quantum mechanical) of hydrogen ligands from one face to another. In $Os(CO)_4(SiMe_3)_2$, a large distortion from regular octahedral geometry is not expected in view of the known structures of *cis*- and *trans*-$Ru(CO)_4(GeCl_3)_2$.[10] While a different mechanism seems indicated, we can at present only speculate on what it may be.

A trigonal twist mechanism, traversing a trigonal prismatic intermediate, is one possibility, although it is not generally thought to be an attractive one energetically.[1,9,11] Another possibility is that the trimethylsilyl group might migrate across a carbonyl carbon, *via* a kind of pseudo-five-coordinate, acyl-type intermediate. Such a possibility for ligand interchange in $XMn(CO)_5$ systems has in fact been suggested.[12] Since ^{13}CO does not exchange with $Os(CO)_4(SiMe_3)_2$ during isomerization as it would be expected to do in a normal five-coordinate intermediate, the species postulated must be transitory in character, or not "fully" five coordinate. A shift of the trimethylsilyl group to carbon would be related to the nonrigid behavior of cyclopentadienyltrimethylsilane and related compounds.[13] A discussion of other possible mechanisms, including turnstile rotations,[14] does not seem justified at the present time.

We have investigated the effect of replacing the methyl groups on silicon by chlorine atoms.[15] For $Os(CO)_4(SiMe_2Cl)_2$, the coalescence temperature is raised to between 120 and 140°; the barrier to isomerization in $Os(CO)_4(SiMeCl_2)_2$ is sufficiently high that the isomers are separable at room temperature; a cis form of $Os(CO)_4(SiCl_3)_2$ was not detected.[16] We have also reexamined the reported[6] cis and trans isomers of the tin derivative, $Os(CO)_4(SnMe_3)_2$, and find them to be nonrigid, with a coalescence temperature approximately the same as that of $Os(CO)_4(SiMe_3)_2$.

A search for other examples of nonrigidity in octahedral systems is in progress, and it is anticipated that variable temperature ^{13}C nmr spectroscopy will play a key role in these investigations.

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The Detection of Intermediates During the Conversion of Propane-1,2-diol to Propionaldehyde by Glyceroldehydrase, a Coenzyme B_{12} Dependent Reaction

Sir:

Recently there has been[1,2] renewed discussion of the mechanism of dioldehydrase,[3] an enzyme which requires as coenzyme, 5′-deoxyadenosylcobalamin, and catalyzes the conversion of L- or D-propane-1,2-diol to propionaldehyde, and ethylene glycol to acetaldehyde. Elegant experiments[4] have traced the fate of the hydrogen which migrates in these conversions: the C-1 hydrogen of the substrate is transferred to C-5′ of the coenzyme, where it becomes one of three equivalent hydrogens from which a C-2 hydrogen of product is ultimately derived.

We have isolated and purified[5] an enzyme closely related to dioldehydrase, *viz.*, a glyceroldehydrase[6] from *Aerobacter aerogenes* (No. 572 PZH), which, in addition to those reactions catalyzed by dioldehydrase, converts glycerol to β-hydroxypropionaldehyde.

The electronic absorption spectrum of a solution containing propane-1,2-diol and the glyceroldehydrase holoenzyme is similar to that reported[7,8] for propanedioldehydrase and by a detailed examination of the spectrum at wavelengths longer than 600 nm, we have identified[9] the species present (accounting for at least 80% of the enzyme-bound coenzyme present initially), as "base-on" B_{12r} *i.e.*, Co(II)cobalamin which has the 5,6-dimethylbenzimidazole coordinated. We have measured the absorption spectrum as a function of time, simultaneously monitoring the formation of propionaldehyde from propane-1,2-diol (Figure 1). The apoenzyme was incubated anaerobically with substrate, and a solution of 5′-deoxyadenosylcobalamin was added.[10] The pronounced lag[11] between the addition of coenzyme and both the attainment of the maximum rate of formation of product and the generation of the maximum concentration of Co(II)cobalamin is presumably connected with the slow binding of coenzyme to form the holoenzyme. Using the absorption bands at 611 and 655 nm diagnostically,[9] the concentration of Co(II)cobalamin increases to a steady-state value, concomitant with the formation of propionaldehyde. When all the substrate had been consumed, the concentration of Co(II)cobalamin decreased, and the coenzyme reformed, although not completely. When more substrate was added, Co(II)cobalamin was again formed.

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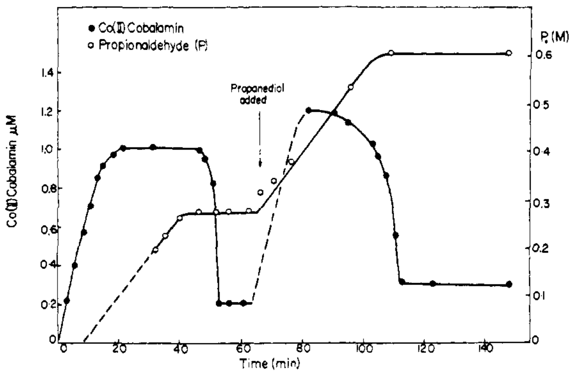

Figure 1. The time dependence of the formation of Co(II)cobalamin and propionaldehyde in a system consisting of glyceroldehydrase, 0.30 mg/ml (activity 82 units mg^{-1}),[11] coenzyme B_{12}, 2.1 μM, and propanediol, 0.273 M in 2.55 ml (0.1 M) of tricine buffer, pH 8.2 at 293°K. The concentration of Co(II)cobalamin generated on binding of coenzyme to apoenzyme was determined[9] by difference spectroscopy. The system was thoroughly degassed before addition of the coenzyme and maintained so until the concentration of Co(II)cobalamin reached a constant value, when small aliquots were removed for analysis for propionaldehyde.

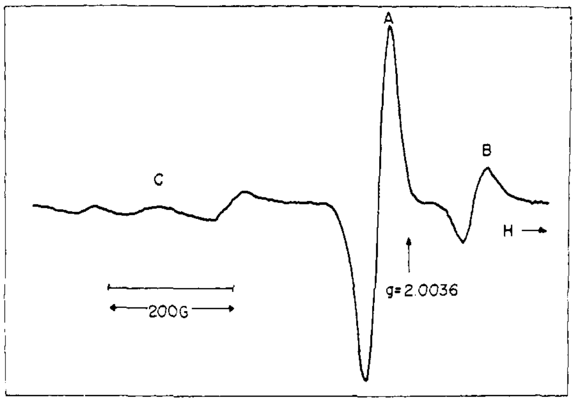

Figure 2. The epr spectrum, measured at 115°K using X-band radiation, of the species generated on addition of coenzyme B_{12} (final concentration 74.4 μM) to a reaction mixture containing glyceroldehydrase, 9.8 mg/ml (activity 70 units mg^{-1}), and propane-1,2-diol (0.664 M) in a total volume of 0.31 ml of tricine buffer (1 M).

The epr spectrum of the holoenzyme in the presence of substrate (Figure 2) increased in intensity to a maximum steady-state value, and then *disappeared* when all the substrate had been consumed. On addition of more substrate it reappeared. It is dominated by two derivative lines, A and B, with g values of 1.944 and 2.035, line widths of 39 and 36 G, respectively, and separated by 150 G, and a broad resonance C at low field with a g value of ~2.3, due presumably to Co(II)-cobalamin, which has[12] a prominent resonance, g = 2.32.

The two derivative lines at high field, A and B, are strikingly similar to those observed[13] in another cobamide-dependent enzyme, ribonucleotide reductase, in which the resonances had g values of 1.965 and 2.032 with a frequency-independent separation of 110 G. The derivative lines might, therefore, represent the interaction of an impaired electron with one proton.[14] The concentration of unpaired electrons was[13] very low in the ribonucleotide reductase; in glyceroldehydrase, double integration gives a value of 0.5 electron/coenzyme B_{12}. However, decreased intensities may be characteristic of radicals close to paramagnetic metal ions in polycrystalline materials.[15]

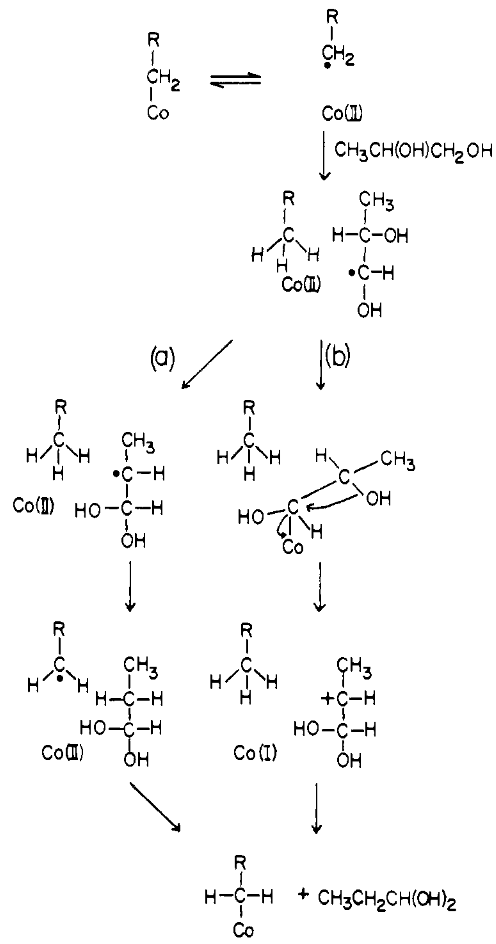

Figure 3. Possible mechanisms for the conversion of propane-1,2-diol to propionaldehyde by glyceroldehydrase.

The evidence presented here provides considerable support for the initial homolytic fission of the cobalt–carbon bond of the coenzyme, as suggested elsewhere[16] for a related enzyme, ethanolamine deaminase. The formation of cobalt(II)cobalamin and the 5′-deoxyadenosyl radical by interaction of the coenzyme with the apoenzyme, induced perhaps, by the substrate, would be followed by hydrogen transfer to give 5′-deoxyadenosine, which has been detected under certain conditions,[8,16,17] and the substrate radical. No experiment to date distinguishes between the possibilities shown in Figure 3: (a) the shift of OH as a radical to C-2, and the subsequent hydrogen abstraction to give product and re-form coenzyme; (b) the formation of a Co–C bond to substrate, followed by a 1,2 shift to give product and a cobalt corrinoid, which in the present case, would be Co(I)cobalamin, since the hydroxyl would shift, presumably, as an anion. The last stage in

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the mechanism requires the transfer of hydrogen from 5′-deoxyadenosine to substrate with the re-formation of the coenzyme Co–C bond. This step seems unlikely because the methyl group is normally considered inert. We would like to emphasize that, held close to the cobalt by the protein, this may not be so and the metal atom may be involved directly in the activation of the C_5′-methyl group.

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An Investigation of the Trans Effect in Some Cobalt(III) Complexes by ^{19}F Nuclear Magnetic Resonance Spectroscopy

Sir:

Cis and trans effects in six-coordinate cobalt(III) complexes have been observed[1] mainly in studies of the thermodynamics and kinetics of replacement reactions. We have previously reported[2–4] investigations by ^{1}H nmr spectroscopy of the cis effect in corrinoids,[2] cobalt(III) dimethylglyoximates,[3] and cobalt(III) Schiffs base complexes.[4] However, ^{1}H chemical shifts are small and their interpretation is sometimes complicated[4] by "through-space" effects such as those due to the ring currents of aromatic ligands and the electric field associated with dipoles in the complex. ^{19}F chemical shifts, on the other hand, are larger and in meta- and para-substituted fluorobenzenes, for example, have been used[5–7] to investigate the σ- and π-donor properties of substituents, inasmuch as they can be separated. Thus the meta shift, Δ_m, may be considered[6] a σ-electron effect parameter, while the difference between the para, Δ_p, and meta shifts, $(\Delta_p - \Delta_m)$, has been termed[6] a π-electron-effect parameter. The availability[8] of aryl derivatives of cobalt(III) complexes of the type *m*-(*p*-) $FC_6H_4Co(III)\{(DO)(DOH)pn\}X$ (1), where {(DO)(DOH)pn} is diacetylmonoximeimino diacetylmonoximatoiminopropane-1,3 and X is an anionic ligand, has made possible an investigation of the trans effect and allows a comparison with a similar study[9] of cis and trans effects in square-planar *trans-m-* (*p*-) fluorophenylbis(triethylphosphine)platinum complexes.

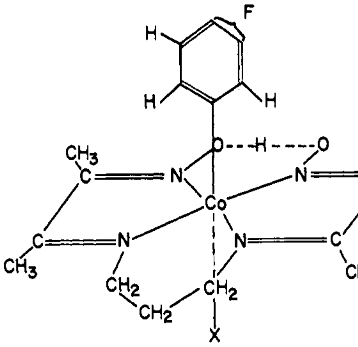

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Table I. ^{19}F Nmr Chemical Shifts[a] of *m*-Fluoroaryl–Cobalt(III)[b] and –Platinum(II) Complexes

	m-FC_6H_4Co-{(DO)(DOH)pn}X		m-FC_6H_4Pt-$(P(C_2H_5)_3)_2X$[c]	
X	In CH_2Cl_2	In $(CH_3)_2SO$	In $(CH_3)_2CO$	In C_6H_{12}
CH_3	3·05	3·05	3·93	4·26
m-FC_6H_4	1·99	2·05	3·07	
OCN (or NCO)	*d*	0·98	2·30	2·48
Br	*d*	0·68	1·97	2·34
SCN (or NCS)	*d*	0·52	1·75	1·90
I	*d*	0·50	1·56	2·00

[a] Relative to C_6H_5F. [b] The complexes were characterized by ^{1}H nmr spectroscopy and had satisfactory elemental analyses. [c] From ref 9. [d] Not sufficiently soluble.

Table II. ^{19}F Nmr Chemical Shifts[a] of *p*-Fluoroaryl–Cobalt(III)[b] and –Platinum(II) Complexes

	p-FC_6H_4Co-{(DO)(DOH)pn}X			p-$FC_6H_4Pt(P(C_2H_5)_3)_2X$[c]		
X	In CH_2Cl_2	In $(CH_3)_2SO$	$(\Delta_p - \Delta_m)$[d]	In $(CH_3)_2CO$	In C_6H_{12}	$(\Delta_p - \Delta_m)$[e]
CH_3	11·3	11·3	8·25	11·7	11·7	7·77
p-FC_6H_4	10·4	10·6		10·8	10·8	
OCN (or NCO)	*f*	9·72	8·74	10·1	10·2	7·80
I	9·46	9·73	9·23	9·54	9·70	7·98
Br	9·46	9·73	9·05	9·86	10·0	7·89
SCN (or NCS)	*f*	9·29	8·77	9·29	9·20	7·54

[a] Relative to C_6H_5F. [b] The complexes were characterized by ^{1}H nmr spectroscopy and had satisfactory elemental analyses. [c] From ref 9. [d] Data derived from measurements in $(CH_3)_2SO$. [e] Data derived from measurements in $(CH_3)_2CO$. [f] Not sufficiently soluble.

The ^{19}F chemical shifts Δ_m and Δ_p of the Co(III) complexes are given in Tables I and II, together with comparable data[9] for the Pt(II) complexes. Considered as substituents of fluorobenzene, both the Co(III) and the Pt(II) complexes behave as strong donors (relative to hydrogen) particularly when they are para substituents. The Δ_m values suggest that the Co(III) complexes are consistently poorer σ donors (better σ acceptors) than the Pt(II) complexes, but, most interestingly, the effect of the trans ligand X is qualitatively the same in both sets of complexes, with the resultant σ donation (to the aryl ligand) decreasing in the order $CH_3 >$ *m*-$FC_6H_4 >$ OCN(NCO)[10] > Br > SCN(NCS)[10] > I and shown in Figure 1a. The previous investigation[3] of the cis effect had concluded that the

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