

ble involvement of **1** and/or **3** in this scheme is indicated by the finding that **1** catalyzed the trimerization of 2-butyne as well as oligimerization to tetra-, penta-, and hexamers which remain to be fully characterized structurally.

NOTE ADDED IN PROOF. Through private communications, we have learned that compound **1** has been prepared in other laboratories: H. F. Klein and H. Schmidbaur (personal communication from H. Schmidbaur) and by Dr. S. Ittel (personal communication from S. Ittel).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation, Grant No. MPS73-08943 A02.

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- (1) E. L. Muettterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974).
- (2) (a) Very pale green needles; identified by complete elemental analysis; (b) 70% yields; (c) electron and chemical ionization mass spectra.
- (3) We found no evidence in our product for $H_2Fe[P(CH_3)_3]_4$,⁴ a compound that has a similar physical appearance, volatility, and infrared Fe-H stretch.
- (4) H. F. Klein, *Angew. Chem.*, **82**, 885 (1970).
- (5) At 90 MHz, the spectrum may be described as a doublet of triplets with the triplets further split into doublets. Tentative assignments of $H(Fe-H)-P$ coupling constants for **1** are $J_{HP_a} = 70$ Hz, $J_{HP_b} \approx J_{HP_c} = 56$ Hz, and $J_{HP_d} = 26$ Hz.
- (6) At 90 MHz, the unique CH_2 resonance (**1**) and four CH_3 resonances (doublets) were resolved.
- (7) Macroscale cryoscopic molecular weight determination with benzene solvent in a Vacuum Atmospheres "Dri Lab" with an argon atmosphere (Theory: 360, Found: 328, 370).
- (8) (a) J. Chatt and J. N. Davidson, *J. Chem. Soc.*, 843 (1965). (b) The molecular weight in benzene (ebullioscopic) was reported as slightly higher than theory for a monomer.
- (9) F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J. Chem. Soc., Chem. Commun.*, 755 (1974).
- (10) When the NMR spectrum of **1** was examined in the presence and absence of internal $P(CH_3)_3$, there was no detectable difference in line shapes of the resonances characteristic of **1**. However, the internal $P(CH_3)_3$ resonance broadened in the higher temperature ranges ($>-50^\circ$) and was slightly shifted from the normal $P(CH_3)_3$ position. In contrast, the $^{31}P\{^1H\}$ spectrum of $P(CH_3)_3$ alone in toluene remained sharp over this temperature range. We tentatively propose that there is an equilibrium of the type $1 \rightleftharpoons Fe[P(CH_3)_3]_4$ which shifts to the right as T increases, with k_1 small with respect to the NMR time scale and small with respect to k_2 (K small). We further propose that the equilibrium $P(CH_3)_3 + Fe[P(CH_3)_3]_4 \rightleftharpoons Fe[P(CH_3)_3]_5$ extant with rates large with respect to the NMR time scale and with the equilibrium shifting to the right with temperature decrease. The four- and five-coordinate species in the latter equilibrium would be probably paramagnetic (T_d) and definitely diamagnetic (D_{3h}), respectively. A paramagnetic species, $Fe[P(CH_3)_3]_4$, present in low concentrations could account for broadening and shifting of the $P(CH_3)_3$ resonance.
- (11) Fully defined by the DNMR ^{31}P spectra.
- (12) Mass spectral and NMR characterization.
- (13) Wherein an intermediate $Fe[P(CH_3)_3]_3(CH_3CN)_2^{2+}FeCl_4^{2-}$ is tentatively proposed as indicated by analysis of the intermediate.
- (14) 1H NMR ($CH_3)_4Si$ reference: C- CH_3 , -1.95 (s, 6); N-H, -6.73 (broad, 2 H); and P- CH_3 , -1.23 (m, 27 H). Inequivalence of P atoms was not seen at -110 to $+20^\circ$ so the molecule is fluxional. Infrared C=N stretch 1560 cm^{-1} . Phosphine ligands are tightly bound; there is no fast ligand exchange (NMR time scale) between **2** and $P(CH_3)_3$ in toluene at 80° .
- (15) An analogous linear diimine metal complex has been described recently. P. A. Finn, M. S. King, P. A. Kilty, and R. E. McCarley, *J. Am. Chem. Soc.*, **97**, 220 (1975).

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Received February 7, 1975

New Peripheral Metal Complexes Related to Chlorophyll

Sir:

Coordination of metal ions to the four central nitrogen atoms of the porphyrin tetrapyrrole macrocycle has been the generally recognized mode of metal complex formation in chlorophyll and related compounds.¹ We report here new metal complexes of the chlorophyll macrocycle in which the metal is bound to the β -ketoester system of ring V and which we therefore term peripheral complexes.

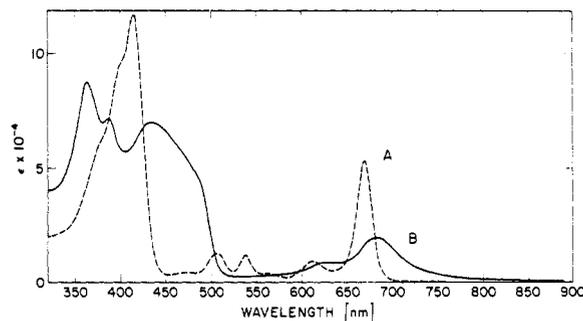
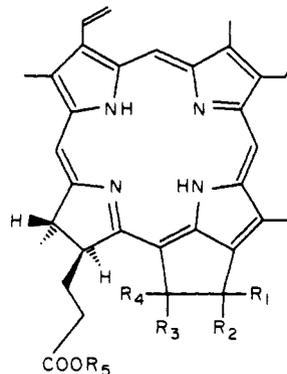


Figure 1. Uv-visible absorption spectra of pheophytin a (**1**) in dry pyridine (A, - - -), and its peripheral magnesium complex (**7**) (B, —) in dry pyridine, saturated with anhydrous $Mg(ClO_4)_2$. Spectrum A is the typical chlorin spectrum.

During metalation studies of pheophorbides of the a series to the respective chlorophyllides by the method of Baum et al.,² we noticed that the substrates can be divided into two classes on the basis of their spectral response to Mg^{2+} . Compounds of the first class dissolve in pyridine saturated with $Mg(ClO_4)_2$ to give brown solutions with the uv-visible spectrum typical of pheophorbides (i.e., Figure 1A). Compounds of the second class, by contrast, give under the same conditions bright green solutions in which the red band is broadened and shifted to significantly longer wavelengths and the Soret band is split into two complex band systems extending from 350 to 500 nm (Figure 1B).

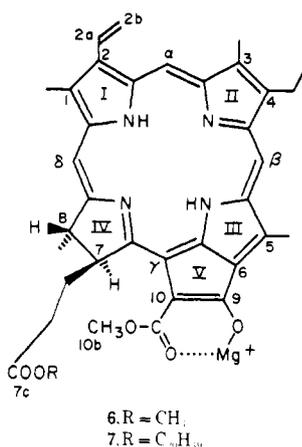
The spectral response to pyridine- Mg^{2+} is determined by whether or not the pheophorbides contain an enolizable β -ketoester system in ring V. Pheophytin a (**1**) and methylpheophorbide a (**2**) form green solutions, and similar pronounced spectral changes are observed in pheophytin b, and bacteriopheophytins a and b.³ These compounds all contain an intact ring V β -ketoester system capable of enolization. However, pyromethylpheophorbide a (**3**),⁴ 9-desoxo-9-hydroxymethylpheophorbide a (**4**),⁵ and 10-methoxymethylpheophorbide a (**5**)⁶ give brown solutions in pyridine with spectra unaffected by the presence or absence of $Mg(ClO_4)_2$. In the latter compounds, ready enolization of the β -ketoester system is prevented by elimination of either the C-10 ester C=O or the C-9 keto C=O functions or by substitution of the enolizable 10-H by an alkoxy group. We conclude from this chemical evidence that the observed



No.	Compound	R_1, R_2	R_3	R_4	R_5
1	Pheophytin a	=O	H	COOCH ₃	phytyl
2	Methylpheophorbide a	=O	H	COOCH ₃	CH ₃
3	Pyromethylpheophorbide a	=O	H	H	CH ₃
4	9-Desoxo-9-hydroxymethylpheophorbide a	H, OH	H	COOCH	CH ₃
5	10-Methoxymethylpheophorbide b	=O	OCH ₃	COOCH ₃	CH ₃

spectral change is due to a new chemical species rather than to a solvent effect⁷ and that the intact enolizable β -ketoester system is necessary to form the species which give rise to the unusual uv-visible spectrum. β -Dicarbonyl compounds are excellent chelating agents, and therefore a structure in which Mg^{2+} is bound to the peripheral β -ketoester system seemed plausible. Such a structure (**6**) is supported by the ir and NMR spectra of the new complexes. This structure further is consistent with the predicted red shifts for both $\Delta 9,10$ and $\Delta 10,10a$ enols⁸ and the loss of fluorescence observed both in the Molisch phase test intermediate⁹ and the peripheral complexes.

The ir spectrum of methylpheophorbide a (**2**) in [²H₅]pyridine shows a band at 1741 cm⁻¹ (the 7b- and 10-carbomethoxy ester C=O functions) and a band at 1703 cm⁻¹ assigned to the free 9-keto group.¹⁰ If **2** is dissolved in a dry solution of Mg(ClO₄)₂ in pyridine, the ester band is reduced in intensity by about 50% and shifted to 1735 cm⁻¹, and the keto band has disappeared. Instead, a strong band at 1626 cm⁻¹ is observed. As the position and intensity of this band are typical for chelates of β -dicarbonyl compounds,¹¹ we ascribe it to the chelated C=O vibration in structure **6**. Addition of water regenerates the original ir spectrum.



The ¹H NMR spectrum of the Mg(II) peripheral complex of methylpheophorbide a (**6**) (Table I) supports the proposed chelate structure as well. The C-10 proton resonance has vanished from the spectrum, but both N-H proton resonances are still present, as required by structure **6**.¹² The incremental chemical shifts of **6** as compared to **2**¹³ indicate a uniformly reduced ring current probably resulting from the electron-withdrawing effect of the chelate. The opposite incremental shifts of the 10b-CH₃, 7-H, and 8-CH₃ protons are explained by the steric consequences from chelate formation. These involve not only a coplanar conformation of the 10-COOCH₃ group with the macrocycle but also an induced conformation change¹⁴ of ring IV due to increased steric hindrance between the substituents at C- γ and C-7. This brings these three sets of protons more into the plane of the macrocycle, and thus in a strongly deshielded region.¹³

The peripheral complexes are decomposed by water and by Mg(II) chelating agents such as pentan-2,4-dione. Titration with water has been followed by fluorescence, uv-visible and ¹H NMR spectroscopy over a wide concentration and temperature range, and all data confirm an equilibrium only between the free pheophorbide a and its peripheral complex. The equilibrium between **2** and **6** can be probed in detail by ¹H NMR spectroscopy, which shows two distinct sets of resonances even at elevated temperatures. In no case were resonances of a third compound (e.g., a dinuclear peripheral complex) observed.

Table I. ¹H NMR Spectra (δ (ppm)) Relative to TMS of Methylpheophorbide a (**2**) in [²H₅] Pyridine and of its Peripheral Complex (**6**) in [²H₅] Pyridine, Saturated with Mg(ClO₄)₂^a

	Peripheral		$\Delta\delta$	Multiplicity
	Methylpheo- phorbide 2	Mg com- plex 6		
β -H	9.75	9.01	+0.74	s
α -H	9.57	8.83	+0.74	s
δ -H	8.71	8.00	+0.71	s
2a-H	8.08	7.77	+0.31	dd, $J = 11, 17$ Hz
2b-H _A	6.23	6.06	+0.17	dd, $J = 2, 17$ Hz
2b-H _B	6.05	5.87	+0.18	dd, $J = 2, 11$ Hz
10-H	6.61	—	—	s
7-H	4.29	4.65	-0.36	m(d)
8-H	4.42	4.10	+0.32	q, $J = 7$ Hz
10b-CH ₃	3.76	3.83	-0.07	s
7d-CH ₃	3.52	3.38	+0.14	s
5-CH ₃	3.42	3.11	+0.31	s
3-CH ₃	3.21	2.95	+0.26	s
1-CH ₃	3.08	2.83	+0.25	s
8-CH ₃	1.66	1.73	-0.07	d, $J = 7$ Hz
4-CH ₃	3.54	3.29	+0.25	q, $J = 7$ Hz
4a-CH ₃	1.53	1.39	+0.14	t, $J = 7$ Hz
N-H ¹²	+0.74	2.44	-1.70	s, broad
	-1.48	2.04	-3.52	s, broad

^a A positive sign of the incremental shifts ($\Delta\delta$) denotes high-field shifts.

Surprisingly, chlorophyll a itself does not form a peripheral complex with Mg(II), although it has an intact β -ketoester system. This finding seems to be complementary to the observation that pheophorbides which can form the peripheral complexes cannot be metalated with Mg(ClO₄)₂ in refluxing pyridine,² while pheophorbides lacking this system react smoothly.¹⁵ It would appear that the central N-atoms and the peripheral β -ketoester system compete and that the steric consequences of peripheral complex formation prevent insertion of Mg(II) into the macrocycle, and vice versa. Mg is comparatively loosely bound to the chlorophyll macrocycle,¹⁶ so that minor changes in the molecule can unbalance the system. The corresponding Zn chlorophyllides are considerably more stable, and indeed, the peripheral Zn(II) complex of **2** is converted upon standing at room temperature to the chlorophyllide with the centrally bound metal. In this process, the free pheophorbide is irreversibly removed from the equilibrium with the peripheral complex over a period of hours. With Cu(II), Mn(II), and Ni(II) no peripheral complex has been observed, as these metals are bound instead to the central N-atoms from the beginning. The generality of the peripheral interaction of Mg²⁺ with intact β -ketoester systems in the Mg-free chlorophyll derivatives may explain its insertion into the porphyrin precursors of chlorophyll prior to the biosynthesis of ring V.¹⁷

Enolization of the β -ketoester system in chlorophylls and their derivatives is considered responsible for the easy ¹H/²H exchange and epimerization at C-10,¹⁸ leading to the presence of diastereomeric Chl a' and related pigments¹⁹ with inverted configuration at C-10 (7,10-cisoid).⁶ Enolization is further responsible for the oxidation²⁰ at C-10, for ring V cleavage,²¹ and for the color change in the Molisch phase test,^{9,22} and photosynthetic models have been advanced involving enol participation in oxygen evolution.²³ The formation of peripheral metal complexes is a new aspect of chlorophyll chemistry which may be involved in the generation of red-shifted chlorophyll species in vitro and in vivo. More detailed studies of this system and its possible role in chlorophyll aggregation²⁴ and reactivity are in progress.

Acknowledgment. This work was carried out under the auspices of the Energy Research and Development Admin-

istration. We gratefully acknowledge the award of a stipend to H.S. (at Gesellschaft fuer Molekularbiologische Forschung, D3301 Stöckheim, West Germany) by the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg. We thank V. J. Heintz and P. R. Edwards for technical assistance while participating in the Argonne Undergraduate Research Program. Dr. P. S. Song kindly communicated data before publication.

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Received February 24, 1975

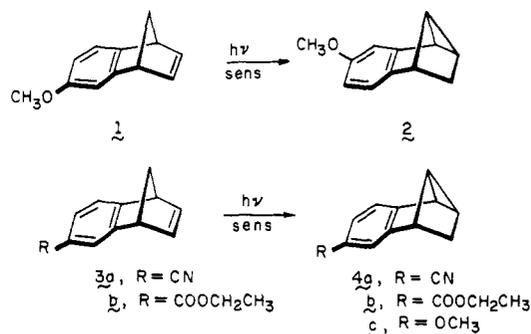
Substituent Control of Regiospecific Pathways in Di- π -methane Photorearrangements Which Utilize Benzo-Vinyl Bonding Schemes

Sir:

So vaguely understood are polar substituent influences on π -electron distribution in electronically excited molecules, that this question now commands consideration as a major unsettled issue in organic photochemistry. Intriguing subtleties are to be anticipated since photoexcited species possess electronic distributions quite unlike those of their ground state progenitors.¹ Currently, little basis exists for

predicting which course a $\pi \rightarrow \pi^*$ rearrangement will take when proximal electron-withdrawing or -donating substituents are introduced.² With regard to this question, we have uncovered striking crossovers in otherwise fully regiospecific product formation which result upon substituent alteration from cyano to methoxy in the di- π -methane photorearrangements of the benzenorbornadiene³ and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene systems.⁴

Sensitized irradiation (3500 Å) through Pyrex of dilute benzene solutions of **1**,⁵ **3a**,⁶ and **3b** resulted in ready photoisomerization with formation of a *single* product in each instance. Sensitizers ranging in triplet energy from 65.5 (thioxanthone) to 73.6 kcal/mol (acetophenone) were utilized. Direct irradiation at various wavelengths proved ineffective. The 1H NMR spectrum (CCl_4) of **2**, which consists of a highly structured aromatic pattern (δ 6.30-6.92, 3 H), a methoxyl singlet (3.70, 3 H), and higher field multiplets centered at 3.19 (2 H), 2.75 (1 H), 2.38 (1 H), 1.88 (1 H), and 0.74 (1 H), differs notably from that of **4c**, particularly



in the downfield sector. The latter anisole was prepared from **4b** by sequential saponification, reaction with methyl-lithium, Baeyer-Villiger rearrangement, hydrolysis, and exposure to dimethyl sulfate in alkali. Treatment of **4a** with methylmagnesium iodide produced the identical acetyl derivative, thus completing the requisite interconversions. Absolute positional assignment to the substituents in **2** and **4** follows principally from direct 1H NMR spectral comparisons with the homologous compounds of unequivocal structure described below. Simultaneous irradiation of benzenorbornadiene, **1** and **3a**, under controlled conditions revealed no substantial differences in the individual rates of starting material disappearance or product formation.⁷

To further assess this dramatic change in bonding preference, the photochemistry of **5** and **8** was also examined. Initial detailed studies with the parent hydrocarbon of this series⁴ revealed its triplet state ($E_T = 69-74$ kcal/mol) to enjoy the capacity for bifurcate reactivity. In this instance, bond reorganization along the di- π -methane pathway leading to cyclopropane product is slightly favored (1.2:1) over the ($\pi_2 + \pi_2$) bonding process which gives rise to benzo-basketene. The photorearrangements of **5** and **8** were conducted analogously and likewise followed closely by gas chromatography. As with the hydrocarbon, ether **5** was unreactive to sensitization by benzophenone ($E_T = 69$ kcal/mol); however, this was not the case with nitrile **8**, a finding which signals the lower triplet energy of this diene. Direct irradiation failed to promote these isomerizations in both instances.

Whereas triplet excitation of **5** provided a 0.8:1 mixture of **6** (oil) and **7** (mp 53-54°), nitrile **8** gave only **9** (mp 62-63.5°). Complete structure elucidation of **9** was achieved by single-crystal X-ray analysis, its crystals belonging to a triclinic space group with $a = 9.608$ (1) Å, $b = 7.995$ (1) Å, $c = 8.324$ (1) Å, $\alpha = 112.79$ (1)°, $\beta = 112.07$ (1)°, and $\gamma = 84.03$ (1)°. A calculated and measured density indicated