contribution to the overall energy barrier by the germylene rotation step is likely. Gladysz[15] discusses a very similar situation concerning the equilibria involving the germylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}GePh_2)]^+TfO^-$: $\Delta G^{\ddagger}_{268} = 52.7$ kJ mol^{-1} for the exchange of the diastereotopic germyl phenyl groups in this complex, ascertained by coalescence studies of the variable-temperature ^{13}C NMR spectra, and is described in terms of both triflate dissociation and germylene rotation, a separation of these terms being similarly impossible.

We previously reported a dynamic NMR study of a similar fluxional process occurring in a bis(germylene)iron complex, $[Cp'(CO)Fe\{GeMe_2{\cdots}O(Me){\cdots}GeMe_2\}]$, where both germylene moieties are considered to rotate.[17] In that paper, the thermodynamic parameters were evaluated for a fluxional cycle comprising rotation of both germylene moieties. Recalculation of these for rotation of only one germylene allows a better comparison of the energies with those of the (silylene)(germylene) complexes. It is clear that while $\Delta S^{\ddagger}$ for the bis(germylene) complex (27 J K^{-1} mol^{-1}) is virtually equivalent to that for the methoxy(silylene)(germylene) complex (see Table I), due to the virtually equivalent degrees of freedom in the transition states, both $\Delta H^{\ddagger}$ (95 kJ mol^{-1}) and $\Delta G^{\ddagger}_{298}$ (87 kJ mol^{-1}) are much greater. This is consistent with the proposed structures for the two complexes: The bis(germylene) complex has equivalent Ge--O bonds, whereas the (silylene)(germylene) complex is considered to be weighted toward a methoxy(silyl)(germylene) complex, strengthening the Si–O bond at the expense of the Ge–O bond. This is due to stronger Si–O bonding compared with Ge–O bonding and also indicates greater stability of the germylene ligand compared to the silylene ligand. It should be noted that the same conclusion as the latter has been drawn by Pannell from the extensive study on the photolysis of (silylgermyl)- and (germylsilyl)iron complexes, $CpFe(CO)_2GeMe_2SiR_3$ and $CpFe(CO)_2SiMe_2GeR_3$ (R = Me, Ph).[16] These reactions almost exclusively afforded monosilyl complexes $CpFeSiMe_nR_{3-n}$, and the formation of $CpFeGeMe_nR_{3-n}$ was negligible. These observations were reasonably explained on the assumption that the equilibria between (silyl)(germylene) and (germyl)(silylene) intermediates favor the former, from which recombination of CO yields the $CpFe(CO)_2SiMe_nR_{3-n}$ complexes.

Acknowledgment. We thank the Japan Society for the Promotion of Science for the award of a J.S.P.S. Postdoctoral Fellowship for Foreign Researchers in Japan to J.R.K. This work was supported by Grants-in-Aid for Encouragement of Young Scientists, No. 02963001, and for Scientific Research on Priority Areas of Unusual Organic Valency, No. 03233201, from the Ministry of Education, Science and Culture. We thank the Shin-Etsu Chemical Co., Ltd., and the Asai Germanium Research Institute, respectively, for gifts of silicon and germanium compounds.

OM910697K

Syntheses of Methylcyclopentadienyl Derivatives of Lanthanides (Ln = La–Nd) and Crystal Structures of $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpNd(THF)]$ and $[Li(DME)_3][MeCpLa(NPh_2)_3]$

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Received October 24, 1991

The reaction of $LnCl_3{\cdot}2LiCl$ with 1 equiv of MeCpNa in THF gives the complexes $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpLn(THF)]$ (Ln = Nd (1), La (2)) in good yield. These precursors react further with 2 equiv of $LiNPh_2$ to produce the new complexes $[Li(DME)_3][MeCpLn(NPh_2)_3]$ (Ln = La (3), Pr (4), Nd (5)). They have been characterized by elemental analyses and IR and NMR spectra, as well as by structural analyses of 1 and 3. The chloride 1 crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 12.130$ (5) Å, $b = 17.343$ (5) Å, $c = 17.016$ (5) Å, $\beta = 108.54$ (3)°, $V = 3393.87$ Å^3, $Z = 4$, and $D_c = 1.45$ g/cm^3. Least-squares refinement led to a final R value of 0.051 ($I \geqslant 3\sigma(I_o)$) for 2004 independent reflections. Complex 3 crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 18.335$ (6) Å, $b = 16.576$ (5) Å, $c = 17.461$ (6) Å, $\beta = 96.04$ (3)°, $V = 5277.17$ Å^3, $D_c = 1.26$ g/cm^3, $Z = 4$, and $R = 0.057$ ($I \geq 2.5\sigma(I_o)$) for 3378 reflections. The structure of 3 consists of discrete ion pairs $[Li(DME)_3]^+$ and $[MeCpLa(NPh_2)_3]^-$ with average La–N and La–C(ring) distances of 2.459 (8) and 2.84 (1) Å, respectively.

Introduction

Organolanthanide chemistry has undergone rapid growth in recent years. However, much of the work has been concentrated on the smaller and later lanthanide elements. Because of the lanthanide constriction effect and coordinative unsaturation, the important precursor lanthanide cyclopentadienyl and smaller substituted cyclopentadienyl chlorides of the early lanthanides have not been easily synthesized. Now it has been found that some approaches can be used to prepare such kinds of complexes for early lanthanides. These include the use of bulkier ligands such as C_5Me_5,[1,2] $C_5Me_4C_3H_7$,[3] $(Me_3Si)_2Cp$,[4] ^tBuCp,[5]

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0276-7333/92/2311-2483$03.00/0

MeOCH$_2$CH$_2$Cp,[6] bridging ligands,[7-9] etc. These complexes are more soluble and frequently have thermal stability higher than that of their simple Cp analogues. These ligands are very useful for synthesis but are more expensive and indirect than Cp.

Yi reported that LnCl$_3$·2LiCl, instead of LnCl$_3$, reacts with 1 equiv of CpNa to give an anionic simple cyclopentadienyl early-lanthanide dichloride.[10,11] However, no further studies were reported using this method. Because of the higher solubility of LnCl$_3$·2LiCl in THF, the heterogeneous reaction of LnCl$_3$ with CpNa can be transformed into a homogeneous reaction of LnCl$_3$·2LiCl with CpNa, which may protect against disproportionation reactions. Here we report a study of the reaction of LnCl$_3$·2LiCl with 1 equiv of MeCpNa in THF, the successful isolation of the precursor complexes [(THF)$_2$Li(μ-Cl)$_2$]$_2$[MeCpLn(THF)] (Ln = Nd (1), La (2)) using a similar method, and the further reaction products [Li(DME)$_3$][MeCpLn(NPh$_2$)$_3$] (Ln = La (3), Pr (4), Nd (5)) formed by the transmetalation reaction of [(THF)$_2$Li(μ-Cl)$_2$]$_2$[MeCpLn(THF)] with LiNPh$_2$. The crystal structures of 1 and 3 have been determined by single-crystal X-ray analysis.

Experimental Section

All complexes described below are extremely air- and moisture-sensitive; thus, all manipulations were performed under the protection of purified, oxygen-free argon using Schlenk techniques. Solvents were dried with anhydrous CaCl$_2$ and then refluxed over sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous LnCl$_3$ and the complex LnCl$_3$·2LiCl·nTHF were prepared according to literature procedures.[12,13] MeCpNa was prepared by the reaction of freshly cracked MeCpH with sodium in THF. LiNPh$_2$ was obtained by the reaction of HNPh$_2$ with n-BuLi in a solution of THF, hexane, and toluene.

Analysis of lanthanide was carried out by complexometric titration, of chloride by Volhard's method, and of Li by using a Shimadzu atomic absorption spectrometer. Infrared spectra (KBr pellet) were recorded on a Digilab FTS-20E (1 and 2) and Alpha Centauri spectrometer (3–5). NMR spectra were obtained on a JEOL FX-100 instrument and referenced to TMS in THF-d_8.

[(THF)$_2$Li(μ-Cl)$_2$]$_2$[MeCpNd(THF)] (1). To 10 mL of a THF solution of NdCl$_3$·2LiCl (4.069 mmol) was added 2.4 mL (4.16 mmol) of a THF solution of MeCpNa. After it was stirred for 24 h at room temperature and centrifugated, the purple supernatant solution was concentrated and an appropriate amount of hexane was added until the solution turned a bit turbid. The mixture was cooled to −10 °C to effect crystallization, and large purple crystals of 1 were produced in 49% yield (1.47 g). Anal. Calcd for C$_{26}$H$_{47}$O$_5$Cl$_4$Li$_2$Nd: Nd, 19.52; Cl, 19.19. Found: Nd, 19.88; Cl, 20.80. Mp: 58–60 °C. IR (cm^{-1}): 3010 (w), 2960 (s), 2860 (s), 1680 (s), 1642 (s), 1625 (s), 1490 (s), 1455 (s), 1440 (s), 1035 (s), 880 (s), 820 (s), 770–760 (s).

[(THF)$_2$Li(μ-Cl)$_2$]$_2$[MeCpLa(THF)] (2). This compound was prepared analogously to the description above, from 25 mL of a THF solution of LaCl$_3$·2LiCl·nTHF and 5.2 mL of a THF solution of MeCpNa (9.6 mmol), and stirred for 24 h at room temperature. After workup, the solution was cooled to −78 °C to effect crystallization. The colorless transparent square crystals were collected at about −50 °C and dried under vacuum for a long time. However, this compound 2 had lost THF, and only a yellow powder (4.3 g, 77%) was obtained. Anal. Calcd for C$_{14}$H$_{23}$O$_2$Cl$_4$Li$_2$La: La, 26.84; Cl, 27.40. Found: La, 26.90; Cl, 26.37. IR (cm^{-1}): 3060 (s), 2865 (s), 2710 (w), 2695 (w), 2160 (w), 1630 (s), 1460 (s), 1450 (s), 1445 (s), 1175 (w), 1065 (w), 1043 (s), 1032 (w), 875 (m), 822 (m), 765 (s), 620 (m). ^{1}H NMR (THF-d_8): δ 2.22 (s), 5.83–5.93 (d). ^{13}C NMR (THF-d_8): δ 114.66 (s), 113.96 (s), 15.79 (s). 2 is insoluble in other conventional deuterated solvents such as benzene-d_6, toluene-d_8, DCCl$_3$, etc. The signal for THF coordinated to metal ions was not detected.

[Li(DME)$_3$][MeCpLa(NPh$_2$)$_3$] (3). To a THF solution of 2, prepared in the same way as described above, from 25 mL of a THF solution of LaCl$_3$·2LiCl (6.93 mmol) and 4.6 mL of a THF solution of MeCpNa (6.93 mmol), was added from a syringe 58 mL of a solution of LiNPh$_2$ (13.86 mmol) in THF, hexane, and toluene. The mixture was stirred for 30 h. After the solvent was pumped off, the solid product was extracted with DME. The extract solution was treated dropwise with hexane until it became slightly turbid and was then cooled to −10 °C. Bright yellow square crystals of 3 (2.2 g, 31.8%) were collected. Anal. Calcd for C$_{54}$H$_{67}$O$_6$N$_3$LiLa: La, 13.91; Li, 0.695. Found: La, 13.77; Li, 0.70. Mp: 152–154 °C. IR (cm^{-1}): 3450 (s), 3400 (s), 3083 (s), 3044 (s), 2927 (s), 2891 (s), 2824 (m), 2543 (w), 1934 (w), 1596 (s), 1103 (s), 1081 (s), 1027 (s), 995 (m), 977 (m), 875 (s), 749 (s), 693 (s). ^{1}H NMR (THF-d_8): δ 7.30–6.60 (m), 6.50–6.30 (m), 3.23–3.26 (d), 1.83 (s).

[Li(DME)$_3$][MeCpPr(NPh$_2$)$_3$] (4). In a manner analogous to that described for 3, to a THF solution of [(THF)$_2$Li(μ-Cl)$_2$]$_2$[MeCpPr(THF)] at −78 °C, formed from the reaction of PrCl$_3$·2LiCl (5.38 mmol) in 25 mL of THF with a THF solution of MeCpNa (5.4 mmol), was slowly added a solution of LiNPh$_2$ (10.76 mmol) in 33 mL of THF, hexane, and toluene. The reaction mixture was stirred for 3 h. The temperature was then allowed to rise to room temperature over a period of 5 days. The solvent was removed under vacuum, and the green solid product was extracted with 10 mL of toluene and 4 mL of DME. Yellow-green crystals were collected from the extract solution at −10 °C. Yield: 1.87 g (34.8%). Anal. Calcd for C$_{54}$H$_{67}$O$_6$N$_3$LiPr: Pr, 14.08; Li, 0.694. Found: Pr, 14.57; Li, 0.698. Mp: 154–156 °C. IR (cm^{-1}): 3394 (s), 3343 (s), 3199 (w), 3045 (s), 2983 (m), 2928 (s), 2891 (s), 2824 (m), 1935 (w), 1595 (s), 1495 (s), 1459 (s), 1417 (m), 1367 (m), 1312 (s), 1245 (m), 1192 (m), 1154 (m), 749 (s), 693 (s).

[Li(DME)$_3$][MeCpNd(NPh$_2$)$_3$] (5). This complex was prepared by addition of 34 mL of a solution of LiNPh$_2$ (14.9 mmol) in THF, hexane, and toluene to 26 mL of a THF solution of 1 (7.45 mmol) at −78 °C for 2.5 h. The solution was then stirred for another 16 h at room temperature. The purple mixture was concentrated to a thick oil and extracted with a large amount of toluene. The extracted oil was dried under vacuum and extracted with DME again. Blue-purple crystals could be obtained from the concentrated DME solution at −10 °C. Yield: 2.53 g (33.8%). Anal. Calcd for C$_{54}$H$_{67}$O$_6$N$_3$LiNd: Nd, 14.36; Li, 0.69. Found: Nd, 14.83; Li, 0.71. Mp: 134–136 °C. IR (cm^{-1}): 3385 (w), 3022 (w), 1933 (w), 1594 (s), 1494 (s), 1459 (w), 1416 (w), 1367 (w), 1311 (m), 1244 (w), 1173 (w), 1155 (w), 1074 (w), 1027 (w), 965 (w), 874 (m), 747 (s), 691 (s).

X-ray Data Collection, Structure Determination, and Refinement for 1 and 3. A purple-red crystal of 1 measuring 0.28 × 0.23 × 0.22 mm was selected by using a device reported by Jin,[14] glued on the top of a glass fiber, and transferred onto a goniometer head mounted on a Nicolet R3 M/E diffractometer equipped with a low-temperature device. A crystal of 3 measuring 0.26 × 0.30 × 0.26 mm was sealed under argon in a thin-walled glass capillary. Unit cell parameters and their standard deviations were determined from the angular settings of 25 reflections in the range 5° ≤ 2θ ≤ 25° and refined by least squares. From the systematic absences the space group was determined to be $P2_1/n$ for 1 and $P2_1/c$ for 3. All intensity data were measured at 173

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Table I. Crystal and Data Collection Parameters for 1 and 3

formula	$C_{26}H_{47}O_5Cl_4Li_2Nd$	$C_{54}H_{67}O_6N_3LiLa$
fw	738.88	998.84
space group	$P2_1/n$	$P2_1/c$
a, Å	12.130 (5)	18.335 (6)
b, Å	17.343 (5)	16.576 (5)
c, Å	17.016 (5)	17.461 (6)
β, deg	108.54 (3)	96.04 (3)
V, Å^3	3393.87	5277.17
Z	4	4
D_c, g/cm^3	1.45	1.26
$F(000)$, e	1272	2019
μ, cm^{-1}	18.69	8.65
cryst dimens, mm	0.28 × 0.23 × 0.22	0.26 × 0.30 × 0.26
diffractometer	Nicolet R3 M/E	
radiation (λ, Å)	Mo Kα (0.710 69)	
monochromator	graphite	
measure temp, K	173	298
2θ limits, deg	3–50	3–48
data set, *hkl*	0–15, 0–21, −21 to 20	0–20, 0–19, −21 to +21
scan mode	ω	ω
no. of unique data	3025	8156
no. of obsd data	2004 ($I \geq 3\sigma(I_o)$)	3378 ($I \geq 2.5\sigma(I_o)$)
correctns	Lp	Lp and abs
no. of refined params	301	591
av Δ/σ, final cycle	0.022	0.107
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.051	0.057
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}$	0.054	0.048
weighting scheme	$1/(\sigma^2(F_o) - 0.0006F_o^2)$	$1/(\sigma^2(F_o) + 0.0002F_o^2)$

K for 1 and 298 K for 3 with Mo Kα radiation (graphite monochromator, λ = 0.710 69 Å) in the ω-scan mode and corrected for Lorentz and polarization effects for 1 and for Lorentz, polarization, and absorption effects for 3. Two reference reflections were measured every 68 reflections during data collection. No significant decay was observed for either of them. However, only two-thirds of the complete set of data for 1 was collected because the single crystal was blown off the glass fiber by cooled N_2 steam. Crystal data and experimental details of the structure determinations are listed in Table I.

The heavy atoms were found by Patterson methods. The positions of all non-H atoms were revealed by successive Fourier and difference Fourier syntheses. Hydrogen atoms were introduced in calculated positions and assigned isotropic thermal parameters (U = 0.05 Å^2). All positional parameters and temperature factors for non-H atoms were refined anisotropically with full-matrix least-squares methods and converged to the final R = 0.051 (maximum Δ/σ = 0.022, in final cycle) for 1 and 0.057 (maximum Δ/σ = 0.107, in final cycle) for 3. The final difference Fourier map of 3 showed no peak higher than 0.54 e Å^{-3} or less than −0.42 e Å^{-3}. Final coordinates of the non-H atoms are given in Tables II and III. All calculations were carried out on an Eclipse S/140 microcomputer with the SHELXTL 83 computer program system.

Results and Discussion

Syntheses. $LnCl_3{\cdot}2LiCl{\cdot}nTHF$ reacts with 1 equiv of MeCpNa in THF to give the complex $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpLn(THF)]$ (eq 1), which further reacts with 2 equiv of $LiNPh_2$ in a solution of THF, hexane, and toluene, leading to $[Li(DME)_3][MeCpLn(NPh_2)_3]$ after workup (eq 2). 2 crystallizes from THF at −78 °C, giving

$$LnCl_3{\cdot}LiCl{\cdot}nTHF + MeCpNa \rightarrow [(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpLn(THF)] \quad (1)$$
$$La = Nd\ (1),\ La\ (2)$$

$$[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpLn(THF)] + 2LiNPh_2 \rightarrow [Li(DME)_3][MeCpLn(NPh_2)_3] \quad (2)$$
$$Ln = La\ (3),\ Pr\ (4),\ Nd\ (5)$$

the complex with five coordinated THF molecules in good yield. After the complex was dried for prolonged periods under vacuum, three coordinated THF molecules were lost, and only the yellow powder $MeCpLaCl_2{\cdot}2LiCl{\cdot}2THF$ was obtained. The same behavior is observed for complex 1. These complexes are very soluble in THF.

Table II. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms (with Esd's in Parentheses) for 1

	x	y	z	U_{eq},[a] Å^2
Nd	0.0760 (1)	0.7261 (1)	0.8379 (1)	0.036 (1)
Li1	−0.088 (3)	0.5538 (9)	0.788 (1)	0.06 (2)
Li2	0.351 (3)	0.814 (1)	0.931 (1)	0.04 (1)
Cl1	0.0028 (4)	0.6213 (1)	0.7081 (1)	0.038 (2)
Cl2	0.2147 (4)	0.7746 (2)	0.9932 (2)	0.046 (2)
Cl3	−0.0635 (4)	0.6355 (2)	0.9020 (2)	0.046 (2)
Cl4	0.2724 (4)	0.7637 (2)	0.7944 (2)	0.050 (2)
O11	−0.2516 (9)	0.5463 (4)	0.7324 (4)	0.042 (5)
O21	0.349 (1)	0.9257 (4)	0.9320 (4)	0.051 (5)
O41	0.204 (1)	0.6102 (4)	0.8935 (4)	0.060 (6)
O51	−0.034 (1)	0.4482 (4)	0.8132 (4)	0.061 (6)
O61	0.506 (1)	0.7709 (4)	0.9756 (4)	0.055 (6)
C12	−0.316 (2)	0.6043 (8)	0.6763 (8)	0.074 (9)
C13	−0.440 (2)	0.5944 (7)	0.6690 (7)	0.08 (1)
C14	−0.425 (2)	0.5718 (7)	0.7570 (7)	0.09 (1)
C15	−0.325 (1)	0.5240 (7)	0.7830 (7)	0.050 (8)
C22	0.326 (2)	0.9660 (6)	0.9997 (7)	0.07 (1)
C23	0.324 (2)	1.0493 (7)	0.9797 (8)	0.069 (9)
C24	0.277 (2)	1.0489 (7)	0.8863 (8)	0.065 (9)
C25	0.326 (2)	0.9769 (6)	0.8618 (6)	0.052 (8)
C31	−0.135 (2)	0.8062 (6)	0.7898 (7)	0.043 (8)
C32	−0.056 (2)	0.8518 (6)	0.8526 (7)	0.073 (9)
C33	0.032 (1)	0.8806 (5)	0.8228 (6)	0.045 (8)
C34	0.011 (1)	0.8550 (6)	0.7423 (7)	0.029 (7)
C35	−0.087 (1)	0.8098 (6)	0.7212 (6)	0.036 (8)
C36	−0.069 (2)	0.8655 (9)	0.9366 (8)	0.08 (1)
C42	−0.053 (2)	0.3920 (6)	0.7494 (7)	0.08 (1)
C43	−0.032 (1)	0.3148 (6)	0.7903 (6)	0.043 (8)
C44	−0.038 (2)	0.3315 (7)	0.8753 (7)	0.10 (1)
C45	−0.021 (2)	0.4100 (7)	0.8877 (7)	0.13 (1)
C52	0.268 (2)	0.5667 (8)	0.8512 (8)	0.08 (1)
C53	0.350 (3)	0.526 (2)	0.906 (1)	0.22 (2)
C54	0.336 (2)	0.530 (1)	0.9872 (1)	0.15 (2)
C55	0.234 (2)	0.5778 (7)	0.9762 (7)	0.05 (1)
C62	0.579 (2)	0.7504 (7)	0.9260 (7)	0.061 (9)
C63	0.668 (2)	0.701 (1)	0.9774 (9)	0.09 (1)
C64	0.675 (2)	0.717 (1)	1.0605 (9)	0.10 (1)
C65	0.552 (2)	0.7402 (8)	1.0572 (7)	0.055 (9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The ^1H NMR spectrum of 2 exhibits characteristic signals for C_5H_4 at δ 5.83–5.93 (d) and for CH_3 at δ 2.22 (s). The ^{13}C NMR spectrum exhibits signals at δ 114.66 for the tertiary carbon of the MeCp ring, at δ 113.96 for the other four carbon atoms of the MeCp ring, and at δ 15.79 for the carbon of the methyl group, which agreement with the corresponding values in $[Li(THF)_3][C_5Me_5Lu^tBuCl]$.[15] Because of the insolubility of 2 in other conventional solvents such as benzene-d_6, toluene-d_8, $DCCl_3$, etc. THF-d_8 had to be used for these measurements. Thus, the signal of THF coordinated to metal ions was obscured by or underwent exchange with the intense signal of free THF. The ^1H NMR spectrum of 3 shows the signals assign to C_6H_5 at δ 7.30–6.60 (m), to MeC_5H_4 at δ 6.50–6.30 (m), to DME at δ 3.26 (s) and 3.23 (s), and to CH_3 at δ 1.83 (s).

These complexes are thermally stable but decompose when exposed to air and moisture. They are soluble in polar solvents such as THF or DME but not in hydrocarbons or aromatic solvents such as hexane, benzene, and toluene. They are moderately soluble in diethyl ether.

Crystal Structure. Because of the presence of Li ion, 1 contains the cluster moiety $Li(\mu\text{-}Cl)_2Nd(\mu\text{-}Cl)_2Li$, which is formed from two $[(THF)_2Li]^+$ cations coordinated to a

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Table III. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms (with Esd's in Parentheses) for Complex 3

	x	*y*	*z*	U_{eq},[a] Å^2
La	0.2399 (1)	0.0374 (1)	0.2961 (1)	0.060 (1)
N1	0.2273 (4)	−0.0736 (5)	0.3880 (4)	0.069 (4)
N2	0.1389 (4)	0.0185 (5)	0.1947 (4)	0.068 (4)
N3	0.3422 (4)	0.0260 (5)	0.2156 (4)	0.072 (3)
O1	0.1551 (4)	0.4935 (5)	0.2303 (4)	0.105 (4)
O2	0.2994 (4)	0.4558 (5)	0.2156 (4)	0.123 (4)
O3	0.2387 (4)	0.4409 (4)	0.3892 (4)	0.113 (4)
O4	0.3541 (4)	0.5370 (6)	0.3848 (4)	0.140 (4)
O5	0.1767 (4)	0.6178 (5)	0.3685 (5)	0.116 (4)
O6	0.2707 (4)	0.6405 (4)	0.2584 (4)	0.102 (4)
Li	0.246 (1)	0.530 (1)	0.311 (1)	0.094 (8)
C1	0.1719 (5)	−0.0939 (6)	0.4332 (5)	0.064 (4)
C2	0.1011 (5)	−0.0590 (6)	0.4193 (6)	0.080 (5)
C3	0.0439 (7)	0.0829 (8)	0.4585 (8)	0.091 (6)
C4	0.0560 (6)	−0.1428 (7)	0.5166 (6)	0.101 (6)
C5	0.1227 (6)	−0.1785 (7)	0.5334 (7)	0.104 (6)
C6	0.1794 (6)	−0.1530 (6)	0.4922 (5)	0.078 (5)
C7	0.3003 (5)	−0.0863 (6)	0.4139 (5)	0.071 (5)
C8	0.3318 (5)	−0.0712 (6)	0.4881 (6)	0.091 (5)
C9	0.4068 (6)	−0.0771 (7)	0.5090 (7)	0.115 (6)
C10	0.4512 (6)	−0.0976 (8)	0.4540 (8)	0.135 (7)
C11	0.4217 (6)	−0.1108 (7)	0.3798 (7)	0.116 (6)
C12	0.3474 (5)	−0.1081 (6)	0.3593 (6)	0.080 (5)
C13	0.1300 (5)	0.0899 (6)	0.1534 (6)	0.068 (4)
C14	0.0643 (5)	0.1322 (6)	0.1494 (6)	0.087 (5)
C15	0.0570 (6)	0.2081 (7)	0.1144 (6)	0.098 (6)
C16	0.1162 (6)	0.2417 (7)	0.0844 (6)	0.097 (6)
C17	0.1807 (6)	0.1981 (7)	0.0872 (6)	0.089 (5)
C18	0.1877 (6)	0.1247 (6)	0.0121 (5)	0.081 (5)
C19	0.0937 (4)	−0.0463 (6)	0.1724 (5)	0.060 (4)
C20	0.0507 (5)	−0.0507 (6)	0.1021 (5)	0.078 (5)
C21	0.0084 (6)	−0.1151 (6)	0.0825 (6)	0.093 (6)
C22	0.0041 (6)	−0.1796 (7)	0.1301 (7)	0.102 (6)
C23	0.0470 (5)	−0.1786 (6)	0.2006 (6)	0.092 (6)
C24	0.0917 (5)	−0.1125 (6)	0.2203 (6)	0.080 (5)
C25	0.3942 (5)	0.0900 (6)	0.2253 (5)	0.069 (4)
C26	0.4348 (5)	0.1071 (7)	0.2936 (1)	0.087 (5)
C27	0.4805 (6)	0.1743 (7)	0.3037 (7)	0.108 (6)
C28	0.4870 (6)	0.2257 (7)	0.2453 (7)	0.104 (6)
C29	0.4493 (5)	0.2104 (7)	0.1763 (7)	0.094 (6)
C30	0.4043 (5)	0.1427 (6)	0.1643 (6)	0.081 (5)
C31	0.3557 (5)	−0.0367 (7)	0.1690 (5)	0.070 (4)
C32	0.4251 (5)	−0.0591 (6)	0.1475 (6)	0.082 (5)
C33	0.4337 (7)	−0.1273 (7)	0.1035 (7)	0.102 (7)
C34	0.3779 (7)	−0.1755 (7)	0.0801 (8)	0.109 (7)
C35	0.3099 (6)	−0.1563 (6)	0.1000 (6)	0.102 (6)
C36	0.2970 (6)	−0.0886 (6)	0.1427 (5)	0.079 (5)
C37	0.2678 (6)	0.2005 (6)	0.3407 (6)	0.091 (5)
C38	0.1927 (6)	0.1973 (6)	0.3121 (7)	0.099 (6)
C39	0.1534 (6)	0.1549 (6)	0.3618 (6)	0.099 (6)
C40	0.2031 (5)	0.1313 (6)	0.4232 (6)	0.089 (5)
C41	0.2730 (6)	0.1603 (6)	0.4107 (6)	0.088 (5)
C42	0.3429 (7)	0.1543 (9)	0.4674 (7)	0.141 (8)
C43	0.0801 (5)	0.523 (1)	0.2257 (7)	0.141 (7)
C44	0.1727 (7)	0.4519 (9)	0.1633 (7)	0.146 (7)
C45	0.2433 (8)	0.4054 (9)	0.1807 (8)	0.138 (8)
C46	0.3722 (7)	0.4217 (9)	0.2246 (8)	0.154 (8)
C47	0.1726 (7)	0.3895 (8)	0.3947 (7)	0.134 (7)
C48	0.3007 (8)	0.4279 (9)	0.4479 (8)	0.160 (8)
C49	0.3599 (7)	0.4860 (8)	0.4462 (7)	0.148 (8)
C50	0.4070 (6)	0.6000 (9)	0.3851 (8)	0.141 (7)
C51	0.1474 (7)	0.6042 (9)	0.4414 (7)	0.125 (7)
C52	0.1988 (9)	0.6958 (8)	0.3550 (9)	0.153 (9)
C53	0.2213 (7)	0.7053 (7)	0.2744 (8)	0.143 (8)
C54	0.3066 (8)	0.6516 (9)	0.1888 (7)	0.149 (8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised $\mathbf{U}_{ij}$ tensor.

$[MeCpNd(THF)Cl_4]^{2-}$ anion as shown in Figure 1. Important bond lengths and the angles are listed in Table IV.

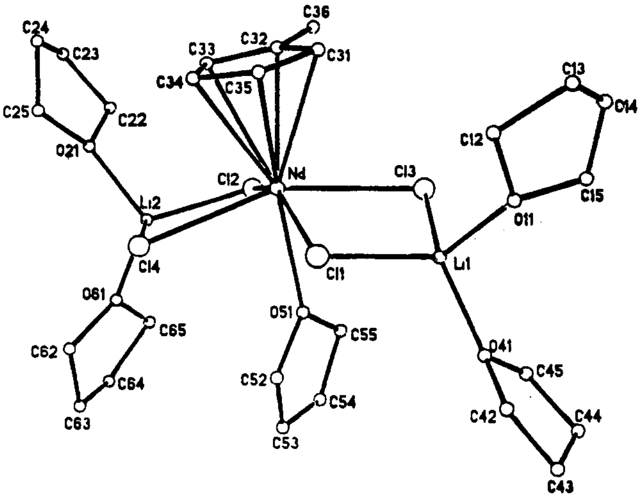

Figure 1. Crystal structure of the complex $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpNd(THF)]$.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpNd(THF)]$ (1)

Nd–Cl1	2.778 (2)	Nd–Cl2	2.774 (3)
Nd–Cl3	2.774 (4)	Nd–Cl4	2.788 (5)
Nd–O51	2.529 (9)	Nd–C31	2.80 (2)
Nd–C32	2.76 (2)	Nd–C33	2.73 (1)
Nd–C34	2.73 (1)	Nd–C35	2.73 (1)
Li1–Cl1	2.31 (3)	Li1–Cl3	2.35 (2)
Li2–Cl2	2.33 (3)	Li2–Cl4	2.38 (2)
Li2–O21	1.94 (2)	Li2–O61	1.94 (3)
Li1–O11	1.91 (3)	Li1–O41	1.95 (2)
Cl1–Nd–Cl2	154.0 (1)	Cl3–Nd–Cl4	156.4 (1)
Cl1–Nd–Cl3	82.0 (1)	Cl2–Nd–Cl4	82.6 (1)
Cl1–Nd–Cl4	91.5 (1)	Cl2–Nd–Cl3	93.3 (1)
Cl1–Nd–O51	77.3 (2)	Cl2–Nd–O51	76.7 (2)
Cl3–Nd–O51	77.3 (3)	Cl4–Nd–O51	79.2 (3)
Li1–Nd–O51	69.5 (5)	Li1–Nd–O51	78.3 (4)
Cl1–Li1–Cl3	102.7 (8)	Cl1–Li1–O11	111.1 (8)
Cl1–Li1–O41	115 (2)	Cl1–Li2–Cl4	103 (1)
Cl2–Li2–O21	106 (1)	Cl2–Li2–O61	116.9 (9)

Table V. Selected Bond Lengths (Å) and Angles (deg) for $[Li(DME)_3][MeCpLa(NPh_2)_3]$ (3)

La–N1	2.469 (8)	La–N2	2.443 (7)
La–N3	2.467 (7)	La–C37	2.85 (1)
La–C38	2.81 (1)	La–C39	2.83 (1)
La–C40	2.85 (1)	La–C41	2.88 (1)
N1–C1	1.39 (1)	N1–C7	1.38 (1)
N2–C13	1.39 (1)	N2–C19	1.39 (1)
N3–C25	1.43 (1)	N3–C31	1.36 (1)
Li–O1	2.14 (2)	Li–O2	2.37 (2)
Li–O3	2.03 (2)	Li–O4	2.26 (2)
Li–O5	2.23 (2)	Li–O6	2.12 (2)
N1–La–N2	105.1 (2)	N1–La–N3	116.3 (3)
N2–La–N3	96.1 (2)	cent[a]–La–N1	106.0
cent–La–N2	108.8	cent–La–N3	121.0
C1–N1–C7	121.2 (8)	C13–N2–C19	118.7 (7)
C25–N3–C31	118.7 (8)	C1–N1–La	132.3 (6)
C7–N1–La	99.9 (6)	C13–N2–La	107.9 (5)
C19–N2–La	133.4 (6)	C25–N3–La	114.5 (6)
C31–N3–La	126.6 (6)	C42–C41–La	120.2 (8)

[a] Cent indicates the centroid of the methylcyclopentadienyl ring.

The lanthanide ion Nd^{3+} is coordinated by one methylcyclopentadienyl, four bridging chlorides, and one THF to form a distorted octahedron with a formal coordination number of 8. It seems that the $Li(\mu\text{-}Cl)_2Ln(\mu\text{-}Cl)_2Li$ cluster moiety stabilizes the simple cyclopentadienyl chloride of the light lanthanide. Nd–C(ring) distances are in the range 2.73 (1)–2.80 (2) Å (average 2.75 (1) Å). Nd–Cl distances are in the range 2.774 (3)–2.788 (5) Å (average 2.778 (3) Å). Both of the average Nd–C(ring) and Nd–Cl distances are in agreement with the corresponding values of Nd–C(ring) = 2.77 (2) Å and Nd–Cl = 2.78 (1) Å in the complex $[(THF)_2Li(\mu\text{-}Cl)_2]_2[CpNd(THF)]$.[10]

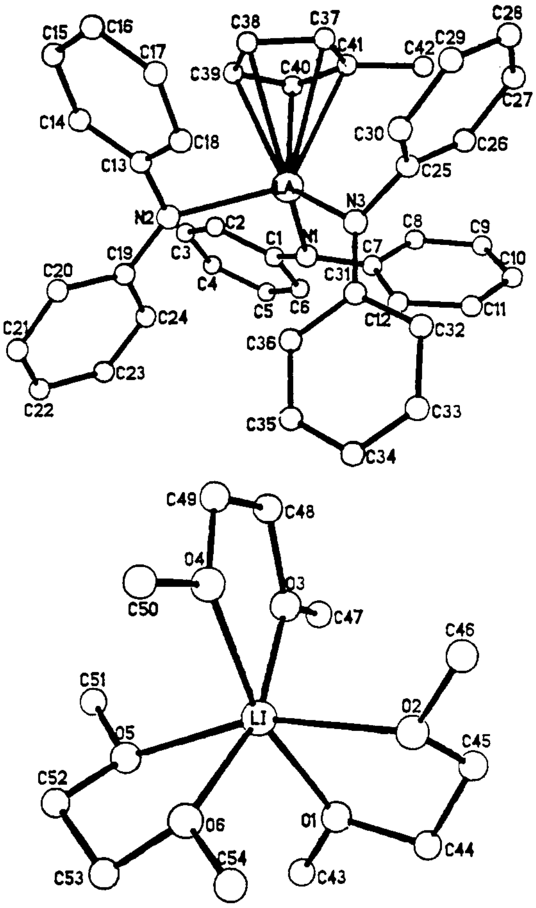

Figure 2. Crystal structure of the complex [Li(DME)$_3$][MeCpLa(NPh$_2$)$_3$].

Complex 3 consists of a disconnected ion pair formed by the [MeCpLa(NPh$_2$)$_3$]$^-$ anion and lithium cation coordinated by DME ligands which are disordered. The molecular structure of 3 is shown in Figure 2. Important bond lengths and angles are given in Table V. In the anion, the central lanthanide metal is surrounded by one methylcyclopentadienyl and three diphenylamido groups to form a distorted tetrahedron with the angles cent(MeCp ring)–La–N1 = 106.0°, cent–La–N2 = 108.8°, and cent–La–N3 = 121.0°. The angle cent–La–N3 is much larger than cent–La–N1 and cent–La–N2. This may be because of the steric congestion by the methyl group located at the N3 side. Although it is larger than the distances of C42 to N1 (4.48 Å), N3 (4.88 Å), C25 (4.55 Å), C26 (3.70 Å), C29 (4.54 Å), C30 (4.86 Å), the distance of C42 to the plane C25–C26–C27–C28–C29–C30 (2.81 Å) is very small. The La–N–C angles La–N1–C1 = 132.3 (6)°, La–N1–C7 = 99.9 (6)°, La–N2–C13 = 107.9 (5)°, La–N2–C19 = 133.4 (6)°, La–N3–C25 = 114.5 (6)°, and La–N3–C31 = 126.6 (6)° clearly deviate from the idealized value of 120° for a trigonal-planar nitrogen atom. This may be caused by repulsion between the six phenyl rings with the inequalities in La–N–C angles also possibly reflecting electronic effects.[16]

The La–N distances are in the range 2.443 (7)–2.469 (8) Å, and the average La–N distance is 2.459 (7) Å. This is the first example of an organolanthanum complex containing a La–N σ bond to our knowledge. The comparison of the distance can only be made with other lanthanide amido complexes. $C_5Me_5Ce(N(SiMe_3)_2)_2$ has a Ce–N distance of 2.353 Å,[17] and the ion pair complex [Li(THF)$_4$][(C$_5$H$_5$)$_2$Lu(NPh$_2$)$_2$] has a Lu–N distance of 2.291 (7) Å.[18] Since La^{3+} is approximately 0.04 and 0.23 Å larger than Ce^{3+} and Lu^{3+}, respectively, the present La–N bond distance is somewhat larger than the 2.353 Å in $C_5Me_5Ce[N(SiMe_3)_2]_2$ and shorter than the 2.291 Å in [Li(THF)$_4$][C$_5$H$_5$)$_2$Lu(NPh$_2$)$_2$]. This is reasonable because the steric congestion in 3 is somewhat larger than that in the former and smaller than that in the latter.

Acknowledgment. We thank the Chinese National Foundation of Natural Science for financial support.

Registry No. 1, 141583-55-3; 2, 141557-11-1; 3, 141557-13-3; 4, 141557-15-5; 5, 141583-57-5; MeCpH, 26519-91-5; NHPh$_2$, 122-39-4.

Supplementary Material Available: Tables of bond lengths and angles, temperature factors, and positional parameters for H atoms for 1 and 3 (12 pages). Ordering information is given on any current masthead page. Tables of structure factors are available from the authors.

OM910667H

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