

# A general synthesis and crystal structure of $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$ <sup>☆</sup>

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## Abstract

The preparation of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  from  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  and  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Mg}$  is described and compared to published routes to other  $\text{Cp}_3\text{Ln}$  (Ln = lanthanide) compounds. The title compound is monomeric in the solid state with three  $\eta^5$ -bound cyclopentadienyl rings which show some unusual distortions while maintaining idealized  $\text{C}_{3h}$  symmetry. The crystals are monoclinic, in the space group  $\text{P}2_1/\text{n}$ , with the unit cell  $a$  10.803(3)  $b$  19.493(6)  $c$  17.946(5) Å,  $\beta$  104.35(2)°,  $Z$  = 4. Anisotropic refinement of all heavy atoms with 361 parameters and 3420 reflections yielded  $R$  = 4.62%.

**Keywords:** Cerium; Trivalent metallocene; Crystal structure

## 1. Introduction

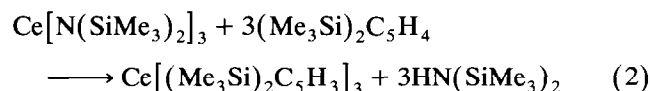
Preparation of the trivalent metallocenes of the lanthanide metals  $\text{Cp}'_3\text{M}$ , where  $\text{Cp}'$  is a general representation for  $\text{C}_5\text{H}_5$  and its substituted derivatives, inevitably involves the reaction of the anhydrous metal chloride with an alkali-metal cyclopentadienide [1,2]. The solid-state structures of the base-free metallocenes are rather interesting since the metallocenes of the larger metals tend to form polymeric structures and this tendency diminishes from left to right across the series. For example,  $\text{Cp}_3\text{Pr}$  is an infinite polymer with two terminal ( $\eta^5$ -bonded  $\text{C}_5\text{H}_5$  groups and a third  $\text{C}_5\text{H}_5$  group bridging two metal centers in an  $\eta^5$ - and an  $\eta^2$ -fashion [3a] whereas  $\text{Cp}_3\text{Yb}$  is a monomer with idealized  $D_{3h}$  symmetry [3b]. In general, as the substituents on the cyclopentadienyl group increase in number and in steric bulk, the degree of association decreases and monomeric metallocenes are obtained, but synthetic difficulties are encountered.

The largest trivalent lanthanide, cerium, provides an interesting series of metallocenes for which to examine the synthetic difficulties and how they have been sur-

mounted. The cerium metallocenes also illustrate how the substituents on the cyclopentadienyl ring change the physical properties, such as volatility and color, of the metallocene. The simplest derivative,  $\text{Cp}_3\text{Ce}$ , is an orange-yellow solid that is insoluble in benzene [1a]. The solid-state structure is unknown but it is presumably a polymer similar in structure to its praseodymium analog. The  $(\text{MeC}_5\text{H}_4)_3\text{Ce}$  derivative is monomeric in the gas phase but is a tetramer in the solid state [4]. It is soluble in toluene and the solution color depends upon the temperature, at  $-30^\circ\text{C}$  it is yellow, at  $25^\circ\text{C}$  it is green, and at  $50^\circ\text{C}$  it is blue. Increasing the size of the substituent on the cyclopentadienyl group to  $\text{Me}_3\text{SiC}_5\text{H}_4$  or  $\text{Me}_3\text{CC}_5\text{H}_4$  gives monomeric metallocenes that are blue or purple, respectively, and  $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{Ce}$  is a monomer [4]. All of these metallocenes are readily prepared by reaction between anhydrous  $\text{CeCl}_3$  and an alkali-metal cyclopentadienide (eqn. (1)).



This synthetic route does not yield the metallocene,  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ , in pure form but this blue monomer was prepared by the Brønsted acid-base reaction shown in eqn. (2).



Extension of this acid-base reaction to  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  was not possible since  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_4$  did not

<sup>1</sup> This paper is dedicated to Prof. Dr. Herbert Schumann on the occasion of his 60th birthday, with special thanks for all he has done for lanthanide organometallic chemistry and for making the senior author's visits to his institute possible.

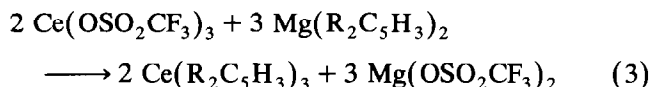
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react with  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ce}$  in refluxing toluene, even though the  $pK_a$  values suggest that the reaction would be exothermic; in DMSO the  $pK_a$  values of  $(\text{Me}_3\text{Si})_2\text{NH}$  and  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_4$  are 26 [5a] and 22 [5b], respectively. It seemed possible that only two  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$  rings could be attached to cerium since the salt elimination methodology yields dimeric  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{Ce}_2(\mu\text{-Cl})_2$  [6]. In this context it is noteworthy that only two sterically voluminous pentamethylcyclopentadienyl groups can be attached to cerium by the salt elimination methodology [7].

Bruno has developed the use of  $\text{CeI}_3$  as a better starting material, than  $\text{CeCl}_3$ , for some metallocene syntheses [8]. This starting material does not yield the binary metallocenes  $(\text{R}_2\text{C}_5\text{H}_3)_3\text{Ce}$ , where  $\text{R} = \text{Me}_3\text{Si}$  or  $\text{Me}_3\text{C}$ , but instead gives the dimers,  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{Ce}_2(\mu\text{-I})_2$  [6b]. In this paper we show that reaction of anhydrous cerium tris-triflate and the magnesium metallocenes in tetrahydrofuran is the method of choice for the high yield synthesis of  $(\text{R}_2\text{C}_5\text{H}_3)_3\text{Ce}$ ,  $\text{R} = \text{Me}_3\text{Si}$ ,  $\text{Me}_3\text{C}$  (eqn. (3)). Only two literature reports describe the use of lanthanide triflates in organometallic synthesis,  $\text{Cp}_2\text{Lu}(\text{OSO}_2\text{CF}_3)(\text{thf})$  (Ref. [9a]) and  $\text{Cp}_4\text{Y}_2(\mu\text{-OSO}_2\text{CF}_3)_2$  (Ref. [9b]).

## 2. Synthesis and physical properties

The addition of 1.5 molar equivalents of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Mg}$  to  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  yields a purple solution from which  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  may be isolated as royal blue crystals from hexane in 74% yield (eqn. (3))

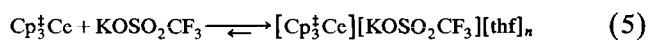


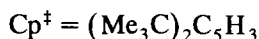
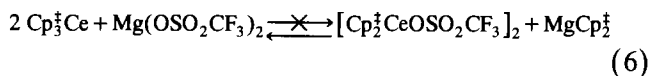
The base-free metallocene sublimes at ca. 200°C under dynamic diffusion pump vacuum and it gives a molecular ion in the EI mass spectrum. Its melting point of 214–217°C is slightly less than that of its  $\text{Me}_3\text{Si}$  analog (see below).

The  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  at 30°C shows resonances due to the  $\text{Me}_3\text{C}$ - groups at  $-4.63$  ( $\nu_{1/2} = 18$  Hz) and the  $\text{A}_2\text{B}$  ring protons at 17.0 ( $\nu_{1/2} = 45$  Hz) and 25.8 ( $\nu_{1/2} = 34$  Hz), respectively. These chemical shifts are close to those reported for the  $\text{Me}_3\text{Si}$  analog of  $-4.48$ , 17.2, and 26.9, respectively, at the same temperature and in the same solvent, [4]. This similarity indicates that in solution these molecules have the same electronic ground state and similar geometries [10]. The chemical shifts in both metallocenes are linear when plotted as a function of the inverse of absolute temperature, i.e. they follow the Curie Law. No change in the line shape is observed over this temperature range ( $-95$ – $95^\circ\text{C}$ ) indicating that the rings are either freely rotating or they are static and equivalent by symmetry.

Since cerium triflate is such a useful starting material for  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$ , we extended the synthetic route to the known  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$  [4]. Mixing  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Mg}$  and  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  in a 1.5:1 molar ratio yields a blue solution from which  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$  may be isolated by crystallization from hexane in 70% yield (eqn. (3)). This newer synthesis is more efficient since the yield is higher and the number of steps is less. Since this metallocene can be prepared in larger quantities, in pure form, its physical properties can be examined [11]. It is noteworthy that the melting point, previously reported as 210–213°C is low by 16°C.

The reaction between  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  and magnesium metallocenes is the best synthetic route that we have been able to develop for these two cerium metallocenes. As in much of lanthanide chemistry, reaction conditions, solvents, starting reagents, etc. play important and often mysterious roles [12]. This is also true in our quest to develop good synthetic routes that give high yields of pure cerium metallocenes. Initially we studied the reaction of  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3\text{K}$ . Mixing  $\text{CeCl}_3$  with the potassium reagent in thf yields mixtures of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{Ce}_2(\mu\text{-Cl})_2$  [6a] and  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$ . Use of a large excess of the potassium reagent did not drive the reaction to completion, suggesting that an equilibrium is involved. Mixing  $\text{CeI}_3(\text{thf})_3$  and an excess of  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3\text{K}$  in thf also gives a mixture of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{Ce}_2(\mu\text{-I})_2$  [6b] and  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$ . Use of equimolar proportions of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Mg}$  and  $\text{CeI}_3(\text{thf})_3$  in thf yields  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{Ce}_2(\mu\text{-I})_2$  in pure form. However, use of excess magnesium reagent again yields mixtures of both products. Cerium triflate and  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3\text{K}$  also failed to produce pure  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$ . Only in the case of  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  and 1.5 molar equivalents of magnesium metallocene is pure  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  obtained. Once pure  $(\text{R}_2\text{C}_5\text{H}_3)_3\text{Ce}$  is available a series of qualitative reactions was examined (eqns. (4–6)). Each of these experiments was performed in thf at 60°C and was monitored by  $^1\text{H}$  NMR spectroscopy. Treatment of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  with  $\text{KCl}$  or  $\text{KI}$  regenerated the equilibria that had prevented purification of the target compound. Addition of potassium triflate to  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  produced a yellow solution which partially reverts to  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  when the solvent is removed under reduced pressure. No detectable  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeOSO}_2\text{CF}_3$  is formed [6b]. If the color of the 1:1 adduct is yellow then an equilibrium such as that shown in eqn. (5) is reasonable. In contrast, when  $\text{Mg}(\text{OSO}_2\text{CF}_3)_2$  was added to  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  the solution remained blue and no  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{CeOSO}_2\text{CF}_3$  was observed.





These qualitative experiments can be interpreted in the following way. Chloride and iodide are better ligands for cerium than is triflate and the halides can compete with the cyclopentadienyl anion thermodynamically and kinetically. The triflate ligand is useful in the synthetic reactions described in this manuscript because it is a poor ligand (Lewis base) and a bad electrophile, which are the reasons why triflate salts are so useful in coordination chemistry [13].

The magnesium metallocene used in this work,  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Mg}$ , has not been previously reported. It is made in a manner similar to that used to prepare  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Mg}$  [14a] or  $(\text{Me}_5\text{C}_5)_2\text{Mg}$  [14b].

### 3. Solid-state structure

An ORTEP diagram of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  is shown in Fig. 1. Table 1 shows a detailed comparison between the geometrical parameters for  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  and  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$ , crystal data are given in Table 2, and positional parameters are in Table 3. Although both metallocenes crystallize in the monoclinic crystal system, they are not isomorphous since  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  crystallizes in the space group  $P2_1/n$  and the silicon analog crystallizes in the space group  $I2/c$  [4]. In addition, all three of the  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$  groups in  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  are ordered whereas in  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$  only two are ordered. Thus, in  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  the unique C-H atom pair in each five-membered ring is related by a  $C_3$  rotation axis and the molecule has idealized  $C_{3h}$  symmetry.

The cerium-ring centroid distances in the  $\text{Me}_3\text{C}$  compound average 2.59 Å, 0.02 Å longer than in the  $\text{Me}_3\text{Si}$

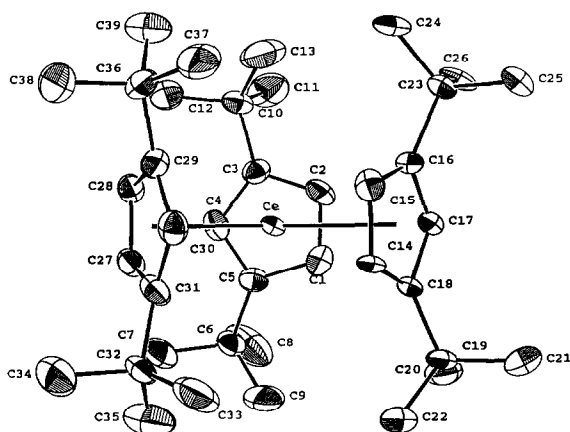


Fig. 1. ORTEP drawing of  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$  with 50% probability ellipsoids.

Table 1  
Structural comparison of  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$  and  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$

	$\text{Me}_3\text{Si-}$	$\text{Me}_3\text{C-}$
Ce-ring centroid	2.57	2.59
Centroid-Ce-centroid	120°	120°
Ce-C	2.83	2.86
Ring C-(Si or C)	1.89	1.53
Out-of-plane bend for substituents	14.0° avg. (18.5°)	19.0° avg. 28.8°
	18.1°	25.2°
	15.2°	20.2°
	7.3°	17.2°
	6.7°	11.9°
$\theta$ (angle between $C_5$ -axis and Ce-centroid vector)	15.2°	10.5°
	25.3°	3.9°
	(18.9°)	11.6°
		13.5°

<sup>a</sup> Numbers in parentheses are from the disordered  $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$  ring.

compound. A similar pattern is observed for the Ce- $C_{\text{ring}}$  (av.) bond distances, 2.86(1) Å and 2.83(1) Å. Thus the  $\text{Me}_3\text{C}$ -substituted ring is further away from cerium, consistent with the larger steric cone angle of  $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$ . The centroid-Ce-centroid angles are 120° in both compounds. The  $C_5$ -rings are planar but the  $\text{Me}_3\text{Si-}$  and  $\text{Me}_3\text{C-}$  groups are bent out of the plane of the ring by an average of 14° and 19°, respectively. The planes of the five-membered rings are also canted so that the vectors normal to the planes and passing through their centroids do not intersect the cerium position (Fig.

Table 2  
Crystallographic data for  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$

Space group	$P2_1/n$
<i>a</i>	10.803(3) Å
<i>b</i>	19.493(6) Å
<i>c</i>	17.946(5) Å
$\alpha$	90°
$\beta$	104.35(2)°
$\gamma$	90°
<i>V</i>	3661.2(36) Å <sup>3</sup>
<i>Z</i>	4
<i>FW</i>	672.047 g mol <sup>-1</sup>
<i>d</i> (calc)	1.219 g cm <sup>-3</sup>
$\mu$ (calc)	12.843 cm
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
Monochromator	highly oriented graphite
Scan range, type	3° < 2 $\theta$ < 45°
Scan speed	5°/min
Scan width (°)	$\Delta\theta = 0.78 + 0.35 \tan \theta$
Reflections collected	5246 (+ <i>h</i> , + <i>k</i> , <i>l</i> )
Unique reflections	4763
Reflections with <i>I</i> > 3 $\sigma$	3644
<i>R</i>	4.62%
<i>R<sub>w</sub></i>	5.38%
<i>R<sub>all</sub></i>	7.25%
GOF	2.075
Largest $\Delta/\sigma$ in final least squares cycle	0.02

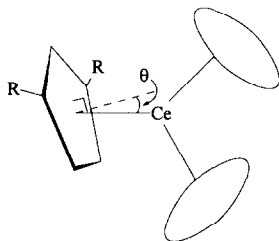


Fig. 2. The dotted line is coincident with the  $C_5$ -axis and the solid line connects cerium and the ring centroid.  $R = Me_3C$ ,  $\theta = 3.9^\circ$ ,  $11.6^\circ$  and  $13.5^\circ$ ;  $R = Me_3Si$ ,  $\theta = 15.2^\circ$ ,  $25.3^\circ$  and  $19^\circ$  (the third ring is disordered).

2). The result is to move the ring substituents farther away from the center of the molecule and to move the two equivalent, unsubstituted ring positions closer to the

center of the molecule. Thus, the geometrical changes in these two compounds are small and subtle, presumably the net result of minimizing intramolecular repulsions as the size and electronic effects of the substituents change.

#### 4. Experimental

Experimental procedures were carried out as previously described [4].

##### 4.1. Preparation of $[(Me_3C)_2C_5H_3]_2Mg$

A heptane solution of dibutylmagnesium (Aldrich) (250 ml, 0.90 M, 250 mmol) was added to di-tert-

Table 3  
Positional and thermal parameters for  $[(Me_3C)_2C_5H_3]_3Ce$

Atom	x	y	z	B(A <sup>2</sup> )
Ce	0.17375(1)	0.21417(1)	0.07024(1)	1.723(8)
C1	0.0392(8)	0.3286(5)	0.0002(5)	2.9(2)
C2	0.1567(8)	0.3276(5)	-0.0229(5)	2.8(2)
C3	0.2523(7)	0.3495(5)	0.0391(5)	2.4(2)
C4	0.1970(8)	0.3620(5)	0.1011(5)	2.8(2)
C5	0.0658(7)	0.3512(4)	0.0775(5)	2.3(2)
C6	-0.0332(8)	0.3764(5)	0.1188(5)	3.1(2)
C7	0.022(1)	0.3865(6)	0.2034(5)	4.5(3)
C8	-0.080(1)	0.4458(7)	0.0852(7)	6.7(3)
C10	0.3879(8)	0.3694(5)	0.0342(5)	2.7(2)
C11	0.374(1)	0.4292(6)	-0.0226(6)	5.5(3)
C12	0.4709(9)	0.3929(6)	0.1102(6)	4.5(3)
C13	0.4516(9)	0.3106(6)	0.0036(7)	5.7(3)
C14	0.0630(7)	0.0905(4)	0.0144(4)	2.0(2)
C15	0.1799(8)	0.0910(4)	-0.0066(5)	2.3(2)
C16	0.1669(7)	0.1373(5)	-0.0695(4)	2.2(2)
C17	0.0453(7)	0.1649(5)	-0.0837(4)	2.3(2)
C18	-0.0235(7)	0.1354(4)	-0.0331(4)	2.0(2)
C19	-0.1685(7)	0.1355(5)	-0.0465(4)	2.2(2)
C20	-0.2268(8)	0.2056(5)	-0.0687(5)	3.4(2)
C21	-0.2214(8)	0.0855(6)	-0.1124(6)	4.0(3)
C22	-0.2077(8)	0.1089(6)	0.0244(5)	3.9(2)
C23	0.2540(7)	0.1377(5)	-0.1257(4)	2.2(2)
C24	0.3941(8)	0.1261(5)	-0.0855(5)	3.3(2)
C25	0.2087(8)	0.0772(5)	-0.1811(5)	3.4(2)
C26	0.2391(8)	0.2033(5)	-0.1723(5)	3.6(2)
C27	0.2450(7)	0.2229(5)	0.2290(4)	2.5(2)
C28	0.3611(7)	0.2226(4)	0.2070(4)	2.2(2)
C29	0.3857(7)	0.1542(5)	0.1863(4)	2.5(2)
C30	0.2817(8)	0.1148(4)	0.1930(5)	2.5(2)
C31	0.1955(8)	0.1545(5)	0.2215(4)	2.6(2)
C32	0.0945(8)	0.1265(5)	0.2607(4)	2.7(2)
C33	0.033(1)	0.0618(6)	0.2236(5)	4.9(3)
C34	0.163(1)	0.1104(6)	0.3439(6)	5.0(3)
C35	-0.007(1)	0.1791(7)	0.2613(6)	5.5(3)
C36	0.5151(7)	0.1247(5)	0.1823(5)	2.7(2)
C37	0.5033(9)	0.0608(6)	0.1338(6)	4.5(3)
C38	0.5846(9)	0.1068(6)	0.2648(6)	5.0(3)
C39	0.5956(9)	0.1774(6)	0.1507(6)	4.3(3)
Cp1	0.14220(1)	0.34380(1)	0.03900(1)	
Cp2	0.08630(1)	0.12380(1)	-0.03570(1)	
Cp3	0.29380(1)	0.17380(1)	0.20680(1)	

butylcyclopentadiene [15] (89.37 g, 501 mmol). Upon addition the mixture began to evolve butanes and warmed slightly. The mixture was heated to reflux for 24 h at which point no further gas evolution was detected [16]. The clear solution was cooled to  $-40^{\circ}\text{C}$  producing large colorless crystals (39.1 g, 41% yield). Concentrating the mother liquor by one half and cooling produced a second crop of crystals (39.1 g, 83% yield). The compound sublimes at  $120^{\circ}\text{C}$  at  $10^{-3}$  Torr. m.p.  $138\text{--}141^{\circ}\text{C}$ . Anal. calc. for  $\text{C}_{26}\text{H}_{42}\text{Mg}$ : C, 82.4; H, 11.2%. Found: C, 82.5; H, 11.2%. IR 1635m, 1545m, 1295w, 1250s, 1230m, 1200s, 1160w, 1085w, 1050m, 1025m, 975w, 935m, 805s, 760m, 740s, 695s, 675m, 500s, 410m, 345w, 245w.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ ) 1.31 (s, 18H), 5.94 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR 133.7 (ring C), 103.0 (ring C), 99.9 (ring C), 32.49 ( $\text{CMe}_3$ ), 32.56 ( $\text{CMe}_3$ ). The E.I. mass spectrum showed a molecular ion at  $m/e = 378$  amu. The parent ion isotopic cluster was simulated: (calc. %, obs. %); 378 (100, 100), 379 (42.2, 41.7), 380 (21.8, 21.5), 381 (5.0, 4.9).

#### 4.2. Preparation of $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$

Hydrated cerium triflate was prepared from  $\text{Ce}_2(\text{CO}_3)_3$  (Strem) and aqueous triflic acid [17]. Coordinated water was removed by finely grinding  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3 \cdot x\text{H}_2\text{O}$  and heating it to  $200^{\circ}\text{C}$  under vacuum. The resulting white powder was examined by IR spectroscopy to ensure that no hydroxide stretches remained ( $1650\text{ cm}^{-1}$ ).

#### 4.3. Preparation of $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$

To a mixture of anhydrous  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  (7.54 g, 12.8 mmol) and  $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{Mg}$  (7.30 g, 19.3 mmol) was added 150 ml of thf. The reaction mixture was stirred for 24 h, gradually producing a purple solution and a small amount of white precipitate. The solution was filtered and the solvent was removed under reduced pressure. The residue was extracted with 150 ml of hexane and the resulting purple solution was filtered and cooled to  $-40^{\circ}\text{C}$ , giving royal blue crystals (2.4 g, 28% yield). Concentrating and cooling the mother liquor yielded two additional crops of crystals (2.6 g and 1.4 g, 74% yield). The solvent was removed from the mother liquor and additional product was sublimed from the residue ( $200^{\circ}\text{C}$  at  $10^{-3}$  Torr). m.p.  $214\text{--}217^{\circ}\text{C}$ . IR: 1305w, 1255s, 1240w, 1205m, 1160m, 1090w, 1055m, 1025m, 930m, 810s, 740s, 700w, 680w, 665m, 610w, 490w, 430w, 355m, 250m.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ )  $-4.63$  (18H,  $\nu_{1/2} = 12$  Hz),  $17.0$  (2H, ( $\nu_{1/2} = 45$  Hz),  $25.8$  (1H, ( $\nu_{1/2} = 34$  Hz). Anal. Calc. for  $\text{C}_{39}\text{H}_{63}\text{Ce}$ : C, 69.7; H, 9.45%. Found C, 69.4; H, 9.70%. The EI mass spectrum showed a molecular ion at  $m/e = 671$ . The parent ion isotopic cluster was

simulated: (calc. %, obs. %); 671 (100, 100), 672 (44, 41), 673 (22, 23), 674 (7, 7)

#### 4.4 Preparation of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ce}$

To a mixture of anhydrous  $\text{Ce}(\text{OSO}_2\text{CF}_3)_3$  (2.73 g, 4.65 mmol) and  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Mg}$  [14a] (3.09 g, 6.98 mmol) was added 100 ml of thf. The reaction mixture was stirred for 24 h, gradually producing a royal blue solution and a small amount of white precipitate. The solution was filtered and the solvent was removed under reduced pressure. The residue was extracted with 150 ml of hexane, filtered, and concentrated to a volume of 80 ml and cooled to  $-40^{\circ}\text{C}$ . Royal blue crystals were formed (1.7 g, 48% yield). Concentrating and cooling the mother liquor produced a second crop of crystals (0.83 g, 71% yield). The compound sublimes at  $200^{\circ}\text{C}$  at  $10^{-3}$  Torr. m.p.  $226\text{--}228^{\circ}\text{C}$ . IR: 1325w, 1245s, 1210w, 1205w, 1070s, 920s, 835s, 780m, 755m, 695m, 645m, 625w, 485m, 380m, 360w, 335w, 305m, 280w, 245w. Anal. calc. for  $\text{C}_{33}\text{H}_{63}\text{Ce}$ : C, 51.6; H, 8.26%. Found: C, 49.3; H, 8.18%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ )  $-4.47$  (18H, ( $\nu_{1/2} = 5$  Hz),  $17.1$  (2H, ( $\nu_{1/2} = 44$  Hz),  $26.8$  (1H, ( $\nu_{1/2} = 28$  Hz). The EI mass spectrum showed a molecular ion at  $m/e = 767$  amu. The molecular ion isotopic cluster was simulated:  $m/e$  (calc. %, obs. %); 767 (100, 100), 768 (67, 69), 769 (54, 48), 770 (25, 24), 771 (11, 10).

#### 4.5. X-Ray structure of $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_3\text{Ce}$

Blue crystals of the compound were grown from a saturated hexane solution which was cooled slowly to  $-40^{\circ}\text{C}$ . The crystals were immersed in Paratone N and a single crystal, measuring  $0.30 \times 0.40 \times 0.41$  mm was selected and mounted on the end of a glass capillary. The mounted crystal was cooled to  $-124^{\circ}\text{C}$  in a nitrogen cold stream on an Eraf-Nonius CAD-4 diffractometer. The crystal was centered manually and an automated peak search and indexing routine was used to determine the cell parameters. (Table 1)

After further centering based on Friedel pairs, a total of 5246 reflections were collected and converted to structure factors and their estimated standard deviations by correcting for scan speed, background, and Lorentz-polarization effects [18]. Two of the three intensity standards showed a linear 5.9% decay (the third standard was noisy but did not contradict this observation) and the data were corrected accordingly. An empirical absorption correction was applied based on azimuthal scans which showed  $I_{\min}/I_{\max} = 0.76$ . Redundant data, totaling 295 reflections, and systematic absences ( $h,0,l$ ),  $h+l$  odd, and  $(0,k,0)$ ,  $k$  odd, totaling 188 reflections were removed leaving 4763 unique data of which 3420 showed  $F_o > 3\sigma_{F_o}$ .

The cell volume suggested that the unit cell con-

tained four molecules. The cerium atoms were located by solving the Patterson map and the remainder of the heavy atoms were located in a single difference Fourier search. Refinement of these positions yielded no significant changes. Hydrogen positions were calculated based on idealized geometry and were used in structure factor calculations but were not refined by least-squares.

The final residuals for 361 variables applied to 3420 unique data with  $F_o > 3\sigma F_o$ , were  $R = 4.62\%$ ,  $R_w = 5.38\%$ , and  $GOF = 2.075$ . The  $R$  value for all data including “unobserved” reflections was 7.25%. Inspection of the residuals ordered in the ranges of  $\sin\theta/\lambda$ ,  $F_o$ , and parity as well as values of the individual indices showed no obvious trends.

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