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

Supporting Information

Kinetic Modelling of Cobalt-Catalyzed Propene Hydroformylation: A Combined *Ab Initio* and Experimental Fitting Protocol

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1. Fitting results for models M0 – M6

Table S1. The 'raw' *ab initio* values for M0. The 'raw' *ab initio* enthalpies and entropies for all species are obtained by carrying out a linear fit of the *ab initio* Gibbs energies at three temperatures 383, 403 and 423 K (taken from [Szlapa and Harvey, *Chem. Eur. J.* **2018**, 24, 17096–17104]).

Species	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔG (kJ mol^{-1}) 383 K
1	–17.991	0.010878	–22.157
TS2	–21.336	–0.168283	43.116
3	0.000	0.000000	0.000
TS4	150.632	0.096896	113.521
5	144.657	0.156086	84.876
TS6	153.977	0.134296	102.542
7	39.521	0.014178	34.091
TS8	66.643	0.014703	61.012
9	40.294	0.018707	33.129
TS10	67.571	0.013981	62.216
11	38.179	0.018050	31.266
TS12	84.362	–0.024861	93.884
13	–45.361	–0.122480	1.549
TS14	86.497	–0.030637	98.231
15	–45.132	–0.130684	4.920
TS16	9.958	–0.130028	59.759
17	–4.354	–0.124777	43.436
TS18	7.956	–0.135279	59.768
19	–12.874	–0.127731	36.047
TS20	0.021	–0.247322	94.745

21	–89.117	–0.270492	14.481
TS22	–4.739	–0.257299	93.807
23	–95.378	–0.276990	10.709
TS24	17.695	–0.258021	116.517
25	31.270	–0.119263	76.948
TS26	10.970	–0.263141	111.753
27	26.466	–0.120707	72.697
TS28	81.047	–0.100622	119.585
29	18.304	0.023301	9.380
TS30	83.211	–0.109483	125.143
TS31	–14.803	–0.269245	88.318
TS32	–14.040	–0.274693	91.167

Table S2. The fitted Δ*H* (in kJ mol^{-1}), Δ*S* (in kJ mol^{-1} K^{-1}, and Δ*G* (in kJ mol^{-1}) values and change with respect to 'raw' *ab initio* values for M1.

Species	Δ*H* (fitted and change)		Δ*S* (fitted and change)		Δ*G* (fitted and change) 383K	
1	–14.389664	3.601336	0.029768	0.018890	–25.790950	–3.633676
TS2	–24.225498	–2.889498	–0.178672	–0.010389	44.205918	1.089529
TS4	144.644342	–5.987658	0.116890	0.019994	99.875589	–13.645243
TS6	148.230787	–5.746213	0.146050	0.011754	92.293509	–10.248123
TS12	87.934709	3.572709	–0.040464	–0.015603	103.432487	9.548724
TS14	85.855227	–0.641773	–0.049135	–0.018498	104.674107	6.443136
TS31	–16.997378	–2.194378	–0.263049	0.006196	83.750403	–4.567432
TS32	–15.530868	–1.490868	–0.264915	0.009778	85.931734	–5.235685

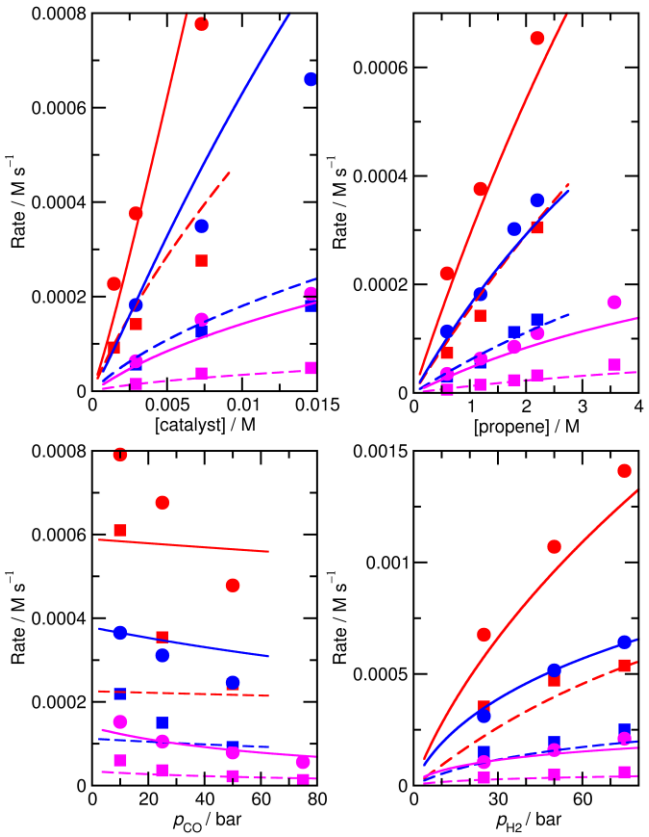


Figure S1. Predicted (lines) and experimental (points) rates for formation of n-butyraldehyde and iso-butyraldehyde under a range of different experimental conditions for M1. Experimental conditions: Top left: p_{CO}=p_{H2}=50 bar, [propene]=1.19 M; Top right: p_{CO}=p_{H2}=50 bar, [catalyst]=0.00292 M; Bottom left: p_{H2}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M; Bottom right: p_{CO}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M. Red, 423 K; Blue, 403 K; Magenta, 383 K. Experimental rates for n-butyraldehyde are shown as circles, and for iso-butyraldehyde as squares. Calculated rates for n-butyraldehyde are shown as solid lines, and for iso-butyraldehyde as dashed lines.

Table S3. The derivative of RMS error with respect to Δ*H* and *T*Δ*S* for all species for 'raw' *ab initio* model M0 (*T*=403 K).

Species	$\frac{\partial \chi}{\partial \Delta H}$	$\frac{\partial \chi}{\partial (T\Delta S)}$
1	–0.0101	0.0101
TS2	0.0000	0.0000
3	–0.0449	0.0444
TS4	0.0128	–0.0126
5	0.0000	0.0000
TS6	0.0314	–0.0308
7	0.0000	0.0000
TS8	0.0000	0.0000
9	0.0000	0.0000
TS10	0.0000	0.0000
11	0.0000	0.0000
TS12	–0.0005	0.0004
13	–0.0010	0.0011
TS14	0.0035	–0.0034
15	–0.0001	0.0001
TS16	0.0000	0.0000
17	0.0000	0.0000
TS18	0.0000	0.0000
19	0.0000	0.0000
TS20	0.0000	0.0000
21	–0.0003	0.0003
TS22	0.0000	0.0000
23	–0.0002	0.0002
TS24	0.0110	–0.0115
25	0.0000	0.0000
TS26	0.0043	–0.0037
27	0.0000	0.0000
TS28	–0.0002	0.0002
29	0.0000	0.0000
TS30	0.0000	0.0000
TS31	–0.0055	0.0050
TS32	0.0000	0.0001

Table S4. The fitted Δ*H* (in kJ mol^{-1}), Δ*S* (in kJ mol^{-1} K^{-1}, and Δ*G* (in kJ mol^{-1}) values and change with respect to 'raw' *ab initio* values for M2.

Species	Δ*H* (fitted and change)		Δ*S* (fitted and change)		Δ*G* (fitted and change) 383K	
1	–16.014568	1.976432	0.017351	0.006473	–22.659872	–0.502598
TS4	144.691500	–5.940500	0.109756	0.012860	102.655095	–10.865737
TS6	149.521605	–4.455395	0.145778	0.011482	93.688691	–8.852941
TS12	88.688418	4.326418	–0.037836	–0.012975	103.179540	9.295777
13	–39.838624	5.522376	–0.135150	–0.012670	11.923750	10.374910
TS14	86.486169	–0.010831	–0.047713	–0.017076	104.760289	6.529318
15	–49.124168	–3.992168	–0.147646	–0.016962	7.424222	2.504250
TS24	12.007198	–5.687802	–0.266910	–0.008889	114.233824	–2.283219
TS26	15.322114	4.352114	–0.256758	0.006383	113.660240	1.907237
TS31	–14.966906	–0.163906	–0.279899	–0.010654	92.234229	3.916394
TS32	–15.020022	–0.980022	–0.270948	0.003745	88.752971	–2.414448

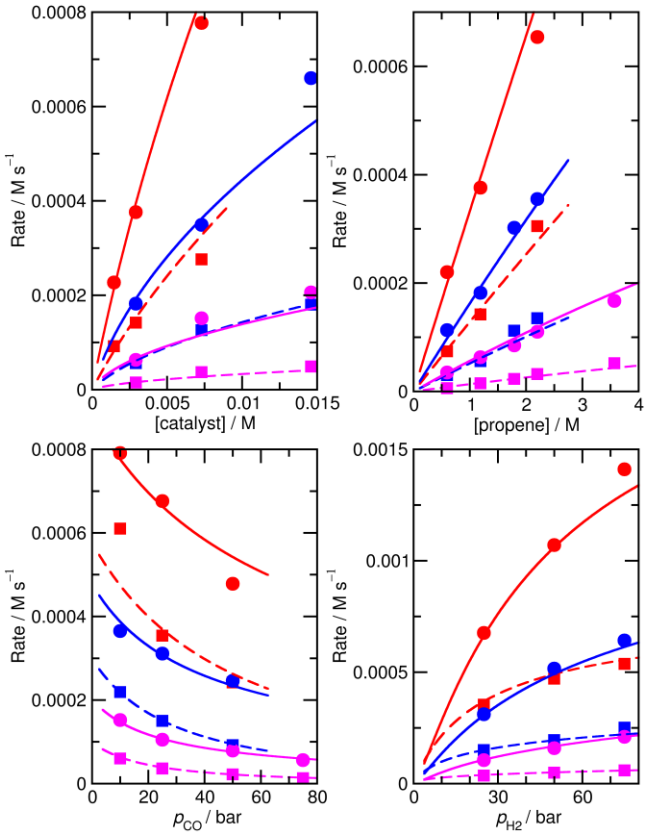


Figure S2. Predicted (lines) and experimental (points) rates for formation of n-butyraldehyde and iso-butyraldehyde under a range of different experimental conditions for M3. See Fig. S1 for full reaction conditions.

Table S5. The fitted Δ*H* (in kJ mol^{-1}), Δ*S* (in kJ mol^{-1} K^{-1}, and Δ*G* (in kJ mol^{-1}) values and change with respect to 'raw' ab initio values for M3.

Species	Δ*H* (fitted and change)		Δ*S* (fitted and change)		Δ*G* (fitted and change) 383K	
1	–103.717457	–85.726457	–0.187143	–0.198021	–32.041688	–9.884414
TS2	–67.643823	–46.307823	–0.316470	–0.148187	53.564187	10.447798
3	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
TS4	21.107150	–129.524850	–0.031809	–0.128705	33.289997	–80.230835
5	73.701667	–70.955333	0.019139	–0.136947	66.371430	–18.504632
TS6	42.634569	–111.342431	–0.127224	–0.261520	91.361361	–11.180271
7	–20.942124	–60.463124	–0.137915	–0.152093	31.879321	–2.211505
TS8	16.256047	–50.386953	–0.117291	–0.131994	61.178500	0.166749
9	–46.553247	–86.847247	–0.144202	–0.162909	8.676119	–24.453100
TS10	38.660157	–28.910843	–0.138899	–0.152880	91.858474	29.642197
11	–30.095600	–68.274600	–0.152778	–0.170828	28.418374	–2.847476
TS12	21.677860	–62.684140	–0.203173	–0.178312	99.493119	5.609356
13	–88.696355	–43.335355	–0.320201	–0.197721	33.940628	32.391788
TS14	32.683266	–53.813734	–0.174592	–0.143955	99.552002	1.321031
15	–102.658070	–57.526070	–0.279403	–0.148719	4.353279	–0.566693
TS16	–53.465496	–63.423496	–0.275658	–0.145630	52.111518	–7.647206
17	–75.847933	–71.493933	–0.271067	–0.146290	27.970728	–15.464863
TS18	–49.702281	–57.658281	–0.291084	–0.155805	61.782891	2.015034
19	–76.197572	–63.323572	–0.285335	–0.157604	33.085733	–2.961240
TS20	–80.913112	–80.934112	–0.401196	–0.153874	72.744956	–22.000370
21	–132.709007	–43.592007	–0.433525	–0.163033	33.331068	18.849632
TS22	–86.792662	–82.053662	–0.404624	–0.147325	68.178330	–25.628187
23	–169.751462	–74.373462	–0.434083	–0.157093	–3.497673	–14.206843
TS24	–10.913633	–28.608633	–0.310738	–0.052717	108.099021	–8.418022
25	–29.880405	–61.150405	–0.268748	–0.149485	73.050079	–3.897650
TS26	–52.618547	–63.588547	–0.403353	–0.140212	101.865652	–9.887351
27	–34.684405	–61.150405	–0.270192	–0.149485	68.799131	–3.897650
TS28	52.117085	–28.929915	–0.261735	–0.161113	152.361590	32.776364
29	–42.846405	–61.150405	–0.126184	–0.149485	5.482067	–3.897650
TS30	25.666324	–57.544676	–0.239066	–0.129583	117.228602	–7.914387
TS31	–15.870633	–1.067633	–0.419118	–0.149873	144.651561	56.333726
TS32	–85.545022	–71.505022	–0.423836	–0.149143	76.784166	–14.383253

For M4, it is worth noting that we performed multiple partially unconstrained gradient-based minimizations with different optimization parameters to ensure it indeed reach the global minimum. Among these fittings having the same RMS error of 13.4%, the fitted values for **TS4** are always different but that for other species are always constant, suggesting **TS4** does not have an effect on the final RMS error.

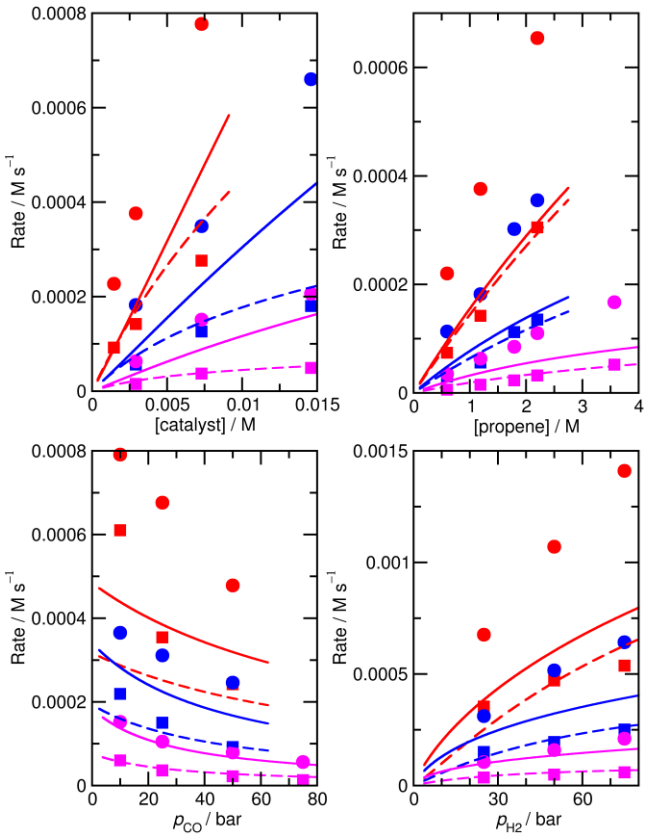


Figure S3. Predicted (lines) and experimental (points) rates for formation of n-butyraldehyde and iso-butyraldehyde under a range of different experimental conditions for MN. See Fig. S1 for full reaction conditions.

Table S6. The derivative of RMS error with respect to Δ*H* and *T*Δ*S* for all species for 'new' *ab initio* model MN (*T*=403 K).

Species	$\frac{\partial\chi}{\partial\Delta H}$	$\frac{\partial\chi}{\partial(T\Delta S)}$
1	–0.0086	0.0090
TS2	0.0000	0.0000
3	0.0025	–0.0001
TS4'	0.0013	–0.0014
5'	0.0000	0.0000
TS6'	–0.0124	0.0108
7	0.0000	0.0000
TS8	0.0000	0.0000
9	0.0000	0.0000
TS10	0.0000	0.0000
11	0.0000	0.0000
TS12	0.0041	–0.0039
13	–0.0026	0.0027
TS14	–0.0261	0.0251

15	–0.0003	0.0003
TS16	0.0000	0.0000
17	0.0000	0.0000
TS18	0.0000	0.0000
19	0.0000	0.0000
TS20	0.0000	0.0000
21	–0.0005	0.0006
TS22	0.0000	0.0000
23	–0.0004	0.0004
TS24	0.0553	–0.0550
25	0.0000	0.0000
TS26	–0.0477	0.0465
27	0.0000	0.0000
TS28	–0.0002	0.0002
29	0.0000	0.0000
TS30	0.0000	0.0000
TS31	0.0399	–0.0391
TS32	–0.0041	0.0039

Table S7. The fitted Δ*H* (in kJ mol^{-1}), Δ*S* (in kJ mol^{-1} K^{-1}, and Δ*G* (in kJ mol^{-1}) values and change with respect to 'new' *ab initio* values for M5.

Species	Δ*H* (fitted and change)		Δ*S* (fitted and change)		Δ*G* (fitted and change) 383K	
1	–22.192219	–4.201219	0.010664	–0.000214	–26.276447	–4.119173
TS4'	68.394891	–6.105109	–0.064470	0.015530	93.086902	–12.053098
TS6'	60.124311	–9.175689	–0.088148	–0.020148	93.885165	–1.458835
TS12	89.401823	5.039823	–0.029146	–0.004285	100.564635	6.680872
13	–42.225191	3.135809	–0.125091	–0.002611	5.684745	4.135905
TS14	84.938495	–1.558505	–0.045165	–0.014528	102.236579	4.005608
15	–49.668348	–4.536348	–0.119154	0.011530	–4.032376	–8.952348
TS24	18.043603	0.348603	–0.242710	0.015311	111.001553	–5.515490
TS26	12.292856	1.322856	–0.250426	0.012715	108.206128	–3.546875
TS31	–14.194753	0.608247	–0.278362	–0.009117	92.418007	4.100172
TS32	–11.913796	2.126204	–0.265711	0.008982	89.853471	–1.313948

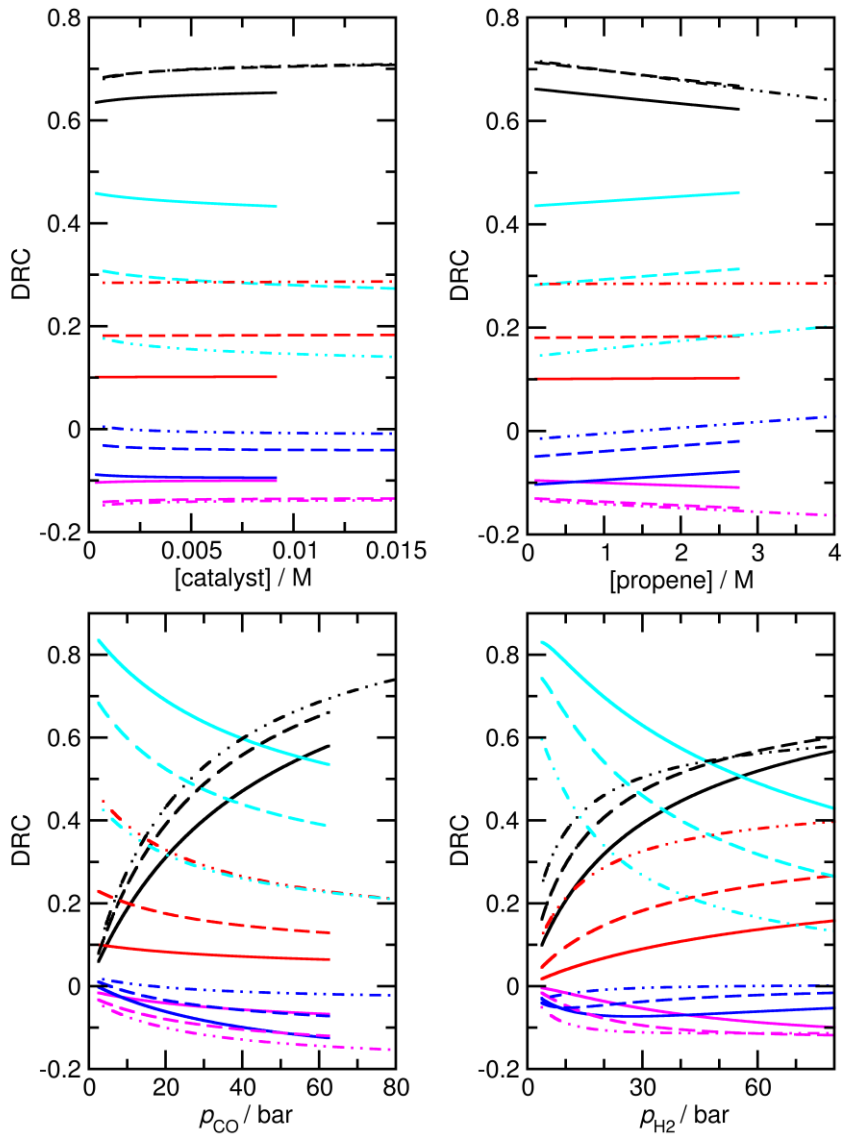


Figure S4. Calculated degree of rate control (DRC) values for formation of n-butyraldehyde for M5 under a range of different experimental conditions. Experimental conditions: Top left: p_{CO}=p_{H2}=50 bar, [propene]=1.19 M; Top right: p_{CO}=p_{H2}=50 bar, [catalyst]=0.00292 M; Bottom left: p_{H2}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M; Bottom right: p_{CO}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M. Black, step 3; Red, step 6; Magenta, step 7; Cyan, step 12; Blue, step 13; Solid lines, 423 K; Dashed lines, 403 K; Dash double-dotted lines, 383 K.

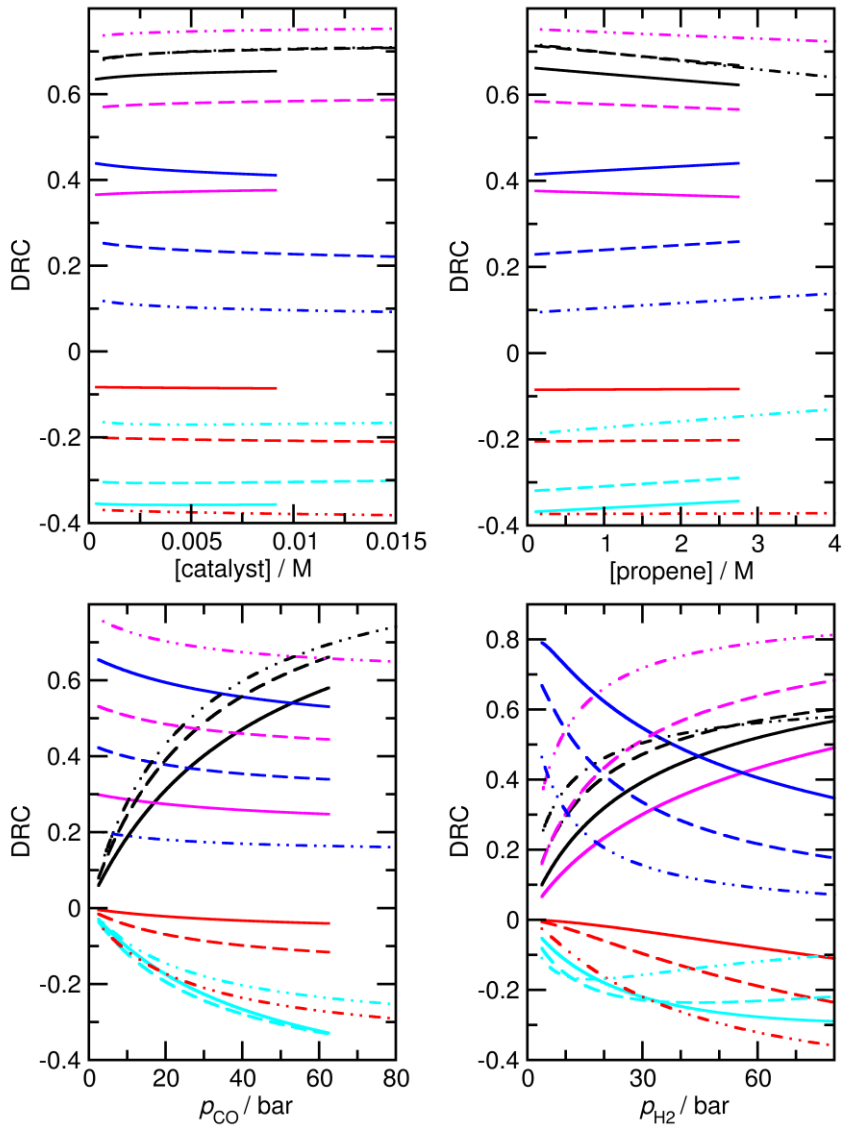


Figure S5. Calculated degree of rate control (DRC) values for formation of iso-butyraldehyde for M5 under a range of different experimental conditions. Experimental conditions: Top left: p_{CO}=p_{H2}=50 bar, [propene]=1.19 M; Top right: p_{CO}=p_{H2}=50 bar, [catalyst]=0.00292 M; Bottom left: p_{H2}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M; Bottom right: p_{CO}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M. Black, step 3; Red, step 6; Magenta, step 7; Cyan, step 12; Blue, step 13; Solid lines, 423 K; Dashed lines, 403 K; Dash double-dotted lines, 383 K.

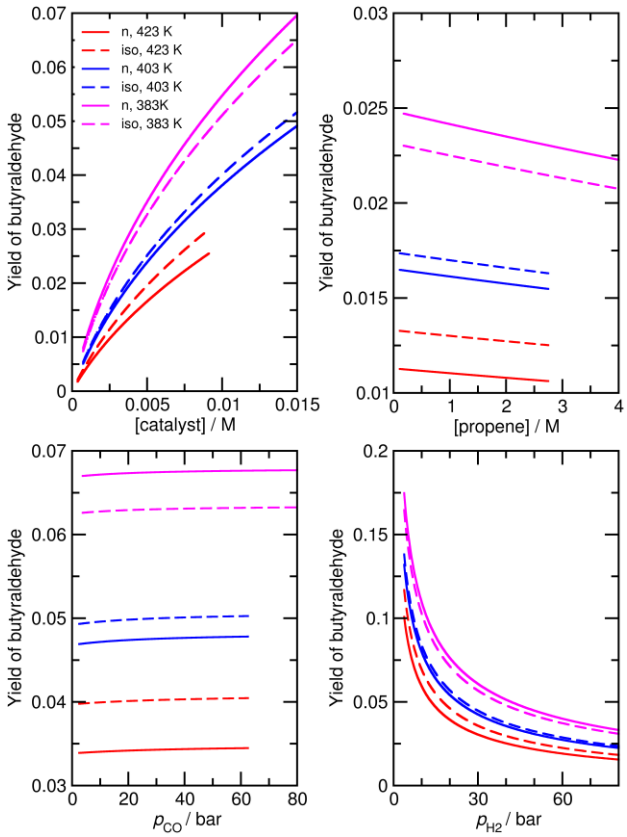
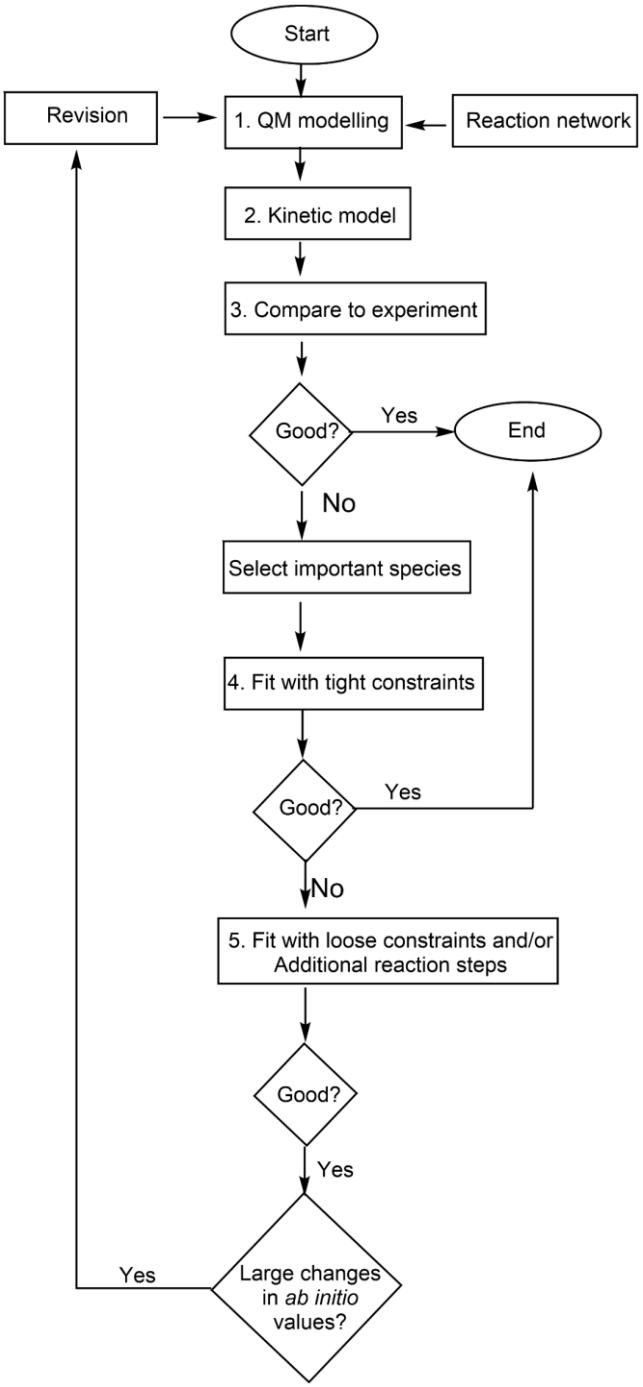


Figure S6. Predicted yield of n- and iso-butyraldehyde through alternative bimetallic mechanism under a range of different experimental conditions for M5. Experimental conditions: Top left: p_{CO}=p_{H2}=50 bar, [propene]=1.19 M; Top right: p_{CO}=p_{H2}=50 bar, [catalyst]=0.00292 M; Bottom left: p_{H2}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M; Bottom right: p_{CO}=25 bar, [catalyst]=0.0073 M, [propene]=1.19 M. Red, 423 K; Blue, 403 K; Magenta, 383 K; Solid lines, n-butyraldehyde; Dashed lines, iso-butyraldehyde.

Table S8. The fitted Δ*H* (in kJ mol^{-1}), Δ*S* (in kJ mol^{-1} K^{-1}, and Δ*G* (in kJ mol^{-1}) values and change with respect to 'new' *ab initio* values for M6.

Species	Δ*H* (fitted and change)		Δ*S* (fitted and change)		Δ*G* (fitted and change) 383K	
1	–15.990040	2.000960	0.027545	0.016667	–26.539650	–4.382376
TS4'	69.620580	–4.879420	–0.090418	–0.010418	104.250539	–0.889461
TS6'	63.409041	–5.890959	–0.079511	–0.011511	93.861691	–1.482309
TS12	85.825950	1.463950	–0.038588	–0.013727	100.605187	6.721424
13	–47.123422	–1.762422	–0.133762	–0.011282	4.107308	2.558468
TS14	84.027440	–2.469560	–0.047411	–0.016774	102.185887	3.954916
15	–47.315941	–2.183941	–0.146031	–0.015347	8.613953	3.693981
TS24	15.968126	–1.726874	–0.246735	0.011286	110.467488	–6.049555
TS26	14.379286	3.409286	–0.244643	0.018498	108.077375	–3.675628



Scheme S1. Flowchart of our protocol.

2. Cartesian coordinates and total energies

In the table below, E and G(383 K) values are electronic energies and Gibbs energies calculated at 383 K, respectively (B3LYP-D3BJ/6-311G(d)). Note that **TS4'** and **$HCo(CO)_3$(propene)** were already reported in [Szlapa and Harvey, *Chem. Eur. J.* **2018**, 24, 17096–17104].

CO
E: -113.346962
G(383 K): -113.367529

C	0.000000	0.000000	-0.643975
O	-0.000000	-0.000000	0.482982

$HCo(CO)_3$_C2V
E: -1723.459194
G(383 K): -1723.468982

Co	0.000000	0.000000	0.271922
H	0.000000	0.000000	1.785676
C	0.000000	1.746603	0.588571
O	0.000000	2.849993	0.867945
C	-0.000000	-1.746603	0.588571
O	-0.000000	-2.849993	0.867945
C	-0.000000	-0.000000	-1.496444
O	-0.000000	-0.000000	-2.637358

$HCo(CO)_4$_C3V
E: -1836.858366
G(383 K): -1836.862874

Co	0.000000	0.000000	0.184766
H	0.000000	0.000000	1.665397
C	0.000000	1.767501	0.456143
O	0.000000	2.879923	0.700971
C	1.530701	-0.883750	0.456143
O	2.494086	-1.439961	0.700971
C	0.000000	0.000000	-1.613721
O	0.000000	0.000000	-2.750703
C	-1.530701	-0.883750	0.456143
O	-2.494086	-1.439961	0.700971

Propene_CS
E: -117.942737
G(383 K): -117.892845

C	0.000000	0.473432	0.000000
C	-1.289483	0.152100	0.000000
H	-1.619534	-0.883491	0.000000
H	-2.066804	0.908955	0.000000
H	0.278444	1.526848	0.000000
C	1.135555	-0.505375	0.000000
H	1.776649	-0.367687	0.877784
H	0.778162	-1.537879	0.000000
H	1.776649	-0.367687	-0.877784

$HCo(CO)_3$(propene)
E: -1841.443345
G(383 K): -1841.377127

Co	0.198712	0.032272	-0.138144
H	-0.316182	-0.062166	-1.522291
C	-0.485836	1.662491	-0.310827
O	-0.978654	2.676158	-0.490706
C	1.721165	-0.302062	-1.000380
O	2.653223	-0.521705	-1.620458
C	0.851312	0.158519	1.538490
O	1.262523	0.239577	2.597100
C	-1.565280	-0.983149	0.430453
H	-1.715956	-0.790932	1.489660
C	-0.570800	-1.896036	0.082835
H	-0.017614	-2.420198	0.853123
H	-0.613182	-2.400959	-0.875460
C	-2.770711	-0.708477	-0.431665
H	-3.598904	-1.360004	-0.128973
H	-3.118335	0.322945	-0.341350
H	-2.560889	-0.899984	-1.485733

$HCo(CO)_3$(toluene)
E: -1995.133927
G(383 K): -1995.02949

Co	-1.039300	0.204151	-0.134290
H	-1.618308	0.572657	-1.462846
C	-2.362970	-0.955932	-0.235169
O	-3.298407	-1.608966	-0.318429
C	-1.102276	1.954457	0.042590
O	-1.250837	3.085831	0.132436
C	-0.421944	-0.218386	1.492141
O	-0.036468	-0.485345	2.529706
C	2.177150	-1.836267	0.352361
H	2.620175	-2.597565	0.985171
C	2.640520	-0.512131	0.435102
C	1.165101	-2.169749	-0.525512
C	0.596247	-1.174214	-1.345749
H	0.809399	-3.191435	-0.596358
H	-0.083326	-1.454196	-2.140312
C	2.106814	0.485439	-0.363554
C	1.069257	0.145400	-1.268420
H	0.776784	0.863056	-2.024973
H	3.432003	-0.267941	1.136375
C	2.583104	1.909180	-0.286095
H	2.888093	2.281501	-1.268530
H	1.784598	2.568861	0.069482
H	3.431381	2.014032	0.391956

Toluene
E: -271.647314
G(383 K, 1M): -271.557062

C	-0.004751	0.911576	0.000000
C	-0.007295	0.194184	1.199681
C	-0.007295	-1.198157	1.202713
C	-0.006665	-1.900406	-0.000000

C	-0.007295	-1.198157	-1.202713
C	-0.007295	0.194184	-1.199681
H	-0.010979	0.733061	2.142889
H	-0.011862	-1.735094	2.145893
H	-0.009806	-2.985346	-0.000000
H	-0.011862	-1.735094	-2.145893
H	-0.010979	0.733061	-2.142889
C	0.028401	2.419236	0.000000
H	-0.465021	2.831716	0.883090
H	1.058715	2.791220	0.000000
H	-0.465021	2.831716	-0.883090

TS6'

E: -2113.077729

G(383 K): -2112.906424

Co	-0.618191	-0.204079	0.090826
H	-1.107115	0.314299	1.430881
C	-0.877330	1.500149	-0.299463
O	-1.119225	2.598984	-0.494810
C	-0.813409	-1.735076	0.967341
O	-1.006334	-2.678141	1.580427
C	0.072944	-0.776545	-1.436856
O	0.543511	-1.132646	-2.413990
C	2.357735	1.191607	0.544660
C	3.061882	0.960584	-0.641118
H	3.296058	1.797626	-1.292354
C	2.051066	0.094514	1.357491
C	2.465765	-1.192021	1.009483
H	2.223703	-2.026916	1.658799
C	3.464241	-0.322572	-0.997631
C	3.172344	-1.404698	-0.169018
H	3.483487	-2.405624	-0.447513
C	-3.790732	-0.238046	0.090816
C	-3.379841	-0.683815	-1.095831
H	-3.124860	-1.724993	-1.255975
H	-3.843435	-0.939990	0.920897
H	-3.307451	-0.027346	-1.957926
C	-4.188557	1.172036	0.394886
H	-3.572732	1.587272	1.199221
H	-4.087300	1.819547	-0.478542
H	-5.227750	1.220021	0.737072
H	4.001355	-0.480346	-1.926797
H	1.517284	0.254248	2.287673
C	1.977901	2.589772	0.957381
H	2.827577	3.102746	1.419498
H	1.661422	3.192212	0.103070
H	1.163251	2.586469	1.683828

TS4'

E: -2108.477881

G(383 K): -2108.377292

Co	-0.954803	-0.100352	-0.197763
H	-1.347169	0.337881	-1.592881
C	-1.205343	-1.690794	-0.972728
O	-1.377891	-2.663872	-1.538275
C	-0.952387	1.657262	-0.000940
O	-0.976548	2.795866	0.057037
C	-0.455392	-0.595989	1.435350
O	-0.116987	-0.902527	2.479726
C	-3.571189	-0.136642	0.427333
O	-4.117552	0.854617	0.455678
C	2.578683	-1.639350	0.461567
C	1.982249	-1.431832	-0.777104
C	2.976990	-0.541507	1.222287
C	1.784149	-0.134102	-1.254472
H	1.664107	-2.277624	-1.377039
C	2.795227	0.749697	0.736963
H	3.428184	-0.692259	2.197113
C	2.209708	0.974445	-0.512899
H	1.344958	0.017519	-2.234282
H	3.116571	1.598257	1.333669
C	2.086741	2.369531	-1.067203
H	3.043271	2.706757	-1.479180
H	1.349098	2.420974	-1.869918
H	1.793924	3.087254	-0.298011
H	2.721949	-2.646240	0.837876