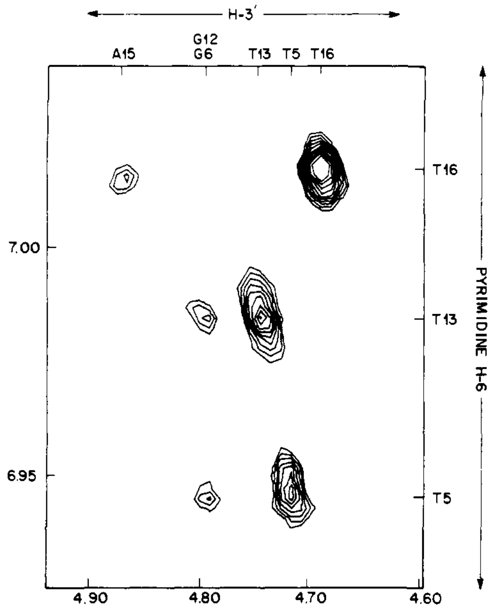

Figure 1. Portion of 2D NOESY spectrum showing indirect NOE's between thymidine H6 protons and H3′ protons. The characteristic geometry of B DNA implies that the larger effect is seen with the H3′ of its own sugar, the smaller effect with the H3′ of the 5′-flanking sugar. The oligonucleotide was made 6 mM in 200 mM KCl, 50 mM potassium phosphate (pD 7.4), 1 mM EDTA, and 1 mM sodium azide. The 2D experiment was a modification of the pure phase method of States et al.[3,7] and performed at 30 °C. The mixing time was 300 ms. 4096 points were sampled over 5000-Hz sweep width in t_2. After Fourier transformation on the fly, 1024 points containing the aromatic region were extracted and stored. 512 T_1 values were obtained and zero filled to 1024. A mild convolution difference with parameters GM2, EM100, and 0.9 was applied.

observed in this region of the NOESY spectrum. The H4′ resonances from pyrimidines (3.90–4.15 ppm) occur upfield to those from purines (4.22–4.36 ppm), with the exception of the terminal adenosines (A_1 and A_{17}), whose sugars may be in a different configuration.[7] As to the H1′ resonances, those from cytosines tend to be upfield to those from thymidines; likewise, the H1′ resonances from guanosines are upfield to those from adenosines.[7] Thus the two-dimensional H4′–H1′ region of the NOESY spectrum roughly partitions into four subsections corresponding to the four bases.[15]

O_L1 is the first complete operator DNA sequence for which H3′ and H4′ assignments have been made.[16] Since these protons lie on the outer surface of the sugar–phosphate backbone, they may be involved in ligand binding. In addition, H3′ assignments may be used to assign the scalar-coupled ^{31}P resonances by one-dimensional[17] and two-dimensional heteronuclear correlated methods.[5] These ^{31}P resonances are known to be sensitive to DNA conformation and interactions.[18–21] For these reasons we anticipate that this method will be of considerable utility in understanding the solution structure and dynamics of biologically important oligonucleotides such as O_L1.

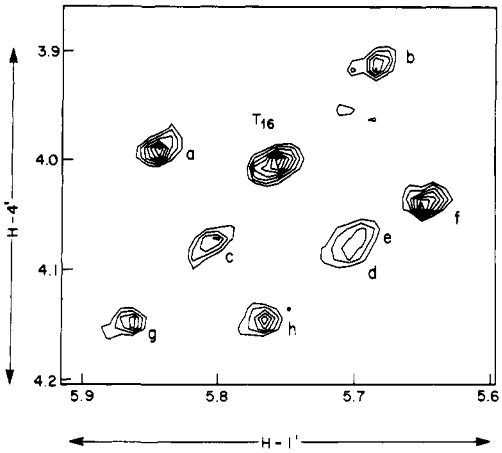

Figure 2. Portion of 2D NOESY spectrum showing indirect NOE's between pyrimidine H1′ and H4′ sugar protons. The conditions were the same as in Figure 1. H1′ assignments, obtained by the sequential method,[7] thus extend to the H4′ protons. The assignments shown are (a) T_2, (b) T_1 and T_{17}, (c) C_9, (d) C_6, (e) C_{12}, (f) T_{13} and T_5, (g) T_{15}, and (h) C_3. In the experiment the mixing time was 350 ms. Resolution enhancement was achieved in both dimensions by convolution difference with parameters 2, 20, and 1.

Acknowledgment. All spectra were taken at the 498 Megahertz facility of the Francis Bitter National Magnet Laboratory, supported by NIH Grant RR-00995 and NSF Contract C670. This work was supported in part by grants from the National Institutes of Health to M.K. (GM-30804) and to R.T.S (AI-16892). M.A.W. was partially supported by an NIH Medical Sciences Training Grant to Harvard Medical School.

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[15] In addition to the strong NOE's observed between the H1′ and H4′ protons of the same sugar, weak cross-relaxation is observed between the H1′ of one sugar and the H4′ proton of the 3′-neighboring sugar on the same strand. Such NOE's, which may be used as consistency checks, illustrate that each sugar is not rigorously an independent relaxation sink, but only nearly so. The H1′ of A_{13}, for example, weakly cross-relaxes with an H4′ at 4.06 ppm, confirming the assignment of the latter to C_{12}, its 3′ neighbor. In standard B DNA, the distance from H1′ to the H4′ of the same sugar is 3.6 Å whereas the distance to the H4′ of the 3′-neighboring sugar is 4.2 Å. The strength of the latter NOE is therefore expected to be ≈40% of the former. In the single-crystal studies of Dickerson and Drew[9] the mean distances are 2.9 and 4.7 Å, implying an intensity ratio of 17:1. Although individual distances vary by as much as 0.9 Å relative to the mean value, the H1′ is always closer to its own H4′.

[16] The H3′ and H4′ resonances have been completely assigned with the exception of C_6 and G_{10}; the H3′ assignments of these bases are unclear due to limited resolution (manuscript in preparation).

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Synthesis and Crystallographic Characterization of an Unsolvated, Monomeric Bis(pentamethylcyclopentadienyl) Organolanthanide Complex, $(C_5Me_5)_2Sm$[1,2]

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The 1968 discovery of uranocene, $U(C_8H_8)_2$,[4] and the subsequent synthesis of the related lanthanide complexes,[5] $Ln(C_8H_8)_2^-$, demonstrated that eight-carbon rings rather than five-carbon rings were the appropriate size to form bis(ring) sandwich complexes of the f elements. This is quite reasonable given the strong preference of these large metals for high coordination numbers and typically 8–10 ligand electron pairs.[6,7] Bis(cyclopentadienyl)

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(1) Dedicated to the memory of Professor Earl L. Muetterties, whose untimely death occurred on the date this structure was solved, Jan 12, 1984.

(2) Presented in part at the Industrial Associates Conference on Recent Trends in Heterogeneous and Homogeneous Catalysis, California Institute of Technology, March 21–23, 1984.

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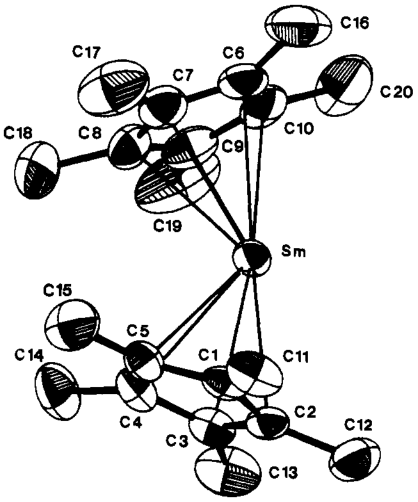

Figure 1. ORTEP view of $(C_5Me_5)_2Sm$ showing the numbering scheme. Hydrogen atoms are omitted for clarity.

f-element sandwich complexes analogous to ferrocene would be so coordinatively unsaturated that they would be expected to have limited stability. Although a wide variety of bis(cyclopentadienyl) f-element complexes are known,[6,7] nearly all have additional ligands in their coordination sphere. Even the unsolvated $(C_5H_5)_2Ln$ complexes of Eu,[8] Yb,[8,9] and Sm,[10] which are analogous in formula to ferrocene, are likely to have coordination numbers larger than 6 via oligomerized structures. The insolubility of the Eu and Sm derivatives and the oligomerized 10-coordinate structure of the solvated $[(CH_3C_5H_4)_2Yb(THF)]_n$[11] support this contention. We describe here the first structure of a divalent bis(cyclopentadienyl) f-element complex free of any additional coordinating solvent molecules or other bases. This species represents the closest f-element analogue to cyclopentadienyl transition-metal metallocenes.

As part of our general investigation of low-valent lanthanide chemistry,[12,13] we have examined the metal vapor reaction of samarium with C_5Me_5H. The primary product of this reaction upon workup with THF was the purple solvated species $(C_5Me_5)_2Sm(THF)_2$ (I),[14] although small amounts of a green complex, II, analyzing as the nonsolvated species $(C_5Me_5)_2Sm$, were also obtained prior to the addition of THF.[15] Recently, we examined the high-temperature stability of I in vacuo (10^{-5} torr) and found that II could be obtained in good yield from I by desolvation and sublimation. As I is heated to 75 °C, a pressure surge occurs, and at 85 °C THF-free II sublimes as a dark green solid. The highest yield of II, 74% based on I, was obtained when the sublimation was done at 125 °C.[16,17] The sublimate was identified as $(C_5Me_5)_2Sm$ by spectroscopic methods[18] and by its reaction chemistry. It reacts cleanly with THF to form I in quantitative yield[19] and reacts with D_2O to form only D_2.[20] II is so reactive with traces of THF that we handle it only in a THF-free glovebox.

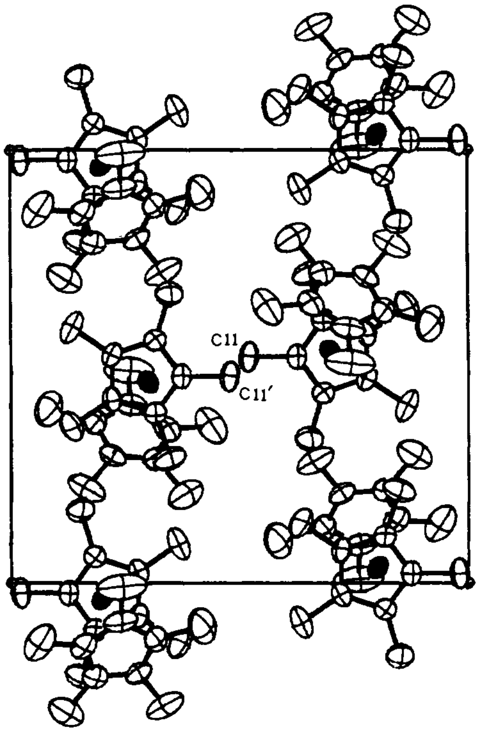

Figure 2. Side-by-side approach of two $(C_5Me_5)_2Sm$ units via C(11) as seen in a packing diagram projected down the "A" axis.

X-ray-quality crystals of II were obtained by resublimation at 100 °C in a sealed tube at 4×10^{-5} torr. The crystallographically determined structure of II (Figure 1)[21] confirmed its formulation as an unsolvated bis(pentamethylcyclopentadienyl) complex, i.e., decamethylsamarocene. In the solid state, the two C_5Me_5 rings are not parallel, as in $(C_5Me_5)_2Fe$,[22] but instead have a bent metallocene structure.[23] The ring centroid–Sm–ring centroid

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(16) In contrast, $(C_5H_5)_2Sm(THF)$ is reported to decompose upon desolvation.[10] Partial desolvation of $(C_5Me_5)_2Yb(THF)_2$ to $(C_5Me_5)_2Yb(THF)$ at 90 °C has been reported: Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652–653.

(17) The major samarium byproduct isolated after this sublimation is the crystallographically characterized oxide $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$: Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.*, submitted for publication.

(18) ^1H NMR (C_6D_6) δ 1.53 (br, s; $\Delta\nu_{1/2}$ = 20 Hz); in toluene-d_8 $\Delta\nu_{1/2}$ = 9 Hz. ^{13}C NMR (toluene-d_8) δ −98.18 (s, $C_5(CH_3)_5$) and 99.04 (q, J = 130 Hz, $C_5(CH_3)_5$). Cf. $(C_5Me_5)_2Sm(THF)_2$ δ −73.7 (s, C_5Me_5), 94.62 (q, J = 117 Hz, $C_5(CH_3)_5$). IR (KBr, cm^{-1}): 2970 (s), 2923 (s), 2869 (s), 1440 (s), 1260 (m), 1240 (m), 1130 (s), 1060 (s), 1020 (w), 805 (s), 790 (s). UV–vis ($CH_3C_6H_5$): The only maximum observed was a broad absorbance at 599 nm (ϵ 250).

(19) Addition of one drop of THF-d_8 instantly changed the color of a solution of II from dark green to purple, and the ^1H NMR spectrum of the product exhibited a sharp singlet at 2.09 ppm ($\Delta\nu_{1/2}$ = 9 Hz), consistent with the reported spectrum of I.[14]

(20) Deuterolysis yields 0.32 mol of D_2 per gram atom of Sm (64% yield) with no HD observed. In comparison, deuterolysis of I yields D_2 in 90% yield;[15] deuterolysis of $\{[(C_5H_5)_2LnH]_3H\}\{Li(THF)_4\}$ (Ln = Y, Lu) gives HD in 60% yield: Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015–2017. Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *Ibid.*, in press.

(21) The space group is the monoclinic $P2_1/n$ with $a = 9.815$ (3) Å, $b = 13.436$ (9) Å, $c = 14.163$ (8) Å, $\beta = 94.98$ (4)°, $U = 1860.8$ Å^3, and $D_c = 1.50$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement on the basis of 2636 absorption-corrected unique reflections with $I > 3.0\sigma(I)$ yielded a final $R = 0.035$, $R_w = 0.049$. Evidence for 13 hydrogens was observed, and at least one hydrogen per methyl group was located. The rest were inserted in calculated positions. Hydrogen atoms were not included in the refinement. All other atoms were refined with anisotropic temperature factors.

(22) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892–897. $(C_5Me_5)_2Mn$ also contains parallel rings but they are distorted and slightly slipped from the metal center so that the C–C ring distances range from 1.409 to 1.434 Å and the Mn–C bond lengths vary from 2.105 to 2.118 Å.

angle is 140.1° compared to 136.7° for the disolvated analogue, I.[14,24] The average cyclopentadienyl C–Sm bond length in II is 2.79 (1) Å compared to 2.86 (3) Å in I.[14] The difference in these distances is consistent with the reduced ligand crowding in II due to the loss of two THF molecules.[25]

Examination of a packing diagram for II (Figure 2) indicates that the closest approach of one $(C_5Me_5)_2Sm$ molecule to the samarium center of another molecule occurs through the C(11) methyl group.[26] This Sm–C(11)′ distance is 3.22 (1) Å.[27] The smallest calculated separation of a hydrogen on C(11) to the distant samarium is 2.80 Å. In comparison, the longest crystallographically observed agostic metal–hydrogen interaction cited in a recent review is 2.29 Å.[28–30] The closest intermolecular contact between the methyl groups of adjacent molecules (3.34 (1) Å) is, however, significantly less than the sum of the appropriate van der Waals radii (ca. 4.0 Å).[31] We are pursuing the synthesis of closely related compounds in order to determine the importance of this and other factors to the geometry of the molecule.

The high degree of coordinative unsaturation found in $(C_5Me_5)_2Sm$, unprecedented in f-element chemistry, combined with the fact that Sm(II) is the most strongly reducing of the accessible divalent lanthanides,[32] makes decamethylsamarocene a highly reactive species. It should be an ideal molecule for examining the full potential of organosamarium(II) chemistry.

Acknowledgment. We thank the National Science Foundation for support of this research and the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.). We especially thank Professor R. J. Doedens for his help and advice with the crystal structure determination.

Supplementary Material Available: Tables of crystal data, bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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(27) For comparison, the tetrameric structure of $[(CH_3C_5H_4)_3Nd]_4$ arises from the interaction of a carbon atom of an η^5-cyclopentadienyl ring in one $(CH_3C_5H_4)_3Nd$ unit with the metal of an adjacent $(CH_3C_5H_4)_3Nd$ unit at a distance of 2.990 (7) –2.978 (7) Å. The average Nd–C (η^5) distance is 2.79 (5) Å: Burns, J. H.; Baldwin, W. H.; Fink, F. H. *Inorg. Chem.* **1974**, *13*, 1916–1920. The Nd–C distances holding $(C_8H_8)_2Nd^-$ to $(C_8H_8)Nd(THF)_2^+$ in a tight ion pair are 2.69 (2), 2.89 (2), and 3.02 (2) Å in comparison to the Nd–C distances in the η^8-C_8H_8 Nd units of 2.68 (1), 2.79 (1), and 2.68 (1) Å: De Kock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625–631. Nd^{3+} is approximately 0.115 Å smaller than Sm^{2+}: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 982, 1002.

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^{13}C NMR Spectroscopy of "Transition-State Analogue" Complexes of *N*-Acetyl-L-phenylalaninal and α-Chymotrypsin

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Enzymes are predicted to bind transition-state structures more tightly than the ground-state structures and hence a "transition-state analogue", a molecule that resembles the transition state, should have a higher affinity for the enzyme than the substrate or product analogue structures.

Peptide aldehydes related to substrates have proven to be potent inhibitors of serine proteases,[1–4] and it has been suggested that the tighter binding of the aldehydes derives from stabilization of a hemiacetal tetrahedral adduct (resembling the transition state) formed between the enzyme active site serine and the aldehyde carbonyl. In a collaborative experiment, Chen et al.[5] applied proton NMR spectroscopy to the interaction of *N*-benzoyl- and *N*-acetyl-L-phenylalaninals with α-chymotrypsin (Cht) and [195-dehydroalanine]α-chymotrypsin. From line width changes and cross-saturation effects, it was shown that these specific aldehyde transition-state analogues do bind as the hemiacetal to Cht. Proton NMR signals for the hemiacetal structures were never directly observed and were only inferred from the selective cross-saturation experiments.[5,6] However, in a proton and fluorine NMR investigation of *N*-acetyl- and *N*-benzoyl-DL-*p*-fluorophenylalaninal binding to Cht, Gorenstein and Shah[3] provided the first direct observation of signals (fluorine) representing the hemiacetal structure and the noncovalent Michaelis complex.

The wide range and diagnostic power of ^{13}C NMR suggested that structural assignment of the complex could be made for an aldehyde inhibitor binding to Cht, and we now report ^{13}C NMR spectra which allows us to monitor for the first time two interconverting forms for the hemiacetal complex. During the course of our studies a related ^{13}C NMR study of an aldehyde transition-state analogue binding to papain appeared.[7]

The ^{13}C NMR spectrum of the *N*-acetyl-L-phenylalaninal-*1*-^{13}C[8] (prepared from L-phenylalanine-*1*-^{13}C (90% ^{13}C enriched) reveals that a substantial amount (92 ± 2%) of hydrate (δ(C) 91.6 from Me_4Si) is present in Me_2SO-d_6 (20%) together with a small signal (8 ± 2% at 203.6 ppm) for the free aldehyde, which is in agreement with our previous assignments for the ^{19}F NMR spectrum for *N*-acetyl-DL-*p*-fluorophenylalaninal in Me_2SO-d_6 (20%). Addition of the *N*-acetyl-L-phenylalaninal to Cht at 30 °C resulted in the appearance of a new signal at ~94.0 ppm and broadening of the signal at ~203.6 ppm (Figure 1).

The new signal at ~94.0 ppm and the 203.7 ppm signal are assigned to the hemiacetal signal and noncovalent Michaelis complex, respectively (Scheme I), on the basis of the chemical shifts of analogous systems and earlier NMR studies.[3,4,6]

Note that the signals of enzyme-bound complexes are >25 Hz broader than the hydrate signal and also that the noncovalent enzyme-bound complex is broader by about 25 Hz at pH 5 than the free aldehyde signal at 203.6 ppm in the absence of Cht. This broadening of the ^{13}C signals for the enzyme complexes is at-

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