structure in the solid as shown in Figure 4. The Au(1) atom is 3.404 (2) Å from Au(2). However, it is 4.658 Å from the Hg atom of the neighboring molecule. The preference of the Au^{III} center for a Au^{I} rather than a Hg^{II} center is apparent here. The Hg–Au(2)–Au(1) axis is nonlinear by about 16°.

The formation of mixed-valence compounds by oxidative addition of halogen to Au^{I} compounds has been observed previously.[2,3c,13] In some dinuclear gold complexes it has been established[13c–e] that mixed-valence Au^{I}–Au^{III} species are formed by the disproportionation of Au^{II}–Au^{II} intermediates. The mechanism of the formation of **3** is not yet understood.

We have found that the PF_6^- and $AuCl_4^-$ anions in **3** and **3a**, respectively, can be readily replaced by other dianionic metal complexes such as $Pt(i\text{-}MNT)_2^{2-}$ (i-MNT = 1,1-dicyano-2,2-dithioethene) to form new heteronuclear one-dimensional compounds. The structural characterizations of these new interesting materials are under way.

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Supplementary Material Available: Tables of anisotropic thermal parameters and positional and thermal parameters of hydrogen atoms for **2** and **3** (4 pages); listings of structure factors for **2** and **3** (42 pages). Ordering information is given on any current masthead page.

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Structural Studies on Cyclopentadienyl Compounds of Trivalent Cerium: Tetrameric $(MeC_5H_4)_3Ce$ and Monomeric $(Me_3SiC_5H_4)_3Ce$ and $[(Me_3Si)_2C_5H_3]_3Ce$ and Their Coordination Chemistry

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The coordinated tetrahydrofuran in $(MeC_5H_4)_3Ce(THF)$ can be removed by Me_3Al in a Lewis acid–base reaction or by the "toluene-reflux method" to give base-free $(MeC_5H_4)_3Ce$ which is a monomer in the gas phase though a tetramer in the solid state: monoclinic, $P2_1/a$, with a = 12.497 (5) Å, b = 26.002 (8) Å, c = 9.664 (3) Å, β = 97.33 (3)°; R = 0.041 for 2117 data, $F^2 > 2\sigma(F^2)$. The structure is made up of a cyclic tetramer in which two MeC_5H_4 rings are η^5-bonded to each cerium atom and one MeC_5H_4 ring is bridging two cerium atoms such that the MeC_5H_4 ring is η^5-bonded to one cerium and η^1-bonded to the other. With larger cyclopentadienyl groups, the binary metallocenes $(\eta^5\text{-}Me_3SiC_5H_4)_3Ce$, $(\eta^5\text{-}Me_3CC_5H_4)_3Ce$, and $[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3Ce$ are monomeric in the gas phase and the solid state. The structure of the latter is based upon a trigonal-planar geometry; the crystals are monoclinic, $I2/c$, with a = 22.752 (5) Å, b = 11.386 (3) Å, c = 17.431 (4) Å, β = 105.70 (3)°, R = 0.046 for 2519 data, and $F^2 > 3\sigma(F^2)$. All of the binary metallocenes form 1:1 complexes with isocyanides and organocyanides, and the crystal structure of two of them have been determined; $(MeC_5H_4)_3Ce(CNCMe_3)$ is monoclinic, $P2_1/c$, with a = 14.259 (3) Å, b = 9.382 (2) Å, c = 17.652 (3) Å, β = 106.16 (3)°, R = 0.050 for 1501 data, and $F^2 > 3\sigma(F^2)$, and $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$ is also monoclinic, $P2_1/c$, with a = 11.462 (3) Å, b = 17.146 (4) Å, c = 26.826 (6) Å, β = 112.93 (3)°, R = 0.047 for 2437 data, and $F^2 > 3\sigma(F^2)$.

The solid-state structures of the trivalent lanthanide (including scandium and its congeners) metallocenes, $(C_5H_5)_3M$, are unusual as only in a few cases are their crystal structures as expected, i.e., monomeric with each C_5H_5 group η^5-bonded to the metal so that the coordination number is nine (defining a C_5H_5 group as occupying three coordination sites) and the geometry about the metal atom as trigonal planar (defining the centroid of a C_5H_5 group as occupying one coordination site). The structures of the light lanthanide (praseodymium) and lanthanium tris(cyclopentadienyl) compounds are polymers with two terminal C_5H_5 groups η^5-bonded to the metal while a third C_5H_5 group is bridging two metal centers in a η^5 and a η^1 or η^2 fashion so as to form a zigzag polymer.[1a–c] The bridging cyclopentadienyl group allows the metal atom to increase its coordination number from nine in the monomer to either ten or eleven in the polymer. The structure of the middle lanthanide, samarium, appears to have a similar structure though the low quality of the data prevents any detailed conclusion.[1d] The heavier lanthanides (Er, Tm)

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are structurally similar with bridging C_5H_5 groups that are η^5 to one metal and η^1 to the adjacent metal in the polymeric zigzag chain with the M to η^1-C distance increasing with decreasing metal radius.[1e] At ytterbium, $(C_5H_5)_3Yb$[1f] and $(MeC_5H_4)_3Yb$[1j] are monomeric with the expected structure, i.e., an idealized D_{3h} symmetry metallocene with each C_5H_5 group being bonded in an η^5 fashion. Another type of polymeric structure is found in the tris(cyclopentadienyl) compound of the heaviest and smallest lanthanide, lutetium. The structure consists of two η^5-bonded, terminal C_5H_5 groups and a bridging C_5H_5 group that is η^1-bonded to each metal center so that the coordination number is eight.[1g] The geometry of the bridging C_5H_5 group in polymeric Cp_3Lu is similar to that found in dimeric Cp_3Sc.[1h] The change in structure may be rationalized on the basis of steric effects; viz., the largest metal centers prefer to have the highest coordination numbers, consistent with tolerable intramolecular repulsions. As the size of the metal atom contracts, the coordination number decreases since intramolecular ligand–ligand repulsions increase. This rationalization requires that the solid-state structure of the trivalent metallocenes will depend upon the size of the substituents on the cyclopentadienyl ring. Only a few structures of substituted, trivalent, binary metallocenes have been published; tris(indenyl) samarium[1i] is monomeric with an idealized trigonal-planar geometry whereas $(C_5H_5)_3Sm$ in polymeric, and, perhaps most interesting of all, $(MeC_5H_4)_3Nd$ is tetrameric with one bridging η^5,η^1-MeC_5H_4 per Nd.[2] There is literature precedence for a correlation between steric bulk of a substituted cyclopentadienyl ring and molecular geometry since C_5H_5Tl,[3a] C_5H_5In,[3a,b] MeC_5H_4In,[3b] $(Me_3SiC_5H_4)Tl$,[3c] and Me_5C_5Tl[3d] are zigzag polymers whereas Me_5C_5In is a hexamer with the metal atom at the corners of an octahedron,[3e] $[(Me_3Si)_2C_5H_3]Tl$ is also a hexamer but with the metal atoms at the vertices of a hexagon,[3c] and $[(PhCH_2)_5C_5]Tl$ is a monomer.[3f,g] This bewildering set of structures for a large, monovalent metal atom suggests that a study of the solid-state structures of the trivalent metallocenes with different sized substituents on the cyclopentadienyl groups would be rewarding.

In this paper we describe our initial efforts at synthesis and solid-state structure of substituted metallocenes of the largest and lightest lanthanide, cerium(III).

Synthetic Studies. The parent, base-free compound $(C_5H_5)_3Ce$ was prepared from $CeCl_3$ and NaCp in THF followed by sublimation at 230 °C in vacuum.[4a] The orange-yellow compound is insoluble in benzene which suggests that it has a polymeric constitution in the solid phase. Generally, MeC_5H_4 analogues of C_5H_5 metallocenes are more soluble in hydrocarbons,[4b] and this generalization proves to be true in this case. The orange-yellow, base-free complex $(MeC_5H_4)_3Ce$ may be obtained from $(MeC_5H_4)_3Ce(THF)$[5] by displacing the coordinated ether by using the "toluene reflux method"[6] or by Lewis acid–base competition reaction with Me_3Al (eq 1). The base-free compound is soluble in toluene and gives a monomeric molecular ion in the mass spectrum though it is tetrameric in the solid state with a structure related to that of $(MeC_5H_4)_3Nd$ (see below). The color of $(MeC_5H_4)_3Ce$ in toluene is a function of temperature; at −30 °C and below the solution is yellow, at room temperature green, and at 50 °C or higher blue. It is noteworthy that all of the 1:1 coordination compounds of $(MeC_5H_4)_3Ce$ are yellow[5] though the base-free compounds $(RC_5H_4)_3Ce$ where R = Me_3C or Me_3Si and $[(Me_3Si)_2C_5H_3]_3Ce$ are purple, blue, and blue, respectively (see below). The qualitative observation of the change in color of $(MeC_5H_4)_3Ce$ as a function of temperature suggests that at low temperature the molecule is associated into oligomers so that the molecule is at least ten-coordinate, and at high temperature mainly nine-coordinate monomeric species are present in solution. The ^1H NMR spectrum of $(MeC_5H_4)_3Ce$ in toluene is not particularly informative since at +29 °C the methyl and methine resonances are at δ −4.52, 13.0, and 10.6, respectively. On cooling all three resonances move upfield and broaden into the base line by ca. −30 °C and do not become resolved by −85 °C. Clearly, exchange processes are occurring in solution, but the spectrum is not informative about their nature.

$$(MeC_5H_4)_3Ce(THF) + Me_3Al \rightarrow (MeC_5H_4)_3Ce + Me_3Al(THF) \quad (1)$$

Reaction of $CeCl_3$ and $KMe_3SiC_5H_4$ in tetrahydrofuran gives royal blue $(Me_3SiC_5H_4)_3Ce$ which is isolated base-free upon crystallization from hexane. The base-free compound sublimes at 60 °C at 10^{-3} mm, shows a monomeric molecular ion in the mass spectrum, and is isostructural with $(Me_3SiC_5H_4)_3U$ as shown by X-ray powder diffraction studies. The uranium compound is monomeric with idealized D_{3h} symmetry.[7] The methyl and cyclopentadienyl ring resonances of $(Me_3SiC_5H_4)_3Ce$ follow Curie law dependence in the ^1H NMR spectrum to −80 °C. The purple, base-free compound $(Me_3CC_5H_4)_3Ce$ may be prepared similarly; its physical properties are nearly identical with those of its Me_3Si analogue. The size of the substituent on the cyclopentadienyl ring rather than its electronic effect plays the dominant role in determining the degree of association in these metallocenes.

The solid-state magnetic susceptibility of $(Me_3CC_5H_4)_3Ce$ was studied as a function of temperature. The plot of χ_M^{-1} as a function of T is linear from 5 to 30 K with $\mu = 2.14 \pm 0.02\ \mu_B$ and $\theta = -2.96$ and 50–280 K with $\mu = 2.28 \pm 0.01\ \mu_B$ and $\theta = -6.71$ K at a field strength of 5 kG. The value of the magnetic moment at a field strength of 40 kG is not significantly different from the value at 5 kG. The high-temperature magnetic moment is close to that found in several simple inorganic compounds at 27 °C, i.e., $NH_4Ce(SO_4)_2\cdot 4H_2O$ μ is 2.25 μ_B and CeF_3 μ is 2.28 μ_B, though smaller than that found for polymeric $(C_5H_5)_3Ce$ of 2.46 μ_B at −196 and 22 °C[4a] or predicted for the free ion of 2.54 μ_B by Van Vleck.[8a] Cerium(III) is a f^1 ion, and the free ion term symbol is ^2F. Spin–orbit coupling splits this state into two levels with

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$J = {}^5/_2$ (ground state) and $J = {}^7/_2$, the separation of which is ca. 2200 cm^{-1} in the free ion so at 20 °C the $J = {}^7/_2$ state is not populated (kT = 205 cm^{-1} at 20 °C). In the presence of a trigonal crystal field the degeneracy of the $J = {}^5/_2$ state is removed, and the separation between the three crystal field states is small relative to the spin–orbit coupling and kT. At 20 °C each crystal field state is equally populated and a moment of 2.54 μ_B is expected at room temperature for the free ion. The plot of χ_M^{-1} vs T for $(Me_3CC_5H_4)_3Ce$ is linear from 5 to 30 and 50 to 280 K. In the higher temperature regime, all of the crystal field states are populated; as the temperature is lowered, the crystal field states become unevenly populated in the temperature range of 30–50 K, and at 5–30 K the lowest crystal field state is mainly populated.

We have been unable to extend the salt elimination synthesis method to the bulkier metallocene $[(Me_3Si)_2C_5H_3]_3Ce$ since reaction of $[(Me_3Si)_2C_5H_3]_2CeCl$,[9] with various $(Me_3Si)_2C_5H_3^-$ reagents did not yield *pure* $[(Me_3Si)_2C_5H_3]_3Ce$. We have been able to isolate pure $[(Me_3Si)_2C_5H_3]_3Ce$ by using the Brønsted acid–base reaction shown in eq 2. Though the pK_a of the diene is unknown, it must be less than 26, the pK_a of $(Me_3Si)_2NH$ in tetrahydrofuran.[10] The blue, base-free compound is soluble in hexane, gives a monomeric molecular ion in the mass spectrum, and is monomeric in the solid state (see below). The variable-temperature ^{1}H NMR spectrum shows that the Me$_3$Si resonances are equivalent at −80 °C and no broader at −80 °C than at +30 °C, indicating free rotation of the metallocene rings about their pseudo C_5 axis or that the rings are not rotating but are equivalent by symmetry. Further, the ring resonances obey Curie law. Comparison of the physical properties of $(Me_3SiC_5H_4)_3Ce$ and $[(Me_3Si)_2C_5H_3]_3Ce$ is somewhat surprising since the former is more soluble in aliphatic hydrocarbons and has a lower melting point, 69 °C vs 210 °C, than the latter.

$$Ce[N(SiMe_3)_2]_3 + 3(Me_3Si)_2C_5H_4 \rightarrow [(Me_3Si)_2C_5H_3]_3Ce + 3(Me_3Si)_2NH \quad (2)$$

All of these metallocenes form 1:1 coordination compounds with the sterically small alkyl isocyanide and alkyl cyanide ligands; see Experimental Section for details. We have been unable to isolate 1:2 complexes with these ligands though variable-temperature ^{1}H NMR studies show that the resonances in $(MeC_5H_4)_3Ce(L)$ (L = EtCN or EtNC) do not follow Curie law (the chemical shifts are not a linear function of T^{-1}) indicative of equilibria in solution, perhaps between base-free, 1:1 and 1:2 complexes.[11] In contrast, $(MeC_5H_4)_3Ce(CNCMe_3)$ and all of the other isocyanide and cyanide complexes prepared in this study do follow the Curie law from −80 to +80 °C. Although we have not been able to isolate 1:2 complexes, several $(C_5H_5)_3M(L)_2$ complexes, where M is La or Ce and L is MeCN or EtCN, have been isolated. X-ray crystallographic studies show the molecules to have idealized D_{3h} symmetry.[12] These results are readily understandable in terms of steric congestion about the metal atom as a function of the size of the substituents on the cyclopentadienyl ring. Quantitative equilibrium quotient studies will be reported later; however, in the present context, the equilibrium quotient at 30 °C for the reaction shown in eq 3 is 54.

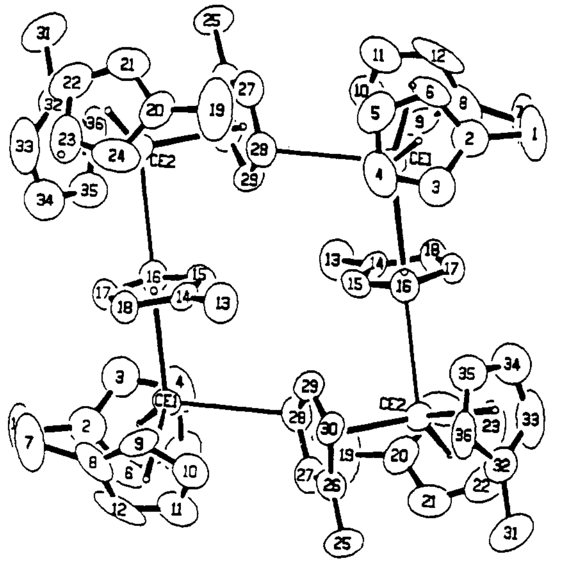

Figure 1. ORTEP diagram of $(\eta^5\text{-}MeC_5H_4)_8(\mu\text{-}\eta^5,\eta^1\text{-}MeC_5H_4)_4Ce_4$ [(50% probability ellipsoids; Cp(1) = ring centroid of C(2–6), Cp(2) = ring centroid of C(8–12), Cp(3) = ring centroid of C(14–18), Cp(4) = ring centroid of C(20–24), Cp(5) = ring centroid of C(26–30), Cp(6) = ring centroid of C(32–36)]: Ce(1)C(2–6,8–12) and Ce(2)C(20–24,32–36) = 2.80 (3) Å (av); Ce–Cp(1,2,4,6) = 2.54 Å; Ce(1)–C(14–18) and Ce(2)–C(26–30) = 2.88 (4) Å (av); Ce–Cp(3,5) = 2.62 Å, Cp(1)–Ce(1)–Cp(2) and Cp(4)–Ce(2)–Cp(6) = 117°; Cp(1)–Ce(1)–Cp(2), Cp(2)–Ce(1)–Cp(3), Cp(4)–Ce(2)–Cp(5), and Cp(6)–Ce(2)–Cp(5) = 116° (av); Ce(1)–C(28) = 3.09 (1) Å; Ce(2)–C(16) = 2.97 (1) Å; Cp(1)–Ce–C(28), Cp(2)–Ce–C(28), Cp(4)–Ce–C(16), and Cp(6)–Ce–C(16) = 100° (av).

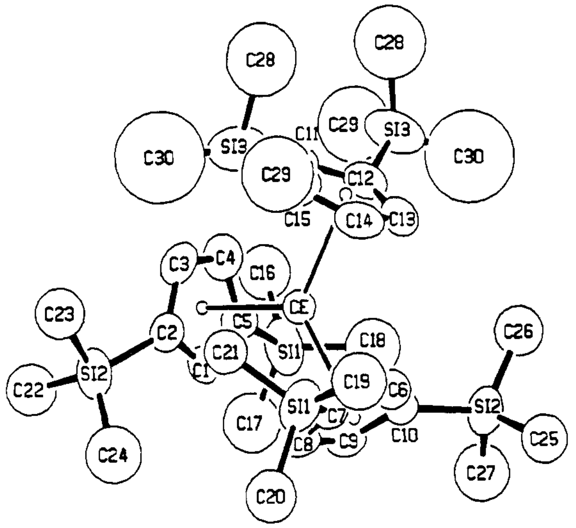

Figure 2. ORTEP drawing of $[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3Ce$ (50% probability ellipsoids): Ce–C = 2.83 (4) Å (av), Ce–ring centroid = 2.57 Å (av), and ring centroid–Ce–ring centroid = 120° (av).

$$(Me_3SiC_5H_4)_3Ce + [(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3) \rightleftharpoons (Me_3SiC_5H_4)_3Ce(CNCMe_3) + [(Me_3Si)_2C_5H_3]_3Ce \quad (3)$$

Solid-State Studies. ORTEP diagrams of $(MeC_5H_4)_3Ce$, $[(Me_3Si)_2C_5H_3]_3Ce$, $(MeC_5H_4)_3Ce(CNCMe_3)$, and $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$ are shown in Figures 1–4, respectively, along with important bond distances and angles; additional bond distances and angles are in the supplementary material. Crystal data are in Table I, and positional parameters are in Tables II–V.

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Table I. Crystallographic Summary and Data Processing

	$(MeC_5H_4)_3Ce$	$[(Me_3Si)_2C_5H_3]_3Ce$	$(MeC_5H_4)_3Ce(CNCMe_3)$	$[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$
a, Å	12.497 (5)	22.752 (5)	14.250 (3)	11.462 (3)
b, Å	26.002 (8)	11.386 (3)	9.382 (2)	17.146 (4)
c, Å	9.664 (3)	17.431 (4)	17.652 (3)	26.826 (6)
β, deg	97.33 (3)	105.70 (2)	106.16 (2)	112.93 (3)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$I2/c$	$P2_1/c$	$P2_1/c$
V, Å^3	3115	4347.1	2266.7	4855.5
d(calcd), g/cm^3	1.610	1.174	1.350	1.165
Z	2	4	4	4
temp, °C	23.0	23.0	23.0	23.0
empirical formula	$C_{72}H_{84}Ce_4$	$C_{33}H_{63}Si_6Ce$	$C_{23}H_{30}NCe$	$C_{38}H_{72}NSi_6Ce$
fw	1509.95	788.51	460.62	851.64
X-ray	Mo Kα	Mo Kα	Cu Kα	Mo Kα
wavelength (K$\bar{\alpha}$), Å	0.710 73	0.710 73	1.541 80	0.710 73
cryst size, mm	0.11 × 0.13 × 0.19	0.15 × 0.20 × 0.35	0.10 × 0.17 × 0.22	0.16 × 0.19 × 0.21
abs coeff, cm^{-1}	29.6	12.4	159.3	11.2
abs corr rnge	1.35–1.47	1.1–1.4	3.1–9.6	
decay corr rnge	0.98–1.02	0.97–1.03	0.92–1.09	0.97–1.02
2θ limits, deg	4–50	4–50	4–120	12–45
scan width, deg (2θ)	$1.4 + 0.693 \tan \theta$	$1.5 + 0.693 \tan \theta$	$1.5 + 0.285 \tan \theta$	$1.5 + 0.693 \tan \theta$
no. of stds	3	3	3	3
no. of rflctns btwn stds	250	250	250	250
stds variatns, %	0.7, 1.9, 1.3	1.1, 1.2, 1.3	5.6, 4.6, 4.7	2.02, 1.36, 1.08
no. of scan data	8184	6949	6744	12793
no. of unique reflctns	4101	3853	3376	6398
no. of nonzero wtd data	2117 [$F^2 > 2\sigma(F^2)$]	2519 [$F^2 > 3\sigma(F^2)$]	1501 [$F^2 > 3\sigma(F_2)$]	2437 [$F^2 > 3\sigma(F_2)$]
P^b	0.03	0.05	0.06	0.05
no. of parameters	343	223	171	415
R(nonzero wtd dat)^c	0.041	0.046	0.050	0.047
$R_w{}^d$	0.034	0.058	0.061	0.050
R (all data)	0.120	0.084	0.118	0.162
goodness of fit^e	1.00	1.54	1.37	1.15
max shift/esd	0.01	0.02	0.01	0.0269
max/min residual, e/Å^3	1.2, −1.5	0.4, −0.3	1.0, −0.7	1.43, −1.40

[a] Unit-cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 23 reflections ($21 < 2\theta < 35$), 24 reflections ($20 < 2\theta < 35$), 25 reflections ($25 < 2\theta < 66$), and 19 reflections ($16 < 2\theta < 34$), respectively. [b] In the least squares, the assigned weights $w = 4F^2[\sigma^2(F^2) + (pF^2)^2]^{-1}$. [c] $R = \sum[|F_o| - |F_c|)/\sum[|F_o|]$. [d] $R_w = \{\sum(|F_o| - |F_c|]^2/\sum(wF_o{}^2)\}^{1/2}$. [e] σ_1 = error in observation of unit weight = $\{\sum(w[|F_o| - |F_c|]^2)/(NO - NV)\}^{1/2}$, where NO is the number of observations and NV is the number of variables.

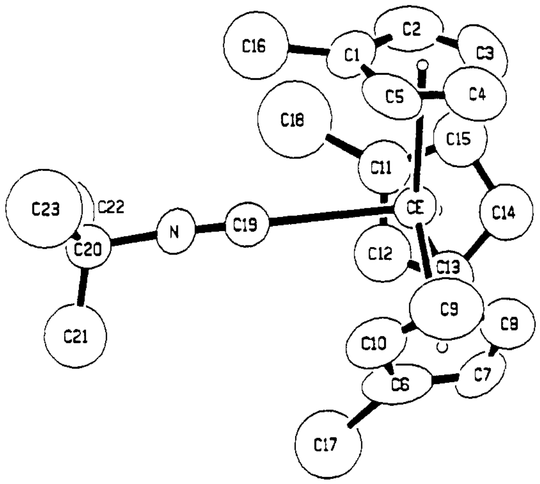

Figure 3. ORTEP drawing of (η^5-$MeC_5H_4)_3Ce(CNCMe_3)$ (50% probability ellipsoids): Ce–C(Cp) = 2.79 (3) Å, Ce–ring centroid = 2.55 Å (av) ring centroid–Ce–ring centroid = 119° (av), Ce–C(19) = 2.71 (2) Å, and ring centroid–Ce–C(19) = 97° (av).

The most striking feature of the four structures is the similarity in bond parameters. The geometry of the three η^5-bonded cyclopentadienyl to cerium units are nearly trigonal planar in each case since the Cp–Ce–Cp angle, where Cp is used as an abbreviation for a ring centroid regardless of the substituent on the cyclopentadienyl group, varies from 117° to 120°, the Cp–Ce distance varies from 2.55 to 2.60 Å, and the cyclopentadienyl–ring carbon to cerium distance varies from 2.79 (3) to 2.87 (3) Å. The geometry of the monomer $[(Me_3Si)_2C_5H_3]_3Ce$ is trigonal planar with idealized D_{3h} symmetry similar to that found in $(Me_3SiC_5H_4)_3U$.[7] Upon coordination of an isocyanide to $[(Me_3Si)_2C_5H_3]_3Ce$ the geometry changes very slightly, the Cp–Ce–Cp angle changes from 120° to 119.5°, and the averaged Ce–C (ring) distance increases 0.04 (3) Å. The geometry of $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$ is the same as

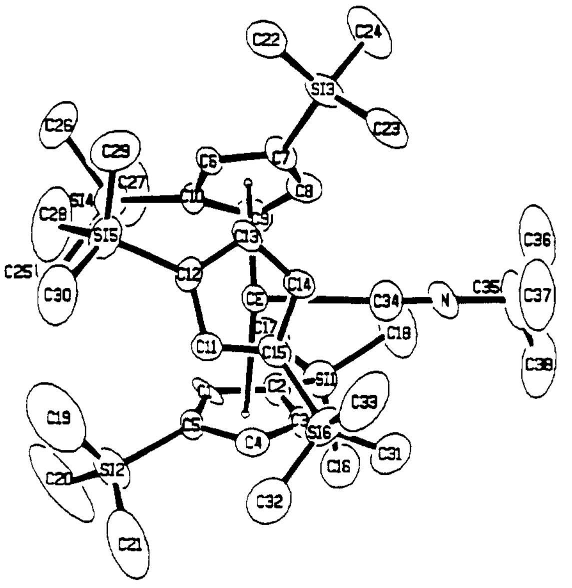

Figure 4. ORTEP drawing of $[\eta^5$-$(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$ (50% probability ellipsoids): Ce–C(Cp) = 2.87 (3) Å (av), Ce–ring centroid = 2.60 Å (av), ring centroid–Ce–ring centroid = 119.5° (av), Ce–C(34) = 2.70 (1) Å, and ring centroid–Ce–C(34) = 94° (av).

Table II. Positional and Thermal Parameters with Estimated Standard Deviations for $(MeC_5H_4)_3Ce$[a]

atom	x	y	z	B_{eq}, Å^2
Ce(1)	0.13433 (6)	0.12673 (3)	0.62232 (8)	3.13 (2)
Ce(2)	−0.27165 (6)	0.08491 (3)	0.25927 (8)	3.19 (2)
C(1)	0.2460 (15)	0.1660 (8)	0.9940 (19)	9.0 (8)
C(2)	0.1462 (13)	0.1476 (8)	0.9152 (18)	5.8 (6)
C(3)	0.1074 (15)	0.0983 (6)	0.8995 (15)	5.0 (6)
C(4)	0.0063 (14)	0.0959 (8)	0.8261 (16)	6.0 (6)
C(5)	−0.0222 (13)	0.1485 (8)	0.7986 (16)	5.5 (6)
C(6)	0.0650 (15)	0.1793 (6)	0.8552 (17)	5.1 (6)
C(7)	0.3924 (17)	0.2016 (8)	0.6745 (20)	10.6 (9)
C(8)	0.2838 (14)	0.2031 (7)	0.5885 (18)	5.2 (6)
C(9)	0.2631 (12)	0.1829 (5)	0.4580 (19)	4.4 (5)
C(10)	0.1570 (15)	0.1943 (6)	0.4031 (16)	5.3 (6)
C(11)	0.1153 (14)	0.2217 (7)	0.5018 (24)	6.3 (7)
C(12)	0.1902 (20)	0.2304 (6)	0.6154 (21)	7.2 (8)
C(13)	0.2291 (11)	0.0541 (6)	0.3039 (15)	5.4 (5)
C(14)	0.2345 (11)	0.0479 (5)	0.4621 (13)	3.5 (4)
C(15)	0.1616 (9)	0.0209 (5)	0.5360 (15)	3.4 (4)
C(16)	0.1999 (11)	0.0227 (5)	0.6801 (15)	4.1 (4)
C(17)	0.2952 (10)	0.0523 (5)	0.6973 (14)	3.8 (5)
C(18)	0.3146 (10)	0.0676 (5)	0.5612 (15)	3.6 (4)
C(19)	−0.3224 (15)	0.1094 (9)	0.6339 (22)	11.9 (10)
C(20)	−0.3792 (12)	0.1028 (8)	0.4951 (17)	5.0 (6)
C(21)	−0.4163 (15)	0.1390 (6)	0.3992 (22)	5.7 (6)
C(22)	−0.4801 (14)	0.1151 (9)	0.2891 (19)	6.3 (7)
C(23)	−0.4759 (14)	0.0624 (9)	0.3192 (23)	6.4 (7)
C(24)	−0.4169 (15)	0.0555 (7)	0.4431 (22)	6.0 (7)
C(25)	−0.1363 (12)	0.2176 (6)	0.2057 (16)	6.3 (6)
C(26)	−0.1152 (11)	0.1681 (5)	0.2828 (15)	4.1 (5)
C(27)	−0.1334 (11)	0.1562 (6)	0.4195 (15)	4.6 (5)
C(28)	−0.0904 (11)	0.1075 (6)	0.4561 (14)	4.5 (5)
C(29)	−0.0421 (9)	0.0898 (6)	0.3396 (17)	4.5 (5)
C(30)	−0.0577 (10)	0.1260 (6)	0.2330 (14)	4.2 (4)
C(31)	−0.4012 (15)	0.1709 (8)	−0.0263 (19)	9.9 (8)
C(32)	−0.3501 (14)	0.1179 (6)	−0.0072 (16)	5.1 (6)
C(33)	−0.4024 (13)	0.0702 (10)	0.0030 (17)	7.3 (8)
C(34)	−0.3296 (17)	0.0315 (7)	0.0047 (16)	6.0 (6)
C(35)	−0.2300 (15)	0.0547 (8)	−0.0063 (16)	5.9 (7)
C(36)	−0.2426 (13)	0.1075 (7)	−0.0162 (15)	4.9 (6)

[a] Anisotropic thermal parameters, $B_{eq} = \sum B_{ij} a_i^* \mathbf{a}_j a_i \cdot \mathbf{a}_j / 3$.

Table III. Positional and Thermal Parameters for $[(Me_3Si)_2C_5H_3]_3Ce$[a]

atom	x	y	z	B/B_{eq}, Å^2
Ce	0	0.15363 (6)	0.250	3.88 (2)[a]
Si(1)	−0.16325 (10)	0.27712 (28)	0.10783 (16)	6.87 (9)[a]
Si(2)	0.07888 (11)	0.30451 (25)	0.06659 (15)	6.23 (8)[a]
Si(3)	−0.12372 (15)	−0.14254 (28)	0.24956 (27)	9.6 (1)[a]
C(1)	−0.0360 (4)	0.2939 (14)	0.1091 (12)	3.7 (5)[a]
C(2)	0.0154 (6)	0.2314 (9)	0.1006 (9)	4.5 (5)[a]
C(3)	−0.0045 (5)	0.1137 (10)	0.0909 (9)	4.9 (5)[a]
C(4)	−0.0652 (5)	0.1086 (11)	0.0961 (9)	5.7 (5)[a]
C(5)	−0.0863 (5)	0.2215 (9)	0.1088 (8)	4.1 (5)[a]
C(6)	0.0377 (6)	0.2598 (21)	0.4054 (14)	5.1 (7)
C(7)	0.0763 (5)	0.3030 (12)	0.3609 (7)	4.2 (5)[a]
C(8)	0.0406 (4)	0.3766(11)	0.3012 (8)	4.7 (5)[a]
C(9)	−0.0193 (5)	0.3798 (11)	0.3099 (7)	4.7 (5)[a]
C(10)	−0.0214 (5)	0.3067 (12)	0.3744 (7)	4.0 (5)[a]
C(11)	−0.0029 (5)	−0.0944 (12)	0.2373 (12)	5.5 (6)[a]
C(12)	−0.0458 (6)	−0.0719 (14)	0.2806 (8)	5.9 (6)[a]
C(13)	−0.0107 (5)	−0.0298 (14)	0.3549 (8)	6.0 (6)[a]
C(14)	0.0511 (6)	−0.0301 (14)	0.3539 (8)	6.1 (6)[a]
C(15)	0.0580 (5)	−0.0710 (16)	0.2805 (8)	5.8 (6)[a]
C(16)	−0.2151 (9)	0.1685 (18)	0.0330 (13)	9.7 (7)
C(17)	−0.1806 (11)	0.4247 (14)	0.0629 (15)	11.6 (8)
C(18)	−0.1871 (11)	0.2591 (25)	0.2003 (11)	10.6 (8)
C(19)	0.1951 (11)	0.2075 (22)	0.4873 (10)	10.6 (8)
C(20)	0.1911 (9)	0.4356 (12)	0.3886 (14)	9.3 (6)
C(21)	0.1803 (8)	0.1993 (17)	0.3047 (9)	6.4 (4)
C(22)	0.0425 (11)	0.3629 (22)	−0.0371 (9)	8.5 (9)
C(23)	0.1377 (10)	0.1924 (19)	0.0630 (17)	8.4 (9)
C(24)	0.1148 (12)	0.4301 (17)	0.1292 (14)	10.6 (8)
C(25)	−0.0374 (10)	0.3225 (23)	0.5428 (8)	7.7 (8)
C(26)	−0.1270 (11)	0.1692 (17)	0.4270 (16)	8.2 (8)
C(27)	−0.1324 (10)	0.4293 (18)	0.3949 (16)	10.7 (8)
C(28)	0.1111 (10)	−0.3012 (19)	0.2579 (13)	17.7 (7)
C(29)	0.1809 (10)	−0.1267 (19)	0.3474 (14)	18.6 (7)
C(30)	0.1510 (14)	−0.113 (3)	0.1758 (19)	27.9 (13)

[a] The equivalent isotropic thermal parameter B_{eq} is derived from the anisotropic values as $B_{eq} = \sum B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j / 3$.

Table IV. Positional and Thermal Parameters for $(MeC_5H_4)_3Ce(CNCMe_3)$[a]

atom	x	y	z	B/B_{eq}, Å^2
Ce	0.24978 (5)	0.19706 (10)	0.33336 (5)	6.81 (3)*
N	0.2322 (9)	−0.0511 (17)	0.1586 (8)	8.2 (5)*
C(1)	0.0911 (21)	0.306 (5)	0.2110 (11)	10.0 (8)*
C(2)	0.1484 (25)	0.415 (6)	0.238 (3)	13.2 (13)*
C(3)	0.145 (3)	0.447 (3)	0.309 (4)	14.3 (15)*
C(4)	0.0843 (22)	0.352 (5)	0.3306 (20)	12.0 (12)*
C(5)	0.0485 (13)	0.2627 (25)	0.2691 (26)	11.0 (10)*
C(6)	0.2888 (20)	−0.066 (3)	0.4109 (19)	12.1 (11)*
C(7)	0.307 (3)	0.029 (4)	0.4712 (16)	13.7 (14)*
C(8)	0.223 (6)	0.095 (4)	0.4698 (23)	13.9 (17)*
C(9)	0.1511 (23)	0.030 (6)	0.417 (4)	14.5 (16)*
C(10)	0.1861 (23)	−0.064 (3)	0.3786 (13)	11.7 (10)*
C(11)	0.4077 (15)	0.293 (3)	0.2793 (13)	11.4 (5)
C(12)	0.4428 (18)	0.181 (3)	0.3246 (18)	13.1 (6)
C(13)	0.4515 (15)	0.2026 (28)	0.3863 (14)	11.2 (5)
C(14)	0.4225 (16)	0.3370 (26)	0.3989 (14)	11.9 (6)
C(15)	0.3944 (16)	0.395 (3)	0.3284 (15)	12.8 (6)
C(16)	0.0481 (28)	0.223 (4)	0.1341 (24)	17.8 (10)
C(17)	0.3581 (28)	−0.180 (4)	0.3892 (22)	18.0 (10)
C(18)	0.393 (4)	0.281 (6)	0.186 (3)	22.6 (15)
C(19)	0.2356 (11)	0.0189 (22)	0.2102 (10)	8.1 (6)*
C(20)	0.2309 (11)	−0.1488 (19)	0.0990 (11)	9.1 (6)*
C(21)	0.2815 (19)	−0.2867 (26)	0.1352 (17)	16.3 (8)
C(22)	0.2954 (20)	−0.086 (4)	0.0501 (17)	18.3 (10)
C(23)	0.1286 (16)	−0.176 (4)	0.0459 (23)	23.3 (15)

[a] The equivalent isotropic thermal parameter B_{eq} (asterisked value) is derived from the anisotropic values as $B_{eq} = \sum B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j / 3$.

that in $(MeC_5H_4)_3Ce(CNCMe_3)$, and the bond parameters change very slightly; the Cp–Ce–C(isocyanide) angles and Ce–C(isocyanide) distance are nearly equal though the averaged Ce–C(ring cyclopentadienyl) distance in $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$ of 2.87 (3) Å is longer than in the MeC_5H_4 analogue of 2.79 (3) Å. The large uncertainty in each datum and the correspondingly large average derivations from the mean value means that these distances are not statistically different to within 3σ. Hence, we do not wish to read too much into these differences though it is reasonable to expect that the larger ligand should be farther from the metal center to minimize intraligand–ligand repulsions.

The most interesting structure of the four is tetrameric $(MeC_5H_4)_3Ce$; the cerium atoms are at the corners of a square, and an inversion center is located in the center of the square; see Figure 1. The structure is composed of MeC_5H_4 rings bonded in a η^5 fashion to each cerium while one of the carbons in one of the η^5-MeC_5H_4 groups is close to that of an adjacent cerium atom with an averaged Ce···C distance of 3.03 (3) Å. Each cerium atom is surrounded by two terminal η^5-MeC_5H_4 groups and a bridging MeC_5H_4 group which is η^5-bonded to a cerium and η^1-bonded to an adjacent cerium such that the averaged bridging η^5-Cp–Ce–η^1-C angle is 100° and the averaged C(16)Ce(1)···C(28) and C(28)Ce(2)···C(16) angle is 91°. In a sense the $(MeC_5H_4)_3Ce$ structure is not dissimilar from that of its Me_3CNC complex; both are ten coordinate, but the Ce–C (isocyanide) is shorter than the Ce–C(η^1-ring cyclopentadienyl) because the isocyanide ligand is smaller and presumably a stronger base than the MeC_5H_4 ligand. The geometry of tetrameric $(MeC_5H_4)_3Ce$ is nearly identical with that of its neodymium analogue $(MeC_5H_4)_3Nd$.[2] The M–C(η^5-MeC_5H_4) distances in $(MeC_5H_4)_3Ce$ are 2.83 (4)

Table V. Positional and Thermal Parameters for $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$[a]

atom	x	y	z	B_{eq}, Å^2
Ce	−0.00675 (7)	0.25155 (9)	0.11692 (2)	2.38 (2)
Si(1)	0.1439 (4)	0.16121 (27)	0.00107 (17)	3.8 (2)
Si(2)	0.3629 (4)	0.3730 (3)	0.17926 (20)	4.8 (2)
Si(3)	−0.3146 (4)	0.10639 (28)	0.12000 (20)	4.3 (2)
Si(4)	0.2312 (4)	0.06448 (28)	0.21413 (17)	4.1 (2)
Si(5)	0.0274 (5)	0.31297 (29)	0.27681 (16)	4.5 (2)
Si(6)	−0.1459 (5)	0.48965 (28)	0.07592 (18)	4.3 (2)
N	−0.2755 (10)	0.2522 (13)	−0.0247 (4)	4.6 (4)
C(1)	0.2355 (11)	0.2422 (12)	0.1046 (5)	2.7 (4)
C(2)	0.1411 (14)	0.2350 (10)	0.0520 (5)	3.1 (6)
C(3)	0.0833 (14)	0.3079 (10)	0.0383 (6)	3.0 (5)
C(4)	0.1333 (15)	0.3593 (9)	0.0824 (6)	3.3 (5)
C(5)	0.2312 (12)	0.3201 (10)	0.1242 (5)	2.6 (5)
C(6)	−0.0390 (19)	0.1185 (11)	0.1766 (8)	2.6 (6)
C(7)	−0.1512 (18)	0.1158 (10)	0.1254 (8)	2.8 (7)
C(8)	−0.1049 (16)	0.0982 (8)	0.0862 (7)	3.1 (6)
C(9)	0.0298 (15)	0.0894 (8)	0.1081 (6)	3.4 (6)
C(10)	0.0734 (15)	0.1011 (8)	0.1652 (5)	2.4 (5)
C(11)	−0.0119 (19)	0.3936 (12)	0.1729 (9)	3.1 (7)
C(12)	−0.0438 (14)	0.3309 (9)	0.2025 (5)	3.1 (5)
C(13)	−0.1674 (13)	0.3038 (9)	0.1684 (6)	3.3 (5)
C(14)	−0.2054 (16)	0.3472 (10)	0.1199 (6)	2.9 (6)
C(15)	−0.1131 (17)	0.4036 (11)	0.1230 (8)	2.6 (6)
C(16)	0.2169 (17)	0.2095 (11)	−0.0417 (6)	5.7 (7)
C(17)	0.2425 (16)	0.0750 (11)	0.0320 (7)	5.2 (7)
C(18)	−0.0192 (18)	0.1261 (13)	−0.0427 (7)	7.2 (8)
C(19)	0.3472 (27)	0.3719 (17)	0.2472 (12)	9.3 (13)
C(20)	0.5166 (20)	0.3218 (16)	0.1937 (12)	12.1 (12)
C(21)	0.367 (4)	0.4696 (21)	0.1601 (16)	23.2 (22)
C(22)	−0.3209 (17)	0.1057 (12)	0.1883 (7)	6.5 (8)
C(23)	−0.4253 (16)	0.1851 (11)	0.0788 (8)	6.3 (7)
C(24)	−0.3760 (1]5)	0.0130 (11)	0.0850 (8)	6.1 (7)
C(25)	0.3662 (18)	0.1383 (13)	0.2401 (8)	5.5 (8)
C(26)	0.2167 (17)	0.0223 (11)	0.2755 (6)	5.7 (7)
C(27)	0.2838 (21)	−0.0160 (14)	0.1802 (8)	8.2 (9)
C(28)	0.1568 (20)	0.2447 (16)	0.2997 (6)	9.1 (8)
C(29)	−0.0980 (21)	0.2748 (13)	0.2993 (7)	8.2 (9)
C(30)	0.0875 (21)	0.4071 (11)	0.3129 (7)	7.6 (8)
C(31)	−0.1660 (17)	0.4656 (10)	0.0057 (7)	5.7 (7)
C(32)	−0.0167 (23)	0.5626 (10)	0.1044 (7)	7.7 (9)
C(33)	−0.2982 (22)	0.5355 (14)	0.0719 (8)	8.4 (10)
C(34)	−0.1963 (12)	0.2553 (14)	0.0177 (6)	3.3 (5)
C(35)	−0.3776 (15)	0.2534 (19)	−0.0780 (6)	5.6 (6)
C(36)	−0.4196 (28)	0.1713 (17)	−0.0893 (10)	11.3 (13)
C(37)	−0.4755 (23)	0.3073 (18)	−0.0764 (9)	9.6 (10)
C(38)	−0.3246 (22)	0.2795 (20)	−0.1169 (8)	11.4 (14)

[a] The equivalent isotropic thermal parameter B_{eq} is derived from the anisotropic values as $B_{eq} = \sum B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j / 3$.

Å and in $(MeC_5H_4)_3Nd$ they are 2.79 (4) Å, the Cp–M–Cp angles are identical at 117°, the averaged M···C(η^1-MeC_5H_4) distances are 3.03 (3) and 2.984 (3) Å, and the Cp–M–C-(η^1-MeC_5H_4) angles are 100° and 81°, respectively. These differences are most reasonably ascribed to the smaller size of neodymium, 0.03 Å in eight-coordination, relative to cerium.[13]

The tetrameric constitution of the $(MeC_5H_4)_3M$ compounds where M is Ce or Nd is to be contrasted with that of the other lanthanide $(C_5H_5)_3M$ compounds which form a continuous series of compounds whose degree of association in the solid state changes from a linear zigzag polymer with coordination number of ten or eleven to monomeric $(C_5H_5)_3Yb$ with coordination number of nine.[1] The reason for this structural change is not readily apparent though we offer the following as a reasonable, qualitative model. We assume that the observed geometry is determined by the conflicting tendency of the metal centers to achieve a maximum coordination number while minimizing the intraligand repulsions. Polymerization is one way to maximize the coordination number of a metal. When the intraligand repulsions become large, the degree of association changes from infinite (in the case of a polymer) to something finite (monomer, dimer, etc.). This simple, qualitative statement can be used to account for the change in structure of the $(C_5H_5)_3M$ compounds (M = La to Lu)[1] since the size of the metal atom monotonically decreases across the 4f transition-metal series. However, $(MeC_5H_4)_3M$ (M = Ce, Nd) and $(C_5H_5)_3Pr$ are both ten coordinate though the praseodymium compound is an infinite polymer in the solid state, whereas its immediate neighbors to the left and right form cyclic tetramers with the MeC_5H_4 ligand. This may be understood in the following manner. On going from a tetrameric structure found for $(MeC_5H_4)_3Ce$ to a polymeric structure related to that found in $(C_5H_5)_3Pr$ for hypothetical $(MeC_5H_4)_3Ce$, the Ce(1)···Ce(2)···Ce(1) angle must increase from ca. 90°, the individual angles at Ce(1) and Ce(2) are 81.3° and 98.8°, respectively, to ca. 115° found in polymeric $(C_5H_5)_3M$ (M = La, Pr).[1] This opening, assuming that all other distances and angles remain essentially constant, will force the MeC_5H_4 groups to be closer to each other, a situation that is tolerated in the sterically smaller C_5H_5 structures. In the cerium and neodymium structures ten coordination is achieved by bending the Ce···Ce···Ce angle by ca. 25° to form the cyclic tetrameric structure.

Experimental Section

All synthetic work was done under an atmosphere of nitrogen. Analytical and spectroscopic studies were done as previously described.[5]

$(MeC_5H_4)_3Ce$. Method A. Trimethylaluminum (3.1 mL of a 0.96 M hexane solution, 3.0 mmol) was added to $(MeC_5H_4)_3Ce(THF)$[5] (1.35 g, 3.00 mmol) in toluene (30 mL). The green-yellow solution turned bright green, the solution was stirred for 1 h, and then the solvent was removed under reduced pressure. The yellow solid was extracted with toluene (50 mL, 50 °C) and filtered, and the filtrate was concentrated to ca. 20 mL (50 °C). Cooling the extract to −20 °C for 3 h, followed by cooling to −80 °C, afforded yellow-orange crystals (0.65 g, 57%), mp 152–153 °C. Anal. Calcd for $C_{18}H_{21}Ce$: C, 57.3; H, 5.61. Found: C, 57.2; H, 5.69. IR: 1315 w, 1305 w, 1237 mw, 1115 w, 1102 w, 1032 m, 970 w, 928 mw, 882 w, 870 w, 830 s, 790 w, 760 s, 742 s, 615 ms, 510 w, 328 m, 230 m cm^{-1}. ^1H NMR (C_6D_6, 29 °C): 13.02 (2 H, $\nu_{1/2}$ = 43 Hz), 10.56 (2 H, $\nu_{1/2}$ = 58 Hz), −4.52 ppm (3 H, $\nu_{1/2}$ = 20 Hz). Mass spectrum (calcd, %, obsd, %): m/e 377 (100, 100), 378 (20.0, 18.5), 379 (14.4, 15.1).

Method B. The yellow solution prepared by dissolving $(MeC_5H_4)_3Ce(THF)$ (1.52 g, 3.38 mmol) in toluene (150 mL) was heated to ca. 100 °C, and the solvent was removed very slowly under reduced pressure (over ca. 2–3 h). As the THF was removed with the toluene, the solution turned greenish blue though the solid residue was yellow-orange. The residue was dissolved in an additional 150 mL of toluene, and the toluene reflux process was repeated. The solid residue was extracted with toluene (60 mL, 50 °C) and filtered, and the filtrate was concentrated to ca. 35 mL. Cooling to −20 °C for 3 h, followed by cooling to −80 °C, afforded yellow-orange crystals (0.93 g, 73%) whose physical properties were identical with those obtained from method A.

$(MeC_5H_4)_3Ce(NCEt)$. Propionitrile (0.14 mL, 3.5 mmol) was added to $(MeC_5H_4)_3Ce(THF)$ (0.76 g, 1.7 mmol) in diethyl ether (30 mL), and the yellow solution was stirred for 30 min. The solvent was removed under reduced pressure, and residue was dissolved in diethyl ether (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to −20 °C afforded yellow crystals (0.44 g, 60%), m.p. 62–65 °C. Anal. Calcd for $C_{21}H_{26}CeN$: C, 58.3; H, 6.06; N, 3.24. Found: C, 58.0; H, 6.01; N, 3.18. IR: 2350 w (br), 2260 s, 2160 w, 2110 w, 1410 m, 1375 s, 1365 mw, 1310 m, 1260 w, 1235 m, 1170 w, 1092 w, 1070 m, 1061 w, 1045 m, 1030 s, 1020 w, 975 w, 928 m, 885 w, 850 m, 822 s, 765 s, 740 s, 617 m, 563 w, 330 s, 240 s, 220 s cm^{-1}. ^1H NMR (C_6D_6, 34 °C): 11.04 (6 H), 7.86 (6 H), −0.65 (9 H), −3.81 (3 H, t, J = 6.8 Hz), −7.24 ppm (2 H, q, J = 6.8 Hz). The last two resonances

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(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

shift toward the diamagnetic region of the spectrum upon addition of excess propionitrile.

$(MeC_5H_4)_3Ce(CNEt)$. This molecule was prepared in a manner similar to that used to prepare the propionitrile complex and crystallized as yellow crystals from hexane (−20 °C) in 58% yield; mp 60–61 °C. Anal. Calcd for $C_{21}H_{26}CeN$: C, 58.3; H, 6.06; N, 3.24. Found: C, 58.5; H, 6.09; N, 3.37. IR: 2320 w (br), 2200 s, 2070 w, 1342 m, 1302 w, 1235 w, 1160 w, 1140 w, 1092 m, 1060 w, 1045 m, 1030 m, 1008 w, 975 w, 929 m, 850 w, 822 s, 765 s, 743 s, 618 m, 500 w, 330 m, 245 m, 223 m cm^{-1}. ^1H NMR (C_6D_6, 34 °C): 10.38 (6 H), 8.31 (6 H), −0.73 (9 H), −3.61 (3 H), −5.86 ppm (2 H, d, J = 6 Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition to excess ethyl isocyanide.

$(MeC_5H_4)_3Ce(CNCMe_3)$. This compound was prepared in a manner similar to that used to prepare the ethyl isocyanide complex and crystallized from hexane (−20 °C) as yellow needles in 74% yield; mp 108–110 °C. Anal. Calcd for $C_{23}H_{30}CeN$: C, 60.0; H, 6.16; N, 2.85. Found: C, 60.4; H, 6.43; N, 3.13. IR: 2175 s, 2060 w, 1670 w (br), 1300 w, 1233 m, 1195 m, 1165 w, 1150 w, 1060 w, 1042 m, 1028 m, 970 m, 925 m, 888 w, 848 m, 812 s, 748 s, 720 m, 697 w, 612 m, 567 w, 525 m, 417 w, 411 m, 322 s, 240 m, 218 s cm^{-1}. ^1H NMR (C_6D_6, 30 °C): 10.53 (6 H, $\nu_{1/2}$ = 24 Hz), 7.99 (6 H, $\nu_{1/2}$ = 28 Hz), −0.57 (9 H, $\nu_{1/2}$ = 10 Hz), −4.13 ppm (9 H, $\nu_{1/2}$ = 5 Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of *tert*-butyl isocyanide.

$(Me_3SiC_5H_4)_3Ce$. Potassium (trimethylsilyl)cyclopentadienide (40.3 mL of a 0.74 M solution in tetrahydrofuran, 30.0 mmol) was added to a suspension of cerium trichloride (2.45 g, 9.94 mmol) in tetrahydrofuran (50 mL). The suspension became yellow after ca. 15 min and was stirred for 18 h. The solvent was removed under reduced pressure. The yellow residue was extracted with hexane (120 mL) and the blue-green solution was filtered. While the filtrate was concentrated, a yellow solid began to crystallize which is presumably the THF adduct. All of the hexane was removed under reduced pressure, and the yellow-green residue was melted in a water bath (85 °C) under dynamic vacuum which produced a viscous, dark blue solution. The solution was cooled to room temperature, and the blue solid was dissolved in hexane (15 mL) and filtered, and the filtrate was concentrated to ca. 3 mL. Cooling the filtrate to −80 °C yielded a royal blue solid (3.7 g, 68% yield), mp 69–70 °C. The compound sublimed at 60 °C at 10^{-3} mm. Anal. Calcd for $C_{24}H_{39}CeSi_3$: C, 52.2; H, 7.12. Found: C, 51.9; H, 7.33. IR: 1360 m, 1310 w, 1245 s, 1058 w, 1039 s, 975 w, 950 w, 900 s, 830 s, 780 w, 765 s, 750 m, 720 w, 698 w, 685 m, 630 w, 622 m, 420 m, 340 m, 310 m, 250 w, 220 m cm^{-1}. ^1H NMR (C_6D_6, 32 °C): 24.12 (2 H, $\nu_{1/2}$ = 34 Hz), 5.15 (2 H, $\nu_{1/2}$ = 34 Hz), −8.30 ppm (9 H, $\nu_{1/2}$ = 8 Hz). The mass spectrum showed a monomeric molecular ion in the mass spectrum: m/e (calcd, %, obsd, %): 551 (100, 100), 552 (42.0, 28.3), 553 (30.9, 16.8), 554 (0, 10.0). Powder pattern data (Table VI) show that the cerium compound is isostructural with the uranium compound.[7]

$(Me_3SiC_5H_4)_3Ce(NCEt)$. Propionitrile (0.03 mL, 0.83 mmol) was added to $(Me_3SiC_5H_4)_3Ce$ (0.46 g, 0.83 mmol) dissolved in hexane (30 mL). The dark blue solution immediately turned yellow. The solution was stirred for 30 min, and then the solvent was removed under reduced pressure. The yellow residue was dissolved in hexane (50 mL) and the solution was filtered. Cooling the filtrate to −20 °C yielded small yellow needles (0.34 g, 67% yield), mp 126–128 °C. Anal. Calcd for $C_{27}H_{44}CeNSi_3$: C, 53.4; H, 7.31; N, 2.31. Found: C, 52.3; H, 7.07; N, 2.80. IR: 2260 s, 1360 m, 1308 m, 1242 s, 1178 s, 1070 w, 1060 w, 1038 s, 970 w, 900 s, 830 s, 785 w, 750 m, 720 m, 685 m, 638 s, 632 m, 620 s, 560 w, 420 s, 320 s, 250 w, 220 s cm^{-1}. ^1H NMR (C_6D_6, 30 °C): 13.63 (6 H, $\nu_{1/2}$ = 21 Hz), 6.59 (6 H, $\nu_{1/2}$ = 21 Hz), −2.25 (27 H, $\nu_{1/2}$ = 4 Hz), −3.61 (3 H, t, J = 7 Hz), −6.86 ppm (2 H, q, J = 7 Hz). The last two resonances shift toward the diamagnetic region of the spectrum with addition of propionitrile.

$(Me_3SiC_5H_4)_3Ce(CNEt)$. The compound was made in a manner similar to that used for preparation of the propionitrile complex and crystallized from hexane (−20 °C) as yellow crystals in 63% yield; mp 121–123 °C. Anal. Calcd for $C_{27}H_{44}CeNSi_3$: C, 53.4; H, 7.31; N, 2.31. Found: C, 52.5, H, 7.37; N, 2.11. IR: 2200 m, 1310 w, 1257 w, 1245 s, 1175 m, 1090 w, 1060 w, 1040 s, 937 w, 900 s, 830 s, 765 s, 750 m, 720 w, 685 w, 640 w, 623 m, 605 w, 422 m, 320 m cm^{-1}. ^1H NMR (C_6D_6, 28 °C): 13.71 (6 H, $\nu_{1/2}$ = 30 Hz), 6.13 (6 H, $\nu_{1/2}$ = 30 Hz), −2.17 (27 H, $\nu_{1/2}$ = 6 Hz), −3.91 (3 H, $\nu_{1/2}$ = 16 Hz), −6.52 ppm (2 H, $\nu_{1/2}$ = 23 Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of ethyl isocyanide.

Table VI

			U		Ce	
index			d_{hkl}(calcd)	d_{hkl}(measd)	d_{hkl}(measd)	int (Ce)
2	0	0	11.315	11.518	11.226	s
2	1	0	10.550		10.495	w−
0	2	1	7.300	7.329	7.345	s
1	2	1	6.946	6.903	6.929	s
2	4	0	6.131	6.121	6.130	s
2	3	1	5.550	5.540	5.574	s−
3	2	1	5.245	5.216	5.246	m−
3	3	1	4.867	4.861	4.894	w
4	4	0	4.471	4.446	4.462	m
1	6	1	4.141	4.143	4.201	s−
6	1	0	3.741	3.712	3.719	s−
2	8	0	3.471	3.470	3.486	w−
4	7	0	3.358	3.354	3.357	w−
5	6	1	3.083	3.074	3.079	w+
1	10	1	2.737	2.736	2.747	m+
2	2	3	2.680	2.675	2.692	m
3	8	2	2.590	2.578	2.592	w+
0	6	3	2.433	2.478	2.483	w+
2	6	3	2.378	2.395	2.381	w
4	12	0	2.234	2.290	2.232	w
6	5	3	2.102	2.159	2.102	w+
1	4	4	2.016	2.056	2.026	w+
2	10	3	1.992	2.008	1.992	m+
3	14	1	1.944	1.954	1.946	m+

$(Me_3SiC_5H_4)_3Ce(CNCMe_3)$. This compound was prepared in a manner similar to that of the ethyl isocyanide analogue and crystallized as yellow needles from hexane (−20 °C) in 76% yield; mp 111–113 °C. Anal. Calcd for $C_{29}H_{48}CeNSi_3$: C, 54.8; H, 7.62; N, 2.21. Found: C, 54.1; H, 7.32; N, 2.30. IR: 2170 s, 1370 s, 1360 m, 1305 w, 1240 s, 1188 w, 1172 m, 1058 w, 1038 s, 900 s, 828 s, 781 m, 762 s, 745 m, 718 w, 686 m, 638 w, 620 m, 525 w, 420 m, 330 w, 315 m, 240 w cm^{-1}. ^1H NMR (C_6D_6, 30 °C): 13.25 (6 H, $\nu_{1/2}$ = 22 Hz), 6.52 (6 H, $\nu_{1/2}$ = 26 Hz), −2.14 (27 H, $\nu_{1/2}$ = 6 Hz), −3.80 ppm (9 H, $\nu_{1/2}$ = 5 Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of *tert*-butyl isocyanide.

$(Me_3CC_5H_4)_3Ce$. Potassium *tert*-butylcyclopentadienide (43 mL of a 0.66 M solution in THF, 28 mmol) was added, via syringe, to $CeCl_3$ (2.34 g, 9.49 mmol) suspended in THF (50 mL). The suspension became grayish purple after ca. 30 min. The suspension was stirred for 18 h, and the solvent was removed under reduced pressure. The purple residue was extracted with hexane (1 × 90 mL, 1 × 30 mL, 50 °C) and filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to −80 °C afforded a purple solid (3.72 g, 78%), mp 85 °C. In order to obtain a solid product, it is sometimes necessary to melt the crude product under vacuum to remove all of the THF. Anal. Calcd for $C_{27}H_{39}Ce$: C, 64.4; H, 7.80. Found: C, 64.8; H, 7.85. IR: 1680 m, 1575 m, 1360 s, 1267 s, 1200 m, 1189 w, 1155 s, 1045 s, 1040 s, 1017 m, 975 w, 912 m, 850 w, 818 s, 710 m, 670 s, 610 w, 587 w, 448 m, 370 m, 350 m, 257 m cm^{-1}. ^1H NMR (C_6D_6, 33 °C): 21.80 (2 H, $\nu_{1/2}$ = 31 Hz), 7.74 (2 H, $\nu_{1/2}$ = 30 Hz), −9.35 ppm (9 H, $\nu_{1/2}$ = 10 Hz). The EI mass spectrum showed a molecular ion at m/e 803 amu.

$[(Me_3Si)_2C_5H_3]_3Ce$. To $[(Me_3Si)_2N]_3Ce$[14] (0.85 g, 1.4 mmol), dissolved in diethyl ether (30 mL), was added, via syringe, bis(trimethylsilyl)cyclopentadiene (1.0 mL, 4.2 mmol). The solution was stirred for 15 h. During this time the solution color gradually turned from yellow to green and finally to blue with the presence of a small amount of white precipitate. The diethyl ether was removed under reduced pressure. The blue solid was dissolved in hexane (30 mL) and filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the filtrate to −20 °C, followed by further

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[14] (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021. (b) Fjeldberg, T.; Andersen, R. A. *J. Mol. Struct.* **1985**, *129*, 93.

cooling to −80 °C, afforded blue crystals (0.33 g, 31%). Concentrating the mother liquor to ca. 5 mL and cooling to −20 °C afforded an additional 0.19 g (18%) of product, mp 210–213 °C. Anal. Calcd for $C_{33}H_{63}CeSi_6$: C, 51.6; H, 8.26. Found: C, 49.3; H, 8.18. This is the best analysis that we have been able to get; in our experience molecules with high Si to C ratios are difficult to oxidize completely. IR: 1372 s, 1360 m, 1315 w, 1241 s, 1205 w, 1150 w, 1073 s, 1012 w, 970 w, 915 s, 830 s, 771 m, 745 m, 718 w, 684 m, 632 m, 612 w, 475 m, 371 w, 348 w, 295 w, 270 m cm^{-1}. ^{1}H NMR (C_6D_6, 30 °C): 26.9 (1 H, $\nu_{1/2}$ = 30 Hz), 17.2 (2 H, $\nu_{1/2}$ = 36 Hz), −4.48 ppm (18 H, $\nu_{1/2}$ = 7 Hz). The EI mass spectrum showed a molecular ion at *m/e* (calcd, %, obsd, %) 767 (100, 100), 768 (67.3, 68.5), 769 (54.3, 47.8), 700 (25.4, 25.2), and 771 (11.3, 9.80).

$[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$. This compound was prepared in a manner similar to that used to prepare the other isocyanide complexes and crystallized as yellow blocks from hexane (−20 °C) in 78% yield; mp 223–226 °C (upon heating the yellow solid turned green then blue from ca. 150–190 °C). IR: 2205 w, 2170 s, 2065 w, 1402 w, 1372 s, 1363 mw, 1315 mw, 1243 s, 1203 m, 1072 s, 1055 mw, 970 vw, 918 s, 831 s, 815 s, 771 m, 750 ms, 720 w, 681 m, 632 ms, 617 m, 521 w, 480 ms, 368 m, 350 w, 325 w, 295 m, 230 vw cm^{-1}. Anal. Calcd for $C_{38}H_{72}CeNSi_6$: C, 53.6; H, 8.52; N, 1.64. Found: C, 53.4; H, 8.60; N, 1.62. ^{1}H NMR (C_6D_6, 30 °C): 12.8 (1 H, very broad; $\nu_{1/2} \approx$ 150 Hz), 11.7 (2 H, $\nu_{1/2} \approx$ 50 Hz), −0.94 (18 H, $\nu_{1/2}$ = 8 Hz), −3.11 ppm (3 H, $\nu_{1/2}$ = 15 Hz).

X-ray Crystallography. $(MeC_5H_4)_8(\mu\text{-}MeC_5H_4)_4Ce_4$. A yellow, air-sensitive crystal was sealed inside a thin-walled quartz capillary under argon and mounted on a modified Picker FACS-1 automated diffractometer equipped with a Mo X-ray tube and a graphite monochromator. A set of θ–2θ scan data was collected and corrected for absorption (analytical method)[15] and Lorentz and polarization effects. The cerium atom positions were obtained from three-dimensional Patterson maps, and subsequent least-squares refinements and difference electron density maps were used to determine the positions of the remaining atoms. All of the non-hydrogen atoms were assigned anisotropic thermal parameters in the full-matrix, least-squares refinement procedures; hydrogen atoms were included in fixed estimated positions with estimated isotropic thermal parameters. No extinction correction was indicated and none applied. Details of the refinements and other crystallographic data are given in Table I for all of the structures reported in this paper.

$[(Me_3Si)_2C_5H_3]_3Ce$. An air-sensitive, blue crystal was sealed inside a thin-walled quartz capillary under argon and mounted on a modified Picker FACS-1 automated diffractometer equipped with a Mo X-ray tube, and the data were collected and processed as described above. A full-matrix, least-squares program was used to refine the atomic parameters. The first refinements were done in space group *Ic*, but subsequent difference Fourier maps showed disorder in the cyclopentadienyl rings and in some of the methyl groups. The structure was ultimately refined in the centric space group *I*2/*c* with disorder taken into account. The three silicon atoms and the methyl carbon atoms [C(28), C(29), C(30)] were placed in the general position with full occupancy; the remaining carbon atoms were placed in general positions with half occupancy. Since there was overlap of the carbon atoms onto other carbon atoms in disordered positions, it was necessary to impose Si–C and C–C distance restraints[16] in the least-squares refinements. Hydrogen atoms were included in their estimated positions with estimated isotropic thermal parameters but were not refined. No extinction correction was indicated and none was made. The scattering factors and anomalous dispersion terms used were taken from ref 17.

$(MeC_5H_4)_3Ce(CNCMe_3)$. An air-sensitive, yellow crystal was sealed inside a thin-walled quartz capillary under argon and mounted on a modified Picker FACS-1 automated diffractometer equipped with a Cu X-ray tube and a graphite monochromator. The data were collected and processed as described above. The hydrogen atoms were included in their estimated positions with estimated isotropic thermal parameters but were not refined. The methyl carbon atoms of the isocyanide group were poorly resolved, and the distances to their next nearest neighbors were restrained in the least-squares refinements.[16] All 139 data below $(\sin\theta)/\lambda$ = 0.20 were given zero weight because of large discrepancies due to absorption errors that were not well accounted for by the absorption correction. No extinction correction was indicated and none was made.

$[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$. An air-sensitive crystal was sealed inside a thin-walled quartz capillary under argon and mounted on a modified Picker FACS-1 automated diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The data were collected and processed as described above. An absorption correction was not made. All of the non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms were included in their estimated positions with estimated isotropic thermal parameters but were not refined.

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Registry No. $(MeC_5H_4)_3Ce$, 123810-47-9; $(MeC_5H_4)_3Ce(NCEt)$, 123810-48-0; $(MeC_5H_4)_3Ce(CNEt)$, 123810-49-1; $(MeC_5H_4)_3Ce(CNCMe_3)$, 123810-50-4; $(Me_3SiC_5H_4)_3Ce$, 123810-51-5; $(Me_3SiC_5H_4)_3Ce{\cdot}NCEt$, 123810-52-6; $(Me_3SiC_5H_4)_3Ce(CNEt)$, 123810-53-7; $(Me_3SiC_5H_4)_3Ce(CNCMe_3)$, 123810-54-8; $(Me_3CC_5H_4)_3Ce$, 123810-55-9; $[(Me_3Si)_2C_5H_3]Ce$, 123810-56-0; $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$, 123810-57-1; $(MeC_5H_4)_8(\mu\text{-}MeC_5H_4)_4Ce_4$, 123810-58-2; $(MeC_5H_4)_3Ce(THF)$, 113811-04-4; $[(Me_3S)_2N]_3Ce$, 41836-21-9; potassium (trimethylsilyl)cyclopentadienide, 101630-43-7; cerium trichloride, 7790-86-5; potassium *tert*-butylcyclopentadienide, 117012-90-5; bis(trimethylsilyl)cyclopentadiene, 38927-85-4.

Supplementary Material Available: Tables of thermal parameters, hydrogen positional parameters, bond lengths, bond angles, and least-squares planes and crystal data (26 pages); structure factor tables (34 pages). Ordering information is given on any current masthead page.

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