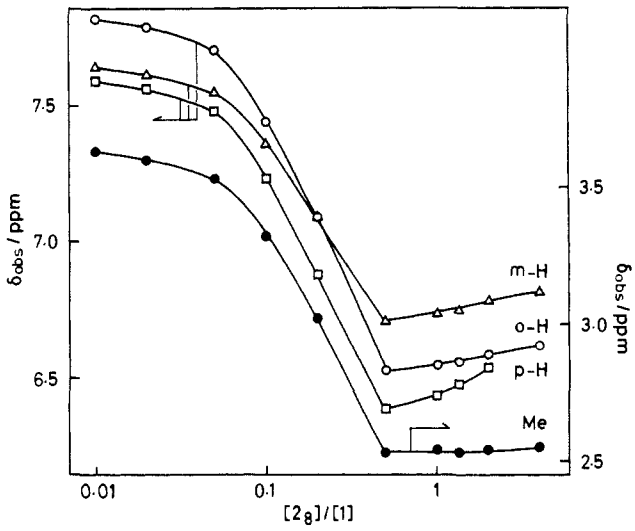

Figure 2. Plots of δ_{obsd} versus $[\mathbf{2}_8]/[\mathbf{1}]$. The concentration of $\mathbf{2}_8$ was maintained constant (1.10 mM) while that of **1** was varied (0.25–100 mM): D_2O 25 °C, pD 7.3 with 0.1 M phosphate buffer, internal standard DSS.

higher magnetic field with increasing $[\mathbf{2}_4]/[\mathbf{1}]$ ratio. This indicates that **1** is included in the cavity of $\mathbf{2}_4$ and undergoes the effect of the ring current of the benzene components. The observed chemical shift (δ_{obsd}) appears as an average of the free **1** (δ_{free}) and the complexed **1** ($\delta_{complex}$).[16] We thus determined that K at 25 °C assuming the formation of a 1:1 complex: $K = 5.39 \times 10^3$ M^{-1}.[17] The similar plots of δ_{obsd} versus $[\mathbf{2}_4]/[\mathbf{1}]$ were made at 0, 40, 60, and 80 °C in addition to 25 °C, and the K values were determined at each temperature. The plot of ln K versus T^{-1} shows a good linear relationship with $r = 0.99$. This indicates the formation of the 1:1 complex. The ΔH and ΔS were determined from the slope ($-\Delta H/R$) and the intercept ($\Delta S/R$) by the least-squares procedure: $\Delta H = -6.2$ kcal mol^{-1} and $\Delta S = -3.6$ cal mol^{-1} deg^{-1}. From these thermodynamic parameters we obtained the most reliable binding constant at 25 °C (Table I).[18]

The NMR peaks for $\mathbf{2}_6$ also shifted to higher magnetic field with increasing $[\mathbf{2}_6]/[\mathbf{1}]$ ratio, and the plot of ln K versus T^{-1} showed a good linear relationship. Thus, we could determine the K for the 1:1 complex with $\mathbf{2}_6$ (Table I). In contrast, the plot for $\mathbf{2}_8$ showed an unusual biphasic dependence (Figure 2): the NMR peaks shifted to higher magnetic field at $[\mathbf{2}_8]/[\mathbf{1}] < 0.5$, while the slight downfield shift occurred at $[\mathbf{2}_8]/[\mathbf{1}] > 0.5$. The biphasic dependence with a break point at $[\mathbf{2}_8]/[\mathbf{1}] = 0.5$ supports the formation of a 1:2 $\mathbf{2}_8/\mathbf{1}$ complex. We thus assumed the following two-step association scheme and estimated K_1 and K_2 independently. The results are summarized in Table I.

$$\mathbf{1} + \mathbf{2}_8 \overset{K_1}{\rightleftharpoons} \mathbf{1}\cdot\mathbf{2}_8 \quad (1)$$

$$\mathbf{1}\cdot\mathbf{2}_8 + \mathbf{1} \overset{K_2}{\rightleftharpoons} (\mathbf{1})_2\cdot\mathbf{2}_8 \quad (2)$$

The formation of the 1:2 complex with $\mathbf{2}_8$ is primarily attributed to the large ring size. Therefore, the flexibility also plays an important role in the binding of the second guest molecule. It is shown that β- and γ-cyclodextrins can include two guest molecules in the cavity.[19-21] In these 1:2 complexes the K_1 is usually smaller than the K_2.[19-21] It is seen from Table I, on the other hand, that the K_1 is almost equal to the K_2. This implies that the two "pinched" half-cavities[1] in $\mathbf{2}_8$ can interact with **1** flexibly in an "induced-fit" manner (eq. 3).[22]

In conclusion, the present study demonstrated that the association properties of water-soluble calixarenes are conveniently estimated by the NMR measurements and that only $\mathbf{2}_8$ can form the 1:2 complex with **1**. This suggests that calixarene cavities are capable of molecular recognition.

(16) The ^1H NMR studies and the conductance measurements indicated that $\mathbf{2}_4$, $\mathbf{2}_6$, and $\mathbf{2}_8$ do not form the micelle-like aggregate under the experimental conditions.

(17) For the complexation process $\mathbf{1} + \mathbf{2}_n \rightleftharpoons \mathbf{1}\cdot\mathbf{2}_n$, $\delta_{obsd} = \delta_{free}(([\mathbf{2}_n]_0 - [\mathbf{1}\cdot\mathbf{2}_n])/[\mathbf{2}_n]_0) + \delta_{complex}([\mathbf{1}\cdot\mathbf{2}_n]/[\mathbf{2}_n]_0)$ where $[\mathbf{2}_n]_0$ is the initial concentration of $\mathbf{2}_n$. Thus, $\delta_{obsd} = [\mathbf{2}_n]_0 + [\mathbf{1}]_0 + K^{-1} \pm (([\mathbf{2}_n]_0 + [\mathbf{1}]_0 + K^{-1})^2 - 4[\mathbf{2}_n]_0[\mathbf{1}]_0)^{1/2}(2[\mathbf{1}]_0)^{-1}(\delta_{complex} - \delta_{free}) + \delta_{free}$ where $[\mathbf{1}]_0$ is the initial concentration of **1**. The K was determined from this relationship by the computer-assisted nonlinear least-squares procedure.

(18) The T_c values of $\mathbf{2}_4$ (9 °C: 1.10×10^{-2} M) were enhanced in the presence of 4.60 M LiCl (26 °C), 4.70 M NaCl (25 °C), 2.30 M KCl (20 °C), and 3.80 M CsCl (17 °C), but the effect of **1** (T_c 65 °C) was incomparably greater than that of these alkali metal cations.

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Oxygen-Atom Transfer from Nitrous Oxide. Synthesis and Structure of a Zirconocene Oxametallacyclobutene Complex

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Interactions between nitrous oxide and oxophilic, early-metal d^0 systems (where oxidation at the metal center is formally precluded) can produce interesting reactivity at the ligand sites. We recently reported examples of reactions between nitrous oxide and transition-metal complexes that result in addition of the oxygen atom of N_2O to coordinated ligands instead of formation of metal oxides.[1] While studying the reaction of N_2O with $Cp^*_2Hf(D)(Ph)$ (**1**; $Cp^* = \eta^5$-C_5Me_5), we observed that the deuterium label in **1** scrambles into the phenyl hydrogen positions (at about 40 °C) well before the onset of the reaction between N_2O and **1** (that gives $Cp^*_2Hf(OH)(Ph)$ and $Cp^*_2Hf(H)(OPh)$ at about 80 °C).[1] In the light of related zirconocene[2] and tantalocene[3] chemistry, an intermediate benzyne complex is strongly implicated in the scrambling process.[4] Moreover, we have found that the reaction

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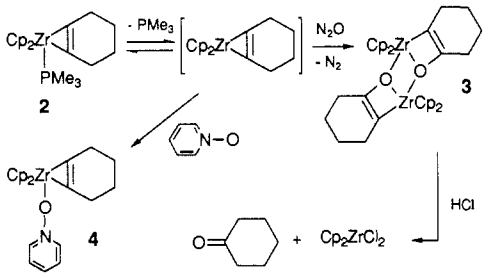
Scheme I



of N_2O with **1** does not appear to be a general one; other simple zirconocene and hafnocene carbyls (alkyls, vinyls, alkynyls) show no tendency toward insertion of an O-atom into the metal–carbon bond,[5] suggesting that the observed reactivity of N_2O with **1** to give $Cp^*_2Hf(H)(OPh)$ might result from the action of N_2O on the benzyne intermediate. This notion led us to investigate the reactions of nitrous oxide with the readily available "strained-ring" zirconium metallacycles $Cp_2Zr(L)(PMe_3)$ ($Cp = \eta^5$-C_5H_5; L = benzyne, cyclohexyne).[2,6] N_2O reacts under mild conditions (20 °C) with the benzyne derivative $Cp_2Zr(C_6H_4)(PMe_3)$, but the reaction is not a clean one. The analogous reaction between N_2O and the cyclohexyne adduct, however, is well behaved and yields an unprecedented oxametallacyclobutene derivative of zirconocene, the synthesis and structure of which we report here.

Nitrous oxide reacts (1 atm, 20 °C, 12 h) with toluene solutions of $Cp_2Zr(C_6H_8)(PMe_3)$ (**2**)[6] to afford colorless $[Cp_2Zr(OC_6H_8)]_2$ (**3**), with elimination of N_2 (1 equiv/Zr) and PMe_3, as shown in Scheme I.[7] The reaction proceeds quantitatively when monitored by ^1H NMR spectroscopy, with isolated yields of **3** ranging from about 50–60%. The formulation of **3** as an oxametallacyclobutene follows directly from its spectral (^1H, ^{13}C NMR; IR; MS), analytical, and reactivity characteristics and was confirmed by a single-crystal X-ray diffraction study.[8] Further chemical evidence that an oxygen atom has been added to the cyclohexyne ligand is provided by treatment of **3** with an excess of HCl, resulting in formation of cyclohexanone (GC/MS; ^1H NMR) and production of Cp_2ZrCl_2, shown in Scheme I.

Oxametallacycles of the transition metals have been the subject of considerable research activity and speculation, primarily because of their possible importance as intermediates in metal-catalyzed oxidation chemistry and in Wittig-type metathesis reactions.[9] Although a few examples of oxametallacyclobutane complexes have been reported, like $(AsPh_3)_2\overline{Pt\{OC(CN)_2C(CN)_2\}}$,[10] $(PPh_3)_2\overline{Pt(CH_2OCH_2)}$,[11] $Cp^*(PMe_3)\overline{Ir(OCMe_2CH_2)}$,[12] and $Cp_2\overline{Ti\{OC(CH_2)CH_2\}}$,[13] **3** represents the first example of an oxametallacyclobutene species.

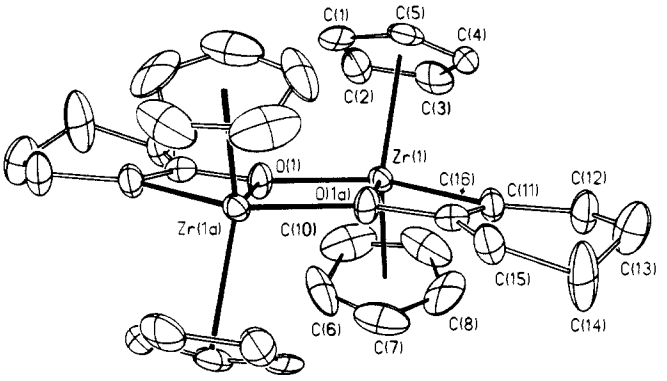


Figure 1. Molecular structure of one of two crystallographically independent (but chemically similar) centrosymmetric molecules of $C_{32}H_{36}O_2Zr_2$ (**3**): Zr(1)–O(1), 2.159 (8); Zr(1)–O(1a), 2.227 (7); Zr(1)–centroid(1–5), 2.26 (1); Zr(1)–centroid(6–10), 2.24 (1); Zr(1)–C(11), 2.284 (10); C(11)–C(12), 1.52 (2); C(12)–C(13), 1.50 (2); C(13)–C(14), 1.43 (2); C(14)–C(15), 1.52 (2); C(15)–C(16), 1.488 (14); C(11)–C(16), 1.309 (17); C(16)–O(1a), 1.387 (13) Å. Cent–Zr(1)–cent, 127.7 (4); O(1)–Zr(1)–O(1a), 64.4 (3); O(1)–Zr(1)–C(11), 124.1 (4); O(1a)–Zr(1)–C(11), 59.7 (4); Zr(1)–O(1)–Zr(1a), 115.6 (3); Zr(1)–C(11)–C(16), 93.5 (8); Zr(1)–O(1a)–C(16), 93.8 (6); Zr(1)–O(1)–C(16a), 150.4 (6); O(1a)–C(16)–C(11), 112.9 (9)°.

Several features of the molecular structure of **3**, shown in Figure 1, are noteworthy. There are two crystallographically independent dimers in the unit cell, each lying on a center of symmetry; the intramolecular metrical parameters for the two, however, are quite similar, so only one will be discussed in detail here (see Supplementary Material for a complete listing of bond angles and distances for both). The C(11)–C(16) bond length (1.31 (2) Å) is typical of a C–C double bond, and the other five C–C bond distances in the cyclobutene ring (av 1.49 Å) are typical of single bonds.[14] The C(16)–O(1a) bond length (1.387 (13) Å) is in the range found in several related ketene and oxametallacycle structures.[15] Oxametallacyclo*heptene* complexes of zirconocene are mononuclear in solution and the solid state,[16] whereas a structurally characterized oxametallacyclo*pentane* derivative possesses a dimeric structure similar to that of **3**.[17] It seems to be a general trend that contraction of the oxametallacycle ring size favors, probably for steric reasons, dimerization via Zr_2O_2 linkages.[18] The oxametallacyclobutene ring is, as expected, essentially planar, with the maximum deviation from the least-squares plane being 0.016 Å for C(16). The Zr_2O_2 ring in **3** is necessarily planar, with one long (2.227 (7) Å) and one short (2.159 (8) Å) Zr–O bond ($\Delta = 0.07$ Å). Interestingly, the shorter bond, Zr(1)–O(1), is the one that *is not* in the oxametallacyclobutene ring. The central Zr_2O_2 plane and the adjacent $ZrOC_2$ planes are nearly coplanar, with dihedral angles of 1.8°.

It is important to note that, although the oxidation of **2** to **3** is a facile reaction when N_2O is employed as the oxidant, it is not observed for other common oxygenating reagents. Dioxygen reacts rapidly with solutions of **2** to give a complex mixture of products, and the "dipolar" O-transfer reagent pyridine-*N*-oxide (O–NC_5H_5) reacts smoothly with **2** to simply displace the coordinated PMe_3 ligand, affording crystalline $Cp_2Zr(C_6H_8)(O$-$NC_5H_5)$ (**4**) in good yield (Scheme I).[7] In contrast to the pro-

(5) Complexes of the formula $Cp^*_2M(H)(R)$ (M = Zr, Hf) do, however, generally react to give $Cp^*_2M(OH)(R)$. Vaughan, G. A.; Hillhouse, G. L., unpublished results.

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tonolysis of **3** that gives cyclohexanone, **4** reacts with HCl to give Cp_2ZrCl_2 and cyclohexene (GC/MS; ^1H NMR), demonstrating that the O-atom has not been transferred to a Zr-C bond in this complex.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE-8520329) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (17718-AC3), is appreciated by G.L.H. Support from the National Institutes of Health (GM 34917), the Camille and Henry Dreyfus Fund, the American Cancer Society (for a Junior Faculty Research Award), and Firmenich SA is gratefully acknowledged by S.L.B. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant (NIH-CA-14599).

Supplementary Material Available: Experimental details and tables of atomic coordinates, bond angles and distances, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages); table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Synthesis of (-)-Oxetanocin

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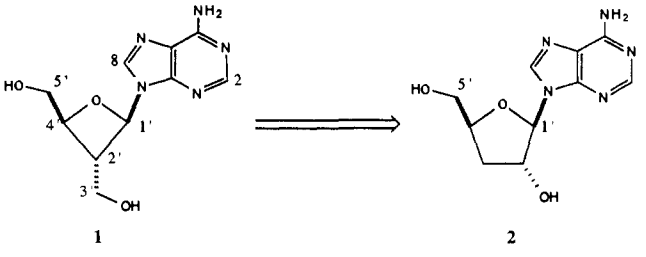
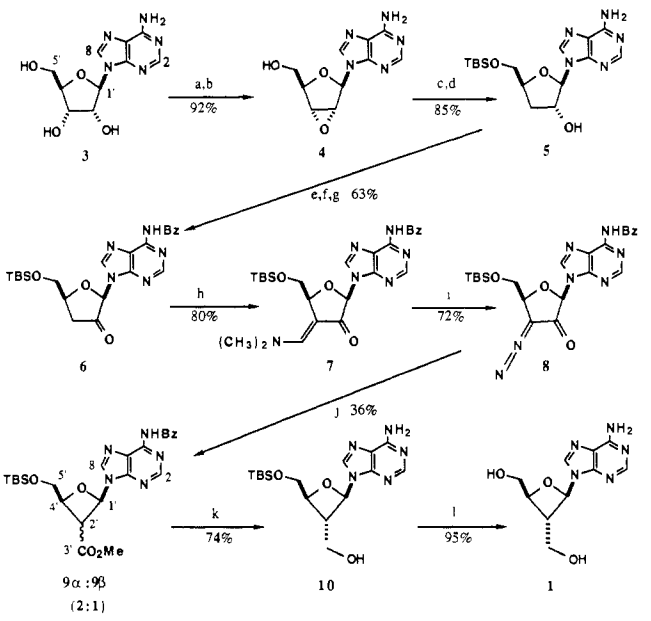
Oxetanocin inhibits the in vitro replication of human immunodeficiency virus (HIV), the causative agent of AIDS.[1,2] X-ray crystallographic analysis[3] of material produced by a strain of *Bacillus megaterium*[4] has established oxetanocin's structure as compound **1**. This unprecedented oxetanosyl-*N*-glycoside presents



1 **2**

new challenges in the synthesis of nucleosides[5] and branched chain carbohydrates.[6] These difficulties are evident in the 19-step Nippon Kayaku synthesis,[7,8] which produces oxetanocin in an overall yield of 0.008%. We report here an alternative synthesis of oxetanocin which should supply sufficient material for the elaboration and biological testing of derivatives.

Scheme I. Synthesis of (-)-Oxetanocin[a]



[a] (a) 2-Acetoxyisobutyryl bromide, CH_3CN; (b) resin$^+OH^-$, MeOH; (c) TBSCl, C_6H_5N; (d) $LiEt_3BH$, THF; (e) BzCl, C_6H_5N; (f) 1 N aqueous NaOH, 1,4-dioxane; (g) $CH_3CH_2NCN(CH_2)_3N(CH_3)_2HCl$, Cl_2CHCO_2H, DMSO, C_6H_6; (h) $(CH_3O)_2CHN(CH_3)_2$; (i) $CF_3SO_2N_3$; (j) *hν*, >280 nm, MeOH; (k) $NaBH_4$, EtOH; (l) TMSCl, MeOH.

Recognition of oxetanocin as a structural isomer of cordycepin (**2**)[9,10] suggested ring contraction as the pivotal synthetic transformation.

Although treatment of cordycepin with *tert*-butyldimethylsilyl chloride[11] in pyridine provided the nucleoside **5** directly, a more economical route utilized (-)-adenosine as the starting material. Thus, addition of 4.0 equiv of α-acetoxyisobutyryl bromide to a suspension of (-)-adenosine in acetonitrile containing 1.1 equiv of H_2O at room temperature followed by treatment of the ethyl acetate extract with BioRad AG-1-X8 (OH^-) resin in methanol afforded a 92% yield of crystalline 2′,3′-anhydroadenosine (**4**) in the manner described by Robins.[12] Silylation of the 5′-hydroxyl group prior to reduction of the epoxide[13] with 4.0 equiv of $LiEt_3BH$ in THF at room temperature facilitated isolation of the required 3′-deoxynucleoside **5** in an overall yield of 85%. The corresponding 2′-deoxynucleoside was not detected. Treatment of compound **5** with 4.0 equiv of benzoyl chloride in pyridine for 3 h at room temperature gave a mixture of di- and tribenzoates, which, without purification, was selectively O-deacylated by aqueous 1 N NaOH in dioxane.[14] Moffatt oxidation[15] of the resulting N-protected alcohol was carried out in 1 h by adding 0.2 equiv of dichloroacetic acid every 15 min to 5.0 equiv of 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride dissolved in a 1:1 mixture of DMSO and benzene. After dilution with dichloromethane, the excess carbodiimide was easily removed by washing with water acidified to pH 3. Chromatography of the organic residue on silica gel with ethyl acetate/hexane afforded the ketone **6** in 63% overall yield from the alcohol **5**.

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