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# Preparation of $(Me_3CC_5H_4)_4M_2(\mu\text{-}Me)_2$ (M = Ce or U) and the Crystal Structure of the Cerium Derivative**

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**This manuscript is dedicated to Professor M.F. Lappert, one of the pioneers in synthesis of f-element compounds with bridging methyl groups, on the occasion of his 65th birthday.

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## Abstract

The bridging methyl compound, $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$, is prepared from $(Me_3CC_5H_4)_3Ce$ or $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ and MeLi in hydrocarbon solvents. The solid state x-ray structure of the cerium methyl [orthorhombic, $C_{mca}$, a = 23.477(4) Å, b = 9.599(2) Å, and c = 16.457(3) Å, V = 3708.7 Å$^3$, Z = 4] shows that the methyl groups bridge the two $(Me_3CC_5H_4)_2Ce$ units, such that the geometry at cerium is four coordinate and pseudo-tetrahedral, in a symmetrical fashion. The Ce-C(μ-Me) distance is 2.665(6) Å and the Ce-C(μ-Me)-Ce angle is 89.9(3)°. All of the hydrogen atoms were located and refined isotropically; C-H (ave.) = 0.85 Å and H-C-H (ave.) = 108° for the bridging methyl group. The geometry of the bridging methyl group in $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ is similar to that in $Me_4Al_2(\mu\text{-}Me)_2$. The uranium methyl is prepared in the reaction of $(Me_3CC_5H_4)_3U$ and MeLi. The cerium and uranium methyls are unstable in the gas phase and in benzene solution since they rearrange to $(Me_3CC_5H_4)_3M$ (M = Ce or U) and other materials.

Bridging alkyl groups in general and bridging methyl groups in particular have played an important role in organometallic chemistry [1]. Several compounds are known in which a methyl group bridges two identical metal fragments, some examples in the p- and d-block metals are $Me_4Al_2(\mu\text{-}Me)_2$ [2] $(allyl)_2Ni_2(\mu\text{-}Me)_2$ [3a], $(cod)_2Rh_2(\mu\text{-}Me)_2$ [3b], and $(Me_5C_5)_2Cr_2(\mu\text{-}Me)_2(Me)_2$ [3c]. In f-block metals, only a few compounds are known in which a methyl group bridges two lanthanide centers; two compounds have been characterized by X-ray crystallography, $Cp_4Yb_2(\mu\text{-}Me)_2$ [4a,4b] and $(Me_5C_5)_4Lu_2(\mu\text{-}Me)(Me)$ [4c,4d], and they have very different solid state structures. In the ytterbium compound the Yb-C-Yb angle is 86.6(5)° and the Yb-C distances are 2.49(2) and 2.54(2) Å. Although the hydrogen atoms on the bridging carbon atoms were not located in the X-ray structure, they were located and refined in the isomorphous yttrium compound [4a], yielding the conclusion that the bridging methyls in these two compounds are similar to those in $Me_4Al_2(\mu\text{-}Me)_2$. In contrast, the geometry of the bridging methyl group in $(Me_5C_5)_4Lu_2(\mu\text{-}Me)(Me)$ is very different since the Lu-C-Lu angle is 170(4)° and the Lu-C distances are very asymmetric, 2.44(1) and 2.76(1) Å [5]. Though the hydrogens were not located in the X-ray structure of the lutetium compound, the methyl group geometry is likely to be similar to that in $(Me_5C_5)_2Yb(\mu\text{-}Me)Be(Me_5C_5)$, where the hydrogens were located and refined, in which the idealized symmetry of the bridging methyl is $C_{3v}$ [6]. In contrast to the small number of compounds with methyl groups bridging two identical or similar f-block metal centers, a large number are known in which the methyl group bridges an f-block metal and a main-group metal [7].

The lack of suitable synthetic routes is probably responsible for the slow development of this field. Two principal synthetic routes have been developed, the metathetical exchange (eq. 1) [4a,4b] and the group displacement reaction (eq. 2) [4b]. Synthesis of $(Me_5C_5)_4Lu_2(\mu\text{-}Me)(Me)$ is a variation of the reaction in eq. 2, as shown in eqs. 3-5 [4c,4d].

$$Cp_4Yb_2(\mu\text{-}Cl)_2 + 2MeLi \rightarrow Cp_4Yb_2(\mu\text{-}Me)_2 + 2LiCl \qquad (1)$$

$$2Cp_2Yb(\mu\text{-}Me)_2AlMe_2 + 2py \rightarrow Cp_4Yb_2(\mu\text{-}Me)_2 + 2Me_3Al(py) \quad (2)$$

$$(Me_5C_5)_2Lu(\mu Me)_2AlMe_2 + thf \rightarrow (Me_5C_5)_2Lu(Me)(thf) + Me_3Al(thf) \quad (3)$$

$$(Me_5C_5)_2Lu(Me)(thf) + NEt_3 \rightarrow (Me_5C_5)_2Lu(Me)(NEt_3) + thf \quad (4)$$

$$2(Me_5C_5)_2Lu(Me)(NEt_3) \rightarrow (Me_5C_5)_4Lu_2(\mu Me)(Me) + NEt_3 \quad (5)$$

When applied to other lanthanide metals, the synthetic route symbolized by eq. 1 often yields addition compounds such as $Cp_2M(\mu\text{-}Me)_2Li$, particularly for the lighter lanthanides [7a-7j]. The synthetic route symbolized by eq. 2 has been applied to the lanthanides from dysprosium through ytterbium (including yttrium), but the method fails for the lighter lanthanides and scandium [4a,4b].

A potentially useful synthetic route is suggested by the work of Jonas, who has shown that d-transition metal metallocenes are useful synthetic reagents since the $C_5H_5$- anion can function as a leaving group [8]. Jonas' work suggests that the base-free metallocenes of the 4f-transition metals, $(RC_5H_4)_3M$, might be useful starting materials for synthesis of cyclopentadienyl metal methyls as illustrated in eq. 6.

$$(RC_5H_4)_3M + nR'Li \rightarrow ((RC_5H_4)_{3-n}MR'n + nLi(RC_5H_4) \quad (6)$$

The utility of the synthetic method is that the substituted cyclopentadienyl lanthanides are usually soluble in hydrocarbons and their lithium derivatives are usually insoluble in these solvents. The reaction of trivalent f-block metallocenes with lithium alkyls in ethereal solvents has been studied briefly by others. Addition of $LiCMe_3$ in $Et_2O$-thf to $Cp_3Nd(thf)$ gives $Cp_2NdCMe_3(thf)$ though other lithium alkyls do not give isolable compounds [9a]. Lithium alkyls and $Cp_3Pr$ give addition compounds, $LiCp_3PrR$, in thf [9b] as do some trivalent uranium metallocenes [9c]. In contrast, methyllithium and $(MeC_5H_4)_3U(thf)$ in presence of $Me_2NCH_2CH_2NMe_2$ give the anion $\{[(MeC_5H_4)_3U]_2Me\}^-$ in which the bridging methyl group is symmetrically disposed between the two heavy metal centers [9d].

The difficulty with the synthetic efforts just described is that the unsubstituted base-free metallocenes are not soluble in hydrocarbons though very soluble in thf and LiCp has

similar solubility properties. Hence, preparation of substituted-cyclopentadienyl compounds of the trivalent f-block metals that are soluble in hydrocarbons and the corresponding lithium compounds that are insoluble in hydrocarbons offers hope that the reaction illustrated in eq. 6 could be developed into a useful synthetic method. In this paper we describe the application of this strategy for the synthesis of $(Me_3CC_5H_4)_4M_2(\mu\text{-}Me)_2$, where M is Ce or U.

**Synthetic Studies.**

Addition of one molar equivalent of MeLi in diethyl ether to a hexane solution of $(Me_3CC_5H_4)_3Ce$ [10a] at 25°C gives a light colored precipitate (assumed to be $Me_3CC_5H_4Li$) and an orange colored solution. The orange solution yields orange crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$, see Figure 1, on cooling to -80°C in 65% yield. The alkyl can be prepared in a similar yield by reaction of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$ [10b] and MeLi; in this case, insoluble $LiSCHMe_2$ is formed. As the thiolate is made from $(Me_3CC_5H_4)_3Ce$ and $Me_2CHSH$, the direct reaction of the metallocene and MeLi is more convenient. Curiously, addition of MeLi to $(Me_3CC_5H_4)_3Ce$ at -25°C followed by warming to +25°C gives a yellow product (that contains lithium) that we have been unable to purify.

The cerium methyl melts at 125°C without decomposition, the electron impact mass spectrum is identical to that of $(Me_3CC_5H_4)_3Ce$ indicating that rearrangement occurs in the source of the mass spectrometer. A similar rearrangement occurs in solution. Dissolution of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ in $C_6D_6$ and monitoring the $^1H$ NMR spectrum at +30°C within 20 minutes of dissolution shows a spectrum that contains four resonances at δ21.8, 16.3, -5.8, and -48.2 in area ratio of 6:6:27:3 which are attributed to the two types of ring methyne, $Me_3C$, and the Ce-Me protons, respectively. During the course of a day at +30°C, these four resonances disappear and three new resonances appear at δ21.8, 7.83, and -9.57 in an area ratio of 2:2:9, respectively, due to $(Me_3CC_5H_4)_3Ce$ [10a]. During this time the solution becomes yellow and cloudy. The alkyl is redistributing its ligands in

solution (and in the mass spectrometer) according to the reaction shown in eq. 7 though the only observed

$$3(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2 \rightarrow 4(Me_3CC_5H_4)_3Ce + \text{"}Me_3Ce\text{"} \qquad (7)$$

resonances in the $^1H$ NMR spectrum are due to the methyl compound and the metallocene. Equation 7 is a minimum since the identity of the yellow precipitate is not necessarily "$Me_3Ce$". The half-time for the reaction in $C_6D_6$ or $C_6D_{12}$ is ca. 2h in each case indicating that the rate of ligand redistribution is not solvent dependent.

The ligand redistribution prevents a detailed examination of the reaction chemistry of the cerium methyl compound. As an example, the methyl reacts with dihydrogen, but the isolated product is the metallocene, $(Me_3CC_5H_4)_3Ce$. The detailed reaction chemistry and indeed even the constitution in solution of these alkyls must wait until we can learn how to prevent the ligand redistribution reaction.

The uranium metallocene, $(Me_3CC_5H_4)_3U$ [10b], behaves like its cerium analogue. Addition of methyllithium in diethyl ether to $(Me_3CC_5H_4)_3U$ in hexane at -20°C (the addition at 20°C gives a similar result) gives a green solution from which dark green crystals of $(Me_3CC_5H_4)_2UMe$, m.p. = 111°C, are obtained by cooling the hexane solution. The mass spectrum shows a molecular ion for the rearranged product, $(Me_3CC_5H_4)_3U$, as was observed in the case of the cerium compound. The solid state infrared spectra of the cerium and uranium compounds are superimposible so it is likely that both compounds have similar solid state structures, viz., dimers with the methyl groups bridging the two $(Me_3CC_5H_4)_2M$ centers.

A $C_6D_6$ solution of the uranium compound at 30°C shows resonances at δ8.08, 1.11, -20.0, and -139.3 in an area ratio of 6:6:27:3 due to the ring methyne, ring-t-butyl, and uranium methyl, respectively. With time the intensity of these resonances diminish and new resonances due to $(Me_3CC_5H_4)_3U$ and other unidentified resonances appear. As in the case of the cerium alkyl, the half-time is ca. 2h. In each of the methyls, we assign the most shielded (highest field) resonance to the methyl group bonded to the paramagnetic

metal center. Terminal methyl groups resonate in this general region [11]. In the present case, it is impossible to know if the chemical shifts are typical of bridging methyl groups since the ligand redistribution processes complicate all experiments designed to study solution equilibria, such as a dimer $\rightleftharpoons$ 2 monomer equilibrium, and the observed chemical shifts might be averaged values.

## X-Ray Crystallographic Study.

An ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ is shown in Figure I. Positional parameters are in Table I, thermal parameters are in Table II, some bond distances and angles are listed in Table III, and crystal data are in Table IV. The dimer crystallizes in the orthorhombic space group $C_{mca}$; the mirror plane passes through C(10) making the two top $Me_3CC_5H_4$ and two bottom $Me_3CC_5H_4$ groups equivalent, and the two-fold rotation axis is orthogonal to this plane, making the top and bottom $Me_3CC_5H_4$ groups equivalent. In this space group C(10) is located on a special position at -x, -y, -z so that only two of the hydrogen atoms, H(15) and H(15') attached to C(10) are related by symmetry; H(14) is unique. All of the non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms were located and refined isotropically.

The averaged Ce-C distance to the $Me_3CC_5H_4$ ligand is 2.80 ± 0.04 Å. The Ce to $Me_3CC_5H_4$ ring centroid distance is 2.53 Å and the ring centroid-Cerium-ring centroid angle is 130°. These bond distances and angles are identical, within 1σ, to the equivalent parameters found in $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}ECHMe_2)_2$, where E is oxygen or sulfur [10b]. The $Ce_2C(10)_2$ ring is planar; the Ce-C(10)-Ce and C(10)-Ce-C(10) angles are 91.1(3)° and 88.9(3)°, respectively, and square; the Ce-C(10) distance is 2.665(6) Å. The Ce···Ce distance is 3.805(2) Å, 0.04 Å longer than in $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}OCHMe_2)_2$ and 0.64 Å longer than in $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}SCHMe_2)_2$. The refined C-H distances on the $Me_3CC_5H_4$ ring range from 0.86(4) Å to 1.03(6) Å with an averaged value of 0.93 Å with an averaged deviation from the mean of 0.05 Å. In the bridging methyl group the two

unique C-H distances are 0.84(9) Å and 0.87(6) Å. The H-C-H angles are 101(5)° and 115(8)°, equal to within 3σ.

The structural parameters for compounds of the f-block metals with bridging methyl groups are shown in Table V. The structural values for $Me_4Al_2(\mu\text{-}Me)_2$ are included for comparison. The structural features for the bridging methyl groups in the two lanthanides and the two yttrium compounds are similar. As cerium is the largest metal center in the compounds in Table V the Ce-C (μ-Me) distance and the Ce-C(μ-Me)-Ce angle is the largest. The C-H distances and H-C-H angles in the compounds in which the hydrogen atoms were located and refined are also similar. Comparison of the structural parameters to those in $Me_4Al_2(\mu\text{-}Me)_2$ are particularly informative. The acute Al-C-Al angle and the relatively long Al-C bridging distance is generally accepted to be the structural criterion for three center-two electron bonding, viz.,the electron in the σ-molecular orbital of a methyl group combines with two σ-symmetry orbitals and an electron in two metal centers to give three new molecular orbitals, the lowest in energy combination that is occupied by the two electrons is metal-carbon bonding. The H-C-H angles in all three compounds are similar as are the C-H distances; these parameters are equal given the large uncertainty in the individual datum. In addition, the M-C(μ-Me)-M angles range from 76° to 91°, the largest being for the largest metal center, and they all are less than tetrahedral values.

It seems reasonable to conclude that the bridge bonding is similar in all of the compounds listed in Table V. This is not to say that the bonding is "covalent" in all of these compounds since an "ionic" bond model would likely give similar solid state crystallographic values; compare, for example, the solid state structures of tetrameric MeNa with that of MeLi [13]. Indeed X-ray crystallography is not a particularly good technique for answering detailed questions about electronic structure. Our intent is to say that the bond parameters are similar in the compounds in Table V and therefore the bonding is similar also.

An X-ray crystallographic study of a compound purported to be $(Me_3CC_5H_4)_4Nd_2(\mu\text{-}Me)_2$ was published after the work in this manuscript was completed [14]. Comparison between the cerium methyl and the purported neodymium methyl casts doubt on formulation of the latter as a pure compound. The neodymium compound was prepared by the reaction of $(Me_3CC_5H_4)_2NdCl$, generated from $NdCl_3$ and $NaMe_3CC_5H_4$ in tetrahydrofuran, with MeLi in diethyl ether. Although the microanalytical data indicated no chloride, the crystal used in the X-ray crystallographic study presents several difficulties that could be resolved by postulating that the sites purported to be occupied exclusively by the methyl groups are, in fact, partially occupied by methyl and chloride groups. In the neodymium compound the Nd-C(Me) distances are unequal, 2.70(2)Å and 2.53(2)Å. In the cerium compound the two crystallographically equivalent methyl groups have a Ce-C(Me) distance of 2.665(6)Å. Since neodymium is ca. 0.03Å smaller than cerium in a given coordination number, a Nd-C(Me) distance of 2.63Å is expected [15]. Indeed, the metal to ring carbon distances fulfill this expectation, Ce-C($Me_3CC_5H_4$) (ave.) = 2.80 ± 0.04Å and Nd-C($Me_3CC_5H_4$) (ave.) = 2.78 ± 0.05Å, but the large average deviation from the mean renders this comparison meaningless. The anisotropic thermal parameters for the bridging methyl groups in the neodymium structure are grossly different, the atom with the shorter distance of 2.53(2)Å has U eq. of 136(22) and the longer distance of 2.70(2)Å is associated with a smaller U eq. of 41(9). Further, all of the unique hydrogen atoms were located and refined isotropically in the cerium methyl whereras none of them were found in the neodymium structure.

One way to rationalize the unusual results attributed to the methyl groups in the neodymium compound is to postulate that the sites purported to be occupied by methyl groups are partially occupied by methyl and chloride groups. Therefore the site with the lower U eq. and longer Nd-C distance has more chloride than the other site explains the asymmetric distances and thermal parameters. The crystal structure of $(Me_3CC_5H_4)_4Nd_2(\mu\text{-}Cl)_2$ has not been reported, but the Ce-Cl and Pr-Cl distances in

$[(Me_3C)_2C_5H_3]_4Ce_2(\mu\text{-}Cl)_2$ and $(Me_3CC_5H_4)_4Pr_2(\mu\text{-}Cl)_2$ are 2.868(4)Å and 2.864(2)Å, respectively [16]. Since the radius of Nd is ca. 0.03Å less than that of Ce, a Nd-Cl distance of 2.84Å is expected. In addition, the Ce-Cl distance is ca. 0.2Å longer than the Ce-C(Me) distance in these two similar molecules, and it is to be expected that a similar pattern of bond distances would hold for neodymium as well. Indeed, inspection of a compilation of M-Cl and M-C(Me) bond distances shows the inequality, M-Cl > M-Me, is always true [17].

It seems that the problems with X-ray structure of $(Me_3CC_5H_4)_4Nd_2(\mu\text{-}Me)_2$ can be ascribed to a synthetic method that yields a compound in which the bulk, as judged by chloride analysis, is chloride-free but a single crystal that is not chloride-free. This difficulty can be surmounted by developing synthetic methods in which the halide is not the learning group; two approaches are described in this manuscript.

## Experimental Section

All of the compounds were handled as previously described by using techniques and instruments previously described [10].

**$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$**. Method A: To $(Me_3CC_5H_4)_3Ce$ [10a] (1.22g, 2.42 mmol) dissolved in hexane (25 mL) was added, via syringe, MeLi (2.60 mL of a 0.91 M solution in hexane, 2.4 mmol). The purple solution color immediately turned brown and then orange with the formation of a light-colored precipitate. The solution was stirred for 45 min, then the solvent was removed under reduced pressure. The orange solid was extracted with hexane (60 mL), filtered, and the filtrate was concentrated to ca. 45 mL. Cooling the extract to -20° for two hours followed by cooling to -80°C for 6-8 hours yielded orange crystals (0.64g, 67%), m.p. 125-129°C. Anal. Calcd. for $C_{38}H_{58}Ce_2$: C, 57.4; H, 7.35. Found: C, 57.6; H, 7.37. IR: 1300w, 1272m, 1195w, 1150m, 1045m, 1035m, 1012m, 970w, 910w, 848w, 815w, 808m, 760s, 750s, 720m, 672s, 465m, 450m, 367w, 350w, 295m, 255m $cm^{-1}$. $^1H$ NMR ($C_6D_6$, 30°C): 21.80 (4H, $\nu_{1/2}$ =

20 Hz), 16.28 (4H, $\nu_{1/2}$ = 20 Hz), -5.75 (18H, $\nu_{1/2}$ = 7 Hz), -48.23 (3H, $\nu_{1/2}$ = 70 Hz). This compound decomposes to $(Me_3CC_5H_4)_3Ce$ and an uncharacterized yellow solid in solution. The E.I. mass spectrum does not give a parent molecular ion; thehighest mass fragment corresponds to $(Me_3CC_5H_4)_3Ce$ (M/e = 503 amu).

Method B: To $[(Me_3CC_5H_4)_2CeSCH(Me)_2]_2$ [10b] (1.30g, 1.42 mmol) dissolved in hexane (50 mL) was added, via syringe, MeLi (3.12 mL of a 0.91M solution in diethyl ether, 2.8 mmol). The magenta solution color turned orange with the formation of a light-colored precipitate. The solution was stirred for 30 min, then the solvent was removed under reduced pressure. The orange solid was extracted with hexane (50 mL), filtered, and the filtrate was concentrated to ca. 40 mL. Cooling the extract to -20°C followed by cooling to -80°C afforded orange crystals (0.73g, 65%). All physical properties and analytical results were identical to those observed in Method A.

**$(Me_3CC_5H_4)_4U_2(\mu\text{-}Me)_2$**. To $(Me_3CC_5H_4)_3U$ [10a] (0.92g, 1.5 mmol) dissolved in hexane (30 mL) was added, via syringe, MeLi (1.68 mL of a 0.91M solution in hexane, 1.53 mmol). The green solution color lightened slightly upon addition, and a green precipitate formed. The suspension was stirred for 40 min, then the solvent was removed under reduced pressure. The dark green solid was extracted with hexane (25 mL), filtered, and the filtrate was concentrated to ca. 20 mL. Cooling the extract to -20° afforded dark green crystals (0.25g, 33%), m.p. 111-115°C. An additional 0.13g (17%) of product can be obtained by concentrating the mother liquor to ca. 10 mL and cooling to -20°C. Anal. Calcd. for $C_{38}H_{58}U_2$: C, 46.1; H, 5.90. Found: C, 46.5; H, 5.98. IR: 1300w, 1270m, 1195w, 1150m, 1041mw, 1032mw, 1012mw, 970w, 908mw, 848w, 812m, 806m, 760s, 750s, 718m, 667s, 468w, 450w, 350w, 288m, 245w $cm^{-1}$. $^1H$ NMR ($C_6D_6$, 30°C): 8.08 (4H, $\nu_{1/2}$ = 50 Hz), 1.11 (4H, $\nu_{1/2}$ = 50 Hz), -20.02 (18H, $\nu_{1/2}$ = 11 Hz), -139.25 (3H, $\nu_{1/2}$ = 68 Hz). This compound decomposes to $(Me_3CC_5H_4)_3U$ and other uncharacterized products in solution.

**X-Ray Crystallography**. A yellow, air-sensitive crystal of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ 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 $\theta$–$2\theta$ scan data was collected and corrected for absorption (analytical method [18]) and Lorentz and polarization effects. The cerium atom positions were obtained from three-dimensional Patterson maps and subsequent least-squares refinements and difference maps were used to determine the positions of the remaining atoms. All of the non-hydrogen atoms were assigned anisotropic thermal parameters with the full-matrix, least-squares refinement procedures. The hydrogen atom positional parameters were estimated and these were included in the least-squares refinement, and they were refined isotropically. No extinction correction was indicated and none applied. Details of the refinements and other crystallographic data are in Table IV. The observed and calculated structure factors are available on request from R.A. Andersen.

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Figure I. ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$. The non-hydrogen atoms represent 50% probability ellipsoids and the refined hydrogen atoms represent arbitrary sized spheres. The hydrogen atoms located on C(1,3, 4,5) are numbered H(1,2,3,4), those on C(7,8,9) are numbered H(5,6,7,8,9,10,11,12,13) and those on C(10) are numbered H(14,15).

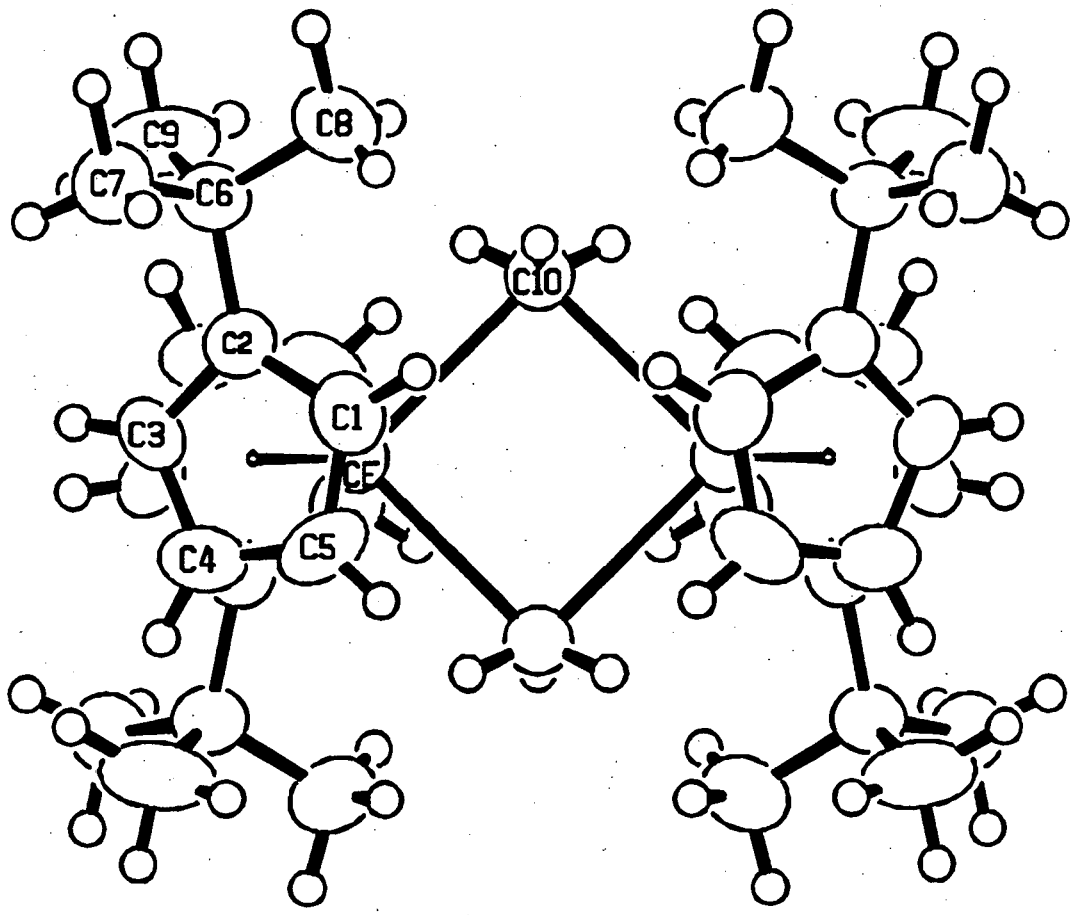

Table I. Positional Parameters with Estimated Standard Deviations for

$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$*

| Atom | x | y | z |
|---|---|---|---|
| Ce | 0.08104(1) | 0 | 0 |
| C1 | 0.08498(24) | 0.2954(4) | -0.0048(6) |
| C2 | 0.13239(24) | 0.2594(5) | 0.0438(3) |
| C3 | 0.17062(24) | 0.1890(5) | -0.0063(8) |
| C4 | 0.1478(3) | 0.1838(6) | -0.0848(4) |
| C5 | 0.0955(3) | 0.2472(6) | -0.0837(4) |
| C6 | 0.14466(26) | 0.3061(5) | 0.1312(3) |
| C7 | 0.1885(4) | 0.4234(9) | 0.1268(5) |
| C8 | 0.0908(4) | 0.3654(9) | 0.1716(5) |
| C9 | 0.1672(6) | 0.1854(10) | 0.1799(5) |
| C10 | 0 | 0.0334(8) | 0.1117(5) |
| H1 | 0.0541(17) | 0.343(4) | 0.0161(29) |
| H2 | 0.2050(19) | 0.158(4) | 0.004(6) |
| H3 | 0.1658(22) | 0.141(6) | -0.1298(29) |
| H4 | 0.0697(16) | 0.262(5) | -0.1197(24) |
| H5 | 0.1749(28) | 0.496(8) | 0.102(4) |
| H6 | 0.2247(23) | 0.390(6) | 0.106(4) |
| H7 | 0.1978(22) | 0.450(5) | 0.184(3) |
| H8 | 0.0678(29) | 0.289(7) | 0.183(4) |
| H9 | 0.0727(27) | 0.422(7) | 0.136(4) |
| H10 | 0.1018(25) | 0.404(6) | 0.227(4) |
| H11 | 0.2052(27) | 0.158(6) | 0.153(3) |
| H12 | 0.137(3) | 0.143(8) | 0.199(5) |
| H13 | 0.1752(20) | 0.213(5) | 0.233(4) |
| H14 | 0 | 0.119(10) | 0.123(6) |
| H15 | 0.0312(23) | 0.007(7) | 0.135(3) |

*Estimated standard deviations in this and subsequent tables are indicated in parentheses.

Table II. Thermal Parameters with Estimated Standard Deviations for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Ce | 3.380(14) | 2.431(11) | 3.768(14) | 0 | 0 | 0.34(5) |
| C1 | 4.77(23) | 2.61(14) | 5.59(27) | -0.07(17) | 0.6(6) | 0.5(4) |
| C2 | 4.25(26) | 2.76(19) | 3.94(23) | -0.38(21) | -0.16(25) | 0.18(21) |
| C3 | 3.81(21) | 3.56(17) | 4.4(4) | -0.61(17) | 1.1(5) | -0.3(4) |
| C4 | 6.5(4) | 3.90(28) | 3.54(29) | -1.49(27) | 0.59(29) | -0.08(24) |
| C5 | 6.8(4) | 3.73(24) | 4.21(29) | -1.74(28) | -1.9(3) | 1.26(23) |
| C6 | 4.80(27) | 3.39(22) | 4.12(26) | -0.06(22) | 0.10(24) | -0.71(20) |
| C7 | 5.4(4) | 5.9(4) | 6.3(4) | -1.6(3) | 0.0(4) | -2.6(4) |
| C8 | 6.5(5) | 6.5(4) | 5.5(4) | -1.3(4) | 1.3(3) | -1.9(3) |
| C9 | 11.5(8) | 6.6(4) | 3.8(4) | 1.4(5) | -1.1(4) | -0.1(3) |
| C10 | 4.0(4) | 3.1(5) | 3.9(3) | 0 | 0 | -0.20(26) |

| Atom | B (iso) | Atom | B (iso) | Atom | B (iso) |
|---|---|---|---|---|---|
| H1 | 3.5(11) | H6 | 6.9(18) | H11 | 6.0(17) |
| H2 | 4.9(12) | H7 | 6.3(16) | H12 | 8.4(30) |
| H3 | 4.1(14) | H8 | 9.9(24) | H13 | 5.9(16) |
| H4 | 2.4(10) | H9 | 7.3(22) | H14 | 8.9(33) |
| H5 | 8.7(25) | H10 | 7.2(17) | H15 | 9.3(18) |

The temperature factor has the form:

$T = -\Sigma\,(h_i h_j B_{ij} a_i^* a_j^*)/4$ for the anisotropic case and $T = -B(\sin\theta/\lambda)^2$ for the isotropic case.

**Table III. Bond Distances (Å) and Bond Angles (degrees) for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C-10 | - Ce | 2.665(6) | C4 | - C3 | 1.398(13) | C7 | - H6 | 0.97(5) |
| C4 | - Ce | 2.741(6) | C5 | - C4 | 1.370(8) | C7 | - H7 | 1.00(5) |
| C5 | - Ce | 2.765(6) | C9 | - C6 | 1.505(9) | C8 | - H8 | 0.93(7) |
| C3 | - Ce | 2.779(5) | C7 | - C6 | 1.528(9) | C8 | - H9 | 0.90(6) |
| C1 | - Ce | 2.838(4) | C8 | - C6 | 1.538(9) | C8 | - H10 | 1.01(6) |
| C2 | - Ce | 2.859(5) | C1 | - H1 | 0.92(4) | C9 | - H11 | 1.03(6) |
| C5 | - C1 | 1.401(10) | C3 | - H2 | 0.88(5) | C9 | - H12 | 0.87(7) |
| C2 | - C1 | 1.413(8) | C4 | - H3 | 0.95(5) | C9 | - H13 | 0.94(6) |
| C3 | - C2 | 1.394(10) | C5 | - H4 | 0.86(4) | C10 | - H14 | 0.84(9) |
| C6 | - C2 | 1.535(6) | C7 | - H5 | 0.87(7) | C10 | - H15 | 0.87(6) |
| Ce | - Ct[a] | 2.532 | Ce | - Ce | 3.805 | ave Ce | - C(Cp) | 2.80(5) |

[a]Ct represents the centroid of the cyclopentadienyl ring made up of atoms C1 through C5.

**Angles**

| | | | | | |
|---|---|---|---|---|---|
| C10-Ce -C10 | 88.9(3) | C2 -C1 -H1 | 122(3) | C6 -C8 -H9 | 109(4) |
| C2 -C1 -C5 | 107.7(6) | C5 -C1 -H1 | 130(3) | C6 -C8 -H10 | 108(4) |
| C1 -C2 -C3 | 107.0(6) | C2 -C3 -H2 | 130(7) | H8 -C8 -H9 | 110(6) |
| C1 -C2 -C6 | 127.4(6) | C4 -C3 -H2 | 122(7) | H8 -C8 -H10 | 104(5) |
| C3 -C2 -C6 | 125.1(7) | C3 -C4 -H3 | 125(3) | H9 -C8 -H10 | 119(5) |
| C2 -C3 -C4 | 108.5(6) | C5 -C4 -H3 | 127(3) | C6 -C9 -H11 | 105(3) |
| C3 -C4 -C5 | 108.4(6) | C1 -C5 -H4 | 117(3) | C6 -C9 -H12 | 106(5) |
| C1 -C5 -C4 | 108.4(6) | C4 -C5 -H4 | 134(3) | C6 -C9 -H13 | 111(3) |
| C2 -C6 -C7 | 107.3(5) | C6 -C7 -H6 | 112(3) | H11-C9 -H12 | 138(7) |
| C2 -C6 -C8 | 111.1(5) | C6 -C7 -H7 | 107(3) | H11-C9 -H13 | 108(5) |

| | | | | | |
|---|---|---|---|---|---|
| C2 -C6 -C9 | 109.9(5) | H5 -C7 -H6 | 115(6) | H12-C9 -H13 | 87(5) |
| C7 -C6 -C8 | 107.6(6) | H5 -C7 -H7 | 108(6) | H14-C10-H15 | 101(5) |
| C7 -C6 -C9 | 110.8(7) | H6 -C7 -H7 | 103(5) | H14-C10-H15 | 101(5) |
| C6 -C7 -H5 | 112(5) | C6 -C8 -H8 | 106(5) | H15-C10-H15 | 115(8) |
| Ce -C10 -Ce | 91.1(3) | Ct[a] -Ce -Ct | 130.4 | Ct -Ce -C10 | 108.3 |
| Ct -Ce -C10[b] | 106.5 | | | | |

[a]Ct represents the centroid of the cyclopentadienyl ring made up of atoms C1 through C5.

[b]Atom at -x, -y, -z.

The hydrogen atoms located on C(1,3,4,5) are numbered H(1,2,3,4), those on C(7,8,9) are numbered H(5,6,7,8,9,10,11,12,13), and those on C(10) are numbered H(14,15).

**Table IV. Crystallographic Summary and Data Processing for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$**

| | |
|---|---|
| a, Å[a] | 23.477(4) |
| b, Å | 9.599(2) |
| c, Å | 16.457(3) |
| cryst syst | orthorhombic |
| space group | Cmca |
| volume, $Å^3$ | 3708.7 |
| d(calcd), $g/cm^{-3}$ | 1.424 |
| Z | 4 |
| temp (°C) | 23.0 |
| empirical formula | $C_{38}H_{58}Ce_2$ |
| f(000) | 1608 |
| fw | 795.13 |
| color | orange |
| reflection rules | hkℓ : h+k = 2n; hkO: h = 2n; hOℓ : ℓ = 2n |
| x-ray | MoKα (graphite monochromated) |
| wave-length (Kα1,Kα2), A | 0.70930, 0.71359 |
| crystal size (mm) | 0.12 x 0.14 x 0.16 |
| crystal faces, dist (mm), face | ± (1 1 1) .062; ± (1 1-1) .074; ± (1-1-1) .069; |
| to origin inside crystal | ± (1-1 1) .080; ± (0 0 1) .060 |
| abs coeff, $cm^{-1}$ | 24.85 |
| abs corr range | 1.24-1.35 |
| cryst decay corr range | 0.96-1.02 |
| diffractometer | modified Picker FACS-1 |
| 2θ limits, ° | 5.0-55.1 |
| sinθ λ, min, max | 0.061, 0.651 |

Table IV (continued)

| | |
|---|---|
| hkl limits | h 0, 30; k -12, 12; ℓ 0, 21 |
| scan type | θ-2θ |
| scan width, ° | 1.50 + 0.693 x tan θ |
| no. of standards | 3 |
| no. reflections between stds | 1000 |
| variation of standards (%) | 2.92 0.57 0.72 |
| no. scan data | 4268 |
| no. unique reflections | 2204 |
| $R_{int}$[b] | 0.046 |
| no. non-zero weighted data | 1016 ($F^2 > 2\sigma(F^2)$) |
| p[c] | 0.020 |
| extinction k[d] | $1.2 \times 10^{-6}$ |
| max % extinction corr | 0.8% |
| no. parameters | 152 |
| R (non-zero wtd dat)[e] | 0.023 |
| Rw[f] | 0.020 |
| R (all data) | 0.109 |
| Goodness of fit[g] | 1.00 |
| max shift/esd in least-square | 0.08 |
| max/min in diff map ($e/A^3$) | 0.71, -0.75 |

(a) Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved MoKα components of 18 reflections ($22 < 2\theta < 30$).

(b) $R_{int}$ = agreement factor between equivalent or multiply measured reflections = Sum [I(hkl) - I(hkl)ave]/Sum[I(hkl)ave].

Table IV (continued)

(c) In the least-squares, the assigned weights to the data are $1.0/[\sigma(F)]^2$ 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 $(Fobs)corr = (1 + kI)Fobs$, where I is the uncorrected intensity and Fobs is the observed scattering amplitude.

(e) $R = \Sigma[|Fobs| - |Fcal|] / \Sigma|Fobs|$

(f) $Rw = \sqrt{\{\Sigma[w \times |Fobs| - |Fcal|]^2 / \Sigma(w \times Fobs^2)\}}$

(g) $\sigma_1$ = error in observation of unit weight = $\sqrt{\{\sigma(w \times [|Fobs| - |Fcal|]^2/(n_o-n_v)\}}$, where $n_o$ is the number of observations and $n_v$ is the number of variables.

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