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Lanthanide Carbene Halides through Protonolysis of Ln−N Bonds by Imidazolium Salts: Synthesis and Structure of Salicylaldiminato-Functionalized N-Heterocyclic Carbene Lanthanide Bromides

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Summary: The three salicylaldiminato-functionalized N-heterocyclic carbene lanthanide bromides L_2LnBr *(Ln = Nd (**2**), Sm (**3**), Er (**4**); L =* [3,5-$^tBu_2$-2-(O)$C_6H_2CH{=}NCH_2CH_2$(C{NCHCHN^{i}Pr})]) *with early to late lanthanide metals were conveniently synthesized in moderate yields by a protonolysis strategy via the direct reaction of* LiLn(N^{i}Pr$_2$)$_4$ *with* [H$_2$L]Br *(**1**). All complexes were characterized by X-ray crystal determinations.*

Lanthanide halides with the general formula of L'_nLnX_{3-n} (L' = anionic ligand; n = 1, 2) are well-known to be important precursors for further transformations into a wide range of organolanthanide derivatives. However, the synthesis of these types of complexes with anionic functionalized N-heterocyclic carbene ligands (NHC) has been quite limited. The first amino-functionalized NHC cerium halides [CeL^1(N[SiMe$_3$]$_2$)(μ-X)]$_2$ (X = Br, I; L^1 = ^{t}BuNCH$_2$CH$_2$[C{^{t}BuN(CHCH)N}]),[1] the related neodymium iodide [NdL^2(N(SiMe$_3$)$_2$)(μ-I)]$_2$ (L^2 = ^{t}BuNCH$_2$CH$_2$[C{NC(SiMe$_3$)CHN^{t}Bu}]),[2] and the yttrium complexes YL^3(N{SiMe$_3$}$_2$)Cl and YL^{3}Cl$_2$ (L^3 = N{CH$_2$CH$_2$(1-C[NCHCHNMes]}$_2$)[3] were successfully prepared by the reaction of the corresponding carbene amide complexes with LiX or Me$_3$SiI. It was noticed, though, that no analogue with a late lanthanide metal has been reported, as the above approaches are not valuable for them.[4] Furthermore, no bis-carbene lanthanide halide has yet been synthesized. Therefore, it is highly desirable to develop an efficient method to access (NHC)$_n$-LnX$_{3-n}$ complexes with early to late lanthanide metals.

The utility of imidazolium salts for the preparation of transition-metal carbene complexes via protonolysis of suitable ligand−metal bonds, such as Cp−M,[5] indenyl−M,[6] and amido−M,[7] has been well documented. This approach has been proven to provide a good opportunity for accessing the corresponding d-block transition-metal halides, as no extra step is required and no byproduct produced. However, no example for the application of this approach to lanthanide carbene halide complexes has yet been reported, even though the protonolysis of lanthanide complexes by amines,[1,2,8] phenols,[9] and indenes[10] has been developed as a common protocol to carbene complexes of lanthanides. The reaction of Cp$_3$Yb with 2 equiv of 1,3-dimesitylimidazolium chloride (Imid$_2$Cl) was reported by the Cowley group to afford the salt [Imid$_2$Cp][Cp$_2$YbCl$_2$] instead of the desired carbene complex.[11] Considering the fact that the bonding of lanthanides to a free NHC ligand is weak and the bonding of a metal to an NHC with a pendant anionic functionalized group becomes stronger,[8a] we decided to explore a protonolysis strategy with an anion-functionalized imidazolium salt, with the hope of accessing a new route to lanthanide carbene halides. We began our research on the protonolysis of Ln−N bonds by using salicylaldimino-functionalized imidazolium salts, because this ligand is already known to play the role of a tridentate NHC ligand in Ni complexes via the coordination of O, N, and C$_{\text{carbene}}$ to the center metal,[12] and a tridentate NHC ligand binds to the central metal with stronger NHC−metal affinity as compared to a bidentate NHC.[3] Indeed, the strategy turned out to be successful. The target lanthanide carbene bromides L$_2$LnBr (Ln = Nd, Sm, Er; L = [3,5-^{t}Bu$_2$-2-(O)C$_6$H$_2$CH$=$NCH$_2$CH$_2$(C{NCHCHN^{i}Pr})]) with early to late lanthanide metals were synthesized in moderate yields via the direct reaction of LiLn(N^{i}Pr$_2$)$_4$ with [H$_2$L]Br (**1**). Here we wish to report these results.

Results and Discussion

The anionic lanthanide amide LiLn(N^{i}Pr$_2$)$_4$ was used as the substrate, since this amide has proven to be valuable in preparing NHC lanthanide complexes[9] and was the desired starting

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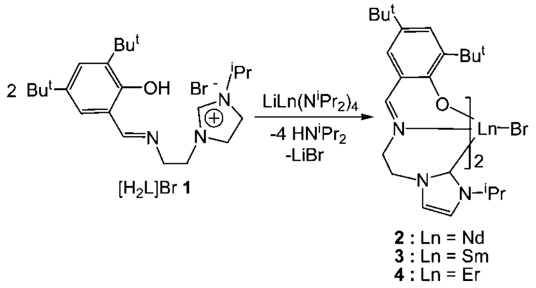
Scheme 1



material for the synthesis of a bis-NHC lanthanide halide. The salicylaldimino-functionalized imidazolium salt **1** was synthesized by a published method.[12] Treatment of a yellow suspension of **1** in THF with 0.5 equiv of a THF solution of $\mathrm{LiNd(N^{i}Pr_2)_4}$, which was synthesized by the reaction of anhydrous $\mathrm{NdCl_3}$ with $\mathrm{LiN^{i}Pr_2}$ in a 1:4 molar ratio[13] at −40 °C for 1 h and then at room temperature for another 4 h, afforded a red-brown solution. The bromide $\mathrm{L_2NdBr}$ (**2**) could be isolated as colorless crystals upon extraction with toluene and then crystallization from a mixture of toluene and THF in 61% yield. Elemental analysis confirmed that no amido group remained in the product (Scheme 1).

The paramagnetism of the complex precludes ^{13}C NMR spectroscopic identification of the carbenoid carbon. The same situation was also found in the cases of Nd, Ce, and Sm complexes reported previously.[1,2,8a] A further confirmation for the synthesis of **2** was obtained by X-ray structure determination. The molecular structure of **2** with important bond distances and angles is shown in Figure 1. It can be seen that the ligand L adopts a tridentate coordination mode (O, N, $\mathrm{C_{carbene}}$), and the seven-coordinated saturated sphere around the Nd metal precludes the formation of a dimer via a bromide bridge that is usually observed in lanthanide halide complexes. The geometry around the neodymium metal can be best described as a capped octahedron with one $\mathrm{C_{carbene}}$ atom (C(10)) in the capping position. Two N-heterocyclic rings are located on the opposite positions with a C(10)−Nd−C(10A) angle of 176.5(1)°, deviating from 180° due to the steric demand of two chelate salicyaldimino metal rings. The Nd−Br bond is almost perpendicular to the C(10)−Nd−C(10A) axis with an angle of 88.3(7)°. The two Nd−NHC bond distances in **2** are equal to 2.717(3) Å, which is about 0.070 Å shorter than the values reported for other neodymium−NHC bonds when the difference in ionic radii of an Nd ion with different coordination numbers is considered: for example, 2.609(3) Å for the four-coordinated $\mathrm{NdL^1[N(SiMe_3)_2]_2}$ and 2.656(5) Å for the five-coordinated $\mathrm{[NdL^2\{N(SiMe_3)_2\}(\mu\text{-}I)]_2}$.[2] The shorter $\mathrm{Nd-C_{carbene}}$ bond indicates that the metal−NHC binding is enforced by the tridentate NHC ligand. The Nd−Br bond distance of 2.962(7) Å is longer than the 2.771(2) Å and 2.778(2) Å found in ytterbocene bromide[14] if the ionic radii difference between Nd and Yb is considered, which may attribute to the more crowded coordination sphere around the Nd atom. The Nd−O distance of 2.242(2) Å is consistent with the values found in the related Schiff base complexes, while the Nd−N bond distance of 2.666(3) Å is slightly longer than those found in seven-coordinated Nd Schiff base complexes.[15]

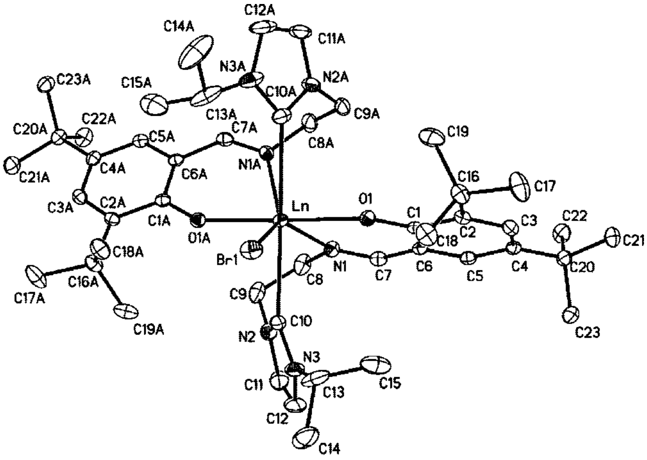


Figure 1. Crystal structure of **2** (Ln = Nd) and **3** (Ln = Sm) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2**: Nd1−O1 = 2.242(2), Nd1−N1 = 2.666(3), Nd1−C10 = 2.717(3), Nd1−Br1 = 2.9615(7), O1−C1 = 1.316(3), N1−C7 = 1.285(4), N2−C10 = 1.366(4), N3−C10 = 1.357(4); O1−Nd1−N1 = 69.49(7), O1−Nd1−C10 = 95.09(9), O1−Nd1−Br1 = 93.25(5), N1−Nd1−Br1 = 144.17(5), N1−Nd1−C10 = 63.48(9), C10−Nd1−Br1 = 88.27(7), O1−Nd1−O1A = 173.50(10), C10−Nd1−C10A = 176.53(14). Selected bond lengths (Å) and angles (deg) for **3**: Sm1−O1 = 2.215(4), Sm1−N1 = 2.571(5), Sm1−C10 = 2.685(6), Sm1−Br1 = 2.976(1), O1−C1 = 1.310(7), N1−C7 = 1.279(8), N2−C10 = 1.371(8), N3−C10 = 1.364(8); O1−Sm1−N1 = 70.52(15), O1−Sm1−C10 = 128.44(17), O1−Sm1−Br1 = 138.97(11), N1−Sm1−Br1 = 89.00(11), N1−Sm1−C10 = 74.23(18), C10−Sm1−Br1 = 74.85(13), O1−Sm1−O1A = 82.1(2), C10−Sm1−C10A = 149.7(3).

The success in the synthesis of **2**, which is the first example of a bis-carbene lanthanide halide, prompted us to evaluate the generality of the protonolysis approach to lanthanide halides. The same reactions with middle and late lanthanide metals were tested, with Sm and Er metals serving as representatives of middle and late lanthanide metals, respectively. Thus, the amide complexes $\mathrm{LiSm(N^{i}Pr_2)_4}$ and $\mathrm{LiEr(N^{i}Pr_2)_4}$ were synthesized by the same method to give yellow and pink crystals, respectively. The reaction of **1** with $\mathrm{LiSm(N^{i}Pr_2)_4}$ and $\mathrm{LiEr(N^{i}Pr_2)_4}$, respectively, was then conducted in toluene and went smoothly to give the corresponding red-brown and dark brown solutions, from which the yellow crystals were obtained in moderate yields, respectively. Elemental analyses revealed that no amido group remained in these complexes and the formulas were consistent with $\mathrm{L_2SmBr}$ (**3**) and $\mathrm{L_2ErBr}$ (**4**) (Scheme 1). The carbenoid carbon in both complexes cannot be identified by ^{13}C NMR because of the paramagnetism of the two metals. A further confirmation for **3** and **4** was obtained by X-ray diffraction. Both complexes exhibit capped-octahedral geometries similar to that for **2**. Interestingly, the angle $\mathrm{C_{carbene}-Ln-C_{carbene}}$ (C(10)−Ln−C(10A)) is remarkably dependent on the ionic radii of the central metals, as can be seen by comparison of the structures of **2**−**4**: the angle of C(10)−Ln−C(10A) decreases from 176.5(1)° for Nd and 149.7(3)° for Sm to 75.6(3)° for Er, in parallel with decreasing ionic radii. In addition, differences among the complexes regarding the arrangement of the coor-

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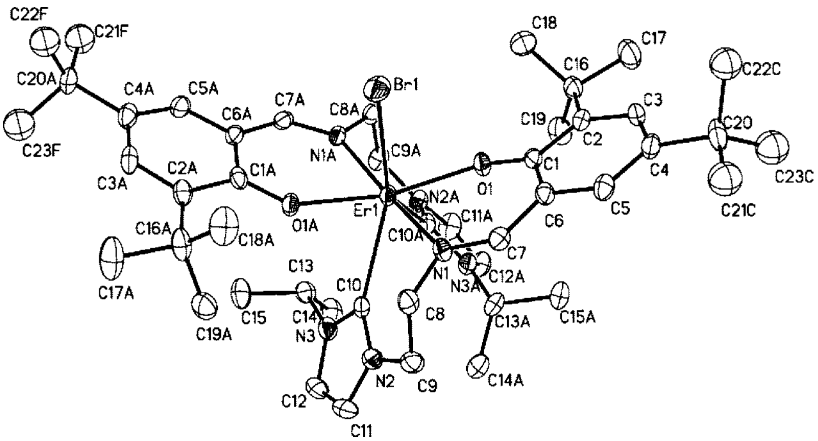
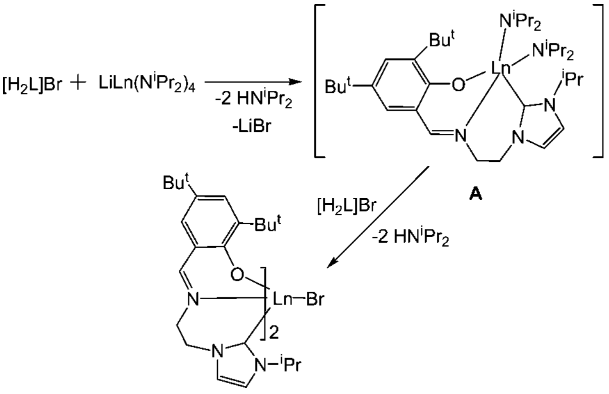


Figure 2. Crystal structure of **4** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Er1−O1 = 2.200(5), Er1−N1 = 2.440(6), Er1−C10 = 2.568(7), Er1−Br1 = 2.886(1), O1−C1 = 1.296(8), N1−C7 = 1.291(9), N2−C10 = 1.377(9), N3−C10 = 1.348(9); O1−Er1−N1 = 74.44(18), O1−Er1−Br1 = 121.24(19), O1−Er1−Br1 = 81.83(13), N1−Er1−Br1 = 86.74(13), N1−Er1−C10 = 73.4(2), C10−Er1−Br1 = 142.20(16), O1−Er1−O1A = 163.7(3), C10−Er1−C10A = 75.6(3).

Scheme 2. Possible Mechanism



dinating groups were also observed. For example, the capping position was occupied by one $C_{carbene}$ atom (C(10)) in both **2** and **3** but by the bromo atom in **4**; the two N-heterocyclic rings are located on opposite sides in **2** and **3** but on the same side in **4** (Figure 2), as can be seen from the C(10)−Ln−C(10A) angle. These differences in structure among **2**−**4** may reflect the demand for a more crowded coordination sphere around smaller metal centers. The Sm−$C_{carbene}$ bond distance of 2.685(6) Å is shorter than the 2.588(2) Å reported for the four-coordinated $SmL^1[(NSiMe_3)_2]_2$[8a] when the difference in ionic radii between the two complexes is considered. The value is comparable to that for **2** if the deviation of ion radius between Nd and Sm is taken into account. To the best of our knowledge, this is the first example of the synthesis and molecular structure of lanthanide NHC halides with a late metal and also the first crystal structure for an Er−NHC complex, and therefore the comparison of Er−$C_{carbene}$ bond distances can only be made with those for other lanthanide metal complexes. The Er−$C_{carbene}$ bond distance of 2.568(7) Å is comparable to those found in **2** and **3**, when the differences in ion radii among the three metals are taken into account.[16]

The synthetic pathway for **2**−**4** (Scheme 2) can be rationalized as follows: $LiLn(N^iPr_2)_4$ reacts first with **1** to afford the intermediate **A** via 2 equiv of amine elimination by both reaction of LiN^iPr_2 with imidazolium salt and the reaction of $Ln(N^iPr_2)_3$ with salicylaldimine. The intermediate **A** then reacts further with another 1 equiv of **1** to afford the bis-NHC bromide via the protonolysis of an Ln−N bond by the imidazolium salt. Attempts to isolate **A** by the reaction of $LiNd(N^iPr_2)_4$ with **1** in a 1:1 molar ratio and the reaction of **2** with $LiNd(N^iPr_2)_4$ in a 1:1 molar ratio, respectively, were unsuccessful; the former reaction still afforded **2**, although with lower yield, while the latter case gave an indefinite mixture. These results indicate that **A** is not stable enough in the present case.

Conclusion

In conclusion, we have presented a protonolysis strategy to access NHC lanthanide halides by the direct reaction of lanthanide amides with imidazolium salts. This route is valuable for complexes with early to late lanthanide metals. To the best of our knowledge, this is the first example of the synthesis of lanthanide NHC halides with early to late metals using a common method. Further study concerning the utility of this protonolysis of other suitable ligand−lanthanide bonds to synthesize NHC lanthanide complexes is now underway.

Experimental Section

General Considerations. All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. H_2LBr and $LiLn(N^iPr_2)_4$ were synthesized according to literature methods. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument.

Structure Determination. A suitable single crystal was sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(2) K. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using the programs SHELXS-97 and SHELXL-97, respectively. Crystal data and collection details and main refinement parameters are given in Table 1.

Preparation of L_2NdBr (2). A Schlenk flask was charged with **1** (0.91 g, 2.02 mmol), THF (25 mL), and a stir bar. To this suspension was added dropwise a solution of $LiNd(N^iPr_2)_4$ (0.84 M, 1.20 mL) in THF at −40 °C. The reaction mixture was stirred

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Table 1. X-ray Crystallographic Data for Complexes 2−4

	2	**3**	**4**
formula	$C_{46}H_{68}BrN_6O_2Nd$	$C_{58}H_{92}BrN_6O_5Sm$	$C_{54}H_{84}BrErN_6O_4$
mw	961.21	1183.64	1128.44
temp (K)	193(2)	193(2)	193(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	11.8146(17)	19.365(2)	13.1047(18)
b (Å)	15.281(2)	21.987(3)	14.4727(19)
c (Å)	26.667(4)	14.4724(17)	29.969(4)
α (deg)	90	90	90
β (deg)	100.577(3)	92.193(3)	98.948(3)
γ (deg)	90	90	90
V ($Å^3$)	4732.5(12)	6157.6(13)	5614.7(13)
Z	4	4	4
density (Mg/m^3)	1.349	1.277	1.335
abs coeff (mm^{-1})	1.982	1.65	2.253
no. of rflns	22 607	29 930	25 957
no. of unique rflns	4322	5637	5127
no. of params	263	318	297
R1 ($I > 2\sigma(I)$)	0.0354	0.0706	0.0658
wR2 (all data)	0.0668	0.1501	0.1536

for 1 h and gradually warmed to room temperature for an additional 4 h. The red-brown solution was evaporated to dryness and extracted with toluene. The toluene solution was concentrated, and drops of THF were added for crystallization. The product was obtained as colorless crystals at 15 °C (0.59 g, 61%); mp 224−227 °C dec under Ar. Anal. Calcd for $C_{46}H_{68}BrN_6O_2Nd$: C, 57.43; H, 7.07; N, 8.74. Found: C, 57.56; H, 7.38; N, 8.50.

Preparation of L_2SmBr (3). Complex **3** was prepared by an procedure analogous to that described above, except **1** (0.93 g, 2.08 mmol) and $LiSm(N^iPr_2)_4$ (0.80 M, 1.30 mL) were used. Yellow crystals that were suitable for X-ray diffraction were obtained from toluene/THF at −5 °C after a few days (0.66 g, 54%); mp 223−227 °C dec under Ar. Anal. Calcd for $C_{58}H_{92}BrN_6O_5Sm$: C, 58.85; H, 7.77; N, 7.10. Found: C, 58.12 ; H, 7.51; N, 7.58.

Preparation of L_2ErBr (4). Complex **4** was prepared by an procedure analogous to that described for **2**, except **1** (0.94 g, 2.10 mmol) and $LiEr(N^iPr_2)_4$ (0.84 M, 1.25 mL) were used. Yellow crystals were obtained upon crystallization from toluene/THF at room temperature after a few days (0.57 g, 48%); mp 225−228 °C dec under Ar. Anal. Calcd for $C_{54}H_{84}BrErN_6O_4$: C, 57.48; H, 7.44; N, 7.44. Found: C, 57.31; H, 7.38; N, 7.40.

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Supporting Information Available: CIF files giving crystallographic data for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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