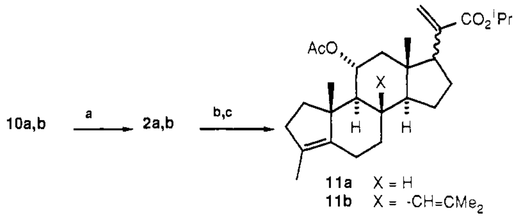
Scheme II

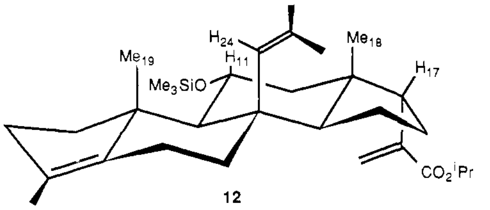


(a) To give **2a**: 2 mol equiv of MeLi in Et_2O, –78 °C then repeat; 91% crude. To give **2b**: 10 mol of equiv MeLi, –40 °C; 99% crude. (b) See under "**Cyclizations**" in text. (c) Ac_2O (10 mol equiv), 0.1 mol equiv of DMAP, 1:2 Et_3N/C_6H_6.

the phosphonate **8**,[4] the products **9a**,**b**[5] both being isolated as 2:3 mixtures of *E* and *Z* isomers. Conversion to the enones **10a**,**b**[5] and thence to the desired carbinols **2a**,**b**[5a,10] (see Scheme II) was achieved by established methodology.[2,9]

Cyclizations. The optimal cyclization conditions[10] were applied in the following preparative experiments. The dehydration product of **2a** (i.e., the cyclopentadiene[10]) was treated with 20% TFA in 1:1 CF_3CH_2OH/CH_2Cl_2 at –20 °C for 24 h to produce, after acetylation followed by HPLC, **11a**[5] in 20% yield as a 1:1 mixture of C-17 epimers. It is particularly noteworthy that *only 1–2% of* ***11a*** *was formed after a reaction time of 1 h, whereas the cyclization of* ***2b*** *appeared to be complete within 1 min*, even though the conditions (5% TFA, CH_2Cl_2, –20 °C) were milder. Also in striking contrast, no side products were observed in the cyclization of either **2b** or its dehydration product.[10] After a reaction time of 1 h, the procorticoid **11b**[5] was isolated, after acetylation and flash chromatography, in 80–83% yield as a 9:1 mixture of C-17 α:β isomers.

The 17α-epimer of **11b** was separated from the β-isomer by HPLC[11] and crystallized from ethanol as very fine needles (mp 148–151 °C) which, unfortunately, proved to be unsuitable for single-crystal X-ray structure analysis. However, the validity of structure **11b** is supported by the unambiguously established constitution of the analogous compound derived from **1b**[1] as well as of related C-11-hydroxy cyclization products.[2] Moreover, strong corroborative evidence was obtained by use of the nuclear Overhauser effect. Thus, the trimethylsilyl ether **12**[5] afforded the NOE data displayed in Table I. The enhancements are fully consistent with the relative stereochemistry assigned to **12**. Particularly significant is the transannular enhancement observed at H_{11} upon irradiation of the C-S auxiliary's vinyl proton (H_{24}) and vice versa.



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In conclusion, the unprecedented high yield for the cyclization of a *pro*-C-11-OH polyene substrate, namely **2b**, points to the potential of applying the concept to the synthesis of corticoids. To this end, removal of the auxiliary is under investigation, as is the use of alternative (e.g., heteroatom) auxiliaries.[12] The enormous cyclization rate enhancement of **2b** is a first-order anchimeric effect due to the C-S auxiliary. In forthcoming disclosures relatively small rate increases, due to second-order effects,[13] are observed when the C-S auxiliary is at the once-removed position from the initiator. Thus the rate of cyclization was enhanced by >10-fold when the methyl at *pro*-C-13 of **2c** was replaced by an isobutenyl group.[14] These first- and second-order rate effects indicate that there is considerable cationic character at *pro*-C-8 and *pro*-C-13 in the transition state, otherwise the isobutenyl auxiliary would not be effective in lowering the activation energy. The same argument applies to the effect of external point-charge stabilization in the proposed mechanism of the enzymic cyclization.[15]

Table I. NOE Enhancements for **12** at 400 MHz

site of irradiation	observed (+%)				
	H_{11}	H_{24}	H_{17}	Me_{18}	Me_{19}
H_{11}		13	0	1	0
H_{24}	19		2	2	2
H_{17}	4	0		2	0
Me_{18}	7	7.3	7		0
Me_{19}	7	5.3	2	0	

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this research.

Registry No. **2a**, 109787-69-1; **2a** (dehydration product, *Z*), 109801-33-4; **2a** (dehydration product, *E*), 109801-31-2; **2b**, 109787-70-4; **2b** (dehydration product, *Z*), 109801-34-5; **2b** (dehydration product, *E*), 109801-32-3; **3**, 43001-29-2; **4**, 109787-71-5; **5**, 109787-72-6; **6a**, 109787-73-7; **6a** (diacetate), 109787-84-0; **6a** (monoacetate), 109787-85-1; **6b**, 109787-79-3; **6c**, 109787-80-6; **6c** (dibenzoate), 109787-86-2; **6c** (monobenzoate), 109787-87-3; **7a**, 109787-74-8; **7b**, 109787-81-7; **8**, 109271-06-9; **9a** (*E*), 109801-29-8; **9a** (*Z*), 109787-88-4; **9a** (diketone, *E*), 109801-30-1; **9a** (diketone, *Z*), 109787-92-0; **9b** (*E*), 109787-82-8; **9b** (*Z*), 109787-89-5; **9b** (diketone, *E*), 109787-93-1; **9b** (diketone, *Z*), 109787-94-2; **10a** (*E*), 109787-75-9; **10a** (*Z*), 109787-90-8; **10b** (*E*), 109787-83-9; **10b** (*Z*), 109787-91-9; **11a** (α), 109787-76-0; **11a** (β), 109837-92-5; **11b** (α), 109787-77-1; **11b** (β), 109837-93-6; **12**, 109787-78-2; (2-methylpropenyl)bromozinc, 109801-35-6; 5-methylhex-5-ene-1,4-diol, 100590-28-1.

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(10) Attempts to chromatograph the carbinols **2a**,**b** generally resulted in variable amounts of dehydration of the tertiary allylic alcohol giving the corresponding cyclopentadienes which are intermediates in the cyclization of the carbinols (see p 69 of ref 9 for evidence in a related series). Yield optimization was carried out on the crude carbinols **2a**,**b** by using a 15-m, SE54 capillary column (hydrogen as carrier) for VPC analysis. The methyl ether of either cholestanol or stigmasterol was used as internal standard.

(11) HPLC separation was performed on a DuPont Zorbax SIL, normal phase column with use of 5% ether in hexanes as eluant.

(12) Cf. ref 1.

(13) Cf. Barlett, P. A.; Brauman, J. I.; Johnson, W. S.; Volkmann, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 7502–7504.

(14) Johnson, W. S.; Newton, C., unpublished observation.

(15) Cf. ref 1, footnote 22. The concept as applied to the enzymic conversion of 2,3-oxidosqualene to protolanosterol involves axial delivery of negative point-charge stabilizers by the enzyme as depicted in Figure 1. The expected transition state stabilization, as inferred from our rate data, nicely accounts for the (otherwise disfavored) boat ring-B as well as the non-Markownikov ring-C cyclization. Thus the charges **b** (directed to *pro*-C-8) and **c** (directed to *pro*-C-13) guide the course of the reaction by being delivered only to the α-face of the substrate. It is further postulated that stabilization by charge **a**, delivered to the β-face at *pro*-C-10, may be important in enhancing the rate and efficiency of the overall process by a first-order effect of the sort disclosed in the present paper.

$(Me_5C_5)_2Yb(\mu\text{-}Me)Be(C_5Me_5)$: A Model for Methane Coordination?

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The concept of NH_3 or CH_3^- acting as a classical Lewis base by donating a pair of electrons in a σ-symmetry orbital to a vacant

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Table I, Bond Length and Bond Angle Comparison

compd	YbC(C_5Me_5),[a] Å	YbC-(centrd), Å	(centrd)-Yb(centrd), Å	BeC(C_5R_5),[a] Å	BeC-(centrd), Å	BeC(Me), Å
$(Me_5C_5)_2Yb{\cdot}MeBe(C_5Me_5)$	2.68 ± 0.1	2.39	145	1.88 ± 0.01	1.45	1.705 (6)
$(Me_5C_5)_2Yb$[8b]	2.621 ± 0.006	2.33	158			
$MeBe(C_5H_5)$[7a]				1.923 (3)	1.50	1.706 (3)
$(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$[9a]	2.66 ± 0.01	2.37	144			
$(Me_5C_5)_2Yb(MeC{\equiv}CMe)$[9a]	2.659 ± 0.009	2.38	143			

[a] Average value.

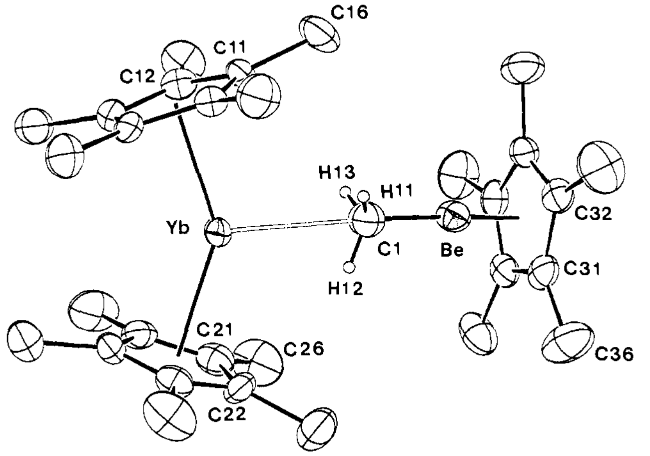

Figure 1. ORTEP diagram of $(Me_5C_5)_2Yb{\cdot}MeBe(C_5Me_5)$. Some bond lengths and angles are as follows: Yb–H(1) = 2.54 (4) Å, Yb–H (2) = 2.51 (5) Å, Yb–H(3) = 2.71 (6) Å, C–H(1) = 0.92 (4) Å, C–H(2) = 0.90 (5) Å, C–H(3) = 0.73 (6) Å, YbC(1)H(1) = 66.5 (2.4)°, YbC(1)H(2) = 64.2 (3.0)°, YbC(1)H(3) = 78.2 (5.0)°, BeC(1)H(1) = 115.2 (2.4)°, BeC(1)H(2) = 113.0 (3.1)°, BeC(1)H(3) = 103.5 (5.0)°, H(1)C(1)H(2) = 104.7 (3.8)°, H(1)C(1)H(3) = 99.6 (5.3)°, and H(2)C(1)H(3) = 120.6 (5.6)°.

σ-symmetry orbital on a metal fragment is a fundamental principle of inorganic coordination and organometallic chemistry. Molecular hydrogen can act as a nonclassical Lewis base by donating its electron pair in a σ-molecular orbital and a Lewis acid by accepting electrons into its σ^*-molecular orbital, a situation not unlike that found in ethylene, though ethylene is a π-donor and acceptor,[1] This simple analogy is a useful way to rationalize the bonding in molecular hydrogen compounds.[2] Classification of ligands according to their frontier orbitals can be extended to methane whose t_2 orbitals can act as σ-donors and t_2^* orbitals can act as acceptors.[1,3] From symmetry, the preparation of a methane complex is not absurd,[4] the difficulty being that methane lacks a permanent dipole moment and the first ionization energy is ca. 3 eV higher than ammonia.[5]

One strategy for synthesis of a substituted methane complex, $M \leftarrow CH_3X$, is to choose a ligand or a group X whose electronegativity is less than that of a methyl group so that the permanent dipole moment is in the direction of carbon rather than X. A convenient molecule is $MeBe(C_5Me_5)$[6] since it is monomeric, as is $MeBe(C_5H_5)$; therefore, no steric effects will prevent coordination, and it presumably has a dipole moment.[7] A convenient Lewis acid is $(Me_5C_5)_2Yb$ since it is a bent metallocene in gas phase;[8] therefore, the reorganization energy of bending is small, and this $4f^{14}$ metallocene forms coordination complexes with olefins and acetylenes.[9]

Addition of $(Me_5C_5)_2Yb$ to $MeBe(C_5Me_5)$ in pentane does not result in a visible color change although $(Me_5C_5)_2Yb{\cdot}MeBe(C_5Me_5)$,[10a] mp 224–227 °C, may be isolated as dark orange prisms on cooling a concentrated pentane solution to −25 °C. An ORTEP diagram is shown in Figure 1.[10b] The complex may be viewed as being formed by bringing the $MeBe(C_5Me_5)$ fragment up to the $(Me_5C_5)_2Yb$ fragment in a linear fashion; the YbC(1)Be angle is 177.2 (3)°. The geometry of the fragments in the complex in the solid state is very weakly perturbed relative to the individual parts as determined by gas electron diffraction (Table I). The principle perturbations are that the Yb–C(C_5Me_5) distance lengthens by ca. 0.06 Å and the (Me_5C_5)ring centroid–Yb–(Me_5C_5)ring centroid closes by ca, 13°.

The most interesting structural feature is the geometry of the methyl group that bridges the two metal centers. The Yb···C distance of 2.766 (4) Å is close to the average Yb–C(C_2H_4)

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(6) (a) Prepared from $ClBe(C_5Me_5)$[6b] and MeLi in diethyl ether and isolated by crystallization from pentane or by sublimation at 30–40 °C/10^{-2} mm: M^+ 159; ^1H NMR (C_6D_6, 20 °C) δ 1.76 (30 H), −1.23 (3 H); ^{13}C NMR (C_6D_6, 20 °C) δ 108.0 (Mr_5C_5), 8.75 (Me_5C_5), the Be–Me resonance was not observed. (b) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31–37.

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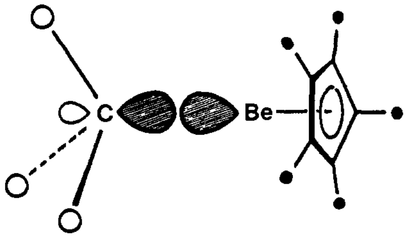
(10) Anal. Calcd for $C_{31}H_{48}BeYb$: C, 61.8; H, 8.04. Found: C, 62.1; H, 8.10. (a) $(M - 15)^+ = 588$; ^1H NMR (C_6D_6, 20 °C, 89.56 MHz) δ 2.02 (30 H), 1.76 (15 H), −1.13 (3 H, $\nu_{1/2}$ = 30 Hz); ^{13}C NMR (C_6D_6, 20 °C, 22.50 MHz) δ 112.8 (s, YbC_5Me$_5$), 108.7 (s, BeC_5Me$_5$), 10.84 (q, J_{CH} = 124 Hz, YbC$_5$$Me_5$), 8.93 (q, J_{CH} = 126 Hz, BeC$_5$$Me_5$). The resonance due to MeBe was not observed. The ^1H NMR spectrum (C_7D_8, 90 °C) shows three resonances at δ 1.93, 1.81, and −1.41 ($\nu_{1/2}$ = 9 Hz). On cooling to −25 °C the Me–Be resonance broadened into the base line and did not reappear at −70 °C. The Me_5C_5 resonances were broadened at −70 °C. One molar equivalent of $MeBe(C_5Me_5)$ was added to the complex in a ^1H NMR tube in C_6D_6. Only a single resonance for MeBe was observed at δ −1.15, indicating that intermolecular chemical exchange is rapid. (b) The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 11.265 (1) Å, b = 11.102 (1) Å, c = 24.125 (3) Å, β = 82.904 (9)°, V = 2994 (1) Å^3, Z = 4, d(calcd) = 1.34 g cm^{-3}, and μ = 31.28 cm^{-1}. The data were collected on a Nonius CAD-4 diffractometer with Mo Kα X-rays (λ = 0.71073 Å) at −80 °C. The structure was solved from Patterson and electron density maps and refined by full-matrix least squares to a conventional R factor of 0.023 (R_w = 0.028 and GOF = 1.74) by using 3176 absorption corrected data, where $F_o^2 > 3\sigma(F_o^2)$, against 311 variables. The R values for all 3886 unique reflections was 0.044. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the Me_5C_5 rings were placed in idealized positions and given isotropic thermal parameters 1.3 times those of the carbons to which they were attached. They were included in the structure factor calculations, but they were not refined. The hydrogen atoms on C(1) were placed and refined with isotropic thermal parameters.

distance of 2.781 ± 0.006 Å in $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$[9a] and is shorter than the average Yb—C(MeC≡CMe) distance of 2.85 ± 0.01 Å in $(Me_5C_5)_2Yb(MeC{\equiv}CMe)$.[9b] The hydrogen atoms on C(1), which were located and refined isotropically, are close to the ytterbium atom with an average Yb···H distance of 2.59 ± 0.08 Å which is identical with the closest Yb···H distance of 2.61 ± 0.02 Å found in $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$.[9a] In addition the average YbCH angle is 69.6 ± 5.7°, the BeCH angle is 110.6 ± 4.7°, and the HCH angle is 108.3 ± 8.2°. The X-ray crystallographic data are consistent with the HOMO of $MeBe(C_5Me_5)$, shown below, acting as a σ-donor toward the Lewis acid $(Me_5C_5)_2Yb$. The geometry of the bridging methyl group is very



similar to that found in $Li_4B_4(\mu\text{-}Me)_8(Me)_8$ by X-ray and neutron diffraction[11a] and perhaps in $(Me_5C_5)_4Lu_2(\mu\text{-}Me)(Me)$[11b] (though the hydrogen atoms were not located in the X-ray structure) though different from that found in $Cp_4Zr_2(\mu\text{-}Me)[OCH(CH_2CMe_3)]_2AlMe_2$ in which the Zr(μ-Me)Zr angle is ca. 148°.[11c]

In solution, the resonance in the ^1H NMR spectrum due to the briding methyl group is deshielded by 0.1 ppm relative to free $MeBe(C_5Me_5)$. The complex is undergoing rapid intermolecular chemical exchange to -70 °C.[10a]

Acknowledgment. We thank the Fannie and John Hertz Foundation for a fellowship (C.J,B.) and Dr. F, J. Hollander for his help with the X-ray crystallographic study, This work was supported by the Director, Office of Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U,S. Department of Energy under Contract DE-AC03-76SF0098.

Supplementary Material Available: Tables of positional parameters, thermal parameters, and bond lengths and bond angles (8 pages). Ordering information is given on any current masthead page.

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Long-Distance Magnetic Exchange between Chromium(III) Atoms Bridged by $H_3O_2^-$ Ligands

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We report an unexpected long distance antiferromagnetic coupling between chromium(III) atoms in hydroxoaqua complexes. It has recently[2,3] been established that the so-called hydroxoaqua complexes are not mononuclear in the solid state (and concentrated aqueous solution[2e,f]) as their classical formulation implies but binuclear or polynuclear; the hydroxo ligand of one metal atom merges with the aqua ligand of a neighboring metal atom to form an $H_3O_2^-$ bridging ligand, by means of a very strong hydrogen bond (2.4-2.5 Å).

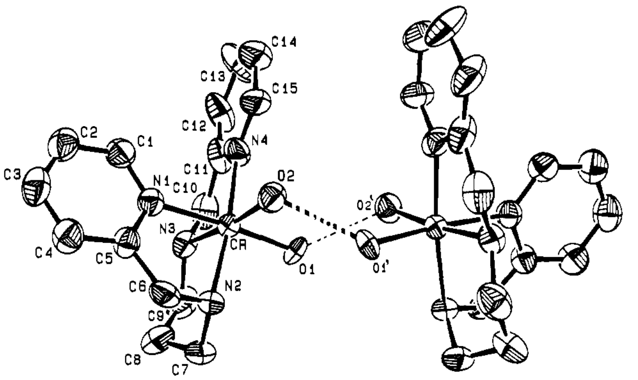

Figure 1, The structure of β-*cis*-$[(bispictn)Cr(H_3O_2)_2Cr(bispictn)]^{4+}$ as found in **2**. The O···H···O bonds in the $H_3O_2^-$ units are represented by the dashed lines.

Table I, Structural Data for **1** and **2**

compd	O-O($H_3O_2^-$), Å	M-O($H_3O_2^-$), Å	M-M, Å	M-O···O-M torsnl angle, deg
1[a]	2.50 (1)	1.932 (7)		60.4
	2.48 (1)	1.934 (7)	5.118 (2)	90.1
2[b]	2.472 (5)	1.906 (3)		
		1.961 (4)	4.797 (1)	

[a] Reference 3. [b] This work.

The present investigation was conducted on two chromium(III) "hydroxo-aqua" complexes whose structures were determined by single-crystal X-ray studies: **1**, α-*cis*-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4{\cdot}2H_2O$ [pico = (2-picolylamine), and **2**, β-*cis*-$[(bispictn)Cr(H_3O_2)_2Cr(bispictn)]I_4{\cdot}4H_2O$ [bispictn = *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine].[4a] Preparation and structure of **1** were reported elsewhere.[3] Structure **2** is presented in Figure 1,[4b] Some important distances and angles of **1** and **2** are listed in Table I. Both have a double-bridged dimeric structure with a Cr to Cr separation of 5,118 and 4.797 Å, respectively. This configuration is typical for most *cis*-hydroxoaqua complexes.[2d] The hydrogen bond of $H_3O_2^-$ in **1** and **2** is very short, as expected (Table I).

The magnetic susceptibilities of powdered samples of **1** and **2** in the temperature range 1,7-300 K were measured by the Faraday method at a field strength of 12 000 Oe. As an example, data for **2** are presented in Figure 2, The date exhibit a decreasing magnetic moment at low temperatures, which has been interpreted in terms of magnetic saturation at 13 kG combined with anti-

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(4) (a) Bispictn was prepared as reported earlier.[5b] Compound **2** was prepared by base hydrolysis of *cis*-β-$[Cr(bispictn)Cl_2]Cl{\cdot}2H_2O$ and precipitation with excess NaI. Recrystallization from water yielded orange-red crystals. *cis*-β-$[Cr(bispictn)Cl_2]Cl{\cdot}2H_2O$ was prepared by the same procedure employed for *cis*-α-$[Cr(bispictn)Cl_2]Cl{\cdot}3H_2O$.[5b] (b) Compound **2** is monoclinic, space group $P2/n$ with a = 9.076 (1) Å, b = 10.714 (1) Å, c = 23.660 (3) Å, β = 96.03 (2)°, and Z = 2. The structure was refined by least-squares methods by using 2910 unique reflections with $I > 3\sigma(I)$ to a conventional R factor of 3.76%.

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