Supporting Information

Chemoselective Hydrogenation of Aldehydes under Mild, Base-Free Conditions – Manganese Outperforms Rhenium

Mathias Glatz,[†] Berthold Stöger,[§] Daniel Himmelbauer,[†] Luis F. Veiros,[‡] and Karl Kirchner*[, †]

[†]Institute of Applied Synthetic Chemistry, [§]X-Ray Center, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, AUSTRIA, and [‡]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais No. 1, 1049-001 Lisboa, PORTUGAL

General experimental information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in a MBraun inert-gas glovebox. Hydrogen (99.999% purity) was purchased from Messer Austria and used as received. The solvents were purified according to standard procedures.[1] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. All aldehyde substrates were obtained from commercial sources and purified by distillation prior to use. Complexes *cis*-[Mn(PNP-*i*Pr)$(CO)_2$H] (**Mn1**),[2] *cis*-[Mn(PNP^{Me}-*i*Pr)$(CO)_2$H] (**Mn2**),[2] *cis*-[Mn(PNP^{CH2}-*i*Pr)$(CO)_2$Br] (**3**)[3] and *cis*-[Re(PNP^{CH2}-*i*Pr)$(CO)_2$Cl] (**5**)[4] were prepared according to the literature. ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AVANCE-250, 400, and AVANCE-600 spectrometers. ^{19}F{^{1}H} NMR spectra are referenced externally to trifluorotoluene (0.05%) (δ = 0 ppm). ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to residual protio-solvent, and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{31}P{^{1}H} NMR spectra are referenced externally to H_3PO_4 (85%) (δ = 0).

General procedure for the hydrogenation of aldehydes. All hydrogenation reaction were carried out in a Carl Roth 100 mL stainless steel autoclave containing a 20mL screw cap vial equipped with a septum, a small stirring bar and a 10 inch needle (gauge 18) connecting the vial on the bottom with the head of the autoclave for injecting the reaction solution. The autoclave was evacuated, flushed 3 times with argon gas before use. For a typical experiment, the reaction solution was prepared inside a glovebox by mixing the substrate (2.0 mmol), ethanol (3 mL), the catalyst (1 mL, 0.10 μM stock solution in EtOH). The catalyst stock solutions were freshly prepared and readily used. For a typical experiment, including addition of base, the substrate (2.0 mmol), ethanol (2 mL), the catalyst (1 mL, 0.10 μM stock solution in EtOH) and the base (1 mL, 0.30 μM stock solution in EtOH) were mixed. The resulting solution was taken up in a syringe via a twelve-inch needle (gauge 22), removed from the glovebox and injected into the autoclave under a slight flow of argon. The autoclave was then purged three times with H_2 gas before the final pressure was adjusted to the specified value and the reaction was carried for the stated time. Afterwards, the hydrogen gas was released, the vial was taken out of the autoclave and the solution was filtered over aluminum oxide. The solvent was then slowly removed under reduced pressure. The residue was analyzed by ^{1}H NMR and yields were determined by integration of the spectra after addition of mesitylene (2.0 mmol) as internal standard or by ^{19}F NMR spectroscopy.

Synthesis

***cis*-[Mn(PNP^{CH2}-*i*Pr)$(CO)_2$H] (Mn3).** To a suspension of *cis*-[Mn(PNP^{CH2}-*i*Pr)$(CO)_2$Br] (**3**) (212 mg, 0.40 mmol) in toluene (15 mL), a 1 M THF-solution of Na[$HBEt_3$] (0.4 mL, 0.4 mmol) is added at 0°C. After gas evolution, the solution turns clear and is stirred for 1h. The insoluble solids are removed by filtration over celite. The solvent is then removed under reduced pressure and the colorless product was washed with cold *n*-pentane (20 mL). The pale solid is dried under reduced pressure to obtain an off-white powder. Yield: 160 mg (90 %). Anal. Calcd. for $C_{21}H_{36}MnNO_2P_2$ (451.40). C, 55.88; H, 8.04; N, 3.10. Found: C, 55.90; H, 8.06; N, 3.10.^{1}H NMR (250 MHz, δ, C_6D_6, 20 °C) 6.61 (t, J_{HH} = 7.3 Hz, 1H, py[4]), 6.35 (d, J_{HH} = 7.5 Hz, 2H, py[3,5]), 2.92 (m, 4H, C*H*), 2.26 (m, 2H, C*H*), 2.04 (m, 2H, C*H*), 1.29 (m, 18H, CH_3), 0.98 (m, 6H, CH_3), -4.27 (t, J_{HP} = 48.1 Hz, 1H, Mn-*H*). ^{13}C{^{1}H} NMR (151 MHz, δ, C_6D_6,

20 °C) 235.3 (m, *C*O), 227.8 (m, *C*O), 162.9 (vt, J_{CP} = 6.7 Hz, py^{2,6}), 132.8 (s, py^4), 118.1 (s, py^{3,5}), 40.5 (vt, J_{CP} = 6.1 Hz, *C*H$_2$), 28.8 (vt, J_{CP} = 8.6 Hz, *C*H), 26.4 (vt, J_{CP} = 10.9 Hz, *C*H), 19.0 (s, *C*H$_3$), 18.7 (s, *C*H$_3$), 18.6 (s, *C*H$_3$),17.8 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (101 MHz, δ, C_6D_6, 20 °C) 110.8 (s, 2P). IR (ATR, cm^{-1}): 1975 (ν_{CO}), 1801 (ν_{CO}).

***cis*-[Re(PNP-*i*Pr)(CO)$_2$Cl] (4).** A suspension of PNP-*i*Pr (136 mg, 0.4 mmol) and Re(CO)$_5$Cl (144 mg, 0.4 mmol) in dioxane (15 mL) is stirred in a closed vessel at 120°C for 18 h. The suspension is evaporated to dryness and the solid washed with Et$_2$O (10 ml) and *n*-pentane (20 mL). The colorless powder is recrystallized from acetone/*n*-pentane. Yield: 191 mg (77%). Anal. Calcd. for $C_{19}H_{33}ClN_3O_2P_2Re$ (619.09).C, 36.86; H, 5.37; N, 6.79. Found: C, 36.90; H, 5.37; N, 6.77.^{1}H NMR (600 MHz, δ, dmso-d$_6$, 20 °C) 8.41 (s, 2H, N*H*), 7.30 (t, J_{HH} = 8.0 Hz, 1H, py^4), 6.29 (d, J_{HH} = 8.0 Hz, 2H, py^{3,5}), 3.01 (m, 2H, C*H*), 2.60 (m, 2H, C*H*), 1.33 (dd, *J* = 12.8, 6.9 Hz, 6H, C*H*$_3$), 1.29 (dd, *J* = 16.0, 8.3 Hz, 6H, C*H*$_3$), 1.27 (dd, *J* = 17.3, 7.6 Hz, 6H, C*H*$_3$), 1.12 (dd, *J* = 15.0, 7.3 Hz, 6H, C*H*$_3$).^{13}C{^{1}H} NMR (151 MHz, δ, dmso-d$_6$, 20 °C) 208.0 (m, *C*O), 195.3 (vt, J_{CP} = 7.8 Hz, *C*O), 162.3 (vt, J_{CP} = 7.4 Hz, py^{2,6}), 139.6 (s, py^4), 97.7 (s, py^{3,5}), 27.3 (vt, J_{CP} = 15.0 Hz, *C*H), 26.1 (vt, J_{CP} = 14.3 Hz, *C*H), 20.0 (vt, J_{CP} = 3.8 Hz, *C*H$_3$), 19.8 (vt, J_{CP} = 4.3 Hz, *C*H$_3$), 18.7 (s, *C*H$_3$), 16.81 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (101 MHz, δ, dmso-d$_6$, 20 °C) 99.7 (2P). IR (ATR, cm^{-1}): 1918 (ν_{CO}), 1804 (ν_{CO}).

***cis*-[Re(PNP-*i*Pr)(CO)$_2$H] (Re1).** A solution of 1M Na[HBEt$_3$] in THF (0.3 ml, 0.3 mmol) is added to a suspension of *cis*-[Re(PNP-*i*Pr)(CO)$_2$Cl] (**4**) (186 mg, 0.3 mmol) in benzene (15 mL) at 0 °C. The colorless solution is allowed to reach room temperature, and stirred for 1 h. After filtration over celite, the solvent is removed under reduced pressure. The crude product is washed three times with cold *n*-pentane (30 mL). The final colorless powder is dried under reduced pressure. Yield: 162 mg (92%). Anal. Calcd. for $C_{19}H_{34}N_3O_2P_2Re$ (584.65). C, 39.03; H, 5.86; N, 7.19. Found: C, 39.11; H, 5.91; N, 7.15.^{1}H NMR (250 MHz, δ, C_6D_6, 20 °C) 6.69 (t, J_{HH} = 8.0 Hz, 1H, py^4), 6.29 (d, J_{HH} = 8.0 Hz, 2H, py^{3,5}), 4.45 (s, 2H, N*H*), 2.09 (m, 2H, C*H*), 1.76 (m, 2H, C*H*), 1.32-1.14 (m, 18H, C*H*$_3$), 1.03 (dd, *J* = 15.0, 7.0 Hz, 6H, C*H*$_3$), -3.84 (t, J_{HP} = 24.9 Hz, H, Re*H*). ^{13}C{^{1}H} NMR (151 MHz, δ, C_6D_6, 20 °C) 205.7 (m, *C*O), 198.9 (vt, J_{CP} = 6.5 Hz, *C*O), 161.0 (vt, J_{CP} = 7.6 Hz, py^{2,6}), 136.0 (s, py^4), 95.7 (vt, J_{CP} = 2.0 Hz, py^{2,6}), 33.4 (vt, J_{CP} = 13.7 Hz, *C*H), 32.2 (vt, J_{CP} = 14.8 Hz, *C*H), 19.2 (vt, J_{CP} = 4.4 Hz, *C*H$_3$), 19.0-18.7 (m, C*H*$_3$), 18.2 (s, *C*H$_3$).^{31}P{^{1}H} NMR (101 MHz, δ, C_6D_6, 20 °C) 117.0 (2P). IR (ATR, cm^{-1}): 1875 (ν_{CO}), 1805 (ν_{CO}).

***cis*-[Re(PNP^{CH2}-*i*Pr)(CO)$_2$H] (Re2).** A solution of 1M Na[HBEt$_3$] in THF (0.3 mL, 0.3 mmol) is added to a suspension of *cis*-[Re(PNP^{CH2}-*i*Pr)(CO)$_2$Cl] (**5**) (186 mg, 0.3 mmol) in benzene (15 mL) at 0 °C. The yellow solution is allowed to reach room temperature, and stirred for 1 h. After filtration over Celite, the solvent is removed under reduced pressure. The crude product is washed three times with cold *n*-pentane (30 mL). The final yellow powder is dried under reduced pressure. Yield: 165 mg (95 %). Anal. Calcd. for $C_{21}H_{36}ReNO_2P_2$ (582.67). C, 43.29; H, 6.23; N, 2.40. Found: C, 43.38; H, 6.27; N, 2.35. ^{1}H NMR (250 MHz, δ, C_6D_6, 20 °C) 6.68 (t, J_{HH} = 7.7 Hz, 1H, py^4), 6.37 (d, J_{HH} = 7.6 Hz, 2H, py^{3,5}), 3.29 (m, 2H, C*H*$_2$), 2.99 (m, 2H, C*H*$_2$), 2.11 (m, 2H, C*H*), 1.85 (m, 2H, C*H*$_2$), 1.99 (m, 15H, C*H*$_3$), 0.96 (m, 9H, C*H*$_3$), -2.56 (t, J_{HP} = 22.8 Hz, 1H, Re-*H*). ^{13}C{^{1}H} NMR (151 MHz, δ, C_6D_6, 20 °C) 208.2 (m, *C*O), 204.9 (m, *C*O), 162.9 (vt, J_{CP} = 6.0 Hz, py^{2,6}), 133.8 (s, py^4), 118.1 (vt, J_{CP} = 4.5 Hz, py^{3,5}), 44.3 (vt, J_{CP} = 10.2 Hz, *C*H$_2$), 29.1 (vt, J_{CP} = 12.1 Hz, *C*H), 27.7 (vt, J_{CP} = 13.7 Hz, *C*H), 19.6 (vt, J_{CP} =

2.4 Hz, CH_3), 19.0 (s, CH_3), 18.9 (s, CH_3), 18.3 (s, CH_3), 18.2 (s, CH_3). $^{31}P\{^1H\}$ NMR (101 MHz, δ, C_6D_6, 20 °C) 62.1 (s, 2P). IR (ATR, cm^{-1}): 1895 (ν_{CO}), 1821 (ν_{CO}).

Computational Details. The computational results presented have been achieved in part using the Vienna Scientific Cluster (VSC). Calculations were performed using the GAUSSIAN 09 software package[5] and the PBE0 functional without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock[6] exchange with DFT[7] exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[8] The basis set used for the geometry optimizations consisted of the Stuttgart/Dresden ECP (SDD) basis set[9] to describe the electrons of Mn, and a standard 6-31G(d,p) basis set[10] for all other atoms. Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel *et al*,[11] following extensive searches of the Potential Energy Surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. The electronic energies were converted to free energy at 298.15 K and 1 atm by using zero point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level. Solvent effects (ethanol) were considered in all calculations using the Polarizable Continuum Model (PCM) initially devised by Tomasi and coworkers[12] with radii and non-electrostatic terms of the SMD solvation model, developed by Truhlar *et al*.[13] Three-dimensional representations of the orbitals were obtained with the program Molekel.[14]

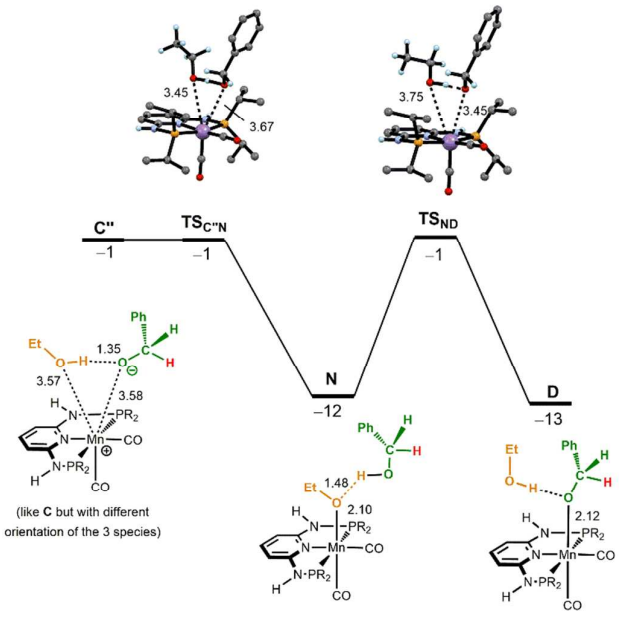


Figure S1: Free energy profile calculated for the formation of the O-coordinated benzaldehyde intermediate, **D**. The free energy values (kcal/mol) are referred to the initial reactants (**A**) and relevant distances (Å) are presented.

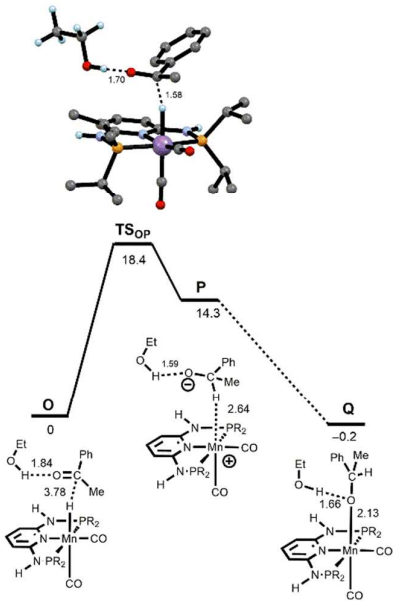


Figure S2: Free energy profile calculated for the hydrogenation of acetophenone catalyzed by the hydride complex **A + acetophenone (O)**. Relevant distances (Å) are presented.

Crystal Structure Determination. A pre-selected single crystal of **Re1**·C_6H_6 (CCDC 1815730) was embedded in perfluorinated polyether and mounted on a Kapton micro mount. X-ray diffraction data were measured in a stream of nitrogen at T = 100 K on a Bruker APEX-II diffractometer[15] with Mo-$K\alpha$ radiation. After integration of the data with the program SAINT, an absorption correction based on the semi-empirical "multi-scan" approach was performed with the SADABS program.[15] The crystal structure was solved using the dual space approach implemented in SHELXT[16] and was refined against F^2 using the Jana2006 software package.[17] The H atoms connected to C atoms were placed geometrically and refined in the riding model approximation. Amine-H atoms were located in difference Fourier maps and the N-H distances restrained to 0.870(1) Å. The hydride was likewise located in difference Fourier maps and refined without constraints, using the atomic form factor for H^-. All non-hydrogen atoms were refined anisotropically. Molecular graphics were generated with the program MERCURY.[18] Crystal data and experimental details are given in Table S1.

Table S1. Details for the crystal structure determination of **Re1**·C_6H_6.

	Re1·C6H6
formula	$C_{25}H_{40}N_3O_2P_2Re$
fw	662.8
cryst.size, mm	0.15×0.06×0.04
color, shape	colourless, needle
crystal system	Orthorhombic
space group	$P2_12_12_1$ (no. 19)
a, Å	10.1881(7)
b, Å	13.7426(11)
c, Å	20.6392(16)
V, Å^3	2889.7(4)
T, K	100
Z,Z'	4,1
ρ_{calc}, g cm^{-3}	1.5234
μ, mm^{-1} (MoKα)	4.340
F(000)	1328
absorption corrections, T_{min}-T_{max}	multi-scan, 0.52–0.84
θ range, deg	2.23–27.30
no. of rflns measd	11 512
R_{int}	0.0558
no. of rflns unique	6403
no. of rflns $I>2\sigma(I)$	4528
no. of params / restraints	309 / 2
R ($I > 2\sigma(I)$) [a]	0.0484
R (all data)	0.0764
wR ($I > 2\sigma(I)$)	0.0991
wR (all data)	0.1115
GooF	1.11
Diff.Four.peaks	-1.10 / 2.27
CCDC no.	1815730

[a] $R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma w(F_o^2 - F_c^2) / \Sigma[w(F_o^2)^2]\}^{½}$, GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{½}$

Figure S3: ^{1}H NMR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$Cl] (**4**) (600 MHz, dmso-d$_6$)

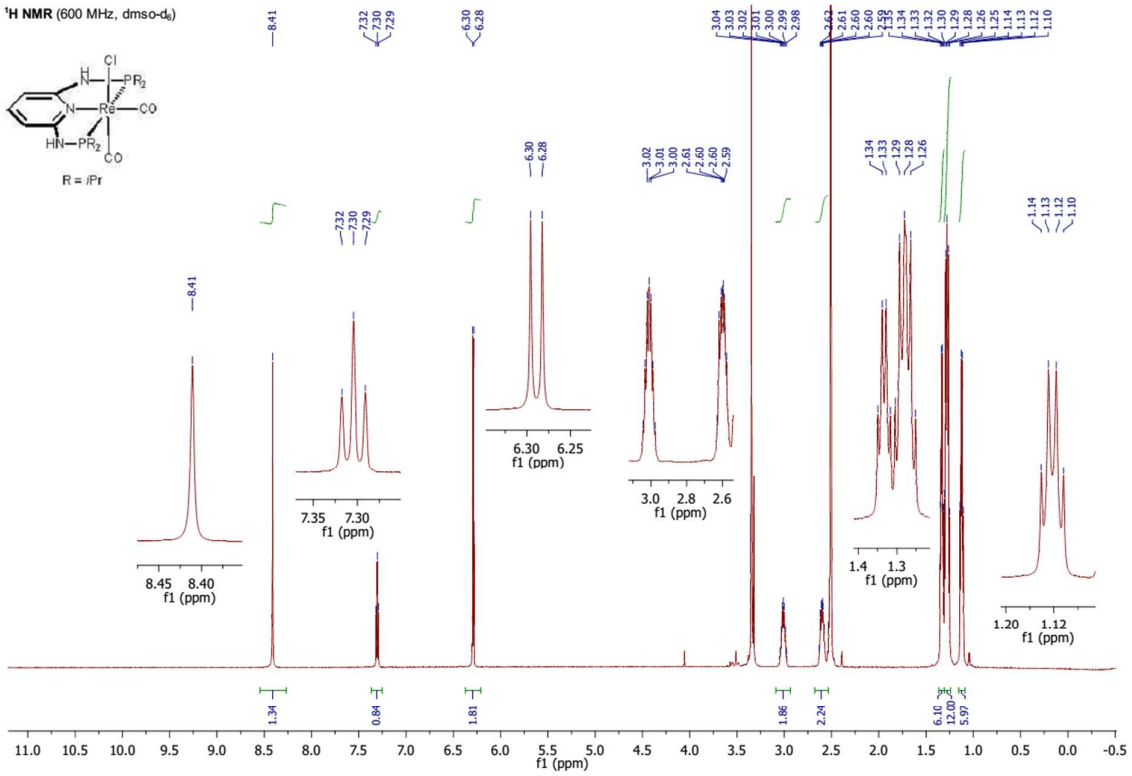


Figure S4: ^{13}C{^{1}H} NMR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$Cl] (**4**) (151 MHz, dmso-d$_6$)

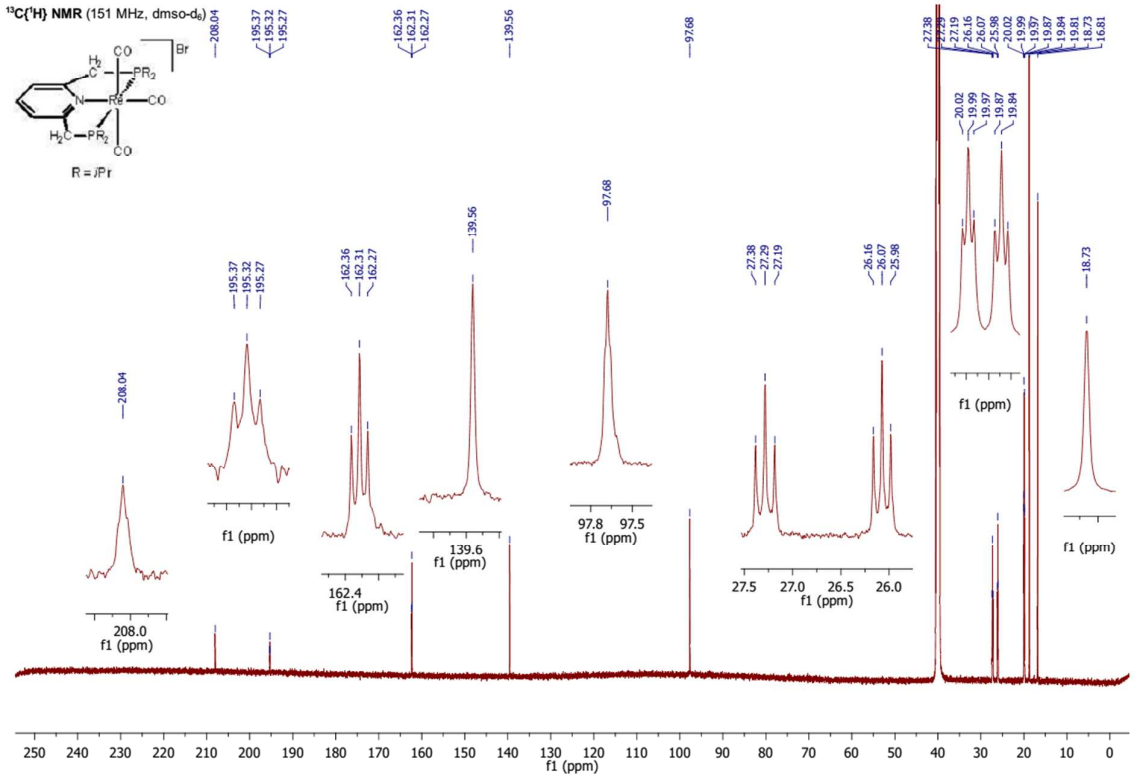


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$Cl] (**4**) (101 MHz, dmso-d$_6$)

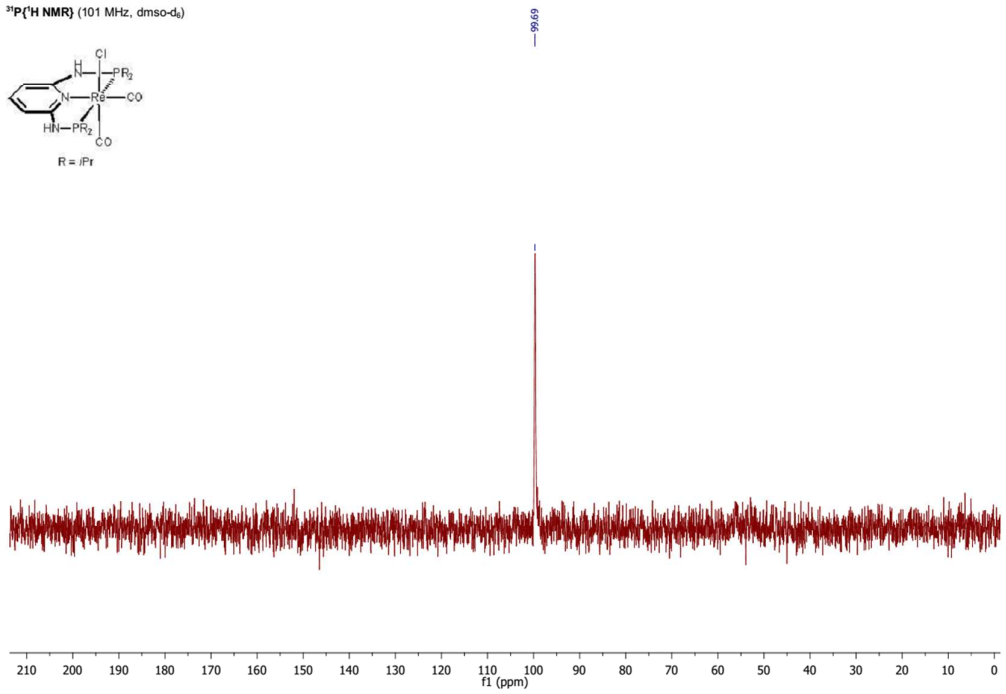


Figure S6: IR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$Cl] (**4**)

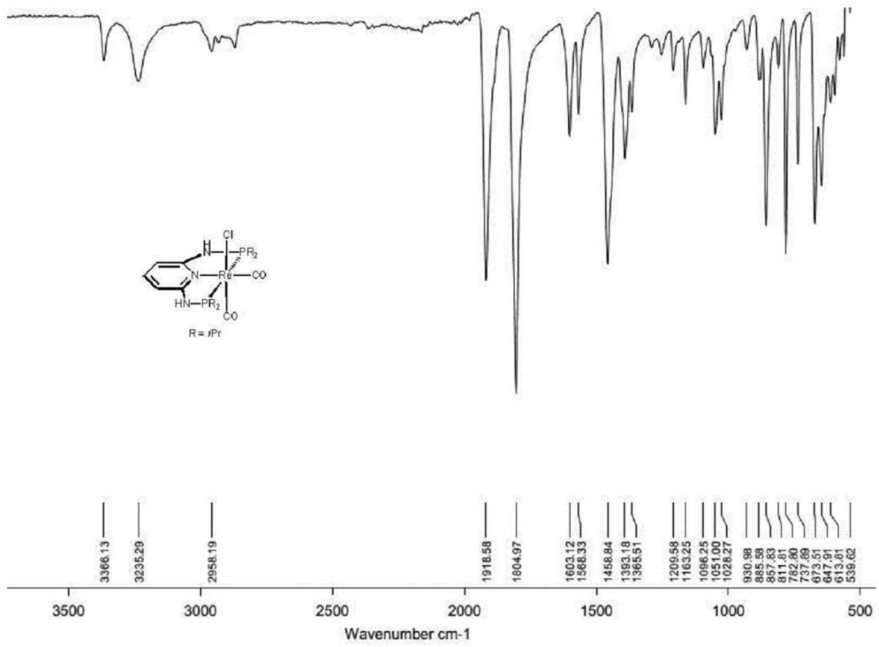


Figure S7: ^{1}H NMR spectrum of *cis*-[Mn(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Mn3**) (250 MHz, C_6D_6)

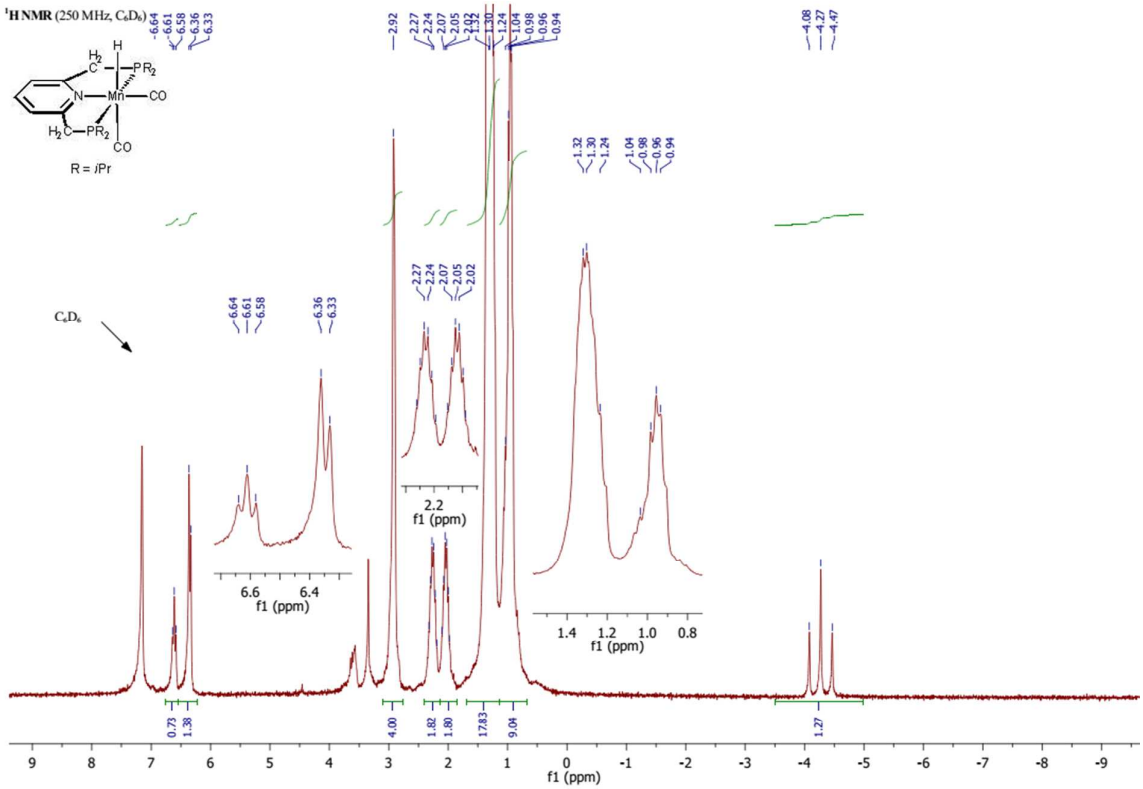
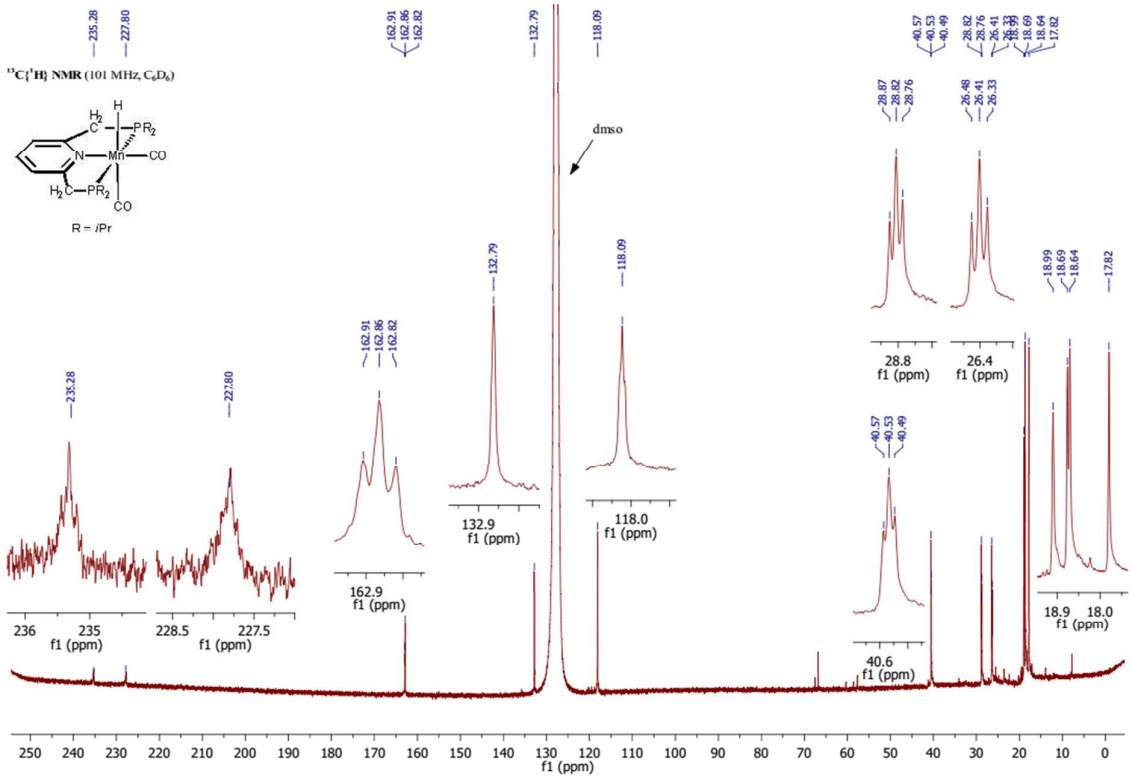
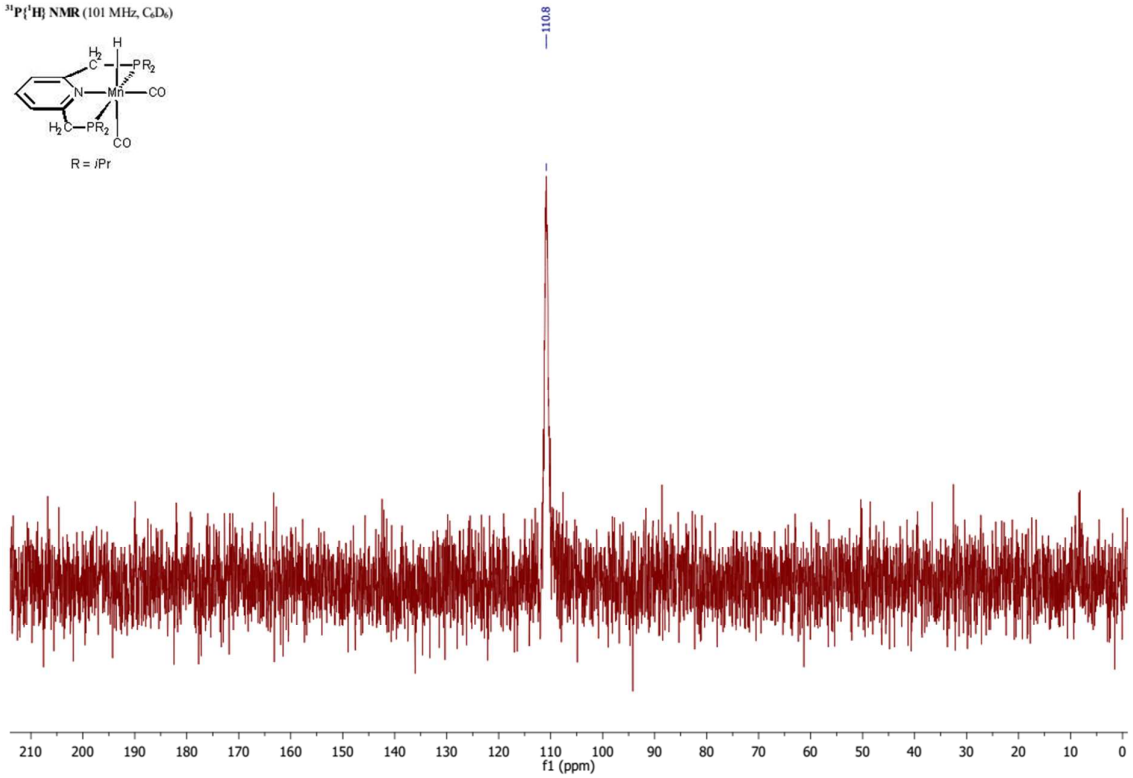


Figure S8: ^{13}C{^{1}H} NMR spectrum of *cis*-[Mn(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Mn3**) (151 MHz, C_6D_6)



1 **Figure S9: $^{31}P\{^{1}H\}$ NMR** spectrum of *cis*-[Mn(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Mn3**) (101 MHz, C_6D_6)



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3 **Figure S10: IR** spectrum of *cis*-[Mn(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Mn3**)

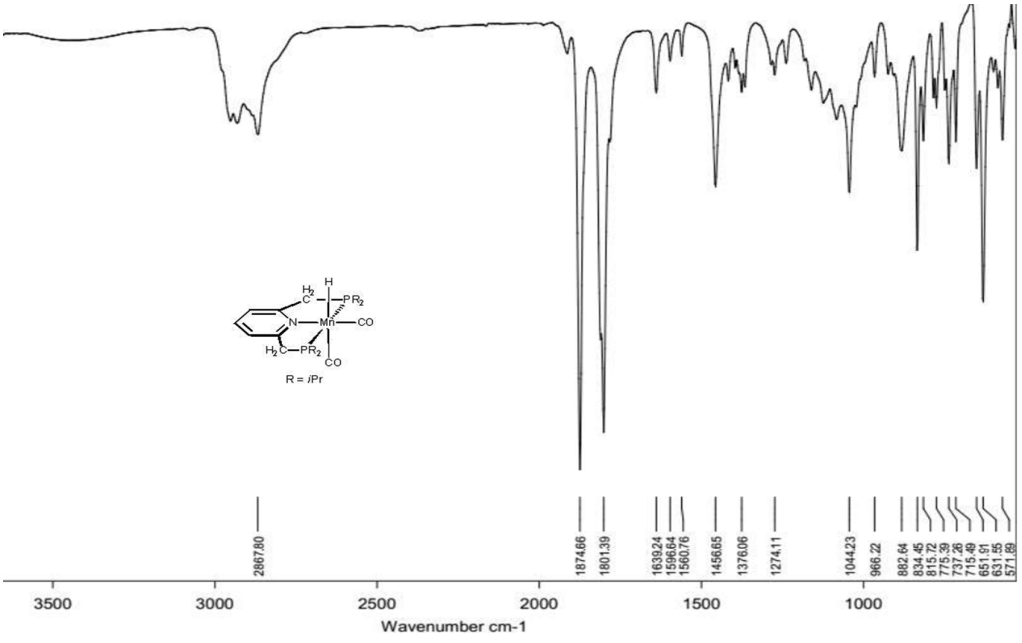

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Figure S11: ^{1}H NMR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$H] (**Re1**) (250 MHz, C_6D_6)

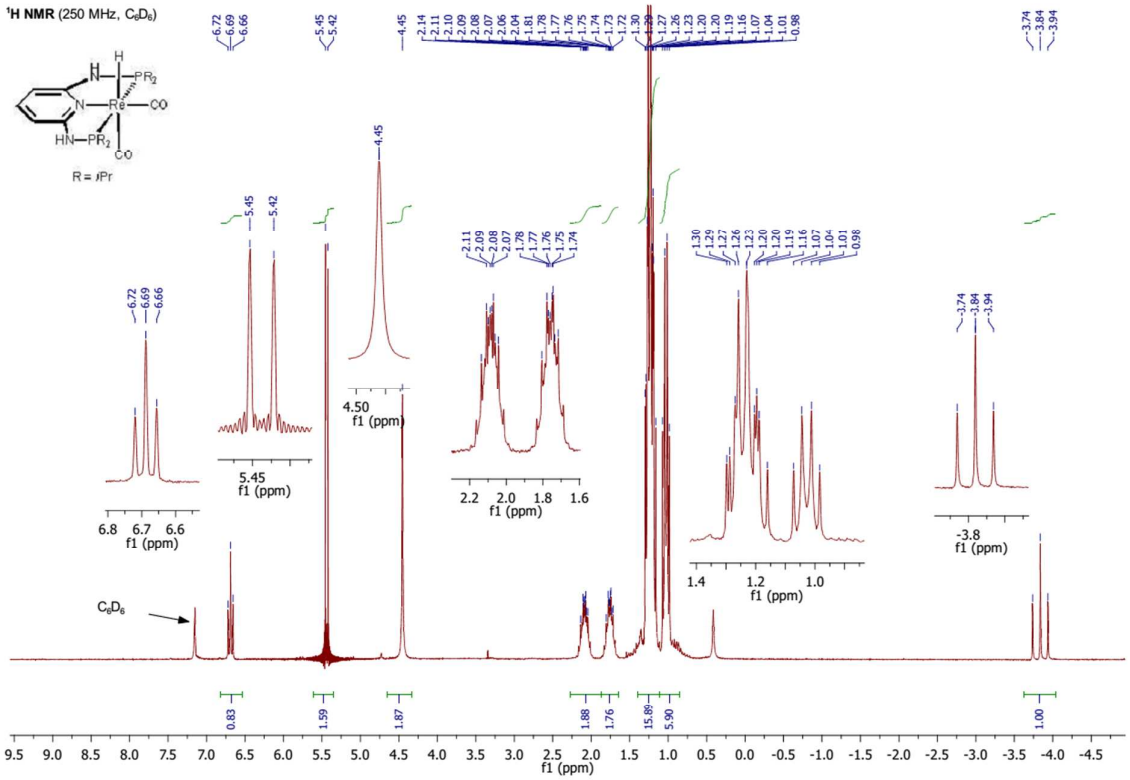


Figure S12: ^{13}C{^{1}H} NMR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$H] (**Re1**) (151 MHz, C_6D_6)

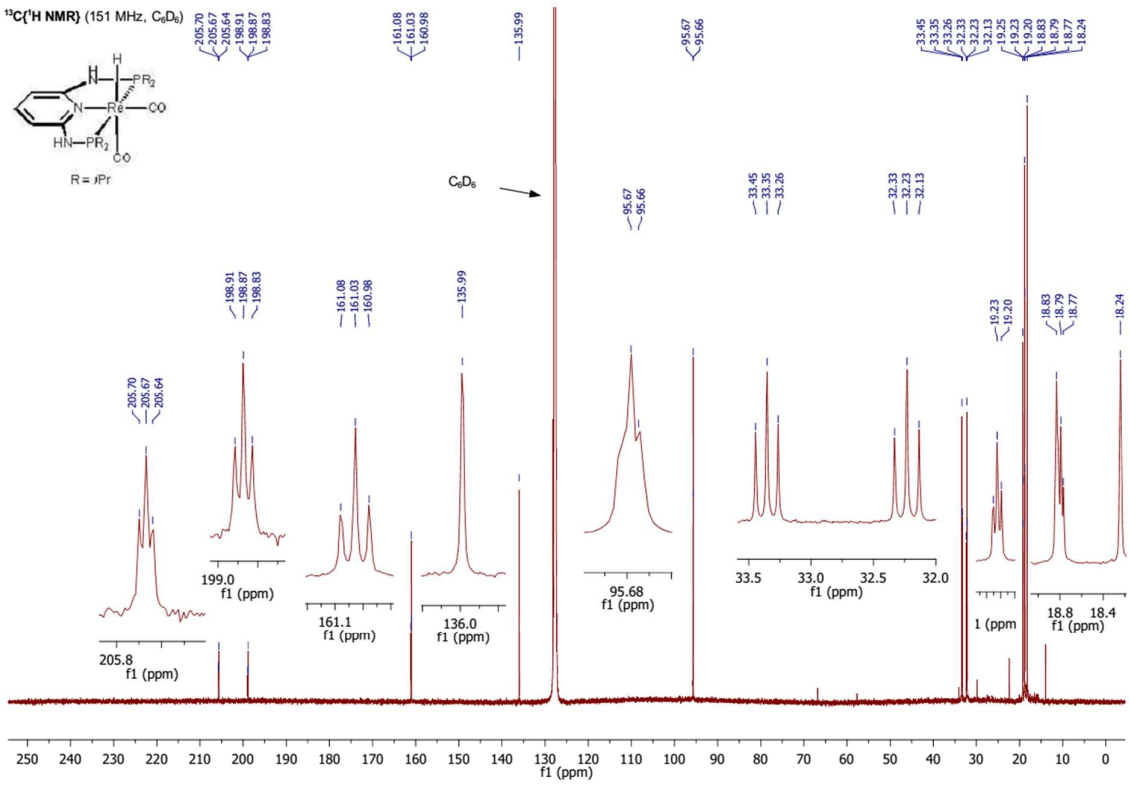


Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$H] (**Re1**) (101 MHz, C_6D_6)

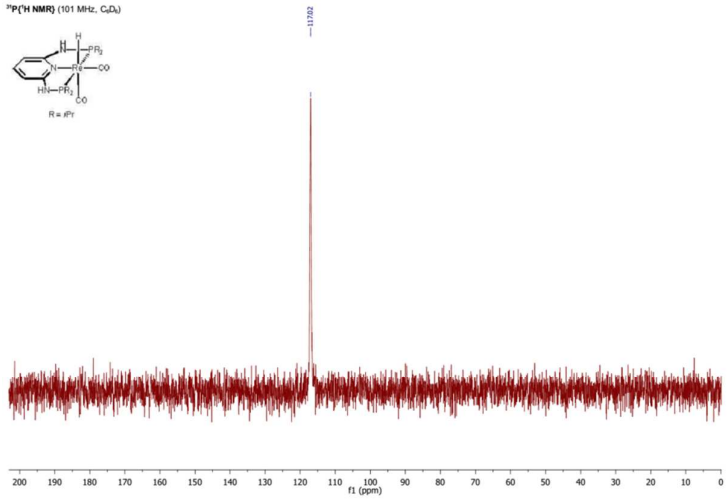


Figure S14: IR spectrum of *cis*-[Re(PNP^{NH}-*i*Pr)(CO)$_2$H] (**Re1**)

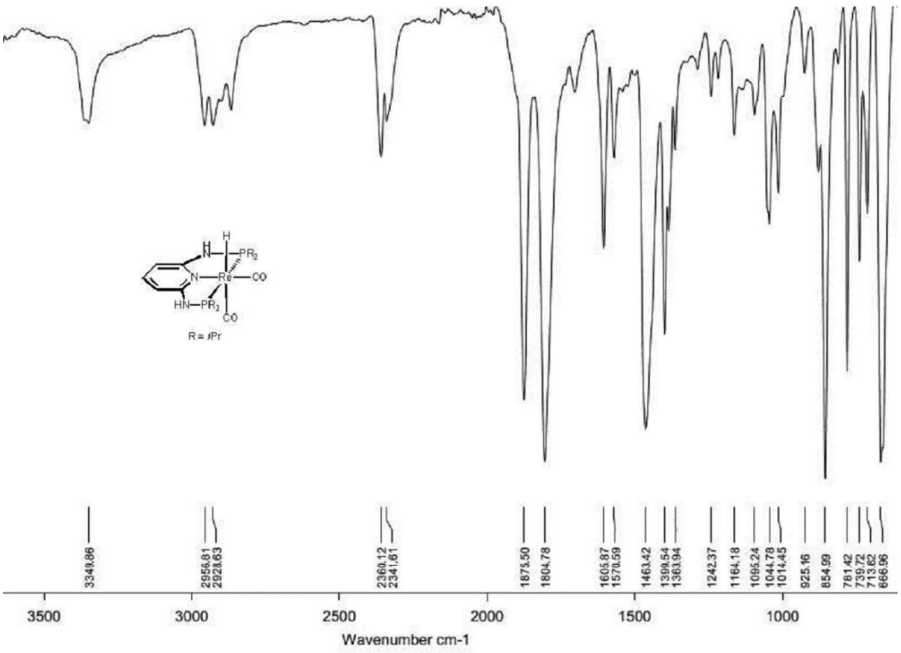


Figure S15: ^{1}H NMR spectrum of *cis*-[Re(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Re2**) (250 MHz, C_6D_6)

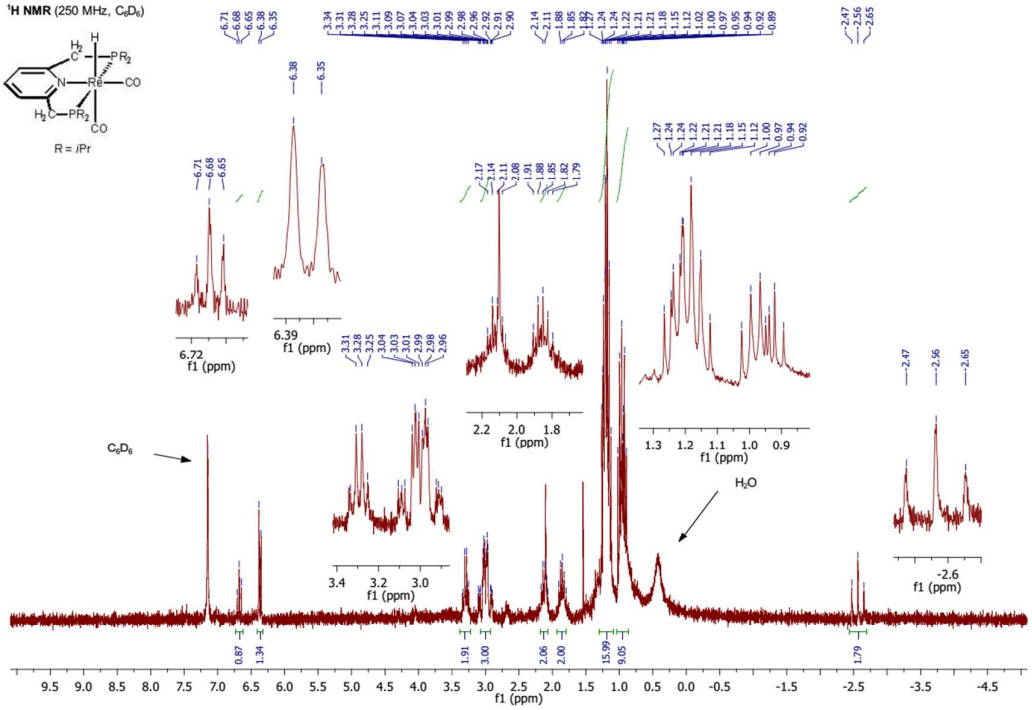


Figure S16: ^{13}C{^{1}H} NMR spectrum of *cis*-[Re(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Re2**) (151 MHz, CD_2Cl_2)

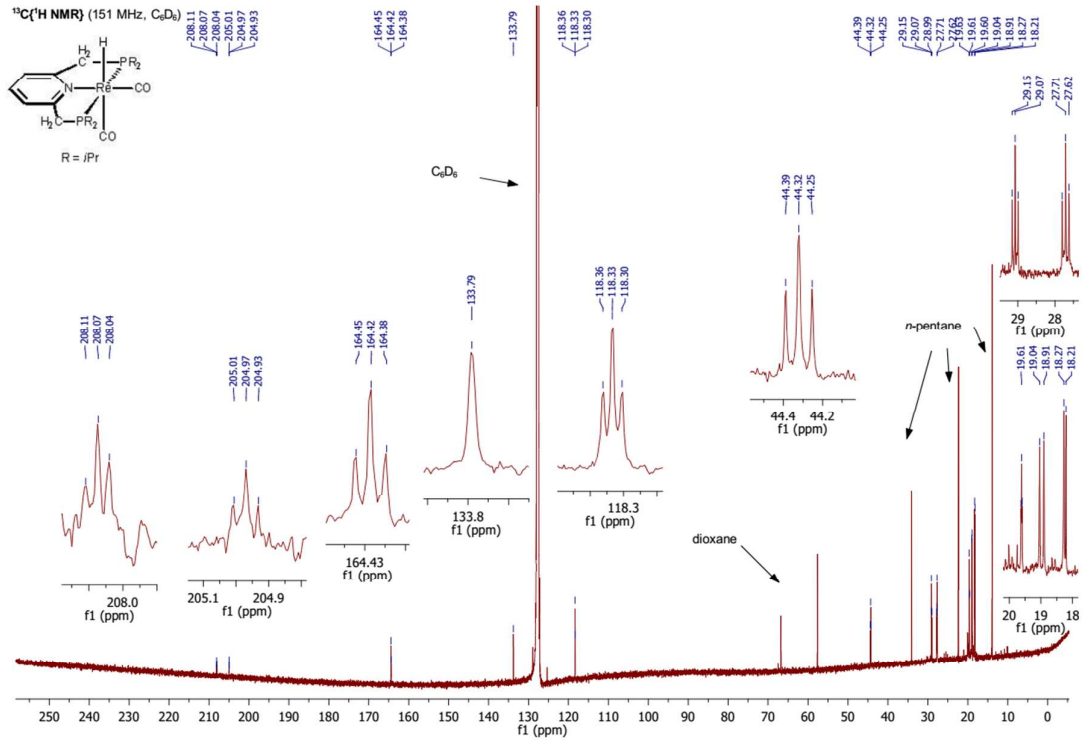


Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-[Re(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Re2**) (101 MHz, CD_2Cl_2)

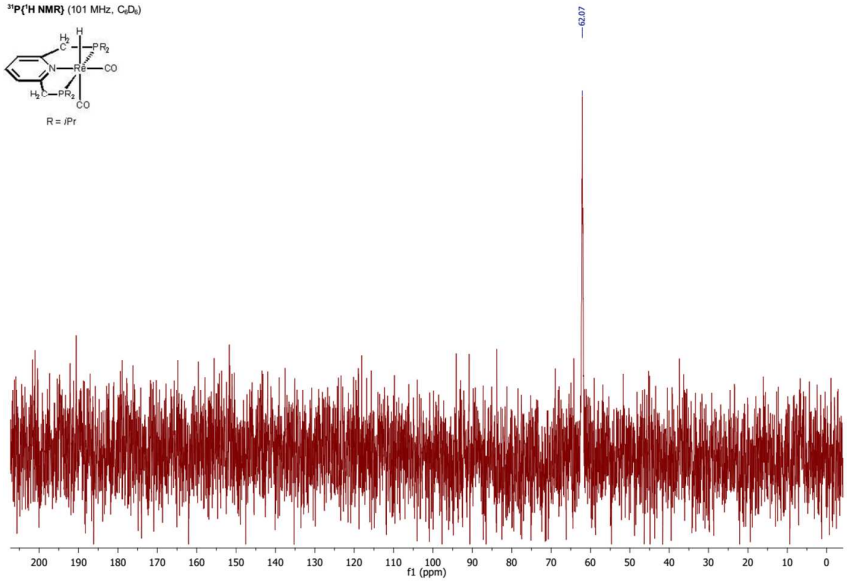
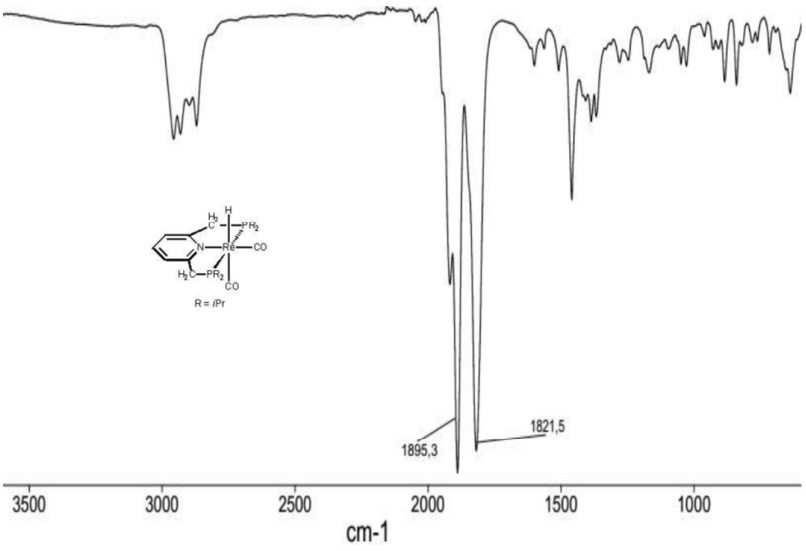


Figure S18: IR spectrum of *cis*-[Re(PNP^{CH2}-*i*Pr)(CO)$_2$H] (**Re2**)



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