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Triple Hydrogen Atom Abstraction from Mn-NH₃ Complexes Results in Cyclophosphazenium Cations

Brian J. Cook[a], Samantha I. Johnson[a], Geoffrey M. Chambers[a], Werner Kaminsky[b], and R. Morris Bullock*[a]

All hydrogen atoms of the NH₃ in [Mn(depe)₂(CO)(NH₃)]⁺ are abstracted by 2,4,6-tri-*tert*-butylphenoxyl radical, resulting in the isolation of a rare cyclophosphazenium cation [(Et₂P(CH₂)₂PEt₂)N]⁺, in 76% yield. An analagous reaction is observed for [Mn(dppe)₂(CO)(NH₃)]⁺. Computations suggest insertion of NHₓ into a Mn-P bond provides the thermodynamic driving force. Contextualization of this reaction provides insights on catalyst design and breaking strong N-H bonds.

Storing energy in chemical bonds is attractive for safely transporting energy generated from renewable, intermittent sources such as wind and solar.[1] Conversion of chemical energy to electrical power generally involves proton-coupled electron transfer (PCET) reactions.[2] Ammonia (NH₃) is an energy-rich molecule, providing carbon-free energy when oxidized in fuel cells.[3] Seminal studies by Meyer and co-workers on Ru/Os complexes reported molecular complexes that oxidize NH₃, and Chirik and co-workers reported Mo-NH₃ reactions, yet additional examples remain sparse.[4] A few molecular catalysts were reported recently.[5] Fundamental studies of cleavage of N-H bonds in M-NH₃ complexes are needed.

We have been exploring the abstraction of hydrogen atoms from metal-bound NH₃ complexes using the 2,4,6-tri-*tert*-butylphenoxyl radical (ArO•; BDFE of ArO-H = 77 kcal/mol in CH₃CN).[2b] Hydrogen atom abstraction (HAA) from [CpMo^{II}(P$^{Ph}_2$N$^{tBu}_2$)(CO)(NH₃)]⁺ gives a Mo^V-nitride that is trapped by ArO•.[6] Hydrogen atom abstractions from [(PY5)Mo(NH₃)]²⁺ generate N₂[7] while catalytic N₂ formation (TON ~10) was found using [Cp*Ru^{II}(P$^{tBu}_2$N$^{Ph}_2$)(NH₃)]⁺.[5c] We seek earth-abundant metals for these transformations rather than precious metals. Precedent for Mn-based NH₃ oxidation includes the synthesis of Mn^V(salen)(N);[8] N-N coupling from transient [Mn^{VI}(salen)(N)]⁺

has been demonstrated under strongly oxidizing conditions.[9] Our prior work in electrocatalytic oxidation of H₂ using Mn^I complexes[10] provided impetus to study oxidation of the corresponding NH₃ complexes.

Addition of NH₃ gas to [Mn(depe)₂(CO)]B(C₆F₅)₄[10b,10c,11] (depe = 1,2-bis(diethylphosphino)ethane) in PhF results in an immediate color change from dark blue to pale yellow. The NH₃ complex *trans*-[Mn(depe)₂(CO)(NH₃)]B(C₆F₅)₄ (**1**) was isolated in 86% yield. Analogous reactions with [Mn(dppe)₂(CO)]BAr$^F_4$ (dppe = 1,2-bis(diphenylphosphino)ethane, Ar^F = (3,5-(CF₃)₂C₆H₃) led to [Mn(dppe)₂(CO)(NH₃)]⁺ (**2**); both complexes were fully characterized. The IR spectra (Figures S10, S22) confirm NH₃ binding, with a bathochromic shift in ν_{CO} compared to the starting complex, as well as bands assigned to N-H at 3386 cm⁻¹ for **1** and 3346 cm⁻¹ for **2**. When ¹⁵NH₃ is used, sharp singlets at −416 (**1-¹⁵N**) and −395 ppm (**2-¹⁵N**) are observed by ¹⁵N{¹H} NMR spectroscopy (Figures S13, S20). The *trans* geometry of the NH₃ and CO ligands is confirmed by single crystal x-ray diffraction (Figure 1). The less electron-rich Mn in **2** has a shorter Mn-N bond (2.149(2) Å) than in **1** (2.218(7) Å); both are significantly longer than *fac*-[Mn(CO)₃(NH₃)₃][Mn(CO)₅] (Mn-N: 2.096(7) Å), the only other structurally characterized Mn^I-NH₃ complex.[12] The electrochemistry of **1** and **2** was characterized by cyclic

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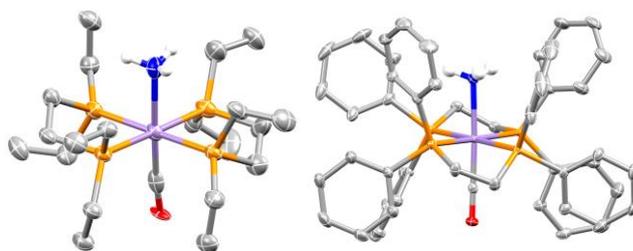b. *Department of Chemistry, University of Washington, Box 951700, Seattle, WA 98195, USA.*

Figure 1. ORTEP drawing (50% ellipsoid probability) of **1** (left) and **2** (right). Counterions, solvent guests and hydrogen atoms on carbon are not shown.

voltammetry (Figures S58-S59), which features a reversible $Mn^{II/I}$ couple at −0.130 V vs. $Cp_2Fe^{+/0}$ for **1** and an irreversible oxidation ($E_{p,a}$ +0.120 V) for **2**. The ~250 mV anodic shift from **1** to **2** is consistent with a less electron-rich Mn^I center. The origin of chemical irreversibility in **2** is possibly due to oxidatively-induced CO dissociation, as formation of $[Mn(diphosphine)_2(CO)_2]^+$ has been reported in this system.[11a,11b] The i_{pa} of this process increases substantially upon addition of exogenous DBU, indicating possible deprotonation after oxidation (Figures S60, S61).[13] Accordingly, we turned our attention to concerted removal of H^+/e^- by hydrogen atom abstraction (HAA) using the ArO• radical.

Treatment of a PhF solution of **1** with ArO• (3 equiv.) at 22 °C results in the rapid disappearance of the dark blue color of ArO•, turning pale yellow over the course of 5 min. Assaying the reaction by $^{31}P\{^1H\}$ NMR spectroscopy after sequential addition of 1, 2, or 3 equiv. of ArO• (Figure S34), the peak corresponding to **1** disappears, and a singlet at +83.5 ppm grows in. A small preparative scale reaction results in the isolation of an off-white solid in 76% yield. The yield was optimized by dropwise addition of a dilute Mn solution to a saturated ArO• solution in PhF (Figure 2). Formation of 2,4,6-tri-*tert*-butylphenol (ArOH) is confirmed and assayed by ^1H NMR and IR spectroscopy (Figures S37, S38). The other observable Mn species in this reaction is $[Mn(depe)_2(CO)_2]^+$,[11a,11b] whose formation can be suppressed under optimized reaction conditions (see Supplementary Information). The major product was confirmed by x-ray
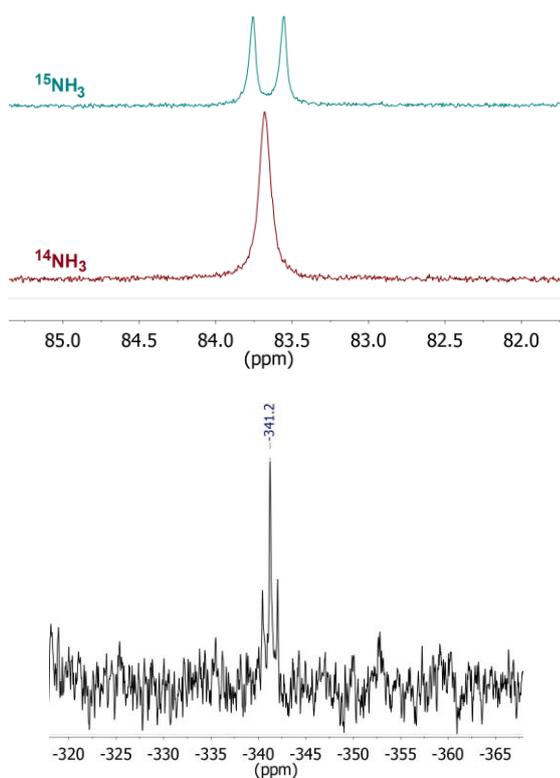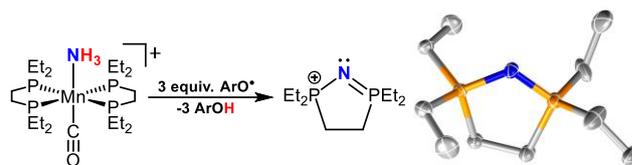
Figure 3. Synthesis and ORTEP drawing (50% probability) of phosphazenium cation **3**. Hydrogens and $B(C_6F_5)_4^-$ are not shown.

diffraction as the cyclophosphazenium cation, $[(Et_2P(C_2H_4)PEt_2)N]B(C_6F_5)_4$ (**3**), resulting from N-migratory insertion and coupling to a diphosphine ligand (Figure 3). The P-N bond lengths (1.619(2) and 1.604(2) Å) are between P-N single and P=N double bonds (~1.8 and 1.5 Å respectively).[14] The sp^2-hybridized nitrogen in **3** has a lone pair, but is no longer coordinated to Mn. The fate of the "Mn(depe)(CO)" fragment is not yet determined.

When the $^{15}NH_3$ isotopologue, **1-^{15}N**, is treated with 3 equiv. ArO•, a doublet instead of a singlet grows in at +83.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Figure 2, top)**.** The coupling constant ($^1J_{PN}$ = 40.6 Hz) is similar to those found for the P-N single bonds in phosphatriazenes.[15] The $^{15}N\{^1H\}$ NMR spectrum (Figure 2, bottom) shows a triplet at −341 ppm resulting from coupling to two equivalent ^{31}P nuclei, with J_{PN} (40.5 Hz) in excellent agreement with the ^{31}P NMR spectrum for the generation of **3-^{15}N** from **1-^{15}N**. Finally, the shift of a peak at 1125 cm^{-1} to 1098 cm^{-1} in the IR spectra using **1-^{15}N** instead of **1** is consistent with P-N multiple bonding (Figures S29-S31). The spectroscopic characterization is in full agreement with cyclophosphazenium generation upon triple HAA from **1**.

In contrast to **1**, the reaction between **2** and ArO• (3 equiv.) requires approximately 72 h for complete consumption of ArO•, even though **2** is completely consumed within the first 5 min at 22 °C, as judged by *in situ* IR spectroscopy (Figures S52-S57). The only other Mn-CO containing species observed is assigned to $[Mn(dppe)_2(CO)_2]^+$ at 1897 cm^{-1}, which forms rapidly upon mixing (Figure S54). Monitoring the reaction progress by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S39, S41), the disappearance of **2** and growth of the peak at +78.9 ppm corresponding to $[Mn(dppe)_2(CO)_2]^+$ occurs within the first 2 h, followed by the growth of another species at +63.5 ppm at longer reaction times (Figures S44-S48). The amount of $[Mn(dppe)_2(CO)_2]^+$ generated in the reaction is constant after 2 h (Figures S45, S47); indicating that another Mn species (that shows no resonance in the $^{31}P\{^1H\}$ NMR spectrum between −50 and +200 ppm) reacts further with excess ArO•. The generation of $[Mn(dppe)_2(CO)_2]^+$ in the reaction was further confirmed by x-ray diffraction of single crystals grown from the reaction mixture (Figure S6). When **2-^{15}N** is used, a doublet grows in at +63.5 ppm; this chemical shift is in excellent agreement with the only known cyclophosphazenium cation, $[(Ph_2P(CH_2)_2PPh_2)N]^+$.[14] This assignment was further corroborated by its $^{15}N\{^1H\}$ NMR spectrum (Figure S40), which features a triplet that is downfield shifted (−336 ppm) compared to the Et derivative. Single crystal x-ray diffraction confirmed the solid-state structure as $[(Ph_2P(C_2H_4)PPh_2)N]BAr^F_4$, **4** (Figure S5).

Figure 2. (top): $^{31}P\{^1H\}$ NMR spectral comparison of the reaction between **1** and **1-^{15}N** with 3 equiv. ArO•. $^{15}N\{^1H\}$ NMR spectrum of the latter. For full spectrum, see Figures S35 and S36**.**

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To probe the effect of diphosphine methylene chain length, we synthesized a mixed bis(diphosphine) complex, [Mn(dppp)(dppm)(CO)(^{15}NH$_3$)]$^+$ (**5**) (dppp = 1,2-bis(diphenylphosphino)propane; dppm = 1,2-bis(diphenylphosphino)methane).[11c] Treatment of **5** with ArO$^\bullet$ (3 equiv.) results in the disappearance of both starting material peaks in the ^{31}P{^{1}H} NMR spectrum, but only one doublet (+25 ppm) grows in (Figure S26). This observation suggests that not all diphosphine ligands are susceptible to cyclophosphazenium formation, and stability of the cyclophosphazenium ring is a factor.[16] Our results demonstrate this reaction to be applicable to various diphosphine ligands that can generate cyclophosphazenium cations of different ring sizes and phosphorus substituents.

DFT computations (Scheme 1) are helpful in evaluating the thermochemistry and assessing the stage at which insertion may occur. Calculations employed dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) to avoid additional configurations from ethyl group rotations. Starting from Mn-NH$_3$ complex **A**, the ΔG for abstraction of the three hydrogen atoms by ArO$^\bullet$ are uphill by 11.6, 14.1, and 14.2 kcal/mol, respectively (Scheme 1).[5c,6,17] These values suggest three consecutive uphill HAA steps to generate the Mn^{IV}-nitrido **D** (followed by insertion) is not likely in the current system. Thus, two alternative paths were considered for nitrogen insertion: from the Mn^{II}-amido (**B**) or the Mn^{III}-imido (**C**) intermediates (Schemes 2, S1). Imido insertion (**C**→**F**) into the Mn-P bond is favorable by 28.9 kcal/mol. Hydrogen atom abstraction from **F** (ΔG = −11.4 kcal/mol) is much more favorable than from the Mn^{III}-imido complex (**C**). We also considered concerted migratory insertion/N-H oxidative addition of the NH$_2$ ligand to Mn (**B**→**E**), which is 5.3 kcal/mol more favorable than **B**→**C**. N-H oxidative addition from M-NH$_3$ complexes and migratory insertions of amido ligands have literature precedent.[18,19] Subsequent HAA (**E**→**F**) is favorable by 23.6 kcal/mol. Either pathway is energetically feasible, indicating that **C** and **E** are both plausible intermediates; a more detailed study would be necessary to determine which pathway occurs. Finally, we also interrogated metal-free H atom abstraction steps (Scheme S1) and found those to be less thermodynamically favorable; we postulate all HAA steps occur on Mn-NH$_x$ or Mn-NH$_x$-P species.

The large thermodynamic driving force afforded by the migratory insertion assists in lowering the energy for removing all three hydrogen atoms from these Mn species. This conclusion agrees with our experimental observations, as no intermediates are spectroscopically observed prior to formation of the cyclophosphazenium product. Apparently, cyclophosphazenium is not a strong ligand; it has a lone pair on nitrogen but is cationic. Dissociation of cyclophosphazenium from a formally Mn^0 center is interesting, considering the Lewis relationship to *N*-heterocyclic carbene ligands.

Reports of cyclophosphazenium cations are rare.[14,16] The first method of cyclophosphazenium synthesis used excess CCl$_4$ and NH$_3$,[16] while more recent reports utilize halogen-induced silylphosphinimine cyclization[14a] and [NO]BF$_4$ reduction.[14b] Under our conditions, we observed no reaction between free diphosphine (dppe or depe) and NH$_3$ in the presence of 4 equiv.
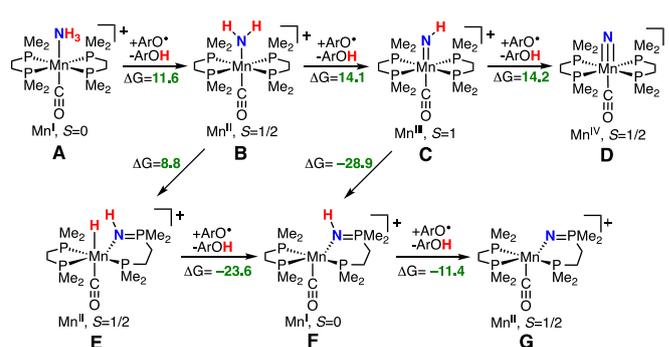
Scheme 1. Computed free energy changes (kcal/mol) for HAA and insertion reactions starting from [Mn(dmpe)$_2$(CO)(NH$_3$)]$^+$ (**A**).

ArO$^\bullet$ (Figures S42-S43), confirming that Mn is required for the high yield of cyclophosphazenium. In the previously reported procedures, only products with P-Ph substituents were produced, thus our introduction of alternative substituents on phosphorus diversifies cyclophosphazenium synthesis.

Terminal Mn-imido and Mn-nitrido species lower-valent than Mn^V are exceedingly rare. Meyer's and Smith's groups have independently reported Mn^{IV}-nitrido species; Mn^{III}-nitrido, while observable at low temperatures, is not isolable in those systems.[20] Formation of the corresponding Mn^{IV}-nitrido complex (**D**) is not favored in our system, as migratory insertion from a lower-valent Mn is strongly favored.[21] The inaccessibility of Mn^{IV}-nitrido is similar the Meyer/Hamman-Smith systems, where Ru^{IV}-imido, rather than Ru^V-nitrido, is implicated as the critical intermediate.[4a,5b,17] Intramolecular migratory insertion of transient metal-nitrido and metal-imido species is well documented,[21-22] but to the best of our knowledge, double insertion into two M-P bonds is unprecedented. Interestingly, the final HAA step from our proposed Mn^I-iminophosphorane (**F**) is thermodynamically favorable after insertion, introducing ligand-cooperativity effects to assist lowering N-H BDFEs of metal-bound NH$_x$ species.

We have synthesized and fully characterized a series of Mn^I-NH$_3$ complexes. Triple hydrogen-atom abstraction by an aryloxyl radical results in insertion into two Mn-P bonds, giving a rare cyclophosphazenium heterocycle. DFT calculations reveal insertion at a Mn^{III}-imido intermediate is highly favorable, and the resulting species has a significantly weakened N-H bond.

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Conflicts of interest

The authors declare no conflicts of interest.

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Graphic for Table of Contents

All three hydrogen atoms of the NH_3 ligand of $[Mn(depe)_2(CO)(NH_3)]^+$ are abstracted by an organic radical, giving a rare cyclophosphazenium cation, $[(Et_2P(CH_2)_2PEt_2)N]^+$; computations suggest that insertion of NH_x into a Mn-P bond provides a strong thermodynamic driving force.