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Nitridomanganese(V) Complexes: Design, Preparation, and Use as Nitrogen Atom-Transfer Reagents

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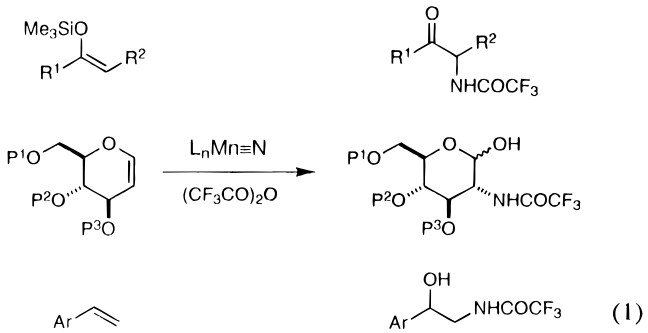
Oxidation of organic substrates by direct oxygen-atom transfer from transition-metal complexes is of fundamental importance and has been subject to intensive investigation.[1] Highly selective methods for alkene epoxidation and dihydroxylation have been described and are commonly employed in synthesis.[2,3] By contrast, significantly fewer reagents and protocols are available for the analogous nitrogen-atom-transfer process, despite the enormous potential utility of such methodology.[4] Recent efforts by other groups to develop general olefin amination strategies have led to impressive advances in both metal-catalyzed hydroxyamination and aziridination.[5,6] Our interest in this area has resulted in the preparation and characterization of novel nitridomanganese complexes which may be activated for nitrogen-atom transfer. Pivotal to the success of this research has been the development of new protocols for the construction of these manganese nitride (Mn≡N) reagents. These systems have proven to be versatile and effective aminating agents with different classes of olefins which include both silyl enol ethers and glycals (eq 1). The following account documents these findings and highlights the unique chemistry of these complexes as nitrogen-atom-transfer reagents.



(1)

Background

Our desire to develop novel nitrogen-atom-transfer reagents was fueled by the potential application of aziridination and amination technologies for chemical synthesis together with the paucity of available strategies for effecting such transformations.[4,6] To this end, we became interested in a report by Groves of a nitridomanganese(V) porphyrin system ((TMP)Mn≡N) **2,** which, when reacted with trifluoroacetic anhydride (TFAA), transferred CF_3CON to *cis*-cyclooctene to furnish the *N*-trifluoroacetyl-protected aziridine **3** (Figure 1).[7] This example of a metal nitrenoid coupling with an olefin was unique and did not appear to be plagued by competing insertion and C−H abstraction reactions typically observed in processes thought to involve nitrenoid intermediates.[4,6a,i] Additionally, because of the apparent similarity between this aziridination reaction and related oxo-transfer processes, it was thought that the expansive body of information on metal-catalyzed epoxidation reactions would provide an invaluable guide for the development of this work.[1a,8] In this regard, particular attention was paid to the numerous

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(1) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981. (b) Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 1097. (c) Murahashi, S.-I.; Naota, T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995, Vol. 12, p 1177.

(2) (a) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; p 159. (b) Jørgensen, K. A. *Chem. Rev. (Washington, D.C.)* **1989**, *89*, 431.

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(6) (a) Mansuy, D.; Mahy, J.-P. In *Metalloporphyrins Catalyzed Oxidations*; Montanari, F., Casella, L., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; p 175. (b) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742 and references therein. (c) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326. (d) Nishikori, H.; Katsuki, T. *Tetrahedron Lett.* **1996**, *37*, 9245 and references therein. (e) O'Connor, K. J.; Wey, S.-J.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001. (g) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744. (h) Atkinson, R. S.; Grimshire, M. J.; Kelly, B. J. *Tetrahedron* **1989**, *45*, 2875. (i) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517.

(7) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Groves, J. T.; Takahashi, T.; Butler, W. M. *Inorg. Chem.* **1983**, *22*, 884. (c) Takahashi, T. Ph.D. Dissertation, The University of Michigan, Ann Arbor, MI, 1985.

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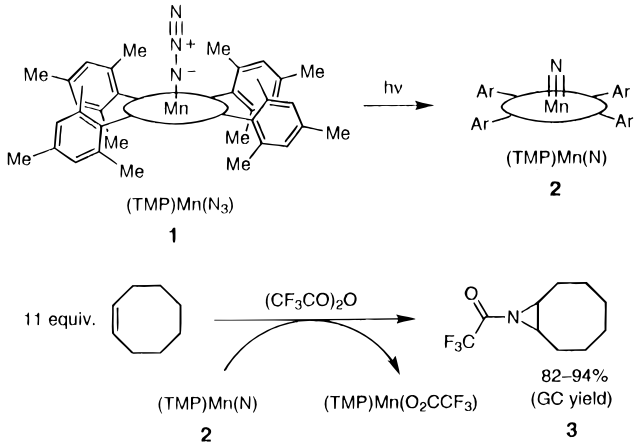
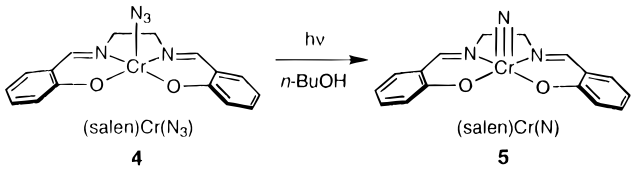


FIGURE 1. Aziridination of cyclooctene with (TMP)Mn(N) (2).

examples of olefin epoxidation catalyzed by non-porphyrin Mn and Fe complexes.[1a,2a,9] Thus, by analogy, it seemed reasonable that manganese nitrides other than porphyrin-based systems such as (TMP)Mn(N) **2** could be utilized as nitrogen-transfer reagents. At the time we became involved with this project, however, only porphyrin- and phthalocyanine-derived nitrido Mn(V) complexes had been prepared.[7,10,11]

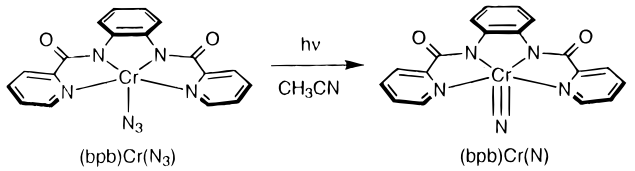
Inspired by the elegant application of (TMP)Mn(N) for the aziridination of *cis*-cyclooctene, we were aware, however, of certain features which would diminish the utility of such nitrogen-transfer technology as a general, practical method. First, the aziridination reaction of cyclooctene prescribed the use of a large excess of the starting olefin. For an inexpensive olefin such as cyclooctene, this requirement may not represent a limitation, but for more elaborate, less available alkenes, a process in which the olefin substrate serves as the limiting reagent is desirable. Second, the formation of (TMP)Mn(N) had been accomplished by irradiation of the corresponding Mn(III) azide **1** (Figure 1). This photolysis reaction afforded good yields of the Mn(V) nitride but was limited to small-scale production of this compound.[7] A method amenable to large-scale synthesis of the nitrido complex would be necessary, however, because of its requirement as a stoichiometric reagent in the aziridination reaction at the current level of development. Finally, the difficulties associated with the preparation and functionalization of porphyrin ligands, coupled with the prohibitive cost of these materials, rendered the porphyrin-based compounds impractical for our purposes.[12] Alternative Mn complexes with inexpensive, readily derivatizable ligand systems were, therefore, considered.

In our efforts to find non-porphyrin ligands suitable for the formation of a highly oxidized Mn(V) nitrido species, we became interested in a report by Arshankow and Poznjak of a salen Cr(V) nitride **5** which had been prepared photolytically from (salen)$Cr^{III}(N_3)$ (**4,** eq 2).[13,14]



(2)

In the absence of X-ray crystallographic data, assignment of this complex as (salen)Cr^{V}(N) was based on electron paramagnetic resonance spectroscopy, which supported a d^1 valence configuration, and infrared spectroscopy, which established the presence of a Cr−N triple bond ($\nu_{Cr\equiv N}$ = 1012 cm^{-1}). Subsequently, Che had described a second non-porphyrin nitrido chromium compound, (bpb)Cr^{V}(N) (**7**), derived from the tetradentate 1,2-bis(2-pyridinecarboxamido)benzene (bpb) ligand (eq 3).[15] This

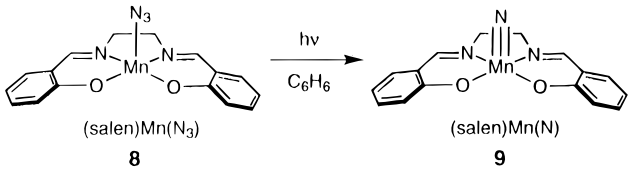


(3)

was prepared in a fashion analogous to that of the (salen)-Cr(N) complex and had been characterized by single-crystal X-ray analysis. The fact that both the (salen)Cr(N) and the (bpb)Cr(N) were stable to air and moisture and could be handled on the benchtop was noteworthy. On the basis of these findings, we speculated that analogous nitridomanganese systems could be constructed.

Preparation and Characterization of Salen-Derived $Mn^{V}\equiv N$ Complexes

Following the protocol delineated by Arshankow and Poznjak, (salen)Mn^{V}(N) (**9**) was successfully prepared upon irradiation of the corresponding (salen)$Mn^{III}(N_3)$ (**8,** eq 4). Although formation of **9** was possible under these



IR: $\nu_{Mn\equiv N}$ = 1047 cm^{-1}

(4)

conditions, isolated yields of this compound were low (<35%). This, together with the need for preparative

(9) (a) Katsuki, T. *J. Mol. Catal. A* **1996**, *113*, 87. (b) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (c) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.

(10) (a) Buchler, J. W.; Dreher, C.; Lay, K.-L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1155. (b) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318. (c) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J. A.; Scheidt, W. R. *Inorg. Chem.* **1983**, *22*, 888.

(11) Grunewald, H.; Homborg, H. *Z. Anorg. Allg. Chem.* **1992**, *608*, 81 and references therein.

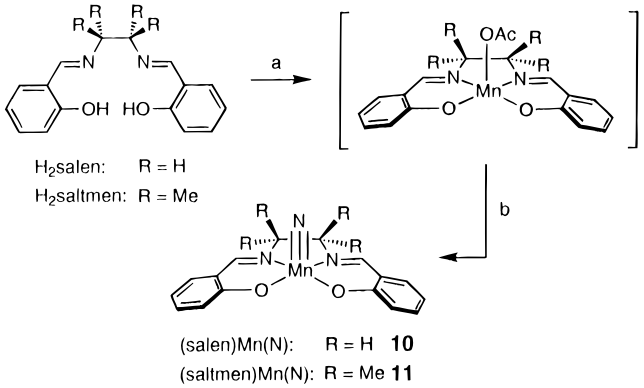
(12) For example, 2,3,7,8,12,13,17,18-octaethylporphyrin manganese(III) chloride may be purchased for $566/gram from Aldrich Chem. Co.

(13) Arshankow, S. I.; Poznjak, A. L. *Z. Anorg. Allg. Chem.* **1981**, *481*, 201. (Salen)Cr(N) has also been prepared by intermetal nitrogen-atom-transfer, see: Neely, F. L.; Bottomley, L. A. *Inorg. Chim. Acta* **1992**, *192*, 147.

(14) (salen)Mn(N) = nitrido[*N,N′*-ethylenebis(salicylideneaminato)]-manganese(V); (saltmen)Mn(N) = nitrido[*N,N′*-(1,1,2,2-tetramethyl)-ethylenebis(salicylideneaminato)]manganese(V).

(15) Che, C.-M.; Ma, J.-X.; Wong, W.-T.; Lai, T.-F.; Poon, C.-K. *Inorg. Chem.* **1988**, *27*, 2547.

Scheme 1[a]



[a] (a) $Mn(OAc)_2 \cdot 4H_2O$, MeOH; (b) 15 M NH_4OH, Clorox bleach, 80−85%.

quantities of the manganese nitride, required the development of an alternative method for the synthesis of (salen)Mn(N).

Oxidation of both Cr(III) and Mn(III) porphyrin complexes with NaOCl in the presence of NH_4OH had been reported to yield the corresponding Cr(V) and Mn(V) nitrides.[10] This method for M≡N bond formation possessed two salient features which were ideal for our purposes: (1) experimental simplicity and (2) amenability to large-scale synthesis. However, it was unclear as to whether the salen ligand could withstand such strongly alkaline (pH = 14), oxidizing reaction conditions.[16] Nevertheless, upon treatment of a dark brown suspension of (salen)Mn^{III}(OAc) with NH_4OH and Clorox bleach, nitride **10** was provided as an emerald green solid (Scheme 1).[17] By following this procedure, multigram quantities of **10** could be prepared; however, the low solubility of this compound in most organic solvents made its isolation and purification difficult. It was possible to avoid such problems by synthesizing the H_2saltmen ligand, in which the ethylenediamine backbone of salen was replaced with 2,3-diamino-2,3-dimethylbutane. The corresponding nitrido Mn(V) complex **11** derived from H_2saltmen was prepared in a single operation by sequential treatment with $Mn(OAc)_2 \cdot 4H_2O$ then NH_4OH and bleach. Under these conditions, the desired nitride, (saltmen)Mn(N) (**11**), could be isolated as a dark green microcrystalline solid in overall yields of 80−85%.[18]

The (saltmen)Mn(N) complex **(11)**, like the parent (salen)Mn(N) (**10**), was found to be remarkably stable to both air and H_2O. ^1H and ^{13}C NMR spectra recorded for the two complexes showed sharp resonances in the usual range for chemical shifts, consistent with a diamagnetic complex of low-spin d^2 configuration. Infrared spectroscopic analysis established the Mn≡N stretching frequency at 1047 cm^{-1} for **10** and **11**, similar to that reported for the analogous nitridomanganese porphyrin species (ca. 1050 cm^{-1}).[7a,c,10a] The structures of **10** and **11** were confirmed by single-crystal X-ray analysis (**10** shown in Figure 2). X-ray data show both compounds to be monomeric, each having a Mn−N bond length of 1.51 Å,

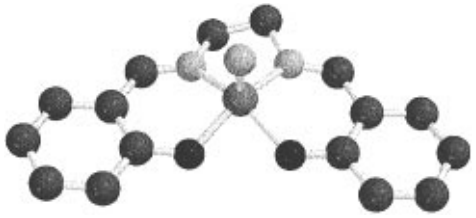


FIGURE 2. Drawing of the X-ray structure of (salen)Mn(N) (10).[21]

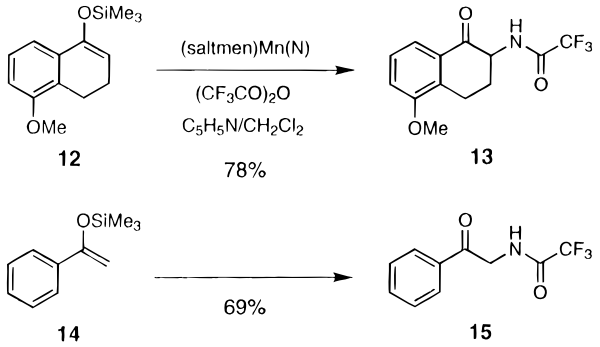


FIGURE 3. Reactions of (saltmen)Mn(N) with representative silyl enol ethers 12 and 14.

consistent with the assignment of a formal Mn≡N triple bond.[19] At the time of their preparation, **10** and **11** represented the first non-porphyrin nitridomanganese(V) complexes to be synthesized and crystallographically characterized.[20]

Amination of Electron-Rich Olefins

Preliminary investigations into the use of (saltmen)Mn(N) (**11**) as a nitrogen-transfer reagent suggested that electron-rich alkenes, such as ketone silyl enol ethers (e.g., **12** and **14**), would serve as optimal substrates for amination (Figure 3).[17] A protocol was developed in which trifluoroacetic anhydride (TFAA) was added to a solution of **11**, enol silane, and pyridine. Under these conditions, consumption of the starting materials occurred rapidly at temperatures as low as −30 °C. The corresponding *N*-trifluoroacetylated α-amino ketones were furnished in yields typically ranging from 50 to 78%. The role of pyridine in these reactions with silyl enol ethers is believed to be twofold: as a base to scavenge adventitious CF_3CO_2H which would cause decomposition of the starting enol ethers and as a catalyst which promotes acylation of the nitrido moiety at low temperature. The successful amination of silyl enol ethers with (saltmen)Mn(N) affirms that reactions involving activation and transfer of nitrogen from manganese nitrides are not unique to porphyrin-derived species.

As a general strategy for the preparation of α-amino ketones, this amination method has several appealing features: (1) the facile preparation of large quantities of the starting Mn nitrido reagent **11**; (2) the use of the silyl enol ether substrate as the limiting reagent; and (3) mild reaction conditions. Additionally, the trifluoroacetyl residue serves as a convenient amine protecting group which may be readily cleaved.[22]

(16) Collins, T. J. *Acc. Chem. Res* **1994**, *27*, 279.
(17) The nature of this dark brown Mn(III) species has not been established and is drawn as such for convenience.
(18) Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915.
(19) Mn≡N distances of 1.51 Å have been reported for (TpMPP)Mn(N) and (OEP)Mn(N); see refs 10b and 10c, respectively.
(20) The crystal structure of a triazacyclononane nitridomanganese(V) complex appeared concurrently, see: Niemann, A.; Bossek, U.; Haselhorst, G.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 906.

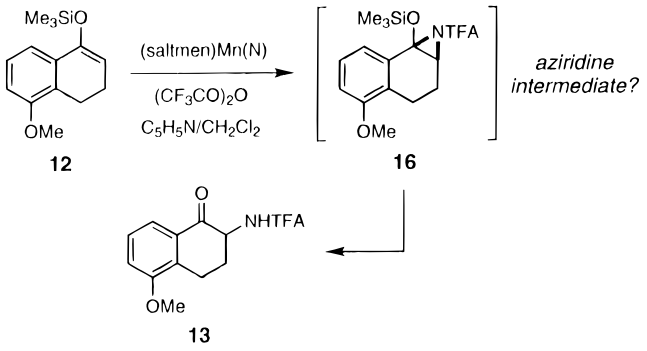


FIGURE 4. Proposed intermediate in the silyl enol ether amination reaction.

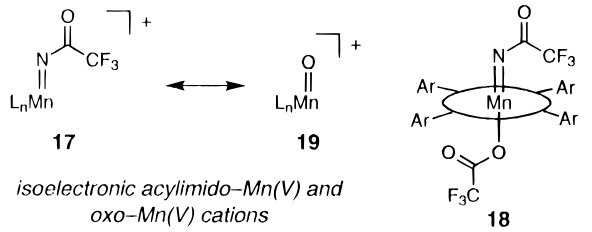


FIGURE 5. Reactive intermediates in Mn-mediated nitrogen- and oxygen-atom-transfer processes.

The generation of α-amino ketones from the reaction of silyl enol ethers with (saltmen)Mn(N) and TFAA is consistent with a mechanism which formally involves aziridination of the enol ether followed by ring opening and loss of the silyl group (Figure 4).[23] The intermediate aziridine **16** is expected to be quite labile and, as a consequence, has not been isolated in any of the reactions recorded.[24] In a related process, Evans has reported reactions of enol silanes with PhI=NTs and catalytic $CuClO_4$, the same reagent combination which furnishes aziridine products in reactions with unfunctionalized olefins such as styrene and cyclohexene.[6b,c,g] In accord with our observations, when silyl enol ethers were reacted with $CuClO_4$ and PhI=NTs, *N*-(*p*-tolylsulfonyl) α-amino ketone products were produced exclusively.[6b,g]

The amination of silyl enol ethers with (saltmen)Mn(N), as the analogous reaction of cyclooctene with (TMP)Mn(N) and TFAA (vide supra), is presumed to proceed via initial formation of a reactive *N*-(trifluoroacetyl)imido manganese species **17** (Figure 5).[7a,c,25] Subsequent transfer of the CF_3CON group to the olefin with concomitant generation of a reduced, Mn(III) complex completes this process. Groves has provided spectroscopic evidence (IR, UV−visible) which supports the formulation of an *N*-acylimido complex **18** as the first-formed product upon reaction of a solution of (TMP)Mn(N) with TFAA.[7a] The intermediate $Mn{=}NCOCF_3^+$ (**17**) is isoelectronic with the putative Mn(V)−oxo cation **19**, a highly reactive species thought to be responsible for olefin epoxidation in Mn−porphyrin- and Mn−salen-catalyzed reactions.[1a,8e,9c,26] Because of this relationship, it has been speculated that the mechanism for CF_3CON and oxygen-atom transfer to an olefin in these processes are analogous.[6i,7a,c]

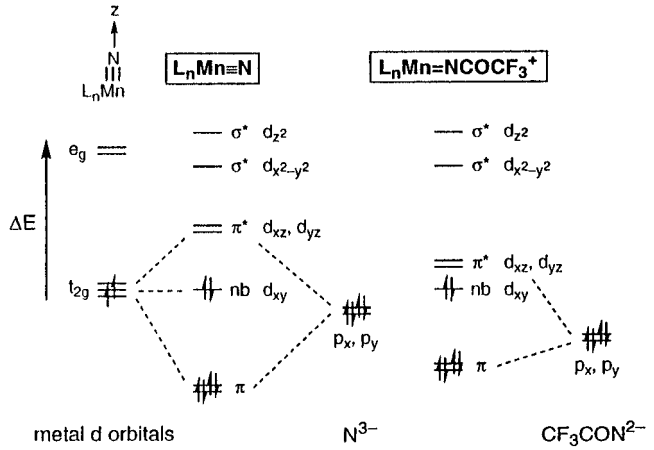


FIGURE 6. MO diagrams for nitrido 11 and imido 17 manganese complexes.

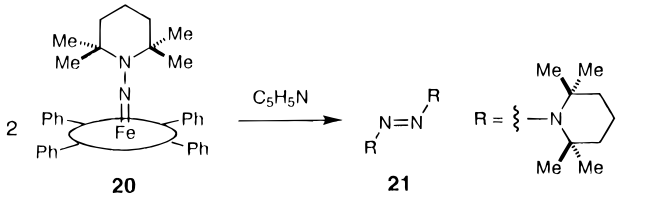
The ability of Mn≡N complexes to effect nitrogen-atom transfer when activated with TFAA may be understood from simple, qualitative molecular orbital (MO) arguments. To a first approximation, the molecular orbitals for **11** and **17** are arranged as shown in Figure 6.[27] Importantly, the t_{2g} metal orbitals together with the N^{3-} p_x and p_y MO's form a set of doubly degenerate π-bonding and π^*-antibonding orbitals (d_{xz}, d_{yz}) and a singly degenerate nonbonding orbital (d_{xy}). The d^2 valence configuration for Mn(V) requires filling the nonbonding d_{xy} MO, leaving the π^* as the lowest unoccupied MO (LUMO). *N*-Acylation of the nitrido ligand (N^{3-}) is expected to weaken its π-donor strength and to result in a lowering of the π^* manifold.[7a,c] This shift in the MO energies results in an increase in the oxidizing potential of the acylimido species **17** relative to the parent nitrido. Thus, an olefin with an appropriate reduction potential would be capable of interacting with the unoccupied π^* level, necessarily causing $Mn{=}NCOCF_3$ bond rupture and concomitant CF_3CON transfer.[8b,25,28]

Methodology for 2-Amino Sugar Synthesis

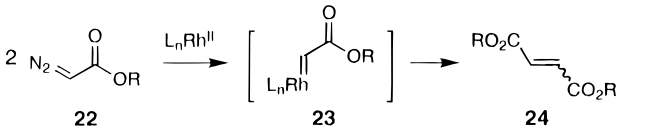
Our interest in further exploring the chemistry of these novel manganese compounds, and in finding additional applications for these reagents, provided impetus to test the reactivity of the Mn≡N systems with other olefins. We were particularly attracted to the possibility of employing these methods for nitrogen-atom transfer to glycal substrates. Amination of these carbohydrate-derived olefins with (saltmen)Mn(N) would provide a direct method for

(21) The figure shown was drawn using the SPARTAN program and is an exact representation of the X-ray crystal structure.
(22) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991; p 353.
(23) This reaction is analogous to the Rubottom epoxidation, see: Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319.
(24) A product which has been assigned as the *N*-trifluoracetylated aziridine was isolated from the reaction of (saltmen)Mn(N) (**26**) with TFAA and *p*-methoxystyrene.
(25) 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.
(26) (a) Pospisil, P.; Carsten, D. H.; Jacobsen, E. N. *Chem. Eur. J.* **1996**, *2*, 974. (b) Jacobsen, E. N.; Deng, L.; Furukawa, Y.; Martínez, L. E. *Tetrahedron* **1994**, *50*, 4323. (c) Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1988**, *110*, 8628. (d) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.
(27) (a) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.
(28) For a leading reference on the mechanism of metal−oxo transfer reactions, see: Bruice, T. C. *Aldrichim. Acta* **1988**, *21*, 87.

the preparation of 2-amino sugars.[29] Given the prevalence and importance of this saccharide structural motif in both naturally occuring and synthetic materials, a general glycal amination methodology of this type would potentially find widespread use for the preparation of such products.[28a,30] Initial attempts to aminate tri-*O*-benzylglucal using (saltmen)Mn(N) (**11,** Scheme 1) were, however, unsuccessful. The failure of this reaction was attributed to the greatly diminished reactivity of the glycal compared to unfunctionalized vinyl ethers such as dihydropyran.[31] As a result, we speculated that the reactive manganese species was being consumed in side reactions which occurred at a rate faster than the desired alkene amination step. Examination of other atom-transfer processes provides support for such a hypothesis. In this regard, Mansuy has reported the bimolecular decomposition of an Fe(II)−nitrene complex **20** to give a diazene product **21** (eq 5).[32] Similarly, dimerization of metal carbenoids **23** to give olefins **24** is a common occurrence in cyclopropanation reactions with diazo alkanes **22** (eq 6).[33] With reactive metal−oxo species



(5)



(6)

25, the formation of oxo-bridged products **26** is well-precedented and is often a highly favorable process (eq 7).[1a,34,35] It seemed reasonable, therefore, that trifluoroacetylated (saltmen)Mn(N) (**17**) could be susceptible to these types of bimolecular reactions (Figure 7). If the rates

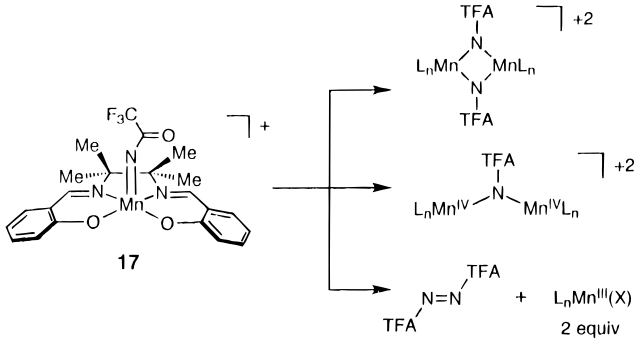


FIGURE 7. Possible bimolecular processes involving 17.

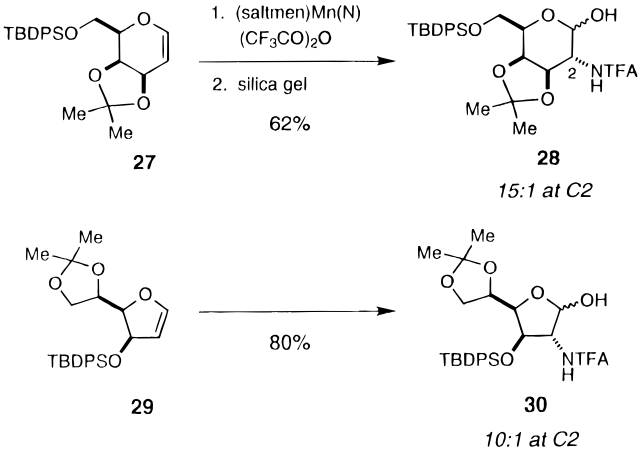
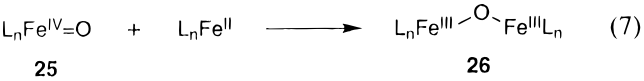


FIGURE 8. Representative examples of glycal amination reactions.

of these processes were significantly faster than the rate of alkene amination, no olefin-derived products would be expected to form.[36]



(7)

A potential solution was considered to favor the transfer of CF_3CON from nitridomanganese systems to the less reactive glycal starting materials. This approach required maintaining a high concentration of the glycal relative to the activated manganese complex **17**. Such a difference in concentration might then allow the rate of olefin amination to effectively compete with the rates of other deleterious processes. In practice, this could be accomplished by slow addition of the (saltmen)Mn(N) reagent to a solution containing both glycal and TFAA.[37]

When these conditions were implemented, successful amination of the glycals was observed (Figure 8). Both furanose and pyranose glycal starting materials (e.g., **27** and **29**) proved to be effective substrates for the reaction. The resulting *N*-trifluoroacetylated 2-amino sugars were isolated in yields consistently ranging from 60−80% and in diastereoselectivities from 6:1 → 15:1 at C2.[38] In each of these reactions, the CF_3CON group was introduced

(29) For leading references on the preparation of 2-amino sugars, see: (a) Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1380. (b) Griffith, D. A.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1996**, *118*, 9526. (c) Leblanc, Y.; Labelle, M. In *Cycloaddition Reactions in Carbohydrate Chemistry*; Giuliano, R. M., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1990; Vol. 494, p 81.

(30) (a) Danishefsky, S. J.; Roberge, J. Y. *Pure Appl. Chem.* **1995**, *67*, 1647. (b) Banoub, J.; Boullanger, P.; Lafont, D. *Chem. Rev. (Washington, D.C.)* **1992**, *92*, 1167.

(31) We have found that CF_3CON may be transferred to 3,4-dihydro-2*H*-pyran (45−50% yield) by following a previously described protocol (see ref 17). Under identical conditions, no reaction was observed when tri-*O*-benzylglucal was employed as the substrate.

(32) Mansuy, D.; Battioni, P.; Mahy, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 4487. Also, see: Mahy, J.-P.; Battioni, P.; Mansuy, D.; Fisher, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *106*, 1699.

(33) (a) Maxwell, J. L.; Brown, K. C.; Bartley, D. W.; Kodadek, T. *Science* **1992**, *256*, 1544. (b) Doyle, M. P.; Van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787 and references therein.

(34) (a) Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344 and references therein. (b) Davies, J. E.; Gatehouse, B. M. *Acta Crystallogr.* **1973**, *B29*, 1934. A μ-aza bridged Fe^{III}(salen) dimer has also been crystallographically characterized, see: Nichols, P. J.; Fallon, G. D.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1988**, *27*, 2795.

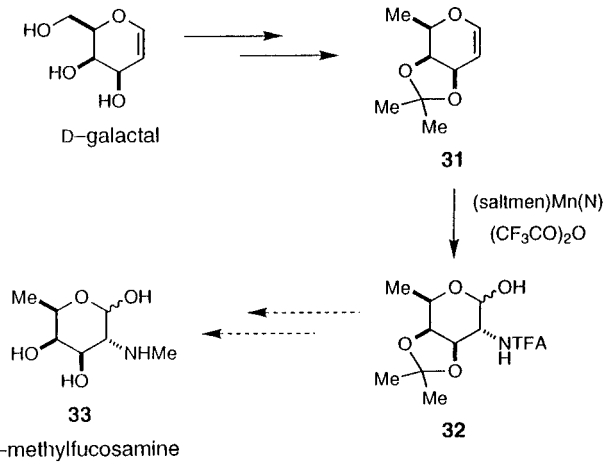
(35) μ-Oxo-bridged Mn dimers have been characterized in reactions with PhI═O, see: (a) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510. (b) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3515.

(36) This assumes that decomposition of the acylated nitrido species **17** does not occur through intramolecular processes. (a) Mahy, J.-P.; Battioni, P.; Bedi, G.; Mansuy, D.; Fisher, J.; Weiss, R.; Morgenstern-Badarau, I. *Inorg. Chem.* **1988**, *27*, 353. (b) Mahy, J.-P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079.

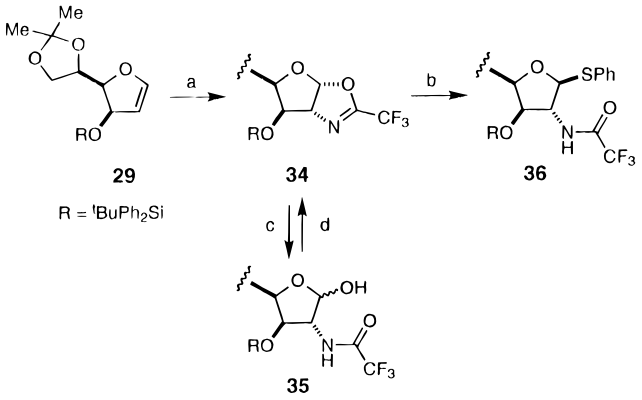
(37) An analogous, slow addition procedure is typically used for alkene cyclopropanation; see ref 32b.

(38) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 3179.

Scheme 2



Scheme 3[a]



[a] (a) (saltmen)Mn(N), $(CF_3CO)_2O$, 2,6-di-*tert*-butyl-4-methylpyridine; (b) PhSH, $BF_3{\cdot}OEt_2$; (c) aqueous AcOH, THF; (c) CH_3SO_2Cl, Et_3N, CH_2Cl_2.

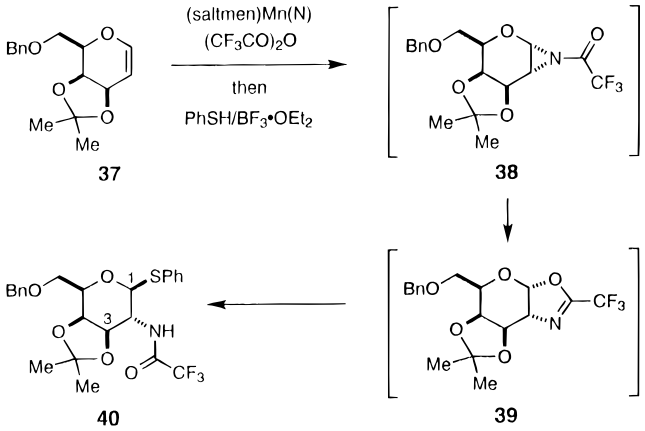
opposite the preexisting allylic stereocenter to give the 2,3-*trans* configuration.

As a demonstration of the utility of this method, we have devised an expeditious synthesis of *N*-methyl-D-fucosamine (**33**), a 2-amino monosaccharide found commonly in nature (Scheme 2). The preparation of **33** is highlighted by the single-step conversion of the protected D-fucal **31** to the *N*-trifluoroacetylated amino alcohol **32** with the (saltmen)Mn(N) system.

In accord with earlier results obtained with silyl enol ethers, we were unable to observe aziridine products when glycals were reacted with (saltmen)Mn(N) and TFAA. The possible intermediacy of an aziridine along the reaction coordinate, however, cannot be discounted as such a compound is expected to be highly reactive and susceptible to nucleophilic ring opening.[28a,b,39] In an effort to elucidate the mechanistic course of this reaction, we have characterized a stable furanose-derived oxazoline intermediate **34** (Scheme 3). This oxazoline is readily hydrolyzed with aqueous AcOH to give alcohol **35**. In addition, **34** can be reacted with thiophenol (PhSH) in the presence of $BF_3{\cdot}OEt_2$ to provide, exclusively, *trans*-phenylthioglycoside **36** (80%). We have demonstrated that amide alcohol **35** may be converted to the oxazoline upon treatment with methanesulfonyl chloride, thus providing

(39) *N*-Carbomethoxy aziridines generated from glycals have been shown to react with alcohols to give methyl glycoside products, see: Kozlowska-Gramsz, E.; Descotes, G. *Can. J. Chem.* **1982**, *60*, 558.

Scheme 4



further confirmation of the structural assignment of **34**. For the six-membered ring glycals, both the putative aziridine and oxazoline products have eluded isolation, but evidence for the formation of either of these structures under the reaction conditions has been procured. To this end, amination of glycal **37** was performed and an electrophilic intermediate intercepted in situ with PhSH (Scheme 4). The resulting thioglycoside **40** was isolated solely as the β-epimer with *trans* 1,2 stereochemistry. Generation of **40** supports the intervention of either an aziridine **38** or an oxazoline **39** in this reaction sequence. The isolation of **34** (described above) would seem to suggest that oxazoline **39** is serving as the glycosyl donor in this coupling reaction with PhSH but does not, however, preclude formation of aziridine **38**.

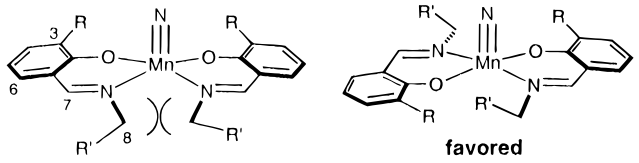
Second-Generation Nitridomanganese(V) Complexes

Our interest in constructing new nitridomanganese complexes was fueled by a desire to find systems capable of performing nitrogen-atom transfer to additional substrates. Ideally, these new complexes would be unable to participate in deleterious bimolecular reactions, thereby obviating the need for a slow addition procedure. To address this issue, we considered developing ligands which would provide a pocket or picket fence for the Mn≡N moiety.[40] Bidentate Schiff base ligands, H−^{3}R−sal−R′,[41] prepared from substituted salicylaldehydes and primary amines, were chosen because of their accessibility and their amenability to numerous structural and electronic modifications (Figure 9).[42] Importantly, molecular models indicated that the imine donors in these complexes would be disposed *trans* to one another to avoid an unfavorable steric interaction (Figure 9). The conformational degrees of freedom about the N_{imine}−C8 and C8−R′ bonds could be restricted by substitution at the 3-position on each aryl ring (R ≠ H). It was hoped that

(40) A similar strategy has been successfully employed to inhibit the dimerization reaction of metal−oxo species, see: (a) Momenteau, M.; Reed, C. A. *Chem. Rev. (Washington, D.C.)* **1994**, *94*, 659. (b) Collman, J. P.; Gagne, R. R.; Halbert, T. R.; Marchon, J.-C.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 7868.

(41) H−3R−sal−R′ is used to designate substitution on the salicylimine, as shown in Figure 9.

(42) For elegant studies of electronic tuning in metal catalysts, see: (a) Jacobsen, E. N.; Zhang, W.; Güler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703. (b) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.



steric interaction disfavors cis configuration

FIGURE 9. Non-covalent interactions bias ligand orientation.

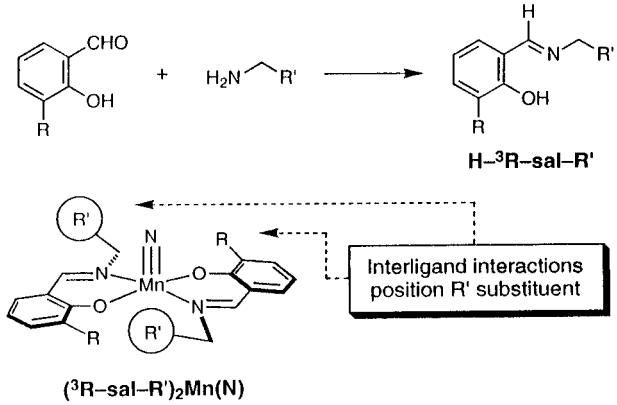
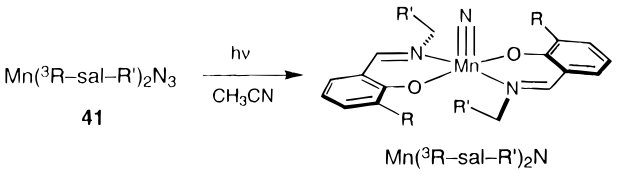


FIGURE 10. Readily prepared Schiff base ligands with "picket-fence"construction.

such interligand, noncovalent interactions would serve as a conformational lock to define a picket-fence arrangement around the nitrido unit (Figure 10). This approach was based largely on elegant work by Still, which demonstrated the use of intramolecular steric "ratcheting" to reduce conformational heterogeneity in acyclic receptor molecules.[43] A particularly attractive feature of this strategy was that it avoided lengthy ligand syntheses which would otherwise be needed to generate fixed picket-fence ligand systems.

An initial synthetic plan for the generation of Schiff base-derived nitrido complexes (^{3}R−sal−R′)$_2$Mn(N) (**43**) was employed which involved the photochemical extrusion of dinitrogen from the corresponding Mn(III) azide starting materials **41** (eq 8).[44] Although formation of small



(8)

quantities (5−10 mg) of the nitrido species were possible under these conditions, a more efficient preparative method was desirable. Attempts to form nitrido Mn(V) derivatives of (^{3}R−sal−R′)$_2$Mn(X) (X = OAc, Cl, N_3) using NH_4OH and Clorox bleach were, however, entirely unsuccessful. We assumed that the labile Mn(III) starting materials were not capable of withstanding such strongly alkaline (pH = 14) and oxidizing reaction conditions.

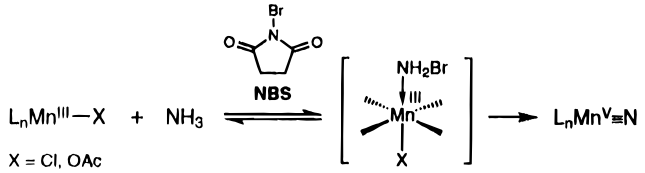


FIGURE 11. Putative mechanism for Mn≡N formation with NH_3 and *N*-bromosuccinimide.

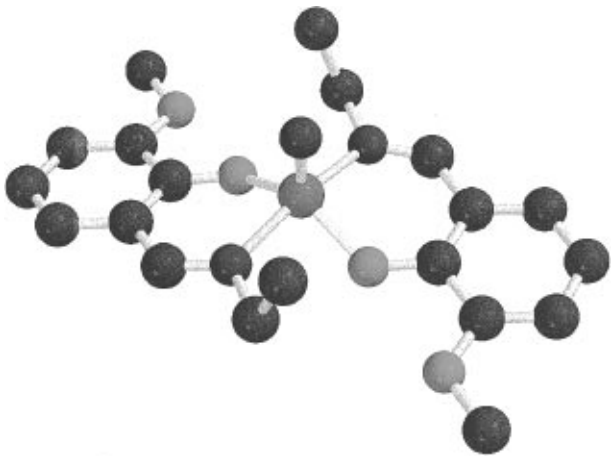
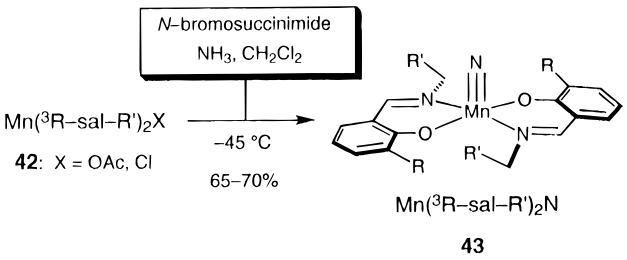


FIGURE 12. Drawing of the X-ray structure of (^{3}MeO−sal−Me)$_2$Mn(N) (44).[20]

Fortunately, it was discovered that preparation of (^{3}R−sal−R′)$_2$Mn(N) (**43**) from (^{3}R−sal−R′)$_2$Mn(X) (**42**) (X = OAc, Cl) could be effected using gaseous NH_3 and the commodity chemical *N*-bromosuccinimide (eq 9).[45] We



(9)

speculated that this reaction occurred through an oxidative dehydrogenation mechanism involving a Mn-coordinated bromamine (NH_2Br) intermediate (Figure 11).[10c,46] In support of this hypothesis, it was found that other halogenating agents including *tert*-butyl hypochlorite (*t*-BuOCl) and *N*-bromoacetamide ($CH_3CONHBr$) could also be employed as oxidants in this process. By following this new protocol, (^{3}R−sal−R′)$_2$Mn(N) were readily accessed in yields of 65−70%.[47]

Schiff base-derived nitridomanganese complexes (^{3}MeO−sal−Me)$_2$Mn(N) (**44**) and (^{3}Ph−sal−Ph)$_2$Mn(N) (**45**) have been prepared using NH_3 and NBS, and their stuctures unambiguously established by single-crystal X-ray diffraction (Figures 12 and 13). Nitrides **44** and **45** are representative of only a few crystallographically char-

(43) (a) Wang, X.; Erickson, S. D.; Iimori, T.; Still, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 4128. (b) Iimori, T.; Still, W. C.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 3439.

(44) For a comprehensive review on the preparation and characterization of transition-metal nitrido complexes, see: (a) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955.

(45) PhI=O and Cl_2 have also been employed; see refs 10b and 11, respectively.

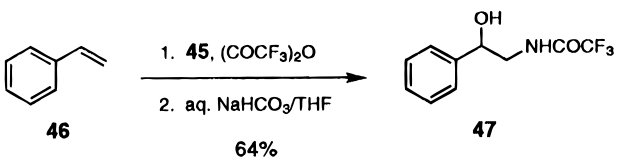
(46) Clemens, D. F.; Woodford, W.; Dellinger, E.; Tyndall, Z. *Inorg. Chem.* **1969**, *8*, 998.

(47) We have recently communicated this work, see: Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M.; Day M. W. *Angew. Chem.* **1997**, *109*, 1772.

FIGURE 13. Drawing of the X-ray structure of (^{3}Ph−sal−Ph)$_2$Mn(N) (45).[20]

acterized Mn(V) compounds.[10,17,19,48] In **44**, the formation of a metal−nitrogen triple bond is confirmed by an observed Mn≡N distance of 1.54 Å and a Mn≡N infrared stretch of 1047 cm^{-1}, both of which compare favorably with analogous data for known porphyrin and salen adducts.[7,10,17] Importantly, this structure shows the nitrido moiety tucked between each of the N_{imine}−Et groups, illustrative of the type of structural topography which was desired. To examine the effect of varying the steric environment about the Mn≡N unit (^{3}Ph−sal−Ph)$_2$Mn(N) (**45**) was designed and synthesized. The X-ray structure of **45** is similar to that of **44** in two regards: (1) the ligand configuration about the Mn center and (2) the distorted trigonal bipyramidal Mn coordination geometry.[49] One apparent difference between **44** and **45**, however, is that the benzyl groups in **45** are not symmetrically disposed about the nitrido ligand, suggesting that the N_{imine}−CH_2 bond has some degree of flexibility. Further optimization of the ligand system is expected to increase the conformational homogeneity in these complexes and to furnish the desired picket-fence nitridomanganese structures.

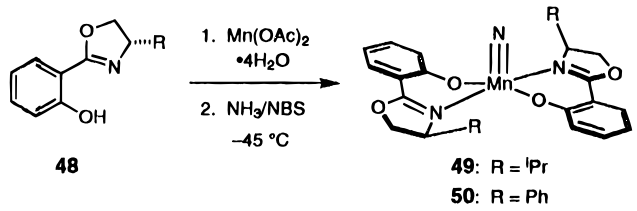
Bidentate Schiff base nitridomanganese complexes have been tested for their efficacy as nitrogen-atom-transfer agents. In this regard, (^{3}Ph−sal−Ph)$_2$Mn(N) (**45**) was added to a solution containing both TFAA and a *single* equivalent of styrene (**46**) to give the *N*-trifluoroacetyl amino alcohol **47** in an exceptional 64% yield (eq 10). The amination of styrene with a nitridomanganese reagent is unprecedented, and serves as a demonstration of the potential of these systems as reagents for olefin amination.[7a,c]



46 *1 equiv* — **47** — 64%

(10)

With the discovery of a new, mild method for Mn≡N bond formation, it has been possible to prepare chiral



48

FIGURE 14. First-generation chiral nitridomanganese reagents.

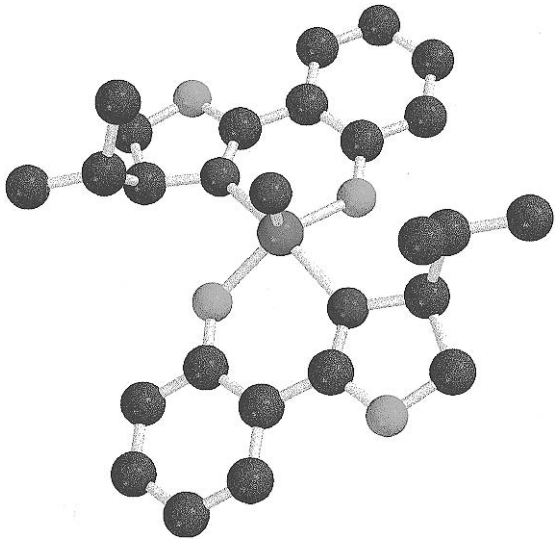


FIGURE 15. Drawing of the X-ray structure of oxazoline−Mn≡N 49.[20]

nitridomanganese complexes **49** and **50** (Figure 14) from readily available, optically active bidentate oxazoline ligands **48**.[50] The X-ray crystal structure of one of these compounds, **49**, has been solved (Figure 15) and reveals certain features in common to those of (^{3}MeO−sal−Me)$_2$Mn(N) (**44**) and (^{3}Ph−sal−Ph)$_2$Mn(N) (**45**). These include both Mn≡N bond length (1.50 Å) and Mn coordination geometry (distorted trigonal bipyramid). The successful construction of these systems highlights the utility of the NH_3/NBS protocol and suggests that additional nitrido complexes with unique structures and reactivities will be accessible. Moreover, these chiral Mn nitrides afford the opportunity to address mechanistic issues regarding the transfer of CF_3CON as it relates to ligand morphology and product stereoselectivity.

Conclusion

Nitridomanganese(V) complexes have been prepared and demonstrated to function effectively as reagents for alkene amination. These results attest to the fact that nitrogen transfer is not exclusive to porphyrin or salen systems and can be achieved using simple, easily constructed Mn≡N coordination complexes. A pivotal part of this research has been the development of a new protocol for the oxidative conversion of Mn(III) precursors to the desired nitrido Mn(V) products. Application of this methodology has made possible the preparation of several novel Mn nitrides, including complexes derived from bidentate

(48) (a) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899.

(49) The crystals of **45** produced weak data which prevented complete refinement of this structure. However, the overall structure is confirmed.

(50) For the synthesis of these ligands, see: Bolm, C.; Wieckhardt, K.; Zehnder, M.; Glasmacher, D. *Helv. Chim. Acta* **1991**, *74*, 717.

Schiff base and chiral oxazoline ligands. This latter class of compounds has potential use as asymmetric olefin amination reagents and as important probes for mechanistic investigations. Further elaboration of the chemistry described, herein, is expected to yield additional nitridometal reagents with uniquely designed ligand systems. It is hoped that such efforts will ultimately furnish complexes capable of performing nitrogen-atom transfer to substrates of all types.

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