Supporting Information

belonging to the paper

Reversible cyclometalation at Rh^{I} as Motif for Metal-Ligand Bifunctional Bond Activation and Base-free Formic Acid Dehydrogenation

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1) Synthesis and Characterization of New Compounds

Complex 2, $Rh_2(SCH_2CH_2CH_2S)(CO)_2(\kappa^1$-*P*-2-phenyl-6-((di-*tert*-butylphosphino)-methyl)pyridine)).

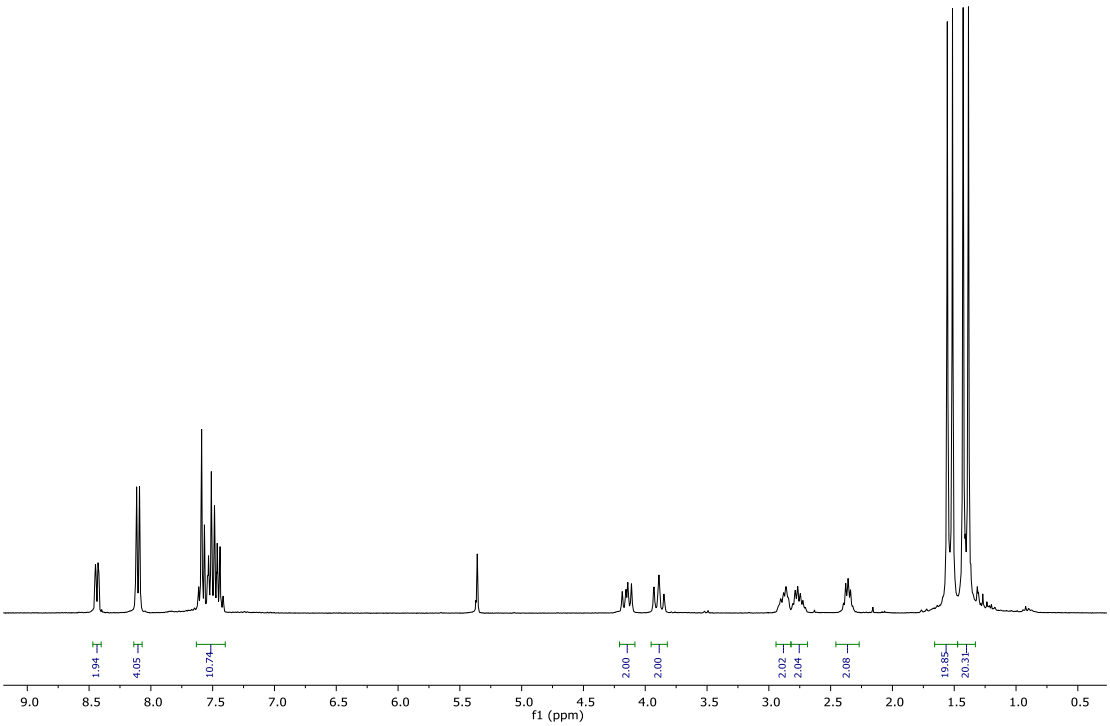


Fig. S1. ^{1}H NMR spectrum of complex **2** (methylene chloride-d_2, 300 MHz , 298 K).

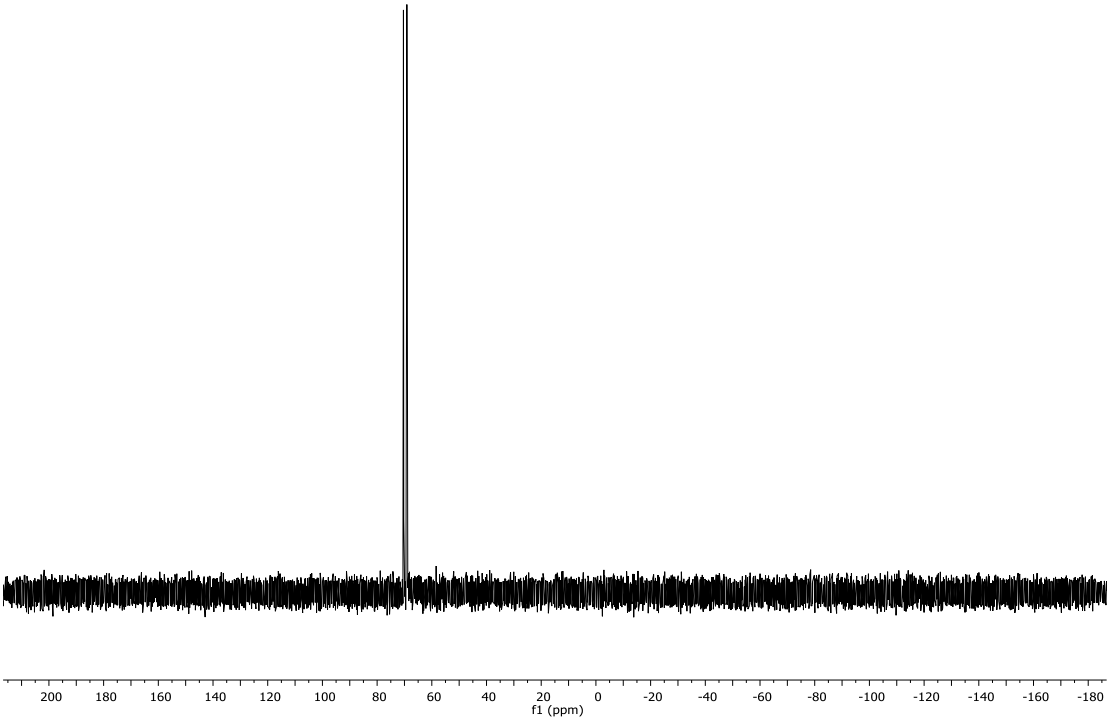


Fig. S2. ^{31}P NMR spectrum of complex **2** (methylene chloride-d_2, 121 MHz, 298 K).

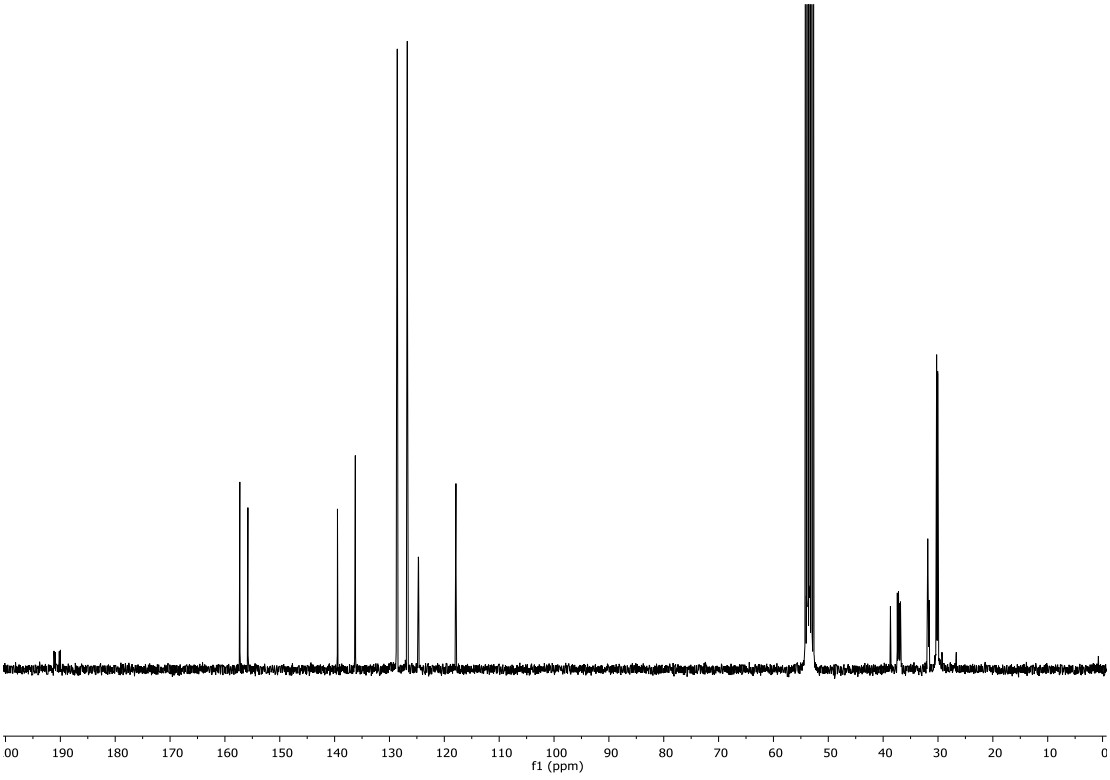


Fig. S3. ^{13}C{^{1}H} NMR spectrum of complex **2** (methylene chloride-d_2, 75 MHz, 298 K).

Complex 3, Rh(NHSO$_2$CF$_3$)(CO)(κ^2-*P*,*N*-2-phenyl-6-((di-*tert*-butylphosphino)-methyl)pyridine))

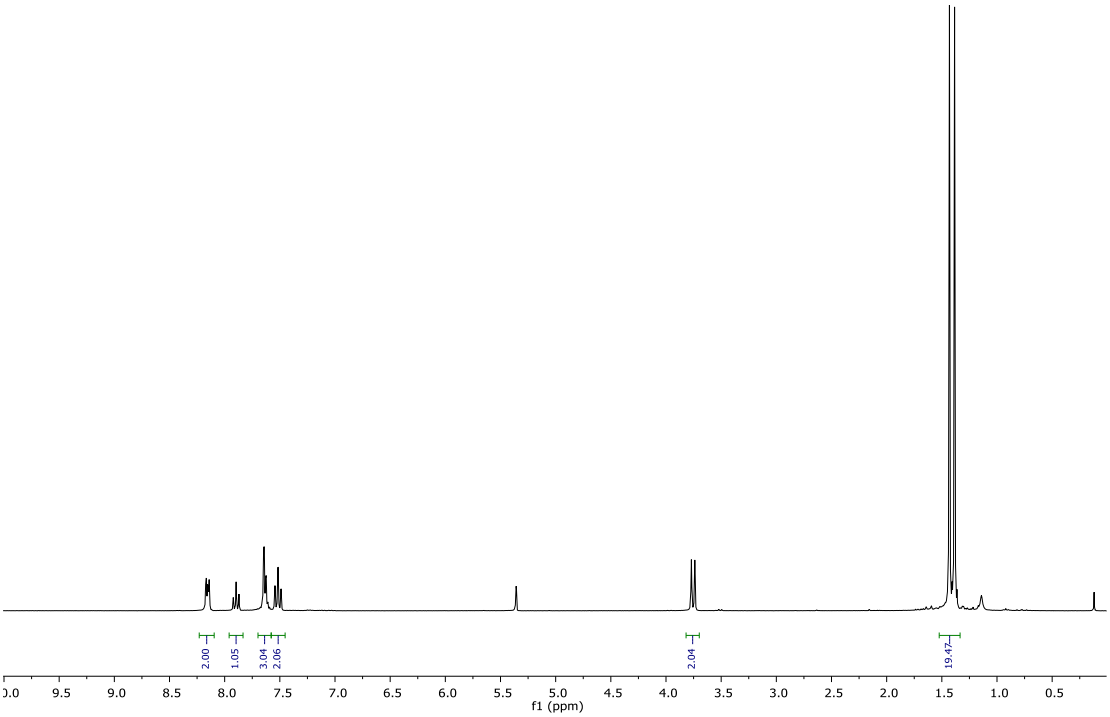


Fig. S4. ^{1}H NMR spectrum of complex **3** (methylene chloride-d_2, 300 MHz, 298 K).

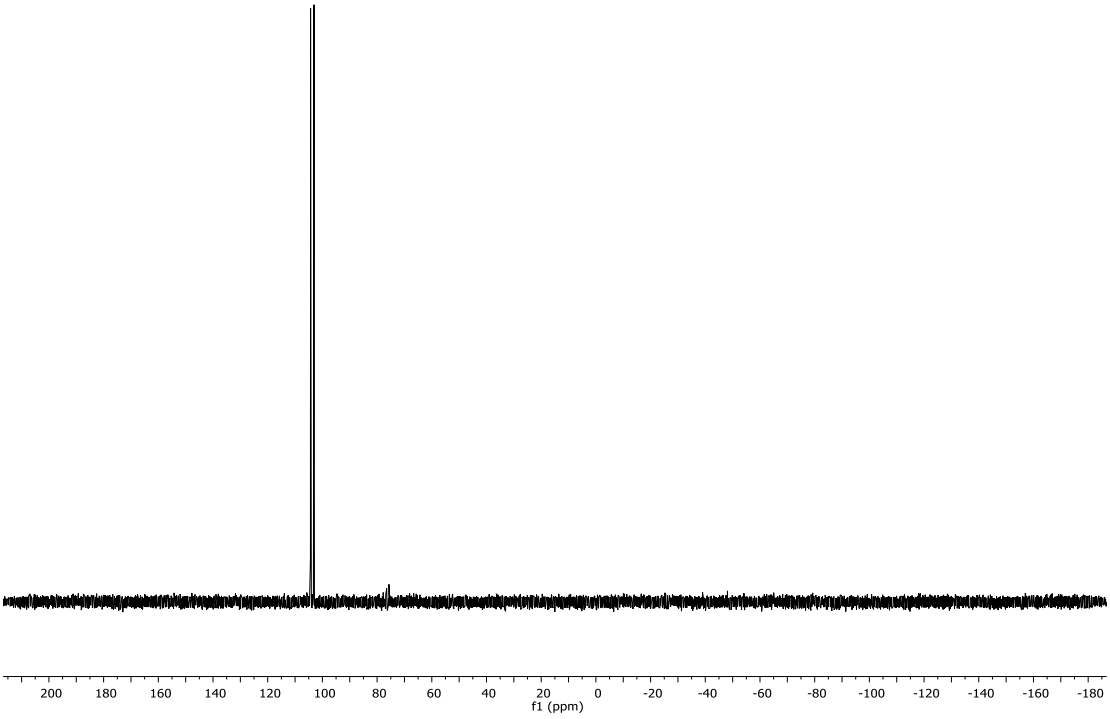


Fig. S5. ^{31}P NMR spectrum of complex **3** (methylene chloride-d_2, 121 MHz, 298 K).

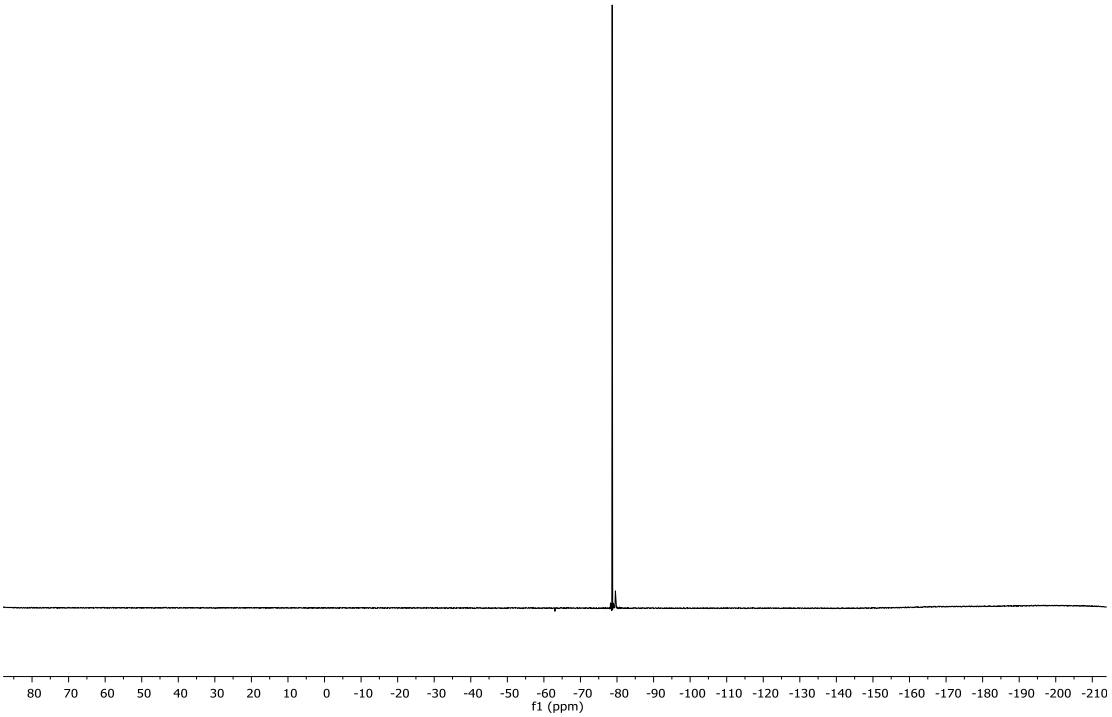


Fig. S6. ^{19}F NMR spectrum of complex **3** (methylene chloride-d_2, 282 MHz, 298 K).

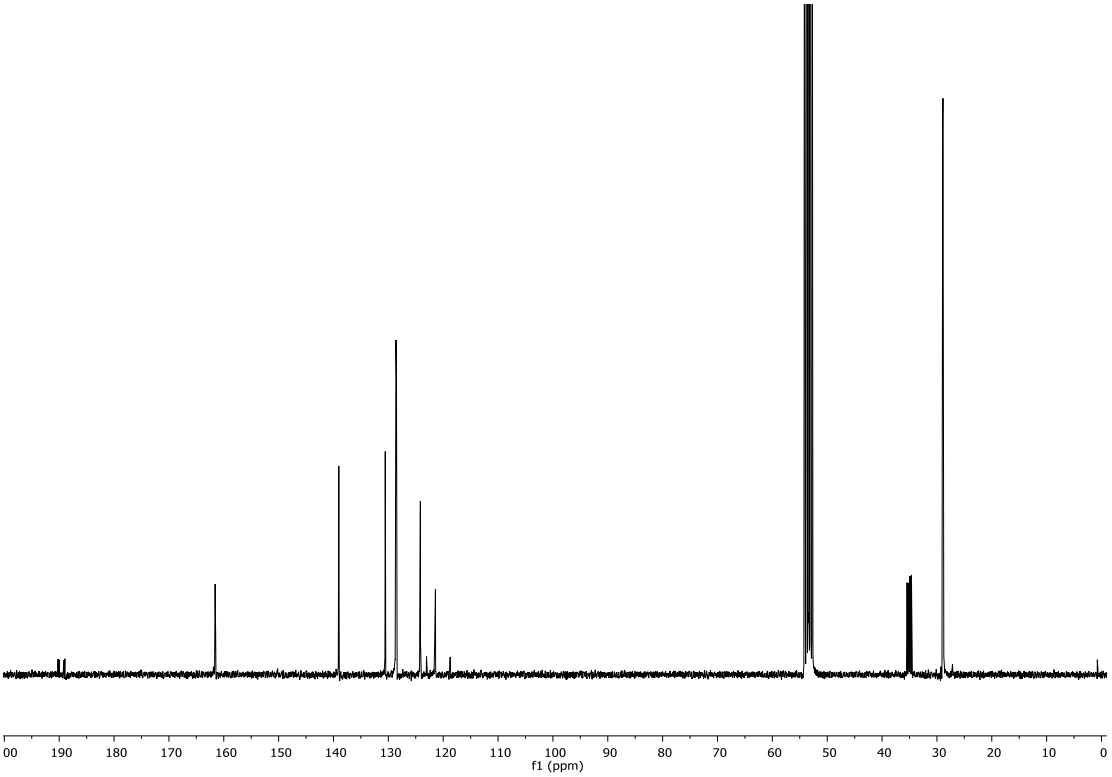


Fig. S7. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** (methylene chloride-d_2, 75 MHz, 298 K).

Complex 4, Rh(OCH(O))(CO)(κ^2-*P,N*-2-phenyl-6-((di-*tert*-butylphosphino)-methyl)pyridine))

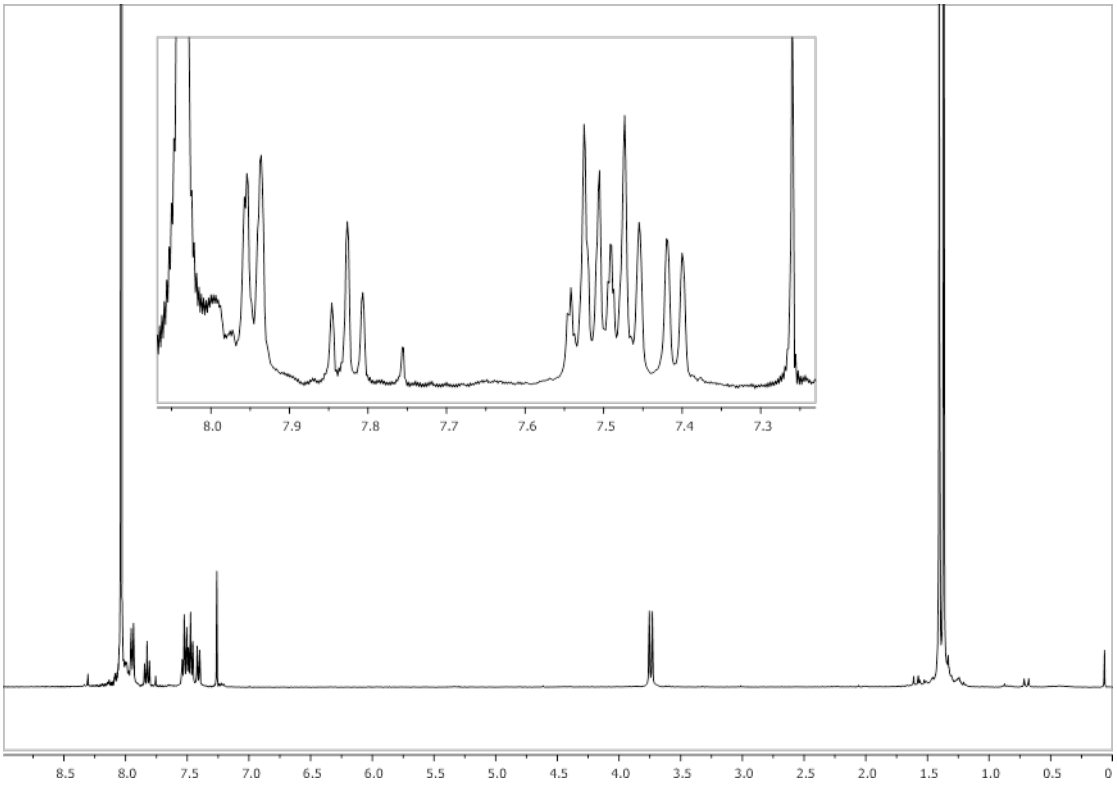


Fig. S8. ^{1}H NMR spectrum of complex **4** ($CDCl_3$, 400 MHz, 298 K).

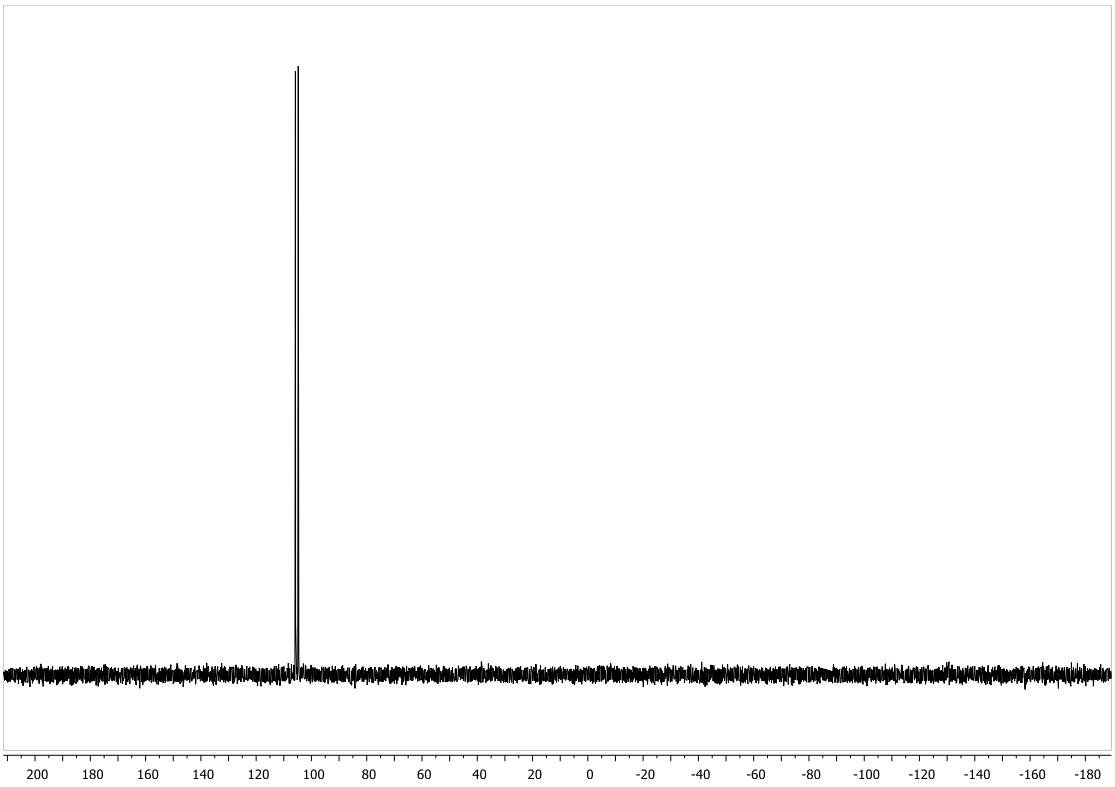


Fig. S9. ^{31}P NMR spectrum of complex **4** ($CDCl_3$, 162 MHz, 298 K).

Complex 4-*d*, Rh(OCH(O)(CO)(κ^2-*P*,*N*-2-phenyl-6-((di-*tert*-butylphosphino)-methyl)pyridine))-*d*

To a solution of **3** (4.4 mg, 10 μmol) in $CDCl_3$ (0.6 mL) was added formic acid-d_1 or formic acid-d_2 (9.2 mg, 200 μmol), resulting in an immediate color change from red to yellow at room temperature. Due to its unstable nature, this species was only characterized *in situ* using NMR spectroscopy.

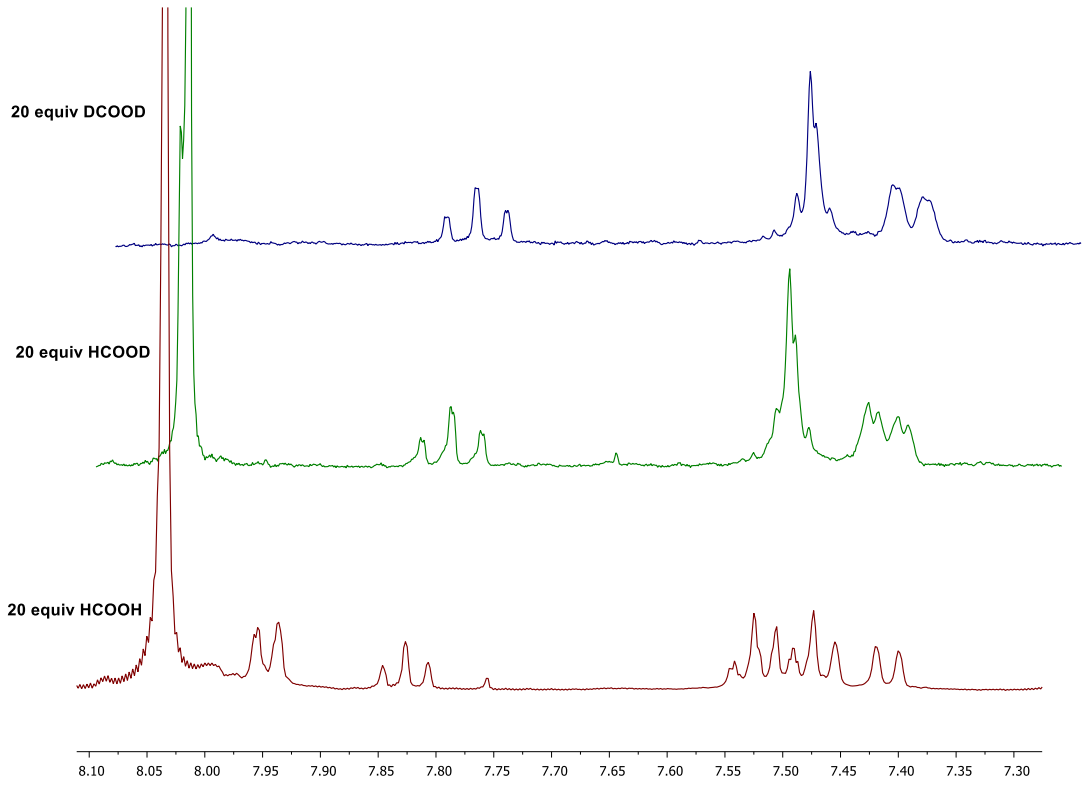


Fig. S10. Aromatic region of ^{1}H NMR spectra of complex **4** and **4-*d*** ($CDCl_3$, 300 MHz, 298 K). Spectra are stacked under an angle of 5°.

Complex 5, Rh(Cl)(CO)(κ^2-*P*,*N*-2-methyl-6-((di-*tert*-butylphosphino)methyl)-pyridine))

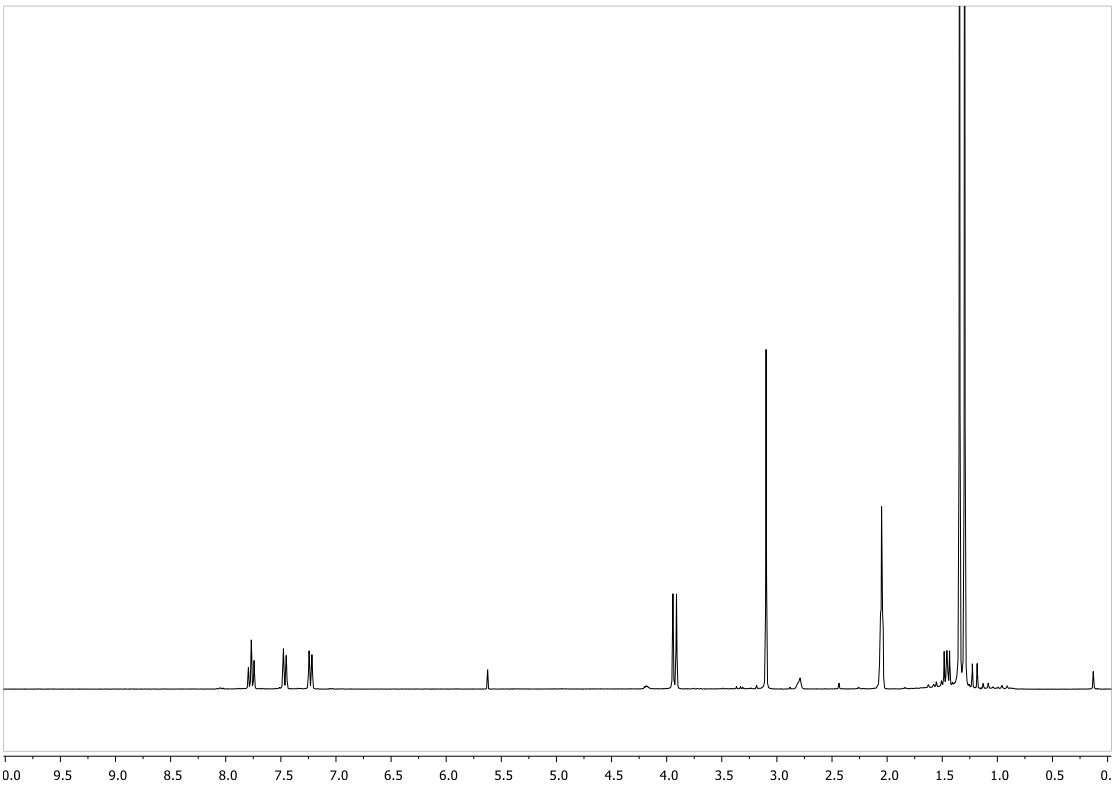


Fig. S11. ^{1}H NMR spectrum of complex **5** (acetone-d_6, 300 MHz, 298 K).

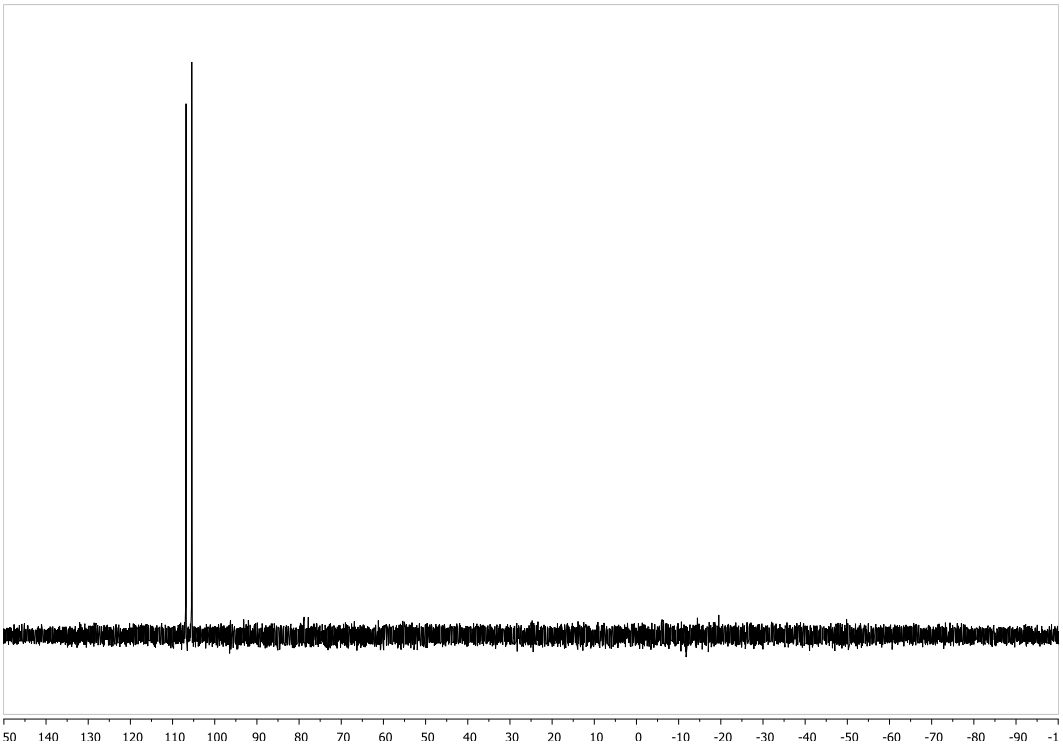


Fig. S12. ^{31}P NMR spectrum of complex **6** ($CDCl_3$, 121 MHz, 298 K).

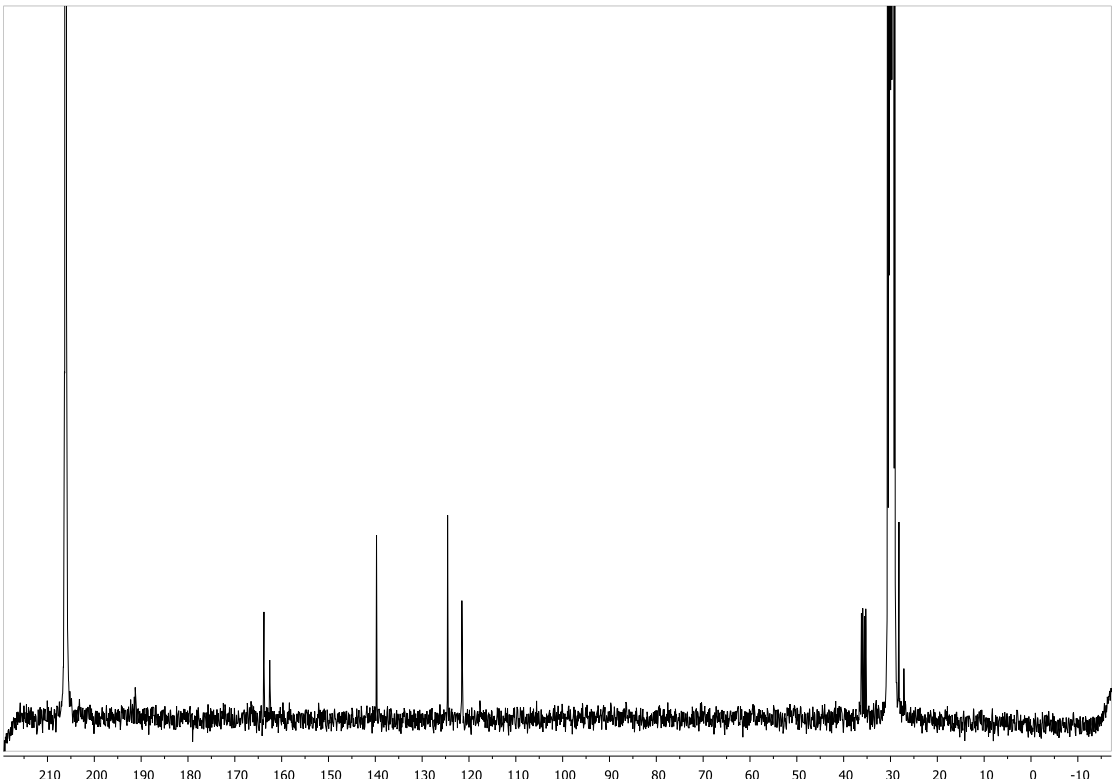


Fig. S13. $^{13}C\{^{1}H\}$ NMR spectrum of complex **5** (acetone-d_6, 75 MHz, 298 K).

2) Catalytic dehydrogenation of formic acid

2.1 Standard catalytic experiment and control experiments

Typically, compound **1** (10 μmol) was added to the solvent (1 mL) in a 5 mL schlenk equipped with a condenser and connected to a water replacement setup.[S1] The reaction mixture was heated to required temperature and stirred for 10 minutes. Formic acid was added to the reaction mixture (75 μL, 2 mmol) or the azeotrope HCOOH/Et_3N 5:2 was added to the reaction mixture (187 μL, 2 mmol HCOOH) and evolved gas was collected. In the case of complex RhCl(CO)(PN), first 1 equivalent of potassium *tert*-butoxide in THF (1M) was added at RT to abstract the chloride ligand. After 5 min stirring, 75 μL HCOOH was added. The mixture was rapidly heated to 75 ºC and the evolved gas was collected.

The setup was calibrated with a Brooks flowmeter type 1054-3C and evolved gases were analyzed with a G·A·S Compact GC (Rt-MSieve 5A 20 m × 0.32 mm + Rt-Q-bond 2 m × 0.32 mm). The amounts of mol converted were determined from the volumes of gas collected using equation *1a* and *1b*.

$$V_{H2} = \frac{RT}{p} + b - \frac{a}{RT} = 24.49\ \frac{L}{mol} \qquad 1a$$

R: 8.3145 m^3 Pa•mol^{-1}•K^{-1}

T: 298.15 K

p: 101325 Pa

b: 26.7 • 10^{-6} m^3•mol^{-1}

a: 2.49 • 10^{-10} Pa•m^3•mol^{-2}

$$V_{CO2} = \frac{RT}{p} + b - \frac{a}{RT} = 24.42\ \frac{L}{mol} \qquad 1b$$

R: 8.3145 m^3 Pa•mol^{-1}•K^{-1}

T: 298.15 K

p: 101325 Pa

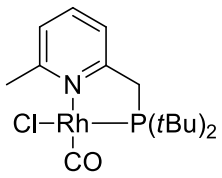
b: 42.7 • 10^{-6} m^3•mol^{-1}

a: 36.5 • 10^{-10} Pa•m^3•mol^{-2}

Table S1. HCOOH dehydrogenation activity of 3[a]

Entry	Catalyst	Additive	TOF (h^{-1})[b]
1	Complex **1**	-	169 ± 12
2	Complex **1**	Et_3N	155 ± 20
3	RhCl(CO)(PN)	-	3
4	RhCl(CO)(PN)	1 equiv KO*t*Bu	112 ± 4
5	Rh(CO)(PNN*)	-	4
6	Rh(CO)(PCP)	-	0

[a] Catalyst (0.01 mmol), HCOOH (2 mmol), (Et_3N (0.8 mmol)), dioxane (1mL), 75 °C. Experiments are performed at least in duplo. [b] TOFs were determined from the slope of the curve around 20% conversion.



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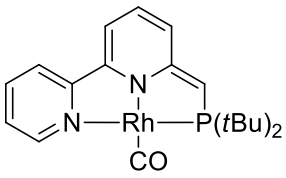

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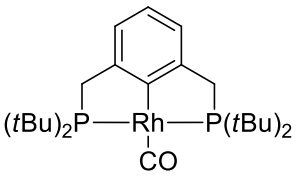

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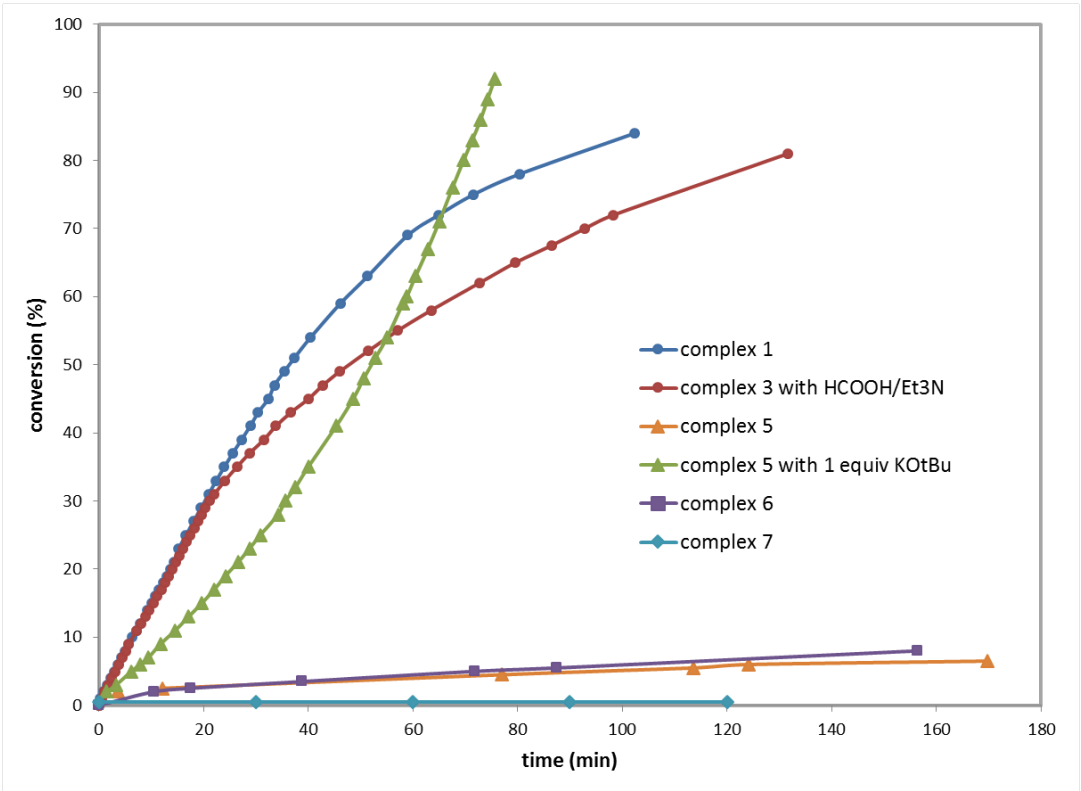

Fig. S14. Dehydrogenation curves of entries 1-6 (table S1).

2.2 Catalytic dehydrogenation experiment with recharging of HCOOH

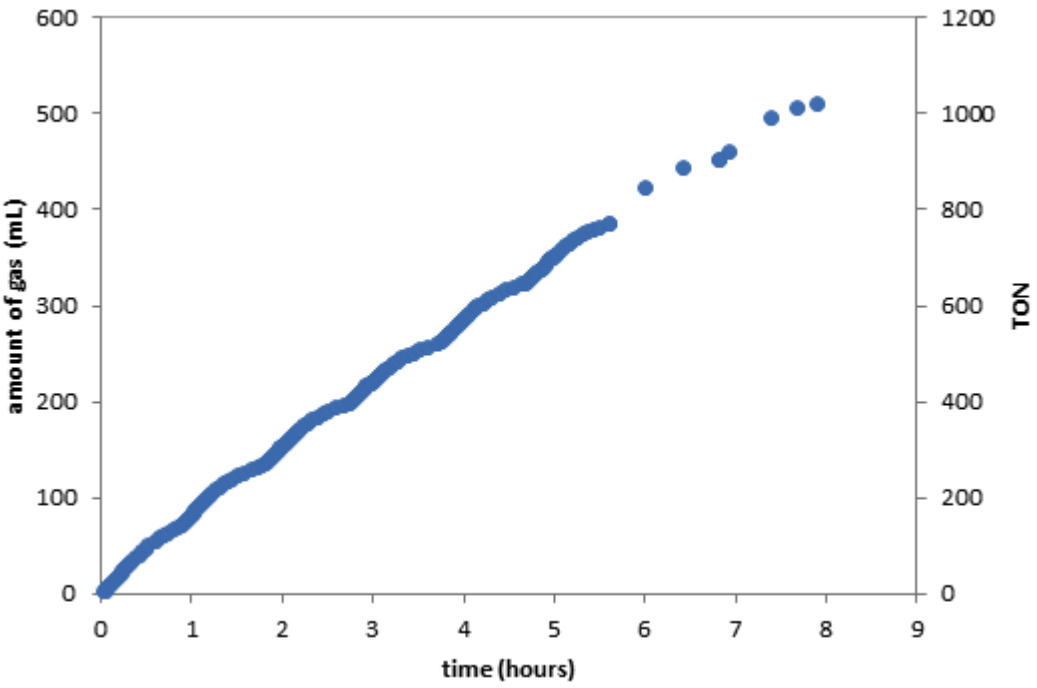

Fig. S15. Curve of a longer time catalytic experiment with complex **1** with intermittent addition of formic acid. Every time, around 65% conversion, 1.3 mmol of extra HCOOH is added. Only after the 7th cycle, some loss in activity is observed.

2.3 Catalytic experiment with H^{13}COOH followed by NMR

A catalytic experiment is performed with H^{13}COOH to rule out the formation of ^{13}CO or new Rh-^{13}CO species. A 10 mm HP sapphire NMR tube is charged with 0.02 mmol complex **1** (0.02 mmol), H^{13}COOH (4 mmol), and dioxane-d8 (2 ml). The tube is not completely closed to prevent buildup of pressure and in the NMR machine it is quickly heated to 75 ºC.

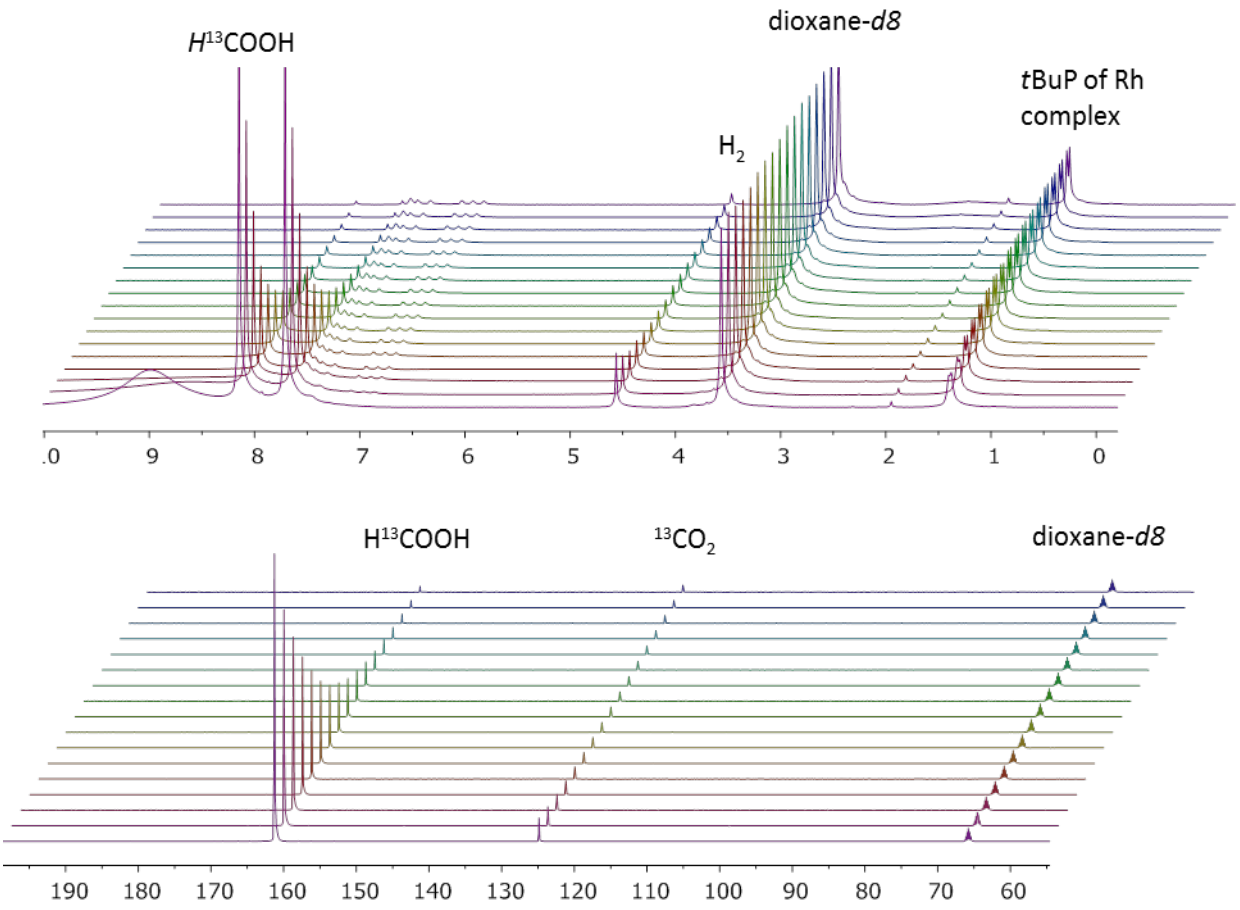

Fig. S16. Catalytic experiment using $H^{13}COOH$, monitored by ^{1}H NMR (top) and ^{13}C NMR (lower) over the course of 2.5 h. Spectra are stacked under an angle of 20°.

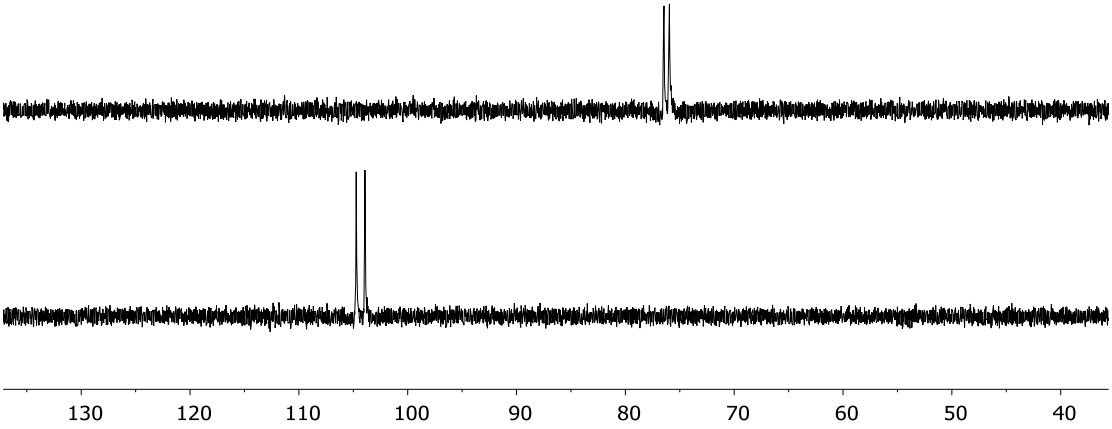

Fig. S17. ^{31}P NMR spectra of the reaction (see S15) before (lower) and after (top) catalysis.

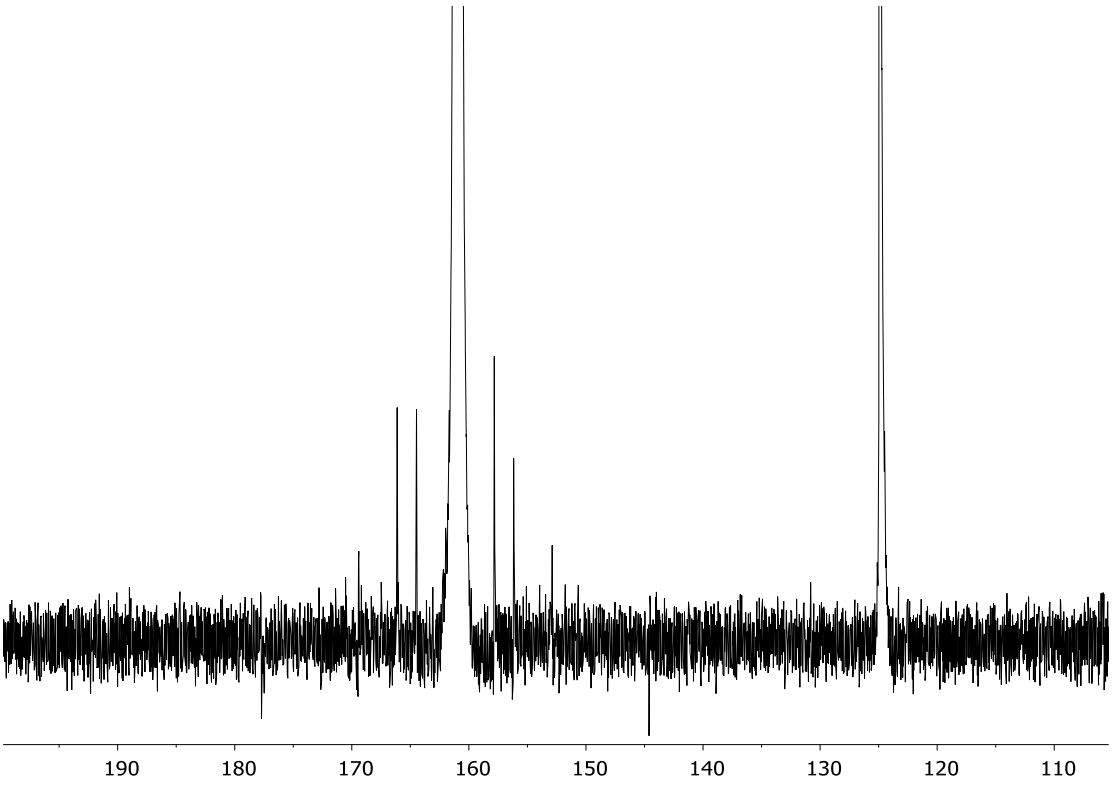

Fig. S18. Zoom-in of ^{13}C NMR spectrum: no free CO (around 185 ppm) is detected.

2.4 Catalytic experiment followed by IR

A catalytic experiment was monitored by in situ HP-IR in an autoclave equipped with an IR cell.[S2] The autoclave was charged with 6 mL dioxane (or THF) and pressurized with 2 bars of helium (to fill the IR cell) and heated to 75 ºC (60 ºC for THF). A blank spectrum was recorded. Thereafter, the pressure was slowly released and complex **1** (0.03 mmol) and HCOOH (6 mmol) dissolved in 1 mL dioxane (or THF) were added to the autoclave before repressurizing with 2 bars of helium.

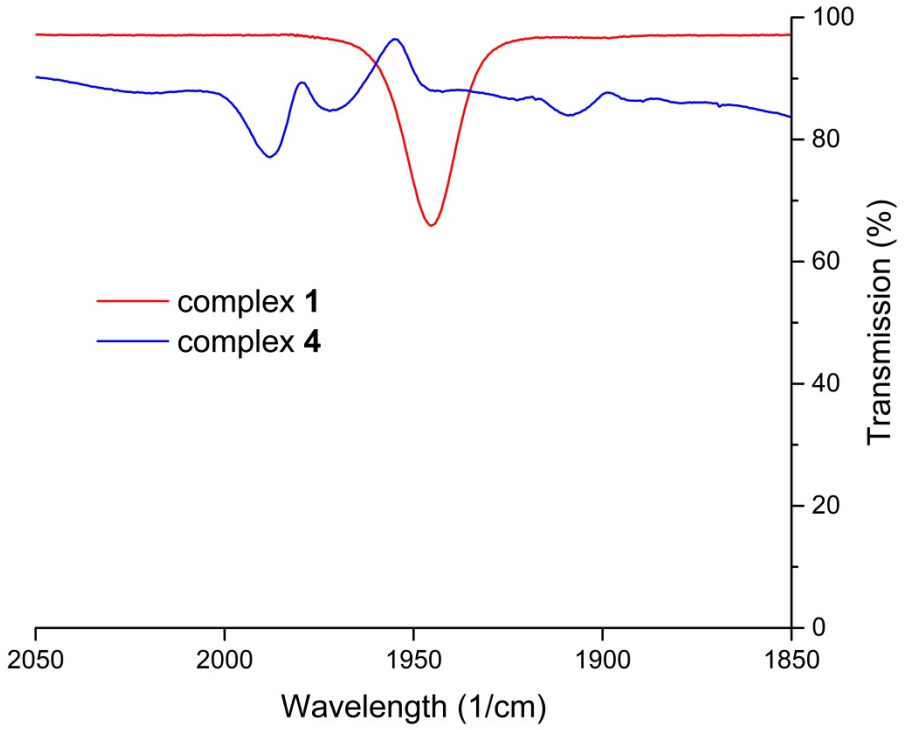

Fig. S19. IR spectra of complex **1** (red) and complex **4** (blue) measured in dioxane.

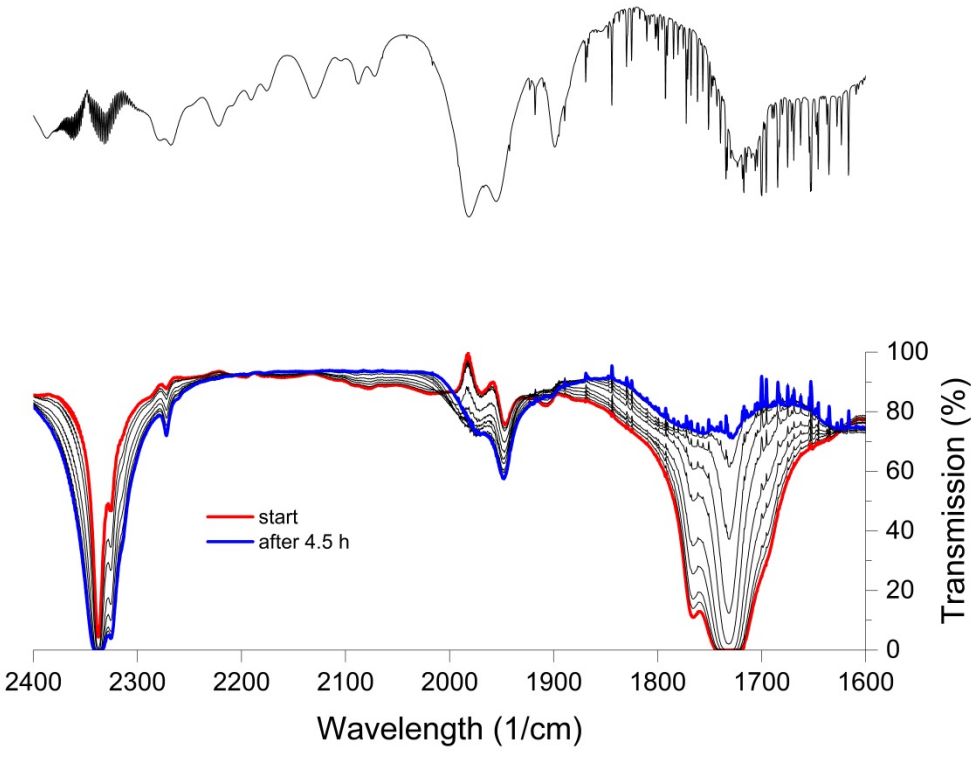

Fig. S20. Zoom-in of the IR spectrum between 1600 and 2400 cm^{-1} from a catalytic dehydrogenation reaction in dioxane. The spectrum of dioxane is depicted (top) to show that the solvent residual peaks interfere with the Rh-CO peaks (lower). The red spectrum in the lower figure is recorded at the start of catalysis and the blue one after 4.5 h. The picture shows that the concentration of CO_2 (peak at 2330 cm^{-1}) increases over time and that the concentration of HCOOH (peak at 1730 cm^{-1}) decreases.

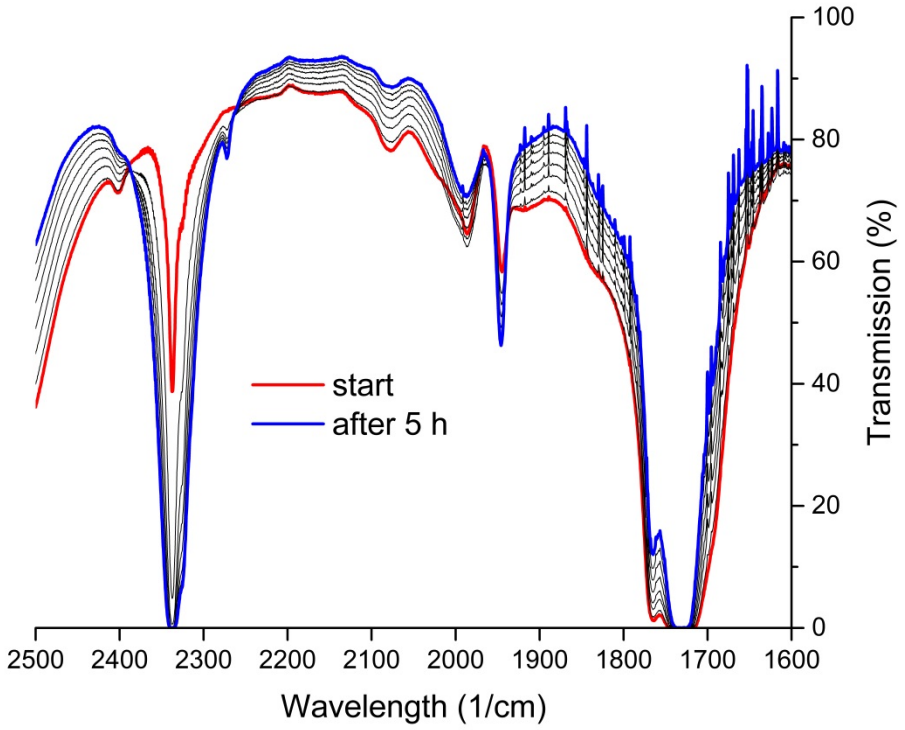

Fig. S21. Zoom-in of the IR spectrum between 1600 and 2500 cm^{-1} from a catalytic dehydrogenation reaction in THF over a time-span of 5 h. The red spectrum is recorded at the start and the blue after 5 h. In this case the solvent does not interfere with the Rh-CO signals and it is clear the only two Rh-CO peaks present can be attributed to complex **1** (1945 cm^{-1}) and complex **4** (1989 cm^{-1}). The concentration of complex **4** slowly decreases, as it converts back to complex **1**.

3) DFT Calculations

3.1 Protonation of complex 1 by HCOOH

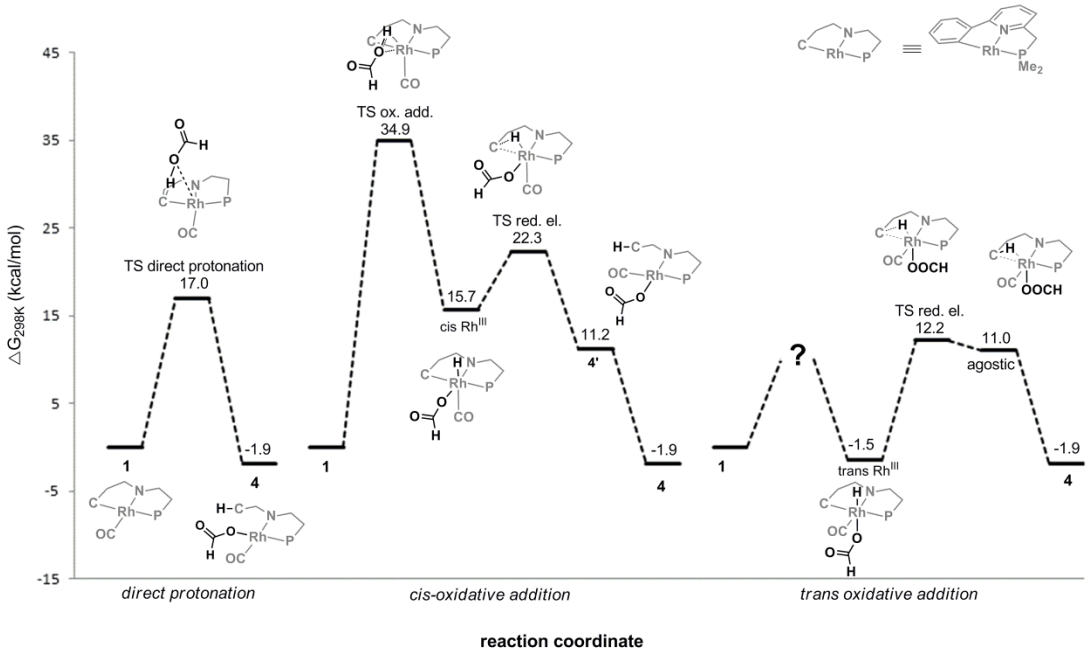

Fig. S22. Energy surfaces of the reaction of HCOOH with **1**. This reaction can either occur through direct protonation of the Rh-C bond or through oxidative addition of HCOOH to form a Rh^{III} intermediate. From these results it can be ruled out that protonation occurs via *cis* oxidative addition because the TS-barriers are too high. The pathway from the trans Rh^{III} intermediate has low-lying TS-barriers (lower than direct protonation) but the TS for oxidative addition could not be located because the energy of charged species is highly overestimated in gas-phase calculations.

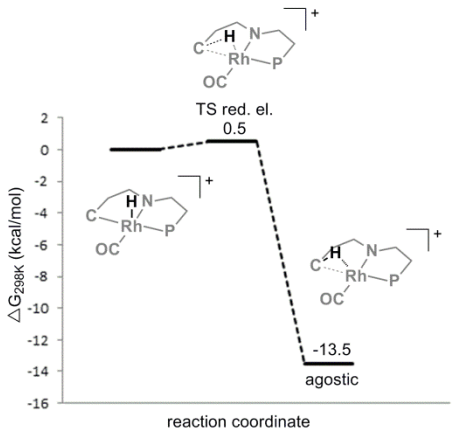

Fig. S23. Energy profile for the protonation of the Rh-C bond when the metal is protonated first, forming a 5-coordinated Rh^{III} cation with the formate as counterion. These calculations show that if protonation occurs at the metal, the subsequent protonation of the ligand by reductive elimination is almost barrierless.

3.2 Energy profiles of dehydrogenation of HCOOH by complex 1

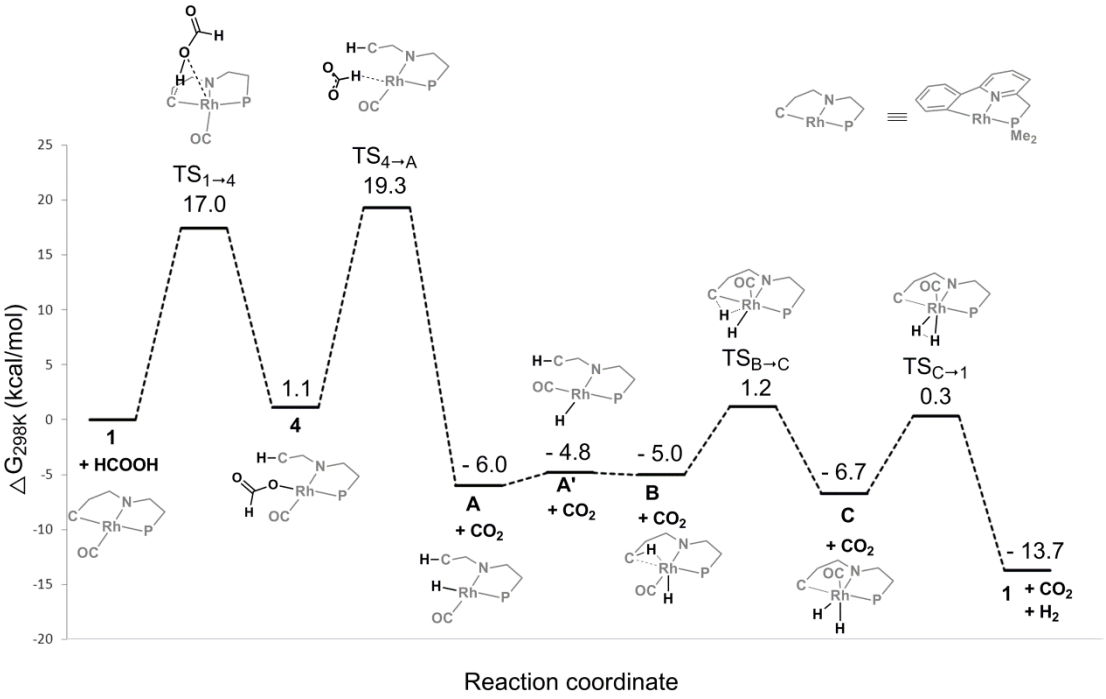

Fig. S24. Energy profile of the dehydrogenation of HCOOH following the cooperative pathway via reversible cyclometalation.

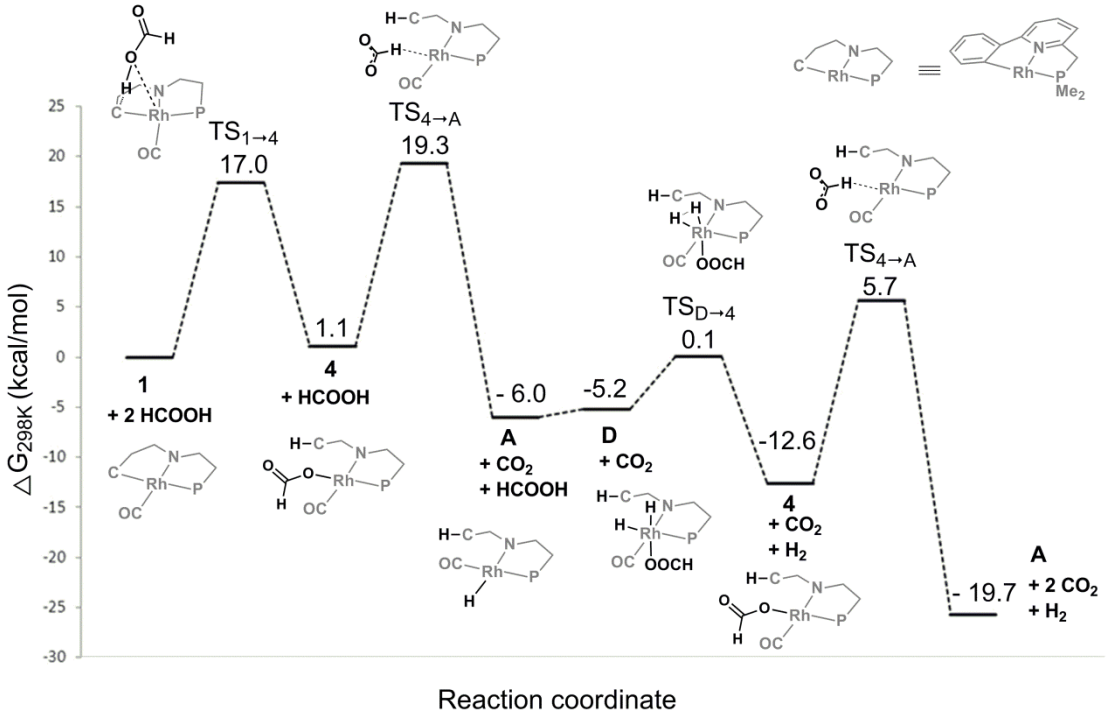

Fig. S25. Energy profile of the dehydrogenation of HCOOH following a non-cooperative pathway.

3.3 Coordinates

Complex 1

SCF Energy = -1163.1782257350

H	1.2013245	0.1618491	-4.4756807
C	0.8542495	0.1475054	-3.4416432
N	-0.0027930	0.0921706	-0.8104852
C	-0.0967540	-0.7910387	-3.0337657
C	1.3509822	1.0687945	-2.5261499
C	0.9115003	1.0371718	-1.1941114
C	-0.5205855	-0.7861241	-1.7041530
H	-0.5169765	-1.5114857	-3.7345077
H	2.0865344	1.8092669	-2.8349721
C	-1.6041728	-1.7018615	-1.1970604
P	-1.4597621	-1.9254729	0.6519176
C	-0.4963284	-3.4881355	0.7912175
H	0.5014759	-3.3241909	0.3641753
H	-0.9907138	-4.3223934	0.2716122
H	-0.3741393	-3.7388071	1.8530112
C	-3.1496878	-2.4724045	1.1226833
H	-3.8480974	-1.6367592	0.9872440
H	-3.1450863	-2.7446057	2.1865878
H	-3.4844046	-3.3368787	0.5305730
Rh	-0.4136732	0.0161044	1.2342693
C	-0.7254223	0.0481870	3.0368519

O	-0.9368022	0.0655680	4.1823575
C	1.3317077	1.9365960	-0.1205986
C	2.0360825	3.6214938	1.9844775
C	0.7768245	1.6813593	1.1717214
C	2.2194157	3.0057249	-0.3380002
C	2.5717846	3.8500325	0.7116015
C	1.1588736	2.5544535	2.2049665
H	2.6376570	3.1891070	-1.3301468
H	3.2575683	4.6806857	0.5405992
H	0.7637268	2.4018901	3.2106235
H	2.3056609	4.2814639	2.8121455
H	-1.6210668	-2.6561684	-1.7441318
H	-2.5789021	-1.2130979	-1.3632288

TS1→4(direct protonation)

SCF Energy = -1353.0317506610

H	0.8796057	0.4219491	-4.9270067
C	0.7542920	0.2630100	-3.8553788
N	0.4241687	-0.1372033	-1.1505634
C	0.1961930	-0.9273786	-3.3865491
C	1.1846480	1.2326267	-2.9509546
C	1.0202299	1.0070854	-1.5814215
C	0.0541545	-1.1135812	-2.0098530
H	-0.1028758	-1.7179940	-4.0732570
H	1.6666905	2.1449878	-3.2980485
C	-0.4012860	-2.3890198	-1.3714156
P	-1.1349175	-2.0439247	0.3062010
C	-0.9238142	-3.6145166	1.2063624
H	0.1571815	-3.8088994	1.2713511
H	-1.4219123	-4.4420542	0.6809479
H	-1.3455891	-3.5132654	2.2146910
C	-2.9415994	-1.9116571	0.0154951
H	-3.1359581	-1.0570856	-0.6449795
H	-3.4460434	-1.7305923	0.9736417
H	-3.3396758	-2.8308731	-0.4384391
Rh	0.1060633	-0.2954807	0.8991110
C	-0.2792425	-0.3843394	2.6874159
O	-0.5540774	-0.4473895	3.8156333
C	1.4764782	1.8884562	-0.4950422
C	2.3072152	3.4602962	1.6696075
C	1.6563249	1.2781452	0.7855525
C	1.7084304	3.2569295	-0.6720301
C	2.1242166	4.0380680	0.4086509
C	2.0748952	2.0953850	1.8496645
H	1.5388206	3.7276822	-1.6423942
H	2.3001658	5.1053519	0.2670072
H	2.2352240	1.6431386	2.8297175
H	2.6323863	4.0778633	2.5084006
H	0.5138535	-2.9735097	-1.1413384
H	-1.0602602	-2.9848299	-2.0180040
C	2.5681613	-2.0950591	0.8029748
H	2.5602341	-2.0302447	1.9240699
O	2.2577950	-3.1730664	0.2708768
O	2.9130337	-1.0067845	0.1889322
H	2.2134710	0.0802412	0.7037708

Complex 4

SCF Energy = -1353,065977747

H	0,7596006	-0,2773191	-5,1638508
C	0,4456511	-0,3637686	-4,12301
N	-0,3809657	-0,573448	-1,4654955
C	-0,0355052	-1,5760884	-3,6264641
C	0,5616094	0,7173869	-3,259095
C	0,1657579	0,5906224	-1,9182334
C	-0,4384994	-1,6540166	-2,2946643
H	-0,1059314	-2,4582611	-4,261898
H	1,0013569	1,6569858	-3,5903652
C	-0,9424424	-2,9399831	-1,6932863
P	-0,6226936	-2,8832836	0,1394747
C	1,1254742	-3,4399339	0,2776796
H	1,7664375	-2,7195655	-0,2473766
H	1,2705547	-4,4433626	-0,1493798
H	1,4142999	-3,4486292	1,336758
C	-1,5548861	-4,305053	0,8136471
H	-2,6269465	-4,1371256	0,6518089
H	-1,3783906	-4,3586924	1,8961791
H	-1,2464012	-5,2512061	0,3469149
Rh	-1,235525	-0,8139286	0,5120476
C	-1,8701848	-1,1837919	2,1859766
O	-2,2226394	-1,5516269	3,2289943
C	0,3958563	1,6863386	-0,9595601
C	0,763976	3,7486384	0,9022169
C	0,9006227	1,4066127	0,3229928
C	0,107895	3,0144434	-1,3086265
C	0,2818721	4,0377831	-0,3785461
C	1,0797572	2,4334088	1,2479242
H	-0,3162049	3,2359288	-2,2891517
H	0,0206013	5,0622553	-0,6461558
H	1,4410875	2,199933	2,2489693
H	0,8808494	4,5479102	1,634736
H	-0,4981865	-3,8136857	-2,194577
H	-2,0369206	-3,0053447	-1,8032335
H	1,1342205	0,3755249	0,5984973
C	-2,3154678	1,8252245	1,3231512
H	-2,7723455	2,7989851	1,0185374
O	-2,1129201	1,0591389	0,2906133
O	-2,062551	1,5978109	2,5059463

TS cis ox. add. HCOOH to Rh(PNC)(CO)

SCF Energy = -1353,000793

H	1,8404641	-0,4203358	0,7951167
C	1,2628922	-0,2445834	1,7030348
N	-0,1854582	0,1729146	4,0339235
C	0,2066382	-1,0969993	2,0437929
C	1,5531686	0,8390993	2,5211095
C	0,8186618	1,0495786	3,6978557
C	-0,5211221	-0,854369	3,2056769
H	-0,0663658	-1,9386942	1,4081794
H	2,3493617	1,5339884	2,2588165

C	-1,7390095	-1,6517108	3,5867738
H	-2,6248861	-1,1553403	3,1532628
P	-1,9925395	-1,5882949	5,4308424
C	-0,9631253	-2,9922936	6,0040082
H	0,0870733	-2,7757226	5,7673432
H	-1,2634352	-3,9299828	5,5139724
H	-1,0732021	-3,0844281	7,0902621
C	-3,7022471	-2,1895553	5,6646974
H	-4,4021716	-1,4670513	5,2254936
H	-3,8815779	-2,2401493	6,7461307
H	-3,8573613	-3,1807154	5,214942
Rh	-1,2032034	0,5709133	5,7711142
C	-2,8753254	1,548175	5,582697
O	-3,8939021	2,0894981	5,4867432
C	0,9852741	2,1425887	4,6402547
C	1,1530754	4,1750294	6,5484786
C	0,060643	2,1669835	5,7211082
C	1,9807666	3,1337791	4,5306972
C	2,062903	4,1456996	5,4801778
C	0,1624147	3,1974256	6,6632996
H	2,6964724	3,111835	3,7062769
H	2,8334304	4,9128309	5,3954706
H	-0,5350429	3,2299892	7,5022853
H	1,2192912	4,9703303	7,2938568
H	-0,0785948	-0,1194997	6,7987376
O	-0,4118205	0,3002917	8,0302782
C	-1,1515944	-0,4961191	8,7745686
O	-2,013224	-1,2940164	8,4281403
H	-0,8929533	-0,3498191	9,8489681
H	-1,6993025	-2,6737398	3,1827939

Rh^{III} intermediate from cis ox. add. HCOOH to Rh(CNP)(CO)

SCF Energy = -1353,034571

H	1,3388346	-0,0197272	0,5078984
C	0,8931561	0,0496179	1,500694
N	-0,2267552	0,2102952	4,0208161
C	-0,0625931	-0,8869361	1,9074781
C	1,2730254	1,0657117	2,3667517
C	0,7086601	1,1416025	3,6507209
C	-0,6213419	-0,7772967	3,1792772
H	-0,382575	-1,6910339	1,2460903
H	2,0178575	1,8002365	2,0661938
C	-1,7080332	-1,7013014	3,6693112
H	-2,6849577	-1,2706467	3,3891233
P	-1,7323266	-1,7921974	5,5310499
C	-0,6655087	-3,2247121	5,9274639
H	0,343202	-3,022569	5,5455051
H	-1,0521782	-4,1590245	5,4959174
H	-0,6009551	-3,3209145	7,0192799
C	-3,4188995	-2,4041526	5,9014075
H	-4,1507896	-1,6389876	5,6120023
H	-3,5014082	-2,5600195	6,9853661
H	-3,6405854	-3,347871	5,3820841
Rh	-0,8865195	0,3366736	5,9603298
C	-2,5055476	1,3722753	5,5696692

O	-3,4297777	2,0069599	5,3053658
C	1,031614	2,1189998	4,6814029
C	1,5644476	3,8700261	6,7877244
C	0,380755	1,9419377	5,9296397
C	1,9411934	3,1803061	4,5007272
C	2,2012572	4,0539667	5,5507297
C	0,6614531	2,8197133	6,9769233
H	2,445033	3,3263386	3,5431449
H	2,9027045	4,877534	5,4131184
H	0,1772683	2,6655702	7,9426775
H	1,7780273	4,5543353	7,6114172
H	0,4773795	-0,4077792	6,3334912
O	-1,1165583	0,4727265	8,0071061
C	-2,2756262	0,2610993	8,5822042
O	-2,4612311	0,2619428	9,789831
H	-3,1273998	0,0741633	7,8694524
H	-1,6392352	-2,6893326	3,1917946

TS cis red. el.

SCF Energy = -1353,021877

H	1,2604069	-0,0011259	0,5145452
C	0,8176308	0,0634718	1,5088675
N	-0,3112841	0,2189067	4,0310242
C	-0,1583318	-0,8609168	1,9052084
C	1,2277595	1,0492171	2,3925691
C	0,6641384	1,1196097	3,6794478
C	-0,7172423	-0,7579781	3,1744048
H	-0,4887508	-1,6537683	1,2354894
H	2,0003762	1,7616912	2,1090664
C	-1,7895225	-1,6862456	3,6780898
H	-2,7767629	-1,2290415	3,4920596
P	-1,6792572	-1,841215	5,534586
C	-0,4861016	-3,2114427	5,7864866
H	0,4803111	-2,914261	5,3586635
H	-0,8261657	-4,1490896	5,3225237
H	-0,3484774	-3,3649645	6,8648569
C	-3,2850804	-2,5920175	5,9957092
H	-4,0895099	-1,8809334	5,7669484
H	-3,2863677	-2,7698004	7,0794297
H	-3,4667023	-3,5419503	5,4722393
Rh	-1,0388065	0,3721708	5,9389652
C	-2,6905006	1,2246526	5,3969507
O	-3,6009518	1,7035028	4,8632069
C	1,0506681	2,0378077	4,7350765
C	1,6908893	3,6890985	6,9024874
C	0,4720586	1,7896102	6,0173084
C	1,9364868	3,1193258	4,5620412
C	2,2507014	3,9418307	5,636298
C	0,8205842	2,6213055	7,096641
H	2,3679991	3,3275344	3,581238
H	2,9298731	4,783345	5,4976125
H	0,3886293	2,4152918	8,0768486
H	1,9385479	4,3422533	7,7413865
H	0,5725764	0,3346977	6,3541762
O	-1,3317712	0,4136634	7,9642606

C	-2,4893456	0,6926214	8,5192586
O	-2,7000169	0,6566277	9,7212216
H	-3,2984891	0,9755911	7,7917849
H	-1,7651331	-2,6515461	3,1522029

Complex 4'

SCF Energy = -1353,042377

H	1,461491	-0,1005498	0,6791489
C	0,945271	-0,0486491	1,6378008
N	-0,3961388	0,0957299	4,1028752
C	-0,0462483	-0,9737071	1,965893
C	1,2824351	0,9187385	2,5766121
C	0,6213145	0,9648203	3,8105274
C	-0,7019622	-0,8827073	3,1910249
H	-0,3285672	-1,7647433	1,271783
H	2,0883738	1,6276318	2,3919084
C	-1,7868026	-1,853678	3,573296
H	-2,7712831	-1,4251222	3,3239131
P	-1,7747426	-2,0214659	5,4188587
C	-0,5529733	-3,3592269	5,7305261
H	0,4271496	-3,0439949	5,3486666
H	-0,8482028	-4,3026664	5,2483302
H	-0,4689803	-3,5158182	6,8138901
C	-3,3687021	-2,7572237	5,9072005
H	-4,1793354	-2,1158403	5,5402563
H	-3,4073962	-2,7438991	7,0048287
H	-3,4903352	-3,7829127	5,5321765
Rh	-1,4827925	0,1838924	5,8750607
C	-1,9202775	2,0065827	5,6511236
O	-2,2703753	3,0570293	5,3029906
C	1,0390958	1,935813	4,8416579
C	1,7980944	3,7872389	6,8076151
C	1,2869836	1,5119953	6,1611106
C	1,1940513	3,2916649	4,5174906
C	1,5625728	4,2140279	5,4980591
C	1,667968	2,434269	7,1349274
H	0,9747128	3,6301598	3,5037425
H	1,650714	5,2701993	5,24154
H	1,8530605	2,0956642	8,1546061
H	2,0800676	4,5094919	7,5746713
H	1,193071	0,4545231	6,4138383
O	-2,4228558	-0,1450436	7,6332286
C	-2,867302	0,7930106	8,4466322
O	-3,3506203	0,5708691	9,5447436
H	-2,7672778	1,8362541	8,0474681
H	-1,67819	-2,8048273	3,0311585

Rh^{III} intermediate form trans ox. add. HCOOH to Rh(PNC)(CO)

SCF Energy = -1353,065207

H	0,5911203	0,2880259	0,5466286
C	0,4676426	0,1810137	1,6249328
N	0,1129742	-0,0734639	4,3470188
C	-0,0896832	-0,9873437	2,1534491
C	0,8735408	1,1999191	2,4769428
C	0,6969845	1,0616524	3,8629838

C	-0,2462561	-1,0940447	3,5344552
H	-0,3915672	-1,8114837	1,5085259
H	1,3186204	2,1091326	2,0776067
C	-0,7468201	-2,3489966	4,2028625
H	-1,4088966	-2,9257736	3,5414892
P	-1,5390465	-1,9615009	5,8430848
C	-1,4291559	-3,5356404	6,767479
H	-0,376368	-3,7481565	6,9920875
H	-1,8683771	-4,3726285	6,2062576
H	-1,9684975	-3,4161404	7,7164176
C	-3,3131562	-1,793807	5,4470477
H	-3,4244865	-0,9613018	4,7403063
H	-3,848122	-1,5232448	6,3661997
H	-3,7207204	-2,7186076	5,0152596
Rh	-0,3475787	-0,0233054	6,3703643
C	-0,6402703	0,0414182	8,2016524
O	-0,7084591	0,0382726	9,353219
C	1,0960855	2,020002	4,8891438
C	1,8680591	3,7401624	6,9455626
C	0,7826974	1,679186,2347389	
C	1,7797674	3,2140505	4,5937885
C	2,1651193	4,0724989	5,6183621
C	1,1844589	2,5578003	7,2465611
H	2,0169654	3,4757519	3,5607791
H	2,695914	4,9965797	5,3873117
H	0,9599288	2,3282404	8,2890455
H	2,1707445	4,4096009	7,7533657
H	0,9539188	-0,838368	6,7059999
O	-2,0327304	1,1988767	5,7073775
C	-3,0479545	1,2841467	6,5028396
O	-3,2331412	0,7027717	7,5798344
H	-3,8330042	1,9757027	6,1075562
H	0,1245669	-2,9849886	4,434207

TS trans red. el.

SCF Energy = -1353,040694

H	0,6985622	0,261477	0,54674
C	0,5370609	0,162244	1,6205605
N	0,0888067	-0,0789083	4,337196
C	-0,0978225	-0,9755968	2,1334445
C	0,9764701	1,1527655	2,4868101
C	0,7497607	1,0215327	3,8670687
C	-0,2993072	-1,0789572	3,5068764
H	-0,4187487	-1,7843314	1,4781279
H	1,4901135	2,0326777	2,1042463
C	-0,8639327	-2,3172331	4,1527828
H	-1,6146453	-2,8020612	3,5119649
P	-1,5376786	-1,9602969	5,8534327
C	-1,3174503	-3,5379564	6,7565483
H	-0,2461121	-3,7304981	6,8935782
H	-1,7874484	-4,3798825	6,2275766
H	-1,7796666	-3,4335363	7,7472176
C	-3,3441088	-1,8637106	5,5989921
H	-3,5391074	-1,0579098	4,8797863
H	-3,8128226	-1,5750531	6,5483967

H	-3,7532855	-2,8152187	5,2307546
Rh	-0,4425577	-0,006173	6,3372519
C	-0,8053228	-0,0629726	8,1515078
O	-0,9393351	-0,13663	9,2979928
C	1,1807038	1,9562705	4,8998062
C	1,9229619	3,680086	6,9845467
C	0,918628	1,5855975	6,2552296
C	1,8038739	3,1851441	4,6199365
C	2,1723751	4,0417174	5,6517851
C	1,3133723	2,4641606	7,2810943
H	1,9883156	3,4857589	3,5873177
H	2,6513336	4,9941859	5,4231421
H	1,1292268	2,1865047	8,3197101
H	2,2068754	4,3555476	7,7933115
H	1,1828731	0,2242862	6,6037227
O	-2,1898432	1,2062537	5,5894657
C	-3,1896762	1,3188442	6,3957424
O	-3,369645	0,7659248	7,4900595
H	-3,9784432	2,0093776	5,9997709
H	-0,0383538	-3,0364305	4,2885085

Trans agostic complex

SCF Energy = -1353,045933

H	0,8203903	0,1531658	0,5781805
C	0,6269425	0,0597069	1,6470526
N	0,1232337	-0,18506	4,3686757
C	-0,0279573	-1,0726763	2,1497242
C	1,0514365	1,0455574	2,5266348
C	0,7906333	0,9133937	3,8992618
C	-0,253574	-1,1794718	3,5176678
H	-0,3440018	-1,8781255	1,4877546
H	1,5993371	1,9150985	2,1670526
C	-0,8530743	-2,4093196	4,1461435
H	-1,6175456	-2,8649412	3,4993626
P	-1,5174115	-2,033892	5,8413571
C	-1,4318746	-3,6318741	6,73166
H	-0,3828471	-3,9250566	6,8593287
H	-1,9841534	-4,4198788	6,1983819
H	-1,876608	-3,4926915	7,7260351
C	-3,3119596	-1,7880588	5,5923508
H	-3,4467752	-0,9903731	4,8505905
H	-3,7450754	-1,4155601	6,5294868
H	-3,8084468	-2,7113845	5,2584512
Rh	-0,4685829	-0,1732956	6,3649675
C	-0,9026801	-0,3773048	8,1380018
O	-1,1366414	-0,547669	9,2620716
C	1,1959219	1,8833408	4,9157428
C	1,7337154	3,7242022	6,9763599
C	1,3173494	1,449266	6,2616545
C	1,3677729	3,2462505	4,6269576
C	1,6359323	4,1562919	5,6450928
C	1,5872676	2,3747212	7,2801984
H	1,2311876	3,6069671	3,6066112
H	1,743772	5,215106	5,4077509

H	1,676309	2,0246197	8,3088625
H	1,9269095	4,4463039	7,7706701
H	1,4627675	0,3550334	6,4895068
O	-1,6045749	1,7023169	5,8943795
C	-2,7892299	1,7690302	6,403059
O	-3,3626075	0,9659959	7,1517618
H	-3,3287304	2,7012168	6,0902388
H	-0,050527	-3,1539513	4,2829631

Protonated Rh(PNC)(CO)

SCF Energy = -1163,559211

H	0,6385975	0,2483171	0,5506571
C	0,4978957	0,1511822	1,6273802
N	0,116408	-0,0848021	4,347931
C	-0,0739128	-1,008976	2,1553993
C	0,9021423	1,1756475	2,4774122
C	0,7108836	1,0477254	3,8581584
C	-0,2415106	-1,1131247	3,5349545
H	-0,3710799	-1,8341817	1,51022
H	1,3635445	2,0750858	2,0751189
C	-0,7505819	-2,3663289	4,1957746
H	-1,424362	-2,9299595	3,535575
P	-1,5374067	-1,9863229	5,83442
C	-1,4734967	-3,5498803	6,7690168
H	-0,4289509	-3,8008423	6,9927642
H	-1,9367191	-4,3689954	6,2016192
H	-2,0116512	-3,4211832	7,7172485
C	-3,3072521	-1,7344879	5,4427401
H	-3,4142996	-0,884973	4,7551301
H	-3,8573964	-1,507008	6,3649676
H	-3,7361934	-2,6335175	4,9784138
Rh	-0,2779356	-0,0479268	6,3813479
C	-0,5435586	0,0107595	8,2254107
O	-0,6718801	0,0264297	9,3674452
C	1,0967763	2,0158349	4,8847365
C	1,8442433	3,7495357	6,9507567
C	0,8261548	1,6606831	6,2364875
C	1,7129593	3,2423814	4,591077
C	2,0850453	4,1054395	5,6216266
C	1,2231464	2,5311916	7,2559334
H	1,9077445	3,5327575	3,5578582
H	2,5700988	5,0526751	5,3869337
H	1,0554083	2,2734959	8,3021496
H	2,1452946	4,4183796	7,7580339
H	1,046995	-0,729134	6,6926685
H	0,1098494	-3,0208775	4,4156361

TS red. el. from protonated Rh(PNC)(CO)

SCF Energy = -1163,55761

H	0,6072721	0,2554993	0,557171
C	0,4826937	0,1486658	1,6348932
N	0,1476681	-0,1147671	4,3600796
C	-0,0881012	-1,0129585	2,1606832
C	0,9057372	1,1625507	2,4888021
C	0,7338769	1,0197939	3,8703665

C	-0,2324251	-1,1305297	3,541939
H	-0,40276	-1,8285929	1,5116148
H	1,3669835	2,0630941	2,0887017
C	-0,7454413	-2,3815393	4,2029267
H	-1,4340387	-2,9368575	3,5507557
P	-1,5129726	-1,9866598	5,8474215
C	-1,4979364	-3,5466806	6,7870992
H	-0,4614337	-3,8343858	7,0026034
H	-1,996812	-4,348086	6,224527
H	-2,0234242	-3,3943851	7,7388863
C	-3,2733487	-1,6671345	5,4660599
H	-3,3512976	-0,8124098	4,7813611
H	-3,8096168	-1,4217455	6,3916982
H	-3,7361757	-2,549144	5,0018635
Rh	-0,1829692	-0,1134756	6,4080654
C	-0,4307997	-0,1256179	8,2512933
O	-0,5561304	-0,1397327	9,3948004
C	1,1334982	1,9807793	4,8994352
C	1,8765012	3,7122088	6,9759674
C	0,9282477	1,6007865	6,2541239
C	1,6772219	3,2419304	4,6114998
C	2,0470418	4,1022363	5,6455508
C	1,3290393	2,4594334	7,2802081
H	1,809936	3,5636912	3,5779545
H	2,4756185	5,0764934	5,4116525
H	1,2168391	2,1645405	8,3235536
H	2,1780149	4,3792672	7,784284
H	1,34305	-0,2003063	6,6623107
H	0,109443	-3,0449623	4,4168493

Agostic complex from protonated Rh(PNC)(CO)

SCF Energy = -1163,583258

H	0,8521674	0,1272508	0,5555729
C	0,6900721	0,0283291	1,6289776
N	0,2934484	-0,2398235	4,3480762
C	0,0329569	-1,0957228	2,1359875
C	1,1403797	1,0200323	2,4985766
C	0,9229675	0,8684566	3,8701675
C	-0,1505937	-1,2141502	3,5131575
H	-0,3259019	-1,8807915	1,4719598
H	1,6620625	1,8996287	2,1249653
C	-0,8119797	-2,3915028	4,1742586
H	-1,5814682	-2,8462171	3,5342252
P	-1,4985103	-1,8796673	5,8297174
C	-1,6293892	-3,4077425	6,8087009
H	-0,6275737	-3,8135977	6,9939198
H	-2,2449986	-4,1520015	6,2842928
H	-2,0958525	-3,1711589	7,7740183
C	-3,2238557	-1,3806185	5,5015945
H	-3,2325691	-0,5375092	4,7995051
H	-3,6895537	-1,0560649	6,4407948
H	-3,7958703	-2,2204042	5,081756
Rh	-0,0801679	-0,280472	6,3873423
C	-0,4506658	-0,4039799	8,191823
O	-0,6944263	-0,50728	9,3163117

C	1,2838669	1,8505506	4,9077454
C	1,7172895	3,6758205	7,0120412
C	1,5675939	1,3924528	6,2232956
C	1,2385472	3,2288942	4,6705118
C	1,4605565	4,1307315	5,7147516
C	1,7810217	2,3050362	7,2650625
H	0,9867355	3,6035801	3,6778347
H	1,4163464	5,2016013	5,514916
H	2,0170744	1,9351466	8,2626199
H	1,8801394	4,3892931	7,8195361
H	1,8785195	0,3289012	6,3903875
H	-0,0553691	-3,1660011	4,3825993

TS4→A

SCF Energy = -1353.0294257350

H	0.7110063	-0.0089370	-5.0845503
C	0.4402583	-0.1609394	-4.0392167
N	-0.2769047	-0.5396468	-1.3655025
C	0.0516156	-1.4195624	-3.5827766
C	0.5090707	0.8880606	-3.1310331
C	0.1655723	0.6766838	-1.7881237
C	-0.3023363	-1.5787874	-2.2439154
H	0.0085643	-2.2761120	-4.2547956
H	0.8630354	1.8728912	-3.4319085
C	-0.7436377	-2.9165951	-1.7070228
P	-0.5545369	-2.8975280	0.1350933
C	1.2008717	-3.3653738	0.3998456
H	1.8408283	-2.6014657	-0.0600879
H	1.4251261	-4.3502302	-0.0373300
H	1.4061219	-3.3856317	1.4777634
C	-1.4721771	-4.3640723	0.7206397
H	-2.5380137	-4.2323945	0.4975856
H	-1.3551035	-4.4448804	1.8091213
H	-1.0975196	-5.2816371	0.2452597
Rh	-1.2410659	-0.8906929	0.5847683
C	-1.8362261	-1.4161064	2.2114978
O	-2.1847881	-1.8054658	3.2523962
C	0.3316507	1.7578097	-0.7999914
C	0.6266626	3.8017249	1.0912396
C	0.9709951	1.5025988	0.4251920
C	-0.1461071	3.0482644	-1.0722058
C	-0.0090242	4.0608895	-0.1254073
C	1.1216538	2.5239164	1.3623019
H	-0.6926496	3.2354048	-1.9970136
H	-0.4312127	5.0457663	-0.3236544
H	1.6151726	2.3166410	2.3123575
H	0.7201601	4.5925246	1.8360776
H	-0.1995743	-3.7411231	-2.1937169
H	-1.8189401	-3.0595707	-1.9012829
H	1.3445290	0.5002245	0.6401387
C	-2.4678524	1.4514466	0.5403306
H	-1.6241676	0.9864991	1.2639982
O	-2.8003474	0.6847715	-0.4125821
O	-2.8066426	2.5806391	0.8714028

Complex A

SCF Energy = -1164.3621204360

H	0.2870347	0.2120260	-4.7322007
C	0.1274418	0.1466135	-3.6553866
N	-0.2881811	-0.0169725	-0.8937609
C	-0.4225865	-1.0045410	-3.0874201
C	0.5065307	1.1896215	-2.8205593
C	0.3055896	1.0873092	-1.4347659
C	-0.6121706	-1.0636171	-1.7080591
H	-0.7076699	-1.8561463	-3.7042383
H	1.0013791	2.0738315	-3.2196891
C	-1.1635249	-2.2867025	-1.0329445
P	-0.3641937	-2.4338019	0.6504953
C	1.2331042	-3.2634023	0.2310144
H	1.8241887	-2.5867640	-0.4009937
H	1.0822025	-4.2169943	-0.2977940
H	1.7967691	-3.4478969	1.1552283
C	-1.3079443	-3.7974789	1.4351379
H	-2.3350887	-3.4554837	1.6143089
H	-0.8521743	-4.0314988	2.4065866
H	-1.3172551	-4.7043014	0.8132937
Rh	-0.7100480	-0.2400871	1.2146987
C	-1.3020293	-0.4008409	2.9222422
O	-1.6893566	-0.5291743	4.0142451
C	0.7762608	2.1374462	-0.5187425
C	1.6660908	4.1259106	1.2550670
C	1.3466406	1.7878078	0.7210228
C	0.6613663	3.4967723	-0.8552399
C	1.0977296	4.4838617	0.0270329
C	1.7906980	2.7789723	1.5979937
H	0.1859931	3.7825866	-1.7950655
H	0.9820397	5.5357067	-0.2370777
H	2.2274380	2.4919675	2.5547689
H	2.0077773	4.8996449	1.9440530
H	-1.0411438	-3.1806735	-1.6629314
H	-2.2380038	-2.1494939	-0.8280698
H	-1.3449632	1.2426478	1.2975252
H	1.4727285	0.7298259	0.9835254

Complex A'

SCF Energy = -1164.3622544360

H	0.0727682	0.5480600	-4.7750995
C	0.1056736	0.3768701	-3.6982909
N	0.1669152	-0.0525939	-0.9752548
C	-0.0718227	-0.9147485	-3.1882403
C	0.3185497	1.4408990	-2.8307881
C	0.3429612	1.2159292	-1.4427461
C	-0.0270154	-1.1001842	-1.8074558
H	-0.2344493	-1.7654563	-3.8491902
H	0.4476170	2.4495221	-3.2196310
C	-0.1456051	-2.4519328	-1.1489559
P	-0.8249721	-2.2997607	0.5879209
C	-0.3365775	-3.9028420	1.3364698
H	0.7551628	-3.9275204	1.4474303

H	-0.6683058	-4.7602762	0.7327828
H	-0.7832990	-3.9723788	2.3371485
C	-2.6317751	-2.4977008	0.3484210
H	-2.9860469	-1.6695730	-0.2785220
H	-3.1294623	-2.4206179	1.3237114
H	-2.8840256	-3.4595737	-0.1211431
Rh	-0.0099509	-0.2125678	1.1404699
C	1.7263708	-0.7103271	1.7952080
O	2.7010139	-0.9935727	2.3522807
C	0.5144663	2.2283518	-0.4016788
C	0.8167184	4.0927663	1.6556653
C	0.3840448	1.7969503	0.9523297
C	0.7934283	3.5772622	-0.6991180
C	0.9462182	4.5067555	0.3230868
C	0.5380010	2.7581350	1.9603616
H	0.9011337	3.9034351	-1.7355610
H	1.1660785	5.5487790	0.0877598
H	0.4372796	2.4569080	3.0033778
H	0.9353783	4.8193402	2.4625707
H	0.8683237	-2.8691845	-1.0229039
H	-0.7170523	-3.1597084	-1.7672703
H	-1.5275110	0.3142602	1.0287961
H	-0.4350197	-0.1131646	2.6547871

Complex B

SCF Energy = -1164.3333811050

H	0.444891	0.515565	-4.842156
C	0.282208	0.372723	-3.773946
N	-0.152363	-0.007503	-1.035724
C	-0.196754	-0.860784	-3.284381
C	0.514422	1.403827	-2.881194
C	0.317117	1.208656	-1.499424
C	-0.429470	-1.006801	-1.928819
H	-0.405205	-1.689811	-3.960544
H	0.845127	2.378480	-3.238503
C	-1.066733	-2.242599	-1.343579
P	-0.803130	-2.310245	0.485462
C	0.717908	-3.303682	0.722024
H	1.550607	-2.782760	0.233307
H	0.609774	-4.316131	0.305642
H	0.933974	-3.364714	1.796885
C	-2.116807	-3.408211	1.121634
H	-3.092019	-2.956098	0.906376
H	-2.005699	-3.487289	2.210856
H	-2.051339	-4.410753	0.675388
Rh	-0.605844	-0.179400	1.017094
C	-0.101467	-0.395476	2.815604
O	0.054783	-0.548076	3.962597
C	0.565572	2.190011	-0.472399
C	1.133799	3.950456	1.664764
C	0.009731	1.953334	0.834627
C	1.399042	3.312597	-0.659536
C	1.687999	4.176178	0.385916

C	0.291526	2.874466	1.877105
H	1.857905	3.482067	-1.635107
H	2.350858	5.026278	0.220777
H	-0.166050	2.716168	2.854109
H	1.363920	4.631421	2.485614
H	-0.726070	-3.161216	-1.843571
H	-2.160249	-2.171778	-1.476685
H	-2.222765	-0.374319	0.994687
H	-1.103984	1.565960	0.873829

TSB→C

SCF Energy = -1164.3482768790

H	-0.0099617	0.5099641	-4.7556117
C	0.0650445	0.3422852	-3.6804821
N	0.2500074	-0.0881095	-0.9554987
C	-0.0567309	-0.9559373	-3.1613902
C	0.2591097	1.4127579	-2.8208283
C	0.3409721	1.1895211	-1.4322439
C	0.0426704	-1.1411105	-1.7867663
H	-0.2239202	-1.8109699	-3.8154943
H	0.3220537	2.4277754	-3.2099688
C	-0.0650753	-2.4826385	-1.1135647
P	-0.8014036	-2.2746882	0.5954686
C	-0.4685268	-3.9069963	1.3655169
H	0.6132927	-4.0133083	1.5185202
H	-0.8410368	-4.7391798	0.7501580
H	-0.9574469	-3.9384212	2.3481386
C	-2.6090695	-2.3556342	0.2670511
H	-2.8808379	-1.5047618	-0.3712795
H	-3.1498764	-2.2558476	1.2171321
H	-2.9009453	-3.2960491	-0.2240144
Rh	0.2388923	-0.2921335	1.1602315
C	1.9513278	-0.9089343	1.7016085
O	2.9508010	-1.3001099	2.1455121
C	0.4523369	2.2113923	-0.4037817
C	0.6309348	4.0957419	1.6611141
C	0.2678479	1.7863243	0.9553264
C	0.7319814	3.5622546	-0.6907375
C	0.8289244	4.4992807	0.3287297
C	0.3403006	2.7711951	1.9651676
H	0.8982953	3.8765213	-1.7229270
H	1.0578442	5.5398535	0.0970434
H	0.1780141	2.4730284	3.0011405
H	0.7085717	4.8295756	2.4659462
H	0.9491980	-2.8781310	-0.9327789
H	-0.6055333	-3.2115164	-1.7352138
H	-0.9219230	0.9156132	1.1295719
H	-0.0609208	-0.3080675	2.7079331

Complex C

SCF Energy = -1164.3622535950

H	0.0673624	0.5484623	-4.7751511
C	0.1016955	0.3770936	-3.6984123
N	0.1664715	-0.0528004	-0.9755034
C	-0.0753738	-0.9145642	-3.1883263

C	0.3159284	1.4409352	-2.8310208
C	0.3421498	1.2157500	-1.4430423
C	-0.0287839	-1.1002201	-1.8076298
H	-0.2390800	-1.7651279	-3.8491980
H	0.4446172	2.4495932	-3.2198776
C	-0.1469782	-2.4520042	-1.1491375
P	-0.8248287	-2.2996419	0.5882911
C	-0.3372259	-3.9032223	1.3361642
H	0.7545409	-3.9289557	1.4462408
H	-0.6702413	-4.7602309	0.7325947
H	-0.7831950	-3.9724988	2.3371781
C	-2.6319189	-2.4960242	0.3500110
H	-2.9857723	-1.6676337	-0.2767511
H	-3.1288812	-2.4183512	1.3255919
H	-2.8854011	-3.4576801	-0.1193208
Rh	-0.0082814	-0.2129100	1.1403963
C	1.7281615	-0.7109377	1.7945525
O	2.7025113	-0.9936436	2.3524283
C	0.5151687	2.2279830	-0.4020484
C	0.8204378	4.0920642	1.6551904
C	0.3862503	1.7964501	0.9520750
C	0.7941114	3.5768652	-0.6996542
C	0.9483805	4.5061950	0.3224850
C	0.5417356	2.7574618	1.9600650
H	0.9006489	3.9031456	-1.7361988
H	1.1682115	5.5482002	0.0870087
H	0.4422166	2.4561170	3.0031836
H	0.9403078	4.8185051	2.4620485
H	0.8669696	-2.8694516	-1.0239840
H	-0.7191380	-3.1596254	-1.7669603
H	-1.5256228	0.3146956	1.0304169
H	-0.4319422	-0.1134536	2.6550232

TSC→1

SCF Energy = -1164.3484381460

H	0.0412581	0.5804069	-4.8181172
C	0.0641547	0.4065053	-3.7416927
N	0.0866654	-0.0317544	-1.0085636
C	-0.1290085	-0.8843082	-3.2329961
C	0.2963891	1.4611444	-2.8680851
C	0.3083035	1.2316547	-1.4815810
C	-0.0972308	-1.0748023	-1.8539077
H	-0.2876120	-1.7338772	-3.8967528
H	0.4604909	2.4668280	-3.2518238
C	-0.1877218	-2.4347059	-1.2102911
P	-0.7786474	-2.3190627	0.5569127
C	-0.1737044	-3.8958734	1.2739274
H	0.9211185	-3.8585666	1.3387908
H	-0.4827003	-4.7675613	0.6787781
H	-0.5724477	-3.9949471	2.2922561
C	-2.5866428	-2.6130960	0.4135329
H	-3.0225912	-1.7993389	-0.1803294
H	-3.0342015	-2.5817855	1.4156951
H	-2.8131503	-3.5801990	-0.0590315
Rh	-0.0482027	-0.1983985	1.1131427

C	1.4604574	-0.6382358	2.1699638
O	2.3262354	-0.9035894	2.8991893
C	0.5361254	2.2264457	-0.4394012
C	0.9878649	4.0433884	1.6388258
C	0.4635123	1.7749258	0.9125171
C	0.8293573	3.5759552	-0.7220335
C	1.0541213	4.4808365	0.3083579
C	0.6959358	2.7097649	1.9313432
H	0.8881586	3.9211207	-1.7562592
H	1.2837797	5.5226507	0.0815746
H	0.6503072	2.3869785	2.9724341
H	1.1690609	4.7496470	2.4520012
H	0.8331623	-2.8491263	-1.1433854
H	-0.7865338	-3.1371600	-1.8085327
H	-1.6370425	0.3545928	1.3465075
H	-1.1938085	0.1840827	2.2457622

Complex D

SCF Energy = -1354.2432148450

H	0.2665727	0.0412870	-4.9666703
C	0.1469479	-0.0730753	-3.8888594
N	-0.1696173	-0.3610988	-1.1180169
C	-0.3256371	-1.2617752	-3.3486743
C	0.4625561	0.9695637	-3.0231181
C	0.3091366	0.8010662	-1.6443763
C	-0.4899157	-1.3825557	-1.9662040
H	-0.5996346	-2.1005193	-3.9872703
H	0.8436653	1.9204583	-3.3917273
C	-1.1026439	-2.6268261	-1.3940788
P	-0.5849403	-2.8947899	0.3572876
C	0.9126447	-3.9454726	0.2475072
H	1.6963512	-3.3876692	-0.2819278
H	0.7118164	-4.8883244	-0.2813401
H	1.2746638	-4.1674411	1.2600529
C	-1.8909078	-3.9818709	1.0213915
H	-2.8143705	-3.3875021	1.0305879
H	-1.6367299	-4.2737007	2.0486413
H	-2.0249113	-4.8836755	0.4076108
Rh	-0.5685590	-0.6194446	1.0148576
C	-0.7828201	-0.6872433	2.8217289
O	-0.8833986	-0.7103419	3.9740299
C	0.6781461	1.9259893	-0.7483836
C	1.3619758	4.0743477	0.9083248
C	1.8496886	1.8777219	0.0183327
C	-0.1366512	3.0646576	-0.7009792
C	0.2000875	4.1311670	0.1348364
C	2.1898155	2.9495063	0.8424774
H	-1.0508756	3.0944623	-1.2955764
H	-0.4501999	5.0053083	0.1850203
H	3.1001250	2.9039722	1.4414661
H	1.6234938	4.9069172	1.5626184
H	-0.9141001	-3.4962043	-2.0397750
H	-2.1951051	-2.4546308	-1.3414715
H	-0.6486967	0.9535791	1.2264677
H	2.4801529	0.9893064	-0.0206195

C	-3.1047571	-0.1034729	-0.5351495
H	-2.8308535	0.9809963	-0.4351269
O	-2.6596677	-0.8693920	0.4196284
O	-3.7661365	-0.4895650	-1.5003755
H	0.9588334	-0.4963506	1.3187343

TSD→4

SCF Energy = -1354.2334385130

H	1.1366277	-0.2013705	-4.8633704
C	0.7934418	-0.2408955	-3.8290061
N	-0.0626417	-0.3508728	-1.1528611
C	0.0917117	-1.3423879	-3.3520198
C	1.0168032	0.8226370	-2.9640443
C	0.5702128	0.7597730	-1.6366972
C	-0.3348790	-1.3745261	-2.0220401
H	-0.1419384	-2.1848214	-4.0015700
H	1.5127153	1.7312378	-3.3013941
C	-1.1497391	-2.5267336	-1.5283994
P	-0.8428108	-2.8262803	0.2572366
C	0.6142521	-3.9450636	0.2975404
H	1.4673589	-3.4298142	-0.1620715
H	0.4167028	-4.8876489	-0.2352576
H	0.8692750	-4.1647629	1.3425058
C	-2.2143561	-3.8995553	0.7996181
H	-3.1416602	-3.3240718	0.6889660
H	-2.0645354	-4.1611386	1.8557922
H	-2.2564786	-4.8215897	0.2022894
Rh	-0.5105633	-0.6740539	0.9618806
C	-0.8299040	-1.1737233	2.6807659
O	-1.0409891	-1.5159078	3.7694964
C	0.7845208	1.9511049	-0.7815433
C	1.2116272	4.2682432	0.7370760
C	2.0746040	2.4887403	-0.6550219
C	-0.2961278	2.5867268	-0.1459464
C	-0.0775411	3.7437676	0.6013196
C	2.2890321	3.6361347	0.1113788
H	-1.2962037	2.1554203	-0.2150318
H	-0.9219632	4.2302697	1.0906857
H	3.2986843	4.0340570	0.2207351
H	1.3771644	5.1673862	1.3322217
H	-1.0182929	-3.4201438	-2.1546840
H	-2.2145976	-2.2178578	-1.5277041
H	0.3909900	0.6888378	1.4161896
H	2.9165313	1.9875028	-1.1362450
C	-3.4945874	-0.1205791	0.0529399
H	-4.3700248	0.5712938	-0.0521371
O	-2.4702637	0.4490570	0.5715172
O	-3.6293071	-1.2974791	-0.3344492
H	0.9861495	-0.1249120	1.3913392

H2

SCF Energy = -1.1775301292

H	0.0000000	0.0000000	1.0043423
H	0.0000000	0.0000000	0.2536572

CO2

SCF Energy = -188.6877079720

O	0.0038657	0.0480430	0.7605969
C	-0.0052988	-0.0659520	-0.4052461
O	-0.0145398	-0.1799544	-1.5711390

Formic acid

SCF Energy = -189.8644923955

C	0.0000000	-0.0034369	1.0523458
O	0.0000000	0.1053390	-0.1502717
H	0.0000000	0.8363973	1.7743649
O	0.0000000	-1.1754383	1.7353308
H	0.0000000	-1.8940105	1.0658597

4) References

S1 S. Fukuzumi, T. Kobayashi, T. Suenobu, *J. Am. Chem. Soc.* 2010, **132**, 1496-1497.

S2 P. C. J. Kamer, A. van Rooy, G. C. Schoemaker, P. W. N. M. van Leeuwen, *Coord. Chem. Rev.* 2004, **248**, 2409-2424.