



Supporting Information

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Saturated vs. Unsaturated: Ligand Addition to the Saturated Metal Site in an Unsaturated Binuclear Metal Complex**

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Experimental Section

General Data. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR were recorded on a Varian Mercury 400 spectrometer operating at 400.1 and 161.9 MHz, respectively. $^{13}\text{C}\{^1\text{H}\}$ NMR were recorded on a Varian Mercury 300 spectrometer operating at 75.5 MHz. Proton and phosphorus decoupled $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$ NMR and the variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were recorded on a Varian Inova 500 spectrometer operating at 125.8 MHz. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were externally referenced against 85% *ortho*- H_3PO_4 . Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. Electrospray mass spectrometric measurements were obtained on a MicroMass Q-ToF spectrometer. ^{13}CO (99 % ^{13}C , <5 % ^{18}O) was purchased from Aldrich and was used as received. Tri-*t*-

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butyl phosphine, PtBu_3 , was purchased from Strem and was used without further purification. The tri-*t*-butyl phosphine was handled under nitrogen and stored at $-80\text{ }^\circ\text{C}$ under nitrogen. $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_3$ was prepared according to the published procedure.^[1] Product separations were performed by thin layer chromatography (TLC) in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Preparation of $\text{Re}_2(\text{CO})_6(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **1.** Under an atmosphere of nitrogen, $\text{Re}_3(\text{CO})_{12}(\mu\text{-H})_3$ (50.3 mg, 0.056 mmol) and PtBu_3 (50 μL , 0.201 mmol) were dissolved in 20 mL of octane. The reaction mixture was heated to reflux for 6 h. The solvent was removed *in vacuo*, and the products were separated by TLC by using a 5:1 hexane/methylene chloride solvent mixture to yield in order of elution: 15.4 mg (31 % yield) of orange $\text{Re}_2(\text{CO})_6(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **1**, and 5.3 mg of a yellow band (currently being characterized). Spectral data for **1**: IR ν_{CO} (cm^{-1} in hexane): 2079 (s), 1993 (vs), 1969 (vs), 1954 (vs), 1923 (s), 1850 (s). ^1H NMR (400 MHz, [D8]toluene, rt, TMS): δ = 1.37 (d, $^3J(\text{P,H}) = 14\text{ Hz}$, 18 H; CH_3), 1.24 (d, $^3J(\text{P,H}) = 12\text{ Hz}$, 27 H; CH_3), -4.46 (dd, $^2J(\text{P,H}) = 12\text{ Hz}$, $^2J(\text{P,H}) = 5\text{ Hz}$, hydride 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, [D8]toluene, rt, 85% *ortho*- H_3PO_4): δ = 139.68 (d, $^2J(\text{P,P}) = 99\text{ Hz}$, 1P, $\mu\text{-PtBu}_2$), 84.31 (d, $^2J(\text{P,P}) = 99\text{ Hz}$, 1P, PtBu_3). Mass Spec. EI/MS m/z . 888. The isotope pattern is consistent with the presence of two rhenium atoms.

Preparation of $\text{Re}_2(\text{CO})_7(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **2.** Carbon monoxide gas (1 atm) was bubbled through a solution of **1** (15.4 mg, 0.017 mmol) in 20 mL of hexane. Within a few minutes the orange colored solution turned to yellow and then almost colorless. The CO gas was purged through this solution for a total of 10 min and an IR spectrum after

this time indicated complete conversion of the starting material **1**. The solvent was removed *in vacuo*, and the product was separated by TLC by using a 5:1 hexane/methylene chloride solvent mixture to yield 15.4 mg (97 %) of colorless **2**. Spectral data for **2**: IR ν_{CO} (cm⁻¹ in hexane): 2079 (m), 2018 (w), 1983 (m), 1974 (vs), 1953 (s), 1914 (m), 1908 (m). ¹H NMR (400 MHz, [D8]toluene, rt, TMS): **d** = 1.53 (d, ³J(P,H) = 14 Hz, 18 H; CH₃), 1.38 (d, ³J(P,H) = 12 Hz, 27 H; CH₃), -14.01 (dd, ²J(P,H) = 15 Hz, ²J(P,H) = 8 Hz, hydride 1H). ³¹P{¹H} NMR (162 MHz, [D8]toluene, rt, 85% *ortho*-H₃PO₄): **d** = 120.84 (d, ²J(P,P) = 71 Hz, 1P, μ -PtBu₂), 63.05 (d, ²J(P,P) = 71 Hz, 1P, PtBu₃). The isotope pattern is consistent with the presence of two rhenium atoms. The assignments of the respective ³¹P resonances were appropriately made from the selective phosphorus decoupled ¹H{³¹P}NMR experiments which showed the doublet at 1.53 ppm collapse into a singlet when the resonance at 120.84 ppm the ³¹P spectrum was irradiated. Accordingly, the doublet at 1.38 ppm collapsed into a singlet when the resonance at 63.05 ppm in the ³¹P spectrum was irradiated. Mass Spec. EI/MS *m/z*. 916. The isotope pattern is consistent with the presence of two rhenium atoms.

Conversion of 2 to 1. Compound **2** (15.0 mg, 0.016 mmol) in 10 mL of heptane was heated to reflux for 1½ h. IR at this time showed complete conversion of the starting material **2** to **1**. The solvent was removed *in vacuo*, and the product was separated by TLC by using a 5:1 hexane/methylene chloride solvent mixture to yield 14.0 mg (96 %) of orange **1**.

Preparation of ^{13}C enriched $\text{Re}_2(\text{CO})_7(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **2.** A 15.0 mg amount of **1** was dissolved in 25 mL of heptane in a 100 mL side-arm flask. The flask was evacuated and then filled with ^{13}CO . This solution was stirred for 30 min at room temperature during which time the color of the solution turned from orange to almost colorless affording ^{13}C enriched $\text{Re}_2(\text{CO})_7(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **2**. The ^{13}CO gas was then removed and the heptane solution heated to reflux for 1½ h under a purge of nitrogen to afford ^{13}C enriched $\text{Re}_2(\text{CO})_6(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **1**. The flask was then cooled to room temperature, evacuated and filled again with ^{13}CO and stirred for 30 min at room temperature. These series of steps were repeated 3 times to increase the enrichment still further. The heptane solvent was then removed *in vacuo*, and the ^{13}C enriched $\text{Re}_2(\text{CO})_7(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **2** was purified by TLC by using a 5:1 hexane/methylene chloride solvent mixture.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at room temperature is shown in Figure S1b. The splitting of the observed resonances is due to ^{31}P coupling. Selective phosphorus decoupled $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$ NMR experiment revealed that the three resonances at 188.6 ppm ($^2J(\text{P2,C})$ 25.9 Hz), 187.2 ppm ($^2J(\text{P2,C})$ 5.9 Hz) and 185.4 ppm ($^2J(\text{P2,C})$ 6.8 Hz) are coupled only to the bridging phosphorus atom P2. While the two resonances at 199.3 ($^2J(\text{P1,C})$ 8.0 Hz, $^2J(\text{P2,C})$ 5.5 Hz) and 195.7 ppm ($^2J(\text{P1,C})$ 5.2 Hz, $^2J(\text{P2,C})$ 3.0 Hz) are coupled to both P1 and P2. The three resonances coupled only to P2 are assigned to the carbonyl ligands on Re1 and they are too far away to observe coupling to P1. The resonance at 188.6 ppm is assigned to (CO)14 as this ligand is trans to P2 and therefore exhibits the largest P-C coupling of all ($^2J(\text{P2,C})$ 25.9 Hz). The resonance at 187.2 ppm is assigned to the two equivalent (CO)11 and (CO)13 ligands based on their large peak intensity and the

resonance at 185.4 ppm is assigned to (CO)12. The two resonances that show coupling to both phosphorus atoms are assigned to the carbonyls on Re2. The two equivalent CO ligands (CO)21 and (CO)23 are assigned to the resonance at 199.3 ppm because of the relative peak intensity and the resonance at 195.7 ppm is assigned to (CO)22.

Selective Addition of ^{13}CO to **1.** An unenriched sample of **1** (15.0 mg, 0.017 mmol) was dissolved in approximately 0.5 mL of toluene- d_8 in a 5 mm NMR tube and sealed with a rubber septum. The NMR tube was evacuated and filled with ^{13}CO . The NMR tube was shaken and within minutes the orange colored solution turned almost colorless. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at this time showed only one resonance at 187.2 ppm indicating that the site of CO addition was on Re1, see Figure S1a.

Preparation of ^{13}CO enriched $\text{Re}_2(\text{CO})_6(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **1.** The ^{13}CO enriched $\text{Re}_2(\text{CO})_7(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **2** prepared above was dissolved 10 mL of heptane and heated to reflux for 1½ h. The solvent was removed *in vacuo*, and the product was purified by TLC by using a 5:1 hexane/methylene chloride solvent mixture. A mass spectrum of this sample of **2** showed that it was enriched with ^{13}CO at the amount of approximately 30% which is consistent with the method of preparation.

Variable Temperature $^{13}\text{C}\{^1\text{H}\}$ NMR for Compound **1.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **1** in the carbonyl region at various temperatures is shown in Figure S2. The limiting spectrum at -110 °C shows two sharp resonances at 188.7 ppm and 190.5 ppm which are assigned to (CO)12 and (CO)14 respectively. There are two very broad

resonances in the baseline at 201 ppm and 208 ppm for (CO)21 and (CO)22 and another very broad resonance in the baseline at 186 ppm for (CO)11 and (CO)13. These are pairs of CO's that are exchanging with each other but not with the other CO ligands in the complex. The exchange process is very rapid and one would have to go much lower in temperature to reach the slow exchange limit. The coalescence temperature for this process appears is estimate to be at -100 °C and the rate of exchange at the coalescence temperature (k_c) was estimated by using the expression $k_c = \pi \Delta\nu_0 / (2)^{1/2}$, where $\Delta\nu_0$ is the chemical shift difference between the maxima of the two broad resonances observed at -110 °C. Substitution of k_c in the Eyring equation provides the free energy of activation for the process at the coalescence temperature ΔG^\ddagger (at 173 K) = 7.3 kcal / mol. As the temperature is raised, the two broad resonances coalesce and sharpen at -40 °C. This process represents one of three dynamical processes occurring in compound **1**. A second dynamical process occurs in the temperature range -40 °C – +50 °C. At 10 °C the three resonances at 187.8, 188.7 and 190.5 ppm start to broaden and as the temperature is raised, they average to a broad resonance at 50 °C. This second dynamical process is a result of all the CO's on Re1 exchanging. While this second dynamical process is occurring, yet a third dynamical process begins as is apparent in the broadening of the peak at 204.2 ppm. This indicates that the CO's on Re2 are starting to exchange with the CO's on Re1. As the temperature is raised to 108 °C, the two resonances coalesce and at 140 °C they are averaged and begin to sharpen into a single resonance. This third dynamical process shows that the CO ligands in **1** are now exchanging between the two rhenium centers.

Preparation of $\text{Re}_2(\text{CO})_6(\text{NCMe})(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})$, **3.**

Compound **1** (9.9 mg, 0.011 mmol) was dissolved in approximately 0.6 mL of acetonitrile in a medium vial (1 dram size, 3.7 mL). The solution was then concentrated to about half the volume and placed in a freezer at $-25\text{ }^\circ\text{C}$ for ~ 2 days to yield 8.5 mg (82 % yield) of light yellow/colorless crystals of **3**. Spectral data for **3**: IR ν_{CO} (cm^{-1} in acetonitrile): 2018 (w), 2000 (s), 1909 (vs), 1889 (sh). ^1H NMR (400 MHz, CD_3CN , rt, TMS): δ = 1.60 (d, $^3J(\text{P,H}) = 12$ Hz, 27 H; CH_3), 1.50 (t, $^3J(\text{P,H}) = 13$ Hz, 18 H; CH_3), -11.76 (dd, $^2J(\text{P,H}) = 16$ Hz, $^2J(\text{P,H}) = 9$ Hz, hydride 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN , rt, 85% *ortho*- H_3PO_4): δ = 114.09 (d, $^2J(\text{P,P}) = 67$ Hz, 1P, $\mu\text{-PtBu}_2$), 65.26 (d, $^2J(\text{P,P}) = 67$ Hz, 1P, PtBu_3). The ^1H NMR when taken on a 300 MHz instrument, the triplet (overlapping doublet of doublets) splits into a doublet of doublets. Mass Spec. ES^+/MS calcd. for M^+ , $[\text{Re}_2(\text{CO})_6(\text{NCMe})(\text{PtBu}_3)(\mu\text{-PtBu}_2)(\mu\text{-H})]^+$ 929, found 929. The isotope pattern is consistent with the presence of two rhenium atoms. NOTE: Compound **3** goes back to **1** when acetonitrile is removed.

At $45\text{ }^\circ\text{C}$ the triplet (overlapping doublet of doublets) becomes a doublet indicating that the ^tBu groups on the bridging P are now equivalent.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** having all CO sites partially enriched with ^{13}CO , was obtained by dissolving the ^{13}CO enriched sample of **1** in CD_3CN . The spectrum with the peak assignments is shown in Figure S3. There are six resonances all of equal intensity for the six inequivalent CO ligands. Just as in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **2** the three higher field resonances at 193.5 ppm, 196.2 ppm and 196.8 ppm are assigned to the CO's on Re1. The large coupling of ($^2J(\text{P2,C})$ 38.5 Hz) for the peak at 196.8 is attributed to (CO)13 which is trans to the bridging phosphine atom P2. The lower field

resonances at 200.1, 201.9 and 203.1 ppm are assigned to the CO's on Re2. The resonances at 201.9 and 203.1 ppm are assigned to either (CO)11 and (CO)13. It is interesting to note that these two CO ligands were equivalent in compound **2** at 195.7 ppm, however now they are inequivalent due to the lowering in symmetry produced by the presence of the NCMe ligand.

Crystallographic Analyses: Red single crystals of **1** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at -25 °C. Colorless single crystals of **2** were obtained by slow evaporation of diethyl ether at -25 °C. Colorless single crystals of **3** were obtained by slow evaporation from a methylene chloride/acetonitrile/heptane solution at -25 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.^[2] Correction for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 , by using the SHELXTL software package.^[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Compound **1** crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with either of the space groups *Pnma* or *Pna2₁*. The structure could only be solved in the latter space group. The hydrido ligand was located and refined successfully with isotropic thermal parameters.

Compounds **2** and **3** crystallized in the monoclinic crystal system. The systematic absences in the intensity data identified the unique space group *P2₁/c*. The hydrido ligands in both compounds were located and refined successfully with isotropic thermal parameters.

Molecular Orbital Calculations. A single point molecular orbital calculation on **1** was performed on the molecular structure as derived from the single crystal x-ray diffraction analysis. PH₃ was used in place of PtBu₃ in these calculations. The molecular orbital calculations reported herein were performed by using the Fenske-Hall method.^[4] Contracted double- ζ basis sets were used for the Re 5d, P 3p, and C and O 2p atomic orbitals. The Fenske-Hall molecular orbital method is an approximate self-consistent-field (SCF) nonempirical method that is capable of calculating molecular orbitals for very large transition metal systems and has built-in fragment analysis routines that allow one to assemble transition metal cluster structures from the ligand-containing fragments.

References

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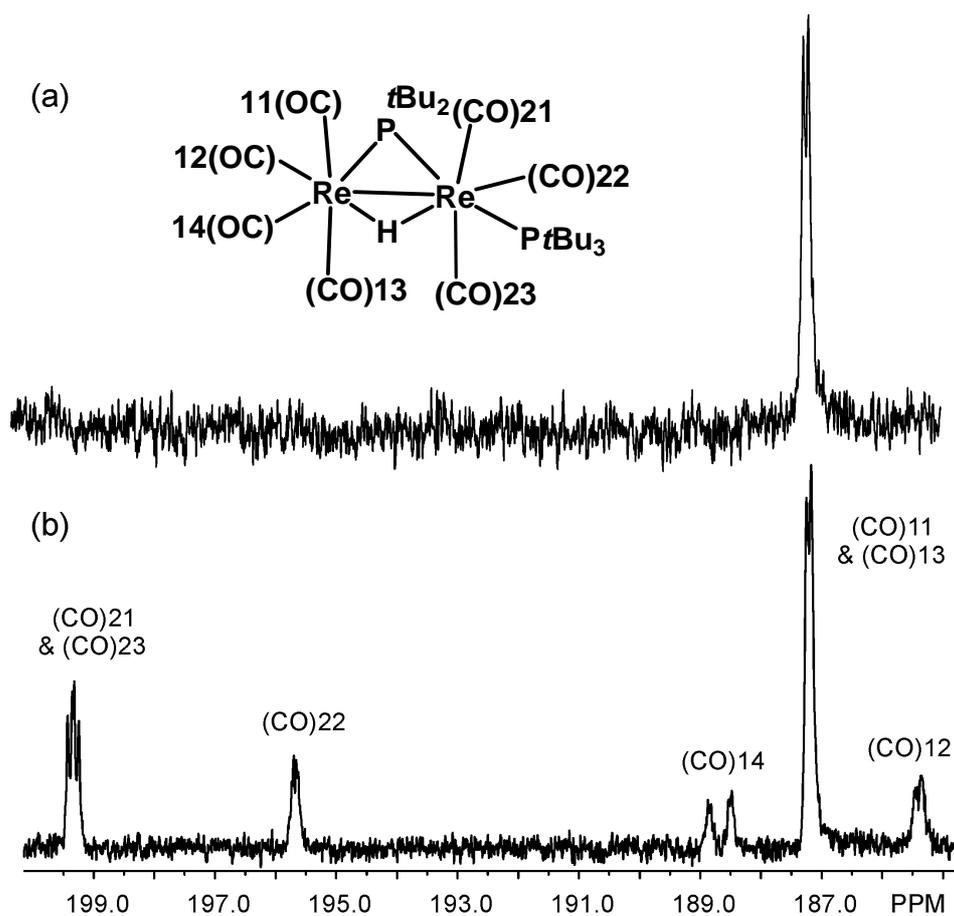


Figure S1. (a) ^{13}C $\{^1\text{H}\}$ NMR spectrum of a sample of **2** formed by the addition of CO enriched with ^{13}CO . (b) A ^{13}C NMR spectrum of **2** having all CO sites enriched with ^{13}CO .

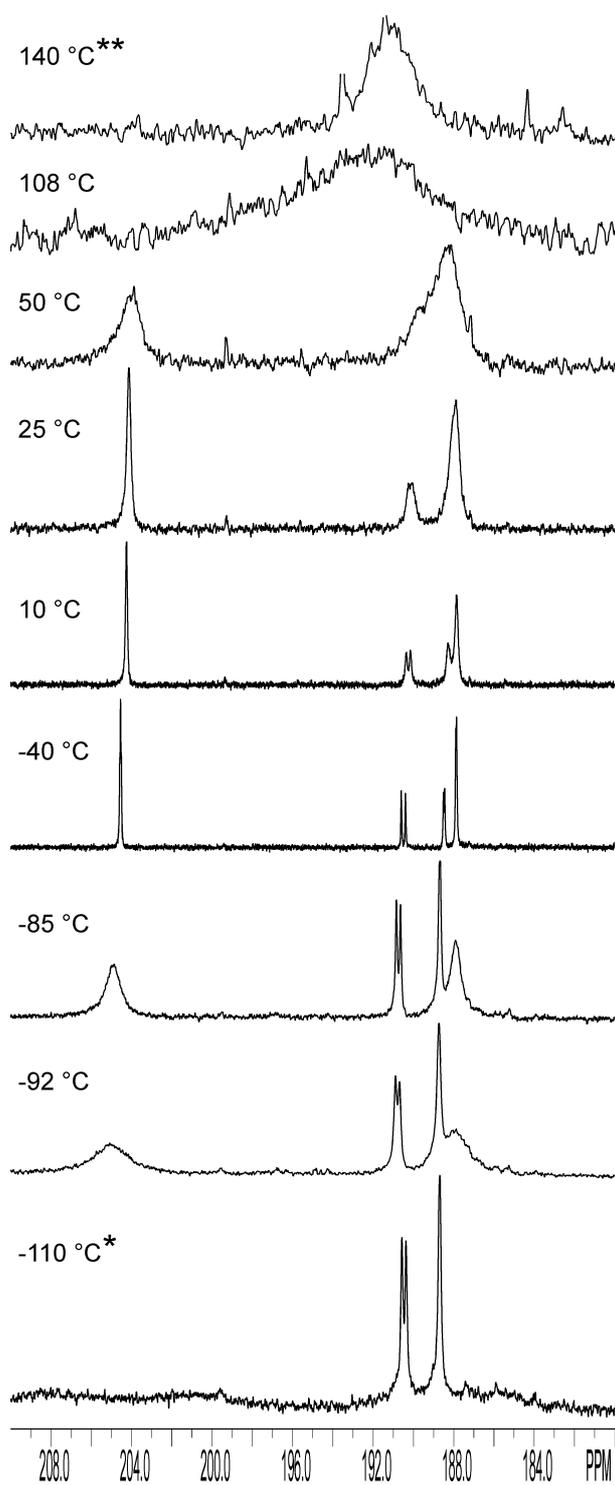


Figure S2. Variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for compound **1** in $[\text{D}_8]$ toluene solvent.

*The spectrum at -110 °C was recorded in diethyl ether solvent with a drop of CD_2Cl_2 .

** The spectrum at 140 °C was recorded in xylene solvent with a drop of $[\text{D}_8]$ toluene.

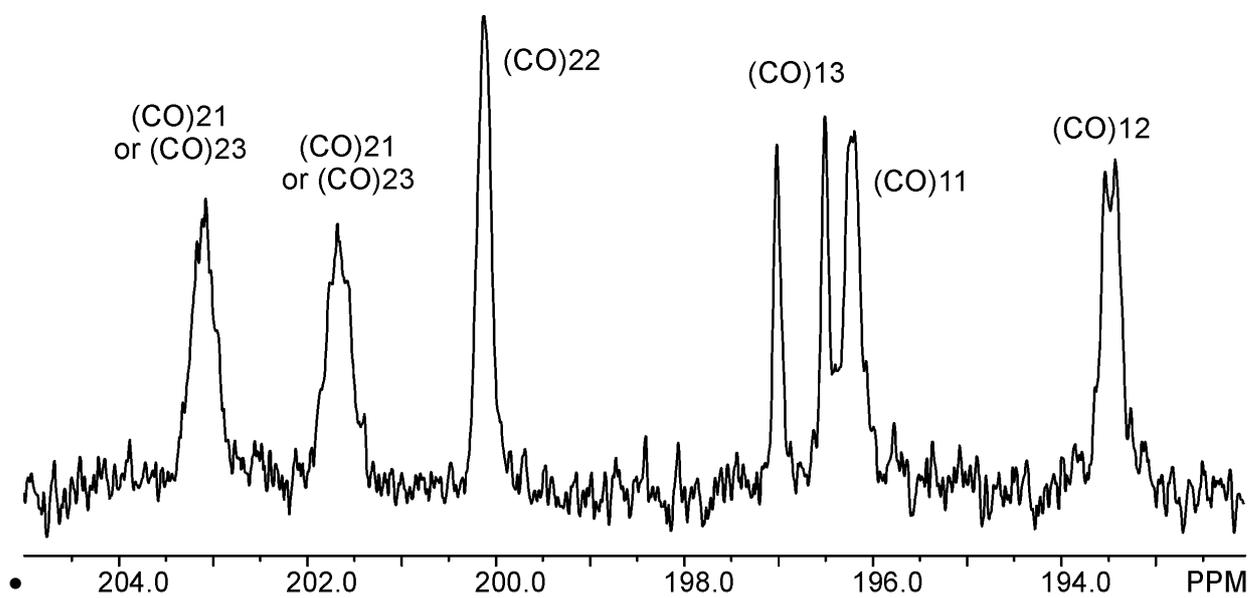


Figure S3. A ^{13}C { ^1H } NMR spectrum of **3** in the CO region. The CO sites were enriched approx 30% with ^{13}C . Recorded in CD_3CN solvent.

Table 1. Crystallographic Data for Compounds 1, 2 and 3.

	1	2	3
Empirical formula	Re ₂ P ₂ O ₆ C ₂₆ H ₄₆	Re ₂ P ₂ O ₇ C ₂₇ H ₄₆	Re ₂ P ₂ O ₆ N ₁ C ₂₈ H ₄₉
Formula weight	888.97	916.98	930.02
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Lattice parameters			
a (Å)	21.1976(10)	16.4619(4)	11.0279(4)
b (Å)	17.2257(8)	11.8441(3)	29.6026(10)
c (Å)	8.8901(4)	16.9897(4)	10.7886(3)
β (deg)	90	93.057(1)	105.577(1)
V (Å ³)	3246.2(3)	3307.88(14)	3392.63(19)
Space group	<i>Pna2</i> ₁ (# 33)	<i>P2</i> ₁ / <i>c</i> (# 14)	<i>P2</i> ₁ / <i>c</i> (# 14)
Z value	4	4	4
ρ _{calc} (g / cm ³)	1.819	1.841	1.821
μ (Mo Kα) (mm ⁻¹)	7.583	7.441	7.261
Temperature (K)	294	294	294
2Θ _{max} (°)	56.90	56.62	56.60
No. Obs. (I > 2σ(I))	7338	7468	7412
No. Parameters	345	362	356
Goodness of fit	1.078	1.061	1.101
Max. shift in cycle	0.002	0.001	0.002
Residuals*: R1; wR2	0.0279; 0.0626	0.0217; 0.0539	0.0227; 0.0532
Absorption Correction,	Multi-scan	Multi-scan	Multi-scan
Max/min	1.000/0.512	1.000/0.582	1.000/0.832
Largest peak in Final Diff. Map (e ⁻ / Å ³)	2.390	1.588	1.201

$$*R = \frac{\sum_{hkl} (|F_{obs}| - |F_{calc}|)}{\sum_{hkl} |F_{obs}|}; R_w = \left[\frac{\sum_{hkl} w (|F_{obs}| - |F_{calc}|)^2}{\sum_{hkl} w F_{obs}^2} \right]^{1/2}, w = 1/\sigma^2(F_{obs}); GOF = \left[\frac{\sum_{hkl} w (|F_{obs}| - |F_{calc}|)^2}{(n_{data} - n_{vari})} \right]^{1/2}.$$