Electronic Supplementary Material (ESI) for Chemical Communications

Tandem decarboxylative hydroformylation – hydrogenation reaction employing a supramolecular catalyst system

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Supporting Information

I	**General**	**2**
II	**General Procedure for α,β-unsaturated acid Hydroformylation-Hydrogenation Catalysis**	**3**
III	**Isolation and Characterization of Products**	**4**
IV	**Chemoselective hydroformylation-hydrogenation of α,β-unsaturated acid**	**7**
V	**Optimization of the Reaction Conditions**	**7**
VI	**Determination of association constant**	**8**
VII	**Kinetic study**	**9**
VIII	**NMR experiments**	**11**
IX	**DFT-Calculations**	**13**

I General

All reagents were commercially available unless otherwise noted. *N*-(6-diphenylphosphanylpyridine-2-carbonyl)-guanidine (1), *N*-(3-diphenylphosphanylbenzoyl)-guanidine (3), *N*-(2-diphenylphosphanylbenzoyl)-guanidine (4), *N*-(5-Diphenylphosphanyl-pyrrole-2-carbonyl)-guanidine (2), (*E*)-5-Methylhex-2-enoic acid, (*E*)-Oct-2-enoic acid, (*E*)-9-(*tert*-Butyldimethyl-silyloxy)non-2-enoic acid, (*E*)-Dodec-2-enedioic acid, (*E*)-8-Oxonon-2-enoic acid, (*E*)-9-Benzyloxynon-2-enoic acid, Benzoic acid (*E*)-8-carboxy-oct-7-enyl ester were prepared according to literature procedure (*L1*). All reactions were carried out under argon 5.0 (Südwest-Gas) atmospheres in dried glassware. Air and moisture sensitive liquids and solutions were transferred *via* syringe. All solvents were dried and distilled by standard procedures. Solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished on Merck silica gel Si 60® (200-400 mesh).

Nuclear magnetic resonance spectra were acquired on a Bruker AMX 400 (400.132 MHz and 101.626 MHz for ^{1}H and ^{13}C respectively) and were referenced according to internal TMS standard. Data for ^{1}H-NMR are reported as follows: chemical shift (δ in ppm), multiplicity (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ in ppm), multiplicity and coupling constant (Hz).

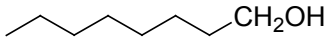
II General Procedure for α,β-unsaturated acid Hydroformylation-Hydrogenation Catalysis

Decarboxylative Hydroformylation-Hydrogenation experiments were performed in a parallel autoclave equipped with glass inlets. The solutions were prepared by charging a Schlenk flask with [$Rh(CO)_2acac$] (1 mg, $4x10^{-3}$ mmol), ligand ($4x10^{-2}$ mmol), if appropriate internal standard (1,3,5-trimethoxybenzene-NMR or tetradecane-GC) and solvent (2 ml). Then the substrate (0.4 mmol) was added and the mixture was stirred for 5 minutes under argon. The solution was transferred into the autoclave *via* syringe under an atmosphere of argon. The autoclave was purged three times with synthesis gas (CO/H_2 = 1:1), and the reaction was conducted as specified in the text. For kinetic measurements the samples were taken and analyzed by NMR (after dilution with $CDCl_3$).

III Isolation and Characterization of Products

All the products were obtained according to the general procedure for α,β-unsaturated acid hydroformylation-hydrogenation.

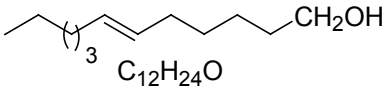
Octanol



$C_8H_{18}O$
Mol. Wt.: 130,23

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (washed with CH_2Cl_2/Et_2O = 2:1) as a colorless liquid in 150 mg (96%) yield.
NMR data are in accordance with those previously reported (*L2*).

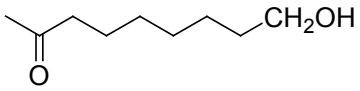
Dodec-6-en-1-ol



$C_{12}H_{24}O$
Exact Mass: 184,18

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (washed with CH_2Cl_2/Et_2O = 2:1) as a colorless liquid in 72 mg (98%) yield.
^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.93 Hz, 3H), 1.26-1.37 (m, 10H), 1.53-1.57 (m, 2H), 1.90-1.93 (m, 5H), 3.62 (t, *J* = 6.5 Hz, 2H), 5.34 (m, 2H).
^{13}C-NMR (100.626 MHz, $CDCl_3$): δ = 14.4, 20.60, 25.71, 27.08, 29.12, 29.78, 32.88, 63.11, 129.20, 131.74.
NMR data are in accordance those previously reported (*L3*).

8-Oxo-nonanol

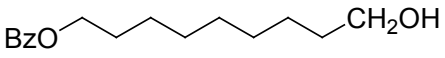


$C_9H_{18}O_2$
Mol. Wt.: 158,24

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (2× washed with CH_2Cl_2-Et_2O = 10:1) as a colorless liquid in 187 mg (95%) yield.
^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 1.25 (m, 6H), 1.5 (m, 4H), 2.11 (s, 3H), 2.4 (t, *J* = 6.4 Hz, 2H), 3.6 (t, *J* = 6.5 Hz, 2H).
^{13}C-NMR (100.626 MHz, $CDCl_3$): δ = 23.78, 25.60, 29.15, 29.21, 29.90, 32.73, 43.78, 62.9, 209.38.

NMR data are in accordance with those previously reported (*L4*).

Benzoic acid 9-ol-nonyl ester



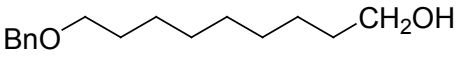
$C_{16}H_{24}O_3$
Mol. Wt.: 264,36

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (2× washed with CH_2Cl_2-Et_2O = 8:1) as a colorless liquid in 313 mg (99%) yield.

^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 1.28 (m, 8H), 1.37 (m, 2H), 1.49 (m, 2H), 1.69 (m, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 4.24 (t, *J* = 6.5 Hz, 2H), 7.34-7.38 (m, 2H), 7.46-7.49 (m, 1H), 7.95-7.98 (m, 2H).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ = 25.77, 26.09, 28.78, 29.26, 29.40, 29.52, 32.85, 63.11, 65.18, 128.40, 129.6, 130.6, 132.8, 166.78. NMR data are in accordance with those previously reported (*L5*).

9-Benzyloxy-1-nonanol



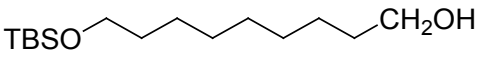
$C_{16}H_{26}O_2$
Mol. Wt.: 250,38

The title compound was isolated by flash chromatography (cyclohexane-Et_2O = 1:1) as a colorless liquid in 324 mg (99%) yield.

^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 1.23-1.28 (m, 12 H), 1.49-1.53 (m, 4H), 3.39 (t, *J* = 6.5 Hz, 2H), 3.5 (t, *J* = 6.5 Hz, 2H), 7.19-7.27 (m, 5H).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ = 25.79, 26.25, 29.42, 29.46, 29.60, 29.82, 32.88, 63.12, 70.58, 72.9, 127.53, 127.69, 128.4, 138.78. NMR data are in accordance with those previously reported (*L6*).

9-(*tert*-Butyl-dimethyl-silanyloxy)-1-nonanol



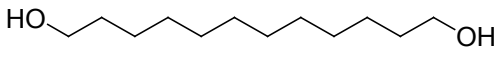
$C_{15}H_{34}O_2Si$
Mol. Wt.: 274,51

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (2× washed with CH_2Cl_2) as a colorless liquid in 322 mg (98%) yield.

^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 0.05 (s, 6H), 0.89 (s, 9H), 1.29 (m, 10H), 1.51-1.57 (m, 4H), 3.59 (t, *J* = 6.4 Hz, 2H), 3.63 (t, *J* = 6.5 Hz, 2H).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ = -5.16, 18.47, 25.81, 26.07, 29.45, 29.66, 32.89, 32.96, 63.17, 63.40. NMR data are in accordance with those previously reported (*L7*).

Dodecane-1,12-diol



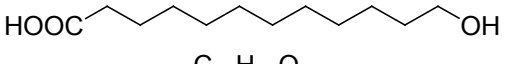
$C_{12}H_{26}O_2$
Exact Mass: 202,19

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (2× washed with CH_2Cl_2/Et_2O) as a colorless liquid in 79 mg (98%) yield.

^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 1.26-1.36 (m, 20 H), 1.52-1.59 (m, 4H), 3.63 (t, *J* = 6.5 Hz, 4H).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ = 25.8, 29.49, 29.62, 29.65, 32.89, 63.17. NMR data are in accordance with those previously reported (*L8*).

12-Hydroxy-dodecanoicacid



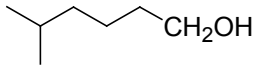
$C_{12}H_{24}O_3$
Exact Mass: 216,17

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (petroleum ether/Et_2O/MeOH= 100:50:1) as a colorless liquid in 84 mg (98%) yield.

^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 1.23-1.28 (m, 14 H), 1.43-1.52 (m, 4H), 2.21(t, *J* = 7.3 Hz, 2H), 3.4 (t, *J* = 6.5 Hz, 2H).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ = 24.45, 25.45, 28.5, 28.69, 28.87, 28.92, 29.03, 32.50, 32.60, 33.64, 60.67, 174.43. NMR data are in accordance with those previously reported (*L9*).

5-Methyl-hexan-1-ol



$C_7H_{16}O$
Exact Mass: 116,12

The title compound was isolated by filtration of the reaction mixture over a short silicagel column (2× washed with CH_2Cl_2) as a colorless liquid in 45 mg (99%) yield.

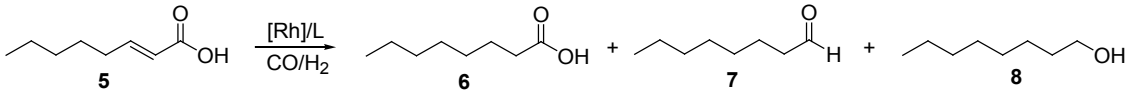
^{1}H-NMR (400.132 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 7.3 Hz, 6 H), 1.16-1.22 (m, 2 H), 1.30-1.38 (m, 2H), 1.5-1.58 (m, 3H) 3.64 (t, *J* = 6.3 Hz, 2H).

^{13}C-NMR (100.612 MHz, $CDCl_3$): δ = 22.6, 23.6, 28.04, 33.17, 38.8, 63.20. NMR data are in accordance with those previously reported (*L10*).

IV Chemoselective hydroformylation-hydrogenation of α,β-unsaturated acid

First, the reaction of oct-2-enoic acid (**5**) under standard hydroformylation conditions (15 bar CO/H_2) was examined. Using $[Rh(CO)_2(acac)]/PPh_3$ as a catalyst gave the saturated acid as the only product (Table 1, entry 1). Furthermore, the combination of triphenylphosphine and acylguanidine (**9**) lead to the saturated acid as a major product (Table 1, entry 2). Under the same conditions, catalyst based on ligand **4** showed very low activity (1% conversion) (Table 1, entry 3). Using ligand **1** or **2**, a mixture of products was obtained (Table 1, entry 4, 5). Total conversion for alcohol was obtained using ligand **3** under the same hydroformylation conditions (Table 1, entry 6).

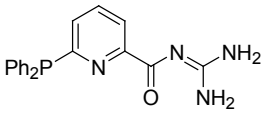
Table 1: Tandem decarboxylative hydroformylation-hydrogenation reaction of oct-2-enoic acid



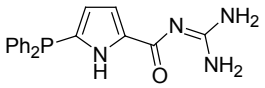
5 **6** **7** **8**

Entry[a]	Ligand	**6**[%]	**7** [%]	**8** [%]
1	PPh_3	99	0	0
2	PPh_3+ **9**	89	2	9
3	**4**	<1	0	0
4	**2**	29	15	55
5	**1**	0	88.5	11.5
6	**3**	0	0	>99

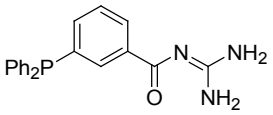
[a] Conditions: $[Rh(CO)_2acac]$/L/**5** = 1:10:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 29 h, 40°C.



1



2



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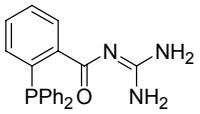

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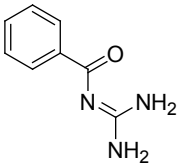


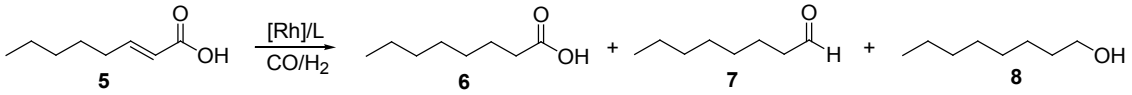
9

V Optimization of the Reaction Conditions

Influence of various reaction parameters on the decarboxylative hydroformylation of **5** catalyzed by $[Rh(CO)_2acac]$/**3** has been studied (Table 2). At 15 bar, 29 hours are necessary to get a total conversion with a complete selectivity for the alcohol **8** (Table 3, entry 1). Using higher pressure (20 bar or 30 bar CO/H_2, 40°C), complete conversion of **5** had occurred after 24 h but lower selectivity for the formation of **8** was observed, with the presence of 5% and 13% of saturated acid, respectively (Table 2, entries 2-3). Using

higher substrate concentration (0.6 M) affected neither the reactivity nor the selectivity (Table 3, entry 4). With higher substrate to metal ratio [$Rh(CO)_2acac$]/**3**/substrate = 1/10/200), we can get the alcohol after 29 hours with 94% of conversion and 6% of aldehyde (table 2, entry 5). Addition of small amounts of the strong acid CF_3SO_3H had a negative effect on the selectivity and we obtained the saturated acid as a major product (Table 2, compare entry 6). Then, we tested various ligand mixtures. Rhodium catalysts derived from ligand mixtures of **3** and **2** as well as **3** and **1**, respectively, did not give any improvement. However, the best catalyst for the title reaction was obtained employing a mixture of ligands **1** and **2**. This new catalyst system is significantly more active and allowed to reduce the catalyst loading to 0.5 mol% (Table 2, entries 7-10). Following the general procedure for α,β-unsaturated acid hydroformylation-hydrogenation the results summarised in table 2 were obtained.

Table 2: Influence of reaction conditions.

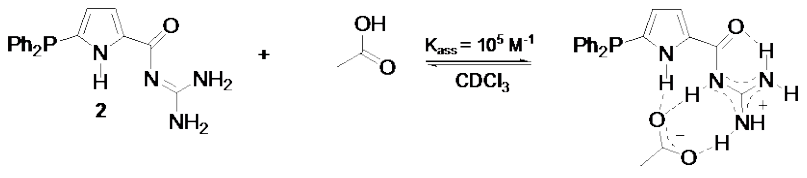


Entry[a]	Ligand	Pressure (CO/H_2)	[$Rh(CO)_2acac$]:**L:5**	C_0	**6** [%]	**7** [%]	**8** [%]
1 [b]	**3**	15	1:10:100	0.2	0	0	99
1	**3**	15	1:10:100	0.2	0	12	88
2	**3**	20	1:10:100	0.2	5	0	95
3	**3**	30	1:10:100	0.2	13	0	87
4	**3**	30	1:10:100	0.6	19	0	81
5[b]	**3**	15	1:10:200	0.2	0	6	94
6[c]	**3**	20	1:10:100:5	0.2	93	0	7
7	**3:2**	15	1:5:5:100	0.2	24	0	76
8	**3:1**	15	1:5:5:100	0.2	0	21	79
9	**2:1**	15	1:5:5:100	0.2	0	0	99
10 [d]	**2:1**	15	1:5:5:200	0.2	0	0	99

[a] Conditions: CH_2Cl_2 (2 ml), 24 h, 40°C . [b] t = 29h, [c] acid = CF_3SO_3H = 5 eq, [d] t = 26h.

VI Determination of association constant

By NMR study:



Ligand **2** was dissolved in $CDCl_3$ (TMS, 0.6 ml, c_0(**2**) = 0.011 M). Titration was carried out by addition of acetic acid (0-6 eq.) to the solution of **2** and recording the ^1H NMR (500 MHz, 40°C) spectra after each

addition. We have observed a shift of hydrogen signal of the pyrrole moiety of **2** (figure 1) (NH signals are broad due to exchange process).

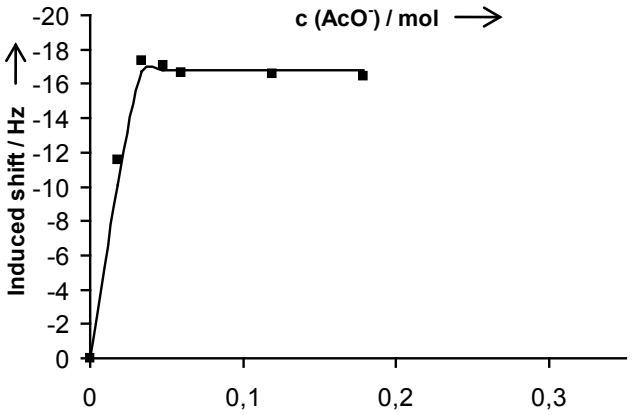
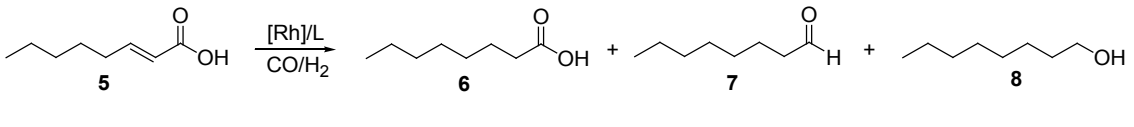
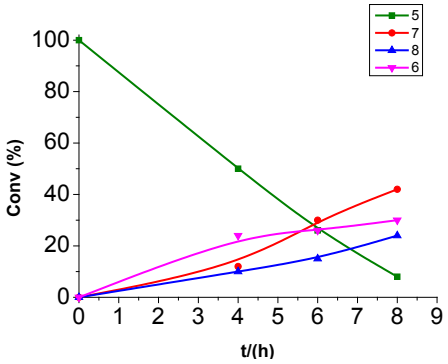


Fig. 1. Titration binding curve signal H3 of the ligand **2**.

We observe linear shift up to 1 eq. AcOH, and then no change for higher concentrations. This could be interpreted as quantitative proton transfer and association (Kass $>10^5$ M^{-1}).

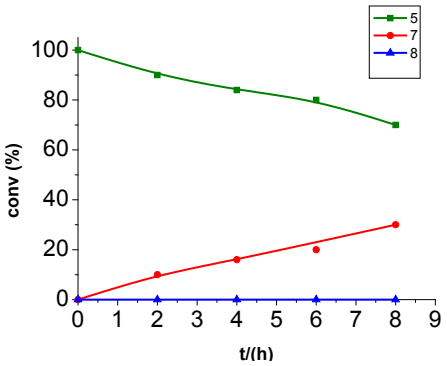
VII Kinetic study





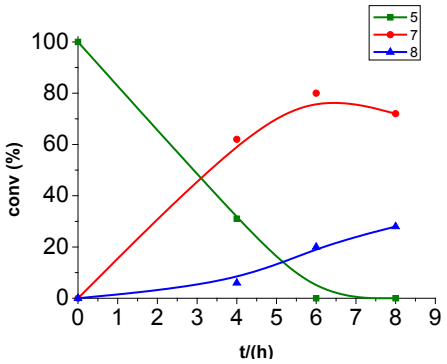
t (h)	5	6	7	8
0	100	0	0	0
4	50	12	10	24
6	26	30	15	26
8	8	42	24	30

Reaction progress followed by ^{1}H NMR. Conditions : [$Rh(CO)_2acac$]/**2**/substrate = 1:10:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 40°C.



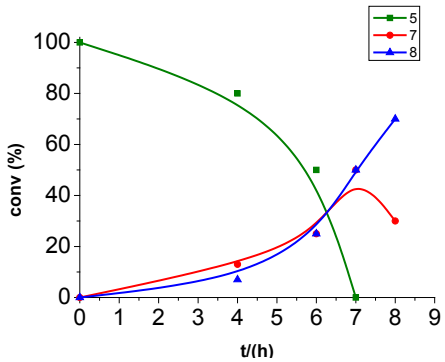
t (h)	5	7	8
0	100	0	0
2	90	10	0
4	84	16	0
6	80	20	0
8	70	30	0

Reaction progress followed by ^{1}H NMR. Conditions : [Rh(CO)$_2$acac]/**1**/substrate = 1:5:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 40°C.



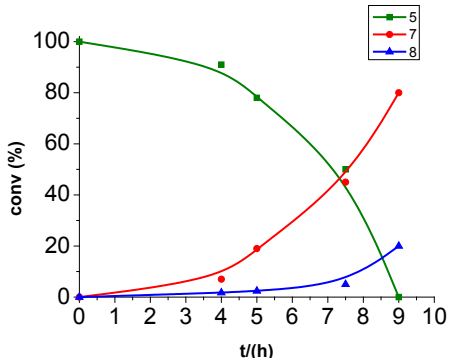
t (h)	5	7	8
0	100	0	0
4	31	62	6
6	0	80	20
8	0	72	28

Reaction progress followed by ^{1}H NMR. Conditions : [Rh(CO)$_2$acac]/**1:2**/substrate = 1:5:10:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 40°C.



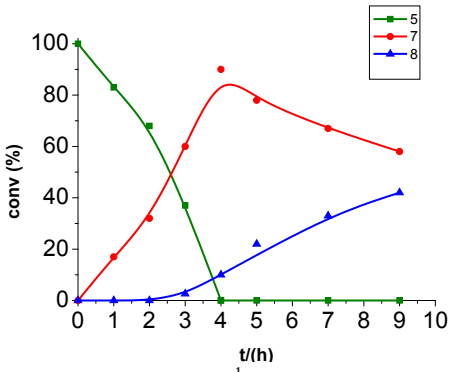
t (h)	5	7	8
0	100	0	0
4	80	13	7
6	50	25	25
7	0	50	50
8	0	30	70

Reaction progress followed by ^{1}H NMR. Conditions : [Rh(CO)$_2$acac]/**1:2**/substrate = 1:5:5:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 40°C.



t (h)	5	7	8
0	100	0	0
4	91	7	1,7
5	78	19	2,4
7,5	50	45	5
9	0	80	20

Reaction progress followed by ^{1}H NMR. Conditions : [Rh(CO)$_2$acac]/**2:1**/substrate = 1:5:10:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 40°C.

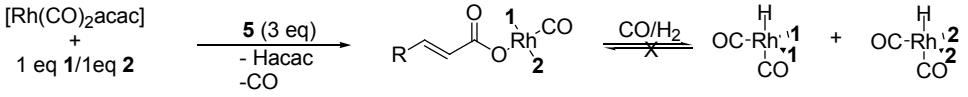


t	**5**	**7**	**8**
0	100	0	0
1	83	17	0
2	68	32	0
3	37	60	2,6
4	0	90	10
5		78	22
7		67	33
9		58	42

Reaction progress followed by ^{1}H NMR. Conditions : [Rh(CO)$_2$acac]/**3**/substrate = 1:10:100, c_0(substrate)= 0.2 M, CH_2Cl_2 (2 ml), 15 bar CO/H_2 (1:1), 40°C.

VIII NMR experiments

Rhodium complexes



[Rh(CO)$_2$acac] (7.6 mg, 2.9x10^{-3} mmol), lignad **2** (10 mg, 2.9x10^{-3} mmol) and ligand **1** (10.3 mg, 2.9x10^{-3} mmol) were suspended in $CDCl_3$ under argon. After addition of **5** (3 eq), dissolution of the compounds was observed and the mixture was analyzed using NMR spectroscopy. Only the Trans complex was observed by ^{31}P NMR and ^{1}H NMR.

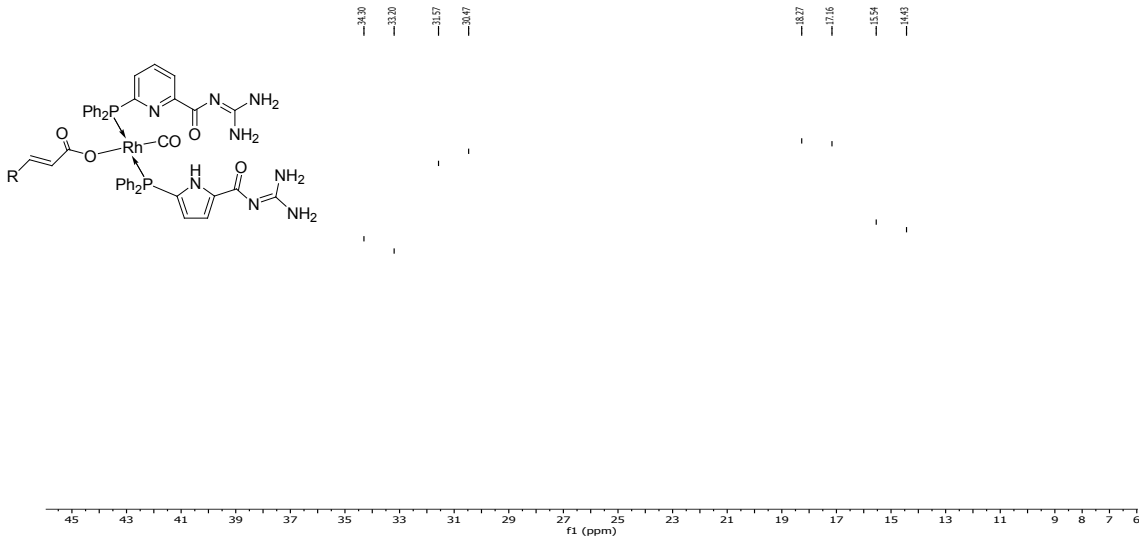


Fig. 2. ^{31}P NMR (161,984 MHz, $CDCl_3$) spectrum of Rh complexe with ligands **1** and **2**.

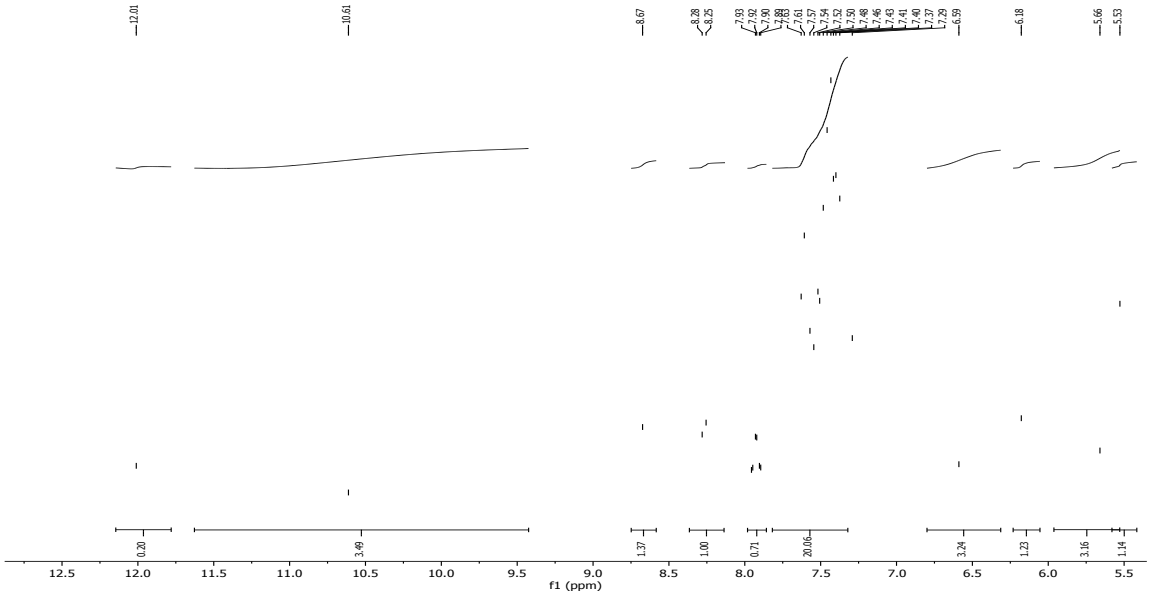


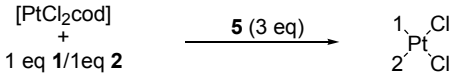
Fig. 3. ^{1}H NMR ($CDCl_3$) spectrum of Rh complexe with ligands **1** and **2**.

Then, a mixture of $[Rh(CO)_2acac]$ (7.6 mg, $2.9x10^{-3}$ mmol), lignad **2** (10 mg, $2.9x10^{-3}$ mmol) and ligand **1** (10.3 mg, $2.9x10^{-3}$ mmol) was suspended in $CDCl_3$, three equivalent of **5** was added to dissolve the mixture. The resulting solution was transferred to a screw-capped NMR tube by a syringe under CO atmosphere (15-40 bar) to take ^{31}P and ^{1}H NMR spectrum. No signals were observed in the rhodium-hydride spectrum (-9 to -10 ppm) and very broad signals were observed by ^{31}P NMR (due to a fast equilibrium).

Platinum complexes

$[PtCl_2COD]$ (11 mg, $2.9x10^{-3}$ mmol), lignad **2** (10mg, $2.9x10^{-3}$ mmol) and Ligand **2** (10.3mg, $2.9x10^{-3}$ mmol) were suspended in $CDCl_3$ under argon. After addition of **5** (3 eq.), dissolution of the compounds was observed and the mixture was analyzed using NMR spectroscopy.

Only the cis complex was observed by ^{31}P NMR: $\delta = 2.7$ and 3.4 ppm, $J_{P\text{-}P} = 19.6$ Hz, $J_{Pt\text{-}P} = 3820$ Hz.



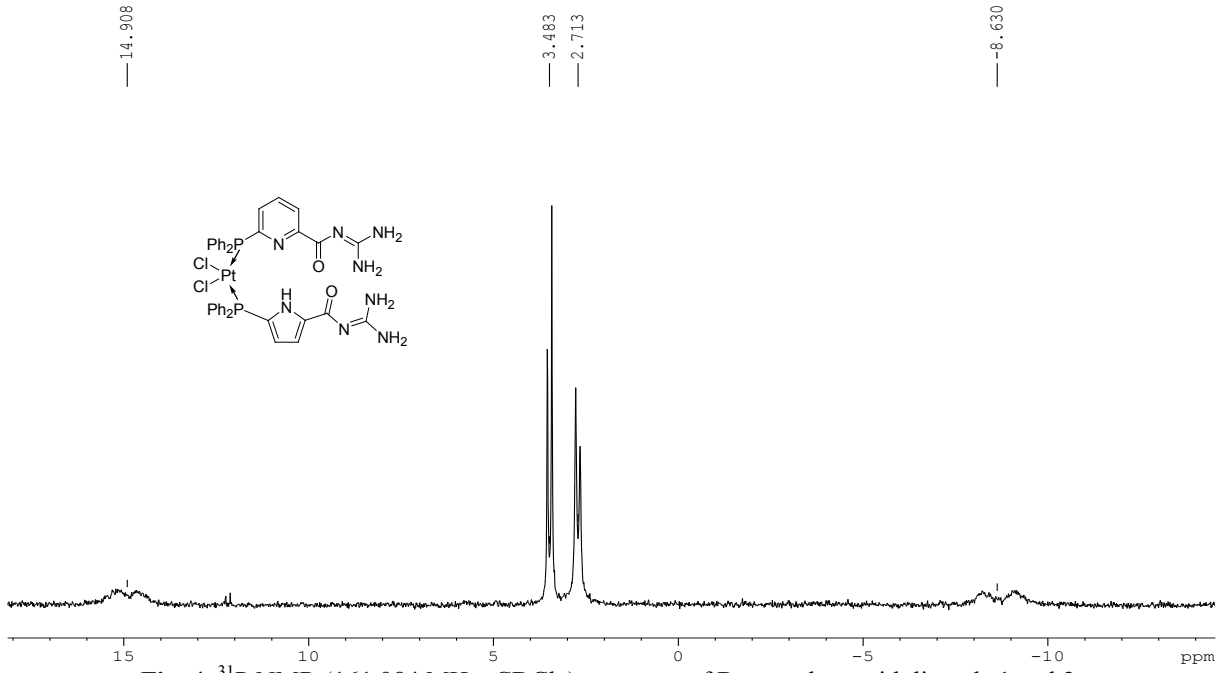
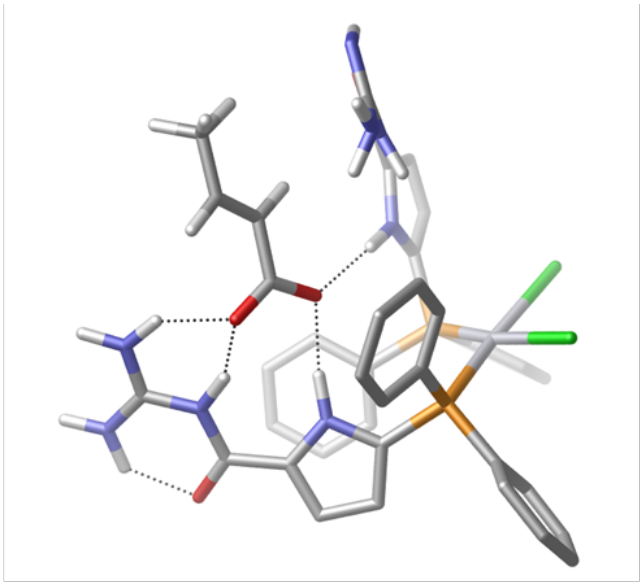


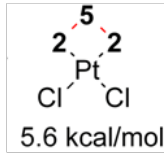
Fig. 4. ^{31}P NMR (161,984 MHz, $CDCl_3$) spectrum of **Pt** complexe with ligands **1** and **2**.

IX DFT-Calculations

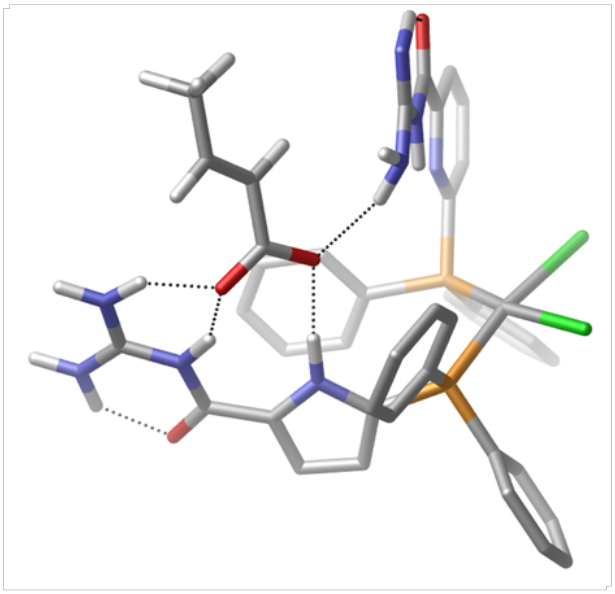
All structures are fully optimized by using Density Functional Theory (DFT) with the B3LYP[11] functional. All calculations were carried out with the all-electron 6-31G(d,p)[12] basis set for C, H, N, O, and P atoms and an Hay-Wadt core potential together with the associated [3s3p2d] basis set (LANL2DZ)[13] for Cl, Pt and Rh. Thermodynamic corrections are calculated at the same level of theory from a harmonic vibrational analysis. Transition states and minimum structures were identified by the presence or absence of one imaginary frequency. To account for solvent effects, the PCM model for CH_2Cl_2 was used (also for the geometry optimizations). All electronic structure calculations were carried out using the Gaussian09[1] suite of programs with the grid=ultrafine and the scf=tight option.

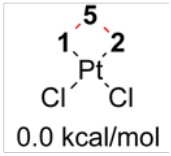
Optimizes structures of the platinum complexes



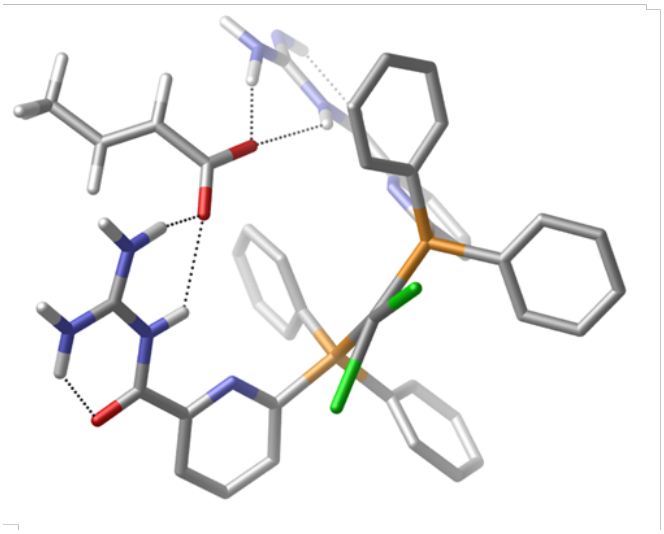


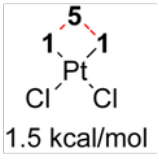
5.6 kcal/mol





0.0 kcal/mol





1.5 kcal/mol

Cartesian coordinates

[(**2**)(**1**)(**5**)$PtCl_2$]

P	-1.66645	0.85348	1.34917
P	-0.76728	-1.60206	-1.22597
C	-0.34427	0.14429	2.42314
C	0.08714	-2.47569	0.12483
C	1.58443	-0.77719	4.24253
C	-0.62626	-0.93895	3.27208
C	0.33260	-1.39199	4.17791
C	1.88616	0.27113	3.37148
H	-1.59819	-1.41795	3.24648
H	0.09716	-2.22315	4.83523
H	2.32415	-1.12352	4.95808
C	0.67745	-4.01106	1.66535
C	-0.35194	-3.61858	0.80203
N	1.35686	-2.17773	0.55194
C	1.72969	-3.11203	1.49784
H	-1.30036	-4.11144	0.65615
C	2.98961	-3.21440	2.23208
H	0.69314	-4.85874	2.33393
C	3.90602	0.22889	-0.33640
O	4.58875	-0.85047	-0.22843
O	2.64300	0.26690	-0.31108
N	4.06446	-2.45917	1.77504
O	3.08504	-3.96720	3.20948
H	4.02211	-1.90521	0.87762
C	5.29613	-2.40486	2.37360
N	6.19976	-1.61963	1.79560
H	5.91344	-1.11123	0.94567
H	7.14003	-1.56014	2.15494
C	4.64195	1.52079	-0.49590
H	4.04507	2.42091	-0.37642
C	5.94424	1.60630	-0.79678
H	6.50237	0.67934	-0.92492
N	5.55244	-3.09890	3.47617
H	6.45560	-3.05080	3.92260
H	4.80718	-3.70058	3.82199
C	6.69943	2.88439	-0.99570
H	7.52119	2.97013	-0.27311
H	7.16064	2.91166	-1.99076
H	6.05227	3.75977	-0.89353
H	1.88819	-1.33843	0.24087
C	-3.20326	0.56032	2.31581
C	-3.23603	0.80078	3.70270
C	-4.36447	0.09789	1.67869
C	-4.40900	0.59367	4.42761
H	-2.34644	1.13902	4.22360

C	-5.53348	-0.11915	2.41133
H	-4.35930	-0.07994	0.61008
C	-5.55964	0.13134	3.78347
H	-4.42052	0.78817	5.49565
H	-6.42295	-0.47976	1.90402
H	-6.47064	-0.03416	4.35073
C	-2.02688	-2.85446	-1.71736
C	-1.88161	-3.66393	-2.85096
C	-3.17574	-2.98635	-0.92000
C	-2.86703	-4.59977	-3.17419
H	-1.01203	-3.56430	-3.48986
C	-4.15174	-3.92939	-1.24137
H	-3.31160	-2.34721	-0.05311
C	-3.99959	-4.73774	-2.37081
H	-2.74721	-5.21737	-4.05923
H	-5.03395	-4.02428	-0.61549
H	-4.76384	-5.46558	-2.62628
C	0.53803	-1.57681	-2.51992
C	1.33378	-2.72271	-2.70576
C	0.76604	-0.44741	-3.31548
C	2.31988	-2.74219	-3.69096
H	1.18592	-3.60003	-2.08425
C	1.76064	-0.47041	-4.29568
H	0.16487	0.44168	-3.17722
C	2.53369	-1.61563	-4.48929
H	2.92273	-3.63452	-3.82947
H	1.92948	0.41486	-4.90018
H	3.30440	-1.63010	-5.25434
C	-1.30402	2.67702	1.45938
C	-1.96140	3.57349	2.30979
C	-1.58420	4.91681	2.27951
H	-2.75569	3.24064	2.96533
C	0.01317	4.36002	0.59445
C	-0.57970	5.32760	1.40581
H	-2.08057	5.63502	2.92416
H	-0.26045	6.36009	1.33193
Cl	-2.53810	0.13697	-3.32613
Cl	-3.48026	2.35370	-0.87595
Pt	-1.94087	0.37199	-0.90658
N	-0.33628	3.06800	0.62676
C	1.07418	4.74974	-0.40562
O	1.48279	5.90661	-0.49473
N	1.48758	3.70089	-1.17761
H	1.02906	2.81849	-0.96542
H	2.86357	0.74312	3.40102
C	0.93283	0.72798	2.46098
H	1.18840	1.53167	1.78262
C	2.40733	3.74560	-2.24949

N	2.52502	2.50322	-2.85022
H	2.47334	1.69934	-2.23007
N	3.03437	4.77650	-2.67714
H	2.74187	5.59463	-2.14407
H	3.31201	2.45904	-3.48419

[(**1**)$_2$(**5**)$PtCl_2$]

P	-1.94075	0.81586	-0.99625
P	-0.45135	-1.67372	1.13590
C	-3.65431	0.50775	-1.60950
C	-1.19597	2.16937	-1.97981
C	0.30259	-0.43714	2.25667
C	0.80886	-3.02980	1.35792
C	-0.50618	4.38107	2.41190
C	-6.28058	-0.02581	-2.45060
C	-4.35325	-0.60461	-1.10751
C	-4.27847	1.33481	-2.55345
C	-5.58476	1.06658	-2.96923
C	-5.66054	-0.86228	-1.51940
H	-3.87188	-1.28275	-0.40979
H	-3.75064	2.17854	-2.98082
H	-6.05314	1.71292	-3.70535
H	-6.18733	-1.72409	-1.12110
H	-7.29559	-0.23116	-2.77713
C	-0.06697	4.25430	-3.47470
C	-0.01066	1.96293	-2.69554
C	-1.79678	3.44240	-1.99340
C	-1.23889	4.47447	-2.74489
C	0.54753	3.00343	-3.44114
H	0.47428	0.99574	-2.67008
H	-2.69455	3.63597	-1.41548
H	-1.71458	5.45039	-2.75349
H	1.46820	2.83179	-3.99001
H	0.36889	5.06076	-4.05702
C	1.78520	1.24176	3.93858
C	0.33111	-0.66797	3.64636
C	1.04225	0.62111	1.71688
C	1.78382	1.45338	2.56072
C	1.05734	0.17801	4.48137
H	-0.19644	-1.51142	4.07869
H	1.07523	0.80103	0.64843
H	2.35364	2.26247	2.11878
H	1.06475	-0.00183	5.55217
H	2.35881	1.89454	4.59005
C	2.80868	-4.89023	1.61445
C	0.58314	-4.16362	2.14791
N	1.97597	-2.79878	0.74926
C	2.93745	-3.72080	0.85916

C	1.60772	-5.10083	2.28335
H	-0.36952	-4.31659	2.63936
C	4.19085	-3.51436	0.06326
H	1.46084	-5.98828	2.89015
H	3.62686	-5.59835	1.65643
C	3.37574	1.90798	-0.73520
O	3.33940	0.64246	-0.92206
O	2.37112	2.61040	-0.44955
O	-0.64132	5.07885	3.41891
N	0.49000	4.50987	1.49084
C	1.53908	5.47010	1.51812
H	0.47498	3.83660	0.72787
N	2.36917	5.32598	0.43191
H	2.48255	4.38102	0.04233
C	-2.00215	-2.30913	1.88815
C	-4.44739	-3.30364	2.84465
C	-2.67774	-1.65178	2.92724
C	-2.57721	-3.46066	1.31555
C	-3.78687	-3.95649	1.79954
C	-3.89396	-2.15072	3.40163
H	-2.26753	-0.75125	3.36744
H	-2.08151	-3.95887	0.48750
H	-4.21581	-4.84907	1.35461
H	-4.40514	-1.63376	4.20806
H	-5.39113	-3.68991	3.21756
N	4.25293	-2.31637	-0.62637
O	5.06743	-4.37386	0.01235
H	3.48406	-1.65866	-0.48397
C	5.21147	-1.97634	-1.56206
N	5.09350	-0.79517	-2.13200
H	3.21648	5.87045	0.51421
H	4.39088	-0.08275	-1.71820
N	1.69616	6.39333	2.39577
H	0.93553	6.34849	3.07144
C	4.69311	2.62710	-0.83720
H	4.63579	3.68221	-1.10114
C	5.87432	2.08174	-0.52202
H	5.89626	1.03571	-0.22014
N	6.17797	-2.84344	-1.85136
H	6.88854	-2.60821	-2.52718
H	6.19720	-3.72613	-1.34942
H	5.78500	-0.51219	-2.81185
C	7.18861	2.80354	-0.52255
H	7.08193	3.84251	-0.84744
H	7.63863	2.80074	0.47834
H	7.90872	2.30726	-1.18567
Pt	-0.86575	-1.24306	-1.09868
Cl	-0.16487	-3.60156	-1.58757

Cl	-1.32512	-1.06751	-3.55403
C	-1.50575	3.29179	2.09904
C	-2.57828	3.08108	2.96996
N	-1.33324	2.59307	0.97192
C	-3.50798	2.10126	2.63644
H	-2.66542	3.68448	3.86510
C	-2.23485	1.66189	0.64335
C	-3.34368	1.38009	1.45248
H	-4.36064	1.90642	3.27906
H	-4.07156	0.63393	1.16115

[(**2**)$_2$(**5**)PtCl$_2$]

P	1.35812	-0.87507	1.56438
P	1.15844	1.08526	-1.54544
C	0.66011	0.57623	2.45461
C	0.61713	2.47543	-0.50536
C	-0.19586	2.66626	4.11208
C	1.49020	1.68634	2.68102
C	1.06229	2.72467	3.50500
C	-1.03063	1.57327	3.87746
H	2.47692	1.73212	2.23009
H	1.71250	3.57628	3.67868
H	-0.52291	3.47278	4.76111
C	0.43590	4.49160	0.48877
C	1.28053	3.68860	-0.28931
N	-0.60579	2.53587	0.10920
C	-0.72892	3.76383	0.72464
H	2.25321	3.95118	-0.67497
C	-1.88076	4.26624	1.46903
H	0.61511	5.49904	0.83408
C	-3.43097	0.42039	-0.05362
O	-3.85488	1.61039	-0.24587
O	-2.21315	0.13969	0.16912
N	-3.07543	3.57552	1.29110
O	-1.79444	5.26722	2.18895
H	-3.16074	2.79876	0.57905
C	-4.25931	3.87374	1.90583
N	-5.30428	3.12097	1.56972
H	-5.15823	2.38692	0.86907
H	-6.22070	3.29924	1.95118
C	-4.42525	-0.69166	-0.08546
H	-4.07339	-1.65984	0.25437
C	-5.68411	-0.53823	-0.52074
H	-5.98425	0.45151	-0.86299
N	-4.34009	4.85693	2.79364
H	-5.21136	5.07701	3.25162
H	-3.49749	5.40863	2.94340
C	-6.71923	-1.61780	-0.58522

H	-7.57634	-1.36716	0.05297
H	-7.11435	-1.71390	-1.60405
H	-6.32580	-2.58978	-0.27671
H	-1.25611	1.72819	0.16108
C	2.80425	-1.23084	2.64659
C	2.60591	-1.38892	4.02954
C	4.10763	-1.25073	2.13319
C	3.69404	-1.59947	4.87551
H	1.60640	-1.34120	4.44970
C	5.19546	-1.44260	2.98796
H	4.27167	-1.12683	1.06982
C	4.99119	-1.62525	4.35607
H	3.52821	-1.73306	5.94020
H	6.20124	-1.45380	2.57912
H	5.83837	-1.78104	5.01737
C	2.55706	1.87310	-2.44290
C	2.40605	2.44454	-3.71214
C	3.80563	1.92599	-1.80322
C	3.49193	3.06858	-4.33038
H	1.45254	2.39831	-4.22603
C	4.88363	2.55997	-2.42056
H	3.93560	1.46260	-0.82950
C	4.72853	3.13157	-3.68627
H	3.36839	3.50227	-5.31816
H	5.84523	2.59757	-1.91772
H	5.57034	3.61747	-4.17040
C	-0.26246	0.89858	-2.70123
C	-0.95747	2.03941	-3.14086
C	-0.68207	-0.36693	-3.13597
C	-2.03864	1.91328	-4.01330
H	-0.66057	3.02679	-2.80239
C	-1.76853	-0.48827	-4.00443
H	-0.15070	-1.25208	-2.81012
C	-2.44697	0.64960	-4.44572
H	-2.56332	2.80260	-4.34883
H	-2.08137	-1.47546	-4.33113
H	-3.29128	0.55300	-5.12191
Cl	2.56571	-1.39352	-3.06465
Cl	2.72116	-3.25209	-0.20303
Pt	1.88481	-0.94128	-0.69608
C	-2.67070	-4.16734	0.58123
O	-3.36458	-5.05615	1.07677
N	-2.86424	-3.67815	-0.69957
H	-2.13300	-3.10058	-1.09449
H	-2.00886	1.52155	4.34612
C	-0.60759	0.52958	3.05032
H	-1.25969	-0.31982	2.88547
C	-3.91257	-4.04023	-1.57932

N	-3.89118	-3.25232	-2.72689
H	-3.77225	-2.25856	-2.56040
N	-4.76692	-4.97624	-1.41458
H	-4.54740	-5.48487	-0.55850
H	-4.69505	-3.44029	-3.31365
C	-1.53576	-3.57918	1.31115
C	-0.79364	-4.20923	2.30152
N	-0.93393	-2.37049	1.02232
C	0.29056	-3.36699	2.61695
H	-0.99759	-5.19367	2.69664
C	0.17698	-2.22742	1.82590
H	-1.38011	-1.58308	0.52998
H	1.09498	-3.57885	3.30449

TS_Hydrometallation_prolinear

Rh	-0.07488	-0.11674	0.01875
P	2.17717	-1.05496	-0.20585
P	-2.00573	-1.52651	0.17683
C	3.48164	0.04203	-0.98912
C	-3.55398	-0.64571	-0.28866
C	5.29716	1.83169	-2.05956
N	3.52865	1.29882	-0.51197
C	4.31388	-0.36272	-2.04730
C	5.22678	0.54358	-2.58414
C	4.41980	2.15992	-1.02582
H	4.25510	-1.37080	-2.43645
H	5.87907	0.24324	-3.39845
C	4.44837	3.55986	-0.45993
H	5.99134	2.57562	-2.43057
C	-5.59043	0.09055	-0.95545
C	-4.80596	-1.06083	-0.77322
N	-3.58043	0.71075	-0.18818
C	-4.80820	1.19226	-0.58830
H	-5.09611	-2.08231	-0.97342
C	-5.17468	2.60394	-0.66890
H	-6.60606	0.14369	-1.32129
C	-0.77138	3.00395	0.00010
O	-1.88195	2.60588	0.50172
O	-0.40292	4.20737	0.05702
O	5.32679	4.35921	-0.78293
N	3.42188	3.83015	0.40124
C	3.17080	5.06235	1.05636
H	2.81058	3.04444	0.60078
N	1.93365	5.05209	1.67676
H	1.15658	4.68853	1.11754
N	-4.17182	3.51278	-0.30435
O	-6.28964	2.97777	-1.05196
H	-3.24478	3.16595	0.06345
C	-4.23417	4.86822	-0.39639

N	-3.12481	5.54885	-0.09985
H	-2.22668	5.08239	0.08836
H	1.72298	5.95692	2.07946
H	-3.12977	6.55691	-0.14282
N	3.97371	6.05746	1.13072
H	4.85075	5.82234	0.66823
C	0.09353	2.03153	-0.75208
H	1.13091	2.33881	-0.84635
C	-0.45009	1.31359	-1.85023
H	-1.53175	1.35451	-1.96799
N	-5.36139	5.47339	-0.75778
H	-5.40061	6.47186	-0.89432
H	-6.14841	4.86906	-0.98553
C	0.31968	1.22184	-3.15823
H	-0.05492	0.41795	-3.79824
H	0.21080	2.16587	-3.70551
H	1.38495	1.05557	-2.97924
H	-2.76482	1.28494	0.11796
C	2.46168	-2.64686	-1.11420
C	3.61013	-3.43941	-0.93014
C	1.49998	-3.06389	-2.04457
C	3.78705	-4.61390	-1.66139
H	4.36699	-3.14038	-0.21175
C	1.67837	-4.23899	-2.78013
H	0.60146	-2.47097	-2.18160
C	2.82111	-5.01610	-2.58938
H	4.67823	-5.21548	-1.50660
H	0.91614	-4.54855	-3.48884
H	2.95908	-5.93303	-3.15515
C	-2.15533	-3.01298	-0.92527
C	-2.12416	-4.32400	-0.43019
C	-2.24349	-2.81889	-2.31477
C	-2.18520	-5.41478	-1.30291
H	-2.05781	-4.50112	0.63795
C	-2.31525	-3.90724	-3.18353
H	-2.26330	-1.81140	-2.72115
C	-2.28479	-5.21167	-2.67937
H	-2.16157	-6.42359	-0.90069
H	-2.39532	-3.73728	-4.25353
H	-2.33898	-6.05997	-3.35537
C	-2.39009	-2.21827	1.85172
C	-3.70054	-2.37125	2.33111
C	-1.31996	-2.62160	2.66650
C	-3.93241	-2.91264	3.59710
H	-4.54199	-2.06210	1.71998
C	-1.55434	-3.17543	3.92648
H	-0.29996	-2.49557	2.31616
C	-2.86144	-3.31890	4.39635

H	-4.95182	-3.01662	3.95763
H	-0.71445	-3.48309	4.54261
H	-3.04446	-3.73955	5.38086
C	2.92315	-1.42564	1.45497
C	2.61583	-2.64963	2.07708
C	3.68215	-0.48544	2.16858
C	3.06891	-2.92938	3.36696
H	2.03011	-3.39589	1.54884
C	4.13457	-0.76884	3.46004
H	3.91836	0.47359	1.72169
C	3.83240	-1.98990	4.06440
H	2.82644	-3.88452	3.82443
H	4.72594	-0.02885	3.99199
H	4.18533	-2.20718	5.06821
H	-0.31177	-0.28183	-1.60367
C	0.00905	0.34540	1.86147
O	0.06087	0.65076	2.97888

TS_Hydrometallation_probranched

Rh	0.19583	-0.71881	-1.01489
P	2.52796	-0.30617	-0.59880
P	-1.18696	-1.65517	0.77489
C	0.32504	-2.29276	-2.06453
C	3.11348	1.44144	-0.92828
C	-2.91972	-1.94016	0.22056
O	0.39216	-3.24866	-2.72298
C	3.95478	4.04937	-1.19437
N	2.50068	2.39774	-0.20575
C	4.13267	1.74532	-1.84330
C	4.54664	3.06988	-1.98410
C	2.92991	3.66259	-0.32451
H	4.60576	0.96042	-2.41965
H	5.33507	3.32569	-2.68540
C	2.32585	4.72322	0.56852
H	4.26097	5.08753	-1.23270
C	-4.98553	-2.62493	-0.41749
C	-3.77636	-3.05014	0.16191
N	-3.58568	-0.88112	-0.31504
C	-4.85437	-1.26504	-0.70819
H	-3.53858	-4.04559	0.50600
C	-5.82122	-0.35502	-1.28608
H	-5.86600	-3.22072	-0.61222
C	-1.65223	2.18928	-0.80041
O	-2.87659	1.81750	-0.77023
O	-1.20225	3.18966	-0.20107
H	0.03254	0.79897	-0.36730
O	2.98435	5.72929	0.84721
N	1.06313	4.46932	1.01345

C	0.31511	5.30093	1.89027
H	0.56630	3.67957	0.59584
N	-0.92468	4.75674	2.16229
H	-1.34670	4.19573	1.42277
N	-5.31275	0.93491	-1.54429
O	-6.99668	-0.64543	-1.52638
H	-4.30652	1.12260	-1.42738
C	-6.04967	2.06238	-1.73167
N	-5.38663	3.21569	-1.64396
H	-4.43503	3.19371	-1.27869
H	-1.54493	5.41430	2.61412
H	-5.85041	4.10100	-1.78122
N	0.71240	6.39291	2.43366
H	1.66987	6.58086	2.14136
C	-0.64604	1.41100	-1.64579
H	0.20829	2.03287	-1.90480
C	-1.02022	0.41393	-2.57597
H	-2.04532	0.05646	-2.51327
N	-7.34594	1.98713	-2.00172
H	-7.92355	2.81373	-2.02613
H	-7.75385	1.05433	-2.01721
C	-0.40677	0.36345	-3.96029
H	-0.45226	-0.63816	-4.39515
H	-0.95454	1.03534	-4.63736
H	0.63920	0.68383	-3.94816
H	-3.19874	0.07012	-0.37039
C	3.70320	-1.29553	-1.64482
C	4.87088	-1.88621	-1.13655
C	3.40779	-1.46188	-3.00927
C	5.71637	-2.62393	-1.96932
H	5.12491	-1.77437	-0.08843
C	4.26119	-2.18416	-3.84392
H	2.50200	-1.02427	-3.41798
C	5.41717	-2.77251	-3.32443
H	6.61123	-3.07992	-1.55532
H	4.01734	-2.29546	-4.89661
H	6.07637	-3.34512	-3.97035
C	-0.75235	-3.34482	1.39782
C	-0.35206	-3.57435	2.72363
C	-0.73348	-4.42380	0.49496
C	0.04573	-4.84905	3.13720
H	-0.35204	-2.76062	3.44026
C	-0.34796	-5.69743	0.91345
H	-1.02325	-4.27375	-0.53979
C	0.04562	-5.91482	2.23679
H	0.34969	-5.00571	4.16834
H	-0.35077	-6.51880	0.20268
H	0.35102	-6.90540	2.56058

C	-1.50810	-0.68774	2.32559
C	-2.52264	-1.04971	3.23029
C	-0.74797	0.46047	2.58373
C	-2.76233	-0.28096	4.36830
H	-3.12894	-1.93060	3.04037
C	-0.99313	1.23540	3.72150
H	0.02828	0.75380	1.88357
C	-1.99847	0.86489	4.61468
H	-3.54926	-0.57066	5.05893
H	-0.41255	2.13670	3.89175
H	-2.19332	1.46830	5.49668
C	3.21361	-0.57267	1.10590
C	2.70199	-1.64636	1.85050
C	4.22874	0.21556	1.67182
C	3.19504	-1.93290	3.12431
H	1.90979	-2.25783	1.42971
C	4.71117	-0.06146	2.95321
H	4.65017	1.04825	1.11902
C	4.19798	-1.13665	3.68185
H	2.78663	-2.77123	3.68113
H	5.49072	0.56357	3.37945
H	4.57514	-1.34991	4.67786

Model Substrate_Guanidin adduct

C	1.57389	-0.26888	-0.00004
O	0.69722	-1.14707	-0.00011
O	1.32271	1.02380	-0.00014
C	3.00410	-0.64587	-0.00002
H	3.18877	-1.71658	-0.00004
C	4.01208	0.23701	0.00005
H	3.76586	1.29720	0.00006
C	5.46435	-0.11884	0.00012
H	5.96548	0.30779	-0.87756
H	5.96539	0.30776	0.87785
H	5.62235	-1.20044	0.00011
H	0.29407	1.22488	-0.00014
N	-1.20255	1.65899	-0.00016
N	-2.03144	-0.48130	0.00010
C	-2.25803	0.90124	0.00006
N	-3.54634	1.30055	0.00025
H	-4.27410	0.59437	0.00017
H	-3.77000	2.28242	-0.00013
H	-1.43476	2.64891	-0.00017
H	-1.03284	-0.75466	0.00015
C	-2.96467	-1.47430	0.00010
H	-2.49490	-2.47027	0.00003
O	-4.18535	-1.33313	-0.00014

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