Facile N···N Coupling of Manganese(V) Imido Species

Shek-Man Yiu, William W. Y. Lam, Chi-Ming Ho, and Tai-Chu Lau*

Contribution from the Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong, China

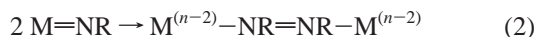Received September 6, 2006; E-mail: bhtclau@cityu.edu.hk

Abstract: (Salen)manganese(V) nitrido species are activated by electrophiles such as trifluoroacetic anhydride (TFAA) or trifluoroacetic acid (TFA) to produce N_2. Mechanistic studies suggest that the manganese(V) nitrido species first react with TFAA or TFA to produce an imido species, which then undergoes N···N coupling. It is proposed that the resulting manganese(III) μ-diazene species decomposes via internal redox to give N_2 and manganese(II). The manganese(II) species is then rapidly oxidized by manganese(V) imide to give manganese(III) and CF_3CONH_2 (for TFAA) or NH_3 (for TFA).

Introduction

N···N coupling between metal nitrides (eq 1), which involves a three-electron change between each metal and nitrogen, is of fundamental interest.

$$2\ M\equiv N \rightarrow M^{(n-3)}-N\equiv N-M^{(n-3)} \qquad (1)$$

The factors that control the kinetics of this coupling reaction would also be relevant to the reverse dinitrogen cleavage process. Coupling between metal nitrides has been reported for that of osmium,[1-3] ruthenium,[4] and iron;[5] a heterocoupling reaction between Os≡N and Mo≡N has also been observed.[6] In contrast, the analogous coupling reaction for metal imides (eq 2) has yet to be demonstrated.

$$2\ M=NR \rightarrow M^{(n-2)}-NR=NR-M^{(n-2)} \qquad (2)$$

In principle, imide coupling should also be a feasible process, at least for R groups and ancillary ligands that are small enough so that steric effects are not a problem. We report here kinetic and mechanistic studies of N···N coupling reaction of (salen)-manganese(V) imido species, which are generated from reaction of the corresponding nitrido species with electrophiles such as trifluoroacetic anhydride (TFAA) or trifluoroacetic acid (TFA). Manganese(V) nitrido complexes containing porphyrin and salen ligands have received much attention in recent years because of their use as amination reagents.[7-12] In the presence of electrophiles such as TFAA or TFA, these nitrido complexes are converted to the corresponding imido species, which can

transfer the imido group to electron rich alkenes. However, very often a high concentration of the substrate relative to the active manganese species is required for these amination reactions, and it has been suggested that the reactive manganese(V) imido species may be consumed in various side reactions.[9d] Indeed, we observed that in the absence of organic substrates, these (salen)manganese(V) imido species undergo a clean N···N coupling reaction.

The following manganese nitrido complexes were investigated:

1   **2**

3   **4**
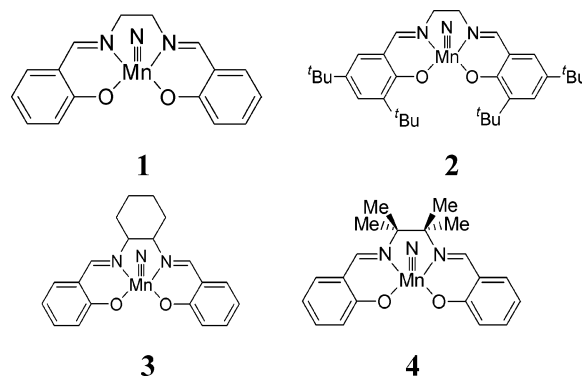
Experimental Section

Materials. All chemicals were of reagent grade unless otherwise noted. (Salen)manganese(V) nitrido complexes were synthesized according to a literature method.[9a] The Schiff base ligands were prepared

(1) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605−4610.
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(11) Svenstrup, N.; Bøgevig, A.; Hazell, R. G.; Jørgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, *11*,1559−1566.
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by reacting the diamine with two equivalents of the corresponding salicylaldehyde in ethanol. Dichloromethane, 1,2-dichloroethane, acetonitrile, acetone, tetrabutylammonium hexafluorophosphate, and *trans*-β-methylstyrene were of reagent grade and were further purified according to standard methods.[13] Trifluoroacetic acid, trifluoroacetic anhydride, 1,2-diaminoethane, 1,2-diaminocyclohexane, 3,5-*tert*-butylsalicylaldehyde, salicylaldehyde, and manganese(II) acetate tetrahydrate were obtained from Aldrich and were used as received. 2,3-Diamino-2,3-dimethylbutane was synthesized according to a literature procedure.[14]

Instrumentation. Gas chromatographic analyses were performed on a HP 6890 gas chromatograph equipped with a HP-5MS (30 m × 0.25 mm i.d.), a HP-FFAP (25 m × 0.2 mm i.d.), a molsieve 5A (25 m × 0.32 mm i.d.) or a Carboplot (25 m × 0.53 mm i.d.) column. GC-MS measurements were carried out on a HP 6890 gas chromatograph interfaced to a HP 5973 mass selective detector. Kinetic experiments were performed by using either a Hewlett-Packard 8452A diode array spectrophotometer or an Applied Photophysics DX-17MV stopped-flow spectrophotometer. Electrospray ionization mass spectrometry (ESI/MS) was performed on a PE SCIEX API 365 mass spectrometer. The samples were continuously infused with a syringe pump at a constant flow rate of 5 μL min^{-1} into the pneumatically assisted electrospray probe with nitrogen as the nebulizing gas. ^{1}H NMR spectra were recorded on a Varian (300 MHz) FT NMR spectrometer. Elemental analyses were done on an Elementar Vario EL Analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet Avatar 360 FTIR spectrophotometer. Ion chromatographic analyses were performed on a Dionex LC 20 ion chromatograph equipped with a GP 40 gradient pump, a Dionex IonPac CS12A analytical column (4 mm × 250 mm) and a Dionex ED 40 electrochemical detector. Suppression of the eluent was achieved with a Dionex cation CSRS ULTRA II self-regenerating suppressor (4 mm).

Procedure for N···N Coupling Reactions. Isolation and Analysis of Products. All experiments were carried out under argon, unless otherwise specified. TFAA/TFA was added using an airtight syringe to a green solution of (salen)manganese(V) nitrido complex dissolved in a solvent. The reaction temperature was maintained by a water bath. The volume of the gas produced was measured using a gas burette. The gas was analyzed by GC and GC/MS.

Mn^{2+} and NH$_4^+$ were analyzed by ion chromatography after extraction with water. Trifluoroacetamide and aziridines were analyzed by GC and GC/MS.

The manganese product after N···N coupling reaction of [Mn^V(N)(^{t}-Bu$_4$salen)] (**2**) was isolated by the following procedure. The reaction mixture was filtered and the filtrate was evaporated to dryness under vacuum at room temperature. The residue was purified by column chromatography using silica gel (CH$_2$Cl$_2$/acetone) and recrystallized from methanol/water to give [Mn^{III}(^{t}Bu$_4$salen)CF$_3$CO$_2$]·CH$_3$OH as a brown crystalline solid. Anal. Calcd for C$_{35}$H$_{50}$N$_2$O$_5$F$_3$Mn: C, 60.86; H, 7.29; N, 4.06. Found: C, 60.55; H, 7.25; N, 4.19.

The amount of carbon monoxide produced after N···N coupling reaction was detected by the following procedure. TFAA (0.75 mmol) was added into a green solution of **2** (0.15 mmol) in 1,2-dichloroethane (3 mL) in a 10 mL reaction vessel equipped with a septum at 22 °C in air. After 5 min, 50 μL of gas was withdrawn from the head space of the reaction vessel using a gastight syringe and then analyzed by GC/MS and GC/TCD.

Kinetics. The kinetics of the coupling reaction was monitored by using a HP 8452A diode array spectrophotometer. The *formation* of the intermediate was monitored at 370 nm under pseudo-first-order conditions with the concentration of TFAA in at least 10-fold excess of that of **2**. Ionic strength was maintained with ^{n}Bu$_4$NPF$_6$. The reaction follows first-order kinetics, and the pseudo-first-order rate constant,

Table 1. TFAA-Activated N···N Coupling of (Salen)manganese(V) Nitrido Complexes^a

compound	% yield of N$_2$^{b}	reaction time (min)
1	73 ± 2	35
2	72 ± 2	5
3	53 ± 2	45
4	0	−

^{a} Reaction conditions: Mn^V(N), 0.25 mmol; TFAA, 1.25 mmol; 1,2-dichloroethane, 10 mL; T = 0 °C. ^{b} Percent yield of N$_2$ was calculated by assuming 2 mol of Mn^V(N) produce 1 mol of N$_2$.

k_{obs}, was obtained by nonlinear least-squares fits of A_t to time t according to the equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively. The *decay* of the intermediate was also monitored at 370 nm, however it appears to be biphasic. The method of initial rate was applied to determine the order of the reaction according to the equation $A = a_0 + a_1t + a_2t^2 + ... + a_9t^9$.[15]

The kinetics of the aziridination of *trans*-β-methylstyrene by [Mn^V(N)(^{t}Bu$_4$salen)] in the presence of TFAA were studied by using an Applied Photophysics DX-17MV stopped-flow spectrophotometer. The concentration of *trans*-β-methylstyrene (0.1 to 0.8 M) was in large excess of [Mn^V(N)(^{t}Bu$_4$salen)] (8 × 10^{-5} M). The reaction progress was monitored by observing absorbance changes at 370 nm.

Results and Discussion

1. TFAA-Activated N···N Coupling of (Salen)manganese-(V) Nitrido Complexes. 1.1. Products and Stoichiometry. [Mn^V(N)(salen)] (**1**) is stable for weeks in common organic solvents at room temperature. However, when 5 equiv of TFAA were added to a suspension of **1** in 1,2-dichloroethane under argon at room temperature, the green solid gradually dissolved to give a dark brown solution and gas bubbles could be seen. The gas evolved was determined to be N$_2$ by GC and GC/MS. When the 98% ^{15}N-labeled complex [Mn^V(^{15}N)(salen)] was used, the gas evolved was found to be a mixture of ^{14}N^{15}N and ^{15}N$_2$ in the ratio of 1:20, indicating that both N atoms come from Mn^V≡N. These observations are consistent with a N···N coupling reaction of **1** upon activation by TFAA. This coupling reaction also occurs with other (salen)manganese(V) nitrido species. The results in Table 1 show that introducing *tert*-butyl groups on 3- and 5- positions of salen does not affect the coupling reaction. The longer reaction time for **1** than **2** is probably due mainly to its low solubility in ClCH$_2$CH$_2$Cl. On the other hand, the cyclohexylene-bridged salen complex **3** gives a lower yield and a slower rate. Moreover, addition of TFAA to a dark-green solution of [Mn^V(N)(saltmen)] (**4**) did not result in any color change nor formation of gas bubbles, indicating that N···N coupling does not occur readily for this nitrido species. The dark-green solution eventually turned brown after several days. Simple molecular modeling (Chem3D) shows that there are little steric effects to N···N coupling by *tert*-butyl groups in the aromatic rings but there can be substantial effects from substituents in the ethylene bridge, which are closer to the nitrido moiety.

Among the complexes **1**−**4**, [Mn^V(N)(^{t}Bu$_4$salen)] (**2**) was used to study the coupling reaction in detail because of its good solubility in various organic solvents. Because the only gas detected by GC and GC/MS is N$_2$ with a yield of 72%, attempts

(13) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.
(14) Sayre, R. *J. Am. Chem. Soc.* **1955**, *77*, 6689−6690.

(15) (a) Lee, D. G.; Lee, E. J.; Chandler, W. D. *J. Org. Chem.* **1985**, *50*, 4306−4309. (b) Chandler, W. D.; Lee, E. J.; Lee, D. G. *J. Chem. Ed.* **1987**, *64*, 878−881.
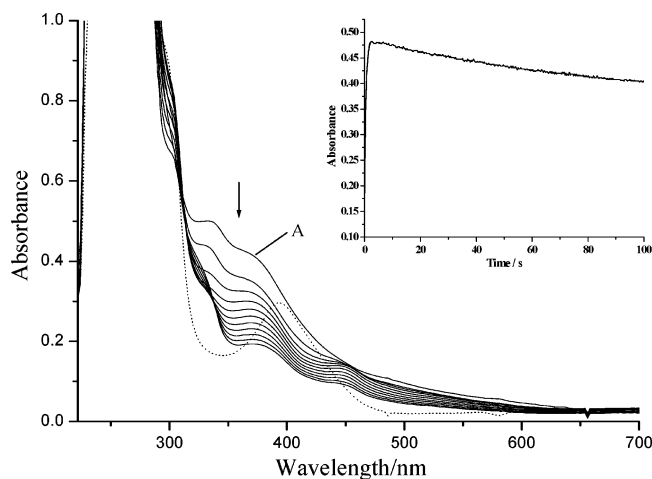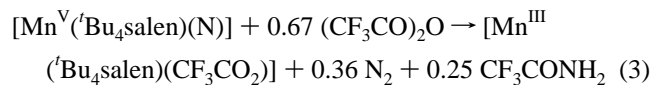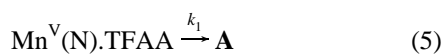
Figure 1. Spectral changes at 288-s intervals for the reaction between **2** (4 × 10⁻⁵ M) and TFAA (0.1 M) in ClCH₂CH₂Cl at 298.0 K and $I =$ 0.1 M. (Dotted line is the spectrum before adding TFAA.) (Insert) Kinetic trace at 370 nm.

were made to search for the remaining 28% nitrogen atoms in the solution. Analysis of the organic products in the reaction mixture by GC and GC/MS showed the presence of (25 ± 2)% of CF₃CONH₂, thus the mass balance for nitrogen is 97 ± 2%. Also, it was found that (67 ± 2)% of TFAA was consumed in the reaction. The yields are based on the number of moles of **2** used. There is no difference in the yields between reactions performed under argon or in air. From the reaction mixture, [Mn^{III}(ᵗBu₄salen)(CF₃CO₂)] was isolated in 93 ± 2% yield. The net result as observed experimentally is represented by eq 3, which is not balanced.

$$[Mn^V(^tBu_4salen)(N)] + 0.67\,(CF_3CO)_2O \rightarrow [Mn^{III}$$

$$(^tBu_4salen)(CF_3CO_2)] + 0.36\,N_2 + 0.25\,CF_3CONH_2 \quad (3)$$

1.2 Kinetic Studies. The kinetics of the coupling reaction were investigated by UV/vis spectrophotometry. Repetitive scanning of the UV/vis spectrum of a solution of **2** and TFAA in ClCH₂CH₂Cl at 298.0 K revealed the rapid formation of an intermediate (**A**) with λ_{max} at 334 and 370 nm, which then slowly decayed (Figure 1). The maximum absorbance for **A** is the same for [TFAA] ranging from 0.025 to 0.1 M, suggesting that the formation of **A** is quantitative at these TFAA concentrations.

The formation of **A** was monitored at 370 nm, and it was found to follow pseudo-first-order kinetics. The pseudo-first-order rate constant (k_{obs}) is independent of ionic strength (0.01–0.1 M) but increases with [TFAA], and kinetic saturation occurs at [TFAA] > 0.1 M (Figure 2). The plot of $1/k_{obs}$ vs $1/$[TFAA] is linear, this is consistent with a preassociation step prior to the formation of the intermediate **A** as shown in eq 4 and eq 5; the rate law is shown in eq 6. A nonlinear least-squares fit of the data to eq 6 gives $k_1 = (6.4 ± 0.3)$ s⁻¹ and $K_f = (36 ± 5)$ M⁻¹ at 298.0 K.

$$Mn^V(N) + TFAA \underset{}{\overset{K_f}{\rightleftharpoons}} Mn^V(N).TFAA \quad (4)$$

$$Mn^V(N).TFAA \xrightarrow{k_1} \mathbf{A} \quad (5)$$

$$-\frac{d[Mn^V(N)]}{dt} = k_{obs}[Mn^V(N)] = \frac{k_1K_f[TFAA]}{1 + K_f[TFAA]}[Mn^V(N)] \quad (6)$$

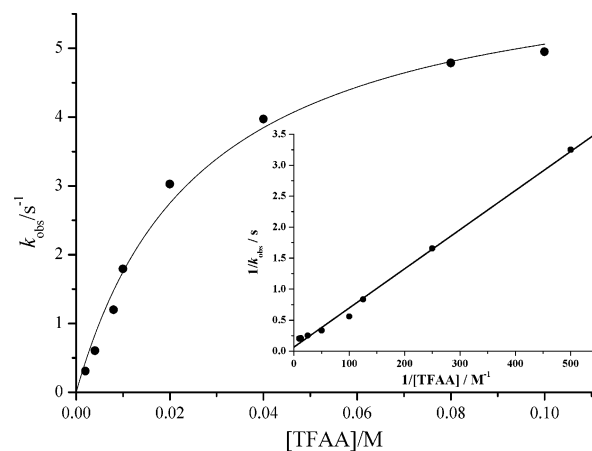**Figure 2.** Plot of k_{obs} vs [TFAA] for the formation of the intermediate (**A**) between **2** (2 × 10⁻⁴ M) and TFAA in ClCH₂CH₂Cl at 298.0 K and $I =$ 0.1 M. (Insert) Corresponding plot of $1/k_{obs}$ vs $1/$[TFAA] (slope = (6.32 ± 0.17) × 10⁻³; *y*-intercept = (6.46 ± 3.48) × 10⁻²; $r = 0.998$).
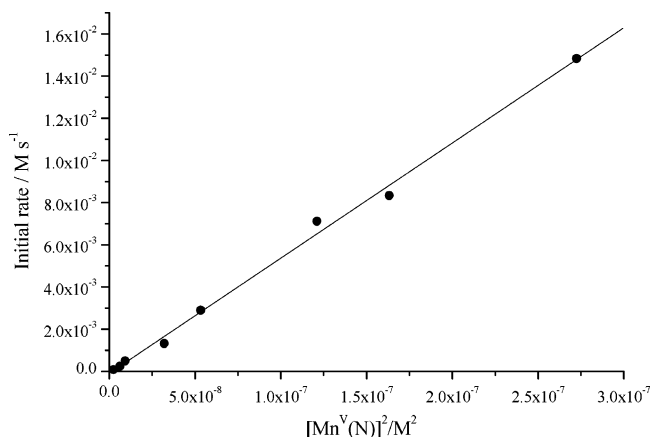
Figure 3. Plot of initial rate vs [Mn^V(N)]² for the reaction between **2** and TFAA (0.10 M) in ClCH₂CH₂Cl at 298.0 K and $I =$ 0.1 M (slope = (5.46 ± 0.15) × 10⁴; *y*-intercept = −(0.95 ± 1.66) × 10⁻⁴; $r = 0.998$).

On the other hand, the decay of the intermediate **A** appears to be biphasic; spectral changes show an isosbestic point at 312 nm for approximately the first half-life of the decay, which shifts to 313 and 338 nm on further reaction. The final spectrum is similar to that of [Mn^{III}(ᵗBu₄salen)(CF₃CO₂)]. The first phase of the decay does not obey first-order kinetics, and the method of initial rates was used to determine the order of the reaction.[15] A plot of initial rate against [Mn^V(N)]² ([Mn^V(N)] = 5 × 10⁻⁵ − 5 × 10⁻⁴ M) gives a straight line (Figure 3), indicating a second-order rate law:

$$-\frac{d[\mathbf{A}]}{dt} = 2k_2[Mn^V(N)]^2 = 2k_2[\mathbf{A}]^2 \quad (7)$$

The [Mn^V(N)] is taken as equal to [**A**] because the formation of **A** from Mn^V(N) is quantitative. At 298.0 K, [TFAA] = 0.10 M, $I =$ 0.1 M, and k_2 is found to be (2.7 ± 0.2) × 10⁴ M⁻¹ s⁻¹. k_2 is independent of ionic strength ($I = 0 − 0.1$ M). The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, obtained from the plot of ln (k_2/T) vs $1/T$, are found to be 6.9 ± 0.4 kcal mol⁻¹ and −(15 ± 1) cal K⁻¹ mol⁻¹ respectively at [TFAA] = 0.10 M.

The effect of [TFAA] on the initial rate has also been investigated (Figure 4). There is a slight increase in initial rate on increasing the concentration of TFAA from 2 × 10⁻² to 3 × 10⁻¹ M; this is probably due to medium effects.

1.3. N···N Coupling vs Aziridination. To gain more insight into the nature of the intermediate **A**, the kinetics of the coupling reaction were carried out in the presence of *trans-β*-methylstyrene (0.1−0.8 M). The same intermediate **A** was observed and the rate constant for the appearance of this intermediate is the same as in the absence of the alkene. However, the decay of the intermediate **A** is first order in **A** when an excess of the olefin is used (Figure 5). The pseudo-first-order rate constant depends linearly on [*trans-β*-methylstyrene], and the second-order rate constant is $(7.74 \pm 0.03) \times 10$ M^{-1} s^{-1} at 298.0 K (Figure 5). The product was also analyzed by GC and GC/MS and it was found that the corresponding *N*-trifluoroacetyl aziridine was formed in 80% yield (based on **2**). These results strongly suggest that **A** is an imido species, which is capable of transferring the imido group to an alkene. At [*trans-β*-methylstyrene] < 0.1 M, however, clean pseudo-first-order kinetics were not observed, suggesting that N···N coupling is competing with aziridination, as illustrated in Scheme 1**1.4. Mechanism of N···N Coupling.** On the basis of the above experimental results, a proposed mechanism for the coupling reaction is shown in eqs 8−11; the overall reaction is represented by eq 12.

$$(8)$$

$$(9)$$

$$(10)$$

$$(11)$$

$$(12)$$
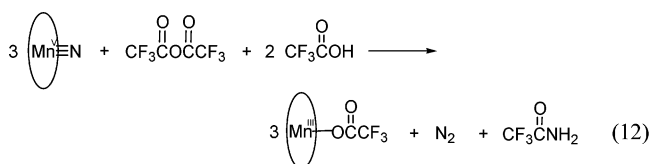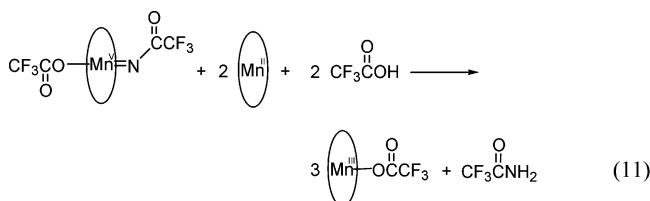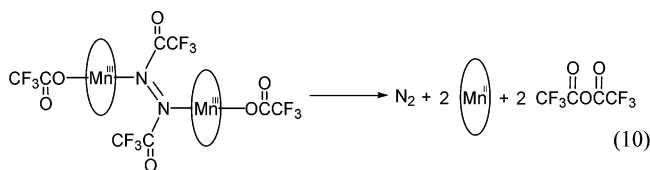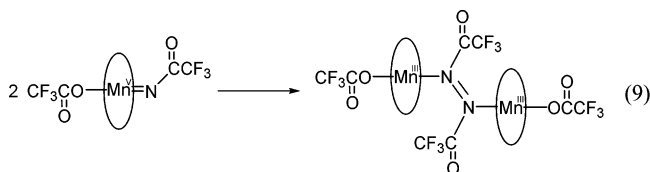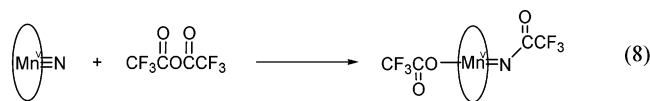
The first step (eq 8) is the reaction of **2** with TFAA to produce an imido species (**A**) Mn^V=$NCOCF_3$; this is supported by its ability to react with an alkene to produce an aziridine.

The next step (eq 9) is coupling of the imido species to produce a manganese(III) *μ*-diazene species. This is supported by a rate law that is second order in the imido species. Although a second-order rate law is also consistent with nitrido−imido
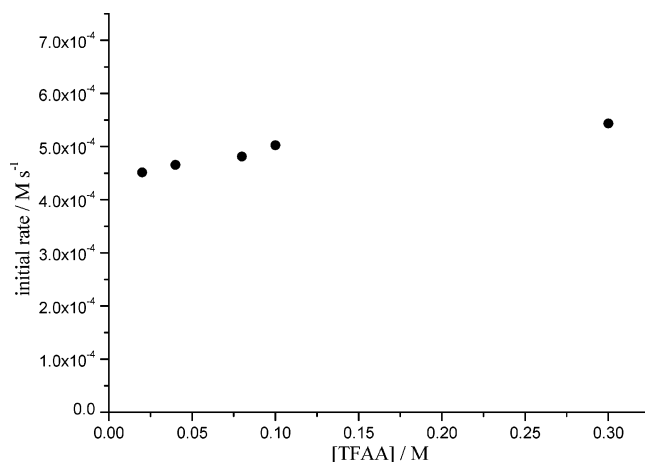

Figure 4. Plot of initial rate vs [TFAA]. [**2**] = $(9.84 \times 10^{-5}$ M) in $ClCH_2CH_2Cl$ at 298.0 K and $I = 0.1$ M.
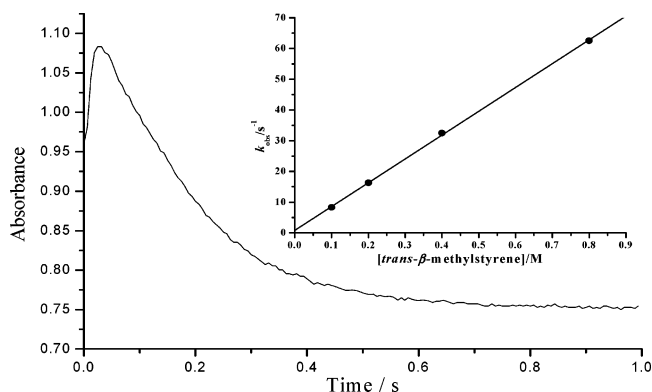

Figure 5. Absorbance change vs time trace at 370 nm during the reaction of **2** (8×10^{-5} M) with *trans-β*-methylstyrene (0.1 M) in the presence of TFAA (0.1 M) at 298.0 K in $ClCH_2CH_2Cl$. (Insert) Plot of k_{obs} vs [*trans-β*-methylstyrene].

coupling, this pathway can be neglected. UV/vis spectral studies suggest that formation of the imido species is quantitative at the TFAA concentrations used in our studies. Moreover the rate of the coupling reaction is insensitive to [TFAA] (0.02−0.3 M), which is consistent with an imido−imido coupling process. For nitrido−imido coupling a bell-shape relationship between rate and [TFAA] is expected, since the amount of TFAA governs the relative amounts of nitride and imide in the solution.

Imido coupling should produce initially a manganese(III) *μ*-diazene species, however, attempts to detect such a species by various techniques including mass spectrometry were unsuccessful. Because N_2 is produced immediately after addition of TFAA to Mn^V≡N without an induction period, it is reasonable to assume that the manganese(III) *μ*-diazene species rapidly decomposes via intramolecular electron transfer according to eq 10. A two-electron oxidation of CF_3CON=$NCOCF_3$ would produce N_2 and 2 mol of CF_3CO^+; the latter species would be highly unstable. Thus, it is proposed that the reaction is initiated by nucleophilic attack of $CF_3CO_2^-$ on coordinated CF_3CON=$NCOCF_3$, which would produce N_2 and 2 mol of TFAA. Production of TFAA would also satisfy the experimental stoichiometry of the reaction. Apart from internal redox, prior dissociation of coordinated CF_3CON=$NCOCF_3$ to give free diazene followed by intermolecular electron transfer is also a possibility. Free CF_3CON=$NCOCF_3$ is known to be unstable

Scheme 1
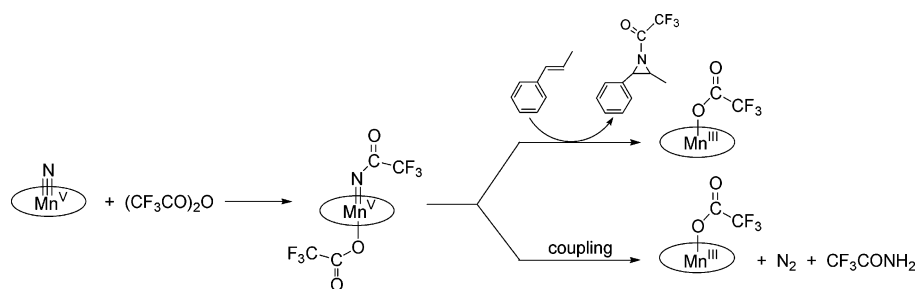
Table 2. TFA-Activated N···N Coupling of (Salen)manganese(V) Nitrido Complexes[a]

compound	% yield of N$_2$[b]	reaction time (min)
1	93 ± 2	30
2	72 ± 2	3
3	58 ± 2	40
4	35 ± 2	90

[a] Reaction conditions: Mn^V(N), 0.25 mmol; TFA, 1.25 mmol; 1,2-dichloroethane, 10 mL; $T = 22$ °C. [b] Percent yield of N$_2$ was calculated by assuming 2 mol of Mn^V(N) produce 1 mol of N$_2$.

and decomposes to give C$_2$F$_6$, CO, and N$_2$.[16] By using GC/MS and GC/TCD, 0.4 ± 0.1 mol % of CO was detected in the head space of the reaction vessel (the yield was calculated based on the amount of Mn^V≡N). Although this is a very small amount, it is reproducible and is well above the detection limit of the GC used (~0.05 mol %). No CO was detected in the absence of Mn^V≡N or TFAA. This result suggests the existence of a trace amount of free diazene; it also provides some support for the proposed formation of a manganese(III) μ-diazene species.

Decomposition of the manganese(III) μ-diazene species would result in the formation of Mn(II), however [Mn^{III}(^{t}Bu$_4$salen)-(CF$_3$CO$_2$)] is produced quantitatively. We propose that Mn(II) is oxidized rapidly by Mn^V=NCOCF$_3$ according to eq 11.[17] This is supported by the detection of CF$_3$CONH$_2$ in the reaction mixture, which may be produced by the reduction of Mn^V=NCOCF$_3$ to Mn^{III}−NCOCF$_3$ (the CF$_3$CON$^-$ ligand has a −1 charge in both Mn oxidation states) followed by protonation with TFA (presumably formed by hydrolysis of TFAA by trace water in the solvent).[18]

The overall stoichiometry of the proposed mechanism (eq 12) can be compared with the experimental results (eq 3). The observed yield of N$_2$ (72 ± 2) % is in reasonable agreement with the yield of 67% according to eq 12. Moreover, the observed amount of TFAA consumed (69%) is in good agreement with the predicted value (67%), assuming that the two moles of TFA consumed come from hydrolysis of one mole of TFAA by trace water in the solvent. On the other hand, the observed yield of 25% for CF$_3$CONH$_2$ is lower than the predicted yield of 33%. The slightly higher yield of N$_2$ and the lower yield of CF$_3$CONH$_2$ than expected can be accounted for by the oxidation of some Mn(II) to Mn(III) by trace O$_2$ in the
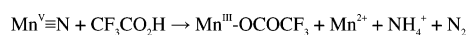
(16) Young, J. A.; Durrell, W. S.; Dresdner, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 2105−2109.
(17) Attempts to study this reaction independently did not give any reproducible results. If [Mn^V(^{t}Bu$_4$salen)(N)] was mixed with TFAA first before adding [Mn^{II}(^{t}Bu$_4$salen)], N···N coupling of Mn^V=NCOCF$_3$ occurred rapidly. On the other hand, there was a direct reaction between [Mn^V(^{t}Bu$_4$salen)(N)] and [Mn^{II}(^{t}Bu$_4$salen)] if they were mixed first.
(18) Under our experimental conditions, the presence of around 0.01 wt % of H$_2$O in the solvent is enough to produce 25% of CF$_3$CONH$_2$. Attempts to add water to the system to study the effects resulted in lower yields of all products.

reaction vessel instead of by Mn(V). [Mn^{II}(^{t}Bu$_4$salen)] is known to be very air-sensitive, and this side reaction would lead to more N$_2$ and less CF$_3$CONH$_2$ production.

2. TFA-Activated N···N Coupling of (Salen)manganese-(V) Nitrido Complexes. 2.1. Products and Stoichiometry. N···N coupling also occurs readily when TFA (instead of TFAA) is added to (salen)manganese(V) nitrido complexes. Addition of 5 equiv of TFA to a solution of **1** (0.25 mmol) in 1,2-dichloroethane (10 mL) under argon at room temperature resulted in the evolution of 93% of N$_2$ after 30 min (assuming 2 mol of Mn^V≡N produce 1 mole of N$_2$). Using ^{15}N-labeling, it is shown that both nitrogen atoms in N$_2$ come from Mn^V≡N. As in activation by TFAA, the yield of N$_2$ and the reaction rate depend on the structure of the salen ligand (Table 2). The longer reaction time for **1** than **2** is probably due to its low solubility, whereas the low yields and rates for **3** and **4** are probably due to steric effects; as expected, these effects are less than in TFAA-activated reactions because of a less-bulky imido intermediate. The reactions of **1** and **2** have been studied in more detail.

Analysis of products in the solution by ion chromatography (after extraction with water) showed the presence of NH$_4^+$ and Mn^{2+}(aq). In a separate experiment, the solution after reaction was evaporated to dryness, and recrystallization of the residue produced [Mn^{III}(L)(CF$_3$CO$_2$)] (L = salen or ^{t}Bu$_4$salen). The yields of the various products for compound **1** and **2** are summarized in Scheme 2. For both compounds, there is excellent mass balance for manganese and nitrogen.

2.2. Kinetic Studies. As in the case of TFAA-activated reaction, the spectral changes for a solution containing **2** and TFA in ClCH$_2$CH$_2$Cl at 298.0 K reveal the rapid formation of an intermediate (**B**) with λ_{max} at 330 and 372 nm, which then slowly decays (Figure 6). The UV/vis spectra of the intermediates **B** and **A** are rather similar (see also Figure 1). The maximum absorbance for **B** is the same for [TFA] ranging from 0.025 to 0.1 M; this suggests that formation of **B** is quantitative at these TFA concentrations.

The formation of the **B**, however, is too fast to be followed even by stopped-flow techniques. The decay of **B**, monitored at 372 nm, did not obey first-order kinetics, and the method of initial rates was applied. A plot of initial rate against [Mn^V-(N)]^2 gives a straight line (Figure 7), indicating a second-order rate law. The slope of the line gives the second-order rate constant k_2', which is equal to (1.4 ± 0.1) × 10^4 M^{-1} s^{-1} at 298.0 K and [TFA] = 0.10 M. The activation parameters $\Delta H^\ddagger$

Scheme 2

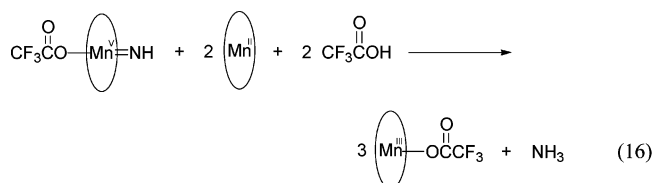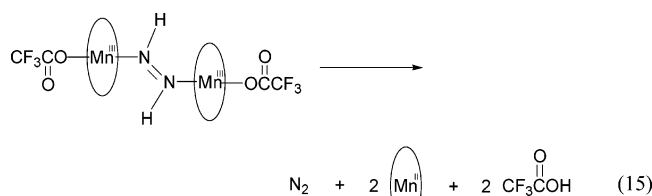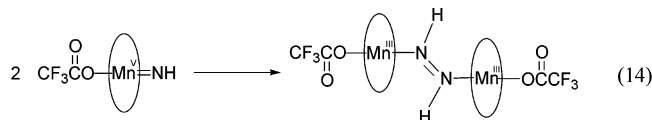Mn^V≡N + CF$_3$CO$_2$H → Mn^{III}-OCOCF$_3$ + Mn^{2+} + NH$_4^+$ + N$_2$

1	22%	76%	7%	93%
2	81%	18%	27%	72%

and $\Delta S^\ddagger$ are found to be 8.8 ± 0.7 kcal mol^{-1} and $-(10 \pm 2)$ cal K^{-1} mol^{-1}, respectively, at [TFA] = 0.10 M. These values are similar to that for TFAA-activated reaction, although **B** should be less bulky than **A**.

2.3. Mechanism of N⋯N Coupling. Based on the experimental results a proposed mechanism for the TFA-activated coupling reaction of **2**, which is similar to the TFAA-activated reaction, is shown in eqs 13−16, the overall reaction is represented by eq 17.

$$Mn^V{\equiv}N \ + \ CF_3\overset{O}{\underset{}{C}}OH \ \longrightarrow \ CF_3\overset{O}{\underset{}{C}}O{-}Mn^V{=}NH \quad (13)$$

$$2 \ CF_3\overset{O}{\underset{}{C}}O{-}Mn^V{=}NH \ \longrightarrow \ CF_3\overset{O}{\underset{}{C}}O{-}Mn^{III}{-}N{=}N{-}Mn^{III}{-}O\overset{O}{\underset{}{C}}CF_3 \quad (14)$$

$$CF_3\overset{O}{\underset{}{C}}O{-}Mn^{III}{-}N{=}N{-}Mn^{III}{-}O\overset{O}{\underset{}{C}}CF_3 \ \longrightarrow$$

$$N_2 \ + \ 2 \ Mn^{II} \ + \ 2 \ CF_3\overset{O}{\underset{}{C}}OH \quad (15)$$

$$CF_3\overset{O}{\underset{}{C}}O{-}Mn^V{=}NH \ + \ 2 \ Mn^{II} \ + \ 2 \ CF_3\overset{O}{\underset{}{C}}OH \ \longrightarrow$$

$$3 \ Mn^{III}{-}O\overset{O}{\underset{}{C}}CF_3 \ + \ NH_3 \quad (16)$$

$$3 \ Mn^V{\equiv}N \ + \ 3 \ CF_3\overset{O}{\underset{}{C}}OH \ \longrightarrow$$

$$3 \ Mn^{III}{-}O\overset{O}{\underset{}{C}}CF_3 \ + \ N_2 \ + \ NH_3 \quad (17)$$
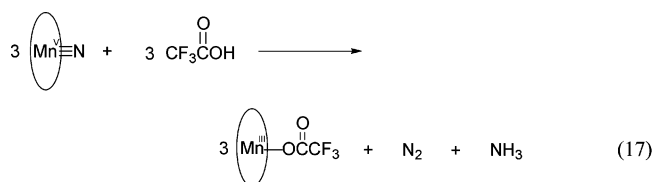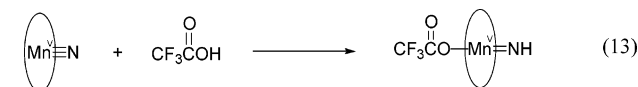
The first step is the formation of the imido species Mn^V=NH (eq 13). This step is expected to be very fast. This proposed intermediate is supported by our previous studies, which show that in the presence of TFA, (salen)manganese(V) nitrido complexes can transfer an NH group to an alkene to give an aziridine.[12] The next step is coupling of the imido species to produce a manganese(III) μ-diazene species (eq 14), which is supported by a second-order rate law. An imido−nitrido coupling mechanism can be ruled out because UV/vis spectral studies suggest that formation of the imido species is quantitative at the TFA concentrations used in our studies. Attempts to detect the proposed manganese(III) μ-diazene species were unsuccessful, although trans-[(μ-N$_2$H$_2$){CpMn(CO)$_2$}$_2$][19] and [(μ-N$_2$H$_2$){Fe("N$_H$S$_4$")}$_2$][20] have been reported. N$_2$H$_2$ is a strong reducing agent; hence, it is not unreasonable to assume that, in this case, the μ-diazene species undergoes rapid internal redox to give N$_2$ (eq 15). Free N$_2$H$_2$ is known to decompose to give N$_2$, N$_2$H$_4$, and a small amount of H$_2$; in acid solution, HN$_3$ is

(19) Sellmann, D. *J. Organomet. Chem.* **1972**, *44*, C46−C48.
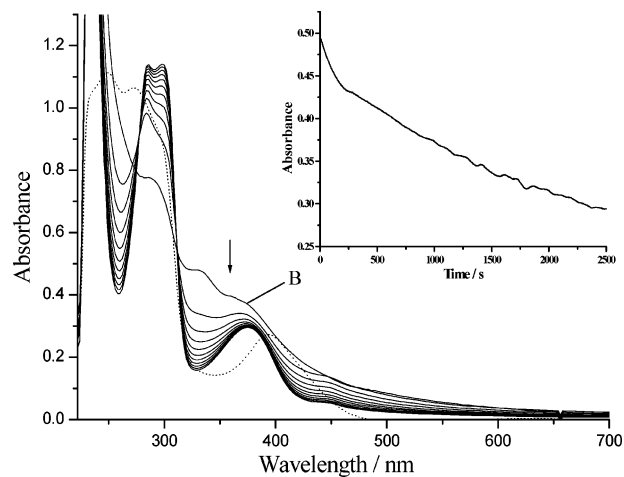(20) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271−1272.

Figure 6. Spectral changes at 144 s intervals for the reaction between **2** (4×10^{-5} M) and TFA (0.1 M) in ClCH$_2$CH$_2$Cl at 298.0 K and I = 0.1 M. (Dotted line is the spectrum before adding TFA.) (Insert) Kinetic trace at 372 nm.
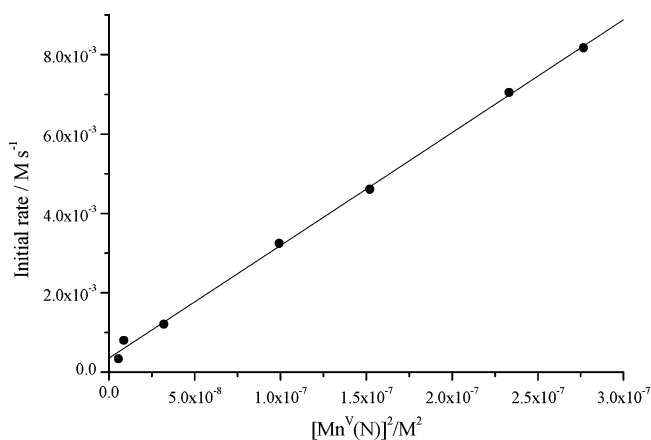

Figure 7. Plot of initial rate vs [Mn^V(N)]^2 for the reaction of **2** with TFA (0.10 M) in ClCH$_2$CH$_2$Cl at 298.0 K and I = 0.1 M (slope = $(2.84 \pm 0.05) \times 10^4$; y-intercept = $(3.56 \pm 0.07) \times 10^{-4}$; r = 0.999).

also produced.[21] Because we were unable to detect any N$_2$H$_4$, H$_2$, or N$_3^-$ from the reaction mixture, we conclude that free N$_2$H$_2$ was either not produced or was more readily oxidized by Mn^{III}. NH$_3$ is proposed to come from the reduction of [Mn^V(NH)(L)(CF$_3$CO$_2$)] by [Mn^{II}(L)] (L = salen or ^{t}Bu$_4$salen) in the presence of TFA (eq 16). According to eq 17, the yield for N$_2$ and NH$_3$ should be 67 and 33%, respectively, which are slightly different from the results for **2** but very different for that of **1**. Because Mn^{2+} ions were detected, these discrepancies can be readily accounted for by a demetalation reaction of [Mn^{II}(L)] by TFA according to eq 18.

$$[Mn^{II}(L)] \ + \ 2CF_3CO_2H \ \rightarrow \ Mn(CF_3CO_2)_2 \ + \ H_2L \quad (18)$$
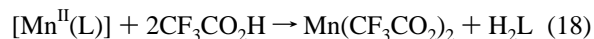
This is supported by the detection of Mn^{2+} ions using ion chromatography. Control experiments show that Mn^{2+} does not reduce Mn^V=NH, and reaction of **1** or **2** with TFA in the presence of an equivalent amount of Mn(CF$_3$CO$_2$)$_2$ did not result in an increase in the yield of NH$_3$. Demetalation would result

(21) Holleman, A. F.; Wiberg, E. In *Inorganic Chemistry*; Academic Press: New York, 2001; p 630.
(22) Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104,* 4487−4489.

in less Mn^V=NH being reduced to give NH_3 but more N⋯N coupling to produce more N_2. Independent experiments using $[Mn^{II}(L)]$ also indicate that this demetalation indeed occurs in the presence of TFA, with that of $[Mn^{II}(salen)]$ occurring more readily than $[Mn^{II}({}^tBu_4salen)]$. By lower the reaction temperature to 0 °C, the amount of N_2 (69 ± 2)% and NH_3 (30 ± 2)% from **2** are in good agreement with the predicted values, presumably demetalation is slowed down.

3. Concluding Remarks. We have presented a definitive example of N⋯N coupling of imido species. Imido species generated from (porphyrin)manganese(V) nitrido complexes have been reported to slowly decompose with time to the corresponding manganese(III) porphyrin complexes; it is possible that N⋯N coupling also occurs for these species.[8] An iron-(II) nitrene (or iron(IV) hydrazido) complex Fe(TPP)(N−NC_9H_18) (TPP = tetraphenylporphyrin, NC_9H_{18} = 2,2,6,6-tetramethylpiperidyl) was reported to give $Fe(TPP)(py)_2$ and $C_9H_{18}N−N$=$N−NC_9H_{18}$ upon treatment with pyridine (py);[22] this reaction may also occur by coupling of the iron nitrene complex. On the other hand, stable (imido)manganese(V) corrole complexes have recently been reported.[23] These complexes contain bulky 2,4,6-trisubstituted phenylimido groups, so N⋯N coupling is not expected to occur.

Our results show that facile N⋯N coupling occurs for imido species derived from the (salen)manganese(V) nitrido complexes **1** and **2**. This probably explains why amination experiments are usually performed with **4**, which forms an imido species that is much more stable with respect to N⋯N coupling.[9] In some cases, the more bulky tosyl anhydride (Ts_2O) is used as the activating reagent for alkene amination, which gives better yields than TFAA.[10,11]

The reverse process of N⋯N coupling, i.e., cleavage of a μ-diazene species to produce imido species, is also of interest, and there are a number of systems reported in the literature that undergo N=N splitting via μ-diazene intermediates.[24]

Supporting Information Available: Tables S1−5 and Figures S1−5. This material is available free of charge via the Internet at http://pubs.acs.org.

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