	332.4	
			134.5	182.2	205.6	274.5	341.4	
			136.1	179.4	203.4	278.2		
			133.1	180.0	208.2	273.8		
			130.1		207.0	278.5		
	Average		133.2	181.3	205.7	274.8	336.9	
−45	k_{obs}, s^{-1}		93.21	135.4	151.5	205.4	258.2	
			95.95	135.7	150.7	207.5	252.6	
			90.53	137.6	157.4	216.1	247.7	
			91.00	139.3	157.7	216.7	254.9	
			91.30	137.0	154.9	203.3	257.4	
	Average		92.40	137.0	154.0	209.8	254.2	
−50	k_{obs}, s^{-1}		82.57		101.6	165.0	188.2	229.3
			84.25		101.0	167.8	188.0	227.3
			83.52		101.8	165.2	194.7	231.1
			84.23		102.1	167.4	197.6	234.4
						153.4		
	Average		83.6		101.6	163.8	192.1	230.5

Table S2. Comparison of experimental and computed structural metrics

	$[Ni(pyN_2^{Me2})(OH)]^-$			$[Ni(pyN_2^{Me2})(OCO_2H)]^-$ (P2*)					
Method/basis set	Ni—N(py)	Ni—N(amide)	Ni—O1	Ni—N(py)	Ni—N(amide)	Ni—O2	C—O1	C—O2	C=O3
experimental*	1.826(3)	1.911(2)	1.825(3)	1.817(4)	1.896(4)	1.871(4)	1.293(6)	1.253(7)	1.286(7)
B3LYP/6-31G(d)	1.816	1.926, 1.929	1.791	1.816	1.916	1.856	1.375	1.286	1.236
(DMF solvation)	1.820	1.917, 1.923	1.803	1.818	1.913	1.864	1.375	1.284	1.237
B3LYP/DGDZVP	1.845	1.955, 1.959	1.822	1.838	1.947	1.883	1.383	1.287	1.239
(DMF Solvation)	1.847	1.941, 1.956	1.843	1.839	1.942	1.896	1.384	1.284	1.241
BP86/6-31G(d)	1.790	1.897, 1.903	1.786	1.793	1.894	1.857	1.387	1.300	1.247
(DMF solvation)	1.792	1.898, 1.890	1.794	1.795	1.891	1.862	1.385	1.300	1.247
BP86/DGDZVP	1.819	1.931, 1.938	1.823	1.819	1.930	1.888	1.396	1.301	1.249
(DMF solvation)	1.822	1.919, 1.932	1.838	1.822	1.927	1.896	1.396	1.299	1.251

*Both experimental structures and all calculated P2 geometries are C_s symmetric.