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Resurgence of Organomanganese(I) Chemistry. Bidentate Manganese(I) Phosphine−Phenol(ate) Complexes

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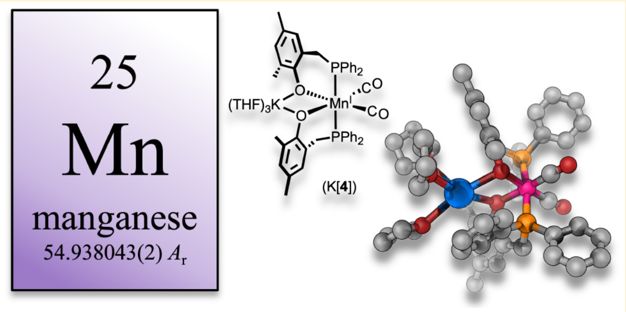
Supporting Information



ABSTRACT: As part of the United Nations 2019 celebration of the periodic table of elements, we are privileged to present our studies with the element manganese in this Forum Article series. Catalysis with organomanganese(I) complexes has recently emerged as an important area with the discovery that pincer manganese(I) complexes that can activate substrates through metal−ligand cooperative mechanisms are active (de)hydrogenation catalysts. However, this rapidly growing field faces several challenges, and we identify these in this Forum Article. Some of our efforts in addressing these challenges include using alternative precursors to $Mn(CO)_5Br$ to prepare manganese(I) dicarbonyl complexes, the latter of which is usually a component of active catalysts. Specifically, the synthesis of a new bidentate phosphine−phenol ligand along with its corresponding coordination chemistry of five new manganese(I) complexes is described. The complexes having two phenol−phenolate moieties interact with the secondary coordination sphere to enable facile loss of the bromido ligand and even one of the CO ligands to afford manganese(I) dicarbonyl centers.

■ INTRODUCTION

Celebrating Manganese in the Year of the Periodic Table. The United Nations has proclaimed 2019 as the *Year of the Periodic Table* to celebrate the 150th anniversary of the periodic table. We are privileged with the opportunity to showcase manganese in this *Inorganic Chemistry* Forum Article that commemorates humankind's achievement of codifying the chemical elements. Manganese is a first-row transition metal that has been used since prehistoric times in the form of black mineral pigments found in a variety of locations around Europe.[1] Manganese was one of the first elements identified, having been systematically discovered in 1774 by Scheele and Gahn.[2] In modern times, it finds practical application in metallurgy and a variety of areas in society. Manganese is an element that touches almost every field of chemistry, but as inorganic chemists, we are primarily interested in its chemical properties. Hence, the following discussion on manganese contains our limited perspective with an emphasis on homogeneous organometallic manganese(I) chemistry.

In keeping with the theme of *The Year of the Periodic Table*, we first turn to the periodic table to intuit the types of properties manganese is expected to have. Manganese is unique among the first-row transition metals because it has no naturally occurring second-row congener, and rhenium (its third-row congener) is one of the least abundant transition metals in the Earth's crust.[3] In its common 2+ formal oxidation state, manganese is additionally unique, owing to its half-filled 3d subshell. Except in the most unusual of cases,[4,5] the five d electrons are in a high-spin configuration, resulting in a nullification of ligand-field stabilization. In other words, the frontier orbitals of high-spin manganese(2+) complexes are not very different from complex to complex, and thereby the chemistry is not as versatile and is often viewed as less interesting than nearby first-row metals.[6] This chemical nature has even earned manganese the nickname the "black-sheep" of divalent transition organometals,[7] sharing more similarities with organomagnesium and organozinc than nearby organo-transition metals.

The similarity to redox inert divalent metals enables it to replace various 2+ cations like zinc(II), calcium(II), and magnesium(II) as a structural component to proteins.[8] However, unlike magnesium and zinc, manganese has rich redox chemistry with accessible d counts from d^8 to d^0 without evoking exotic oxidation states. This has significant implications to life on Earth because a critical component of the molecular machinery in photosynthesis is a tetranuclear Mn_4CaO center that oxidizes water to O_2.[9] Additionally, it is becoming widely recognized that Mn^{II} is a crucial metal ion for microbial growth and function.[10]

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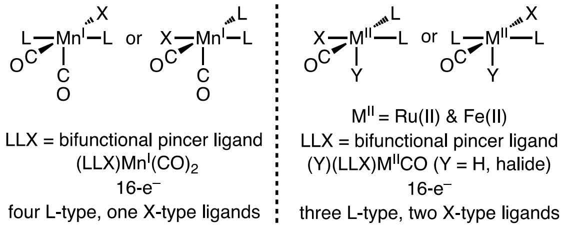
Examples of mononuclear molecular manganese complexes with unambiguous Mn^{n+} oxidation states with d counts from d^8 to d^0 include the following: [Mn^{-1}(CO)$_3${CNAr^{Dipp}}$_2$]$^-$ (Ar^{Dipp} = 2,6-[2,6-(iPr)$_2$C$_6$H$_3$]$_2$C$_6$H$_3$),[11] [Mn^0(CO)$_3${CNAr^{Dipp}}$_2$],[12] CpMn^I(CO)$_3$ (Cp = cyclopentadienyl),[13] Mn^{II}Cp$_2$,[14] Mn^{III}(acac)$_3$ (acac = acetylacetonate),[15] [Mn^{IV}Me$_6$]$^{2-}$,[16] [Mn^V(O)H$_3$buea]$^-$ (H$_3$buea = tris[(*N′-tert*-butylureaylato)-*N*-ethylene]amine),[17] [Mn^{VI}(N*t*Bu)$_4$]$^{2-}$,[18] and [Mn^{VII}(N*t*Bu)$_3$Cl].[18] Much of the fundamental research in organometallic chemistry relied on the element manganese. For instance, the substitution chemistry of six-coordinate d^6 Mn(CO)$_5$X was instrumental in the discovery of the cis effect.[19] Migratory insertions was first observed on the MeMn(CO)$_5$ complex, and the first M−M bond in a molecular species was discovered with Mn$_2$(CO)$_{10}$.[20,21]

Molecular manganese complexes have an important role in industrial chemistry on a massive scale as catalysts in radical-chain aerobic oxidations[22] and as an antiknock fuel additive.[23] In the latter case, methylcyclopentadienylmanganese(I) tricarbonyl was produced on an industrial scale to replace tetraethyllead, demonstrating that organomanganese(I) complexes can be economically produced in large quantities. To this end, manganese has the potential to compete with expensive metals in nearly every corner of homogeneous catalysis, whether it be coupling reactions,[24] C−H bond activation,[25] epoxidations,[26] small-molecule activation,[27] and more. This potential is limited only by available knowledge, of which is lacking because, in our opinion, the chemistry of manganese has lagged behind the other transition metals.[28] Thus, there is ample reason to explore the fundamental chemistry of manganese, and only time will tell what kind of new reactions manganese will catalyze to open possible avenues toward replacing toxic and expensive metals in synthesis.

Resurgence of Organomanganese(I) Chemistry. An excellent example of how this can unfold is the discovery that Mn^I ions are useful in a variety of (de)hydrogenation reactions previously performed by ruthenium, iron, and cobalt pincer catalysts.[29] This finding, which came decades after the first analogous ruthenium examples,[30] stimulated a resurgence of catalysis with organomanganese(I). Langer and Zell recently discussed some of the unique properties of manganese(I) compared to analogous d^6 ruthenium(II) and iron(II) systems that will enable this new chemistry.[31] One of the most important differences is that 16-electron manganese(I) complexes can support four neutral L-type ligands instead of three. The general formulation for a 16-electron manganese(I) catalyst is Mn^I(XL$_2$)(CO)$_2$, where XL$_2$ is the supporting bifunctional ligand(s) (Chart 1). In contrast to M^{2+} (Fe, Ru) 16-electron catalysts, the formulation is Y−M^{II}(XL$_2$)(CO), where Y is a supporting X-type ligand (e.g., hydride). Manganese(I) accommodates an extra L-type ligand, and therefore bidentate ligands are sufficient in stabilizing catalysts of the metal−ligand cooperative (MLC) sort.[32] For the 2+ ions, the supporting ligand needs to contain at least two strong-field L-type ligands to keep the complexes low-spin (for iron). This aspect of manganese has many added benefits including flexibility in ligand design, and phosphine-free bidentate NN ligands can be employed.[33,34] Collectively, this new and growing body of data surrounding manganese(I) (de)hydrogenation catalysts led us to explore uncharted areas with the goal of uncovering new applications of manganese in areas such as energy and catalysis.

Chart 1



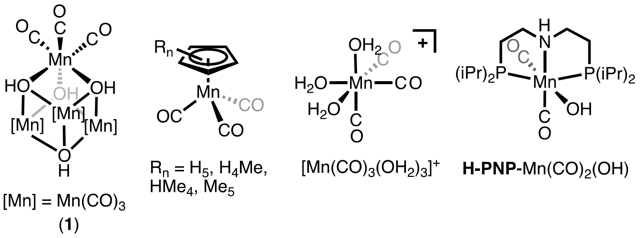
Besides the fact that manganese(I) chemistry has lagged behind the organometallic chemistry of other first-row transition metals (e.g., iron, cobalt, nickel, etc.), some of the major challenges facing catalysis with organomanganese(I) are as follows: (i) The only relevant manganese(I) precursor for catalysts is Mn(CO)$_5$Br, which is rather expensive and is derived from Mn$_2$(CO)$_{10}$. (ii) All of the bifunctional ligands used in MLC manganese(I) systems rely exclusively on anionic N-atom donors for the bifunctional activation of substrates. (iii) Synthetic routes to prepare the catalytically active 16-electron manganese(I) dicarbonyl complex are lacking. These generally require "luck of the draw" syntheses, where coordination of a tridentate ligand produces the required precatalyst formulation. Recently, Kirchner and co-workers demonstrated that "bifunctional ligands" are not even necessary to enact hydrogenation chemistry with manganese(I) precatalysts,[35] and thus the search for novel ligands and less expensive precursor materials should constitute major foci in the resurgence of organomanganese(I) chemistry.

In this report, we detail some of the new efforts ongoing in our laboratory to address these three challenges. First, two synthons derived from Mn$_2$(CO)$_{10}$ are used to prepare manganese(I) catalysts; the first of these is the in situ prepared butterfly tetranuclear complex described below, and the other is MeMn(CO)$_5$. Second, we have been exploring phenolic-based phosphine ligands to augment the nitrogen-only heteroatoms found in bifunctional systems. Finally, the phenolic platform interacts with the secondary coordination sphere and appears to modulate the liberation of bromido ligands and even carbonyl ligands. This work is an extension of an earlier report where we prepared a tridentate bis(phosphine)−phenol (POP) pincer ligand.[36] The resulting POP-Mn complexes were constrained in their geometry, which limited access to dicarbonyl catalysts. To relax the constraints imposed by the POP system, we synthesized a new bidentate monophosphine ligand that affords access to a variety of coordination modes including manganese(I) dicarbonyl complexes.

RESULTS AND DISCUSSION

Alternative Precursors to Mn(CO)$_5$Br To Access Manganese(I) Catalysts. Our roots in exploring the fundamental chemistry of organomanganese(I) centers originated from our interest in the finding that cymantrene [CpMn(CO)$_3$] can mediate a stoichiometric water-splitting reaction by the action of, presumably, a single photon.[37] Using a variety of organomanganese(I) complexes with and without water-derived ligands (e.g., Chart 2), we showed that only certain heteronuclear Mn^I-OH complexes produce H$_2$ under photochemical conditions. In particular, the tetramer [Mn(CO)$_3$(μ_3-OH)]$_4$ (1) exhibited unique behavior in that it was

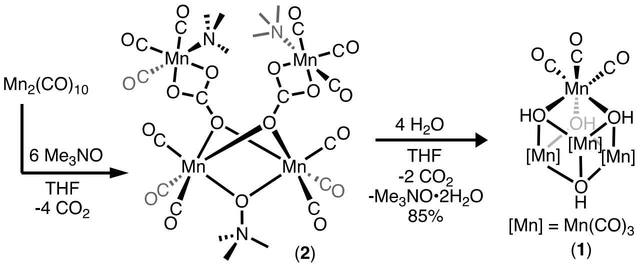
Chart 2. Manganese(I) Complexes with and without Water-Derived Ligands Tested for Photochemical H_2 Production[39,40]



the only complex that produced H_2 gas under rigorously dry conditions through a CO-photolysis-induced H-atom-transfer reaction.[38,38] This prompted our investigation into the formation mechanism of the tetramer so as to develop an atom-precise methodology to install labeled D and ^{18}O atoms in **1**.

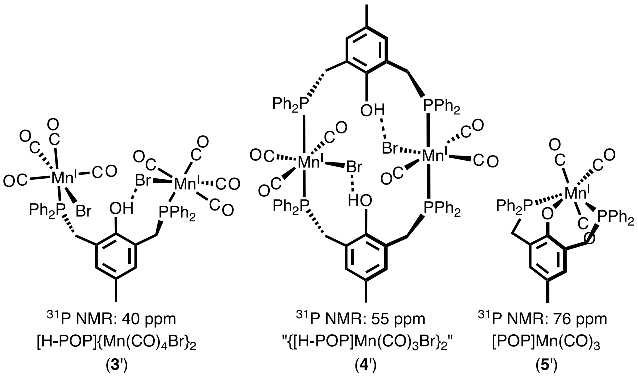
During this initial study, we discovered a novel tetranuclear butterfly complex (**2**) with bridging carbonato ligands derived exclusively from $Mn_2(CO)_{10}$ and Me_3NO (Scheme 1). The formation of carbonate from $Mn_2(CO)_{10}$ and Me_3NO was unexpected because it implied the formation of CO_3^{2-} from CO_2 and Me_3NO, which is not possible without a reductant. Therefore, it was presumed that the Mn^0 centers were the source of electrons and, indeed, **2** contained four $Mn^I(CO)_3$ fragments charge-balanced by two carbonato groups. In addition to two capping NMe_3 ligands, the structure also contained a rare μ_2-$ONMe_3$ ligand. The treatment of **2** with exactly 4 equiv of water resulted in complete conversion to the tetramer **1** and $Me_3NO{\cdot}2H_2O$, providing a synthetic route to the fully deuterated and partially ^{18}O-labeled tetramer.[41]

Scheme 1. Butterfly Complex En Route to 1[41]

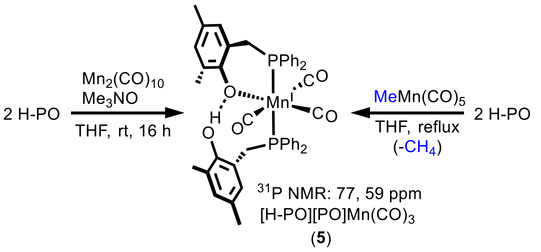


The reaction of **2** with water to yield **1** suggested an acid–base chemistry, where the basic carbonato ligand moieties in **2** deprotonated the incoming water molecules, thus installing the OH group in the $Mn^I(CO)_3$ fragments. We envisioned the applicability of this route for direct activation of the Brønsted acidic bonds on various ligand platforms for generation of the corresponding manganese(I) tricarbonyl complexes. Such manganese(I) tricarbonyl complexes are often precursors for generation of the manganese(I) dicarbonyl active catalyst in MLC chemistry.[42] In fact, treating **2** with our phenolic pincer ligand, tridentate bis(phosphine) phenol−2,6-bis-[(diphenylphosphino)methyl]-4-methylphenol (H-POP), instead of water, led to deprotonation of the phenol group as expected and yielded $[POP]Mn(CO)_3$ (**5′**; Scheme 2).[36] Following the same procedure as that for our new bidentate phenolic ligand, monophosphine phenol−2-[(diphenylphosphino)methyl]-4,6-dimethylphenol (H-PO), led to the generation of an analogous tricarbonyl compound, $[H\text{-}PO][PO]Mn(CO)_3$ (**5**; Scheme 3), the synthetic details of which are described in the next section.

Scheme 2. Previously Reported POP-Mn^I Complexes[36]



Scheme 3. Single-Step Preparation of the H-PO Complex 5



Although complex **2** is an interesting alternative synthon to $Mn(CO)_5Br$, the workup for such reactions can be problematic owing to low yields and/or residual Me_3NO. On our quest for higher yielding routes, in an earlier report, we explored the applicability of $MeMn(CO)_5$ as a manganese(I) synthon and found that the $MeMn(CO)_5$ complex is able to rapidly install $Mn^I(CO)_n$ groups in Brønsted acidic ligands.[43] $MeMn(CO)_5$ can be derived directly from $Mn_2(CO)_{10}$ in good yield using NaK and MeI in a glovebox, although $MeMn(CO)_5$ itself is air-stable. Besides its high price, the use of $Mn(CO)_5Br$ can be disadvantageous because it is typically required to prepare H-$LMn(Br)(CO)_2$ (H-L = tridentate bifunctional pincer ligand) and then must be activated with a strong base (e.g., KO*t*Bu) to generate the active 16-electron manganese(I) dicarbonyl complex (Chart 1). Alternatively, $MeMn(CO)_5$ circumvents the need to prepare the precatalyst because CH_4 is readily liberated. For instance, refluxing $MeMn(CO)_5$ with 1 equiv of H-POP or 2 equiv of H-PO yielded the corresponding tricarbonyl complexes **5′** and **5**, respectively, via the release of CH_4 (Schemes 3 and 4). This method's usefulness extends into a variety of applications that include the activation of N−H, O−H, and even C−H bonds on preligands; a summary from our previous report with $MeMn(CO)_5$ as an alternative synthon is shown in Scheme 4.

Coordination Chemistry of [H-PO]Mn^I Complexes. As stated, we synthesized the tridentate H-POP as a supporting ligand for manganese(I) complexes. One of the key findings from that study was that the Mn−O−C bond angle of the mononuclear complex **5′** was much smaller (103.4°) than those of other POP-Mn^I complexes from the same report (≈120−124°). The result was that the monomeric complex **5′** readily formed the inert dimer $\{5'\}_2$ or was otherwise unstable

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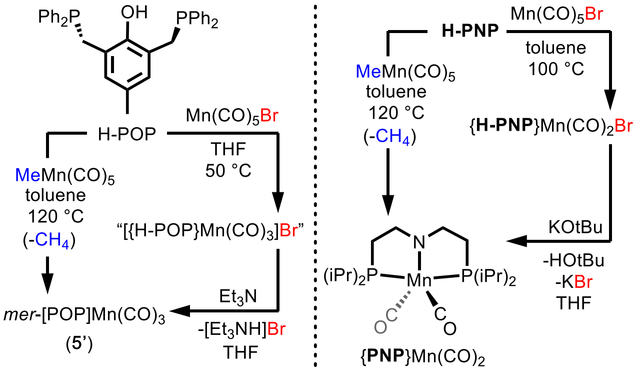
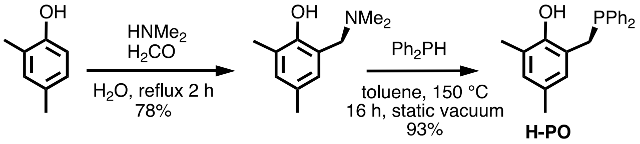
Scheme 4. Expedient Route to Catalysts with $MeMn(CO)_5$[43]



toward our attempts to generate highly active dicarbonyl analogues. For this reason, we designed H-PO to be a less constrained platform. The procedure uses 2,4-dimethylphenol in a Mannich reaction with dimethylamine and formaldehyde and produces the preligand 2-[(dimethylamino)methyl]-4,6-dimethylphenol (H-NO). H-NO was converted into H-PO through treatment with diphenylphosphine in toluene at 150 °C in 93% yield as an air-sensitive white crystalline solid (Scheme 5).

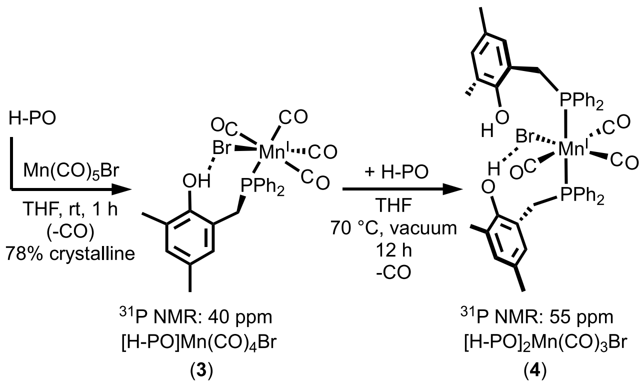
Scheme 5. Synthesis of H-PO



A simple ligand substitution between $Mn(CO)_5Br$ and H-PO occurs at room temperature in tetrahydrofuran (THF) in under 1 h. The result is liberation of CO and clean formation of a new complex assigned as the monomeric [H-PO]Mn-$(CO)_4Br$ (**3**) in quantitative yield [$^{31}P\{^1H\}$ NMR = 40 ppm; the attenuated-total-reflectance Fourier transform infrared (ATR-FTIR) ν_{CO} splitting pattern matches that of tetracarbonyl coordination; Figures S4–S6]. This molecule was not characterized by X-ray diffaction (XRD), but because of its NMR and FTIR spectroscopic similarities to the previously reported complex **3′** ($^{31}P\{^1H\}$ NMR = 40 ppm),[36] a proposed structure is shown in Scheme 6.

Attempts to remove another molecule of CO from the tetracarbonyl compound **3** and form the tricarbonyl [H-PO]$Mn(CO)_3Br$ and induce coordination of the phenolic OH were unsuccessful (e.g., through heating, vacuum, Me_3NO, etc.).[44] Instead, **3** converts into $[H\text{-}PO]_2Mn(CO)_3Br$ (**4**; $^{31}P\{^1H\}$ NMR = 55 ppm) and other unidentified products. The same complex can be formed through the treatment of $Mn(CO)_5Br$ with 2 equiv of H-PO at 70 °C under static vacuum for 12 h (Scheme 6). Notably, in our previous report with the H-POP system, we prepared a complex with spectroscopic features nearly identical with those of **4** ($^{31}P\{^1H\}$ NMR = 55 ppm; the ATR-FTIR ν_{CO} splitting pattern matches *mer*-CO coordination) and was overall consistent with a $\{[H\text{-}POP]Mn(CO)_3Br\}_2$ (**4′**) formulation for which we proposed a dimeric structure with meridional CO coordination (Scheme 2).

Scheme 6. Coordination of H-PO with $Mn(CO)_5Br$



The XRD structure for **4** (Figure 1) supports our hypothetical structure for **4′** (Scheme 2). Both of the OH moieties in the XRD structure are directed toward the bromido ligand, with one having a short O···Br distance [O···Br = 3.386(1) Å] indicating hydrogen-bonding interaction. The remaining coordination sites on manganese are occupied by three CO ligands in a meridional fashion, consistent with the ATR-FTIR spectrum, which additionally contains two different ν_{OH} at 3350 and 3460 cm^{-1} that are tentatively assigned as the hydrogen-bonded OH and the free OH moiety, respectively (Figure S9). The singular peak in the ^{31}P NMR spectrum for **4** indicates that the hydrogen-bonding group is not static in solution (Figure S8).

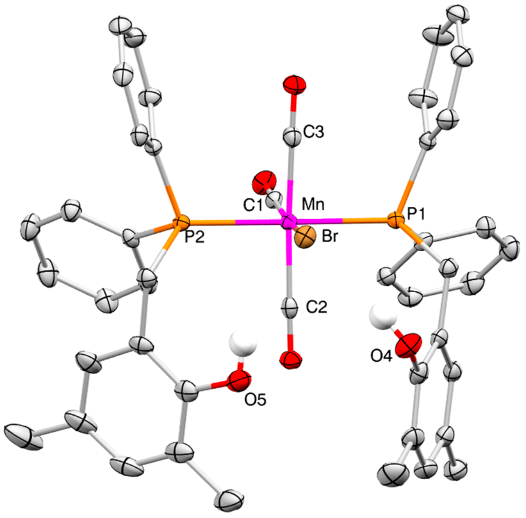


Figure 1. X-ray crystallographically determined molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Mn–P1 2.3079(4); Mn–P2 2.314(4); Mn–Br 2.5473(5); Mn–C1 1.784(2); Mn–C2 1.858(1); Mn–C3 1.866(1); O5···Br 3.386(1); O4···Br 3.220(1); P1–Mn–P2 179.09(2); C1–Mn–C3 88.73(7); C1–Mn–C2 94.75(7); C2–Mn–C3 175.92(7). Ellipsoids are shown at 50% probability and nonphenol H atoms removed for clarity.

Heating a solution of **4** in THF at 100 °C for 12 h under static vacuum causes the formation of a new compound, **5**, via the release of one molecule of HBr. The $^{31}P\{^1H\}$ NMR spectrum of **5** showed two peaks at 77 and 59 ppm corresponding to the P atom on the phenolate PO and phenolic H-PO ligands, respectively (Figure S11). The molecular structure determined from XRD (Figure 2) is consistent with that from ATR-FTIR for meridional tricarbonyl coordination. The broad OH stretch around 2500

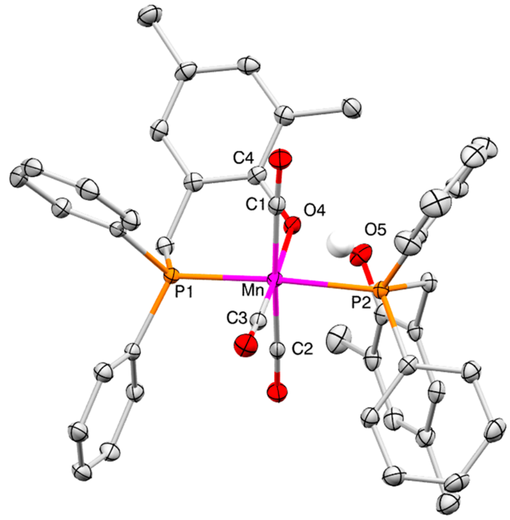


Figure 2. X-ray crystallographically determined molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Mn−P1 2.2798(6); Mn−P2 2.3035(6); Mn−O4 2.063(1); Mn−C1 1.854(2); Mn−C2 1.865(2); Mn−C3 1.777(1); O4···O5 2.580(1); P1−Mn−P2 172.55(3); Mn−O4−C4 122.39(8); C1−Mn−C2 173.85(6); C1−Mn−C3 90.36(6); C2−Mn−C3 95.55(6). Ellipsoids are shown at 50% probability and nonphenol H atoms removed for clarity.

cm^{-1} in the ATR-FTIR (Figure S12) spectrum possibly suggests that the free OH group is hydrogen-bonded to the O atom on the adjacent ligand, again consistent with a short O··· O distance [2.580(1) Å] in the crystal structure.

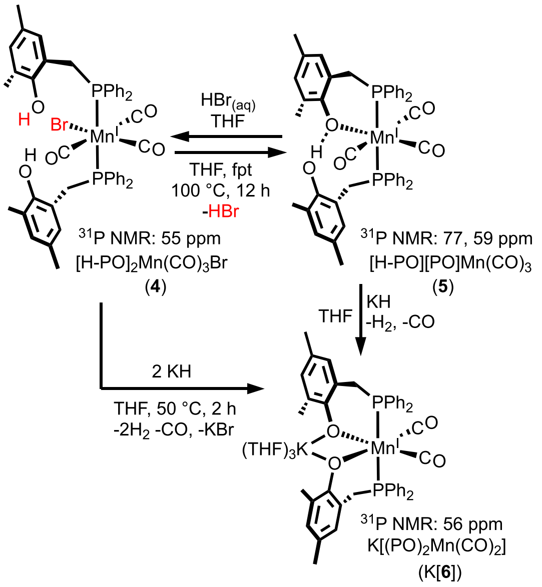
5 closely resembles **5′** from our previous work except that the phenolic C−O−Mn bond angle (103.4° in **5′**) is less constrained in **5** (122.4°).[36] In the previous report, we showed that **5′** reversibly reacts with HX (X = Cl, Br, I) to form $\{[H\text{-}POP]Mn(CO)_3X\}_2$. Similarly, **5** reacts with HBr to reform **4**. The reversible addition of HBr to **5** and **5′** is presumably enabled by the incorporation of interactions in the secondary coordination sphere. For instance, $Mn(CO)_5Br$ does not readily release its bromido ligand, which typically requires the use of Ag^+ salts. Additionally, molecules like H-PNP-Mn-$(CO)_2Br$ (H-PNP = bis[(2-diisopropylphosphino)ethyl]-amine; Scheme 4) require the addition of KO*t*Bu to liberate a Br ion and HO*t*Bu. Hence, the interconversion of **4** and **5** may indicate that secondary coordination sphere interactions modulate the energies associated with the liberation of bromide.

Synthesis of Manganese(I) Dicarbonyl Complexes. Treating **4** with 2 equiv of KH or **5** with 1 equiv of KH led to complete deprotonation of the H-PO ligand(s) to generate a dicarbonyl compound, $K[(PO)_2Mn(CO)_2]$ (K[**6**]; $^{31}P\{^1H\}$ NMR = 56 ppm; Scheme 7 and Figures S13−S15), and the salt readily recrystallizes from THF at −35 °C. Crystallographic data revealed a *cis*-dicarbonyl compound with two PO ligands coordinated to Mn and K ions (Figure 3). The K ion is additionally coordinated by three THF molecules, the latter of which can be removed with dynamic vacuum at 40 °C.

The formation of manganese(I) dicarbonyl complexes is challenging. Recently, manganese(I) dicarbonyl complexes have been shown to be excellent catalysts for a variety of hydrogenative and dehydrogenative reactions. However, their synthesis is not readily accessible through typical methods used to liberate CO (e.g., from a tricarbonyl) through photochemical or chemical means.[42] Rather, coordination reactions with tridentate ligands using $Mn(CO)_5Br$ is one of the few methods that allows access to such dicarbonyl compounds. In our previous report with the tridentate H-POP preligand, we were unsuccessful in preparing POP-$Mn(CO)_2$ from the tricarbonyl complex despite having a density functional theory (DFT)-computed Mn−CO bond dissociation free energy (BDFE) of only 11 kcal/mol (Table 1). Rather, attempts at liberating CO from **5′** using light or Me_3NO resulted in formation of the dimer $\{5'\}_2$.[36] Thus, the preparation of the dicarbonyl $[6]^-$ using H-PO was somewhat unexpected.

The regulation of the secondary sphere and incorporation of two phenolate−phosphine ligands appear to enable the

Scheme 7. Regulated Secondary Coordination Spheres of 4 and 5 and the Synthesis of Dicarbonyl K[6]



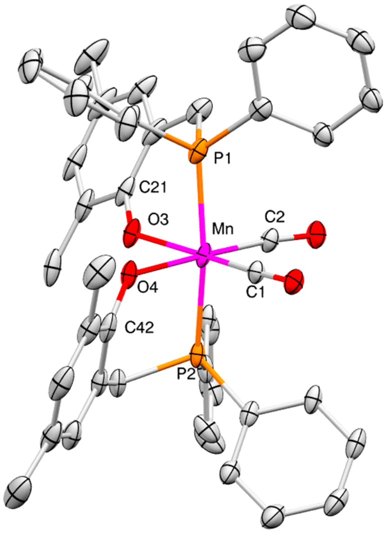


Figure 3. X-ray crystallographically determined molecular structure of the anion $\{[PO]_2Mn(CO)_2\}^-$ ($[6]^-$). Selected bond lengths (Å) and angles (deg): Mn−P1 2.2761(8); Mn−P2 2.2750(6); Mn−O3 2.075(1); Mn−O4 2.068(2); Mn−C1 1.748(2); Mn−C2 1.761(2); P1−Mn−P2 168.43(3); Mn−O3−C21 133.7(1); Mn−O4−C42 131.8(1); C1−Mn−C2 86.7(1); O3−Mn−O4 81.40(6). Ellipsoids are shown at 25% probability. THF molecules and K and H atoms are not shown for clarity.

Table 1. Free Energies for Mn–CO Dissociation[a]

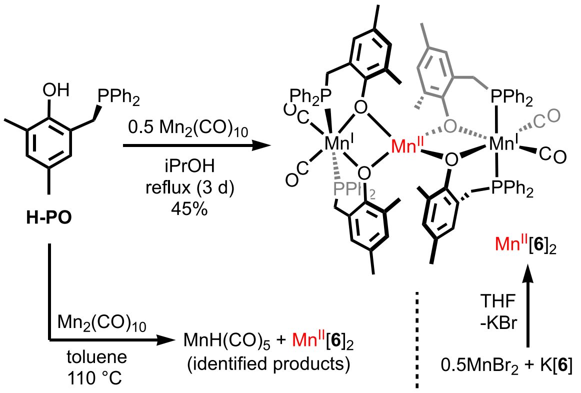
complex[b]	DFT[c]	experiment
Mn–CO → Mn + CO		
5 to **7** + CO	18	
5′ to **7′**+ CO	11	
[**5**-H]$^-$ to [**6**]$^-$ + CO[d]	−8	
[Mn(CO)$_6$]$^+$ to [Mn(CO)$_5$]$^+$ + CO	30[e]	32[f]

[a] Energies in kcal/mol, standard conditions; complex **7** and **7′** are the products of CO dissociation from **5** and **5′**, respectively. [b] K ions are excluded from the calculations. [c] B3LYP 6-31G* with the SMD solvation model for toluene. [d] Free energy for the intramolecular ligand substitution reaction. [e] Gas-phase free energy = 31 kcal/mol. [f] Gas-phase BDFE$_{M-CO}$.[45]

formation of dicarbonyl complexes. To gain additional insight into these factors, we used DFT computations to compare the CO dissociation energies. As a benchmark, we computed a CO dissociation energy of 30 kcal/mol for [Mn(CO)$_6$]$^+$, which is close to the experimental Mn–CO BDFE of 32 kcal/mol (Table 1).[45] The loss of CO from the POP complex **5′** is only 11 kcal/mol. This low energy might be due to constraints on the complex imposed by the short C–O–Mn angle discussed above. This assumption is based on the analogous PO complex **5**, which does not have the constrained C–O–Mn angle and has a larger CO dissociation energy of 18 kcal/mol. However, the conversion of [**5**-H]$^-$ (in silico removal of a proton from **5**) to [**6**]$^-$ is exergonic (−8 kcal/mol). Note that this free energy for conversion of the deprotonated form of **5** ([**5**-H]$^-$) into [**6**]$^-$ is an intramolecular ligand substitution reaction, not a Mn–CO BDFE.

Within the context of preparing dicarbonyl complexes with "alternative synthons", the treatment of 2 equiv of H-PO with Mn$_2$(CO)$_{10}$ in refluxing isopropyl alcohol affords a paramagnetic bis(dicarbonyl) complex Mn^{II}[**6**]$_2$ (Scheme 8), where one Mn^{II} ion sits between two [**6**]$^-$ molecular anions (connectivity determined from XRD; Figure S17). The intermediates involved were not identified, but heating (110 °C) 1:1 H-PO/Mn$_2$(CO)$_{10}$ in toluene-d_8 produced a solution with a ^{1}H NMR signal at −7.9 ppm (Figure S19), which is consistent with the formation of Mn(CO)$_5$H. We propose that an oxidative addition of the phenolic O–H bond across a Mn^0–Mn^0 bond furnishes a hydride, and unidentified species lead to the Mn^{II}[**6**]$_2$ product. The same paramagnetic bis(dicarbonyl) complex Mn^{II}[**6**]$_2$ can be prepared by the treatment of K[**6**] with 0.5 equiv of MnBr$_2$, serving as an additional support for its molecular identity in the absence of a ^{1}H NMR spectrum or a high-quality XRD structure.

Scheme 8. Preparation of Paramagnetic Bis(dicarbonyl)



CONCLUSIONS

Being the third most abundant transition metal, next to iron and titanium, manganese is in a position to replace expensive and toxic metals in many fields including catalysis. To achieve this goal, new knowledge regarding the fundamental coordination and reaction chemistry of organomanganese complexes must be pursued. Three challenges that we identified are (i) the dearth of manganese precursors in forming active manganese(I) pincer catalysts, (ii) the similarity in bifunctional ligands all relying on N atoms, and (iii) the lack of methods to prepare manganese(I) dicarbonyl complexes.

In addressing these challenges, we first demonstrated that MeMn(CO)$_5$ is a versatile synthon that can be used to directly prepare a variety of coordinated ligand–metal complexes. We also showed that by using a mixture of Mn$_2$(CO)$_{10}$ with excess Me$_3$NO under anhydrous conditions, a basic manganese(I) carbonato intermediate is generated that also serves as an excellent synthon for manganese(I) complexes. It was even possible to generate a manganese(I) dicarbonyl complex directly with H-PO and Mn$_2$(CO)$_{10}$ by the presumed oxidative addition of a phenolic O–H bond by the Mn–Mn bond. Our ongoing studies with phenolic-based phosphine complexes show promise because the bidentate [PO]$^-$ and H-PO ligands afforded several different coordination modes, including simple access to the rare manganese(I) dicarbonyl motif. We proposed that one facet of the phosphine–phenolate platform is that modulation of the secondary coordination sphere facilitates the liberation of ligands to the Mn^I center. New synthetic routes and knowledge about the fundamental chemistry of dicarbonyl complexes are important in the resurgence of organomanganese(I) chemistry, where they have shown to be active catalysts for a variety of transformations and are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reagents were procured from commercial sources and used without further purification unless otherwise noted. Solvents were purified and collected from a PPT solvent system and stored over 3 Å molecular sieves. Molecular sieves and basic alumina were activated at 200 °C under vacuum (<100 mTorr) for 48 h before use. Unless noted, all of the samples were prepared under nitrogen in a VAC Genesis glovebox or argon using standard Schlenk-line techniques. Deuterated solvents were degassed by a freeze–pump–thaw method and stored in the glovebox in Strauss flasks. NMR experiments were performed on Varian Mercury 300 MHz and Inova 400 MHz spectrometers. Transmission electron microscopy and ATR-FTIR spectra were collected inside of a VAC Atmospheres Omni glovebox using a Bruker Alpha IR spectrometer with an ALPHA-P Platinum ATR module (diamond crystal). Cyclic voltammetry was obtained using a SP-200 Bio-Logic potentiostat. Electron paramagnetic resonance (EPR) spectra were collected on an EMX Bruker X-band spectrometer on frozen solutions at 77 K.

Computational Methods. All calculations were performed using *QChem 4.4* and visualized using *IQmol 2.11.1*,[46] and the B3LYP functional, 6-31G* basis set, and solvent model based on density (SMD) solvation model were used for toluene. Geometry optimizations for manganese complexes were performed using the crystal coordinates (the K ion was excluded in the calculation of [**6**]$^-$ and the deprotonated form of **5**) or constructed directly in the *IQmol* visualizer (homoleptic Mn–CO complexes) as the starting points. Frequency calculations were performed on all structures to ensure no imaginary frequencies. Single-point energy calculations were used to

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obtain the final electronic energy (enthalpy) and corrected by adding the total enthalpy obtained from the frequency calculation (298 K). Free energies (298 K) additionally required the total entropy from the frequency calculation and energy of solvation in toluene.

Synthetic Procedures. *Synthesis of 2-[(Dimethylamino)-methyl]-4,6-dimethylphenol (H-NO).* In a 50 mL round-bottomed flask, open to air, 2,4-dimethylphenol (1.8 g, 15 mmol) and dimethylamine (40 wt % aqueous solution, 3.8 mL, 30 mmol) were mixed together at 0 °C. Formaldehyde (37 wt % aqueous solution, 2 mL, 25.6 mmol) was added, and the mixture was allowed to stir at room temperature for 30 min, followed by reflux at 100 °C for 2 h. After cooling to room temperature, NaCl was added to separate the organic and aqueous layers. The top organic layer was collected, dried over anhydrous Na_2SO_4, and later dried under vacuum to yield pure H-NO as an oil (2.1 g, 78% yield). ^{1}H NMR ($CHCl_3$-d_1, 400 MHz, 298 K, ppm): δ 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.31 (s, 6H, CH_3), 3.58 (s, 2H, CH_2), 6.62 (s, 1H, CH), 6.86 (s, 1H, CH).

Synthesis of Monophosphine Phenol–2-[(Diphenylphosphino)-methyl]-4,6-dimethylphenol (H-PO). In a 25 mL Strauss tube, H-NO (500 mg, 2.8 mmol, 1 equiv) and diphenylphosphine (624 mg, 3.35 mmol, 1.2 equiv) were dissolved in toluene (1 mL). The solution was freeze−pump−thawed once and then heated at 150 °C for 16 h. After cooling to room temperature, the solvent was evaporated under vacuum to obtain a viscous oil to which petroleum ether (10 mL) was added, and the solution was stored at −35 °C. The white crystals formed were collected using a frit and washed with cold petroleum ether. Concentrating the washes under vacuum and storing again at −35 °C yielded more white crystals (835 mg, 93% yield in total). The washes were combined, and the solvent was pumped off to recover residual diphenylphosphine, which was used for later H-PO syntheses. ^{1}H NMR ($CH_2Cl_2d_2$, 400 MHz, 298 K, ppm): δ 2.08 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.39 (s, 2H, CH_2), 5.11 (s, 1H, OH), 6.50 (s, 1H, CH), 6.76 (s, 1H, CH), 7.35−7.42 (10H, $(C_6H_5)_2P$). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, 101 MHz, 298 K, ppm): δ 16.08 (s), 20.50 (s), 31.56 (d, J = 18.18 Hz), 122.99 (d, J = 7.07 Hz), 124.94 (d, J = 1.01 Hz), 129.60 (d, J = 9.09 Hz), 130.11 (d, J = 3.03 Hz), 133.14 (d, J = 24.24 Hz), 138.31 (s), 138.48 (s), 150.82 (s). $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2-d_2, 121 MHz, 298 K, ppm): δ −16.9.

*Synthesis of [H-PO]Mn(CO)$_4$Br (**3**).* To a solution of $Mn(CO)_5Br$ (47 mg, 0.17 mmol, 1 equiv) in THF was added H-PO (50 mg, 0.16 mmol, 1 equiv), and the reaction was stirred for 1 h at room temperature. Evolution of the bubbles ceased within this 1 h. Layering the solution under hexane and storing the vial at −35 °C yielded orange crystals of **3** (76 mg, 78% crystalline yield). ^{1}H NMR (CH_2Cl_2-d_2, 300 MHz, 298 K, ppm): δ 1.86 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 4.03 (d, 2H, CH_2), 5.62 (s, 1H, CH), 5.71 (s, 1H, CH), 6.71 (s, 1H, OH), 7.48−7.60 (10H, $(C_6H_5)_2P$). $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2-d_2, 121 MHz, 298 K, ppm): δ 40.34. ATR-FTIR (cm^{-1}): 3370, 2089, 2006, 1956, 1913.

*Synthesis of [H-PO]$_2$Mn(CO)$_3$Br (**4**).* To a solution of $Mn(CO)_5Br$ (20 mg, 0.073 mmol, 1 equiv) in THF was added H-PO (51 mg, 0.16 mmol, 2.2 equiv). The reaction mixture was subjected to three freeze−pump−thaw cycles and then heated at 70 °C overnight. THF was removed under vacuum, and the yellow-orange residue was washed with petroleum ether. Drying the solid yielded pure **4** (60 mg, 96% yield). Crystals suitable for XRD were obtained by layering a THF solution of the compound under hexane at room temperature. ^{1}H NMR (CH_2Cl_2-d_2, 300 MHz, 298 K, ppm): δ 1.89 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 4.07 (d, 2H, CH_2), 5.67 (s, 1H, CH), 5.76 (s, 1H, CH), 6.68 (s, 1H, OH), 7.3−7.6 (10H, $(C_6H_5)_2P$). $^{31}P\{^{1}H\}$ NMR (THF, 121 MHz, 298 K, ppm): δ 55.29. Anal. Calcd (found) for **4**, $C_{45}H_{42}BrMnO_5P_2$: C, 62.88 (62.89); H, 4.92 (5.22); N, 0.00 (none found). ATR-FTIR (cm^{-1}): 3460, 3350, 2045, 1962, 1920.

*Synthesis of [H-PO][PO]Mn(CO)$_3$ (**5**).* $Mn(CO)_5Br$ (17 mg, 0.06 mmol, 1 equiv) and H-PO (40 mg, 0.12 mmol, 2 equiv) were dissolved in THF (1 mL). After stirring at room temperature for 1 h, the reaction mixture was subjected to three freeze−pump−thaw cycles and then heated at 100 °C overnight. The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture showed complete conversion to **5**. Compound **5** was isolated by layering the solution under hexane and growing yellow crystals at room temperature (30 mg, 62% crystalline yield). Slight variations in the temperature led to the formation of unidentified byproducts. A cleaner synthesis pathway is achieved using Et_3N. To a solution of $Mn(CO)_5Br$ (20 mg, 0.073 mmol, 1 equiv) in THF was added H-PO (51 mg, 0.16 mmol, 2.2 equiv). The reaction mixture was subjected to three freeze−pump−thaw cycles and then heated at 70 °C overnight. To this in situ prepared complex **4** was added excess Et_3N (35 μL), leading to the immediate precipitation of $[Et_3NH]Br$. The reaction was stirred for 5 min and the solution filtered using a fine frit. The solvent was removed under vacuum and the residue washed with methanol. Drying the residue under vacuum yielded pure **5** (52 mg, 92% yield) which shows poor solubility in solvents like THF, toluene, dichloromethane (CH_2Cl_2), and acetonitrile. Crystals suitable for XRD were obtained by layering a solution of **5** in CH_2Cl_2 under diethyl ether at room temperature. ^{1}H NMR (toluene-d_8, 300 MHz, 298 K, ppm): δ 1.87 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 3.56 (m, 4H, CH_2), 5.36 (s, 1H, CH), 6.54 (s, 1H, CH), 6.75 (s, 2H, CH), 6.89−7.59 (20H, $(C_6H_5)_2P$), 10.56 (s, 1H, OH). $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 121 MHz, 298 K, ppm): δ 59.50, 77.33. Anal. Calcd (found) for **5**·1.5toluene ($C_{55.5}H_{53}MnO_5P_2$): C, 72.70 (72.47); H, 5.83 (5.89); N, 0.00 (0.44, trace Et_3N from the reaction). ATR-FTIR (cm^{-1}): 2540, 2045, 1962, 1892.

*Synthesis of THF$_3$·K[(PO)$_2$Mn(CO)$_2$] (THF$_3$·K[**6**]).* To a solution of $Mn(CO)_5Br$ (90 mg, 0.33 mmol, 1 equiv) in THF (2 mL) was added H-PO (220 mg, 0.69 mmol, 2.1 equiv). After evolution of the gases ceased, the solution was subjected to one cycle of freeze−pump−thaw and heated at 70 °C for 12 h. $^{31}P\{^{1}H\}$ NMR of the reaction mixture showed complete conversion to **4**. Excess KH (40 mg, 1.00 mmol, 3 equiv) was added to this in situ prepared **4**, and the reaction mixture was stirred until evolution of the bubbles stopped, during the course of which a yellow precipitate formed. The reaction was then heated at 50 °C for 2 h. The yellow precipitate eventually dissolved, and the solution turned bright orange. The reaction mixture was filtered using a frit. Concentrating the filtrate (1 mL) and layering it under petroleum ether afforded crystals of THF_3·K[**6**] (269 mg, 90% crystalline yield). Crystals suitable for XRD were obtained by storing the concentrated filtrate at −35 °C. ^{1}H NMR (CH_2Cl_2-d_2, 300 MHz, 298 K, ppm): δ 1.65 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.22 (d, 1H, CH_2), 3.80 (d, 1H, CH_2), 6.66 (s, 1H, CH), 6.90 (s, 1H, CH), 7.27−7.78 (10H, $(C_6H_5)_2P$). $^{31}P\{^{1}H\}$ NMR (THF, 121 MHz, 298 K, ppm): δ 56.07. Anal. Calcd (found) for THF_3·K[**6**] ($C_{56}H_{64}KMnO_7P_2$): C, 66.92 (66.25); H, 6.42 (6.14); N, 0.00 (none found). ATR-FTIR (cm^{-1}): 1894, 1802.

*Synthesis of Mn^{II}[(PO)$_2$Mn^{I}(CO)$_2$]$_2$ (Mn[**6**]$_2$).* To a solution of H-PO (66 mg, 0.2 mmol, 2 equiv) in 2 mL of isopropyl alcohol was added $Mn_2(CO)_{10}$ (40 mg, 0.1 mmol, 1 equiv), and the reaction was refluxed at 95 °C for 3 days. The solution was filtered using a frit to collect the orange precipitate of Mn[**6**]$_2$ (47 mg, 45% yield). The precipitate was dissolved in a benzene/toluene mixture, layered under hexane, and stored at −35 °C to yield orange needlelike crystals. Anal. Calcd (found) for Mn[**6**]$_2$ ($C_{88}H_{80}Mn_3O_8P_4$): C, 68.00 (68.29); H, 5.19 (5.34); N, 0.00 (none found). ATR-FTIR (cm^{-1}): 1928, 1846.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00941.

NMR, ATR-FTIR, and EPR spectra, connectivity structure of Mn^{II}[**6**]$_2$, DFT-optimized structures, and X-ray crystallography (PDF)

Crystallographic structure (MOL)

Crystallographic structure (MOL)

Crystallographic structure (MOL)

Crystallographic structure (MOL)

Accession Codes

CCDC 1906794–1906796 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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