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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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Abstract

The bridging methyl compound, $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$, has been 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 shows that the methyl groups bridge the two $(Me_3CC_5H_4)_2Ce$ units in a symmetrical fashion in such a way that the geometry at cerium is four coordinate and pseudo-tetrahedral. The Ce–C(μ-Me) distance is 2.665(6) Å and the Ce–C(μ-Me)–Ce angle is 89.9(3)°. All 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 was obtained from the reaction of $(Me_3CC_5H_4)_3U$ with MeLi. The cerium and uranium methyls are unstable in the gas phase and in benzene solution, since they rearrange to give $(Me_3CC_5H_4)_3M$ (M = Ce or U) and other materials.

1. Introduction

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 for 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]. For 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 $(Me_5C_5)_2Yb(\mu\text{-}Me)Be(Me_5C_5)$ (for which 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, metathetical exchange (eqn. (1)) [4a,4b] and the group displacement (eqn. (2)) [4b]. Synthesis of $(Me_5C_5)_4Lu_2(\mu\text{-}$

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* This paper 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.

* Reference number with asterisk indicates a note in the list of references.

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Me)(Me) is a variant of the reaction in eqn. (2), as shown in eqns. (3)–(5) [4c,4d].

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

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

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

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

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

When applied to other lanthanide metals, the synthetic route represented by eqn. (1) often yields addition compounds such as $Cp_2M(\mu\text{-}Me)_2Li$, particularly for the lighter lanthanides [7a–7j]. The route represented by eqn. (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 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's 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 eqn. (6).

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

The value of this method lies in the fact that the substituted cyclopentadienyl lanthanides are usually soluble in hydrocarbons and their lithium derivatives 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 products [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 $\{[(MeC_5H_4)_3U]_2\text{-}Me\}^-$ in which the bridging methyl group is symmetrically located 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 in which the corresponding lithium compounds are insoluble offers hope that the reaction illustrated in eqn. (6) could be developed into a useful synthetic method. In this paper we describe the application of this strategy for the synthesis of $(Me_3CC_5H_4)_4Me_2(\mu\text{-}Me)_2$, where M is Ce or U.

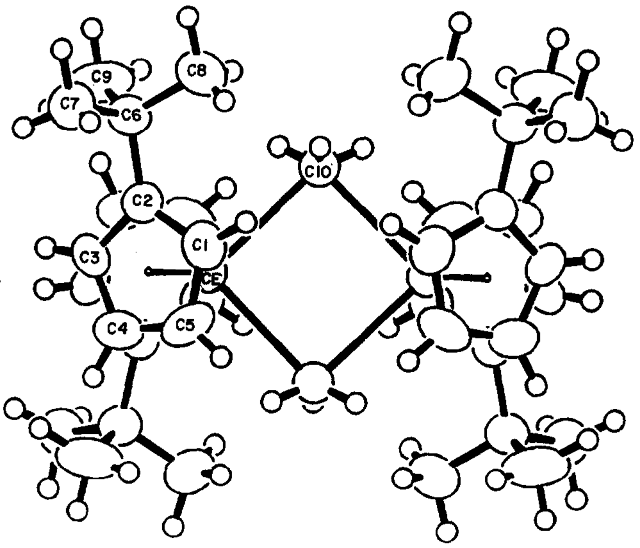

Fig. 1. ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$. The non-hydrogen atoms represent 50% probability ellipsoids and the refined hydrogen atoms represent arbitrary sized spheres. The hydrogen atoms located on C(1, 3, 4, 5) are numbered H(1, 2, 3, 4), those on C(7, 8, 9) are numbered H(5,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

2. 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 on cooling to −80°C yields orange crystals of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ (see Fig. 1) in 65% yield. The metal 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 (which 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

TABLE 1. Positional parameters with estimated standard deviations for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ [a]

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)

[a] Estimated standard deviations in this and subsequent tables are indicated in parentheses.

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. Dissolving $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ in C_6D_6 and monitoring the ^1H NMR spectrum at +30°C within 20 min of dissolution produce a spectrum that contains four resonances, at δ 21.8, 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 one day at +30°C, these four resonances disappear and three new resonances appear, at δ 21.8, 7.83, and −9.57, in an area ratio of 2:2:9, due to $(Me_3CC_5H_4)_3Ce$ [10a]. During this time the solution becomes yellow and cloudy. The alkyl is undergoing ligand redistribution in solution (and in the mass spectrometer) according to the reaction shown in eqn. (7) though the only observed resonances in the ^1H NMR spectrum are due to the methyl compound and the metallocene. Eqn. (7) is a minimum representation, 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.* 2 h in each case, indicating that the rate of ligand redistribution is not solvent dependent.

$$3(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2 \longrightarrow 4(Me_3CC_5H_4)_3Ce + \text{“}Me_3Ce\text{”} \quad (7)$$

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, $(Me_3CC_5H_4)_3Ce$. Study of the detailed reaction chemistry of these alkyls and, indeed, even determination of their constitution in solution, must await the finding of some way of preventing 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 which upon cooling yields dark green crystals of $(Me_3CC_5H_4)_2UMe$, m.p. = 111°C. 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 δ 8.08, 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 intensities 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.* 2 h. 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 whether 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 ⇌ 2 monomer equilibrium, and the observed chemical shifts may be averaged values.

3. X-Ray crystallographic study

An ORTEP diagram of $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$ is shown in Fig. 1. Positional parameters are shown in Table 1, some bond distances and angles in Table 2, and crystal data in Table 3. 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 average 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 1 σ, 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) 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) and 0.87(6) Å. The H–C–H angles are 101(5)° and 115(8)°, equal to within 3 σ.

The structural parameters for compounds of the f-block metals with bridging methyl groups are shown in Table 4; the values for $Me_4Al_2(\mu\text{-}Me)_2$ are included for comparison. The structural features of the bridging methyl groups in the two lanthanides and the two yttrium compounds are similar. As cerium is the largest metal atom in the compounds in Table 4 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 with 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 within the large uncertainty in the individual values. In addition, the M–C(μ-Me)–M angles range from 76° to 91°, the

TABLE 2. Bond distances (Å) and angles (degrees) for $(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$

C10–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(2)	ave Ce–C(Cp)	2.80(5)
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).

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 4. This is not to say that the bonding is "covalent" in all of them, since an "ionic" bond model would probably give similar solid state crystallographic values; compare, for example, the solid state structures

TABLE 3. 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
F.W.	795.13
Color	orange
Reflection rules	$hkl: h + k = 2n$; $hk0: h = 2n$; $h0l: l = 2n$
X-ray	Mo Kα (graphite monochromated)
Wave-length (Kα1, Kα2), Å	0.70930, 0.71359
Crystal size, mm	0.12 × 0.14 × 0.16
Crystal faces, dist (mm), face to origin inside crystal	± (1 1 1) 0.062; ±(1 1 −1) 0.074; ±(1 −1 −1) 0.069; ±(1 −1 1) 0.080; ±(0 0 1) 0.060
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
$\sin \theta$ λ, min, max	0.061, 0.651
hkl limits	h 0, 30; k −12, 12; l 0, 21
Scan type	θ–2θ
Scan width, °	$1.50 + 0.693 \cdot \tan \theta$
No. 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]	$1.2 \cdot 10^{-6}$
Max % extinction corr.	0.8%
No. parameters	152
R (non-zero wtd. dat.) [e]	0.023
R_w [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 Mo Kα components of 18 reflections ($22 < 2\theta < 30°$). [b] R_{int} = agreement factor between equivalent or multiply measured reflections $= \Sigma[I(hkl) - I(hkl)\text{ave}]/\Sigma[I(hkl)\text{ave}]$. [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 $(F_{obs})\text{corr} = (1 + kI)F_{obs}$, where I is the uncorrected intensity and F_{obs} is the observed scattering amplitude. [e] $R = \Sigma[|F_{obs}| - |F_{cal}|]/\Sigma|F_{obs}|$. [f] $Rw = \sqrt{\{\Sigma[w \cdot |F_{obs}| - |F_{cal}|]^2/\Sigma(w \cdot F_{obs}^2)\}}$. [g] σ_1 = error in observation of unit weight $= \sqrt{\{\sigma(w \cdot [|F_{obs}| - |F_{cal}|]^2)/(n_o - n_v)\}}$, where n_o is the number of observations and n_v is the number of variables.

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 intention is to say that the bond parameters are similar in the compounds in Table 4 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 gave no indication of the presence of chloride, the data from the crystal used in the X-ray crystallographic study presented 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) 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.* 0.03 Å smaller than cerium in a given coordination number, a Nd–C(Me) distance of 2.63 Å is expected [15]. Indeed, the metal to ring carbon distances fulfill this expectation, $Ce\text{-}C(Me_3CC_5H_4)$ (ave.) = 2.80 ± 0.04 Å and $Nd\text{-}C(Me_3CC_5H_4)$ (ave.) = 2.78 ± 0.05 Å, 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, whereas none of them were found in the neodymium structure.

As indicated above one way to rationalize the unusual results attributed to the methyl groups in the neodymium compound is to postulate that the sites assumed 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, which would account for 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) and 2.864(2) Å, respectively [16]. Since the radius of Nd is *ca.* 0.03 Å less than that of Ce, a Nd–Cl distance of 2.84 Å is expected. In addition, the Ce–Cl distance is *ca.* 0.2 Å 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 M–Cl is always longer than M–Me [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.

4. Experimental section

Experimental techniques and instruments were as previously described [10].

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

Method A: To a solution of $(Me_3CC_5H_4)_3Ce$ [10a] (1.22 g, 2.42 mmol) in hexane (25 ml) was added, from

TABLE 4. Bond distances and angles in $M_2(\mu\text{-}Me)_2$ compounds

Compound	M–C (Å)	M–C–M (deg)	C–M–C (deg)	C–H (ave.) (Å)	H–C–H (ave.) (deg)	Ref.
$(Me_3CC_5H_4)_4Ce_2(\mu\text{-}Me)_2$	2.665(6)	91.1(3)	88.9(3)	0.85	108	this work
$(C_5H_5)_4Yb_2(\mu\text{-}Me)_2$	2.51(4)	86.6(5)	93.4(5)	–	–	4b
$(C_5H_5)_4Y_2(\mu\text{-}Me)_2$	2.55(1)	87.7(3)	92.3(3)	0.98	108	4b
$(Me_2C_5H_3)_4Y_2(\mu\text{-}Me)_2$	2.60(1) 2.62(2)	86.6(4)	93.4(4)	–	–	12
$Me_4Al_2(\mu\text{-}Me)_2$	2.124(1)	75.7(1)	104.3(1)	0.93	101	2d

a syringe, MeLi (2.60 ml of a 0.91 M solution in hexane, 2.4 mmol). The purple solution immediately turned brown and then orange, with formation of a light-colored precipitate. The solution was stirred for 45 min and the solvent then removed under reduced pressure. The orange solid was extracted with hexane (60 ml), and the extract was filtered, the filtrate being concentrated to *ca.* 45 ml. The extract was kept at −20° for two hours and then at to −80°C for 6–8 h to yield orange crystals (0.64 g, 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 EI mass spectrum does not give a parent molecular ion; the highest mass fragment corresponds to $(Me_3CC_5H_4)_3Ce$ ($m/e = 503$ amu).

Method B: To a solution of $[(Me_3CC_5H_4)_2CeSCH(Me)_2]_2$ [10b] (1.30 g, 1.42 mmol) in hexane (50 ml) was added, from a syringe, MeLi (3.12 ml of a 0.91 M solution in diethyl ether, 2.8 mmol). The magenta solution 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) and the extract filtered and concentrated to *ca.* 40 ml. The extract was kept at −20°C then cooled to −80°C to give orange crystals (0.73 g, 65%). All physical properties and analytical data were identical to those of the product from Method A.

4.2. $(Me_3CC_5H_4)_4U_2(\mu\text{-}Me)_2$

To a solution of $(Me_3CC_5H_4)_3U$ [10a] (0.92 g, 1.5 mmol) in hexane (30 ml) was added, from a syringe, MeLi (1.68 ml of a 0.91 M solution in hexane, 1.53 mmol). The initially green solution color lightened slightly during the addition, and a green precipitate formed. The suspension was stirred for 40 min, and the solvent then removed under reduced pressure. The dark green solid was extracted with hexane (25 ml) and the extract was filtered, and concentrated to *ca.* 20 ml. Cooling of the extract to −20°C afforded dark green crystals (0.25 g, 33%), m.p. 111–115°C. An additional 0.13 g (17%) of product was 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 in solution to $(Me_3CC_5H_4)_3U$ and other uncharacterized products.

4.3. 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 θ–2θ 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 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 4. Tables of thermal parameters and lists of observed and calculated structure factors are available from R.A. Andersen.

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