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

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Abstract

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 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 gas phase and 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, $F^2 > 3\sigma(F^2)$. All of the binary metallocenes form 1:1 complexes with isocyanides and organocyanides and the crystal structure of two of them have been done; $(MeC_5H_4)_3Ce(CNCMe_3)$ 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, $F^2 > 3\sigma(F^2)$ 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, 2437 data, $F^2 > 3\sigma(F^2)$.

The solid state crystal 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 zig-zag 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) 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 zig-zag chain with the M to η^1-C distance increasing with decreasing metal radius.[1e] At ytterbium, $(C_5H_5)_3Yb$ is 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.[1f] 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 intramolecualr 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 $(C_5H_5)_3Sm$ is 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] Me_5C_5Tl[3d] are zig-zag 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 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, gives a monomeric molecular ion

$$(MeC_5H_4)_3Ce(thf) + Me_3Al \rightarrow (MeC_5H_4)_3Ce + Me_3Al(thf) \qquad (1)$$

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 ^{1}H 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, δ 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.

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 ^{1}H 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 5-30K with $\mu = 2.14 \pm 0.02$ B.M. and $\theta = -2.96$K and 50–280K with $\mu = 2.28 \pm 0.01$ B.M. and θ = -6.71K at a field strength of 5 kgauss. The value of the magnetic moment at a field strength of 40 kgauss is not significantly different from the value at 5 kgauss. 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 B.M. and CeF_3 μ is 2.28 B.M., though smaller than that found for polymeric $(C_5H_5)_3Ce$ of 2.46 B.M. at -196 and 22°C[4a] or predicted for the free ion of 2.54 B.M. by Van Vleck.[8a] Cerium(III) is a f^1 ion and the free ion term symbol is $^2F_{5/2}$. Spin-orbit coupling splits this state into two levels with 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 presence of a cubic 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 2.54B.M. 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 5-30K and 50-280K. 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 30-50K and at 5-30K 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 Bronstad acid-base reaction shown in eq. 2. Though the pKa of

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

the diene is unknown, it must be less than 26, the pka 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 ^1H NMR spectrum shows that the Me_3Si 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. 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.

All of these metallocenes form 1:1 coordination compounds with the sterically small alkylisocyanide and alkylcyanide ligands, see Experimental Section for details. We have been unable to isolate 1:2 complexes with these ligands though variable temperature ^1H 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 1:1 and 1:2 complexes.[11] In contrast, $(MeC_5H_4)_3Ce(CNCMe_3)$ and all of other isocyanide and

cyanide complexes prepared in this study do follow Curie law from -80°C 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

$$(Me_3SiC_5H_4)_3Ce + [(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3) \leftrightarrow$$
$$(Me_3SiC_5H_4)_3Ce(CNCMe_3) + [(Me_3Si)_2C_5H_3]_3Ce \qquad (3)$$

is 54.

X-Ray Crystallography. 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 I-IV, respectively, along with important bond distances and angles; additional bond distances and angles are in the Supplementary Material. Positional parameters are in Table I and crystal data are in Tables II-V.

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 unit is nearly trigonal planar in each case since the Cp-Ce-Cp, where Cp is used as an abbreviation for a ring centroid regardless of the substituent on the cyclopentadienyl group, angle varies from 117° to 120°, the Cp-Ce distance varies from 2.55Å to 2.60Å, 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 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 just 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 intra-ligand-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 I. 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 is 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 better base than the MeC_5H_4 ligand. The geometry of tetrameric $(MeC_5H_4)_3Ce$ is nearly identical to 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)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)Å 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, 0.03Å 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 zig-zag 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 intra-ligand repulsions. Polymerization is one way to maximize the coordination number of metal. When the intra-ligand repulsions become large, the degree of association changes from infinite (in the case of a polymer) to something less than infinite (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 0.96M hexane solution, 3.0 mmol) was added to $(MeC_5H_4)_3Ce(thf)$[5] (1.35g, 3.00 mmol) in toluene (30 mL). The green-yellow solution turned bright green, and the solution was stirred for 1 hr then the solvent was removed under reduced pressure. The yellow solid was extracted with toluene (50 mL, 50°C), filtered, and the filtrate was concentrated to ca. 20 mL (50°C). Cooling the extract to -20°C for 3 hr, followed by cooling to -80°C afforded yellow-orange crystals (0.65g, 57%),

m.p. 152-153°C. Anal. Calcd. for $C_{18}H_{21}Ce$: C, 57.3; H, 5.6l. Found: C, 57.2; H, 5.69. IR: 1315w, 1305w, 1237mw, 1115w, 1102w, 1032m, 970w, 928mw, 882w, 870w, 830s, 790w, 760s, 742s, 615ms, 510w, 328m, 230m cm^{-1}. ^1H NMR (C_6D_6, 29°C): 13.02 (2H, $\nu_{1/2}$ = 43 Hz), 10.56 (2H $\nu_{1/2}$ = 58 Hz), -4.52 (3H, $\nu_{1/2}$ = 20 Hz). Mass spec (m/e calculated intensity, observed intensity): 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) (1.52g, 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 hr). 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), filtered, and the filtrate was concentrated to ca. 35 mL. Cooling to -20°C for 3 hr, followed by cooling to -80°C afforded yellow orange crystals (0.93g, 73%) whose physical properties were identical to 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) (0.76g, 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 (0.44g, 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: 2350w (br), 2260s, 2160w, 2110w, 1410m, 1375s, 1365mw, 1310m, 1260w, 1235m, 1170w, 1092w, 1070m, 1061w, 1045m, 1030s, 1020w, 975w, 928m, 885w, 850m, 822s, 765s, 740s, 617m, 563w, 330s, 240s, 220s cm^{-1}. ^1H NMR (C_6D_6, 34°C): 11.04 (6H), 7.86 (6H), -0.65 (9H), -3.81 (3H, t, J = 6.8 Hz), -7.24 (2H, q, J = 6.8 Hz). The last two resonances 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, m.p. 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: 2320w (br), 2200s, 2070w, 1342m, 1302w, 1235w, 1160w, 1140w, 1092m, 1060w, 1045m, 1030m, 1008w, 975w, 929m, 850w, 822s, 765s, 743s, 618m, 500w, 330m, 245m, 223m cm^{-1}. ^1H NMR (C_6D_6, 34°C): 10.38 (6H), 8.31 (6H), -0.73 (9H), -3.61 (3H), -5.86 (2H, d, J = 6 Hz). The last two resonances shift towad the diamagnetic region of the spectrum upon addition of excess ethylisocyanide.

$(MeC_5H_4)_3Ce(CNCMe_3)$. This compound was prepared in a manner similar to that used to prepare the ethylisocyanide complex and crystallized from hexane (-20°C) as yellow needles in 74% yield, m.p. 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: 2175s, 2060w, 1670w (br), 1300w, 1233m, 1195m, 1165w, 1150w, 1060w, 1042m, 1028m, 970m, 925m, 888w, 848m, 812s, 748s, 720m, 697w, 612m, 567w, 525m, 417w, 411m, 322s, 240m, 218s cm^{-1}. ^1H NMR (C_6D_6, 30°C): 10.53 (6H, $\nu_{1/2}$ = 24 Hz), 7.99 (6H, $\nu_{1/2}$ = 28 Hz), -0.57 (9H, $\nu_{1/2}$ = 10 Hz), -4.13 (9H, $\nu_{1/2}$ = 5 Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of t-butylisocyanide.

$(Me_3SiC_5H_4)_3Ce$. Potassiumtrimethylsilylcyclopentadienide (40.3 mL of a 0.74M solution in tetrahydrofuran, 30.0 mmol) was added to a suspension of cerium trichloride (2.45g, 9.94 mmol) in tetrahydrofuran (50 mL). The suspension became yellow after ca. 15 min and was stirred for 18h. The solvent was removed under reduced pressure. The yellow residue was extracted with hexane (120 mL) and the blue-green solution was filtered. While concentrating the filtrate, 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), filtered, and the filtrate was concentrated to ca. 3 mL. Cooling the filtrate to -80°C yielded a royal blue solid (3.7g, 68% yield), m.p. 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: 1360m, 1310w, 1245s, 1058w, 1039s, 975w, 950w, 900s, 830s, 780w, 765s, 750m, 720w, 698w, 685m, 630w,

622m, 420m, 340m, 310m, 250w, 220m cm^{-1}. ^1H NMR (C_6D_6, 32°C): 24.12 (2H, $\nu_{1/2}$ = 34 Hz), 5.15 (2H, $\nu_{1/2}$ = 34 Hz), -8.30 (9H, $\nu_{1/2}$ = 8 Hz). The mass spectrum showed a monomeric molecular ion in the mass spectrum: M/e(calcd. %, obsvd. %): 551 (100,100); 552 (42.0, 28.3); 553 (30.9, 16.8); 554 (0, 10.0). Powder pattern data, given below, show that the cerium compound is isostructural with the uranium compound.[7]

Index			U d_{hkl}(calc)	U d_{hkl}(meas)	Ce d_{hkl}(meas)	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+

$\underline{(Me_3SiC_5H_4)_3Ce{\cdot}NCEt}$. Propionitrile (0.03 mL, 0.83 mmol) was added to $(Me_3SiC_5H_4)_3Ce$ (0.46g, 0.83 mmol) dissolved in hexane (30 mL). The dark blue solution immediately turned yellow. The solution was stirred for 30 min 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 (0.34g, 67% yield), m.p. 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: 2260s, 1360m, 1308m, 1242s, 1178s, 1070w, 1060w, 1038s, 970w, 900s, 830s, 785w, 750m, 720m, 685m, 638s, 632m, 620s, 560w, 420s, 320s, 250w, 220s cm^{-1}. ^1H NMR (C_6D_6, 30°C): 13.63 (6H, $\nu_{1/2}$ = 21 Hz), 6.59 (6H, $\nu_{1/2}$ = 21 Hz), -2.25 (27H, $\nu_{1/2}$ = 4 Hz), -3.61 (3H, t, J = 7 Hz), -6.86 (2H, 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, m.p. 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: 2200m, 1310w, 1257w, 1245s, 1175m, 1090w, 1060w, 1040s, 937w, 900s, 830s, 765s, 750m, 720w, 685w, 640w, 623m, 605w, 422m, 320m cm^{-1}. ^1H NMR (C_6D_6, 28°C): 13.71 (6H, $\nu_{1/2}$ = 30 Hz), 6.13 (6H, $\nu_{1/2}$ = 30 Hz), -2.17 (27H, $\nu_{1/2}$ = 6 Hz), -3.91 (3H, $\nu_{1/2}$ = 16 Hz), -6.52 (2H, $\nu_{1/2}$ = 23 Hz). The last two resonances shift toward the diamagnetic region of the spectrum upon addition of ethylisocyanide.

$(Me_3SiC_5H_4)_3Ce(CNCMe_3)$. This compound was prepared in a manner similar to that of the ethylisocyanide 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: 2170s, 1370s, 1360m, 1305w, 1240s, 1188w, 1172m, 1058w, 1038s, 900s, 828s, 781m, 762s, 745m, 718w, 686m, 638w, 620m, 525w, 420m, 330w, 315m, 240w cm^{-1}. ^1H NMR (C_6D_6, 30°C): 13.25 (6H, $\nu_{1/2}$ = 22 Hz), 6.52 (6H, $\nu_{1/2}$ = 26 Hz), -2.14 (27H, $\nu_{1/2}$ = 6 Hz), -3.80 (9H, $\nu_{1/2}$ = 5 Hz). The last resonance shifts toward the diamagnetic region of the spectrum upon addition of t-butylisocyanide.

$(Me_3CC_5H_4)_3Ce$. Potassium t-butylcyclopentadienide (43 mL of a 0.66M solution in thf, 28 mmol) was added, via syringe, to $CeCl_3$ (2.34g, 9.49 mmol) suspended in thf (50 mL). The suspension became greyish-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 (1x90 mL, 1x30 mL, 50°C), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -80°C afforded a purple solid (3.72g, 78%), m.p. 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: 1680m, 1575m, 1360s, 1267s, 1200m, 1189w, 1155s, 1045s, 1040s, 1017m, 975w, 912m, 850w, 818s, 710m, 670s, 610w, 587w, 448m, 370m, 350m, 257m cm^{-1}. ^1H NMR (C_6D_6, 33°C): 21.80 (2H, $\nu_{1/2}$ = 31 Hz), 7.74 (2H, $\nu_{1/2}$ = 30 Hz), -9.35 (9H, $\nu_{1/2}$ = 10 Hz). The E.I. mass spectrum showed a molecular ion at M/e = 803 amu.

$[(Me_3Si)_2C_5H_3]_3Ce$. To $[(Me_3Si)_2N]_3Ce$[14] (0.85g, 1.4 mmol) dissolved in diethyl ether (30 mL) was added, via syringe, bis-trimethylsilylcyclopentadiene (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), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the filtrate to -20°C followed by further cooling to -80°C afforded blue crystals (0.33g, 31%). Concentrating the mother liquor to ca. 5 mL and cooling to -20°C afforded an additional 0.19g (18%) of product, m.p. 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: 1372s, 1360m, 1315w, 1241s, 1205w, 1150w, 1073s, 1012w, 970w, 915s, 830s, 771m, 745m, 718w, 684m, 632m, 612w, 475m, 371w, 348w, 295w, 270m, cm^{-1}. ^1H NMR (C_6D_6, 30°C): 26.9 (1H, $\nu_{1/2}$ = 30 Hz), 17.2 (2H, $\nu_{1/2}$ = 36 Hz), -4.48 (18H, $\nu_{1/2}$ = 7 Hz). The E.I. mass spectrum showed a molecular ion at M/e (calc %, obsvd %): 767 (100,100); 768 (67.3, 68.5); 769 (54.3, 47.8); 700 (25.4, 25.2); 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, m.p. 223-226°C (upon heating the yellow solid turned green then blue from

ca. 150-190°C). IR: 2205w, 2170s, 2065w, 1402w, 1372s, 1363mw, 1315mw, 1243s, 1203m, 1072s, 1055mw, 970vw, 918s, 831s, 815s, 771m, 750ms, 720w, 681m, 632ms, 617m, 521w, 480ms, 368m, 350w, 325w, 295m, 230vw 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. ^1H NMR (C_6D_6, 30°C): 12.8 (1H, very broad; $\nu_{1/2} \approx 150$ Hz), 11.7 (2H, $\nu_{1/2} \approx 50$ Hz), -0.94 (18H, $\nu_{1/2} = 8$ Hz), -3.11 (3H, $\nu_{1/2} = 15$ 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. A list of the atomic coordinates is given in Table II, and further details are given in the Supplementary Material.

$I(Me_3Si)_2C_5H_3]_3Ce$. 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 a graphite monochromator. A set of θ-2θ scan data was collected and corrected for Lorentz and polarization effects, and absorption (analytical method).[15] The cerium atom position was 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. 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 I2/c with disorder taken into account. The three silicon atoms and the methyl carbon atoms (C28, C29, C30) 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. Details of the refinements and other crystallographic data are given in Table I, a list of the atomic coordinates is given in Table III, and further details are given in the Supplementary Material.

$\underline{(MeC_5H_4)_3Ce(CNCMe_3)}$. 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. A set of θ-2θ scan data was collected and corrected for Lorentz and polarization effects, and absorption (analytical method).[15] The cerium atom position was 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. A full-matrix, least-squares program was used to refine the atomic parameters. 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. The scattering factors and anomalous dispersion terms used were taken from ref. 17. Details of the refinements and other crystallographic data are given in Table I, a list of the atomic coordinates is given in Table IV, and further data are given in the Supplementary Material.

$[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$. 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. A set of θ-2θ scan data was collected and corrected for Lorentz and polarization effects. An absorption correction was not made. The cerium atom position was 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. A full-matrix, least-squares program was used to refine the atomic parameters. 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. The scattering factors and anomalous dispersion terms used were taken from ref 17. Details of the refinements and other crystallographic data are given in Table I, and a list of the atomic coordinates is given in Table V. Further details are given in the Supplementary Material.

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Supplementary Material Available. Thermal parameters, Bond Lengths and Bond Angles, least-squares planes and structure factor tables (55 pages)

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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, °	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	$P2_1/c$	$P2_1/c$
volume, $Å^3$	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	MoKα	MoKα	CuKα	MoKα
wave-length (K$\bar{\alpha}$),Å	0.71073	0.71073	1.54180	0.71073
crystal size (mm)	.11x.13x.19	.15x.20x.35	.10x.17x.22	.16x.19x.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, °	4-50	4-50	4-120	12-45
scan width, °2θ	1.4+0.693tanθ	1.5+0.693tanθ	1.5+0.285tanθ	1.5+0.693tanθ
# of stds	3	3	3	3
# rflctns btwn stds	250	250	250	250
stds variations (%)	0.7,1.9,1.3	1.1,1.2,1.3	5.6,4.6,4.7	2.02,1.36,1.08

Table I, continued.

no. scan data	8184	6949	6744	12793
no. unique reflctns	4101	3853	3376	6398
# non-zero 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. parameters	343	223	171	415
R(non-zero wtd dat)[c]	0.041	0.046	0.050	0.047
Rw[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
mx/mn residual(e/A^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 MoKa 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] $R = \sum[||Fobs|-|Fcal||]/\sum[|Fobs|]$

[d] $Rw = \sqrt{\{\sum[w(|Fobs|-|Fcal|]^2/\sum(wFobs^2)\}}$

[e] σ_1 = error in observation of unit weight = $\sqrt{\{\sum(w[|Fobs|-|Fcal|]^2)/(no-nv)\}}$, where no is the number of observations and nv is the number of variables.

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

Atom	x	y	z	Beq
Ce1	0.13433(6)	0.12673(3)	0.62232(8)	3.13(2)
Ce2	-0.27165(6)	0.08491(3)	0.25927(8)	3.19(2)
C1	0.2460(15)	0.1660(8)	0.9940(19)	9.0(8)
C2	0.1462(13)	0.1476(8)	0.9152(18)	5.8(6)
C3	0.1074(15)	0.0983(6)	0.8995(15)	5.0(6)
C4	0.0063(14)	0.0959(8)	0.8261(16)	6.0(6)
C5	-0.0222(13)	0.1485(8)	0.7986(16)	5.5(6)
C6	0.0650(15)	0.1793(6)	0.8552(17)	5.1(6)
C7	0.3924(17)	0.2016(8)	0.6745(20)	10.6(9)
C8	0.2838(14)	0.2031(7)	0.5885(18)	5.2(6)
C9	0.2631(12)	0.1829(5)	0.4580(19)	4.4(5)
C10	0.1570(15)	0.1943(6)	0.4031(16)	5.3(6)
C11	0.1153(14)	0.2217(7)	0.5018(24)	6.3(7)
C12	0.1902(20)	0.2304(6)	0.6154(21)	7.2(8)
C13	0.2291(11)	0.0541(6)	0.3039(15)	5.4(5)
C14	0.2345(11)	0.0479(5)	0.4621(13)	3.5(4)
C15	0.1616(9)	0.0209(5)	0.5360(15)	3.4(4)
C16	0.1999(11)	0.0227(5)	0.6801(15)	4.1(4)
C17	0.2952(10)	0.0523(5)	0.6973(14)	3.8(5)
C18	0.3146(10)	0.0676(5)	0.5612(15)	3.6(4)
C19	-0.3224(15)	0.1094(9)	0.6339(22)	11.9(10)
C20	-0.3792(12)	0.1028(8)	0.4951(17)	5.0(6)
C21	-0.4163(15)	0.1390(6)	0.3992(22)	5.7(6)

Table II, continued.

C22	-0.4801(14)	0.1151(9)	0.2891(19)	6.3(7)
C23	-0.4759(14)	0.0624(9)	0.3192(23)	6.4(7)
C24	-0.4169(15)	0.0555(7)	0.4431(22)	6.0(7)
C25	-0.1363(12)	0.2176(6)	0.2057(16)	6.3(6)
C26	-0.1152(11)	0.1681(5)	0.2828(15)	4.1(5)
C27	-0.1334(11)	0.1562(6)	0.4195(15)	4.6(5)
C28	-0.0904(11)	0.1075(6)	0.4561(14)	4.5(5)
C29	-0.0421(9)	0.0898(6)	0.3396(17)	4.5(5)
C30	-0.0577(10)	0.1260(6)	0.2330(14)	4.2(4)
C31	-0.4012(15)	0.1709(8)	-0.0263(19)	9.9(8)
C32	-0.3501(14)	0.1179(6)	-0.0072(16)	5.1(6)
C33	-0.4024(13)	0.0702(10)	0.0030(17)	7.3(8)
C34	-0.3296(17)	0.0315(7)	0.0047(16)	6.0(6)
C35	-0.2300(15)	0.0547(8)	-0.0063(16)	5.9(7)
C36	-0.2426(13)	0.1075(7)	-0.0162(15)	4.9(6)

[a] Anisotropic thermal parameters, $Beq = \sum B_{ij} a_i^* a_j^* a_i \cdot a_j / 3$

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

Atom	x	y	z	B/Beq
Ce	0	0.15363(6)	0.250	3.88(2)[a]
Si1	-0.16325(10)	0.27712(28)	0.10783(16)	6.87(9)[a]
Si2	0.07888(11)	0.30451(25)	0.06659(15)	6.23(8)[a]
Si3	-0.12372(15)	-0.14254(28)	0.24956(27)	9.6(1)[a]
C1	-0.0360(4)	0.2939(14)	0.1091(12)	3.7(5)[a]
C2	0.0154(6)	0.2314(9)	0.1006(9)	4.5(5)[a]
C3	-0.0045(5)	0.1137(10)	0.0909(9)	4.9(5)[a]
C4	-0.0652(5)	0.1086(11)	0.0961(9)	5.7(5)[a]
C5	-0.0863(5)	0.2215(9)	0.1088(8)	4.1(5)[a]
C6	0.0377(6)	0.2598(21)	0.4054(14)	5.1(7)
C7	0.0763(5)	0.3030(12)	0.3609(7)	4.2(5)[a]
C8	0.0406(4)	0.3766(11)	0.3012(8)	4.7(5)[a]
C9	-0.0193(5)	0.3798(11)	0.3099(7)	4.7(5)[a]
C10	-0.0214(5)	0.3067(12)	0.3744(7)	4.0(5)[a]
C11	-0.0029(5)	-0.0944(12)	0.2373(12)	5.5(6)[a]
C12	-0.0458(6)	-0.0719(14)	0.2806(8)	5.9(6)[a]
C13	-0.0107(5)	-0.0298(14)	0.3549(8)	6.0(6)[a]
C14	0.0511(6)	-0.0301(14)	0.3539(8)	6.1(6)[a]
C15	0.0580(5)	-0.0710(16)	0.2805(8)	5.8(6)[a]
C16	-0.2151(9)	0.1685(18)	0.0330(13)	9.7(7)
C17	-0.1806(11)	0.4247(14)	0.0629(15)	11.6(8)
C18	-0.1871(11)	0.2591(25)	0.2003(11)	10.6(8)
C19	0.1951(11)	0.2075(22)	0.4873(10)	10.6(8)
C20	0.1911(9)	0.4356(12)	0.3886(14)	9.3(6)

Table III, continued.

C21	0.1803(8)	0.1993(17)	0.3047(9)	6.4(4)
C22	0.0425(11)	0.3629(22)	-0.0371(9)	8.5(9)
C23	0.1377(10)	0.1924(19)	0.0630(17)	8.4(9)
C24	0.1148(12)	0.4301(17)	0.1292(14)	10.6(8)
C25	-0.0374(10)	0.3225(23)	0.5428(8)	7.7(8)
C26	-0.1270(11)	0.1692(17)	0.4270(16)	8.2(8)
C27	-0.1324(10)	0.4293(18)	0.3949(16)	10.7(8)
C28	0.1111(10)	-0.3012(19)	0.2579(13)	17.7(7)
C29	0.1809(10)	-0.1267(19)	0.3474(14)	18.6(7)
C30	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 $B_{eq} = \sum B_{ij} a_i^* a_j^* \, a_i \cdot a_j / 3$

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

Atom	x	y	z	B/B_{eq}
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) *
C1	0.0911(21)	0.306(5)	0.2110(11)	10.0(8) *
C2	0.1484(25)	0.415(6)	0.238(3)	13.2(13)*
C3	0.145(3)	0.447(3)	0.309(4)	14.3(15)*
C4	0.0843(22)	0.352(5)	0.3306(20)	12.0(12)*
C5	0.0485(13)	0.2627(25)	0.2691(26)	11.0(10)*
C6	0.2888(20)	-0.066(3)	0.4109(19)	12.1(11)*
C7	0.307(3)	0.029(4)	0.4712(16)	13.7(14)*
C8	0.223(6)	0.095(4)	0.4698(23)	13.9(17)*
C9	0.1511(23)	0.030(6)	0.417(4)	14.5(16)*
C10	0.1861(23)	-0.064(3)	0.3786(13)	11.7(10)*
C11	0.4077(15)	0.293(3)	0.2793(13)	11.4(5)
C12	0.4428(18)	0.181(3)	0.3246(18)	13.1(6)
C13	0.4515(15)	0.2026(28)	0.3863(14)	11.2(5)
C14	0.4225(16)	0.3370(26)	0.3989(14)	11.9(6)
C15	0.3944(16)	0.395(3)	0.3284(15)	12.8(6)
C16	0.0481(28)	0.223(4)	0.1341(24)	17.8(10)
C17	0.3581(28)	-0.180(4)	0.3862(22)	18.0(10)
C18	0.393(4)	0.281(6)	0.186(3)	22.6(15)
C19	0.2356(11)	0.0189(22)	0.2102(10)	8.1(6) *
C20	0.2309(11)	-0.1488(19)	0.0990(11)	9.1(6) *
C21	0.2815(19)	-0.2867(26)	0.1352(17)	16.3(8)
C22	0.2954(20)	-0.086(4)	0.0501(17)	18.3(10)

Table IV, continued.

C23	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. * $B_{eq} = \sum B_{ij})a_i^* a_j^* \, a_i \cdot a_j/3$

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

Atom	x	y	z	B_{eq}
Ce	-0.00675(7)	0.25155(9)	0.11692(2)	2.38(2)
Si1	0.1439(4)	0.16121(27)	0.00107(17)	3.8(2)
Si2	0.3629(4)	0.3730(3)	0.17926(20)	4.8(2)
Si3	-0.3146(4)	0.10639(28)	0.12000(20)	4.3(2)
Si4	0.2312(4)	0.06448(28)	0.21413(17)	4.1(2)
Si5	0.0274(5)	0.31297(29)	0.27681(16)	4.5(2)
Si6	-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)
C1	0.2355(11)	0.2422(12)	0.1046(5)	2.7(4)
C2	0.1411(14)	0.2350(10)	0.0520(5)	3.1(6)
C3	0.0833(14)	0.3079(10)	0.0383(6)	3.0(5)
C4	0.1333(15)	0.3593(9)	0.0824(6)	3.3(5)
C5	0.2312(12)	0.3201(10)	0.1242(5)	2.6(5)
C6	-0.0390(19)	0.1185(11)	0.1766(8)	2.6(6)
C7	-0.1512(18)	0.1158(10)	0.1254(8)	2.8(7)
C8	-0.1049(16)	0.0982(8)	0.0862(7)	3.1(6)
C9	0.0298(15)	0.0894(8)	0.1081(6)	3.4(6)
C10	0.0734(15)	0.1011(8)	0.1652(5)	2.4(5)
C11	-0.0119(19)	0.3936(12)	0.1729(9)	3.1(7)
C12	-0.0438(14)	0.3309(9)	0.2025(5)	3.1(5)
C13	-0.1674(13)	0.3038(9)	0.1684(6)	3.3(5)
C14	-0.2054(16)	0.3472(10)	0.1199(6)	2.9(6)
C15	-0.1131(17)	0.4036(11)	0.1230(8)	2.6(6)
C16	0.2169(17)	0.2095(11)	-0.0417(6)	5.7(7)

Table V, continued.

C17	0.2425(16)	0.0750(11)	0.0320(7)	5.2(7)
C18	-0.0192(18)	0.1261(13)	-0.0427(7)	7.2(8)
C19	0.3472(27)	0.3719(17)	0.2472(12)	9.3(13)
C20	0.5166(20)	0.3218(16)	0.1937(12)	12.1(12)
C21	0.367(4)	0.4696(21)	0.1601(16)	23.2(22)
C22	-0.3209(17)	0.1057(12)	0.1883(7)	6.5(8)
C23	-0.4253(16)	0.1851(11)	0.0788(8)	6.3(7)
C24	-0.3760(15)	0.0130(11)	0.0850(8)	6.1(7)
C25	0.3662(18)	0.1383(13)	0.2401(8)	5.5(8)
C26	0.2167(17)	0.0223(11)	0.2755(6)	5.7(7)
C27	0.2838(21)	-0.0160(14)	0.1802(8)	8.2(9)
C28	0.1568(20)	0.2447(16)	0.2997(6)	9.1(8)
C29	-0.0980(21)	0.2748(13)	0.2993(7)	8.2(9)
C30	0.0875(21)	0.4071(11)	0.3129(7)	7.6(8)
C31	-0.1660(17)	0.4656(10)	0.0057(7)	5.7(7)
C32	-0.0167(23)	0.5626(10)	0.1044(7)	7.7(9)
C33	-0.2982(22)	0.5355(14)	0.0719(8)	8.4(10)
C34	-0.1963(12)	0.2553(14)	0.0177(6)	3.3(5)
C35	-0.3776(15)	0.2534(19)	-0.0780(6)	5.6(6)
C36	-0.4196(28)	0.1713(17)	-0.0893(10)	11.3(13)
C37	-0.4755(23)	0.3073(18)	-0.0764(9)	9.6(10)
C38	-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. * $B_{eq} = \sum B_{ij})a_i^* a_j^* \, \mathbf{a}_i \cdot \mathbf{a}_j/3$

Figure Captions

Figure I. 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 centroids 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 (ave.); Ce-Cp(1,2,4,6) = 2.54Å; Ce(1)-C(14-18) and Ce(2)-C(26-30) = 2.88(4)Å (ave.); Ce-Cp(3,5) = 2.62Å; 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° (ave.); Ce(1)-C(28) = 3.09(1)Å; Ce(2)-C(16) = 2.97(1)Å; Cp(1)-Ce-C(28), Cp2-Ce-C(28), Cp4-Ce-C(16), Cp6-Ce-C(16) = 100° (ave.)

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

Figure III. ORTEP drawing of $(\eta^5\text{-}MeC_5H_4)_3Ce$ $(CNCMe_3)$, 50% probability ellipsoids, Ce-C(Cp) = 2.79(3)Å, Ce-ring centroid = 2.55Å (ave.) ring centroid-Ce-ring centroid = 119° (ave.), Ce-C(19) = 2.71(2)Å, ring centroid-Ce-C(19) = 97° (ave.)

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

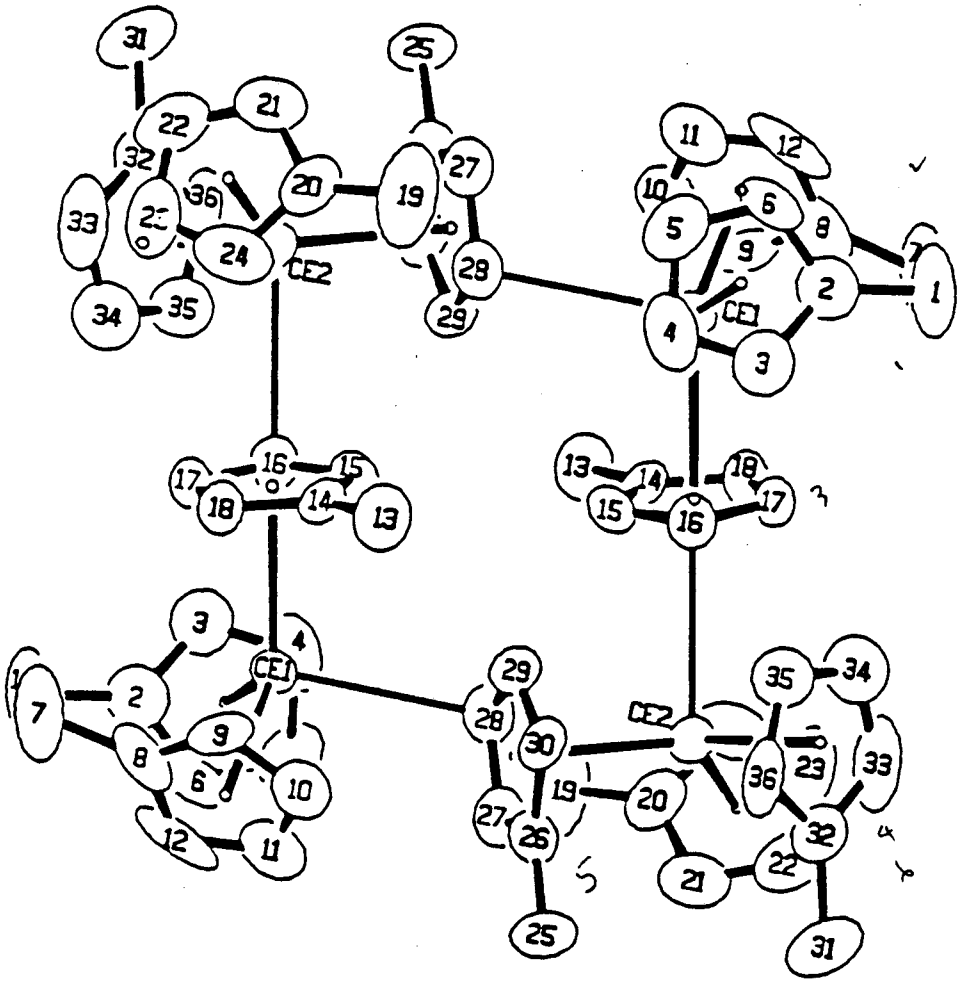
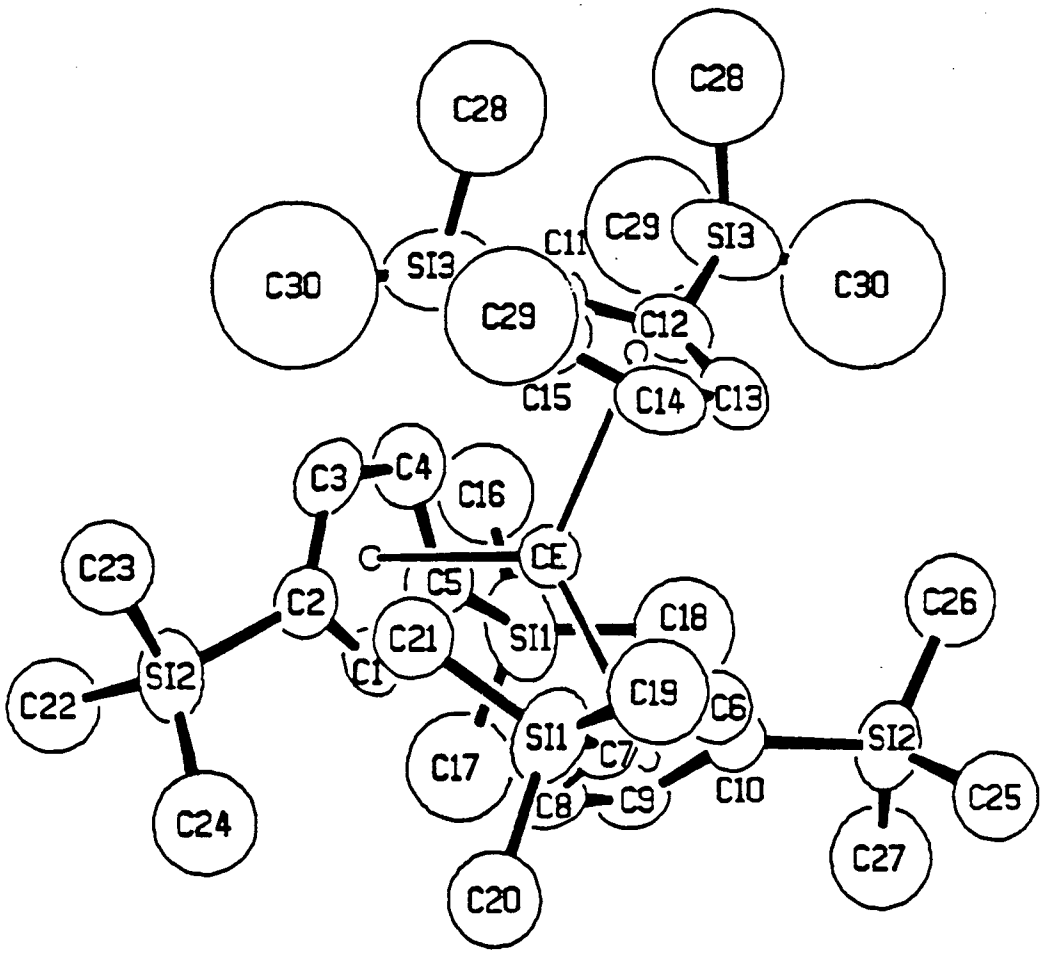


Figure 1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C18
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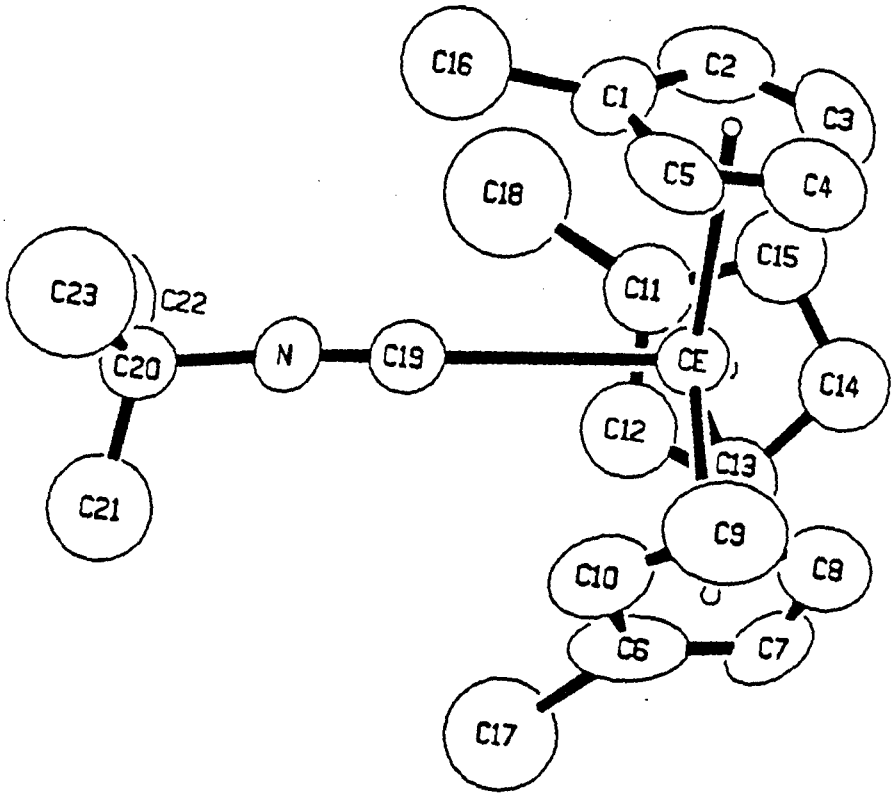
C27
C20

Figure 2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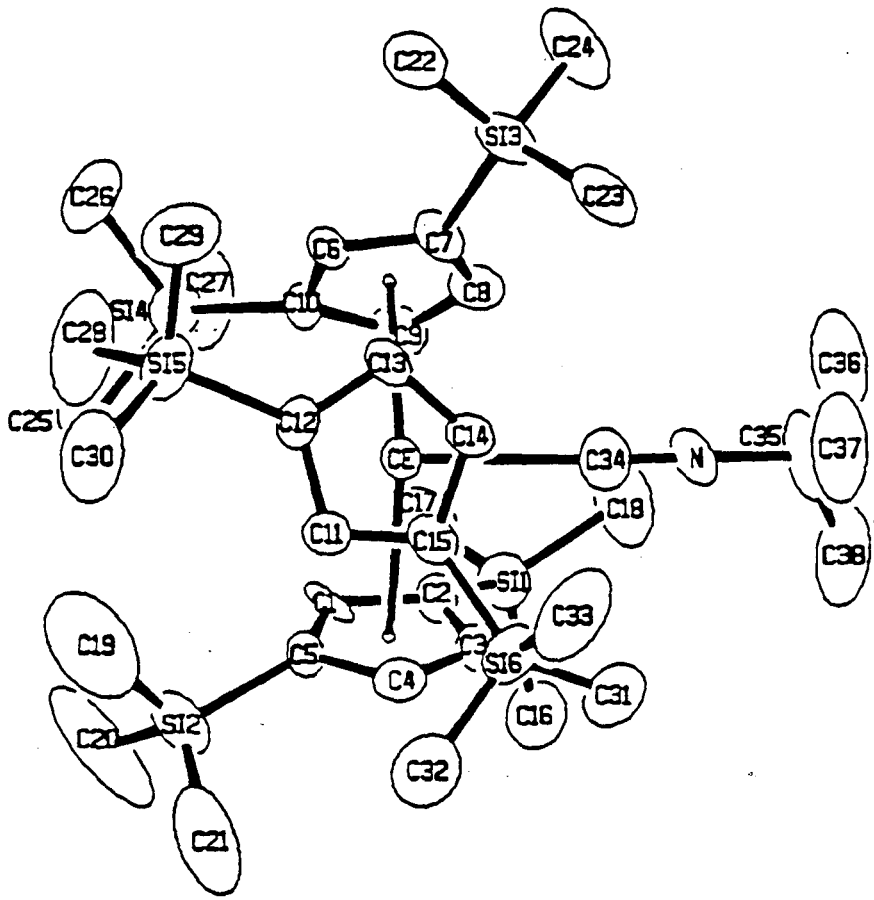
C17

Figure 3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C2
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C19
C5
C4
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SI6
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Figure 4

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