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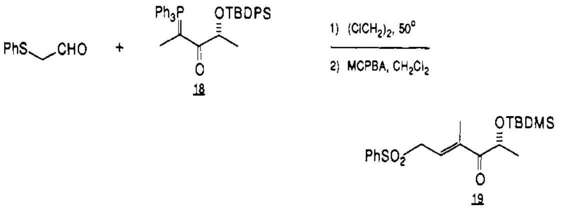
339B in which a palladium-catalyzed alkylation can resolve the question of the stereochemistry of C(11) (see Scheme II). Hydroxyl-directed epoxidation of the trifluoroacetate salt of **9** with trifluoroperacetic acid provided the vinyl epoxide **17**.[14,18]

Transfer of stereochemistry from C(6) to C(11) requires (1) selective palladium initiated ionization from one conformer of the vinyl epoxide, (2) alkylation to be faster than equilibration of the π-allylpalladium intermediates, and (3) regioselective C–C bond formation at C(11) even though this generates a sterically congested exocyclic double bond. Construction of the alkylation partner **19**,[14] proceeds in a straightforward manner (eq 2) from



(2)

the known Wittig reagent **18**[7b] and phenylthioethanal.[19] Palladium(0)-catalyzed condensation of the vinyl epoxide **17** and allyl sulfone **19** *under neutral conditions, surprisingly also benefits from the addition of water*. Unlike the cyclization of **8**, the addition of water might have prevented generation of the requisite nucleophile since the basicity of the medium is limited to that of hydroxide in THF containing water. However, the success of the alkylation demonstrates that such concerns are unwarranted. Direct reductive desulfonylation of the crude alkylation product **20** provides a homogeneous ketone **21**.[14] Thus, faithful transfer of the stereochemical information from C(6) to C(11) using the palladium template has occurred. Threo-selective reduction as previously reported[7b] was accompanied by concommitant desilylation of the *tert*-butyldiphenylsilyl group to give *allo*-pumiliotoxin 339B, $[\alpha]_D^{26}$ +7.0, $[\alpha]_{577}^{26}$ +9.0°, $[\alpha]_{435}^{26}$ +17.0° (*c* 0.20, CH_3OH).[20] Comparisons of the ^1H and ^{13}C NMR spectra of our sample to those of authentic (+)-**1** confirm their identity.

The present work establishes the geometric boundary for endo-type palladium-catalyzed cycloalkylations to be between five and six and suggests an astonishing similarity of a palladium cationic leaving group to a conventional leaving group. The virtue of the palladium template to control conformational behavior and thereby transmit stereochemical information along conformationally mobile systems[21] demonstrates the uniqueness of "palladium leaving groups". With respect to pumiliotoxin, the use of palladium-catalyzed alkylations of vinyl epoxides provides a facile entry into the basic indolizidine ring system, allows a concise convergent strategy, and controls the creation of the proper stereochemistry at C(11) by chirality transfer. We believe this sequence is potentially a quite general approach to this intriguing alkaloid family.

Acknowledgment. We thank the National Institutes of Health, General Medical Sciences Institute, for their generous support of our programs. We thank Professor Larry Overman and Dr. Steven W. Goldstein for detailed experimental procedures for their synthesis of *allo*-pumiliotoxin B, for spectra of authentic samples, and for unpublished rotation data.

Supplementary Material Available: Characterization data (IR, ^1H NMR, and MS) for **8**, **9**, **17**, **19**, and **21** (2 pages). Ordering information is given on any current masthead page.

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(18) A major byproduct in which the 10,11 rather than the 6,7 double bond has been epoxidized arises. The stereochemistry of **15** derives from the successful completion of the synthesis. For an amino-olefin epoxidation, see: Quick, J.; Khandelwal, Y.; Meltzer, P. C.; Weinberg, J. S. *J. Org. Chem.* **1983**, *48*, 5199.

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Induced Dimerization of Tetrakis(*p*-sulfonatophenyl)porphine and Metalloderivatives by a Polyammonium Macrocycle [32]-$N_8H_8^{8+}$

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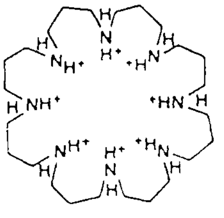
Received February 3, 1989

In this communication we report the induced dimerization of negatively charged porphyrins in *micromolar* concentrations by a 32-membered highly protonated macrocycle.

Polyammonium macrocycles and macropolycycles have been most studied as anion receptors.[1] The macrocycle 1,5,9,13,17,21,25,29-octaazacyclodotricontane [32]-N_8 is octaprotonated in weakly acid solution $N_8H_8^{8+}$, **1**, and binds strongly to multicharged anions.[2-4] Modification of electrochemical[4,5] and photochemical[6] properties as well as chemical reactivity[7,8] of the complexed anion has been reported.

It occurred to us that there might be strong electrostatic attraction between $N_8H_8^{8+}$ and the negatively charged porphyrin **2** (a) R = SO_3^-, H_2TPPS^{4-}. Examination of space-filling models (compare **1** and **2**) shows that the $-SO_3^-$ groups are quite close to alternating NH_2^+ groups on the macrocycle. Spectral titration of H_2TPPS^{4-} with $N_8H_8^{8+}$ (prepared according to ref 3) at pH 6.0[9] gave an isosbestic at 403 nm and indicated formation of a single, very stable, 2:1 adduct (eq 1). A similar behavior was



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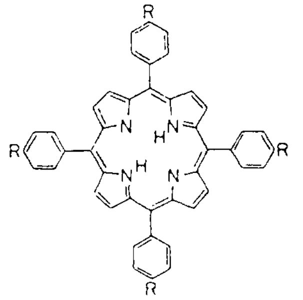

2a R = SO_3^-
2b R = CO_2^-

$$2H_2TPPS^{4-} + N_8H_8^{8+} \rightleftarrows (H_2TPPS^{4-})_2 \cdot NH_8^{8+} \qquad K_1 \quad (1)$$

observed when the visible region was utilized. The value of K_1

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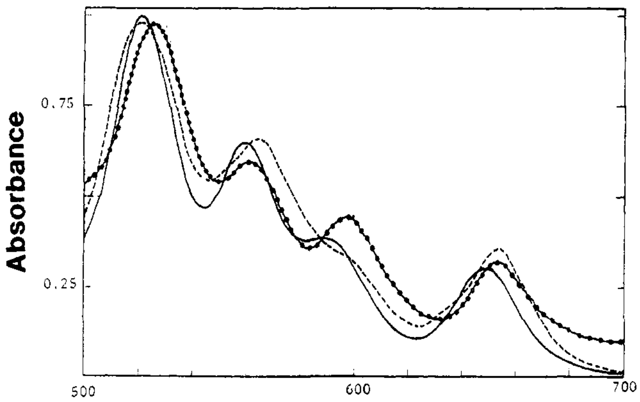

Figure 1. Spectra of the following: (a) H_2TPPS^{4-} (10 μM) + $N_8H_8^{8+}$ (5–7.2 μM) pH 6.1 in 1.0 mM MES, 10-cm cell path (–•–); (b) H_2TPPS^{4-} (10 μM) + 18-crown-6 ether (8–12 mM) pH 6.1 in 0.02 M KCl, 10-cm cell path (– –); and (c) H_2TPPS^{4-} (1.0 mM) in 0.1 M KCl, pH 6.1, 0.1-cm cell path. Similar absorbance characteristics if 2.5 mM H_2TPPS^{4-} and 0.2 M Na_2SO_4 were used (—).

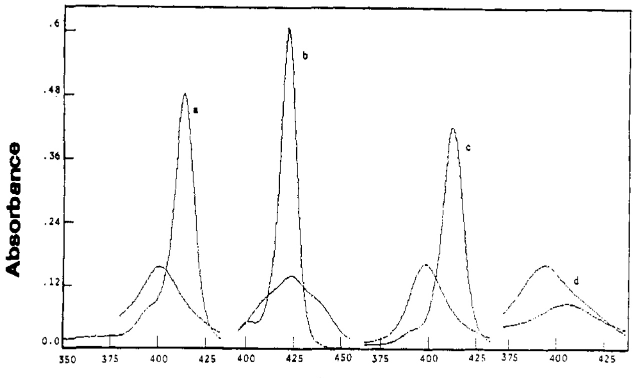

Figure 2. Spectra of porphyrins, metalloporphyrins, and $N_8H_8^{8+}$ 2:1 adducts (a) H_2TPPS^{4-}, (b) $Zn(TPPS)^{4-}$, (c) $Cu(TPPS)^{4-}$, and (d) Fe-$(TPPS)^{3-}$. All solutions contained 1.0 μM porphyrins and 1.0–2.0 μM $N_8H_8^{8+}$ at pH 5.5–6.0 with no added electrolyte. 1.0-cm cell path. The adducts have reduced absorbances compared with the free porphyrins or metalloporphyrins.

(M^{-2} at 25 °C) was $10^{14.4\pm0.6}$ at low $I \sim 10^{-5}$ and $10^{11.3\pm0.8}$ in 0.1 M KCl. The visible spectrum of the adduct resembled closely that of a concentrated solution of H_2TPPS^{4-} (1–2.5 mM) in KCl (0.1 M)[10] and that of a mixture of H_2TPPS^{4-} (10 μM) 18-crown-6 (8–12 mM) and KCl (0.02 M),[13] Figure 1. It is clear that the macrocycle $N_8H_8^{8+}$ has induced dimerization of the anionic porphyrin *at remarkably low concentrations* of both reactants. It is unclear whether in the adduct, $(H_2TPPS^{4-})_2{\cdot}N_8H_8^{8+}$, the polyamine is sandwiched between the porphyrin. Whether it is or not, it appears reasonable that there is a Π–Π interactive face-to-face structure for the porphyrins because of the large absorbance band shifts (Figure 2).[13] For steric and electrostatic reasons, it is likely that one porphyrin ring system is rotated approximately 45° relative to the other. The dimers formed in concentrated solutions[10] and by addition of crown ether[13] also have similar spectral characteristics in the Soret region with a maximum at 412 nm, $\epsilon = 2.1 \times 10^5$ M^{-1} cm^{-1} ref 12 and 413 nm, $\epsilon = 2.5 \times 10^5$ M^{-1} cm^{-1}, respectively. The dimer formed by attachment of the porphyrin to $N_8H_8^{8+}$ has markedly different characteristics with a substantial blue shift, Figure 2. Some indirect evidence that one side of the polyamine macrocycle is open in the adduct (i.e., it is not sandwiched) is afforded by kinetic studies of the dissociation of the adduct to monomeric H_2TPPS^{4-} by anions X^{n-} which can combine with $N_8H_8^{8+}$. The results can be interpreted in terms of the formation of another adduct (eq 2) which has dimer spectral characteristics for $X^{n-} = SO_4^{2-}$, $K_2 = 56$ M^{-1} and for X^{n-}

$$(H_2TPPS^{4-})_2 + N_8H_8^{8+} + X^{n-} \rightleftarrows (H_2TPPS^{4-})_2{\cdot}N_8H_8^{8+}{\cdot}X^{n-} \qquad K_2 \quad (2)$$

$= Fe(CN)_6^{4-}$, $K = 1.2 \times 10^5$ M^{-1} in 0.1 M KCl and pH = 6.0. It would be difficult to visualize this interaction were the amine sandwiched. The porphyrin **2a** is diprotonated at pH 3.0,[14-16] and titration of H_4TPPS^{2-} with $N_8H_8^{8+}$ using both Soret and visible regions indicates a strong complex with stoichiometry $(H_4TPPS^{2-})_4{\cdot}N_8H_8^{8+}$. There are marked absorbance band shifts from monomeric H_4TPPS^{2-}, which are duplicated in the Q-region with concentrated H_4TPPS^{2-} solutions (0.25 mM, 0.1 M KCl, $\epsilon_{708nm} = 9.2 \times 10^4$ M^{-1} cm^{-1}), although the band intensities are quite different. Formation of a tetramer of H_2TPPS^{2-} at high concentrations (~0.1 M) at pH 7.0 has been postulated from ^1H NMR studies.[12]

The interaction of $N_8H_8^{8+}$ with the Zn(II), Cu(II), and Fe(III) derivatives of H_2TPPS^{4-} was also examined at pH 5.5–6.0. Marked spectral changes were observed (Figure 2) with sharp isosbestic points. Titration curves in the Soret and visible regions indicated that only a 2:1 metalloporphyrin:$N_8H_8^{8+}$ adduct was formed in all cases, even in micromolar concentration of reactants provided the ionic strength was maintained low. Dimerization of $Zn(TPPS)^{4-}$ is only evident at ~0.3 mM concentrations, and the dimerization constant is small (2.2×10^2 M^{-1} at pH 7.0 and $I = 0.10$ M).[12] Dimerization of $Cu(TPPS)^{4-}$ has also been previously reported with dimerization constants at 25 °C of 6.7×10^4 M^{-1} (pH 7.0 and $I = 0.5$ M)[11] and 4.1×10^4 M^{-1} (pH 7.0 and $I = 0.10$ M).[12] A concentrated solution of $Zn(TPPS)^{4-}$ has absorbance maxima at 558 nm ($\epsilon = 1.8 \times 10^3$ M^{-1} cm^{-1}) and 597 nm ($\epsilon = 0.8 \times 10^3$ M^{-1} cm^{-1}), and a concentrated solution of $Cu(TPPS)^{4-}$ has a maximum at 547 nm ($\epsilon = 1.0 \times 10^4$). These characteristics resemble closely those of the corresponding polyamine-induced dimers.

A 2:1 adduct of $Fe(TPPS)(OH_2)^{3-}$, ref 17, and $N_8H_8^{8+}$ formed at pH 5.5 and 3.0 with the same spectrum (Figure 2). The *red* shift in the Soret region and, more significantly, the absence of spectral differences between a 10 μM (10 cm cell) and 1 mM (0.1 cm cell) solution of $Fe(TPPS)^{3-}$ indicated that the dimer formed may be of the μ-oxo form rather than the stacking type. The latter has been invoked in relatively high concentration in acid.[18] The μ-oxo dimer normally appears when solutions of the iron(III) porphyrin are adjusted to pH $\gtrsim 6.5$.[17] Attachment of a $N_8H_8^{8+}$ species to $Fe(TPPS)(OH_2)^{3-}$ might be expected to reduce the pK_a value of 7.0[17] markedly (even by 2–3 units), and the hydroxo product could condense with another $Fe(TPPS)(OH_2)^{3-}$ to give the μ-oxo form even at pH's 3–4 (eq 3). All amine-induced dimers

$$Fe(TPPS)(OH_2)^{3-} + N_8H_8^{8+}{\cdot}Fe(TPPS)(OH)^{4-} \rightarrow N_8H_8^{8+}{\cdot}Fe(TPPS)\text{–}O\text{–}Fe(TPPS)^{8-} + H^+ \quad (3)$$

dissociate on addition of anions which associate with the amine (vide supra), and even 0.1 M KCl will dissociate the adducts which have been formed by using micromolar concentrations of reactants in the absence of added electrolyte. This behavior contrasts sharply with that of the dimers prepared from high concentrations of porphyrins or by addition of 18-crown-6 ether,[13] when in both cases

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(10) The monomer, dimer equilibrium for H_2TPPS^{4-} is now well-established,[11-13] although literature values of the dimerization constant vary. At 25 °C, $K_D = 9.6 \times 10^4$ M^{-1} ($I = 0.05$ M[11]) and 2.2×10^4 M^{-1} ($I = 0.10$ M[12]). Even with the lower value, millimolar solutions of H_2TPPS^{4-} will contain $\gtrsim$ 90% dimer.

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added KCl facilitates formation of the dimer.[19]

No spectral changes occur when H_2TPPS^{4-} is treated with $N_8H_4^{4+}$ (pH ~ 8.5[2,3]) nor when H_4TPPS^{2-} is mixed with the smaller macrocycle 1,4,7,10,13,16-hexaazacyclooctadecane in the tetraprotonated form (pH ~ 3.5[20]). There is no spectral interaction between $N_8H_8^{8+}$ and H_2TMPyP^{4+}(tetrakis(*N*-methylpyrid-4-yl)porphine cation), but H_2TPPC^{4-} **2b**, R = CO_2^-(tetrakis(4-carboxyphenyl)porphine anion),[19,21] gives similar spectral changes to that of H_2TPPS^{4-} when treated with $N_8H_8^{8+}$. It has been found that the chemical reactivity and photochemical properties of $TPPS^{4-}$ and metalloderivatives[22-24] are markedly modified in the amine-induced dimer. These are manifest in, for example, reduced rates of interaction of the porphyrin with metal ions and in the loss of the relatively long lifetime of the first excited triplet.[24] These studies are continuing.

Acknowledgment. This work was supported by a National Science Foundation grant (CHE-8613217) which is gratefully acknowledged.

Supplementary Material Available: Spectral titration of H_2TPPS^{4-} by $N_8H_8^{8+}$ at 25 °C and a table of spectral characteristics of H_2TPPS^{4-}, H_4TPPS^{2-}, and metalloderivatives and their adducts with $N_8H_8^{8+}$ (2 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of $Cp_3Co_3(CO)_2$

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Received February 1, 1989

An extensive series of triangular clusters having the general form $(CpM)_3(CO)_2$ is known which exhibits a variety of interesting structural and spectroscopic properties.[1] The formal valence electron count for these neutral clusters may be varied from 46 (M = Co) to 49 (M = Ni). The lower electron count clusters appear to be stabilized by electron-rich ligands such as pentamethylcyclopentadiene (Cp*) as opposed to cyclopentadiene (Cp). We have recently developed a synthetic route into more reactive $46e^-$ clusters which contain at least one Cp ligand.[2] Here we describe the synthesis, structure, magnetic properties, and surprising reactivity of $(CpCo)_3(CO)_2$, **1**.

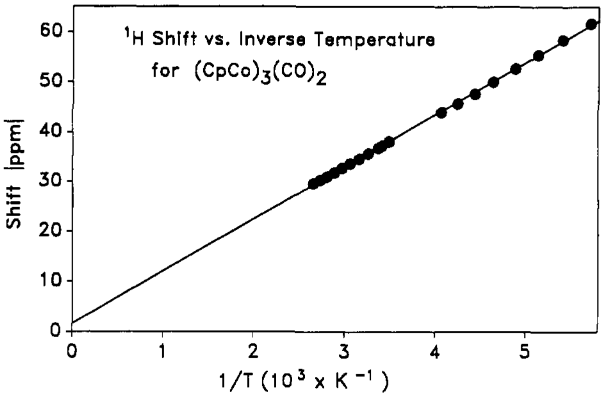
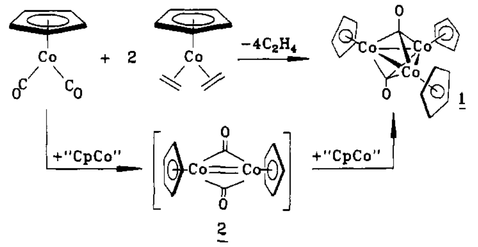


Figure 1. Paramagnetically induced temperature dependence of the ^1H NMR spectrum of **1**. The diamagnetic reference position for the Cp ring protons of **1** was assumed to be 5 ppm. The paramagnetic shift is defined according to the following equation: $\delta_{obsd} = \delta_{dia} + \delta_{para}$.

Scheme I



Although the title complex is quite oxygen sensitive and spontaneously decomposes when dissolved in all organic solvents investigated thus far, it may be conveniently synthesized by the reaction of $CpCo(C_2H_4)_2$ and $CpCo(CO)_2$ as summarized in Scheme I.

The reaction must be conducted by using hexane as the major solvent to cause the trinuclear complex to precipitate as it is formed. In this way, yields of **1** as high as 70% may be obtained. The formation of the trinuclear product occurs in a stepwise manner involving formation of the known dinuclear complex[3] $[CoCp(\mu\text{-}CO)]_2$, **2**, as an intermediate.[4]

The carbonyl stretch for **1** is observed at 1725 cm^{-1} in KBr and 1710 cm^{-1} in toluene. This value is approximately 70 cm^{-1} lower than the stretch observed for **2** and is consistent with a change in the coordination geometry of the carbonyls from doubly to triply bridging.[5] The mass spectrum (EI) of **1** shows a small peak at *m*/*e* = 428 corresponding to the parent ion as well as prominent peaks for **2** and $(CoCp)_4(CO)_2$,[6] **3**. The thermal decomposition

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(4) Addition of $CpCo(C_2H_4)_2$ to the preformed dinuclear intermediate produces the tricobalt cluster. A satisfactory elemental analysis for **1** has been obtained.

(5) These values are close to those reported for complexes similar to **1** which contain triply bridging carbonyls: $Cp_3Ni_3(CO)_2$,[1a] 1742; $CpCoCp_2Ni_2(CO)_2$,[1a] 1737; $Cp^*{}_3Co_3(CO)_2$,[1b] 1680 cm^{-1}.

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