Table I. Selected Bond Distances (Å) and Angles (deg) for $(C_5H_5)_3Ce(OCMe_3)$ (4)[a]

Ce(1)–O(1)	2.045 (6)	Ce(1)–C(1)	2.790 (9)
Ce(1)–C(2)	2.752 (11)	Ce(1)–C(3)	2.741 (10)
Ce(1)–C(4)	2.777 (14)	Ce(1)–C(5)	2.783 (12)
Ce(1)–C(9)	2.749 (10)	Ce(1)–C(10)	2.757 (12)
Ce(1)–C(11)	2.746 (15)	Ce(1)–Cn(1)	2.518
Ce(1)–Cn(2)	2.505	O(1)–C(6)	1.441 (13)
O(1)–Ce(1)–Cn(1)	103.5	O(1)–Ce(1)–Cn(2)	101.7
Cn(1)–Ce(1)–Cn(2)	116.9	Cn(1)–Ce(1)–Cn(1′)	111.8
Ce(1)–O(1)–C(6)	176.3 (6)		

[a] Cn(1) is the centroid of the C(1), C(2), C(3), C(4), C(5) ring. Cn(2) is the centroid of the C(9), C(10), C(11), C(10′), C(9′) ring.

atom roughly define a tetrahedron. $Cp_3Ce(OCMe_3)$ and the Cp_3UZ complexes differ, however, in the nature of their distortion from pure tetrahedral symmetry. Cp_3UZ complexes typically have near C_{3v} symmetry at uranium with Cn–U–Cn angles near 100° and Cn–U–Z angles near 117°.[1,30–36] In contrast, the solid-state structure of $Cp_3Ce(OCMe_3)$ has (a) a mirror plane through Ce, C(11), O(1), C(6), and C(8), (b) Cn–Ce–Cn angles of 116.9° and 111.8°, and (c) Cn–Ce–O angles of 103.5° and 101.7° (Table I).

The average Ce–C(ring) distance, 2.76 (2) Å, can be compared to U–C(ring) averages of 2.68–2.74 Å in Cp_3UZ complexes.[1,30–36] The relationship of the cerium(IV) distance to the uranium(IV) distances in these tetravalent complexes parallels the relationship of the cerium(III) and uranium(III) distances in the six trivalent complexes $(MeC_5H_4)_3ML$ where M = U and Ce and L = PMe_3,[37,38] $P(OCH_2)_3CEt$,[39] and quinuclidine.[39] In all of these cases, the cerium distances are longer than expected on the basis of Shannon's radii for halide and chalcogenide complexes[40] which show cerium to be slightly smaller than uranium. However, the crystallographic differences are small and statistically insignificant. The Ce–C(ring) distance in 4 can also be compared to the 2.81 (4) Å average Ce–C distance in $Cp_3Ce(THF)$.[41,42] According to Shannon,[40] ten-coordinate Ce(IV) is 0.18 Å smaller than ten-coordinate Ce(III). On this basis, the expected Ce–C average length in 4 would be 2.63 Å. The 2.045 (6) Å Ce–O distance is more difficult to assess since there are no structurally characterized Ce(IV) alkoxide complexes of comparable coordination number.[23,43] The 176.3 (6)° Ce–O(1)–C(6) angle is typical of lanthanide, actinide, and early-transition-metal alkoxide complexes which contain short metal–oxygen distances.[44]

The synthetic results described here demonstrate that ceric ammonium nitrate derived alkoxide nitrate complexes are useful precursors to cerium(IV) organometallic compounds. The structural results establish that complete crystallographic data can be obtained on isolable organometallic complexes of Ce(IV). When more structural data on Ce(IV) organometallics are obtained, it should be possible to determine if Ce(IV) bond distance parameters can be assessed in the same way as other f-element organometallic complexes.

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Supplementary Material Available: Synthetic and structural details, tables of crystal data, positional parameters, bond distances and angles, and thermal parameters, and a disordered ORTEP plot (11 pages); a listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(37) Stults, S. D.; Zalkin, A. *Acta Crystallogr.* **1987**, *C43*, 430–432.

(38) Brennan, J.; Zalkin, A. *Acta Crystallogr.* **1985**, *C41*, 1038–1040.

(39) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1329–1334.

(40) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

(41) Evans, W. J.; Deming, T. J.; Olofson, J. M.; Ziller, J. W., unpublished results.

(42) The same argument can be made with the 2.82 (4) Å average La–C distance in isostructural $Cp_3La(THF)$ (Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383–392) and with the 2.80 (2) Å average Pr–C distance in $Cp_3Pr(THF)$ (Fan, Y.; Lu, P.; Jin, Z.; Chen, W. *Sci. Sin.* **1984**, *27B*, 993–1001).

(43) Stecher, H. A.; Sen, A.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 1132–1133.

(44) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim Acta* **1985**, *110*, 191–195 and references therein.

Additions and Corrections

Crystal Structure of $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$: Corrigendum[1]

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Summary: The crystal structure of this compound, originally described in the noncentrosymmetric space group *Pa*, is correctly described as centrosymmetric, space group *P2/a*. Refinement in space group *P2/c*, the standard setting of *P2/a*, has led to much more reasonable geometry than reported for the *Pa* refinement: the bridging H atoms form a square rather than a rectangle, and the bond lengths and angles in the permethylcyclopentadienyl ring are now normal.

The crystal structure of this interesting compound, which contains a Ru–Ru triple bond as well as four H atoms bridging between the Ru atoms, has recently been reported.[2] A surprising feature of the structure was the arrangement of the bridging H atoms, which appeared to form a rectangle with two short H···H distances (0.84 and

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(1) Contribution No. 7614 from the Arthur Noyes Laboratory of Chemical Physics.

(2) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, 2243–2245.

Table I. Coordinates (×10^4), Space Group *P*2/*c* (*a* = 10.053, *b* = 8.521, *c* = 12.291 Å, *β* = 108.519°)

atom	*x*	*y*	*z*	U_{eq}[a] or *B*, Å^2
Ru	1102 (0.2)	2380 (0.2)	2262 (0.2)	106 (0.4)
C(1)	3118 (3)	1241 (3)	2582 (3)	141 (5)
C(2)	3345 (3)	2871 (3)	2877 (3)	170 (5)
C(3)	2719 (3)	3772 (3)	1867 (3)	182 (6)
C(4)	2102 (3)	2706 (4)	931 (2)	157 (4)
C(5)	2352 (3)	1136 (3)	1386 (3)	134 (5)
C(6)	3685 (4)	−126 (4)	3361 (3)	232 (6)
C(7)	4169 (4)	3496 (5)	4034 (3)	281 (7)
C(8)	2764 (5)	5524 (4)	1771 (4)	304 (9)
C(9)	1416 (4)	3140 (74)	−305 (3)	250 (7)
C(10)	1959 (4)	−363 (4)	715 (3)	207 (6)
H(1)	0	3555 (67)	2500	1.4 (11)[b]
H(2)	0	1044 (68)	2500	2.0 (12)[b]
H(3)	504 (48)	2367 (67)	3349 (40)	4.5 (12)[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(\alpha_i^* a_j^*)(\vec{\mathbf{a}}_i\cdot\vec{\mathbf{a}}_j)]$. [b] Isotropic displacement parameter, *B*.

0.99 Å) and two long ones (1.80 and 2.23 Å); however, the NMR measurements indicate no H–H bonds, and the compound was presumed to be a hydride rather than an η^2-bonded H_2 complex. Another disturbing feature, apparent only from the supplementary material, was the bond lengths in the Cp rings which ranged from 1.295 (7) to 1.537 (6) Å, suggesting pronounced localization of the double bonds. These surprising features are a result of refinement in an incorrect space group.

The structure was originally described in space group *Pa* (monoclinic; *a* = 12.291 (2) Å, *b* = 8.521 (1) Å, *c* = 10.053 (2) Å, *β* = 108.519 (12)°, *Z* = 2). It is correctly formulated in space group *P*2/*a* (which is described here in the conventional *P*2/*c*, No. 14). After the change in space group, refinement led to a much more reasonable structure: normal bond lengths in the C_5Me_5 rings and the expected square arrangement for the bridging H atoms.

Refinement was based on the 2391 F_o values recovered from the supplementary material; the starting coordinates were also recovered from the supplementary material, symmetrized, and averaged. Full-matrix refinement in *P*2/*c* led to an *R* of 0.0240 for 169 parameters, compared to an *R* of 0.0222 for 335 parameters in the *Pa* refinement. Most of the difference between the two *R*'s is presumably due to round off of the F_o values; they were listed only to the nearest whole number, so the average round-off error of 0.25 e is competitive with the average value of $|F_o - F_c|$, 0.84 e. A difference map showed no excursions greater than 0.3 e Å^{-3} except for a cloverleaf arrangement—two peaks of +1.0 and two of −1.0 e Å^{-3}—around the ruthenium atom, a pattern that is typical of absorption errors.

Final *P*2/*c* coordinates are given in Table I. The Ru–H distances are statistically equal, averaging 1.61 (4) Å, as are the H···H distances, 1.47 (6) Å, and the Ru–H–Ru angles, 100 (2)°. Thus, the arrangement is that expected for bridging hydrides, as also shown by the NMR measurements.[2]

A final comment: the earlier refinement in space group *Pa* led to coordinates that were in error by more than 0.1 Å for some of the C atoms, which is over 30 standard deviations; the discrepancies were far larger for the H atoms. These errors were the result of the near singularities involved when a nearly centrosymmetric model is refined in a noncentrosymmetric space group.[3,4] And while the peculiar arrangement of the H atoms that resulted from the earlier refinement might well be blamed (as the original authors did) on the inherent difficulties in locating hydrogen atoms from X-ray diffraction data, the distortions in the Me_5Cp rings[5] must have arisen from other causes and should have made the authors (and, perhaps, the referees as well) suspicious as to the choice of space group. The importance of careful scrutiny of all experimental results cannot be overemphasized.

Registry No. $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$, 116887-45-7.

Supplementary Material Available: Tables of coordinates for the H atoms and of anisotropic U_{ij} terms for the heavier atoms and a listing of bond lengths and angles (3 pages). Ordering information is given on any current masthead page.

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(3) Ermer, O.; Dunitz, J. *Acta Crystallogr., Sect. A* **1970**, *A26*, 163.

(4) Schomaker, V.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1933–1934.

(5) Besides the irregularities in the ring C–C distances, the C(ring)–C(ring)–C(Me) bond angles show large variations in the *Pa* description, ranging from 115° to 137°. In the *P*2/*c* description the range is from 125.3 (3)° to 126.5 (3)°.