Table I. Kinetic Parameters for Quenching of DCA* by Benzylstannanes **1a-e**[a]

X	k_q^f	α	$\frac{k_1 k_p}{(k_{-1} + k_r + k_p)}$	$k_q^p = \alpha k_q^f$	$k_q^r = (1 - \alpha)k_q^f$
Cl	3.8	0.91 ± 0.08	3.5 ± 0.5	3.5 ± 0.3	0.3 ± 0.3
F	5.9	0.55 ± 0.05	2.5 ± 0.4	3.2 ± 0.3	3.1 ± 0.3
H	7.9	0.45 ± 0.04	2.8 ± 0.5	3.5 ± 0.4	4.8 ± 1
CH_3	10	*b*	*b*	*b*	*b*
CH_3O	21	0.11 ± 0.01	2.7 ± 0.5	2.1 ± 0.2	18 ± 1

[a] Rate constants are given in units of $M^{-1}\ s^{-1} \times 10^{-9}$. [b] Not determined.

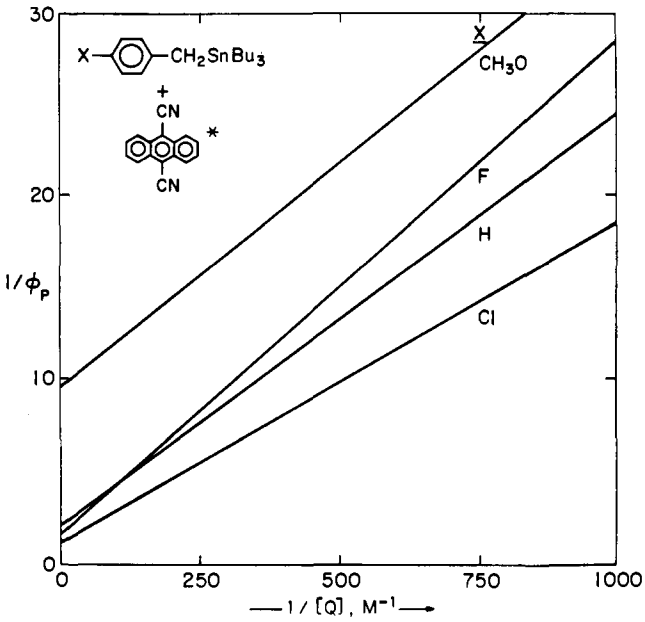

Figure 1. Plot of inverse quantum yield for DCA disappearance (ϕ_p^{-1}) vs. inverse quencher concentration ($[Q]^{-1}$) for the photoreaction DCA* + **1**.

radiationless decay to ground states (k_r) or to photoproduct(s) (k_p). Analysis according to this sequence provides the parameters listed in Table I: k_q^f derived from fluorescence quenching represents overall bimolecular exciplex decay, attenuated by exciplex reversibility, through both product-forming and non-product-forming channels; α, the efficiency of product formation at $[Q]_\infty$, and $k_1k_p/(k_1 + k_{-1} + k_p)$, the pseudo-rate constant for product-forming steps, arise from ϕ_p^{-1} vs. $[Q]^{-1}$ plots. Multiplication of k_q^f by α yields k_q^p, the overall rate constant for product-forming channels, and conversely the quantity $(1 - \alpha)k_q^f$ corresponds to radiationless but non-product-forming channels.[11]

The following trends emerge. Although the overall rate constant for deactivation (k_q^f) increases rapidly as the substituent X becomes more electron donating, the efficiency of product formation (α) simultaneously decreases. We find, quite surprisingly, that k_q^p is nearly invariant with substituent X in **1**, but that k_q^r strongly depends on the nature of X, varying by a factor of 50 from X = Cl to X = OCH_3.

A degree of insight into the peculiar behavior of the (**1**-DCA)* system is provided by assuming[12] that $k_1 = k_{dif}$ (that is, exciplex formation occurs with diffusional efficiency), in which case eq 2 and 3 obtain:

$$k_q^f/(k_{dif} - k_q^f) = (k_r + k_p)/k_{-1} \quad (2)$$

$$\alpha(k_r + k_p)/k_{-1} = k_p/k_{-1} \quad (3)$$

With this assumption the values in Table II are derived. These data indicate that exciplex reversibility strongly depends on the nature of the substituent X in **1**: as X becomes increasingly electron donating, exciplex reversion to S_1 and Q (k_{-1} channel) becomes increasingly unlikely, while decay via radiationless channels (k_r or k_p) becomes dominant. These results strongly implicate a charge-stabilized exciplex intermediate in the photophysical decay of the (**1**-DCA)* system and provide valuable insight into the electronic factors which contribute to various modes of exciplex decay.

Table II. Exciplex Reversibility vs. Radiationless Decay[a]

X	$(k_r + k_p)/k_{-1}$	k_p/k_{-1}
Cl	0.61	0.55
F	1.4	0.79
H	3.8	1.7
CH_3	ind[b]	*c*
CH_3O	ind[b]	ind[b]

[a] Derived from parameters in Table I assuming that $k_1 = k_{dif}$; see text. [b] For these substituents $k_q^f \sim k_{dif}$ so that application of eq 2 becomes indeterminant. The values are >5. [c] Not determined.

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(8) Oily yellow solid: IR 2230 cm^{-1} (CN); NMR ($CDCl_3$) δ 8.4-8.2 and 7.8-7.5 (m, 8 H), 2.0-0.8 (m, 27 H).
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David F. Eaton

Contribution No. 2753
E. I. du Pont de Nemours and Company
Central Research and Development Department
Wilmington, Delaware 19898

Received January 2, 1980

Double-Bond Participation in Cyclopent-3-enyl Tosylate

Sir:

There has been essentially universal agreement that π participation in cyclopent-3-enyl systems is entirely absent

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(1)

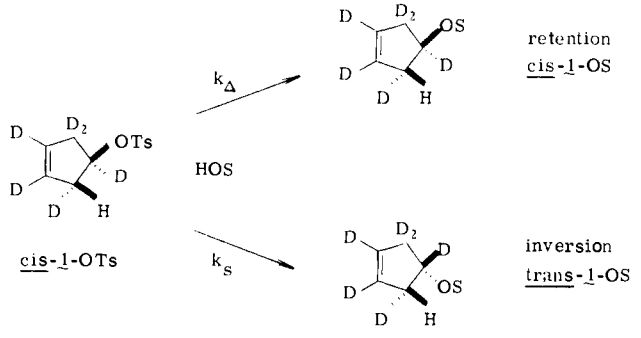
during solvolysis (eq 1). Rate retardations, in comparison with the corresponding saturated cyclopentyl system, were reported by Winstein and Sonnenberg for the tosylate,[1] by Bartlett and Rice for the bromide,[2] and by Hanack and Schneider for the nosylate.[3] No bicyclic material was found among the solvolysis products.[3] The apparent failure of the system to exhibit double-bond participation, despite its formal resemblance to the strongly participating *anti*-7-norborn-2-enyl system, was attributed to a nearly planar conformation of the cyclopentenyl ring[3] and to enhanced angle strain.[2] These arguments have led many authorities to accept the cyclopent-3-enyl system as totally lacking double-bond participation.[4] We now report that double-bond participation is quite strong in the solvolysis of cyclopent-3-enyl tosylate and that this participation may be even stronger than in the widely accepted case of cyclohex-3-enyl tosylate.[5,6]

Previous approaches have relied upon rates and product structures. We sought to examine the stereochemistry of the reaction. The only products of the solvolysis are the homoallylic material (major), whose structure corresponds to the starting material, and its allylic isomer (minor). The starting material, the ions with and without π participation, and the homoallylic product are all achiral and hence lack a stereochemical handle. To avoid steric factors associated with the introduction of an alkyl group to serve as the stereochemical handle, we used a variation of our proton label method.[5] All of the protons on cyclopentadiene were exchanged for deuterium. A single proton and the leaving group functionality then were introduced by hydroboration with diisopinocamphenylborane.[7] Reaction with tosyl chloride produced cyclopent-3-enyl-*1,2,2,3,4,5-d*$_6$ tosylate (*cis*-**1**-OTs), in which the 5 proton and the tosylate group are cis to each other.

Solvolysis of this derivative by solvent participation (k_s) would give an inverted product (*trans*-**1**-OS). Solvolysis by double-bond participation through a homoallylic ion (k_Δ) would give a retained product (*cis*-**1**-OS) (Scheme I). These structures can be readily distinguished by the resonance position of the 5 proton. In the inverted product this proton is trans to the OS group; in the retained product the relationship is cis.

We carried out the formolysis of *cis*-**1**-OTs under buffered conditions (KOCHO) at 35 °C. The allylic and homoallylic products were separated by preparative high pressure liquid chromatography. In the unlabeled case, the resonances of the 2,5 protons overlapped at 60 MHz. The spectrum at 360 MHz, however, produced two well-spaced multiplets. To determine which resonance corresponded to the proton cis to the formyloxy group and which to the trans proton, we prepared a deuterated formate of known stereochemistry. Reaction of the deuterated *cis*-**1**-OH with formyl fluoride[8] produced the cyclopent-3-enyl formate in which the lone proton was cis to the formyloxy group, *cis*-**1**-OCHO. The 360-MHz spectrum of this material lacked the low-field multiplet from the 2,5 resonance region. The formate product from the solvolysis of the deuterated *cis*-**1**-OTs lacked the same low-field multiplet. The complete void in this spectral region at 360 MHz for the reaction product showed that the formolysis of cyclopent-3-enyl tosylate proceeds with >99% retention (*cis*-**1**-OTs → *cis*-**1**-OCHO). The corresponding saturated system, cyclopentyl brosylate, solvolyzes in trifluoroethanol with complete inversion, as determined by a similar deuterium procedure.[9] Thus introduction of the double bond alters the mechanism from an ion pair k_s process to complete π participation. Formolysis of the corresponding six-membered ring, cyclohex-3-enyl tosylate, proceeds with about only 40% retention under similar conditions.[5] Consequently, participation may be considerably stronger in the symmetrical five-membered case than in the unsymmetrical six-membered case.[10]

Scheme I



The observation of retention demands a participation mechanism in the formolysis of cyclopent-3-enyl tosylate, contrary to previous conclusions.[1-4] The analogy with the *anti*-7-norborn-2-enyl system is not entirely inappropriate after all. Cyclopentene itself is nonplanar,[11] contrary to the previous description,[3] and the 1 substituent should exaggerate the nonplanarity (eq 2). Double-bond participation produces a

(2)

symmetrical bishomocyclopropenyl ion, whereas the analogous six-membered ring produces an unsymmetrical homoallylic ion in which π overlap is stronger at one end of the double bond than at the other. These structural differences may bring about stronger π participation for the five- than for the six-membered-ring system. The absence of the bicyclic product is no deterrent to the π participation mechanism, since reaction of the solvent at the 1 position (to produce **1**-OS) is as much in accord with the mechanism as reaction at the 3,4 positions to produce the bicyclic product. The absence of a rate enhancement may be attributed to the fact that double-bond participation must compete with an almost equally strong solvent participation. Likewise in the six-membered system, cyclohex-3-enyl tosylate, a rate retardation was almost always observed (in comparison with cyclohexyl tosylate), even in the highly ionizing, poorly nucleophilic solvent hexafluoro-2-propanol.[5]

It should be pointed out that much of the earlier work was done in acetic acid,[3] which is more strongly nucleophilic than formic acid. Furthermore, the work of Bartlett and Rice was done in water.[2] The high nucleophilicity and low ionizing power of water make it quite likely that, under their specific conditions, the dominant mechanism was solvent participation (k_s). Mechanistic generalizations, however, were not warranted on the basis of the relative rates.

In summary, we have found that formolysis of cyclopent-3-enyl tosylate proceeds with >99% retention. Consequently, double-bond participation is favored by several kilocalories/mole over solvent participation as the mechanism for formolysis. This system provides another example in which participation occurs without a rate enhancement.[12] In borderline cases, stereochemistry provides a more subtle test for participation than do rate comparisons.

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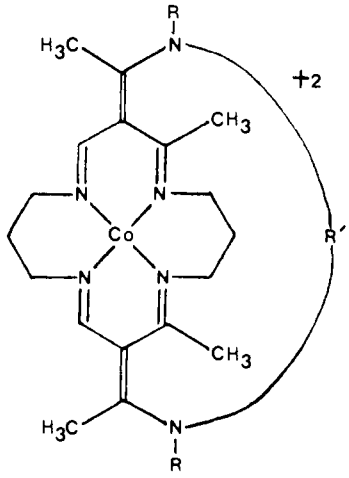
(14) National Science Foundation Undergraduate Research Participant from Barat College, Lake Forest, Ill., 1978.

Joseph B. Lambert,*[13] Rodney B. Finzel, Catherine A. Belec[14]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201
Received January 25, 1980

Synthesis and Structure of Totally Synthetic Coboglobin Models

Sir:

The ability of cobalt(II)-substituted hemoglobin and myoglobin to reversibly bind oxygen has provided new probes for the study of the metal atom site in these heme proteins.[1] Cobalt is similarly important in the development of totally synthetic heme protein models. Using the templating action of nickel(II), we have recently prepared and reported a new family of *superstructure* ligands (structure I) that have been



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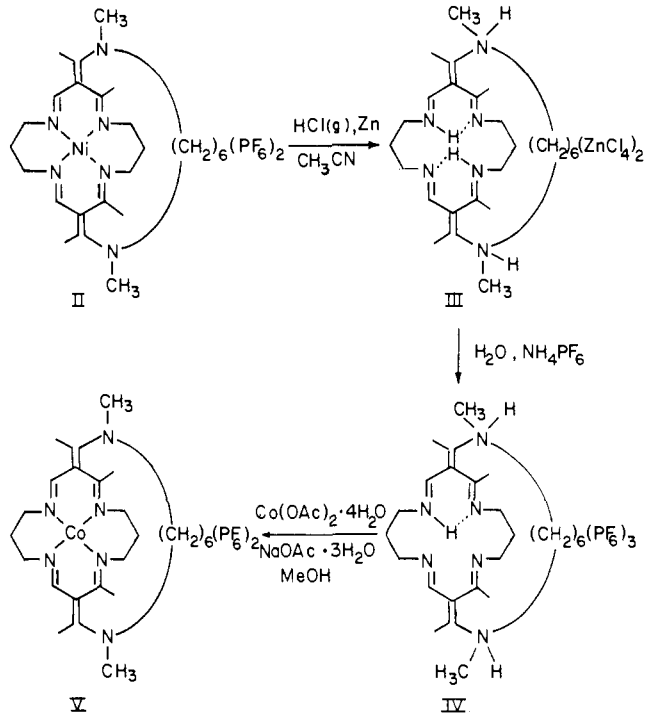
designed to emulate the active sites of heme proteins.[2] We report here the synthesis and characterization of the cobalt complexes of these unusual ligands, wherein the bridge group R′ provides a protected void, or "dry cave", near the metal atom, which is intended to shelter small ligands from interactions with other cobalt centers or with solvent. Two critical questions that we faced in developing the dry cave ligand system were (1) can the ligand be removed intact from the Ni(II) template and, more importantly, can it be chelated around the more interesting (from a bioinorganic standpoint) Co(II), again without degradation or isomerization and (2) does the dry cave structure that we have designed into these ligands actually perform the desired function—is the bridging group sufficiently rigid and appropriately positioned to permit the coordination of small molecules in the cavity while restricting the entry and coordination mode of other potential ligands? We report here that the answers to both questions are unequivocally in the affirmative.

Scheme I



The synthesis of the cobalt(II) complexes proceeds according to Scheme I (shown for the $-(CH_2)_6-$ bridged compound with CH_3 groups on the bridging nitrogens).[3] The yield of the orange microcrystalline product was 1.34 g (68%). Anal. Calcd for $CoC_{26}H_{44}N_6P_2F_{12}$; C, 39.55; H, 5.62; N, 10.64. Found: C, 39.56; H, 5.89; N, 10.61. This complex is a 2:1 electrolyte in CH_3CN (λ 282 at 25 °C) and has a magnetic moment of 2.49 β. Its ESR spectrum is reported in the following communication.[4]

The cobalt(II) complex prepared in this way was subjected to a complete X-ray structure determination.[5] While the structure is flawed by limitations associated with a disorder in the PF_6^- counterions, a number of highly significant results are nevertheless firmly established. Of primary importance, the ligand is not altered when removed from nickel and coordinated to cobalt(II) (Figures 1 and 2). The cobalt(II) is four coordinate and square planar and the dry cave is clearly evident. It is ~6.65 Å wide (measured between nonbridgehead vinyl carbons) with the height varying from 4.83 (back) to 5.60 Å (front). The saddle shape of the basic macrocycle is largely responsible for formation of the cavity in the structure.

Since cobalt(III) is very nearly always six coordinate, we have chosen to form the complexes of that ion to prove that small ligands can be accommodated in the dry cave. The cobalt(II) complex can be oxidized in the presence of the small ligands X^- = NCS^-, N_3^-, and NCO^- to form the corresponding cobalt(III) complexes $Co^{III}(L)X_2^+$, where L = the dry cave ligand. The oxidation can be accomplished with a variety of reagents, including Ce^{4+}, $NOPF_6$, and air (24 h). These diamagnetic complexes are 1:1 electrolytes in acetonitrile solution. Also in solution, the infrared spectrum of the

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