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Studies on organolanthanide complexes

XLVI *. Synthesis and characterization of N-containing ring-linked biscyclopentadienyl lanthanide and yttrium chlorides

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Abstract

Four new title complexes, $[CH_3N(CH_2CH_2C_5H_4)_2LnCl]_2$ (Ln = Y, Yb, Sm, Nd), were synthesized by using amine-linked biscyclopentadiene, $CH_3N(CH_2CH_2C_5H_5)_2$, as ancillary ligands and fully characterized by elemental analyses, MS, IR and ^1H NMR. Their spectroscopies indicate that these complexes are chloride-bridged dimers and the two amine-linked cyclopentadienyl rings coordinate to one metal in a chelating fashion with intramolecular coordination from the nitrogen atom to the metal.

1. Introduction

The chemistry and application to synthetically useful organic transformations and polymerization of organolanthanide complexes containing Ln–H, Ln–C and Ln–N bonds have become the most active field of organolanthanide chemistry [1–7]. Because organolanthanide chlorides are the most important precursors for such complexes, the synthesis and reactivity of the chlorides have been widely studied, especially for the early rare earth metals owing to their higher reactivities. Following this approach, a series of ring-bridged biscyclopentadienyl ligands, which are effective in avoiding the proportionation of the early lanthanide chlorides and derivatives, have been developed [8–24].

It has been suggested [10,11,24,25] that the presence of the bridging group should prevent the complexes from undergoing intermolecular ligand redistribution, decrease the torsional mobility of the cyclopentadienyl ring and open the coordination sphere around the central metal, and therefore favour the availability of coordination sites for an additional ligand or intermediate coordinated substrates and enhance the possibility of acquiring more stable, but also catalytically more active, organolanthanide complexes. These promising features are strengthened when the rigidity of the bridging chain increases and/or a heteroatom is introduced into the chain [13,17]. At this time, it is of significance to systematically investigate the effects of the rigidity of the bridging chain and the coordination from the heteroatom to the lanthanide metal upon the torsional mobility of the cyclopentadienyl rings and the potential for opening the coordination sphere of the lanthanide metal. As a part of this work, we report the synthesis and characterization of four new amine-linked biscyclopentadienyl lanthanide and yttrium chlorides, and briefly discuss the influence of intramolecular coordination from the nitrogen atom to the central metal on the above-mentioned properties.

2. Results and discussion

The title complexes $[CH_3N(CH_2CH_2C_5H_4)_2LnCl]_2$ [Ln = Y (**1**), Yb (**2**), Sm (**3**), Nd (**4**)], were prepared in high yields by treating anhydrous $LnCl_3 \cdot n$THF ($n = 0$, 3 or 4) with the disodium salt, $CH_3N(CH_2CH_2C_5H_4)_2$-Na_2 (**5**), under the given conditions. The disodium salt (**5**) was prepared by the reaction of $Na(C_5H_5)$ with

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$CH_3N(CH_2CH_2Cl)_2$ (**6**) followed by treatment with excess sodium sand, crystallizing from the solution of 1,2-dimethoxyethane (DME). The synthesis of **6**, based on the replacement of the OH groups of $CH_3N(CH_2CH_2OH)_2$ by treatment with $SOCl_2$, was carried out by the literature method [26]. The whole procedure is presented in eqns. (1)–(4).

$$CH_3N(CH_2CH_2OH)_2 + 2SOCl_2 \xrightarrow{CHCl_3} \underset{(\mathbf{6})}{CH_3N(CH_2CH_2Cl)_2} \qquad (1)$$

$$\underset{(\mathbf{6})}{CH_3N(CH_2CH_2Cl)_2} + 2Na(C_5H_5) \xrightarrow[0-10°C]{THF} CH_3N(CH_2CH_2C_5H_5)_2 \qquad (2)$$

$$CH_3N(CH_2CH_2C_5H_5)_2 + 2Na \xrightarrow[\text{room temperature } -45°C]{THF} \underset{(\mathbf{5})}{CH_3N(CH_2CH_2C_5H_4)_2Na_2} \qquad (3)$$

$$\underset{(\mathbf{5})}{2CH_3N(CH_2CH_2C_5H_4)_2Na_2} + 2LnCl_3 \cdot nTHF \xrightarrow[-30°C-\text{room temperature}]{THF} [CH_3N(CH_2CH_2C_5H_4)_2LnCl]_2 \qquad (4)$$

Ln = Y (**1**), Yb (**2**), $n = 0$; Ln = Sm (**3**), $n = 3$; Ln = Nd (**4**), $n = 4$

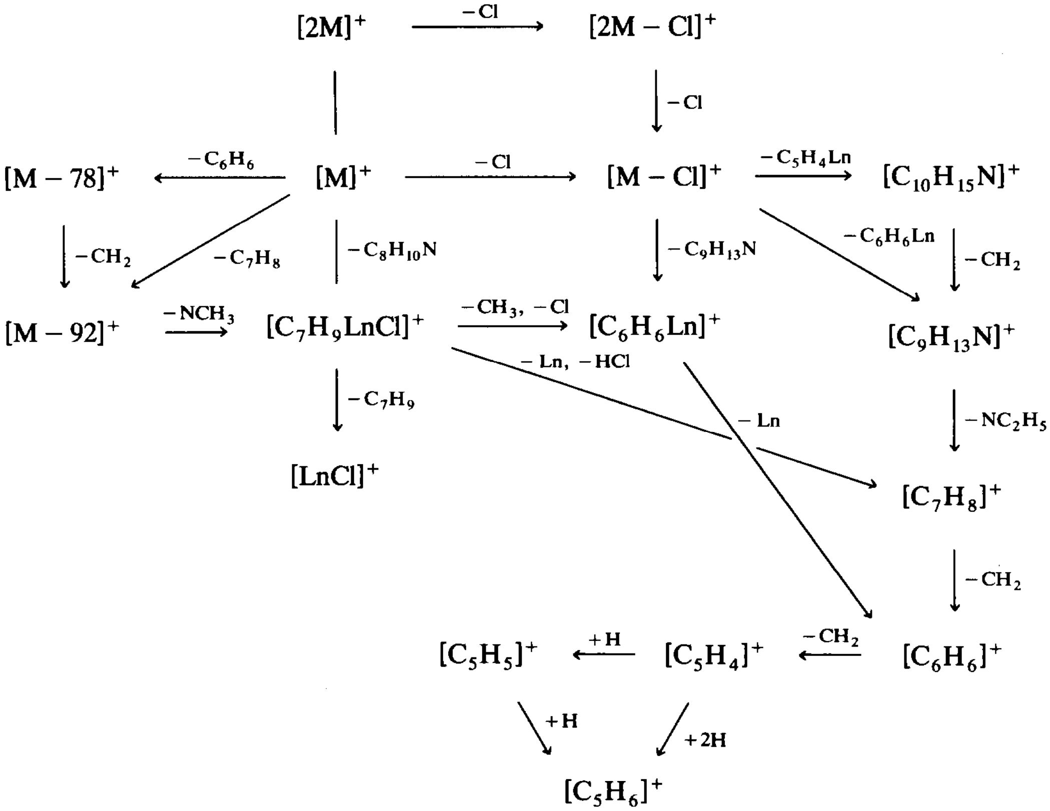
Using the amine-linked biscyclopentadiene as ancillary ligands, complexes of the type $(\eta^5\text{-}C_5H_5)_2LnCl$ are readily accessible to neodymium and the later rare earth metals. However, efforts to obtain their La- and Pr-congeners under similar conditions have failed and a new type of binuclear cyclopentadienyl lanthanide complex, $[CH_3N(CH_2CH_2C_5H_4)_2Ln]_2(CH_2CH_2C_5H_4)_2NCH_3$, have been obtained, which will be published elsewhere [27]. A similar observation also appears when $O(CH_2CH_2C_5H_5)_2$ is used as the ancillary ligand [13], and suggests that these two chelating ligands have similar effects on avoiding intermolecular ligand redistribution.

Although the four new complexes are still sensitive to air and moisture, their stabilities are much improved when compared with the corresponding $(C_5H_5)_2LnCl$ and $CH_2(CH_2C_5H_4)_2LnCl \cdot THF$. They also possess good thermal stability and can be sublimed at 200–220°C/5×10^{-4} mmHg.

The complete mass spectra of these complexes were obtained. The fact that they all showed a dimer molecular ion $[2M]^+$ and/or the fragment $[2M - Cl]^+$, suggests that these complexes are dimer in the solid and vapour states. It can be seen from the data that the mass spectra of all the complexes give very high relative intensity peaks of $[M]^+$ and $[M - Cl]^+$, indicating that this type of lanthanide chloride is relatively stable and the Ln–Cl bond is probably more easily cleaved under the MS conditions. This feature differs from our previous observation for the mass spectra of $(C_5H_5)_2LnCl$ and $(CH_3C_5H_4)_2LnCl$, in which the Cp–Ln bond is more easily cleaved [28], and this may result from intramolecular coordination between the nitrogen atom and the lanthanide metal.

The fragmentation of these chlorides is very similar and is shown in Scheme 1. Their fragmentation patterns are in good agreement with Fischer's results of a mass spectrometric study on the ring-linked biscyclopentadienyl lanthanide chlorides $[(CH_3)_2Si(C_5H_4)_2Ln(\mu\text{-}Cl)]_2$ [29]. This has led to the conclusion that the two amine-linked cyclopentadienyl rings coordinate to one metal ion in a chelating fashion and the two metal ions are linked via two bridging chloride ligands [29], as shown in Fig. 1.

The IR spectra of complexes **1–4** and the disodium salt (**5**) were measured from 4000 to 180 cm^{-1} and showed very similar features. The complexes exhibit several characteristic absorption peaks in the low frequency region and the absorption peak at about 250 cm^{-1} is assigned to a characteristic absorption of the π-bond between the cyclopentadienyl group and the lanthanide metal [30]. It is noticeable that the characteristic absorption of the π-bond in complex **1** is shifted to 280 cm^{-1}, which is in agreement with those of $(C_5H_5)_2YCl$, $(CH_3C_5H_4)_2YCl$, $CH_2(CH_2C_5H_4)_2Y^tBu \cdot THF$, $O(CH_2CH_2C_5H_4)_2YCl$ and $m\text{-}C_6H_4(CH_2C_5H_4)_2YCl \cdot THF$ reported in our previous work [12,13,17]. The characteristic absorption peaks due to cyclopentadienyl and the bridging amine groups are evidently present. The characteristic cyclopentadienyl absorptions appear at about 3080, 1445, 1030 and 760 cm^{-1} in complexes 1–4, and at 3055, 1445, 1021 and 719 cm^{-1} in the disodium salt, which implies the transfer of charge from the Cp ligand to the central metal and the bonding formed between them. It is worth noting that the absorption peaks due to the C–H vibration of the Cp ring at about 3080 cm^{-1} in complexes 2–4 have a shoulder peak; particularly in **1** two peaks appear at 3100 and 3079 cm^{-1}, respectively. This suggests that the four hydrogen atoms in the Cp ring are not equal. The absorption peaks of the C–N stretching vibration for the complexes are assigned at about 1208 and 1127 cm^{-1} and shift to a lower frequency compared with those of the disodium salt, with $\Delta\nu = 8$ and 33 cm^{-1}, respectively, implying the presence of an intramolecular coordination bond from the



Scheme 1. Fragmentation pattern of the complexes.

nitrogen atom in the chelating chain to the lanthanide metal [13]. Unfortunately, the characteristic absorption of the Ln–Cl bond has not yet been clearly assigned.

The ^1H and ^{13}C NMR spectra of complex **1** and the disodium salt (**5**) were measured using perdeuterotetrahydrofuran as solvent. The results show that when the complex is formed, the signals of hydrogen and carbon at $N-CH_3$ and $N-CH_2$ shift to a lower field ($\Delta\delta = 0.38$ and 0.22 ppm for ^1H; $\Delta\delta = 7.41$ and 5.15 ppm for ^{13}C, respectively), indicating the existence of an intramolecular coordination bond (Fig. 1) [13,21]. The Cp signals also shift to a lower field, suggesting that the negative charge of the Cp ring is transferred to Ln^{3+}. It is interesting that the signals of the four hydrogen atoms at the Cp ring were split into three peaks at 5.80 (m, 4H), 5.93 (m, 2H) and 6.12 (m, 2H), respectively. This suggests that the hydrogen atoms at the α- and α'-positions are not homomagnetic, differing from our previous observations [13,14,17]. The ^{13}C NMR spectra gives a similar result, with the signals of carbon at the α- and α'-positions at 112.24 and 113.47 ppm, respectively.

As reported [31,32], the $\Delta\delta$ value between the α- and β-protons of the Cp ring implies the distribution of charge on cyclopentadienyl and torsional mobility of the Cp ring, and an increase in the $\Delta\delta$ value means a decrease in the torsional mobility of the Cp ring. The values for some ring-bridged lanthanocene chlorides are compared and the data are listed in Table 1. From Table 1, we have found that when a chain containing nitrogen is introduced into the bridged biscyclopenta-

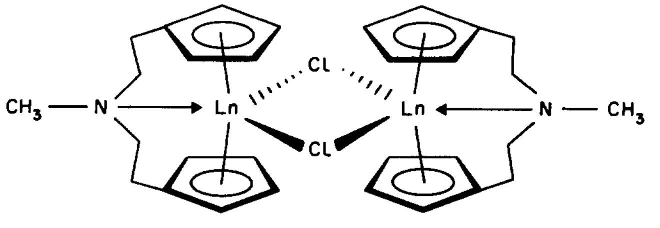


Fig. 1.

TABLE 1. Correlation of the bridging chain with ring-proton splitting

Complex	n	$\Delta\delta$ [a]	Reference
$(CH_2)5(C_5H_4)_2YCl\cdot THF$	5	0.07	14
$O(CH_2CH_2C_5H_4)_2YCl$	4+0	0.14	13
m-$C_6H_4(CH_2C_5H_4)_2YCl\cdot THF$	5	0.22	17
$CH_3N(CH_2CH_2C_5H_4)_2YCl$	4+N	0.23 [b]	This work

[a] $\Delta\delta = \delta_{\alpha-H} - \delta_{\beta-H}$. [b] $\Delta\delta = 1/2(\delta_{\alpha-H} + \delta_{\alpha'-H}) - \delta_{\beta-H}$.

dienyl ligand, because of the formation of an intramolecular coordination bond, the $\Delta\delta$ value obviously increases compared with those of the complexes with the same chain length. This together with the difference in the chemical shifts of the α- and α'-H atom implies that the torsional mobility of the Cp ring decreases, thus probably favouring the opening of the coordination sphere of the lanthanide metal and the availability of more reactive organolanthanide complexes [21]. In the case of the chain containing a benzene ring, the rigidity of the chain is strengthened and results in an increase in $\Delta\delta$ [17].

In conclusion, using N-containing bridged biscyclopentadiene as an ancillary ligand, complexes of type $[CH_3N(CH_2CH_2C_5H_4)_2LnCl]_2$ are readily accessible for neodymium and the later lanthanides. Fragmentation patterns of these complexes indicate that they are chloride-bridged dimers in the solid and/or vapour states. The IR and NMR spectra imply the presence of intramolecular coordination from the nitrogen atom to the central metal, resulting in a decrease in the torsional mobility of the Cp ring and offering an opportunity of obtaining more stable, but also more reactive organolanthanide species. Further investigations focusing on the chemistry of the amine-linked biscyclopentadienyl lanthanide derivatives are underway in order to obtain the more reactive species.

Experimental details

All operations were carried out under purified argon using Schlenk techniques. All solvents were refluxed and distilled either over finely divided $LiAlH_4$ or over blue sodium benzophenone under argon immediately before use. Anhydrous lanthanide chlorides were prepared from the oxides by the published procedure [33]. *N*-Methyl-2,2′-dichloroethyl amine was obtained by the literature method based on the replacement of the hydroxyl groups of *N*-methyldiethanol amine by treatment with $SOCl_2$ [26]. C_5H_5Na was prepared in the usual manner from freshly distilled monomeric cyclopentadiene and sodium sand in THF.

Melting points or thermal decomposition temperatures were determined in sealed argon-filled capillaries and were uncorrected. IR spectra were recorded on Perkin–Elmer 983 and Digilab FTS-20/E Fourier transform IR spectrometers with Nujol and Fluorolube mulls and were examined between disc-shaped CsI crystals; the mulls were prepared in an argon-filled glovebox. Mass spectra were recorded on a Finnigan 4021 spectrometer at EI, $T = 50$–300°C, EM = 1.3 kV. ^1H and ^{13}C NMR spectra were obtained on a FX-90Q (90 MHz) spectrometer referenced to external Me_4Si in THF-d_8. THF-d_8 (E. Merck for NMR spectroscopy) was dried over a Na/K alloy and degassed by freeze-thaw cycles on a vacuum line.

Metal analyses of the complexes were accomplished using a direct complexometric titration procedure with disodium EDTA [30]. Carbon and hydrogen analyses were performed by the combustion method in an aluminium tube.

3.1. Disodium 2,2′-(N-methyldiethyleneamine)biscyclopentadienide, $CH_3N(CH_2CH_2C_5H_4Na)_2$ (5)

Into a solution of C_5H_5Na (0.20 mol) in 100 ml of THF, a solution of 15.6 g (0.10 mol) of $CH_3N(CH_2CH_2Cl)_2$ in 40 ml of THF was added dropwise at 0–10°C and the mixture was stirred overnight at room temperature. The mixture was centrifuged and the sodium chloride formed was separated from the solution. The light brown solution thus obtained was allowed to react with 6.9 g (0.30 mol) of sodium sand in 50 ml THF at room temperature for 2 h and then at 45°C for 10 h. A nearly colourless solution was thus obtained. After the solvent was removed, the residue was dissolved in 60 ml of DME by slightly heating. The solution was set aside overnight and the white needles formed were separated and dried under a vacuum (21.5 g, 61%). Anal. Found: C, 65.30; H, 8.56. $C_{19}H_{29}NO_2Na_2$ calc.: C, 65.31; H, 8.36%. IR: 3055m, 2922s, 2840s, 2786s, 1460m, 1445m, 1216m, 1196w, 1160w, 1096s, 1021s, 933s, 896s, 784vs, 719vs, 675m, 630m, 597m, 300s cm^{-1}. ^1H NMR (THF-d_8, TMS): δ 5.40 (m, 8H); 2.60 (t, 4H); 2.48 (t, 4H); 2.12 (s, 3H). ^{13}C NMR (THF-d_8, TMS): δ 30.33 (CH_2); 41.16 (NCH_3); 64.51 (NCH_2); 104.06, 104.71, 118.42 (C_5H_4).

3.2. 2,2′-(N-Methyldiethyleneamine)biscyclopentadienyl yttrium chloride (1)

A THF solution of an equivalent of 2,2′-(*N*-methyldiethyleneamine)biscyclopentadienyl disodium was added slowly to a suspension of 2.36 g (12.0 mmol) of YCl_3 in 60 ml of THF at −30°C. The reaction mixture was stirred for 2 h at −30 to −20°C, then allowed to warm to room temperature and stirred overnight. The Schlenk flask was centrifuged, and the precipitate was separated from the solution, which was reduced in volume to about 15 ml. Addition of 40 ml of n-hexane gave a white solid which was washed with hexane (20 ml × 2) and dried *in vacuo* to give a white solid, 2.94g. Yield 73%. Melting point 143–145°C. Anal. Found: C, 52.66; H, 5.88; Cl, 10.42; Y, 26.24. $C_{15}H_{19}NClY$ calc.: C, 53.35; H, 5.67; Cl, 10.50; Y, 26.33%. *m/e*: 639 (1.76, $[2M - Cl]^+$), 337 (51.46, $[M]^+$), 302 (85.35, $[M - Cl]^+$), 259 (12.55, $[M - C_6H_6]^+$), 244 (22.17, $[M - C_7H_8]^+$), 217 (9.57, $[C_7H_9YCl]^+$), 167 (1.89, $[C_6H_6Y]^+$), 149 (13.22, $[C_{10}H_{15}N]^+$), 136 (19.34, $[C_9H_{13}N]^+$), 124 (7.69, $[YCl]^+$), 91 (14.98, $[C_7H_8]^+ - 1$), 77 (5.08, $[C_6H_6]^+ - 1$), 66 (100, $[C_5H_6]^+$). IR: 3100m, 3079m, 2917s, 2825s, 1461m, 1449s, 1330m, 1279m, 1208m, 1147w, 1127m, 1077m, 1064m, 1049m, 1033s, 1005m, 940s, 871m, 849m, 827s, 774vs, 763vs, 679m, 549m, 522m, 455m, 359m, 280s, 224m cm^{-1}. ^{1}H NMR (THF-d_8, TMS): δ 6.12 (m, 2H); 5.93 (m, 2H); 5.80 (m, 4H); 2.70 (m, 8H); 2.50 (s, 3H). ^{13}C NMR (THF-d_8, TMS): δ 27.76 (CH_2); 48.57 (NCH_3); 69.66 (NCH_2); 105.49, 112.24, 113.47, 127.93 (C_5H_4).

3.3. 2,2′-(N-Methyldiethyleneamine)biscyclopentadienyl ytterbium chloride (2)

The procedure followed was similar to that for **1**. A red solid (**2**) was obtained in 78% yield. Melting point 150–154°C. Anal. Found: C, 42.28; H, 4.69; Cl, 8.43; Yb, 41.40. $C_{15}H_{19}NClYb$ calc.: C, 42.71; H, 4.54; Cl, 8.40; Yb, 41.02%. *m/e*: 808 (4.89, $[2M-Cl]^+$), 422 (89.92, $[M]^+$), 387 (100, $[M-Cl]^+$), 344 (17.24, $[M-C_6H_6]^+$), 322 (1.74, $[M-C_7H_8]^+$), 308 (33.76, $[C_7H_9YbCl]^+ + 6$), 252 (3.08, $[C_6H_6Yb]^+$), 209 (46.16, $[YbCl]^+$), 149 (10.17, $[C_{10}H_{15}N]^+$), 136 (72.48, $[C_9H_{13}N]^+ + 1$), 91 (17.52, $[C_7H_8]^+ - 1$), 77 (5.60, $[C_6H_6]^+ - 1$), 65 (2.46, $[C_5H_5]^+$). IR: 3071m, 2923m, 2857m, 1462m, 1448m, 1419w, 1363m, 1330w, 1279w, 1228w, 1208m, 1146w, 1127w, 1075m, 1065m, 1039m, 1033m, 1005m, 940m, 831s, 785vs, 764vs, 681m, 549w, 458w, 403w, 378w, 358w, 300w, 247m, 215m cm^{-1}.

3.4. 2,2′-(N-Methyldiethyleneamine)biscyclopentadienyl samamium chloride (3)

After 1.77 g (6.89 mmol) of $SmCl_3$ in 40 ml of THF was stirred at room temperature for 24 h, a THF solution of an equivalent of 2,2′-(*N*-methyldiethyleneamine)biscyclopentadienyl disodium was added slowly into the suspension at −30°C. The mixture was stirred at −30 to −20°C for 2 h, then allowed to warm to room temperature and stirred overnight. The work-up procedure followed was similar to that for **1**. Compound **3** was obtained as an orange solid in 76% yield. Decomposition temperature 197–200°C. Anal. Found: C, 45.70; H, 4.71; Cl, 8.20; Sm, 38.22. $C_{15}H_{19}NClSm$ calc.: C, 45.14; H, 4.80; Cl, 8.88; Sm, 37.67%. *m/e*: 800 (1.91, $[2M]^+$), 765 (3.55, $[2M-Cl]^+$), 400 (57.63, $[M]^+$), 365 (80.79, $[M-Cl]^+$), 322 (11.83, $[M-C_6H_6]^+$), 308 (8.17, $[M-C_7H_8]^+$), 286 (100, $[C_7H_9SmCl]^+ + 6$), 230 (4.10, $[C_6H_6Sm]^+$), 187 (51.91, $[SmCl]^+$), 91 (6.23, $[C_7H_8]^+ - 1$), 78 (2.29, $[C_6H_6]^+$), 65 (2.52, $[C_5H_5]^+$). IR: 3098m, 2921m, 2859m, 1465m, 1445m, 1376m, 1208m, 1148w, 1127w, 1050m, 1031m, 1005m, 941w, 826m, 758vs, 679m, 247w, 220w cm^{-1}.

3.5. 2,2′-(N-Methyldiethyleneamine)biscyclopentadienyl neodymium chloride (4)

The procedure followed was similar to that for **3**. Compound **4** was obtained as a pale purple solid in 86% yield. Decomposition temperature 215–220°C. Anal. Found: C, 46.03; H, 4.97; Cl, 9.53; Nd, 36.29. $C_{15}H_{19}NClNd$ calc.: C, 45.84; H, 4.87; Cl, 9.02; Nd, 36.70%. *m/e*: 782 (4.05, $[2M]^+ + 2$), 390 (34.93, $[M]^+$), 355 (100, $[M-Cl]^+$), 312 (33.79, $[M-C_6H_6]^+$), 299 (72.68, $[M-C_7H_8]^+$), 270 (84.88, $[C_7H_9NdCl]^+$), 220 (4.22, $[C_6H_6Nd]^+$), 177 (42.65, $[NdCl]^+$), 136 (16.68, $[C_9H_{13}N]^+ + 1$), 91 (14.39, $[C_7H_8]^+ - 1$), 77 (10.54, $[C_6H_6]^+ - 1$), 65 (5.10, $[C_5H_5]^+$). IR: 3084m, 2974m, 2916m, 2855s, 2806s, 1460m, 1445s, 1415m, 1370m, 1208m, 1147w, 1128w, 1049m, 1030m, 1004m, 940m, 825s, 784s, 757vs, 679m, 624w, 546w, 460w, 350w, 222m cm^{-1}.

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