Nitrogen Transfer from a Nitridomanganese(V) Complex: Amination of Silyl Enol Ethers

J. Du Bois,† Jason Hong,† Erick M. Carreira,*,† and Michael W. Day‡

Contribution No. 9155, Arnold and Mabel Beckman Laboratory for Chemical Synthesis and Beckman Institute, X-Ray Crystallography Laboratory California Institute of Technology Pasadena, California 91125

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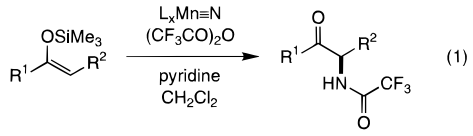
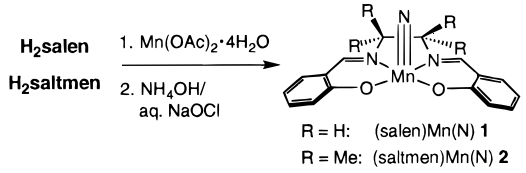
Metal-catalyzed oxygen atom-transfer reactions are of fundamental interest in both chemistry and biology.[1] Detailed investigations of the mechanism of oxygen atom transfer in biological systems have led to the generation of synthetic models capable of performing analogous oxidation chemistry.[2] This work has fueled the development of valuable synthetic methodology specifically with regard to alkene epoxidation, a reaction for which numerous protocols exist.[3] In contrast, fewer methods are available for the related metal-mediated nitrogen atom-transfer reaction, despite the utility of such technology in synthesis.[4,5] Herein, we describe the preparation of two novel nitridomanganese(V) salen-derived complexes that can be activated for nitrogen transfer with trifluoroacetic anhydride (TFAA).[6,7] When this activation process is conducted in the presence of certain silyl enol ethers, rapid formation of *N*-trifluoroacetyl α-amino ketone products is observed (eq 1).



(1)

In one of the earliest examples of nitrogen atom-transfer chemistry, Groves and Takahashi elegantly described the use of nitrido[*meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinato]-manganese(V), (TMPMnN), for the aziridination of *cis*-cyclooctene.[8] Formation of TMPMnN was effected by irradiation

Scheme 1



($\lambda \geq 290$ nm) of the corresponding [porphyrinato]Mn(III) azide. Isolation of nitrido−Mn(V) adduct and subsequent treatment of a solution of this complex with cyclooctene (11 equiv) and TFAA (1.2 equiv) afforded the *N*-trifluoroacetylated aziridine product. Following this example, we have prepared the nitrido−Mn(V) species (**1**) derived from (salen)MnN_3. The choice of salen as a ligand followed from the work of Arshankow and Poznjak, who had previously prepared (salen)$Cr^{V}N\cdot H_2O$ by photolysis of the (salen)$Cr^{III}N_3\cdot 2H_2O$ complex.[9,10] Although formation of (salen)$Mn^{V}N$ (**1**) was possible by the Arshankow−Poznjak protocol, isolated yields of the desired manganese nitride were low (<35%).

An alternative method for the preparation of **1** was developed which offered significant improvement over the photolysis procedure. Oxidation of both Cr(III) and Mn(III) porphyrin complexes with either NaOCl or PhIO in the presence of NH_4OH had been reported to yield the corresponding Cr(V) and Mn(V) nitrides.[11,12] In a similar fashion, treatment of a methanolic suspension of (salen)$Mn^{III}Cl$ with NH_4OH (15 M, 15 equiv) and aqueous NaOCl (Clorox bleach, 6 equiv) provided nitride **1** as an emerald green solid. With this procedure, multigram quantities of **1** could be prepared; however, the low solubility of this compound in most organic solvents (CH_2Cl_2, EtOAc, CH_3CN, Et_2O) made its isolation and purification difficult. It was possible to circumvent such problems by synthesizing the ligand in which the ethylenediamine backbone of salen was replaced with 2,3-diamino-2,3-dimethylbutane.[13] Condensation of this diamine with salicylaldehyde (2 equiv) furnished the H_2saltmen ligand as a yellow crystalline solid (96%).[7] The nitrido-Mn(V) complex (**2**) derived from H_2-saltmen was prepared in a single operation by first reacting $Mn(OAc)_2\cdot 4H_2O$ with a solution of the ligand in methanol to give an air-oxidized (saltmen)Mn(III) intermediate.[14] Subsequent treatment of the resulting dark brown solution with NH_4OH and Clorox bleach afforded the desired Mn(V) nitride **2** (Scheme 1). Following purification, the product was isolated as a dark green microcrystalline solid (in up to 20 g scale) in overall yields which consistently ranged from 80 to 85%.[15]

The (saltmen)Mn(N) complex **2**, like the parent **1**, is remarkably stable to both air and H_2O. ^1H and ^{13}C NMR spectra recorded for the two complexes show sharp resonances in the usual range for chemical shifts, consistent with a diamagnetic complex of low-spin d^2 configuration. Infrared spectroscopic

† Arnold and Mabel Beckman Laboratory for Chemical Synthesis.

‡ Beckman Institute, X-Ray Crystallography Laboratory.

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(6) For a review of nitrido metal complexes, see: (a) Dehnicke, K.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. See also: Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(7) Salen = *N*,*N*′-ethylenebis(salicylideneaminato); saltmen = *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(salicylideneaminato).

(8) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2074. (b) Groves, J. T.; Takahashi, T.; Butler, W. M. *Inorg. Chem.* **1983**, *22*, 884.

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(14) The nature of this dark brown Mn(III) species has not been established. For an analogous reaction in which the resulting Mn(III)−salen complex was isolated and characterized following treatment with LiCl, see: Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296.

(15) A detailed experimental procedure for the preparation of both H_2-saltmen and **2** is provided in the supporting information.

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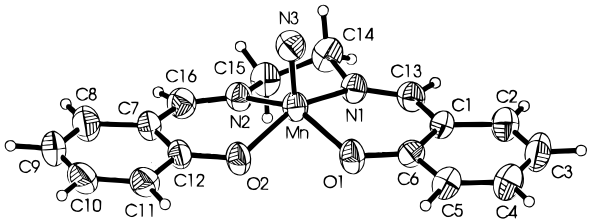
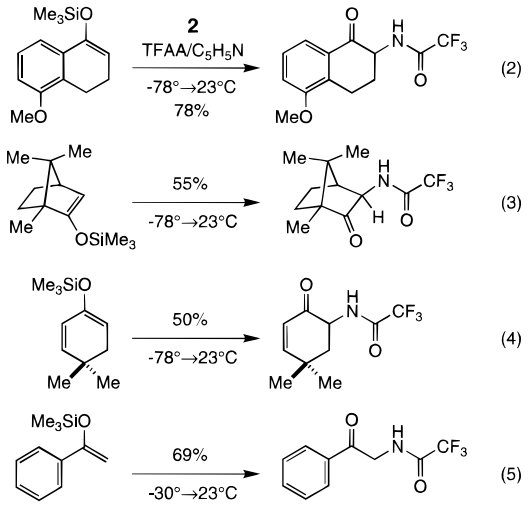


Figure 1. ORTEP diagram of (salen)Mn(N) **1** displaying 50% probability ellipsoids.

analysis established the Mn≡N stretching frequency at 1047 cm^{-1} for **1** and **2**, similar to that reported for the analogous nitridomanganese porphyrin species (∼1050 cm^{-1}).[8a,11b] The structures of **1** and **2** were confirmed by single crystal X-ray analysis (ORTEP for **1** shown in Figure 1).[16] X-ray data show both compounds to be monomeric, each having a Mn−N bond length of 1.51 Å, consistent with the assignment of a formal Mn≡N triple bond.[17] To the best of our knowledge, **1** and **2** represent the first non-porphyrin nitridomanganese(V) complexes to be synthesized and crystallographically characterized.[18]

Preliminary investigations into the use of **2** (or **1**) as a nitrogen-transfer reagent suggested that electron-rich alkenes, such as ketone silyl enol ethers, would serve as optimal substrates for amination. Treatment of a solution of **2** (2 equiv), 1 equiv of a Me_3Si enol ether, and pyridine (3 equiv) in CH_2Cl_2 with TFAA (2.4 equiv) at reduced temperature (ca. −30 °C) led to rapid consumption of the starting materials and provided the corresponding *N*-trifluoroacetylated α-amino ketone (eqs 2−5).[19,20] This reaction, like the analogous reaction of cyclooctene with TMPMnN and TFAA (*vide supra*), may proceed via initial formation of a reactive *N*-trifluoroacetylimidomanganese species with subsequent transfer of the CF_3CON group to the olefin substrate.[8a,21] Although currently limited to certain enol silanes, the amination method described has several appealing features, which include (i) the facile preparation of large quantities of the starting Mn−nitrido reagent **2**; (ii) the use of the silyl enol ether substrate as the limiting reagent (1 equiv); and (iii) the mild reaction conditions employed. Additionally, the trifluoroacetyl residue serves as a useful amine protecting group which may be cleaved under mild conditions.



We have described the facile preparation of two novel nitridomanganese(V) salen-derived complexes that serve as reagents for the amination of electron-rich enol ethers, and in doing so, we have demonstrated that reactions involving activation and transfer of nitrogen from metal nitrides are not unique to porphyrin-derived species. The ease with which both the structural and electronic properties of the salen ligand may be varied by simple substitutions of either the salicylaldehyde or ethylenediamine moieties should allow for the preparation of other nitrido−metal reagents that display increased reactivity. Efforts along these lines are currently in progress.

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Supporting Information Available: Experimental procedures for the preparation of H_2saltmen and **2** are included, spectral and analytical data for *N*-trifluoroacetyl α-amino ketone products, and crystallographic data for **1** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be donwloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) Crystal data for (salen)MnN (**1**): emerald green crystals were deposited by slow evaporation of a CH_2Cl_2 solution of **1**; space group $P2_1/c$; cell constants $a = 9.496(3)$, $b = 12.313(3)$, and $c = 12.857(4)$ Å; $\beta = 103.61°$; $V = 1461.1(7)$ $Å^3$, $Z = 4$. A total of 4023 observations were collected (Mo Kα, $2\theta_{max} = 44°$, $-9 \le h \le 9$, $0 \le k \le 12$, $-13 \le l \le 13$) and merged to 1781 unique reflections ($R_{merge} = 0.038$, $GOF_{merge} = 1.05$). The structure was solved by direct methods (SHELXS-86) and refined ansiotropically (SHELXL-93) to $R = 0.061$ with GOF = 1.304. Additional information is given in the supporting information.

(17) A Mn−N distance of 1.51 Å has been reported for the (5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5*H*,15*H*-porphyrinato)nitridomanganese(V) compound, see ref 11b.

(18) The preparation of a nitrido−Mn(V) phthalocyanine complex has been reported; however, its structure was only established by UV and resonance Raman spectroscopy. Grunewald, H.; Homborg, H. *Z. Anorg. Allg. Chem.* **1992**, *608*, 81. A stable Mn(V) oxo complex has been crystallographically characterized, see: Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899.

(19) Following is a general procedure for the amination of the silyl enol ethers shown in eqs 2−5: A solution of **2** (1.0 mmol, 2 equiv) in 3.0 mL of CH_2Cl_2 was cooled to −78 °C. Pyridine (1.5 mmol) was added, followed by a solution of the silyl enol ether (0.5 mmol) in 2.0 mL of CH_2Cl_2. Freshly distilled TFAA (1.2 mmol) was then added dropwise to the dark green mixture. The solution was allowed to warm slowly from −78 °C to 23 °C over a 3−4 h period. During this time, the reaction mixture turned dark brown. Silica gel (800 mg) and Celite (800 mg) were added, along with 25 mL of *n*-pentane. The dark brown slurry was stirred vigorously at 23 °C for 30 min before being filtered through a 20 mm × 40 mm plug of silica gel using Et_2O (4 × 10 mL) as eluent. Concentration of the filtrate under reduced pressure afforded a pale yellow residue, which was purified by chromatography on silica gel. In one case (eq 5), a higher yield of the desired product was obtained if the reaction was initially run at −30 °C (3:2 H_2O/ethylene glycol−dry ice) and only a catalytic amount of pyridine (62 μmol) was employed.

(20) The camphor-derived product (eq 3) has been shown by ^1H NMR difference NOE experiments to be the exo isomer. In addition, the product was found to be identical (^1H and ^{13}C NMR, IR) to authentic material which was prepared according to a known procedure for a related compound: Chittenden, R. A.; Cooper, G. H. *J. Chem. Soc. C*, **1970**, 49.

(21) For mechanistic studies on the reaction of TFAA with nitrido−Cr and Mn porphyrin complexes, see: (a) Bottomley, L. A.; Neely, F. L. *Inorg. Chem.* **1990**, *29*, 1860. (b) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 6748.