

Activation of H₂ with Manganese(I)-Phosphido Complexes

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Abstract: Metal-ligand cooperativity (MLC) predominantly occurs across transition-metal amido moieties. In contrast, there are few reports of activation of H₂ or substrate across metal–phosphido linkages, and all of the first-row metal examples use *N*-heterocyclic phosphido donors. In this report, we highlight a discovery of the first MLC dihydrogen activation with first-row transition metal M-PR₂ (R = alkyl or aryl) complexes using dinuclear Mn(I)-bisphosphido complexes. In addition, we demonstrate that oxidative addition of P–Cl bond leads to the same Mn(I)-bisphosphido complexes at elevated temperatures, enabling a simple and versatile strategy for in-situ reduction of phosphine chlorides to phosphine using dihydrogen, a process that appears general having success with both diaryl- and dialkyl-phosphines.

Metal-ligand cooperative (MLC) dihydrogen activation is important for its utility in organic synthesis and implications in hydrogen storage.¹ A majority of transition-metal-based systems that use the MLC paradigm rely on H₂ activation across M–amido linkages (Figure 1, top) and only a handful of examples of MLC-based H₂ activation involving M–phosphido linkages with second and third-row metals are known known (M = Zr,² Hf,³ Ru,^{4,5} Ir⁵). Examples with first-row metals are even more rare. The only example includes the work of Thomas⁷ and coworkers that used a tridentate pincer scaffold with a central *N*-heterocyclic phosphido (NHP) donor on a Co complex. The reverse reaction, photochemical H₂ formation, was demonstrated using a Mn(H)–*N*(H)-heterocyclic phosphine,⁸ which was prepared by sequential hydride and proton addition to a Mn–NHP complex. The NHP ligands temper the basicity of unruly phosphido ligands (Figure 1, middle), but this strategy precludes readily available diaryl and dialkyl phosphido groups in MLC.

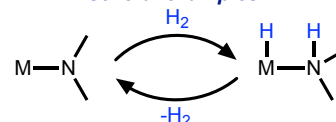
We hypothesized that the use of highly electron deficient metal centers, or those substantially compensated with a plethora of electron withdrawing supporting ligands, could stabilize phosphido groups enough to enable H₂ activation across M–P linkages. We recognized that dinuclear Mn(I) complexes bearing phosphido bridges such as [Mn(CO)₄(μ-PR₂)₂] (1, R = Ph; 5, R = *i*Pr) are well-suited to this end. Such dinuclear Mn(I) phosphido complexes have been known for a long time now. For instance, 1 was prepared first in 1964 by Hayter by reacting Mn₂(CO)₁₀ with Ph₂P–PPh₂ or treating Na[Mn(CO)₅] with ClPh₂P,⁹ and since then some alternative syntheses for 1 and related compounds have been discovered.^{10,11,12} Although some reactions surrounding the chemistry of 1 have been reported,¹³ its reaction with dihydrogen has not been studied. We therefore endeavored to test the hypothesis that 1 can activate H₂ in an MLC-type mode and report the results herein.

In addition to reporting a rare example H₂ activation across a first-row metal–phosphido bond, we discovered that Mn₂(CO)₁₀ will oxidatively add P–Cl bonds in ClPR₂ (R = Ph or *i*Pr) to form the bis-phosphido complexes. The utility of this reaction is the *in-situ* reduction of secondary phosphine chlorides to secondary phosphines using molecular dihydrogen and commercially

available Mn complexes. Conventionally, this reduction is accomplished using strong hydride donors (such as LiAlH₄), require laborious work-ups, and demand strict oxygen and moisture free conditions.¹⁴

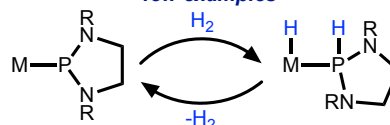
common metal-ligand cooperative H₂ activation

several examples



metal-ligand cooperative H₂ with *N*-heterocyclic phosphido

few examples



metal-ligand cooperative H₂ with phosphido ligands

unknown for first-row metals

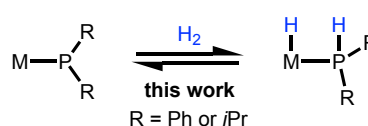
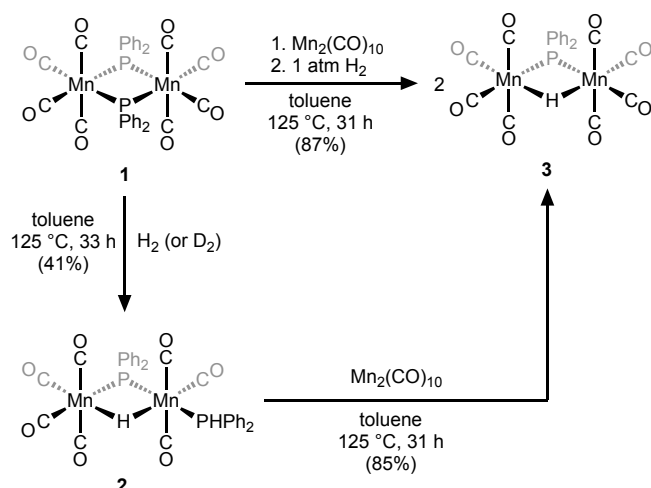


Figure 1. Conventional metal-ligand cooperative (MLC) activation occurs across M–amido linkages (top). First-row metals known to activated H₂ across M–P bonds rely on *N*-heterocyclic phosphido (NHP) ligands (middle). This work describes the first example of M–PR₂ MLC activation of H₂ where M = first-row metal and R = alkyl or aryl substituent (bottom).

To test H₂ activation across Mn–P bonds, 1 was subjected to heating under an H₂ atmosphere which resulted in the formation of 2 in moderate yields (Scheme 1). The moderate yield is partly due to the insolubility of 1 in the reaction medium and also the reversibility of the reaction (*vide infra*). The ¹H NMR spectrum of 2 contains a resonance at -16.17 ppm (1H, *dd*, *J*_{PH} = 30, 30 Hz), which appears as an apparent triplet, but is actually a doublet corresponding to a single bridging hydride coupled to two chemically inequivalent phosphorus atoms, i.e. the bridging phosphido group (*J*_{P-H} = 30 Hz) and the L-type phosphine (*J*_{P-H} = 29 Hz). The ³¹P{¹H} NMR spectrum of 2 contains two resonances, one at 43.8 ppm (bs) corresponding to the L-type diphenyl phosphine and another at 165 ppm (bs) corresponding to the bridging phosphido group. The ¹H NMR spectrum also contains a doublet at 6.78 ppm with a large coupling (*J*_{PH} = 350 Hz) indicative of a P–H bond. Since the ³¹P and ³¹P{¹H} spectra show broad singlets (*Δw*_{1/2} = 100 Hz), presumably due to quadrupolar

coupling with the two manganese nuclei ($I = 5/2$), the J_{P-P} coupling constants were not determined. Similar peak broadening induced by neighboring Mn nuclei ($I = 5/2$) is well documented for related compounds.^{15,19} Collectively, along with the ATR-FTIR spectrum, the formulation of **2** is $\{[\text{Mn}(\text{CO})_4(\mu\text{-H})(\mu\text{-PPh}_2)\{\text{Mn}(\text{CO})_3(\text{Ph}_2\text{PH})\}]\}$ (Scheme 2). The characterization data also matches the spectroscopic assignment for the same compound isolated by Mays as an intermediate during the photolytic reaction of $[(\text{Cp})(\text{CO})_2\text{Ru-Mn}(\text{CO})_5]$ with diphenylphosphine (Ph_2PH).¹⁶

Scheme 1. H_2 and PH activation w/ dinuclear Mn/P system

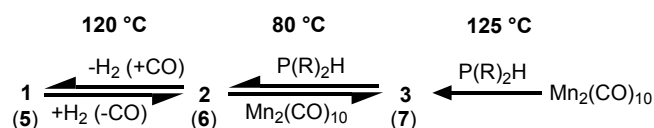


The monodentate phosphine in **2** can be further carried on in useful chemistry. For instance, the known complex $\{[\text{Mn}(\text{CO})_4(\mu\text{-H})(\mu\text{-PPh}_2)\{\text{Mn}(\text{CO})_4\}]\}$ (**3**) is typically prepared by reacting $\text{Mn}_2(\text{CO})_{10}$ with diphenylphosphine (Ph_2PH).¹⁷ To demonstrate the utility of **2** as a phosphine synthon, **2** was allowed to react with $\text{Mn}_2(\text{CO})_{10}$ and the product was **3**, isolated in 85% yield. Likewise, a mixture of **1**, $\text{Mn}_2(\text{CO})_{10}$, and H_2 resulted in direct formation of **3** in 87% yield (Scheme 2).

As noted above, the formation of **2** from **1** and dihydrogen does not go to completion and one reason was stated to be the poor solubility of **1**. However, there also appears to be reversibility that precludes complete conversion (Scheme 2). To test this hypothesis, we examined the possibility of **2** thermally converting back to **1** with loss of H_2 . When **3** is treated with an equivalent of free diphenylphosphine (Ph_2PH) at 80 °C, clean and near quantitative conversion to **2** is observed (Figure S22). However, if the reaction is carried out at 120 °C, **1** is detected as the major product, as observed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy, along with a small amount of **2** and H_2 (Figures S23 and S24).

This reversibility is akin to that observed for somewhat related osmium-phosphido/phosphine complex.¹⁸ However, the closely related cyclohexyl analogue of **2** appears not to exhibit the same reversibility.¹⁹ Thus, we suspect the P-H bond activation and H_2 activation across M-P bonds is likely both steric and electronically controlled by the phosphorus substituents (*vide infra*).

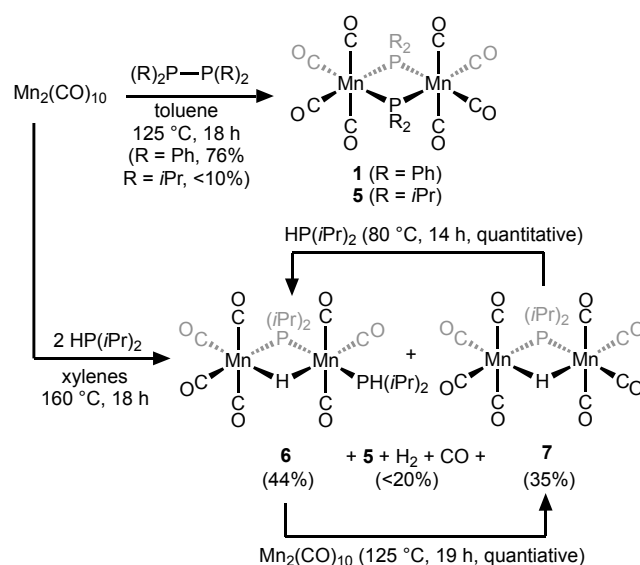
Scheme 2. Observed reversibility of Mn-P/ H_2 activation



To test this, we sought to prepare **5** via various known routes for related compounds (Scheme 3). Following an analogous procedure used to prepare **1**, oxidative addition of

tetraisopropylbisphosphide $[(i\text{Pr})_2\text{P-P}(i\text{Pr})_2]$ across $\text{Mn}_2(\text{CO})_{10}$ shows formation of **5** as a minor product (Scheme 3, top) as evidenced by the broad peak at -34.8 ppm in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum (Figure S25). Another route used to prepare $[\text{Mn}(\text{CO})_4(\mu\text{-PR}_2)]_2$ ($\text{R} = \text{Ph}, \text{Me}$) uses $\text{Na}[\text{Mn}(\text{CO})_5]$ and ClPR_2 .⁹ Hence, we attempted a similar reaction with $\text{Cl}(i\text{Pr})_2\text{P}$ but detected only a minor amount of **5** on ^{31}P -NMR spectrum and $[(i\text{Pr})_2\text{P-P}(i\text{Pr})_2]$ was the major product observed (Figure S26). This indicates that **5** is likely the major product but that it reductively eliminates $[(i\text{Pr})_2\text{P-P}(i\text{Pr})_2]$. Alternatively, following an analogous procedure used to prepare $[\text{Mn}(\text{CO})_4(\mu\text{-PCy}_2)]_2$,²⁰ refluxing $\text{Mn}_2(\text{CO})_{10}$ and two equivalents of diisopropylphosphine $[(i\text{Pr})_2\text{PH}]$ in xylene yielded a mixture of two main products, $\{[\text{Mn}(\text{CO})_4(\mu\text{-H})(\mu\text{-P}(i\text{Pr})_2)\{\text{Mn}(\text{CO})_3(\text{PH}(i\text{Pr})_2)\}]\}$ (**6**) and $\{[\text{Mn}(\text{CO})_4(\mu\text{-H})(\mu\text{-P}(i\text{Pr})_2)\{\text{Mn}(\text{CO})_4\}]\}$ (**7**), and minor quantities of **5** (Scheme 3, bottom). GC analysis of the reaction headspace shows the presence of CO and H_2 (Figure S29). Overall, the observations summarized in Scheme 2 and Scheme 3 support the general reversible MLC activation of H_2 and P-H bonds across dinuclear (formally) monovalent Mn-centers.

Scheme 1. Synthesis of **5**, **6**, & **7**



To confirm the identity of **6** and **7**, we synthesized the new complexes independently. Complex **7** was prepared in high yield by the direct reaction of $\text{Mn}_2(\text{CO})_{10}$ with $(i\text{Pr})_2\text{PH}$ and Me_3NO in toluene (Scheme 4). The presence of a bridging hydride in **7** was confirmed by a doublet at -16.76 ppm ($J_{P-H} = 30$ Hz) in the ^1H NMR and the bridging phosphido group shows a very downfield resonance at 190.5 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figures S16 and S17), overall consistent with known analogs and **3**.^{19,21} Additionally, the structure was confirmed using single-crystal XRD (Figure 2). Both the Mn(I) centers are hexa-coordinated with a $\text{Mn}\cdots\text{Mn}$ distance of 2.94 Å, which is comparable to the $\text{Mn}\cdots\text{Mn}$ distance reported for **3** (2.95 Å) and other dialkyl-phosphido bridged analogues,^{19,22} however, this short distance is not a M-M bond but a 3-centered 2-electron bond in the usual formalism for bridging hydride ligands.

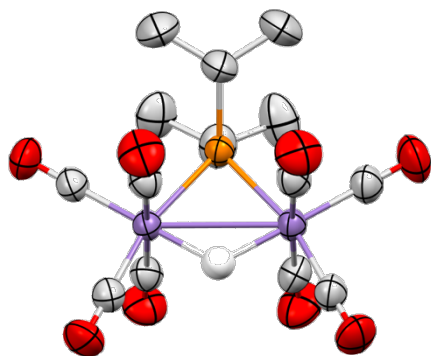
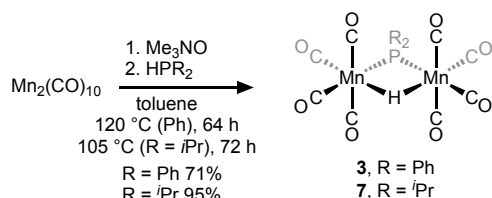


Figure 2. Molecular structure of **7** with H-atoms (except the bridging hydride) omitted for clarity. Thermal ellipsoids shown at 50% probability. Color scheme: white = H; grey = C; red = O; orange = P; purple = Mn. Selected distances and angles: Mn···Mn = 2.9378(5) Å; Mn1–P = 2.2991(5) Å; Mn2–P = 2.2994(6) Å; Mn1–P–Mn2 = 79.41(2)°.

Scheme 2. Independent synthesis of **3** and **7**

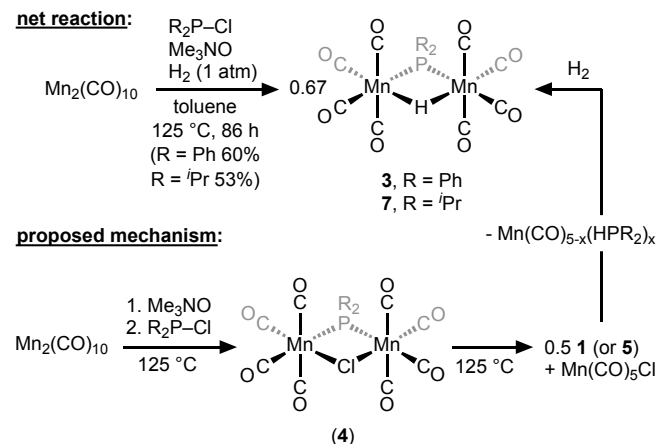


Reaction of **7** and one equivalent of (*i*Pr)₂PH at 80 °C leads to the near quantitative formation of the new complex **6** (Figures S11–S15). Complexes **6** and **7** behave similarly to **2** and **3** (see Scheme 1 and Scheme 2), except that attempts to convert **7** into **5** (analogous to conversion of **3** to **1**) is significantly lower yielding (Figures S30 and S31).

We also tested the ability of Mn₂(CO)₁₀ to activate P–Cl bonds. We treated Mn₂(CO)₁₀ with one equivalent of chlorodiphenylphosphine (Cl(Ph)₂P) under an H₂ atmosphere. Originally, we hypothesized the formation of the known compound [{Mn(CO)₄}(μ-Cl)(μ-PPh₂){Mn(CO)₄}] (**4**)²³ as an intermediate which could subsequently activate H₂, liberate HCl, and form **3**. When we performed this experiment, **3** formed but only in maximum yield of 60% along with other yellow byproducts including **1** (< 5%). Inclusion of base had no effect on the reaction, and we did not observe the expected conjugate acid formation (e.g., no [Et₃NH]Cl formed with inclusion of Et₃N).

To account for these observations, we propose the mechanism in Scheme 5. Namely, Mn₂(CO)₁₀ and ClPh₂P react to initially form **4** that subsequently dissociates leading to the formation of **1** and presumably Mn(CO)₅Cl, the latter of which giving rise to the other yellow byproducts. H₂ activation across the Mn–P bond of **1** is thus expected to give **2**, which in the presence of unreacted Mn₂(CO)₁₀ ultimately yields **1** as the final product; dihydrogen activation was confirmed using D₂ furnishing [{Mn(CO)₄}(μ-D)(μ-PPh₂){Mn(CO)₄}] **3**^D (Figures S36–S38). The maximum theoretical yield for **3** predicted by this mechanism is 66.67% based on Mn₂(CO)₁₀ and is overall consistent with our isolated yields of **3** (ref. SI for further discussion). It is also worth noting that although **4** (R = Ph) is a known compound, it is prepared at room temperature via pathways eschewing P–Cl bond activation.²³ Likely, **4** decomposes in the forcing conditions required to activate the P–Cl bonds which do not cleave until elevated temperatures.

Scheme 5. Net reaction and proposed mechanism for P–Cl bond oxidative addition and subsequent MLC across Mn–P bonds (see SI for full net rxn)



Collectively, these reactions point to a versatile H₂ activation mode using diaryl-substituted phosphido ligands. We wanted to test if this reaction was general and turned to the commonly used (*i*Pr)₂PCl to prepare analogous isopropyl complexes. Thus, treating a mixture of Mn₂(CO)₁₀ and (*i*Pr)₂PCl with H₂ and heating resulted in formation of the new species **7** in 53% yield.

To summarize, we demonstrated herein the first example of MLC-based H₂ activation in first-row transition-metal dialkyl- and diaryl-phosphido complexes. We confirmed this using simple Mn starting materials and simple phosphines showing that NHP's are not necessarily required to engender MLC capability to first-row metal phosphido groups. Additionally, we established P–Cl bond activation and reduction to phosphines. Together, the MLC activation of H₂ using readily available phosphine and phosphine chloride complexes at dinuclear Mn centers appears to have potential versatile applications.

Acknowledgements

Supported by NSF CAREER award 1847933.

Keywords: Phosphido • H₂ activation • manganese • first-row metals

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General considerations

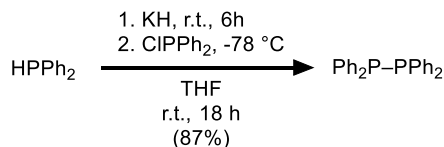
All chemicals were used as purchased from chemical vendors unless otherwise noted. Sodium sand,¹ Na[Mn(CO)₅],² and Cl(*i*Pr)₂P³ were synthesized according to reported procedures. Anhydrous trimethylamine-*N*-oxide (Me₃NO) was obtained by drying the purchased hydrate in a dean stark apparatus; absence of water was confirmed using ATR-FTIR spectroscopy. All manipulations were carried out in a nitrogen filled Genesis VAC glovebox or using Schlenk techniques to ensure dry and oxygen-free conditions, unless otherwise stated. Dry, oxygen-free solvents were obtained from a PPT solvent purification system and were purified and stored over 3 Å molecular sieves. The sieves were activated at 200 °C under vacuum for 48 hours prior to use. NMR spectra were obtained on Varian Mercury 300 MHz, Inova 500 MHz, Bruker Ascend-400 (400 MHz), or Bruker Ascend-500 (500 MHz) spectrometers. All proton NMR spectra are referenced to TMS, or hexamethyldisiloxane (HMDSO) as internal standards or residual solvent peaks (marked with an “*”). ATR-FTIR spectra were collected using a Bruker Alpha IR spectrometer with the “ATR Platinum” insert adapter (diamond crystal) housed inside a nitrogen filled VAC Atmospheres glovebox. Head space gas chromatography analyses were performed using a PerkinElmer Clarus 580 GC. Volumetric measurements were carried in analytic grade glassware. CHN combustion analysis was performed by Robertson MicroLit Laboratories, NJ USA.

Crystallographic methods

Low-temperature X-ray diffraction data for [Mn(CO)₄](μ-H)(μ-P(*i*Pr)₂){Mn(CO)₄} (Rlacy39) was collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu Kα radiation (λ = 1.54184 Å) from a PhotonJet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.⁴ The structures were solved through intrinsic phasing using SHELXT⁵ and refined against F² on all data by full-matrix least squares with SHELXL⁶ following established refinement strategies.⁷ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Rlacy39 contains disordered solvent molecules of toluene that were included in the unit cell but could not be satisfactorily modeled. Therefore, those molecules were treated as diffuse contributions to the overall scattering without specific atom positions using the solvent mask routine in Olex2.⁸

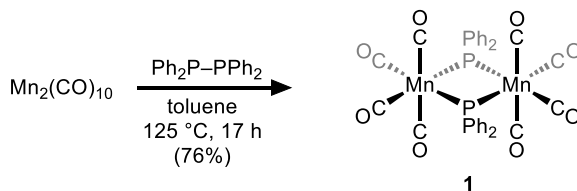
Syntheses and Reactions:

Synthesis of tetraphenylbisphosphide [(PPh₂)₂]:



In a glovebox, a 50 mL round bottom flask with a stir bar was charged with diphenylphosphine (Ph₂PH) (100 mg, 0.54 mmol, 1.0 eq.) and 2.0 mL dry THF. To this solution, KH (22 mg, 0.55 mmol, 1.0 eq.) was added with vigorous stirring. The reaction was stirred at room temperature for 6 h during which time the reaction turned bright red-orange with the formation of KPPH₂. The solution was cooled to -78 °C by immersion in a dry-ice/isopropanol bath and chlorodiphenylphosphine (ClPPh₂) (0.1 mL, 120 mg, 0.54 mmol, 1.0 eq.) was added. The reaction was then allowed to rise to room temperature overnight and stirred for 18h. Copious amount of white precipitate formation is seen. The THF was removed *in-vacuo* and the flask was brought into a glovebox. The residue extracted with petroleum (5 mL X 2 fractions) and benzene (5 mL X 2 fractions). All organic fractions were combined and all volatiles stripped off *in vacuo* to yield tetraphenylbisphosphide ((Ph₂P)₂) (173 mg, 87%). Spectra matched literature values.⁹

Synthesis of [Mn(CO)₄(μ-PPh₂)₂] (1):



Synthesis was adapted from a prior report by Hayter with modifications in work-up procedure.¹⁰ In our hands the procedure affords a much higher yield of **1**. In a glovebox, a 25 mL reaction bomb equipped with a stir bar was charged with dimanganese decacarbonyl ([Mn₂(CO)₁₀]) (67 mg, 0.17 mmol, 1.0 eq.) and dissolved in 3.0 mL dry toluene. To this solution, anhydrous trimethylamine-*N*-oxide (Me₃NO) (13 mg, 0.17 mmol, 1.0 eq.) was added

with vigorous stirring followed by tetraphenyl bisphosphide ((Ph₂P)₂) (62 mg, 0.17 mmol, 1.0 eq.). The solution turned red upon addition of Me₃NO and evolution of gas bubbles could be seen. The reaction was stirred at 125 °C for 17h. Complex **1** precipitates upon cooling to room temperature as a yellow micro-crystalline solid which was filtered and then washed with two 1 mL fractions of petroleum ether. The precipitate was dried *in-vacuo* and characterized (**1**, 89 mg, 76%).

¹H-NMR (CDCl₃, 400 MHz, ppm): δ 7.67 (s, 4H, aromatic), 7.27 (m, 6H,).

³¹P{¹H}-NMR (C₆D₆, 161 MHz, ppm): δ -40.1 (bs, Δ*w*_{1/2} = 636 Hz).

ATR-FTIR (ν_{CO}, cm⁻¹): 2048, 2000, 1988, 1973, 1957, 1942.

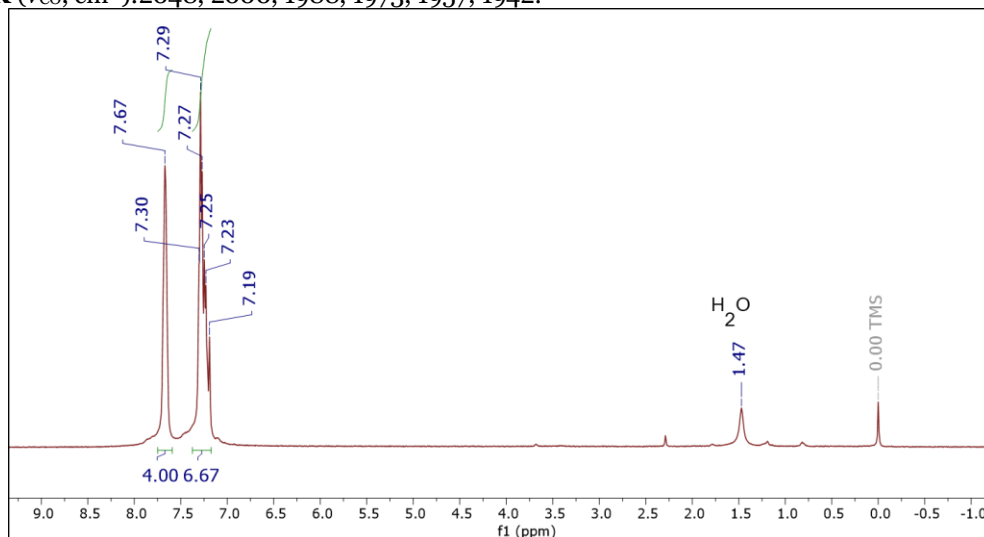


Figure S1: ¹H-NMR spectrum of **1** in CDCl₃.

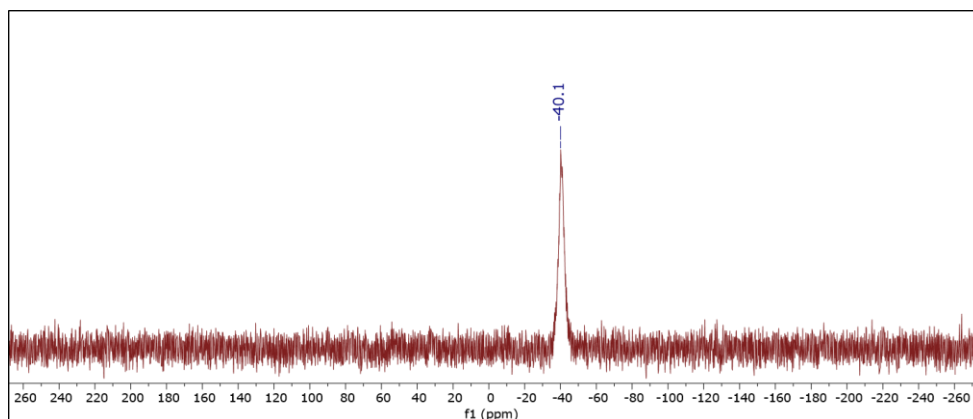


Figure S2: ³¹P{¹H}-NMR spectrum of **1** in CDCl₃.

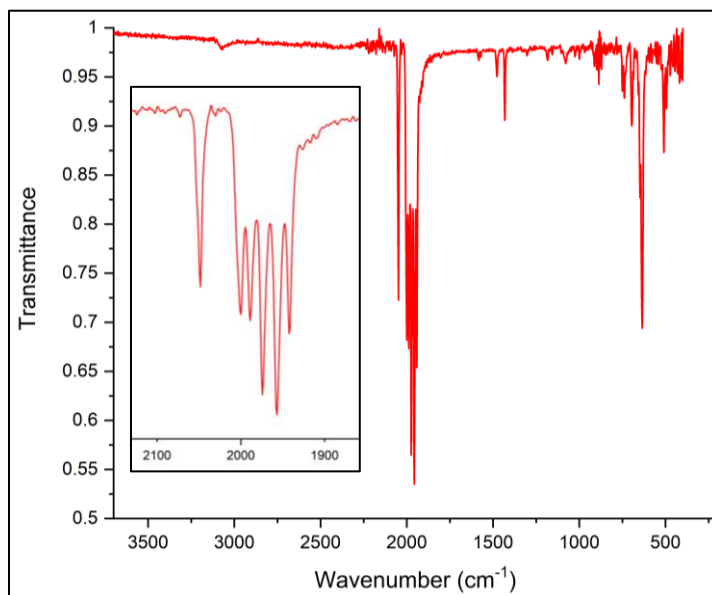
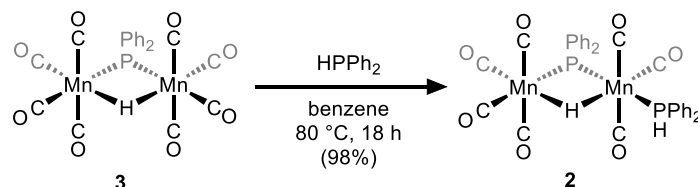


Figure S3: ATR-FTIR spectrum of **1**; inset: magnified region for CO stretches.

Synthesis of $[\{\text{Mn}(\text{CO})_4\}(\mu\text{-H})(\mu\text{-PPh}_2)\{\text{Mn}(\text{CO})_3(\text{HPPh}_2)\}]\textbf{(2)}$:



In a glovebox, a 25 mL Schlenk bomb equipped with a stir bar was charged with $[\{\text{Mn}(\text{CO})_4\}(\mu\text{-H})(\mu\text{-PPh}_2)\{\text{Mn}(\text{CO})_3\}]\textbf{(3)}$ (147 mg, 0.28 mmol, 1.0 eq.) and dissolved in 3.0 ml dry benzene. To this solution, diphenylphosphine (Ph_2PH) (53 mg, 0.28 mmol, 1.0 eq.) was added and the reaction was stirred at 80 °C for 18 h. The reaction was cooled down and filtered. The filtrate was pumped on under vacuum leaving behind a yellow solid, **2** (187 mg, 98 %). ^1H NMR data matches with the literature reported values.¹¹

^1H -NMR (C_6D_6 , 300 MHz, ppm): δ 8.21 (dd, $J_{\text{P-H}} = 11$ Hz, $J_{\text{H-H}} = 7$ Hz, 4H, aromatic), 7.55 (dd, $J_{\text{P-H}} = 11$ Hz, $J_{\text{H-H}} = 7$ Hz, 5H, aromatic), 7.00 (m, 11H, aromatic), 6.78 (d, $J_{\text{P-H}} = 350$ Hz, 1H, $\text{Ph}_2\text{P-H}$), -16.17 (t, $J_{\text{P-H}} = 30$ Hz, 1H, $\mu\text{-H}$).

$^1\text{H}\{^3\text{P}\}$ -NMR (43.8 ppm resonance decoupled) (C_6D_6 , 300 MHz, ppm): δ 8.21 (dd, $J_{\text{P-H}} = 11$ Hz, $J_{\text{H-H}} = 7$ Hz, 4H, aromatic), 7.56 (d, 5H, $J_{\text{H-H}} = 7$ Hz, aromatic), 7.00 (m, 11H, aromatic), 6.78 (s, 1H, $\text{Ph}_2\text{P-H}$), -16.17 (t, $J_{\text{P-H}} = 30$ Hz, 1H, $\mu\text{-H}$).

$^1\text{H}\{^3\text{P}\}$ -NMR (166.1 ppm resonance decoupled) (C_6D_6 , 300 MHz, ppm): δ 8.21 (d, $J_{\text{H-H}} = 7$ Hz, 4H, aromatic), 7.56 (dd, $J_{\text{P-H}} = 11$ Hz, $J_{\text{H-H}} = 7$ Hz, 5H, aromatic), 6.97 (m, 11H, aromatic), 6.75 (d, $J_{\text{P-H}} = 350$ Hz, 1H, $\text{Ph}_2\text{P-H}$), -16.17 (t, $J_{\text{P-H}} = 30$ Hz, 1H, $\mu\text{-H}$).

$^3\text{P}\{^1\text{H}\}$ -NMR (C_6D_6 , 121 MHz, ppm): δ 166.1 (bs, $\Delta w_{1/2} = 103$ Hz), 43.8 (bs, $\Delta w_{1/2} = 98$ Hz).

^3P -NMR (C_6D_6 , 121 MHz, 298 K, ppm): δ 166.1 (bs), 43.8 (d, $J_{\text{P-H}} = 350$ Hz).

ATR-FTIR (ν_{CO} , cm^{-1}): 2073, 1980, 1936, 1915.

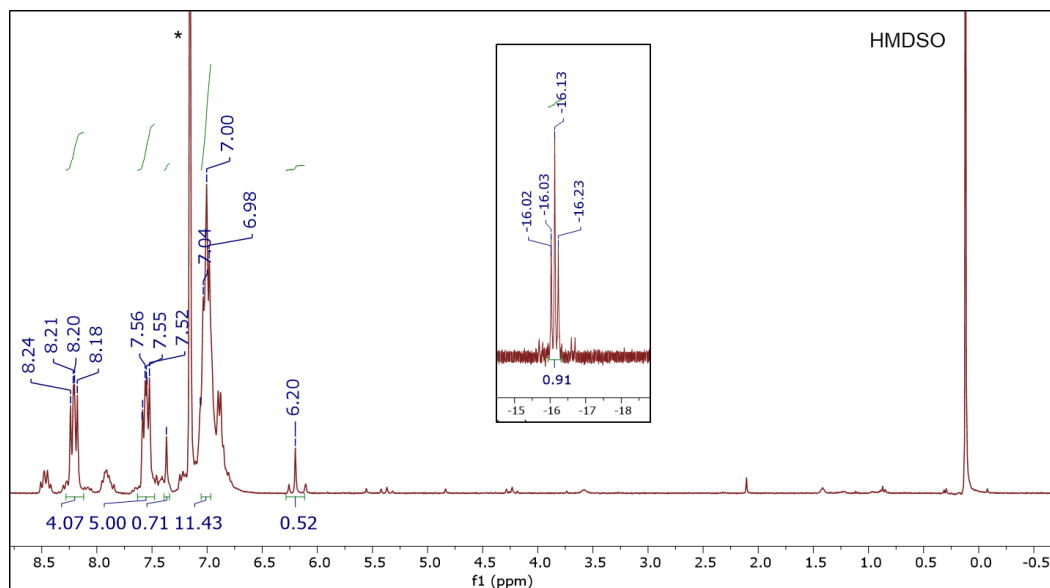


Figure S4: ^1H -NMR spectrum of **2**. Inset: hydride region.

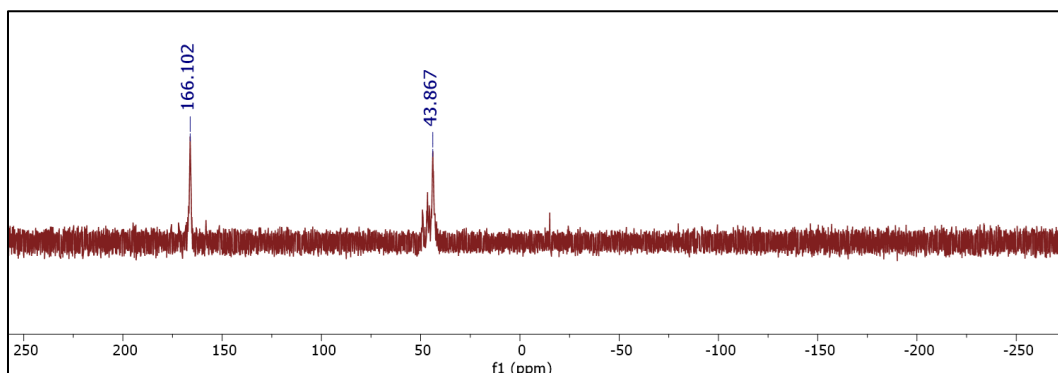


Figure S5: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **2** in CDCl_3 .

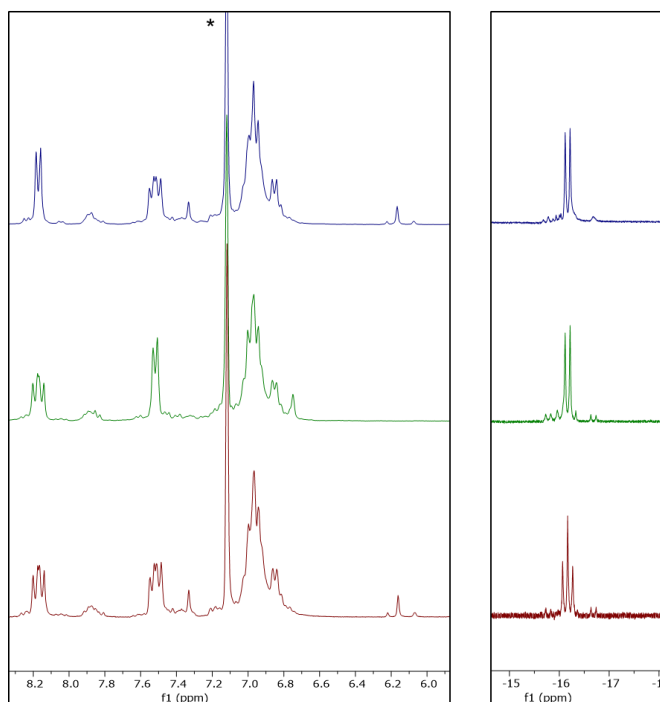


Figure S6: $^1\text{H}\{^{31}\text{P}\}$ -NMR spectra with selective decoupling. Red: $^1\text{H}\{^{31}\text{P}\}$ spectrum (for reference); green: ^{31}P -resonance at 43.8 ppm decoupled, note the doublet at 6.78 ppm is now a singlet; blue: ^{31}P -resonance at 166 ppm decoupled. Note that the hydride couples to both inequivalent ^{31}P -nuclei.

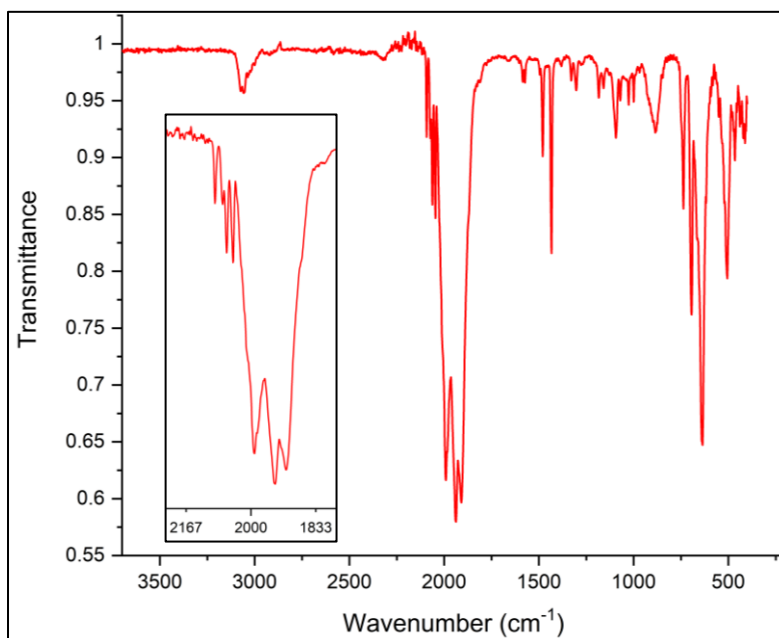
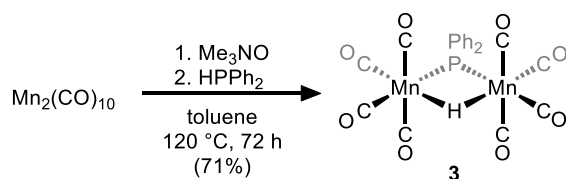


Figure S7: FTIR-ATR spectrum of **2**, inset: magnified region for CO stretches.

Synthesis of $[\{\text{Mn}(\text{CO})_4\}(\mu\text{-H})(\mu\text{-PPh}_2)\{\text{Mn}(\text{CO})_4\}]$ (**3**):



A synthesis reported earlier¹² was modified; toluene was used instead of decalins, trimethyl amine was used to facilitate CO liberation, and the reaction was carried out in a closed vessel. A 25 mL Schlenk bomb equipped with a stir bar was charged with dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (546 mg, 1.40 mmol, 0.98 eq.) and dissolved in 7 mL dry toluene. To this solution, anhydrous trimethylamine-*N*-oxide (Me_3NO) (107 mg, 1.42 mmol,

1.0 eq.) was added in one portion upon which the solution turned red-orange along with evolution of bubbles. Diphenylphosphine (Ph_2PH) (265 mg, 1.42 mmol, 1.0 eq.) was added in a dropwise fashion with vigorous stirring. The reaction was stirred open to the glovebox atmosphere for 2 min, sealed, and stirred at 120 °C for 72 h. The reaction was cooled down and filtered. The residue washed with 5 mL toluene. All the organic fractions were combined, and the volatiles were pumped off under vacuum leaving behind a yellow solid. The solid was re-dissolved in benzene and lyophilized to give a yellow powder of **3** (519 mg, 71%). ^1H -NMR data matches with the values reported in literature.

^1H -NMR (C_6D_6 , 300 MHz, ppm): δ 7.93 (dd, $J_{\text{H-H}} = 11$, $J_{\text{P-H}} = 7$ Hz, 4H, aromatic), 6.88 (m, 6H, aromatic), -16.64 (d, $J_{\text{P-H}} = 31$ Hz, 1H, $\mu\text{-H}$).

$^1\text{H}\{^3\text{P}\}$ -NMR (C_6D_6 , 300 MHz, ppm): δ 7.93 (d, $J = 7$ Hz, 4H, aromatic), 6.88 (m, 6H, aromatic), -16.64 (s, 1H, $\mu\text{-H}$).

$^3\text{P}\{^1\text{H}\}$ -NMR (C_6D_6 , 121 MHz, ppm): δ 156.7 (bs, $\Delta w_{1/2} = 121\text{Hz}$).

ATR-FTIR (ν_{CO} , cm^{-1}): 2092, 2061, 2047, 1990, 1944.

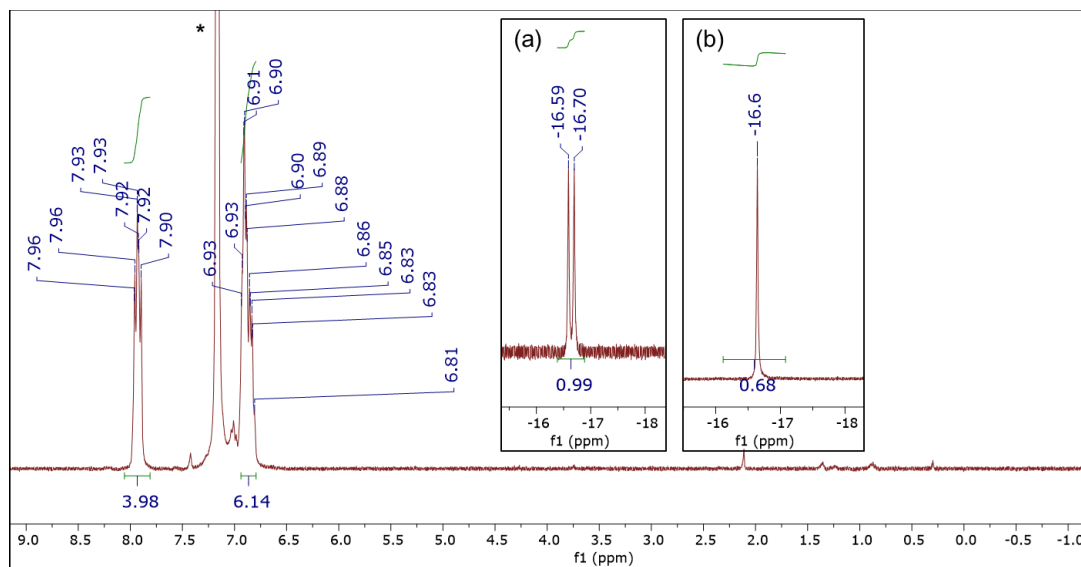


Figure S8: ^1H -NMR spectrum of **3**. Inset: hydride region, (a) ^{31}P coupled; (b) ^{31}P decoupled.

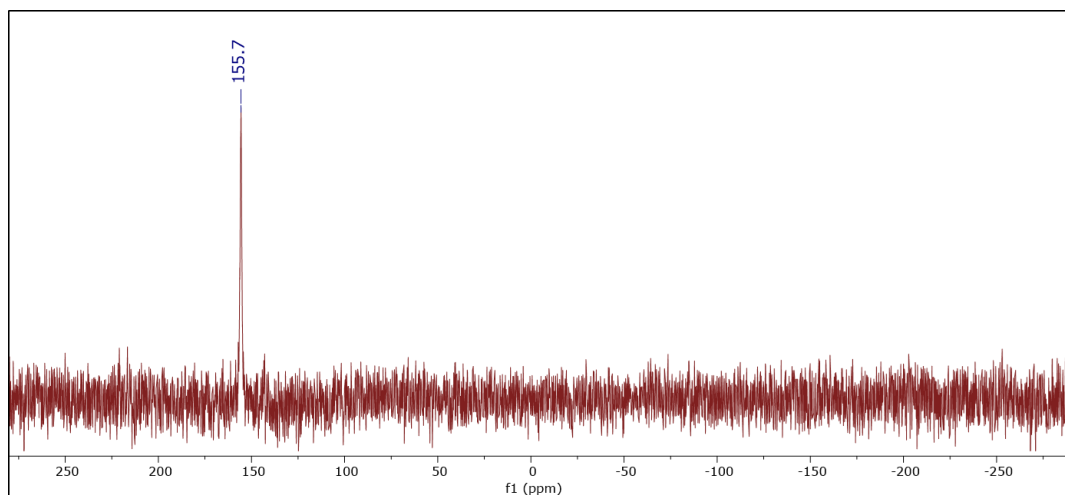


Figure S9: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **3**.

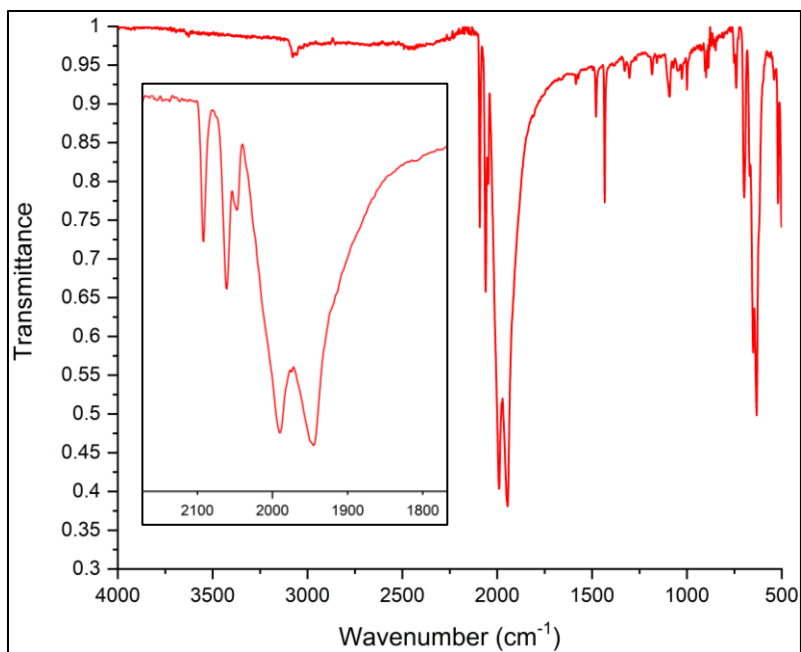
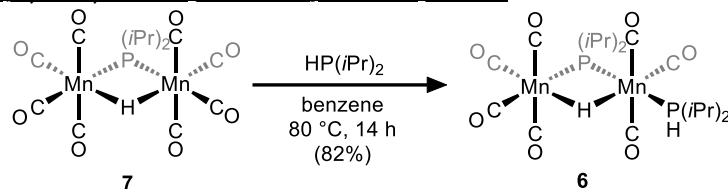


Figure S10: ATR-FTIR spectrum of **3**. Inset: magnified region for CO stretches.

Synthesis of $[\{\text{Mn}(\text{CO})_4\}(\mu\text{-H})(\mu\text{-P}(\text{iPr})_2)\{\text{Mn}(\text{CO})_3(\text{HP}(\text{iPr})_2)\}]$ (**6**):



A 25 mL Schlenk bomb equipped with a stir bar was charged with $[\{\text{Mn}(\text{CO})_4\}(\mu\text{-H})(\mu\text{-P}(\text{iPr})_2)\{\text{Mn}(\text{CO})_4\}]$ (**7**) (127 mg, 0.28 mmol, 1.0 eq.) and dissolved in 2.0 ml benzene. To this solution, diisopropylphosphine ($(\text{iPr})_2\text{PH}$) (35 mg, 0.29 mmol, 1.0 eq.) was added with stirring. The reaction was sealed and stirred at 80 °C for 14 h. The reaction was then brought into the glovebox and filtered. All the volatiles stripped off *in vacuo* to leave behind a yellow oil, **2** (152 mg, 82%).

^1H -NMR (C_6D_6 , 500 MHz, ppm): δ 4.26 (dt, $J_{\text{P-H}} = 322$ Hz, $J_{\text{H-H}} = 5$ Hz, 1H, $(\text{iPr})\text{P-H}$), 2.38 (pd, $J_{\text{P-H}} = 2.0$ Hz, $J_{\text{H-H}} = 7$ Hz, 2H, $\mu\text{P}-(\text{CH}-(\text{CH}_3)_2)_2$), 2.08 (qd, $J_{\text{P-H}} = 7$, $J_{\text{H-H}} = 5.3$ Hz, 2H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.53 (ddd, $J_{\text{P-H}} = 18$, $J_{\text{H-H}} = 14$, 7 Hz, 12H, $\mu\text{-P}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.07 (ddd, $J_{\text{P-H}} = 34$, $J_{\text{H-H}} = 16$, 7 Hz, 12H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), -16.69 (t, $J_{\text{P-H}} = 28$ Hz, $\Delta w_{1/2} = 10$ Hz, 1H, $\mu\text{-H}$).

^1H -NMR (C_6D_6 , 300 MHz, ppm): δ 4.26 (dt, $J_{\text{P-H}} = 322$ Hz, $J_{\text{H-H}} = 5$ Hz, 1H, $(\text{iPr})\text{P-H}$), 2.38 (pd, $J_{\text{P-H}} = 2$ Hz, $J_{\text{H-H}} = 7$ Hz, 2H, $\mu\text{P}-(\text{CH}-(\text{CH}_3)_2)_2$), 2.08 (qd, $J_{\text{P-H}} = 7$, $J_{\text{H-H}} = 5$ Hz, 2H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.53 (ddd, $J_{\text{P-H}} = 14$, $J_{\text{H-H}} = 11$, 7 Hz, 12H, $\mu\text{-P}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.06 (ddd, $J_{\text{P-H}} = 16$, $J_{\text{H-H}} = 21$, 7 Hz, 12H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), -16.69 (t, $J_{\text{P-H}} = 28$ Hz, $\Delta w_{1/2} = 10$ Hz, 1H, $\mu\text{-H}$).

$^1\text{H}\{^{31}\text{P}\}$ -NMR (63.1 ppm resonance decoupled) (C_6D_6 , 300 MHz, ppm) δ 4.25 (t, $J_{\text{H-H}} = 5$ Hz, 1H, $(\text{iPr})\text{P-H}$), 2.38 (pd, $J_{\text{P-H}} = 2$ Hz, $J_{\text{H-H}} = 7$ Hz, 2H, $\mu\text{P}-(\text{CH}-(\text{CH}_3)_2)_2$), 2.06 (dp, $J_{\text{H-H}} = 7$ Hz, 2H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.53 (ddd, $J_{\text{P-H}} = 14$, $J_{\text{H-H}} = 11$, 7 Hz, 12H, $\mu\text{-P}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.06 (dd, $J_{\text{H-H}} = 21$, 7 Hz, 12H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), -16.69 (d, $J_{\text{P-H}} = 30$ Hz, $\Delta w_{1/2} = 10$ Hz, 1H, $\mu\text{-H}$).

$^1\text{H}\{^{31}\text{P}\}$ -NMR (196.9 ppm resonance decoupled) (C_6D_6 , 300 MHz, 298 K, ppm): δ 4.25 (dt, $J_{\text{P-H}} = 321$ Hz, $J_{\text{H-H}} = 5$ Hz, 1H, $(\text{iPr})\text{P-H}$), 2.38 (p, $J_{\text{H-H}} = 7$ Hz, 2H, $\mu\text{P}-(\text{CH}-(\text{CH}_3)_2)_2$), 2.08 (qd, $J_{\text{P-H}} = 7$, $J_{\text{H-H}} = 5$ Hz, 2H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.53 (dd, $J_{\text{H-H}} = 11$, 7 Hz, 12H, $\mu\text{-P}-(\text{CH}-(\text{CH}_3)_2)_2$), 1.06 (ddd, $J_{\text{P-H}} = 21$, $J_{\text{H-H}} = 16.0$, 7.0 Hz, 12H, $\text{HP}-(\text{CH}-(\text{CH}_3)_2)_2$), -16.69 (d, $J_{\text{P-H}} = 26$ Hz, $\Delta w_{1/2} = 10$ Hz, 1H, $\mu\text{-H}$).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6 , 121 MHz, 298 K, ppm): δ 196.9 (bs, $\Delta w_{1/2} = 146$ Hz), 63.1 (bs, $\Delta w_{1/2} = 143$ Hz).

^{31}P -NMR (C_6D_6 , 121 MHz, 298 K, ppm): δ 196.9 (bs, $\Delta w_{1/2} = 176$ Hz), 63.1 (d, $J_{\text{P-H}} = 321$ Hz, $\Delta w_{1/2} = 167$ Hz).

ATR-FTIR (ν_{CO} , cm^{-1}): 2064, 2009, 1965, 1943, 1910.

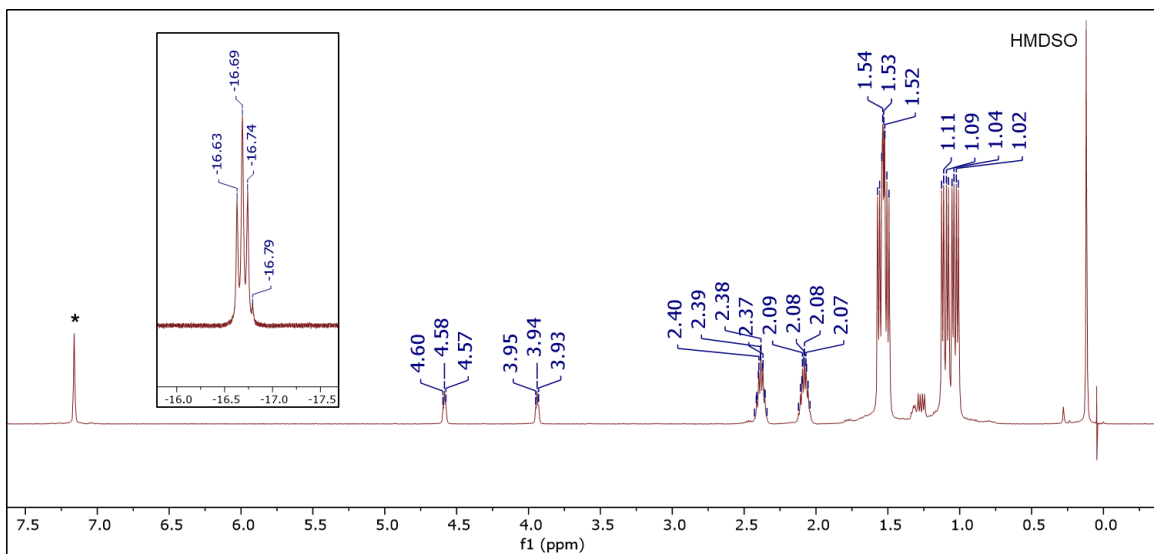


Figure S 11: ^1H -NMR spectrum of **6**.

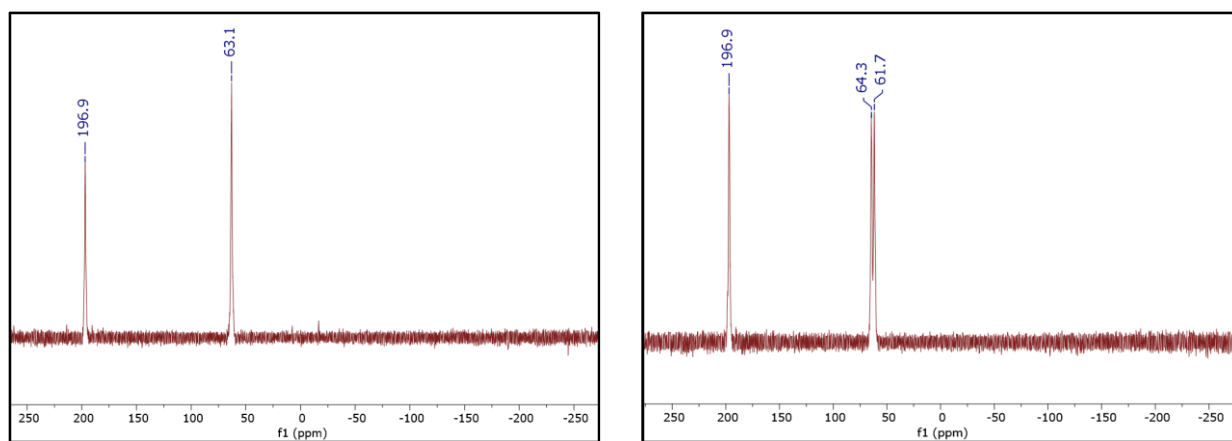


Figure S 12: Left: $^{31}\text{P}\{^1\text{H}\}$ -NMR of **6**; right: ^{31}P -NMR of **6**.

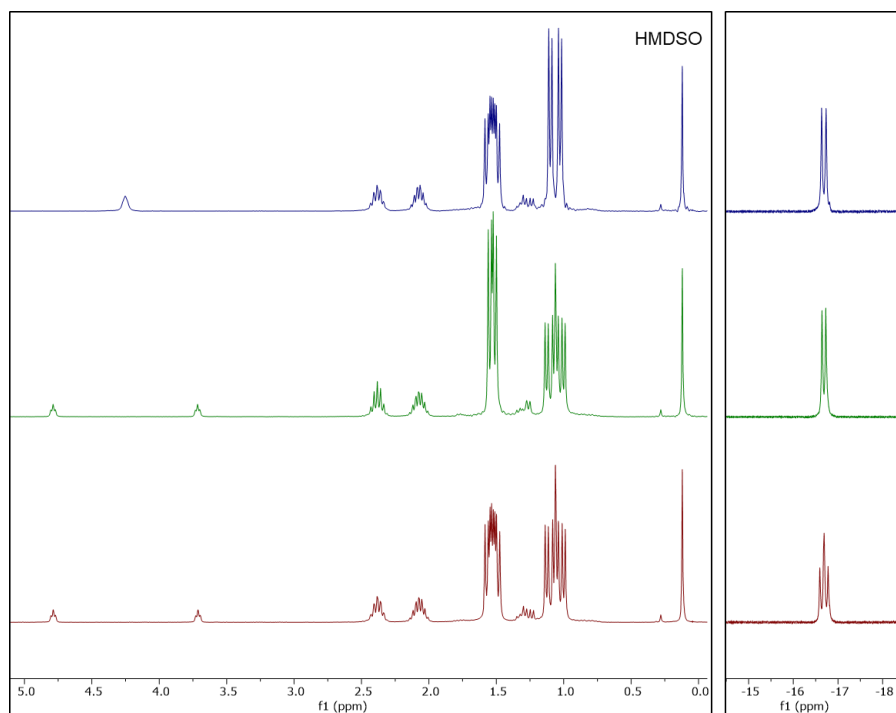


Figure S 13: Red: ^1H -NMR spectrum (for reference); green: ^1H -NMR spectrum with ^{31}P -resonance at 196.9 ppm decoupled; blue: ^1H -NMR spectrum with ^{31}P -resonance at 63.1.

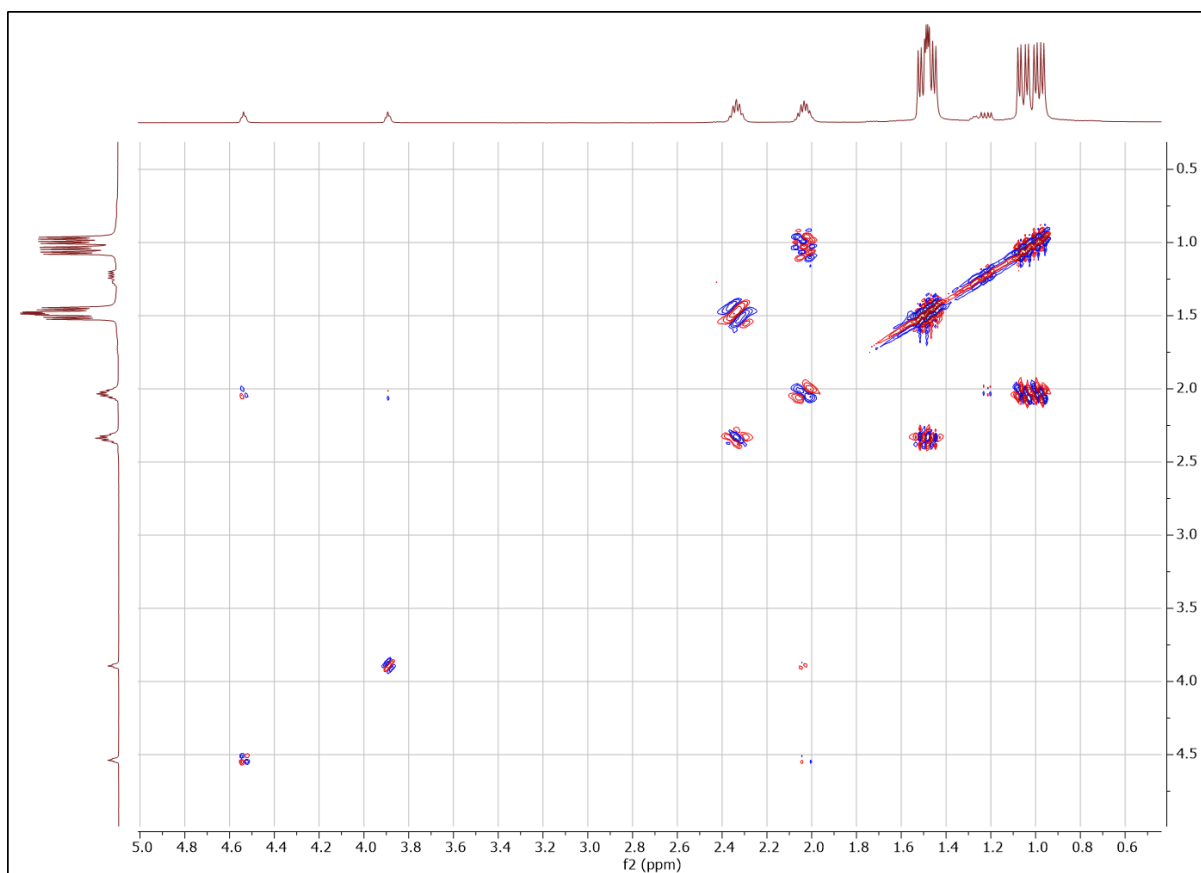


Figure S 14: Gradient double quantum filtered (g-DQF)-COSY NMR spectrum of **6**.

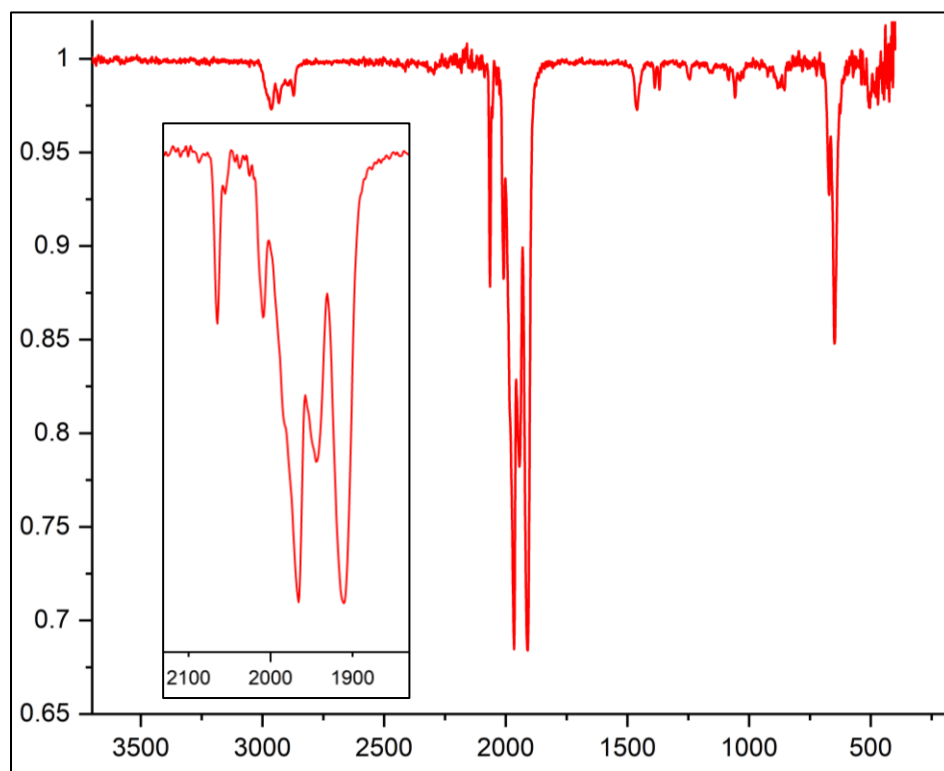
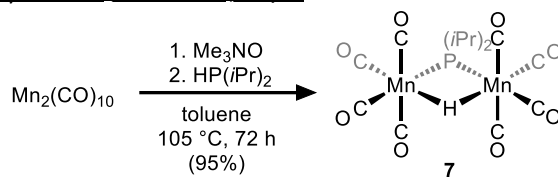


Figure S 15: ATR-FTIR of **6**; inset: magnified region for CO stretches.

Synthesis of $[Mn(CO)_4(\mu-H)(\mu-P(iPr)_2)]_2$ (**7**):



The reaction was carried out analogous to the synthesis of **3**. A 50 mL Schlenk bomb equipped with a stir bar was charged with dimanganese decacarbonyl ($[Mn_2(CO)_{10}]$) (965 mg, 2.47 mmol, 1 eq.) and dissolved in 13 mL dry toluene. To this solution, anhydrous trimethylamine-*N*-oxide (Me_3NO) (194 mg, 2.58 mmol, 1.0 eq.) was added (whereupon the solution turned red and gas bubbles evolved) followed by the dropwise addition of diisopropylphosphine ($(iPr)_2PH$) (295 mg, 2.49 mmol, 1.0 eq.). The reaction was stirred open to the glovebox atmosphere for 2 minutes. The reaction was then sealed and stirred at 105 °C for 72 h. The Schlenk bomb was then cooled to room temperature, the reaction was filtered and the residue washed with two 5 mL fractions of toluene. All the organic fractions were combined and the volatiles stripped off under vacuum leaving behind a yellow solid. The solid material was dissolved in benzene and lyophilized to give a yellow powder, **7** (1063 mg, 95%).

1H -NMR (C_6D_6 , 500 MHz, ppm): δ 2.05 (m, 2H, P-CH-), 1.25 (dd, $J_{H-H} = 7$, $J_{P-H} = 15$ Hz, 12H, $-CH_3$), -16.76 (d, $J_{P-H} = 30$ Hz, 1H, $\mu-H$).

$^1H\{^31P\}$ -NMR ($CD_3C_5D_5$, 300 MHz, ppm): δ 2.05 (m, 2H, P-CH-), 1.26 (d, $J_{H-H} = 7$, 12H, $-CH_3$), -16.76 (s, 1H, $\mu-H$).

$^31P\{^1H\}$ -NMR (C_6D_6 , 121 MHz, ppm): δ 190.5 (bs, $\Delta w_{1/2} = 149$ Hz).

ATR-FTIR (ν_{CO} , cm^{-1}): 2087, 2053, 1981, 1947, 1918.

CHN-Analysis [Calc. (found)] for $(C_{14}H_{15}Mn_2O_8P)$: %C 37.19 (37.35), %H 3.34 (3.88).

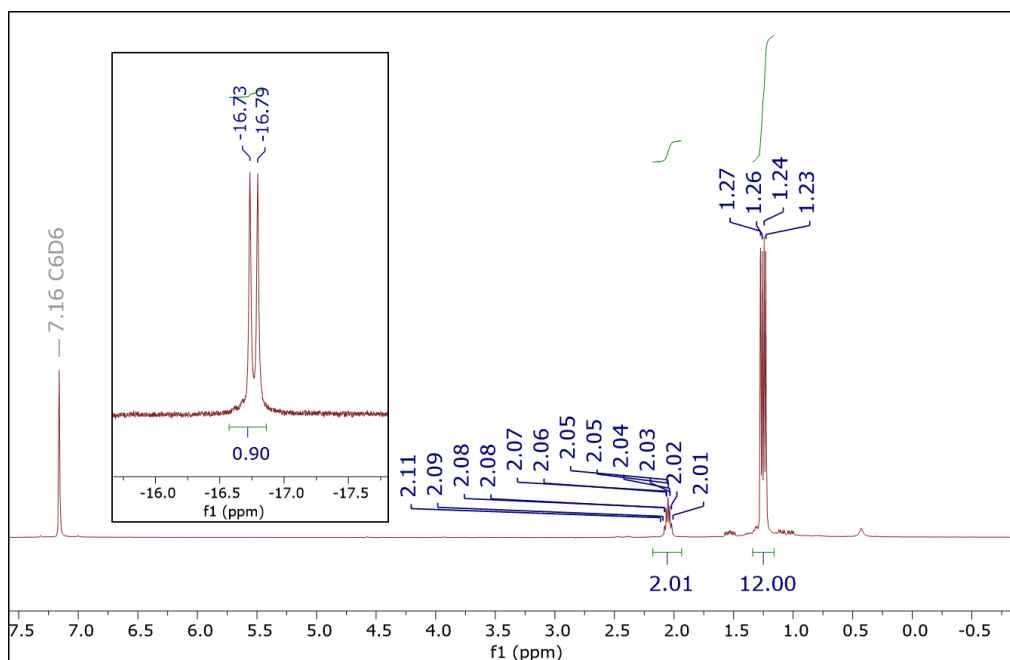


Figure S16: 1H NMR of **7**. Inset: hydride region.

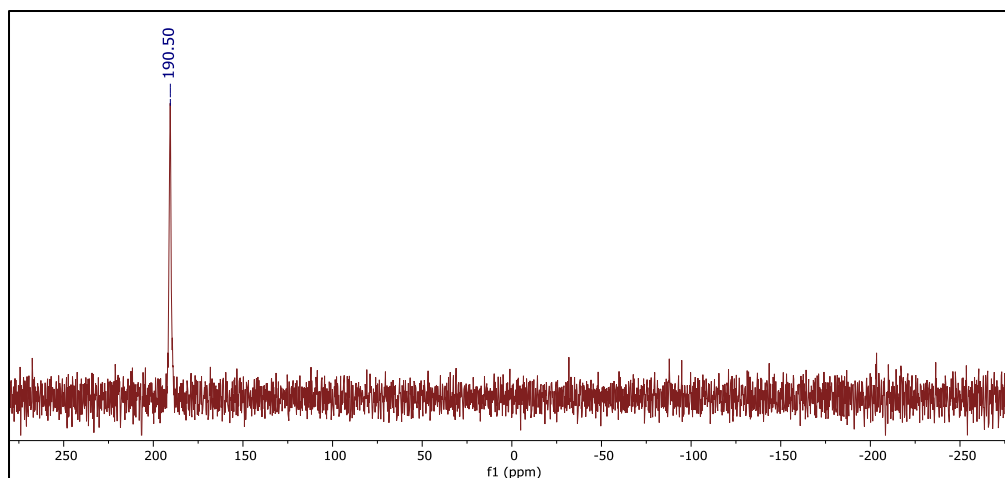


Figure S17: $^{31}\text{P}\{^1\text{H}\}$ NMR of **7**

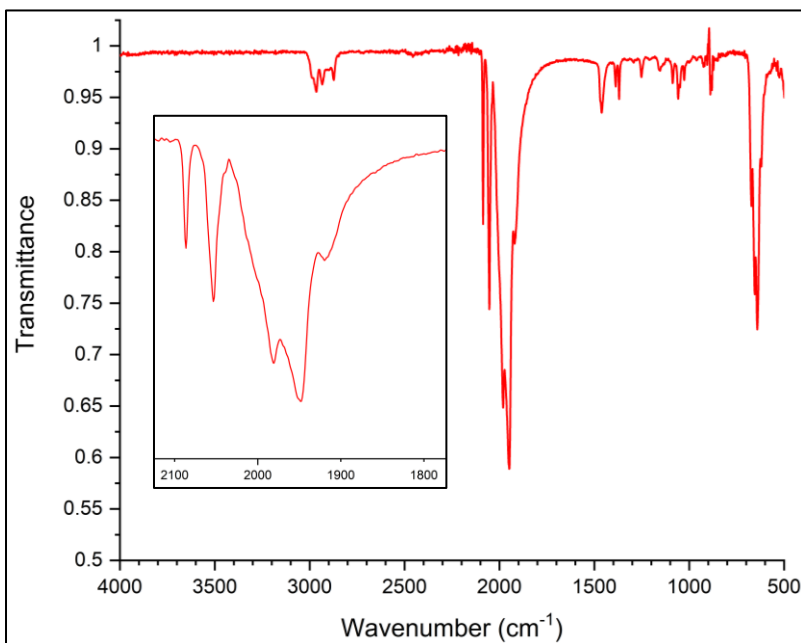
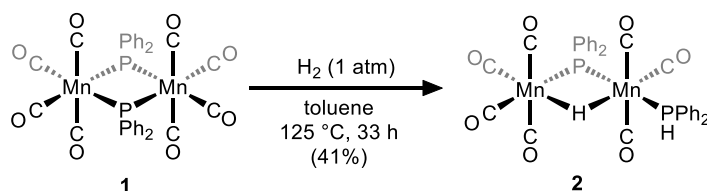


Figure S18: ATR-FTIR for **7**. Inset: magnified region for CO stretches.

Reaction of **1** with H_2 (D_2):



A 25 mL Schlenk bomb equipped with a stir bar was charged with **1** (40 mg, 0.057 mmol) and toluene (2 mL). The vessel was sealed, subjected to three freeze-pump-thaw cycles, H_2 (or D_2) was introduced at 1 atm pressure and the reaction vessel was sealed. The reaction was heated at 125 °C for 33 h. The reaction was then cooled to room temperature whereupon precipitate of unreacted **1** forms. The reaction was then filtered and the residue washed with two 1 mL fraction of petroleum ether. All the organic layers were combined and volatiles pumped off under vacuum to give a yellow powder of **2** (16 mg, 41%), or **2^D**. Identity of **2** was confirmed based on ATR-FTIR, ^1H -NMR, and $^{31}\text{P}\{^1\text{H}\}$ -NMR data.

In the case of **2^D**, the reaction mixture was transferred to an NMR tube with a D_2O insert and ^2H -NMR was collected. The reaction was thereafter stripped of all volatiles and analyzed via ^1H -NMR and ATR-FTIR.

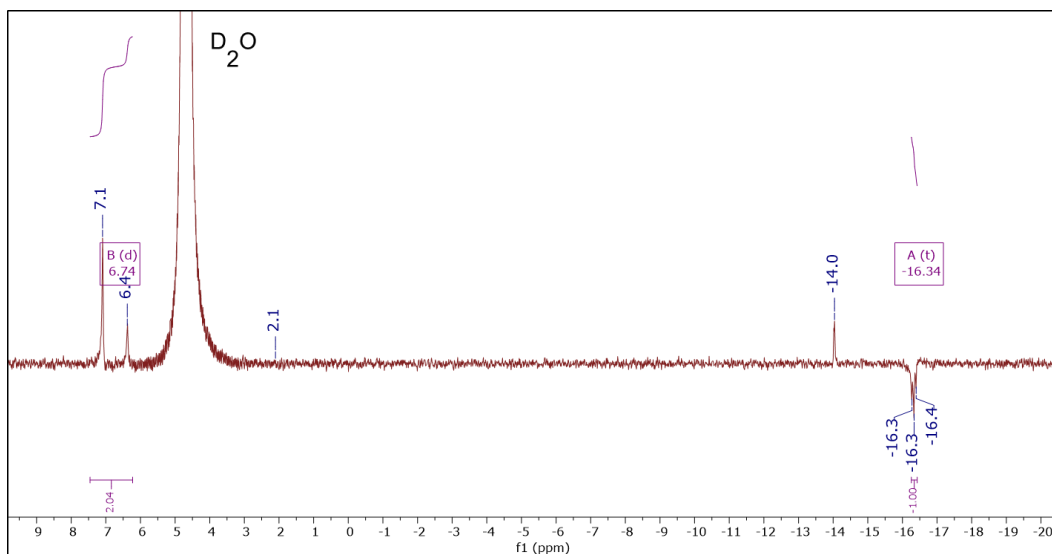


Figure S19: ^2H -NMR of 2^{D} with D_2O insert.

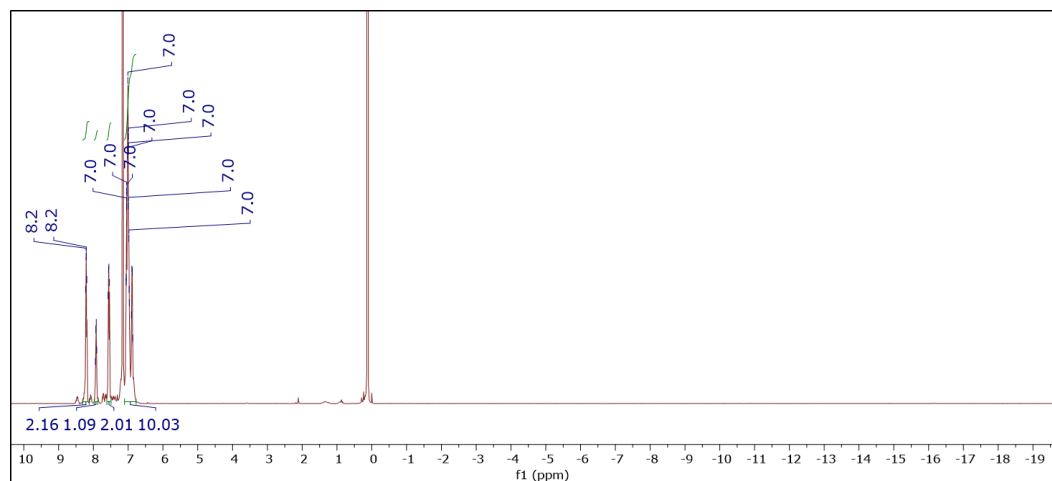


Figure S20: ^1H NMR of 2^{D} Note the absence of the resonances corresponding to the bridging hydride and the P-H in the L-type diphenylphosphine.

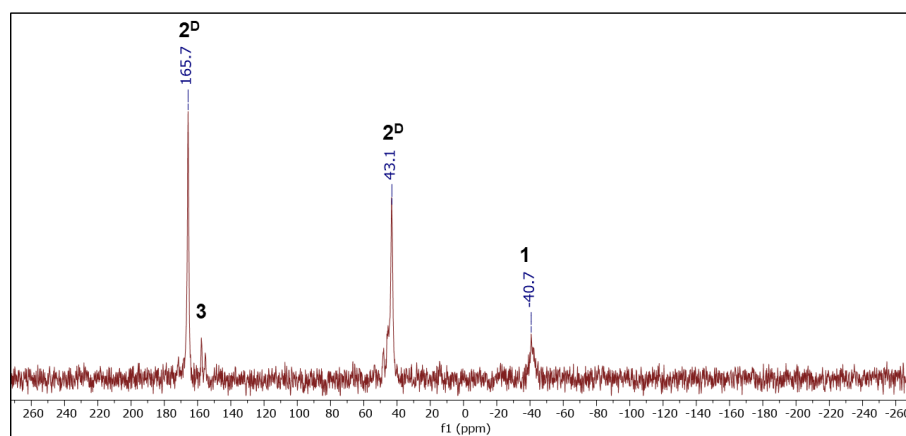
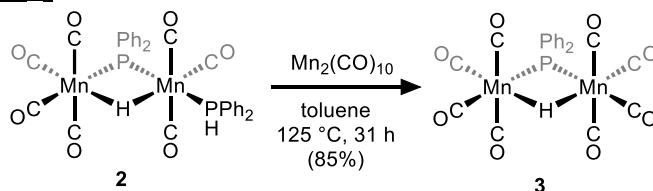


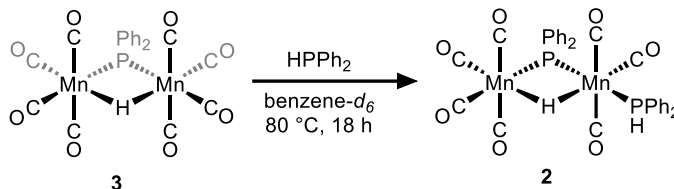
Figure S21: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the reaction mixture.

Reaction of **2** with $\text{Mn}_2(\text{CO})_{10}$:



A Schlenk bomb equipped with a stir bar was charged with **2** (36 mg, 0.054 mmol, 1 eq.), $\text{Mn}_2(\text{CO})_{10}$ (21 mg, 0.054 mmol, 1 eq.), and toluene (2 mL). The reaction was stirred at 125 °C for 31 h. The reaction was then cooled to room temperature and filtered. The residue was washed with two 1 mL fraction of toluene. All the organic layers were combined and volatiles removed *in vacuo* to leave behind a yellow powder, **3** (48 mg, 85%). Identity of **3** was confirmed based on ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectroscopy.

Reaction of **3** with HPPH_2 at 80 °C:



In a nitrogen filled glovebox, **3** (14 mg, 0.027 mmol, 1 eq) was added to a J-Young NMR tube and dissolved in benzene- d_6 (C_6D_6). To this solution, diphenylphosphine (Ph_2PH) (6 mg, 0.032 mmol, 1.1 eq.) was added and the tube sealed. The reaction was followed by ^1H -NMR. Heating the reaction at 60 °C for 3 h shows very little formation of **2**. Heating at 80 °C for 18 h show formation of **2**.

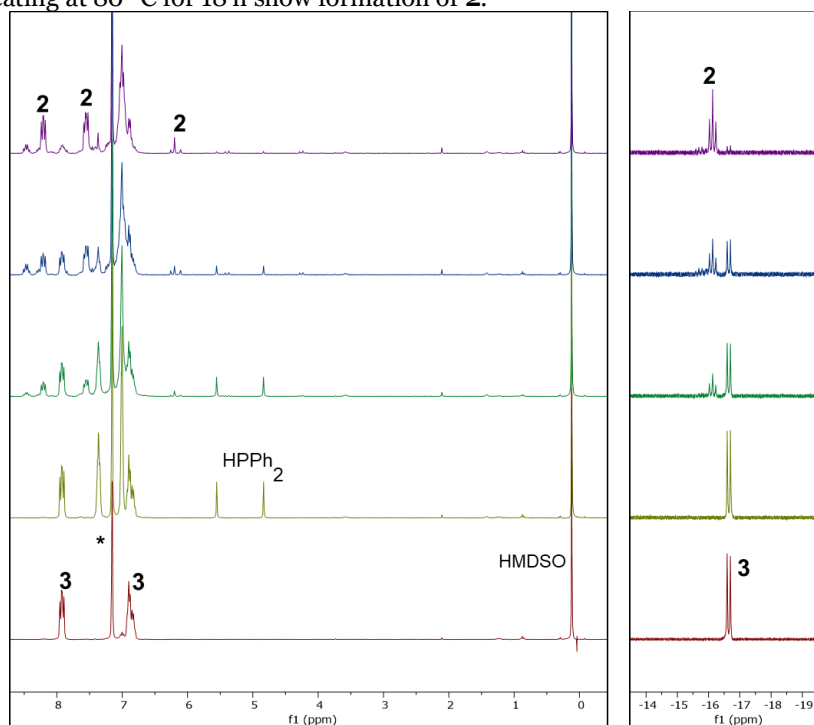
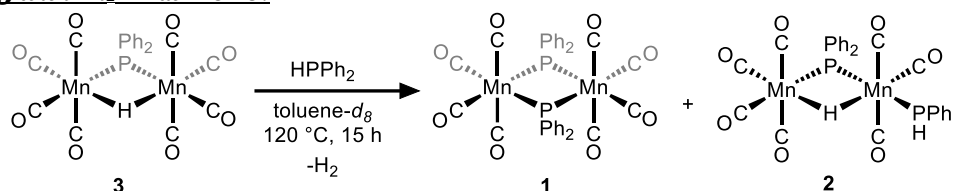


Figure S22: ^1H -NMR spectra of the reaction mixture. Red: before Ph_2PH addition; green: after HPPH_2 addition; teal: after 3 h heating at 80 °C; blue: after 7 h heating at 80 °C, purple: after 18 h heating at 80 °C. The hydride doublet at -16.6 ppm was monitored for the consumption of **3** and the triplet at -16.1 ppm was monitored for the formation of **2**.

Reaction of **3** with Ph_2PH at 120 °C:



In a nitrogen filled glovebox, **3** (24 mg, 0.046 mmol, 1.0 eq) was added to a J-Young NMR tube and dissolved in toluene- d_8 ($\text{CD}_3\text{C}_6\text{D}_5$). To this solution, diphenylphosphine (Ph_2PH) (9 mg, 0.048 mmol, 1.0 eq.) was added. The reaction was heated at 120 °C for 15 h. Upon cooling the reaction to room temperature, copious amount of yellow crystalline powder forms. The reaction was analyzed using NMR and shows the formation of **1** and a small amount of **2**. The reaction was then subjected to two freeze-pump-thaw (FPT) cycles and ^1H -NMR collected. The singlet at 4.5 ppm disappears confirming the presence of dihydrogen.

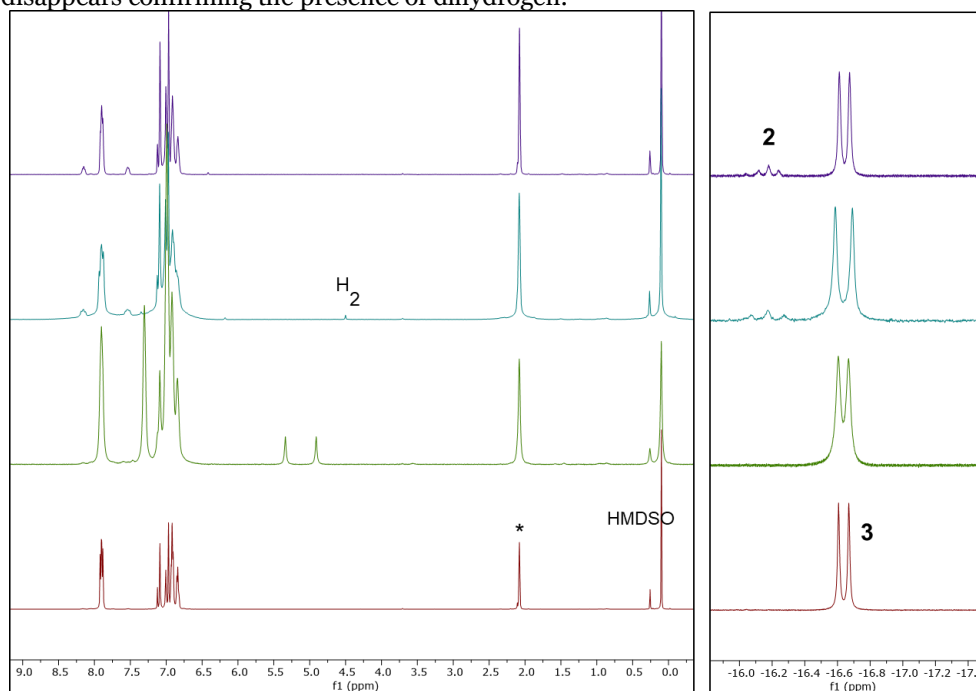


Figure S23: ^1H -NMR spectra for reaction of **3** with HPPH_2 . Red: **3** before any manipulations; green: post HPPH_2 ; teal: reaction mixture post heating at 120 °C for 15 h; purple: reaction mixture post two FPT cycles, note the absence of the singlet at 4.5 ppm corresponding to H_2 .

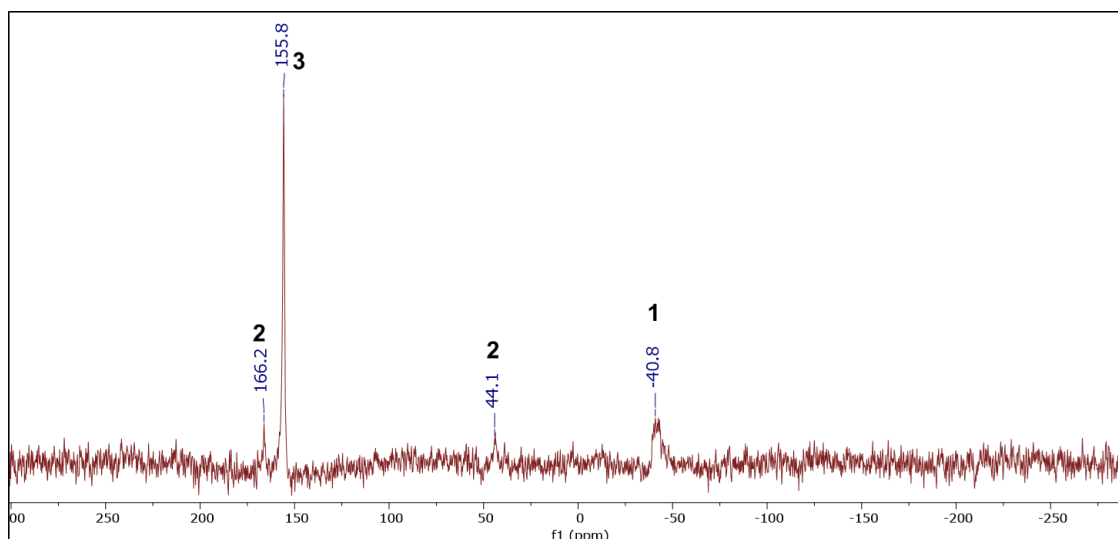
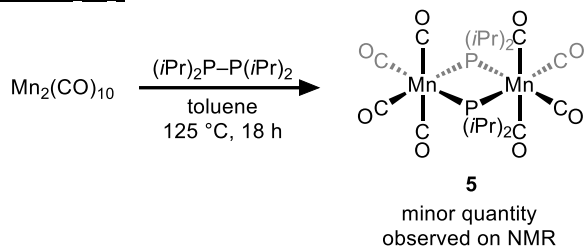


Figure S24: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the reaction mixture.

Reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with $((i\text{Pr})_2\text{P})_2$:



A 25 mL Schlenk bomb equipped with a stir bar was charged with dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (100 mg, 0.26 mmol, 1 eq), tetraisopropyl bisphosphide $((i\text{Pr})_2\text{P})_2$ (600 mg, 0.26 mmol, 1 eq), and 2 mL toluene. The reaction was stirred at 125 °C for 18 h. An ^1H and ^{31}P -NMR analysis of the reaction shows unreacted $((i\text{Pr})_2\text{P})_2$ and formation of a minor quantity of **5**.

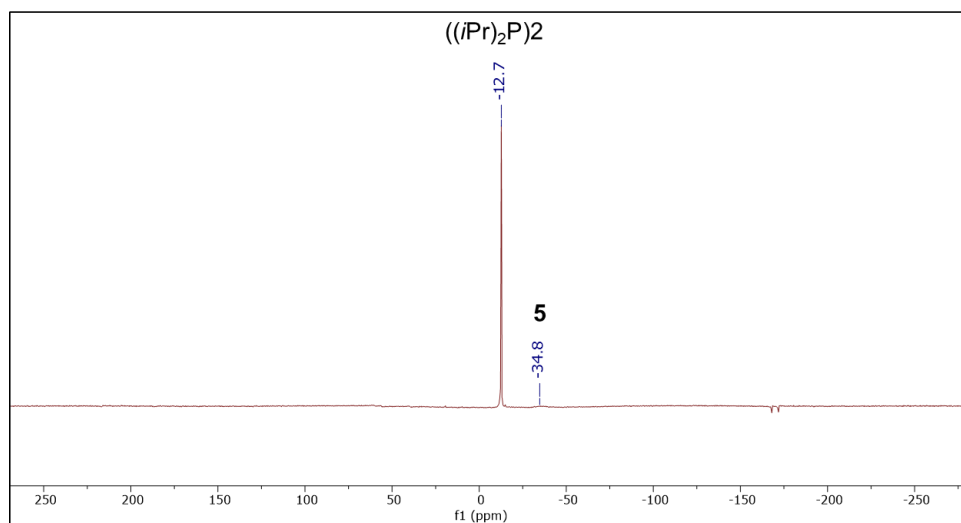
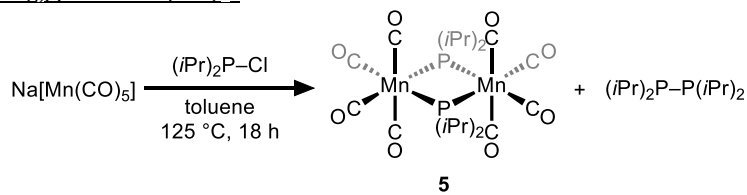


Figure S 25: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the reaction between $[\text{Mn}_2(\text{CO})_{10}]$ and $((i\text{Pr})_2\text{P})_2$.

Reaction of $[\text{Na}\{\text{Mn}(\text{CO})_5\}]$ with $\text{ClP}(i\text{Pr})_2$:



A 25 mL Schlenk bomb equipped with a stir bar was charged with sodium pentacarbonylmanganate ($[\text{Na}\{\text{Mn}(\text{CO})_5\}]$) (78 mg, 0.37 mmol, 1 eq) and toluene (4 mL, alumina dried right before use). To this reaction, chlorodiisopropylphosphine ($\text{ClP}(i\text{Pr})_2$) (60 μL , 58 mg, 0.37 mmol, 1 eq) was added. The reaction was sealed and stirred at 125 °C for 18 h. The reaction mixture analyzed using ^{31}P -NMR spectroscopy which shows the formation of tetraisopropyl bisphosphido $((i\text{Pr})_2\text{P})_2$, **5** (minor product), and two other minor unidentified products (**Figure S 26**).

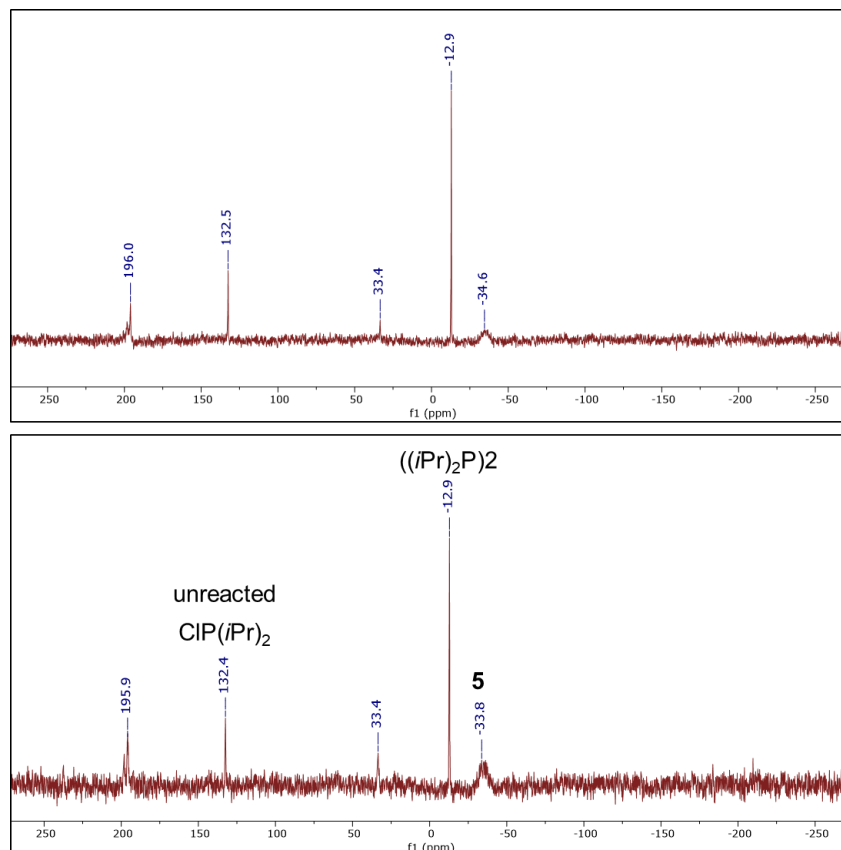
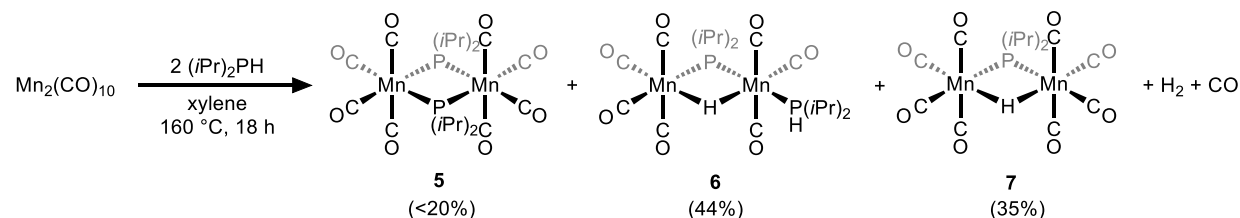


Figure S 26: NMR spectra of the reaction between $[\text{Na}\{\text{Mn}(\text{CO})_5\}]$ with $\text{Cl}(\text{iPr})_2\text{P}$. Top: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum; bottom: ^{31}P -NMR spectrum.

Reaction of $[\text{Mn}_2(\text{CO})_{10}]$ with 2 eq. $(\text{iPr})_2\text{PH}$:



A 25 mL Schlenk bomb with a stir bar was charged with dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (101 mg, 0.26 mmol, 1 eq), diisopropylphosphine $(\text{iPr})_2\text{PH}$ (62 mg, 0.52 mmol, 2 eq), and xylenes (4 mL). The reaction was sealed and stirred at 160 °C for 18 h. The reaction was cooled brought into a glovebox and a sample of the headspace was obtained for GC-analysis. The xylenes were stripped off *in vacuo*, residue redissolved in toluene and volatiles stripped off to remove traces of xylenes. The residue was dissolved in C_6D_6 analyzed by ^1H and ^{31}P -NMR spectroscopy. The spectra show the formation of **5** (<20%), **6** (44%), and, **7** (35%). Yields calculated based on ^1H -NMR.

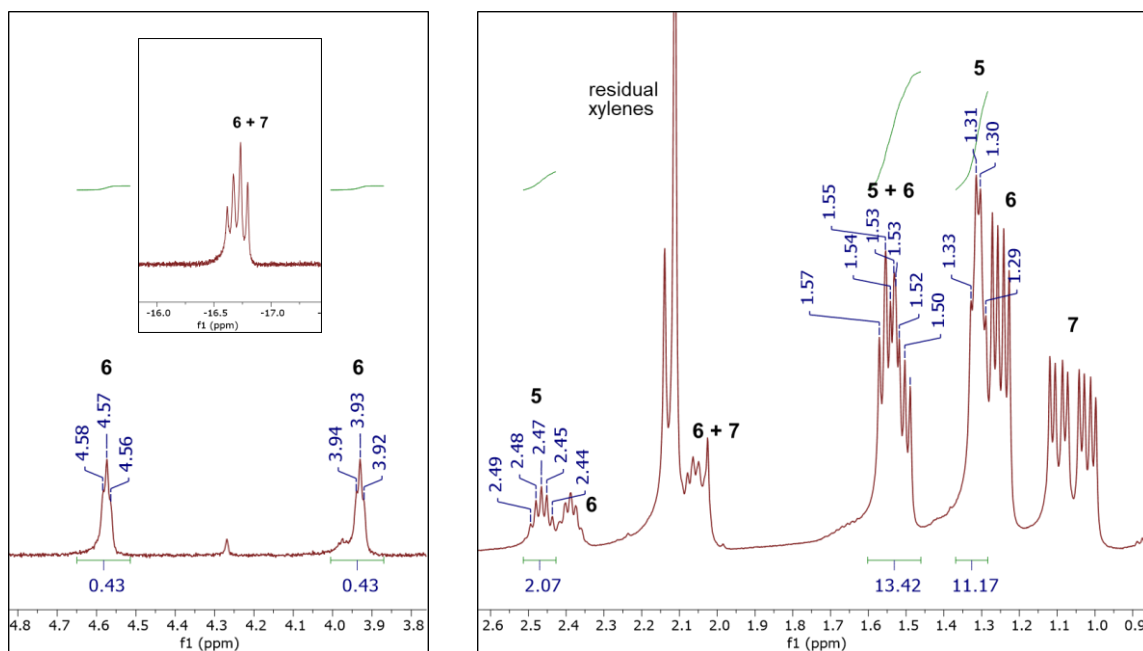


Figure S27: ^1H -NMR spectrum of the reaction mixture. Inset: hydride region.

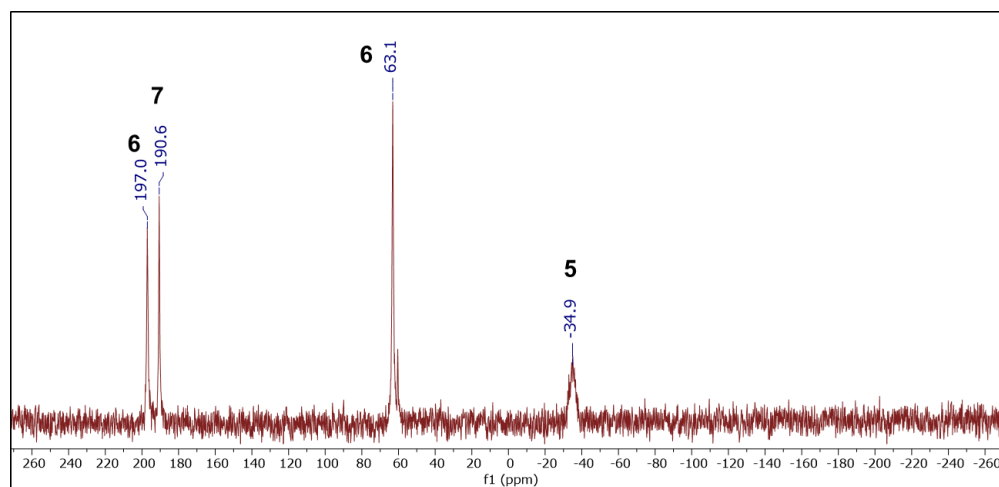


Figure S28: $^{31}\text{P}\{^1\text{H}\}$ -NMR of the reaction mixture.

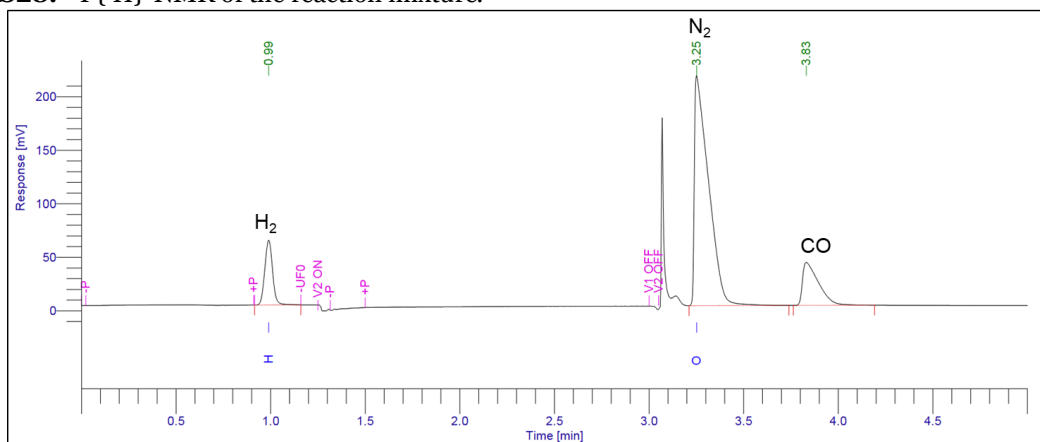
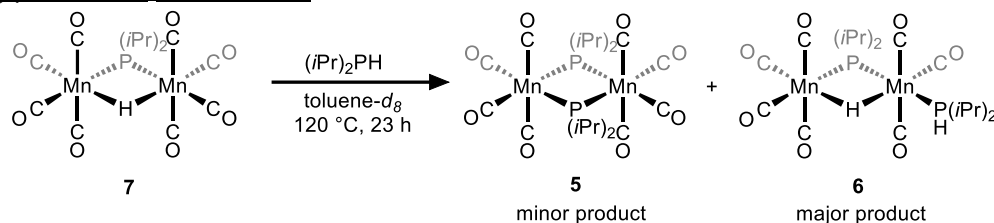


Figure S29: Gas chromatogram for the reaction headspace.

Reaction of **7** with $(i\text{Pr})_2\text{PH}$ at 120 °C:



In a nitrogen filled glovebox, **7** (20 mg 0.044 mmol, 1 eq.) was transferred to an NMR tube with a J-Young adapter and dissolved in toluene- d_8 (0.6 mL). Diisopropylphosphine (6 mg 0.051 mmol, 1.1 eq) was added to this solution and the NMR tube shut off. The reaction was heated at 120 °C. Almost complete conversion to **6** is observed within 2 h. Further heating for 23 h shows only minor formation of **5** in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectra.

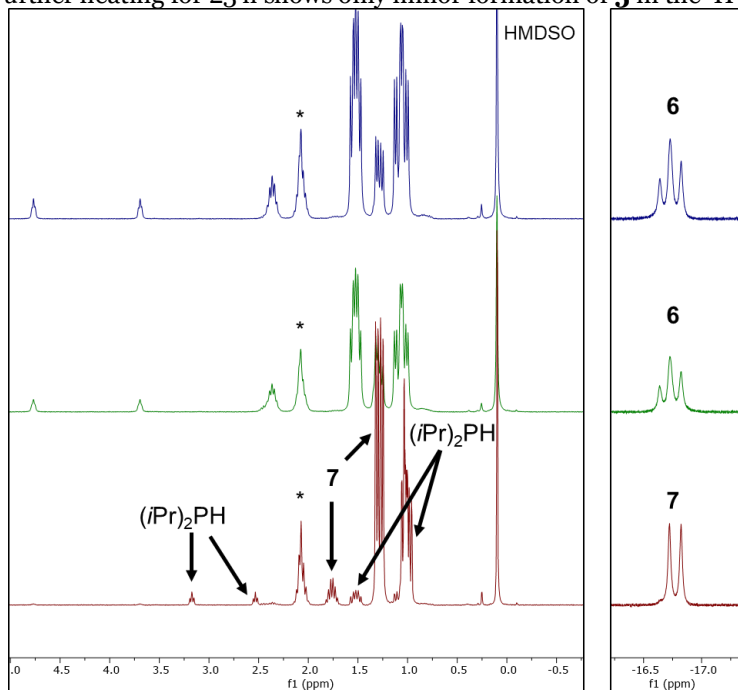


Figure S30: ^1H -NMR spectrum of the reaction mixture in toluene- d_8 at 300 MHz. Bottom: before heating; middle: after 2 h of heating at 120 °C; top: after 23 h heating at 120 °C.

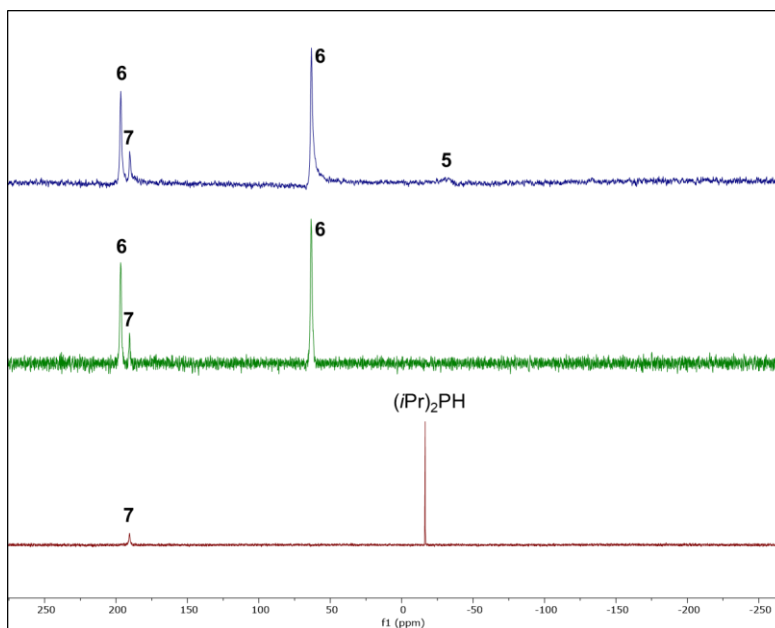
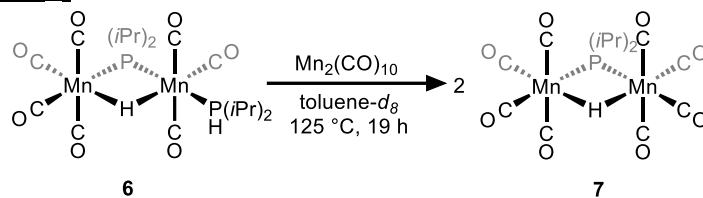


Figure S31: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the reaction mixture in toluene- d_8 at 121 MHz. Red: before heating; green: after heating at 120 °C for 2 h; blue: after heating at 120 °C for 23 h.

Reaction of **6** and $\text{Mn}_2(\text{CO})_{10}$:



In a nitrogen filled glovebox, **6** (33 mg 0.061 mmol, 1 eq.) was transferred to a J-Young NMR tube and dissolved in toluene- d_8 . Dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (22 mg 0.061 mmol, 1 eq) was added and the reaction was heated at 120 °C for 19 h. The reaction was analyzed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectroscopy.

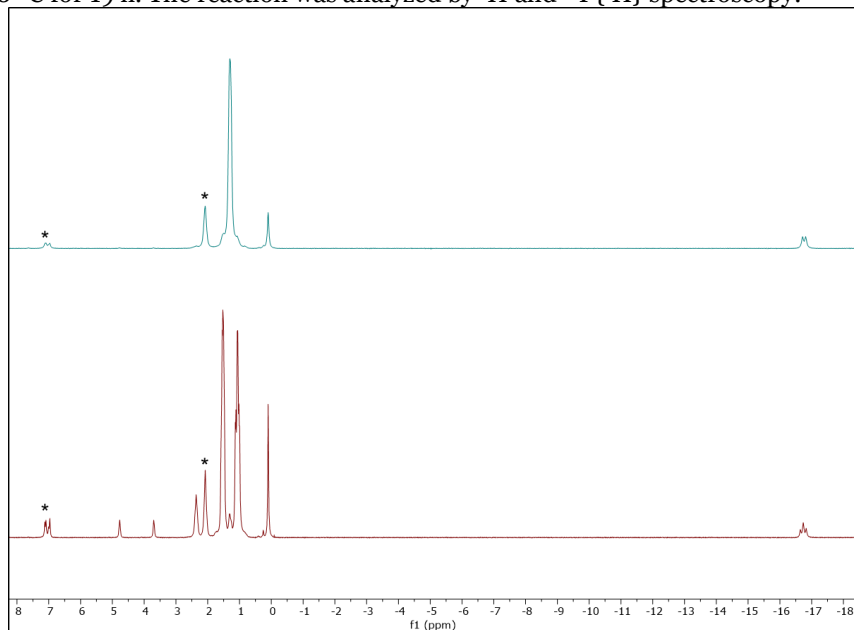


Figure S32: ^1H -NMR spectrum of the reaction mixture in toluene- d_8 at 300 MHz. Red: before heating; blue: after heating at 120 °C for 19 h (the methine peak for **7** and residual solvent methyl peak overlap)

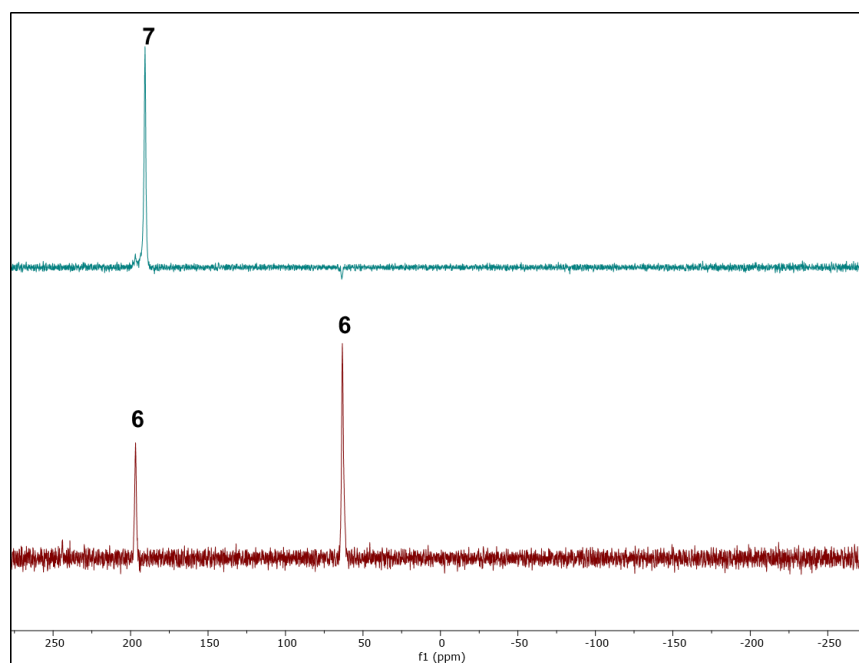
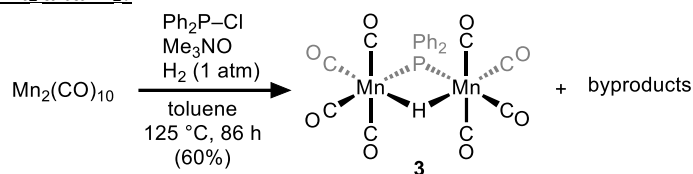


Figure S33: $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the reaction mixture in toluene- d_8 at 121 MHz. Red: before heating; blue: after heating at 120 °C for 19 h.

Synthesis of **3** using ClPPh₂ and H₂:



A 25 mL Schlenk bomb equipped with a stir bar was charged with dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (102 mg, 0.26 mmol., 1 eq.) and dissolved in 3 mL dry toluene. To this solution, anhydrous trimethylamine-*N*-oxide (Me_3NO) (22 mg, 0.29 mmol., 1.1 eq.) was added followed by chlorodiphenylphosphine (ClPh_2P) (57 mg, 0.26 mmol., 1 eq.) with vigorous stirring. The reaction was then subjected to three freeze-pump-thaw cycles and H_2 was introduced at 1 atm. The reaction vessel was then sealed and stirred at 125 °C for 86 h. The reaction was filtered to obtain a yellow solid and a yellow filtrate. The yellow solid (61 mg) is an unidentified byproduct. The yellow filtrate was reduced to dryness *in vacuo* to give a yellow solid, **3** (82 mg, 60%). The yellow by-product had broad featureless NMR spectra potentially indicative of paramagnetic impurities (e.g. no signals observed in ^{31}P -NMR) (Figure S34).

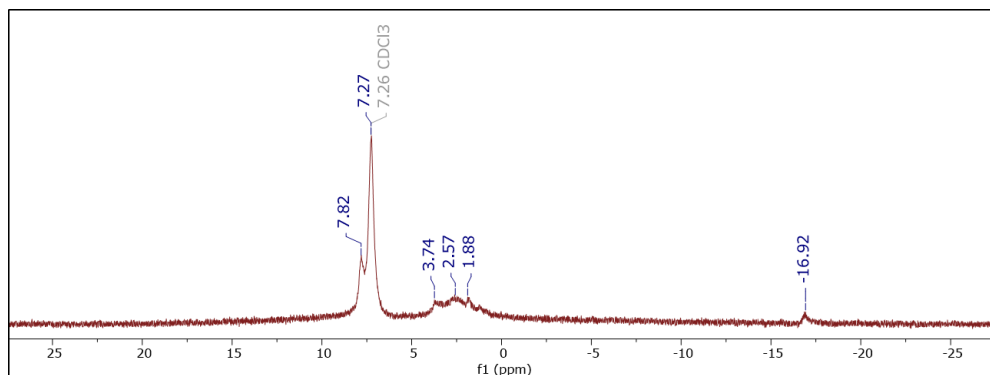


Figure S34: ^1H -NMR of byproducts (contains some **3**).

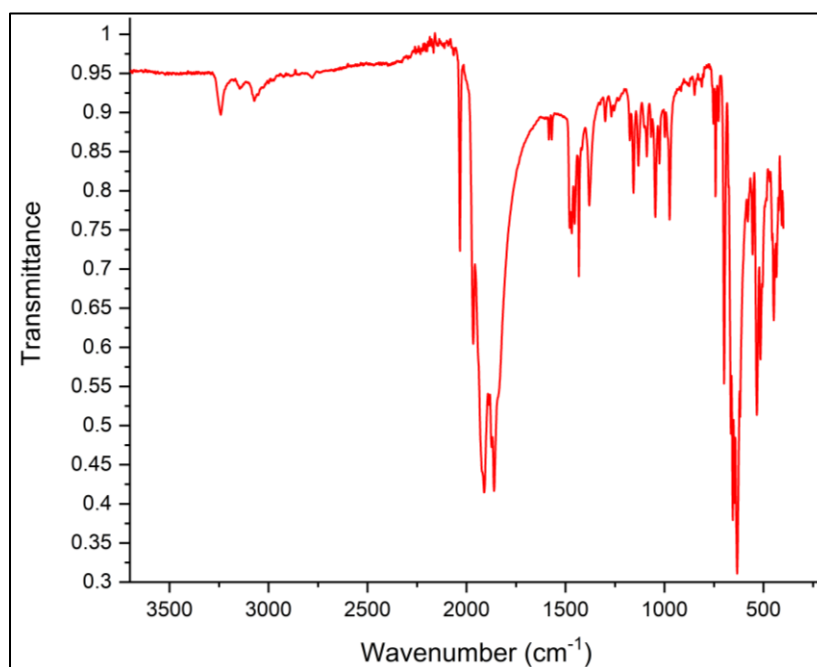
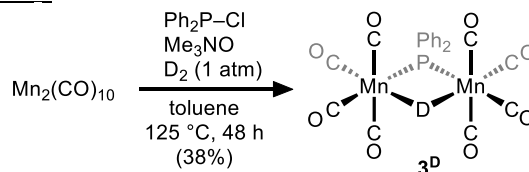


Figure S35: ATR-FTIR spectrum of decomposition product mixture.

Synthesis of **3** using ClPPh₂ and D₂:



A Schlenk bomb equipped with a stir bar was charged with dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (41 mg, 0.105 mmol), trimethylamine-*N*-oxide (Me_3NO) (9 mg, 0.120), and chlorodiphenylphosphine (ClPPh_2) (24 mg, 0.108 mmol) were used in 2 mL dry toluene and D_2 was added at one atmosphere. The reaction yielded **3^D** (21 mg, 38%), identity confirmed using ^1H , ^2H and $^{31}\text{P}\{^1\text{H}\}$ NMRs.

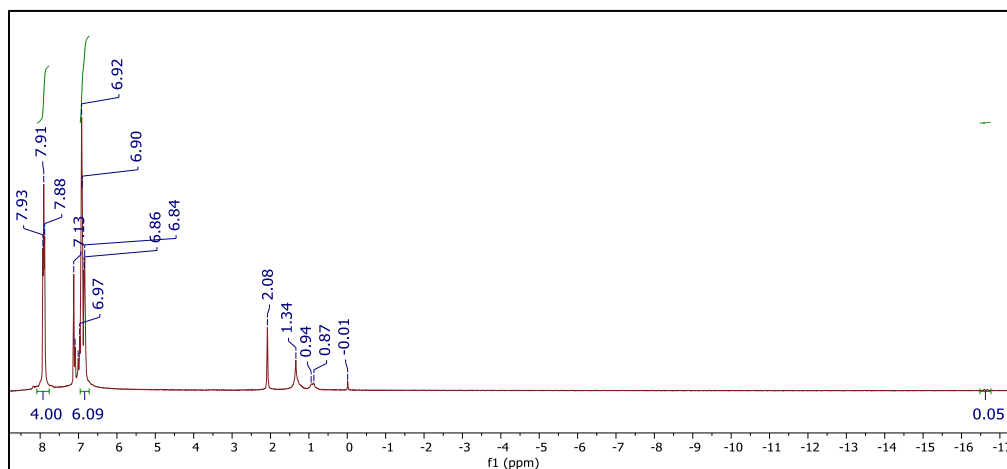


Figure S36: ^1H -NMR of **3^D**. Inset: hydride region, note that the integration for the hydride region is 0.05 H instead of 1 H as compared to the rest of the spectrum indicative of 95% deuterium incorporation.

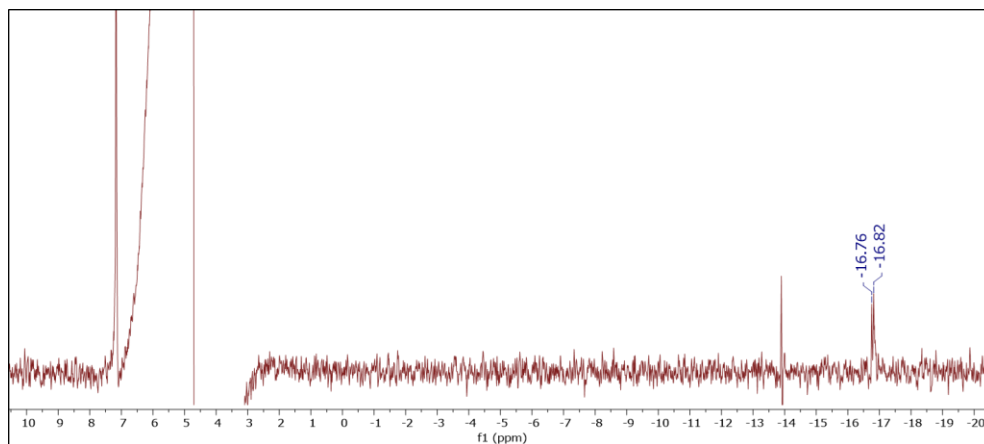


Figure S37: ^2H -NMR of **3^D**. D_2O insert used to lock and shim the instrument.

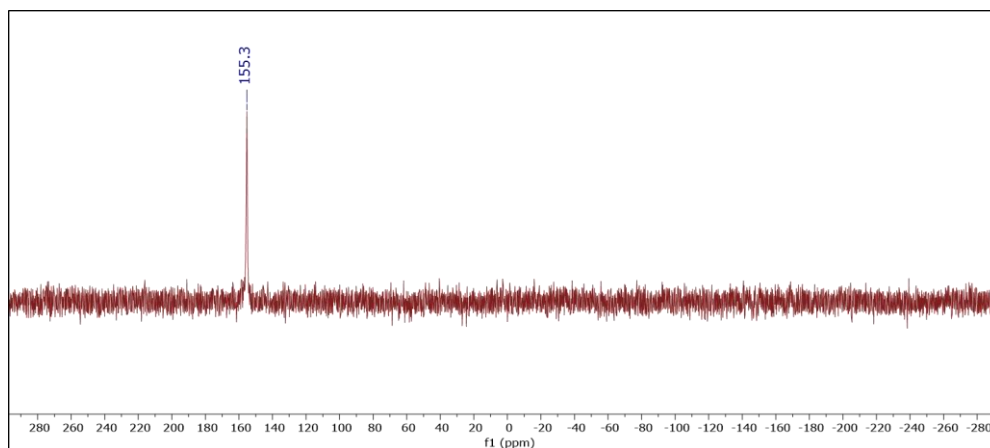
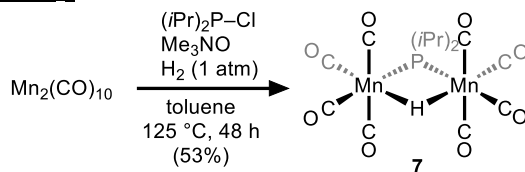


Figure S38: $^{31}\text{P}\{^1\text{H}\}$ NMR of **3^D**.

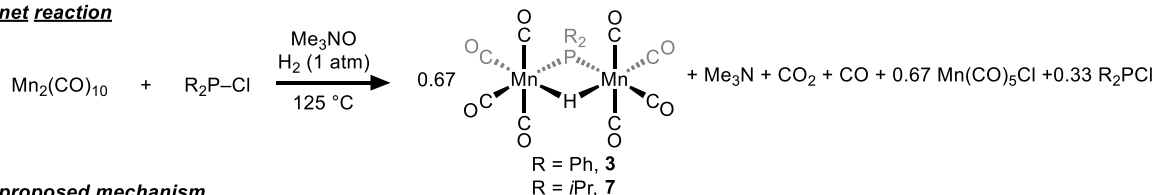
Synthesis of **7** using $\text{ClP}(\text{iPr})_2$ and H_2 :



The procedure was analogous to the synthesis of **3** starting from ClPPh_2 . Dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) (43 mg, 0.109 mmol, 1 eq.), chlorodiisopropylphosphine ($\text{ClP}(\text{iPr})_2$) (16 mg, 0.107 mmol, 1.0 eq.), and 2 mL toluene were used. **7** (25 mg, 53 %) was isolated from .

Discussion on the proposed reaction mechanism and the maximum possible yield of $[\{\text{Mn}(\text{CO})_4\}(\mu\text{-H})(\mu\text{-PR}_2)\{\text{Mn}(\text{CO})_4\}]$ (3** or **7**)**

net reaction



proposed mechanism

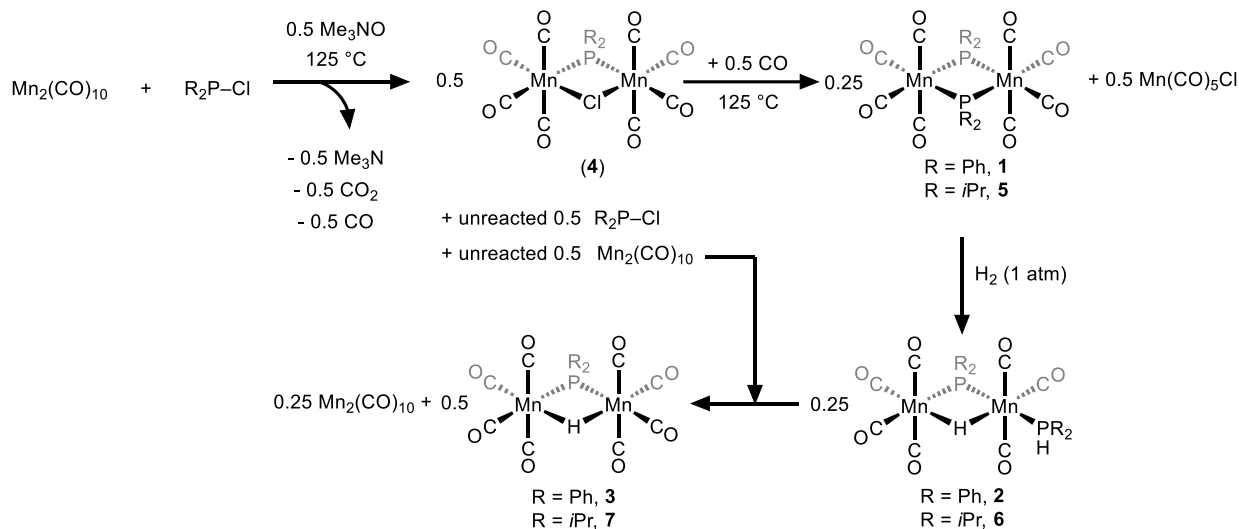


Figure S39: Proposed reaction mechanism.

The mechanism proposed in Figure S39 results in 0.25 eq. of unreacted $\text{Mn}_2\text{CO}_{10}$ which can be taken further on to products (**3** or **7**). Therefore, the theoretical yield of **3** or **7** is the sum...

$$\begin{aligned} \text{Yield of } \mathbf{3} \text{ or } \mathbf{7} &= \frac{1}{2} + \frac{1}{8} + \frac{1}{32} + \frac{1}{128} + \dots \infty = \frac{1}{2} + \frac{1}{2^3} + \frac{1}{2^5} + \frac{1}{2^7} + \dots \infty = \sum_{n=0}^{\infty} \frac{1}{2^{2n+1}} \\ &= \sum_{n=0}^{\infty} \frac{1}{(2^{2n})(2^1)} = \frac{1}{2} \sum_{n=0}^{\infty} \left(\frac{1}{2}\right)^{2n} = \frac{1}{2} \sum_{n=0}^{\infty} \left(\left(\frac{1}{2}\right)^2\right)^n = \frac{1}{2} \sum_{n=0}^{\infty} \left(\frac{1}{4}\right)^n = \frac{1}{2} \times S \\ \text{where } S &= \sum_{n=0}^{\infty} \left(\frac{1}{4}\right)^n \end{aligned}$$

It can be seen that the terms in the summation form a geometric progression (G.P.) of the form

$$a_0 r^0, a_0 r^1, a_0 r^2, a_0 r^3, \dots \infty$$

where $a_0 = 1$ and $r = 1/4$. Since $r < 1$, the G.P. is therefore convergent. As n approaches infinity, the sum of the infinite G.P. is given by:

$$S = \frac{a_0}{(1+r)} = \frac{1}{\left(1 - \frac{1}{4}\right)} = \frac{4}{3}$$

$$\text{Thus, yield of } \mathbf{3} \text{ or } \mathbf{7} = \frac{1}{2} \times S = \frac{1}{2} \times \frac{4}{3} = 0.6\bar{6}$$

This implies that if we started with 1 mole of $\text{Mn}_2(\text{CO})_{10}$, then we can at most get 0.67 moles of product (**3** or **7**). Therefore, based on $\text{Mn}_2(\text{CO})_{10}$ the yield of the reaction is:

$$\% \text{ Yield of } \mathbf{3} \text{ or } \mathbf{7} = \frac{\text{Mol. of } \mathbf{3} \text{ or } \mathbf{7} \text{ produced}}{\text{Mol. of } \text{Mn}_2(\text{CO})_{10} \text{ used}} \times 100 = \frac{0.6\bar{6}}{1} \times 100 = 66.6\bar{6} \%$$

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