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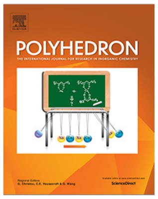

Salt elimination reactions do not always eliminate. Mechanistic study of the reaction of $NdCl_3$ with sodium *N*,*N*-dimethylaminodiboranate

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Dedicated to Bill Jones for his outstanding contributions to synthetic and mechanistic organometallic chemistry.

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ABSTRACT

Treatment of neodymium trichloride ($NdCl_3$) in tetrahydrofuran with 3 equiv of sodium *N*,*N*-dimethylaminodiboranate, $Na[(H_3B)_2NMe_2]$, which we will refer to as NaL, followed by solvent removal and extraction with pentane, affords a solution of the trisubstituted product $NdL_3(thf)$ in excellent yield. Although this transformation appears to be a straightforward salt metathesis/elimination reaction, the reaction mixture in thf surprisingly does not contain the ultimate $NdL_3(thf)$ product; instead the only aminodiboranate species present are the monosubstituted Nd compound $NdLCl_2(thf)_3$ and two equivalents of unreacted NaL. A series of ^{11}B NMR experiments in thf show that the monosubstituted product is formed under thermodynamic control: elimination of the first equivalent of salt is thermodynamically downhill but the subsequent two salt elimination reactions are thermodynamically uphill. Consistent with this view, the salt elimination reactions are reversible: treatment of isolated samples of $NdL_3(thf)$ with NaCl in tetrahydrofuran generates the same $NdLCl_2(thf)_3$ monosubstituted product, along with two equivalents of the aminodiboranate salt NaL. The reversibility of the salt elimination reaction can be attributed to the solvation of the sodium cations by tetrahydrofuran, and the affinity of the Lewis acidic lanthanide centers for tetrahydrofuran and chloride relative to the aminodiboranate anion. The importance of the sodium-solvent and lanthanide-solvent interactions to the thermodynamics of salt elimination reactions is confirmed by the finding that the reaction of $NdCl_3(thf)_2$ with 3 equiv of NaL in diethyl ether proceeds – even in the reaction solution – to the fully substituted $NdL_3(thf)$ product.

1. Introduction

One of the most common and useful reactions in inorganic chemistry is the salt elimination reaction – also known as a salt metathesis reaction – which is one variety of the larger class of transformations known as double decomposition or double replacement reactions. In a typical salt elimination reaction, a metal derivative of one reagent (MA) is treated with a halide derivative of a second (BX) to form the desired product (AB) and salt (MX):

$$MA + BX \rightarrow AB + MX$$

Often, the salt MX precipitates from the solvent in which the reaction is carried out, and the insolubility of the salt byproduct is regarded as an important factor in the overall driving force for the reaction [1–7]. For this reason, silver halides are a popular choice for the elimination product if water is the solvent, but alkali metal halides such as NaCl are popular choices for reactions carried out in organic solvents (in contrast, LiCl is appreciably soluble in highly solvating organic solvents such as tetrahydrofuran, and in such cases precipitation will not contribute to the driving force for the exchange). Such salt elimination reactions are so common that, as far as we are aware, they have not been the subject of a review in the last 100 years, and often are employed in reaction sequences without comment.

It is generally assumed that the reaction products in salt elimination reactions are formed in the initial reaction mixture, and that the workup procedure simply separates the desired product from the salt. This assumption is particularly alluring if the workup procedure merely involves removing the reaction solvent and treating the solid residue with an innocuous extractant such as a saturated hydrocarbon. Here we discuss an interesting counterexample to this general expectation.

We have recently reported that the reaction of lanthanide trihalides in tetrahydrofuran with 3 equiv of sodium *N*,*N*-dimethylaminodiboranate, $Na[(H_3B)_2NMe_2]$, which we will refer to as NaL, followed by removal of the solvent and extraction with pentane, affords solutions from which the volatile tris(*N*,*N*-dimethylaminodiboranate)lanthanide complexes, $LnL_3(thf)$, can be isolated by crystallization in good (often 50–70%) yield [8].

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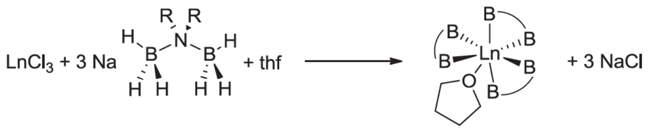

NaL **LnL$_3$(thf)**

The LnL$_3$(thf) compounds can be easily desolvated to form the binary aminodiboranates LnL$_3$, which are highly volatile and useful precursors for the chemical vapor deposition of lanthanide-containing thin films [9].

In the course of synthesizing the lanthanide tris(aminodiboranate) compounds, we discovered that the reaction mechanism is not as simple as the reaction stoichiometry above would suggest.

2. Results and discussion

2.1. Products of the reaction of NdCl$_3$ with Na[(H$_3$B)$_2$NMe$_2$]

Treatment of neodymium trichloride, NdCl$_3$, with 3 equiv of sodium *N,N*-dimethylaminodiboranate (NaL) in tetrahydrofuran for 15 h affords a blue solution. Removal of the solvent and extraction of the resulting residue with pentane gives a purple-colored extract whose ^{11}B{^{1}H} NMR spectrum (Fig. 1a) shows a single strong peak[1] at δ 106, which is assignable to the known trisubstituted compound NdL$_3$(thf) [9]. This chemical shift is identical to that seen when isolated samples of NdL$_3$(thf) are dissolved either in pentane or in tetrahydrofuran. The ^{11}B NMR chemical shift of this product is affected by the paramagnetic nature of the f^3 Nd^{III} center; for comparison, the chemical shift of the diamagnetic sodium salt NaL is δ −10 [10,11]. The reaction seems to proceed nearly quantitatively, although the isolated yields of the NdL$_3$(thf) product are typically 50–70%. These observations are consistent with the expectation that the reaction of NdCl$_3$ with 3 equiv of NaL in thf directly affords NaL$_3$(thf), and that no further changes in speciation occur upon workup.

Interestingly, however, examination of the ^{11}B{^{1}H} NMR spectrum of the crude NdCl$_3$ + 3 NaL reaction solution in thf does not show a peak at δ 106 due to the expected NdL$_3$(thf) product, even after extended reaction times. Instead, a there is a peak at δ 43 due to some other neodymium aminodiboranate species (**1**), and a strong resonance at δ −10 due to unreacted NaL (Fig. 1b). No change in the spectrum occurs even after the reaction solution is stirred for 7 days. These results indicate that—to our surprise—the final product NdL$_3$(thf) is not formed upon combining the two reactants (as is typical in salt elimination reactions), but instead is formed during a subsequent step in the reaction workup procedure. In order to further understand the mechanistic details of this reaction, we investigated the identity of species 1 and exactly when the final NdL$_3$(thf) product is formed.

In the ^{11}B{^{1}H} NMR spectrum of the crude NdCl$_3$ + 3 NaL reaction mixture in thf, the peak due to unreacted NaL has about twice the integrated area as the peak due to **1**. This result suggests that only one of the three equivalents of NaL has reacted with NdCl$_3$ to form the new neodymium aminodiboranate species **1**. To obtain support for this conclusion, we treated NdCl$_3$ with only one equivalent of NaL in thf. The ^{11}B{^{1}H} NMR spectrum of the resulting reaction solution shows a significant peak at δ 43 due to **1** but essentially no NaL. These results support the contention that **1** has the stoichiometry NdLCl$_x$(thf)$_y$. Whether **1** is a cation, an electrically neutral complex, or an anion depends on the number of halide ligands bound to the metal center.

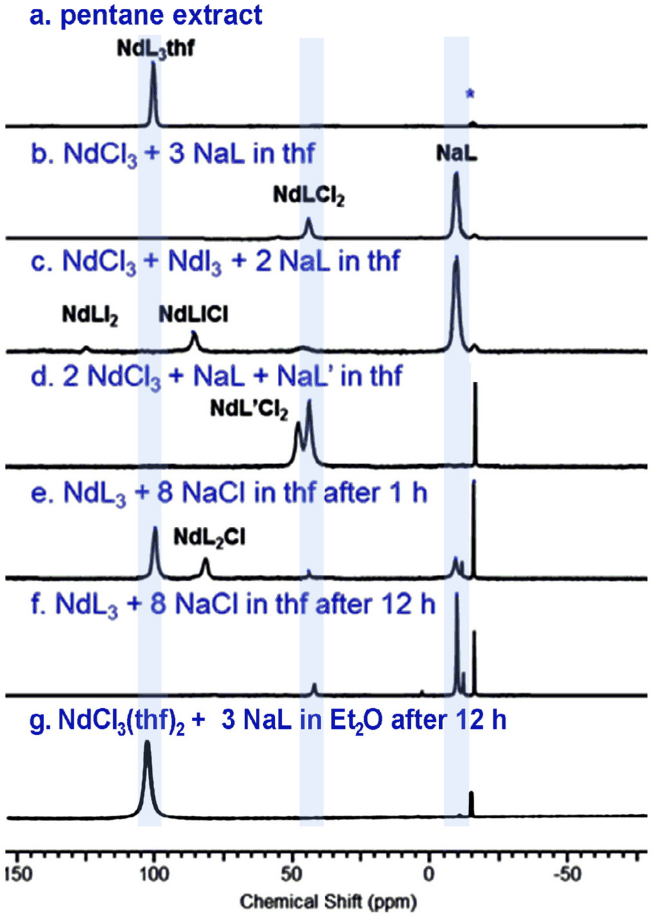

Fig. 1. Room temperature 128 MHz ^{11}B NMR spectra of the products of the reactions of NdX$_3$ with sodium *N,N*-dimethylaminodiboranate (NaL) in tetrahydrofuran. Spectrum (a) was obtained after removing the thf and extracting the residue with pentane; the remaining spectra are those of the indicated reaction mixtures. The symbol L′ stands for the piperidyldiboranate group, and the asterisk indicates impurities due to hydrolysis. The vertical stripes are guides for the eye.

Similar results are obtained upon treatment of the iodide starting material NdI$_3$(thf)$_{3.5}$ with 3 equiv of NaL in thf. The ^{11}B{^{1}H} NMR spectrum of the crude reaction mixture contains no peak at δ 106 due to NdL$_3$(thf), but instead contains a peak at δ 125 due to some other neodymium aminodiboranate species (**2**) and a resonance at δ −10 due to unreacted NaL, also in roughly a 1:2 ratio. The relative integrals again suggest that, of the three equivalents of NaL added, only one equivalent has reacted with the Nd trihalide to form **2**, and that the latter therefore has the stoichiometry NdLI$_x$(thf)$_y$. Removal of the thf solvent and extraction of the residue with pentane affords the desired product NdL$_3$(thf) in good yield. Therefore, the reactions of Nd trihalides with NaL proceed by the same pathway irrespective of the nature of the halide.

2.2. Determination of the stoichiometries of species *1* and *2*

Attempts to isolate **1** (or its iodo analogue **2**) from the reaction mixtures have so far been unsuccessful. Therefore, we have employed other strategies to establish their compositions. In order to determine the number of halide ligands bound to the Nd center, we carried out experiments in which both chloride and iodide ions were present. Because the reaction pathway does not depend on the identity of the halide, it should be possible to determine the number of metal-bound halides in the NdLX$_x$(thf)$_y$ species by

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[1] No resonance due to NaL is observed in this spectrum because it is insoluble in pentane and is left behind during the extraction step.

counting the number of $^{11}B\{^1H\}$ NMR peaks due to neodymium-containing species; we have previously employed this approach with success in other chemical systems [12]. Specifically: (1) if only two species are present, one must be the neodymium chloro complex and the other the iodo complex, and the Nd centers must bear only one halide ligand; (2) if three species are present, one must be the neodymium dichloro complex, one must be the chloro-iodo complex, and the other must be the diiodo complex, so that the Nd centers must bear two halide ligands; (3) if four species are present, then the Nd centers must bear three halide ligands, etc.

The mixed-halide experiment was carried out in two ways. First, an equimolar mixture of $NdCl_3$ and $NdI_3(thf)_{3.5}$ was treated with 2 equiv of NaL per Nd in thf for 16 h. The $^{11}B\{^1H\}$ NMR spectrum of the resulting mixture shows three resonances due to Nd aminodiboranate complexes (Fig. 1c): one at δ 43 due to the all-chloro species **1**, one at δ 125 due to the all-iodo species **2**, and a third resonance about half-way between these two, at δ 85, which is assigned as a mixed halide complex.

$$NdCl_3 + NdI_3 + 2\,NaL \xrightarrow{thf} \begin{array}{ll} NdLCl_2(thf)_3\ \mathbf{(1)} & \delta\ 43 \\ NdLICl(thf)_3 & \delta\ 85 \\ NdLI_2(thf)_3\ \mathbf{(2)} & \delta\ 125 \end{array}$$

These same three species are formed when $NdCl_3$ is treated with 1 equiv of NaL and then with 2 equiv of NaI. Thus, we can conclude that the reaction of neodymium trihalides with NaL in thf affords intermediates of stoichiometry $NdLX_2(thf)_y$ in which the Nd centers are coordinated to two halide ligands.

Similarly, the number of aminodiboranate ligands coordinated to the Nd centers in **1** was confirmed by treating $NdCl_3$ with a 1:1 mixture of two different aminodiboranate anions, sodium *N*,*N*-dimethylaminodiboranate (NaL) and sodium piperidyldiboranate (NaL′). The $^{11}B\{^1H\}$ NMR spectrum of the resulting thf solution shows two peaks: one at δ 43 due to **1** (which bears the ligand L), and one at δ 48 due to a second species **1′** that presumably contains the ligand L′ (Fig. 1d). The absence of resonances due to a third species in this mixture is consistent with the conclusion that only one aminodiboranate ligand is bound to the metal centers. From these results, species **1** is established to have the stoichiometry $NdLCl_2(thf)_y$.

As mentioned above, we have been unable to isolate solid samples of **1**, in part because this compound is too soluble in thf. We have, however, been able to obtain crystals of a similar compound with an aminodiboranate ligand that gives less soluble metal complexes. Thus, treatment of $ErCl_3$ with the unsubstituted aminodiboranate salt $Na[(H_3B)_2NH_2]$ in thf gives a pink solution from which crystals of $Er[(H_3B)_2NH_2]Cl_2(thf)_3$ can be isolated (see below). Like species **1**, this compound bears one aminodiboranate ligand and two halide ions per metal center, and also three thf ligands (see below). The crystal structure suggests that species **1** is also ligated by three thf ligands, for an overall stoichiometry of $NdLCl_2(thf)_3$.

2.3. When is $Nd[(H_3B)_2NMe_2]_3(thf)$ formed?

The above results show that the reaction of $NdCl_3$ with 3 equiv of sodium *N*,*N*-dimethylaminodiboranate, NaL, in thf results in replacement of only one of the chloride ligands to afford solutions of the monosubstituted complex $NdLCl_2(thf)_3$. Subsequent removal of the thf solvent and extraction with pentane gives the trisubstituted product $NdL_3(thf)$ in good yield. We were interested to determine at what point in the workup this latter product is formed. There are two possibilities: either during the thf removal step or during the pentane extraction step.

In an initial attempt to distinguish these possibilities, we carried out the following experiment. We treated $NdCl_3$ in thf with 3 equiv of NaL, removed the solvent until the reaction products were thoroughly dry, and then redissolved the residue in thf. The resulting solution gives a $^{11}B\{^1H\}$ NMR spectrum identical with that in Fig. 1b: only the monosubstituted species $NdLCl_2(thf)_3$ (**1**) and 2 equiv of unreacted NaL are seen. If one assumes that elimination of NaCl is chemically irreversible (which seemed reasonable owing to the high lattice energy of NaCl and the consequently large thermodynamic driving force associated with its formation), then this redissolution experiment suggests that $NdL_3(thf)$ is not formed until the pentane extraction step.

To obtain additional evidence about when $NdL_3(thf)$ is formed, we treated $NdCl_3$ with 3 equiv of NaL in thf, removed the solvent, and obtained a magic angle spinning (MAS) ^{11}B NMR spectrum of the resulting solid residue (Fig. 2). The spectrum contains only one major peak, which appears at δ 86. This peak corresponds to the *trisubstituted* product $NdL_3(thf)$, as shown by an independent MAS NMR study of purified samples of this latter compound. The ca. 20 ppm difference between the chemical shift in the solid state and that seen in solution is consistent with the differences seen in heteronuclear NMR spectra of other paramagnetic compounds, and is attributed in part to paramagnetic shielding effects and in part to the effect of rotor heating in the magic angle spinning experiment (chemical shifts of paramagnetic compounds often being strongly temperature-dependent) [13–16].

This result provides conclusive evidence that, in the reaction of $NdCl_3$ with 3 equiv of NaL in thf, the $NdL_3(thf)$ product is formed upon removal of thf, and that the pentane extraction merely serves to separate this species from sodium chloride and other reaction byproducts. At first glance, this finding seems inconsistent with the result of the thf redissolution experiment described above. In order to reconcile the two results, we are forced to the following conclusion: removal of thf from the reaction solution gives a mixture of $NdL_3(thf)$ and sodium chloride, but that addition of thf to this mixture reverses the salt elimination reaction and regenerates the monosubstituted species $NdLCl_2(thf)_3$ and NaL:

$$NdL_3(thf) + 2\,NaCl + 2\,thf \rightarrow NdLCl_2(thf)_3 + 2\,NaL$$

To confirm that this salt elimination reaction is reversible, we mixed a solid sample of purified $NdL_3(thf)$ with an excess of commercial NaCl and then added thf. After the mixture had been stirred for 1 h, the solution gave a $^{11}B\{^1H\}$ NMR spectrum with peaks at δ 43 and δ 86, which we assign to the monosubstituted compound $NdLCl_2(thf)_3$ (1) and the disubstituted compound $NdL_2Cl(thf)_y$, respectively (Fig. 1e). After the mixture had been stirred for 12 h, the only species observable in the $^{11}B\{^1H\}$ NMR spectrum were the monosubstituted product 1 and NaL (Fig. 1f). This result clearly shows that the salt elimination reaction can be reversed in thf. Similar equilibrium processes in salt elimination reactions have been proposed to exist in other lanthanide systems [17].

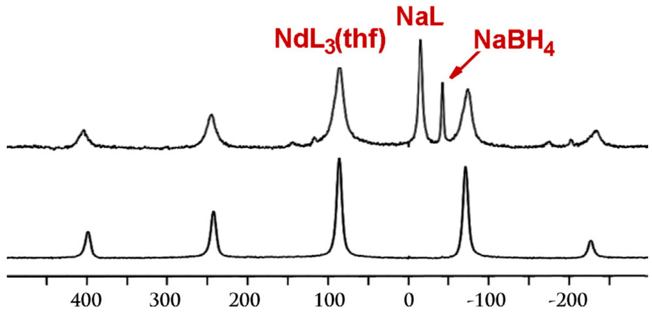

Fig. 2. Solid state 96 MHz MAS ^{11}B NMR spectrum at 15 kHz of (a) crude residue from the reaction of $NdCl_3$ with 3 equiv of NaL after removal of the thf solvent, and (b) a purified sample of $NdL_3(thf)$. The unlabeled peaks are spinning sidebands due to $NdL_3(thf)$. The integrations (including the spinning sidebands) suggest that very little (<10%) NaL remains in the crude residue.

We are led to the conclusion that the monosubstituted species $NdLCl_2(thf)_3$ is a thermodynamic (rather than kinetic) product of the reaction of $NdCl_3$ with 3 equiv of NaL. The reaction of **1** with the two remaining equivalents of NaL to afford the trisubstituted product $NdL_3(thf)$ and NaCl occurs only after the removal of thf.

$$NdCl_3(thf)_4 + 3\ NaL \xrightarrow[\text{- NaCl}]{\text{thf}} NdLCl_2(thf)_3 + 2\ NaL \underset{\text{add thf}}{\overset{\text{remove thf}}{\rightleftharpoons}} NdL_3(thf) + 2\ NaCl$$

2.4. Thermodynamics of the salt elimination reaction

Why does conversion of the monosubstituted product $NdLCl_2(thf)_3$ to the trisubstituted product $NdL_3(thf)$ occur only upon removal of the thf solvent? And why is the salt elimination reaction reversible? Normally, one assumes that the insolubility of salts such as NaCl in organic solvents helps to drive such reactions [18–21]. In fact, the solubility of NaCl in tetrahydrofuran is small: 6 mg/L [22]. The low solubility reflects the high lattice energy of NaCl compared to the interaction of its ionic components with the solvent. Tetrahydrofuran coordinates to sodium cations, and many hexacoordinate $Na(thf)_6$ cations have been crystallographically characterized [23–25]. Evidently, NaCl is insoluble in thf because the solvation of the chloride ions by this solvent is relatively poor.

In salt elimination reactions, however, additional energy terms become important. In the present case, lanthanide ions are strong Lewis acids, and are known to form strong bonds to halide anions. For example, the reaction of sodium pentamethylcyclopentadienide ions with lanthanide trichlorides often gives salts of stoichiometry $[Na(thf)_x][Cp^*_2LnCl_2^-]$, and conversion to electrically neutral Cp^*_2LnCl species requires special treatment such as refluxing in toluene, which drives off the thf and promotes the elimination of the alkali metal halide [26–28]. In addition, lanthanide ions form strong bonds to thf and other coordinating solvents [29,30]: in particular, $NdCl_3$ forms the tetra-adduct $NdCl_3(thf)_4$ [31].

Quantitative thermodynamic studies would be required to explain why the reaction of $NdCl_3$ with 3 equiv of NaL proceeds to the $NdLCl_2(thf)_3$ stage and then stops. But some inferences can be drawn from the observations above. In each step in the salt elimination sequence we have studied, one Nd—Cl bond and one Nd—thf bond are broken, and the liberated coordination sites are occupied by a chelating aminodiboranate ligand. A reasonable explanation of why the salt elimination reaction stops after the first step is that each step results in an increase in the strengths of the remaining Nd—Cl and/or Nd—thf bonds. Because of these additional energy terms, replacement of subsequent chloride–thf ligand pairs after the first pair becomes thermodynamically unfavorable.

The stability of $NdLCl_2(thf)_3$ toward further salt elimination reactions with the aminodiboranate anion must be a consequence of (1) the Lewis acidity of the Nd center and its affinity for tetrahydrofuran and chloride, (2) the solvation of the sodium ions by tetrahydrofuran, and also (3) the thermodynamics associated with replacement of a Cl–thf ligand pair with an aminodiboranate anion. Removal of tetrahydrofuran leads to the loss of the sodium solvation shell and an open coordination site on the lanthanide center, making NaCl precipitation and the formation of the trisubstituted $NdL_3(thf)$ thermodynamically favorable.

These conclusions suggest that the second and third salt elimination steps should become more thermodynamically favorable if the solvent is less able to solubilize the Na cations or attach less strongly to the Nd center. To test this hypothesis, we carried out the reaction of $NdCl_3(thf)_2$ with 3 equiv of NaL in the less strongly coordinating solvent diethyl ether. The reaction solution rapidly changes color from blue to purple, and a $^{11}B\{^1H\}$NMR spectrum of the solution shows a single intense peak at δ 106 (Fig. 1g) corresponding to the fully substituted product $NdL_3(thf)$. This experiment strongly supports the contention that the solvation of the sodium cations and the strength of the metal-solvent bonds are important factors in determining the thermodynamics of salt elimination reactions.

2.5. Synthesis and characterization of $Er[(H_3B)_2NH_2]Cl_2(thf)_3$

Isolation of the mono-substituted $NdLCl_2(thf)_3$ species is difficult because it is highly soluble in thf and it converts to NdL_3 in other solvents. In order facilitate crystallization of this $NdLCl_2(thf)_3$ species from thf, one strategy is to replace the methyl groups on the N,N-dimethylaminodiboranate ligand with groups that will lower the solubility in thf. Therefore, we investigated the analogous reaction with the parent (unsubstituted at nitrogen) aminodiboranate salt $Na[(H_3B)_2NH_2]$ [32] In order to test the generality of our observations, we also changed the lanthanide metal to erbium. Thus, treatment of $ErCl_3$ with 3 equiv of $Na[(H_3B)_2NH_2]$ in thf gives a pink solution, from which large pink blocks of the monosubstituted compound $Er[(H_3B)_2NH_2]Cl_2(thf)_3$, **3**, can be isolated. A $^{11}B\{^1H\}$ NMR spectrum of **3** in thf gives a peak at δ −176.2 (fwhm = 250 Hz). As we will show below, we are able to isolate this monosubstituted product because intermolecular hydrogen bonding interactions lower its solubility in thf.

A single-crystal X-ray diffraction study of **3** (Tables 1 and 2) confirms that only one chloride has been displaced by the aminodiboranate ligand (Fig. 3). If the aminodiboranate ligand is

Table 1
Crystallographic data for $Er[(H_3B)_2NH_2]Cl_2(thf)_3{\cdot}thf$, **3**.

Formula	$C_{16}H_{40}B_2Cl_2NO_4Er$
FW (g mol^{-1})	570.27
T (K)	193(2)
wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.9649(4)
b (Å)	21.9294(8)
c (Å)	11.2331(4)
β (deg)	90.552(2)
V (Å^3)	2454.59(16)
Z	4
ρ_{calc} (g cm^{-3})	1.543
μ (mm^{-1})	3.655
R_{int}	0.0815
Absorption correction	face-indexed
Maximum minimum transmission factors	0.477/0.204
Data/restraints/parameters	5678/1/267
Goodness-of-fit on F^2	1.073
R_1 $[F_o^2 > 2\sigma(F_o^2)]$[a]	0.0229
wR_2 (all data)[b]	0.0554
Maximum, minimum $\Delta\rho$ (e Å^{-3})	0.957/−0.783

[a] $R_1 = \sum|F_o| - |F_c||/|\sum|F_o|$ for reflections with $F_o^2 > 2\ \sigma(F_o^2)$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$ for all reflections.

Table 2
Selected bond lengths and angles for Er[$(H_3B)_2NH_2$]Cl_2(thf)$_3$·thf, **3**.

Bond lengths (Å)			
Er(1)—B(1)	2.775(4)	Er(1)—O(1)	2.366(2)
Er(1)—B(2)	2.791(4)	Er(1)—O(2)	2.3954(19)
Er(1)—H(11)	2.35(3)	Er(1)—O(3)	2.364(2)
Er(1)—H(12)	2.39(3)	Er(1)—Cl(1)	2.5956(7)
Er(1)—H(21)	2.36(3)	Er(1)—Cl(2)	2.5922(7)
Er(1)—H(22)	2.37(3)	N(1)—H(1)	0.84(2)
Bond angles (°)			
O(1)—Er(1)—O(2)	75.46(7)	O(1)—Er(1)—B(1)	133.95(10)
O(3)—Er(1)—O(1)	148.96(7)	O(1)—Er(1)—B(2)	78.98(10)
O(3)—Er(1)—O(2)	73.50(7)	O(2)—Er(1)—B(1)	150.54(10)
O(1)—Er(1)—Cl(1)	86.30(5)	O(2)—Er(1)—B(2)	154.44(11)
O(2)—Er(1)—Cl(1)	81.03(5)	O(3)—Er(1)—B(1)	77.09(10)
O(3)—Er(1)—Cl(1)	89.60(5)	O(3)—Er(1)—B(2)	132.06(11)
O(1)—Er(1)—Cl(2)	84.45(5)	Cl(1)—Er(1)—B(1)	97.15(8)
O(2)—Er(1)—Cl(2)	82.13(5)	Cl(1)—Er(1)—B(2)	96.94(8)
O(3)—Er(1)—Cl(2)	90.63(5)	Cl(2)—Er(1)—B(1)	100.08(8)
Cl(2)—Er(1)—Cl(1)	162.37(3)	Cl(2)—Er(1)—B(2)	95.97(8)
B(1)—Er(1)—B(2)	54.99(13)		

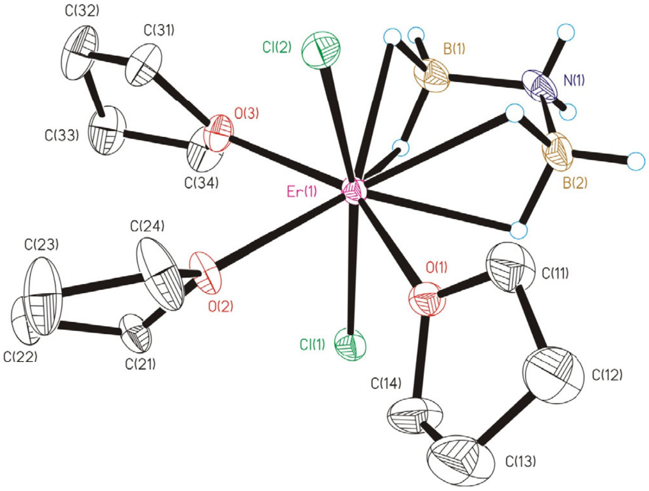

Fig. 3. Molecular structure of Er[$(H_3B)_2NH_2$]Cl_2(thf)$_3$, **3**. Ellipsoids are drawn at the 35% probability level. The hydrogen atoms attached to carbon have been removed for clarity.

considered to be bidentate, then the coordination geometry of **3** is a distorted pentagonal bipyramid, in which the two chlorine atoms occupy the axial sites (the "trans" Cl—Er—Cl angle is 162.37(3)°). The boron atoms occupy two mutually cis cites in the pentagonal girdle, the other three sites being occupied by thf ligands. The Er···B distances are 2.775(4) and 2.791(4) Å, and the Er—O distances to the coordinated thf molecules range from 2.364(2) to 2.395(2) Å; these distances are similar to those observed in other erbium aminodiboranate complexes [9]. A non-coordinated thf molecule is also present per formula unit, which is corroborated by the observation that isolated blocks of **3** turn from clear to opaque (indicative of desolvation) when they are exposed to a dynamic vacuum.

The crystal structure of **3** reveals that there are significant intermolecular hydrogen bonding interactions between the chlorine atoms and the N—H groups of the $(H_3B)_2NH_2^-$ ligands in adjacent molecules (Fig. 4). The H···Cl distance of 2.568 Å is significantly shorter than the 2.95 Å sum of the van der Waals radii, and the N···Cl distance of 3.387 Å compares well to the hydrogen-bonded N···Cl distance of 3.35 Å observed in ammonium chloride [33]. The hydrogen bonding in **3** can also be observed by IR spectroscopy: the N—H stretching band at 3148 cm^{-1} is shifted to lower energy relative to those of 3306 and 3265 cm^{-1} seen for Na($H_3BNH_2BH_3$) [32]. The strong hydrogen bonding in **3** probably lowers its solubility in tetrahydrofuran, thus making it easier for us to crystallize it from this solvent.

3. Conclusions

Treatment of $NdCl_3$ with 3 equivalents of NaL (L = *N,N*-dimethylaminodiboranate) in thf does not produce solutions of the trisubstituted product NdL_3(thf) as expected, but reacts to form the partially substituted intermediate $NdLCl_2$(thf)$_3$. NMR studies show that the reaction proceeds to completion in the solid state only after thf is removed from the reaction mixture. In addition, treatment of isolated NdL_3(thf) with excess NaCl in thf reverses the reaction to form the same $NdLCl_2$(thf)$_3$ compound. These results contradict the typical assumption in salt elimination reactions carried out in organic solvents that the precipitation of the NaCl byproduct drives the reaction. The coordination of the Na cations

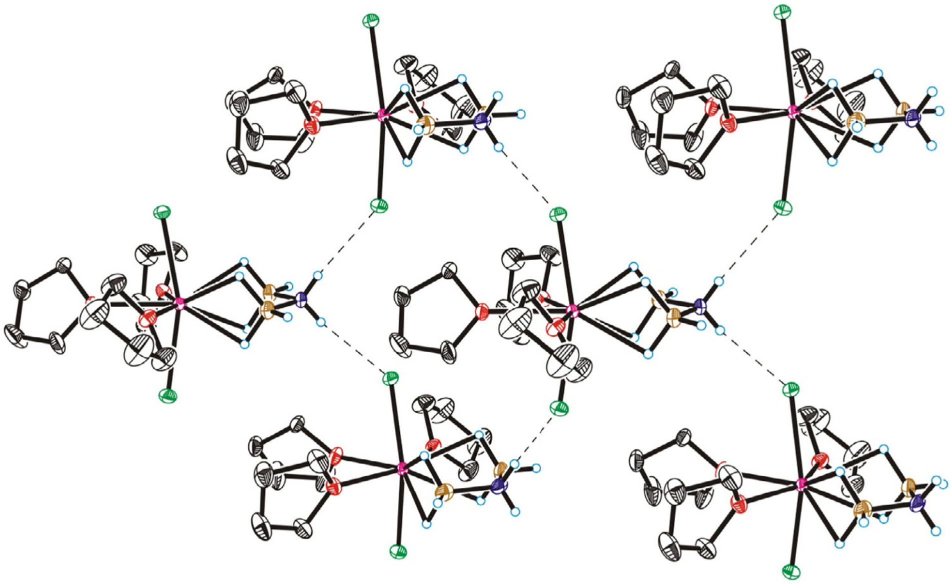

Fig. 4. Intermolecular N—H···Cl interactions observed for Er[$(H_3B)_2NH_2$]Cl_2(thf)$_3$, **3**. Ellipsoids are drawn at the 35% probability level. The hydrogen atoms attached to carbon have been removed for clarity.

by thf and the affinity of the metal center for chloride and tetrahydrofuran are important factors in dictating whether salt elimination reactions are thermodynamically favorable or unfavorable. Salt elimination reactions become more thermodynamically favorable if the solvent is less able to coordinate to the Na cations and the metal center. Consistent with this conclusion, we find that, in the less strongly coordinating solvent diethyl ether, $NdCl_3(thf)_2$ reacts with 3 equiv of NaL to afford solutions of the fully substituted product $NdL_3(thf)$. We believe this is a general effect, supported not only by our results but also by empirical observations in other systems: salt elimination reactions involving lanthanide metals are likely to be most effective in poorly coordinating solvents.

4. Experimental

All manipulations were carried out using standard Schlenk and drybox techniques under an atmosphere of dry argon. All glassware was dried in an oven at 150 °C, assembled hot, and allowed to cool under vacuum before use. Tetrahydrofuran and pentane were distilled under nitrogen from sodium/benzophenone and degassed with argon immediately before use. Anhydrous $NdCl_3$ (Strem) was used as received. Literature routes were used to prepare $NdCl_3(thf)_2$ [34], $NdI_3(THF)_{3.5}$ [35], $Na[(H_3B)_2NMe_2]$ [10], $Na[(H_3B)_2NC_5H_{10}]$ [8], and $Na[(H_3B)_2NH_2]$ [32].

The solution ^1H and ^{11}B NMR data were obtained on a Varian Unity 400 instrument at 400 and 128 MHz, respectively. The solid state ^{11}B MAS NMR data were collected on a General Electric GN300WB instrument at 96 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (^1H) or $BF_3{\cdot}Et_2O$ (^{11}B). The IR spectra were recorded on a Nicolet Impact 410 infrared spectrometer as Nujol mulls between KBr plates. Elemental analyses were carried out by the University of Illinois Microanalytical Laboratory.

4.1. Reaction of $NdCl_3$ with NaL in tetrahydrofuran

Tetrahydrofuran solutions of $NdCl_3$ (0.1 mM) and $Na[(H_3B)_2NMe_2]$ (0.3 mM) were combined at 0 °C and warmed to room temperature. Aliquots were taken periodically from the blue reaction mixtures, transferred to NMR tubes, and examined by ^{11}B and $^{11}B\{^1H\}$ NMR spectroscopy at room temperature. The blue reaction mixture was taken to dryness under vacuum to yield a purple solid, which was packed in a 4 mm Teflon rotor under inert gas and examined using ^{11}B MAS NMR spectroscopy.

Experiments involving $NdI_3(thf)_{3.5}$ and $Na[(H_3B)_2NC_5H_{10}]$ were conducted similarly.

4.2. Reaction of $NdL_3(thf)$ with NaCl in tetrahydrofuran

To a flask charged with NaCl (0.46 g, 7.9 mmol) and $Nd[(H_3B)_2NMe_2]_3(thf)$ (0.40 g, 1.0 mmol) at 0 °C was added tetrahydrofuran (15 mL). The purple suspension, which quickly turned blue, was stirred and warmed to room temperature. After 1 h, an aliquot was transferred to an NMR tube and examined by $^{11}B\{^1H\}$ NMR spectroscopy at room temperature. The stirring was continued for another 12 h, at which point another aliquot was examined by $^{11}B\{^1H\}$ NMR spectroscopy.

4.3. Reaction of $NdCl_3(thf)_2$ with NaL in diethyl ether

To a suspension of $NdCl_3(thf)_2$ (0.40 g, 1.0 mmol) at 0 °C in diethyl ether (15 mL) was added a solution of $Na[(H_3B)_2NMe_2]$ (0.28 g, 3.0 mmol) in diethyl ether (15 mL). The light blue suspension, which quickly turned purple, was warmed to room temperature and stirred for 18 h. An aliquot was taken and analyzed by ^{11}B NMR spectroscopy showed the presence of $NdL_3(thf)$ and no other significant amount of boron-containing species. The mixture was taken to dryness to yield a light purple solid, which was then extracted with pentane (2 × 15 mL). The extracts were filtered and combined, and the clear purple solution was concentrated to ca. 10 mL and cooled to −20 °C to afford large, lavender-colored crystals. The mother liquor was concentrated to ca. 5 mL and cooled to −20 °C to yield an additional crop of crystals. Yield: 0.17 g (43%). Analytical and spectroscopic properties are consistent with those reported previously for $NdL_3(thf)$ [8].

4.4. (Aminodiboranato)dichlorotris(tetrahydrofuran)erbium(III) tetrahydrofuran solvate, $Er[(BH_3)_2NH_2]Cl_2(thf)_3{\cdot}thf$

To a mixture of $ErCl_3$ (0.30 g, 1.1 mmol) in tetrahydrofuran (15 mL) cooled to 0 °C was added a solution of $Na[(H_3B)_2NH_2]$ (0.23 g, 3.5 mmol) in tetrahydrofuran (15 mL). The light pink suspension was warmed to room temperature and stirred for 24 h. The mixture was filtered and the clear, pink filtrate was concentrated to 10 mL and cooled to −20 °C to yield 0.14 g of small, light pink blocks. The mother liquor was concentrated to 6 mL and cooled to −20 °C to yield an additional 0.10 g of crystals. The crystals were placed under dynamic vacuum overnight, which resulted in the partial loss of the co-crystallized non-coordinated thf molecule observed in the diffraction studies. During this time the clear pink blocks turned opaque. Yield: 0.24 g (41%). *Anal.* Calc. for $Er[(H_3B)_2NH_2]Cl_2(thf)_{3.3}$: C, 30.5; H, 6.67; N, 2.69; Cl, 13.6. Found: C, 30.6; H, 6.87; N, 3.29; Cl, 13.9%. ^1H NMR (thf-d_8, 20 °C): δ −0.03 (br s, fwhm = 35 Hz, NH_2), 1.70 (br s, fwhm = 110 Hz, β-CH_2), 3.76 (br s, fwhm = 160 Hz, OCH_2). ^{11}B NMR (thf-d_8, 20 °C): δ −176.2 (br s, fwhm = 250 Hz, BH_3). IR (cm^{-1}): 3275 vs, 3247 vs, 3148 m, 2388 vs, 2306 m, 2281 m, 2236 vs, 1587 m, 1347 w, 1290 s, 1230 s, 1188 s, 1150 s, 1081 w, 1017 vs, 957 w, 919 m, 855 vs, 771 w, 673 w, 447 w.

4.5. Crystallographic information for $Er[(H_3B)_2NH_2]Cl_2(thf)_3{\cdot}thf$ [36]

The monoclinic lattice and systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$) were uniquely consistent with the space group $P2_1/n$, which was confirmed by the success of the subsequent refinement. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o)]^2 + (0.0112P)^2 + 2.0347P\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The chemically equivalent N—H distances were constrained to be equal within 0.01 Å. The largest peak in the final Fourier difference map (0.96 e $Å^{-3}$) was located 0.99 Å from Er1.

5. Supporting information

CIF file for the structure of **3**. This material has been previously reported [33]: DOI – 10.1021/ja1016427, CCDC identifier – 812707.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.01.046.

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