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J Am Chem Soc. Author manuscript; available in PMC 2024 December 16.

Published in final edited form as:

J Am Chem Soc. 2024 May 01; 146(17): 11616–11621. doi:10.1021/jacs.4c03411.

Manganese(III) Nitrate Complexes as Bench-Stable Powerful Oxidants

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Abstract

We report herein a convenient one-pot synthesis for the shelf-stable molecular complex $[Mn(NO_3)_3(OPPh_3)_2]$ (**2**) and describe the properties that make it a powerful and selective one-electron oxidation (deelectronation) reagent. **2** has a high reduction potential of 1.02 V versus ferrocene (MeCN) (1.65 vs normal hydrogen electrode), which is one the highest known among readily available redox agents used in chemical synthesis. **2** exhibits stability toward air in the solid state, can be handled with relative ease, and is soluble in most common laboratory solvents such as MeCN, dichloromethane, and fluorobenzene. **2** is substitutionally labile with respect to the coordinated (pseudo)halide ions enabling the synthesis of other new Mn(III) nitrato complexes also with high reduction potentials ranging from 0.6 to 1.0 V versus ferrocene.

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The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c03411.

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

Accession Codes

CCDC 2338924–2338930 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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Introduction.

Single-electron oxidation, sometimes referred to as deelectronation,[1] is one of the most fundamental reactions in chemistry. Most very strong oxidants (>0.8 V; all potentials vs $FeCp_2$ unless noted) such as main group fluorides (e.g., AsF_6) or transition-metal hexafluoride compounds (WF_6, PtF_6, etc.) are impractical because they are difficult to synthesize and/or handle in standard laboratory settings.[2] Nitrosonium and Ag^+ salts of weakly coordinating anions (WCAs) are also established reagents for deelectronation,[3] but, as with most strong oxidants, oxidation is often accompanied by side reactions in addition to electron removal. Some recent progress toward more selective single-electron oxidants such as [TCNQ·4B(C_6F_5)$_3$] (TCNQ = tetracyanoquinodimethane), [phenazine^F] [Al(OR^F)$_4$] (phenazine^F = perfluoro-5,10-bis(perfluorophenyl)-5,10-dihydrophenazine), and aminium-cation carborane-anion pairs, like T13,[4] have been reported, but the multistep syntheses and air and moisture sensitivities limit their utility.[5] Hence, the search for selective single-electron oxidants continues, driven by the need for ease of synthesis and handling while maintaining high reduction potentials.

We noted that a characteristic of the Mn(III) ion is its high reduction potential, a property that is critical to life,[6] battery materials,[7] and oxidation in organic transformations such as alkene difunctionalization,[8] alkene epoxidation,[9] and free-radical additions and cyclizations.[10] Within this framework of reactivity, we recently observed that the mononuclear Mn(III) complex [$Mn^{III}Cl_3(OPPh_3)_2$] (**1**) is a potent Cl-atom transfer reagent[11] and mediates C–H chlorination in specific cases,[12] properties that appear to be intrinsic to the highly reactive $MnCl_3$ entity. We reasoned that the coordination of pnictogen-oxide ylide triphenylphosphine oxide (Ph_3PO) enabled the room-temperature stabilization of highly reactive $MnCl_3$, which otherwise decomposes above −40 °C.[13] As an extension of this rationale, we hypothesized that analogous Mn(III) complexes with weakly coordinating pseudohalide ligands could likewise exhibit desirable bench-stability characteristics while maintaining some of the intrinsic chemical properties, such as the high reduction potential.

Exploring this hypothesis with nitrate as the anion, reported herein, resulted in successful gram-scale synthesis of [$Mn^{III}(NO_3)_3(OPPh_3)_2$] (**2**) and demonstration of desirable bench-stability and redox properties for oxidation. **2** has a strikingly high reduction potential of 1.02 V in MeCN (1.65 vs NHE) (Figure 1), which is one of the highest among available stoichiometric oxidants.[14] While other reactants with higher potentials are known,[5] **2** can be synthesized in a single step on the bench from commercially available reactants, is capable of open-to-air manipulations, and is soluble in common laboratory solvents. The byproducts of oxidation with **2** are [$Mn^{II}(NO_3)_2(OPPh_3)_2$] (**9**) and non-nucleophilic nitrateion.[15] Except for use in exotic cases, where extremely electrophilic products are generated, **2** is an important addition to the growing class of powerful oxidants. **2** also is substitutionally labile with respect to halide/pseudohalide ion metathesis enabling the synthesis of new Mn(III) nitrato[16] complexes, effectively allowing us to tune the reduction potential in a series of strong to very strong oxidants spanning 0.6 to 1.0 V.

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Synthesis and Characterization of $[Mn^{III}(NO_3)_3(OPPh_3)_2]$.

A procedure to prepare what is nominally $[Mn^{III}(NO_3)_3]$ (**3**) has been known since 1972,[17] but it requires the use of highly toxic and inconvenient reagents like N_2O_5 and N_2O_4 and requires storage below −14 °C (Figure 2). **2** was synthesized from $[Mn^{III}(NO_3)_3]$ via this cumbersome route and, aside from a solid-state magnetic measurement and select vibrational data, virtually nothing was known about it prior to this work.[17] Motivated by the premise that **2** would exhibit a kind of tempered stability like **1**, we aimed to develop convenient ways of preparing **2** and new pnictogen-oxide stabilized complexes of Mn(III); pyridine-*N*-oxide (Opy), Ph_3PO, and triphenylarsine oxide (Ph_3AsO) were the chosen ligands for this study.

Two convenient routes to **2** were devised, both using an acetonitrile solution of trimethylsilylnitrate (Me_3SiONO_2) generated *in situ* from $AgNO_3$ and Me_3SiCl.[18] In the first route, 36 equiv of Me_3SiONO_2 was added to $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 2HOAc\cdot 4H_2O$ (**Mn_{12}**)[19] and then treated with 24 equiv of Ph_3PO to give **2** in low yields (26% crystalline). The more efficient second route is analogous to the one-pot synthesis that we developed for **1** (Scheme 1),[11] employing Me_3SiONO_2 instead of Me_3SiCl. Adding Me_3SiONO_2 to a mixture of $Mn(OAc)_2$ and $KMnO_4$ in a 16:4:1 ratio formed a brown solution, presumably containing **3**, and upon addition of Ph_3PO **2** was obtained in good yields. The reaction is scalable; we routinely perform syntheses that furnish 6 g of crude product (73%, Figure 2) which after recrystallization in a glovebox furnishes 5 g (63%) of crystalline, analytically pure material. In the solid state, **2** is stable to air and can be stored for months without noticeable change on the bench (Figure S5). Performing an entire synthesis (8 g scale) on a Schlenk line under Ar followed by open-to-air filtration does not diminish the yield of the crude product.

X-ray diffraction (XRD) characterization of red-brown crystals of **2** revealed a pseudo-square-pyramidal geometry with the Ph_3PO ligands in the *cis* position (Figure 2), similar to **1**.[11] The solid-state ATR-FTIR spectrum of **2** contains a characteristic P–O stretch at 1436 cm^{-1} as well as nitrato stretches at 1528, 1260, and 951 cm^{-1}. The solution-state magnetic moment of **2** in DCM is consistent with a high-spin Mn(III) center (μ_{eff} = 5.46 μ_B), and the X-band EPR spectrum (77 K) is silent.

Synthesis of Other Mn(III) Nitrato Complexes.

Mn(III) nitrato complexes with other pnictogen-oxide ligands were synthesized via **3** that was prepared directly from $Mn(OAc)_2$ and $KMnO_4$ (Scheme 2). Addition of 2 equiv of Ph_3AsO to **3** produced $[Mn^{III}(NO_3)_3(OAsPh_3)_2]$ (**4**) in 61% crystalline yield. XRD analysis of deep purple crystals of **4** revealed a pseudo-trigonal-bipyramidal geometry with the Ph_3AsO ligands in the *trans* position (Figure 3). Addition of 2 equiv of Opy to **3** did not produce the expected $[Mn^{III}(NO_3)_3(Opy)_2]$, and instead the mononitrato Mn(III) complex salt $[Mn^{III}(NO_3)(MeCN)(Opy)_4][Mn^{II}(NO_3)_4]$ (**5**) was obtained in 64% crystalline yield (Figure 3). The six-coordinate manganese center of **5** is in the +3 oxidation state. The bond lengths and angles of the other manganese center are consistent with the known anion $[Mn^{II}(NO_3)_4]^{2-}$.[20] While **2** and **4** are bench stable in the solid state, **5** readily undergoes

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hydration when exposed to air. Furthermore, **2** and **4** are soluble in polar organic solvents like DCM, MeCN, and THF while **5** is only soluble in MeCN, consistent with its salt-like state in contrast to neutral **2**. In fact, **2** is soluble in fluorobenzene (2.8 mg/mL) and is sparingly soluble in toluene and benzene (<1 mg/mL).

We also prepared mixed nitrato dichlorido Mn(III) complexes via halide/pseudohalide metathesis (Scheme 3). Reaction of **1** and **2** in a 2:1 ratio cleanly produces **6** (Figure 3). Similarly, complex $[Mn^{III}Cl_2(NO_3)(OAsPh_3)_2]$ (**8**) was synthesized from **4** and $[Mn^{III}Cl_3(OAsPh_3)_2]$ (**7**) (Figure 3).[21]

Electrochemical Investigation of the Mn(III) Complexes.

The complexes prepared here were analyzed with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in DCM, MeCN (Figure 4), and THF (Figure S47). The reduction potentials are remarkably high and span the range of 0.6 to 1.0 V (Table 1).

To confirm that **2** acts as a one-electron oxidant, we titrated a solution of ferrocene with **2** and found that one equivalent was required to cleanly generate $FeCp_2^+$ in DCM (Figure 4). The same titration was conducted for $[Fe^{II}(bipy)_3](PF_6)_2$ (0.66 V in MeCN) and N(4-bromophenyl)$_3$ (0.70 V in DCM), and likewise a clean one-electron transformation occurred to $[Fe^{III}(bipy)_3]^{3+}$ [22] and N(4-bromophenyl)$_3^{+\bullet}$, respectively.

The byproducts of oxidation with **2** are a weakly coordinating nitrate anion and **9**, which are easy to separate from reaction mixtures and will not likely interfere with subsequent chemistries if they are still present. The potentials of oxidants like $KMnO_4$ or ceric ammonium nitrate (CAN) in aqueous $HClO_4$ that are more powerful than **2** are only available in aqueous conditions, and such comparisons with aqueous oxidants are misleading. For instance, the $E_{1/2}$ for tetrabutylammonium ceric nitrate (CTAN)[23] is 0.6 V (Figure 1) in MeCN and DCM and requires addition of strong acids like HOTf to achieve higher oxidizing strength in organic solvent.[24]

C–H Nitrooxylation and Stability Limits of 2.

Single-electron oxidation is not the only reaction that **2** mediates. We found that **2** and **4** react with certain benzylic C–H bonds to form nitrate esters (nitrooxylation) (Scheme 4, Table 2).[25]

Hexamethylbenzene (HMB) was chosen as model substrate to investigate this reactivity since it has a weak benzylic C–H bond dissociation free energy (BDFE) in MeCN of 81.0 kcal/mol[26] and low ionization potential (IP) of 7.85 eV.[27] Reaction of HMB with two equiv of **2** in DCM afforded quantitative conversion to 2,3,4,5,6-pentamethylbenzyl nitrate in 5 min (entry 1). The same reaction but with **4** gave only 58% conversion in 24 h (entry 2). Reaction of 1 equiv of **2** with HMB resulted in 50% conversion (entry 3) consistent with the proposed mechanism (*vide infra*). Due to the efficiency and short reaction time of **2** mediated nitrooxylation of HMB, it can serve as an effective batch control for the purity of **2** (entry 4; see Supporting Information for details).

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The reactivity of **2** with benzylic C–H bonds is limited, boding well for use of **2** as a selective single-electron oxidant. For example, **2** did not react with a range of benzylic substrates (e.g, aromatic aldehydes, ketones, or esters; Scheme 4), even under thermal (refluxing DCM) or photolytic (100 W Xe-arc lamp) conditions. Other substrates affording clean nitrooxylation were *tert*-butyldiphenylsilane (TBDPS) protected *p*-cresol and mesitylene (Scheme 4). One possible mechanism of the reaction with HMB is a C–H cleavage akin to what has been proposed for Ni(IV) nitrato-mediated C–H cleavage by Jackson and Wang,[28] chlorination of HMB using **1** by us,[12] and CF_3 functionalization of arenes using Ag^{2+} photooxidants by Nocera.[29] The first equivalent of **2** cleaves a C–H bond forming nitric acid and a benzylic radical, the latter of which couples with a second molecule of **2** explaining the need for two equivalents of **2** and observation of **9** as the byproduct in HMB nitrooxylation. Given that **2** has an $E_{1/2,\mathrm{MeCN}}$ of 1.02 V and HNO_3 has a $pK_{a,\mathrm{MeCN}}$ of 9.4,[30] the H atom abstracting ability (i.e., effective BDFE) is estimated to be 89 kcal/mol.[26] This bond energy is high enough for C–H nitrooxylation of HMB, but it is not so high as to interfere with selective single-electron oxidation under a wide range of conditions (most C–H strengths are above 89 kcal/mol). An alternative mechanism to C–H activation could initiate with single-electron oxidation of HMB to form the $HMB^{+\bullet}$ given its low IP.[27] **2** also reacts, albeit slowly, with mesitylene (IP = 8.39 eV) but is stable in dry fluorobenzene (IP = 9.19 eV), DCM (IP = 11.35 eV), and MeCN (IP = 12.20 eV),[31,32] which puts an upper limit of single-electron oxidation of <9.2 eV.[33] This high IP and low $BDFE_{eff}$ reflects the high stability of **2** toward air and common organic solvents while maintaining its potent oxidizing ability. In addition to this and the other properties of **2** that we have described herein, it is plain that **2** and other Mn(III) nitrato complexes are ideal powerful oxidants for organometallic chemists.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

NSF grant CHE-1847933, NIH-R21-GM141685-01, and the University at Buffalo (UB) provided support. X-ray diffraction (XRD) System Rigaku XtaLAB Synergy-S was purchased with NSF award CHE-2216151. A Q-exactive GC-Orbitrap tandem MS was purchased using NSF CHE-1919594 by the UB Chemistry Instrument Center (CIC). The Bruker Ascend-500 NMR spectrometer in the UB Magnetic Resonance Center was purchased with NSF CHE-2018160.

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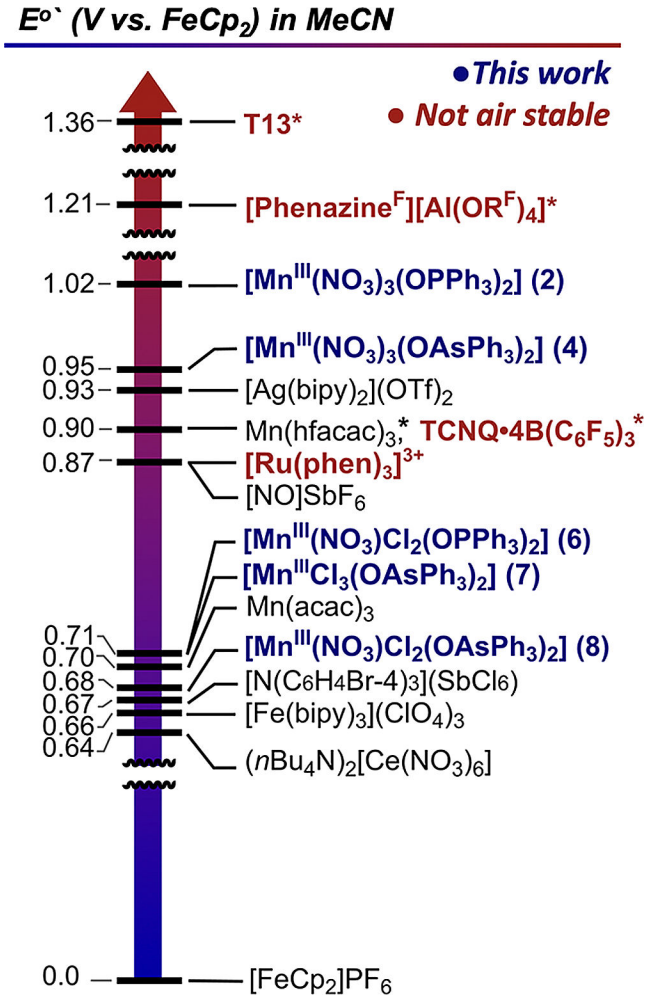

Figure 1.

Reduction potentials of common air-stable oxidants in MeCN (see the text for citations). (*) Potentials in DCM.

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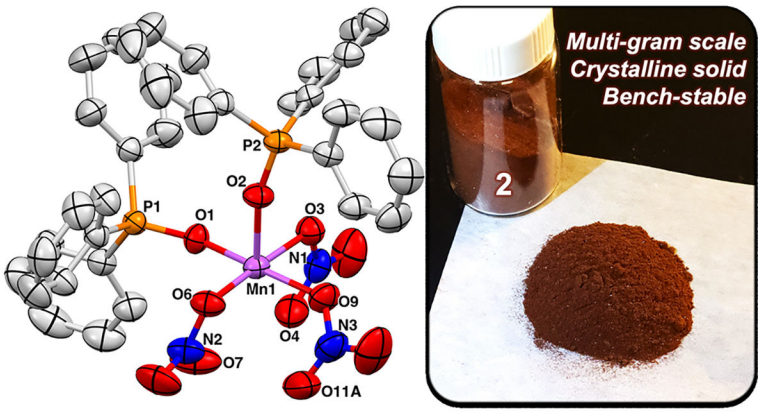

Figure 2.

X-ray crystal structure of **2** (ellipsoids shown at 50% probability; H atoms omitted and only one component of disordered atoms for clarity) and material isolated from multigram scale synthesis.

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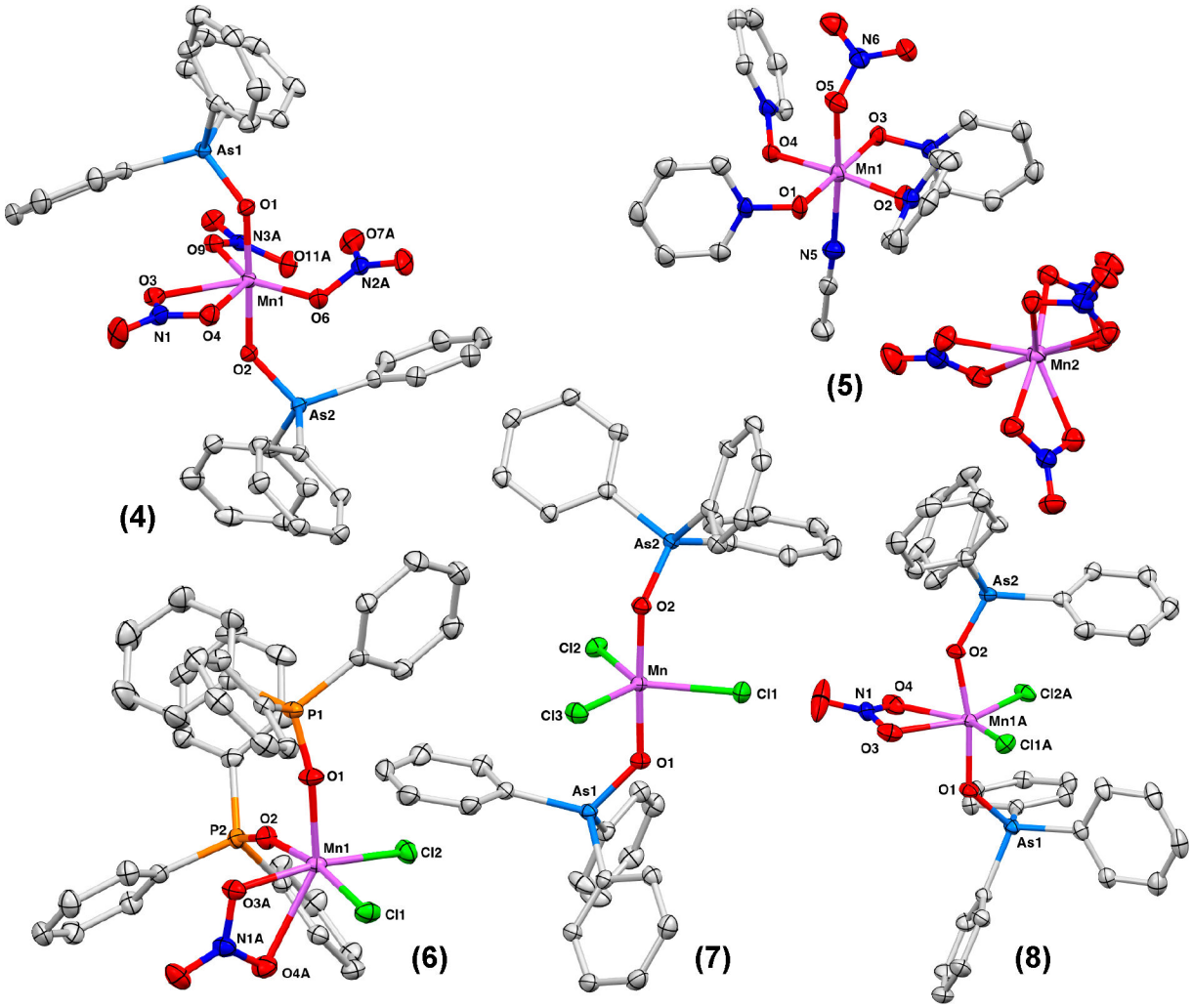

Figure 3.

Molecular structures determined with XRD for **4–8** (ellipsoids shown at the 50% probability). H atoms are omitted, and only one component of disordered atoms is shown for clarity.

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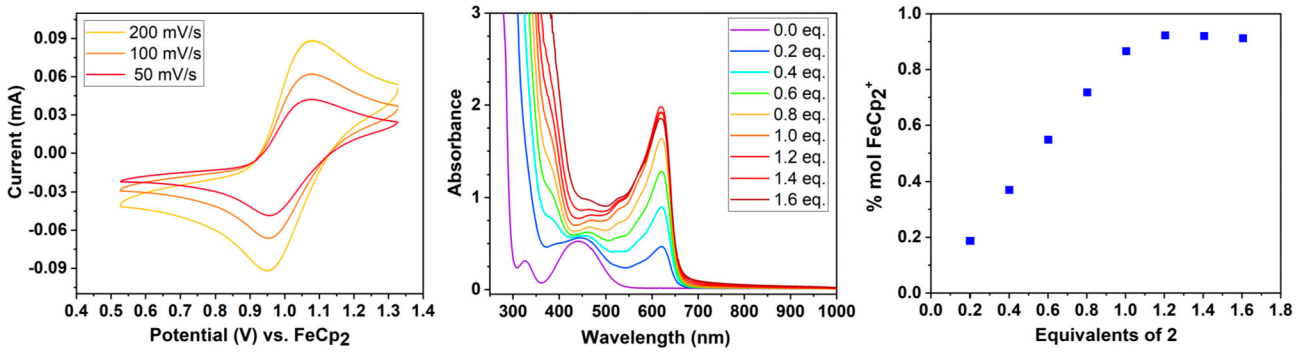

Figure 4.

(Left) Cyclic voltammograms of 0.006 M **2** in MeCN with 0.500 M [nBu$_4$N][PF$_6$] (see Supporting Information for details). (Middle & right) Titration of **2** with ferrocene in DCM showing one-to-one stoichiometry.

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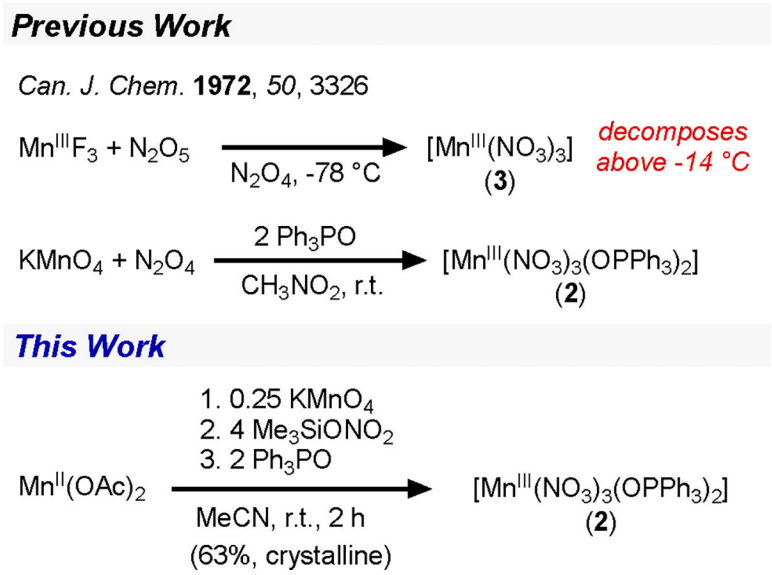

Scheme 1.
Synthesis of 2

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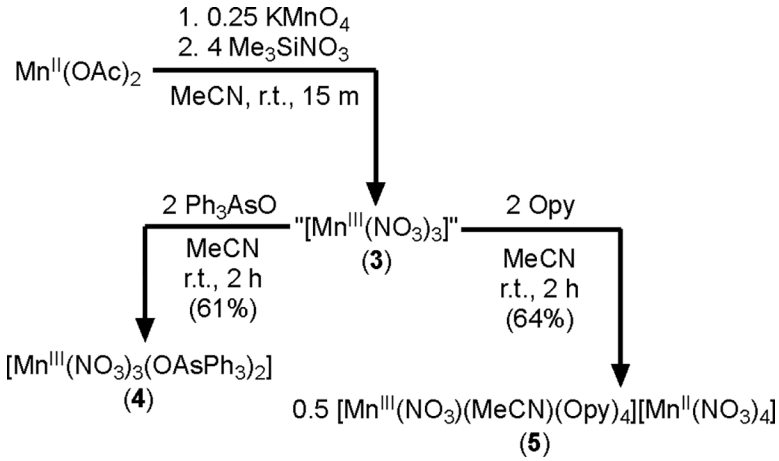
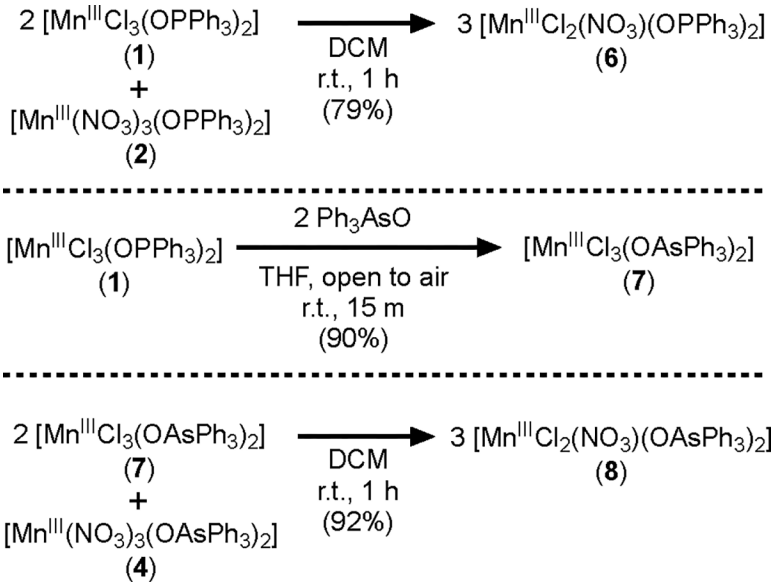


Scheme 2.
Synthesis of 3–5



Scheme 3.
Synthesis of 6–8

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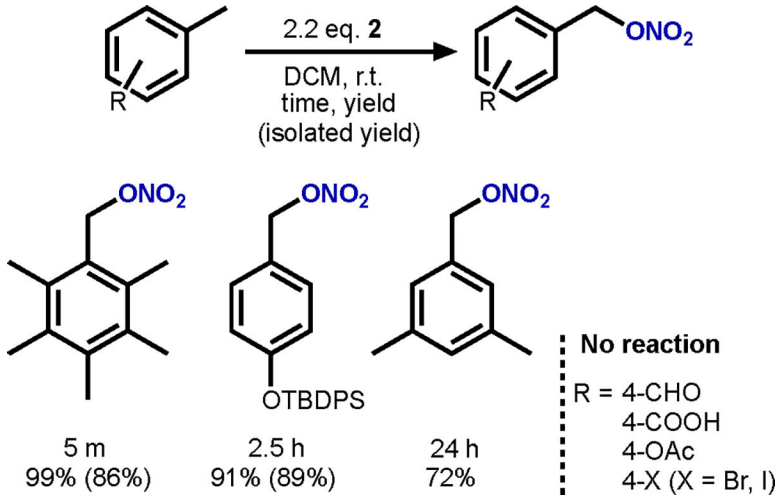

Scheme 4.

C–H Nitrooxylation Mediated by 2

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Table 1.

Reduction Potentials for Mn(III) Complexes

Complex	$E_{1/2}$ (V vs $FeCp_2$)	
	MeCN	DCM
$[Mn^{III}(NO_3)_3(OPPh_3)_2]$ (**2**)[a]	1.02	0.96
$[Mn^{III}(NO_3)_3(OAsPh_3)_2]$ (**4**)	0.95	0.91
$[Mn^{III}(NO_3)(MeCN)(Opy)_4][Mn^{II}(NO_3)_4]$ (**5**)	1.02	
$[Mn^{III}(NO_3)(Cl)_2(OPPh_3)_2]$ (**6**)	0.72	0.68
$[Mn^{III}(Cl)_3(OAsPh_3)_2]$ (**7**)	0.72	0.78
$[Mn^{III}(NO_3)(Cl)_2(OAsPh_3)_2]$ (**8**)	0.68	0.68

[a]Potentials of **2** in MeCN measured in triplicate were within 1 mV. Potentials in DCM measured in triplicate varied by ±10 mV. Electrolyte: 0.5 M $[nBu_4N][PF_6]$. Analyte conc.: 6 mM.

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Table 2.

Nitrooxylation of HMB with Mn(NO3)3 Complexes[a]

Entry	Complex	% yield
1	**2**	99
2	**4** [b]	58
3	**2** (1 equiv)	50
4	**2** (crude)	82

[a]Conditions shown in Scheme 4.

[b]24 h. Average yields for duplicated runs determined by ^{1}H NMR.