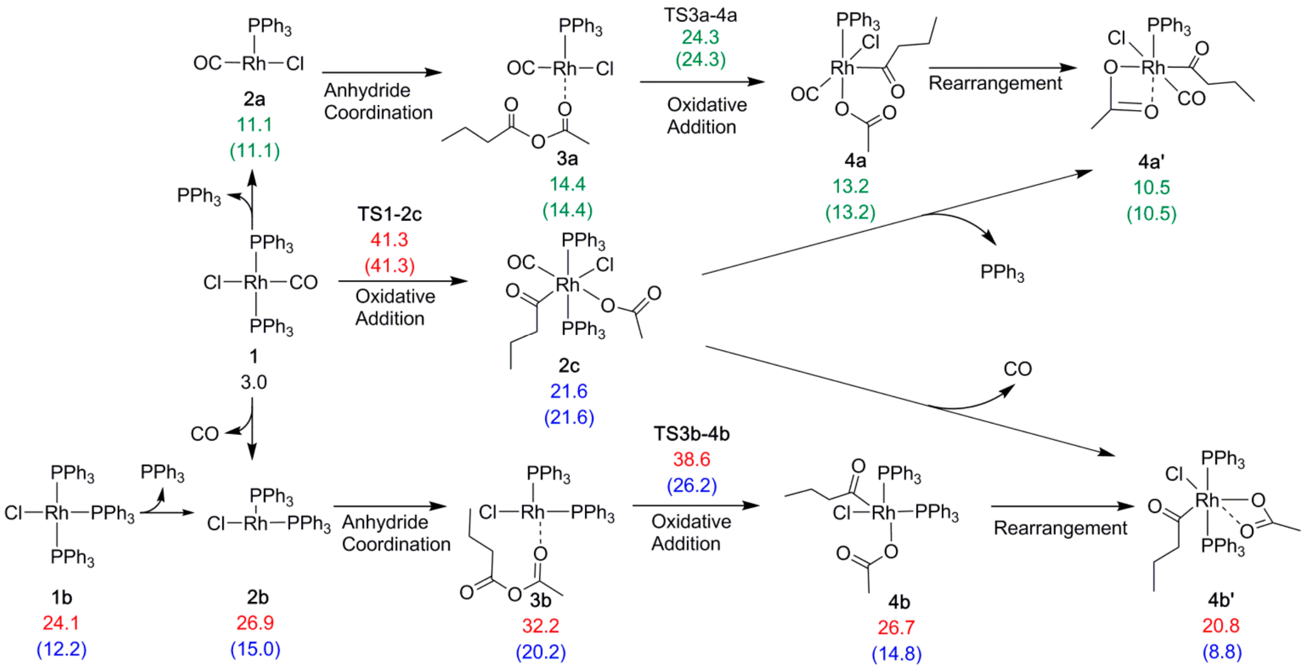
Supplementary Materials: The Mechanism of Rh-catalyzed Transformation of Fatty Acids to Linear Alpha Olefins.

Sondre H. Hopen Eliasson, Anamitra Chatterjee, Giovanni Occhipinti and Vidar R. Jensen

1. Rh reaction pathways

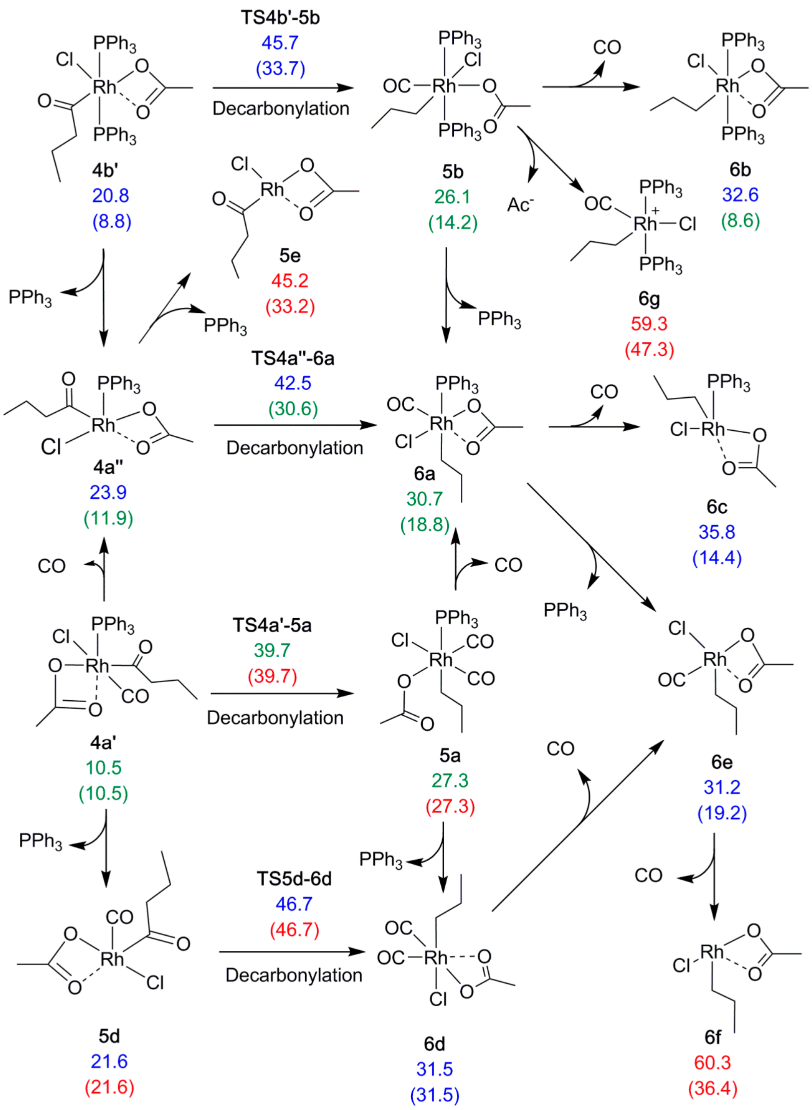
To find the most favored pathway for the Rh catalyzed decarbonylative dehydration many different possibilities, presented in the following, were explored. The free energy of the most favorable route(s) is colored in green, while energies of highly unfavorable species and pathways are colored in red. Other energies have been given a blue tint. The pathway reported in the manuscript corresponds to the pathway labeled "a" in the following. Except where otherwise indicated, all reported energies are Gibbs free energies calculated at 523 K, with butanoic acid as continuum solvent (termed ΔG_{BA}). The values in parentheses are the energies calculated using a CO pressure of 10^{-5} atm as described in the Computational Method section.

a) Oxidative addition.



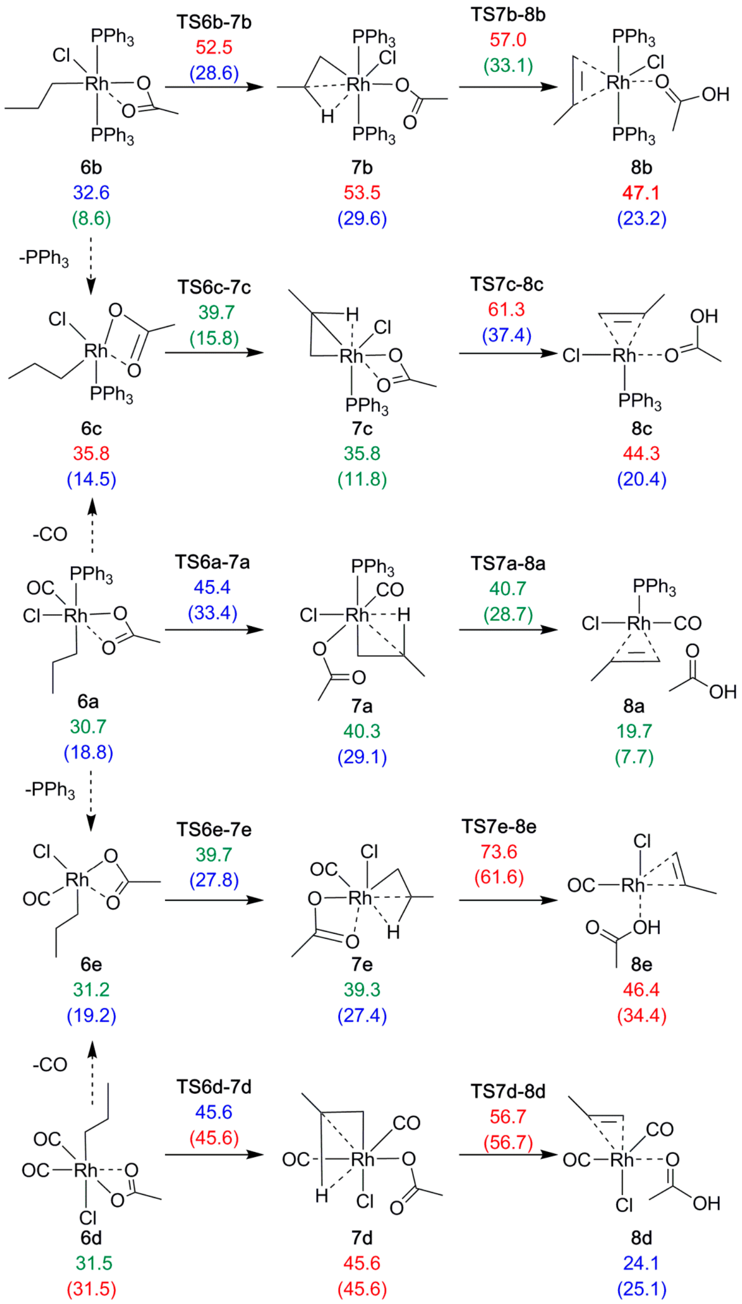
Scheme S1. The investigated pathways for oxidative addition of mixed anhydride.

b) Decarbonylation.



Scheme S2. The investigated pathways for decarbonylation.

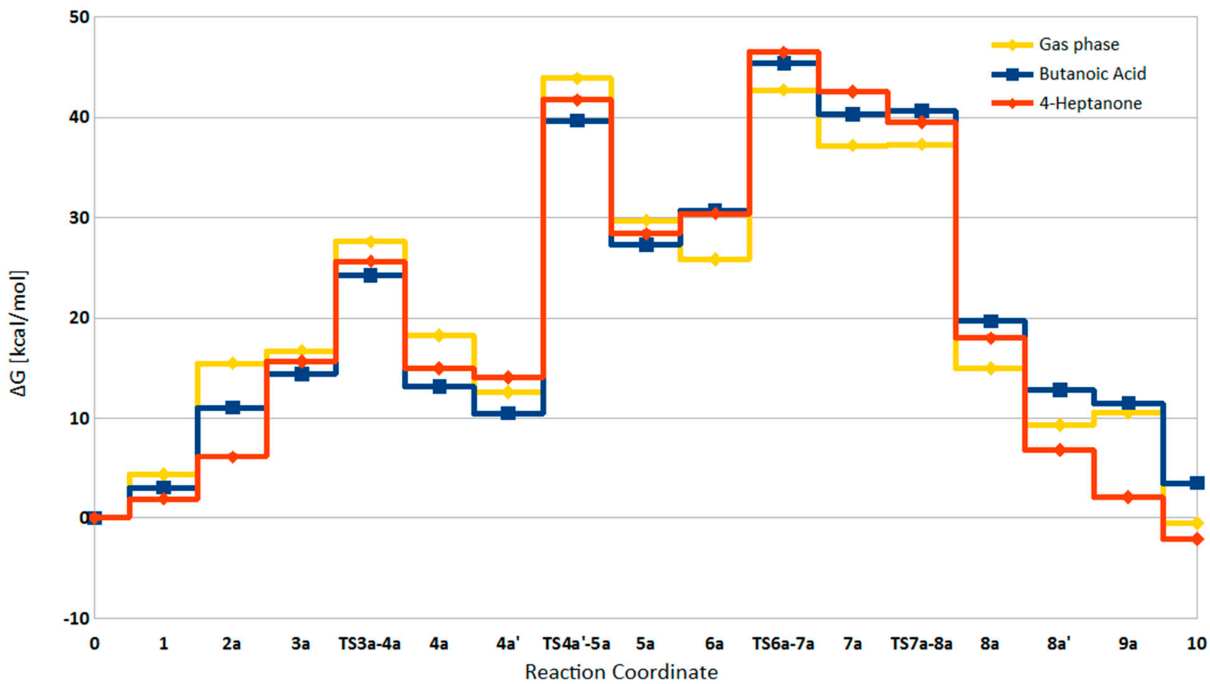
c) Alkene formation.



Scheme S3. The investigated pathways for β-hydrogen transfer to form alkene.

2. **The energy profile for the Rh-Mechanism in gas phase and butanoic acid and 4-heptanone solvent.**

The decarbonylative dehydration reactions are typically carried out in neat substrates and anhydride additives, i.e., without solvent. In other words, the reaction environment is dominated by the substrate and the additive (here: butanoic acid and acetic anhydride, respectively) and the acetic acid produced by the reaction. We have modeled this environment by using two solvents with different dielectric constants, butanoic acid (BA, ε = 2.85) and 4-heptanone (4-Hep, ε = 12.26), respectively, for which parameters are available in Gaussian 09. The corresponding free energy profiles of Rh-catalyzed decarbonylative dehydration in Scheme S4 are quite similar, with slightly higher barriers in general for the reaction modeled in 4-heptanone.



Scheme S4. The free energy profile for Rh-catalyzed decarbonylative dehydration as calculated in gas phase, butanoic acid (SMD model) and 4-heptanone solvent (SMD model) using the M06L functional and QZ basis sets.

3. The free energies for the reaction using different functionals and modified BJ-dampening.

SP calculations were performed using different DFT functionals (see the Computational Method section) to investigate the influence on the ΔG_{BA} for species of pathway **a**. The functionals investigated were PBE [1,2], B3LYP [3] and M06L [4-6]. PBE was used in combination Grimme's empirical dispersion term D3 in combination with Becke-Johnson damping [7], using both the original (termed D3-BJ) and the modified [8] (termed D3-(M)BJ) parameters. B3LYP was used in combination with D3-(M)BJ. The functionals were found to reproduce similar trends, but with some differences. M06L gave the overall lowest barrier for the rate-determining step, but gave, together with B3LYP, a higher de-carbonylation barrier compared to the PBE functional. For the oxidative addition, B3LYP was the outlier. The effect of the modified damping parameters was limited as PBE-D3(M)BJ and PBE-D3BJ in general gave energies in close agreement.

Table S1. The Gibbs free energies (kcal/mol) of the main species in butanoic acid solvent (SMD-model) at 523 K, calculated using different DFT functionals.

Species	PBE-D3BJ	B3LYP-D3(M)BJ	M06L	PBE-D3(M)BJ
0	0.0	0.0	0.0	0.0
1	2.8	2.7	3.0	2.8
2	16.6	19.7	11.1	21.1
3	21.4	21.5	14.4	24.1
TS3-4	22.2	28.5	24.3	23.4
4'	9.9	14.6	10.5	10.3
TS4'-5	34.3	41.6	39.7	34.8
5	22.9	28.1	27.3	20.9
6	34.4	33.6	30.7	36.7
TS6-7	49.5	47.5	45.4	51.4
7	43.4	42.1	40.3	45.0
TS7-8	39.3	41.3	40.7	40.3
8	24.6	21.8	19.7	27.0
8'	18.9	16.9	12.8	21.7
9	21.5	17.6	11.5	26.6
10	7.6	0.6	3.5	8.3

4. Energies of all species

Table S2. The electronic energy and free energy in a.u. calculated for the solvents (SMD-model), butanoic acid (BA) and 4-heptanone (4-Hep), and in gas phase. Calculations were performed with the M06L functional with QZ basis sets. Free energy calculated at 523 K.

Species	E(Gas Phase)	E(BA)	E(4-Hep)	G(Gas Phase)	G(BA)	G(4-Hep)
MA	-460.5042843	-460.5029881	-460.5176	-460.4172857	-460.4159896	-460.4306015
PPh_3	-1036.501858	-1036.507937	-1036.519006	-1036.312966	-1036.319045	-1036.330114
CO	-113.3485452	-113.3359949	-113.3444143	-113.3802592	-113.3677089	-113.3761283
BA	-307.8115738	-307.8135656	-307.8222835	-307.7485168	-307.7505086	-307.7592264
Propene	-117.9395724	-117.9397813	-117.942485	-117.9030978	-117.9033067	-117.9060103
AcOH	-229.1567229	-229.1592332	-229.169882	-229.141733	-229.1442433	-229.1548921
Ac_2O	-381.856609	-381.8537243	-381.8684754	-381.817451	-381.8145662	-381.8293174
AcO^-	-228.5923073	-228.6589378	-228.6798309	-228.5906698	-228.6573003	-228.6781934
1	-2757.071683	-2757.082413	-2757.111887	-2756.660443	-2756.671173	-2756.700647
2a	-1720.511493	-1720.521085	-1720.545596	-1720.329746	-1720.339338	-1720.36385
3a	-2181.051202	-2181.056167	-2181.085301	-2180.745081	-2180.750046	-2180.779180
TS3a-4a	-2181.035992	-2181.042545	-2181.071544	-2180.727743	-2180.734296	-2180.763295
4a	-2181.0467	-2181.05611	-2181.084476	-2180.742573	-2180.751982	-2180.780348
4a’	-2181.056956	-2181.061485	-2181.087053	-2180.751684	-2180.756212	-2180.781781
TS4’a-5a	-2181.007812	-2181.015746	-2181.043721	-2180.7018	-2180.709733	-2180.737709
5a	-2181.028852	-2181.033958	-2181.063446	-2180.724359	-2180.729466	-2180.758954
4a’’	-2067.651966	-2067.668488	-2067.688056	-2067.350697	-2067.367219	-2067.386787
TS4a’’-6a	-2067.630565	-2067.639393	-2067.661559	-2067.328615	-2067.337444	-2067.35961
6a	-2067.651191	-2067.657121	-2067.680477	-2067.350328	-2067.356258	-2067.379614
TS6a-7a	-2067.624228	-2067.633807	-2067.654854	-2067.323375	-2067.332955	-2067.354001
7a	-2067.632795	-2067.641596	-2067.66078	-2067.332211	-2067.341012	-2067.360196
TS7a-7a'	-2067.628549	-2067.637953	-2067.66078	-2067.329807	-2067.339211	-2067.362038
7a'	-2067.64211	-2067.650802	-2067.673704	-2067.343445	-2067.352138	-2067.375039
TS7a'-8a	-2067.630298	-2067.6386	-2067.663347	-2067.3326	-2067.340902	-2067.365648
TS7a-8a	-2067.630312	-2067.638721	-2067.663364	-2067.332023	-2067.340432	-2067.365075
8a	-2067.664733	-2067.671059	-2067.696565	-2067.367568	-2067.373894	-2067.3994
8a’	-1838.487015	-1838.492787	-1838.514414	-1838.234822	-1838.240593	-1838.26222
1b	-3680.210544	-3680.231629	-3680.260911	-3679.56783	-3679.588915	-3679.618197
2b	-2643.652908	-2643.675346	-2643.700997	-2643.242964	-2643.265402	-2643.291053
3b	-3104.191897	-3104.208899	-3104.235654	-3103.656039	-3103.673040	-3103.699795
TS3b-4b	-3104.181405	-3104.199876	-3104.225731	-3103.644238	-3103.662710	-3103.688564
4b	-3104.197519	-3104.217673	-3104.225731	-3103.661546	-3103.681701	-3103.689758
4b’	-3104.209859	-3104.227847	-3104.252933	-3103.673211	-3103.691199	-3103.716285
TS4b’-5b	-3104.171401	-3104.18635	-3104.212954	-3103.636575	-3103.651524	-3103.678128
5b	-3104.202875	-3104.216915	-3104.245808	-3103.668608	-3103.682648	-3103.711542
6b	-2990.818793	-2990.835085	-2990.858024	-2990.288407	-2990.304699	-2990.327638
TS6b-7b	-2990.786422	-2990.80381	-2990.82531	-2990.255508	-2990.272896	-2990.294396

7b	-2990.785804	-2990.80204	-2990.825816	-2990.255024	-2990.271261	-2990.295037
TS7b-8b	-2990.776621	-2990.792344	-2990.817661	-2990.25005	-2990.265772	-2990.291089
8b	-2990.797756	-2990.813345	-2990.839146	-2990.265912	-2990.281501	-2990.307302
9b	-2875.004799	-2875.016633	-2875.045464	-2874.520934	-2874.532767	-2874.561598
TS1-2c	-3217.546511	-3217.561455	-3217.592786	-3217.006406	-3217.02135	-3217.052681
2c	-3217.580027	-3217.595966	-3217.627642	-3217.041577	-3217.057515	-3217.089191
6c	-1954.263658	-1954.27902	-1954.298064	-1953.965185	-1953.980548	-1953.999591
TS6c-7c	-1954.257063	-1954.272673	-1954.288554	-1953.958636	-1953.974246	-1953.990127
7c	-1954.265317	-1954.279304	-1954.295065	-1953.966547	-1953.980533	-1953.996295
TS7c-8c	-1954.221037	-1954.233994	-1954.252739	-1953.926914	-1953.939871	-1953.958616
8c	-1954.253601	-1954.264741	-1954.284376	-1953.955749	-1953.966888	-1953.986524
5d	-1144.493223	-1144.4953	-1144.518011	-1144.417425	-1144.419502	-1144.442213
TS5d-6d	-1144.457923	-1144.455237	-1144.477712	-1144.382108	-1144.379421	-1144.401897
6d	-1144.484509	-1144.479322	-1144.503139	-1144.408836	-1144.403649	-1144.427465
TS6d-7d	-1144.458205	-1144.455539	-1144.479186	-1144.383941	-1144.381276	-1144.404923
7d	-1144.456751	-1144.454427	-1144.478924	-1144.383623	-1144.381299	-1144.405796
TS7d-8d	-1144.440722	-1144.435487	-1144.460199	-1144.368755	-1144.36352	-1144.388232
8d	-1144.497263	-1144.487408	-1144.511462	-1144.425295	-1144.415441	-1144.439495
5e	-1031.074686	-1031.087539	-1031.103391	-1031.001381	-1031.014234	-1031.030086
6e	-1031.105227	-1031.108686	-1031.125937	-1031.0326	-1031.036059	-1031.05331
TS6e-7e	-1031.09436	-1031.096622	-1031.110664	-1031.020633	-1031.022896	-1031.036938
7e	-1031.095099	-1031.096172	-1031.111883	-1031.022478	-1031.023552	-1031.039263
TS7e-8e	-1031.036847	-1031.036349	-1031.05242	-1031.010244	-1030.968975	-1030.985046
8e	-1031.077618	-1031.081148	-1031.099458	-1031.008709	-1031.012239	-1031.030549
6f	-917.6774244	-917.6924607	-917.6924607	-917.6073244	-917.6223607	-917.6223607
6g	-2875.423143	-2875.46786	-2875.508578	-2874.927857	-2874.972574	-2875.013291
Pd_1	-4273.754605	-4273.771938	-4273.804088	-4272.880946	-4272.898279	-4272.930429
Pd_2	-2200.668712	-2200.678967	-2200.700648	-2200.258349	-2200.268604	-2200.290285
Pd_3	-2661.198721	-2661.212059	-2661.235511	-2660.660606	-2660.673944	-2660.697396
Pd_TS3-4	-2661.188138	-2661.203815	-2661.228114	-2660.652024	-2660.667702	-2660.692
Pd_4	-2661.208432	-2661.224667	-2661.24845	-2660.672576	-2660.688811	-2660.712594
Pd_4'	-2661.214252	-2661.229675	-2661.253548	-2660.679711	-2660.695134	-2660.719008
Pd_4''	-1624.676916	-1624.684073	-1624.705069	-1624.371904	-1624.379061	-1624.400057
Pd_TS4''-5	-1624.643861	-1624.650293	-1624.670313	-1624.341832	-1624.348264	-1624.368284
Pd_5	-1624.664978	-1624.66907	-1624.689664	-1624.363269	-1624.36736	-1624.387954
Pd_6	-588.1290868	-588.1228221	-588.1383892	-588.0538157	-588.047551	-588.0631181
Pd_TS6-8	-588.0980855	-588.0908256	-588.1066388	-588.0269829	-588.0197229	-588.0355362
Pd_8	-588.1221798	-588.1130032	-588.1301152	-588.0502063	-588.0410297	-588.0581417
Pd_8'	-1395.485308	-1395.483547	-1395.503128	-1395.233532	-1395.231771	-1395.251352
Pd_9	-1277.520941	-1277.517252	-1277.536379	-1277.338645	-1277.334957	-1277.354084
Pd_10	-3350.596519	-3350.606511	-3350.639653	-3349.954637	-3349.964629	-3349.997771

5. References

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