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General Synthesis and Metal Complexes of Fused-Ring Bicyclic Cyclopentadienes

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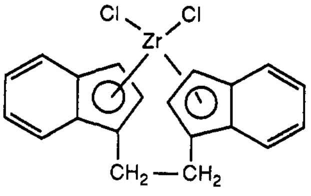
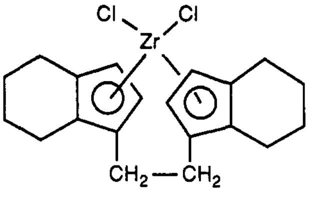
A simple new synthesis of cyclopentadienes possessing fused hydrocarbon $(CH_2)_n$ chains is based upon rearrangement of spirolactones. These latter compounds can be made from commercially available oxiranes in a three-step procedure. Cyclopentadienes containing five- and six-membered alkylidene groups, $-(CH_2)_5-$ and $-(CH_2)_6-$, respectively, in 1,2-positions were thus prepared. They were employed as precursors to generate ligands L for novel neodymium and zirconium complexes of the types L_2ZrCl_2, $(L_2NdCl)_2$, and L_3Nd. Single-crystal X-ray structures of these complexes are reported.

Introduction

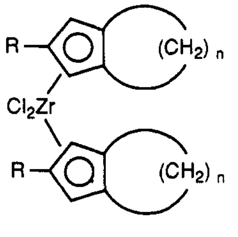
The so-called "stereorigid" zirconocene-type catalysts of propene polymerization for highly isotactic polymers of tunable molecular weight have attracted enormous attention in both basic research and industry.[1-3] A prototypal complex is the C_2-symmetrical indenyl complex **A**, which exhibits particularly interesting catalytic properties if employed in combination with methylalumoxane as a cocatalyst.[4]



A



B



C (=9)

While tetrahydroindenyl derivatives **B** are easily accessible through simple hydrogenation of the indenyl precursor compounds,[5] no synthesis of larger ring systems (type **C**) was previously known. We now describe the first efficient route to fused-ring derivatives **6** of cyclopentadiene and their use as π-ligands in novel zirconium and neodymium complexes.

Results and Discussion

A. Fused-Ring Cyclopentadienes. The reaction sequence is given in Scheme I. Oxiranes **1a,b** are easily available precursor compounds.[6,7] Spirolactones **4** are known to rearrange to cyclic enones **5** in media such as polyphosphoric acid and concentrated sulfuric acid.[8] These are easily reduced to allylic alcohols that spontaneously eliminate water to give the dienes **6**.

The importance of a 2-methyl group in zirconocene-type complexes to polymerize propene with high isotacticity has been noted.[9-11] Therefore, our synthetic method outlined in Scheme I had to take care of this aspect.

The epoxides **1a** and **1b** were derived from commercially available, cheap ketones.[12] They were transformed into the ring-expanded products **2a** and **2b** by treatment with the sodium salt of diethyl malonate in ethanolic solution. The intermediates **2** were anionic, the negative charge being centered at the most acidic site in the molecule,

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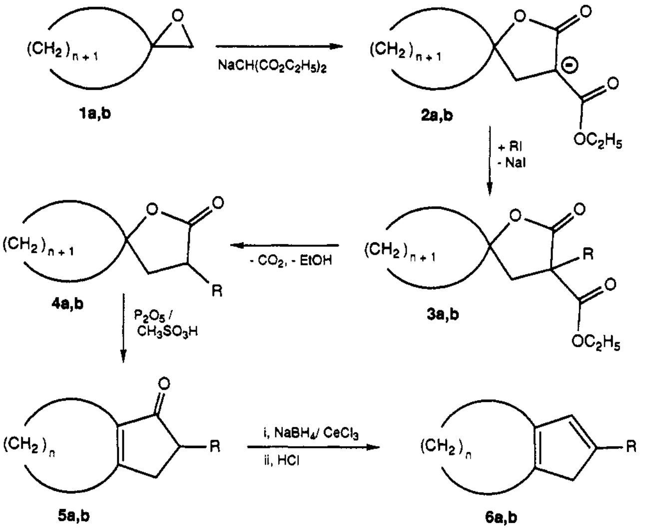
Scheme I[a]



n		Salts	
		Li	K
5	6a	7a	8a
6	6b	7b	8b

[a] R = CH_3.

which is the carbon atom between the two carboxy groups. The anions **2a,b** were then alkylated with methyl iodide to give **3a,b**. Spontaneous decarboxylation with concomitant loss of ethanol yields the intermediate lactones **4a,b**. This one-pot procedure holds promise of working as a *general route* to derivatives other than R = CH_3.

The desired enones **5a** and **5b**, respectively, were obtained *via* rearrangement of the lactones by virtue of polyphosphoric acid or Eaton's reagent (methane-sulfonic acid/P_2O_5) (Scheme I). The products of the Nazarov cyclization were characterized by their ^{1}H NMR spectra. A doublet centered at ca. 1 ppm is assigned to the methyl group of the five-membered ring. This signal is well separated from the complicated set of signals of the methylene and of the methyne protons and allows an assessment of isomeric purity. A gas chromatogram showed only *one* product peak. A ^{13}C NMR spectrum indicated that the synthesis following Scheme I yields the enones **5a** and **5b** as the only isomers. By reduction of **5a,b** with either $LiAlH_4$ or $NaBH_4/CeCl_3$ *three* isomers of the cyclopentadienes **6a,b** are obtained (Figure 1). The isomer ratios are different for the two enones **5a** (n = 5) and **5b** (n = 6).

In the three possible isomers, the methyl group is connected to an sp^2-hybridized ring carbon atom in two cases: **i1** and **i2** (Chart I). The methyl group of isomer **i3** (which is attached to an sp^3 carbon) should exhibit the lowest chemical shift in the ^{13}C NMR spectrum. By inspection of the ^{13}C NMR spectrum of the mixture the first signal appears at 14.50 ppm. With regard to its low intensity and shift range, it is attributed to the methyl group of isomer **i3** (ca. 10%). The signals at 15.61 and 16.78 ppm are compatible with sp^2-bonded methyl groups of isomers **i1** and **i2** with regard to intensity and chemical shift. The signal count in the vinylic range is rationalized by use of DEPT 135 (Chart I). There are nine CH signals, five of which are sp^2 CH groups. Six high-intensity CH signals are attributed to isomers **i1** and **i2**, of which three are vinylic CH groups. Five out of the eight high-intensity vinylic sp^2 carbons of isomers **i1** and **i2** are absent in the DEPT spectrum, leaving three sp^2 CH groups.

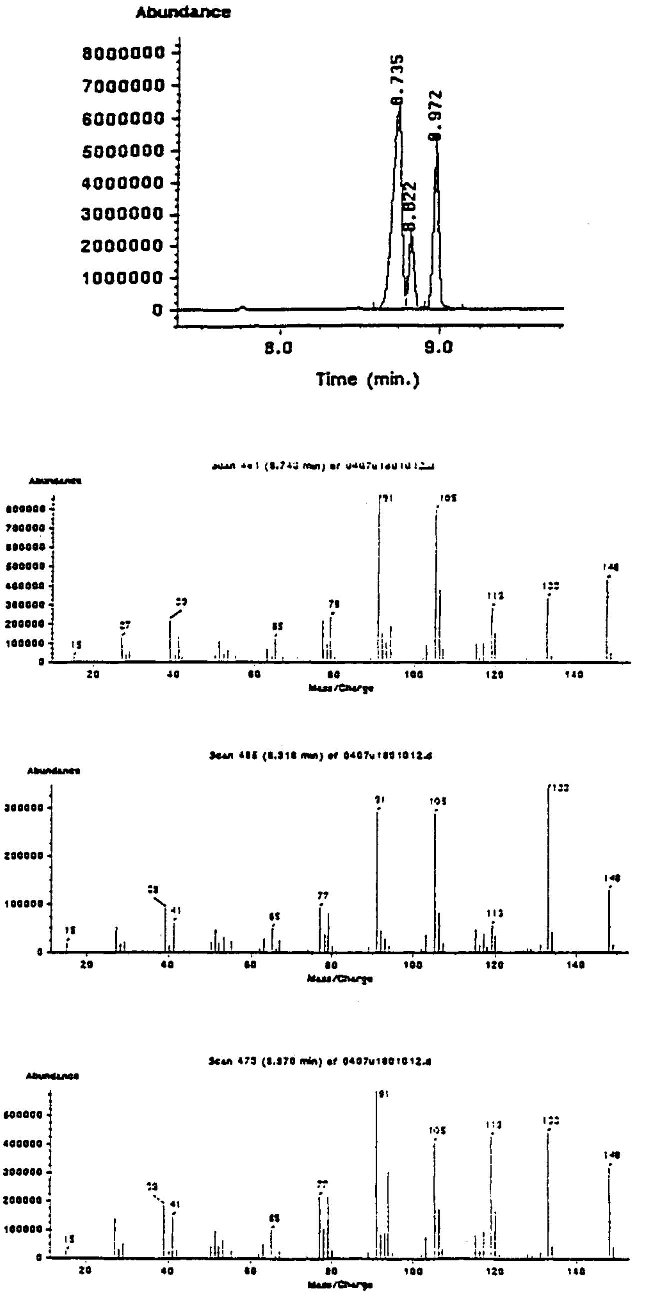
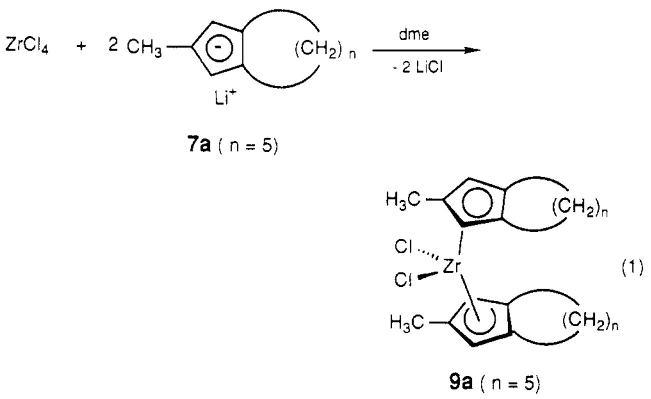


Figure 1. GC/MS graphs for cyclopentadiene **6a** (isomers **i1**, **i2**, and **i3**).

B. Zirconium Complex. The zirconocene-type complex **9a** (n = 5), prepared from **6a** by reaction of 2 equiv of the corresponding lithium salt **7a** with zirconium tetrachloride in dimethoxyethane (eq 1; dme = 1,2-dimethoxyethane), exhibits only three signals for CH_2 groups in the ^{13}C NMR spectrum (δ 28.73, 30.72, and 32.23 ppm). No special conformation is thus adopted at room temperature. The presence of two fused-ring cyclopentadienyl ligands is shown by the mass spectrum which exhibits the parent ion peak at m/z 456 of correct isotopic pattern.

Single crystals of **9a** were obtained by dissolving 226 mg of white, thin needles from the purified reaction product in 3.5 mL of hot toluene. Slow cooling from 60 °C to room temperature over a period of several days yielded colorless, rod-shaped crystals.

In the crystal, the molecules conform to 2-fold rotation symmetry. The seven-membered rings of the annelated



7a (n = 5)

(1)

9a (n = 5)

cyclopentadienyl ligands lie on opposite sides of the $(MeCp)_2ZrCl_2$ fragment and are folded in a chair conformation such that the C5–C6–C7 fragments are parallel to their respective Cp rings (see Figure 2a). The hydrogen atoms were found to assume conventional axial and equatorial positions for the chair conformation. It is of interest that the Cp fragments are eclipsed (see Figure 2b) and that the methyl substituents are directed toward the back of the metallocene unit, away from the chlorine atoms. Thus, the bulky seven-membered rings lie toward the front of the molecule but appear to avoid close contacts with the chlorine atoms by virtue of the chair conformation by being folded away from the center of the molecule.

Perhaps as a result of the considerable bulk of the seven-membered ring, or because of slight folding of the Cp fragment, the zirconium atom lies closer to C2 and C3 of the Cp ring (Zr–C2 = 2.485(2) Å, Zr–C3 = 2.495(2) Å) than to C1, C3a, and C8a (Zr–C1 = 2.536(2) Å, Zr–C3a = 2.552 (2) Å, Zr–C8a = 2.597(2). A least-squares planes calculation for the five Cp ring carbon atoms gives a relatively high χ^2 value of 58.5, the atoms C3 and C8a lying approximately 0.01 Å above the average plane (i.e. away from the Zr atom) and atoms C1, C2, and C3a below the plane. The "ring slippage" amounts to 0.12 Å. The angle between the average Cp rings is 52.09°. Such an effect is well-known in these complexes,[13] but in the present case it appears that C8a, which carries the bulk of the seven-membered ring at the front of the molecule, is pushed further away from the center of the molecule. Note that there is a short Cl···H81 contact of 2.67(3) Å.

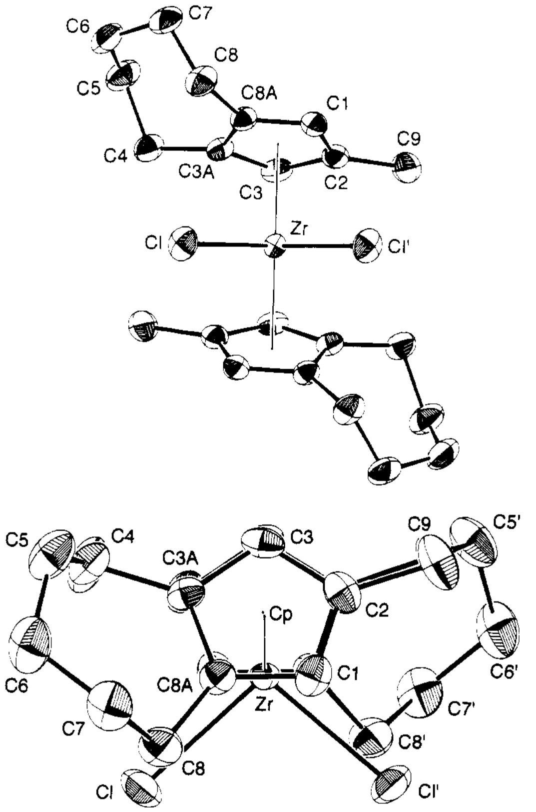
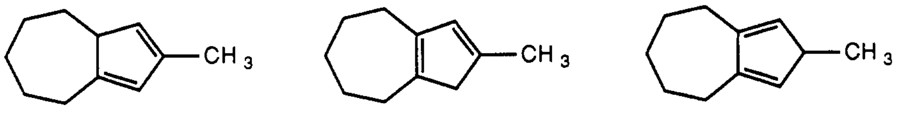


Figure 2. ORTEP plots with 50% probability ellipsoids and numbering of the ligand system: (a, top) molecule of compound **9a** viewed down the dibsector of the Cl–Zr–Cl′ angle, showing the 2-fold rotation symmetry and chair conformation of the annelated cyclopentadienyl ligands; (b, bottom) molecule of compound **9a** viewed from above, showing the position of the ligand rings with respect to the Cl_2Zr unit.

The coordination environment of the zirconium is similar to that found in other $(RCp)_2ZrCl_2$ metallocenes with bulky R groups.[13,14] For a comparative list of structural parameters of some zirconium and titanium metallocenes, see Gallucci et al.[13a] A list of bond lengths and angles for **9a** is given in Table I; atomic coordinates are compiled in Table II.

We find a Zr–Cl distance of 2.445(1) Å, Zr–C distances ranging from 2.485(2) to 2.597(2) Å, Zr–Cp = 2.230(1) Å,

Chart I



i1 i2 i3

	i1	i2	i3
quart. sp^2 - C	2	3	2
sp^3 - CH	1	2	1
vinyl. sp^2 - CH	2	1	2
composition (parts)	5	4	1
high intensity ^{13}C-Signals	DEPT: 3 vinyl. sp^2 - CH, $\Sigma = 6$ CH		
Sum of ^{13}C-Signals	DEPT: 5 vinyl. sp^2 - CH, $\Sigma = 9$ CH		

Table I. Selected Bond Distances (Å) and Angles (deg) for the Zirconium Complex 9a[a]

	Bond Distances (Å)		
Zr–Cl	2.445(1)	Zr–C1	2.536(2)
Zr–C2	2.485(2)	Zr–C3	2.495(2)
Zr–C3A	2.552(2)	Zr–C8A	2.597(2)
Zr–Cp	2.230		
C1–C2	1.415(3)	C1–C8A	1.411(2)
C2–C3	1.407(3)	C2–C9	1.502(3)
C3–C3A	1.414(2)	C3A–C4	1.495(3)
C3A–C8A	1.424(2)	C4–C5	1.535(3)
C5–C6	1.520(4)	C6–C7	1.518(3)
C7–C8	1.536(3)	C8–C8A	1.500(3)
	Bond Angles (deg)		
Cl–Zr–Cl′	97.74(2)	C2–C1–C8A	109.4(2)
Cl–Zr–Cp	104.8	C3A–C8A–C8	125.6(2)
Cl′–Zr–Cp	106.1	C4–C3A–C8A	124.7(2)
Cp–Zr–Cp′	132.2	C3A–C4–C5	111.7(2)
C1–C2–C3	106.5(2)	C4–C5–C6	115.0(2)
C1–C2–C9	126.0(2)	C5–C6–C7	116.9(2)
C3–C2–C9	127.4(2)	C6–C7–C8	114.6(2)
C2–C3–C3A	109.6(2)	C7–C8–C8A	112.0(2)
C3–C3A–C4	127.6(2)	C1–C8A–C3A	107.3(2)
C3–C3A–C8A	107.1(2)	C1–C8A–C8	126.7(2)

[a] Cp = centroid of cyclopentadienyl fragment. Primed atoms (e.g. Cl′) indicate the symmetry operation $-x, y, {}^1/_2 - z$.

Table II. Fractional Atomic Coordinates for zirconium Complex 9a

atom	x/a	y/b	z/c	U(eq), Å^2
Zr	0	0.04415(3)	$^1/_4$	0.0209
Cl	−0.00291(3)	−0.19607(8)	0.13084(4)	0.0411
C1	0.12436(9)	0.0487(3)	0.3062(1)	0.0324
C2	0.09185(9)	0.2276(3)	0.2515(1)	0.0326
C3	0.07895(9)	0.3391(3)	0.3142(1)	0.0301
C3A	0.10150(9)	0.2303(3)	0.4055(1)	0.0269
C4	0.1044(1)	0.2999(4)	0.4980(2)	0.0375
C5	0.1794(1)	0.3232(4)	0.5942(2)	0.0496
C6	0.2165(1)	0.1285(5)	0.6461(2)	0.0525
C7	0.2336(1)	−0.0059(4)	0.5863(2)	0.0464
C8	0.1702(1)	−0.0998(3)	0.4877(2)	0.0403
C8A	0.13119(9)	0.0490(3)	0.4011(1)	0.0282
C9	0.0791(1)	0.2904(5)	0.1505(2)	0.0498
Cp[a]	0.10557	0.17895	0.33572	

[a] Cp = centroid of the atoms C1, C2, C3, C3A, and C8A.

and angles Cl–Zr–Cl′ = 97.74(2)° and Cp–Zr–Cp′ = 132.2°. Three comparable zirconocenes with bulky Cp substituents are known: an isocyclopentadiene,[13] a camphor-substituted Cp,[13] and a 1-methylcyclohexyl-substituted derivative.[14] Zr–Cl distances in these complexes are 2.441(1) and 2.446(1) Å,[13] 2.425(4)–2.434(4),[13] and 2.457(1) Å, respectively,[14] while the corresponding Cl–Zr–Cl′ angles are 95.00(3)°,[13] 91.3(1) and 90.6(1)°,[13] and 93.5(1)°.[14] The Zr–C distances are 2.477(3)–2.537(3) Å,[13] 2.43(1)–2.67(1) Å,[13] and 2.455(2)–2.599(2) Å.[14] The bond distances found in the current complex are therefore typical, although the Cl–Zr–Cl′ angle is slightly larger than those found in the literature. It is of interest that in each of these complexes[13,14] the bulky substituents lie away from the chlorine atoms and to opposite sides of the molecule, in contrast to the present molecule, in which the seven-membered rings lie slightly toward the chlorine atoms.

C. Neodymium Complexes. Organolanthanoid complexes of the type "Cp_2LnCl", also known as lanthanocene(III) chlorides, are key intermediates (precursors) in the synthesis of "Cp_2LnX" systems (e.g. X = alkyl, hydride, alkoxide, amide).[15,16] Of considerable current interest in the fields of both homogeneous catalysis[17] and olefin polymerization[18] are two classes of compounds, namely the alkyl and hydride derivatives "Cp_2LnR" and "$(Cp_2LnH)_2$", respectively, where Ln = an "early" lanthanide metal. Unsubstituted and substituted, particularly bridging,[19] cyclopentadienyl ligands provide a stable framework in these compounds. Lanthanocene(III) chlorides with fused-ring cyclopentadienyl groups are only known for the indenyl system[20] and the related derivatives heptamethylindenyl[21] and tetrahydroindenyl.[22]

The novel neodymium(III) fused-ring cyclopentadienyl complexes **10a** and **10b** have been synthesized by reaction of $NdCl_3$ with 2 equiv of **7a** and **7b**, respectively (eq 2a). When it is heated, the reaction mixture (suspension) changes color from pink to blue. The complexes were isolated, after evaporating the solvent, by sublimation at 270–290 °C/10^{-3} mmHg as blue crystals. The thermal stability and sublimation behavior are comparable to those of other highly substituted lanthanocene(III) chlorides (e.g. $[Nd(Cp^tBu_2)_2(\mu\text{-}Cl)]_2$, >300 °C dec; $[Ln\{Cp(SiMe_3)_2\}_2(\mu\text{-}Cl)]_2$, ca. 250–280 °C/$10^{-3}$ mmHg (sublimes); $[YCp^*_2(\mu\text{-}Cl)]_2$, 285 °C/$10^{-5}$ mmHg (sublimes); $[CeCp^*_2(\mu\text{-}Cl)]_2$,

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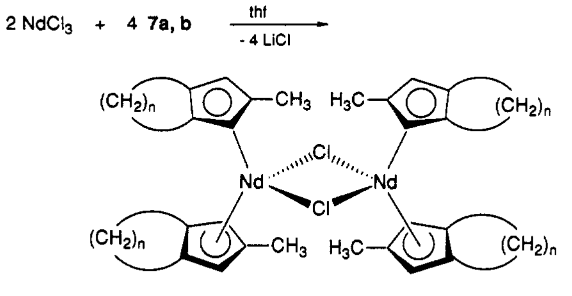
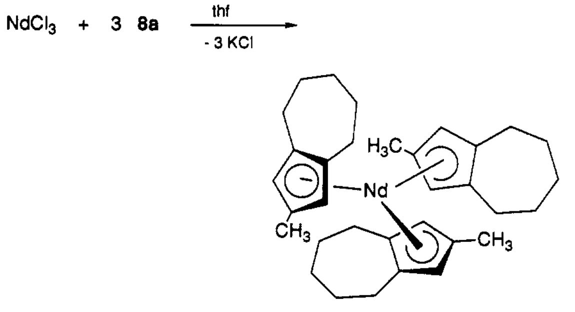


(2a)

10a (n = 5)
10b (n = 6)

300–320 °C/10^{-4} mmHg (sublimes)).[23–28] Both **10a** and **10b** are soluble in ethers such as THF but less soluble in aromatic hydrocarbons and insoluble in aliphatic hydrocarbons.

The potassium salts of cyclopentadienyls are preferred, however, due to greater reactivity toward lanthanoid chlorides than the analogous lithium or sodium salts.[21] Thus, **8a** was used to synthesize the homoleptic, sterically very crowded neodymium complex **11a**. **8a** was prepared from KH and **6a** in THF and was isolated as a white powder. The product did not contain a coordinated solvent (THF). Reaction of $NdCl_3$ and 3 equiv of **8a** in tetrahydrofuran at room temperature gives a green-purple solution (eq 2b).



(2b)

11a

Like **10a** and **10b**, **11a** can be isolated by sublimation (ca. 210 °C/10^{-3} mmHg) of the reaction residue and is obtained as greenish purple crystals in excellent yield (92%). **11a** is even slightly soluble in aliphatic hydrocarbons. Complexes **10a,b** and **11a** are all highly sensitive toward moisture and air (immediate color change to yellow!). The mass spectra for the neodymium complexes exhibit the parent ion, and no peak attributable to a THF adduct is observed.

Suitable crystals of **11a** were grown from a *n*-hexane solution through slow evaporation of the solvent. The molecular structure is shown in Figure 3. Bond lengths and selected bond angles are collected in Table III and atomic coordinates in Table IV.

11a is monomeric in the crystal and possesses a trigonal-planar coordination geometry around neodymium. The trivalent neodymium ion lies in the plane of the three cyclopentadienyl centroids (Cp–Nd–Cp = 120.47, 120.01, 119.47°). The same geometry is seen for the tris(indenyl) complex $Sm(C_9H_7)_3$[20c] and the monomeric (RCp)–lanthanoid[29] and –actinoid derivatives[30] $Yb(MeCp)_3$, $Ce[(SiMe_3)_2Cp]_3$, $Sm[(SiMe_3)_2Cp]_3$, $Sm(Cp^*)_3$, $U(SiMe_3Cp)_3$, and $Th[(SiMe_3)_2Cp]_3$. While $Yb(MeCp)_3$ is monomeric in the crystal, the corresponding complex of the larger neodymium has a tetrameric structure.[31] Fusion of a five-membered ring to the cyclopentadienyl ligand restricts the possibility of intermolecular interaction, and therefore **11a** can retain a monomeric structure. In contrast to $Yb(MeCp)_3$, **11a** does not show any preferred orientation of the methyl groups.

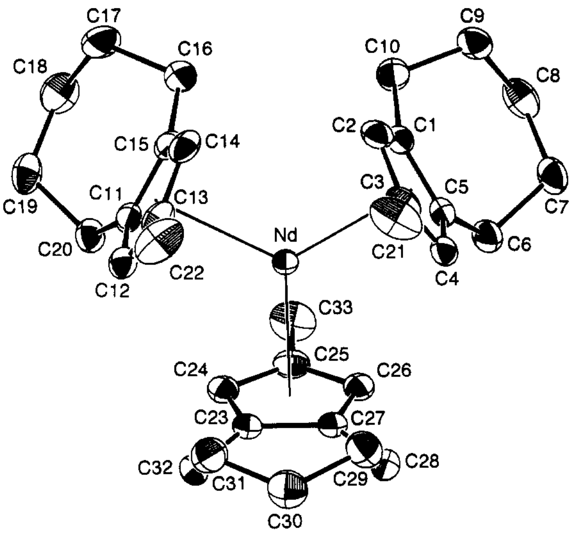


Figure 3. Thermal ellipsoid plot at 50% probability level for **11a**.

Table III. Selected Bond Distances (Å) and Angles (deg) for the Neodymium Complex 11a[a]

Bond distances (Å)			
Nd1–C1	2.820(2)	Nd1–C2	2.792(2)
Nd1–C3	2.748(2)	Nd1–C4	2.744(2)
Nd1–C5	2.801(2)	Nd1–C11	2.780(2)
Nd1–C12	2.769(2)	Nd1–C13	2.771(2)
Nd1–C14	2.774(2)	Nd1–C15	2.769(2)
Nd1–C23	2.823(2)	Nd1–C24	2.761(2)
Nd1–C25	2.732(2)	Nd1–C26	2.776(2)
Nd1–C27	2.830(2)	Nd–C(ring 1)	2.781(2)
Nd–C(ring 2)	2.773(2)	Nd–C(ring 3)	2.784(2)
Nd–Cp1	2.517	Nd–Cp2	2.502
Nd–Cp3	2.514		
Bond Angles (deg)			
Cp1–Nd–Cp2	120.47	Cp2–Nd–Cp3	119.47
Cp1–Nd–Cp3	120.01		

[a] Cp = centroid of cyclopentadienyl fragment.

The average Nd–C(Cp) bond distances are 2.781(2) (ring 1, C1–C5), 2.773(2) (ring 2, C11–C15), and 2.784(2) Å (ring 3, C23–C27). With the exception of atom C15, the longest Nd–C bonds are those where the seven-membered ring is fused (see Figure 3). The average Nd–C distances are comparable to those in $[Nd(MeCp)_3]_4$ (2.795(8) Å),[31] [Nd-

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Table IV. Fractional Atomic Coordinates for Neodymium Complex 11a

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Nd	0.12908(1)	0.129643(4)	0.230511(9)	0.0202
C1	0.3348(2)	0.05293(7)	0.3306(2)	0.0255
C2	0.4255(2)	0.09388(8)	0.3750(2)	0.0292
C3	0.3528(3)	0.11782(8)	0.4498(2)	0.0314
C4	0.2158(3)	0.09073(8)	0.4525(2)	0.0282
C5	0.2044(3)	0.05061(7)	0.3797(2)	0.0253
C6	0.0910(3)	0.00902(8)	0.3688(2)	0.0331
C7	0.1810(3)	−0.03716(8)	0.4170(2)	0.0358
C8	0.2729(3)	−0.05935(8)	0.3397(2)	0.0400
C9	0.4208(3)	−0.03271(8)	0.3281(2)	0.0356
C10	0.3827(3)	0.01416(8)	0.2604(2)	0.0346
C11	0.1455(2)	0.15782(7)	0.0103(2)	0.0250
C12	0.1407(3)	0.20025(8)	0.0716(2)	0.0290
C13	0.2882(3)	0.20508(8)	0.1642(2)	0.0323
C14	0.3843(3)	0.16542(9)	0.1585(2)	0.0314
C15	0.2977(2)	0.13587(8)	0.0660(2)	0.0271
C16	0.3606(3)	0.09217(9)	0.0225(2)	0.0354
C17	0.3758(3)	0.0980(1)	−0.1022(2)	0.0448
C18	0.2143(3)	0.0973(1)	−0.2009(2)	0.0455
C19	0.0988(3)	0.13869(9)	−0.2057(2)	0.0367
C20	0.0254(3)	0.14130(8)	−0.1034(2)	0.0310
C21	0.4180(4)	0.1614(1)	0.5214(3)	0.0529
C22	0.3414(4)	0.2469(1)	0.2457(3)	0.0534
C23	−0.1768(2)	0.17433(8)	0.1920(2)	0.0263
C24	−0.1915(2)	0.14376(8)	0.0958(2)	0.0285
C25	−0.1822(3)	0.09647(8)	0.1348(2)	0.0300
C26	−0.1643(2)	0.09808(7)	0.2565(2)	0.0278
C27	−0.1594(2)	0.14574(7)	0.2931(2)	0.0256
C28	−0.1574(3)	0.16271(8)	0.4135(2)	0.0322
C29	−0.0422(3)	0.20348(9)	0.4645(2)	0.0383
C30	−0.0915(3)	0.25119(9)	0.4053(2)	0.0425
C31	−0.0789(3)	0.25606(8)	0.2810(2)	0.0407
C32	−0.2000(3)	0.22732(8)	0.1855(2)	0.0331
C33	−0.1905(3)	0.0527(1)	0.0612(3)	0.0471

$(^t\mathrm{BuCp})_2(\mu\text{-OH})]_2$ (2.761(2) Å),[32] and $[\mathrm{Nd}(^t\mathrm{BuCp})_2(\mu\text{-CH}_3)]_2$ (2.78(6) Å).[33] The average Nd–Cp(ring centroid) distance is 2.511 Å. As in complex **9a**, the seven-memberd rings form a chair conformation.

The metal complexes described in this paper are potential catalysts in olefin polymerization. Catalytic investigations are underway.

Experimental Section

General Remarks. Manipulations of organic compounds were performed in air. The dienes were distilled under purified, dry argon prior to use. As the lithium and potassium salts of the fused-ring cyclopentadienes and the neodymium complexes are *extremely air-sensitive*, the manipulations with these substances were carried out either under an atmosphere of pure and dry argon, using standard high-vacuum techniques, or a glovebox (N_2 atmosphere).[32] Solvents were predried and freshly vacuum-transferred from Na/K alloy. Anhydrous $NdCl_3$ (Johnson Matthey) was used as purchased. $ZrCl_4$ (Merck) was sublimed prior to use. KH, purchased as a 35 wt % suspension in mineral oil (Aldrich), was washed several times with toluene and *n*-hexane until a white color was obtained and then dried under high vacuum and finally stored in a glovebox.

Elemental analyses were performed by the microanalytical laboratory of our institute. IR spectra were recorded as Nujol mulls between CsI plates (metal complexes) or fluid films (organic compounds) using a Nicolet 5DX-FT or a Perkin-Elmer 283D spectrometer, calibrated with polystyrene film. Mass spectra were obtained on a Varian-MAT 311A spectrometer (EI method) and a Varian-MAT 90 spectrometer (CI, FI method). The organic syntheses were assisted by gas chromatographic analyses using a Beckman HP5890 instrument with HP5970 mass filter. For all analyses the following temperature program was used: 170 °C, 1 min; 170–200 °C, 10°/min; 200–250 °C, 40°/min (helium 200 kPa, column HP-1 50 m, 0.2 mm and film 0.33 mm cross-linked methylsilicone). NMR spectra were measured on a JEOL JMN-GX 400 or a Bruker WP100 spectrometer. ^{13}C NMR assignments were confirmed by DEPT135 (+, CH_3, CH; −, CH_2; 0 quaternary carbons).

Synthesis. 1. Synthesis of Lactones 4. General Procedure. In a three-necked vessel of 2.5-L volume equipped with a reflux condenser and a dropping funnel, 16.5 g (0.71 mol) of sodium metal was dissolved in 550 g of dry, freshly distilled ethanol, to which 113.7 g (0.71 mol) of diethyl malonate was then added to the hand-warm solution. A jelly precipitate of sodium diethyl malonate formed after a few minutes. Epoxide (0.71 mol) was then dropped into this mixture at room temperature, and the mixture was refluxed for 6 h with mechanical stirring. After 2 h a heavy snow white precipitate formed. More ethanol was added if stirring was no longer possible for viscosity reasons. Methyl iodide (85 g, 0.75 mol) was introduced through the dropping funnel, after the mixture was allowed to reach room temperature again. The white lactonate anion dissolves to a yellow oil. The mixture was stirred overnight and then refluxed for 2 h. The reflux condenser was replaced by a distillation bridge (Liebig condenser), and most of the solvent was distilled off. If the liquid separated white masses, a slight vacuum was applied. Sodium hydroxide (200–300 mL, 25% solution in water) was introduced, and distilling was continued. If most of the ethanol was distilled off, a viscous oil remained in the vessel. This oil was separated, and the water phase was extracted two times with ether. The combined organic phases were added to the oil. After drying with sodium sulfate and removal of the solvent, vacuum distillation yielded a nearly colorless product. Some more carboxylic acid was obtained, if the water phase was treated with acid to pH 1. The white solid acid can also be decarboxylated by distillation.

(a) Lactone 4a: bp 112 °C (2 mm Hg); yield 94.3 g (75–80%). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.8. Found: C, 72.9; H, 9.9. Gas chromatography (retention time, min): 12.06, $C_{11}H_{18}O_2$, *m*/*e* 182 (M^+). MS: *m*/*e* 182 (M^+), 125 (M_b), 153, 139, 112, 96, 81, 78, 41, 27. IR (cm^{-1}): $\tilde{\nu}$ 2292 s, 2863 m, 1768 vs, 1458 m, 1378 m, 1312 w, 1284 w, 1237 m, 1175 m, 1152 m, 1030 m, 1006 m, 987 m, 936 m-s. ^1H NMR (100 MHz, $CDCl_3$, 25 °C): δ 1.08 (d, J = 6.9 Hz, 3H), 1.39, 1.43 ("d", 12H), 1.87, 2.08, 2.25, 2.30, 2.47, 2.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C [DEPT]): δ 15.1 [(+) CH_3], 21.4, 21.8, 28.7, 37.6, 40.0, 42.5, 46.1 [(−) CH_2], 39.5 [(+) CH], 87.0 [(0) quat *C*], 178.8 [(0) $C{=}O$].

(b) Lactone 4b: bp 166 °C (10 mmHg); yield 114.11 g (82%). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.00; H, 10.19. Found: C, 73.47; H, 10.44. Gas chromatography (retention time, min): 13.40, $C_{12}H_{20}O_2$, *m*/*e* 196 (M^+). MS: *m*/*e* 196 (M^+), 125 (M_b), 178, 153, 139, 110, 96, 82, 78, 55, 41, 27. ^1H NMR (100 MHz, $CDCl_3$, 25 °C): δ 1.08 (d, J = 7.2 Hz, 3H), 1.39 ("s", 14H), 2.61, 2.51, 2.45, 2.38, 2.30, 2.19, 2.09 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C [DEPT]): δ 15.7 [(+) CH_3], 21.8, 22.1, 24.4, 27.8, 27.9, 33.8, 34.9, 37.4 [(−) CH_2], 41.6 [(+) CH], 87.5 [(0) quat *C*], 179.3 [(0) $C{=}O$].

2. Synthesis of Enones 5. General Procedure. An 18-g (0.48-mol) amount of P_2O_5 was added in small portions to 150 mL of technical-grade methanesulfonic acid (99%). The mixture was vigorously stirred. A 45-mL (ca. 0.27-mol) amount of lactone **4a** or **4b** was then added dropwise; the mixture immediately became warm and developed a red color. A temperature of nearly 70 °C was reached and was subsequently maintained by means of an oil bath. After 2 h the dark melt was poured into a total of 600 g of an ice/water mixture containing 20 wt % of sodium carbonate. The yellow emulsion was extracted three times with ether; the organic phases were combined and dried over magnesium sulfate. The mixture was then filtered and the solvent stripped off. The deeply colored resulting oil was vacuum-distilled by a short-path distillation; the oil bath temperature should be kept as low as possible to avoid decomposition.

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[32] For details, see; Herrmann, W. A.; Anwander, R.; Kleine, M.; Öfele, K.; Riede, J.; Scherer, W. *Chem. Ber.* **1992**, *125*, 2391–2397.

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(a) Enone 5a: bp 105 °C (1 mmHg); yield 45.8 g (93%). Gas chromatography (retention time, min): 12.93, $C_{11}H_{16}O$, *m/e* 164 (M^+). MS: *m/e* 164 (M^+), 136 (M_b), 149, 121, 108, 93, 79, 67, 42, 39, 27. IR (cm^{-1}): $\tilde{\nu}$ 2921 s, 2850 s, 1700 vs, 1648 vs, 1445 s, 1393 s, 1285 m, 1209 w, 1134 w, 1068 w, 969 m, 879 w, 823 w. ^1H NMR (100 MHz, $CDCl_3$, 25 °C): δ 0.82 (d, J = 7.25 Hz, 3H), 1.30, 2.10 ("m", 13H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C [DEPT] δ 15.2 [(+) CH_3], 34.2 [(+) CH], 28.4, 28.6, 37.8, 39.5, 40.0 [(−) CH_2], 161.2 [(0) $C{=}C$], 173.0 [(0) $C{=}C$], 210.0 [(0) $C{=}O$].

(b) Enone 5b: bp 125 °C (1 mmHg); yield 47.5 g (89%, crude yield). Gas chromatography (retention time, min): 11.9, $C_{12}H_{18}O$, *m/e* 178 (M^+). MS: *m/e* 178 (M^+), 163 (M_b), 149, 132, 121, 106, 93, 78, 66, 54, 38, 28. IR (cm^{-1}): $\tilde{\nu}$ 2929 vs, 2857 vs, 1700 vs, 1644 vs, 1450 vs, 1379 s, 1312 s, 1218 m, 1185 m, 1125 m, 1097 s, 979 s, 935 m, 920 s, 873 m, 853 m, 815 w, 756 w, 673 m, 626 w, 541 w. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.99 (d, J = 7.1 Hz, 3H), 1.31, 1.63 ("d", 12H), 2.09, 2.20, 2.31, 2.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C [DEPT]): δ 16.5 [(+) CH_3], 19.8, 22.0, 25.4, 25.6, 28.3, 29.8 [(−) CH_2], 39.5 [(+) CH], 138.8 [(0) $C{=}C$], 173.1 [(0) $C{=}C$], 211.0 [(0) $C{=}O$].

3. Fused-Ring Cyclopentadienes 6a and 6b. General Procedure. A 0.1-mol amount of the enone **5a** or **5b** was dissolved in 50 mL of methanol. A 23.8-g (0.1-mol) amount of $CeCl_3{\cdot}7H_2O$ was dissolved in 70 mL of methanol with stirring and heating to ca. 30 °C. Both solutions were put together in a large vessel and chilled in an ice bath. Using a solid-addition funnel, 3.7 g (0.1 mol) of $Na[BH_4]$ was added in pieces (200-mg portions) into the solution over 1.5 h. The suspension foams and produces gas. Approximately 30 min after the last addition of reducing agent, the white suspension was heated to 50 °C for 2 h. The resulting solution was checked for unreacted enone by gas chromatography. When all enone had reacted, some drops of concentrated hydrochloric acid were added to adjust pH 2–3 in order to destroy any excess sodium borohydride. The emulsion was concentrated on a rotary evaporator using a slight vacuum. The resulting white mass was extracted three times with ether by thorough shaking. The organic phases were dried over magnesium sulfate, the mixture was filtered, and the ether was distilled off under normal pressure. The resultant yellow oil was distilled at a vacuum of 1 mmHg.

(a) Diene 6a: bp 81 °C (1 mmHg); yield 8.52 g (61%). Gas chromatography (retention time, min): 8.73, 8.82, 8.97, $C_{11}H_{16}$, *m/e* 148 (M^+), 6:1:4. MS: *m/e* 148 (M^+), 133, 119, 105, 91 (M_b), 79, 65, 52, 39; second isomer *m/e* 148 (M^+), 133, 119, 105, 91, 79, 65, 52; third isomer *m/e* 148 (M^+), (M_b), 133 (M_b), 119, 105, 91, 79, 65, 52, 39, 27. IR (cm^{-1}): $\tilde{\nu}$ 3137 w, 1639 w, 1444 s, 1376 m, 1279 w, 1227 w, 1205 w, 1182 w, 1182 w, 1147 w, 1090 w-m, 982 w, 959 m-w, 902 m-w, 885 w, 868 w, 811 w. ^1H NMR (100 MHz, $CDCl_3$, 20 °C): δ 1.72, 1.83, 2.00, 2.19, 2.40, 2.84, 5.60, 5.69, 5.90. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ 14.5, 15.6, 76.8, 27.3, 28.3, 29.1, 30.0, 30.1, 31.4, 32.2, 35.1, 42.9, 45.4, 49.8, 117.6, 129.3, 132.7, 133.9, 139.8, 141.3, 145.0, 155.2.

(b) Diene 6b: bp 91 °C (1 mmHg); yield 12.73 g (78%). Gas chromatography (retention time, min): 9.76, 9.80, 10.14, $C_{12}H_{18}$, *m/e* 162 (M^+), 6:3:1. MS: *m/e* 162 (M^+), 147, 134, 119, 104, 91 (M_b), 79, 65, 51, 41; second isomer *m/e* 162 (M^+), 147, 134, 119, 104, 91 (M_b), 79, 65, 51, 41, 27; third isomer *m/e* 162 (M^+), 147, 134 (M_b), 119, 104, 91, 79, 65, 51, 41, 27.

4. Synthesis of Lithium and Potassium Salts of 6a,b. (a) Lithium Salts 7 of Dienes 6. General Procedure. A 0.1-mol amount of a mixture of the isomeric dienes was dissolved in 100 mL of *n*-hexane in a Schlenk tube. The solution was cooled to −10 °C. A solution of 69 mL of 1.6 M *n*-butyllithium (for **7a**) in *n*-hexane was transferred into the Schlenk tube *via* cannula over 30 min. The initial colorless liquid became turbid. A white, fine solid separated. After 3 h of stirring at room temperature, the mixture was refluxed for 1 h, during which time the solid formed coarse grains. The solid was filtered from the solution on a glass frit. It was thoroughly washed three times with 30 mL of *n*-hexane and finally dried *in vacuo*.

7a: yield 11.96 g (79%). Anal. Calcd for $C_{11}H_{15}Li$: C, 85.70; H, 9.74; Li, 4.88. Found: C, 83.86; H, 9.52; Li, 4.70. IR (Nujol, cm^{-1}): $\tilde{\nu}$ 1305 (sh) w, 1280 w, 1252 w, 1158 w, 1122 w, 1083 w, 1068 w, 971 (br) w, 953, 810 s, 723 m, 658 m, 597 w, 490 (br) m, 468 (br) m.

(b) Potassium Salt 8a of Diene 6a. In a glovebox, KH (0.80 g, 19.95 mmol) was placed in a two-necked 100-mL flask equipped with a reflux condenser, a magnetic stirbar, a gas inlet, and a pressure-equalizing 50-mL dropping funnel, the last item being charged with diene **6a** (2.87 g, 20.0 mmol). The reaction apparatus was removed from the glovebox, and both KH and the cyclopentadiene were mixed with 30 mL of tetrahydrofuran by means of a syringe. The suspension of KH was cooled to 0 °C and treated dropwise over 30 min with the solution of the cyclopentadiene. Gas (H_2) began to be generated, and a yellowish color appeared. After the mixture was stirred for 30 min at 0 °C and, subsequently, for 2 h at room temperature, the gas evolution stopped. The THF was removed from the filtered yellow solution under reduced pressure to afford an almost off-white powder. This solid was washed with *n*-hexane and dried under high vacuum (10^{-3} mbar) for 4 h. The product **8a** (yield 2.3 g, 65%; mp 245 °C) immediately turns drak brown upon exposure in air. Anal. Calcd for $C_{11}H_{15}K$: C, 70.90; H, 8.11. Found: C, 70.0; H, 7.89. IR (Nujol, cm^{-1}): $\tilde{\nu}$ 3050 vs, 1506 m, 1441 vs, 1358 s, 1346 s, 1318 m, 1299 s, 1272 m, 1240 s, 1209 m, 1167 w, 1130 w, 1114 m, 1086 m, 1065 w, 1018 w, 969 m, 951 m, 945 (sh) m, 919 w, 878 w, 862 w, 847 m, 819 m, 793 m, 734 vs, 693 (sh) m, 630 vs, 597 w, 572 w, 491 w, 394 m, 345 w, 285 s, 220 vs. ^1H NMR (400 MHz, THF-d_8, 20 °C): δ 1.46 (m, 4H), 1.71 (m, 2H), 1.96 (s, 3H), 2.45 (m, 4H), 4.99 (s, 2H).

5. Zirconium Complex 9a. A 466-mg (2-mmol) amount of freshly sublimed $ZrCl_4$ was dissolved in 30 mL of 1.2-dimethoxyethane (dme), and the solution was then cooled to −10 °C. After 20 min of stirring, all solid materials disappeared, and the solution was further cooled to −40 °C. A suspension of 612 mg (4 mmol) of **7a** in cold DME (−40 °C) was added to the solution *via* a cannula. The solution was warmed to room temperature over 2 h and stirred overnight. Then the solution was refluxed for a period of 3 h, during which time a precipitate of lithium chloride appeared. The supernatant solution was decanted, and the solvent was completely stripped off. A 30-mL portion of methylene chloride and, after 10 min of stirring, 10 mL of concentrated HCl were added. After 20 min, the organic phase was separated, dried over sodium sulfate, and then filtered. Upon removal of the solvent a yellow, "semicrystalline" mass was obtained and recrystallized from a hot mixture of methylene chloride (14 mL) and benzene (6 mL). Short white needles was obtained by slow cooling to room temperature: mp 236 °C; yield 560 mg (63%). Anal. Calcd for $C_{22}H_{30}Cl_2Zr$: C, 57.90; H, 6.6; Cl, 15.30; Zr, 20.0. Found: C, 57.08; H, 6.54; Cl, 15.63; Zr, 19.75. IR (KBr, cm^{-1}): $\tilde{\nu}$ 3097 s, 2905 vs, 2851 s, 1439 s, 1379 w, 1337 w, 1313 w, 1277 w, 1175 w, 1121 m, 1091 w, 1031 w, 959 w, 917 w, 875 s, 839 w, 833 w, 755 m. MS (EI): *m/e* 461 (2.45%), 460 (10.93), 459 (6.03), 458 (23.72), 457 (12.84), 456 (35.51), 455 (15.10), 454 (33.18), 418 (M_b), 405, 382, 307, 271, 269, 242, 202, 188, 147, 117, 105, 91, 77, 67. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.21, 1.52, 1.80, 1.92, 2.08 (m, 6H), 2.56 (t, 4H), 5.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C [DEPT]): δ 15.6 [(+) CH_3], 28.7, 30.7, 32.2 [(−) CH_2], 117.9 [(+) CH], 121.9 [(0) C–CH_2], 133.14 [(0) C–CH_3].

6. Neodymium Complex 10a. In a glovebox, solid **7a** (0.67 g, 4.35 mmol) and $NdCl_3$ (0.55 g, 2.19 mmol) were added together in a 100-mL flask. On a high-vacuum line 30 mL of THF was vacuum-transferred into the flask. The suspension was slowly warmed to room temperature with stirring under an argon atmosphere. Reflux of the colorless mixture for 40 h resulted in a pale blue suspension. After the solvent was removed *in vacuo*, the resulting solid was dried under high vacuum for 4 h. Sublimation of the residue at 270 °C at 10^{-3} mmHg afforded blue crystals of the desired product: yield 0.23 g (22%). Anal. Calcd for $C_{44}H_{60}Cl_2Nd_2$: C, 55.73; H, 6.38. Found: C, 56.48; H, 7.29. MS (EI): *m/e* 942 (M^+, 0.6%), 795 ($[M - H^7Cp^2CH_3]^+$, 7.6), 471 ($M/2^+$, 2.8), 436 ($M/2 - Cl^+$, 100), 324 ($[M/2 - H^7Cp^2CH_3]^+$, 16.8), 289 ($[M/2 - H^7Cp^2CH_3 - Cl]^+$, 3.0), 105 ($C_8H_9^+$, 50.0).

7. **Neodymium Complex 10b.** In a glovebox, **7b** (1.45 g, 8.62 mmol) and $NdCl_3$ (1.21 g, 4.83 mmol) were added together in a 100-mL flask. On a high-vacuum line 50 mL of THF was condensed onto the solids. Warming to room temperature gave rise to a greenish color. After it was stirred at room temperature for another 2 h, the suspension was refluxed for 16 h, which procedure presumably enhances the reaction by converting oligomeric $NdCl_3$ to a more soluble form. The color changed to blue-violet. Upon cooling, the solvent was removed under reduced pressure (1 mmHg) and the resulting blue powder was dried in vacuo for another 2 h. The residue was transferred to a sublimation tube in the glovebox and the tube attached to a high-vacuum line. Sublimation started at ca. 280–290 °C at 10^{-3} mmHg. Blue transparent crystals of **10b** were formed on hot glass walls, whereas on the cooled sublimation finger a small amount of green homoleptic **11b** was sublimed (mass spectra [*m/e* 625]!). Separation of the two complexes proved easy: extraction of the mixture with *n*-hexane resulted in a green solution of the homoleptic complex, while **10b** remained as a blue powder (yield 2.05 g, 85%). Anal. Calcd for $C_{48}H_{68}Cl_2Nd_2$: C, 57.40; H, 6.82; Cl, 7.1. Found: C, 57.45; H, 6.96; Cl, 7.6 (6.8). IR (Nujol, cm^{-1}): $\tilde{\nu}$ 3065 s, 3055 s, 1313 m, 1279 m, 1248 m, 1222 w, 1175 w, 1160 m, 1137 m, 1115 w, 1082 w, 1065 w, 1046 w, 1032 w, 980 w, 965 w, 951 w, 885 w, 863 w, 839 w, 811 vs, 775 m, 759 m, 687 w, 633 m, 590 w, 516 w, 414 w, 315 m. MS (EI): *m/e* 998 (M^+, 0.9%), 837 ($[M - {}^{8}Cp^{2}CH_3]^+$, 11.1), 499 ($M/2^+$, 0.7), 464 ($[M/2 - Cl]^+$, 97.1), 338 ($[M/2 - {}^{8}Cp^{2}CH_3]^+$, 4.8), 303 ($[M/2 - {}^{8}Cp^{2}CH_3 - Cl]^+$, 1.5), 105 ($C_8H_9^+$, 8.3).

8. **Neodymium Complex 11a.** In a glovebox, **8a** (1.85 g, 9.93 mmol) and $NdCl_3$ (0.83 g, 3.31 mmol) were added together in a 100-mL flask. The flask was attached to a high-vacuum line, 40 mL of THF was vacuum-transferred into the flask, and the resulting mixture was warmed to room temperature with stirring under an argon atmosphere. The brownish suspension was stirred for 40 h, during which time a voluminous white precipitate appeared together with a brown-violet solution. The solvent was removed *in vacuo* (1 mmHg), and the resulting green residue was further dried under high vacuum (10^{-3} mmHg) for about 2 h. In a glovebox, the residue was loaded into a sublimation tube equipped with a Teflon valve. The tube was removed from the glovebox, attached to a high-vacuum line, placed under a dynamic vacuum, and slowly heated. Green transparent crystals of $Nd({}^{7}Cp^{2}CH_3)_3$ sublimed at ca. 210 °C at 10^{-3} mmHg (yield 1.78 g, 92%). Anal. Calcd for $C_{33}H_{45}Nd$: C, 67.64; H, 7.74. Found: C, 67.33; H, 7.78. IR (Nujol, cm^{-1}): $\tilde{\nu}$ 3063 s, 1456 vs, 1447 vs, 1366 s, 1340 m, 1309 m, 1298 sh m, 1277 s, 1251 m, 1238 m, 1221 m, 1204 m, 1172 m, 1160 m, 1123 m, 1040 sh m, 1083 m, 1026 m, 964 m, 955 s, 884 m, 848 s, 828 s, 814 vs, 799 s, 782 s, 773 m, 753 m, 688 w, 668 w, 617 s, 590 w, 580 w, 570, 507 w, 488 w, 442 w, 425 m, 390 w, 343 w, 315 sh m, 297 vs, 235 s, 215 s. MS (EI, relative intensity , relative to ^{142}Nd): *m/e* 583 (M^+, 5.9%), 436 ($[M - H^{7}Cp^{2}CH_3]^+$, 100), 289 ($[M - 2H^{7}Cp^{2}CH_3]^+$, 11.7), 105 ($C_8H_9^+$, 44.7).

X-ray Crystallography. The crystals used for structure determinations were sealed in a Lindemann capillary prior to data collection. Reflection data were collected on an Enraf-Nonius CAD4 diffractometer. Details of data collection and refinement are given in Table V. The structures were solved and refined using the program system STRUX-III;[34] this includes SHELX86[35] and SHELX76,[36] with the plotting programs ORTEP II[37] and SCHAKAL.[38] Calculations were carried out on a Microvax 3100 computer. Scattering factors were taken from ref 39. Positions of the metal and chlorine atoms (**9a**) were obtained from the Patterson map, and the remaining atomic positions were determined using difference Fourier syntheses.[35,36] After least-squares refinement of the non-hydrogen atoms,[36] all hydrogen atom positions could be determined from the difference Fourier. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were refined, while their isotropic temperature factors were fixed (free for **11a**) at values calculated from their parent carbon atoms ($1.25U(C_{ring})$ and $1.50U(C_{methyl})$).

Table V. Crystallographic Data for Diffraction Studies of 9a and 11a

	9a (Zr)	**11a** (Nd)
empirical formula	$C_{22}H_{30}Cl_2Zr$	$C_{33}H_{45}Nd$
mol wt	456.6	586.0
color	colorless	blue
cryst size, mm	0.80 × 0.25 × 0.25	0.45 × 0.40 × 0.38
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
temp °C	23	–30
a, Å	23.65(2)	8.585(1)
b, Å	6.6906(5)	28.237(1)
c, Å	15.78(1)	11.885(1)
β, deg	125.44(3)	107.66(1)
V, $Å^3$	2038	2745
Z	4	4
D(calcd), g cm^{-3}	1.49	1.42
λ(Mo K*α* radiation) Å	0.710 73	0.710 73
μ, cm^{-1}	8.0	19.2
F(000)	944	1212
monochromator	graphite, incident beam	
scan type	$\omega/2\theta$	ω
scan time, s	max 90	max 45
scan width, deg	1.50 + 0.20 tan *θ* 25% to each side of the rfln to determine the bkgd	0.7 + 0.30 tan *θ*
θ_{max}, deg	25	25
cor	Lorentz and polarizn and extinction	emp abs cor 0.95–1.00
no. of data collcd	3276 ($+h,+k,\pm l$)	5176 ($\pm h,+k,+l$)
no. of unique data	2856	4605
no. of unique obsd data	2853 ($I > 0.01\sigma(I)$)	4605 ($I > 0.01\sigma(I)$)
no. of params refined	160	353
data to param ratio	17.38	13.05
R^a	0.028	0.019
R_w	0.030	0.016
weighting scheme	$w = 1/\sigma^2(F_o)$	Tukey/Prince
shift/error	<0.0001	<0.00001
largest diff peak, e $Å^{-3}$	+0.55 from Zr atom	+0.34 from C22
largest diff hole, e $Å^{-3}$		–0.32

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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Supplementary Material Available: Tables of complete bond lengths and angles, anisotropic thermal parameters for the non-hydrogen atoms, and hydrogen atom parameters for **9a** and **11a** (10 pages). Ordering information is given on any current masthead page.

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