DOI: 10.1002/ejic.200601167

Synthesis and Crystal Structure of New Early-Lanthanide Organometallic Clusters

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Keywords: Organolanthanide halide clusters / Lithium / Bridging ligands

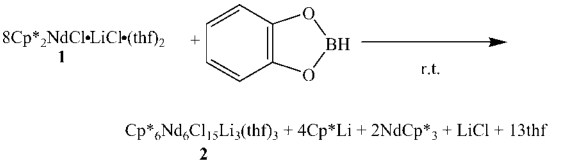
Reaction of $Cp^*{}_2NdCl{\cdot}LiCl{\cdot}2thf$ (**1**) with excess catecholborane affords the hexameric cluster $(Cp^*NdCl_2)_6(LiCl)_3(thf)_3$ (**2**) bearing three types of bridging chloride ions. Heating the reaction mixture affords the tetrameric cluster $[(Cp^*NdCl_2)_4(\mu_4\text{-}Cl)]_2[LiO_2][LiO_2{}^*Li_2O{}^*O_2]$ (**3**), which has the first crystal structure with the $LiO_2{}^+$ motif. Reaction of complex **1** or the analogous Sm complex, **4**, with pinacolborane affords clusters **5a** (Nd) or **5b** (Sm), respectively, a second type of hexameric cluster built from two $CpNd_3Cl_5(thf)$ units bonded by two μ_2-Cl atoms.

Introduction

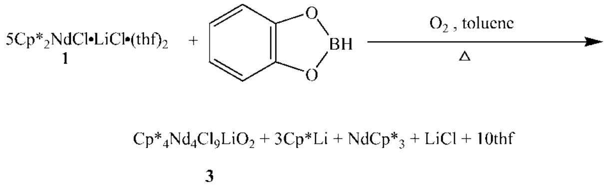
Organometallic rare-earth complexes bearing one Cp* ligand and a heteroatom have received considerable attention in recent years due to their potential use in homogeneous catalysis, especially in the polymerization of olefins.[1] However, the synthesis of mono(Cp) complexes of lanthanides is still a challenging task, because of the relative ease of the synthesis of bis(Cp) complexes and/or their rearrangement into the more thermodynamically stable homoleptic tris(Cp) derivatives.[2] In addition, these metals are also known to form organometallic heteroatom clusters.[3] Recently, Visseaux et al.[4] reported the synthesis and crystal structure of new monocyclopentadienyl lanthanide clusters bearing chlorido or borohydride bridges and up to six Nd or Sm atoms in the metallic backbone. Higher-order lanthanide–halide clusters bearing up to 12 metal atoms in the backbone were reported by Kretschmer et al.[5] In this contribution, we present the crystal structures of four new organolanthanide chlorido clusters as well as the unique counterion $LiO_2{}^+$.

Results and Discussion

We recently reported the synthesis of inclusion complexes of organic ligands with f-elements in which the metal is encapsulated by trianionic triborate–tribenzo crown ethers.[6a] When we attempted to prepare such a macrocyclic complex bearing Nd as the metal center by the reaction of catecholborane (HBcat) with complex **1**, $Cp^*{}_2NdCl{\cdot}LiCl{\cdot}2thf$ [Equation (1a)], we found that the presence of HBcat (neat, no solvent) induced a selective clustering reaction, yielding cubelike blue crystals of cluster **2**, which were analyzed by X-ray crystallography. Cluster **2** crystallizes in the cubic space group $I\bar{4}3d$ (see Table 1 for complete crystallographic data and Figure 1 for selective bond lengths and angles). The X-ray diffraction analysis (Figure 1) revealed a hexameric cluster structure bearing six Nd atoms bridged by 14 chloride ions. In addition, three groups of four chloride ions are bridged by a Li–thf moiety. Each Nd atom is also bonded to one Cp* ligand outside the cluster. The six Nd atoms describe a trigonal prism, which has a central isolated chloride ion (Cl7). The bonds between the Nd atoms and the central Cl atom are considerably longer (3.388 Å) than other Nd–Cl bonds in the cluster (2.92 Å in average, similar to those observed in the literature[4,5]). Each Nd atom has nine coordination sites. Interestingly, the presence of a μ^6-heteroatom in the center of a cluster has been already observed for oxygen,[7] halogen,[8] and selenium.[9]



(1a)



(1b)

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Table 1. Crystallographic data for complexes **2** and **3**.

	2	**3**
Color	blue	pale blue
Size [mm^3]	0.42 × 0.36 × 0.24	0.40 × 0.24 × 0.21
Chemical formula	$C_{75}H_{114}Cl_{15}Li_3Nd_6O_{4.5}$	$C_{42}H_{62}Cl_9Li_{1.33}Nd_4O_{2.5}$
Fw	2505.67	1512.18
Crystal system	cubic	monoclinic
Space group	$I\bar{4}3d$	$C2/m$
T [K]	240.0(1)	230.0(1)
a [Å]	34.407(7)	32.8430(6)
b [Å]	34.407(7)	21.1480(4)
c [Å]	34.407(7)	14.6670(4)
α [°]	90	90
β [°]	90	113.8510(8)
γ [°]	90	90
V [Å^3]	40732(14)	9317.2(4)
Z, D_{calc} [g cm^{-3}]	48, 1.634	6, 1.617
μ (Mo-K_α) [mm^{-1}]	3.435	3.703
θ range [°]	1.387–27.48	1.18–25.05
Limiting indices	$-44 \le h \le 29$; $-37 \le k \le 44$; $-22 \le l \le 35$	$-39 \le h \le 39$; $-23 \le k \le 25$; $-17 \le l \le 17$
Collected reflns./unique	38574/4085	15080/8487
R(int)	0.0870	0.0323
Parameters	324	293
GOF on F^2	1.054	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0426$, $wR_2 = 0.1210$	$R_1 = 0.0771$, $wR_2 = 0.2218$
ρ_{min}, ρ_{max} [e Å^{-3}]	–0.884, 1.359	–2.576, 1.400

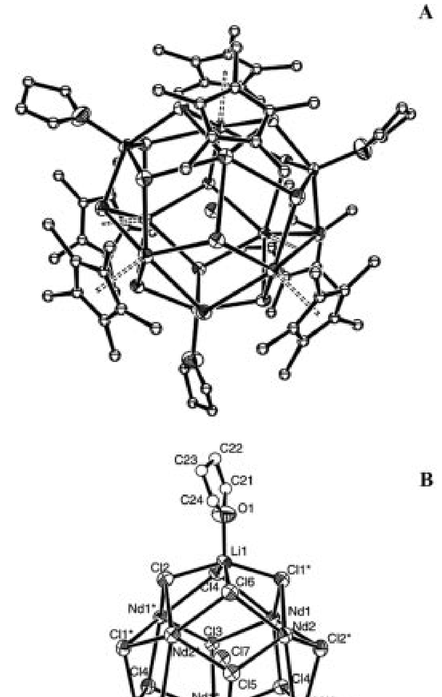


Figure 1. ORTEP representation (50% probability) of the molecular structure of complex **2**. (A) Full structure and (B) with removal of hydrogen atoms and Cp* ligands for clarity. Selected bond lengths [Å] and angles [°]: Nd1–Cl1* 2.898(3), Nd–Cp*(CNT) 2.341(10), Nd1–Cl2 2.882(3), Nd1–Cl5 2.972(4), Nd1–Cl7 3.388(5), Cl–Li 2.488(5), Li1–O1 1.931(6), Nd1–Nd2 4.427(10); Nd1–Cl7–Nd2 80.08(9), Nd1–Cl7–Nd1* 82.63(9), Nd1–Cl1*–Nd2 98.26(9).

The formation of **2** is accompanied by the formation of LiCp*, NdCp*$_3$,[10] and LiCl, as presented in Equation (1a); in contrast, a very small amount of product forms when the reaction is carried out in only a slight excess of the borane. It is important to point out that our attempts to perform the same reaction in the absence of the borane or by adding a strong Lewis acid (Me_3Al) resulted in decomposition products only.

When the same reaction was performed at higher temperatures (in the expectation of lowering the clustering effect) a different cluster was formed [Equation (1b)]. The crystal structure of cluster **3** (Figure 2 and Figure 3) revealed a tetrameric cluster with four Cp*Nd units bridged by eight μ_2-Cl ions. In addition, in the center of the square described by the four Nd atoms lies an isolated μ_4-Cl ion.[11] The unit cell contains two clusters, each with a –1 charge. These charges are counterbalanced by two microstructures of LiO_2^+ ion outside the cluster. In the first structure, the Li^+ ion is bonded to O_2 in a triangular fashion to form the ordered $[LiO_2]^+$. To the best of our knowledge, this is the first solid-state characterization of this motif. The O–Li–O angle is 46.5 °, which is the same as the calculated angle of the LiO_2 radical of 46.5 °.[12] However, the Li–O bond length (1.922 Å) differs significantly from the calculated length (1.76 Å),[12] which is reasonable if it is taken into account that the calculations were done for the LiO_2 radical and not the cationic $[LiO_2]^+$. We believe that the oxygen comes from contamination of the reaction mixture with traces of molecular oxygen in the glove box, where there is

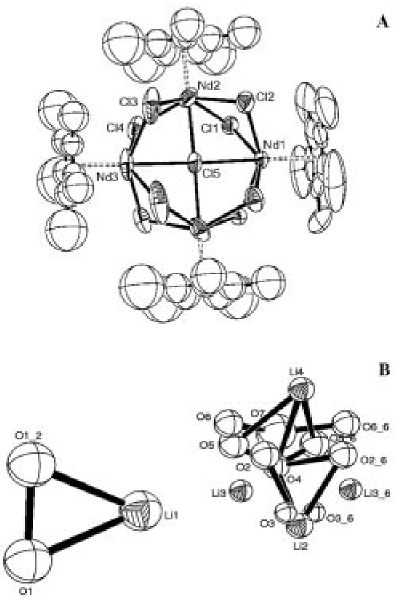


Figure 2. ORTEP representation (30% probability) of the molecular structure of compound **3**. (A) Side view of the anionic cluster; hydrogen atoms were removed for clarity. (B) Top view of both cationic microstructures: the ordered LiO_2^+ (left) and the disordered $LiO_2^+/Li_2O/O_2$ cluster fragment. Selected bond lengths [Å] and angles [°]: Nd1–Cl1 2.877, Nd–Cp*(CNT) 2.414, Nd1–Cl2 2.825, Nd1–Cl5 2.875, O1–Li1 1.943, Nd1–Nd2 4.090, O1–O1_2 1.534; Nd1–Cl5–Nd2 90.75, Nd2–Cl5–Nd3 89.17, Nd1–Cl1–Nd2 91.03, Nd1–Cl2–Nd2 92.32, O1–Li1–O1_2 46.87.

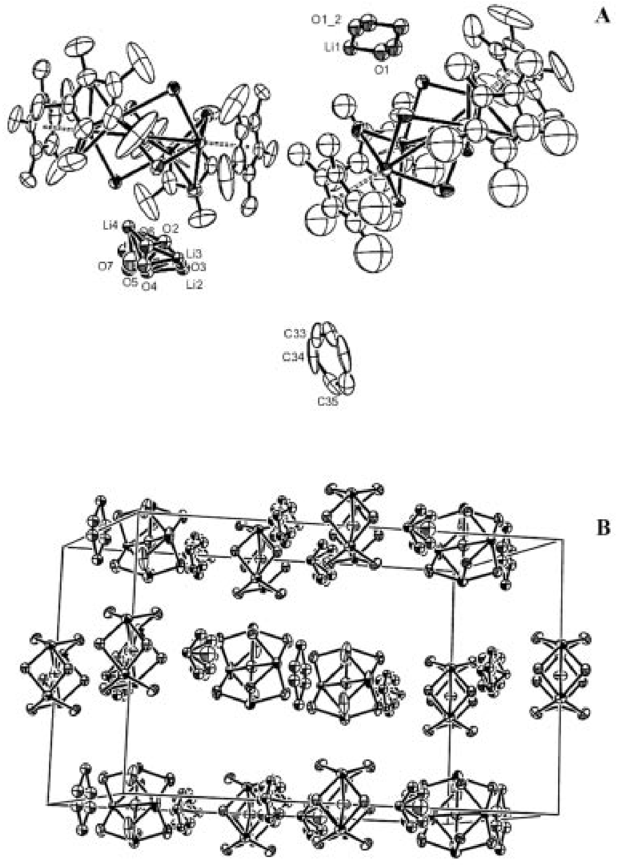
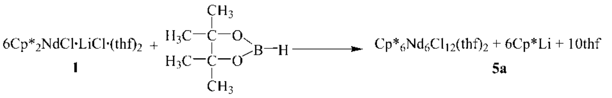
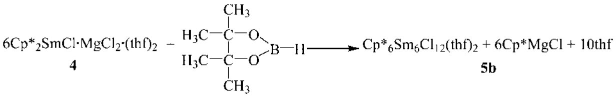


Figure 3. ORTEP representation (30% probability) of (A) the two different cluster units of complex **3**, along with the solvent molecule and the two microstructures of LiO_2^+ and (B) the unit cell of complex **3**. Cp* methyl groups and hydrogen atoms were removed for clarity.


$6Cp^*_2NdCl{\cdot}LiCl{\cdot}(thf)_2$ + HBpin → $Cp^*_6Nd_6Cl_{12}(thf)_2 + 6Cp^*Li + 10thf$ (2a)

1 **5a**


$6Cp^*_2SmCl{\cdot}MgCl_2{\cdot}(thf)_2$ – HBpin → $Cp^*_6Sm_6Cl_{12}(thf)_2 + 6Cp^*MgCl + 10thf$ (2b)

4 **5b**

Table 2. Crystallographic data for complexes **5a** and **5b**.

	5a	**5b**
Color	pale blue	pale red
Size [mm^3]	$0.12 \times 0.12 \times 0.08$	$0.12 \times 0.12 \times 0.08$
Chemical formula	$C_{68}H_{106}Cl_{12}Nd_6O_2$	$C_{68}H_{106}Cl_{12}O_2Sm_6$
Fw	2246.37	2283.09
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
T [K]	230.0(1)	240.0(1)
a [Å]	25.9700(8)	25.8930(11)
b [Å]	20.1800(6)	20.1770(10)
c [Å]	17.2250(7)	17.2360(9)
α [°]	90	90
β [°]	114.213(14)	114.135(3)
γ [°]	90	90
V [Å^3]	8233.0(5)	8217.7(7)
Z, D_{calc} [g cm^{-3}]	4, 1.812	4, 1.845
μ (Mo-K_α) [mm^{-1}]	4.142	4.646
θ range [°]	1.33–21.11	1.59–25.04
Limiting indices	$-26 \le h \le 26$; $-18 \le k \le 20$; $-17 \le l \le 17$	$-30 \le h \le 29$; $-22 \le k \le 24$; $-20 \le l \le 20$
Collected reflns./unique	8114/4465	25676/7259
R(int)	0.0452	0.2122
Parameters	412	398
GOF on F^2	0.932	0.794
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0637$	$R_1 = 0.0567$, $wR_2 = 0.0959$
ρ_{min}, ρ_{max} [e Å^{-3}]	–0.415, 0.528	–1.174, 1.333

no humidity and hence no hydrolysis products were observed. The presence of molecular oxygen can also be inferred from the second cationic microstructure, which shows a highly disordered $Li_3O_5^+$ fragment. This results from the combination of the following motifs: LiO_2^+, Li_2O, and O_2. The formulation of these fragments is postulated according to the occupancies of the different atoms, bond length, angles, and total charge of the unit cell.[13]

Addition of dry oxygen to the reaction mixture allowed us to synthesize complex **3**, although the yield was not predictable. It seems that the most important factor is the concentration of the oxygen dissolved in the solution and not its total amount in the Schlenk tube.

As we have reported,[6] the reaction of the analogous complex **4**, $Cp^*_2SmCl{\cdot}MgCl_2{\cdot}2thf$ with HBcat yields a macrocyclic inclusion complex. To exclude the option of macrocycle formation, we turned our attention to pinacolborane (HBpin), which was found to be inactive in the macrocycle formation reaction.[6a] The reaction of complexes **1** or **4** with excess HBpin at room temperature afforded crystals of the isostructural clusters **5a** (Ln = Nd) or **5b** (Ln = Sm), respectively [Equations (2a) and (2b)], which were characterized by X-ray crystallography. Both clusters crystallize in the monoclinic space group *C*2/*c* with almost identical unit cells (see Table 2 for complete crystallographic data and Figure 4 for selective bond lengths and angles). As depicted in Figure 4, compound **5** is a hexameric cluster built from two symmetric units, which are bonded by two μ_2-Cl ions (Cl6 and Cl6*). Each unit is built from three Ln atoms, two of which are bonded to the two μ_2-Cl ligands, while the third Ln atom has a coordinated thf ligand, maintaining the stereoelectronic saturation of the cluster. In each $(Cp^*Ln)_3Cl_5$ unit, there are two μ_3 (Cl1 and Cl4) and three μ_2 (Cl2, Cl3, and Cl5) bridging chlorido ligands. The structure of the fragment can be regarded as a hexagonal plane of alternating Ln and Cl atoms and two apical Cl ligands bonded to the metal. In the overall structure of the cluster, the six Ln centers adopt a chairlike geometry with Cp*Ln(thf) ends, similar to that of the mixed chlorido/borohydride clusters presented by Visseaux et al.[4] As can be expected from the smaller ionic radii of Sm relative to Nd, the bond lengths in **5b** are slightly shorter than those in **5a**.[14] Regarding the role of borane in the formation of the clusters, we suggest that the thf ligands of complexes **1** and **4** are removed by the borane in order to coordinate the boron atom instead of the Li or Mg salt. Attempts to determine the fate of the Cp* ligation were unsuccessful. The removal of LiCl/MgCl$_2$ and solvent from the starting complex by the strong Lewis acidic borane induces the coordinative unsaturation of the resulting complex. In addition, we propose that the borane fragment has a role in trapping one of the Cp* ligands of the starting complex. These two factors increase the tendency of the remaining Cp*LnCl fragments to form clusters. Attempts to perform the reaction without a borane did not lead to products but rather resulted in decomposition.

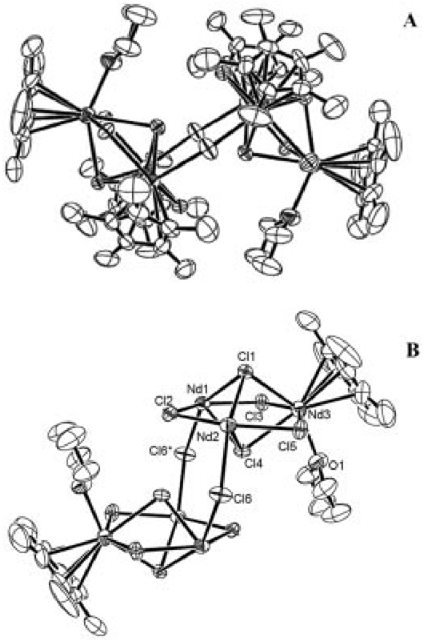


Figure 4. ORTEP representation (50% probability) of the molecular structure of complex **5a**: (A) full structure and (B) with removal of hydrogen atoms and Cp* ligands (bonded to Nd1 and Nd2) for clarity. Selected bond lengths [Å] and angles [°]: Nd–Cl1 2.932, Nd–Cp*(CNT) 2.414(9), Nd–Cl4 2.898(2), Nd1–Cl2 2.795(2), Nd1–Cl3 2.834(2), Nd1–Cl6* 2.758(2), Nd2–Cl6 2.772(2), Nd3–Cl3 2.784(2), Nd3–O1 2.458(6), Nd–Nd 4.122(5); Nd1–Cl1–Nd2 88.58(12), Nd1–Cl4–Nd2 91.59(6), Nd1–Cl2–Nd2 95.81(6), Nd2–Cl6–Nd1* 136.60(9). Complex **5b** shows an isostructural cluster. Selected bond lengths [Å] and angles [°] for complex **5b**: Sm–Cl1 2.884, Sm–Cp*(CNT) 2.361(15), Sm–Cl4 2.912(4), Sm1–Cl2 2.789(3), Sm1–Cl3 2.825(4), Sm1–Cl6* 2.743(3), Sm2–Cl6 2.769(4), Sm3–Cl3 2.771(4), Sm3–O1 2.435(10), Sm–Sm 4.101(7); Sm1–Cl1–Sm2 88.66(9), Sm1–Cl4–Sm2 91.63(9), Sm1–Cl2–Sm2 95.63(9), Sm3–Cl6–Sm1* 137.05(14).

Conclusion

In conclusion, we have presented four new mono-Cp* lanthanide clusters, composed of tetramers or hexamers with chloride ions as the bridging units of the cluster. These complexes are formed by the reaction of a borane with the complexes containing chlorido ligands. In addition, the crystal structure of the unique and unusual LiO$_2^+$ counterion was presented.

Experimental Section

Instruments and Methods: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, in a Schlenk line interfaced with a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1–2 ppm O$_2$). Argon and nitrogen were purified by passage through a MnO oxygen removal column and a Davison 4 Å molecular sieves column. NMR spectra were recorded with Avance 300 and Avance 500 spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted in Teflon valve-sealed tubes (J. Young) after vacuum transfer of the liquids in a high vacuum line.

Reagents and Standards: Hydrocarbon solvents [D$_8$]thf, [D$_6$]benzene, and [D$_8$]toluene (Aldrich) were distilled under nitrogen from over a Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. NdCl$_3$ (Aldrich) was degassed and stored under argon. Catecholborane (HBcat) and pinacolborane (Hbcat) (Aldrich) were used without purification. Cp*$_2$NdCl·LiCl·2thf[15] and Cp*$_2$SmCl·MgCl$_2$·2thf[6c] were prepared according to published procedures.

Crystal Structure Determination – General Procedure: Single crystals immersed in Parathone-N oil were quickly removed with a glass rod and mounted on a KappaCCD diffractometer under a cold stream of nitrogen at 230 K. Data collection was carried out with monochromatized Mo-K_α radiation by using omega and phi scans to cover the Ewald sphere.[16] Accurate cell parameters were obtained with complete collections of intensities and these were corrected in the usual way.[17,18] The structures were solved by direct methods and completed by using successive Fourier difference maps.[19] Refinements were performed anisotropically with respect to the non-hydrogen atoms.[20] Hydrogen atoms were placed at calculated positions and refined by using the riding model until convergence was reached. Figures were prepared with ORTEP.[21]

Syntheses

Cp*$_6$Nd$_6$Cl$_{15}$Li$_3$(thf)$_3$ (2): A Schlenk tube was charged in the glovebox with Cp*$_2$NdCl·LiCl·2thf (35 mg, 0.056 mmol) and HBcat (80 mg, 0.67 mmol). After 24 h at room temperature, the large, cubelike, blue crystalline precipitate was isolated (15 mg, 86%) and characterized by single-crystal X-ray diffraction. ^{1}H NMR (500 MHz, [D$_8$]thf, 298 K): δ = 8.23 (s, 15 H, C$_5$*Me*$_5$) ppm. ^{13}C NMR (125 MHz, [D$_8$]thf, 298 K): δ = 243.6 (s, *C*$_5$Me$_5$), –14.7 (s, C$_5$*Me*$_5$) ppm. $C_{72}H_{114}Cl_{15}Li_3Nd_6O_4$ (2483.5): calcd. C 34.79, H 4.59, Cl 21.44; found C 35.02, H 4.12, Cl 21.21.

[Cp*$_4$Nd$_4$Cl$_9$]$_2$[LiO$_2$]$_2$·Li$_2$O·O$_2$·3C$_6$H$_6$ (3): A Schlenk tube was charged in the glovebox with Cp*$_2$NdCl·LiCl·2thf (35 mg, 0.056 mmol), HBcat (80 mg, 0.67 mmol), and toluene (1 mL) and then heated to 110 °C for a few days. After the heating period, the white precipitate was removed by filtration to leave behind a clear blue solution. The solvent was removed by vacuum, and benzene was added to the tube by vacuum transfer. The tube was allowed to stand at high temperature for 24 h, affording a few pale blue crystals, which were isolated (10 mg, 44%) and characterized by single-crystal X-ray diffraction. ^{1}H NMR (500 MHz, [D$_8$]thf, 298 K): δ = 8.55 (s, 15 H, C$_5$*Me*$_5$) ppm. Attempts to introduce measured amounts of dry oxygen resulted in the same product but in lower yields. When a measured amount or regular-moisture air was introduced into the reaction mixture, no product was observed.

$C_{98}H_{138}Cl_{18}Li_4Nd_8O_7$ (3245.6): calcd. C 36.24, H 4.25, Cl 19.68; found C 35.02, H 4.09, Cl 20.67.

[Cp*$_3$Nd$_3$Cl$_5$(thf)]$_2$(μ$_2$-Cl)$_2$ (5a): A Schlenk tube was charged in the glovebox with Cp*$_2$NdCl·LiCl·2thf (35 mg, 0.056 mmol) and HBpin (80 mg, 0.62 mmol). After 72 h at room temperature, the blue crystalline precipitate was isolated (18 mg, 86%) and characterized by single-crystal X-ray diffraction. ^{1}H NMR (500 MHz, [D$_8$]thf, 298 K): δ = 7.89 (s, 15 H, C_5Me_5) ppm. ^{13}C NMR (125 MHz, [D$_8$]thf, 298 K): δ = 240.5 (s, C_5Me$_5$), –13.2 (s, C$_5Me_5$) ppm. $C_{68}H_{106}Cl_{12}Nd_6O_2$ (2246.37): calcd. C 36.32, H 4.71, Cl 18.96; found C 35.94, H 4.47, Cl 19.11.

[Cp*$_3$Sm$_3$Cl$_5$(thf)]$_2$(μ$_2$-Cl)$_2$ (5b): A Schlenk tube was charged in the glovebox with Cp*$_2$SmCl·MgCl$_2$·2thf (35 mg, 0.054 mmol) and HBpin (80 mg, 0.62 mmol). After 72 h, the colorless crystalline precipitate was isolated (18 mg, 87.8%) and characterized by single-crystal X-ray diffraction. ^{1}H NMR (500 MHz, [D$_8$]thf, 298 K): δ = 2.45 (s, 15 H, C$_5Me_5$) ppm. ^{13}C NMR (125 MHz, [D$_8$]thf, 298 K): δ = 113.8 (s, C_5Me$_5$), 16.3 (s, C$_5Me_5$) ppm. $C_{68}H_{106}Cl_{12}O_2Sm_6$ (2283.09): calcd. C 35.74, H 4.64, Cl 18.65; found C 36.01, H 4.35, Cl 18.11.

Crystal Structure Analysis of Complex 3: A single pale blue crystal was removed from Parathone oil and mounted on the KappaCCD diffractometer under a cold stream of nitrogen at 230 K. Unit cell parameters were determined with 9306 reflections by using Mo-K_α radiation. The complete set of 15080 reflections were collected and processed in the usual way. The structure was solved by direct methods with the program package 'maXus'. After the correct space group *C*2/*m* was established, Fourier maps revealed the positions of the heavy atoms as follows: Nd1, Nd3, and Cl5 on the mirror plane at y = 0 site *i*, Cl6 and Cl7 on the mirror plane at y = 0.5 site *i*, Cl9 on site 2/*m* (*b*) and Nd2, Nd4, Cl1, Cl2, Cl3, Cl4, and Cl8 in general positions. The positions of these heavy atoms were refined anisotropically by using the SHELXL97 program package. The carbon atoms of the Cp* groups found from Fourier difference maps were refined anisotropically, whereas the positions of the methyl hydrogen atoms were calculated and shifted by using the riding model.

At this stage it was clear that the unit cell contains six cluster units of $Nd_4Cl_9Cp*_4$ bearing a charge of –1 by assuming a valence of +3 for the Nd cation. One cluster unit defined by Nd1–Nd3 is located on a mirror plane at y = 0, whereas a second cluster defined by Nd4 occupies a 2/*m* site (*b*), and the overall number of clusters is (½ + ¼)·8 = 6. Careful examination of the difference maps revealed numerous small peaks which could not be assigned easily as Li$^+$ counterions. Three peaks with occupancies of ½ were identified as half benzene rings located on the mirror plane at y = 0. The remaining peaks were found to be grouped into two regions, and they were analyzed by considering the interaction of disordered Li$^+$ ions with oxygen molecules and charged oxygen species. After tedious attempts, the following occupancies were given to the Li and oxygen atoms by constraining the total charge, keeping reasonable geometries for the Li–O species, and meaningful U_{iso} values for the various atomic positions (Table 3).

Table 3. List of atoms and occupancies in one of the counterions for complex **3**.

Atom	Occupancy	U_{iso}	Number of atoms in the unit cell
Li1	0.25	0.072	2
Li2	0.25	0.056	2
Li3	0.25	0.044	2
Li4	0.25	0.055	2
O1	0.50	0.087	4
O2	0.50	0.069	4
O3	0.125	0.038	1
O4	0.25	0.062	2
O5	0.25	0.077	2
O6	0.125	0.0751	–
O7	0.125	0.141	–

This model fulfils the following formula per unit cell: $6LiO_2·Li_2O·O_2$ or $LiO_2·Li_2O·O_2$ per cluster unit. The LiO_2 unit grouped separately is located on a mirror plane and is attributed to the interaction of Li$^+$ with neutral O_2. The second region of grouped peaks contains Li_2O composed of Li$^+$ and O^{-2}. There is also O_2 as a neutral species. In this model only one Li$^+$ neutralizes the charge of one cluster unit.

CCDC-643835, 643836, 643843, 643844 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This research was supported by the Israel Science Foundation Administered by the Israel Academy of Science and Humanities under Contract 1069/05.

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Received: December 10, 2006