Activation of H_2 by a highly distorted Rh^{II} Complex with a new C_3-symmetric tripodal tetraphosphine ligand

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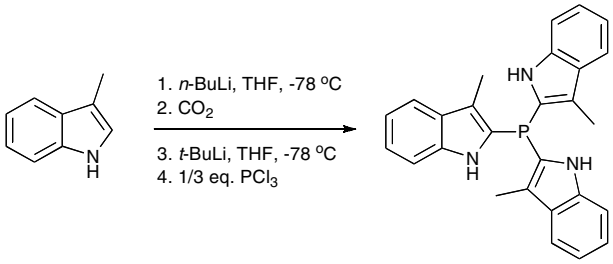
Supplementary Material

I General Experimental Methods

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. All reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and diethyl ether were distilled from sodium benzophenone ketyl; CH_2Cl_2, isopropanol and methanol were distilled from CaH_2, and toluene was distilled from sodium under nitrogen. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. NMR spectra (^1H, ^{31}P and ^{13}C) were measured on a Varian INOVA 500 MHz. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. Elemental analyses were carried out at Kolbe Mikroanalytisches Laboratorium in Mülheim an der Ruhr. Cyclic voltammograms were recorded on an Eco Chemie Autolab PGSTAT10 potentiostat. Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). The spectra were simulated by iteration of the anisotropic g values, (super)hyperfine coupling constants and line widths. We thank Prof. F. Neese for a copy of his EPR simulation program.

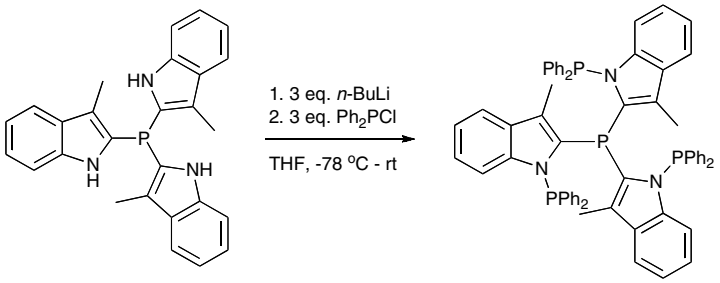
II Synthetic Procedures

Tris-2-(3-methylindolyl)phosphine.[1]



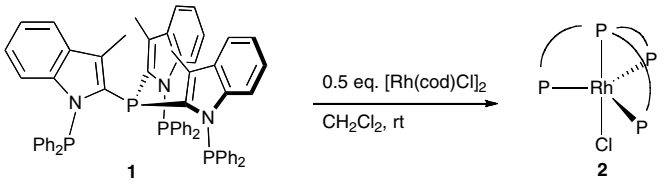
To a solution of 3-methylindole (9.88 g, 75.3 mmol) in THF (200 mL) was added dropwise *n*-BuLi (2.5 M in hexanes, 31.6 mL, 79.1 mmol) at -78 °C. The resulting suspension was stirred at -78 °C for 20 min. Carbon dioxide was bubbled through the suspension for 10 min to give a clear solution, which was allowed to warm to room temperature. The solvent was removed *in vacuo*. The resulting white residue was dissolved in THF (200 mL) and cooled to -78 °C. To this solution, *t*-BuLi (1.6 M in pentanes, 49.4 mL, 79.1 mmol) was added and the resulting orange solution was stirred at -78 °C for 1 h. Phosphorus trichloride (2.19 mL, 25.1 mmol) was added and the reaction mixture was stirred for 16 h allowing to warm to room temperature. The resulting yellow solution was washed with 200 mL sat. aq. NH_4Cl. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude, yellow solid was triturated with MeOH to yield the product as a colourless powder. Yield: 4.29 g (40 %). Spectral and analytical data were identical to literature values.

Tris(*N*-3-methyl-2-indolylphosphino)phosphine (1).



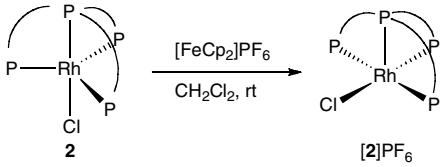
To a solution of tris-2-(3-methylindolyl)phosphine (1.5 g, 3.56 mmol) in THF (50 mL) was added *n*-BuLi (2.5 M in hexanes, 4.28 mL, 10.7 mmol) at -78 °C. The resulting solution was stirred for 1 h and chlorodiphenylphosphine (1.92 mL, 10.7 mmol) was added. The reaction mixture was stirred for 16 h allowing to warm slowly to room temperature. The resulting white suspension was concentrated *in vacuo* and redissolved in $CHCl_3$ (40 mL). The suspension was filtered through a pad of basic alumina, which was rinsed with $CHCl_3$ (2 x 20 mL). The solvent was removed under reduced pressure and the resulting white solid was washed with Et_2O (3 x 10 mL) and dried *in vacuo*. Yield: 2.00 g (58 %). Mp = 267 °C dec. ^{1}H-NMR (500 MHz; $CDCl_3$, 298 K): δ 7.43 (d, J = 7.9 Hz, 3H), 7.24-7.10 (m, 30H), 7.02 (t, J = 7.4 Hz, 3H), 6.83 (t, J = 7.7 Hz, 3H), 6.71 (d, J = 8.3 Hz, 3H), 2.05 (s, 9H). ^{13}C-NMR (126 MHz; $CDCl_3$, 298 K): δ 140.63 (d, J = 10.7 Hz), 136.37-136.22 (m), 136.08 (d, J = 16.8 Hz), 133.78-133.70 (m), 131.93 (t, J = 21.1 Hz), 128.81 (s), 128.31 (t, J = 5.5 Hz), 124.27-124.24 (m), 122.43 (s), 120.04 (s), 118.88 (s), 114.46 (s), 9.81 (s). ^{31}P-NMR (202 MHz; $CDCl_3$, 298 K): δ 37.27 (d, J = 159.2 Hz, 3P), -75.07 (q, J = 159.3 Hz, 1P). Anal. Calcd for the trisphosphine oxide $C_{63}H_{51}N_3O_3P_4$ (%): C 74.04, H 5.03, N 4.11; found: C 74.20, H 5.17, N 4.12. HRMS (FAB) calcd for $[M + H]^+$ $C_{63}H_{52}N_3P_4$, 974.3112; found, 974.3108.

[Rh(1)Cl] (2).



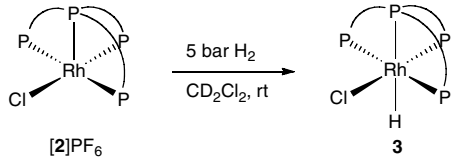
Tetraphosphine **1** (400 mg, 0.41 mmol) and $[Rh(cod)Cl]_2$ (101 mg, 0.21 mmol) are stirred in CH_2Cl_2 (20 mL) for 0.5 h at room temperature. The resulting deep red solution was concentrated under reduced pressure and hexanes (40 mL) were added to precipitate a burgundy-colored solid. The solid was collected by filtration and washed with hexanes (2 x 10 mL). Crystals suitable for X-ray diffraction were obtained from slow diffusion of hexanes into a dichloromethane solution. Yield: 378 mg (83 %). Mp = 303 °C dec. ^{1}H-NMR (500 MHz; $CDCl_3$; 298 K): δ 7.55 (d, J = 8.0 Hz, 3H), 7.05-7.02 (m, 15H), 6.82-6.77 (m, 21H), 6.42 (d, J = 8.5 Hz, 3H), 2.55 (s, 9H). ^{13}C-NMR (126 MHz; $CDCl_3$; 298 K): δ 139.71-139.59 (m), 136.78-136.66 (m), 136.08 (d, J = 8.7 Hz), 129.80-129.74 (m), 128.10 (d, J = 4.9 Hz), 124.14 (s), 122.30-122.25 (m), 121.02 (s), 120.32 (s), 116.25 (s), 10.53 (s). ^{31}P-NMR (202 MHz; $CDCl_3$; 298 K): δ 73.95 (dd, J_{PRh} = 158.8 Hz, J_{PP} = 26.9 Hz, 3P), 43.49 (dq, J_{PRh} = 108.2 Hz, J_{PP} = 26.8 Hz, 1P). Anal. Calcd for the CH_2Cl_2 adduct $C_{64}H_{53}Cl_3N_3P_4Rh$ (%): C 64.20, H 4.46, N 3.51; found: C 64.22, H 4.51, N 3.48. HRMS (FAB) calcd for $[M]^+$ $C_{63}H_{51}ClN_3P_4Rh$, 1111.1777; found, 1111.1771.

[Rh(1)Cl]PF_6 ([2]PF_6).



Complex **2** (100 mg, 0.09 mmol) and ferrocenium hexafluorophosphate (30 mg, 0.09 mmol) are stirred in CH_2Cl_2 (5 mL) for 1 h at room temperature. The resulting deep purple solution was concentrated under reduced pressure. The dark purple residue was washed with Et_2O (3 x 10 mL) and dried *in vacuo*. Crystals suitable for X-ray diffraction were obtained from slow diffusion of hexanes into a dichloromethane solution. Yield: 54 mg (48 %). Mp = 220 °C dec. Anal. Calcd for the CH_2Cl_2 adduct $C_{64}H_{53}Cl_3F_6N_3P_5Rh$ (%): C 57.27, H 3.98, N 3.13; found: C 57.88, H 4.06, N 3.24. HRMS (FAB) calcd for $[M - PF_6]^+$ $C_{63}H_{51}ClN_3P_4Rh$, 1111.1777; found, 1111.1777.

[Rh(1)(H)Cl]PF_6 (3).



Complex [**2**][PF_6] (13 mg, 0.01 mmol) was charged to a 5 mm high-pressure NMR-tube and dissolved in CD_2Cl_2. The tube was put under 5 bar of H_2 and the reaction followed by NMR spectroscopy. Quantitative conversion to complex **8** was observed after 24 h. By comparison with an authentic sample (*vide infra*, different anion), this was characterized as [Rh^{III}(**2**)(H)Cl]PF_6. **[Rh(1)(H)Cl]OTf** was prepared by reaction of **2** (100 mg, 0.09 mmol) with one equiv HOTf (13.5 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) for 2 h. The solvent was evaporated *in vacuo*, and the residue was washed with pentanes. After drying *in vacuo*, a dark-brown solid was obtained. Yield: 88 mg (77 %). ^{1}H-NMR (500 MHz; CD_2Cl_2, 298 K): δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.57 (q, *J* = 6.9 Hz, 4H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.19 (m, 6H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.95 (q, *J* = 6.2 Hz, 4H), 6.91-6.81 (m, 12H), 6.46 (d, *J* = 8.5 Hz, 2H), 6.12 (d, *J* = 8.5 Hz, 1H), 2.75 (d, *J* = 1.6 Hz, 6H), 2.65 (d, *J* = 0.7 Hz, 3H), -6.52 (ddq, *J* = 174.8, 14.6, 7.4 Hz, 1H). ^{13}C-NMR (126 MHz; CD_2Cl_2): δ 140.75 (d, *J* = 13.1 Hz), 140.19 (d, *J* = 6.2 Hz), 136.07 (d, *J* = 11.3 Hz), 135.88 (d, *J* = 9.7 Hz), 132.60 (s), 132.40 (t, *J* = 6.2 Hz), 131.95 (s), 131.01 (d, *J* = 2.5 Hz), 130.69 (t, *J* = 6.6 Hz), 130.61 (s), 130.52 (s), 129.58 (s), 129.58-129.39 (m), 129.19 (s), 129.15 (s), 129.10 (s), 129.07 (d, *J* = 3.8 Hz), 128.84 (s), 128.55 (d, *J* = 2.0 Hz), 127.26 (s), 126.49 (s), 125.47-125.44 (m), 125.27 (s), 123.70 (s), 123.37 (s), 122.19 (s), 122.02 (s), 116.88 (s), 115.53 (s), 11.36 (d, *J* = 19.9 Hz). ^{31}P-NMR (202 MHz; CD_2Cl_2, 298 K): δ 77.13 (dt, *J* = 108.1, 15.9 Hz, 2P), 67.15 (dt, *J* = 91.1, 24.1 Hz, 1P), 26.44 (dq, *J* = 91.6, 19.1 Hz, 1P).

[Rh(1)(D)Cl]PF_6 (3-D). The deuterido complex was prepared according to the procedure described above for hydrido complex **3**, using D_2 instead of H_2. ^{1}H-NMR (500 MHz; CD_2Cl_2, 298 K): δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.71-7.70 (m, 1H), 7.57 (q, *J* = 7.0 Hz, 4H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.23-7.15 (m, 6H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.95 (q, *J* = 6.4 Hz, 4H), 6.91-6.81 (m, 12H), 6.46 (d, *J* = 8.5 Hz, 2H), 6.12 (d, *J* = 8.5 Hz, 1H), 2.74 (d, *J* = 1.4 Hz, 6H), 2.64 (s, 3H). ^{13}C-NMR (126 MHz; CD_2Cl_2, 298 K): δ 140.75-140.64 (m), 135.87-135.79

(m), 132.56 (s), 132.36 (t, J = 6.5 Hz), 131.91 (s), 130.96 (s), 130.65 (t, J = 6.6 Hz), 130.52 (d, J = 11.7 Hz), 129.52 (d, J = 4.5 Hz), 129.43 (t, J = 5.3 Hz), 129.11 (t, J = 5.7 Hz), 129.04 (s), 127.22 (s), 126.46 (s), 125.30 (d, J = 24.9 Hz), 123.66 (s), 123.33 (s), 122.15 (s), 121.98 (s), 116.84 (s), 115.49 (s), 11.36 (d, J = 20.3 Hz). ^{31}P-NMR (202 MHz; CD_2Cl_2): δ 77.24 (dt, J = 107.2, 16.1 Hz, 2P), 67.42-66.62 (m, 1P), 26.44 (dq, J = 91.6, 19.2 Hz, 1P).

III Cyclic Voltammogram of complex 2

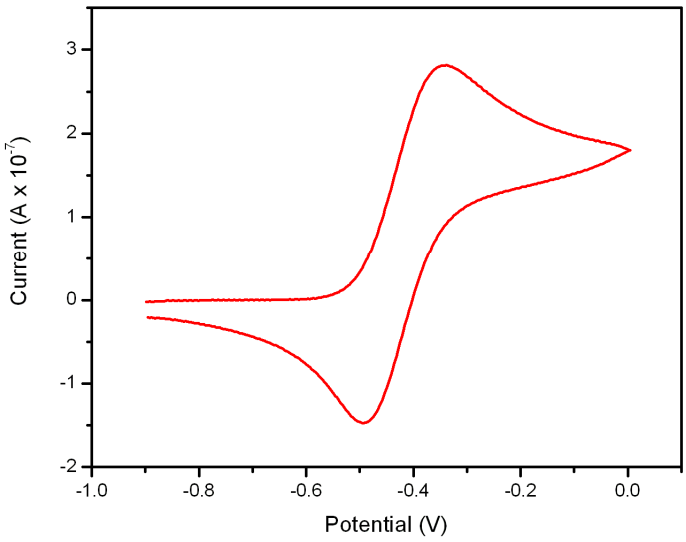


Fig. S1. Cyclic voltammogram of complex **2** [RhCl(**1**)] in CH_2Cl_2 *vs*. Fc/Fc^+ using 0.1 mM nBu$_4$PF$_6$. (v = 0.1 V s^{-1}).

IV Crystallographic Details

For **2**: $C_{63}H_{51}ClN_3P_4Rh$, CH_2Cl_2, Fw = 1197.23, red block, 0.10 x 0.14 x 0.27 mm^3, T = 110 K, Triclinic, *P*-1 (No: 2), a = 11.8086(5), b = 14.6492(4), c = 17.0348(5)Å, α = 83.286(2), β = 87.505(2), γ = 71.163(2)°, V = 2769.79(17)Å^3, Z = 2, Dx = 1.436 g/cm^3, R = 0.0386, wR2 = 0.0767, S = 1.01, ρ(min) = -0.68 e/Å^3, ρ(max) = 0.76 e/Å^3. CCDC 735997.

For [**2**]PF_6: $C_{63}H_{51}ClN_3P_4Rh$, F_6P, 3(CH_2Cl_2), Fw = 1512.06, dark brown block, 0.26 x 0.31 x 0.32 mm^3, T = 110 K, Triclinic, *P*-1 (No: 2), a = 13.2110(6), b = 15.3608(8), c = 17.6791(10)Å, α = 93.963(2), β = 110.874(2), γ = 101.654(3)°, V = 3243.8(3)Å^3, Z = 2, Dx = 1.548 g/cm^3, R = 0.0309, wR2 = 0.0759, S = 1.04, ρ(min) = -0.94 e/Å^3, ρ(max) = 1.04 e/Å^3, CCDC 735998.

V DFT Calculations and Spin Density Plots

The geometry optimizations were carried out with the Turbomole program[2a] coupled to the PQS Baker optimizer[3] Geometries were fully optimized as minima at the bp86[4] level using the Turbomole SV(P) basisset[2c,d] on all atoms EPR parameters[5] were calculated with the ADF[6] program system using the bp86[4] functional with the ZORA/TZP basis set supplied with the program (all electron, core double zeta, valence triple zeta polarized basis set on all atoms), using the coordinates from the

structures optimized in Turbomole as input. Orbital and spin density plots were generated with Molden.[7].

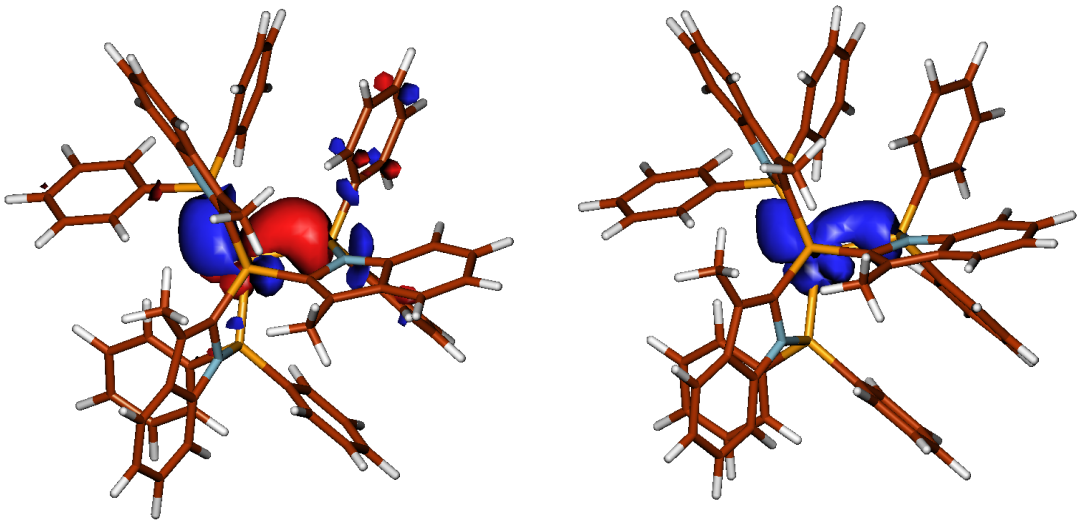


Fig. S2. SOMO (left) and spin density (right) of complex $\mathbf{2}^{+}$ (view along the Cl-Rh-P_1 axis)

Table S1. Experimental and DFT calculated *g*-values, hyperfine coupling constants, *A* [MHz], and spin populations ρ of [**2**]PF_6**.** DFT values are given in italics. The experimental values are least-square "best fit" values obtained by simulation of the experimental X-band EPR spectrum (see Fig. 2).

g-values	Exp. *comp.*	$g_{11} = 2.092$ $g_{11} = 2.085$	$g_{22} = 2.067$ $g_{22} = 2.064$	$g_{33} = 2.005$ $g_{33} = 1.996$
A-tensors	ρ	A_{11}	A_{22}	A_{33}
^{31}P_2 exp. comp.	- *24%*	585 *493*	580 *494*	740 *646*
^{31}P_3 exp. comp.	- *6%*	70 *67*	90 *68*	<70 (NR) *99*
^{31}P_4 exp. comp.	- *3%*	<30 (NR) *23*	59 *27*	<70 (NR) *46*
^{31}P_1 exp. comp.	- *0.4%*	NR ~*9*	NR ~*8*	NR ~*4*
^{103}Rh exp. comp.	– *51%*	20 (NR) *23*	9 (NR) *9*	−40 (NR) *−37*

NR = not resolved, atom labelling of the P-atoms as in Fig. 1

VI NMR spectra of New Complexes and Ligands

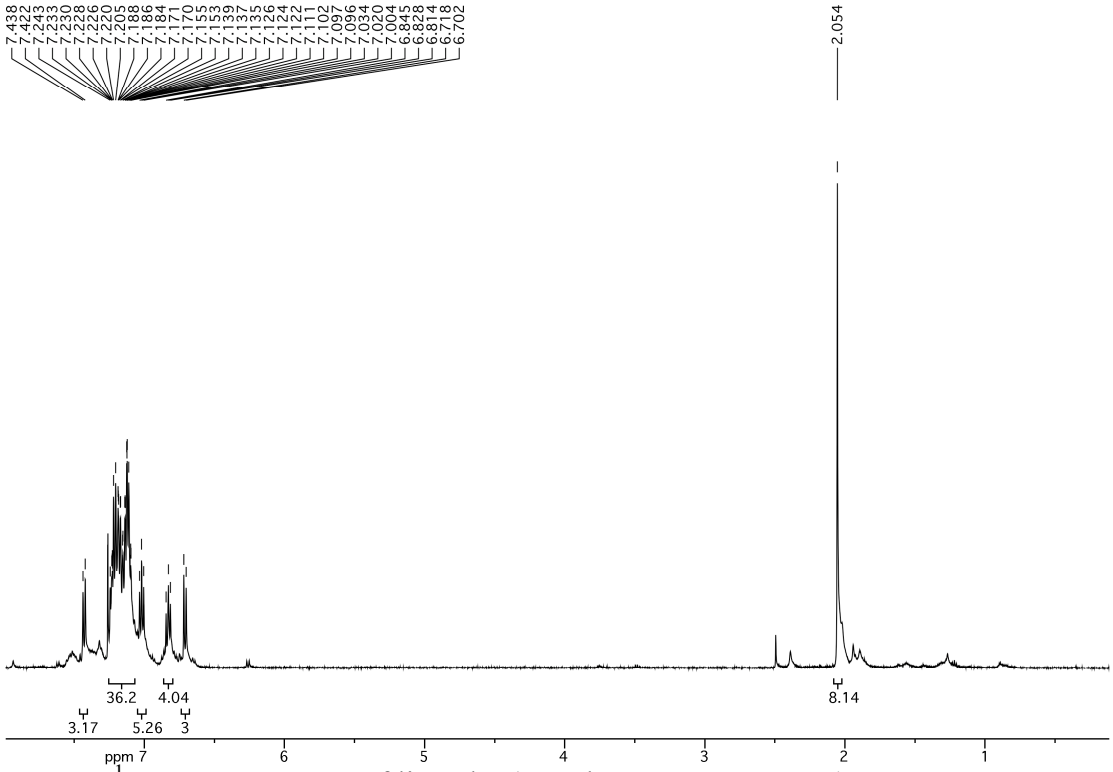


Fig. S3. ^{1}H NMR spectrum of ligand **1** ($CDCl_3$, 500 MHz, 298 K).

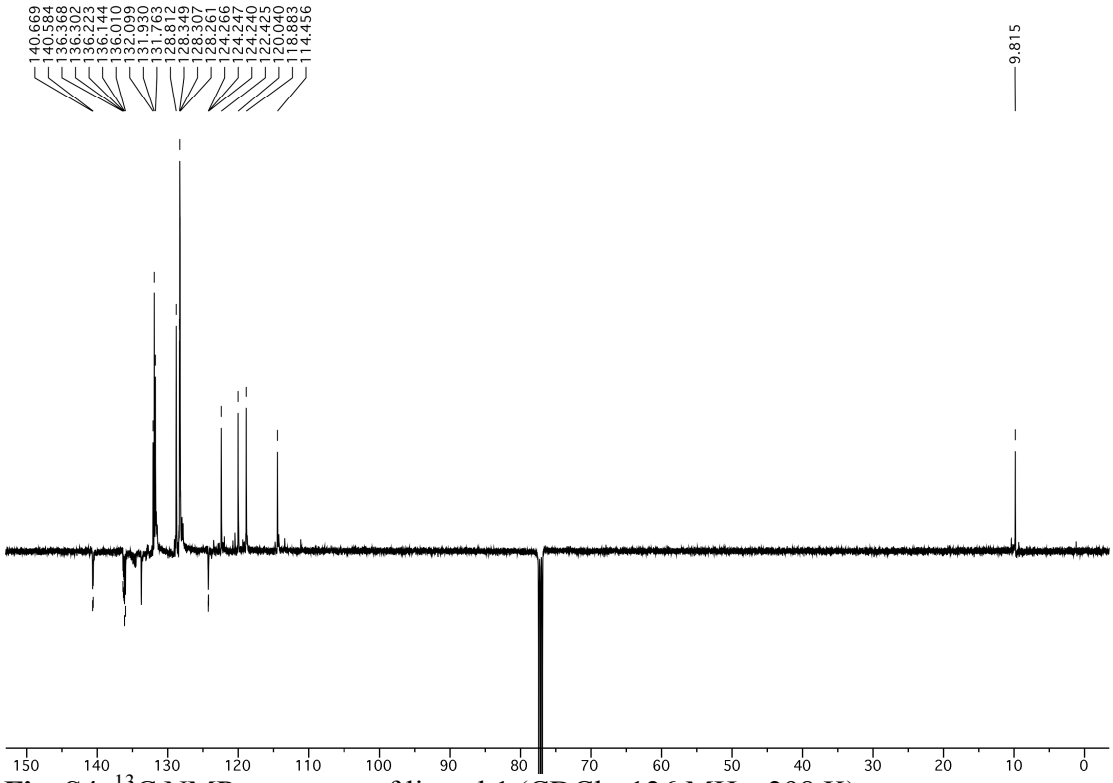


Fig. S4. ^{13}C NMR spectrum of ligand **1** ($CDCl_3$, 126 MHz, 298 K).

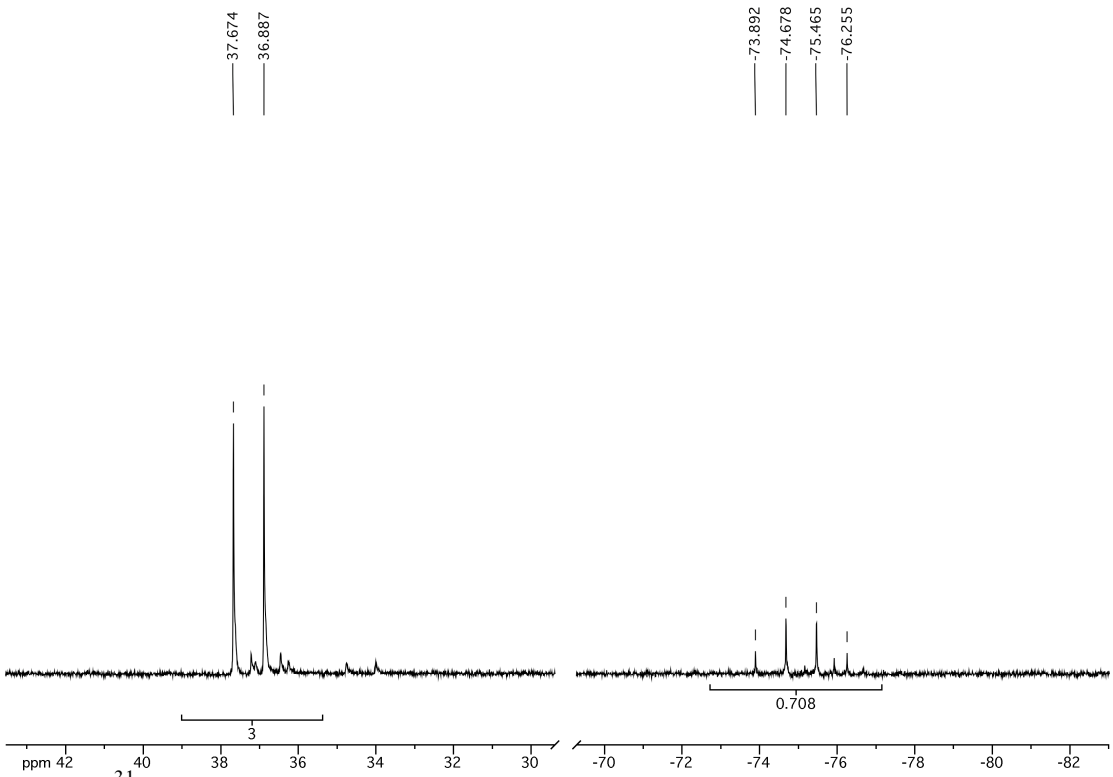


Fig. S5. ^{31}P NMR spectrum of ligand **1** ($CDCl_3$, 202 MHz, 298 K).

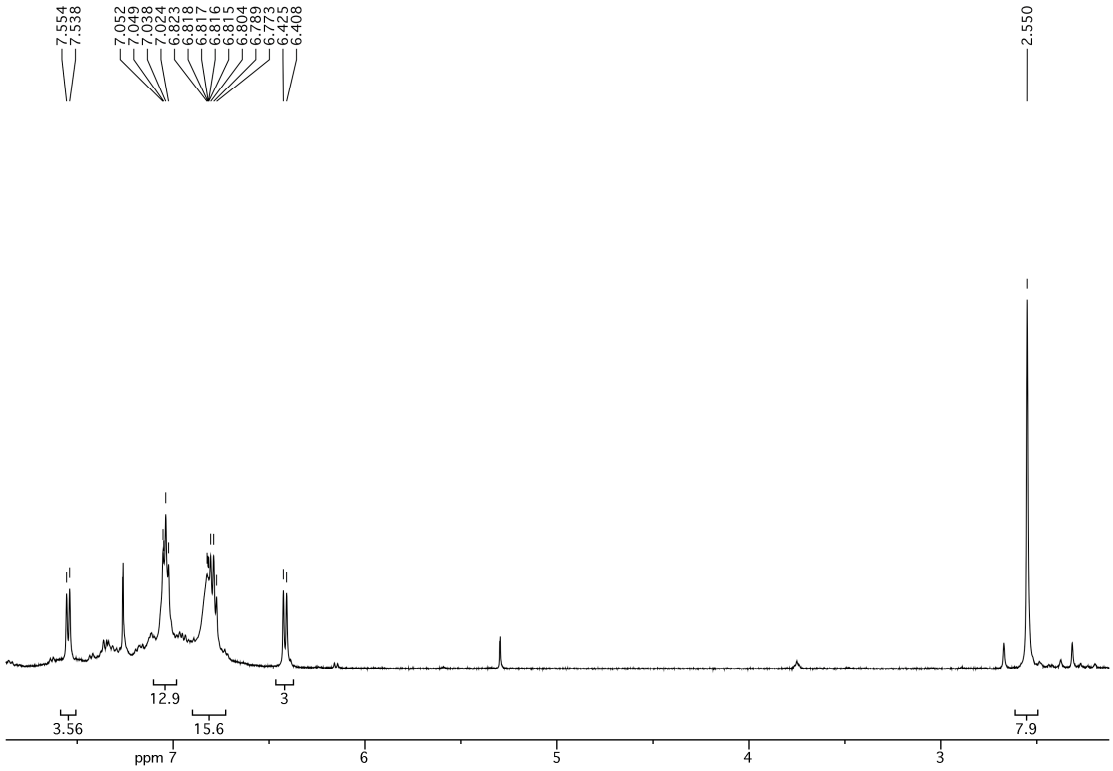


Fig. S6. ^{1}H NMR spectrum of complex **2** ($CDCl_3$, 500 MHz, 298 K).

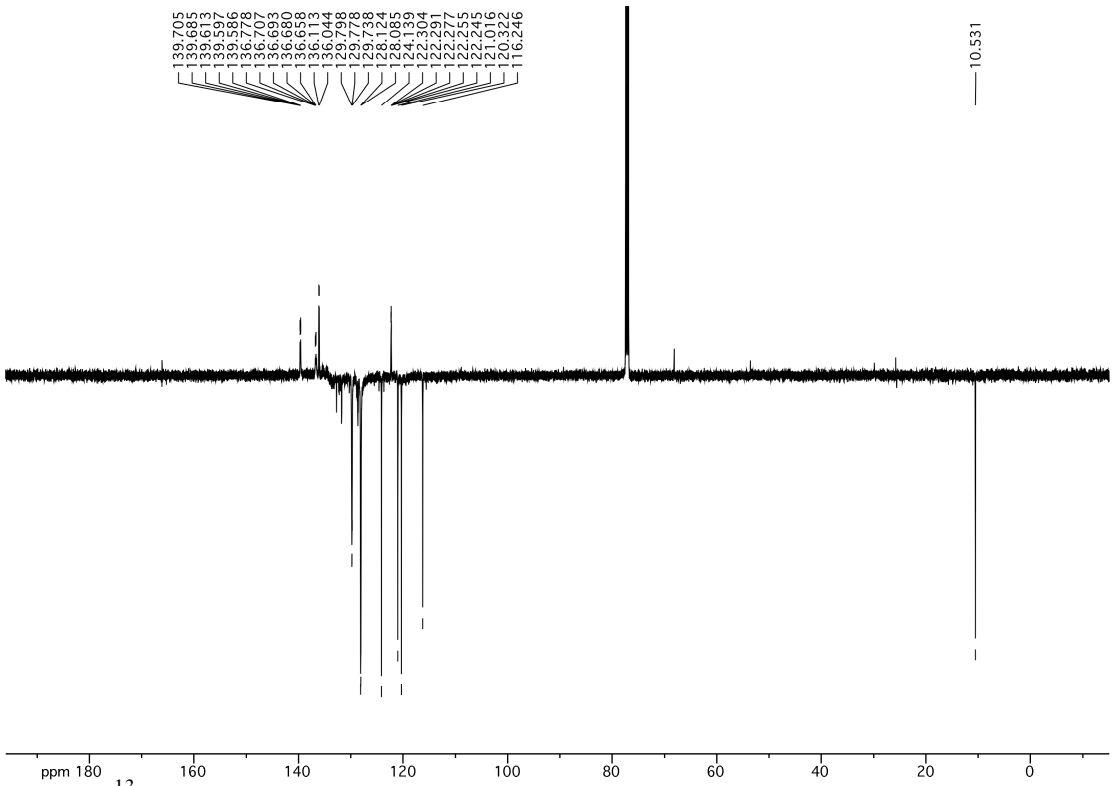


Fig. S7. ^{13}C NMR spectrum of complex **2** ($CDCl_3$, 126 MHz, 298 K).

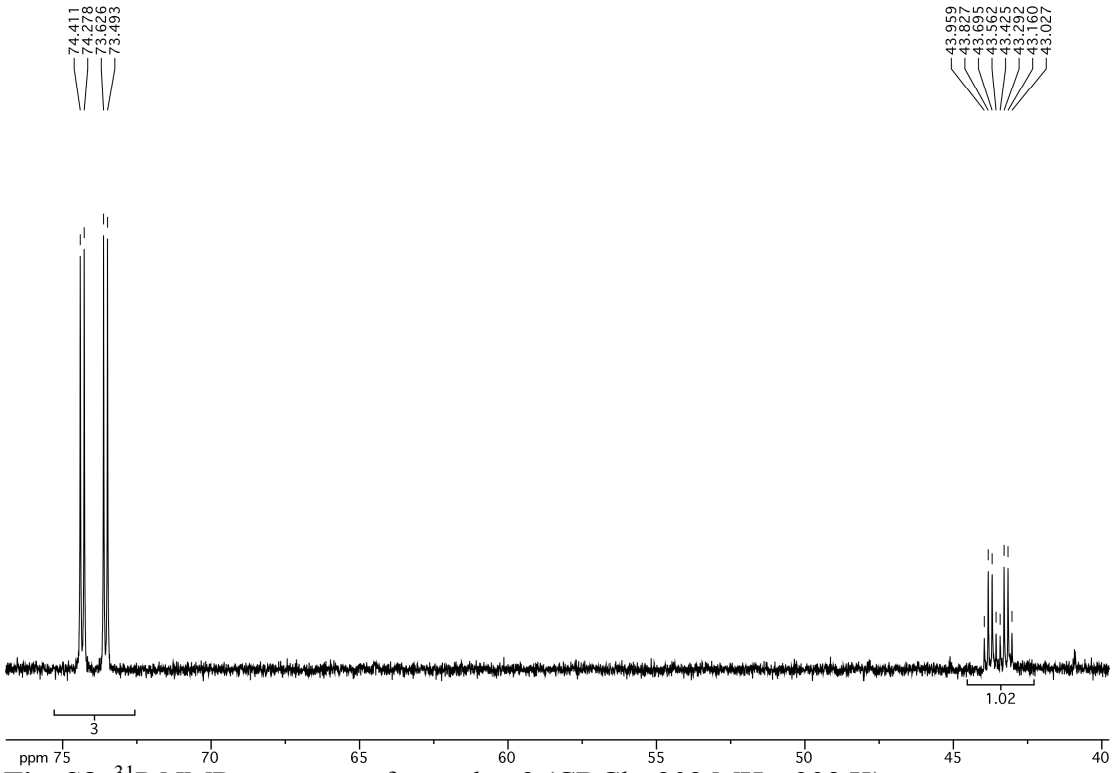


Fig. S8. ^{31}P NMR spectrum of complex **2** ($CDCl_3$, 202 MHz, 298 K).

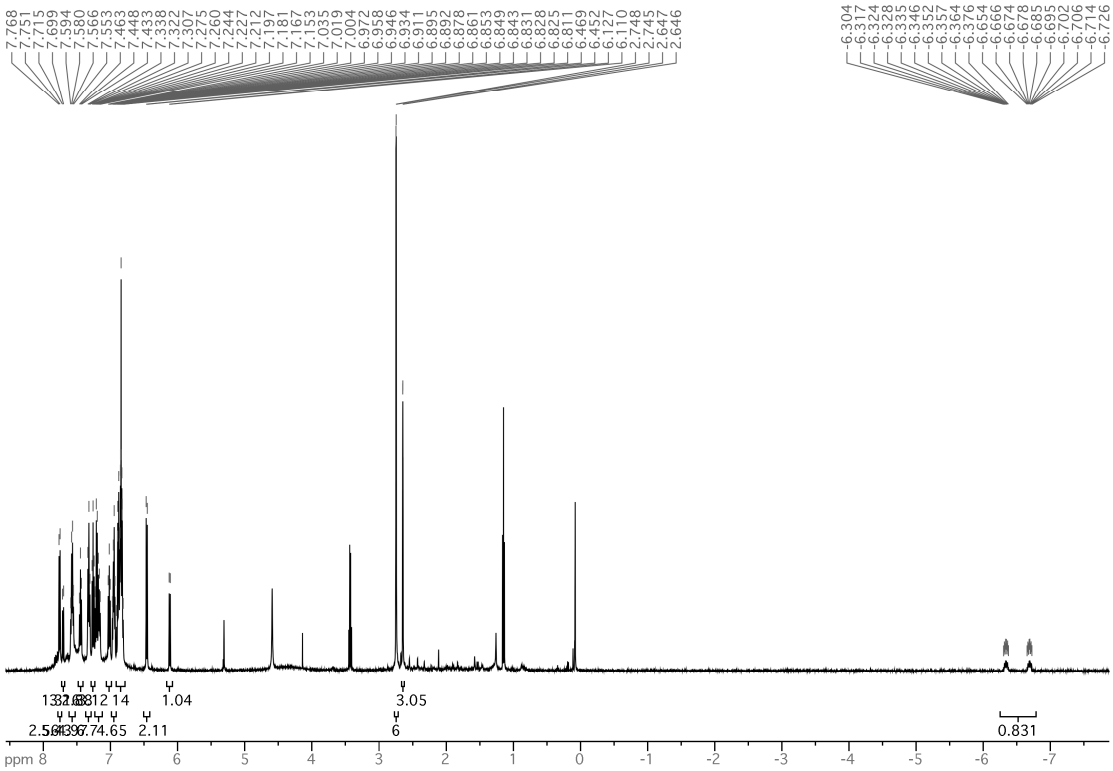


Fig. S9. ^{1}H NMR spectrum of complex **3** (CD_2Cl_2, 500 MHz, 298 K). Et_2O (1.21 and 3.48 ppm), grease (0.07 ppm), and dissolved H_2 (4.59 ppm) are present in small amounts.

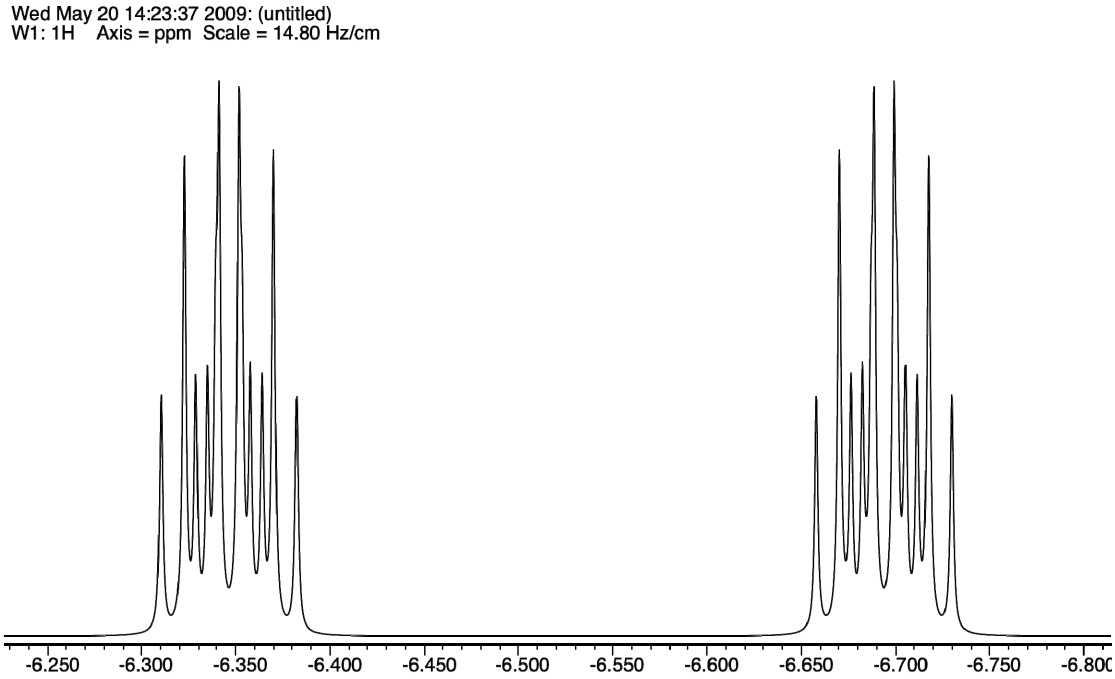


Fig. S10. Simulation of hydride signal generated with gNMR. Coupling constants: J_{RhH} = 9.2 Hz, J_{P1H} = 14.5 Hz, J_{P2H} = 174.8 Hz, J_{P34H} = 6.2 Hz.

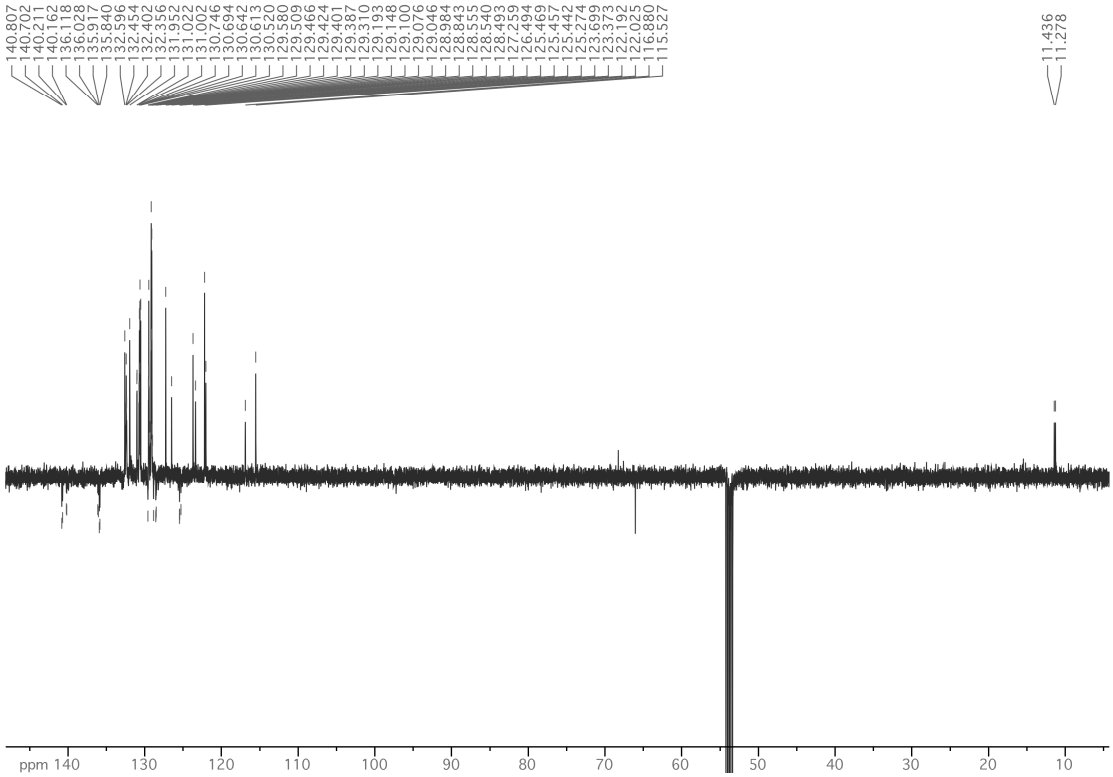


Fig. S11. ^{13}C NMR spectrum of complex **3** (CD_2Cl_2, 126 MHz, 298 K).

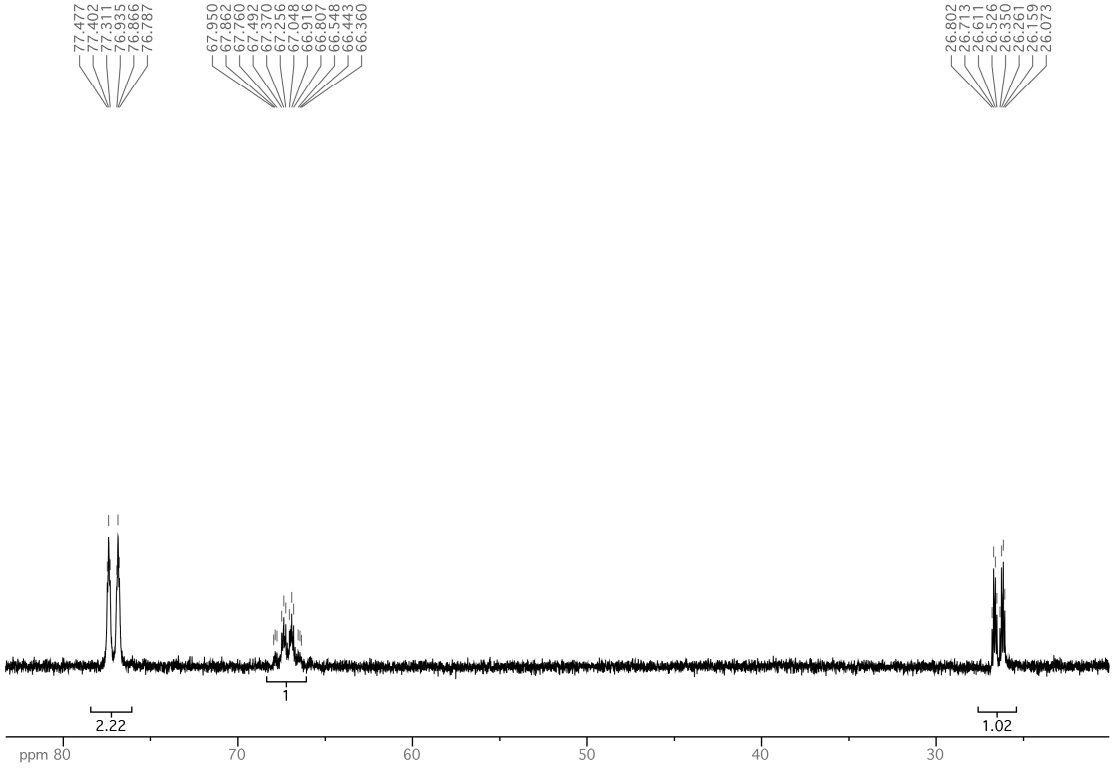


Fig S12. ^{31}P NMR spectrum of complex **3** (CD_2Cl_2, 202 MHz, 298 K).

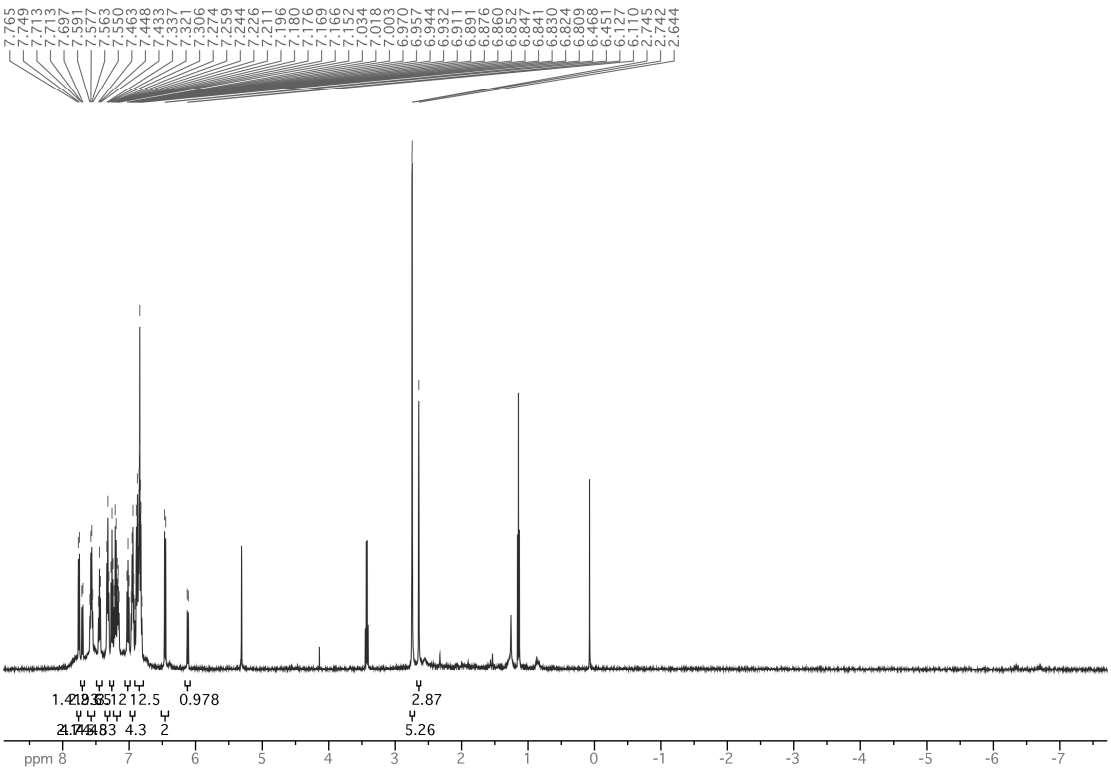


Fig S12. ^{1}H NMR spectrum of complex **3-D** (CD_2Cl_2, 500 MHz, 298 K). Et_2O (1.21 and 3.48 ppm) and grease (0.07 ppm), are present in small amounts.

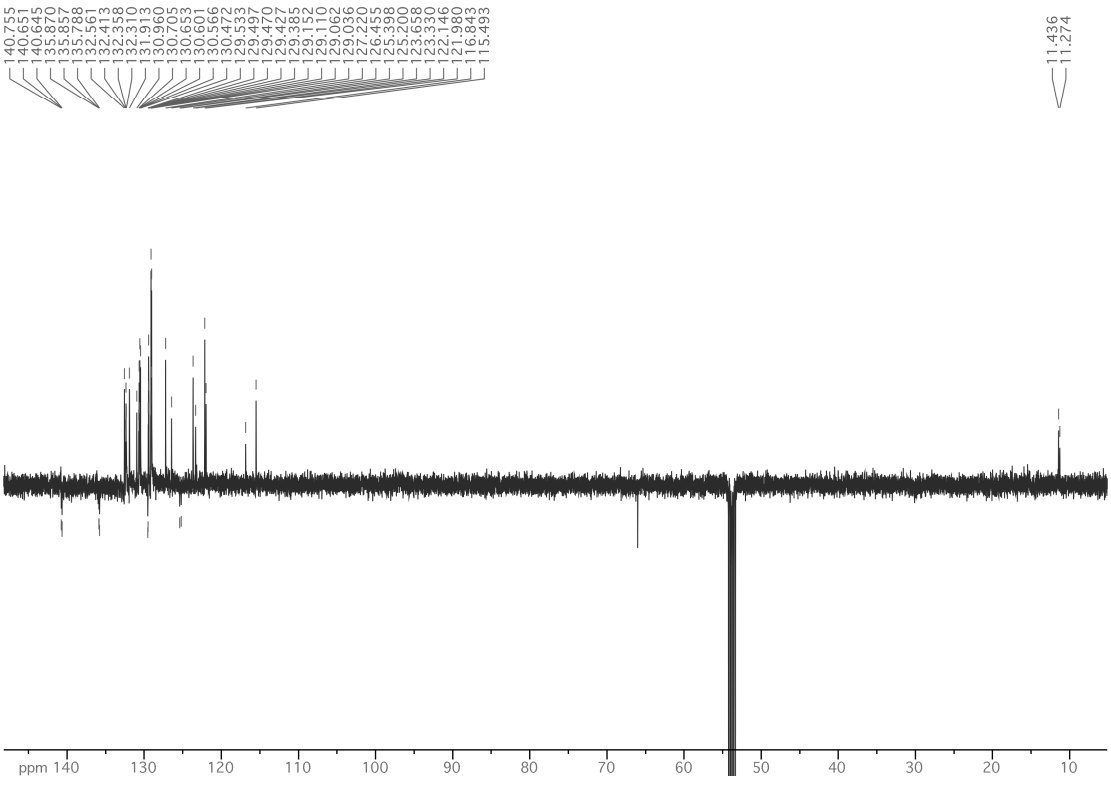


Fig S13. ^{13}C NMR spectrum of complex **3-D** (CD_2Cl_2, 126 MHz, 298 K).

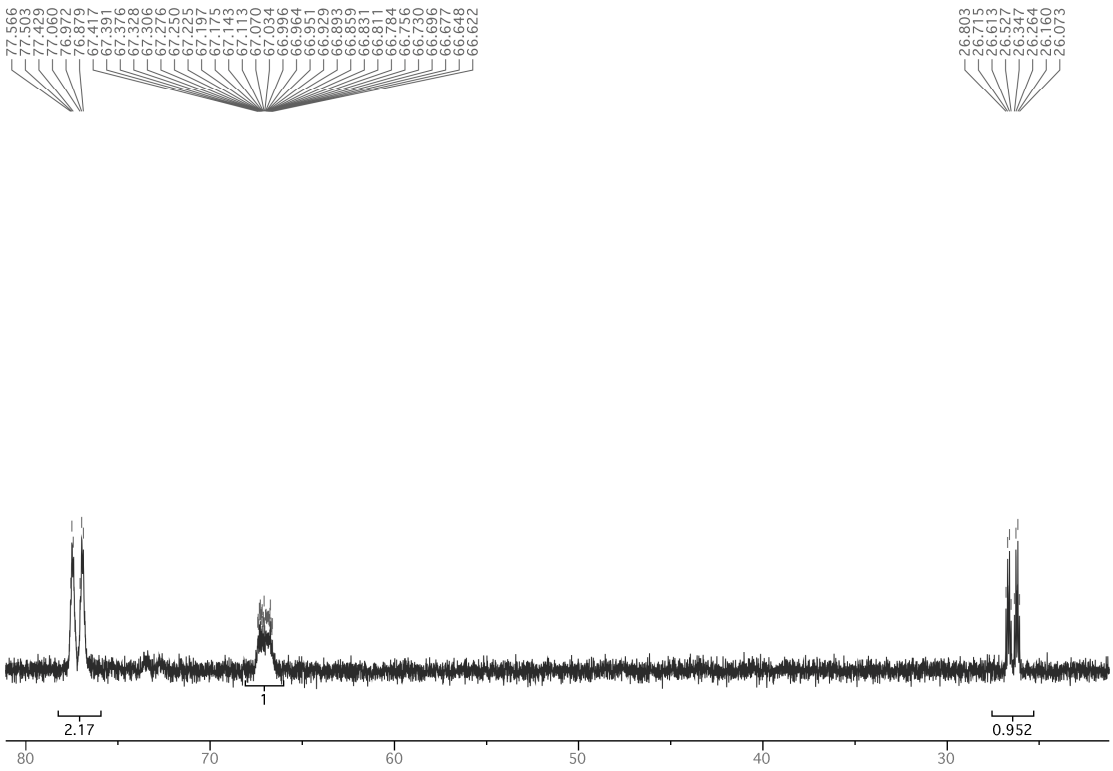


Fig S14. ^{31}P NMR spectrum of complex **3-D** (CD_2Cl_2, 202 MHz, 298 K).

VII References

[1] This compound has been synthesized previously using an aminal protecting group, see: J. O. Yu, C. S. Browning, D. H. Farrar, *Chem. Commun.* **2008**, 1020.

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