complex as in **2a**,**b** and **3** (Scheme II).

While nucleophiles primarily add to the α-carbon of non-sulfur-containing vinylidenes to afford vinyl complexes, nucleophilic addition to the sulfoniovinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)SMe](BF_4)_2$ (**4**) occurs in several ways: (1) Phosphines displace an MeS^+ group to give $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]BF_4$ (**5**). (2) Pyridines displace a methyl from the sulfonium group, forming $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (**1**). (3) Pyridines, mercaptides, and sulfides displace the SMe_2 group. The observation of the π-alkyne intermediate **10i** in mechanistic studies of **4** with SEt_2 and DMAP supports the proposal that the latter reactions proceed by nucleophilic attack at the α-carbon of **4** to form a π-alkyne, which rearranges to the vinylidene product. It is clear from these and previous studies[2] that the presence of MeS groups has a major influence on the reactivity of the vinylidene ligand.

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Supplementary Material Available: Tables of thermal parameters, additional bond angles, and least-squares planes (4 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

Studies on Rare-Earth Allyl Compounds. 6. Syntheses and Structures of the Novel Trinuclear Complexes $(\eta^3\text{-}C_3H_5)_2Ln(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2Mg(tmed)(\mu_2\text{-}Cl)Mg(tmed)$

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A series of new allyllanthanide complexes, $(\eta^3\text{-}C_3H_5)_2LnCl_5Mg_2(tmed)_2$ (where Ln = La, Ce, Pr, Nd, Sm; and tmed = tetramethylethylenediamine), have been prepared by the reaction of anhydrous $LnCl_3$ with allyl Grignard reagents and tmed in THF at 0 °C. They are air- and moisture-sensitive and show the characteristic reactions of allyl metallic compounds with CO_2, H_2O, acetone, etc. The five compounds were characterized by elemental analyses, infrared spectra, mass spectra, and molar conductivities. The structures of three complexes have been determined by X-ray analysis: $(\eta^3\text{-}C_3H_5)_2Ce(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2Mg(tmed)(\mu_2\text{-}Cl)Mg(tmed)$, orthorhombic, space group $P2_12_12_1$, $a = 11.245$ (2) Å, $b = 15.053$ (1) Å, $c = 18.206$ (1) Å, $Z = 4$, $R = 0.043$ for 2371 observed reflections; $(\eta^3\text{-}C_3H_5)_2Ce(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2Mg(ether)_2(\mu_2\text{-}Br)Mg(ether)_2$, monoclinic, space group $C2/c$, $a = 20.223$ (3) Å, $b = 11.333$ (2) Å, $c = 18.917$ (3) Å, $\beta = 122.58$ (2)°, $Z = 4$, $R = 0.088$ for 1663 observed reflections; $(\eta^3\text{-}C_3H_5)_2Nd(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2Mg(ether)_2(\mu_2\text{-}Br)Mg(ether)_2$, monoclinic, space group $C2/c$, $a = 20.203$ (3) Å, $b = 11.286$ (3) Å, $c = 18.925$ (4) Å, $\beta = 122.58$ (2)°, $Z = 4$, $R = 0.072$ for 1904 observed reflections. The complexes have trianglar metallic skeletons bonded together by three bridging and two capping halide atoms. The two allyl groups in the structures are η^3-bonded to the lanthanide ions.

Introduction

During the last three decades, allylnickel and allylpalladium complexes, among others, have been widely used in organic syntheses for the formation of C–C bonds. The success of these complexes in synthetic work mainly depends on their high reactivities.[1] In contrast, allyllanthanide complexes are less known and studied, probably owing to the difficulty of their preparation. However, these complexes may show activities[2] just as high as those of allyl transition-metal complexes.

Earlier we reported the structure of $[Li_2(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$,[3] the first structure of an allyllanthanide complex. Here we report the syntheses, structural studies, and some properties of a novel series of trinuclear allyllanthanide complexes.

Tsutsui[4] used allyl Grignard reagents to synthesize allyllanthanide compounds, but no further developments have been reported since. Three years ago, when lanthanide chlorides were treated with allylmagnesium bromide in ether at 0–5 °C, we found that beautiful crystals grew in these systems, which were characterized as $(\eta^3\text{-}C_3H_5)_2LnX_5Mg_2(Et_2O)_4$ (where Ln = Ce, Nd) by X-ray analysis. However, some difficulties arose in the determinations: these new compounds were mixed together with the white solid $LnCl_3$. Besides, they were difficult to isolate and analyze due to the weakly coordinating Et_2O. There was also the problem that the halide atoms in these crystals might be Cl, Br, or both, which was difficult to determine by routine analysis. Therefore, with allylmagnesium chloride instead of allylmagnesium bromide as the initial material, THF instead of ether as the

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Table I. Elemental Analyses and Physical Properties of the Complexes $Ln(C_3H_5)_2Cl_5Mg_2(tmed)_2$

Ln (compd no.)	color	dec pt, °C	elemental anal., %[a] Ln	Mg	C	H	Cl	N	yield, %
La (3)	pale yellow	>175	20.51 (20.45)	7.07 (7.16)	31.91 (31.82)	6.07 (6.23)	25.74 (26.09)	8.02 (8.25)	50
Ce (4)	orange-red	>170	20.50 (20.59)	7.21 (7.14)	31.92 (31.77)	5.88 (6.22)	25.66 (26.05)	7.90 (8.23)	40
Pr (5)	bright yellow	>160	20.64 (20.68)	7.24 (7.14)	31.90 (31.74)	6.08 (6.21)	25.63 (26.02)	7.95 (8.22)	45
Nd (6)	bright green	>160	21.01 (21.07)	7.14 (7.10)	31.49 (31.58)	5.96 (6.18)	25.70 (25.89)	8.00 (8.18)	49
Sm (7)	rosy violet	>160	21.76 (21.77)	7.44 (7.04)	31.45 (31.30)	6.20 (6.13)	25.34 (25.66)	7.87 (8.11)	45

[a] The values in parentheses are those calculated.

Table II. IR and MS Data for Complexes 3–7

Ln (compd no.)	IR, cm^{-1} [a] ν(C$\cdots$C$\cdots$C)	ν(=C—H)	ν(tmed)	MS, *m/e* (%) $(C_3H_5)^+$	$(tmed)^+$
La (3)	1546 (s)	3058 (w)	3009 (m), 2973 (m), 2875 (m), 2847 (m), 2805 (m), 1026 (s)	41 (20.71)	116 (5.34)
Ce (4)	1545 (s)	3061 (w)	3007 (m), 2973 (m), 2877 (m), 2849 (m), 2807 (m), 1023 (s)	41 (41.67)	116 (5.34)
Pr (5)	1545 (s)	3063 (w)	3007 (m), 2970 (m), 2875 (m), 2845 (m), 2802 (m), 1025 (s)	41 (91.77)	116 (7.29)
Nd (6)	1546 (s)	3065 (w)	3009 (m), 2973 (m), 2875 (m), 2850 (m), 2805 (m), 1026 (s)	41 (48.46)	116 (4.39)
Sm (7)	1546 (s)	3065 (w)	3009 (m), 2966 (m), 2875 (m), 2847 (m), 2805 (m), 1026 (s)	41 (27.73)	116 (4.31)

[a] IR spectra at 400–1400 cm^{-1} as Nujol mulls and at 1400–4000 cm^{-1} as Fluorolube mulls.

solvent, and the large bulky ligand tmed as the precipitating agent, the new series of complexes $(\eta^3\text{-}C_3H_5)_2LnCl_5Mg_2(tmed)_2$ was synthesized.

Experimental Section

The infrared spectra and the mass spectra of these compounds were recorded on a Nicolet FT-IR-5DX spectrophotometer and a Finnigan 4510 GC/MS/DS spectrometer, respectively. The melting points were determined in sealed capillaries filled with nitrogen and not corrected. All the manipulations were carried out under a purified N_2 atmosphere with standard Schlenk techniques. THF and Et_2O were distilled from sodium benzophenone ketyl prior to use. Tetramethylethylenediamine (tmed) was dried by reflux over KOH, distilled, and stored over 4-Å molecular sieves. Allyl bromide and allyl chloride were distilled and stored over 4-Å molecular sieves.

Preparation of Complexes $Ln(C_3H_5)_2X_5Mg_2(Et_2O)_4$ (Ln = Ce (1), Nd (2)). An Et_2O solution (6 mL, 1.7 mmol) of allylmagnesium bromide (excess) was added to 0.1 g (0.4 mmol) of anhydrous $CeCl_3$ or $NdCl_3$ powder. After it stood for 7–10 days at 0–5 °C, the Et_2O solution turned orange (for $CeCl_3$) or green (for $NdCl_3$), and after about 20–30 days, a few single crystals (orange-red for complex 1 and green for complex 2) grew. They were mixed together with the white solid $CeCl_3$ and the pale violet $NdCl_3$, respectively. Crystals suitable for X-ray analysis were chosen and sealed into capillaries.

Preparation and Characterization of $Ln(C_3H_5)_2Cl_5Mg_2(tmed)_2$ (Ln = La (3), Ce (4), Pr (5), Nd (6), Sm (7)). To a suspension of 2.0 g of $LnCl_3$ (8.2 mmol of $LaCl_3$, 8.1 mmol of $CeCl_3$, 8.1 mmol of $PrCl_3$, 8.0 mmol of $NdCl_3$, and 7.8 mmol of $SmCl_3$) in THF was added dropwise 10.4–10.7 mmol of allylmagnesium chloride in THF solution with stirring at 0 °C. The mixture was stirred for an additional 2 h at room temperature and filtered. The solution was concentrated under vacuum, and 2.4 mL (16 mmol) of tmed was added dropwise, producing a precipitate. The complex was filtered, washed with cold THF, and dried under vacuum for 1 h at room temperature to give a crystalline powder. The elemental analyses and physical properties for complexes 3–7 are listed in Table I, IR and MS data in Table II, and molar conductivities in Table III.

Reaction of Complexes 3–7 with CO_2. The chemical properties of these complexes are similar. They show typical characteristics of metal allyl compounds. Into a solution of 0.2 g of complex 4 in 15 mL of THF was passed dry gaseous CO_2 at room temperature for $^1/_2$ h. The orange-red solution turned to a pale suspension, evolving heat. The solvent was removed. The residue was hydrolyzed with 2 N HCl and extracted with Et_2O. The solvent was removed, and 3-butenoic acid was identified. IR (cm^{-1}): 3074, 1716, 1644, 925. MS (relative intensity): *m/e* 86 (M^+, 23.10%). Complex 7 was similarly treated as described for complex 4. IR (cm^{-1}): 3091, 1716, 1644, 925. MS: *m/e* 86 (M^+, 45.29%).

Table III. Molar Conductivities of the Complexes in THF

complex	specific conductivity, Ω^{-1} cm^{-1}	molar conductivity, Ω^{-1} cm^{-1} mol^{-1}	concn, 10^{-3} mol L^{-1}	temp, °C
3	1.85×10^{-6}	0.26	7.14	25
4	5.94×10^{-6}	0.84	7.07	25
5	5.32×10^{-6}	0.67	7.98	25
6	4.97×10^{-6}	0.69	7.16	25
7	4.53×10^{-6}	0.63	7.21	25
a	1.30×10^{-4}	21.2	6.14	2.5
b	3.61×10^{-4}	58.3	6.20	25

[a] $[Li(tmed)_2][Yb(CH_2SiMe_3)_4]$. [b] $[Li(tmed)_2][Ce(C_3H_5)_4]$.

Reaction with Substances Containing Active Hydrogen. To 0.05 g of complex 4 (or 7) was added 0.5 mL of water. Propylene was evolved immediately as a gaseous product. MS: *m/e* 42 (M^+, 73.51% for complex 4; 76.78% for complex 7). To 0.05 g of complex 4 was added 0.5 mL of acetone. Propylene was evolved. MS: *m/e* 42 (M^+, 71.18% for complex 4; 70.55% for complex 7).

X-ray Diffraction Studies. Complexes 1, 2, and 4 were studied with an Enraf-Nonius CAD-4 diffractometer. All the crystallography calculations were carried out on a PDP 11/44 computer with the SDP-PLUS package. The parameters of the unit cell were determined and refined from the setting angles of 25 reflections (θ about 14–18°). Three were used for orientation and intensity control (after every 100 reflections orientation control was checked, and intensity control was carried out every 3600 s) during the data collection. The intensity data were corrected for Lorentz and polarization and empirical absorption effects.

The atomic scattering factors and anomalous dispersion corrections for Nd, Ce, Cl, Br, O, N, C, and H were taken from ref 5.

A summary of crystal data for complexes 1, 2, and 4 is listed in Table IV. The determinations of the structures are described in detail below.

Complex 1. The structure was solved by direct methods and refined by full-matrix least squares (x, y, z, and B_{ij} for Ce, Br, and O atoms and x, y, z, and B for the remaining ones), The final R value was 0.088 for 1663 observed reflections. No attempt was made to locate the hydrogen atoms. Final positional parameters of atoms are given in Table V). (In all the positional parameter tables, the values of the temperature factors with double stars were refined isotropically.) Bond lengths and angles are listed in Table VI. A view of the molecule is shown in Figure 1.

Complex 2. The intensity data were collected in the triclinic space group $P\bar{1}$ with three parameters similar to those of complex 1. The determination was thus performed in the space group $P\bar{1}$

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(5) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.1B and 2.2B.

Table IV. Summary of Crystal Data

	Complexes 1, 2, and 4		
complex	1	2	4
formula	$CeMg_2Br_5C_{22}H_{50}O_4$	$NdMg_2Br_5C_{22}H_{50}O_4$	$CeMg_2Cl_5C_{18}H_{42}N_4$
cryst size, mm	0.05 × 0.1 × 0.12	0.5 × 0.2 × 0.35	0.2 × 0.2 × 0.25
space group	*C*2/*c*	*C*2/*c*	$P2_12_12_1$
a, Å	20.223 (3)	20.203 (3)	11.245 (2)
b, Å	11.333 (2)	11.286 (3)	15.053 (3)
c, Å	18.917 (3)	18.925 (4)	18.206 (2)
β, deg	122.58 (2)	122.58 (2)	
V, $Å^3$	3653.1	3636.0	3081.8
Z	4	4	4
d_{calcd}, g/cm^3	1.758	1.774	1.458
μ(Mo Kα), cm^{-1}	67.407	69.338	19.907
F(000)	1884	1892	1364
transmissn factor, %	80.04–99.82	62.66–99.77	90.95–99.79
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)		
scan mode	ω–2θ	ω–2θ	ω–2θ
θ range, deg	0–25	0–25	0–27
scan range (θ), deg	0.70 + 0.35 tan θ	0.85 + 0.35 tan θ	0.66 + 0.35 tan θ
aperture width, mm	1.50 + 1.05 tan θ	3.00 + 1.05 tan θ	1.98 + 1.05 tan θ
no. of rflens measd	6758	6711	3782
no. of rflns obsd	1663	1904	2371
no. of refined params	109	116	190
final *R*	0.088	0.072	0.043
final R_w	0.101	0.084	0.049
max residuals, e $Å^{-3}$	2.283	0.818	0.746
	Parameters of Unit Cells for Complexes 4, 6, and 7		
complex	4	6	7
formula	$CeMg_2Cl_5C_{18}H_{42}N_4$	$NdMg_2Cl_5C_{18}H_{42}N_4$	$SmMg_2Cl_5C_{18}H_{42}N_4$
a, Å	11.245 (2)	11.194 (1)	11.157 (2)
b, Å	15.053 (3)	15.034 (4)	15.012 (3)
c, Å	18.206 (2)	18.177 (3)	18.168 (2)
α = β = γ, deg	90	90	90

Table V. Positional Parameters in $(C_3H_5)_2CeBr_5Mg_2(Et_2O)_4$ and Their Estimated Standard Deviations (Esd's) in Parentheses[a]

atom	*x*	*y*	*z*	*B*(eq), $Å^2$
Ce	0.7500	0.2500	0.2500	4.62 (4)
Br1	0.7112 (1)	0.0291 (3)	0.1362 (2)	6.22 (7)
Br2	0.9083 (1)	0.1434 (2)	0.2904 (2)	5.43 (6)
Br3	0.7500	−0.2500	0.2500	7.6 (1)
Mg	0.6538 (3)	−0.0652 (6)	0.2272 (4)	4.0 (2)
C1	0.773 (2)	0.358 (4)	0.141 (2)	12 (1)**
C2	0.705 (2)	0.412 (4)	0.130 (2)	11 (1)**
C3	0.643 (2)	0.377 (4)	0.121 (2)	12 (1)**
C4	0.667 (2)	−0.315 (3)	0.383 (2)	7.6 (8)**
C5	0.606 (1)	−0.261 (3)	0.310 (1)	5.9 (6)**
O6	0.6222 (7)	−0.127 (1)	0.3077 (8)	4.7 (4)
C7	0.623 (2)	−0.054 (3)	0.373 (2)	7.0 (8)**
C8	0.537 (2)	−0.043 (3)	0.346 (2)	9 (1)**
C9	0.430 (2)	−0.150 (4)	0.098 (2)	11 (1)**
C10	0.480 (2)	−0.094 (3)	0.078 (2)	8.4 (9)**
O11	0.5591 (8)	−0.146 (2)	0.123 (1)	5.5 (5)
C12	0.559 (2)	−0.293 (4)	0.081 (2)	11 (1)**
C13	0.577 (3)	−0.265 (5)	0.034 (3)	15 (2)**

[a] Double-starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $^4/_3*[a^2B(11) + b^2B(22) + c^2B(33) + ab(\cos\gamma)B(12) + ac(\cos\beta)B(13) + bc(\cos\alpha)B(23)]$.

Table VI. Bond Lengths (Å) and Angles (deg) in $(C_3H_5)_2CeBr_5Mg_2(Et_2O)_4$ with Their Esd's in Parentheses

Bond Lengths

Ce–Br1	3.114 (1)	Br2–Mg	2.613 (3)	C5–O6	1.552 (13)
Ce–Br2	3.109 (1)	Br3–Mg	2.730 (3)	O6–C7	1.483 (14)
Ce–C1	2.65 (2)	Mg–O6	2.066 (7)	C7–C8	1.52 (2)
Ce–C2	2.67 (2)	Mg–O11	2.078 (8)	C9–C10	1.40 (2)
Ce–C3	2.65 (2)	C1–C2	1.41 (2)	C10–O11	1.48 (2)
Br1–Mg	2.758 (3)	C2–C3	1.23 (2)	O11–C12	1.84 (2)
Br1–Mg′	2.770 (4)	C4–C5	1.41 (2)	C12–C13	1.16 (3)

Bond Angles

Br1–Ce–Br1′	72.99 (5)	Ce–Br2–Mg	87.66 (7)
Br1–Ce–Br2	72.53 (3)	Mg–Br3–Mg′	79.8 (1)
Br1–Ce–Br2′	71.04 (3)	Br1–Mg–Br1′	84.15 (9)
Br1–Ce–C1	85.2 (4)	Br1–Mg–Br2	84.57 (9)
Br1–Ce–C1′	145.8 (4)	Br1–Mg–Br3	83.83 (9)
Br1–Ce–C2	96.9 (4)	Br1–Mg–O6	173.3 (3)
Br1–Ce–C2′	169.7 (4)	Br1–Mg–O11	93.5 (3)
Br1–Ce–C3	91.3 (4)	Br1′–Mg–Br2	86.2 (1)
Br1–Ce–C3′	148.2 (5)	Br1′–Mg–Br3	83.59 (9)
Br2–Ce–Br2′	134.24 (4)	Br1′–Mg–O6	89.1 (2)
Br2–Ce–C1	77.5 (4)	Br1′–Mg–O11	174.8 (2)
Br2–Ce–C1′	125.2 (4)	Br2–Mg–Br3	165.3 (1)
Br2–Ce–C2	108.2 (4)	Br2–Mg–O6	94.8 (2)
Br2–Ce–C2′	102.8 (4)	Br2–Mg–O11	98.2 (2)
Brw–Ce–C3	131.2 (4)	Br3–Mg–O6	95.7 (2)
Br2–Ce–C3′	76.3 (5)	Br3–Mg–O11	91.5 (2)
C1–Ce–C1′	124.9 (9)	O6–Mg–O11	93.2 (3)
C1–Ce–C2	30.9 (5)	C1–C2–C3	136 (2)
C1–Ce–C2′	102.9 (6)	C4–C5–O6	111 (1)
C1–Ce–C3	55.1 (6)	Mg–O6–C5	120.3 (6)
C1–Ce–C3′	94.0 (6)	Mg–O6–C7	124.0 (6)
C2–Ce–C2′	93.3 (8)	C5–O6–C7	115.3 (8)
C2–Ce–C3	26.7 (5)	O6–C7–C8	106 (1)
C2–Ce–C3′	98.5 (6)	C9–C10–O11	112 (1)
C3–Ce–C3′	114.2 (9)	Mg–O11–C10	122.2 (7)
Ce–Br1–Mg	85.07 (7)	Mg–O11–C12	126.3 (7)
Ce–Br1–Mg′	84.88 (7)	C10–O11–C12	111 (1)
Ce–Br2–Mg	87.66 (7)	O11–C12–C13	99 (2)

at first. The structure was solved by direct methods and refined by Fourier syntheses; after several cycles of refinements, it was clear that two parts of the molecule were related by a diad. The space group was thus changed to *C*2/*c*. Refinements including an extinction correction converged at *R* = 0.072 for 1904 observed reflections. The final atomic parameters are given in Table VII. Bond lengths and angles are listed in Table VIII. The view of the molecule is similar to that of complex 1 and is not shown here.

Complex 4. The refined parameters of unit cells for these analogues (complexes 3–7) were similar, and thus, the existence of isomorphous compounds was elucidated. The structure of complex 4 was solved by direct methods in the space group $P2_12_12_1$ and refined by least squares. The final *R* value was 0.043 for 2371 observed reflections. Unlike complex 1 or 2, complex 4 crystallized in a polar space group, and the refinement included the determination of the absolute configuration. The final positional

Table VII. Positional Parameters in $(C_3H_5)_2NdBr_5Mg(Et_2O)_4$ and Their Estimated Standard Deviations (Esd's) in Parentheses[a]

atom	*x*	*y*	*z*	*B*(eq), Å^2	mult
Nd	0.500	0.0047 (1)	0.250	5.01 (3)	1.000
Br1	0.65790 (9)	0.1069 (2)	0.2907 (1)	5.93 (5)	1.000
Br2	0.4615 (1)	0.2211 (2)	0.1366 (1)	6.73 (6)	1.000
Br3	0.500	0.4902 (3)	0.250	7.29 (8)	1.000
Mg	0.5969 (3)	0.3175 (5)	0.2735 (3)	4.5 (1)	1.000
C1	0.582 (1)	0.567 (3)	0.112 (1)	8.5 (7)**	1.000
C2	0.643 (1)	0.509 (2)	0.191 (1)	6.2 (5)**	1.000
O3	0.6274 (5)	0.382 (1)	0.1921 (6)	5.4 (3)	1.000
C4	0.627 (1)	0.307 (2)	0.127 (1)	7.2 (6)**	1.000
C5	0.715 (1)	0.289 (3)	0.156 (2)	8.8 (7)**	1.000
C6	0.821 (2)	0.410 (3)	0.405 (2)	10.4 (9)**	1.000
C7	0.771 (1)	0.348 (3)	0.425 (2)	9.4 (8)**	1.000
O8	0.6912 (6)	0.397 (1)	0.3777 (7)	5.6 (3)	1.000
C9	0.695 (3)	0.440 (5)	0.455 (3)	8 (1)**	0.442
C10	0.695 (3)	0.580 (6)	0.451 (3)	8 (2)**	0.442
C9*	0.686 (2)	0.528 (4)	0.408 (2)	6 (1)**	0.558
C10*	0.666 (2)	0.510 (5)	0.469 (3)	8 (1)**	0.558
C11	0.513 (2)	−0.113 (3)	0.135 (2)	11 (1)**	1.000
C12	0.461 (2)	−0.168 (3)	0.143 (2)	12 (1)**	1.000
C13	0.394 (2)	−0.122 (4)	0.115 (2)	12 (1)**	1.000

[a] See footnote *a* of Table V.

Table VIII. Bond Lengths (Å) and Angles (deg) in $(C_3H_5)_2NdBr_5Mg_2(Et_2O)_4$ with Their Esd's in Parentheses

Bond Lengths

Nd–Br1	3.074 (1)	Mg–O3	2.077 (6)	O8–C9	1.49 (3)
Nd–Br2	3.063 (1)	Mg–O8	2.068 (7)	O8–C9*	1.61 (2)
Nd–C11	2.68 (2)	C1–C2	1.486 (15)	C9–C10	1.58 (4)
Nd–C12	2.61 (2)	C2–O3	1.464 (12)	C9–C9*	1.27 (3)
Nd–C13	2.69 (2)	O3–C4	1.486 (12)	C10–C10*	1.15 (3)
Br1–Mg	2.616 (3)	C4–C5	1.56 (2)	C9*–C10*	1.43 (3)
Br2–Mg	2.782 (3)	C6–C7	1.43 (2)	C11–C12	1.30 (2)
Br2–Mg′	2.763 (3)	C7–O8	1.463 (15)	C12–C13	1.26 (2)
Br3–Mg	2.625 (3)				

Bond Angles

Br1–Nd–Br1′	135.91 (4)	Br1–Mg–Br2	85.55 (9)
Br1–Nd–Br2	73.38 (3)	Br1–Mg–Br2′	83.94 (9)
Br1–Nd–Br2′	71.78 (3)	Br1–Mg–Br3	162.6 (1)
Br1–Nd–C11	81.1 (4)	Br1–Mg–O3	96.0 (2)
Br1–Nd–C11′	121.7 (4)	Br1–Mg–O8	98.4 (2)
Br1–Nd–C12	108.2 (4)	Br2–Mg–Br2′	83.60 (8)
Br1–Nd–C12′	104.3 (4)	Br2–Mg–Br3	82.11 (9)
Br1–Nd–C13	128.4 (4)	Br2–Mg–O3	89.0 (2)
Br1–Nd–C13′	77.1 (4)	Br2–Mg–O8	175.0 (2)
Br2–Nd–Br2′	74.21 (5)	Br2′–Mg–Br3	82.53 (7)
Br2–Nd–C11	85.8 (4)	Br2′–Mg–O3	172.6 (2)
Br2–Nd–C11′	149.9 (4)	Br2′–Mg–O8	93.6 (2)
Br2–Nd–C12	101.2 (4)	Br3–Mg–O3	96.0 (2)
Br2–Nd–C12′	175.3 (4)	Br3–Mg–O8	93.4 (2)
Br2–Nd–C13	89.2 (4)	O3–Mg–O8	93.7 (3)
Br2–Nd–C13′	149.5 (4)	C1–C2–O3	112.2 (9)
C11–Nd–C11′	120.5 (8)	Mg–O3–C2	121.0 (6)
C11–Nd–C12	28.3 (4)	Mg–O3–C4	122.6 (6)
C11–Nd–C12′	98.0 (6)	C2–O3–C4	116.1 (7)
C11–Nd–C13	48.8 (5)	O3–C4–C5	106.2 (9)
C11–Nd–C13′	97.5 (5)	C6–C7–O8	110 (1)
C12–Nd–C12′	83.3 (8)	Mg–O8–C7	124.1 (7)
C12–Nd–C13	27.5 (5)	Mg–O8–C9	128 (1)
C12–Nd–C13′	95.3 (6)	Mg–O8–C9*	122.2 (8)
C13–Nd–C13′	115.8 (8)	C7–O8–C9	93 (1)
Nd–Br1–Mg	87.34 (6)	C7–O8–C9*	113 (1)
Nd–Br2–Mg	84.68 (7)	O8–C9–C10	106 (3)
Nd–Br2–Mg′	85.07 (7)	O8–C9*–C10*	105 (2)
Mg–Br2–Mg′	78.72 (9)	C11–C12–C13	120 (2)
Mg–Br3–Mg′	84.1 (1)		

parameters are listed in Table IX and bond distances and angles in Table X. A view of the molecule is shown in Figure 2.

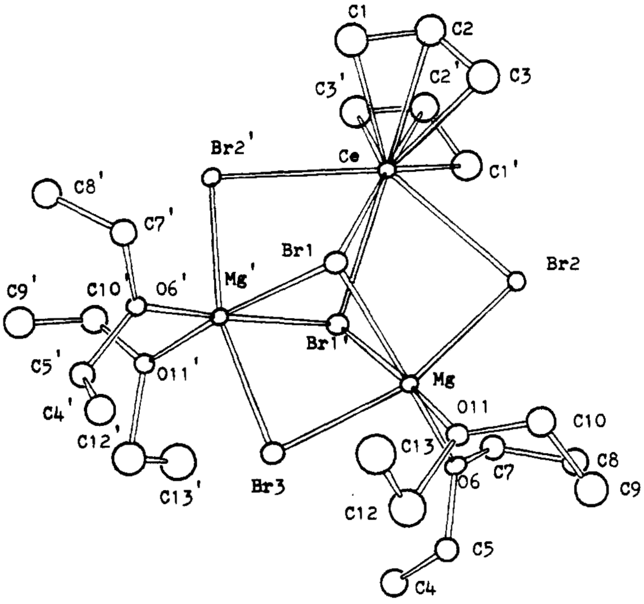

Figure 1. View of the molecule $(\eta^3\text{-}C_3H_5)_2CeBr_5Mg_2(Et_2O)_4$.

Table IX. Positional Parameters in $(C_3H_5)_2CeCl_5Mg_2(tmed)_2$ and Their Estimated Standard Deviations (Esd's) in Parentheses[a]

atom	*x*	*y*	*z*	*B*(eq), Å^2	mult
Ce	0.65231 (6)	0.55720 (5)	0.14384 (5)	3.64 (1)	1.000
Cl1	0.7265 (3)	0.5031 (2)	0.2884 (2)	4.75 (7)	1.000
Cl2	0.7366 (3)	0.5111 (3)	−0.0006 (2)	4.95 (8)	1.000
Cl3	0.7241 (3)	0.3638 (2)	0.1392 (2)	4.11 (6)	1.000
Cl4	0.9176 (2)	0.5427 (2)	0.1487 (2)	3.98 (6)	1.000
Cl5	1.0161 (3)	0.3342 (2)	0.1444 (2)	4.63 (6)	1.000
Mg1	0.8834 (4)	0.4095 (3)	0.2358 (2)	3.60 (9)	1.000
Mg2	0.8934 (3)	0.4170 (3)	0.0524 (2)	3.57 (9)	1.000
N1	1.029 (1)	0.4419 (9)	0.3159 (6)	4.9 (3)	1.000
C1	1.149 (2)	0.440 (1)	0.2833 (9)	6.5 (3)**	1.000
C2	1.010 (1)	0.528 (1)	0.357 (1)	6.2 (3)**	1.000
C3	1.021 (2)	0.368 (1)	0.371 (1)	7.9 (5)**	1.000
C4	0.961 (2)	0.295 (1)	0.358 (1)	10.0 (6)**	1.000
N2	0.857 (1)	0.2926 (7)	0.3089 (6)	4.5 (2)	1.000
C5	0.746 (1)	0.294 (1)	0.351 (1)	6.6 (4)**	1.000
C6	0.858 (2)	0.210 (1)	0.2676 (9)	6.0 (4)**	1.000
N3	1.0437 (9)	0.4639 (7)	−0.0180 (6)	4.0 (2)	1.000
C7	1.018 (1)	0.549 (1)	−0.0561 (9)	6.4 (4)**	1.000
C8	1.155 (2)	0.474 (1)	0.0219 (8)	5.9 (3)**	1.000
C9	1.021 (2)	0.407 (2)	−0.089 (1)	4.2 (5)**	0.526
C10	1.001 (2)	0.304 (2)	−0.059 (2)	4.4 (5)**	0.526
N4	0.886 (1)	0.3061 (7)	−0.0294 (6)	4.6 (3)	1.000
C11	0.769 (1)	0.305 (1)	−0.0726 (9)	5.4 (3)**	1.000
C12	0.907 (2)	0.219 (1)	0.005 (1)	6.5 (4)**	1.000
C9*	1.077 (2)	0.380 (2)	−0.064 (1)	3.7 (5)**	0.474
C10*	0.961 (2)	0.345 (2)	−0.095 (1)	3.6 (5)**	0.474
C21	0.657 (2)	0.718 (1)	0.214 (1)	8.2 (5)**	1.000
C22	0.624 (1)	0.741 (1)	0.142 (1)	6.8 (4)**	1.000
C23	0.699 (2)	0.721 (1)	0.0842 (9)	6.2 (4)**	1.000
C24	0.440 (2)	0.483 (2)	0.195 (1)	10.7 (7)**	1.000
C25	0.414 (2)	0.537 (1)	0.141 (1)	10.5 (6)**	1.000
C26	0.438 (2)	0.554 (1)	0.075 (1)	8.4 (5)**	1.000

[a] See footnote *a* of Table V.

Results and Discussion

Although the structures of complexes 1 and 2 have been determined, the reaction between anhydrous $LnCl_3$ (Ln = Ce, Nd) and the Grignard reagent goes very slowly in ether (eq 1). Unlike the preparation of simple η^3-allyl

$$LnCl_3 + 2C_3H_5MgBr \rightarrow (C_3H_5)_2LnCl_3Br_2Mg_2(Et_2O)_4 \qquad (1)$$

transition-metal complexes, the product here is a novel allyl heterometallic complex. This may be attributed to the requirement for high coordination numbers and the very electropositive character of the lanthanide ions.

In the structural determinations, it was difficult to determine which halides were chloride atoms and which were

Table X. Bond Lengths (Å) and Angles (deg) in $(C_3H_5)_2CeCl_5Mg_2(tmed)_2$ with Their Esd's in Parentheses

Bond Lengths

Ce-Cl1	2.878 (2)	Cl4-Mg2	2.593 (3)	N3-C8	1.45 (1)	Ce-C25	2.69 (1)	N1-C2	1.50 (1)	N4-C12	1.48 (1)
Ce-Cl2	2.880 (2)	Cl5-Mg1	2.506 (4)	Ne-C9	1.57 (2)	Ce-C26	2.72 (1)	N1-C3	1.51 (1)	N4-C10*	1.57 (2)
Ce-C13	3.023 (2)	Cl5-Mg2	2.504 (4)	N3-C9*	1.57 (2)	Cl1-Mg1	2.452 (3)	C3-C4	1.30 (2)	(C9*-C10*)	1.52 (2)
Ce-Cl4	2.993 (2)	Mg1-N1	2.243 (7)	(C9-C9*)	0.88 (2)	Cl2-Mg2	2.458 (4)	C4-N2	1.47 (2)	C21-C22	1.41 (2)
Ce-C21	2.73 (1)	Mg1-N2	2.227 (7)	C9-C10	1.66 (2)	Cl3-Mg1	2.602 (3)	N2-C5	1.46 (1)	C22-C23	1.39 (1)
Ce-C22	2.78 (1)	Mg2-N3	2.237 (7)	C10-N4	1.40 (2)	Cl3-Mg2	2.601 (3)	N2-C6	1.46 (1)	C24-C25	1.31 (2)
Ce-C23	2.74 (2)	Mg2-N4	2.238 (8)	(C10-C10*)	1.03 (2)	Cl4-Mg1	2.586 (3)	N3-C7	1.49 (1)	C25-C26	1.26 (2)
Ce-C24	2.79 (2)	N1-C1	1.48 (1)	N4-C11	1.54 (1)						

Bond Angles

Cl1-Ce-Cl2	132.15 (5)	Cl3-Mg1-N1	176.2 (3)	C21-Ce-C23	52.4 (3)	Mg1-N2-C4	103.6 (8)
Cl1-Ce-Cl3	71.06 (7)	Cl3-Mg1-N2	95.9 (2)	C21-Ce-C24	102.2 (4)	Mg1-N2-C5	114.5 (6)
Cl1-Ce-Cl4	70.31 (7)	Cl4-Mg1-Cl5	81.7 (2)	C21-Ce-C25	97.3 (4)	Mg1-N2-C6	111.5 (5)
Cl1-Ce-C21	79.3 (3)	Cl4-Mg1-N1	97.0 (2)	C21-Ce-C26	104.6 (4)	C4-N2-C5	110.8 (8)
Cl1-Ce-C22	109.0 (3)	Cl4-Mg1-N2	178.5 (2)	C22-Ce-C23	29.1 (3)	C4-N2-C6	109.5 (9)
Cl1-Ce-C23	124.1 (2)	Cl5-Mg1-N1	95.5 (2)	C22-Ce-C24	107.4 (4)	C5-N2-C6	107.0 (8)
Cl1-Ce-C24	80.3 (3)	Cl5-Mg1-N2	96.9 (2)	C22-Ce-C25	89.8 (4)	Mg2-N3-C7	113.3 (6)
Cl1-Ce-C25	105.7 (4)	N1-Mg1-N2	83.2 (4)	C22-Ce-C26	85.0 (4)	Mg2-N3-C8	113.4 (6)
Cl1-Ce-C26	132.3 (3)	Cl2-Mg2-Cl3	83.8 (2)	C23-Ce-C24	130.7 (5)	Mg2-N3-C9	100.0 (7)
Cl2-Ce-Cl3	69.78 (7)	Cl2-Mg2-Cl4	85.4 (1)	C23-Ce-C25	106.4 (5)	Mg2-N3-C9*	103.5 (7)
Cl2-Ce-Cl4	71.41 (7)	Cl2-Mg2-Cl5	160.9 (1)	C23-Ce-C26	90.2 (4)	C7-N3-C8	107.8 (7)
Cl2-Ce-C21	129.5 (3)	Cl2-Mg2-N3	97.8 (2)	C24-Ce-C25	27.4 (5)	C7-N3-C9	93.6 (8)
Cl2-Ce-C22	105.6 (3)	Cl2-Mg2-N4	98.2 (2)	C24-Ce-C26	52.4 (4)	C7-N3-C9*	120.0 (9)
Cl2-Ce-C23	78.0 (2)	Cl3-Mg2-Cl4	83.7 (1)	C25-Ce-C26	27.0 (4)	C8-N3-C9	127.4 (9)
Cl2-Ce-C24	119.4 (4)	Cl3-Mg2-Cl5	81.0 (2)	Ce-Cl1-Mg1	90.83 (9)	C8-N3-C9*	98.3 (9)
Cl2-Ce-C25	106.6 (4)	Cl3-Mg2-N3	177.6 (2)	Ce-Cl2-Mg2	90.94 (9)	N3-C9-C10	106 (1)
Cl2-Ce-C26	82.3 (3)	Cl3-Mg2-N4	98.6 (2)	Ce-Cl3-Mg1	84.85 (8)	N3-C9*-C10*	106 (1)
Cl3-Ce-Cl4	70.37 (5)	Cl4-Mg2-Cl5	81.5 (2)	Ce-Cl3-Mg2	85.16 (8)	C9-C10-N4	103 (1)
Cl3-Ce-C21	149.0 (3)	Cl4-Mg2-N3	94.5 (3)	Mg1-Cl3-Mg2	79.95 (9)	C9*-C10*-N4	107 (1)
Cl3-Ce-C22	171.0 (2)	Cl4-Mg2-N4	175.8 (2)	Ce-Cl4-Mg1	85.78 (8)	Mg2-N4-C10	104.1 (8)
Cl3-Ce-C23	143.5 (2)	Cl5-Mg2-N3	97.1 (3)	Ce-Cl4-Mg2	85.90 (8)	Mg2-N4-C10*	102.0 (7)
Cl3-Ce-C24	81.6 (3)	Cl5-Mg2-N4	95.3 (2)	Mg1-Cl4-Mg2	80.40 (9)	Mg2-N4-C11	112.4 (6)
Cl3-Ce-C25	99.0 (3)	N3-Mg2-N4	83.1 (3)	Mg1-Cl5-Mg2	83.70 (9)	Mg2-N4-C12	112.2 (6)
Cl3-Ce-C26	101.9 (3)	Mg1-N1-C1	113.8 (6)	Cl1-Mg1-Cl3	85.5 (2)	C10-N4-C11	127 (1)
Cl4-Ce-C21	91.7 (4)	Mg1-N1-C2	114.2 (6)	Cl2-Mg1-Cl4	84.4 (1)	C10-N4-C12	90 (1)
Cl4-Ce-C22	100.9 (2)	Mg1-N1-C3	103.4 (6)	Cl1-Mg1-Cl5	161.4 (1)	C11-N4-C10*	94.1 (8)
Cl4-Ce-C23	83.6 (2)	C1-N1-C2	110.0 (8)	Cl1-Mg1-N1	98.3 (2)	C11-N4-C12	109.6 (8)
Cl4-Ce-C24	144.4 (3)	C1-N1-C3	107.8 (9)	Cl1-Mg1-N2	97.1 (2)	C12-N4-C10*	125.3 (9)
Cl4-Ce-C25	169.3 (3)	C2-N1-C3	107.3 (8)	Cl3-Mg1-Cl4	83.9 (1)	C21-C22-C23	119 (2)
Cl4-Ce-C26	153.8 (3)	N1-C3-C4	122 (1)	Cl3-Mg1-Cl5	81.0 (2)	C24-C25-C26	143 (2)
C21-Ce-C22	29.6 (3)	C3-C4-N2	123 (1)				

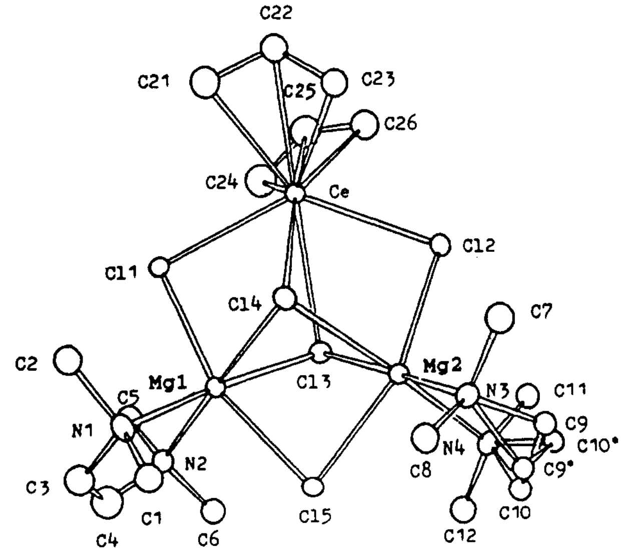

Figure 2. View of the molecule $(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2$.

bromides in the five halide ion sites. It seemed the bond lengths and the temperature factors as well the *R* values favored bromides in all sites. The average bond lengths from Ce to bridging halides (3.114 (1) Å) and to the capping sites (3.109 (1) Å) in complex 1 are about 0.23–0.10 Å longer than those from Ce to the bridging chlorides (2.879 Å) and to the capping chlorides (3.008 Å) in complex 4. The distances from Mg to the Ce bridging sites (2.613 Å) and to the capping sites (2.758 (3), 2.770 (4) Å) are also 0.16–0.17 Å longer than those from Mg to the bridging chlorides (2.456 Å) and to the capping chlorides (2.595 Å) in complex 4. The bond distance from the bridging atom Cl5 to the Mg atom (2.613 Å) is 0.11 Å longer than that (2.505 Å) in complex 4. These differences are comparable to the radii difference of 0.14 Å between bromide and chloride anions. The differences of the relevant lengths between complexes 1 and 2 are about equal to the radii difference of 0.03 Å between Ce^{3+} and Nd^{3+},[6] also supporting the assignment of the halide atoms in complexes 1 and 2 as bromide. Probably, the all-Br forms of complexes 1 and 2 are less soluble than the partial Cl analogues in these systems. Thus, the all-Br forms of complexes 1 and 2 gradually crystallize.

The reaction of $LnCl_3$ (where Ln = La, Ce, Pr, Nd, Sm) and allylmagnesium chloride in the ratio of 1:(1.3–1.5) occurred smoothly in THF at 0 °C. After the residue of $LnCl_3$ was removed, the solution was precipited with tmed. The reaction carried out is shown by eq 2.

$$\mathrm{LnCl_3 + 2C_3H_5MgCl + 2tmed \rightarrow (C_3H_5)_2LnCl_5Mg_2(tmed)_2} \qquad (2)$$

Complexes 3–7 were obtained as bright-colored crystalline powders that are sensitive to air and moisture. They were stable under an N_2 atmosphere, readily soluble in THF and CH_2Cl_2 and slightly soluble in benzene and in toluene, but insoluble in hexane. Their IR and MS

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[6] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

spectra are given in Table II. Two bands at 1545–1546 and 3058–3065 cm^{-1} in the IR spectra are assigned to the characteristic stretching vibrations of ν(C⋯C⋯C) and ν(=C—H), which indicate the existence of allyl groups. The characteristic fragments of the allyl group and tmed also appear in the mass spectra. The molar conductivities of complexes 3–7 were much lower than those of the ionic compounds [Li(tmed)$_2$][Yb(CH$_2$SiMe$_3$)$_4$][6] and [Li(tmed)$_2$][Ce(C$_3$H$_5$)$_4$],[7] indicating the complexes likely exist as neutral molecules in THF.

All the results mentioned above are consistent with the structure determined for complex 4. As shown in Figures 1 and 2, the structure of complex 4 is similar to those of complexes 1 and 2: The lanthanide ion is η^3-bonded by the two allyl groups, while the molecule has a typical trimetallic skeleton completed by three bridging and two capping halide ions. Although the trimetallic feature is not unique in comparison to those in {(Me$_5$C$_5$)U[μ-(CH$_2$)P(Ph)$_2$(CH$_2$)]}$_2$Mg[CH$_2$PMePh$_2$]$_2$(μ_3-O)(μ_2-O)(μ_2-Cl)$_2$[9] and (Me$_2$Si(C$_5$Me$_5$)$_2$NdCl)$_2$Cl$^-$·Li(THF)$_2^+$.[10] The molecular structure is more closed than others. It is also totally different from all the allyllanthanides reported previously.[3,11]

As shown in Table I, the quite high decomposition temperatures of complexes 4–7 (higher than 160 °C) indicate the stabilities of the structures. The bond lengths and angles from the lanthanide to the halide atoms shown in Tables VI, VIII, and X may vary some, depending on the metal and the halide, and show no great stereo interferences exist in the structures. On the other hand, the capping halide ions are in short contact with each other (3.465 (2) Å) and are in contact with the three bridging atoms as well (3.328 (3)–3.433 (3) Å). Obviously, from the point of view of steric congestion, the metals with large radii will be slightly favored. Hence, within the lanthanide series, the early metals such as La, Ce, Pr, Nd, and Sm can form these complexes. Moreover, the congestion will produce some distortion in these molecules, as discussed below.

Like complexes 1 and 2, complex 4 has nearly C_{2v} symmetry with the pseudodiad axis passing through the Ce^{3+} ion and the bridging atom Cl5. (Of the three structures in this paper, complexes 1 and 2 have the real diads of symmetry.) The three bridging chloride atoms Cl1, Cl2, and Cl5 are almost located in the main plane defined by the three metal atoms (at distances −0.022, 0.064, and 0.011 Å from the plane), while Ce, Cl5, and the two capping chloride atoms Cl3 and Cl4 define another plane with a dihedral angle of 90.16° between them. The two capping chloride atoms are 1.7 Å from the main plane on both sides, bonded to all of these metal atoms. There are also two allyl groups and two nitrogen atoms of each tmed molecule above and below the main plane bonded to the Ce and two Mg atoms, respectively.

The average distance from Ce to the bridging chloride atoms Cl1 and Cl2 (2.88 Å) is comparable with that from Nd to the bridging chloride (2.841 Å) in [Na(THF)$_6$][Nd(η^5-C$_9$H$_7$)$_3$(μ-Cl)Nd(η^5-C$_9$H$_7$)$_3$].[12] Bond lengths vary depending on the number, nature, and size of coligands as well the geometry in the system. Subtraction of the eight-coordinate cerium radius, 1.143 Å, from the metal–chloride distances yields an average "effective chloride radius" 1.74 Å in this compound, which is longer than those found in the cyclopentadienyl homometallic bridged dimers Ln(μ_2-Cl)$_2$Ln (1.66[13] and 1.68 Å[14]) and much longer than those observed in Ln(μ_2-Cl)$_2$Li complexes (1.61[15] and 1.64 Å[14]). It is also slightly shorter than that found in the Yb(μ_2-Cl)$_2$Al structure[15] (1.78 Å). The effective chloride radius of the capping atoms in this compound is even longer (1.87 Å). Obviously, the effective chloride radius in the Ln(μ_2-Cl)M systems (M = Li$^+$, Ln^{3+}, Mg^{2+}, Al^{3+}) varies depending on both bonds to the chloride.

As described by Evans,[16] some anomalously long bond lengths found in these structures may be qualitatively explained by the steric interaction in the system. In complex 4, because the chloride atoms are in short contact with each other, nonbonded repulsions among the halide atoms will push the three bridging atoms apart as much as possible and push the capping chlorides away also. It is no wonder that the distances between the lanthanide and chloride atoms will be somewhat stretched. Meanwhile, the bond angles Ce–Cl–Mg and Mg–Cl–Mg will be more or less contracted. The angles Cl–Ce–Cl due to the Coulombic repulsions among these halide atoms will be increased. For comparison, in the trimetallic complex [Me$_2$Si(Me$_4$C$_5$)$_2$NdCl]$_2$ClLi(THF)$_2$,[10] where no μ_3-bonded atoms exist, the effective chloride radii, 1.66 Å in the Nd(μ_2-Cl)Nd system and 1.61 Å in the Nd(μ_2-Cl)Li system, are normal. The bond angles Nd–Cl1–Nd (134.4°), Nd–Cl2–Li (117.9 (4)°) and Cl1–Nd–Cl2 (97.1 (1)°), Cl2–Li–Cl2′ (123.7°) are not special. However, things are quite different in complex 4: the effective chloride radius is certainly stretched, and the angles Ce–Cl1–Mg1, Ce–Cl2–Mg2, and Mg1–Cl5–Mg2 are contracted to 90.93 (9), 90.94 (9), and 83.70 (9)°, while the angles Cl1–Ce–Cl2, Cl1–Mg1–Cl5, and Cl2–Mg2–Cl5 are increased to 132.15 (5), 161.4 (1), and 160.9 (1)°, respectively. Similarly changes are also observed in the compound {(Me$_5$C$_5$)U[μ-(CH$_2$)P(Ph)$_2$(CH$_2$)]}$_2$Mg[CH$_2$PMePh$_2$]$_2$(μ_3-O)(μ_2-O)(μ_2-Cl)$_2$,[9] where the trimetallic nucleus is bonded together by an additional coplanar μ_3-oxygen. Because the μ_3-oxygen atom O2 is in short contact with the three bridging atoms O1, Cl, and Cl′ with distances O1–O2 = 2.60 Å, O1–Cl = 3.07 Å, and O2–Cl = 3.07 Å, an anomalously long effective chloride radius (1.93 Å) is found, the angles U–O1–U′ and U–Cl–Mg are contracted to 108 (1) and 80.8 (5)°, and the angles Cl–U–O1 and Cl–Mg–Cl′ are enlarged to 146.4 (8) and 158 (1)°.

The coordination sphere about the Ce is an irregular octahedron composed to two allyl groups, two bridging chloro ligands, and two capping chloro ligands. The two allyl groups are antipodal to the two weakest bonds Ce–Cl3 and Ce–Cl4 (with angles C22–Ce–Cl3 = 171.0 (2)° and C25–Ce–Cl4 = 169.3 (3)°), which means there are strong interactions between the lanthanide and the allyl groups. The distances from C of the η^3-allyl groups to the Ce (2.69 (1)–2.79 (2) Å) are comparable with those in the complex [Li$_2$(μ-C$_3$H$_5$)(C$_4$H$_8$O$_2$)$_3$][Ce(η^3-C$_3$H$_5$)$_4$][3] (2.712–2.858 Å). The angles of the η^3-allyl groups C21–C22–C23 and C24–

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C25–C26 (119 (2) and 143 (2)°, respectively) are also comparable with those in ref 3 (124.0–135.8°). The dihedral angles between the planes defined by the three-carbon skeleton of the η^3-allyl groups and the plane defined by the metal atom and the two terminal carbon atoms of the η^3-allyl groups are 112 (2)° and 117 (3)°. The high values of the temperature factors of these carbon atoms in the allyl groups mean they are somewhat disordered.

The geometry about the two Mg ions is distorted octahedral with two lengths (2.455 (3) and 2.505 (4) Å) to the bridging atoms Cl1 (or Cl2) and Cl5, two average lengths (2.596 (3) Å) to the two capping atoms, and two average distances (2.236 (7) Å) to the two nitrogen atoms of the tmed molecules. The distances from Mg1 and Mg2 to the bridging chloride atoms Cl1, Cl2, and Cl5 (2.452 (3), 2.458 (4), and 2.505 (4) Å, respectively) and to the two capping atoms Cl3 and Cl4 2.601 (3) and 2.589 (3) Å, respectively) are comparable to those in $[C_2H_5Mg_2Cl_3(THF)_3]_2$[17] (2.47–2.51 and 2.50–2.79 Å, respectively). In addition, the chelating rings Mg–N–C–C–N formed by the tmed molecule and Mg^{2+} bring additional stability to the compound. As shown by their disordered arrangements, these ethylene groups are not rigid. Like some solvent molecules in the lanthanide compounds,[18] they may statistically exist as two conformers.

The appearance of the molecule is quite similar to those of other trinuclear cluster compounds.[19–21] The trianglar conformation of the complex, with full bridging and capping ligands coordinating to the metal atoms, seems to be one of the most favorable schemes in electrostatics.

Further studies of these complexes are ongoing.

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Registry No. **1**, 130095-97-5; **2**, 130063-49-9; **3**, 130063-50-2; **4**, 130063-51-3; **5**, 130063-52-4; **6**, 130063-53-5; **7**, 130063-54-6; C_3H_5MgBr, 1730-25-2; $CeCl_3$, 7790-86-5; $NdCl_3$, 10024-93-8; $PrCl_3$, 10361-79-2; $SmCl_3$, 10361-82-7; C_3H_5MgCl, 2622-05-1; $LaCl_3$, 10099-58-8; 3-butenoic acid, 625-38-7; propylene, 115-07-1.

Supplementary Material Available: Listings of crystal data, thermal parameters, bond distances and angles, least-squares planes, and torsion angles for **1**, **2**, and **4** (56 pages); listings of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Gas-Phase Ion Chemistry of Cr(η^6-arene)$(CO)_3$ Complexes by FTMS Techniques

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The gas-phase reactivities of eight Cr(η^6-arene)$(CO)_3$ complexes (arene = toluene, mesitylene, PhCOOMe, PhCOMe, PhCOEt, PhCO-*n*-Pr, PhCO-*t*-Bu, $PhCH_2COMe$) have been studied by FTMS techniques. Self-condensation processes occur that follow different reaction pathways when the coordinated arene is a hydrocarbon or a phenyl ketone. PhCOOMe and $PhCH_2COMe$ show an intermediate behavior. Reactions with free arenes or propene give substitution of the carbonyl groups, yielding $Cr(arene)(arene')^+$ and $Cr(arene)(propene)^+$, respectively. The extent to which displacement takes place depends on the nature of the original coordinated arene and is higher when it contains a CO group. With suitable free arenes as reagent gases, arene displacement is also observed, producing $Cr(arene')_2{}^+$. The formation of the disubstituted ions depends, once again, on the nature of the coordinated arene as well as on the relative bond energy of Cr^+–arene′ with respect to Cr^+–arene. CID experiments have been performed in order to obtain a sequence of relative binding energies of the arenes to Cr^+. The results are consistent with the electronic and steric properties of the arene ligands, which affect the Cr^+–arene bond strength.

Introduction

In the last decade, an increasing number of studies have been reported on gas-phase ion–molecule reactions involving transition-metal complexes and the reactivity of atomic and coordinated metal ions.[1–5] The rapid growth in this area can be attributed to the development of new experimental methodologies involving techniques such as ion beam,[1,2] flowing afterglow,[3] ion cyclotron resonance (ICR),[4] and Fourier transform mass spectrometry (FTMS).[5] This research has mainly focused on atomic metal cations produced by laser desorption, surface ioni-

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