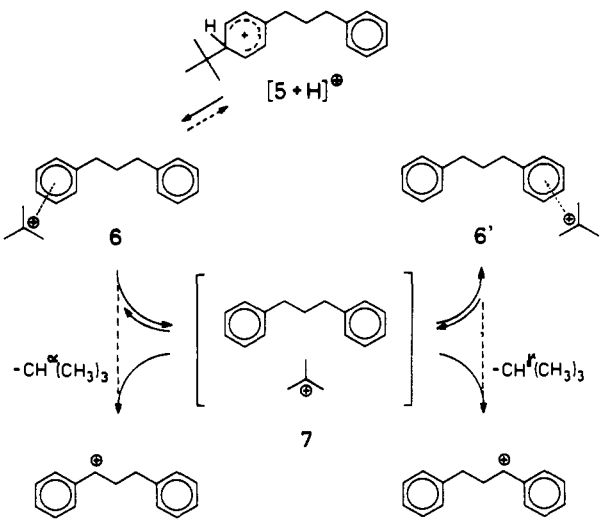
Scheme IV



(k_H/k_D) observed is the same as that reported for simpler alkylbenzenium ions.[8,25]

The overall course of the reaction is illustrated in Scheme IV. Besides interannular proton transfer, which according to our previous studies should operate in $[5 + H]^+$ as well,[6,26] a degenerate interannular transalkylation equilibrium may occur between the primarily formed π complex **6** and its "tautomer", **6'**. In addition, however, an ion-neutral complex (**7**) appears to be involved as the central intermediate since the aliphatic chain of $[5 + H]^+$ does not allow for a "direct" *tert*-butyl ion transfer via a geometry akin to an S_N2 transition state, viz., [arene···$C(CH_3)_3$···arene]$^+$.[6] Such a transition state has been suggested by Kebarle et al.[27] for the *inter*molecular transalkylation between *tert*-butylbenzene and toluene under high-pressure CI conditions.[27,28] We therefore believe that complex **7**, rather than **6** and **6'**, is the actual intermediate in which the hydride abstraction step takes place. Hence, the results presented here corroborate the possibility that intermolecular gas-phase transalkylation reactions may take place via ternary complexes,[29] viz., [arene $C_4H_9^+$ arene'], as truly "disolvated ions".[6,9a,11b,18]

We hope that further investigations into complex-mediated alkyl ion migrations at the "backbone" of larger aryl-substituted alkanes will add further interesting facets to our understanding of the behavior of gas-phase π and ion–molecule complexes.

Acknowledgment. This work was supported by the Forschungsprojekt 2194/26, Universität Bielefeld. Persistent fruitful discussions with Professor Hans-F. Grützmacher and experimental contributions by Matthias Jöckel in an early stage of this work are gratefully acknowledged. We thank Dr. David J. McAdoo for a preprint (ref 11b).

Registry No. 4, 16251-99-3; **5**, 138722-44-8; **5a**, 138722-42-6; **5b**, 138722-43-7; **5c**, 138753-36-3; **5d**, 138722-45-9; $C_4H_9^+$, 14804-25-2; benzhydrol, 91-01-0; 3-(4-*tert*-butylphenyl)-1-phenylpropanone, 138722-46-0; [2,2-$^2H_2$]-3-(4-*tert*-butylphenyl)-1-phenylpropan-1-one, 138722-47-1; 3-(4-*tert*-butylphenyl)-1-[$^2H_5$]phenylpropan-1-one, 138722-48-2.

(25) With [α] and [γ] representing the fractional attack of the *tert*-butyl ion at the α and γ positions of ions $[5 + H]^+$ and with $k_H/k_D \equiv [C_4H_9H^i]/[C_4H_9D^i]$ (i = α or γ), the observed abundance ratios expressed as $[C_4H_9H^\gamma]/[C_4H_9D^\alpha] = ([\gamma]/[\alpha])(k_H/k_D)$ for $[5a + H]^+$ and as $[C_4H_9H^\alpha]/[C_4H_9D^\gamma] = ([\alpha]/[\gamma])(k_H/k_D)$ for $[5b + H]^+$, [α] = 0.52, [γ] = 0.48, and $k_H/k_D = 1.57$.

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Efficient Catalytic Cleavage of RNA by Lanthanide(III) Macrocyclic Complexes: Toward Synthetic Nucleases for in Vivo Applications

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Reagents that cleave RNA by promoting transesterification of the phosphate diester linkage of RNA have been the subject of several recent studies.[1-10] Cleavage of RNA by transesterification has many advantages over oxidative cleavage, including the possibility of religation of fragments, the high degree of selectivity for cleavage of RNA over DNA,[11] and the elimination of diffusible oxygen radicals that are often produced in metal-ion-promoted oxidative cleavage of nucleic acids. The latter two are important advantages because the use of metal complexes that promote oxidative cleavage of nucleic acids may result in destruction of the ligand or tethered recognition molecule.[12] One of the most tantalizing applications of RNA transesterification catalysts is the possibility of forming more potent antisense oligonucleotides by attachment of a catalytic cleaving group.[13] An antisense oligonucleotide with an attached cleaving group able to participate in the *catalytic* destruction (several copies of mRNA per antisense oligonucleotide) of selected sequences of RNA might truly be effective in the inhibition of gene expression. To date, however, many reagents used to cleave RNA are employed in large excess[1-5] and catalytic turnover has not been demonstrated. We report here the first example of a metal complex ($Eu(L^1)^{3+}$) that shows catalytic behavior in RNA transesterification at 37 °C and neutral pH. In addition, several lanthanide(III) complexes of L^1

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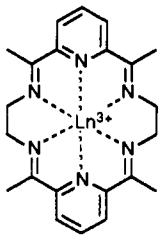
Table I. RNA Cleavage by Lanthanide(III) Complexes and Their Decomposition in Water at 37 °C

complex[a]	pH 2.5[b] (%)	DTPA[c] (%)	ApUp cleavage[d] (%)	A_{12}–A_{18} cleavage[e] (%)
$La(L^1)^{3+}$	0.0	100	20	70
$Eu(L^1)^{3+}$	8.0	20	41	89
$Gd(L^1)^{3+}$	18	36	27	93
$Tb(L^1)^{3+}$	23	63	57	81
$Lu(L^1)^{3+}$	100	100		

[a] Nitrate, or mixed acetate chloride salts; refs 16 and 17. [b] Percent decomposition after 20.5 h, 0.01 M $Ln(L^1)^{3+}$. [c] pH 7.0, percent decomposition after 20.5 h, 0.01 M $Ln(L^1)^{3+}$, 0.02 M DTPA (DTPA = diethylenetriaminepentaacetic acid). [d] Percent cleavage after 4.0 h, 490 μM $Ln(L^1)^{3+}$, 20 μM ApUp, pH = 7.15, 0.01 M HEPES buffer, 0.1 M $NaNO_3$. In the absence of $Ln(L^1)^{3+}$, no cleavage was observed. [e] Percent cleavage after 4.0 h, 200 μM $Ln(L^1)^{3+}$, 190 μM A_{12}–A_{18} (adenosine concentration), pH = 7.00, 0.01 M HEPES buffer. In the absence of $Ln(L^1)^{3+}$, observed cleavage was less than 2%.

that promote transesterification of RNA oligomers are relatively robust toward metal release in solution, a property crucial to in vivo applications.



$Ln(L^1)^{3+}$

Ln = La, Eu, Gd, Tb, Lu

Several metal complexes have been shown to promote the transesterification of simple oligomers of RNA at 37 °C.[6,7] However, in order for a metal complex attached to an oligonucleotide to function in vivo, the complex must be inert to release of the metal ion if the synthetic nuclease is to arrive intact to interact with mRNA. Accordingly, we have searched for metal complexes that promote transesterification of RNA at 37 °C and that may be inert with respect to metal release. We have chosen lanthanide complexes because lanthanide(III) salts are effective in promoting phosphate ester hydrolysis[14] and transesterification of RNA.[15] The hexadentate ligand L^1 forms complexes with all lanthanide(III) ions;[16,17] we have examined five of these for their resistance to decomposition under a variety of conditions.[18,19] After 3 days at 37 °C and pH 7.0, $Lu(L^1)^{3+}$ had completely decomposed, $Gd(L^1)^{3+}$ and $Tb(L^1)^{3+}$ had undergone a moderate degree of decomposition (26% and 36%, respectively), and $La(L^1)^{3+}$ and $Eu(L^1)^{3+}$ had undergone little decomposition (8% and less than 5%, respectively). Experiments performed under more rigorous conditions (see Table I) suggested that $Eu(L^1)^{3+}$ was overall the most inert to metal loss.

Extensive cleavage of the dinucleotide adenylyl-3′,5′-uridine 3′-monophosphate (ApUp) or of oligomers of adenylic acid (A_{12}–A_{18}) was promoted at 37 °C after 4 h by several lanthanide complexes (Table I).[20] These results are remarkable in view of the fact that other hexadentate ligands such as EDTA form lanthanide(III) complexes that are completely inactive in RNA cleavage under similar conditions. Studies suggest that an overall positive charge on the lanthanide complex may be necessary for the complex to be active.[21] Pseudo-first-order rate constants for cleavage of ApUp by 490 μM $Eu(L^1)^{3+}$ or of A_{12}–A_{18} by 160 μM $Eu(L^1)^{3+}$ are 0.14 h^{-1} and 1.5 h^{-1}, respectively. This rate data establishes that $Eu(L^1)^{3+}$ is one of the most efficient metal complexes to promote transesterification of RNA oligomers at 37 °C and neutral pH. Most lanthanide(III), zinc(II), and lead(II) complexes are less efficient in promoting ApUp cleavage,[8,21] as are several copper(II), nickel(II), and zinc(II) complexes in promoting the cleavage of A_{12}–A_{18} under similar conditions.[6,7]

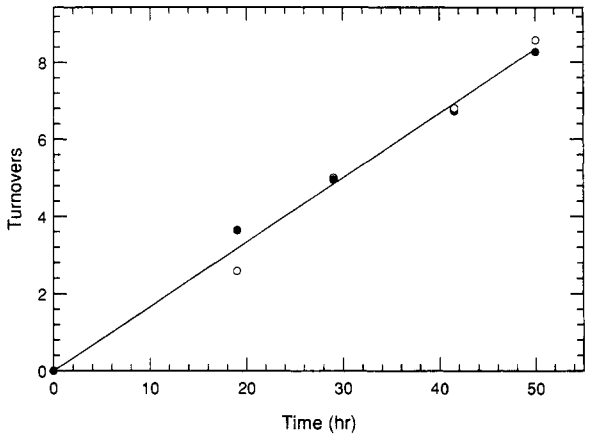


Figure 1. Plot of catalytic turnovers versus time for the cleavage of ApUp by $Eu(L^1)^{3+}$: initial [ApUp] = 2.66×10^{-3} M, [$Eu(L^1)^{3+}$] = 1.20×10^{-4} M, 3.0×10^{-2} M HEPES buffer, pH 7.10, 37 °C. ○, based on [ApUp]; ●, based on sum of [2′,3′-cAMP] and [3′-AMP] products.

While many organic and inorganic reagents cleave RNA when present in excess, cleavage at 37 °C with catalytic amounts of compound has not been demonstrated. Catalytic turnover was studied with ApUp as substrate because all products are easily identified.[8] With catalytic amounts of $Eu(L^1)^{3+}$ (120 μM), the major products were initially adenosine cyclic 2′,3′-monophosphate (2′,3′-cAMP) and uridine 3′-monophosphate. Small amounts of the hydrolysis product adenosine 3′-monophosphate (3′-AMP) were observed after several turnovers. At 10-fold or greater excess of ApUp to $Eu(L^1)^{3+}$, a further increase in dinucleotide concentration resulted in no further increase in the rate of transesterification. Figure 1 shows data for turnovers per hour versus time for the disappearance of dinucleotide or appearance of products 2′,3′-cAMP and 3′-AMP; the straight line that is observed for several turnovers suggests that $Eu(L^1)^{3+}$ shows good catalytic behavior.

In conclusion, macrocyclic lanthanide complexes ($Ln(L^1)^{3+}$) efficiently promote the transesterification of RNA, and the europium(III) complex exhibits true catalytic behavior. Inertness of the macrocyclic complex to metal release changes dramatically throughout the lanthanide series, and studies are underway to better understand the mechanism of dissociation of the lanthanide ion and to inhibit this process. Attachment of these complexes to oligodeoxynucleotides is in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM-46539) for support

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(20) All usual precautions were taken against contamination by ribonucleases, including the sterilization of all glassware, plasticware, and solutions. Reactions with metal complexes run in the presence of excess EDTA showed no RNA cleavage. In the absence of $Ln(L^1)^{3+}$, no cleavage of ApUp was observed over a 3-day period, and less than 2% cleavage of A_{12}–A_{18} was observed after 4 h. The HPLC assay for ApUp cleavage is found in ref 8 and that for A_{12}–A_{18} is in ref 6.

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of this research. We thank Priya Kumar for performing preliminary work.

Registry No. La(L)$^{3+}$, 125897-09-8; Eu(L)$^{3+}$, 138606-01-6; Gd(L)$^{3+}$, 125897-21-4; Tb(L)$^{3+}$, 138606-02-7; Lu(L)$^{3+}$, 138606-03-8; ApUp, 1985-21-3; poly(adenylic acid), 24937-83-5; RNase, 9001-99-4.

Exo and Endo Activation in Glycoside Cleavage: Acetolysis of Methyl α- and β-Glucopyranosides[1]

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Received September 16, 1991

The mechanism of glycoside cleavage is of fundamental importance for the chemical manipulation of sugars[3] and for an understanding of biochemical processes which involve glycosyl transfer.[4,5] This manuscript describes experiments designed (a) to elucidate the preferred site of activation in cleavage of α- and β-glucopyranosides by trapping the oxo–carbenium intermediate(s) arising thereby and (b) to determine the final products arising from the alternate pathways.

The site of anomeric activation in glycoside cleavage is a contentious issue of long standing.[3,6] Early key experiments[7] (appeared to!) establish that activation occurs at the exocyclic oxygen, thereby leading to a cyclic oxo–carbenium ion **1** rather than to the acyclic counterpart, **4**; however, the latter has continued to resurface in a wide range of circumstances.[8]

Central to the question of the activation site is the issue of the relative basicities of the exo and endo oxygens, which is related, in turn, to the anomeric effect(s).[9,10] The FMO rationalization for the latter phenomenon invokes nσ* donation from the oxygen(s) to the C1–O bond.[11] That oxygens which are involved in nσ* donation should be less basic than those not so engaged is a seminal intuitive contribution by Deslongchamps.[12] An ab initio study of dimethoxymethane, carried out in this laboratory,

Scheme I

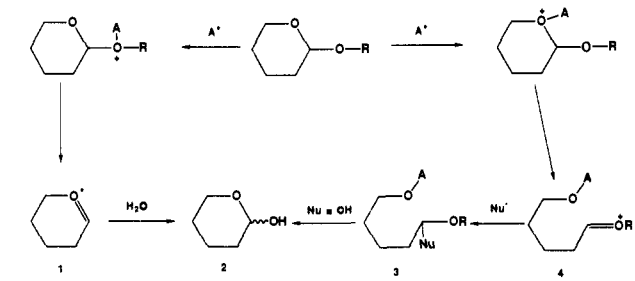

Chart I

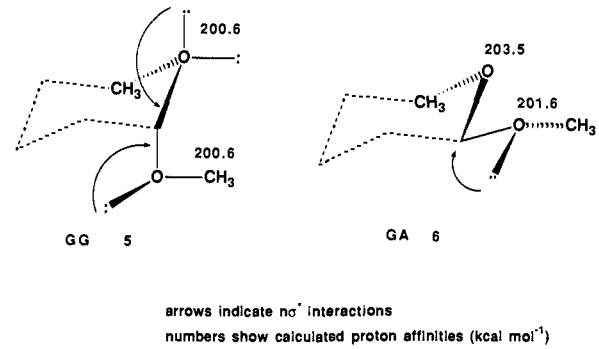

Table I. Percent Distribution of Products in Acetolysis Reaction Mixtures[a-c]

		products[d,e]			
entry	starting material	**7**	**8**	**9**	**10**
i	methyl α-D-glucopyranoside	73	18	8	tr
ii	methyl β-D-glucopyranoside	19	5	48	23
iii	acyl acetal **11a** (epimeric)	2	tr	46	52
iv	acyl acetal **11a** (1*S*)	2	tr	46	52
v	acyl acetal **11a** (1*R*)	2	tr	47	51
vi	dimethyl acetal **11b**			66	34

[a] A 0.1 M solution of anhydrous ferric chloride in acetic anhydride was prepared. The "starting material" was dissolved in this solution to obtain 0.1 M concentration. It was found that addition of one drop of concentrated sulfuric acid reduced the reaction time from 3 to 1.5 h without altering the product composition, and this was done routinely. [b] The composition remained unchanged after standing for 7 days. [c] The composition of each reaction mixture was determined by GLC. [d] Compounds **7–10** were synthesized by known procedures. **7**: Wolfram, M. L.; Thompson, A. *Methods in Carbohydrate Chemistry, II*; Academic Press: New York, **1963**; Vol. 2, p 212. **8**: Moore, J. A.; Dalrymple, D. L.; Rodig, O. R. In *Experimental Methods in Organic Chemistry*; Saunders College Publishing: New York, **1982**; p 32. **9**: Backinowsky, L. V.; Nepogod'ev, S. A.; Shashkov, A. S.; Kochetkov. N. K. *Carbohydr. Res.* **1985**, *135*, 144. **10** was isolated by column chromatography of the product from acetolysis of the β-glucoside and identified by spectral (^{1}H NMR, MS) data. [e] The ^{1}H NMR signals for H-1 of the compounds **7–9** are clearly resolved at 300 MHz: **7** δ 6.30 (d, $J_{1,2}$ = 3.6 Hz), **8** 5.68 (d, $J_{1,2}$ = 8.1 Hz), **9**α 6.42 (d, $J_{1,2}$ = 3.6 Hz), **9**β 6.09 (s), **10** 6.85 (d, $J_{1,2}$ = 5.0 Hz).

has provided support for that postulate by determining the proton affinities for oxygens in the GG and GA rotamers to be as shown in **5** and **6** (Chart I).[13] As indicated by the broken lines, these rotamers correspond to axial and equatorial glycosides, respectively, and as noted by Lemieux,[14] the nσ* donations in **5** are in competition. Accordingly, Praly and Lemieux found that for β-glycosides (i.e., **6**) the exo anomeric effect was stronger than in α-glycosides.[15]

In view of these differences in oxygen basicities, a β-glycoside might be expected to be activated on the ring oxygen and react

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