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Communication

Synthesis of a Bench-Stable Manganese(III) Chloride Compound: Coordination Chemistry and Alkene Dichlorination

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ABSTRACT: The complex $[MnCl_3(OPPh_3)_2]$ (**1**) is a bench-stable and easily prepared source of $MnCl_3$. It is prepared by treating acetonitrile solvated $MnCl_3$ (**2**) with Ph_3PO and collecting the resulting blue precipitate. **1** is useful in coordination reactions by virtue of the labile Ph_3PO ligands, and this is demonstrated through the synthesis of $\{Tpm^*\}MnCl_3$ (**3**). In addition, methodologies in synthesis that rely on difficult or cumbersome to prepare solutions of reactive $MnCl_3$ can be accomplished using **1** instead. This is demonstrated through alkene dichlorinations in a wide range of solvents, open to air, and with good substrate scope. Light-accelerated halogenation and radical sensitive experiments support a radical mechanism involving stepwise Cl-atom transfer(s) from **1**.

INTRODUCTION

In this report, we detail our investigation of the chemical properties of the complex $[MnCl_3(OPPh_3)_2]$ (**1**), a bench-stable blue compound easily prepared in gram quantities open to air (Scheme 1). After its first preparation by a cumbersome low-temperature route in 1976,[1] **1** was lost to obscurity. Now, nearly half a century later, our serendipitous rediscovery led us to the current study. The importance of **1** is found in the simple fact that it enables access to $MnCl_3$, which itself is not thermally stable.[2,3] The lack of Mn(III) starting materials (Chart 1) is unfortunate since it is synthetically useful in a variety of applications including alkene dichlorination,[4] and the Mn^{3+} ion is biologically important.[5]

Scheme 1. Preparative Routes to $MnCl_3(OPPh_3)_2$ (1)

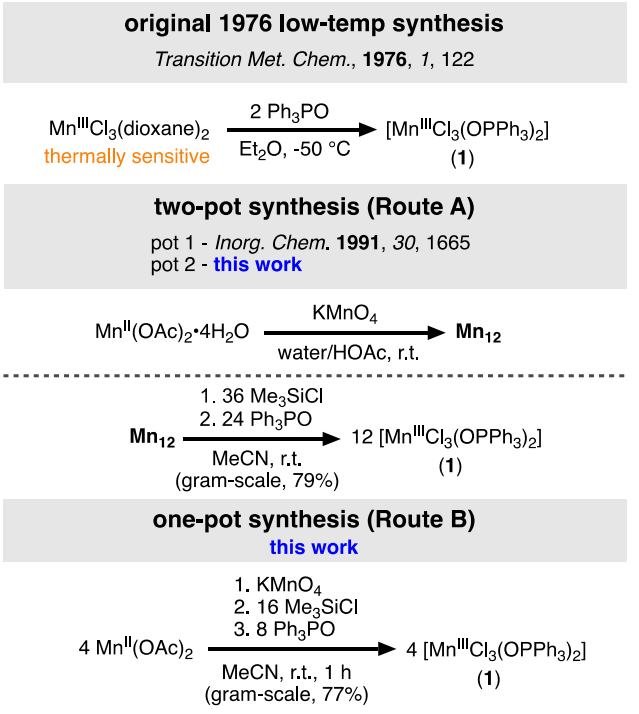

Chart 1. Commercially Available Mn(III) Compounds

molecular precursors	oxides	complexes
• $Mn(acac)_3$	• Mn_2O_3	• Jacobsen's catalyst
• $Mn(acetate)_3{\cdot}2H_2O$	• Mn_3O_4	• tetrapheynylporphyrin Mn(III)
• MnF_3		

new molecular precursor: this work — $[Mn^{III}Cl_3(OPPh_3)_2]$ (**1**)

The challenge with using "$MnCl_3$" is that solutions need to be prepared *and* used immediately and the speciation is often ill-defined precluding precise stoichiometry. Preparation of "$MnCl_3$" is commonly carried out by reduction of MnO_2 or permanganate with gaseous HCl at low temperature, and the compounds prepared this way must be manipulated and stored below −30 °C.[1,6−8] An alternative and more practical preparation of "$MnCl_3$" was developed by Christou and co-workers.[9] Specifically, $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]{\cdot}2HOAc{\cdot}4H_2O$ (**Mn_{12}**) can be treated with Me_3SiCl to afford deep purple solutions of nominally MeCN solvated $MnCl_3$ (**2**).[9] Albeit, **2** is also thermally unstable ($t_{1/2} \approx 1$ h, air and moisture free), is not isolable or separable from reaction byproducts and by virtue of these has imprecise stoichiometry. **2** is nonetheless synthetically useful and has been used to prepare coordination

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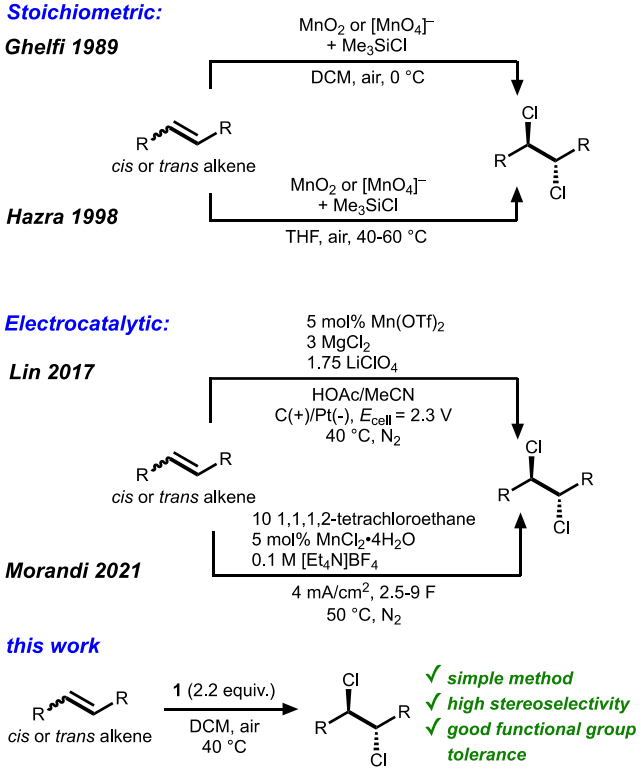
compounds such as $[MnCl_3(bipy)]_n$ and $[Mn^{VII}Cl(NtBu)_3]$.[9,10] Likewise, we found (*vide infra*) that **2** is useful in preparing **1**, which we envisioned to be more useful in chemical synthesis of novel Mn(III) complexes because (*i*) the stoichiometry of reagents can be precisely controlled and (*ii*) labile Ph_3PO ligands are easily exchanged through ligand substitution.

Furthermore, use of **1** affords access to a much wider range of conditions that can be employed in dichlorination reactions used in previous methodologies (Scheme 2). For example,

Scheme 2. Alkene Dichlorination Methods with Mn



"$MnCl_3$" prepared from Me_3SiCl and Mn(II) + high-valent Mn (e.g., MnO_2 or permanganate salts) has been used for alkene dichlorination.[11] However, these methods require low-temperature *in situ* preparation of the ill-defined $MnCl_3$ species, which needs to be used immediately. Also, electrochemical means of generating $MnCl_3$ as a catalytic reagent in dichlorination has been accomplished,[12−14] but such methodologies are not accessible for many contemporary synthetic laboratories and often employ rigorous air and moisture free conditions and/or require acid.

Hence, in this report, we disclose a convenient synthesis of **1** (Scheme 1) and demonstrate its usefulness toward preparation of $MnCl_3$ complexes through a ligand substitution reaction to form {Tpm*}$MnCl_3$ (**3**) (Tpm* = tris(3,5-dimethyl-1-pyrazolyl)methane). We demonstrate the synthetic utility of **1** in alkene dichlorination reactions using a variety of solvent conditions and substrates including those with acid labile functional groups. The reaction appears to be light accelerated, indicating that LMCT charge transfer mediated reactivity avenues are possible.

Synthesis and Characterization of 1. **1** was originally prepared by treating Ph_3PO with $MnCl_3$(1−4-dioxane), the latter of which was prepared at −50 °C and isolated and manipulated at −30 °C, all under air-free conditions (Scheme 1).[1] We have instead prepared **1** by treating **2** with Ph_3PO and isolating the resulting blue precipitate (Scheme 1, route A). All of the steps leading to the isolation of **1** can be conducted open to air with a reagent grade solvent, and in our experience **1** is indefinitely stable under ambient conditions in transparent glass vials. Additionally, a convenient one-pot synthesis of **1** can be accomplished by combining $Mn(OAc)_2$, $KMnO_4$, and Me_3SiCl in a 4:1:16 ratio and treating the resulting mixture with eight equivalents of Ph_3PO (Scheme 1, route B). $MnCl_2$ and/or $SiCl_4$ can be used instead of $Mn(OAc)_2$ and/or Me_3SiCl, respectively, but with diminished yields. Samples of **1** prepared with the improper stoichiometry of reagents leads to contamination of **1** with the known compound $[Mn^{II}Cl_2(OPPh_3)_2]$ (**4**).[15]

Although **1** is a known compound,[1] the only characterization available is CHN analysis and solid-state magnetic moment. Thus, herein we provide the full characterization details. Crystals of **1** suitable for X-ray diffraction were obtained from the blue/green filtrate after synthesis of **1** via route A open to air. XRD analysis revealed square pyramidal geometry (τ_5 = 0.09) with two Ph_3PO groups occupying nonequivalent positions (Figure 1).[16] Since Mn(III) chloride structures

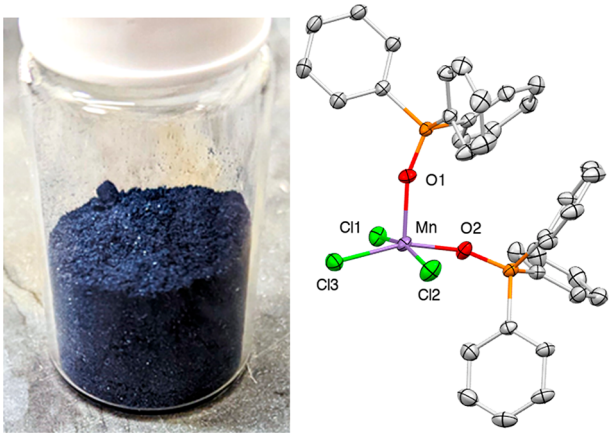


Figure 1. (Left) Air-stable crystalline **1** on the bench. (Right) Molecular structure (ellipsoids 50%) of **1** determined with XRD (H atoms not shown for clarity). Selected bond distances (Å) and angles (deg): Mn−Cl1 = 2.274(1); Mn−Cl2 = 2.263(1); Mn−Cl3 = 2.244(1); Mn−O1 = 2.051(3); Mn−O2 = 1.959(3); Cl3−Mn−O2 = 159.32(9); Cl1−Mn−Cl2 = 164.91(4); O1−Mn−O2 = 97.8(1).

often adopt 6-coordinate octahedral geometries,[17,18] the structure of **1** is rare. **1** dissolves in most polar organic solvents to form intensely colored solutions. Despite the air-stability of **1** in the solid state, solutions are not air stable and lose their color upon standing open to air (SI). Evans-method calculations in DCM are consistent with a high spin Mn(III) center (μ_{eff} = 4.83 μ_B) in the solution-state. UV−vis spectra of **1** in different solvents indicate the major transitions are LMCT, a property that can be leveraged for light-induced chlorine atom transfer. The difference in color of **1** in THF (purple) or MeOH (pink) compared to MeCN and DCM (blue) may indicate changes in coordination.

Applications in Coordination Chemistry. The Ph_3PO ligands in **1** are labile toward ligand substitution (Scheme 3). For this report, we demonstrate this by preparation of the green complex {Tpm*}$MnCl_3$ (**3**), which can be prepared directly from **1** or **2**. X-ray crystallography of **3** reveals its six-

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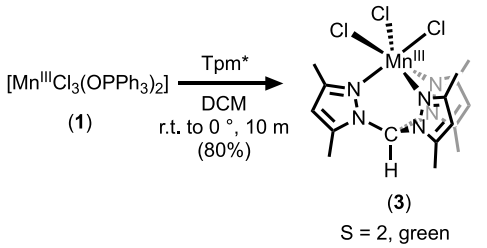
Scheme 3. Use of 1 in Coordination Reactions



coordinate coordination geometry with one elongated Mn−Cl distance (2.45 Å) indicative of the Jahn−Teller effect predicted for an $S = 2$ complex in a pseudo-octahedral ligand field (Figure 2).

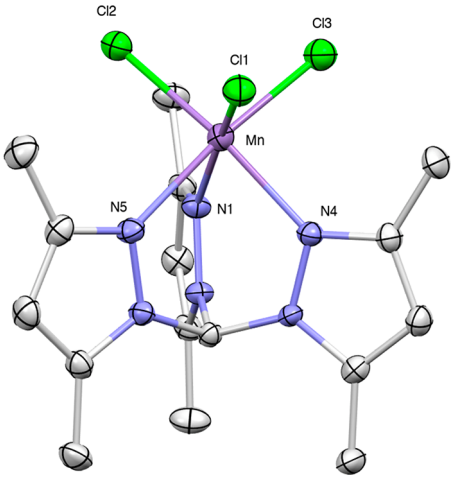
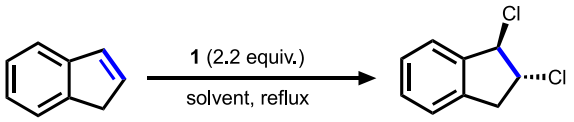


Figure 2. Molecular structure (ellipsoids 50%) of **3** determined with XRD (H atoms and two MeCN solvent molecules not shown). Selected bond distances (Å) and angles (deg): Mn−Cl1 = 2.4510(7); Mn−Cl2 = 2.2465(7); Mn−Cl3 = 2.2748(8); Mn−N1 = 2.321(2); Mn−N4 = 2.101(2); Mn−N5 = 2.138(2); Cl1−Mn−N1 = 168.76(5); Cl2−Mn−N4 = 171.92(6); Cl3−Mn−N5 = 168.70(6).

To our knowledge, **3** is the only $MnCl_3$ complex with a facially coordinating ligand characterized by X-ray crystallography, and it is the first ever prepared using a $MnCl_3$ starting material. The only other comparable compounds are [(tacn)-$MnCl_3$], which was prepared by HCl induced condensation of a multinuclear Mn(III)-oxide complex,[19] and homoleptic "bis" complexes like $[Tp_2Mn]^+$.[20,21] There is significant interest in the *N,N,N/O* facial coordination of Mn(III) ions because of its relevance in a variety of nonheme metalloproteins.[5,22] The lack of compounds like **3** in the literature serve to indicate the difficulty in coordination chemistry with reactive Mn(III). Indeed, **3** exhibits thermal instability.

Applications in Alkene Dichlorination. We also wished to demonstrate the applicability of **1** in alkene dichlorination methodology, which may have advantages compared to other methods (Scheme 2). Optimization of dichlorination with **1** was evaluated using indene as the model substrate (Table 1). Use of less than 2 equiv of **1** resulted in incomplete conversions (e.g., 1 equiv resulted in ∼50% conversion). The reaction can be performed in essentially any common laboratory solvent except water; water caused precipitation of insoluble brown material. The impact of solvent on reaction time is tentatively attributed to solubility (e.g., hexane vs

Table 1. Reaction Optimization[a]



solvent	time	yield[b]
polar protic		
MeOH	5 m	85[c]
polar aprotic		
chloroform	5 m	93
DCM[d]	20 m	99
DCM[e]	20 m	99
DCE	25 m	95
MeCN	120 m	77[c]
THF	150 m	77[c]
ethyl acetate	120 m	95
hydrocarbons		
toluene	20 m	93
benzene	120 m	96
hexanes	22 h	83

[a]Reactions were deemed complete when blue color no longer persisted. [b]Yields determined with ^1H NMR. [c]Isolated yields. [d]Reaction at r.t. required 180 m for same conversion. [e]ACS grade, open to air.

DCM) or a change in composition due to solvent coordination (e.g., THF and MeCN vs DCM). The best results were obtained in DCM or $CHCl_3$.

The scope of the reaction revealed good chemoselectivity, high stereoselectivity, and broad functional group tolerance in appreciable yields (Table 2). 1-Phenylcyclohexene yields a high d.r. for the *anti*-dichloride **7** (>19:1), which is an improvement over Mn-electrocatalysis with a d.r. of 8:1 for the same substrate.[12] Internal and terminal alkenes were successfully chlorinated (**8**−**10**). Allyl ether and oxidatively sensitive functional groups are also tolerated (**11**−**15**). Cyclohexenone furnished the α-halogenated cyclohexenone **16** as the major isolated product. We emphasize that an important facet of **1** is its ability to be accessed and used *without* acid coadditives that are often used in the generation of "$MnCl_3$" methodologies.[11,12] This enabled us to chlorinate silyl protected alcohol alkene **17** without a loss of a silyl functional group and was accomplished on the gram scale. Additionally, substrates **18**−**20** having *N*-containing protecting groups were tolerated. For substrates that did not go do completion in refluxing DCM, $CHCl_3$ and 3 equiv of **1** were used to take the reaction to completion (e.g., **11**, **19**, **20**).

Some shortcomings of **1** are noted. Some reducing functional groups including thioethers, dialkyl sulfone, trialkyl amines, and phosphines are problematic, causing solutions of **1** to decolorize rapidly (≤1 m). The deleterious side reaction(s) is slow enough with thioether **14** that we were successful at isolating the product in ∼20% yields, although outcomes varied. Finally, it appears that **1** can engage in aryl CH halogenation. This was systematically confirmed for naphthalene (Table 2), but it was not observed for any of the other aryl containing substrates used in this study and did not appear to affect yields of aryl containing substrates.

The first report that described **1** indicated sensitivity in daylight.[1] Although we have not observed such sensitivity,[23] there are many examples of light-induced halogen atom extrusion from high-valent metal centers through LMCT

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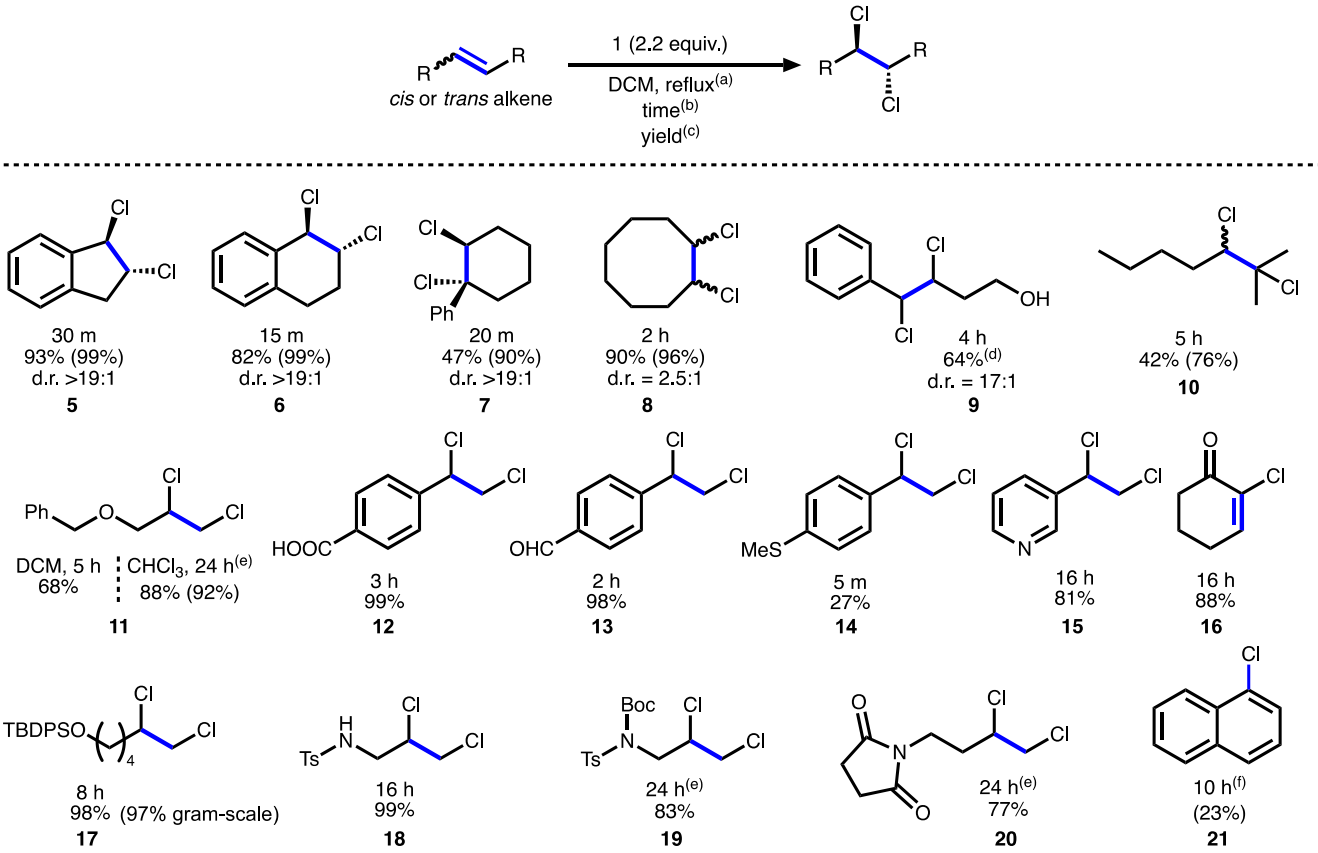
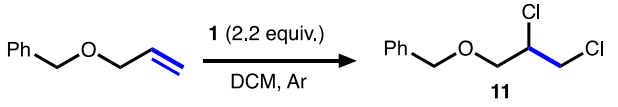
Table 2. Use of 1 in Alkene Dichlorination



[a]Reactions were set up open to air and blanketed with Ar without purging. [b]Reaction time was taken when blue color of 1 was gone. [c]Isolated yields (yields in parentheses determined by ^{1}H NMR). [d]From *trans*-alkene. [e]3 equiv. **1** and $CHCl_3$. [f]Yield determined using GC.

excitation.[24,25] Therefore, we tested light-accelerated chlorine-atom transfer for ((allyloxy)methyl)benzene. The parent conditions of refluxing DCM afforded 68% conversion after 5 h (Table 2, Table 3, entry 5). Broadband irradiation in DCM

Table 3. Light-Accelerated Dichlorination

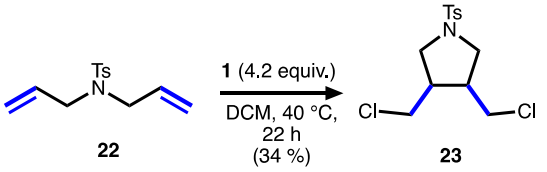


entry	conditions	time	yield (%)
1	r.t., >345 nm	60 m	60
2	r.t., >420 nm	60 m	60
3	r.t., >515 nm	60 m	46
4	r.t., dark	60 m	16
5	40 °C, dark	360 m	68

resulted in a dramatic increase in conversion rate compared to the dark control (entries 1−4). Chlorination of naphthalene is also enhanced by light to afford 1-chloronaphthalene (**21**). For example, the same conversion shown in Table 2 can be afforded in just 1 h using >345 nm.

To test for radical mechanisms, we evaluated *N*-tosyl diallylamine substrate **22**, which yielded cyclized product **23** (Scheme 4). This, and the need for two equivalents of **1** in dichlorinations, serves as strong evidence to support a Mn−Cl atom transfer radical mechanism, essentially the stoichiometric analogue to the one proposed by Lin and co-workers.[12] **4** is the

Scheme 4. Evidence For Radical Mechanism



Mn-containing byproduct of the dichlorination reactions in further support of this hypothesis. As such, it follows that inclusion of **4** may act as an inhibitor when Cl-atom transfer is reversible.[24b] We confirmed this for light accelerated CH chlorination of naphthalene by inclusion of equimolar **1** and **4**. This experiment resulted in a 50% reduction in product yield. To summarize, these observations support a radical mechanism involving stepwise Cl-atom transfer(s) from **1**, as opposed to nucleophilic chloride or electrophilic chloronium transfer (SI).[4,26]

To conclude, this report demonstrates that **1** is a convenient source of "$MnCl_3$" toward new coordination compounds and chlorination reactions. In regard to the former, we used **1** to prepare a unique $MnCl_3$ complex with relevance to *fac*-3-histidine coordination of Mn^{III} in biology. In regard to the latter, the halogen transfer with **1** is exceptionally convenient. The improved d.r. in substrates like 1-phenylcyclohexene over previous methods indicates the role of the ligand. The chlorine atom transfer step is light-accelerated, although further

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optimization is needed to improve the efficiency of desirable light-induced process(es).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08509.

Additional figures, experimental details, and NMR, FTIR, UV−vis spectra, and reaction data (PDF)

Accession Codes

CCDC 2196122 and 2196124−2196125 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 the following competing financial interest(s): A provisional patent application has been filed.

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