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Chemistry of Trivalent Cerium and Uranium Metallocenes: Reactions with Alcohols and Thiols

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Abstract

The trivalent cerium metallocene, $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$, reacts with alcohols, HOR (R = CHMe₂ or Ph), or thiols, HSR (R = CHMe₂, or Ph), to give the dimers $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2$ ($\mu\text{-ER}$)₂ as shown by X-ray crystallography for the isopropoxide and isopropylthiolate derivatives. Crystals of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2$ ($\mu\text{-OCHMe}_2$)₂ are monoclinic, P2₁/c with $a = 11.962(4)$ Å, $b = 14.489(5)$ Å, $c = 12.384(5)$ Å, $\beta = 103.31(3)^\circ$, and $V = 2089$ Å³; the structure was refined by full-matrix least squares to a conventional R-factor of 0.028, 2874 data, $F^2 > 2\sigma(F^2)$. The Ce₂O₂ unit is planar and the geometry about the cerium atom is pseudotetrahedral and the geometry is planar about the oxygen atom. Crystals of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2$ ($\mu\text{-SCHMe}_2$)₂ are also monoclinic, P2₁/n with $a = 14.255(9)$ Å, $b = 13.585(9)$ Å, $c = 11.265(7)$ Å, $\beta = 96.02(5)^\circ$, $V = 2170$ Å³; the structure was refined by full-matrix least squares to a conventional R-factor of 0.028, 2899 data, $F^2 > 2\sigma(F^2)$. The Ce₂S₂ unit is planar and the geometry about cerium is pseudotetrahedral though the geometry is pyramidal at sulfur so that the isopropyl groups are anti relative to the Ce₂S₂ ring. Methanol or water give an insoluble solid, presumably Ce(OMe)₃ or Ce(OH)₃, whereas HECMe₃ (E = O or S) do not react with $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ but the thiol does react with the sterically less bulky metallocene, $(\text{MeC}_5\text{H}_4)_3\text{Ce}$ (thf) to give $(\text{MeC}_5\text{H}_4)_4\text{Ce}_2$ ($\mu\text{-SCMe}_3$)₂. The pK_a's (H₂O) of the organic acids generally predict the thermodynamic outcome of the proton exchange reactions though the latter set of experiments show that kinetic (i.e., steric) factors play a role. The uranium metallocene, $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$, reacts with HSPH at low temperature to give isolable $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{U}_2$ ($\mu\text{-SPh}$)₂ which rearranges in solution to the monomeric, tetravalent species $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USPh}$ and unidentified material. The dimeric intermediate cannot be detected with the sterically smaller metallocene, $(\text{MeC}_5\text{H}_4)_3\text{U}$ (thf), as only $(\text{MeC}_5\text{H}_4)_3\text{UER}$ (ER = OMe, OCHMe₂, OPh, and SCHMe₂) is isolated.

Binary alkoxide derivatives of the 4f-transition metals (lanthanides) traditionally have been prepared by the exchange reaction of a metal halide with either an alkali metal derivative of an alcohol, an alcohol in ammonia, or reaction of the metal with an alcohol.¹ These synthetic methods are not without difficulties due to halide or oxide contamination as well as formation of anionic compounds.² Cyclopentadienylmetal alkoxides have been prepared by metathetical exchange reactions, though difficulties with oxide or halide contamination often makes isolation of pure compounds difficult.³ A clean synthesis of cyclopentadienyl derivatives such as $(\text{Me}_5\text{C}_5)_2\text{Lu}(\text{OCMe}_3)(\text{thf})$, from $(\text{Me}_5\text{C}_5)_2\text{LuMe}_2\text{Li}(\text{thf})_2$ and t-butylalcohol,^{4a,b} and $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OR})$, from $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and diorganoperoxides,^{4c} are useful when the appropriate starting materials are available. Binary thiolates of the lanthanide elements have not been described,⁵ though several cyclopentadienyl derivatives such as $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SR})(\text{NH}_3)$, prepared from $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{NH}_3)_2$ and R_2S_2 and $(\text{Me}_5\text{C}_5)_2\text{Lu}(\text{SCMe}_3)_2\text{Li}(\text{thf})_2$, prepared from the thiol and $(\text{Me}_5\text{C}_5)_2\text{LuMe}_2\text{Li}(\text{thf})_2$, have been isolated.^{4a,b} In addition, $[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Eu}_2(\mu\text{-SCMe}_3)_2$ has been isolated from $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_3$ and the thiol,^{6a} and cerium silylamides have been used to prepare several cerium phenoxides.^{6b} Recently, $(\text{Me}_5\text{C}_5)_2\text{Ce}_2(\text{OCMe}_3)_2(\mu\text{-OCMe}_3)_2$ has been prepared from $(\text{Me}_5\text{C}_5)_2\text{CeCH}(\text{SiMe}_3)_2$ and Me_3COH .^{6c}

It is apparent that there is no generally applicable synthetic route to cyclopentadienyl lanthanide alkoxides or thiolates. Since the equilibrium acidity of many alcohols and thiols in water^{7a} is less than that of cyclopentadiene (pK_a in water is 16^{7c} and in dimethylsulfoxide, dmsO, is 18^{7b}), the reaction of binary metallocenes of the lanthanide metals should provide a general synthetic route to this class of compound. Indeed, this type of reaction has been used to prepare cyclopentadienyl halides, alkynyls, and acetylacetonate derivatives from the metallocenes and ammonium halides, acetylenes, and acetylacetone, respectively, though no alkoxides nor thiolates have been prepared by this route.⁸ It is difficult to use solution equilibrium acidity scales with absolute confidence since these scales depend upon the extent of hydrogen bonding and ion-pairing in solvents such as water^{7a} or dmsO,^{7b} particularly since the reactions of interest in this paper are done in hydrocarbon solvents. The acidity scale in water predicts the course of the reactions in the

experiments described in this paper more satisfactorily than those in dmso. This is illustrated by the observation that the pKa of MeOH in water is 15.5 and in dmso it is 29 and methanol does indeed react with the metallocenes discussed in this paper. The main reason for the large difference in acidity in these two solvents is that hydrogen bonding interactions in water between small, highly charged anions such as methoxide does not change much with change in size of the anion though the negative charge-dipole interaction substantially changes in solvents with high dielectric constants such as dmso. Since the cyclopentadienide anion is charge delocalized, the difference in solvation energies between it and, say, methoxide anion will vary enormously in solvents with high dielectric constants, such as dmso, whereas the hydrogen-bonding interactions in this pair of anions will not vary as much. This qualitative rationalization is consistent with the experimental results described in this paper and helps to understand the reasons for the greater utility of the acidity scale in water rather than that in dmso.

In this paper we describe the synthesis of several $(RC_5H_4)_4Ce_2(\mu-ER)_2$ derivatives, prepared from reaction of $(RC_5H_4)_3Ce$ and alcohols and thiols, and the extension of this synthetic method to the trivalent uranium metallocenes, which gives the tetravalent compounds $(RC_5H_4)_3UER$ as the final product.

Synthetic Studies

Addition of one molar equivalent of isopropanol [$pK_a(H_2O) = 17.1$] to $(Me_3CC_5H_4)_3Ce$ in hexane results in a series of color changes that go from purple to brown to green to yellow followed by precipitation of a yellow solid. Yellow crystals of $(Me_3CC_5H_4)_4Ce_2(\mu-OCHMe_2)_2$ may be isolated in good yield by crystallization of the yellow solid from toluene. Experimental details for the synthesis and characterization of this compound and all of the compounds described in this manuscript are in the Experimental Section and 1H NMR spectroscopic data are shown in Table I. The isopropoxide compound gives a dimeric molecular ion in the mass spectrum and a single crystal X-ray diffraction study shows that the compound is a dimer in solid state with bridging isopropoxide groups, Figure I. Phenol [$pK_a(H_2O) = 10.0$] behaves similarly, giving

yellow $(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeOPh}$ which presumably is dimeric, though we have been unable to observe a molecular ion in the mass spectrum and we have been unable to obtain crystals suitable for a X-ray diffraction study. Addition of MeOH [$\text{pK}_a(\text{H}_2\text{O}) = 15.5$] or H_2O to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ gives a white precipitate, presumably $\text{Ce}(\text{OMe})_3$ or $\text{Ce}(\text{OH})_3$ as, perhaps, its hydrated oxide and the starting material $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ as the only product isolated in low (30-50%) yield, eq. 1.

Further, Me_2CHOH , MeOH , or H_2O behave similarly with $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$, *viz.*, a white precipitate and $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$ are formed. From the color changes, it is apparent that $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$ reacts faster with a given alcohol than does $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ and the former also undergoes ligand redistribution reactions faster than does the latter. *t*-Butyl alcohol [$\text{pK}_a(\text{H}_2\text{O}) = 19.2$] does not react with $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ under reflux in toluene for five days.

Thiols also react with the cerium metallocenes by proton transfer. Addition of one molar equivalent of Me_2CHSH [$\text{pK}_a(\text{H}_2\text{O}) = 10.9$] to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ in hexane slowly gives a magenta colored solution from which magenta colored crystals of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$ may be isolated by crystallization from pentane. A dimeric molecular ion is observed in the mass spectrum and a X-ray study shows that the thiolate is dimeric in solid state with bridging thiolate groups, Figure II. Thiophenol [$\text{pK}_a(\text{H}_2\text{O}) = 6.6$] behaves similarly giving pink $(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{CeSPh}$ which is presumably dimeric though the mass spectrum gives, as the highest mass peak, an ion due to $[\text{M}-(\text{Ph})_2]^+$. Curiously, Me_3CSH [$\text{pK}_a(\text{H}_2\text{O}) = 11.2$] does not react with $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ though it does react with $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$ to give $(\text{MeC}_5\text{H}_4)_2\text{CeSCMe}_3$, which we assume is a dimer with bridging thiolate groups.

The observation that neither Me_3COH nor Me_3CSH react with $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$, though the thiol reacts with the sterically less congested metallocene $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{thf})$, seems to suggest that equilibrium acidities are not always a reliable measure of the extent of reaction and that kinetic factors play a role. This statement is deliberately vague since we do not know the pK_a of either $\text{Me}_3\text{CC}_5\text{H}_5$ or MeC_5H_5 though both will be poorer acids than C_5H_6 , nor do we know the

mechanism of the proton transfer reaction. Relative to mechanism, it has been shown that Cp_2Ni reacts with RSH in an associative, rate determining step followed by a fast proton transfer step.⁹ If we assume a similar mechanism in the cerium compounds, then steric effects in the transition state of an associative substitution mechanism will be important and the lack of reaction of Me_3CSH can be understood as a kinetic effect.

In solution the thiolate dimers undergo chemical exchange. This was shown by mixing the phenylthiolate and isopropylthiolate at room temperature in a 1:1 molar ratio in PhMe-d_8 in an NMR tube at 30°C . The resulting spectrum consists of resonances due to the individual thiolates, most easily monitored by the Me_3C resonance on each species in equal ratios at $\delta=5.06$ for $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2 (\mu\text{-SCHMe}_2)_2$ and $\delta=8.73$ for $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2 (\mu\text{-SPh})_2$ and a new Me_3C resonance at $\delta=7.21$, the intensity of which is twice that of each of the other Me_3C resonances. The other features in the spectrum may be assigned by assuming that it is a 1:1:2 mixture of the components shown in eq. 3. The area ratio

of the resonances due to the three species does not change with temperature and the resonances do not coalesce though the chemical shifts do change as expected for a paramagnetic compound. The ^1H NMR experiment shows that the thiolates do exchange bridging ligands in solution and that once chemical equilibrium is reached, the rate of chemical exchange is either fast or slow on the NMR timescale. The ^1H NMR data do not allow us to distinguish between a mechanism that involves dissociation of the dimers into two monomers then recombination or partial bridge opening followed by exchange then recombination.

The trivalent uranium metallocene $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ behaves different than the cerium metallocenes with alcohols and thiols. In the uranium case, the net result is oxidation of uranium as shown in eq. 3, where ER is OMe , OCHMe_2 ,

OPh, or SCHMe₂. The red (Me₃CC₅H₄)₃USPh derivative was prepared similarly. Experimental details are in the Experimental Section and ¹H NMR data are in Table I. Derivatives of the type Cp₃UER, where E is oxygen or sulfur, have been prepared previously by metathetical exchange reactions so this class of compound is not new though the synthetic reaction in eq. 3 is new.¹⁰ The different type of reaction shown by cerium and uranium metallocenes towards alcohols and thiols most likely reflects the case of oxidizing uranium, the U(IV)/U(III) couple is -0.63 V in aqueous acid whereas the Ce(IV)/Ce(III) couple is +1.74 V.¹¹ Oxidation of trivalent uranium metallocenes to tetravalent compounds has been observed previously; this electron transfer reaction is emerging as a general pattern whenever the resulting tetravalent metallocene is kinetically accessible.¹²

It is noteworthy that the isolated yield of the tetravalent uranium compounds never exceeds ca. 35%. Perhaps the low yields are due to some type of ligand substitution, redistribution reactions shown in eqs. 4, 5, 6. Equation 4 is

a proton transfer reaction analogous to that found in the cerium metallocenes described above and eqs. 5 and 6 show two types of valence disproportionation reactions which would account for the low yield of product; the fate of "(RC₅H₄)₂U" is unknown. An additional reaction, shown in eq. 7 is

not likely since we do not detect hydrogen evolution in the synthetic reaction and the yield of this hypothetical reaction will be higher than that found in the actual reaction.

In order to test these two sets of reactions, viz., the valence disproportionation reactions shown in eqs. 4, 5, 6 or the oxidation by hydrogen reduction reaction in eq. 7, we have done the following experiment. Addition of one molar equivalent of benzenethiol to (Me₃CC₅H₄)₃U in hexane at -25°C results in a color change from green to red and precipitation of a green solid from

the red mother liquor. The green solid was dissolved in toluene at -30°C and crystallized as dark green crystals from that solvent in an isolated yield of 24%. The green crystals were shown to be dimeric $(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{U}_2(\mu\text{-SPh})_2$ by elemental analysis and mass spectroscopy. It is noteworthy that the other uranium compounds reported herein all give monomeric molecular ions. The infrared spectrum of the dimeric uranium compound is virtually superimposable upon that of the cerium analogue, suggesting that the compounds have a similar structure. Dissolution of the green crystals in C_6D_6 followed by observation of the ^1H NMR spectrum shows two sets of $\text{Me}_3\text{CC}_5\text{H}_4$ resonances in a 9:2:2 ratio at δ -17.6, 6.28, -7.58 and δ 2.43, 3.64, -12.2. The former set of resonances was substantially broader, by ca. an order of magnitude, than the latter and the intensity of the former set diminished at the expense of the latter set of resonances with time, concomitant with a color change from green to red. The latter set of resonances is due to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USPh}$; the narrow linewidths are consistent with tetravalent uranium.^{12a} We interpret the NMR experiment in the following way: the initially formed green compound $(\text{Me}_3\text{CC}_5\text{H}_4)_2\text{USPh}$ which is a dimer, prepared by proton transfer according to eq. 4, undergoes a ligand and valence redistribution reaction, either as illustrated in eq. 5 or 6 to give the red isolated product, $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USPh}$, and a sub-valent uranium species which decomposes. Hence, the difference in behavior shown by trivalent uranium and cerium metallocenes with protic acids whose pK_a 's are similar to or less than that of C_5H_6 is due to the M(IV)/M(III) redox couple being more favorable for uranium than cerium in these metallocenes.

Structural Studies

An ORTEP diagram of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OCHMe}_2)_2$ is shown in Figure I and of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$ in Figure II. Positional parameters are in Tables II and III and crystal data are in Table IV. Both compounds are centrosymmetric; the isopropoxide crystallizes in space group $\text{P2}_1/\text{c}$ and the isopropylthiolate in space group $\text{P2}_1/\text{n}$. The Ce_2O_2 and Ce_2S_2 units are planar and the geometry at cerium in both compounds may be described as pseudotetrahedral. The geometry at oxygen in the isopropoxide is planar; since the two independent Ce-O-C(19) angles are

not equal, the geometry at oxygen is not trigonal planar. Planar geometry at oxygen is inevitably observed in bridging alkoxide compounds.¹³ On the other hand, the geometry at sulfur in the isopropylthiolate is pyramidal, since the angles about sulfur sum to 348°, and the isopropyl groups are in an anti-configuration relative to the Ce₂S₂ ring. This is also the usual geometry found in compounds in which the thiolate group bridges two metal centers.^{5,4a}

The two independent Ce-O distances in the isopropoxide are equal, the averaged distance being 2.371 ± 0.001 Å. The two Ce-S distances in the isopropylthiolate are, however, not equal, the individual distances are 2.870(2) Å and 2.894(2) Å, with the average being 2.882 ± 0.006 Å. It is difficult to find examples in the literature of two equivalent molecules that differ only in the identity of the bridging atom. In the gas phase structures of Me₄Al₂(μ-OCMe₃)₂^{14a} and Me₄Al₂(μ-SMe)₂,^{14b} the Al-S distance is 0.51 Å longer than the Al-O distance; exactly the difference found in the cerium molecules described in this paper. The longer Ce-S distance, relative to Ce-O, is responsible for the slight distortions of the coordination geometry that is apparent upon detailed comparison of the two compounds, see Figures I and II.

Experimental Section

All of the compounds were handled as previously described using techniques and instruments previously described.¹⁵

(Me₃CC₅H₄)₄Ce₂(μ-OCHMe₂)₂. To (Me₃CC₅H₄)₃Ce¹⁶ (1.78g, 2.96 mmol) dissolved in hexane (30 mL) was added, via syringe, isopropanol (0.23 mL, 3.0 mmol). The solution color gradually turned from purple to brown to green and finally to yellow, and a yellow precipitate was observed. The suspension was stirred for 6 h, then the solvent was removed under reduced pressure. The yellow solid was dissolved in toluene (50 mL), filtered, and the filtrate was concentrated to ca. 30 mL. Cooling the extract to -20°C for 3 hours, followed by cooling to -80°C yielded yellow micro-crystals (0.83g, 64%), m.p. 240-241°C. Anal. Calcd. for C₄₂H₆₆Ce₂O₂: C, 57.1; H, 7.53. Found: C, 56.9; H, 7.64. IR: 1270s (br), 1155m, 1110m, 1070w, 1048w,

1033w, 950m, 850w, 822m, 810w, 755s, 735m, 673m, 530w, 440w, 335m (br), 258w cm^{-1} . The E.I. mass spectrum showed a molecular ion at $M/e = 882$ amu. The molecular ion isotopic cluster was simulated: M/e (calcd.%, obsvd.%); 882 (100,100); 883 (46.9, 22.3); 884 (36.2, 10.3); 885 (13.6, 28.0).

$(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OPh})_2$. To $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ (0.70g, 1.4 mmol) dissolved in hexane (30 mL) was added phenol (0.13g, 1.4 mmol) dissolved in hexane (10 mL). The purple solution turned yellow upon addition with formation of a yellow precipitate. The suspension was stirred for 4 h, then the solvent was removed under reduced pressure. The yellow solid was extracted with toluene (45 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20°C afforded yellow crystals (0.33g, 50%), m.p. $258\text{-}260^\circ\text{C}$. Anal. Calcd. for $\text{C}_{48}\text{H}_{62}\text{Ce}_2\text{O}_2$: C, 60.6; H, 6.57. Found: C, 61.2; H, 6.59. IR: 1588s, 1575m, 1273m, 1222s, 1160m, 1150w, 1065m, 1048m, 1035m, 1015m, 975w, 915w, 890w, 835m, 818s, 810m, 760s, 735m, 720m, 692m, 672m, 567m, 448m, 350m, 262m cm^{-1} . The E.I. mass spectrum did not show a molecular ion at $M/e = 950$ amu; the observed parent ion was $M/e = 503$ which corresponds to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$.

$(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$. Isopropylthiol (1.00 mL, 10.8 mmol) was added, via syringe, to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{Ce}$ (1.70g, 3.37 mmol) dissolved in hexane (30 mL). The purple solution was stirred for 18 h during which time the color gradually turned to magenta. The solvent was removed under reduced pressure. The pink solid was dissolved in hexane (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C afforded magenta crystals (0.84g, 55%), m.p. $139\text{-}142^\circ\text{C}$. An additional 10-20% can be obtained by concentrating the mother liquor to ca. 7 mL and cooling to -20°C . Anal. Calcd. for $\text{C}_{42}\text{H}_{66}\text{Ce}_2\text{S}_2$: C, 55.1; H, 7.27; S, 7.00. Found: C, 55.3; H, 7.28; S, 6.95. IR: 1272m, 1248w, 1200w, 1152s, 1045m, 1038m, 970w, 910w, 820s, 753s, 672m, 605m, 452w, 353w, 260w cm^{-1} . The E.I. mass spectrum showed a molecular ion at $M/e = 914$ amu. The molecular ion isotopic cluster was

simulated: M/e (calcd.%, obsvd.%); 914 (100,100); 915 (48.4, 49.4); 916 (45.4, 44.6); 917 (18.1, 17.7); 918 (8.1, --).

(Me₃CC₅H₄)₄Ce₂(μ-SPh)₂. To (Me₃CC₅H₄)₃Ce (0.91 g, 1.8 mmol) dissolved in hexane (30 mL) was added, via syringe, thiophenol (0.12 mL, 1.7 mmol). After ca. one min a pink precipitate began to form in the purple solution. The mixture was stirred for 12 h, then the solvent was removed under reduced pressure. The pink residue was dissolved in toluene (30 mL), filtered, and the filtrate was concentrated to ca. 25 mL. Cooling the extract to -20°C afforded pink crystals that crumbled and collapsed to a powder when exposed to vacuum (0.61 g, 69%), m.p. 191-194°C. Anal. Calcd. for C₄₈H₆₂Ce₂S₂: C, 58.6; H, 6.34; S, 6.52. Found: C, 59.1; H, 6.47; S, 6.12. IR: 1570w, 1407w, 1300w, 1273m, 1200w, 1187w, 1165w, 1151m, 1120w, 1078m, 1060w, 1045m, 1038w, 1020m, 970w, 912w, 822m, 775m, 768s, 757mw, 740s, 720mw, 690s, 680m, 483w, 455w, 425w, 258m cm⁻¹. The E.I. mass spectrum did not give a molecular ion at M/e = 983 amu; the observed parent ion corresponds to (Me₃CC₅H₄)₄Ce₂S₂, M⁺ = 796 amu.

(MeC₅H₄)₄Ce₂(μ-SCMe₃)₂. To (MeC₅H₄)₃Ce(thf)¹⁵ (0.84 g, 3.4 mmol) dissolved in diethyl ether (40 mL) was added, via syringe, t-butylthiol (0.38 mL, 3.4 mmol). The solution gradually turned from yellow to brown then to purple. The solution was stirred for 12 h, then the solvent was removed in vacuo. The purple solid was extracted with hexane (2x30mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the extract to -20°C afforded purple crystals (0.31 g, 24%), m.p. 266-268°C (dec). Anal. Calcd. for C₃₂H₄₆Ce₂S₂: C, 49.6; H, 5.98. Found: C, 49.7; H, 5.81. IR: 1300w, 1232w, 1205w, 1168w, 1142s, 1060w, 1040w, 1028m, 970w, 928m, 850w, 820s, 765s, 618m, 588m, 390m, 325m, 250s, 220w cm⁻¹.

(MeC₅H₄)₃UOMe. Methanol (0.08 mL, 2.0 mmol) was added, via syringe, to (MeC₅H₄)₃U(thf)^{12a} (1.15 g, 2.10 mmol) dissolved in diethyl ether (30 mL). The red solution

slowly turned green after addition. The solution was stirred for 20 h, then the solvent was removed under reduced pressure. The green solid was dissolved in hexane (40 mL), filtered, and the filtrate was concentrated to ca. 10 mL. Cooling the extract to -20°C afforded green micro crystals (0.32g, 30%), m.p. $274\text{--}275^{\circ}\text{C}$ (turned brown at 120°C). Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{OU}$: C, 45.1; H, 4.78. Found: C, 44.8; H, 4.78. IR: 1260w, 1248w, 1168w, 1150w, 1070w, 1045w, 1030w, 970w, 930m, 890w, 820s (br), 760s, 608m, 422s, 330s, 225s cm^{-1} . The E.I. mass spectrum showed a molecular ion at $M/e = 506$ amu.

$(\text{MeC}_5\text{H}_4)_3\text{UOCHMe}_2$. This compound was prepared from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and isopropanol in a manner similar to that used to prepare the methoxide, above, and crystallized as flaky-green crystals in 37% yield from hexane (-20°C), m.p. $196\text{--}200^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{28}\text{OU}$: C, 47.2; H, 5.28. Found: C, 47.0; H, 5.11. IR: 1330m, 1240w, 1160m, 1130s, 1065w, 1045m, 1035m, 1030m, 990s, 930w, 885w, 842s, 820m, 760s, 605m, 550s, 450m, 421m, 330s, 228s cm^{-1} . The E.I. mass spectrum showed a molecular ion at $M/e = 534$ amu.

$(\text{MeC}_5\text{H}_4)_3\text{UOPh}$. This compound was prepared in a manner similar to that used to prepare the methoxide, above, and crystallized as green crystals from hexane (-20°C) in 34% yield, m.p. $127\text{--}128^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{24}\text{H}_{26}\text{OU}$: C, 50.7; H, 4.61. Found: C, 50.6; H, 4.53. IR: 1580s, 1300w, 1258s, 1158m, 1150w, 1065w, 1049w, 1029w, 1018w, 995w, 973w, 931w, 884w, 861s, 845w, 838w, 812w, 775m, 762s, 720m, 690m, 600m, 520w, 442w, 337w, 238w cm^{-1} . The E.I. mass spectrum showed a molecular ion at $M/e = 569$ amu.

$(\text{MeC}_5\text{H}_4)_3\text{USCHMe}_2$. The thiolate was prepared from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and isopropylthiol in a manner similar to that used to prepare the methoxide, above, and crystallized as golden-brown flakes from hexane (-20°C) in 27% yield, m.p. $121\text{--}123^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{21}\text{H}_{28}\text{SU}$: C, 45.8; H, 5.13; S, 5.82. Found: C, 44.8; H, 5.13; S, 5.31. IR: 1305w, 1260w, 1235w, 1142m, 1070w, 1045w, 1032m, 972w, 928w, 890w, 863m, 851m, 847m, 795m, 775s, 720s, 624m,

605m, 570w, 440mw, 363mw, 341m, 331m, 242m cm^{-1} . The E.I. mass spectrum showed a molecular ion at $M/e = 550$ amu.

(Me₃CC₅H₄)₃USPh. To (Me₃CC₅H₄)₃U (1.07g, 1.76 mmol) dissolved in hexane (30 mL) was added, via syringe, thiophenol (0.18 mL, 1.8 mmol). The green solution turned red and a light red-brown precipitate formed. The solution was stirred for 5 h, then the solvent was removed under reduced pressure. The red solid was extracted with hexane (30 mL), filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the extract to -20°C afforded red crystals (0.28g, 22%), m.p. 142-143°C. Anal. Calcd. for C₃₃H₄₄SU: C, 55.8; H, 6.24; S, 4.51. Found: C, 52.7; H, 6.32; S, 4.65. IR: 1575m, 1300w, 1272m, 1198w, 1168w, 1155ms, 1070mw, 1052w, 1040w, 1021m, 970m, 838m, 798m, 788m, 772ms, 765s, 739s, 720m, 698m, 678mw, 611m, 482w, 418w, 238mw cm^{-1} . The E.I. mass spectrum showed a weak parent ion at $M/e = 710$ amu.

(Me₃CC₅H₄)₄U₂ (μ -SPh)₂. To (Me₃CC₅H₄)₃U (1.07g, 1.78 mmol) dissolved in hexane (15 mL) and cooled to -25°C was added, via syringe thiophenol (0.18 mL, 1.8 mmol). The solution color turned from green to red upon addition. After ca. 2 min a green precipitate began forming. The suspension was stirred for an additional 15 min, then the precipitate was allowed to settle. The hexane was removed by filtration and the remaining green microcrystalline solid was washed with hexane (2x10 mL, -25°C). The solid was extracted with toluene (45 mL, -30°C). This caused the solution color to become red. The solution was filtered, and the filtrate was concentrated to ca. 30 mL. Cooling to -20°C afforded dark green crystals (0.25g, 24%), m.p. 112-113°C (dec). Anal. Calcd. for C₄₈H₆₂S₂U₂: C, 48.9; H, 5.30; S, 5.44. Found: C, 48.5; H, 5.05; S, 4.24. IR: 1570m, 1405w, 1300w, 1272m, 1200w, 1186w, 1165w, 1150m, 1118w, 1075m, 1062w, 1038m, 1018m, 970w, 912mw, 845w, 821m, 812w, 772m, 763s, 757mw, 740s, 718mw, 690s, 672m, 481mw, 453w, 424w, 239mw cm^{-1} . ¹H NMR (C₆D₆, 28°C): 6.28 (4H, $\nu_{1/2} \approx 50$ Hz), -0.87 (1H), -1.92 (2H, d, $J=6.8$ Hz), -7.58 (4H, $\nu_{1/2} \approx 58$ Hz), -17.63 (18H, $\nu_{1/2} \approx 13$ Hz), -21.07 (2H). The NMR solution color gradually turned red with time. The ¹H NMR spectrum

contained resonances due to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{USPh}$; the integrated intensity of the latter resonances grew with time relative to those of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{U}_2(\mu\text{-SPh})_2$.

$(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{U}$. t-Butyllithium (0.52 mL of a 2.5 M pentane solution, 1.3 mmol) was added to $(\text{Me}_3\text{CC}_5\text{H}_4)_3\text{UCl}^{17}$ (0.85g, 1.3 mmol) in tetrahydrofuran at -70°C . An immediate color change from brown to red was observed. The solution was allowed to warm to room temperature and the green solution was stirred at that temperature for 1 h. The volatile material was removed under reduced pressure and the green residue was extracted with hexane (10 mL). The extract was filtered, the volume of the filtrate was decreased to ca. 5 mL; cooling to -80°C afforded dark green crystals in 90% (0.72g) yield, m.p. $80\text{--}81^\circ\text{C}$. IR: 3080w, 1274s, 1258m, 1198m, 1187w, 1150s, 1040s, 1015m, 901m, 802s, 750vs, 695w, 665m, 455m cm^{-1} . The E.I. mass spectrum contained a molecular ion at 601 amu, though satisfactory elemental analysis could not be obtained. ^1H NMR (C_6D_6 , 29°C): -21.0 (9H, $\nu\ 1/2 = 7\text{Hz}$), -24.2 (2H, $\nu\ 1/2 = 16\text{Hz}$), 9.04 (2H, $\nu\ 1/2 = 16\text{Hz}$).

X-Ray Studies. Air sensitive crystals of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)$, (I) with dimensions $0.22 \times 0.25 \times 0.25$ mm, and $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OCHMe}_2)_2$, (II) with dimensions $0.18 \times 0.15 \times 0.30$ mm were sealed inside 0.3-mm quartz capillaries. A modified Picker FACS-I automated diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation [$\lambda(\text{K}\alpha_1) = 0.70930 \text{ \AA}$, $\lambda(\text{K}\alpha_2) = 0.71359 \text{ \AA}$] was used to collect $\theta\text{--}2\theta$ scan data, 7663 and 7397 scans for the thiolate (I) and the alkoxide (II), respectively, to a 2θ limit of 50° using a scan width of $(1.50 + 0.693 \tan \theta)^\circ$ for (I) and $(1.40 + 0.693 \tan \theta)^\circ$ for (II) on 2θ . Three standard reflections were measured every 250 reflections; the intensities decayed 2% for (I) and 6% for (II) and were corrected accordingly. The data were corrected for Lorentz and polarization effects and absorption (analytical method);¹⁸ the absorption corrections ranged from 1.23 to 1.36 for (I) and from 1.34 to 1.50 for (II).

Cerium positions were located with the use of three dimensional Patterson maps; subsequent least-squares refinements and electron density maps revealed the location of the other

atoms. The structure was refined by full-matrix least-squares using anisotropic thermal parameters on the non-hydrogen atoms, with the exception of the disordered C19 in (II). The estimated positional parameters of the hydrogen atoms on the cyclopentadienyl rings and the hydrogen atom on C19 of (I) were included with isotropic thermal parameters, but were not allowed to vary. The central isopropoxide carbon atom, C19 of (II), refined with anisotropic thermal parameters to a long ellipsoidal shaped atom which strongly suggested disorder; this atom was assumed to be disordered and refined as two isotropic half-atoms. Scattering factors¹⁹ were adjusted for anomalous dispersion. The positional parameters in Tables II and III and crystal data are in Table-IV.

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Supplementary Material Available: Tables of thermal parameters, additional distances and angles, calculated hydrogen positions, the least-square planes, and the observed structure factors. Ordering information is given on any current masthead page.

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Table I.

¹H NMR Data for (RC₅H₄)₄Ce₂ (μ-ER)₂ and (RC₅H₄)₃UER

<u>Compound</u>	<u>δ CH(A)</u>	<u>δ CH(B)</u>	<u>δ R(X)</u>	<u>δ Ligand</u>
(MeC ₅ H ₄) ₄ Ce ₂ (μ-SCMe ₃) ₂	20.54 (≈ 80 Hz)	18.79 (≈ 90 Hz)	4.71 (26 Hz)	-22.22 (9H, 20 Hz)
(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-SCHMe ₂) ₂	21.85 (50 Hz)	20.51 (45 Hz)	-4.96 (17 Hz)	-12.37 (1H) -17.49 (6H, 20 Hz)
(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-SPh) ₂	25.73 (77 Hz)	19.23 (74 Hz)	-8.97 (18 Hz)	2.69 (2H) 1.15 (1H) -4.67 (2H)
(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-OCHMe ₂) ₂	30°C 18.4 (≈ 110 Hz)		0.98 (28 Hz)	-3.87 (1H, 25 Hz) -19.90 (6H, 67 Hz)
	70°C 16.90 (≈ 90 Hz)		0.84 (20 Hz)	-3.25 (1H, 17 Hz) -17.34 (6H, 34 Hz)
(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-OPh) ₂	21.52 (72 Hz)	14.98 (73 Hz)	-4.57 (16 Hz)	-3.41 (1H) -5.03 (2H, d, J=7 Hz) -16.23 (2H)
(MeC ₅ H ₄) ₃ UOMe	-10.60 (6H, 12Hz)	-22.41 (6H, 11Hz)	-0.32 (9H, 8Hz)	45.13 (3H, 12Hz)

Table I. continued.

	δ CH(A)	δ CH(B)	δ R(X)	δ Ligand
(MeC ₅ H ₄) ₃ UOCHMe ₂	-13.93	-23.31	-1.54	55.5 (1H, 20Hz)
	(6H, 8Hz)	(6H, 8Hz)	(9H, Hz)	15.7 (6H, 8Hz)
(MeC ₅ H ₄) ₃ UOPh	-4.75	-11.97	-3.11	4.72(2H, t, J=8Hz)
	(6H, 7Hz)	(6H, 7Hz)	(9H, 3Hz)	3.96 (2H, t, J=8Hz)
				-10.48 (1H)
(MeC ₅ H ₄) ₃ USCHMe ₂	-1.24	-8.77	-1.58	-19.7(6H, d, 7Hz)
	(6H, 7Hz)	(6H, 7Hz)	(9H, 3Hz)	-44.7(1H, m, 7Hz)
(MeC ₅ H ₄) ₃ UOC ₆ F ₅	3.55	-9.92	-5.14	_____
	(6H, 10Hz)	(6H, 9Hz)	(9H, 3Hz)	
(Me ₃ CC ₅ H ₄) ₃ USPh	3.64	-12.16	-2.43	-1.38 (2H)
	(6H, 7Hz)	(6H, 7Hz)	(27H, 4Hz)	-8.43 (1H)
				-21.2(2H, t, 8Hz)

The observed spectra show that A=A', B=B', and X=X' in the AA'BB'X₃ or AA'BB'X₉ spin systems of these complexes. All spectra were recorded in C₆D₆ and referenced relative to tetramethylsilane $\delta=0$ at 30°C with positive values being to high frequency. The A protons are arbitrarily assigned to those farthest downfield. Relative intensities and linewidths at half peak height are given in parentheses.

Table II.

Positional Parameters with Estimated Standard Deviations for $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$

Atom	x	y	z
Ce	0.36143(2)	0.02427(2)	0.06954(2)
S	0.47679(10)	0.10219(11)	-0.10508(15)
C1	0.1902(4)	0.0068(4)	-0.0762(5)
C2	0.1763(4)	-0.0424(4)	0.0311(5)
C3	0.2325(5)	-0.1288(5)	0.0402(6)
C4	0.2808(5)	-0.1327(5)	-0.0600(6)
C5	0.2553(4)	-0.0499(5)	-0.1328(5)
C6	0.1370(4)	0.0966(4)	-0.1275(6)
C7	0.2064(5)	0.1752(6)	-0.1656(8)
C8	0.0780(5)	0.1450(6)	-0.0358(7)
C9	0.0685(6)	0.0619(7)	-0.2368(7)
C10	0.3347(4)	0.0772(4)	0.3084(5)
C11	0.2828(5)	0.1468(5)	0.2320(5)
C12	0.3433(7)	0.2048(5)	0.1753(7)
C13	0.4356(7)	0.1719(7)	0.2164(7)
C14	0.4308(5)	0.0943(6)	0.2949(6)
C15	0.2961(6)	0.0080(5)	0.3997(6)
C16	0.3502(7)	-0.0934(6)	0.4000(8)
C17	0.1903(7)	-0.0108(8)	0.3722(10)
C18	0.3200(10)	0.0601(9)	0.5251(7)
C19	0.4952(8)	0.2314(6)	-0.1453(8)
C20	0.4834(10)	0.3030(7)	-0.0598(10)
C21	0.4591(7)	0.2513(6)	-0.2730(7)

Table III.

Positional Parameters with Estimated Standard Deviations for $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OCHMe}_2)_2$

Atom	x	y	z
Ce	0.13015(2)	0.02736(1)	0.11893(2)
O	-0.07319(29)	0.01614(23)	0.07023(27)
C1	0.2144(4)	-0.0744(4)	0.3244(4)
C2	0.3015(5)	-0.0764(5)	0.2674(5)
C3	0.2686(8)	-0.1272(6)	0.1708(6)
C4	0.1578(10)	-0.1597(4)	0.1659(5)
C5	0.1221(6)	-0.1250(4)	0.2595(5)
C6	0.2208(5)	-0.0383(4)	0.4399(4)
C7	0.3425(7)	-0.0017(6)	0.4901(6)
C8	0.2022(9)	-0.1212(6)	0.5152(5)
C9	0.1330(7)	0.0397(5)	0.4405(6)
C10	0.2505(5)	0.1819(4)	0.2328(5)
C11	0.1332(5)	0.2058(4)	0.2033(6)
C12	0.1042(5)	0.2176(4)	0.0874(6)
C13	0.2015(5)	0.1998(4)	0.0463(5)
C14	0.2942(4)	0.1793(3)	0.1368(4)
C15	0.4212(5)	0.1720(5)	0.1347(5)
C16	0.4620(8)	0.2627(7)	0.0960(10)
C17	0.4947(7)	0.1584(11)	0.2518(8)
C18	0.4428(8)	0.0939(10)	0.0633(15)
C19	-0.1733(9)	0.0316(7)	0.1099(8)
C19 ^a	-0.1241(12)	0.0405(9)	0.1563(11)
C20	-0.1804(5)	0.1337(4)	0.1448(5)
C21	-0.1858(6)	-0.0362(5)	0.1995(5)

Table IV.

Crystallographic Summary and Data Processing for

	(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-SCHMe ₂) ₂	(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-OCHMe ₂) ₂
a, Å ^a	14.255(9)	11.962(4)
b, Å	13.585(9)	14.489(5)
c, Å	11.265(7)	12.384(5)
β, °	96.02(5)	103.31(3)
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /c
volume, Å ³	2169.5	2088.7
d(calcd), g/cm ³	1.401	1.789
Z	2	2
temp (°C)	23	22
empirical formula	C ₄₂ H ₆₆ S ₂ Ce ₂	C ₄₂ H ₆₆ O ₂ Ce ₂
f(000)	932	900
fw	915.36	883.23
color	purple	yellow
abs coeff. cm ⁻¹	22.23	22.16
hkl limits	h-16,16;k0,16;l-13,13	h-14,14;k0,17;l-14,14
no. scan data	7665	7397
no. unique reflections	3847	3707
Rint ^b	0.019	0.021
no. non-zero weighted data	2899 [F ² > 2σ(F ²)]	2874 [F ² > 2σ(F ²)]
p ^c	0.060	0.050
extinction k ^d	1.63 x 10 ⁻⁷	1.99 x 10 ⁻⁷
max % extinction corr	12.6%	12.9%
no. parameters	208	207

Table IV continued.

	(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-SCHMe ₂) ₂	(Me ₃ CC ₅ H ₄) ₄ Ce ₂ (μ-OCHMe ₂) ₂
R (non-zero wtd dat) ^e	0.028	0.028
Rw ^f	0.046	0.042
R (all data)	0.045	0.044
Goodness of fit ^g	1.23	1.30
max shift/esd in least square	0.02	0.003
max/min in diff map (e/Å ³)	0.63,-0.40	0.69,-0.44

^a Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved MoK α components of 31 reflections ($20 < 2\theta < 34$) for the S containing compound and 33 reflections ($20 < 2\theta < 35$) for the O containing compound.

^b $R_{int} = \text{agreement factor between equivalent or multiply measured reflections} = \frac{\sum_i \sum_j [I(hkl)_j - \langle I(hkl) \rangle_i]}{\sum_i [I(hkl)_i]}$

^c In the least squares, the assigned weights to the data, $w = 1.0/[\sigma(F)^2]$, were derived from $\sigma(F^2) = [S^2 + (pF^2)^2]$, where S^2 is the variance due to counting statistics and p is assigned a value that adjusts the weighted residuals of the strong reflections to be comparable to the weak ones.

^d Simple extinction correction has the form $(F_{obs})_{corr} = (1+kI)F_{obs}$, where I is the uncorrected intensity and F_{obs} is the observed scattering amplitude.

^e $R = \text{Sum}[|F_{obs} - |F_{cal}||] / \sum(F_{obs})$.

^f $R_w = \sqrt{\{\sum[w*(|F_{obs}| - |F_{cal}|)^2] / \sum(w_x F_{obs}^2)\}}$

^g $\sigma_1 = \text{error in observation of unit weight} = \sqrt{\{\sum(w_x[|F_{obs}| - |F_{cal}|]^2) / (no-nv)\}}$, where no is the number of observations and nv is the number of variables.

Figure Captions

Figure I. ORTEP diagram of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-OCHMe}_2)$, 50% probability ellipsoids, C(19) is disordered and refined as two isotropic half-atoms, only one conformation of which is shown. $\text{Ce-C (ave.)} = 2.83 \pm 0.04 \text{ \AA}$; $\text{Ce-Cp (cent.)} = 2.58 \text{ \AA}$; $\text{Ce-O} = 2.373(3) \text{ \AA}, 2.369(3) \text{ \AA}$; $\text{Ce}\cdots\text{Ce} = 3.844(2) \text{ \AA}$; $\text{Ce-O-Ce} = 108.3(1)^\circ$; $\text{O-Ce-O} = 71.7(1)^\circ$; $\text{Ce-O-C(19)} = 143.3(5)^\circ, 108.2(5)^\circ$; $\text{Cp (cent.) -Ce-Cp (cent.)} = 128.5^\circ$.

Figure II. ORTEP diagram of $(\text{Me}_3\text{CC}_5\text{H}_4)_4\text{Ce}_2(\mu\text{-SCHMe}_2)_2$, 50% probability ellipsoids. $\text{Ce-C (ave.)} = 2.78 \pm 0.02 \text{ \AA}$; $\text{Ce-Cp (cent.)} = 2.52 \text{ \AA}$; $\text{Ce-S} = 2.870(2), 2.894(2) \text{ \AA}$; $\text{Ce}\cdots\text{Ce} = 4.449(2) \text{ \AA}$; $\text{Ce-S-Ce} = 101.06(6)^\circ$; $\text{S-Ce-S} = 78.94(6)^\circ$; $\text{Ce-S-C(19)} = 128.5(3)^\circ, 118.2(4)^\circ$; $\text{Cp (cent.) -Ce-Cp (cent.)} = 131^\circ$.

Figure I.

Figure II.

Supplementary Material Available for

Chemistry of Trivalent Cerium and Uranium Metallocenes: Reactions with Alcohols and Thiols

Stephen D. Stults, Richard A. Andersen, and Allan Zalkin

Thermal Parameters

Additional Bond Lengths and Distances

Data Processing Summary

Least-Squares Planes

Structure Factor Tables

24 pages

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