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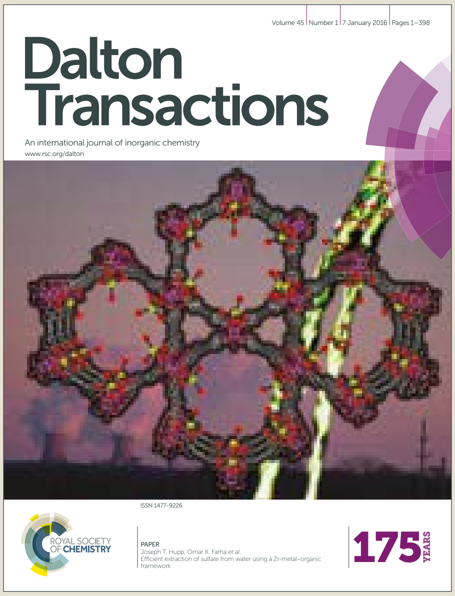

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COMMUNICATION

Pentacarbonylmethylmanganese(I) as a synthon for Mn(I) pincer catalysts

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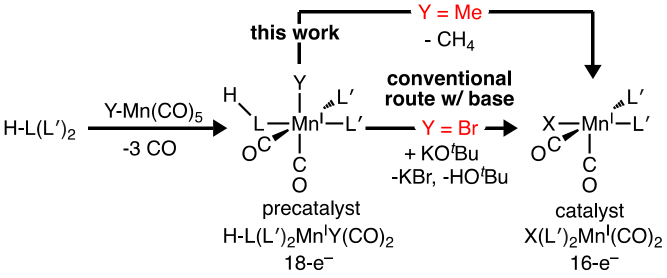
Mn(I) complexes that enable metal-ligand cooperative substrate activation catalyze a range of transformations. Use of $MeMn(CO)_5$ as a synthon in place of typical $Mn(CO)_5Br$ was explored and found to be quite versatile, generating catalytically active species *in situ* by activation of O–H, N–H, and even C–H bonds.

The discovery of metal-ligand cooperativity (MLC) enables green acceptorless (de)hydrogenative transformations.[1,2] The subsequent advent of aromatization-dearomatization MLC with pincer ligands fueled a productive decade of research that used predominantly 16-e⁻ Ru^{II} complexes.[3,4] The recent finding that Mn(I) is also competent in (de)hydrogenation catalysis[5,6] comes on the tails of this research using Ru, which was closely followed by studies with earth abundant transition metals like Fe, Co and Mo.[7,8] These studies are quite timely in an era where replacement of expensive metal ions in catalysis is considered vital. For example, Ru is significantly less abundant than Mn, the latter of which is the third most abundant transition metal in the earth crust.[9] Considering that catalytic (de)hydrogenation for most transition metal ions have been known for decades and that 16-e⁻ Mn(I) species have been known for over 60 years,[10] it is quite surprising that Mn(I) hydrogenation catalysts came so late.

For example, the methyl group in $MeMn(CO)_5$ undergoes reversible migration to a *cis*-carbonyl ligand to generate a 16-e⁻ Mn-acyl complex. However, this complex is not a known (de)hydrogenation catalyst nor does it activate H_2. On the other hand, Mn(I) complexes with "bifunctional ligands" that support metal-ligand cooperative (MLC) substrate activation engage in productive (de)hydrogenation catalysis. Since the 2016 discovery of Milstein,[5] Beller,[6] and others that Mn(I) ions are active (de)hydrogenation catalysts, there has been an explosion of investigations surrounding the chemistry of Mn(I).[8] Collectively, these studies provide the insight that the desired precatalyst formulation is $H–L(L')_2MnY(CO)_2$, where H–L is a neutral ligand that can be deprotonated with KO^tBu, Y is an X-type ligand, and L′ is a neutral spectator ligand that is either CO or derived from the same ligand containing H–L. To our knowledge, the Y group in these previously reported Mn(I) precatalysts is a bromido ligand without exception.[11]

Scheme 1 Use of $MeMn(CO)_5$ in place of the bromide in Mn(I) pincer catalyst preparation.



Pidko identified this facet as one of the major shortcomings of MLC-Mn(I) chemistry, namely that $Mn(CO)_5Br$ and possibly $Mn_2(CO)_{10}$ are the only Mn(I) precursor starting materials.[7c] Both of these Mn precursors, and especially the former, are particularly expensive and not amenable to synthesis in most modern academic synthetic organic/organometallic laboratories. Considering that $Mn(CO)_5Br$ is prepared from $Mn_2(CO)_{10}$, and that the bromido complex is substantially more expensive, other materials derived from $Mn_2(CO)_{10}$ are desirable. Additionally, chemical limitations inherent from using $Mn(CO)_5Br$ or $Mn_2(CO)_{10}$ necessitate new methodologies to generate catalytically active species.

To this end, we envisioned that $MeMn(CO)_5$ as an alternative to $Mn(CO)_5Br$ has several advantages (Scheme 1).

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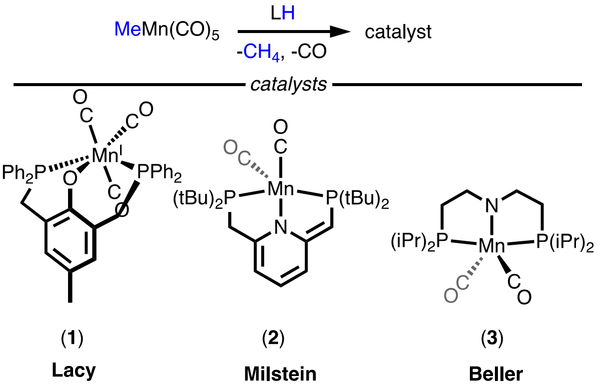
The first is that $MeMn(CO)_5$ can be easily generated from $Mn_2(CO)_{10}$ in good yields. A second advantage is that spontaneous liberation of CH_4 from the metal complex provides an expedient route to the active 16-e^- catalyst from Mn precursor and ligand thereby providing a ligand screening strategy. Herein we report the use of the novel strategy of $MeMn(CO)_5$ to generate catalytically active MLC-Mn(I) complexes. We also report additional new phenolic based pincer phosphine ligands, as a follow-up to an earlier report,[12] that can be directly used to catalyze the Tishchenko reaction. We use these new ligands to showcase the power of the $MeMn(CO)_5$ methodology to screen ligands and bypass potentially laborious coordination chemistry efforts. During these studies we confirmed the presence of Mn-acyl derivatives as intermediates in coordination reactions that eventually lead to the active catalysts upon heating.

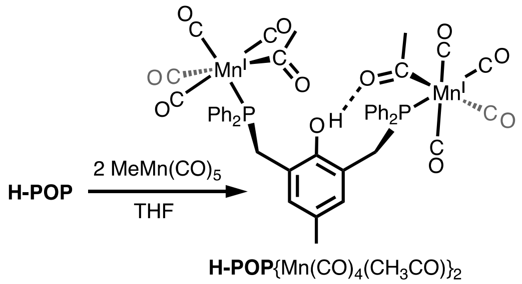
The preparation of $MeMn(CO)_5$ is established in the literature.[13] We adopted a similar strategy, which involves reducing $Mn_2(CO)_{10}$ with an excess of NaK in THF and treating the resulting crude $M[Mn(CO)_5]$ (M = Na, K) material with MeI in diethyl ether. $MeMn(CO)_5$ is rather volatile and easily sublimed to obtain colorless air-stable prisms in good yields (70-90%) when performed on a 500 mg scale.[14] With $MeMn(CO)_5$ in hand, we envisioned that treatment of this Mn precursor with ligands that have been used in catalysis can generate the desired catalytic species via elimination of methane, without any additional reagents. Thus, we treated $MeMn(CO)_5$ with three different pincer ligands in toluene at 120 °C and monitored the reactions using ^1H NMR, $\{^1H\}^{31}P$ NMR, ATR-FTIR and GC headspace analysis, the results of which are discussed below (scheme 2).

Scheme 2 Preparation of active Mn(I) catalysts with $MeMn(CO)_5$ (conditions: toluene at 120 °C; headspace analysis confirmed elimination of CH_4 and CO).



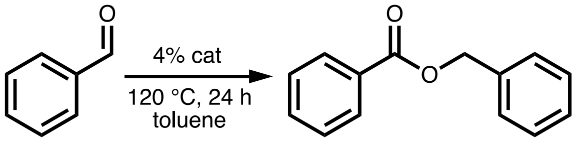
In a previous report,[12] we synthesized bisphosphine phenol and phenolate (POP) Mn(I) complexes and used them in catalyzing the Tishchenko reaction. The parent compound (**POP**)$Mn(CO)_3$ (**1**) of the original report utilized the ligand 2,6-bis[(diphenylphosphino)methyl]-4-methylphenol (**H-POP**). Synthesis of **1** required stepwise coordination reactions and the addition of base (Et_3N) to eliminate an equivalent of HBr. Conveniently, the same complex can be generated cleanly in a single step by treating **H-POP** with 1 equiv. $MeMn(CO)_5$ (Fig S5). We monitored the formation of **1** using $MeMn(CO)_5$ to determine if any acyl or methyl intermediates were present in the synthesis. The reaction between **H-POP** and 2.5 eq. of $MeMn(CO)_5$ monitored using $\{^1H\}^{31}P$-NMR showed complete conversion to a new metal complex within 2 hours at room temperature (^{31}P δ = 48 ppm) (Fig S2). An ATR-FTIR spectrum of this material contains CO stretches of an ill-defined nature and a broad OH stretch at ~ 3400 cm^{-1} indicating that the OH group of the ligand is still present (Fig S3). There are additionally two new peaks ~ 1580 cm^{-1} indicative of an acyl moiety. Collectively, these data suggest a structure similar to the dinuclear complex **H-POP**$\{Mn(CO)_4Br\}_2$ (^{31}P δ = 40 ppm) described earlier,[12] the primary difference being that the bromide is replaced with an acyl group to give **H-POP**$\{Mn(CO)_4(OCMe)\}_2$ (Scheme 3). Indeed, a poor but resolvable structure revealed through connectivity the presence of the acyl functional group and general structure (Fig S4).

Scheme 3 Acyl intermediate observed in the synthesis of **1**.



Treatment of **H-POP** with $MeMn(CO)_5$ in 1:1 ratio in toluene at room temperature led to the generation of the same acyl complex with residual free ligand, which eventually converts into **1** (^{31}P δ = 75 ppm) upon heating at 120 °C. Headspace analysis of the reaction mixture showed the presence of CH_4 along with CO and H_2. Similarly, **1** can be prepared *in situ* using previously optimized conditions for the catalyzed disproportionation of benzaldehyde to benzyl benzoate. For example, a mixture of $MeMn(CO)_5$, **H-POP**, and benzaldehyde in toluene at 120 °C gave conversions nearly identical to those obtained with isolated, crystalline **1** (Scheme 4).

Scheme 4 Ligand screening for Tishchenko reaction with various POP ligands and *in situ* prepared catalyst.



cat prep = $MeMn(CO)_5$ + **L**
mixed in toluene at rt with substrate
(**L = H-POP**, **H-POP**$^{\mathbf{iPr},\mathbf{\textit{p}}\text{-}\mathbf{Me}}$, **H-POP**$^{\mathbf{Ph},\mathbf{\textit{p}}\text{-}\mathbf{OMe}}$)

One of the stated advantages of using $MeMn(CO)_5$ as a synthon is rapid ligand screening compared to studies with the bromide. To demonstrate this, we synthesized two new variants of the parent **H-POP**$^{R,p\text{-}X}$ system (R = Ph & *para*-X = Me for **H-POP**; R=

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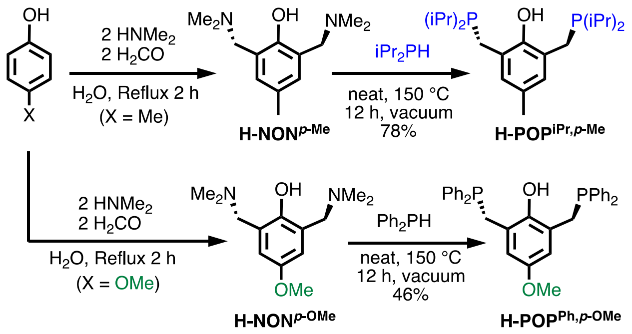
Ph & *para*-X = OMe for **H-POP**$^{Ph,\,p\text{-}OMe}$; R = *i*Pr & *para*-X = Me for **H-POP**$^{iPr,p\text{-}Me}$) and used the three ligands and $MeMn(CO)_5$ to catalyze the Tishchenko reaction of benzaldehyde(Scheme 5; Fig S6-S9). The results using *in situ* generated catalysts are shown in Table 1. While the conversions are modest, it demonstrates that a catalytically active species can in fact be generated using $MeMn(CO)_5$ as a synthon and used to rapidly screen ligands with Mn(I)-MLC catalysts that might otherwise require coordination chemistry studies to obtain purified pre-catalysts. For instance, this rapid screening method allowed us to quickly identify that the **H-POP**$^{iPr,p\text{-}Me}$ ligand furnished the greatest conversion in 24 hours (entry 5 and 6).

Table 1. Ligand screening for Tishchenko reaction using $MeMn(CO)_5$

Entry	Catalyst[a]	Conversion (%)[b]
1	Isolated, crystalline **1**	26[c]
2	none	0
3	**H-POP** + $Mn(CO)_5Br$[d]	0
4	**H-POP** + $MeMn(CO)_5$ (*in situ* **1**)	25
5	**H-POP**$^{iPr,p\text{-}Me}$ + $MeMn(CO)_5$	52
6	**H-POP**$^{iPr,p\text{-}Me}$ + $MeMn(CO)_5$	70[e]
7	**H-POP**$^{Ph,p\text{-}OMe}$ + $MeMn(CO)_5$	17
8	**H-NON**$^{p\text{-}Me}$ + $MeMn(CO)_5$	< 5
9	**H-NON**$^{p\text{-}OMe}$ + $MeMn(CO)_5$	< 5
10	Phenol + $MeMn(CO)_5$	< 5
11	$MeMn(CO)_5$	< 5

(a) see scheme 4 for conditions. (b) conversion determined by ^{1}H-NMR. (c) from ref 12. (d) presence of triethylamine has no effect. (e) 48 hours.

Scheme 5 New POP ligand synthesis.

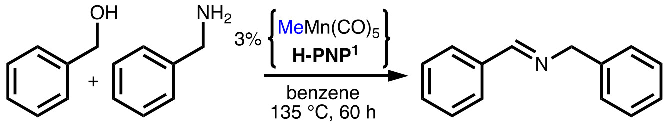


We wished to further demonstrate the versatility of this strategy by using other known, more active Mn(I) catalysts. Consider for example the potential of this application for (pre)catalysts that might be exceedingly difficult to isolate. Using $MeMn(CO)_5$ offers the potential to generate the species under conditions used in substrate conversion. To envision this scenario, we first wanted to demonstrate that known active catalysts could be generated *via* this method.

For this, we used 2,6-bis(di-*tert*-butylphosphinomethyl) pyridine (**H-PNP^1**), the ligand used by Milstein for the first Mn(I) catalyzed dehydrogenation and kicking off this rapidly growing field.[5] Heating a mixture of **H-PNP^1** and $MeMn(CO)_5$ in toluene resulted in elimination of CH_4 (GC) and the {^{1}H}^{31}P-NMR of the reaction mixture showed the presence of (**PNP^1**)$Mn(CO)_3$ (Fig S11), which Milstein demonstrated forms the active catalyst (**2**) after a laborious series of vacuum/reflux procedures. The liberation of CH_4 from **H-PNP^1** to yield (**PNP^1**)$Mn(CO)_3$ (**2CO**) indicates formation and cleavage of C–H bonds in the net reaction and warrants investigation in future studies as it may be important in unraveling the necessary requirements to bring MLC-Mn(I) catalysts into the realm of C–H bond activation.[15]

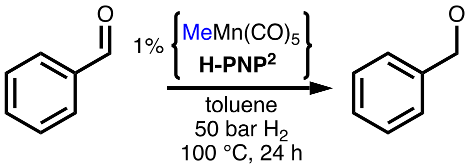
To test the feasibility of generating pincer catalysts with our method under catalytically relevant conditions, we replicated Milstein's original conditions for dehydrogenative coupling between benzyl alcohol and benzylamine.[5] Specifically, when substrates, **H-PNP^1**, and $MeMn(CO)_5$ were mixed together, instead of using pre-isolated **2**, the conversion reached 58% after 60 h (Scheme 6).[16]

Scheme 6 *in situ* generation of **2CO** for dehydrogenative coupling of alcohols and amines



Similar to the above generation of **2CO**, $MeMn(CO)_5$ was treated with bis[(2-diisopropylphosphino)ethyl]amine (**H-PNP^2**), which is the ligand used by Beller in the very first report of Mn(I) catalyzed hydrogenation.[6,17] Treatment of $MeMn(CO)_5$ with **H-PNP^2** in d_8-toluene at 120 °C led to the formation of the red colored active catalyst (**PNP^2**)$Mn(CO)_2$ (**3**) as indicated by {^{1}H}^{31}P NMR (peak at 113 ppm) suggesting elimination of CH_4 via activation of the ligand NH bond (Fig S12). ^{1}H NMR showed the presence of CH_4 as expected, which was also confirmed with GC headspace analysis along with CO. However, to our surprise, the headspace analysis indicated H_2 in the reaction mixture. A close look at the ^{1}H NMR spectrum shows the presence of imine hydrogens, suggestive of dehydrogenation of the 2° amine ligand. This transformation is likely mediated or catalyzed by **3** and explains the non-quantitative conversion. Nevertheless, using this method, crystalline **3** can be obtained in good yield (75% crystalline) and used in catalytic transformations.

Scheme 7 *in situ* catalyst generation and hydrogenation of benzaldehyde with **3**.



3 isolated *via* the above procedure was used in a hydrogenation of benzaldehyde to benzyl alcohol and we found essentially complete conversion in toluene, 50 bar H_2 at 100 °C (Scheme 7). To compare the efficacy of *in situ* catalyst generation, we employed identical conditions except that **PNP^2** and $MeMn(CO)_5$ were mixed with the substrate rather than

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using isolated **3**. To our satisfaction, identical conversions were obtained!

Herein, we demonstrate that $MeMn(CO)_5$ is an excellent Mn(I) precursor to active Mn(I) catalysts with bifunctional ligands. This finding addresses one of the shortcomings in this field, namely that the synthons were limited to $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$. Moreover, the use of $MeMn(CO)_5$ provides an ease of the 16-e^- catalyst preparation that might otherwise be impossible for certain metal-ligand or substrate combinations and will be advantageous in ligand screening, the latter of which we demonstrated in screening POP ligands for the Tishchenko reaction. Related, many of the known 16-e^- Mn catalysts (e.g., **2** and **3**) are air sensitive. $MeMn(CO)_5$ is air stable. Although phosphine ligands are often air sensitive, they are usually stable enough to short exposure to air. Thus, our new method greatly simplifies the application and ligand screening potential of Mn in organic synthesis. We liken this method to wide-spread use of adding $Pd(OAc)_2$ and phosphine ligand with substrate – without the need to synthesize the active Pd catalyst. Hence the use of $MeMn(CO)_5$ is expected to find widespread application in both the areas of organometallic chemistry where the chemistry of the 16-e^- catalyst is sought, but also the organic synthesis field wherein rapid catalyst generation *in situ* is highly desirable.

Acknowledgment

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Conflicts of interest

There are no conflicts to declare.

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14. TOC graphic includes picture of crystals obtained in a 20 mL scintillation vial.
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