Supporting Information

Rh-Catalyzed Linear Hydroformylation of Styrene

Evert Boymans,[a] Michèle Janssen,[a] Christian Müller,[a,b] Martin Lutz,[c] and Dieter Vogt[a,]*

[a] Laboratory of Homogeneous Catalysis, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

[b] Freie Universität Berlin, Institute of Chemistry and Biochemistry, 14195 Berlin, Germany.

[c] Crystal and Structural Chemistry, Utrecht University, 3584 CH Utrecht, The Netherlands.

General Considerations

Chemicals were purchased from Aldrich, Acros, or Merck and used as received. Solvents were taken HPLC grade from an alumina filled, argon flushed column. Styrene was distilled over CaH_2 and degassed prior to use. All preparations were carried out under an argon atmosphere using standard Schlenk techniques.

NMR spectra were recorded on a Varian Mercury 400 spectrometer and chemical shifts are reported referenced to tetramethylsilane and H_3PO_4, respectively.

Maldi-TOF MS were recorded on an Applied Biosystems Voyager System 6020. GC analysis was performed on a Shimadzu GC-17A instrument equipped with an Ultra 2 column (25m x 0.2 mm). Carbon monoxide gas (99.997%) and synthesis gas (CO (99.997%)/H_2 (99.9996%)) were purchased from Praxair.

Synthesis of binaphthol-based diphosphites, L1-L3.

To a solution of the appropriate phenol (14 mmol) in 200 mL of toluene was subsequently added at -10°C PCl_3 (0.95 g, 6.99 mmol) and Et_3N, (6 mL, 43 mmol). The mixture was stirred for 1h. Binaphthol (1.00 g, 3.5 mmol) dissolved in 10 mL of THF was added to the mixture at -10°C. The mixture was stirred for 1h at r.t. The salts were filtered off over a short path of basic alumina (4 cm) and all volatiles were removed *in vacuo*. The ligands were purified by column chromatography (silica 60, heptane/EtOAc, 8/1).

1,1'-Binaphthyl-2,2'-bis(di(o-isopropyl)phosphite) (L1)

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, J=8.8 Hz, 2H), 7.91 (d, J=6.2 Hz, 2H), 7.62 (d, J=8.8 Hz, 2H), 7.43 (t, J=6.6 Hz, 2H), 7.32-7.26 (m, 4H), 7.19 (d, J=7.7 Hz, 4H), 7.02 (t, J=7.3 Hz, 4H), 6.84 (dt, J=8.1 Hz, 4H), 6.70 (d, J=8.1 Hz, 2H), 6.67 (d, J=8.1 Hz, 2H), 3.30 (sept, J=6.2 Hz, 4H), 0.97 (m, 24H)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.9, 148.0, 139.41, 139.37, 134.0, 130.8, 129.7, 127.9, 126.6, 126.29, 126.25, 126.21, 126.16, 126.10, 124.9, 123.8, 121.24, 121.20, 121.15, 120.07, 120.01, 119.95, 119.91, 119.86, 26.64, 26.59, 22.82, 22.78, 22.69

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 131.4 (s)

Maldi-TOF: 885.57 (M-1), 919.60 (M+O_2)

1,1'-Binaphthyl-2,2'-bis(di(o-tert-butylphenyl)phosphite) (L2)

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, J=8.42 Hz, 2H), 7.80 (d, J=8.79 Hz, 2H), 7.45 (d, J=9.15 Hz, 2H), 7.37-7.32 (m, 2H), 7.23-7.17 (m, 8H), 6.91-6.84 (m, 6H), 6.77-6.67 (m, 6H), 1.20 (s, 18H), 1.18 (s, 18H)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.1, 139.6, 134.0, 130.8, 129.8, 127.9, 126.9, 126.7, 126.1, 124.9, 122.9, 120.8, 120.0, 119.8, 119.6, 34.5, 29.9

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 129.4 (s)

Maldi-TOF: 941.37 (M-1), 965.40 (M+Na), 981.39 (M+K)

1,1'-Binaphthyl-2,2'-bis(di(o-[1,3]-dioxan-2-ylphenyl)phosphite) (L3)

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, J=8.79 Hz, 2H), 7.86 (d, J=8.06 Hz, 2H, 7.65 (d, J=9.15 Hz, 2H), 7.55 (dd, J=7.69 Hz, J=1.83 Hz, 2H), 7.52 (dd, J=7.69 Hz, J=1.83 Hz, 2H), 7.36 (dt, J=7.51 Hz, J=1.47 Hz, 2H), 7.29-7.16 (m, 4H), 7.05-6.94 (m, 6H), 6.89 (dt, J=7.69 Hz, J=1.83 Hz, 2H), 6.66 (d, J=8.06 Hz, 2H), 6.52 (d, J=8.05 Hz, 2H), 5.55 (s, 2H), 5.51 (s, 2H), 4.04-3.92 (m, 8H), 3.69-3.51 (m, 8H), 2.13-1.99 (m, 4H), 1.19 (d, J=12.45 Hz, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.81, 147.96, 133.91, 130.82, 129.86, 129.81, 129.71, 127.88, 127.26, 127.19, 126.80, 126.13, 125.06, 123.88, 123.82, 121.20, 119.70, 96.7, 67.2, 26.9, 25.7

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 130.3 (s)

Maldi-TOF: 1061.71 (M-1), 1085.73 (M+Na), 1101.73 (M+K)

2,2'-bis(dipyrrolylphosphinoxy)-1,1'-binaphthyl (L4)

Et_3N (6.5mL, 46.2 mmol) and 1,1'-bi(2-binaphthol) (3g, 10.5 mmol) were dissolved in 30 mL THF and added dropwise to a solution of chlorodipyrrolylphosphine (5.6 g, 30 mmol) at 0^{o}C. The reaction mixture was stirred overnight during which a white suspension formed. Salts were filtered off twice over a short path of basic alumina (4 cm) and all volatiles were evaporated. A white solid was obtained after recrystallization from EtOAc/hexane. Yield: 3 g (4.9 mmol, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, J=8.0 Hz, 4H), 7.45 (t, J=8.0 Hz, 2H), 7.33 (t, J=8.0 Hz, 2H), 7.24 (d, J=8.8 Hz, 2H), 7.17 (d, J=8.8 Hz, 2H), 6.50 (dt, J=8.8 Hz, J=2.0 Hz, 8H), 6.17 (t, J=2.0 Hz, 4H), 6.11 (t, J=2.4 Hz, 4H).

^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 149.2, 133.7, 130.9, 130.5, 128.2, 127.2, 125.9, 125.3, 122.5, 121.2, 119.2, 112.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): 104.98

Maldi-TOF: 609.09 (M-1, 100%), 633.12 (M+Na, 40%)

Spectroscopic data for [Rh(acac)(L)] complexes in $CDCl_3$

[Rh(acac)(L)]	δ(^{31}P) (ppm)	J_{Rh-P} (Hz)	δ(^{31}P) (ppm) Free ligand
L4	129.4	264.5	105.0
L5	127.0	270.5	107.9
L6	124.4	275.6	107.7

X-ray crystal structure determination

Single crystals of [Rh(acac)L4] and [Rh(acac)L6] were obtained and analyzed by single crystal x-ray diffraction. Crystals were obtained from the following procedure:
25 mg of [Rh(acac)$(CO)_2$] (0.097 mmol) was added to5 mL toluene in a Schlenk flask followed by the addition of 0.097 mmol ligand. When the ligand was added, CO bubbles were observed in the solution. To ensure quantitative formation of the desired complex, the reaction was stirred for 5 minutes more. Then toluene was evaporated and the specific solvents for crystallization were used. For [Rh(acac)L4] this was a 1:1 mixture of toluene and methanol, for [Rh(acac)L6] the solvent of choice was acetonitrile. The crystals were grown in approximately two weeks.

X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ at a temperature of 150(2) K. Intensity data were integrated with the Eval15[1] [Rh(L4)(acac)] or Eval14[2] software [Rh(L6)(acac)]. Absorption correction and scaling was performed with SADABS.[3] The structures were solved with Direct Methods using the program SHELXS-97[4] and refined with SHELXL-97[4] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions [Rh(L4)(acac)] or located in difference Fourier maps [Rh(L6)(acac)]. All hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[5]

[Rh(L4)(acac)]. $C_{41}H_{35}N_4O_4P_2Rh \cdot 1.5(C_7H_8)$, Fw = 950.78, pale yellow needle, 0.63 x 0.18 x 0.06 mm^3, orthorhombic, $Pca2_1$ (no. 29), a = 36.3887(6), b = 15.4752(2), c = 16.0031(2) Å, V = 9011.7(2) $Å^3$, Z = 8, D_x = 1.402 g/cm^3, μ = 0.50 mm^{-1}. 107970 Reflections were measured. 20596 Reflections were unique (R_{int} = 0.034), of which 18328 were observed [$I>2\sigma(I)$]. 1319 Parameters were refined. The toluene solvent molecules were refined with a disorder model. 688 Restraints were used for distances, angles and flatness of the toluene molecules and to restrain their displacement parameters approximating isotropic behavior. R1/wR2 [$I > 2\sigma(I)$]: 0.0278 / 0.0601. R1/wR2 [all refl.]: 0.0367 / 0.0638. S = 1.029. The structure was refined as an inversion twin. Flack parameter x = 0.483(11).[6] Residual electron density between -0.28 and 0.32 e/$Å^3$.

[Rh(L6)(acac)]. $C_{44}H_{51}N_4O_5P_2Rh$, Fw = 880.74, yellow block, 0.50 x 0.50 x 0.50 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 11.9548(3), b = 13.3000(3), c = 15.4312(4) Å, α = 84.487(2), β = 74.345(1), γ = 65.005(2) °, V = 2140.82(9) $Å^3$, Z = 2, D_x = 1.366 g/cm^3, μ = 0.52 mm^{-1}. 67184 Reflections were measured. 9867 Reflections were unique (R_{int} = 0.019), of which 8987 were observed [$I>2\sigma(I)$]. 518 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0224 / 0.0559. R1/wR2 [all refl.]: 0.0264 / 0.0579. S = 1.028. EXTI = 0.0051(2). Residual electron density between -0.38 and 0.50 e/$Å^3$.

CCDC 904120 [Rh(L4)(acac)] and 904121 [Rh(L6)(acac)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References:

1 A.M.M. Schreurs, X. Xian, L.M.J. Kroon-Batenburg, *J. Appl. Cryst.* (2010). **43**, 70-82.

2 Duisenberg, A.J.M., Kroon-Batenburg, L.M.J., Schreurs, A.M.M. (2003). *J. Appl. Cryst.* **36**, 220-229.

3 Sheldrick, G. M. (1999). SADABS: Area-Detector Absorption Correction, v2.10, Universität Göttingen, Germany.

4 G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

5 A.L. Spek, *Acta Cryst.* (2009). D**65**, 148-155.

6 H. D. Flack, Acta Cryst. 1983, A39, 876-881.

General procedure for the Rh-catalyzed hydroformylation of styrene.

$[Rh(acac)(CO)_2]$ (1 eq, 14.4 µmol, 3.7 mg) and the ligand (2 eq, 28.8 µmol) were dissolved in 15 mL toluene for the preformation of the catalyst (1 h, 10 bar syn gas, 80°C). Then styrene (2000 eq., 28.8 mmol) was diluted with toluene to 5 mL and added to the catalyst solution. Catalytic conversions were determined by gas chromatography (GC) on an ULTRA 2 column (25 m x 0.20 mm) using decane as an internal standard. Retention times were compared with authentic samples.

Additional experiments for optimizing reaction conditions:

Table 4. Hydroformylation of styrene with $HRhL2(CO)_2$.

Entry	P (CO/H_2)	T_{pref}	$T_{reaction}$	Conv. (%)	TOF (h^{-1})	Hydrogenation (%)	l/b	Selectivity to linear (%)
6	10	100	100	99.9	3619	2.8	2.7	73
7	10	120	120	99.9	7126	8	4.8	83
8	10	140	140	93	-	12	-	-
9	10	80	140	99.9	13874	14	7.1	88
10	5	80	140	95	5895	30	6.7	87
11	20	80	140	99.9	16933	8.6	5.3	84

Conditions: Rh:L:S = 1:2:2000, [Rh] = 0.9 mM, solvent = toluene, l/b ratio is determined by GC after gas-uptake ceased, turnover frequencies (TOF) were determined at 20% conversion and are given in (mol aldehyde)(mol Rh)$^{-1}h^{-1}$.

IR spectra were recorded on an Avatar 360 FT-IR instrument in ATR mode.

10 mg (0.036 mmol) $[Ni(cod)_2]$ and 1 equiv. (0.036 mmol) ligand were dissolved in 3 mL toluene. The slightly yellow solution was purged with CO for 30 s, during which the solution turned colorless. All volatiles were removed in vacuo and the remaining solid was used in the IR measurement in ATR mode.

High pressure FT-IR experiments were recorded on a Shimadzu FT-IR 8300 spectrometer.

$[Rh(acac)(CO)_2]$ (1 eq, 14.4 μmol M: 258 g/mol, 3.7 mg) and the ligand (2 eq, 28.8 μmol) were dissolved in 15 mL 2-methyltetrahydrofuran and subsequently filled into the autoclave. Then, the autoclave was pressurized to 10 bar syngas and the temperature was raised to 80^{o}C, after which the measurements started. Data were corrected by the solvent spectrum at similar conditions.

NMR of the catalyst resting state $HRhL(CO)_2$

In a typical experiment $[Rh(acac)(CO)_2]$ (10 mg, 38.8 μmol) and 1 equivalent of bidentate ligand (38.8 μmol) were dissolved in 2 mL toluene-*d8*. The solution was transferred to a stainless steel 10 mL autoclave and after preformation at 80°C and 10 bar syngas (CO/H_2, 1:1) for 1 hour, the syngas pressure was released and the solution was transferred to into an NMR tube. The Figure below shows the hydride region in the ^{1}H NMR (top) and the ^{31}P NMR spectra (bottom).

NMR of the catalyst resting state $HRhL(CO)_2$ (in the hydride region for ^1H NMR)

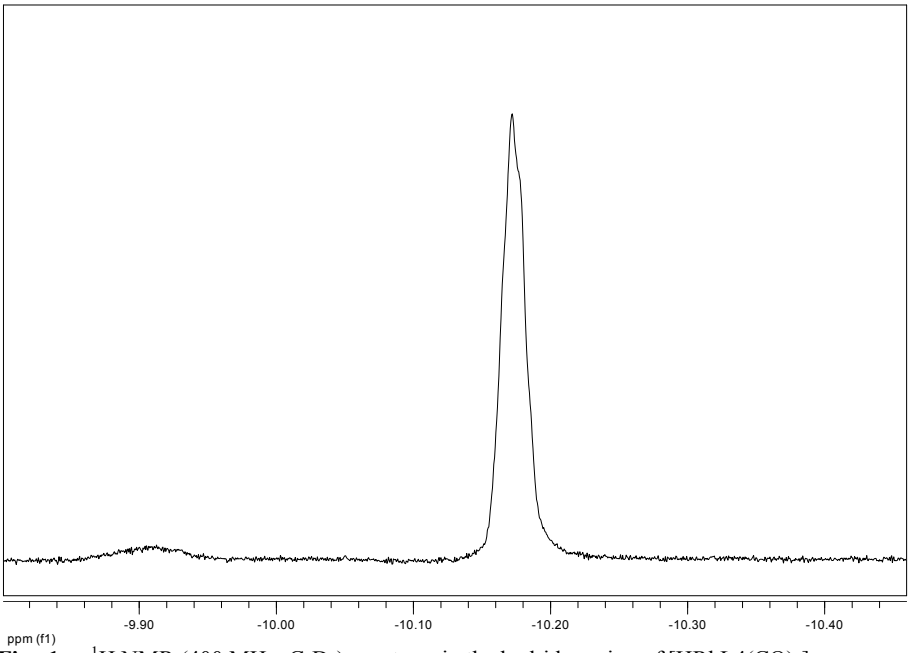

Fig. 1 ^1H NMR (400 MHz, C_7D_8) spectrum in the hydride region of $[HRhL4(CO)_2]$.

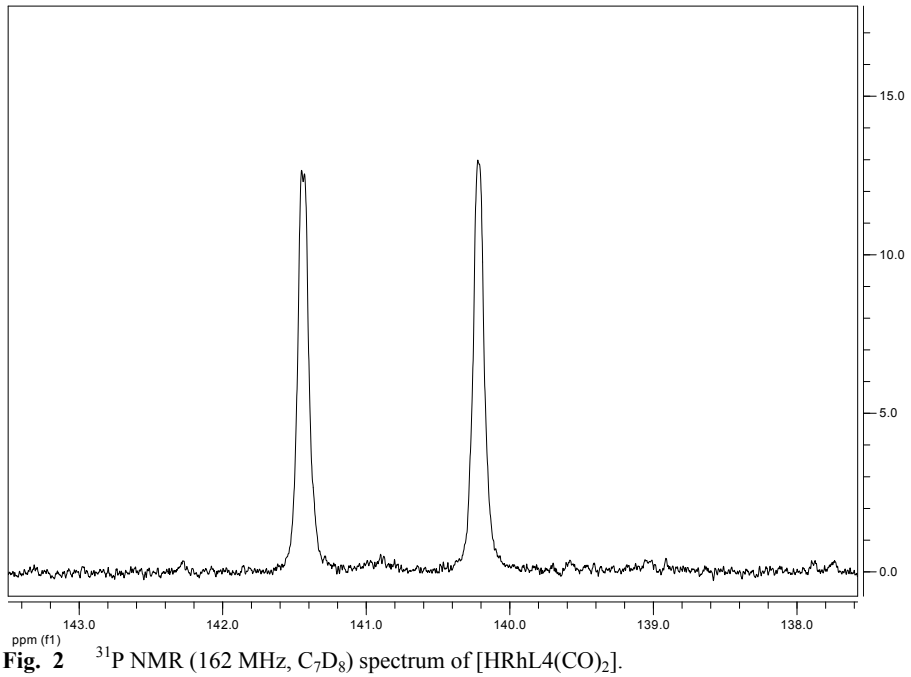

Fig. 2 ^{31}P NMR (162 MHz, C_7D_8) spectrum of $[HRhL4(CO)_2]$.

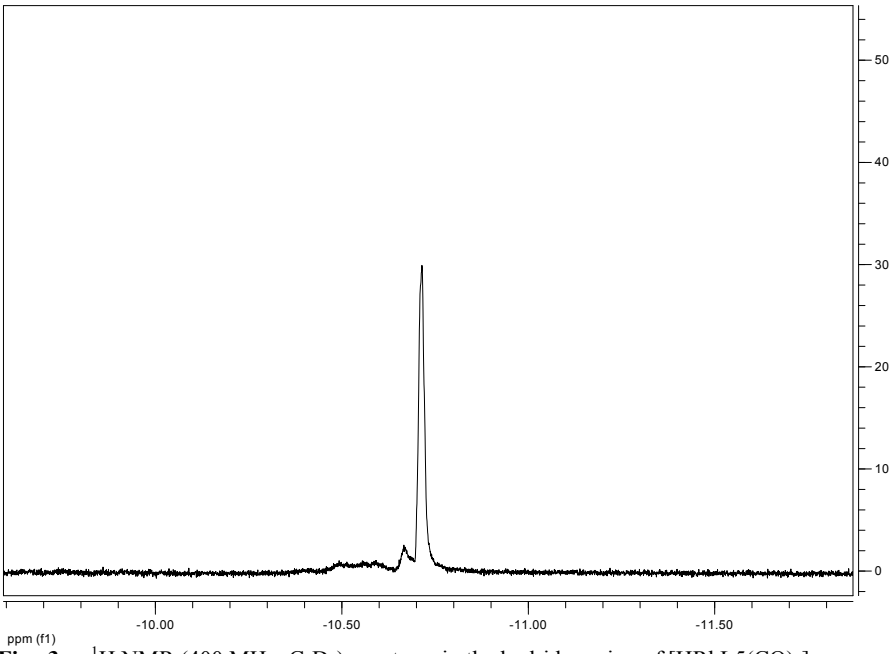

Fig. 3 ^{1}H NMR (400 MHz, C_7D_8) spectrum in the hydride region of $[HRhL5(CO)_2]$.

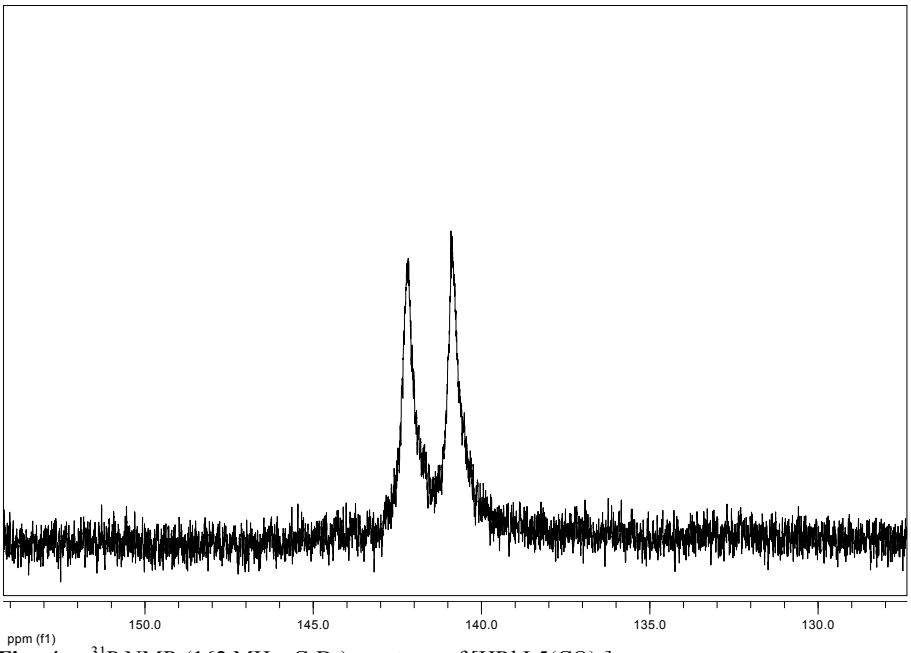

Fig. 4 ^{31}P NMR (162 MHz, C_7D_8) spectrum of $[HRhL5(CO)_2]$.

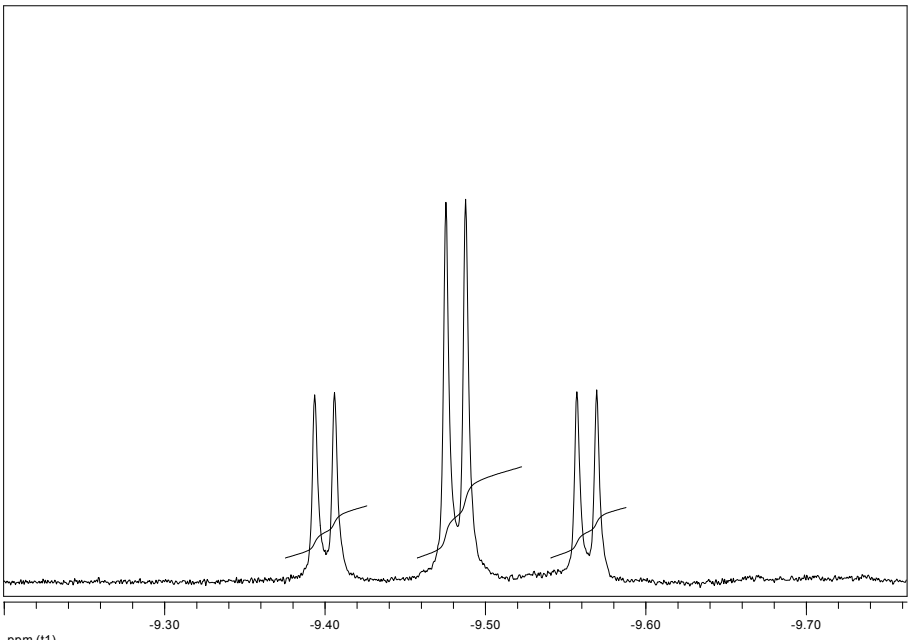

Fig. 5 ^{1}H NMR (400 MHz, C_7D_8) spectrum in the hydride region of [HRhL6(CO)$_2$].

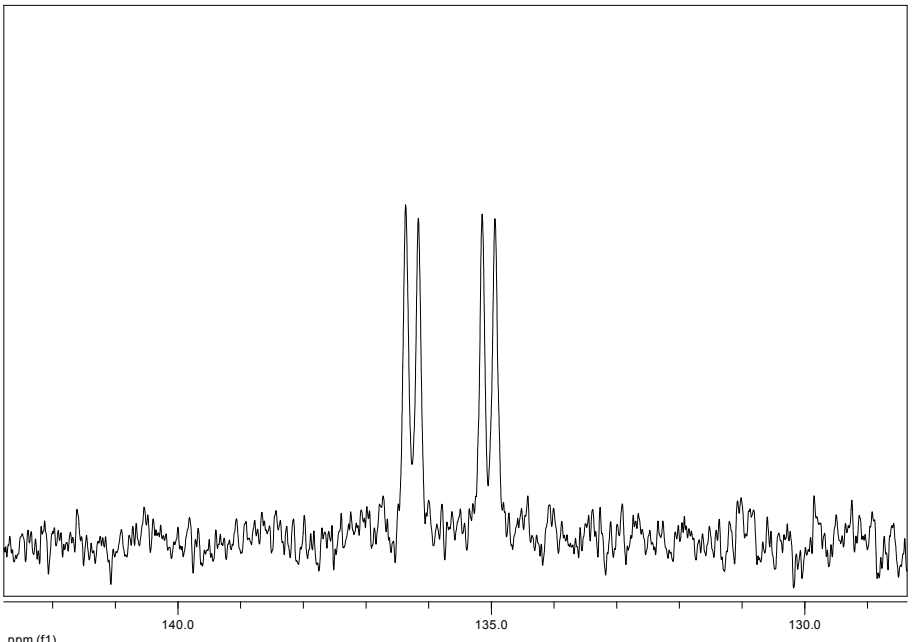

Fig. 6 ^{31}P NMR (162 MHz, C_7D_8) spectrum of [HRhL6(CO)$_2$].