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Asymmetric Transfer Hydrogenation of Ketones With Well-Defined Manganese(I) PNN and PNP Complexes

Karl Z. Demmans, Maxwell E. Olson and Robert H. Morris*

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ABSTRACT

Three new manganese complexes trans-[Mn(P–NH–NH–P)(CO)₂][Br], (14) P–NH–NH–P = (S,S)-PPh₂CH₂CH₂NHCH₂NHCH₂PPh₂, fac-[Mn(P–NH–NH–P)(CO)₂][Br], (15) P–NH–NH₂ = (S,S)-PPh₂(C₆H₄)NHCH₂CH₂NHCH₂PPh₂ and syn-mer-Mn(P–NH–NH₂)(CO)₂Br, (16) P–NH–NH₂ = (S,S)-PPh₂CH₂CH₂NHCH₂CH₂NHCH₂PPh₂ were synthesized and tested for the asymmetric transfer hydrogenation (ATH) of acetophenone in 2-ProH. The ligands have stereogenic centers derived from the starting diamine, (S,S)-DPEN. Complex 16 was shown by NOE NMR experiments to have Mn-Br syn to the N-H of the secondary amine. Only the precatalyst 16, upon reaction with potassium tert-butoxide (KO’Bu) in 2-ProH, generated an active system at 80 °C for the ATH of acetophenone to 1-phenylethanol in an enantiomeric excess (ee) of 42% and thus was selected for further investigation into the mechanism of transfer hydrogenation. The corresponding amido complex Mn(P–N–NH₂)(CO)₂ (17), a borohydride complex syn-mer-Mn(P–NH–NH₂)(CO)₂(BH₄) (18), and an ethoxide complex anti-mer-Mn(P–NH–NH₂)(CO)₂(OEt) (19) were independently synthesized and tested in the ATH of acenaphthene. The amido complex 17 and the borohydride complex 18 displayed similar activity to 16 activated in basic 2-ProH, but the anti NH OEt complex 19 was completely inactive. This result suggested that the NH effect, as described by Noyori, was required to obtain catalytic activity. The syn NH BH₄ manganese complex is one of the most active manganese ATH catalysts to date and can hydrogenate a variety of aromatic ketones, including base-sensitive substrates such as p-acetylbenzoate ethyl ester.

INTRODUCTION

Finding catalysts for the asymmetric hydrogenation of ketones, imines, and alkenes is a valuable pursuit as the enantioselectively pure products are of utmost importance to the fragrance, flavor, and pharmaceutical industries.¹,²,³,⁴,⁵,⁶ These products can be synthesized via asymmetric direct hydrogenation (ADH) under hydrogen gas, and ATH using ethanol or 2-ProH as sacrificial alcohols. Other synthetic routes include ammonia-borane, sodium formate in water, or azetotropic mixtures of formic acid and triethylamine.⁶,⁷,⁸,⁹ Ruthenium, rhodium, and iridium remain the most studied transition metals for the ATH of ketones, but there has been a recent push to use well-defined catalysts based on first-row transition metals.¹⁰,¹¹,¹²,¹³,¹⁴,¹⁵,¹⁶,¹⁷,¹₈,¹₉,₂₀,₂₁,₂₂,₂₃,₂₄,₂₅,₂₆,₂₇,₂₈ To date, there are a rapidly growing number of well-defined iron ATH catalysts but only a few examples based on other first-row transition metals such as nickel,²¹ cobalt,²⁹ or manganese.³⁰,³¹

Notable amongst well-defined manganese hydrogenation catalysts are Beller’s recently reported achiral Mn(P–N–P)(CO)₂Br and [Mn(P–N–P)(CO)₂][Br] (1, Figure 1) precatalysts for the direct hydrogenation (DH) of nitriles, ketones, esters, and aldehydes,³²,³³ as well as a one example for the ADH of ketones with a [MnP*-N–P*](CO)₂][Br] precatalyst containing stereogenic phospholane rings on the phosphorus donors (2, Figure 1).³⁴ Beller’s achiral precatalysts also functioned in the transfer hydrogenation (TH) of ketones at 70 °C in 2-ProH, producing a racemic mixture of alcohols in 24 hours.³⁵ For the DH of esters, Pidko and coworkers synthesized achiral Mn(P–N)(CO)₂Br and [Mn(P–N)(CO)₂][Br] precatalysts, while Milstein and coworkers made achiral Mn(P–N–N)(CO)₂Br precatalysts containing a methylene-pyridine...
moiety to take advantage of their well-known dearomatization-rearomatization mechanism (3 and 4 Figure 1). Clarke and coworkers reported a chiral [Mn(P–NH–N)(CO)]$_3$[Br] precatalyst with a ferrocenyl backbone of the P–NH–N ligand for the ADH of ketones (5, Figure 1). For the TH of ketones, Sortais synthesized Mn(N–Y)(CO)$_3$Br (where Y = N, O) precatalysts (6a,b, Figure 1). Sortais probed the ATH of ketones by stirring bromopentacarbonylmanganese with a variety of chiral diamines in a 1:1 ratio to produce the active species in situ. While the exact structures of the precatalysts were not known, this study demonstrated that manganese catalysts with bidentate chiral diamines yield an ee of the product alcohols of up to 64%. The most active and enantioselective manganese ATH catalyst to date was synthesized by Zirakzadeh and coworkers (characterized as diastereomeric hydrides species 7 and 7', Figure 1). These hydride species required basic conditions to achieve catalytic turnover. In optimized conditions with 0.5 mol% of precatalyst, alcohols with an ee of up to 85% could be obtained at room temperature in only two hours.

![Figure 1. Well-defined manganese precatalysts.](image)

Reported herein are the syntheses, characterizations, and catalytic activities in the ATH of ketones for three new manganese catalysts based on previously reported tetradentate P–NH–NH–P and tridentate P’–NH–NH$_2$, P–NH–NH$_2$ ligands 8–10 (see Figure 2) derived from (S,S)-DPEN.

![Figure 2 P–NH–NH–P, P’–NH–NH$_2$, and P–NH–NH$_2$ ligands.](image)
RESULTS AND DISCUSSION

**Improved Synthesis of the P–NH–NH–P Ligand.** The previously reported synthesis of the P–NH–NH–P ligand 8 required four steps over 7 days, including a protection of the phosphine by oxidation and subsequent deprotection with trichlorosilane in basic conditions resulting in a very poor yield of 8 (Scheme 1).\(^{11}\)

Scheme 1. Previous Synthesis of the P–NH–NH–P Ligand 8

The new synthetic protocol was adapted from the synthesis of the P–NH–NH ligand (10, Figure 2).\(^{12}\) The air- and moisture-stable phosphonium dimer 12 (Scheme 2) was synthesized from the acetal 11 according to the literature.\(^{17}\) All of the subsequent steps were then performed in a single-pot. The dimer 12 was deprotonated in basic methanol to release a diphenylphosphinoacetaldehyde which undergoes an iron-templated condensation reaction with (S,S)-DPEN to produce the \([\text{Fe}(\text{P–N–N–P})(\text{MeCN})_2]^{2+}\) intermediate 13, as previously reported.\(^{17}\) Upon addition of lithium aluminum hydride (LiAlH\(_4\)), the iron(II) was reduced to iron(0) and the imines of the P–N–N–P ligand were reduced to release the P–NH–NH–P ligand 8. The extraction in the workup may be performed open to air and, if completed in less than 2 h, gives 8 with no observable oxidation of the 2-(diphenylphosphinyl)ethyl group as confirmed in the \(^{31}\)P\(^{1}\)H) NMR spectrum. For long-term storage, however, the ligand must be placed under an inert atmosphere.
This alternative synthetic protocol reduced the total amount of time to synthesize the product by five days, replaced the energy-intensive hydroamination step with a simple condensation reaction performed at 28 °C (Scheme 2), and afforded the ligand 8 in moderate yield.

**Synthesis of Manganese Complexes.** Treatment of Mn(CO)₃Br with each ligand 8–10 in toluene at 110 °C afforded the corresponding manganese complexes 14–16 in moderate to high yields as shown in Scheme 3.
Scheme 3. Synthesis of New Manganese Complexes 14–16 with Ligands 8–10

Over the course of the reaction in toluene, complexes 14 and 15 precipitated out of solution to yield the manganese(I) di- or tri-carbonyl bromide salt, respectively. These complexes are greater than 92% pure based on elemental analysis done three times but could not be crystallized to complete purity. Complex 14 has $C_2$ symmetry, making the two diphenylphosphino donors spectroscopically equivalent and producing a singlet in the $^{31}P\{^1H\}$ NMR spectrum. This symmetry, as indicated also by the $^1H$ NMR data, suggested that a trans-carbonyl complex was isolated, and indeed the infrared (IR) spectrum displays the asymmetric and symmetric stretches of the carbonyl ligands at 1930 and 1854 cm$^{-1}$, respectively. The IR spectrum of complex 15 displayed three stretches for the carbonyl ligands at 2032, 1955, and 1914 cm$^{-1}$, which suggested the isolation of the fac-isomer as the IR data matched closely to those of the precatalyst fac-[Mn(P’–N–P)(CO)$_3$][Br] that was crystallographically characterized by Beller and coworkers (1, Figure 1). Our precatalysts cis-$\beta$-[Fe(P’–NH–NH–P)(CO)(Br)][BPh$_4$] (P’–NH–NH–P = 9 with an 2-(diphenylphosphinyl)ethyl arm) also preferentially bend at this aniline nitrogen. Reaction of ligand 10 with Mn(CO)$_3$Br initially formed a precipitate, but after stirring the solution for 4h at 110 °C it redissolved. The complex Mn(P–NH–NH$_2$)(CO)$_2$Br (16) was isolated after removal of the toluene in vacuo and washing with pentane and drying as an analytically pure mixture of diastereomers as indicated by the $^{31}P\{^1H\}$ and $^1H$ NMR spectra and elemental analysis. The mer-(P–NH–NH$_2$)-cis-dicarbonyl structure of the diastereomers was suggested on comparison with the IR spectrum known mer-Mn(P–N–N)(CO)$_2$Br complexes (Table 1).
Table 1. IR Data for the Manganese Complexes 14–16 and Comparison with those of Reported Compounds

<table>
<thead>
<tr>
<th>Manganese Complex&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CO Stretches (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[Mn(P–NH–NH–P)(CO)₂][Br], 14</td>
<td>1930, 1854</td>
<td><em>this work</em></td>
</tr>
<tr>
<td>fac-[Mn(P–NH–NH₂)(CO)₂][Br], 15</td>
<td>2032, 1955, 1914</td>
<td><em>this work</em></td>
</tr>
<tr>
<td>fac-[Mn(P–N–P)(CO)₃][Br], 1</td>
<td>2007, 1933, 1891</td>
<td>33</td>
</tr>
<tr>
<td>mer-[Mn(P*-N–P*)(CO)₃][Br], 2</td>
<td>2009, 1908, 1821</td>
<td>34</td>
</tr>
<tr>
<td>fac-[Mn(P–N)(CO)₃][Br], 6b</td>
<td>2029, 1936, 1911</td>
<td>30</td>
</tr>
<tr>
<td>fac-[Mn(P–N–N)(CO)₂][Br], 5</td>
<td>1921, 1842</td>
<td>37</td>
</tr>
<tr>
<td>mer-Mn(P–NH–NH₂)(CO)₂Br, 16</td>
<td>1915, 1828</td>
<td><em>this work</em></td>
</tr>
<tr>
<td>mer-Mn(P–N–N)(CO)₂Br, 3</td>
<td>1916, 1829</td>
<td>40</td>
</tr>
<tr>
<td>mer-Mn(P–N–N)(CO)₂Br, 4</td>
<td>1909, 1828</td>
<td>39</td>
</tr>
</tbody>
</table>

<sup>a</sup>P* indicates stereogenic phospholane rings on the phosphorus donors.

The 2D NMR spectra for the manganese complexes 14 and 16 were used to assign each proton, excluding aromatic protons (Figure 3), as outlined in the Supporting Information. The isomer of 16 shown in Scheme 3 is calculated by use of density functional theory (DFT) to be 1.4 kcal/mol more stable than the one with Mn–Br *anti* to NH of the secondary amine (labeled 16’ in the Supporting Information). The NMR spectra for manganese complex 15 indicated the presence of a minor diastereomer. Upon heating to 65 °C the <sup>31</sup>P NMR signal of the minor diastereomer disappears, concomitantly with the emergence of a new set of <sup>1</sup>H NMR signals (see the supporting information). This suggested the formation of a manganese complex bearing an uncoordinated phosphine donor which may broaden the <sup>1</sup>H NMR spectrum. A rapid acid-base equilibrium between the highly acidic protonated amino donor bearing a bromo counter anion 15 and the deprotonated manganese complex with hydrogen bromide may also lead to the broadening of the <sup>1</sup>H NMR spectrum in this case.

Figure 3. <sup>1</sup>H NMR resonances for 14 and 16 in DMSO-<em>d</em>₆. Selected 2D NOESY correlations are shown with arrows.

Activity in the ATH of Acetophenone. Manganese complexes 14–16 were tested in the ATH of acetophenone under optimized conditions to compare their catalytic activity. The results are shown in Table 2.
Table 2. Catalyst Screen for Activity in the ATH of Acetophenone at 28 °C and 80 °C

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>ee (%, (R)-alcohol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>28</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>28</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>15</td>
<td>28</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>28</td>
<td>56</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>&gt;99</td>
<td>37</td>
</tr>
</tbody>
</table>

*Reactions performed under argon at 28 °C for 24 h or 80 °C for 1 h. Acetophenone:KO'Bu:manganese complex ratio was 100:1:1. Volume of 2-PrOH = 8 mL. [acetophenone] = 0.312 M; [KO'Bu] = 6.25x10^-4 M; [Mn complex] = 3.13x10^-4 M; [2-PrOH] = 13.1 M. (R)-1-Phenylethanol was the major product. Conversions and ee were determined using a gas chromatograph containing a chiral column. Di-tert-butylbenzene was used as an internal standard.

The catalytic activity of these manganese complexes activated in basic 2-PrOH was sluggish at 28 °C, prompting an increase in the temperature of the reaction vessels to 80 °C. Fac-[Mn(P'-NH–NH2)(CO)3][Br] 15 did not catalyze the ATH of acetophenone under these forcing conditions. trans-[Mn(P–NH–NH–P)(CO)2][Br] 14 produced 1-phenylethanol in a 3% yield, while mer-Mn(P–NH–NH2)(CO)Br 16 displayed high activity in basic 2-PrOH with a poor ee of 37%. Precatalyst 16 contains a bromo ligand which can be labilized upon addition of base to produce an amido manganese complex and potassium bromide, while the manganese salt complexes 14 and 15 do not contain a halide to allow for the facile formation of an open site on the manganese center.

**Activation Studies of Manganese Precatalyst.** Further reactions were performed with 16 to detect possible catalytic intermediates and synthesize a borohydride complex which enters the catalytic cycle without the addition of KO'Bu. The first step in the activation of 16 was the deprotonation of an amine to form a manganese amido complex as shown in Scheme 4.
Upon addition of KOtBu to a bright yellow solution of 16 in THF, there was an immediate colour change to deep red, which is characteristic of 5-coordinate manganese amido complexes. The isolated red solid was very oxygen sensitive and characterized only by IR and NMR spectroscopy. The formation of this amido complex by deprotonation of the secondary amine of 16, rather than the primary amine was established by analysis of the $^1$H NMR resonances (Scheme 4), which were assigned by using 2D $^1$H–$^1$H COSY, 2D $^1$H–$^1$H NOESY, and $^1$H–$^{13}$C HSQC NMR experiments. The IR spectrum of 17 displayed two carbonyl stretches at 1890 and 1808 cm$^{-1}$, which are comparable to those of Mn(P–N–P)(CO)$_2$ and Mn(P–N–N)(CO)$_2$ complexes found in the literature.

Several attempts were made to isolate a hydride species by mimicking catalytic conditions without the addition of the substrate. Three hydride species in minute amounts were observed by $^1$H NMR spectroscopy at –4.12 (d, $^2$J$_{PH}$ = 72 Hz), –4.63 (d, $^2$J$_{PH}$ = 36 Hz), and –4.73 (d, $^2$J$_{PH}$ = 38 Hz), but the structures of these hydride species could not be discerned due to their low concentration in solution. The attempted direct synthesis of a hydride species via a reaction of 16 with sodium triethylborohydride at –78 °C in toluene initially formed a bright yellow solution, but upon warming to 28 °C the solution immediately turned red. Removal of the solvent in vacuo indicated the presence of the amido complex 17 as confirmed in the $^{31}$P{$_^1$H} NMR spectrum. It is proposed that the hydride was formed, but preferentially releases hydrogen gas at 28 °C to form the more stable amido complex. Changing to a less reactive hydride source, sodium borohydride, and stirring the solution for 1.5 h produced the manganese borohydride complex containing the Mn–BH$_4$ syn to the NH of the secondary amine (18 in Scheme 5). The yellow powder of 18 was very sensitive to oxygen and was characterized solely by NMR and IR spectroscopy. The syn isomer is calculated by use of density functional theory to be 3.8 kcal/mol more stable than the one with Mn–BH$_4$ anti to NH of the secondary amine (labeled 18’ in the Supporting Information). If the reaction was stirred for 16 h, then the isolated product was a manganese ethoxide complex containing the Mn–OEt anti to the NH of the secondary amine (19’ in Scheme 5, wherein the apostrophe denotes the anti conformation). The yellow powder of 19’ was also very sensitive to the air and was characterized solely by NMR and IR spectroscopy.
Scheme 5. Synthesis of the Syn Manganese Borohydride Isomer and the Anti Manganese Ethoxide Isomer. The Assignment of the $^1$H NMR (Toluene-$d_8$) Resonances and 2D NOESY Correlations (Arrows)

An ethoxide complex is proposed to form by the loss of BH$_3$ and H$_2$ from 18 to produce the amido complex 17, which then heterolytically cleaves the H–O bond of ethanol to form 19 with a Mn–OEt group syn to the NH of the secondary amine. This complex rearranges to the anti isomer 19', which is calculated by use of density functional theory to be 4.0 kcal/mol more stable than 19 (see Supporting Information). The $^1$H NMR resonances of 18 and 19' could be assigned through analysis of the 2D NMR spectra as outlined in Scheme 5. The $^{31}$P($^1$H) NMR spectrum and CO stretches in the IR spectrum of 19' are similar to the manganese bromide complex 16, while the CO stretches in the IR spectrum of 18 at 1920 and 1836 cm$^{-1}$ were comparable with those of a mer-Mn(P–NH–P)(CO)$_2$(BH$_4$) complex bearing cis-carbonyl ligands which was characterized by X-ray crystallography by Gauvin et al.$^{41}$

Proposed Catalytic Cycle. The borohydride complex 18 and ethoxide complex 19' were independently tested in the ATH of acetophenone at 80 °C without the addition of KOtBu and only 18 produced 1-phenylethanol. The proposed catalytic cycles are presented in Scheme 6 and Scheme 7, respectively.

Scheme 6. Proposed Catalytic Cycle for the ATH of Ketones with 16, 17, and 18

The manganese precatalyst 16 reacts with KOtBu to produce an amido manganese complex 17, potassium bromide, and tert-butanol. In an outer-sphere, six-membered transition state, a proton and hydride are transferred from 2-PrOH to the amido complex to produce the uncharacterized syn NH hydride complex 20 which may benefit from the NH Effect.$^{43}$ The active hydride may also be accessed by
stirring a solution of the borohydride complex 18 or amido complex 17 in 2-PrOH without the need for KO'Bu. In this manner, ketones bearing base-sensitive functional groups could also be asymmetrically reduced (p-acetylbenzoate ethyl ester, Figure 4). In the subsequent step, the manganese hydride species 20 transfers a hydride and proton in either a concerted or step-wise outer-sphere mechanism to the ketone substrate to release the (R)-enantiomerically enriched alcohol product and regenerate the amido complex 17.

Garcia et al. studied the use of several alcohols as sacrificial reductants in the transfer hydrogenation of acetophenone with a nickel catalyst prepared in situ. Using ethanol, they observed the initial production of acetaldehyde which reacts with ethanol to produce ethylacetate. In a similar manner, the ethoxide complex 19' is postulated to release acetaldehyde to produce an anti Mn–H and NH hydride species 20' (Scheme 7), which is proposed to be unreactive with respect to the hydride transfer to the ketone due to the lack of carbonyl activation by an NH group.

Scheme 7. Proposed Formation of an Inactive Hydride Species 20' from 19'

Substrate Scope. With the manganese borohydride complex 18, the ATH of various ketones was performed in heated 2-PrOH without the addition of KO'Bu. The optimized catalysis results are shown in Figure 4.

Figure 4. ATH of Various Ketones with Precatalyst 18

\[ ^{a} \text{Reactions performed under argon at 80 °C. Ketone:18 ratio was 100:1. Volume of 2-PrOH = 8 mL. [ketone] = 0.312 M; [18] = 3.13x10^{-4} M; [2-PrOH] = 13.1 M. (R)-Alcohol was the major species in all cases. Conversions and ee were determined using a gas chromatograph containing a chiral column. Di-tert-butylbenzene was used as an internal standard.} \]
The reduction of acetophenone was rapid at 80 °C, only requiring one hour to produce 1-phenylethanol with a poor ee of 42% (R). The addition of electron donating groups in the para position to the acetyl group on the benzene ring placed electron density near the ketone carbonyl, thus decreasing the electrophilicity of the acetyl carbon and decreasing the rate of catalysis. In contrast, addition of electron withdrawing groups in the meta position of the benzene ring to the acetyl group, enhanced catalytic activity by increasing the electrophilicity of the acetyl carbon. This was observed in both cases for the bromo- and chloro-substituted acetophenone derivatives. Increasing the bulk of the R group of the acetophenone derivative led to lower rates of catalysis (Figure 4), as observed with the lower activity of the catalyst in the reduction of cyclohexylphenylketone or the bromo-substituted acetophenone in contrast to the chloro-substituted acetophenone. The catalyst was also efficient for the hydrogenation of base-sensitive substrate p-acetylbenzoate ethyl ester, producing the ethyl ester alcohol without observation of the transesterification product (see ESI).

Conclusion
New manganese complexes 14–16 were synthesized and tested in the ATH of acetophenone. Only the mer-Mn(P–NH–NH$_2$)(CO)$_2$Br complex 16 displayed moderate activity at 80 °C and was therefore selected to further investigate the mechanism of transfer hydrogenation. The active hydride species could not be isolated, but the 5-coordinate amido complex Mn(P–N–NH$_2$)(CO)$_2$ 17 and the borohydride complex syn-mer-Mn(P–NH–NH$_2$)(CO)$_2$(BH$_4$) 18 were isolated and demonstrated to be active in the ATH of acetophenone without the addition of KO'Bu for the first time with manganese. An ethoxide isomer anti-mer-Mn(P–NH–NH$_2$)(CO)$_2$(OEt) 19' was independently synthesized and found to be inactive for ATH of acetophenone. The proposed catalytic cycle for 18 and 19' relies on the production of a syn Mn–H and NH manganese hydride species for the catalysis to proceed. The borohydride complex 18 is one of the most active manganese ATH catalysts to date and can catalyze the hydrogenation of a variety of ketone substrates including the base-sensitive substrate p-acetylbenzoate ethyl ester. Compared to Sortais and coworker’s manganese ATH catalysts prepared in situ, the catalyst presented herein displayed similar activity and enantioselectivity. The manganese catalyst prepared by Zirakzadeh remained the most active and enantioselective manganese ATH in the literature to date, with an impressive rate of catalysis at 25 °C and an unmatched enantioselectivity.

Experimental Section

General experimental considerations. All manipulations were performed under an inert atmosphere of argon using Schlenk or standard glovebox techniques, unless otherwise stated. Solvents and liquid substrates were dried and degassed via distillation prior to use. All solid substrates were heated to 80 °C under vacuum to remove any traces of water before being stored in the glovebox. The P–NH–NH$_2$ ligand 10 and the orthophenylene P–NH–NH$_2$ ligand 9 were synthesized according to literature. NMR spectra were recorded at ambient temperature and pressure using an Agilent 600 MHz, and 500 MHz spectrometer as well as Bruker Avance-III 400 MHz autosampler. The conversions and ee, using di-tert-butylbenzene as an internal standard, for each reaction were obtained on a Perkin Elmer Clarus 400 Chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m x 2.5 mm), using hydrogen gas as the mobile phase. The IR spectra were recorded on a Bruker Alpha with an ATR-platinum diamond attachment. All experiments were repeated three times for accuracy.
Alternative synthesis of the P–NH–NH–P Ligand (8). This procedure was adapted from the synthesis of (15,2S)-N1′-(2-(diphenylphosphinyl)ethyl)-1,2-diphenylethane-1,2-diamine (P–NH–NH2 ligand, 10).12 In separate vials, the diphenylphosphonium dimer (291 mg, 0.471 mmol, 1 equiv.) and sodium methoxide (51 mg, 0.942 mmol, 2 equiv.) were dissolved in methanol (8 mL), iron (II) tetrafluoroborate hexahydrate (239 mg, 0.707 mmol, 1.5 equiv.) was dissolved in methanol (4 mL), and DPEN (100 mg, 0.471 mmol, 1 equiv.) was dissolved in MeCN (4 mL). All solutions were stirred for 2 min, and then combined in a 100 mL Schlenk flask to produce a purple solution. After stirring for 16 h the solution became red, indicating the formation of [Fe(P–N–N–P)(MeCN)2][BF4]2 (P–N–N–P = Ph2PCH2CHNCH(Ph)CH(Ph)NCHCH3PPh2).17 The solvent was removed in vacuo to leave a red residue. LiAlH4 (89 mg, 2.36 mmol, 5 equiv.) was added as a powder, then the mixture was dissolved in THF (20 mL) and allowed to stir for 1 hour until the solution turned grey and gas evolution ceased. The Schlenk flask was brought from the glovebox to the Schlenk line and placed under a continuous flow of argon. It was placed in an ice bath, and the excess LiAlH4 was quenched by injecting water (deionized, not degassed) via a syringe dropwise to the solution. After 2 mL of water was added in this manner, the solution was dried in vacuo to leave a grey residue. The following extraction can be performed in air in order to dissolve the phosphine does not become oxidized. DCM (not dry or degassed, 50 mL) and water (not degassed, 50 mL) was added to the Schlenk flask in order to dissolve the residue. A DCM/water extraction was performed in a 250 mL separatory funnel, extracting the water layer with DCM (50 mL x 2). All of the DCM fractions were combined, dried with magnesium sulphate, filtered through celite, and then dried in vacuo to isolate the PNNP ligand as a brown oil in a 95% purity as indicated by the singlet in the 31P(1H) NMR spectrum at -20.3 ppm. Yield: 185 mg (62%). Full characterization for 8 can be found in the literature.11

Synthesis of trans-[Mn(P–NH–NH–P)(CO)2][Br] (14). The chiral P–NH–NH–P ligand (15,2S)-N1′,N2′-bis(2-(diphenylphosphinyl)ethyl)-1,2-diphenylethane-1,2-diamine 8 (185 mg, 0.290 mmol, 1 equivalent) was dissolved in toluene (5 mL) and placed into a 50 mL Schlenk flask. In a separate vial, bromopentacarbonylmanganese(I) (80 mg, 0.290 mmol, 1 equiv.) was dissolved in toluene (5 mL) and placed into a 50 mL Schlenk flask. In a separate vial, (diphenylphosphinyl)phenyl)1,2-diphenylethane-1,2-diamine 9 (58 mg, 0.123 mmol, 1 equiv.) was dissolved in toluene (5 mL) and placed into a 50 mL Schlenk flask. In a separate vial,
bromopentacarbonylmanganese(I) (34 mg, 0.123 mmol, 1 equiv.) was dissolved in toluene (8 mL) and then added to the Schlenk flask. This was brought out of the glovebox, placed on the Schlenk line and heated at 110 °C under Ar. After 16 h, the reaction was removed from the oil bath and allowed to cool to 28 °C. The solution was freeze-pump-thawed two times, then brought back into the glovebox. The workup was the same as that of 14 to produce a yellow powder. Several attempts were made to crystallize the product to no avail. Yield: 48 mg (56%). 1H NMR spectrum (600 MHz, DMSO-δ6) δ 7.81 - 6.83 (20H, aromatics from CHPPh and PPh3), 6.81 - 6.17 (4H, aromatics from orthophenylene), 6.03 - 5.57 (br, 2H), 4.77 (br, 1H), 4.49 (br, 1 H), 4.15 (br, 1H). Due to the fluctuation behavior of the complex, all of the peaks were broad. 31P{1H} NMR spectrum (243 MHz, DMSO-δ6) δ 63.9 (s). IR ATR (CO ligand): 2032, 1955, and 1914 cm$^{-1}$.

**Synthesis of syn NH Br mer-Mn(P–NH–NH$_2$)(CO)$_2$(Br) (16).** The chiral PNN ligand (S,S)-Ph$_2$PCH$_2$CH$_2$NHCHPh-CHPhNH$_2$ 10 (620.5 mg, 1.461 mmol, 1 equiv.) was dissolved in toluene (15 mL) and placed into a 100 mL Schlenk flask. In a separate vial, bromopentacarbonylmanganese(I) (401.8 mg, 1.461 mmol, 1 equiv.) was dissolved in toluene (20 mL) and then added to the Schlenk flask. This was brought out of the glovebox, placed on the Schlenk line and heated at 110 °C under Ar. After 4 h, the reaction was removed from the oil bath and allowed to cool to 28 °C. The solution was freeze-pump-thawed two times, and then brought back into the glovebox. The solution was filtered to remove any salt impurities, and then the filtrate was removed in vacuo to yield a bright yellow residue. The residue was stirred in diethyl ether (20 mL) for 16 h, filtered, then dried in vacuo to isolate the product as a yellow powder. Several attempts were made to crystallize the product to no avail. Yield: 800 mg (89%). 1H NMR spectrum (600 MHz, DMSO-δ6) δ 7.80 – 7.00 (br, 40H, aromatic protons), 6.14 (t, 1H, PPh$_2$CH$_2$CH$_2$NH), 5.40 (m, 1H, NH$_2$CHPh), 3.95 (m, 1H, NH$_2$CHPh), 3.81 (pseudo t, 1H, NH$_2$CHPh), 3.36 (m, 1H, PPh$_2$CH$_2$), 2.79 (m, 1H, NHCH$_2$), 2.48 (m, 1H, NHCH$_2$), buried under the DMSO-δ6 signal), 2.42 (m, 1H, PPh$_2$CH$_2$, buried under the DMSO-δ6 signal), 2.07 (pseudo t, 1H, NH$_2$CHPh), 3.1p{1H} NMR spectrum (243 MHz, DMSO-δ6) δ 83.1 (s). 2D 1H-13C HSQC spectrum (500 MHz, DMSO-δ6) displays the two CHPh at (3.95, 66.88) and (3.81, 66.97), the two protons of the CH$_2$ adjacent to the amino donor at (2.79, 45.28) and (2.48, 44.99), the two protons of the CH$_2$ adjacent to the diphenylphosphino donor at (3.36, 29.10) and (2.42, 29.23). There is no cross peak for the three amino protons at 6.14, 5.40, and 2.07 ppm in the HSQC. IR ATR (CO ligand): 1915 and 1828 cm$^{-1}$ and a slight impurity at 2023 cm$^{-1}$ which suggests a side-product. ESI+ Mass Spec [M + Br]$^+$/calc.: 535.1347, actual: 535.13. Elemental Analysis [M]: calc.: 58.55% C, 4.75% H, 4.55% N; actual: 58.24% C, 5.12% H, 4.54% N.

**Synthesis of Mn(P–N–NH$_2$)(CO)$_2$ (17).** Mn(P–NH–NH$_2$)(Br)(CO)$_2$ 16 (425 mg, 0.69 mmol, 1 equiv.) was weighed out in a vial and dissolved in THF (8 mL). In a separate vial, KO'Bu (85.2 mg, 0.76 mmol, 1.1 equiv.) was weighed out and dissolved in THF (2 mL). The KO'Bu solution was added dropwise to the vial containing 16 to form a dark red solution. The solution was stirred for 1 h, then the solvent was removed in vacuo. The residue was redissolved in benzene (3 mL), filtered through celite to remove any solid impurities, and then the filtrate was removed in vacuo. The dark red residue was stirred in pentanes for 16 h. The solution was filtered to isolate the product as a dark red powder. Several attempts were made to crystallize the product to no avail. Yield: 320 mg (87%). 1H NMR spectrum (600 MHz, C$_6$D$_6$) δ 7.71 (dt, $^3$I$_{31}$P = 24, 8 Hz, aromatic protons), 7.30-6.85 (m, overlaps with benzene solvent peak, aromatic protons), 6.58 (d, $^3$I$_{31}$P = 7 Hz, 2H, aromatic protons), 4.02 (d, $^3$I$_{31}$P = 7 Hz, 1H, H$_2$NCHPhCHPhN), 3.31 (m, 1H, H$_2$NCHPh), 2.84 (m, 1H, NCH$_2$), 2.77 (m, 1H, NCH$_2$), 2.47 (m, 1H,
NH₂CHPh), 2.45 (dt, ³JHH = 13 Hz, ³JHH = 7 Hz, 1H, CH₂PPh₂), 2.41 (m, 1H, CH₂PPh₂), 2.05 (m, 1H, NH₂CHPh). ³¹P{¹H} NMR spectrum (243 MHz, CDCl₃) δ 102.8 (s). The 2D ¹H-¹³C HSQC spectrum (500 MHz, CDCl₃) displays the two CHPh protons at (4.02, 79.76) and (3.31, 69.32), the two protons of the CH₂ adjacent to the amino donor are found at (2.84, 54.03) and (2.77, 54.03), and the two protons of the CH₂ adjacent to the diphenylphosphino donor at (2.47, 35.22) and (2.41, 35.20). There is no cross peak for the amino group proton at 2.05 ppm, while no conclusion can be drawn for the amino proton at 2.45 ppm since it is shrouded by the CH proton at 2.47 ppm. IR ATR (CO ligand): 1890 and 1808 cm⁻¹. DART Mass Spec [M]⁺: calc.: 534.1269, actual: 534.2. High resolution mass spectroscopy and elemental analysis could not be performed as the product degrades quickly upon exposure to air.

**Synthesis of syn NH BH₄ isomer mer-Mn(P–NH–NH₂)(CO)₂(BH₄) (18).** Mn(P–NH–NH₂)(Br)(CO)₂ 16 (50 mg, 0.081 mmol, 1 equiv.) was weighed out in a vial, then dissolved in ethanol (4 mL) with toluene (1.3 mL). Sodium borohydride (15 mg, 0.405 mmol, 5 equiv.) was added portion-wise. The solution was stirred for 1.5 h, then filtered through celite to remove any solid impurities. The filtrate was removed in vacuo to yield a yellow-orange powder. The residue was redissolved in THF (5 mL) and filtered to remove excess NaBH₄. The filtrate was concentrated to approx. 1 mL, then pentanes was added dropwise to cause precipitation of the product. The product was isolated via filtration, washed with pentanes (2 mL x 3), then dried in vacuo to obtain a yellow powder. Yield: 38 mg (85%). ¹H NMR spectrum (600 MHz, toluene-d₈) δ 7.95 (t, 2H, aromatic protons, ³JHH = 9 Hz), 7.31 (t, 2H, aromatic protons, ³JHH = 9 Hz), 7.22 – 6.74 (24H, aromatic protons), 6.66 (d, 2H, aromatic protons, ³JHH = 5 Hz), 5.06 (t, 1H, NHCH₂, ³JHH = 12 Hz), 4.08 (t, 1H, NH₂CHPh, ³JHH = 10 Hz), 3.82 (pseudo t, 1H, NH₂CHPhCHPh, ³JHH = 12 Hz), 3.09 (pseudo t, 1H, NH₂CHPh, ³JHH = 10 Hz), 2.77 (m, 1H, NHCH₂), 2.44 (t, 1H, PPh₂CH₂, ³JHH = 15 Hz), 2.31 (m, 1H, NHCH₂), 2.09 (m, 1H, NH₂CHPh, buried under toluene signal), 1.80 (m, 1H, PPh₂CH₂), –1.21 to –1.60 (br, BH₄). ³¹P{¹H} NMR spectrum (243 MHz, toluene-d₈) δ 89.2 (s). ¹¹B NMR spectrum (192 MHz, toluene-d₈) δ -23.9 (br). 2D ¹H-¹³C HSQC spectrum displays the two CHPh at (4.08, 65.01) and (3.82, 74.24), the two protons of the CH₂ adjacent to the secondary amino donor at (2.77, 50.39) and (2.31, 49.58), the two protons of the CH₂ adjacent to the diphenylphosphino donor at (2.44, 31.67) and (1.80, 31.64). There is no cross peak for the three amino protons at 6.14, 5.40, and 2.07 ppm in the HSQC spectrum.

**Synthesis of anti NH OEt isomer mer-Mn(P–NH–NH₂)(CO)₂(OEt) (19’).** Mn(P–NH–NH₂)(Br)(CO)₂ 16 was reacted with NaBH₄ as above, but stirred for 16 h. The workup was the same as for 18 to obtain a yellow powder. Yield: 34 mg (75%). ¹H NMR spectrum (600 MHz, toluene-d₈) δ 8.03 (t, 2H, aromatic protons, ³JHH = 9 Hz), 7.37 (t, 2H, aromatic protons, ³JHH = 9 Hz), 7.22 – 6.74 (24H, aromatic protons), 6.60 (m, 2H, aromatic protons), 4.37 (t, 1H, NHCH₂, ³JHH = 12 Hz), 3.94 (t, 1H, NH₂CHPh, ³JHH = 10 Hz), 3.89 (pseudo t, 1H, NH₂CHPhCHPh, ³JHH = 12 Hz), 3.33 (br, 2H, OCH₂CH₃), 2.79 (m, 1H, NHCH₂), 2.62 (pseudo t, 1H, NH₂CHPh, ³JHH = 10 Hz), 2.54 (t, 1H, PPh₂CH₂, ³JHH = 14 Hz), 2.45 (m, 1H, NHCH₂), 2.27 (m, 1H, NH₂CHPh, buried under toluene signal), 1.87 (m, 1H, PPh₂CH₂), 0.97 (br, 3H, OCH₂CH₃), –1.41 (br, 3H, BH₄). ³¹P{¹H} NMR spectrum (243 MHz, toluene-d₈) δ 84.1 (s). 2D ¹H-¹³C HSQC spectrum displays the two CHPh at (3.94, 64.30) and (3.86, 73.36), the two protons of the CH₂ adjacent to the secondary amino donor at (2.80, 49.30) and (2.44, 49.15), the two protons of the CH₂ adjacent to the diphenylphosphino donor at (2.54, 30.58) and the proton at 1.86 was not found in the 2D ¹H-¹³C HSQC spectrum. There is no cross peak for the three amino protons at 4.36, 2.63, and 2.27 ppm in the HSQC spectrum.

IR ATR (CO ligand):
1916 and 1830 cm\(^{-1}\). High resolution mass spectroscopy and elemental analysis could not be performed as the product degrades quickly upon exposure to air.

**Testing the activity of the compounds 14, 15 and 16 for the ATH of acetophenone (Table 2).** By the Schlenk line, an oil bath was kept at 28 °C or heated to 80 °C. Concurrently, in the glovebox, Stock Solution 1 (SS1) containing a manganese precatalyst 14, 15, or 16 (0.025 mmol) was prepared with DCM (1 mL) and quickly placed into a 1 mL syringe. A 10 mL Schlenk flask was charged with 0.1 mL of SS1 and a magnetic stir bar. The solvent was removed in vacuo to obtain 0.0025 mmol of manganese precatalyst in the Schlenk flask. A syringe was filled with 2-PrOH (7 mL) and the needle was stabbed into a rubber stopper. A second syringe was filled with the acetophenone (0.25 mmol), diluted with 2-PrOH (0.5 mL), and the needle was stabbed into the rubber stopper. A third syringe was filled with KO\(\text{tBu}\) (0.56 mg, 0.005 mmol) dissolved in 2-PrOH (0.5 mL). Once the temperature of the oil bath was stable, the Schlenk flask was brought out of the glovebox and attached to the Schlenk line under Ar. The three syringes were taken out of the glovebox, the 2-PrOH was injected into the Schlenk flask, and then the Schlenk flask was lowered into the oil bath. After stirring for 1 minute, the KO\(\text{tBu}\) was injected into the Schlenk flask, then immediately ketone substrate was injected into the Schlenk flask and the stop watch was started. At this stage the concentrations were calculated to be: \([\text{acetophenone}] = 0.312 \text{ M} ; [\text{Mn complex}] = 3.13 \times 10^{-4} \text{ M} ; [\text{KO\(\text{tBu}\)}] = 6.25 \times 10^{-4} \text{ M} [2\text{-PrOH}] = 13.1 \text{ M} \). After the allotted reaction time, the reaction was removed from heat and opened to air. A 0.1 mL aliquot was taken and added to a GC vial containing di-tert-butylbenzene (0.019 mg, 0.1 mmol) in THF (0.9 mL).

**General procedure for the ATH of ketones using the optimized conditions with no KO\(\text{tBu}\) added (Figure 4).** By the Schlenk line, an oil bath was heated to 80 °C. Concurrently, in the glovebox, Stock Solution 1 (SS1) containing manganese complexes 17, 18, or 19' (0.025 mmol) was prepared with benzene (1 mL) and quickly placed into a 1 mL syringe. A 10 mL Schlenk flask was charged with 0.1 mL of SS1 and a magnetic stir bar. The solvent was removed in vacuo to obtain 0.0025 mmol of manganese precatalyst in the Schlenk flask. A syringe was filled with 2-PrOH (7.5 mL) and the needle was stabbed into a rubber stopper. A second syringe was filled with the ketone substrate (0.25 mmol), diluted with 2-PrOH (0.5 mL), and the needle was stabbed into the rubber stopper. Once the temperature of the oil bath was stable, the Schlenk flask was brought out of the glovebox and attached to the Schlenk line under argon. The two syringes were taken out of the glovebox, the 2-PrOH was injected into the Schlenk flask, and then the Schlenk flask was lowered into the oil bath. After stirring for 1 minute, the ketone substrate was injected into the Schlenk flask and the stop watch was started. At this stage the concentrations were calculated to be: \([\text{acetophenone}] = 0.312 \text{ M} ; [\text{Mn complex}] = 3.13 \times 10^{-4} \text{ M} ; [2\text{-PrOH}] = 13.1 \text{ M} \). After the allotted reaction time, the reaction was removed from heat and opened to air. A 0.1 mL sample was taken and added to a GC vial containing di-tert-butylbenzene (0.019 mg, 0.1 mmol) in THF (0.9 mL).

**Associated Content**

**Supporting Information**

Extended experimental section. Summary of \(^{31}\text{P}^{[1\text{H}]}\) NMR spectra and IR spectra. NMR spectra of newly synthesized compounds and activated complexes. Gas chromatograph readouts for the product alcohols, including an NMR spectrum of the base-sensitive \(\rho\)-acetylenzoate ethyl ester for confirmation of the product alcohol. DFT calculations for the structures of the bromide manganese, borohydride manganese, as well as the ethoxide manganese structures.
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Notes
The authors declare no competing financial interest.

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References


Asymmetric Transfer Hydrogenation of Ketones With Well-Defined Manganese(I) PNN and PNNP Complexes

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Supporting Information

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Attempted Synthesis of Mn(P–NH–NH\textsubscript{2})(CO)\textsubscript{2}(H) mimicking catalytic conditions, (20 and 20’):

\[
\begin{align*}
\text{Mn(P–NH–NH\textsubscript{2})(CO)\textsubscript{2}(H)} &\quad & \text{2-PrOH, 80 °C, 10 min.} & \quad & \text{Three Uncharacterized Hydride Species} \\
\end{align*}
\]

Mn(P–N–NH\textsubscript{2})(CO)\textsubscript{2} 17 (30 mg, 0.056 mmol, 1 equivalent) was weighed out in a 20 mL vial and then 2-PrOH (2 mL) was added. The solution immediately turned yellow presumably due to the formation of an alkoxide complex. The solution was stirred for 10 minutes, then the solvent was removed \textit{in vacuo} to yield a yellow residue. The residue was redissolved in benzene, filtered through celite, and then the filtrate was removed \textit{in vacuo} to yield a mixture of products including a three hydride species.

\(^1\text{H} \text{NMR spectrum (600 MHz, C}_6\text{D}_6 \delta -4.12 \ (d, \ ^2\text{J}_{HP} = 71.6 \text{ Hz}), -4.63 \ (d, \ ^2\text{J}_{HP} = 36 \text{ Hz}), -4.73 \ (d, \ ^2\text{J}_{HP} = 38 \text{ Hz}).}

Attempted independent synthesis of Mn(P–NH–NH\textsubscript{2})(CO)\textsubscript{2}(H) via sodium triethylborohydride, (20 and 20’):

\[
\begin{align*}
\text{Mn(P-NH-NH\textsubscript{2})(CO)\textsubscript{2}(Br)} &\quad & \text{NaHBEt\textsubscript{3}, toluene, -78 °C} & \quad & \text{toluene, 28 °C} \\
\end{align*}
\]

Mn(P-NH-NH\textsubscript{2})(CO)\textsubscript{2}(Br) 16 (50 mg, 0.081 mmol, 1 equivalent) was weighed out in a vial, dissolved in toluene (2 mL), and transferred to a 10 mL Schlenk flask. This was brought out of the glovebox, placed on the Schlenk line, and cooled to −78 °C. In the glovebox, NaHBEt\textsubscript{3} (0.08 mL of 1.0 M in toluene, 0.081 mmol, 1 equivalent) was diluted to 2 mL with toluene, then placed in a syringe. The needle of the syringe was stabbed into a rubber stopper and the syringe was brought out of the glovebox. The solution of NaHBEt\textsubscript{3} was added dropwise to the manganese precatalyst solution. The solution quickly became a lighter yellow colour. This reaction was allowed to warm to 28 °C, upon which the solution turned red indicating the presence of the five-coordinate Mn(P–N–NH\textsubscript{2})(CO)\textsubscript{2} compound 17. This was confirmed to be the only product via the \(^{31}\text{P}(^1\text{H})\text{ and }^1\text{H NMR spectra.}
### Summary of $^{31}\text{P}^{[1\text{H}]}$ NMR Spectrum Chemical Shifts and IR CO Stretch Wavenumbers

Table S1: Summary of $^{31}\text{P}^{[1\text{H}]}$ NMR Spectral Information and IR CO Stretch Wavenumbers

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{31}\text{P}^{[1\text{H}]}$ Spectrum Chemical Shift (ppm)</th>
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<td>trans-[Mn(P–NH–NH–P)(CO)$_2$][Br], 14</td>
<td>77.9</td>
<td>1930, 1854</td>
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<tr>
<td>fac-[Mn(P’–NH–NH$_2$)(CO)$_3$][Br], 15</td>
<td>63.9</td>
<td>2032, 1955, 1914</td>
</tr>
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<td>syn mer-Mn(P–NH–NH$_2$)(CO)$_2$Br, 16</td>
<td>83.1</td>
<td>1915, 1828</td>
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<td>Mn(P–N–NH$_2$)(CO)$_2$, 17</td>
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<td>1890, 1808</td>
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<td>syn mer-Mn(P–NH–NH$_2$)(CO)$_2$(BH$_4$), 18</td>
<td>89.2</td>
<td>1920, 1836</td>
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<tr>
<td>anti mer-Mn(P–NH–NH$_2$)(CO)$_2$(OEt), 19’</td>
<td>84.1</td>
<td>1916, 1830</td>
</tr>
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</table>
NMR Spectra of Newly Synthesized Chemicals

A Note on Solving NMR in the Following Studies:

2D $^1$H–$^{13}$C HSQC spectrum was used to locate the two CHPh o the DPEN backbone in the $^{13}$C range of 70–90 ppm, using the intensity in the $^1$H to discern the major species, medium species, and minor species (when applicable). The 2D $^1$H–$^1$H COSY spectrum was used to discern the connectivity of the DPEN backbone to the side arm, verifying how many protons were attached to each carbon through the HSQC. The 2D $^1$H–$^1$H NOESY spectrum was used to place the protons on either the top or bottom of the plane formed by the PNN ligand, using the DPEN CHPh as an anchor.
Figure S1 NMR and IR Spectroscopy for trans-[Mn(–NH–NH–P)2(CO)2][Br] (14):

(a) $^1$H NMR spectrum (600 MHz, DMSO-$d_6$):
(b) $^1$H NMR spectrum, zoom on CH$_2$, NH, CHPh region:

(c) $^{31}$P$\{^1$H$\}$ NMR spectrum (243 MHz, DMSO-$d_6$):
(d) 2D $^1$H–$^1$H COSY spectrum (600 MHz, DMSO-$d_6$):

(e) 2D $^1$H–$^1$H NOESY spectrum (600 MHz, DMSO-$d_6$):
(f) **2D $^1$H–$^{13}$C HSQC spectrum (500 MHz, DMSO-$d_6$):**

2D $^1$H–$^{13}$C HSQC spectrum displays the two CHPh at (3.04, 67.57), the four protons of the two CH$_2$ adjacent to the amino donor at (3.19, 49.67) and (2.94, 49.69), the four protons of the two CH$_2$ adjacent to the diphenylphosphino donor at (3.57, 22.93) and (3.00, 22.82). There is no cross peak for the two amino protons at 3.75 ppm in the HSQC.

(g) **IR Spectrum:**

The CO stretches of manganese complex 14 are at 1930 cm$^{-1}$ and 1854 cm$^{-1}$. 
Figure S2 NMR and IR Spectroscopy for fac-[Mn(P–NH–NH₂)(CO)]₃[Br] (15):

(a) $^1$H NMR spectrum (600 MHz, DMSO-$d_6$):
(b) Zoom in on $^1$H NMR spectrum (600 MHz, $d_6$-DMSO) between $\delta$ 3.8 ppm – 8.0 ppm:

(c) $^{31}$P($^1$H) spectrum (243 MHz, DMSO-$d_6$):
(d) IR Spectrum:

The CO stretches of manganese complex 15 are at 2032 cm\(^{-1}\), 1955 cm\(^{-1}\), and 1914 cm\(^{-1}\).

(e) \(^{31}\text{P}\{^1\text{H}\}\) Variable temperature NMR spectra heating from 25 °C to 85 °C, then back down to 25 °C.
(f) $^1$H Variable temperature NMR spectra heating from 25 °C to 85 °C, then back down to 25 °C. Asterisks denote areas of change.
Figure S3 NMR and IR Spectroscopy for syn mer-Mn(P–NH–NH$_2$)(CO)$_2$Br (16):

(a) $^1$H NMR spectrum (600 MHz, DMSO-$d_6$):
(b) $^{31}$P-$^1$H NMR spectrum (243 MHz, DMSO-$d_6$):

![31P-1H NMR spectrum](image)

(c) 2D $^1$H-$^1$H COSY spectrum (600 MHz, DMSO-$d_6$):

![2D 1H-1H COSY spectrum](image)
(d) Zoom in on 2D $^1\text{H}^-^1\text{H}$ COSY spectrum (600 MHz, DMSO-$d_6$) between $\delta$ 2.0 ppm – 6.5 ppm:

(e) 2D $^1\text{H}^-^1\text{H}$ NOESY spectrum (600 MHz, DMSO-$d_6$):
(f) Zoom in on 2D $^1$H–$^1$H NOESY spectrum (600 MHz, DMSO-$d_6$) between δ 0.6 ppm – 4.1 ppm:

![2D NOESY spectrum](image)

(g) 2D $^1$H–$^{13}$C HSQC spectrum (500 MHz, DMSO-$d_6$):

2D $^1$H–$^{13}$C HSQC spectrum displays the two CHPh at (3.95, 66.88) and (3.81, 66.97), the two protons of the CH$_2$ adjacent to the amino donor at (2.79, 45.28) and (2.48, 44.99), the two protons of the CH$_2$ adjacent to the diphenylphosphino donor at (3.36, 29.10) and (2.42, 29.23). There is no cross peak for the three amino protons at 6.14, 5.40, and 2.07 ppm in the HSQC. The cross peak at (3.33, 65.41) and the proton with the most upfield shift (1.09 ppm) is from diethyl ether.

![2D HSQC spectrum](image)
The CO stretches of precatalyst 16 are at 1915 cm$^{-1}$ and 1828 cm$^{-1}$. The slight impurity at 2023 cm$^{-1}$ suggests a side-product in the form $[\text{Mn}(\text{P--NH--NH}_2)(\text{CO})_3][\text{Br}]$ was present in small quantities.
NMR Spectra of Base Activation Studies

**Figure S4** NMR and IR Spectroscopy for Mn(P–N–NH$_2$)(CO)$_2$ (17):

(a) $^1$H NMR spectrum (600 MHz, C$_6$D$_6$):
(b) Zoom in on $^1$H NMR spectrum (600 MHz, C$_6$D$_6$) between $\delta$ 1.9 ppm – 4.2 ppm:

(c) $^{31}$P{$^1$H} NMR spectrum (253 MHz, C$_6$D$_6$):
(d) 2D $^1$H–$^1$H COSY spectrum (600 MHz, C$_6$D$_6$):

(e) Zoom in on 2D $^1$H–$^1$H COSY spectrum (600 MHz, C$_6$D$_6$) between $\delta$ 1.9 ppm – 4.2 ppm:
(f) 2D $^1$H–$^1$H NOESY spectrum (600 MHz, C$_6$D$_6$):

(g) Zoom in on 2D $^1$H–$^1$H NOESY spectrum (600 MHz, C$_6$D$_6$) between δ 1.8 ppm – 4.2 ppm:
(h) 2D $^1$H–$^{13}$C HSQC spectrum (500 MHz, C$_6$D$_6$):

2D $^1$H–$^{13}$C HSQC spectrum displays the two CHPh protons at (4.02, 79.76) and (3.31, 69.32), the two protons of the CH$_2$ adjacent to the amino donor are found at (2.84, 54.03) and (2.77, 54.03), and the two protons of the CH$_2$ adjacent to the diphenylphosphine at (2.45, 35.22) and (2.41, 35.20). There is no cross peak for the amino group proton at 2.05 ppm, while no conclusion can be drawn for the amino proton at 2.47 ppm since it is shrouded by the CH$_2$ proton at 2.45 ppm.

(i) IR Spectrum:

The CO stretches of deprotonated complex 17 are at 1890 cm$^{-1}$ and 1808 cm$^{-1}$.
NMR Spectra of Hydride, Borohydride, and Ethoxide Species

Figure S5 NMR and IR Spectroscopy for the attempted synthesis of Mn(P−NH−NH$_2$)(CO)$_2$H (20):

17

2-PrOH, 80 °C, 10 min → Three Uncharacterized Hydride Species

(a) $^1$H NMR spectrum (600 MHz, C$_6$D$_6$):

![NMR Spectrum Image]
(b) Zoom in on $^1$H NMR spectrum (600 MHz, C$_6$D$_6$) in the hydride region
Figure S6 NMR and IR Spectroscopy for syn mer-Mn(P–NH–NH₂)(CO)₂(BH₄) (18):

(a) ¹H NMR spectrum (600 MHz, toluene-d₈):
(b) Zoom in on $^1$H NMR spectrum (600 MHz, toluene-$d_8$) between δ 1.7 ppm – 5.5 ppm:

(c) $^{11}$B NMR spectrum (192 MHz, toluene-$d_8$):
(d) $^{31}$P[$^1$H] NMR spectrum (243 MHz, toluene-$d_8$):

(e) 2D $^1$H–$^1$H COSY spectrum (600 MHz, toluene-$d_8$):
(f) Zoom in on 2D $^1$H–$^1$H COSY spectrum (600 MHz, toluene-$d_8$) between δ 1.6 ppm – 5.3 ppm:

![Zoomed in 2D $^1$H–$^1$H COSY spectrum](image)

(g) 2D $^1$H–$^1$H NOESY spectrum (600 MHz, toluene-$d_8$):

![Zoomed in 2D $^1$H–$^1$H NOESY spectrum](image)
(h) Zoom in on 2D $^1$H–$^1$H NOESY spectrum (600 MHz, toluene-$d_8$) between $\delta$ 1.7 ppm – 5.1 ppm:

(i) 2D $^1$H–$^{13}$C HSQC spectrum (600 MHz, toluene-$d_8$):

Explanation: 2D $^1$H–$^{13}$C HSQC spectrum displays the two CPh at (4.08, 65.01) and (3.82, 74.24), the two protons of the CH$_2$ adjacent to the secondary amino donor at (2.77, 50.39) and (2.31, 49.58), the two protons of the CH$_2$ adjacent to the diphenylphosphino donor at (2.44, 31.67) and (1.80, 31.64). There is no cross peak for the three amino protons at 5.06, 3.09, and 2.09 ppm in the HSQC.
The CO stretches of the borohydride complex 18 are at 1920 cm$^{-1}$ and 1836 cm$^{-1}$. 
Figure S7 NMR and IR Spectroscopy for *anti mer*-Mn(P–NH–NH$_2$)(CO)$_2$(OEt) (19’):

(a) $^1$H NMR spectrum (600 MHz, toluene-$d_8$):
(b) Zoom in on $^1$H NMR spectrum (600 MHz, toluene-$d_8$) between $\delta$ 0.9 ppm – 4.8 ppm:

(c) $^{11}$B NMR spectrum (192 MHz, toluene-$d_8$):
No peaks are present in the $^{11}$B NMR spectrum.
(d) $^{31}\text{P}^{1\text{H}}$ NMR spectrum (243 MHz, toluene-$d_8$):

(e) 2D $^1\text{H}^{1\text{H}}$ COSY spectrum (600 MHz, toluene-$d_8$):
(f) Zoom in on 2D $^1$H–$^1$H COSY spectrum (600 MHz, toluene-$d_8$) between $\delta$ 1.0 ppm – 4.5 ppm:

(g) 2D $^1$H–$^1$H NOESY spectrum (600 MHz, toluene-$d_8$):
(h) Zoom in on 2D $^1$H–$^1$H NOESY spectrum (600 MHz, toluene-$d_8$) between $\delta$ 1.7 ppm – 4.4 ppm:

(i) 2D $^1$H–$^{13}$C HSQC spectrum (600 MHz, toluene-$d_8$):

2D $^1$H–$^{13}$C HSQC spectrum displays the two CHPh at (3.94, 64.21) and (3.89, 73.23), the two protons of the CH$_2$ adjacent to the secondary amino donor at (2.79, 49.38) and (2.45, 48.97), the two protons of the CH$_2$ adjacent to the diphenylphosphino donor at (2.54, 30.42) and no cross peak was found for the proton at 1.87. There is no cross peak for the three amino protons at 4.37, 2.62, and 2.27 ppm in the HSQC spectrum.
IR spectrum:

The CO stretches of the anti ethoxide complex 19' are at 1916 cm\(^{-1}\) and 1830 cm\(^{-1}\).
Gas Chromatograph Readouts for the ATH of Ketones

**Figure S8** Gas chromatograph readout for the ATH of acetophenone.

\[
\text{Oven Temperature: } 130 \, ^{\circ}\text{C}
\]

Retention time: acetophenone: 4.421 min.; \((R)-1\text{-phenylethanol}: 7.329\) min.; \((S)-1\text{-phenylethanol}: 7.752\) min.; ditert-butylbenzene (standard): 10.850 min.
**Figure S9** Gas chromatograph readout for the ATH of *m*-chloroacetophenone.

![Gas chromatograph readout](image)

Oven Temperature: 145 °C

Retention time: *m*-chloroacetophenone: 5.434 min.; *(R)*-1-(*m*-chlorophenyl)ethan-1-ol: 6.920 min.; *(S)*-1-(*m*-chlorophenyl)ethan-1-ol: 7.370 min.; di-tert-butylbenzene (standard): 3.958 min..

**Figure S10** Gas chromatograph readout for the ATH of 3′,5′-bis(trifluoromethyl)acetophenone.

![Gas chromatograph readout](image)

Oven Temperature: 140 °C

Retention time: 3′,5′-bis(trifluoromethyl)acetophenone: 2.939 min.; *(S)*-1-(3′,5′-bis(trifluoromethyl)phenyl)ethanol: 2.804 min.; *(R)*-1-(3′,5′-bis(trifluoromethyl)phenyl)ethanol: 2.972 min.; di-tert-butylbenzene (standard): 4.699 min..
**Figure S11** Gas chromatograph readout for the ATH of p-methylacetophenone.

\[
\text{Oven Temperature: } 130 \, ^\circ\text{C}
\]


**Figure S12** Gas chromatograph readout for the ATH of p-chloroacetophenone.

\[
\text{Oven Temperature: } 145 \, ^\circ\text{C}
\]

Retention time: \(p\)-chloroacetophenone: 4.018 min.; \((R)\)-1-(\(p\)-chlorophenyl)ethan-1-ol: 5.313 min.; \((S)\)-1-(\(p\)-chlorophenyl)ethan-1-ol: 5.771 min.; di-tert-butylbenzene (standard): 2.929 min.
**Figure S13** Gas chromatograph readout for the ATH of p-acetylbenzoate ethyl ester.

Oven Temperature: 180 °C

Retention time: p-acetylbenzoate ethyl ester: 2.686 min.; ethyl (R)-p-(1-hydroxyethyl)benzoate: 5.726 min.; ethyl (S)-p-(1-hydroxyethyl)benzoate: 5.885 min.; di-tert-butylbenzene (standard): 1.853 min..

**Figure S14** Gas chromatograph readout for the ATH of 1-acetonaphthone.

Oven Temperature: 150 °C

Retention time: 1-acetonaphthone: 8.298 min.; (R)-1-(naphthalen-1-yl)ethan-1-ol: 19.331 min.; (R)-1-(naphthalen-1-yl)ethan-1-ol: 21.275 min.; di-tert-butylbenzene (standard): 2.615 min..
**Figure S15** Gas chromatograph readout for the ATH of m-bromoacetophenone.

![Gas chromatograph readout for the ATH of m-bromoacetophenone.](image)

Oven Temperature: 145 °C

Retention time: m-bromoacetophenone: 4.841 min.; (R)-1-(m-bromophenyl)ethan-1-ol: 8.856 min.; (S)-1-(m-bromophenyl)ethan-1-ol: 9.385 min.; di-tert-butylbenzene (standard): 3.621 min..

**Figure S16** Gas chromatograph readout for the ATH of cyclohexylphenylketone.

![Gas chromatograph readout for the ATH of cyclohexylphenylketone.](image)

Oven Temperature: 170 °C

Retention time: cyclohexylphenylketone: 8.169 min.; (R)-cyclohexyl(phenyl)methanol: 8.258 min.; (S)-cyclohexyl(phenyl)methanol: 8.452 min.; di-tert-butylbenzene (standard): 2.223 min..
Figure S17 Gas chromatograph readout for the ATH of p-bromoacetophenone.

![Image of gas chromatograph readout]

Oven Temperature: 145 °C

Characterization of Ethyl p-(1-hydroxyethyl)benzoate Alcohol Product

After catalysis, the reaction solution was cooled to 28 °C. The solvent was removed *in vacuo* and an $^1$H NMR spectrum was taken of the residue without any purification.

*Figure S18* $^1$H NMR of ethyl p-(1-hydroxyethyl)benzoate (600 MHz, CDCl$_3$)
DFT Calculations for the Manganese Bromide, Manganese Borohydride, and Manganese Ethoxide Isomers

Structural Information

The DFT calculations were done with Gaussian09\(^1\) using the functional PBEPBE and the basis set 6-31+G\(^*\) for all atoms apart from the manganese which was treated with the SDD effective core potential. An ultrafine integration grid was employed, and the optimized structures had no imaginary modes. The GIAO method was used to calculate the \(^1\)H NMR isotropic shielding constants. The calculated structures and relative energies of the diastereomers of \(16\) and \(16'\), \(18\) and \(18'\), as well as \(19\) and \(19'\) are shown in the Figure below.

**Figure S19** Structures of pairs of isomers calculated using DFT methods along with their relative energies (the lower of the two for each pair is set as zero energy).

\[ \begin{align*}
16 \Delta G_{\text{rel}} &= 0.0 \text{ Kcal/mol} \\
16' \Delta G_{\text{rel}} &= 1.4 \text{ Kcal/mol} \\
18 \Delta G_{\text{rel}} &= 0.0 \text{ Kcal/mol} \\
18' \Delta G_{\text{rel}} &= 3.8 \text{ Kcal/mol}
\end{align*} \]
$\Delta G_{\text{rel}} = 4.0 \text{ Kcal/mol}$

$\Delta G_{\text{rel}} = 0.0 \text{ Kcal/mol}$
References