

Synthesis of Mn(III)X₃ (X = Cl, Br, I) Compounds with Phosphine (R₃P) Ligands

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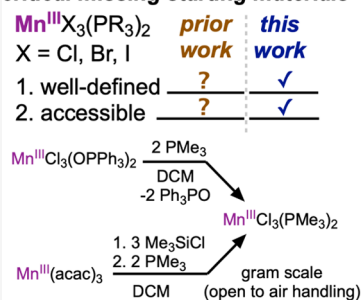
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MnX₃ phosphine compounds are critical missing starting materials



ABSTRACT: This work details the synthesis and characterization of complexes of the form $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$ (X = Cl, Br, I), which is a rare type of coordination compound. Prior to this work, the only mode of synthesis was oxidizing mixtures of $\text{Mn}^{\text{II}}\text{X}_2$ and PR_3 with dry air, but these procedures give low yields and variable outcomes. By taking advantage of the starting material $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (1) and other new strategies, we present robust synthetic protocols for both new and known Mn(III) halido phosphine complexes. In addition to $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$, these include $[\text{Mn}^{\text{III}}\text{Cl}_2(\text{dmpe})_2]^+$ salts and $[\text{LMn}^{\text{II}}\text{X}_3]^-$ manganates (L = phosphine oxide). Furthermore, the full characterization of these $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$ species enabled a definitive revisitation of some controversial chemistry surrounding the compounds and products from the dry air oxidation of certain $\text{Mn}^{\text{II}}\text{X}_2$ and phosphine ligand mixtures.

1. INTRODUCTION

This study describes the synthesis of manganese(III) halido phosphine complexes. The project originated from a thought experiment involving hypothetical Mn alkylidenes. We noted that Mn is surrounded by elements for which alkylidenes and ynes have been prepared and generally engage in C–C coupling reactions. As a starting point, we contemplated a retrosynthetic approach for a Grubbs Gen I type Mn alkylidene (Scheme 1). Whether or not such a target is viable,¹ this mental exercise revealed that the synthesis hypothesis for the Mn(IV) analogue is currently not testable because suitable $[\text{Mn}^{\text{II}}\text{Cl}_2(\text{PR}_3)_n]$ starting materials are missing.

This absence is not from a lack of attempts to prepare them, and the literature contains diverse opinions about their nature.^{2–4} Only a few air sensitive $[\text{Mn}^{\text{II}}\text{X}_2(\text{PR}_3)_n]$ (X = Br, I) complexes have been characterized with crystallography.^{3,5} Controversial aspects of $[\text{Mn}^{\text{II}}\text{X}_2(\text{PR}_3)_n]$ aside, $\text{Mn}^{\text{II}}\text{X}_2/\text{phosphine}$ mixtures have been used to prepare $[\text{Mn}^{\text{III}}\text{X}_3(\text{PMe}_3)_2]$ complexes (X = Cl, Br, or I).^{6,7} Given their well-defined nature⁶ and potential stability toward O₂, we reasoned that these Mn(III) halido phosphine complexes may better serve as starting materials in high-valent organo-

manganese chemistry compared to the Mn(II) counterparts. For example, a retrosynthetic analysis of a hypothetical Mn(V) carbyne complex inspired by Guochen Jia's Re(V) carbynes reveals that $[\text{Mn}^{\text{III}}\text{X}_3(\text{PMe}_3)_2]$ is the first missing link (Scheme 2).⁸ Furthermore, in recognition of the utility of high-valent {MoCl} species in the preparation of Mo-alkyls,⁹ one can make the case for the synthetic utility of {Mn^{III}Cl} species toward similar ends.¹⁰ Unfortunately, the protocols for $[\text{Mn}^{\text{III}}\text{X}_3(\text{PMe}_3)_2]$ lack detail,^{6,7} give variable results (Scheme 3), and are low-yielding, even when the Mn(II) precursors are well-defined/described and uncontroversial.¹⁰

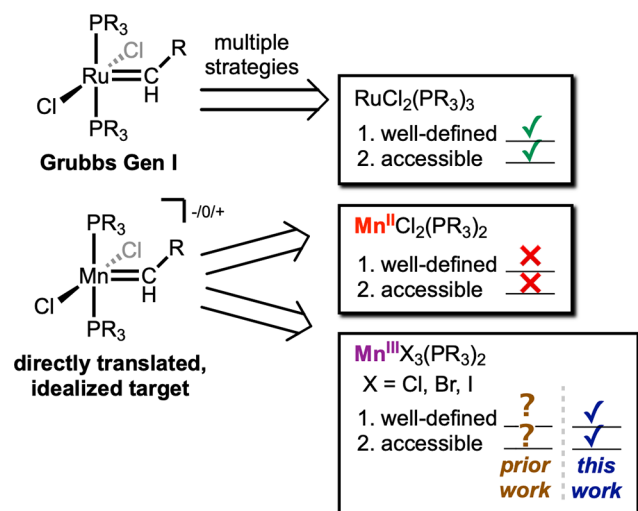
Disregarding issues of viability for the alkylidene/ynone targets or intermediates, these retrosynthetic analyses were an exercise in chemical discovery,¹¹ revealing a knowledge gap in

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Scheme 1. Retrosynthetic Analysis Reveals Knowledge Gap



synthesis. Namely, there are no efficient and/or robust methodologies to prepare Mn(III) halido phosphine starting materials. As part of our growing interest in studying the coordination chemistry of Mn(III), we hypothesized that our recently developed starting material [Mn^{III}Cl₃(OPPh₃)₂] (1) could serve as the ideal candidate from which to develop new synthetic protocols.¹² Testing this hypothesis led to several new discoveries, including addressing the stated knowledge gap and the synthesis of some new Mn(III) halido phosphine complexes.

2. RESULTS AND DISCUSSION

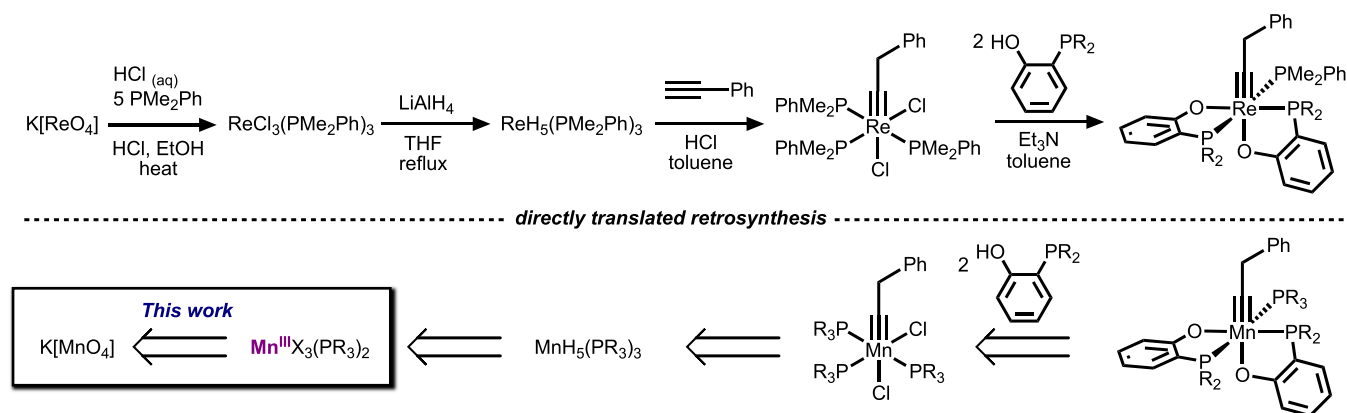
2.1. Note about Mn(II) Halido Phosphine Compounds. [Mn^{II}X₂(PPh₃)_n] complexes have apparently been prepared.¹³ We attempted various syntheses of [Mn^{II}Br₂(PPh₃)_n] but found that, while a complex may form in molten Ph₃P, washing the supposed [Mn^{II}Br₂(PPh₃)_n] material(s) with Et₂O was enough to liberate the phosphine ligand. Hence, we successfully isolated only solvated Mn^{II}Br₂ from reactions with Ph₃P.

We also attempted the synthesis of [Mn^{II}Br₂(PMe₃)_n]. The resulting product is a species consistent with [Mn^{II}Br₂(PMe₃)₂], and it is exceedingly oxygen sensitive, turning deep purple upon addition of air (*vide infra*). In general, there are few well-defined [Mn^{II}X₂(PR₃)_n] com-

pounds,^{3,5} and we suspect the reason is that monodentate phosphine ligands only weakly bind to Mn^{II}X₂ species. Therefore, they do not possess the properties that we sought in an isolable and discrete starting material. By contrast, Mn(II) halido complexes with chelating phosphines and/or cyclopentadienyl¹⁴ and organometallic Mn(II) alkyl phosphine¹⁵ compounds are well-defined materials that could be pursued in a separate study similar to what is shown in Schemes 1 or 2; in fact, others have used Mn(II) halido phosphines to prepare compounds with Mn–C multiple bonds.¹⁶ Instead, we decided to pursue the synthesis and characterization of nominally well-defined [Mn^{III}X₃(PR₃)₂] complexes. For this, we envisioned developing methods discussed herein, allowing for isolation on a 100–1000 mg scale as crystalline solids with potentially enhanced chemical stability (e.g., against air and moisture).

2.2. Early Attempts to Prepare [Mn^{III}X₃(PR₃)₂] Complexes. Previous attempts to prepare well-defined [Mn^{III}X₃(PR₃)₂] complexes with ethereal solutions of Mn^{III}Cl₃ were unsuccessful.¹⁷ Other methods rely on aerobic oxidation of the ill-defined Mn^{II}X₂/phosphine mixtures noted above for [Mn^{III}X₃(PMe₃)₂] (X = Cl, Br, I).⁷ These aerobic oxidations can give varied outcomes,⁴ and so we doubted the viability of this method for our purposes. As a case study, consider the following variable outcomes from reacting Mn^{II}I₂(PR₃)_n with O₂ (Scheme 3, left). Two virtually identical accounts give the [Mn^{III}I₃(PMe₃)₂] complex,^{6,7} others furnish alleged Mn(III) superoxide complexes,¹⁸ others give [{Mn^{II}I₂(PR₃)₄(μ₄-O)] clusters,¹⁹ and still another gives mixed valent Mn(II)/(III) compounds.^{5c} This variability illustrates the difficulty associated with the preparation and isolation of [Mn^{III}X₃(PR₃)₂] compounds through aerobic treatment of the ill-defined Mn(II) precursors. Interpreting these results is also clouded by the noted debate⁴ that is further confused by a labyrinth of studies by McAuliffe²⁰ that often duplicate or cite unpublished works and/or lack characterization/synthetic details. Many aspects of the current study intersect with this labyrinth, but untangling the web is not our intention, and henceforth, we will mostly ignore such intersections except where clarity is afforded.

2.3. Synthesis of Mn^{III}Cl₃ Complexes. Treatment of 1 with 2 equiv of Me₃P in DCM afforded crystals of a maroon-red complex [Mn^{III}Cl₃(PMe₃)₂] (2) (Scheme 3, right) in 44% yield whose trigonal bipyramidal structure was confirmed through X-ray diffraction (XRD) (Figure 1). Evans method of

Scheme 2. Retrosynthesis of Mn(V) Carbyne Inspired by Guochen Jia and Co-Workers' Re(V) Carbyne⁸

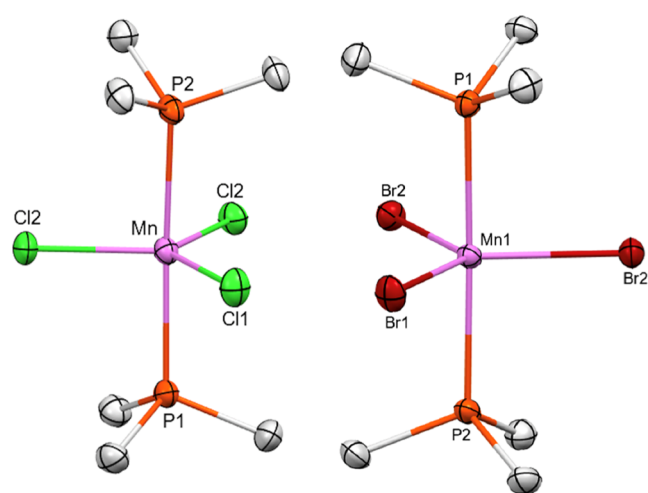
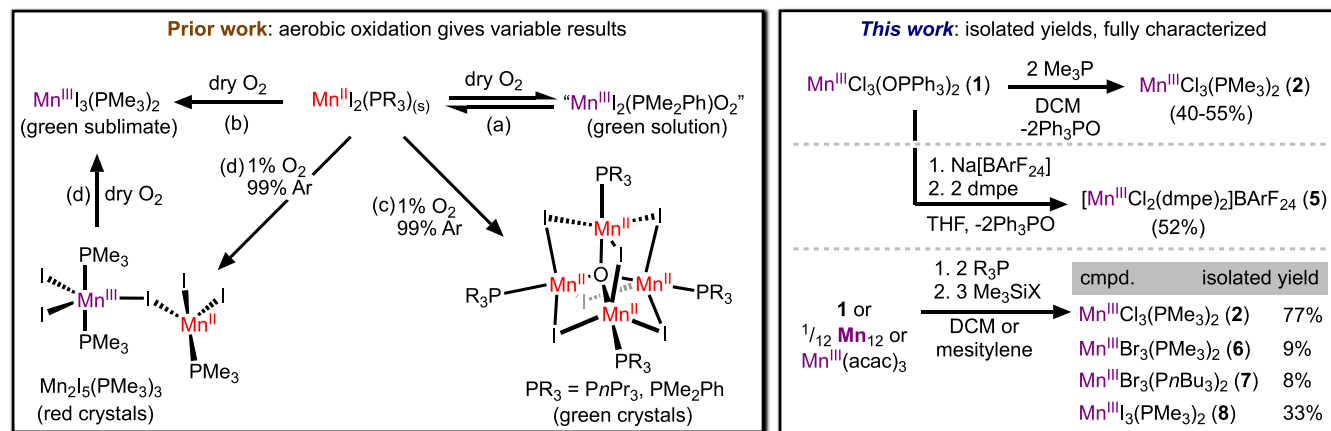
Scheme 3. Previous $\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2$ Synthesis Strategy (a,¹⁸ b,⁶ c,¹⁹ d^{5c}) and This Work

Figure 1. Molecular structure (ellipsoids 50%) of **2** (left) and **6** (right) determined by XRD (H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg) for **2**: Mn–Cl1 = 2.278; Mn–Cl2 = 2.290; Mn–P1 = 2.402; Mn–P2 = 2.418; Cl2–Mn–Cl1 = 115.40; Cl2–Mn–Cl1 = 122.28; P2–Mn–P1 = 176.25. Selected bond lengths (Å) and angles (deg.) for **6**: Mn1–Br1 = 2.418; Mn1–Br2 = 2.434; Mn1–P1 = 2.406; Mn1–P2 = 2.419; Br2–Mn1–Br1 = 121.84; Br2–Mn1–Br2 = 116.30; P2–Mn1–P1 = 177.44. Tau τ_5 parameters are 0.90 for **2** and 0.93 for **6**, respectively.

analytically pure material dissolved in DCM is consistent with a high-spin Mn(III) center in the solution state ($\mu_{\text{eff}} = 4.98 \mu_{\text{B}}$). The compound is not indefinitely stable in solution even under an inert atmosphere ($t_{1/2}$ in DCM = 2 d), but it can be manipulated and stored open to air without decomposition for short periods of time (minimal loss as determined with ^1H NMR and FTIR spectroscopy for periods of <1 d). In the solid state, in or outside of an inert atmosphere, it decomposes to a white material over the course of weeks at room temperature (Figure S4) or ≈ 5 months at -35°C .

Attempts to synthesize other $\text{Mn}^{\text{III}}\text{Cl}_3$ complexes with monodentate phosphines were met with a myriad of results. Highly colored solutions were obtained for Et_3P , $n\text{Bu}_3\text{P}$, Me_2PhP , MePh_2P , and $(\text{MeO})_3\text{P}$ but with half-lives too short to allow for definitive isolation and characterization (Table 1). We compared their UV–vis spectra with those of **2**, and they are similar to such an extent that we tentatively assign them as being isostructural (Figure 2).

Table 1. Half-Life of $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{PR}_3)_2]$ Generated in Solution^a

phosphine	λ_{max} (nm)	half-life
Me_3P	389, 485	2 d
$n\text{Bu}_3\text{P}$	397, 540	2.4 h
Me_2PhP	393, 532	2.0 h
Et_3P	395, 536	1.9 h
MePh_2P	394, 562	216 s
$(\text{MeO})_3\text{P}$	351, 403, 634	768 s
Ph_3P , $(o\text{-tol})_3\text{P}$, $t\text{Bu}_3\text{P}$, Cy_3P , $i\text{Pr}_3\text{P}$, $(\text{OPh})_3\text{P}$, dppe^c	n.a.	$\ll 1$ s ^b
dmpe^c	353, 413, 527 ^d	≈ 5 d

^aHalf-lives were measured using UV–vis at 25°C using *in situ*-generated species by addition of 2 equiv of R_3P to a [0.6 mM] solution of **1** in DCM under an inert atmosphere. ^bAddition caused immediate loss in color ($t_{1/2}$ for Ph_3P species at $-68^\circ\text{C} \approx 533$ s). ^c $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$; $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$. ^dUV–vis spectra measured in THF.

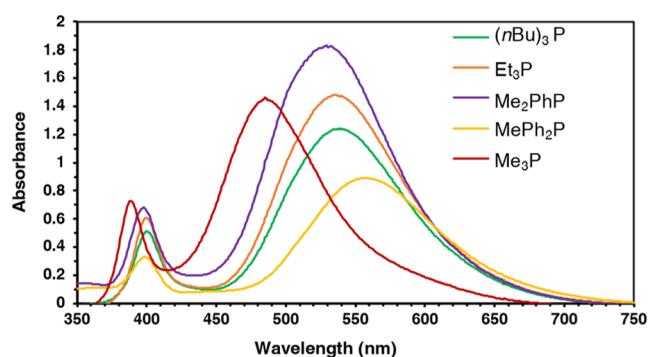


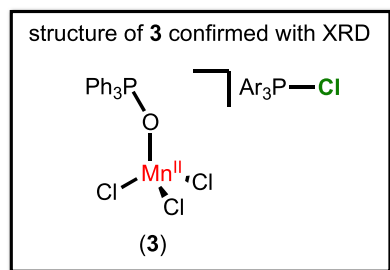
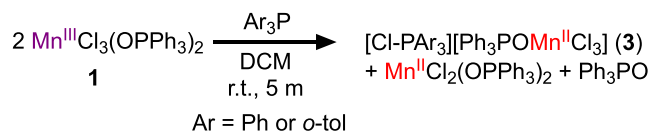
Figure 2. Comparison of UV–vis spectra of species formed from the reaction between **1** and two equivalents of R_3P ($\text{R}_3 = n\text{Bu}_3, \text{Et}_3, \text{Me}_2\text{Ph}, \text{MePh}_2$) with **2** in DCM at room temperature.

Other phosphines, including Ph_3P , $(o\text{-tol})_3\text{P}$, $t\text{Bu}_3\text{P}$, Cy_3P , $i\text{Pr}_3\text{P}$, $(\text{PhO})_3\text{P}$, dppe (1,2-bis(diphenylphosphino)ethane) and dppm (bis(diphenylphosphino)methane), caused immediate loss of color in the solution. For Ph_3P , we additionally carried out the reaction at a low temperature (-68°C) and monitored the reaction with UV–vis. Even at low temperatures, the species that formed rapidly decayed with a half-life of 533 s (Figure S10).

The half-lives of these various compounds do not follow a sensible trend when plotted against the R_3P cone-angle, R_3P^+

reduction potential, or $R_3PH^+ pK_a$. Of the reaction mixtures that furnished tractable products, we observed P–Cl bond formation and P–O bond cleavage/formation alongside reduction of **1**. In all cases involving rapid reduction of **1** in DCM, the known compound $[Mn^{II}Cl_2(OPPh_3)_2]$ formed as the major Mn(II)-containing byproduct.²¹ The same reaction was observed when other solvents like Et₂O, THF, benzene, toluene, and pentane were used. When Ph_3P was used, $[Ph_3P-Cl]^+$ was formed, as confirmed using ³¹P NMR spectroscopy (Figure S11).^{22,23} When (*o*-tol)₃P was used, in addition to $[Mn^{II}Cl_2(OPPh_3)_2]$, crystals of $[(o\text{-tol})_3P-Cl][(Ph_3P-O)-Mn^{II}Cl_3]$ (**3**) were obtained (Scheme 4, Figure 3). Finally, dppe reacted with **1** to generate $[(dppe-O)_3Mn^{II}][Mn^{II}Cl_4]$ (**4**) (dppe-O = the bis-oxide of dppe) (yield = 20%) (Scheme 5, Figure 4). Note that substoichiometric phosphine (0.5 for Ph_3P and 0.25 for dppe) was sufficient to induce complete decomposition of **1**. The implications of this and the lack of correlation between half-life and phosphine property indicate complicated decomposition pathways, and we do not attempt to further rationalize this reactivity of the $Mn^{III}Cl_3(PR_3)_n$ complexes at this stage.

Scheme 4. Products from Reactions with Ar₃P



2.4. Synthesis of $[Mn^{III}Cl_2(dmpe)_2]^+$ Salts. The compound $[Mn^{III}Cl_2(1,2\text{-phenylenebis(dimethylphosphine)})_2]\text{-ClO}_4$ is known,²⁴ and so we attempted to synthesize a few new Mn(III) halido complexes with bidentate phosphines using dppe, dppm, and dmpe (1,2-bis(dimethylphosphino)ethane). Only dmpe afforded a stable Mn(III) compound. This was accomplished by the reaction between **1** and two equivalents of dmpe in THF and inclusion of NaBARF₂₄ affording $[Mn^{III}Cl_2(dmpe)_2][BARF_{24}]$ (**5**) as a stable orange crystalline compound with a yield of 52% (Scheme 5, Figure 5); the PF₆ salt was also prepared in DCM with a yield of 70%. Results from the Evans method in DCM are consistent with an intermediate-spin Mn(III) center in the solution state (*S* = 1). The intermediate spin ground state appears to be common for octahedral Mn(III) cations, since similarly coordinated Mn(III) dimethyl complexes and the homoleptic bis-Tp Mn(III) compounds are *S* = 1.^{25,26} **5** can also be stored in the solid state for ≈ 5 weeks open to air without decomposition (monitored with IR spectroscopy) and is indefinitely stable when stored at −35 °C in an inert atmosphere.

2.5. Synthesis of $Mn^{III}Br_3$ Complexes. Our first trials to prepare $Mn^{III}Br_3$ complexes were our attempts to make $[Mn^{III}Br_3(OPPh_3)_2]$, the bromido analogue of **1**. The reaction

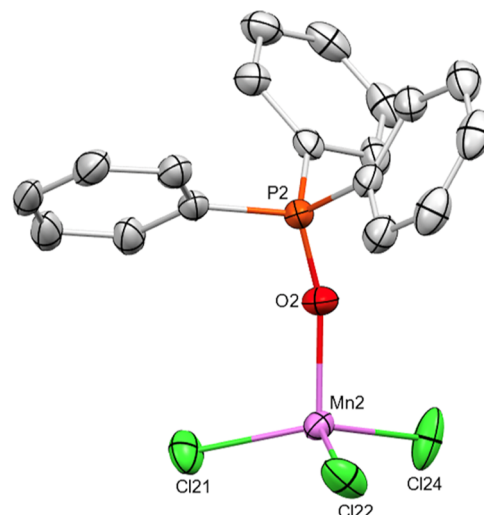
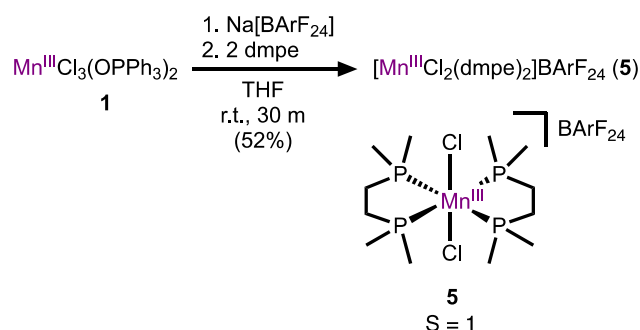
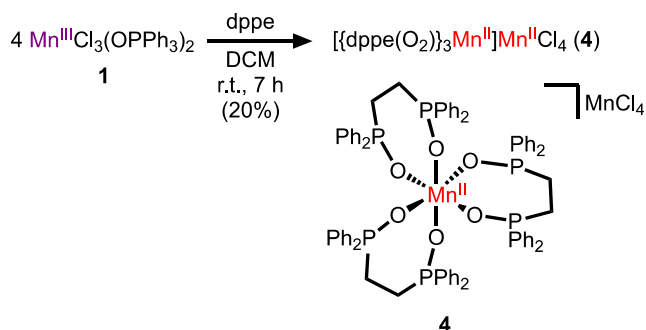


Figure 3. Molecular structure (ellipsoids 50%) of the d⁵ manganate $[Mn^{II}Cl_3(OPPh_3)]^-$ in **3** (*o*-tol₃P⁺Cl⁺ counterion and H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) for **3**: Mn2–O2 = 2.029(2); Mn2–Cl21 = 2.339(7); Mn2–Cl22 = 2.336(6); Mn2–Cl24 = 2.373(4); P2–O2 = 1.496(2); Cl21–Mn2–Cl22 = 116.10(2); Cl21–Mn2–Cl24 = 112.80(1); Cl24–Mn2–Cl22 = 117.40(2); Cl21–Mn2–O2 = 105.12(6).

Scheme 5. Reactions with Bidentate Phosphines



employed was essentially the same as the one used to prepare **1** in our previous study except that Me₃SiBr was used in place of Me₃SiCl.¹² The result of this reaction was the isolation of the known complex $[Mn^{II}Br_2(OPPh_3)_2]$,²¹ Br₂ was an accompanying product (Figure S41). Similarly, when Me₃SiI was used, we isolated $[Mn^{II}I_2(OPPh_3)_2]$ as the major product among other products (i.e., *cis*- $[Mn^{II}(\text{MeCN})_2(OPPh_3)_4](I_3)_2$ (**9a**) and $[Mn^{II}(OPPh_3)_4](I_3)_2$ (**9b**)). Failure to prepare $[Mn^{III}Br_3(OPPh_3)_2]$ and $[Mn^{III}I_3(OPPh_3)_2]$ was corroborated using DFT analysis (Table S1). Specifically, the stability of the desired $[Mn^{III}X_3(OPPh_3)_2]$ relative to the loss of 0.5 X₂, via

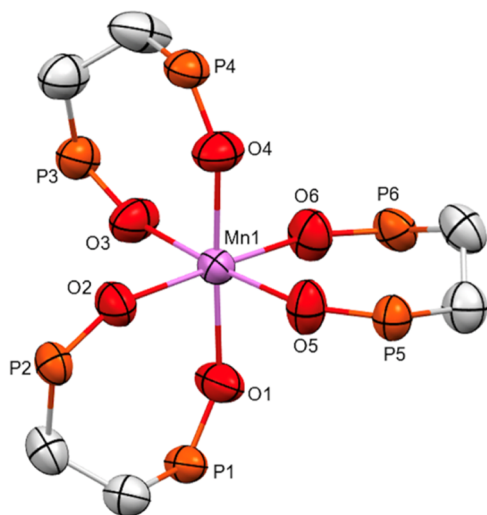


Figure 4. Molecular structure (ellipsoids 50%) of the dication $[\text{Mn}^{\text{II}}(\text{dppe-O})_3]^{2+}$ in **4** determined with XRD ($\text{Mn}^{\text{II}}\text{Cl}_4^{2-}$ counterion, H atoms, and Ph groups in **4** are omitted for clarity). Selected bond lengths (Å) and angles (deg) for **4**: Mn1–O1 = 2.147(4); Mn1–O2 = 2.163(3); Mn1–O3 = 2.154(3); Mn1–O4 = 2.160(4); Mn1–O5 = 2.183(3); Mn1–O6 = 2.125(3); O1–P1 = 1.486(4); O2–P2 = 1.492(3); O3–P3 = 1.483(3); O4–P4 = 1.484(4); O5–P5 = 1.486(2); O6–P6 = 1.477(3); O1–Mn1–O5 = 88.5(1); O2–Mn1–O1 = 89.6(1); O3–Mn1–O2 = 89.9(1); O4–Mn1–O3 = 90.2(1); O6–Mn1–O4 = 90.20(1); O5–Mn1–O3 = 175.5(1).

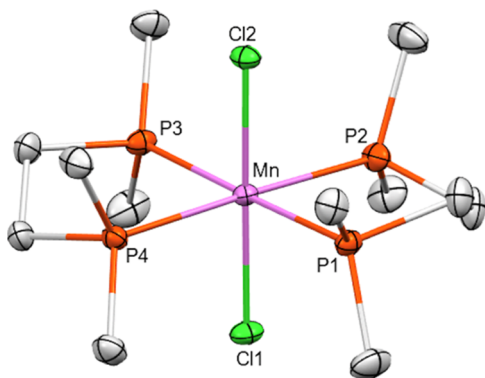
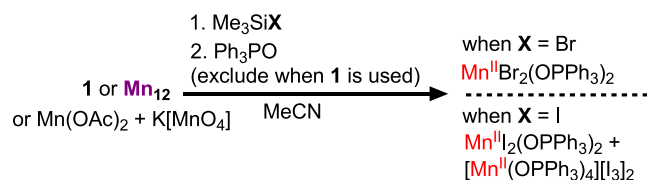


Figure 5. Molecular structure (ellipsoids 50%) of **5** determined with XRD (H atoms and BARF_{24} counterion omitted for clarity). Selected bond lengths (Å) and angles (deg) for **5**: Mn–Cl1 = 2.2438(7); Mn–Cl2 = 2.2374(7); Mn–P1 = 2.3503(8); Mn–P2 = 2.3514(7); Mn–P3 = 2.3508(8); Mn–P4 = 2.3486(7); Cl1–Mn–Cl2 = 179.45(3); P3–Mn–P4 = 83.93(3); P1–Mn–P2 = 84.46(3); P2–Mn–P3 = 96.12(3); P1–Mn–P4 = 95.57(3).

$\text{Br}^\bullet$ or other mechanisms,^{27,28} was evaluated computationally. Only **1** is stable with respect to this transformation, whereas when $\text{X} = \text{Br}$ or I , the reaction to form $\text{Mn}(\text{II})$ and respective X_2 is thermodynamically favorable, all of which is consistent with experimental observation, although the actual mechanisms are likely much more complicated. Scheme 6 summarizes the empirical findings.

The failure to prepare $[\text{Mn}^{\text{III}}\text{X}_3(\text{OPPh}_3)_2]$ ($\text{X} = \text{Br}, \text{I}$) is not surprising considering the well-documented oxidation of bromide with $\text{Mn}(\text{III})$ ions.²⁸ Hence, there are few $\text{Mn}(\text{III})$ complexes that contain even a single Br or I ligand.²⁹ Furthermore, the literature is devoid of $[\text{LMn}^{\text{III}}\text{X}_3]$ ($\text{X} = \text{Br}$ and I) complexes with the exceptions of $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$,⁶ the purported $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PMe}_3)_2]$,⁷ and purported

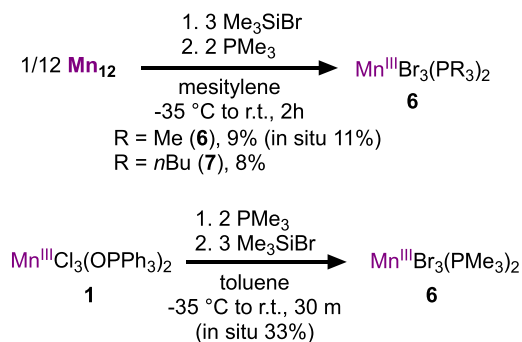
Scheme 6. Attempted Synthesis of $\text{Mn}^{\text{III}}\text{X}_3(\text{OPPh}_3)_2$ ($\text{X} = \text{Br}, \text{I}$) (Generalized Examples)



$[\text{Mn}^{\text{III}}\text{Br}_3(\text{quin-O})_3]$ (quin-O = quinoline-*N*-oxide).³⁰ Therefore, before proceeding with additional syntheses, we performed a DFT analysis for $[\text{Mn}^{\text{III}}\text{X}_3(\text{PMe}_3)_2]$, similar to the one noted for the Ph_3PO system (Table S1). In contrast to the Br and I analogues of **1**, the complexes $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PMe}_3)_2]$ and $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$ are stable against the formation of 0.5 X_2 and encouraged our synthetic pursuit.

Among many trials and reaction conditions, we found that Mn_{12} ($[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HOAc} \cdot 4\text{H}_2\text{O} = \text{Mn}_{12}$)³¹ was best suited to prepare $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PMe}_3)_2]$ (**6**) (yield = 9%) and $[\text{Mn}^{\text{III}}\text{Br}_3(\text{P}n\text{Bu}_3)_2]$ (**7**) (yield = 8%) in the highest isolated yields (Scheme 7). While the isolated yields from

Scheme 7. Synthesis of $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PR}_3)_2]$ Complexes



these reactions are low, reflecting the difficulty of their preparation, the *in situ* yields are relatively higher. For example, we obtained an *in situ* yield of 33% for **6** in toluene starting from 200 mg of **1** in toluene (determined with UV–vis).

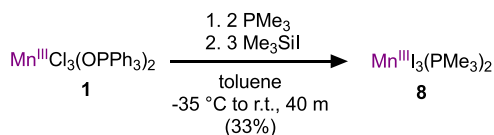
There are some interesting observations worthy of note in the synthesis of **6** and/or **7**. Treatment of Mn_{12} with Me_3SiCl gives a purple metastable solution of $\text{Mn}^{\text{III}}\text{Cl}_3$ that we and others have used to make $\text{Mn}^{\text{III}}\text{Cl}_3$ complexes.^{12,32} The same reaction with Me_3SiBr forms a deep yellow solution that rapidly degrades at room temperature (DCM or MeCN). We suspect, although we have not confirmed, that this solution contains solvated “ $\text{Mn}^{\text{III}}\text{Br}_3$.” At lower temperatures, the solution persists long enough to be treated with various ligands, and we have tried several, such as Me_3P , $n\text{Bu}_3\text{P}$, Et_3P , Ph_3P , dmpe , and dppe . For reactions in DCM or MeCN, the solutions of “ $\text{Mn}^{\text{III}}\text{Br}_3$ ” immediately turned colorless upon reaction with phosphine ligand, and we initially assumed that the $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PR}_3)_2]$ complexes were inaccessible. However, after our DFT analysis noted above, we revisited these reactions but changed the solvent to benzene. Although Mn_{12} is insoluble in benzene, the reaction still proceeds, and upon addition of phosphine, a deep blue or purple solution was formed. We noted that the lifetime of the colored solutions increased upon moving from benzene to toluene and hypothesized that more electron-rich arene solvents could increase the lifetime. Switching to mesitylene allowed for the

stabilization at room temperature of the species when Me_3P or $n\text{Bu}_3\text{P}$ was employed, and we successfully isolated and characterized **6** and **7**. They were successfully characterized by using X-ray diffraction (Figures 2 and S47). Crystalline **6** and **7** are stable to decomposition in open air for about 2 d (as monitored by FTIR spectroscopy) (Figure S29). In an inert atmosphere, these compounds degrade in 6 weeks at room temperature or ≈ 3 months at -35°C .

Foreshadowing our scale-up attempts discussed later, we also noted that $[\text{Mn}^{\text{III}}(\text{acac})_2\text{X}(\text{L})]$ ($\text{L} = \text{H}_2\text{O}$ or no ligand; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been reported.³³ Thus, we used $\text{Mn}^{\text{III}}(\text{acac})_3$ as a starting material for several of the compounds described in this work. Typically, the reactions with $\text{Mn}^{\text{III}}(\text{acac})_3$ give the same product (sometimes in a higher yield) but contain what we suspect is an acac-derived impurity that is difficult to separate. As will be described later, we note this because $\text{Mn}^{\text{III}}(\text{acac})_3$ is a viable candidate to prepare many of the phosphine compounds in this report and might be desirable when acac-derived impurities are not a major concern. By contrast, $\text{Mn}(\text{OAc})_3$ as a starting material afforded trace amounts of $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$ species.

2.6. Synthesis of $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$. Scheme 3 shows the difficulty in preparing $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$ using Mn(II) precursors and aerobic oxidation: the outcomes vary wildly, and, as a result, the literature appears to contain some tongue-and-cheek references to this earlier work.³⁴ To bridge this gap, we attempted the synthesis of $[\text{Mn}^{\text{III}}\text{I}_3(\text{PR}_3)_2]$ complexes using our new methods described above but with iodide. The optimal reaction conditions among many trials use **2** prepared *in situ* in toluene followed by treatment with Me_3SiI (Scheme 8). The product $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$ (**8**) was isolated as a deep

Scheme 8. Synthesis of $\text{MnI}_3(\text{PMe}_3)_2$



green powder (yield = 33%), and XRD quality crystals were grown (Figure S48); in an inert atmosphere, **8** degrades in 1 month at room temperature or ≈ 3 months at -35°C . The characterization data for this known compound differs slightly from the literature but is otherwise consistent with earlier findings (Figures S34–S36).⁶ No other Mn(III) iodido phosphine complexes were successfully synthesized. So, despite the promise that **8** supposedly inspired,³⁴ the $[\text{Mn}^{\text{III}}\text{I}_3(\text{PR}_3)_2]$ compounds are not as promising starting materials as the chlorido analogues.

2.7. Similarities in the UV–vis Spectra of $[\text{Mn}^{\text{III}}\text{Br}_2(\text{PnBu}_3)(\text{O}_2)]$ and $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PnBu}_3)_2]$ (7**).** The UV–vis spectra of the reaction mixtures of “ $\text{Mn}^{\text{III}}\text{X}_2\text{PR}_3$ ” and dry O_2 are said to be those of $[\text{Mn}^{\text{III}}\text{X}_2\text{PR}_3\{\text{O}_2\}]$ complexes.^{4,5,20} Curiously, the reported λ_{max} in $\text{Et}_2\text{O}^{\text{Sc}}$ for $[\text{Mn}^{\text{III}}\text{Br}_2(\text{PnBu}_3)(\text{O}_2)]$ is identical to $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PnBu}_3)_2]$ (**7**) prepared by us here (Figure 6). The spectrum of $[\text{Mn}^{\text{III}}\text{Br}_2(\text{PnBu}_3)(\text{O}_2)]$ in THF^{4a} does not match **7** in THF, although it is strikingly similar (Figure 6). These results suggest that one possible alternative to the $[\text{Mn}^{\text{III}}\text{X}_2\text{PR}_3\{\text{O}_2\}]$ formulation is $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$. We were able to test this hypothesis directly using the complex $[\text{Mn}^{\text{II}}\text{Br}_2(\text{PMe}_3)_2]$ described in Section 2.1. Synthesis, isolation, and subsequent treatment of DCM solvated $[\text{Mn}^{\text{II}}\text{Br}_2(\text{PMe}_3)_2]$ with air formed

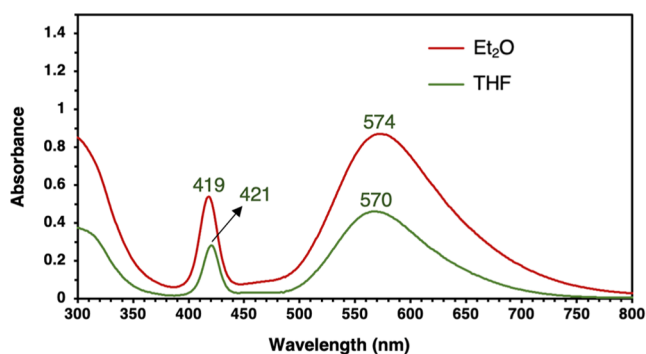


Figure 6. UV–vis spectra of **7** in Et_2O and THF at r.t.

a purple solution with UV–vis features that matched exactly with those of **6** (obtained in 43% *in situ* yield) (Figure S42). The maximum yield for this reaction is 50% because of the starting material. Nevertheless, this method of preparation for **6** is the highest yield so far. Attempts to prepare **2** with air were not as high-yielding, though. For instance, mixtures of anhydrous MnCl_2 and 2 or 4 equiv of Me_3P in DCM reacted with dry air to form a red solution, from which **2** was extracted in 12% yield from the crude product.

While these observations cast serious doubt on the $\text{Mn}^{\text{III}}\text{X}_2\text{PR}_3[\text{O}_2]$ formulation, we avoid making a blanket statement about these supposed superoxides. As was noted in the Introduction section, the results from reactions between $[\text{Mn}^{\text{II}}\text{I}_2(\text{PR}_3)]$ with dry air were reaction-condition and starting material-dependent (Scheme 3), so it is plausible that superoxide compounds exist as products in certain cases.^{4c,d} Unfortunately, a straightforward answer is elusive, and aerobic chemistry was not pursued further here.

2.8. Scaling Up. We achieved our goal of developing Mn^{III} phosphine halido complex syntheses using the new methods described above. However, the above chemistry was only performed on an approximately 100 mg scale, and we desired to scale up certain procedures to advance their utility in synthesis. For this, we chose to focus on Mn(III)-chlorido complexes **2** and **5** because they were the most stable and high yielding.

Complex **5** (either with BArF_4 or PF_6 counteranions) was easily scaled to near-gram quantities using **1** as the starting material (Figure 7). However, the scale-up of **2** was not as straightforward. Many trials using different starting materials (i.e., **1**, $\text{Mn}(\text{OAc})_3$, $\text{Mn}(\text{acac})_3$, and Mn_{12}) and solvents were employed. Only with $\text{Mn}(\text{acac})_3$ and mesitylene were we successful in isolating near-gram quantities of **2**; if DCM is used instead of mesitylene, then **2** is not formed. This was reproducibly accomplished by treating $\text{Mn}(\text{acac})_3$ in mesitylene with 3 equivalents of Me_3SiCl followed by 2 equivalents of Me_3P , which furnished the product **2** in gram quantity (yield = 77%) (Scheme 9, Figure 7).

The crude product **2** synthesized in this manner always contained an organic impurity. By ^1H NMR and FTIR spectral analysis, it is apparent that it is an acac-derived species but could not be removed. Analysis of the CH-combustion data gave satisfactory results if we included 15% $\text{Me}_3\text{Si}(\text{acac})$. The ^1H NMR spectrum of $\text{Me}_3\text{Si}(\text{acac})$ is reported in CCl_4 and is close to the features of the impurity found in crude **2** (Figure S6).³⁵ The GC–MS analysis of crude **2** confirmed the presence of “ $\text{Me}_3\text{Si}(\text{acac})$ -derived” impurity (Figure S8). Attempts to purify by sublimation resulted in degradation (≤ 50 mTorr, 75

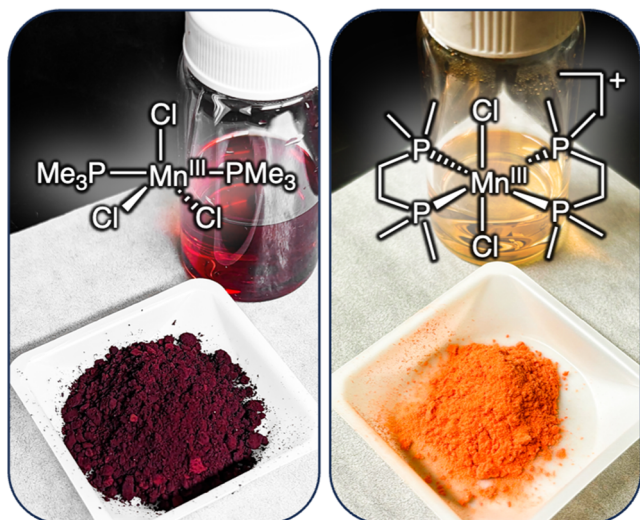
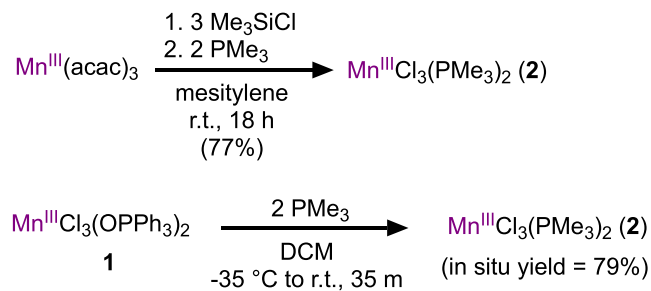


Figure 7. Complex **2** (left) and **5** (right) exposed to air isolated from gram-scale syntheses.

Scheme 9. Scale-Up Synthesis of $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{PMe}_3)_2]$ (2**)**



$^\circ\text{C}$); McAuliffe reported sublimation as a technique to purify and isolate **8**, but we were unsuccessful in reproducing this for **2** and **8**. Importantly, UV–vis, ^1H NMR, and FTIR spectroscopy of the crude product were identical to **2** except for the peaks associated with the $\text{Me}_3\text{Si}(\text{acac})$ -derived impurity (Figures S6 and S7). Attempts to recrystallize led to cocrystallization with white impurities.

The gram-scale reaction between **1** and Me_3P produces **2** in a high *in situ* yield, but purification from Ph_3PO and Mn(II) byproducts was not successful. For example, treatment of 1 g of **1** with 2 equiv of Me_3P in DCM at r.t. afforded **2** in 79% yield, as determined by UV–vis spectroscopy (Scheme 9).

We additionally characterized the white byproduct materials obtained from the scale-up procedures with **1** and Me_3P (and Me_3SiX for $\text{X} = \text{Br}, \text{I}$ for **6** and **8**) using FTIR, $^{31}\text{P}\{^1\text{H}\}$ NMR, and CH-combustion analysis (Figures S37–S40). The results all point to a d^5 manganate species consistent with $[\text{Me}_3\text{PX}][\text{Mn}^{\text{II}}\text{X}_3(\text{OPMe}_3)_n]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $n = 1$ for Cl; $n = 2$ for Br, I), but these are tentative assignments based on the similarities in the chemical and spectroscopic properties of **3** and **4**. To test the feasibility of these d^5 manganates $[\text{Mn}^{\text{II}}\text{X}_3(\text{OPR}_3)_2]^-$, which, prior to this work, were unknown for Cl,³⁶ we treated $[\text{Mn}^{\text{II}}\text{Cl}_2(\text{OPPh}_3)_2]$ with $[(o\text{-tol})_3\text{PCl}]\text{Cl}$ to isolate **3**. This reaction indeed furnished **3**, as determined with characterization by CH-combustion analysis and NMR and FTIR spectroscopy (Figures S43–S45).

3. CONCLUSIONS

This project began with a thought experiment: “what materials are required to prepare high-valent, phosphine-coordinated manganese alkylidene/ynone compounds?” The question was met by a retrosynthetic analysis of Grubbs Gen I $\text{Ru}^{\text{IV}}\text{-(PR}_3\text{)}$ alkylidenes and Jia’s $\text{Re}^{\text{V}}\text{-(PR}_3\text{)}$ alkylidyne and revealed that a potential critical starting material is the $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$ compound class. Prior to this work, these were controversial or unreasonable starting materials. To fill this gap, we successfully found viable, highly reproducible routes to $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$ that rely on $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) or other readily available Mn(III) starting materials. For instance, a gram-scale synthesis of $[\text{Mn}^{\text{III}}\text{Cl}_2(\text{dmpe})_2]^+$ (**5**) used **1**, and the gram-scale synthesis of $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{PMe}_3)_2]$ (**2**) was accomplished with $\text{Mn}(\text{acac})_3$. We also synthesized $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PR}_3)_2]$ ($\text{R} = \text{Me}$ (**6**), $n\text{Bu}$ (**7**)) using a new methodology. Notably, the crystal structures of **6** and **7** are the only structurally characterized materials with the $\text{Mn}^{\text{III}}\text{Br}_3$ motif. This is a rare motif because manganese(III) ions readily oxidize bromide, as we also demonstrated. Finally, we additionally developed a reliable method to prepare the iodo derivative $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$ that used **1** and **2**.

Many different iterations were explored for these syntheses. Invariably, the product was nearly always a mixture of the desired compound $[\text{Mn}^{\text{II}}\text{X}_2(\text{OPPh}_3)_2]$ and a manganate of the general form $[\text{R}_3\text{PX}][\text{Mn}^{\text{II}}\text{X}_3(\text{OPR}_3)_2]$, as determined by crystallography for $\text{X} = \text{Cl}$ and $\text{R} = o\text{-tol}$ for **3** and by CH and $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the products. We did not determine why one set of conditions afforded the desired $[\text{Mn}^{\text{III}}\text{X}_3(\text{PR}_3)_2]$ and others induced near-immediate decomposition into the Mn(II) byproducts. To account for this observation, we simply note that the Mn(III) phosphine complexes are very reactive species—although simultaneously bench stable over convenient lengths of time. These properties bode well for their utility in the synthesis of new compounds.

Finally, the Mn(II) bromido phosphine compound $[\text{Mn}^{\text{II}}\text{Br}_2(\text{PMe}_3)_2]$ studied herein allows for some final points of reflection. The compounds $[\text{Mn}^{\text{II}}\text{Br}_2(\text{PMe}_3)_2]$ and tentatively assigned $[\text{Me}_3\text{PBr}][\text{Mn}^{\text{II}}\text{Br}_3(\text{OPMe}_3)_2]$ were both characterized with CH-combustion analysis and FTIR and NMR spectroscopy. The former species, $[\text{Mn}^{\text{II}}\text{Br}_2(\text{PMe}_3)_2]$, turns purple and infuses the room with the stench of Me_3P when exposed to air, but the latter species, $[\text{Me}_3\text{PBr}][\text{Mn}^{\text{II}}\text{Br}_3(\text{OPMe}_3)_2]$, does not and is essentially air stable. They are clearly different compounds from the reactivity, NMR spectra, and CH analyses, but they have very similar FTIR spectra (Figure S46). Unfortunately, FTIR spectroscopy is one of the best means to characterize difficult-to-crystallize paramagnetic compounds. This is to point out that the nature of the Mn(II) halido phosphine complexes is difficult to parse and likely sparked the early controversies that surround them. In fact, we suspect that the anecdote that “*Mn is hard to work with*” may have sprung from this well of chemistry. For this reason, we advise caution in making blanket statements about their nature.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All chemicals were used as purchased from chemical vendors, unless otherwise noted. $[\text{Mn}_{12}\text{O}_{12}(\text{OAc})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{HOAc}$ (**Mn**₁₂),³¹ bis-(triphenylphosphine oxide)manganese(III) trichloride $[\text{MnCl}_3(\text{OPPh}_3)_2]$ (**1**),¹² $[\text{MnCl}_2(\text{OPPh}_3)_2]$,²¹ acetylacetonate manganese(III) $[\text{Mn}(\text{acac})_3]$,³⁷ triphenylphosphine dichloride

([PPh₃Cl]Cl),²² tri(*o*-tolyl)phosphine dichloride (P{*o*-tolyl}₃Cl₂),³⁸ and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na-BArF₂₄)³⁹ were prepared according to literature procedures. Manipulations of compounds were carried out in a nitrogen-filled Genesis VAC glovebox, kept at or below 1 ppm of H₂O and 5 ppm of O₂, or by using standard Schlenk techniques to ensure dry and very low oxygen conditions. Dry, oxygen-free solvents were obtained from a PPT solvent purification system and were further dried to ≈1 ppm water by storing over 3 Å molecular sieves.⁴⁰ The molecular sieves were activated at 200 °C under vacuum for 48 h prior to use. Deuterated solvents were degassed via three freeze–pump–thaw cycles and stored over sieves in a glovebox. In addition, solvents were passed through a 2 in. column of activated basic alumina loaded in a glass pipet before use. All glassware was kept in an oven maintained at 200 °C for at least 12 h before use. No uncommon hazards were noted during the experiments.

4.2. Instrumentation. NMR experiments were carried out on Varian Mercury-300 MHz, Inova-400 MHz, Inova-500 MHz, Bruker Ascend-400 (400 MHz), or Bruker Ascend-500 (500 MHz) spectrometers. All proton NMR spectra are referenced to either TMS or residual solvent peaks (marked with an asterisk in the SI figures). ATR-FTIR spectra were collected using a Bruker α IR spectrometer with the “ATR Platinum” insert adapter (diamond crystal), which was stored inside a nitrogen-filled VAC Atmospheres glovebox. UV–vis spectra were collected in an Agilent 8154 spectrophotometer, and extinction coefficients were determined using a Beer’s law plot. Chromatographic analyses were carried out on the Thermo Scientific Q-exactive tip GC Orbitrap tandem MS and Thermo Scientific Q-exactive tip LC Orbitrap tandem MS. Elemental combustion analysis (analysis for CHNS) was obtained using a Thermo Scientific FlashEA1112 CHNS analyzer. Compounds were thoroughly dried under vacuum for elemental analysis.

4.3. Crystallographic Methods. Low-temperature X-ray diffraction data for [MnCl₃(PMe₃)₂] (2) (RLacy121), [P(*o*-tol)₃Cl][MnCl₃(OPPh₃)] (3) (RLacy124), [Mn(dppe-O₂)₃][MnCl₄] (4) (Lacy001) [MnCl₂(dmpe)₂] BArF₂₄ (5) (RLacy122), [MnBr₃(PMe₃)₂] (6) (Lacy010), [MnBr₃(P*n*Bu₃)₂] (7) (Lacy009), [MnI₃(PMe₃)₂] (8) (wit_Lacy002), *cis*-[Mn^{II}(OPPh₃)₄(MeCN)₂][I₃]₂·MeCN (9a) (Lacy025), and [Mn^{II}(OPPh₃)₄][I₃]₂ (Lacy031) (9b) were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu K α radiation (λ = 1.54184 Å, for all other structures), from PhotonJet microfocus X-ray sources at 100 K. The diffraction images were processed and scaled using CrysAlisPro software.⁴¹ The structure was solved through intrinsic phasing using SHELXT⁴² and refined against F² on all data by full-matrix least-squares with SHELXL⁴³ following established refinement strategies.⁴⁴ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined by using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). See the SI for more details regarding the disorder in the structure of 7.

4.4. Synthesis of [Mn^{II}Br₂(PMe₃)₂]. Very dry Mn^{II}Br₂ was prepared accordingly. First, MnCO₃ was treated with conc. HBr. The mixture was allowed to evaporate with a gentle heat. The pink residue was pulverized and washed with copious amounts of diethyl ether and then dried under vacuum (≤100 mTorr) with heat (100 °C) for at least 48 h to yield a fine powdery pink solid. MnBr₂, freshly prepared this way, did not contain O–H peaks in the ATR-FTIR spectrum and was used within a few days of preparation since it slowly accumulates moisture upon storage. In a glovebox or on a Schlenk line, Mn^{II}Br₂ (0.520 g, 2.42 mmol) was suspended in 10 mL of dry DCM and treated with 0.25 mL (1 equiv) of Me₃P with stirring. There was no noticeable change. (The mixture became infused with a faint purple color if oxygen impurities were introduced, but this did not affect the outcome of the synthesis.) This treatment with Me₃P was continued, one equivalent at a time, until the solution became fully homogeneous; the final stoichiometry amounted to 1:4 Mn:P, and the total volume of Me₃P was 1 mL. (In a separate, identical reaction,

all four equivalents were added in one portion, which, in this case, it took 20 min for the mixture to become homogeneous.) The mixture was filtered to remove a small amount of undissolved material, and the filtrate was dried to constant weight under vacuum; the mass of the off-white powdered material was determined (0.730 g). ATR-FTIR analysis revealed stretches consistent with coordinated Me₃P. A CH elemental combustion analysis was conducted, and the results were consistent with the adduct formulation of [Mn^{II}Br₂(PMe₃)₂] and thus corresponded to an 85% yield. CH-analysis [calcd (found)] for C₆H₁₈Br₂P₂Mn: %C 19.64 (19.17); %H 4.95 (4.87). ATR-FTIR (cm^{−1}): 2964, 2910, 2805, 1428, 1412, 1299, 1283, 946, 840, 733, 724. The product is sparingly soluble in benzene (≤2 mg/mL); ³¹P{¹H} NMR (C₆H₆, 121 MHz, 298 K): broad peak at δ 13 ppm.

4.5. Synthesis of [Mn^{III}Cl₃(PMe₃)₂] (2) from 1. In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with [Mn^{III}Cl₃(OPPh₃)₂] (1) (0.459 g, 0.640 mmol) and DCM (10 mL) and stirred to afford a dark blue solution. The solution was cooled at −35 °C for 5 min using a glovebox freezer. Trimethylphosphine (0.130 mL, 1.28 mmol) was added to the cooled solution dropwise, and the reaction mixture turned dark red immediately. The resulting mixture was warmed to room temperature, with stirring for 30 min. Then, the dark red solution was filtered to remove a white residue (byproduct identified as [Me₃PCl][Mn^{II}Cl₃(OPMe₃)], 0.021 g, 14%; Figures S37 and S40). Dark red square-shaped crystals were grown via layering the filtrate under petroleum ether (1:1) and stored at −35 °C for ≤20 h (0.089 g, 44% yield). *Note:* Prolonged recrystallizations (more than 24 h) at −35 °C will result in cocrystallization of Ph₃PO and [Mn^{II}Cl₂(OPPh₃)₂]. ¹H NMR (CD₂Cl₂, 500 MHz, ppm): δ −130.69. ³¹P NMR (C₆D₆, 121 MHz, ppm): No signal is observed. Evans method (CD₂Cl₂, 500 MHz, 298 K) μ_{eff} = 4.98 μ_B . ATR-FTIR (cm^{−1}): 2984, 2911, 1403, 1285, 926, 748, 840, 667, 539. UV–vis λ_{max} in DCM [ϵ , M^{−1} cm^{−1}]: 389 (4500), 485 (8875). CH-analysis [calcd (found)] for [Mn^{III}Cl₃(PMe₃)₂] (C₆H₁₈Cl₃P₂Mn): % C 22.99 (22.89); %H 5.79 (5.59).

4.6. Synthesis of [Mn^{III}Cl₃(PMe₃)₂] (2) from [Mn^{III}(acac)₃]. In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with [Mn(acac)₃] (0.200 g, 0.568 mmol) and mesitylene (4 mL) and stirred to afford a dark brown solution at room temperature. Trimethylsilyl chloride (0.216 mL, 1.70 mmol) was added to the solution, with no noticeable color change. After 5 min of stirring, trimethylphosphine (0.116 mL, 1.14 mmol) was added to the reaction mixture. No immediate color change was seen, but a dark red precipitate formed after 18 h of stirring. The reaction mixture was filtered to isolate 2 as a dark red powder (0.154 g, 87%). Characterization data matched that obtained from 1 except contained trace amounts of impurities with weak ν_{CO} (cm^{−1}) stretches at 1655, 1254, and 1223.

4.7. Gram-Scale Synthesis [Mn^{III}Cl₃(PMe₃)₂] (2). **4.7.1. Method A.** *In situ* generation of 2. In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with [Mn^{III}Cl₃(OPPh₃)₂] (1) (0.956 g, 1.33 mmol) and DCM (15 mL) and stirred to afford a dark blue solution. The solution was cooled at −35 °C for 5 min. Trimethylphosphine (0.279 mL, 2.66 mmol) was added dropwise to the cooled solution, and the reaction mixture turned dark red immediately. The resulting mixture was warmed to room temperature, with stirring for 30 min. Then, an aliquot (0.020 mL) from the reaction mixture was transferred into a cuvette with 3.5 mL of DCM, and the UV–vis spectra were collected. From this spectrum, the *in situ* yield of complex 2 was calculated to be 79%.

4.7.2. Method B. *Solid-state isolation of 2.* In a nitrogen-filled glovebox, a round-bottom flask with a stir bar was loaded with [Mn(acac)₃] (1.12 g, 3.18 mmol) and mesitylene (11 mL) and stirred to afford a dark brown solution at room temperature. Trimethylsilyl chloride (1.16 mL, 9 mmol) was added to the solution, and no noticeable color change. After 5 min of stirring, trimethylphosphine (0.659 mL, 8.62 mmol) was added to the reaction mixture. No immediate color change was seen, but a dark red precipitate formed after 18 h of stirring. The reaction mixture was filtered to isolate 2 as a dark red powder (0.896 g, contains 15% Me₃Si(acac), 77%). ¹H NMR (C₆D₆, 500 MHz, ppm) = δ −127.66; peaks from Me₃Si(acac)

impurities (ppm) = 0.12, 2.16. ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. ATR-FTIR (cm^{-1}): 2984, 2911, 1403, 1285, 926, 840, 748, 667, 539; stretches from acac impurities (cm^{-1}) = 1655, 1254, 1223. CH-analysis [calcd (found)] for $2 \cdot \{\text{Me}_3\text{Si}(\text{acac})\}_{0.15}$: %C 25.49 (25.61); %H 6.06 (6.12).

4.8. [(*o*-tolyl) $_3\text{PCl}$][$\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2$] (3). **4.8.1. Method A.** Isolation of a single crystal from **1**. In a nitrogen-filled glovebox, an oven-dried scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) (0.100 g, 0.139 mmol) and DCM (4 mL) and stirred to a dark blue solution. Tri(*o*-tolyl)phosphine (0.018 g, 0.069 mmol) was added, and the solution immediately turned into a colorless, clear reaction mixture. Layering the homogeneous reaction mixture with pentane (1:1) at room temperature led to the formation of crystals containing a mixture of $[\text{MnCl}_2(\text{OPPh}_3)_2]$ and **3** suitable for diffraction. ^{31}P NMR of the reaction mixture containing **3** (CH_2Cl_2 , 500 MHz, 298 K) = δ 70.74 ppm. Note: The difficulty in isolating **3** from the other reaction products prevented us from obtaining any other characterization data from this reaction.

4.8.2. Method B. Independent synthesis from the Mn(II) starting material. In a nitrogen-filled glovebox, an oven-dried scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{II}}\text{Cl}_2(\text{OPPh}_3)_2]$ (0.166 g, 0.243 mmol) and DCM (4 mL) and stirred to a colorless solution. Tri(*o*-tolyl)phosphine dichloride (0.093 g, 0.247 mmol) was added, and the solution was stirred to give a pale yellow homogeneous solution for 2 h. The reaction mixture was reduced to dryness using a vacuum, resulting in a pale yellow, sticky residue. The residue was stirred with benzene (15 mL) to remove excess triphenylphosphine oxide for 30 min, followed by decantation. **3** was isolated as a white powder (0.145 g, 76%). ^1H NMR (CD_2Cl_2 , 500 MHz, 298 K) = δ 8.71, 2.31. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz, ppm): δ 71.20. ATR-FTIR (cm^{-1}): 3054, 2983, 2925, 1591, 1567, 1484, 1471, 1452, 1435, 1384, 1338, 1311, 1285, 1270, 1168, 1138, 1118, 1095, 1079, 1050, 1029, 997, 809, 754, 720, 694, 671, 593, 568, 539, 519, 484, 471, 446. CH-analysis [calcd (found)] for $[(\text{o-tolyl})_3\text{PCl}][\text{Mn}^{\text{II}}\text{Cl}_3(\text{OPPh}_3)_2] \cdot 2\text{C}_6\text{H}_6$ ($\text{C}_{51}\text{H}_{48}\text{Cl}_4\text{P}_2\text{MnO}$): %C 65.47 (65.81); %H 5.17 (5.04).

4.9. Synthesis of [(dppe-*O*) $_3\text{Mn}^{\text{II}}$][$\text{Mn}^{\text{II}}\text{Cl}_4$] (4). In a nitrogen-filled glovebox, an oven-dried scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) (1.20 g, 1.67 mol) and DCM (7 mL) and stirred to afford a dark blue solution. 1,2-bis-(diphenylphosphino)ethane (dppe) (0.173 g, 0.434 mmol) was added, and the mixture was stirred for 7 h. The resulting white precipitate was filtered, washed with DCM, and dried under a vacuum. Slow evaporation of concentrated methanolic solution of the white powder at room temperature gave crystals of **4** (0.257 g, 20%). ^1H NMR (CD_3OD , 500 MHz, 298 K): δ 7.68, 7.17, 7.02, 3.15. ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. CH-analysis [calcd (found)] for $[(\text{dppe-}O)_3\text{Mn}^{\text{II}}][\text{Mn}^{\text{II}}\text{Cl}_4] \cdot (\text{C}_{24}\text{H}_{54}\text{Br}_3\text{P}_2\text{Mn})$: %C 60.72 (61.12); %H 4.70 (4.91).

4.10. Synthesis of $[\text{Mn}^{\text{III}}(\text{dmpe})_2\text{Cl}_2][\text{BarF}_{24}]$ (5). In a nitrogen-filled glovebox, an oven-dried scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) (0.787 g, 1.10 mmol) and NaBarF_{24} (0.972 g, 1.10 mmol). THF (15 mL) was added and stirred thoroughly, resulting in a dark blue solution (there was no indication of NaCl formation). To this, dmpe (0.365 mL, 2.20 mmol) was added, and the color of the reaction mixture turned bright orange immediately. The solution was stirred for 30 min and then filtered to remove a white solid (NaCl). The bright orange filtrate was reduced to dryness using vacuum, resulting in an oily orange residue. The residue was stirred with benzene (20 mL) for 30 min, followed by filtration. The resulting sticky orange material was stirred with petroleum ether (10 mL) for 30 min and filtered to isolate $[\text{Mn}^{\text{III}}(\text{dmpe})_2\text{Cl}_2][\text{BarF}_{24}]$ (**5**) as a bright orange powder (0.734 g, 52%). Crystals suitable for diffraction were grown by the diffusion of petroleum ether (1:1) into a solution of **5** in THF (0.150 g, 18%). ^1H NMR (acetonitrile- d_3 , 500 MHz, ppm): δ -44.57, -38.11. ^{19}F NMR (acetonitrile- d_3 , 472 MHz, ppm) = δ -63.3. ^{11}B NMR (acetonitrile- d_3 , 200 MHz, ppm) = δ -6.6. ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. Evans method (acetone- d_6 , 500 MHz, 298 K) μ_{eff} = 2.73 μ_{B} . ATR-FTIR (cm^{-1}): 3093, 2986, 2914, 1610, 1421, 1353, 1270, 1110, 928, 883, 838. UV-vis λ_{max} in THF

[nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 353 (4621), 413 (3129). CH-analysis [calcd (found)] for $[\text{Mn}^{\text{III}}(\text{dmpe})_2\text{Cl}_2][\text{BarF}_{24}] \cdot (\text{C}_6\text{H}_{18}\text{Cl}_3\text{P}_2\text{Mn})$: %C 39.85 (40.99); %H 3.39 (3.44).

4.11. Synthesis of $[\text{Mn}^{\text{III}}(\text{dmpe})_2\text{Cl}_2][\text{PF}_6]$. In a nitrogen-filled glovebox, an oven-dried scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) (0.251 g, 0.349 mmol) and KPF_6 (0.064 g, 0.349 mmol). DCM (15 mL) was added and stirred thoroughly, resulting in a dark blue solution (there was no indication of KCl formation). To this, dmpe (0.117 mL, 0.698 mmol) was added, and the color of the reaction mixture turned bright orange immediately. The solution was stirred for 30 min and then filtered to remove a white solid (KCl). The bright orange filtrate was reduced to dryness using vacuum, resulting in an oily orange residue. The residue was stirred with benzene (20 mL) for 30 min, followed by filtration. The resulting sticky orange material was stirred with petroleum ether (10 mL) for 30 min and filtered to isolate $[\text{Mn}^{\text{III}}(\text{dmpe})_2\text{Cl}_2][\text{PF}_6]$ as a bright orange powder (0.138 g, 70%). Crystalline solids were grown by layering DCM solution of the complex with pentane (1:1) (0.105 g, 53%). ^1H NMR (CD_2Cl_2 , 500 MHz, ppm): δ -44.84, -38.38. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz, ppm): δ -145.35. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 472 MHz, ppm) = -73.48. ATR-FTIR (cm^{-1}): 2976, 2914, 1610, 1421, 1122, 1087, 933, 898, 877, 827, 729, 714, 648, 556. CH-analysis [calcd (found)] for $[\text{Mn}^{\text{III}}(\text{dmpe})_2\text{Cl}_2][\text{PF}_6] \cdot (\text{THF})_{0.2}$ ($\text{C}_{12}\text{H}_{32}\text{Cl}_2\text{F}_6\text{MnP}_3(\text{C}_4\text{H}_8\text{O})_{0.2}$): %C 26.26 (26.69); %H 5.78 (5.72).

4.12. Synthesis of $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PMe}_3)_2]$ (6). **4.12.1. Method A.** Solid-state isolation of **6**. In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with Mn_{12} (0.141 g, 0.0684 mmol) and mesitylene (10 mL) and stirred into a dark brown heterogeneous solution. The solution was cooled at -35 °C for 5 min. Trimethylsilyl bromide (0.325 mL, 2.46 mmol) was added to the cooled solution dropwise, and the mixture was stirred. Trimethylphosphine (0.167 mL, 1.64 mmol) was added to the cold reaction mixture, and the color immediately changed to deep purple. The resulting mixture was warmed to room temperature, with stirring for 2 h. Then, the dark purple solution was filtered, and the filtrate was collected and concentrated to 3 mL. Dark purple crystals were grown via layering the purple solution with an equal volume of pentane at -35 °C and gave crystals in 5 days (0.032 g, 9% yield). ^1H NMR (toluene- d_8 , 500 MHz, ppm) = No peak seen in the spectrum (scan range = +400 to -400 ppm). ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. Evans method (toluene- d_8 , 500 MHz, 298 K) μ_{eff} = 5.01 μ_{B} . ATR-FTIR (cm^{-1}): 2980, 2908, 1402, 1283, 926, 745, 665. UV-vis λ_{max} in toluene [nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 407 (4595), 517 (6980). CH-analysis [calcd (found)] for $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PMe}_3)_2] \cdot (\text{C}_6\text{H}_{18}\text{Br}_3\text{MnP}_2)$: %C 18.06 (17.72); %H 4.22 (3.87). Note: **6** can also be synthesized by reacting **1** with 2 equiv PMe_3 , followed by Me_3SiBr , as described for **8**. However, the isolation was difficult due to cocrystallization of Mn(II) byproducts.

4.12.2. Method B. In situ preparation of 6. (i) In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) (0.205 g, 0.285 mmol) and toluene (2 mL) and stirred to afford a dark blue heterogeneous solution. The solution was cooled at -35 °C for 5 min. Trimethylphosphine (0.569 mL, 0.570 mmol) was added dropwise to the cooled solution, and the reaction mixture turned dark red immediately. The resulting mixture was warmed to room temperature, with stirring for 5 min. Me_3SiBr (0.042 mL, 0.855 mmol) was added to this solution, leading to an immediate color change to purple, and stirred for 20 min. Then, an aliquot (0.050 mL) from the reaction mixture was transferred into a cuvette with 3.5 mL of toluene, and UV-vis spectra were collected. From this data, the *in situ* yield of complex **6** was calculated to be 33%. (ii) In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with Mn_{12} (0.116 g, 0.056 mmol) and toluene (2.5 mL) and stirred to a dark brown solution. The solution was cooled at -35 °C for 5 min. Trimethylsilyl bromide (0.268 mL, 2.02 mmol) was added to the cooled solution dropwise, and the mixture was stirred. Trimethylphosphine (0.140 mL, 1.34 mmol) was added to the cold reaction mixture, and the color immediately changed to deep purple. The resulting mixture was warmed to room temperature, with stirring for 2 h. Then, an aliquot (0.050 mL) from the reaction

mixture was transferred into a cuvette with 3.5 mL of toluene, and UV–vis spectra were collected. From this data, the *in situ* yield of complex **6** was calculated to be 11%. It is also possible to treat a DCM solution of $[\text{Mn}^{\text{II}}\text{Br}_2(\text{PMe}_3)_2]$ (0.98 mM) with air, which affords **6** in 43% yield, according to UV–vis spectroscopy.

4.13. Synthesis of $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PnBu}_3)_2]$ (7**).** In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with Mn_{12} (0.119 g, 0.057 mmol) and mesitylene (10 mL) and stirred into a dark brown heterogeneous solution. The solution was cooled to -35°C . Trimethylsilyl bromide (0.274 mL, 2.05 mmol) was added dropwise to the solution, followed by the addition of tri(*n*-butyl)phosphine (0.352 mL, 1.38 mmol). The reaction mixture turned deep blue immediately. The resulting mixture was warmed to room temperature with stirring for 2 h. Then, the deep blue solution was filtered, and the filtrate was concentrated to 3 mL and stored at -35°C . Dark blue crystals were grown in 5 d (0.035 mg, 8% yield). The crystals were thoroughly washed with cold (-35°C) pentane and dried before use. Note: The X-ray crystal structure contained disordered interstitial mesitylene molecules (see SI). ^1H NMR (benzene- d_6 , 500 MHz, ppm) = broad peaks at δ - 0.20, 1.14 for 7; δ 2.27 (s, 3H, mes- CH_3), 6.80 (s, 3H, mes- H). ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. Evans method (toluene- d_8 , 500 MHz, 298 K) $\mu_{\text{eff}} = 4.95 \mu\text{B}$. ATR-FTIR (cm^{-1}): 2957, 2928, 2871, 1606, 1464, 1384, 1379, 1307, 1281, 1215, 1204, 1118, 1091, 1058, 1009, 968, 900, 838, 774, 747, 724, 689. UV–vis λ_{max} in mesitylene [m , $\text{M}^{-1} \text{cm}^{-1}$]: 417 (3360), 573 (5576). CH-analysis [calcd (found)] for $[\text{Mn}^{\text{III}}\text{Br}_3(\text{PnBu}_3)_2]$ ($\text{C}_{24}\text{H}_{54}\text{Br}_3\text{P}_2\text{Mn}$): %C 41.22 (40.6); %H 7.78 (7.62); extensive washing of crystals with pentane followed by drying for CH-analysis led to the loss of mesitylene molecules from the crystal lattice.

4.14. Synthesis of $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2]$ (8**).** In a nitrogen-filled glovebox, a scintillation vial with a stir bar was loaded with $[\text{Mn}^{\text{III}}\text{Cl}_3(\text{OPPh}_3)_2]$ (**1**) (0.100 mg, 0.139 mmol) and toluene (10 mL) and stirred to a dark blue heterogeneous solution. The solution was cooled at -35°C . Trimethylphosphine (0.029 mL, 0.28 mmol) was added to the cold reaction mixture, and the color immediately changed to dark red, which indicated the formation of **2**. Trimethylsilyl iodide (0.061 mL, 0.418 mmol) was added dropwise to the *in situ* formed **2**, and a deep green solution was formed (≈ 300 s). The resulting mixture was warmed to room temperature, with stirring for 30 min. Then, the dark green solution was filtered, and the filtrate was reduced to dryness *in vacuo*, giving a deep green powder that corresponded to **8** (0.027 g, 33% yield). Dark green crystals were grown in 8 days via layering the above-mentioned deep green solution with pentane (1:1) at -35°C . ^1H NMR (benzene- d_6 , 500 MHz, 298 K): δ -108.52 ppm. ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. Evans method (toluene- d_8 , 500 MHz, 298 K) $\mu_{\text{eff}} = 5.10 \mu\text{B}$. UV–vis λ_{max} in toluene [m , $\text{M}^{-1} \text{cm}^{-1}$]: 330 (3358), 457 (6229), 578 (11026). ATR-FTIR (cm^{-1}): 2973, 2901, 1407, 1284, 934, 739, 667, 539. CH-analysis [calcd (found)] for $[\text{Mn}^{\text{III}}\text{I}_3(\text{PMe}_3)_2] \cdot 0.2\text{pentane}$ ($\text{C}_{72}\text{H}_{204}\text{I}_3\text{MnP}_2$): %C 13.96 (14.01); %H 3.41 (2.78). Using the same procedure as described for **6** (Method A) except using Me_3SiI , **8** was isolated in 31% yield.

4.15. Synthesis of $[\text{Mn}^{\text{II}}\text{Br}_2(\text{OPPh}_3)_2]$. Mn_{12} (0.050 g, 0.024 mmol, 1 equiv) was stirred with 5 mL of MeCN in a vial to give an intense coffee-brown mixture. Trimethylsilyl bromide (0.115 mL, 0.874 mmol) was added dropwise via a syringe under vigorous stirring to give a deep orange solution. Ph_3PO (0.162 g, 0.583 mmol) was added to the reaction mixture, causing immediate color change to golden yellow and the formation of a pale green solid. After 20 min of stirring at room temperature, the reaction mixture was filtered and the solid was washed with MeCN (2×1 mL) and Et_2O and then dried under vacuum to yield $[\text{Mn}^{\text{II}}\text{Br}_2(\text{OPPh}_3)_2]$ as a pale green solid. The filtrate of the reaction mixture was reduced to 2 mL under a vacuum and stored at room temperature overnight to produce pale green crystals of $[\text{Mn}^{\text{II}}\text{Br}_2(\text{OPPh}_3)_2]$. Combined yield of $[\text{Mn}^{\text{II}}\text{Br}_2(\text{OPPh}_3)_2]$: 0.121 g (54%). ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. The IR spectrum and triboluminescence matched the literature.^{21,45} A similar procedure but starting from $\text{Mn}(\text{OAc})_2$ (0.201 g, 1.16 mmol), KMnO_4 (0.046 g, 0.29 mmol), and

Ph_3PO (0.643 g, 2.31 mmol) in 10 mL of MeCN afforded a brown solution to which Me_3SiBr (610 μL , 4.62 mmol) was added, resulting in the rapid formation of an orange solution and pale green precipitate, $[\text{Mn}^{\text{II}}\text{Br}_2(\text{OPPh}_3)_2]$. Fractional distillation of the filtrate and the subsequent UV–vis spectrum revealed the presence of Br_2 (Figure S41).

4.16. Synthesis of $[\text{Mn}^{\text{II}}\text{I}_2(\text{OPPh}_3)_2]$ and **9 from Mn_{12} and Me_3SiI .** In a 25 mL Schlenk flask equipped with a stir bar, Mn_{12} (0.050 g, 0.024 mmol) was stirred in 8 mL of MeCN under argon to produce a coffee-brown mixture. Trimethylsilyl iodide (0.124 mL, 0.874 mmol) was added dropwise via a syringe under vigorous stirring to give a deep red solution. Ph_3PO (0.162 mg, 0.583 mmol) was added to the reaction mixture under a flow of argon. After 20 min of stirring at room temperature, all volatiles were removed under vacuum to obtain a red sticky oil. The red sticky oil was dissolved in DCM and layered under hexane (open to air) to give deep red crystals of **9b** and light green crystals of $[\text{Mn}^{\text{II}}\text{I}_2(\text{OPPh}_3)_2]$ overnight at room temperature (0.073 g, 29%); the IR spectrum and triboluminescence of the green crystals matched previously reported values of the four-coordinate compound $[\text{Mn}^{\text{II}}\text{I}_2(\text{OPPh}_3)_2]$.^{21,45} The crystals of **9b** were washed with hexane, separated manually, and dried under a vacuum. X-ray crystal structure of **9b** was shown to be $[\text{Mn}^{\text{II}}(\text{OPPh}_3)_4][\text{I}_3]_2$ (Figure S50). Yield of $[\text{Mn}^{\text{II}}(\text{OPPh}_3)_4][\text{I}_3]_2$ **9b**: 0.063 g (22%). ^{31}P NMR (C_6D_6 , 121 MHz, ppm): No signal is observed. ATR-FTIR (cm^{-1}) of $[\text{Mn}^{\text{II}}(\text{OPPh}_3)_4][\text{I}_3]_2$: 3050, 1588, 1483, 1436, 1335, 1310, 1186, 1160, 1133, 1118, 1077, 1067, 1025, 995, 922, 846, 758, 746, 723, 688, 536. CH-analysis (calcd) $[\text{Mn}(\text{OPPh}_3)_4][\text{I}_3]_2$ ($\text{C}_{72}\text{H}_{60}\text{I}_6\text{O}_{24}\text{P}_4\text{Mn}$): %C 44.82 (44.39); %H 3.13 (3.06).

Alternatively, the MeCN reaction mixture was reduced to half volume under vacuum and transferred (open to air) into a vial and left undisturbed overnight. A mixture of deep red crystals of **9a** and light green crystals of $[\text{Mn}^{\text{II}}\text{I}_2(\text{OPPh}_3)_2]$ formed. The crystals were washed with minimal amounts of 1:1 MeCN: Et_2O , separated manually, and an X-ray crystal structure of **9a** revealed it to be *cis*- $[\{\text{Mn}^{\text{II}}(\text{OPPh}_3)_4(\text{MeCN})_2\}][\text{I}_3]_2 \cdot \text{MeCN}$ (Figure S49). These crystals were thoroughly dried under vacuum for 2 days to remove the MeCN ligands. This compound was not further characterized. Note: if fresh Me_3SiI without a brown-reddish discoloration is used, **9** is not obtained, and $[\text{Mn}^{\text{II}}\text{I}_2(\text{OPPh}_3)_2]$ is obtained in greater proportions (90 mg, 36%).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c01820>.

DFT coordinates (XYZ)

Spectroscopic data for novel compounds (PDF)

Accession Codes

CCDC 2346638–2346645 and 2348212 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, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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