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A Mechanistic Study of the Samarium(II)-Mediated Reduction of Aryl Nitro Compounds to the Corresponding Arylamines. The Crystal Structures of $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ and $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$

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Abstract: Treatment of nitrobenzene and other various nitroarenes with 6 equiv of samarium(II) under strictly anhydrous conditions allows for the isolation of aniline or the corresponding arylamine. Reducing the number of samarium(II) equivalents allows for the isolation of intermediate species, e.g., azoarenes or hydrazines. Use of $Sm[N(SiMe_3)_2]_2$, in place of the typically used SmI_2, has allowed for the detailed examination of the aqueous and nonaqueous species formed in this reduction and has been instrumental in delineation of the stepwise reaction mechanism. This is the first time that the reaction intermediates of an organic reaction mediated by samarium(II) have been isolated and analyzed by ^{1}H NMR and X-ray crystallography.

Introduction

The ease with which divalent lanthanide metals are oxidized has caused their compounds to become popular reducing agents in organic synthesis.[1-4] Unfortunately, only a few lanthanides have stable divalent oxidation states (Eu, Sm, and Yb; more recently, soluble Tm(II)[5] and Dy(II)[6] compounds have been described); in this regard, the choice of lanthanide metal is somewhat limited. Samarium is particularly attractive, as it readily reduces a variety of organic moieties including aldehydes,[2] ketones,[7-9] alcohols,[10] and carboxylic acids,[11,12] maintaining excellent chemoselectivity[13] in all cases.

Both aryl[1,14,15] and alkyl[16,17] nitro compounds can be converted to the corresponding amine by using samarium(II) iodide as a reducing agent. The total number of reports in which samarium(II) has been employed as a reducing agent for nitro functionalities is still fairly small, and this may be related to the lack of evidence supporting a specific reaction mechanism. It was previously observed that the reduction of nitro groups may yield hydroxylamines,[18-20] hydrazines,[21,22] azoarenes,[23] or azoxyarenes,[24-27] all of which are intermediates between nitro groups and amines. To date, researchers have reported using 4,[28] 6,[16] 9,[17] or even 20[29] equiv of SmI_2 in order to complete the organic reduction, i.e., form amines from nitro groups. Temperature has also been inconsistently manipulated as a variable; several accounts have indicated that room temperature is sufficient,[17,30] while others suggest that reflux[28,29] or chilled (−50 °C)[31] conditions are required. Reaction times have varied from 3 min[16] to 2 days,[28] although in general most reactions

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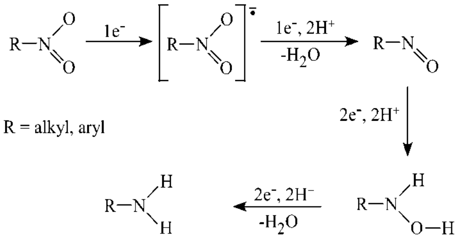
Scheme 1



are run for 7−8 h. A variety of solvents have been employed in these systems; the majority of these are polar (MeOH) or aprotic (THF, DMF). As SmI_2 is only soluble in polar solvents, it is unclear whether these particular solvents are used only to enhance solubility or whether the solvation of the samarium cation is a critical part of the mechanism as has been suggested. Resolution of this point would help establish whether samarium(II) reductants operate as inner- or outer-sphere electron-transfer reagents.[32−34] Obviously, the optimum reaction conditions that are required to successfully convert a nitro group to an amine are still somewhat ill-defined.

Zard proposed a general reaction mechanism[29] that focused exclusively on the reduction occurring at the nitro group and its derivatives (Scheme 1); however, it also required a constant proton source, which in some cases could oxidize a large portion of the samarium(II) to samarium(III) before it could effect the transformation of a nitro group. Zard's mechanism also clearly depicted a rationale for the selective formation of organic moieties that fall on the "continuum" between a nitro group and an amine, including the nitrosyl and hydroxylamine functionalities. Clearly, this mechanistic picture accounts for the stepwise organic transformations that take place, but it does not address the nature of the metal species that are formed throughout the course of the reaction. In a handful of cases, researchers have tentatively proposed the formation of a samarium-containing product in the primary steps of the reduction, typically written as "$I_2SmOSmI_2$",[35] yet there has been no spectroscopic or structural evidence that such a species exists as a byproduct in these reactions.

Typically, SmI_2 has been employed as the source of samarium(II) in organic reactions.[1−3] However, SmI_2 has no proton-containing moieties that would be useful in the ^{1}H NMR assignment of the different species in solution, and little is understood of the reaction mechanism operating in this reduction. To alleviate this problem, we elected to use hexane-soluble $Sm[N(SiMe_3)_2]_2(thf)_2$[36,37] as a source of samarium(II); it possesses distinctive ^{1}H NMR resonances to assist in delineation of reaction intermediates, and it allows use of solvents known to have fairly limited coordination to the metal center. By using this samarium(II) starting material, the reaction mechanism of this reduction has been ascertained by isolating not only the organic products but also the air- and moisture-sensitive samarium(III) coordination compounds formed during reaction with various nitroarenes.

Experimental Section

General Considerations. Unless otherwise specified, all manipulations were performed at Los Alamos National Laboratory under a helium or argon atmosphere with the rigorous exclusion of air and moisture using high-vacuum, Schlenk, or glovebox techniques. ^{1}H NMR spectra were obtained at 25 °C on a Varian Unity 300 spectrometer at 300 MHz and were referenced to the residual proton resonance of C_6D_6 (δ 7.15). Infrared data were obtained on a Digilab FTS-40 spectrometer as Nujol mulls between KBr salt plates. GC/MS data were measured on a HP series 6890 GC system with an HP 5973 mass-selective detector.

Materials. Azobenzene, diphenylhydrazine, 9-nitroanthracene, nitrobenzene, 6-nitrochrysene, 1-nitronaphthalene, 1-nitropyrene, nitrosobenzene, 2-nitrosotoluene, and 4-phenylpyridine *N*-oxide were commercial samples (Aldrich or Acros) and were used as received. $Sm[N(SiMe_3)_2]_2(thf)_2$[36] and $Sm[N(SiMe_3)_2]_3$[38] were prepared as previously described. 1,2,3,4-Di(epoxy)butane was a commercial sample (Aldrich) and was vacuum distilled prior to use. THF, toluene, and hexanes were purified by passing through columns of activated alumina and activated Cu-0226 S copper catalyst (Engelhard).[39] C_6D_6 was vacuum distilled from Na/K (22/78) alloy and stored over 4A molecular sieves prior to use.

Synthesis of $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ (I) by the 1:1 Reaction of Nitrosobenzene with $Sm[N(SiMe_3)_2]_2(thf)_2$. A flask equipped with a stirring bar was charged with $Sm[N(SiMe_3)_2]_2(thf)_2$ (0.125 g, 0.203 mmol), nitrosobenzene (0.022 g, 0.21 mmol), and toluene (25 mL). The solution was stirred vigorously, resulting in an immediate reaction as the deep purple mixture quickly became wine red. The reaction was allowed to continue stirring overnight. The following day, the toluene was removed under vacuum leaving a red oil. Hexanes (5 mL) was added, and the resulting mixture was filtered through a glass wool-filled pipet. The wine-red filtrate was then placed in a freezer (−25 °C) overnight. The following day, dark red X-ray quality crystals of **I** were isolated. Satisfactory elemental analysis was not obtained for this compound as it readily desolvates when removed from the mother liquor: ^{1}H NMR (C_6D_6) δ 2.03 (s, 8H, $\alpha\text{-}C_4H_8O$); −0.11 (s, 8H, $\beta\text{-}C_4H_8O$); −0.73 (s, 72H, $Si(CH_3)_3$). ^{13}C NMR data could not be obtained even with a concentrated sample subjected to a prolonged collection time. Principal IR bands (cm^{-1}) 2947 (s,br), 1243 (m), 981 (m), 832 (m), 722 (m).

Synthesis of I by the 4:1 Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with 1,2,3,4-Di(epoxy)butane. A flask equipped with a stirring bar was charged with $Sm[N(SiMe_3)_2]_2(thf)_2$ (1.029 g, 1.672 mmol), 1,2,3,4-di(epoxy)butane (0.036 g, 0.42 mmol), and toluene (25 mL). The solution was stirred vigorously, leading to a slow reaction as the deep purple mixture changed to deep red over the course of 3 days. The toluene was then removed under vacuum, leaving a dark brown oily solid. Hexanes (5 mL) was added, and the resulting red mixture was filtered through a glass wool-filled pipet. The red hexanes filtrate was then placed in a freezer (−25 °C) overnight. The following day a dark red crystalline solid was isolated and identified as **I**. The mother liquor was also found to contain an appreciable quantity of $Sm[N(SiMe_3)_2]_3$ (**IV**).

Synthesis of $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$ (II) by the 2:1 Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with Azobenzene. A vial was charged with $Sm[N(SiMe_3)_2]_2(thf)_2$ (0.200 g, 0.325 mmol), azobenzene (0.030 g, 0.16 mmol), and toluene (5 mL). Upon vigorous shaking, the deep purple mixture immediately changed to dark red.

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The uniform solution was placed in a freezer (−25 °C) overnight. The following day, dark red X-ray quality crystals of **II** had formed and settled out of the solution. Satisfactory elemental analysis was not obtained for this compound as it readily desolvates if removed from the mother liquor: ^{1}H NMR (C_6D_6) δ 35.8 (s, 2H, $N_2(C_6H_5)_2$); 10.9 (s, 2H, $N_2(C_6H_5)_2$); 4.83 (s, 2H, $N_2(C_6H_5)_2$); 3.55 (s, 2H, $N_2(C_6H_5)_2$); 1.40 (s, 4H, α-C_4H_8O); −0.94 (s, 4H, β-C_4H_8O); −1.97 (s, 72H, $Si(CH_3)_3$); −7.18 (s, 2H, $N_2(C_6H_5)_2$). ^{13}C NMR data could not be obtained even with a concentrated sample subjected to a prolonged collection time.

4:1 Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with Nitrosobenzene (Standard Conditions for Reactions with Nonaqueous Handling). A flask equipped with a stirring bar was charged with $Sm[N(SiMe_3)_2]_2(thf)_2$ (0.500 g, 0.812 mmol), nitrosobenzene (0.022 g, 0.20 mmol), and toluene (25 mL). The solution was stirred vigorously, upon which the deep purple mixture quickly became deep red. After 30 min, the toluene was removed under vacuum to afford a red amorphous solid. Hexanes (5 mL) was added, and the red solution was filtered through a glass wool-filled pipet. The filtrate was subsequently placed in a freezer (−25 °C) overnight. The following day, crystalline **I** was isolated from the red solution. The mother liquor remaining after the removal of the oxo-bridged species was analyzed with ^{1}H NMR and found to contain $[(Me_3Si)_2N]Sm(\mu\text{-}NPh)_2Sm[N(SiMe_3)_2]$ (**III**) and **IV** in a ratio of approximately 1:3. Full details of each experiment run under nonaqueous conditions can be found in the Supporting Information.

Preparation of $Sm[N(SiMe_3)_2]_3$ (IV) by the 4:1 Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with Nitrosobenzene. A flask equipped with a stirring bar was charged with $Sm[N(SiMe_3)_2]_2(thf)_2$ (0.252 g, 0.410 mmol), nitrosobenzene (0.011 g, 0.10 mmol), and toluene (25 mL). The solution was stirred vigorously, leading to an immediate reaction as the deep purple mixture quickly became crimson. After 30 min, the toluene was removed under vacuum to afford a red amorphous solid. Hexanes (5 mL) was added, and the red solution was filtered through a glass wool-filled pipet. The filtrate was subsequently placed in a freezer (−25 °C) overnight. The following day, crystalline **I** was isolated from the red solution. The trisamido complex $Sm[N(SiMe_3)_2]_3$ (**IV**) was then isolated as a fine white powder by returning the mother liquor to the freezer (−25 °C) for 2 h, followed promptly by a cold filtration. X-ray quality crystals of **IV** can be grown by slow evaporation of a hexanes solution at room temperature: ^{1}H NMR (C_6D_6) δ −1.61 (s, 54H, $Si(CH_3)_3$).

1:1 Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with Nitrosobenzene (Standard Conditions for Reactions with Aqueous Processing). A 500-mL Schlenk flask equipped with a stirring bar was charged with $Sm[N(SiMe_3)_2]_2(thf)_2$ (0.500 g, 0.812 mmol) and toluene (150 mL). Into a separate 250-mL Schlenk flask was placed nitrosobenzene (0.087 g, 0.81 mmol) and toluene (30 mL). Under argon, the turquoise nitrosobenzene solution was cannulated into the deep purple samarium(II) solution. The solution was stirred vigorously, upon which the deep purple solution immediately became crimson. The following day, H_2O (50 mL) was added to quench the reaction. The deep red organic phase immediately began to lighten to orange. Both layers were transferred to a separatory funnel. Following agitation, the layers were allowed to separate, and the organic layer was isolated after gravity filtration to remove any insoluble impurities. The aqueous layer was washed with small portions of toluene (15 mL), and the organic layers were combined. The toluene was removed under vacuum, leaving an orange oil. An aliquot of the oil was transferred to a small vial and diluted with Et_2O. Analysis of the solution using GC/MS indicated the presence of two compounds, azobenzene and azoxybenzene. Both compounds were confirmed by comparison of retention times and molecular ion and fragmentation patterns with known standards. Full details of each experiment run with aqueous workup can be found in the Supporting Information.

NMR Study of 2:1 Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with Nitrosobenzene. In an NMR tube, $Sm[N(SiMe_3)_2]_2(thf)_2$ (6.0 mg, 9.8 μmol) was dissolved in C_6D_6. The tube was placed into a freezer (−25 °C) and allowed to solidify overnight. Nitrosobenzene (0.5 mg, 5 μmol) was dissolved in C_6D_6 in a small vial. The nitrosobenzene solution was added to the previously prepared NMR tube, and the tube was returned to the freezer to completely solidify the mixture. The tube was removed from the glovebox and immediately transferred to a small plastic bag containing dry ice for transfer to the instrument. The sample was loaded into the spectrometer and allowed to warm slowly. When the sample was warm enough to be locked and shimmed, data were collected at 5-min intervals for approximately 1.75 h. The initial set of ^{1}H NMR data showed the presence of **I**, **II**, **III**, and **IV**, the intensities of which remained unchanged for the duration of the experiment.

NMR Study of 1:1 Reaction of I with $Sm[N(SiMe_3)_2]_2(thf)_2$. In an NMR tube, $Sm[N(SiMe_3)_2]_2(thf)_2$ (4.0 mg, 6.5 μmol) and $[Sm[N(SiMe_3)_2]_2(thf)]_2O$ (7.0 mg, 6.4 μmol) were dissolved in C_6D_6. The tube was removed from the glovebox and shaken to ensure complete mixing. Examination of the ^{1}H NMR data indicated unreacted starting materials only.

General Procedures for X-ray Crystallography. A suitable crystal of each sample was located, attached to a glass fiber, and mounted on a Bruker P4/CCD/PC diffractometer for data collection at 203 K. Data collection (SMART, Bruker Analytical X-ray Systems, Inc., Madison, WI) and structure solution were conducted at Los Alamos National Laboratory. All calculations were performed using the SHELXTL V5.10 suite of programs (SHELXTL-Plus V5.10, Bruker Analytical X-ray Systems, Inc.). Final cell constants were calculated (SAINT V 4.05, Bruker Analytical X-ray Systems, Inc.) from a set of strong reflections measured during the actual data collection. Relevant crystal and data collection parameters for each of the compounds are given in Appendix A.

The space groups were determined from systematic absences and intensity statistics. A direct-methods solution was calculated that provided most of the non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Absorption corrections were performed with the program SADABS (SADABS, Area-detector Absorption Correction; Bruker Analytical X-ray Systems, Inc.).

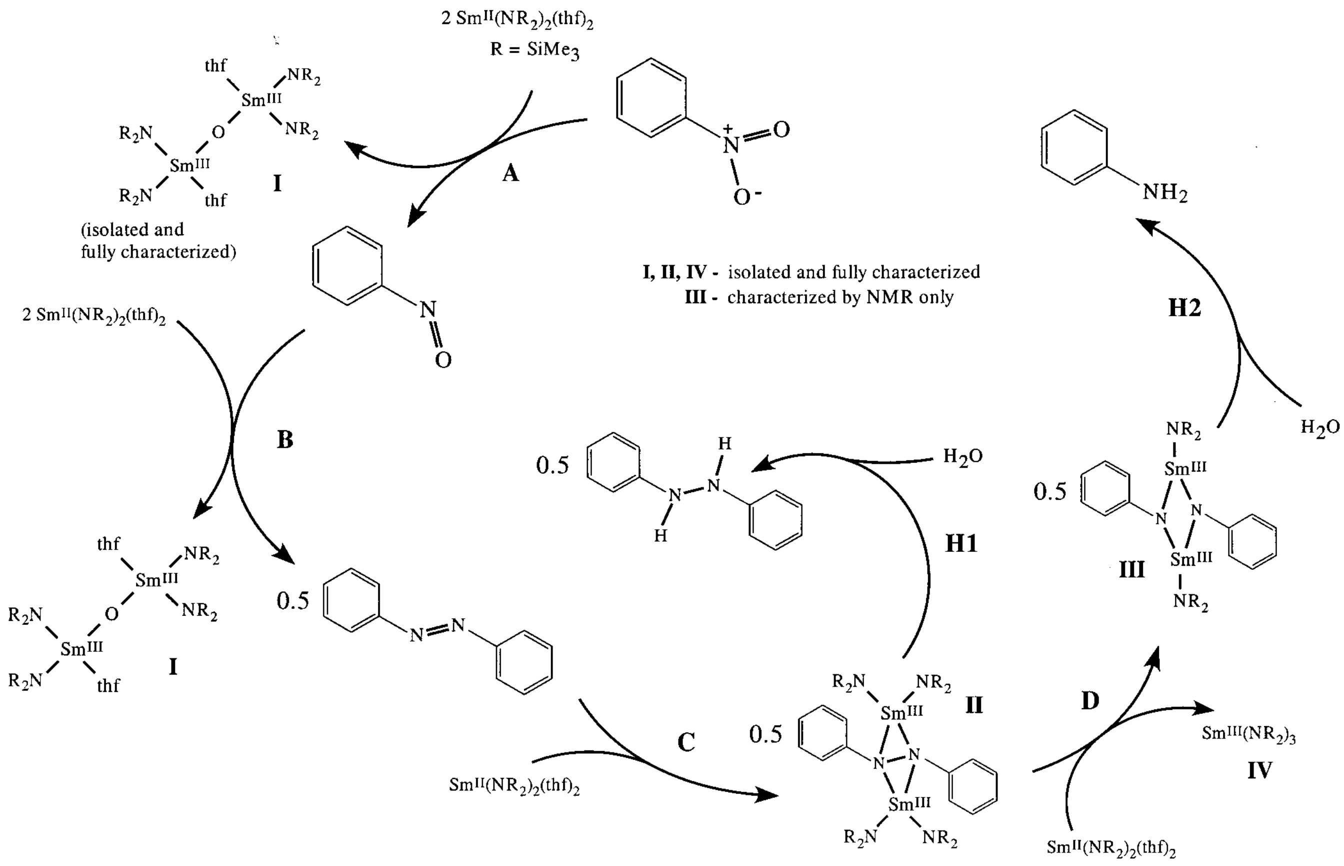
X-ray Crystallography of $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ (I). Dark red crystals of **I** were grown from a saturated hexanes solution at −30 °C. The crystals were extracted from the mother liquor and quickly transferred to a Petri dish filled with a small amount of light mineral oil. A suitable crystal was chosen by examination under a microscope and was attached to a glass fiber using silicone grease.

The space group $P\bar{1}$ was determined according to the methods described in the general procedures. The initial solution revealed the samarium and the majority of all non-hydrogen atom positions. The remaining atoms were found through subsequent Fourier cycles. Hydrogen atoms were placed in fixed positions (0.97 Å for methylene and 0.96 Å for methyl). All hydrogen atoms were refined with isotropic temperature factors fixed at 1.5 (methyl) or 1.2 (methylene) times the equivalent isotropic U of the carbon atom to which they were bound. All other structure solution parameters are as described in the general procedures.

X-ray Crystallography of $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$ (II). Light orange crystals of **II** were grown from a saturated hexanes solution at −30 °C. The crystals were quickly transferred to a Petri dish filled with a small amount of light mineral oil. A suitable crystal was chosen by examination under a microscope and was attached to a glass fiber using a spot of silicone grease.

The space group $P2_1/c$ was determined according to the methods described in the general procedures. The initial solution revealed all of the non-hydrogen atom positions. A severely disordered n-hexane molecule was found in the lattice on a site of inversion. Attempts to

Scheme 2



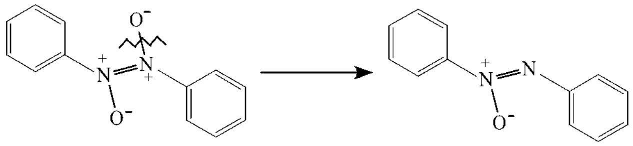
model the lattice *n*-hexane were unsuccessful, and the program PLATON/SQUEEZE was used to remove the *n*-hexane solvent density. All hydrogen atom positions were idealized (C−H = 0.97 Å for methylene, 0.96 Å for methyl, and 0.93 Å for aromatic). Hydrogen atom positions were refined with isotropic temperature factors set at 1.5 (methyl) or 1.2 (methylene, aromatic) times the equivalent isotropic *U* of the carbon atom to which they were bound. All other structure solution parameters are as described in the general procedures.

Results

Reduction of Nitrobenzene to Aniline with Samarium(II). A summary of the reactions in this study with nitrobenzene is found in Scheme 2. Each reduction step is labeled A−D, and the organic products of two intermediates on hydrolysis are indicated as H*n*. Each reduction step in the mechanism will be addressed in detail in subsequent sections. Several nitro-containing organic molecules and their organic intermediates were treated with a variable number of equivalents of samarium(II). The samarium(III) coordination complexes formed in the course of the reduction are also shown, and they are labeled as **I**−**IV**. Although they are not indicated in the scheme, solvent, temperature, and reaction time were also varied throughout the study. In all cases, the mechanism under strictly anhydrous conditions was found to be consistent with that shown at room temperature in toluene for short (10−30 min) reaction times.

Reaction of $Sm[N(SiMe_3)_2]_2(thf)_2$ with Nitro or Nitroso Compounds. When samarium(II) was allowed to react with nitrosobenzene in a 1:1 ratio under nonaqueous conditions, the oxo-bridged species **I** formed. This was unexpected, as the product has two samarium(III) atoms per oxygen, an apparent violation of the reaction stoichiometry. The formation of this complex is consistent with the "$I_2SmOSmI_2$" species that was proposed in previous work.[35] Further analysis of the products with ^1H NMR indicated that several organic products were present. To identify them, a reaction of identical stoichiometry was quenched with H_2O upon completion.

Scheme 3



Analysis with GC/MS confirmed the presence of three compounds, which were identified as nitrosobenzene, azobenzene, and azoxybenzene by comparison with known standards. It might be expected that azoxy- and azobenzene would be possible products of reduction, as azoxybenzene would be produced from the removal of a single oxygen from the dimeric solution structure of nitrosobenzene (Scheme 3). Likewise, azobenzene would form on removal of both oxygen atoms from the nitrosobenzene dimer.

When the ratio of samarium(II) to nitrosobenzene was increased to 2:1 (B, Scheme 2), **I** was again isolated as the only samarium(III)-containing product when nonaqueous conditions were maintained. Aqueous workup, however, afforded azobenzene only, with no azoxybenzene or nitrosobenzene present. Nitrobenzene cleanly forms nitrosobenzene if treated with 2 equiv of samarium(II) (A, Scheme 2); following the conversion, the organic compounds formed from the reduction of nitrobenzene are identical to those found with nitrosobenzene. It is clear that, with nitrobenzene, 4 equiv of samarium(II) is required in

Table 1. Selected Nitro and Nitrosoarenes and ^{1}H NMR Shifts (δ) for Various Hexamethyldisilazido-Containing Products under Nonaqueous Conditions

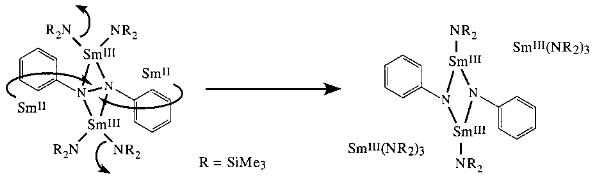
compound	I	II	III	IV
nitrobenzene	−0.73	−1.97	−0.56	−1.61
2-nitrosotoluene	−0.73	−2.07		−1.61
1-nitronaphthalene	−0.73	−2.13	−0.53	−1.61
9-nitroanthracene	−0.73			−1.61
1-nitropyrene	−0.73	−2.24	−0.64	−1.61
6-nitrochrysene	−0.73	−2.41	−0.54	−1.61

order to remove all of the oxygen atoms of the nitro group (A and B, Scheme 2). At this point, azobenzene is the only organic product, and other than **I**, no samarium(III)-containing products are detectable.

Increasing the number of equivalents of samarium(II) produces additional samarium(III) coordination complexes as the reduction of the organic moiety continues. When 3 equiv of samarium(II) are allowed to react with nitrosobenzene, complex **II** forms, which indicates that reduction of the azo N═N double bond has occurred; diphenylhydrazine results on hydrolysis. When 4 equiv of samarium(II) are allowed to react with nitrosobenzene, complexes **III** and **IV** result. Aniline is formed on hydrolysis of complex **III**, indicating the termination of the reduction sequence.

Reaction of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ with Azobenzene. This reaction was examined in the course of the nitroso group reduction by samarium(II) but was also tested independently, i.e., in the absence of nitrosobenzene or **I**. Under nonaqueous conditions, 2 equiv of samarium(II) treated with 1 equiv of azobenzene formed the azo-bridged bimetallic **II** (C, Scheme 2). If the reaction is given aqueous workup at this point, diphenylhydrazine is isolated in quantitative yield (H1, Scheme 2). If nonaqueous conditions are maintained, the introduction of an additional 2 equiv of samarium(II) (D, Scheme 2) leads to the formation of **III** and **IV**; as previously noted, the former produces aniline on hydrolysis (H2, Scheme 2).

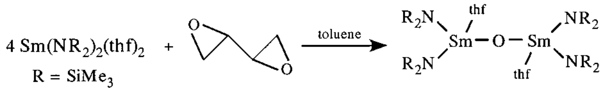
Reduction of Nitroarenes by Samarium(II). With the organic products formed during the nitrobenzene reduction identified, a variety of other nitroarenes were allowed to react with both 4 and 6 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$. The ^{1}H NMR shifts corresponding to the samarium-containing complexes in this series are listed in Table 1. With 4 equiv, each reaction mixture was shown by ^{1}H NMR to contain **I** (peak I) as the predominant species, which forms prior to any other metal-containing complexes. In each case, the nitroarene was cleanly converted to its corresponding azo compound on aqueous workup. On the addition of 6 equiv of samarium(II), additional samarium-containing products were detected. Analysis with ^{1}H NMR confirmed the formation of **IV** (peak IV) and two other sets of compounds containing the organic moiety of the nitroarene starting material (peak II and peak III). Peak II was assigned to the reduced azo-bridged samarium complex similar to species **II** (Scheme 2). Peak III corresponds to the bimetallic complex without a bond between the nitrogen atoms (**III**). This species was not observed with a nitrosotoluene starting material and was only detected in the presence of other organic moieties in extremely pure samples. This may be a reflection of the “amido deficiency” of **III** with respect to **I** and **II**, as during the conversion from **II** to **III**, an amido group is transferred from **II** to the final equivalent of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ to form **III** and **IV** (eq 1). Spectra for 9-nitroanthracene, however, did not contain resonances for the species corresponding to either peak II or III. Aqueous workup of the reaction between Sm and 9-nitroanthracene did afford the expected arylamines; it is possible that the samarium coordination compounds that incorporate the anthracene fragment lack solubility in aromatic solvents.



(1)

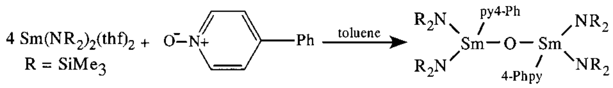
Formation of {Sm[N(SiMe$_3$)$_2$]$_2$(thf)}$_2$(μ_2-O) (I). Crystalline **I** readily formed during the course of this work (A or B, Scheme 2) and crystallized easily from a hexanes solution at −25 °C as deep red blocks. Upon precipitation, it was easily removed from other products for subsequent analysis. The ^{1}H NMR spectrum for **I** is uncomplicated, having one broad singlet (−0.74) corresponding to the methyl protons on the trimethylsilyl groups and two other broad peaks (2.03, −0.11) that were assigned to coordinated thf. Even though the paramagnetic character of the samarium center did not hinder the use of ^{1}H NMR, ^{13}C spectra were unobtainable for all the compounds in this study. **I** readily loses coordinated thf when removed from a solvent layer, so crystals must be stored under the mother liquor or a light mineral oil. Owing to the ready loss of solvent and, presumably, the decomposition that occurs following such a process, satisfactory elemental analysis could not be obtained for **I**.

There was some uncertainty about whether the poor analysis was related to the presence of side products generated in the course of the nitro reduction. To address this possibility, the synthesis of **I** was also attempted by the reaction of 1,2,3,4-di(epoxy)butane with 4 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (eq 2). The major product of the reaction was clearly **I**, but this product, when produced by this alternate synthetic route, was equally susceptible to desolvation/decomposition on removal from the solvent.



(2)

As the coordinated thf ligands appeared to be highly labile, a pyridine-based donor ligand was chosen in an attempt to form a more stable adduct. 4-Phenylpyridine *N*-oxide was allowed to react with 2 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ in toluene (eq 3). The reaction was successful and led to the formation of {Sm[N(SiMe$_3$)$_2$]$_2$(4-phenylpyridine)}$_2$(μ_2-O); repeated attempts at crystallization failed, however, as a brick red powder persistently formed over time. Unfortunately, this powder also decomposed on removal from the solvent; it is unclear whether the initial powder contained trapped lattice solvent or whether the pyridine ligand is lost by desolvation. Consequently, {Sm[N(SiMe$_3$)$_2$]$_2$-



(3)

(4-phenylpyridine)}$_2$(μ_2-O) was characterized with ^{1}H NMR only; it displayed the anticipated pattern consisting of a broad singlet for the trimethylsilyl protons (−0.66 ppm) and broad peaks corresponding to the pyridine ligand.

Formation of [(Me$_3$Si)$_2$N]$_2$Sm(thf)(μ-PhNNPh)Sm[N(SiMe$_3$)$_2$]$_2$ (II). Crystalline **II** was formed on the addition of 1 equiv of azobenzene to 2 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (C, Scheme 2). Alternatively, the compound could be synthesized by the reaction of 1 equiv of nitrobenzene or nitrosobenzene with an appropriate number of equivalents (5 or 3, respectively) of samarium(II). The product was the same regardless of the method used; however, crystals could not be grown when the compound was synthesized from nitro- or nitrosobenzene. Instead, azobenzene and Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ were dissolved in a vial of toluene and immediately placed into a freezer. The following day, red crystals of **II** were isolated and analyzed. The ^{1}H NMR spectrum was characteristic of a paramagnetic substance, as peaks from the phenyl rings spanned a wide range of values. The methyl protons from the trimethylsilyl protons are shifted upfield (−1.9 ppm) from **I** (−0.74 ppm) and the trisamido complex **IV** (−1.6 ppm). As with **I**, elemental analysis of **II** was unsatisfactory, as the crystals quickly lose lattice or loosely bound solvent on removal from a solvent layer.

Formation of [(Me$_3$Si)$_2$N]Sm(μ-NPh)$_2$Sm[N(SiMe$_3$)$_2$] (III) and Sm[N(SiMe$_3$)$_2$]$_3$ (IV). Both of these compounds form on the addition of a sixth equivalent of samarium(II) to a nitro-containing organic molecule (D, Scheme 2). A variety of methods were attempted to isolate and fully characterize **III**, but it has remained elusive. **IV** was isolated from the reaction of 1 equiv of nitrosobenzene and 4 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$. Following the removal of the byproduct **I**, the mother liquor was returned to the freezer. On cooling, **IV** precipitated as a white powder and was isolated by prompt filtration of the cold solution. The ^{1}H NMR spectrum exhibits a single peak (−1.6 ppm), which was assigned to the methyl protons on the trimethylsilyl groups. No coordinated solvent was evident in the NMR spectrum of this compound, which is remarkable when the low coordination number (3) is considered; the solid-state structure, to be discussed in a separate paper, helps to rationalize the lack of solvent coordination. After removal of **IV**, relatively pure **III** was found in the mother liquor, but it could not be isolated as a solid. The ^{1}H NMR peak for **III** (−0.56) was noticeably less intense than the peaks corresponding to **I**, **II**, or **IV**; this is consistent with the loss of a bis(trimethylsilyl)amido group, as highly pure samples indicated an appropriate integration ratio (3:1) for the products. Products **III** and **IV** were also obtainable from the reaction of 2 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ with diphenylhydrazine and presumably could be purified in a similar manner.

^{1}H NMR Studies. Two ^{1}H NMR studies were conducted in the course of this work. The first study was performed in order to investigate the speed of the reduction. A solution of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ in C_6D_6 was prepared and put in an NMR tube. The resulting solution was placed in a freezer overnight. A C_6D_6 solution of nitrosobenzene was subsequently prepared and added to the frozen NMR tube. The mixture was quickly returned to the freezer for 45 min and was transported and loaded in the spectrometer while still frozen. The reaction of 2 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ with nitrosobenzene in C_6D_6 showed that the formation of **I** was nearly instantaneous. On thawing, nearly all of the nitrosobenzene appeared to be have been consumed; **I** and the other samarium amido complexes **II**, **III**, and **IV** were present.

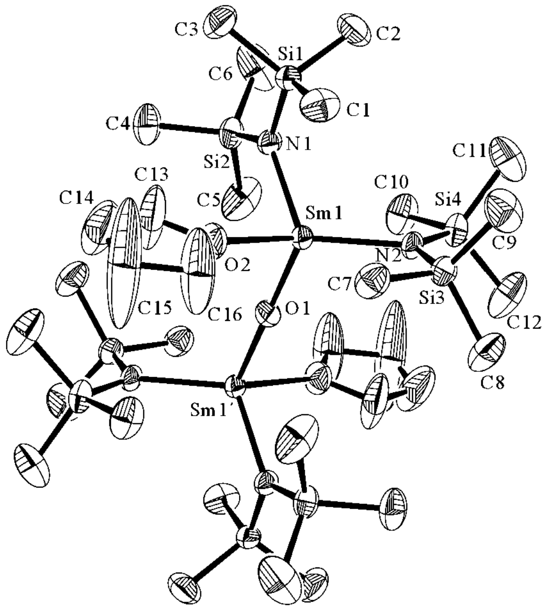
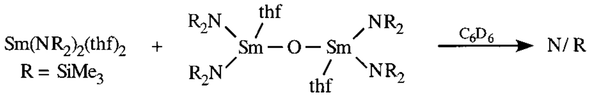


Figure 1. ORTEP drawing of the non-hydrogen atoms of {Sm[N(SiMe$_3$)$_2$]$_2$(thf)}$_2$ (μ_2-O) (**I**), giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 50% level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for {Sm[N(SiMe$_3$)$_2$]$_2$(thf)}$_2$(μ_2-O) (**I**)

atoms	distance	atoms	angle
Sm(1)−O(1)	2.0819(2)	Sm(1)−O(1)−Sm(1)'	180.0
Sm(1)−N(1)	2.322(3)	O(1)−Sm(1)−N(1)	113.20(7)
Sm(1)−N(2)	2.333(3)	O(1)−Sm(1)−N(2)	110.63(8)
Sm(1)−O(2)	2.468(3)	N(1)−Sm(1)−N(2)	113.65(12)
O(1)−Sm(1)−O(2)	93.13(9)		
N(1)−Sm(1)−O(2)	93.22(11)		
N(2)−Sm(1)−O(2)	131.00(12)		

Early in the study, it was unclear whether the oxo-bridged species **I** was an active participant in the reaction or, once formed, did not contribute to the reduction of the azo compounds affected by samarium(II). An NMR tube was prepared containing a sample of **I** and 1 equiv of Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ (eq 4).



$$\underset{R = SiMe_3}{Sm(NR_2)_2(thf)_2} + (R_2N)_2(thf)Sm{-}O{-}Sm(thf)(NR_2)_2 \xrightarrow{C_6D_6} N/R \qquad (4)$$

Data were recorded at every 5 min for a total of 1 h; they showed that the starting materials remained unchanged.

Solid-State Structures. {Sm[N(SiMe$_3$)$_2$]$_2$(thf)}$_2$(μ_2-O) (I). Several small red crystals of **I** suitable for X-ray diffraction study were grown by cooling a concentrated hexanes solution to −25 °C. Selected bond lengths and angles are presented in Table 2. An ORTEP drawing giving the atom numbering scheme used in the text is presented in Figure 1. The molecular geometry consists of two samarium(III) metal centers bridged by a linear Sm−O−Sm linkage. Each metal center also incorporates two bis(trimethylsilyl amido ligands and one coordinated, although disordered, solvent molecule (thf) making each samarium 4-coordinate. The molecular structure is similar to that of the previously reported $[Sm(C_5Me_5)_2]_2(\mu_2\text{-}O)$[40] with one interesting distinction. Evans' compound, which contains η^5-C_5Me_5, had no coordinated solvent on the metals, which may be a reflection of the pentamethylcyclopentadienyl ligands' occupying a larger portion of the coordination sphere than does the amido ligand. Evans was able to isolate the thf solvate in subsequent work,[41] but a structure was not obtained. A related structure was found with a *tert*-butyl isocyanide adduct, $\{Sm(C_5Me_5)_2(CNtBu)\}_2(\mu_2\text{-}O)$,[40] and it compares favorably with **I**. Despite the variable coordination numbers present in the range of complexes, structural comparisons between these compounds remain relevant. The samarium−oxygen bond length for the bridging oxo in $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ is 2.0819(2) Å, which is similar to other structurally verified samarium(III) oxo-bridged compounds, cf. 2.094(1) Å in $[Sm(C_5Me_5)_2]_2(\mu_2\text{-}O)$,[40] 2.101(7) Å in $\{Sm(C_5Me_5)_2(CNtBu)\}_2(\mu_2\text{-}O)$,[40] and 2.078(1) Å in $[Sm(C_9H_7)_2(thf)]_2(\mu_2\text{-}O)$.[42] The Sm−O−Sm angle in $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ is 180° with the oxygen atom lying on an inversion center; this is the same arrangement found in both $[Sm(C_5Me_5)_2]_2(\mu_2\text{-}O)$[40] and $[Sm(C_9H_7)_2(thf)]_2(\mu_2\text{-}O)$.[42] This is in contrast, however, to the structure of $\{Sm(C_5Me_5)_2(CNtBu)\}_2(\mu_2\text{-}O)$, which has a slightly bent Sm−O−Sm angle (174.3(4)°).[40] In all of the structurally verified oxo-bridged structures, the metals are in a distorted tetrahedral environment; $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ follows this pattern, as evidenced by O−Sm−N bond angles that deviate from 109.5° by as much as 21°.

The structure of **I** also appears to have a fairly high degree of coordinative unsaturation; no close contacts were noted. It is surprising then, that the complex so readily loses coordinated thf, since this decreases the coordination number to 3 for each metal center. The great lability of the Sm−O interaction is not reflected in the Sm−O(thf) bond length; at 2.467(3) Å, it is not significantly different from typically observed distances.

Schumann's $\{Lu(C_5H_5)_2(thf)\}_2(\mu_2\text{-}O)$[43] and Fischer's $\{Yb(C_5H_4Me)_2(thf)\}_2(\mu_2\text{-}O)$[44] are the only other oxo-bridged lanthanide bimetallic species that have been structurally characterized, and both compare favorably with **I.** Despite the smaller metal radii, $\{Lu(C_5H_5)_2(thf)\}_2(\mu_2\text{-}O)$ and $\{Yb(C_5H_4Me)_2(thf)\}_2(\mu_2\text{-}O)$ are actually closer structural analogues of **I** than are $[Sm(C_5Me_5)_2]_2(\mu_2\text{-}O)$ or $\{Sm(C_5Me_5)_2(CNtBu)\}_2(\mu_2\text{-}O)$, as each metal has four ligands with a linear M−O−M subunit. It is also notable that the metal (Yb, Lu) has coordinating solvent, since the coordination sphere should be more limited in the case of the smaller lanthanide ions. It can be argued however, that C_5H_5 (or C_5H_4Me) is a markedly smaller ligand than C_5Me_5, so it is not surprising that lutetium (or ytterbium) fills its coordination sphere by scavenging a solvent molecule.

$[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$ (II). Crystals of **II** suitable for X-ray analysis were grown by cooling a concentrated hexanes solution to −25 °C. Selected bond lengths and angles are given in Table 3. An ORTEP drawing giving the atom numbering scheme used in the text is presented in Figure 2. The number of literature reports of reduced azo-bridged bilanthanide compounds is limited, and the majority of the structurally authenticated examples have two such bridging groups.[45−47] In the present case, a single reduced azobenzene bridges two samarium centers, which are each coordinated by two hexamethyldisilazido ligands. Each samarium has been oxidized to the +3 state and displays η^2-interactions with the azobenzene. This is accompanied by the reduction of the N═N double bond to a single bond, as evidenced by the N−N bond distance (1.488(5) Å), which is much closer to that found in hydrazines (1.45 Å) than that found in azobenzenes (1.25 Å).[48,49] Surprisingly, Evans' related compound, $(C_5Me_5)_2Sm(\mu\text{-}PhNNPh)Sm(C_5Me_5)_2$,[46] is not characterized by longer N−N bonds (1.25(1) Å), but rather the N−C(Ph) bond lengthens to 1.58 Å (cf. 1.433 Å in *trans*-azobenzene[49]). In **II**, the N−C(Ph) distance is 1.42 Å, which is very similar to that in free *trans*-azobenzene. Evidently, the reduced organic molecule has more than one energetically accessible bonding mode to the samarium(III) centers. The N−N−Ph bond angle (109°) is also changed on reduction; it is unlike that in the parent azobenzene (120°) but

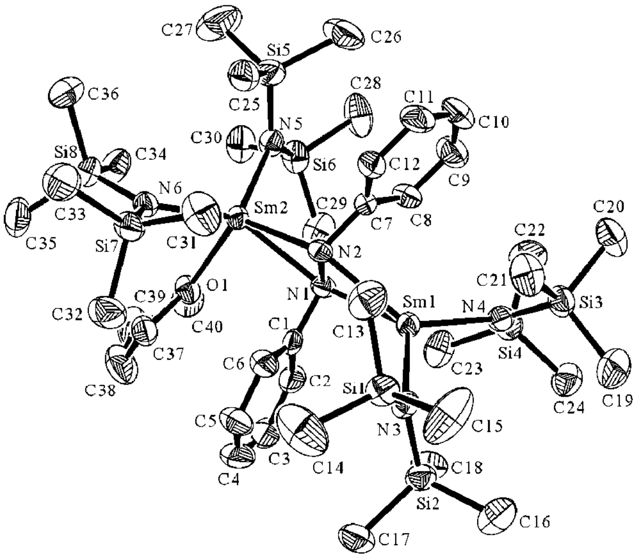


Figure 2. ORTEP drawing of the non-hydrogen atoms of $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$ (**II**), giving the numbering scheme used in the text. Thermal ellipsoids are drawn at the 50% level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$ (**II**)

atoms	distance	atoms	distance
Sm(1)−N(1)	2.461(4)	Sm(1)−C(8)	3.074(5)
Sm(1)−N(2)	2.493(4)	Sm(2)−O(1)	2.460(3)
Sm(2)−N(1)	2.460(4)	N(1)−N(2)	1.488(5)
Sm(2)−N(2)	2.451(4)	N(1)−C(1)	1.421(6)
Sm(1)−C(1)	2.826(5)	N(2)−C(7)	1.426(6)
Sm(1)−C(7)	2.797(5)		
C(1)−N(1)−N(2)	108.7(4)		
C(7)−N(2)−N(1)	110.1(4)		

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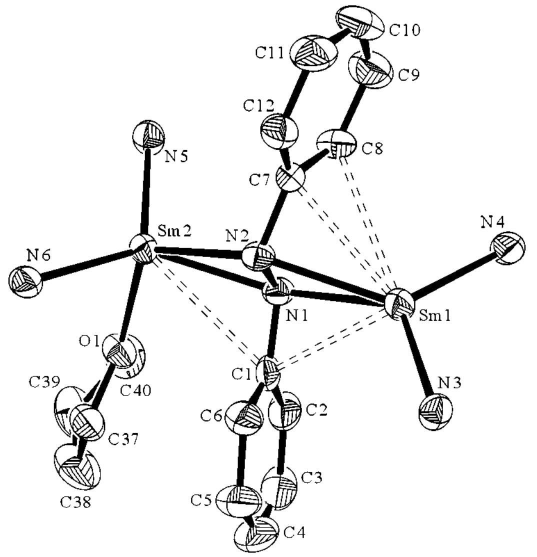

Figure 3. Close contacts in $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh)Sm[N(SiMe_3)_2]_2$ (**II**); trimethylsilyl groups are omitted for clarity.

is remarkably close to the values expected for a tetrahedral atom. The azobenzene is no longer coplanar; i.e., the plane of the arene ring is twisted by 17.5° from the C1−N1−N2 plane. The Sm−N(amido) bond lengths (average 2.28(2)Å) are very similar to those found in other samarium(III) bis(trimethylsilyl)amido complexes, cf. $[C_5Me_5]_2Sm[N(SiMe_3)_2]$ (2.301(3)Å),[50] $[(SiMe_3)_2N]_2Sm(\mu\text{-}COT)Sm[N(SiMe_3)_2]_2$ (average 2.280(3)),[51] $\{[(SiMe_3)_2N]_2Sm(\mu\text{-}X)(thf)\}_2$ X = Cl, Br (average 2.26(1)Å),[52] and $\{[(SiMe_3)_2N]_2Sm(L)\}(\mu\text{-}pinacolate)\{Sm(L)[N(SiMe_3)_2]_2\}$ L = THF, HMPA (average 2.34(2)Å).[53]

Unlike $[C_5Me_5]_2Sm(\mu\text{-}PhNNPh)Sm[C_5Me_5]_2$,[46] **II** also displays several close contacts with the phenyl rings of the reduced azobenzene (Figure 3). Each samarium center has two hexamethyldisilazido ligands in addition to the η^2-interactions with the azobenzene ligand. One samarium (Sm2) has a coordinated thf molecule and displays a close contact with C1 of the azobenzene phenyl ring (3.054(5) Å). The other samarium center (Sm1) has no coordinating solvent; instead it exhibits close contacts with C1, C7, and C8 at distances of 2.826(5), 2.797(5), and 3.074(5) Å, respectively. This is in contrast to $[C_5Me_5]_2Sm(\mu\text{-}PhNNPh)Sm[C_5Me_5]_2$,[46] as no coordinating solvent is found in the latter if crystallized from toluene. When crystallized from a THF solution, a monomeric complex is formed in which the metal center is coordinated to the reduced azobenzene with considerable delocalization.[46] From either crystallization solvent, a bimetallic compound similar to **II**, i.e., with a coordinated thf on one metal center only, is not produced. Presumably, this can again be explained in terms of the steric environment required by the ancillary ligands. C_5Me_5 occupies a larger portion of the coordination sphere than does $[N(SiMe_3)_2]$, and to compensate for the relative coordinative unsaturation, the samarium metal centers in **II** fill their coordination spheres by forming adducts. The other metal evidently satisfies its coordinative unsaturation by forming close contacts with a phenyl ring.

Discussion

Choice of Samarium(II) Source. The reduction of nitro groups is one of many samarium(II)-mediated reactions in organic chemistry.[1,2,54,55] Surprisingly little is known of the reaction intermediates formed in this type of reduction. The standard samarium(II) species used to effect organic transformations is samarium(II) iodide.[1] It is sold commercially as a deep blue THF solution in various molarities and is very effective as a reducing agent. Reactions with samarium(II) iodide are not amenable to detailed mechanistic study with ^1H NMR, as there are no protons with which to identify samarium-containing reaction intermediates; in addition, its derivatives have rather low solubility and do not crystallize well. Samarium(II) bis(hexamethyldisilazide) ($Sm[N(SiMe_3)_2]_2(thf)_2$), on the other hand, has 18 protons per amido group, allowing for the identification of various intermediates, even those formed in low yield. The synthesis of this complex is uncomplicated, requiring only 2 equiv of an alkali metal salt of the hexamethyldisilazide anion and SmI_2 in THF under nonaqueous conditions.[36] Whereas $Sm[N(SiMe_3)_2]_2(thf)_2$ may react differently from SmI_2 in substitution reactions, it should behave similarly as a reducing agent; i.e., the ancillary ligands appear to be uninvolved during electron-transfer reactions. If the ancillary ligands affect the ability of the reagent to reduce organic compounds, $Sm[N(SiMe_3)_2]_2(thf)_2$ should be less active than SmI_2, as access to the metal center is more restricted by the amido ligands. $Sm[N(SiMe_3)_2]_2(thf)_2$ also has markedly better solubility than SmI_2, as it dissolves freely in, and can be recrystallized from, hexanes. This is an intriguing consideration, as some work in samarium-mediated nitro reduction chemistry has suggested that polar solvents (THF, MeOH, HMPA) are needed to effect the transformation to an amine.[16,35] The increased solubility offered by $Sm[N(SiMe_3)_2]_2(thf)_2$ allows for the testing of this hypothesis, as reactions can be run in the absence of these solvents in order to identify any role they may have in the reduction.

Solvent Requirements for the Reduction. The majority of reactions examined in this study were run in toluene in order to determine whether polar solvents were required to assist in the electron-transfer mechanism. The samarium(II)-mediated reduction of nitroarenes does not require polar solvents, as the reaction proceeds in toluene or hexanes. The use of polar solvents (THF, MeOH, HMPA) in prior studies may have been required for the less soluble SmI_2 starting material. Solvent choice is still important with a samarium(II) source, particularly if a nondonor solvent is chosen as the bulk medium. In toluene, a minor amount of H_2O is likely to have a high affinity for most metals. Consequently, it is probable that the metal will be oxidized by the solvent rather than by the organic compound. This is less likely to occur in a donor solvent such as THF, as it has recently been shown that H_2O or MeOH does not compete well with bulk THF for coordination to samarium(II).[56] As a result, anhydrous conditions are critical in reactions with

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Table 4. Products of the Samarium(II)-Mediated Reduction of Nitrobenzene[a]

organic reactant	equiv of Sm(II)	organic products	Sm(III) products[b]
nitrobenzene	2	nitrosobenzene	**I**
nitrosobenzene	1	azo- and azoxybenzene	**I**
nitrosobenzene	2	azobenzene	**I**
nitrosobenzene	3	diphenylhydrazine	**I**, **II**
nitrosobenzene	4	aniline	**I**, **III**, **IV**
azobenzene	2	diphenylhydrazine	**II**
azobenzene	4	aniline	**III**, **IV**
diphenylhydrazine	2	aniline	**III**, **IV**

[a] The products of reactions with intermediates between that of nitrobenzene and aniline are included. [b] See Scheme 2 for structures of **I**-**IV**.

samarium(II) in nonpolar solvents. Further study is clearly needed concerning the solvent requirements for samarium(II)-mediated reductions, as there are conflicting reports in the literature about the number of equivalents required to perform this and other reductions involving divalent samarium.

Temperature and Time Dependence of the Reduction. Most of the literature on samarium(II)-mediated reduction of nitro compounds indicates the need for long reaction times (8−24 h) and refluxing conditions in order to successfully effect the transformation. Neither is strictly necessary in this system, as the reduction is easily accomplished under nonaqueous conditions at room temperature. Small amounts of H_2O may markedly decrease the degree of conversion to an amine; its presence may explain reports of low yields, the necessity for long reaction times, and the isolation of incompletely reduced species.

Reaction times ranging from 30 min to 3 days were used in this study. It is clear that 30 min is more than sufficient to complete the reduction. In fact, the color change evident on oxidation of the purple samarium(II) to the red or yellow samarium(III) usually serves as an excellent indicator of reaction completion. Heating of the reaction is unnecessary, as the reductions all reach completion at room temperature. It is conceivable that more sterically crowded molecules might require solvent reflux, but in general no elevation of temperature is needed.

The Mechanism of Reduction by Samarium(II). All data strongly indicate that a stepwise mechanism is present that requires a stoichiometric amount of samarium(II). The complete reaction mechanism (Scheme 2) begins with nitrobenzene and terminates with aniline. Table 4 lists products of the reaction of samarium(II) with nitrobenzene and with several reaction intermediates. Analysis of the organic products was instrumental in delineating the early steps of this reduction. Aqueous workup at any juncture of the reaction sequence is consistent with this mechanism, as the first 4 equiv of samarium(II) that are used result in the formation of **I** and azobenzene via nitrosobenzene/azoxybenzene. The azo-bridged samarium complex is then transformed to diphenylhydrazine by a fifth equivalent of samarium(II). Hydrolysis of the reaction after the addition of 6 equiv yields aniline and samarium-containing decomposition products.

In the current study, a variety of nitro- or nitroso-containing arenes were allowed to react with $Sm[N(SiMe_3)_2]_2(thf)_2$. In each case, the formation of the oxo-bridged bimetallic **I** was observed. It serves as the counterpart to "$I_2SmOSmI_2$", which has been suggested as an intermediate in other studies.[29] The latter has never been isolated; it may be insufficiently soluble in conventional solvents to make crystallization possible.

The role of samarium in the first part of the reaction mechanism is easily defined. Initially, a single electron from each of the metal centers cleaves the nitrogen−oxygen bond, releasing the oxygen atom. The oxygen dianion is then incorporated into an oxo-bridged compound with two samarium(III) fragments, which yields an electrically neutral complex. Once formed, **I** does not take part in the subsequent reduction sequence, serving as a spectator only.

The next 2 equiv of samarium(II) repeats this process, forming additional **I** in reducing the nitroso functionality. Following the complete removal of all the oxygen from a nitroarene, samarium(II) is free to reduce the N═N double bond present in the resulting azoarene. Two samarium(II) metals are needed per azo compound; however, the coupling of the organic moieties requires only a single equivalent of samarium(II) for this and the subsequent step in the reduction.

Once reduced, the organic ligand formally carries a −2 charge, which is accommodated by the two bridged samarium(III) metal centers. When the final equivalent of samarium(II) is allowed to come in contact with **II**, the N−N single bond is cleaved. The resulting organic moieties each carry a −2 charge, which cannot be balanced by the samarium(III). Since +4 is not an oxidation state readily available to samarium, each bridged metal center releases a hexamethyldisilazido ligand, which is subsequently scavenged by the oxidized sixth equivalent of samarium.

Conclusion

For the first time, both the organic and the inorganic intermediates involved in the reduction of nitroarenes by samarium(II) have been examined under rigorously anhydrous conditions. The reaction mechanism that has been deduced from this study clearly shows that 6 equiv are required to complete the transformation. Our confidence in the correctness of the proposed mechanism was enhanced by the use of $Sm[N(SiMe_3)_2]_2(thf)_2$ in the place of ^1H NMR-silent SmI_2. Analyses of the intermediates by X-ray diffraction and GC/MS have provided a clear understanding of the multiple roles of the samarium reagent in nitro reduction chemistry. This insight into the organic transformations effected by strongly oxophilic lanthanide metals may be applicable to a host of other organic moieties containing oxygen atoms as well as N═N functionalities.

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Supporting Information Available: Complete experimental details for all the synthetic reactions and X-ray crystallographic files, in CIF format, for the structure determination of $\{Sm[N(SiMe_3)_2]_2(thf)\}_2(\mu_2\text{-}O)$ and $[(Me_3Si)_2N]_2Sm(thf)(\mu\text{-}PhNNPh\text{-})Sm[N(SiMe_3)_2]_2$. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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