were then removed in vacuo. The oily residue was extracted with pentane (25 mL) and filtered. The zirconium enolate product **14** (0.29 g) precipitated from the pentane solution at −78 °C together with small amounts of $Cp_2Zr(OPh)_2$ and $Cp_2Zr[OC(Ph){=}CH_2]_2$ which could not be separated. Complex **14** was identified by NMR spectra and its aldol reaction with benzaldehyde (see below): ^1H NMR (C_6D_6) δ 7.81, 7.25, 6.96, 6.75 (aromatic H), 5.98 (Cp), 4.84, 4.22 ($=CH_2$); ^{13}C NMR (C_6D_6) δ 166.0, 165.5 ($C{=}CH_2$, OPh_{ipso}), 139.2 ($=CPh_{ipso}$), 129.8, 125.7, 119.6, 118.6 (aromatic C, some hidden by solvent peaks), 113.1 (Cp), 86.6 ($C{=}CH_2$).

Aldol Condensation Reaction of 14 with Benzaldehyde. Slightly less than 1 molar equiv of benzaldehyde was added to a solution of **14** in benzene-d_6 at ambient temperature. The reaction was complete within 15 min as determined by ^1H NMR spectroscopy. **15**: ^1H NMR (C_6D_6) δ 6.7–7.5 (m, Ph), 5.94, 5.95 (5 H each, Cp), 5.87 (1 H, dd, $^3J_{HH}$ = 2.8, 8.3 Hz, $-OCHPh-$), 3.37 (1 H, dd, $^2J_{HH}$ = 15.8 Hz, $-CH_2-$), 2.75 (1 H, dd, $-CH_2-$).

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Registry No. **1a**, 51177-89-0; **1b**, 63672-39-9; **1c**, 1273-09-2; **1d**, 83076-03-3; **2a**, 71191-32-7; **4a**, 96896-91-2; **4c**, 96896-94-5; **4d**, 96896-93-4; **4e**, 121253-38-1; **4f**, 121253-39-2; **4g**, 121253-40-5; **5a**, 106625-46-1; **5b**, 106625-47-2; **5g**, 121253-46-1; **9**, 121253-41-6; **10**, 121253-42-7; **11**, 37342-97-5; **12**, 109550-91-6; **13**, 52573-30-5; **14**, 121253-43-8; **15**, 121253-45-0; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; H_3CCOPh, 98-86-2; $Ph_3P{=}CH_2$, 3487-44-3; $Cp_2Zr[OC(Ph){=}CH_2]_2$, 121253-44-9; $Cp_2Zr(OPh)_2$, 12303-50-3; PhCHO, 100-52-7; (η^2-1,2-didehydrobenzene)titanocene, 12679-36-6.

Supplementary Material Available: Tables of bond lengths and angles, positional parameters, and temperature factors for the zirconoxycarbene complexes **4g** and **10** (21 pages); listings of calculated and observed structure factors for **4g** and **10** (35 pages). Ordering information is given on any current masthead page.

Synthesis of a Monopentamethylcyclopentadienyl Halide Complex of Calcium. The X-ray Crystal Structure of $[(Me_5C_5)Ca(\mu\text{-}I)(THF)_2]_2$

Michael J. McCormick,[†] S. Craig Sockwell,[†] Caroline E. H. Davies,[†] Timothy P. Hanusa,*[,†] and John C. Huffman[‡]

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and Molecular Structure Center, Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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Potassium pentamethylcyclopentadienide and CaI_2 react in a 3:2 molar ratio in THF to yield a nearly equimolar mixture of the complexes $Cp^*CaI(THF)_2$ and $Cp^*_2Ca(THF)_2$ ($Cp^* = Me_5C_5$). The metallocene can be removed with hexane, leaving the colorless, toluene-soluble organometallic halide in 57% yield. At 20 °C, the equilibrium constant in THF for the system $Cp^*_2Ca(THF)_2 + CaI_2(THF)_2 \rightleftharpoons 2Cp^*CaI(THF)_2$ is 4. $Cp^*CaI(THF)_2$ crystallizes from toluene in the monoclinic space group $P2_1/a$, with a = 14.837 (4) Å, b = 13.022 (4) Å, c = 21.125 (7) Å, β = 98.66 (1)°, and D_{calcd} = 1.47 g cm^{-3} for Z = 4 (dimers). Least-squares refinement on the basis of 4437 observed reflections measured at 118 K led to a final R value of 0.036. Two independent iodide-bridged dimers appear in the asymmetric cell, each with a crystallographically imposed center of inversion. Each calcium in the $[Ca(\mu\text{-}I)]_2$ core is flanked by an η^5-Cp* ring with average Ca–C distances in both dimers of 2.67 (1) Å and by two THF molecules with average Ca–O distances of 2.422 (6) Å in one dimer and 2.387 (7) Å in the other. The Ca–I and Ca–I′ distances differ by 0.06 and 0.146 Å in the two dimers; a quantitative comparison of these values with those in related organolanthanide species provides a method for ranking structural distortions in bridged homometallic dimers.

Introduction

Although an organometallic complex of the alkaline-earth (Ae)[1] element calcium was reported over 80 years ago,[2] the chemistry of organocalcium, -strontium, and -barium compounds remains among the least developed of any similar group of metals.[3] The low solubility in common organic solvents and marginal thermal stability of many Ca, Sr, and Ba complexes have hindered their investigation, so that even the optimum methods of preparation of the long-known "pseudo-Grignard" reagents (RAeX) are still under study.[3,4]

Such experimental problems stem partly from the use of small, compact organic groups as ligands (e.g., Me, Et), which are unable to supply the steric saturation required to stabilize the complexes against irreversible polymerization or decomposition.[5] Consequently, the use of sterically demanding ligands to suppress oligomerization and block decomposition pathways could be expected to im-

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[†] Vanderbilt University.

[‡] Indiana University.

(1) We would like to suggest the use of the symbol "Ae" to represent the alkaline-earth metals, analogous to the use of "Ln" for the lanthanides and "An" for the actinides. The symbol "Ae" emphasizes the common divalent, electropositive nature of these elements and does not conflict with the symbols for the metals Al and Ac.

(2) The synthesis of PhCaI was reported in 1905 (Beckman, E. *Chem. Ber.* **1905**, *38*, 904–906).

(3) For the most recent general review of organometallic Ae chemistry, see: Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Vol. I, Chapter 4.

(4) Mochida, K.; Yamanishi, T. *J. Organomet. Chem.* **1987**, *332*, 247–252 and references therein.

(5) (a) Marks, T. J. *Science* (*Washington, DC*) **1982**, *217*, 989–997. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131–177.

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prove the solubility and kinetic stability of Ae complexes. The recent synthesis of Cp^*_2Ae complexes ($Cp^* = Me_5C_5$; Ae = Ca, Sr, Ba),[6] which unlike the parent metallocenes are hydrocarbon-soluble, testifies to the soundness of this approach.

We have been seeking to exploit the large coordination numbers and Lewis acidity of organometallic species containing the heavy Ae metals through the synthesis of substituted cyclopentadienyl halide and pseudohalide complexes, $(R_5C_5)AeX$. These compounds could stand as analogues to the synthetically important Cp_2LnX and Cp_3AnX species in organolanthanide and -actinide chemistry.[7] We report the synthesis and crystallographic characterization of the monopentamethylcyclopentadienyl complex $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$, which represents the first structurally characterized cyclopentadienyl halide complex of the heavy Ae metals.[8-10]

Experimental Section

All manipulations were performed with the rigid exclusion of air and moisture. Chemicals were handled with high vacuum or Schlenk techniques or in a Vacuum Atmospheres HE-143 drybox equipped with an MO40-1 recirculating purifier. Proton NMR spectra were obtained at 300 MHz with a Bruker NR-300 spectrometer and were referenced to the residual proton resonances of THF-d_8 (δ 3.58) or C_6D_6 (δ 7.15); carbon (^{13}C) NMR spectra were recorded at 50.3 MHz on a Bruker NR-200 spectrometer and were referenced to the residual ^{13}C resonances of C_6D_6 (δ 128.0). Infrared data were obtained on a Perkin-Elmer 1430 spectrometer. Elemental analyses were performed by Analytiche Laboratorien, Engelskirchen, West Germany, or by Galbraith Laboratories, Knoxville, TN.

Materials. Anhydrous calcium iodide (95%) was purchased from Strem Chemicals and heated under vacuum to remove residual amounts of free iodine. KCp^* was prepared from potassium hydride and pentamethylcyclopentadiene. $Cp^*_2Ca(THF)_2$ was prepared from the reaction of KCp^* and CaI_2 in THF.[6c] Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were stirred over sodium or potassium and vacuum transferred before use.

$[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$ from KCp^* and CaI_2. Potassium pentamethylcyclopentadienide (0.500 g, 2.87 mmol) was added to anhydrous CaI_2 (0.702 g, 2.39 mmol) in 125 mL of THF and the mixture stirred for 11 h. The mixture was then filtered through a medium glass frit and the filtrate evaporated to dryness. Toluene (75 mL) was added to the dried solid and the mixture stirred for 20 min. After the mixture was filtered again, the filtrate was cooled to 6 °C and large, colorless crystals of $Cp^*CaI(THF)_2$ (mp >350 °C) began to appear within a week. Analysis indicates that some desolvation of the crystals had occurred and/or that the combustion was not as complete as possible. Calcd for $C_{18}H_{31}CaIO_2$: C, 48.43; H, 7.00; Ca, 8.98; I, 28.43; O, 7.17. Found: C, 48.46; H, 7.69; Ca, 9.61; I, 30.38; O (by difference), 3.86. Loss of THF from organoalkaline-earth complexes is fairly common,[6] and incomplete combustion has been observed in similarly ionic organolanthanide systems.[11] The observed Ca:I ratio of 1.0, however, establishes that the crystals are free from both $Cp^*_2Ca(THF)_2$ and $CaI_2(THF)_2$.

Table I. Crystal Data and Summary of Data Collection for $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$

formula	$C_{36}H_{62}Ca_2I_2O_4$
fw	892.86
color of cryst	colorless
cryst dimens, mm	0.25 × 0.25 × 0.25
space group	$P2_1/a$
cell dimens (at 118 K; 46 reflctns)	
a, Å	14.837 (4)
b, Å	13.022 (4)
c, Å	21.125 (7)
β, deg	98.66 (1)
V, Å^3	4034.98
Z (dimers/cell)	4
D(calcd), g/cm^3	1.470
wavelength, Å	0.71069
abs coeff, cm^{-1}	18.226
type of scan	continuous θ–2θ
scan speed, deg/min	6.0
scan width	1.8 + dispersn
bkgd counting	6 s at extremes of scan
limits of data collectn	$6° \leq 2\theta \leq 45°$
no. of unique intensities	5280
no. with $F > 2.33\sigma(F)$	4437
$R(F)$	0.0358
$R_w(F)$	0.0371
goodness of fit	0.992
max Δ/σ in final cycle	0.05

In solutions of the crystals, both $Cp^*CaI(THF)_2$ and $Cp^*_2Ca(THF)_2$ can be identified in NMR spectra, the latter compound by its proton chemical shifts at δ 2.06 in C_6D_6 (lit.[6c] δ 2.06) and δ 1.88 in THF-d_8.[12] Relative amounts of the complexes were determined by integration of the peak areas. Since the resonance for $Cp^*_2Ca(THF)_2$ generated by disproportionation of crystalline $Cp^*CaI(THF)_2$ is unshifted in C_6D_6 or THF-d_8 relative to the value of pure $Cp^*_2Ca(THF)_2$ in the same solvents, the exchange between the two complexes is evidentally stopped on the room-temperature ^1H NMR time scale. Although $Cp^*_2Ca(THF)_2$ is detectable (4%) in the ^1H NMR of solutions of crystalline $Cp^*CaI(THF)_2$ in C_6D_6 (see below), its low concentration prevents its detection in these solutions by ^{13}C NMR. The resonances assignable to $Cp^*CaI(THF)_2$ are as follows: ^1H NMR (C_6D_6, 20 °C) δ 3.58 (m, 8 H, α-C_4H_8O), 2.32 (s, 15 H, Cp*); 1.35 (m, 8 H, β-C_4H_8O); ^1H NMR (THF-d_8, 20 °C) δ 2.00 (s, Cp*); ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled) δ 114.2 ($C_5(CH_3)_5$), 68.9 (C_4H_8O), 25.4 (C_4H_8O), 11.9 ($C_5(CH_3)_5$)); major IR bands (KBr pellet) 2929 vs, br, 2729 m, 1449 m, 1348 w, 1299 w, 1264 w, 1189 w, 1034 vs, 884 s, 678 w cm^{-1}.

$[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$ from KCp^* and CaI_2 (3:2). Using a procedure similar to that given above, anhydrous CaI_2 (1.000 g, 3.40 mmol) and KCp^* (0.890 g, 5.10 mmol) were stirred in 150 mL of THF overnight. After being filtered through a fine glass frit, the filtrate from the reaction mixture was evaporated to dryness. The residue was then stirred for 2 h in 100 mL of hexane and the mixture filtered again through a fine frit. The retained solid provided 0.86 g (57% yield) of $Cp^*CaI(THF)_2$. Proton NMR of this material in C_6D_6 indicated a $Cp^*CaI(THF)_2$:$Cp^*_2Ca(THF)_2$ ratio of 89:11; because of the Schlenk equilibria in this solvent (see below), the actual purity of the solid is >90%.[13]

$[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$ from $Cp^*_2Ca(THF)_2$ and CaI_2. $Cp^*_2Ca(THF)_2$ (0.155 g, 0.341 mmol) was added to anhydrous CaI_2 (0.100 g, 0.340 mmol) in 30 mL of THF, and the slightly cloudy reaction mixture stirred for 40 h. The reaction mixture was then filtered through a medium glass frit. The filtrate was evaporated to dryness, and ^1H NMR of the residue in THF-d_8 indicated a

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(6) (a) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31–37. (b) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand., Ser. A* **1987**, *A41*, 24–35. (c) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* **1988**, 7(9), 725–730.

(7) Marks, T.l J.; Ernst, R. D. In ref 3; Vol. 3, Chapter 21.3.

(8) Structures of cyclopentadienyl halide complexes of Be and Mg are known. See: (a) Goddard, R.; Akhtar, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1985**, *282*, 149–154. (b) Johnson, C.; Toney, J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *40*, C11–C13.

(9) The synthesis of pentamethylcyclopentadienyl halide complexes of Be and Mg has been described. See ref 6a and: Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

(10) The synthesis of $(C_5H_5)CaI(THF)_2$ from the reaction of CH_3CaI and C_5H_6 was reported some years ago (Bogatskii, A. V.; Chumachenko, T. K.; Derkach-Kozhukhova, A. E.; Lyamtseva, L. N.; Suprinovich, E. S. *Zh. Obshch. Khim.* **1977**, *47*, 2297–2305). Other than its insolubility in hexane, no chemical properties of the light brown solid were described.

(11) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454–4460.

(12) The chemical shift of pure $Cp^*_2Ca(THF)_2$ in THF-d_8 at 20 °C is δ 1.88 (Sockwell, S. C.; Hanusa, T. P., unpublished results).

(13) Even crystalline $Cp^*CaI(THF)_2$ exhibits a $Cp^*CaI(THF)_2$:$Cp^*_2Ca(THF)_2$ ratio of 96:4 when dissolved in C_6D_6; this equilibrium should be considered when assessing the purity of samples by NMR.

Table II. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters (×10 Å^2) for the Non-Hydrogen Atoms in $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$

atom	*x*	*y*	*z*	B_{iso}[a]
Ca(1A)	4624 (1)	4888 (1)	1028 (1)	13
I(2A)	6000.1 (3)	3817.7 (3)	248.9 (2)	17
C(3A)	5422 (4)	6670 (4)	1475 (3)	16
C(4A)	4658 (4)	6538 (5)	1788 (3)	17
C(5A)	4810 (5)	5674 (5)	2194 (3)	19
C(6A)	5672 (4)	5248 (5)	2121 (3)	16
C(7A)	6054 (4)	5879 (5)	1682 (3)	14
C(8A)	5605 (5)	7560 (5)	1058 (4)	23
C(9A)	3855 (5)	7249 (6)	1730 (4)	25
C(10A)	4219 (5)	5370 (6)	2684 (4)	27
C(11A)	6120 (5)	4334 (5)	2465 (4)	22
C(12A)	6989 (5)	5780 (5)	1499 (3)	19
O(13A)	4400 (3)	3178 (3)	1452 (2)	20
C(14A)	4748 (5)	2162 (6)	1342 (4)	31
C(15A)	3912 (6)	1473 (6)	1299 (4)	31
C(16A)	3333 (5)	1980 (6)	1743 (4)	26
C(17A)	3810 (5)	3001 (6)	1928 (4)	26
O(18A)	3003 (3)	4619 (3)	858 (2)	19
C(19A)	2685 (5)	3861 (5)	368 (3)	23
C(20A)	1794 (5)	4263 (6)	21 (4)	26
C(21A)	1421 (5)	4854 (6)	544 (4)	32
C(22A)	2276 (5)	5333 (6)	903 (4)	23
Ca(1B)	789 (1)	4952 (1)	4082 (1)	13
I(2B)	657.7 (3)	3662.9 (3)	5396.0 (2)	17
C(3B)	1010 (4)	3756 (5)	3060 (3)	14
C(4B)	460 (5)	4599 (5)	2807 (3)	17
C(5B)	-378 (4)	4539 (5)	3042 (3)	15
C(6B)	-357 (4)	3662 (5)	3433 (3)	17
C(7B)	503 (4)	3176 (5)	3448 (3)	15
C(8B)	1907 (5)	3485 (6)	2851 (4)	24
C(9B)	696 (5)	5353 (6)	2317 (3)	26
C(10B)	-1158 (5)	5276 (6)	2869 (3)	23
C(11B)	-1127 (5)	3256 (6)	3755 (4)	25
C(12B)	782 (5)	2177 (5)	3797 (3)	21
O(13B)	2335 (3)	4744 (3)	4551 (2)	18
C(14B)	2775 (5)	5361 (5)	5079 (4)	22
C(15B)	3795 (5)	5084 (7)	5129 (5)	37
C(16B)	3815 (5)	4121 (7)	4716 (4)	34
C(17B)	2853 (5)	3797 (6)	4577 (4)	27
O(18B)	1468 (3)	6513 (3)	3776 (2)	21
C(19B)	2348 (5)	6514 (6)	3541 (4)	27
C(20B)	2313 (5)	7413 (6)	3093 (4)	28
C(21B)	1722 (5)	8174 (6)	3381 (4)	27
C(22B)	1001 (5)	7480 (6)	3589 (4)	27

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610.

Table III. Selected Bond Lengths (Å) and Angles (deg) in $[Cp^*CaI(THF)_2]_2$

atoms	distance	
	$[Cp^*CaI(THF)_2]_2$ (A)	$[Cp^*CaI(THF)_2]_2$ (B)
Ca–I	3.1356 (15)	3.1283 (15)
Ca–I′	3.1980 (16)	3.2743 (16)
Ca–O	2.441 (4)	2.373 (5)
Ca–O′	2.403 (4)	2.400 (5)
Ca–C(3)	2.710 (6)	2.722 (6)
Ca–C(4)	2.678 (6)	2.704 (6)
Ca–C(5)	2.643 (7)	2.640 (6)
Ca–C(6)	2.624 (7)	2.625 (6)
Ca–C(7)	2.682 (6)	2.673 (6)
Ca–C(av)	2.67 (1)	2.67 (1)
Ca–centroid	2.38	2.39
O–C(14)	1.452 (8)	1.448 (8)
O–C(17)	1.447 (8)	1.449 (8)
O–C(19)	1.455 (8)	1.466 (8)
O–C(22)	1.439 (8)	1.462 (8)
C(3)–C(4)	1.407 (9)	1.425 (9)
C(3)–C(7)	1.417 (9)	1.412 (9)
C(4)–C(5)	1.411 (9)	1.408 (9)
C(5)–C(6)	1.425 (9)	1.409 (9)
C(6)–C(7)	1.419 (9)	1.420 (9)
C–C (ring, av)	1.416 (20)	1.415 (20)
C(3)–C(8)	1.504 (10)	1.505 (10)
C(4)–C(9)	1.500 (10)	1.505 (10)
C(5)–C(10)	1.507 (10)	1.505 (10)
C(6)–C(11)	1.498 (9)	1.509 (10)
C(7)–C(12)	1.502 (10)	1.522 (9)
C(14)–C(15)	1.523 (11)	1.544 (11)
C(15)–C(16)	1.517 (12)	1.529 (11)
C(16)–C(17)	1.529 (11)	1.475 (11)
C(19)–C(20)	1.505 (10)	1.501 (11)
C(20)–C(21)	1.518 (12)	1.509 (12)
C(21)–C(22)	1.512 (10)	1.515 (11)

atoms	angle	
	$[Cp^*CaI(THF)_2]_2$ (A)	$[Cp^*CaI(THF)_2]_2$ (B)
Ca–I–Ca′	94.59 (4)	97.73 (4)
O(13)–Ca–O(18)	74.57 (16)	77.89 (16)
Ca(1)–O(13)–C(14)	134.5 (4)	123.6 (4)
Ca(1)–O(13)–C(17)	122.0 (4)	125.9 (4)
C(14)–O(13)–C(17)	103.5 (5)	105.5 (5)
Ca(1)–O(18)–C(19)	114.6 (4)	121.6 (4)
Ca(1)–O(18)–C(22)	129.7 (4)	127.0 (4)
C(19)–O(18)–C(22)	108.6 (5)	108.5 (5)
C(4)–C(3)–C(7)	107.9 (6)	107.8 (6)
C(4)–C(3)–C(8)	126.8 (6)	123.5 (6)
C(7)–C(3)–C(8)	124.9 (6)	128.1 (6)
C(3)–C(4)–C(5)	108.5 (6)	108.1 (6)
C(3)–C(4)–C(9)	125.0 (6)	125.6 (6)
C(5)–C(4)–C(9)	126.4 (6)	126.0 (6)
C(4)–C(5)–C(6)	108.0 (6)	108.1 (6)
C(4)–C(5)–C(10)	124.9 (6)	124.5 (6)
C(6)–C(5)–C(10)	126.6 (6)	127.4 (6)
C(5)–C(6)–C(7)	107.3 (6)	108.3 (6)
C(5)–C(6)–C(11)	126.7 (6)	126.7 (6)
C(7)–C(6)–C(11)	125.9 (6)	124.9 (6)
C(3)–C(7)–C(6)	108.2 (6)	107.8 (6)
C(3)–C(7)–C(12)	125.2 (6)	127.5 (6)
C(6)–C(7)–C(12)	126.4 (6)	124.7 (6)
O(13)–C(14)–C(15)	103.9 (6)	104.3 (6)
C(14)–C(15)–C(16)	103.8 (7)	104.8 (6)
C(15)–C(16)–C(17)	104.7 (6)	104.3 (7)
O(13)–C(17)–C(16)	105.5 (6)	104.8 (6)
O(18)–C(19)–C(20)	106.2 (6)	105.4 (6)
C(19)–C(20)–C(21)	102.2 (6)	103.1 (6)
C(20)–C(21)–C(22)	101.8 (6)	101.7 (6)
O(18)–C(22)–C(21)	106.3 (6)	105.4 (6)

$Cp^*CaI(THF)_2$:$Cp^*_2Ca(THF)_2$ ratio of 70:30.

X-ray Crystallography of $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$. General procedures for data collection and reduction have been described previously.[14] A suitable crystal measuring 0.25 × 0.25 × 0.25 mm was located and transferred by using standard inert atmosphere techniques to a Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator. The crystal was cooled to 118 K for characterization and data collection. Relevant crystal and data collection parameters for the present study are given in Table I.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/a$ (alternate setting of $P2_1/c$, No. 14). Subsequent solution and refinement of the structure confirmed this choice.

Data collection was performed by using standard moving-crystal/moving-detector techniques with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Two independent molecules were located in the unit cell. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. A final difference Fourier synthesis was featureless. Positional parameters are supplied in Table II; selected bond distances and angles are listed in Table III.

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[14] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021–1037.

Results and Discussion

Synthesis of Cp*CaI(THF)$_2$ from KCp* and CaI$_2$. Considering that the metathetical reaction of a 2:1 molar ratio of KCp* or NaCp* and CaI$_2$ produces Cp*$_2$Ca(THF, OEt$_2$)$_2$ in high yield (eq 1),[6] simple stoichiometric

$$2\mathrm{KCp}^* + \mathrm{CaI}_2 \xrightarrow{\mathrm{THF}} \underset{1\ (81\%)}{\mathrm{Cp}^*{}_2\mathrm{Ca(THF)}_2} + 2\mathrm{KI}\downarrow \qquad (1)$$

considerations suggest that monopentamethylcyclopentadienyl alkaline-earth halide complexes could be prepared by the reaction of equimolar amounts of KCp* and CaI$_2$.

Stirring an approximately equimolar mixture of KCp* and CaI$_2$ in THF overnight, removing the precipitate, and evaporating the solvent from the filtrate does yield Cp*CaI(THF)$_2$ (2),[15] but 1 and CaI$_2$(THF)$_2$ (3)[16] are present as well. Separation of the compounds by solvent extraction is not easily done, since all three are moderately to easily soluble in THF, and only 1 has any solubility in alkanes. If the crude material is washed with toluene, however, most of 1 and some of 2 is dissolved. On standing, the toluene washings will deposit colorless crystals of 2 in low yield. In the absence of air or moisture, solid samples of 2 are indefinitely stable at room temperature.

The mixture of 1 and 2 obtained from the reaction of KCp* and CaI$_2$ suggests that a Schlenk equilibrium between 1 and 2 exists, as in eq 2. The ^{1}H NMR spectrum

$$\begin{array}{c} 2\mathrm{KCp}^* + 2\mathrm{CaI}_2 \xrightarrow{\mathrm{THF}} 2\mathrm{Cp}^*\mathrm{CaI(THF)}_2 + 2\mathrm{KI}\downarrow \\ \downharpoonleft\upharpoonright \\ \mathrm{Cp}^*{}_2\mathrm{Ca(THF)}_2 + \mathrm{CaI}_2\mathrm{(THF)}_2 \end{array} \qquad (2)$$

of homogeneous 34 and 15 mM THF-d_8 solutions of 2 prepared from crystalline material reveals 1 and 2 in a 1:2 molar ratio. If eq 2 is applicable, an amount of 3 equal to that of 1 must also present in solution. The relative amounts of 1, 2, and 3 in THF-d_8 are then 1, 2, and 1, respectively, and the equilibrium constant K calculated from eq 3 is 4.[17] This is the value expected from a statistical distribution of Cp* rings and iodide ligands and indicates that complete scrambling of the ligands is occurring.

$$K = \frac{[\mathrm{Cp}^*\mathrm{CaI(THF)}_2]^2}{[\mathrm{Cp}^*{}_2\mathrm{Ca(THF)}_2][\mathrm{CaI}_2\mathrm{(THF)}_2]} \qquad (3)$$

Higher Yield Synthesis of Cp*CaI(THF)$_2$. The preparation of 2 is complicated by the Schlenk equilibrium between 1 and 2 (see eq 2) complicates the preparation of the latter in good yield. Although excess CaI$_2$ could be added to the reaction with KCp* in order to suppress the formation of 1, the residual CaI$_2$(THF)$_2$ would seriously contaminate the final product.[18] An alternate approach is to use a 50% molar excess of KCp*, which produces nearly equimolar mixtures of 1 and 2, with little or no 3.[19] Removal of most of the metallocene is accomplished with a hexane wash, leaving 2 in moderately good yield.

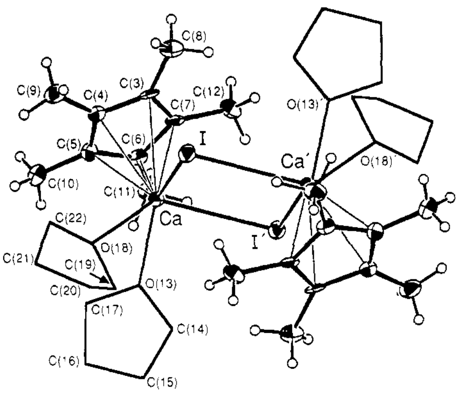

Figure 1. ORTEP view of one of the two independent dimers of [Cp*Ca(μ-I)(THF)$_2$]$_2$ (A), giving the numbering scheme used in the tables. Dimer B is numbered similarly. For clarity, the THF ligands have been rendered as lines.

Synthesis of [Cp*Ca(μ-I)(THF)$_2$]$_2$ from Cp*$_2$Ca(THF)$_2$ and CaI$_2$. Stirring an equimolar mixture of 1 and CaI$_2$ in THF overnight, removing the solvent, and analyzing the material by NMR spectroscopy in THF-d_8 indicates the presence of both 1 and 2 in a ratio of 30:70. This is essentially the same proportion as that from KCp* and CaI$_2$ and supports the appropriateness of eq 2. Although in principle 2 can be prepared from either 1 or KCp*, the use of KCp* avoids the extra steps required to prepare 1.

Relationship of Cp*CaI(THF)$_2$ to Grignard Reagents. The equilibrium between 1, 2, and 3 in THF invites comparison with the behavior of organomagnesium Grignard reagents. In an NMR tube experiment, 2 was found rapidly and completely to dissociate in dioxane-d_8 to form 1 and a white precipitate, presumably the solvate CaI$_2$(dioxane)$_n$. Such behavior is typical of Grignard solutions.[20,21] A saturated solution of crystalline 2 prepared in C$_6$D$_6$ exhibits a 4:96 ratio of 1:2 in its ^{1}H NMR spectrum. Although the ratio of 1:2 in a fairly dilute (11 mM) solution in C$_6$D$_6$ does not change over a 2-week period, greater dilution causes the amount of 1 to increase with time.[22]

Schlenk equilibria and exchange in Grignard systems has been directly observed with various types of NMR

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[15] In this paper, we will use the formula "Cp*CaI(THF)$_2$" to refer to the compound in solution or when only the empirical formula is of interest; no degree of association is implied by it. "[Cp*Ca(μ-I)(THF)$_2$]$_2$" will be used when the structural features in the solid state are discussed.

[16] We will use the formula of the disolvate in the following discussion, although the actual number of THF ligands in solution is probably higher. It might be noted that evaporation of saturated THF solutions of CaI$_2$ produces a material which analyzes as (partially desolvated) CaI$_2$(THF)$_4$. Anal. Calcd for CaI$_2$(THF)$_4$: C, 33.00; H, 5.54. Found (average of two determinations): C, 30.91; H, 5.08. The solubility of anhydrous CaI$_2$ in THF is calculated to be 12.4 g/L (42.2 mmol/L). The presence of CaI$_2$(THF)$_2$ in solution is evidenced by the increase in integrated intensities of THF resonances in ^{1}H NMR spectra measured in C$_6$D$_6$.

[17] Although it is in principle not as accurate a method, an identical value of K was obtained by examining the crude products from the reaction mixtures of KCp* and CaI$_2$ after removal of the THF but without filtering. The ratio of CaI$_2$:KCp* was varied from 1 to 4, and the value of K measured by ^{1}H NMR in THF-d_8 averaged to 4.0.

[18] It is worth noting that the addition of excess iodide (as (^{n}Bu)$_4$N$^+$I$^-$) to the reaction of KCp* and CaI$_2$ in THF has essentially the same effect on the ratio of 1 to 2 as does the addition of excess CaI$_2$. This is an indication that the function of excess iodide may be to drive a dissociative equilibrium such as Cp*CaI(THF)$_2 \rightleftharpoons$ [Cp*Ca(THF)$_n$]$^+$ + [I(THF)$_n$]$^-$ to the left and prevent the formation of 1 from the combination of "[Cp*Ca(THF)$_n$]$^{+}$" with free [Cp*]$^-$.

[19] These amounts, measured by NMR in C$_6$D$_6$, are those expected from the stoichiometric equation 3KCp* + 2CaI$_2 \xrightarrow{\mathrm{THF}}$ Cp*$_2$Ca(THF)$_2$ + Cp*CaI(THF)$_2$ + 3KI $\downarrow$. Schlenk equilibrium is evidently not synthetically important when the KCp*:CaI$_2$ ratio is appreciably greater than one.

[20] Schlenk, W.; Schlenk, W. *Chem. Ber.* **1929**, *62*, 920–924.

[21] Reviews of the early literature on Grignard chemistry may be found in: (a) Wakefield, B. *J. Organomet. Chem. Rev.* **1966**, *1*, 131–156. (b) Ashby, E. C. *Q. Rev., Chem. Soc.*, **1967**, *21*, 259–285.

[22] A nominally 1.9 mM solution of 2, prepared by adding 0.010 g of 2 to 12 mL of C$_6$D$_6$, exhibits a ratio of 1:2 of 35:65 after 8 h. On standing 72 h, the 1:2 ratio changes to 46:54. Owing to precipitation of CaI$_2$(THF)$_2$, a completely clear solution of 2 is never obtained in C$_6$D$_6$. Grignard solutions prepared in hydrocarbons also have R/X > 1 and may decompose on high dilution; see: (a) Glaze, W. H.; Selman, C. M. *J. Organomet. Chem.* **1966**, *5*, 477. (b) Smith, W. N., Jr. *J. Organomet. Chem.* **1974**, *64*, 25.

spectroscopy,[23-25] but Cp*MgI has not been reported, so as to enable comparison of the equilibrium constant for **2** with its organomagnesium analogue. The value for K of 4 calculated for compound **2** in THF-d_8 at ambient temperature, however, is far less than the value of $\sim 10^4$ observed for CpMgCl (^{1}H NMR) or $\sim 10^6$ observed for CpMgBr (^{1}H, ^{25}Mg NMR) in the same solvent.[23d,24] Several factors might be responsible for the large difference in the value for K, including the bulk of Cp vs Cp*, the greater charge density of Mg^{2+} relative to Ca^{2+}, and the nucleophilicity of Br^- vs I^-.[26]

Structure of $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$. To establish structural parameters for this prototypical cyclopentadienyl halide complex, crystals deposited from the toluene wash from KCp* and CaI_2 were collected and subjected to a X-ray structure determination. $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$ crystallizes from toluene as a halide-bridged dimer, in which each calcium atom is coordinated by a single pentamethylcyclopentadienyl ring, two THF molecules, and two bridging iodides. Two independent dimers (A and B) appear in the asymmetric cell, each with a crystallographically imposed center of inversion. An ORTEP view of one complex is displayed in Figure 1.

The average (η^5-Cp*)–Ca distance for both species is 2.67 Å, whereas the average Ca–O(THF) distance is 2.422 (6) Å in one dimer and 2.387 (7) Å in the second dimer. The $[Ca(\mu\text{-}I)]_2$ core is somewhat asymmetric in each dimer, the Ca–I distances differing by 0.062 Å in one case and by 0.146 Å in the other.

Most of the parameters of the individual units are unexceptional. The pentamethylcyclopentadienyl ring in complex A [B] is planar to within 0.009 Å [0.003 Å]. The methyl groups are bent away from the ring plane by an average of 0.11 Å [0.10 Å], leading to an displacement angle of 4.2° [3.8°]. No unusual internal contacts are evident; the closest nonbonded carbon–carbon distance involves a ring methyl group and the α-C of a THF ligand at a distance of 3.48 Å (C10–C17 in dimer A).

The structure of **2** is the first crystallographically characterized monocyclopentadienyl structure of a heavy Ae metal, and only two organocalcium structures are available for comparison. In polymeric Cp_2Ca, each calcium ion is surrounded by two η^5, one η^3, and one η^1 Cp rings, with an average Ca–C(η^5) distance of 2.80 Å.[27] If the Ca^{2+} is considered to be fully nine-coordinate with a radius of 1.18 Å[28] (this is a generous assumption, as the η^1 ring is 3.10 Å from the metal center), the 0.12 Å difference between this value and the seven-coordinate radius of Ca^{2+} (1.06 Å) account satisfactorily for the 0.13 Å shorter Ca–C distance of 2.67 (1) Å in **2**. In the structure of $[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Ca(THF)$,[29] the average Ca–C distance is 2.69 Å, essentially the same as the value in **2**. Other comparisons can be made with the metallocenes $[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2Sr(THF)$[29] and Cp^*_2Ba,[30] which display average Ae–C distances of 2.81 and 2.99 (2) Å, respectively. The differences of 0.15 Å in the radii of seven-coordinate Ca^{2+} and Sr^{2+} and the change of 0.29 Å between the radii of seven-coordinate Ca^{2+} and six-coordinate Ba^{2+} compare favorably with the 0.14 and 0.32 Å differences in the Ae–C bond lengths.

Useful structural comparisons are also possible with divalent organolanthanide species. The average metal–C(Cp*) distances in $[Cp^*Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]_2$ (2.82 (2) Å),[31] $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$ (2.81 (2) Å),[32] $[Cp^*_2Sm(OC_5H_{10})]$ (2.816 (3) Å),[33] $Cp^*_2Yb(MeC{\equiv}CMe)$ (2.659 (9) Å),[34] and $Cp^*_2Yb(THF)$(0.5toluene) (2.66 (2) Å)[35] differ from that found in **2** (2.67 (1) Å) by 0.15, 0.14, 0.15, 0.01, and 0.01 Å, respectively. These values compare well with differences of 0.14, 0.16, and 0.02 Å between the seven-coordinate metal radius of Ca^{2+} and those of Eu^{2+}, Sm^{2+}, and Yb^{2+}, respectively. Similarly, the average M–O(THF) bond lengths in $[Cp^*Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]_2$ (2.62 (1) Å), $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$ (2.64 (2) Å), and $Cp^*_2Yb(THF)$(0.5toluene) (2.412 (5) Å) differ by 0.14, 0.14, and 0.01 Å, respectively, from the average for both dimers in **2** of 2.405 (9) Å, again closely paralleling the difference in metal radii. Such correspondences suggest that the steric environment around the metals in these divalent systems is similar, although with the largest divalent radii of the group, **2** and $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$ must be the most coordinatively unsaturated. The decomposition of dilute hydrocarbon solutions of **2** (see above) may reflect the fact that loss of a THF ligand generates an unstable six-coordinate "Cp*CaI(THF)" species, which then metathesizes to the more sterically saturated $Cp^*_2Ca(THF)_2$ complex.

The similarities of **2** with the isostructural samarium complex $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$ extend beyond metal–C distances. Both it and the calcium species are constructed around a planar $M(\mu\text{-}I)_2M'$ core, with I-M-I′ angles of 82.04° in the samarium complex and 85.41° and 82.27° in the A and B dimers of **2**. The most conspicuous difference between the structures is that the Ca–I bond lengths differ by 0.062 and 0.146 Å in the two conformers of **2**, whereas in $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$ the corresponding Sm–I lengths differ by 0.103 Å. Intriguingly, the asymmetry observed in the two calcium dimers brackets the range of differences in metal–(μ-halide) bond lengths found in the organolanthanide complexes $[(C_8H_8)Ce(THF)(\mu\text{-}Cl)]_2$ (0.080 Å),[36] $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$ (0.103 Å), and $Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2$ (0.136 Å),[37] a series previously proposed as a model of dimer-to-monomer dissociation in complexes containing M_2X_2 centers.[32] Especially counterintuitive is that the difference in M–X bond lengths in the structurally "open" $Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2$ is less than that observed in dimer B of the "closed" **2**, a fact which highlights the difficulty

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[26] No evidence for Schlenk equilibrium is found in the room-temperature ^{1}H NMR spectrum of Cp*CaCl (prepared from Cp^*_2Ca and $CaCl_2$ in THF) in THF-d_8 (McCormick, M. J.; Hanusa, T. P., unpublished results). This result suggests the importance of the identity of the halide to the exchange process, a conclusion supported by the $\sim 10^2$ difference in the value of K for CpMgCl and CpMgBr.

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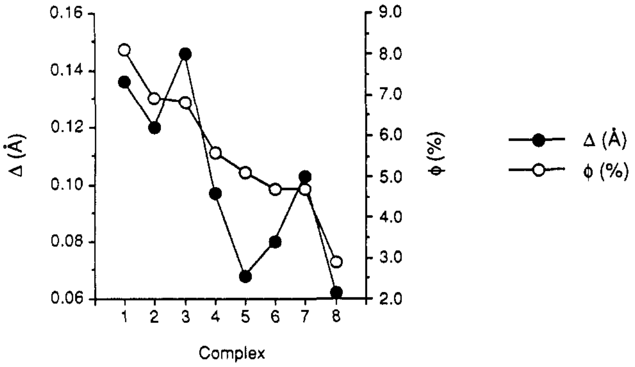

Figure 2. Assymetry in homometallic bridged dimers. Differences in M–X bond lengths are indicated as Δ (black circles) and ϕ (white circles), defined as in the text. The values of Δ (Å) and ϕ (%) for each complex are (1) $Cp^*_2Y(\mu\text{-}Cl)ClYCp^*_2$ (0.136, 8.1, ref 37), (2) $[Cp^*_2ClSm(\mu\text{-}Cl)SmCp^*_2[(MeOCH_2CH_2)_4(OMe)]\text{-}SmCp^*_2]^+$ (0.120, 6.9, ref 39), (3) $[Cp^*CaI(THF)_2]_2$ (B) (0.146, 6.8, this work), (4) $(Cp_2YCl)_2AlH_3{\cdot}Et_2O$ (0.097, 5.6, ref 40), (5) $\{Cp_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (0.068, 5.1, ref 38), (6) $[(C_8H_8)CeCl\text{-}(THF)]_2$ (0.080, 4.7, ref 36), (7) $[Cp^*SmI(THF)]_2$ (0.103, 4.7, ref 32), and (8) $[Cp^*CaI(THF)_2]_2$ (A) (0.062, 2.9, this work).

of drawing structural comparisons between complexes with different metal radii and sets of ligands.

Measures of Asymmetry. Although the simple difference in metal–ligand bond lengths (Δ) is most often used to gauge the degree of asymmetry in bridged dimers, compensation for changes in metal and ligand sizes could be made by calculating the *relative* difference in effective ionic radii of the ligands. That is

$$\phi = \frac{R_{\text{eff}(1)} - R_{\text{eff}(2)}}{0.5(R_{\text{eff}(1)} + R_{\text{eff}(2)})} \qquad (4)$$

where ϕ is a measure of asymmetry and R_{eff}, the "effective ionic radius" of the ligand, equals the difference between the metal–ligand distance and the coordination number adjusted radius of the metal.[37]

The values of Δ (in Å) are plotted in Figure 2 against decreasing values of ϕ (as %) for all known structurally characterized homometallic bridged dimers with $\Delta \geq 0.06$ Å. Two points are especially worthy of note: (1) $Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2$ (Figure 2, number 1) is calculated as having a slightly larger ϕ value than does dimer B of **2** (Figure 2, number 3), even though Δ is smaller for the yttrium complex, and (2) a complex with short metal–ligand distances relative to the size of the metal radius (e.g., $\{Cp_2Y[N{=}C(H)C(CH_3)_3]\}_2$ (Figure 2, number 5),[38] for which the Y^{3+} radius is 1.019 Å and the two Y–N lengths are 2.314 and 2.382 Å)) will possess a relatively large ϕ, even though the absolute difference in metal–ligand lengths (Δ) may be moderate. Thus ϕ can be used both to rank the asymmetry in complexes with large metal ions in a chemically reasonable manner and also to highlight assymetry greater than that apparent from simple metal–ligand bond length differences. Of course, the use of ϕ does not remove the difference in Ca–I lengths in the two dimers of **2**, which appears to stem from crystal packing effects.

Conclusions

In reactions which are typical in early-transition-metal and f-element chemistry, the metathesis of KCp* and CaI_2 can produce either the metallocene $Cp^*_2Ca(THF)_2$ or the monopentamethylcyclopentadienyl dimer complex $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$. The solid-state structure of the latter also has parallels in organolanthanide systems, but in solution it displays Schlenk equilibrium between $CaI_2(THF)_2$ and $Cp^*_2Ca(THF)_2$, inviting comparisons with organomagnesium Grignard reagents. The ability of organometallic Ae complexes to exhibit chemical properties of several different metal families highlights the location of the Ae metals as "bridging elements" between the alkali metals, magnesium, and the f-elements. A major challenge in this area is the determination of those complexes and reaction conditions likely to display most effectively the range of reactivity inherent in organometallic Ae chemistry.

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Registry No. 1, 121232-39-1; 2, 121232-38-0; KCp*, 94348-92-2; CaI_2, 10102-68-8; $[Cp^*Co(\mu\text{-}I)(THF)_2]_2$, 121232-37-9.

Supplementary Material Available: Tables of hydrogen atom fractional coordinates, bond distances and angles involving hydrogen atoms, and anisotropic thermal parameters (11 pages); a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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