**Diazadiene Complexes of the Heavy Alkaline-Earth Metals Strontium and Barium: Structures and Reactivity**

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**ABSTRACT:** 1,4-Diaza-1,3-diene (DAD) complexes of the heavy alkaline-earth metals strontium and barium have been synthesized by direct metalation of N,N'-bis(2,6-diosopropylphenyl)-1,4-diaza-1,3-butadiene (1, =DAD_{Dipp}). The reaction with Sr metal afforded a mixture of the red enediamide-type derivative (DAD_{Dipp})Sr(DME)₂ (2, DME = 1,2-dimethoxyethane) and black (DAD_{Dipp})Sr(DME) (3), which contains two coordinated DAD radical anions. With barium, only the radical anion derivative (DAD_{Dipp})₂Ba(DME) (4) was formed in 82% yield. For the first time, transfer of a DAD radical anion ligand from an alkaline-earth metal to a rare-earth metal has been achieved. Reaction of 4 with [{(Ph₂SiO)₂O₂Li(THF)}₂]HoCl (5) afforded the novel (DAD)holmium bis(disiloxanediolate) complex [{(Ph₂SiO)₂O₂Li(THF)}₂Ho(DAD_{Dipp}) (6). All new complexes (2—4 and 6) have been structurally characterized by X-ray diffraction. In addition, the radical anion complexes 3, 4, and 6 were characterized by their EPR spectra.

## INTRODUCTION

In 1975, tom Dieck et al. surprised the coordination chemistry community with a paper entitled “2,2'-Bipyridyl - a “bad ligand” for metals in low oxidation states.”¹ In this paper the authors demonstrated that the π-acceptor capacity of certain 1,4-diaza-1,3-diene (DAD) ligands such as ‘BuN=CHCH=N‘Bu is about twice as high as that of the traditionally used 2,2'-bipyridine. This particular contribution by one of the pioneers in the field had undoubtedly a significant impact on the development of DAD coordination chemistry. Today, 1,4-diaza-1,3-dienes are well established as highly versatile ligands for nearly every element in the periodic table. The list of stable DAD complexes encompasses main-group metals,² early³ and late⁴ transition metals, and the lanthanides and actinides.⁵ A unique electronic property of the 1,4-diaza-1,3-dienes is that they are redox-noninnocent and can undergo one- and two-electron-reduction steps to afford the corresponding radical anions and the enediamide dianions, respectively, as shown in Scheme 1.⁶

This electronic flexibility combined with the possibility of tuning the steric properties of the diazadiene moiety by introducing various substituents at both carbon and/or nitrogen account for the high versatility of DAD ligands in coordination and organometallic chemistry. Scheme 2 illustrates different coordination modes of DAD ligands which have been reported in the literature.⁷⁻⁹ The neutral σ-chelating coordination mode is most common with late transition metals, especially in low coordination states. Both the dianionic enediamide derivatives and the σ-coordinated radical-anion complexes are known for various s-, p-, and d-block metals and the first-row transition metals. In the vast majority of all metal complexes the diazadienes act as chelating ligands (Scheme 2). In general, nonchelating coordination modes are also possible,⁵ but examples are exceedingly rare.

The chemistry of alkaline-earth-metal DAD complexes has been fairly well developed, especially for magnesium and calcium.⁷,⁸ A large body of research in this area comprises group 2 metal complexes of rigid acenaphthene-based DAD ligands.⁸ The majority of these complexes have been prepared by salt metathesis reactions between the metal dihalides and alkali-metal DAD precursors. Yet another suitable synthetic route is the direct metalation of diazadienes by alkaline-earth metals. While all coordination modes depicted in Scheme 2 have already been realized with alkaline-earth metals, it...
becomes evident that the radical anion and enediamide type complexes generally prevail.\textsuperscript{7} Among the group 2 metals, the DAD coordination chemistry of the heavier elements strontium and barium remains the least developed.\textsuperscript{7b,8c} A recent paper by Mashima et al. reported two synthetic protocols for preparing complexes of Ca, Sr, and Ba with the bulky DAD ligand N,N'-bis(diisopropylphenyl)-1,4-diaza-1,3-butadiene (1, =DAD\textsuperscript{Dipp}).\textsuperscript{9} Salt metathesis reactions of the metal diiodides with 1 equiv of the dipotassium salt of DAD\textsuperscript{Dipp} gave mono- and dinuclear group 2 metal complexes containing the DAD\textsuperscript{Dipp} ligand in its dianionic enediamide form. The second route involved direct metalation of DAD\textsuperscript{Dipp} with the respective alkaline-earth-metal powders in the presence of iodine. This method yielded again the enediamide type complexes [(DAD\textsuperscript{Dipp})M(THF)\textsubscript{4}] for M = Ca, Sr, while barium afforded the iodide-bridged binuclear complex [(DAD\textsuperscript{Dipp})Ba(μ-I)(THF)\textsubscript{2}]\textsubscript{2}, with the DAD\textsuperscript{Dipp} ligand coordinated to barium as a radical anion.\textsuperscript{9}

We report here the synthesis and structural characterization of three new DAD\textsuperscript{Dipp} complexes of Sr and Ba made by direct metalation in the absence of iodine. Moreover, we discovered that the barium complex (DAD\textsuperscript{Dipp})\textsubscript{2}Ba(DME) can be successfully employed as a reagent for transferring the DAD units in the dianionic enediamide-type coordination mode.\textsuperscript{9}

\section*{RESULTS AND DISCUSSION}

Parallel to the investigations by Mashima et al.\textsuperscript{9} we also studied the formation of new DAD\textsuperscript{Dipp} complexes of the heavy alkaline-earth metals Sr and Ba by direct metalation of N,N'-bis(diisopropylphenyl)-1,4-diaza-1,3-butadiene (1, =DAD\textsuperscript{Dipp}). The main difference was that pure Sr and Ba metals were used as chips without activation by addition of iodine. This results are summarized in Scheme 3. When a solution of 1 in DME (=1,2-dimethoxyethane) was stirred with an excess of Sr chips, a deep red color began to develop already after ca. 1 h. In order to ensure complete reaction, stirring was continued for 1 week. Two new strontium DAD complexes could be isolated by fractional crystallization directly from the reaction mixture after removal of unreacted Sr metal.

A minor component (28\% yield) in the product mixture was a red compound which was shown by elemental analysis, spectroscopic data (\textsuperscript{1}H and \textsuperscript{13}C NMR, MS, IR), and X-ray diffraction to be the enediamide derivative (DAD\textsuperscript{Dipp})Sr(DME)\textsubscript{2} (2). Separation of 2 from the second reaction product could be readily achieved, due to its significantly lower solubility in DME. Both elemental analysis and NMR data were consistent with the presence of one DAD\textsuperscript{Dipp} and two DME ligands in the molecule, which was already indicative for enediamide dianion coordination of the diazadiene (coordination mode C in Scheme 2). The highest peak in the EI mass spectrum at m/z 464 (35\% relative intensity) could be assigned to the fragment M\textsuperscript{+} – 2DME, i.e., [(DAD\textsuperscript{Dipp})Sr]\textsuperscript{+}. The \textsuperscript{13}C NMR spectrum of 2 showed a corresponding NCH= resonance at δ 114.5, which is in good agreement with the value reported for (DAD\textsuperscript{Dipp})Sr(THF)\textsubscript{4} (δ 112.7).\textsuperscript{9} In the \textsuperscript{1}H NMR spectrum, the isopropyl protons of the Dipp substituents gave rise to a broad signal at δ 3.98 and a broad singlet at δ 1.09. A very broad singlet at δ 5.12 in the \textsuperscript{1}H NMR spectrum (THF-d\textsubscript{4}) could be assigned to the NCH= protons of the diazadiene backbone, a value typical for dianionic enediamide ligation of DAD’s (cf. δ 5.47 (C\textsubscript{6}D\textsubscript{6}) reported for (DAD\textsuperscript{Dipp})-Sr(THF)\textsubscript{4}).\textsuperscript{9} Particularly notable is the broadening of virtually all signals in the \textsuperscript{1}H NMR spectrum measured at room temperature. In particular, the resonance of the olefinic protons (δ 5.12) was barely distinguishable from the baseline. The same phenomenon has already been noted by Mashima et al. for the complexes [K(DAD\textsuperscript{Dipp})(THF)\textsubscript{2}]Sr(μ-1)(THF)\textsubscript{2} and (DAD\textsuperscript{Dipp})M(THF)\textsubscript{4} (M = Ca, Sr) bearing the DAD ligands in the dianionic enediamide-type coordination mode.\textsuperscript{9}

A single-crystal X-ray diffraction study confirmed the presence of the monomeric strontium diazadiene complex (DAD\textsuperscript{Dipp})Sr(DME)\textsubscript{2} (2). Figure 1 depicts the molecular structure of 2. Crystallographic data for 2–4 and 6 are given in Table 1 in the Supporting Information. The coordination of chelating DAD\textsuperscript{Dipp} and two DME molecules leads to a distorted-octahedral coordination geometry around the central strontium. The Sr–N distances are Sr–N1 = 2.494(2) Å and Sr–N2 = 2.419(3) Å. These can be favorably compared to the Sr–N bond lengths reported for (DAD\textsuperscript{Dipp})Sr(THF)\textsubscript{4} (Sr–N = 2.475(4) and 2.458(5) Å).\textsuperscript{9} The Sr–O distances fall in the narrow range of 2.537(2) – 2.637(2) Å and are unexceptional (cf. Sr–O = 2.448(2) – 2.613(4) Å in (DAD\textsuperscript{Dipp})Sr(THF)\textsubscript{4}).\textsuperscript{9} The most important structural feature of 2 is the long-short-long sequence in the diazadiene backbone corresponding to a NCH=CHN= bonding situation which is typical for dianionic enediamide coordination of DAD ligands (coordination mode C in Scheme 2). Thus with a value of C1–C2 = 1.363(5) Å the central C–C bond is shorter than the two C–N bonds (N1–C1 = 1.384(5) Å, N2–C2 = 1.407(4) Å).
again there is excellent agreement with the corresponding values reported for (DAD$^{3pp}$)M(THF)$_4$ (M = Sr, Ba).\textsuperscript{9} These structural details in combination with the spectroscopic results clearly confirmed the dianionic enediamide coordination of the DAD$^{3pp}$ ligand in 2.

The major product of the reaction of DAD$^{3pp}$ with Sr metal in DME was isolated with 68% yield in the form of dark red (almost black) crystals by crystallization from the concentrated mother liquor after separation of 2. The fact that no meaningful $^1$H NMR spectrum could be obtained gave an early indication for the presence of a radical anion DAD complex. The highest peak in the EI mass spectrum at $m/z$ 929 (30% relative intensity) corresponded to the molecular ion of the bis(DAD) complex (DAD$^{3pp}$)$_2$Sr(DME) (3). The peak with 100% relative intensity at $m/z$ 840 could be easily assigned to the unsolvated ion [(DAD$^{3pp}$)$_2$Sr]$^+$ formed by loss of the coordinated DME, while a peak at $m/z$ 464 (82%) corresponded to [(DAD$^{3pp}$)$^+$. Other prominent peaks were assigned to the fragment ions [DAD$^{3pp}$]$^+$ (m/z 378, 18%) and [DAD$^{3pp}$ − C$_2$H$_5$]$^+$ (m/z 333, 30%). A single-crystal X-ray diffraction study confirmed the presence of the strontium radical anion DAD complex (DAD$^{3pp}$)$_2$Sr(DME) (3) (Figure 2). The coordination geometry around the central Sr atom can again be described as distorted octahedral. In contrast to the long − short − long bonding sequence for the N − C − C − N backbone of the enediamide type coordinated DAD$^{3pp}$ ligand in 2, these three bonds are equalized in 3 (N1 − C1 = 1.321(4) Å, N2 − C2 = 1.330(4) Å, N3 − C31 = 1.326(4) Å). This is typical for the radical anionic coordination of the DAD ligand (coordination mode B in Scheme 2). In the Ba complex [(DAD$^{3pp}$)Ba($\mu$-I)(THF)$_2$]$_2$, which also contains monoanionic DAD ligands, the central C − C bond (1.401(7) Å) is even longer than the C − N bonds (1.343(7) and 1.314(7) Å).\textsuperscript{9} The Sr − N distances fall in the narrow range of Sr − N = 2.600(3) − 2.626(3) Å and are thus significantly longer than those in 2 (Sr − N1 = 2.494(2) Å and Sr − N2 = 2.419(3) Å) and (DAD$^{3pp}$)Sr(THF)$_4$ (Sr − N = 2.475(4) and 2.458(5) Å).\textsuperscript{9} The Sr − O distances are unexceptional with Sr − O1 = 2.578(2) Å and Sr − O2 = 2.588(2) Å (cf. Sr − O = 2.448(2) − 2.613(4) Å in (DAD$^{3pp}$)Sr(THF)$_4$).\textsuperscript{9} The predominant formation of radical anionic 3 in the reaction of DAD$^{3pp}$ with Sr metal in DME is markedly different from the same reaction carried out in the presence of I$_2$ (1 mol%), which led to exclusive formation of

![Figure 1. Molecular structure of (DAD$^{3pp}$)Sr(DME)$_2$ (2). Selected bond lengths (Å) and angles (deg): Sr − N1 = 2.494(2), Sr − N2 = 2.419(3), N1 − C1 = 1.384(5), N2 − C2 = 1.407(4), C1 − C2 = 1.363(5), Sr − O = 2.537(2) − 2.637(2); N1 − Sr − N2 = 74.93(9), Sr − N1 − C1 = 106.4(2), Sr − N2 − C2 = 106.7(2), N1 − C1 − C2 = 126.5(3), N2 − C2 − C1 = 125.2(4); (N1SrN2) − (N1C1C2N2) = 14.6.](image1)

![Figure 2. Molecular structure of (DAD$^{3pp}$)$_2$Sr(DME) (3). Selected bond lengths (Å) and angles (deg): Sr − N1 = 2.613(2), Sr − N2 = 2.600(3), Sr − N3 = 2.626(3), Sr − N4 = 2.613(2), N1 − C1 = 1.321(4), N2 − C2 = 1.330(4), N3 − C31 = 1.326(4), N4 − C32 = 1.325(4), C1 − C2 = 1.396(5), C31 − C32 = 1.403(5), Sr − O1 = 2.578(2), Sr − O2 = 2.588(2); N1 − Sr − N2 = 67.64(8), N3 − Sr − N4 = 66.26(8), Sr − N1 − C1 = 110.4(2), Sr − N2 − C2 = 110.2(2), Sr − N3 − C31 = 111.6(2), Sr − N4 − C32 = 112.2(2).](image2)
The 12-membered Si₆O₆Li₂ inorganic ring system but are significantly displaced, leading to a series of bis-(disiloxanediolate) complexes which have been termed “inorganic lanthanide metallocenes”.11,12 It was shown that this new class of heterobimetallic lanthanide disiloxanediolates shares structural similarities with the well-known bent metalloccenes containing pentamethylcyclopentadienyl (≡C₅Me₅) ligands. The latter form a large and well-investigated class of organolanthanides, with many of them displaying high catalytic activities in various olefin transformations.13 In both cases two bulky ligands are coordinated to the central lanthanide ion in a bent geometry, leaving room for functional groups such as the chloro ligand in [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]HoCl (5). Thus, we reasoned that replacement of the chloro functionality by monoanionic DAD ligands should provide access to an interesting new class of lanthanide bis(disiloxanediolates) of the type [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]Ln(DAD). These would complement the well-known lanthanide metallocene derivatives (C₅Me₅)₂Ln(DAD).5

In fact, treatment of [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]HoCl (5) with the barium reagent 4 (molar ratio 2:1) in toluene according to Scheme 4 at reflux temperature led to the development of a red solution accompanied by formation of a white fine precipitate of BaCl₂. Filtration and subsequent crystallization directly from the concentrated filtrate afforded the desired product [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]Ho-(DADₚₚ) (6) as air-sensitive, orange-red prisms in 57% isolated yield.

The isolation of 6 was facilitated by the virtual insolubility of the barium chloride byproduct in toluene. Because of the strongly paramagnetic nature of the Ho³⁺ ion as well as the presence of a radical anionic DADₚₚ ligand, no useful NMR data (¹H, ¹³C, ²⁹Si) could be gathered for 6. In this case, the EI mass spectrum was also uninformative, showing only the fragment ion m/z 333 [DADₚₚ – C₅H₁₀]⁺ as the highest peak. Fortunately, X-ray-quality single crystals of 6 could be readily grown by slow cooling of a saturated solution in toluene to 2 °C. The X-ray diffraction study (Figure 6) clearly established the successful formation of the target compound [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]Ho(DADₚₚ) (6). For the first time, transfer of a DAD radical anion ligand from an alkaline-earth-metal DAD complexes could perhaps be used as reagents to transfer the DAD ligand to other metals. As a first example in this direction, we studied the reaction between the barium DADₚₚ complex 4 and the chloro-functionalized holmium bis(disiloxanediolate) derivative [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]HoCl (5). Such heterobimetallic lanthanide bis(disiloxanediolates) have been extensively investigated by our group in recent years.11,12 It was found that the small Sc³⁺ and Y³⁺ ions form heterobimetalllic complexes in which the group 3 metal fits into the center of a 12-membered Si₆O₆Li₂ inorganic ring system formed by two lithium disiloxanediolate units. Additional chloro functionalities and solvent molecules are arranged in trans positions. In contrast, medium and large Ln³⁺ ions such as Pr³⁺, Sm³⁺, and Ho³⁺ do not fit into the center of the 12-membered Si₆O₆Li₂ inorganic ring system but are significantly displaced, leading to a series of bis-(disiloxanediolate) complexes which have been termed “inorganic lanthanide metallocenes”.11,12 It was shown that this new class of heterobimetallic lanthanide disiloxanediolates shares structural similarities with the well-known bent metalloccenes containing pentamethylcyclopentadienyl (=C₅Me₅) ligands. The latter form a large and well-investigated class of organolanthanides, with many of them displaying high catalytic activities in various olefin transformations.13 In both cases two bulky ligands are coordinated to the central lanthanide ion in a bent geometry, leaving room for functional groups such as the chloro ligand in [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]HoCl (5). Thus, we reasoned that replacement of the chloro functionality by monoanionic DAD ligands should provide access to an interesting new class of lanthanide bis(disiloxanediolates) of the type [{(Ph₂SiO)₂O}₂{Li(THF)₂}₂]Ln(DAD). These would complement the well-known lanthanide metallocene derivatives (C₅Me₅)₂Ln(DAD).5

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earth metal to a rare-earth metal had been achieved with the synthesis of 6.

As illustrated in Figure 6, the molecular structure of 6 adopts a highly distorted octahedral coordination geometry and features a monoanionic DAD\textsuperscript{Dipp} ligand. Due to the presence of two very bulky ligands, i.e., the 12-membered \([\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li(THF)}_2\}_2\] complex and the sterically demanding DADDipp radical anion, the central Ho\textsuperscript{3+} ion is sterically saturated without addition of a coordinating solvent. The bonding situation within the diazadiene backbone comprises shortened C–N bond lengths (1.319(5) Å) and an elongated central C–C bond length (1.398(9) Å) in accordance with the monoanionic (radical anionic) character of the DAD\textsuperscript{Dipp} ligand in 6. These values are also in good agreement with those reported for \([(\text{DAD Dipp})\text{Ba(μ-I)}(\text{THF})_2]\) (vide supra)\textsuperscript{9} or the previously reported scandium DAD radical anion complex (DADDipp)ScCl\textsubscript{2}(THF)\textsubscript{2} (C–N= 1.338(2) and 1.337(2) Å, C–C = 1.399(2) Å).\textsuperscript{5l} The Ho–N distances in 6 (2.462(3) Å) are in good agreement with those reported for other organoholmium complexes comprising Ho–N bonds.\textsuperscript{14} At 2.243(3) and 2.273(2) Å the Ho–O\textsubscript{dis}= 2.224(4) and 2.205(4) Å due to replacement of the chloro ligand by the bulky DAD\textsuperscript{Dipp} radical anion. The radical anionic coordination mode of the diazadiene ligand in 6 was also proven by the EPR spectrum (Figure 7). The spectrum looks quite similar to that of the barium complex 4 but has slightly different hfc constants and a broader line width. Simulation of the experimental spectrum of 6 results in the hfc constants \(α_N = 6.1 \text{ G}\) for the two \(^{14}\text{N} \) centers and \(α_H = 5.1 \text{ G}\) for the \(^1\text{H} \) atoms (\(g = 2.0033, \nu = 9.769995 \text{ GHz}\)).

### CONCLUSIONS

In summarizing the work reported here, we succeeded in the preparation of three new diazadiene complexes of strontium and barium by direct metalation. In the case of strontium, both monoanionic and dianionic coordination of the redox-active ligand DADDipp was observed, whereas with barium only the radical anion complex (DAD\textsuperscript{Dipp})\textsubscript{2}Ba(DME) (4) could be isolated in excellent yield (92%). These results nicely complement recent findings by Mashima et al.,\textsuperscript{9} making various types of diazadiene complexes of the heaviest alkaline earth metals readily available. Moreover, transfer of a DAD radical anion ligand from an alkaline-earth metal to a rare-earth metal has been achieved for the first time. Reaction of 4 with \([(\text{Ph}_2\text{SiO})_2\text{O}_2\{\text{Li(THF)}_2\}_2]\) afforded the novel \[(\text{DAD ho}lmium \text{ bis(disiloxanediolate)} \) complex \( (DAD\textsuperscript{Dipp})\text{Ho}(DADDipp) \) (6) as the first representative of a new class of DAD complexes. All new complexes (2–4 and 6) have been structurally characterized by X-ray diffraction. The radical anionic coordination mode of the DAD ligand in 3, 4, and 6 was also proven by EPR spectroscopy.

### EXPERIMENTAL SECTION

#### General Procedures
All operations were performed with rigorous exclusion of air and water in oven-dried or flame-dried glassware under...
an inert atmosphere of dry argon, employing standard Schlenk, high-vacuum, and glovebox techniques (MBraun MBLab; <1 ppm O₂, <1 ppm H₂O). THF, DME, and toluene were dried over sodium/benzophenone and freshly distilled under a nitrogen atmosphere prior to use. All glassware was oven-dried at 120 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. The starting materials N,N'-Bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (1; abbreviated DAD); Dipp = 2,6-diisopropylphenyl)⁰¹ and [(Ph₃SiO)₂O]₂[Li(THF)₂]·HoCl(THF)₂ (3)¹¹ were prepared according to published procedures. Strontium and barium metal chips were purchased from Aldrich and used as received. The NMR spectra were recorded in C₆D₆ or THF-d₄ solutions on a Bruker DRX 600 (¹H, 600.1 MHz; ¹³C, 150.9 MHz) or a Bruker-AVANCE-DMX400 instrument (5 mm BB; ¹H, 400.1 MHz; ¹³C, 100.6 MHz).

¹H and ¹³C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. IR (KBr) spectra were recorded in C₆D₆ or THF-d₄ solutions on a Bruker Elexsys E500 EPR spectrometer with an ER077R magnet (75 mm pole cap distance) and an ER047 XG-T microwave bridge. The EPR spectra were measured in toluene. All glassware was oven-dried at 120 °C to use. All glassware was oven-dried at 120 °C. The EPR spectra were recorded on a Bruker Elexsys E500 EPR spectrometer with an ER077R magnet (75 mm pole cap distance) and an ER047 XG-T microwave bridge. The EPR spectra were measured in toluene. All glassware was oven-dried at 120 °C to use.

Synthesis of (DADDipp)Sr(DME)₂ (3). A 2.5 g portion (6.6 mmol) of DADDipp (3) was dissolved in 100 mL of DME, and 0.61 g (7.0 mmol, in excess) of strontium chips was added. The reaction mixture was stirred at room temperature with a glass-coated stirring bar. After 1 h the reaction mixture turned from yellow to deep red. The reaction mixture was stirred for 1 week, and the unconsumed barium together with a gray precipitate were removed by filtration. Partial evaporation of 40 mL of DME and cooling of the deep red solution to 2 °C afforded (DADDipp)Ba(DME) (4) as deep red (almost black) crystals. In this case the formation of the enediamide derivative (DADDipp)-Ba(DME) (4) was not observed. Yield: 3.0 g (92%). Anal. Calcd for C₃₄H₅₆N₂O₄Sr (M = Sr, Ba): C, 63.37; H, 8.76; N, 4.35. Found: C, 64.31; H, 8.39; N, 4.18. Because of the paramagnetic properties of the radical anionic DAD, it was impossible to obtain meaningful ¹H and ¹³C NMR spectra. Mass spectrum (EI): m/z 890 (30%) [M⁺ – DME], 514 (25%) [M⁺ – DAD, DADDipp] (4) (40%) [DADDipp] (2), 353 (100%) [DADDipp – C₇H₇] (EI). IR (KBr disk): w: 3052 w, 2011 w, 2913 s, 2867 s, 2709 w, 1654 s, 1541 s, 1451 s, 1311 m, 1264 s, 1196 w, 1180 w, 1107 w, 1070 m, 1054 w, 1026 w, 982 w, 954 m, 892 m, 859 m, 835 m, 794 s, 755 s, 525 w cm⁻¹. Mp: 155 °C dec.

Synthesis of [(Ph₃SiO)₂O][Li(THF)₂]HoCl(THF)₂ (5). A 0.7 g portion (0.475 mmol) of [(Ph₃SiO)₂O][Li(THF)₂]HoCl (5) and 0.25 g (0.25 mmol) of (DADDipp)Ba(DME) (4) were dissolved in 50 mL of toluene. The reaction mixture was stirred overnight, refluxed for 2 h, and filtered through a P4 glass frit to separate a white precipitate (BaCl₂) from the clear red solution. After the volume of the solution was reduced under vacuum to 5 mL, the product crystallized in the form of orange-red prisms. Yield: 0.5 g (57%). Anal. Calcd for C₃₄H₅₆N₂O₄Sr (M = Sr, Ba): C, 64.31; H, 8.39; N, 4.18. Found: C, 64.31; H, 8.39; N, 4.18. Because of the strongly paramagnetic nature of the Ho⁺ ion, it was impossible to obtain meaningful ¹H, ¹³C, and ²⁸Si NMR data. Mass spectrum (EI): m/z: 333 (100) [DADDipp – C₇H₇], 378 (43) (25), 517 (7), 559 (1), 637 (8), 715 (3), 792 (0.5). IR (KBr disk): 3067 m, 3048 m, 2999 m, 2962 s, 2869 m, 1959 w, 1892 w, 1825 w, 1774 w, 1625 m, 1590 m, 1568 w, 1460 s, 1428 vs, 1384 m, 1362 m, 1316 m, 1348 m, 1319 m, 1196 m, 1119 m, 1119 w, 1083 s, 1034 vs, 1016 vs, 994 w, 821 w, 797 w, 742 s, 701 vs, 683 m, 620 w, 531 vs, 492 vs cm⁻¹. Mp: 95 °C dec.

X-ray Crystallographic Studies. Single crystals of 2-4 were obtained from saturated solutions in DME at 2-5 °C. In the case of 6, single crystals were grown by cooling a saturated toluene solution to 2 °C. The intensity data of 2-6 and 4 were collected on a Stoe IPDS 2T diffractometer with Mo Kα radiation. The data were collected with the Stoe XAREA¹⁶ program using o scans. The space group was determined with the XRED32¹¹ program. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F² using SHELXL-97.¹¹ Data collection parameters are given in Table 1 in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

CIF files and tables giving X-ray structural data for 2-4 and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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