

Table I. Bond Lengths and Angles in 1<sup>a</sup>

bond lengths, pm		bond angles, <sup>b</sup> deg	
P-O	161.1 (3)	O-P-O	113.0 (3)
		N-P-O	96.0 (2)
P-N	170.0 (7)	C-O-P	110.3 (7)
		C-N-P	106.2 (9)
		C-N-C	115.5 (7)
C-O	143.3 (6)	C-C-N	114.3 (14)
		C-C-O	112.7 (9)
C-C <sub>ring</sub>	131.5 (11)	N-P-Pt	124.4 (24)
		O-P-Pt	112.8 (17)
C-N	144.5 (9)	P-Pt-I	86.8 (3)
		P-Pt-P	95.76 (8)
P-Pt	220.3 (2)	I-Pt-I	91.58 (2)
Pt-I	264.5 (3)		

<sup>a</sup>These numbers are averages from the two ADPO ligands. <sup>b</sup>The fold angle about the P-N bonds is 119°.

as a result of coordination to the platinum center to provide an 8-P-4 bonding scheme.

The structure of complex **1** has been verified by single-crystal X-ray structure determination.<sup>8</sup> The solid-state structure of the complex is illustrated in Figure 1.

The ADPO ring system has folded such that the angle between the two five-membered rings is 119°. The two ADPO ligands are essentially identical and representative bond lengths and angles are given in Table I.

It is interesting to note that the N-P bond in the complexed ligand is only 2-pm longer than in 10-P-3 ADPO (168 pm). Fixation of the  $\pi$ -bonds in the ligand rings is also evident from the lengthened C-O and C-N bonds and shortened C-C bonds.

The 10-P-3 ADPO could have provided a phosphorus lone pair to the platinum center without bending;<sup>10</sup> however, this would have two unfavorable consequences. First the planar 10-P-3 ADPO could only provide rather diffuse (low p-orbital character) lone pairs from the phosphorus center while the bent 8-P-3 ADPO provides a single fairly directional phosphorus lone pair (higher p-orbital character).<sup>11</sup> Second the planar 10-P-3 ADPO would yield a sterically congested 10-P-4 complex, whereas the bent 8-P-3 ADPO gives a less hindered 8-P-4 complex.

It should be noted that the existence of the platinum complex **1** shows that there is not inordinate ring strain associated with the bent structure in the ADPO system and that the preference for the planar 10-P-3 structure of the free ligand is largely based on electronic factors. The small energy difference between 8-P-3 and 10-P-3 ADPO is thus overcome by coordination of phosphorus to platinum. The ADPO group can be displaced from the platinum center with triethyl phosphite at -50 °C. However, we saw no evidence of free 8-P-3 ADPO in solution at this temperature.

(8) Two equivalents of 10-P-3 ADPO in toluene were added to a suspension of (COD)PtI<sub>2</sub> (1 equiv) in toluene. The reaction was allowed to stir for 4 h. The toluene was removed in vacuo and the residue recrystallized from benzene. The crystal data (-108 °C) were as follows: C<sub>24</sub>H<sub>40</sub>PtI<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>·1/2C<sub>6</sub>H<sub>6</sub>, monoclinic, space group P2<sub>1</sub>/n, a = 1955.6 (4) pm, b = 1137.0 (6) pm, c = 1668.2 (6) pm,  $\beta$  = 107.27 (2)°, Z = 4, D<sub>c</sub> = 1.82 g/cm<sup>3</sup>, crystal size 0.15 × 0.15 × 0.25 mm. Only the 3745 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The structure was solved by direct methods. The final R factors were R = 0.030 and R<sub>w</sub> = 0.037.

(9) This perspective drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid with the lighting source at infinity so the shadow sizes are meaningful.

(10) Bicyclic 10-P-4 phosphoranides have been shown to coordinate to metal centers with minimal distortion of the idealized phosphoranide geometry; see: Wachter, J.; Mentzen, B. F.; Reiss, J. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 284. We have recently synthesized a complex between 10-Sb-3 ADSbO and platinum in which the planar geometry of the ADSbO group is maintained. Details will be disclosed in subsequent publications.

(11) The two lone pairs in 10-P-3 ADPO can be thought of as essentially sp<sup>2</sup> orbital lone pairs whereas 8-P-3 ADPO has one phosphorus lone pair in an sp<sup>3</sup> orbital.

Apparently the geometrical reorganization of 8-P-3 ADPO to 10-P-3 ADPO is fast on the NMR time scale on concomitant reorganization to 10-P-3 ADPO occurs with displacement from the platinum center.

Work is continuing in this area to address the various factors which control the geometry of the ADPO ligand in metal complexes.

**Acknowledgment.** The X-ray crystal structure analysis was performed by the Molecular Structures Corporation, College Station, TX.

**Supplementary Material Available:** A complete description of the X-ray crystallographic structure determination of **1** and tables of positional and thermal parameters (20 pages). Ordering information is given on any current masthead page.

## ESR and ENDOR of Bacteriopheophytin a Radicals. Implications for Bacteriochlorophylls in Vivo

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The model studies presented here seek to probe effects that the protein environment may induce or impose on the conformation and electronic configuration of photosynthetic chromophores. The cation radicals observed on photooxidation of bacterial reaction centers have been assigned previously to dimeric bacteriochlorophylls (BChl) a or b on the basis of comparisons of ESR and ENDOR characteristics in vivo with those observed for BChl<sup>+</sup> a and b in vitro.<sup>1-5</sup> Recent X-ray results of the *Rhodospseudomonas viridis* reaction center (BChl b) support the dimer formulation for its unoxidized primary donor, P960, and provide evidence of possible interactions between the magnesium and the oxygen of a nearby 2-acetyl group, as well as of ligation by neighboring protein residues.<sup>6</sup> Chlorophylls further interact with their environment by hydrogen bonding of their peripheral carbonyl groups, as evidenced by resonance Raman data.<sup>7</sup> To separate ligation and/or hydrogen bonding effects from the "intrinsic" unpaired spin distributions of BChl radicals, the ENDOR parameters of the cation radical of bacteriopheophytin a (BPheo, a demetalated BChl) have been measured as a function of solvent and temperature.

Comparisons of the BPheo a<sup>+</sup> results with BChl a<sup>+</sup> data suggest that ligation and hydrogen bonding do not significantly alter the unpaired spin distribution of BChl radicals and thus lend validity to the common use of coordinating solvents such as methanol in ENDOR spectroscopy to prevent aggregation and enhance resolution.<sup>8</sup> This insensitivity to ligation also supports theoretical predictions<sup>4,9,10</sup> that the two highest occupied orbitals in BChls

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(8) To our knowledge, all reported ENDOR investigations of BChl cations were carried out in the presence of methanol.

Table I. Major ENDOR Coupling Constants (G)<sup>a,c</sup>

T, K	1-CH <sub>3</sub>	5-CH <sub>3</sub>	H $\beta$	H $\beta$	H $\beta$	H $\beta$
BChl a <sup>+</sup> in 1:6 CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub>						
129	1.77	3.41	NR	NR	NR	NR
153	1.78	3.38	NR	NR	4.74	6.02
163	1.79	3.40	4.23	NR	4.79	5.78
173	1.76	3.45	4.26	NR	4.74	5.79
183	1.76	3.44	4.24	NR	4.71	5.80
213	1.75	3.43	4.19	4.66	4.79	5.83
280	1.70	3.37	4.11	4.65	4.89	5.86
BPheo a <sup>+</sup> in 1:6 CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub>						
129	1.81	3.20	NR	NR	NR	NR
153	1.88	3.18	NR	NR	5.86	6.58
163	1.86	3.22	4.57	4.94	5.76	6.55 (8.29)
183	1.80	3.20	4.52	4.95	5.76	6.73
213	1.79	3.17	4.59	5.08	5.75	6.72
253	1.75	3.17	4.60	5.09	5.71	6.69
BPheo a <sup>+</sup> in CH <sub>2</sub> Cl <sub>2</sub>						
163	1.79	3.20	4.51	4.91	5.74	6.70
173	1.79	3.19	4.52	4.94	5.75	6.69
183	1.78	3.20	4.52	4.97	5.76	6.73
213	1.76	3.16	4.60	5.09	5.80	6.72
253	1.74	3.10	4.61	5.11	5.71	6.69
Comparison of BPheo a <sup>+</sup> at 183 K (well-resolved spectra)						
CH <sub>3</sub> OH/CH <sub>2</sub> Cl <sub>2</sub>	1.80	3.20	4.52	4.95	5.76	6.73
CH <sub>2</sub> Cl <sub>2</sub>	1.78	3.20	4.52	4.97	5.76	6.73 <sup>b</sup>

<sup>a</sup> 1 G = 10<sup>-4</sup> T = 2.8 MHz. <sup>b</sup> Additional proton coupling constants observed are 0.99, 0.81, and 0.26 G.<sup>13</sup> <sup>c</sup> NR = not resolved.

and bacteriochlorins are well separated unlike the situations in porphyrin, chlorin, and chlorophyll cation radicals where admixtures of the two close-lying HOMOs ("a<sub>1u</sub>" and "a<sub>2u</sub>") can be induced by different ligands.<sup>11,12</sup>

Variations observed in only some of the ENDOR coupling constants of the BPheo radicals as a function of temperature are attributed to conformational changes in the flexible skeleton of the macrocycle induced by the solvent matrix. Similar "deformations" are proposed as a mechanism that helps regulate interactions between neighboring electron donors and acceptors in vivo.

ENDOR spectra for BPheo a<sup>+</sup> in CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure 1.<sup>13</sup> Comparable data for BChl a<sup>+</sup><sup>3,5,13</sup> and results obtained in pure CH<sub>2</sub>Cl<sub>2</sub> solutions are listed in Table I. Assignments of the major coupling constants, i.e., those due to the 1- and 5-methyl groups and the four  $\beta$  protons of the saturated rings II and IV (see Figure 2 for structure), are based on reported deuterium substitutions, temperature behavior, molecular orbital

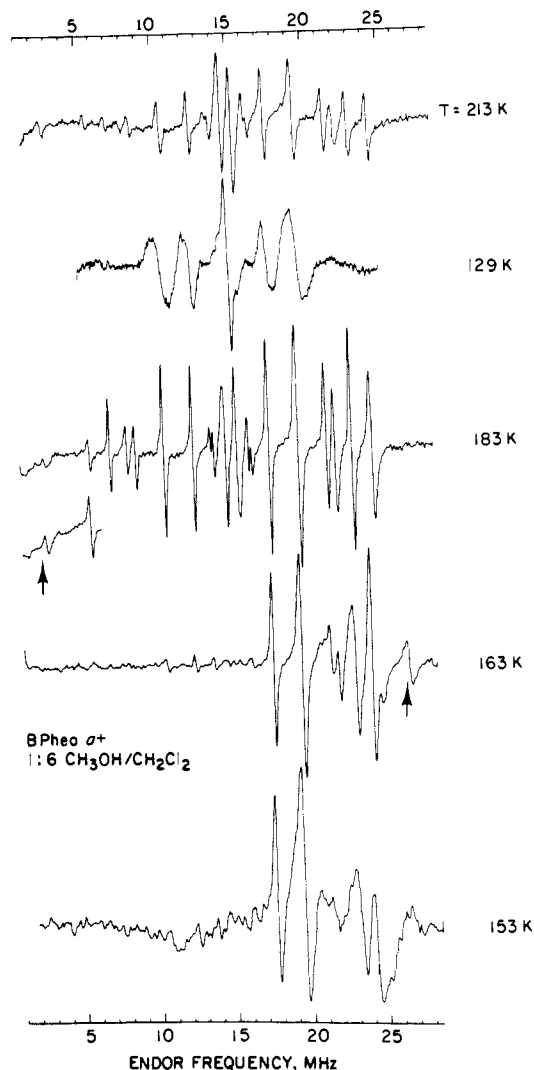
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(13) BChl and BPheo a were prepared as described in ref 14. Cation radicals were generated in 1:6 CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> or pure CH<sub>2</sub>Cl<sub>2</sub> by oxidation with ZnTPP<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, the oxidized salt of zinc tetraphenylporphyrin.<sup>3,4</sup> Because the oxidation potential of ZnTPP<sup>+</sup> is only ~50 mV higher than that of BPheo,<sup>14</sup> small amounts of the ZnTPP<sup>+</sup> radical exist in equilibrium with the BPheo<sup>+</sup> and may contribute to the small proton coupling constants seen in Figure 1. These ZnTPP<sup>+</sup> coupling constants are less than ~1 MHz at all the temperatures used,<sup>11</sup> and therefore do not distort or interfere with the larger BPheo<sup>+</sup> coupling constants listed in Table I. The nitrogen coupling constants of ZnTPP<sup>+</sup> are also significantly larger<sup>11</sup> than the sole nitrogen constant of 1.08 G observed for BPheo<sup>+</sup>. Additional couplings are not resolved; reported a<sub>N</sub> values for BChl<sup>+</sup> range from 0.81 to 1.13 G.<sup>3,5</sup> The BChl<sup>+</sup> proton coupling constants reported here agree well with previous investigations.<sup>3,5</sup> To avoid interference with the ESR spectrum of BPheo<sup>+</sup> shown in Figure 2, (FeTPP)<sub>2</sub>O<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, which is ESR silent at room temperature,<sup>3</sup> was used as oxidizing agent. The iron compound reacts with alcohols and cannot be used in methanolic solutions. ENDOR measurements were made on a Bruker-IBM ER200D spectrometer equipped with a 10-in. magnet, an ER 251 triple-resonance system, a field frequency lock, and an Aspect 2000 data acquisition system.



**Figure 1.** ENDOR spectra of BPheo a<sup>+</sup> in CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>. *T* = 213 K: The four largest coupling constants are assigned to the four  $\beta$  protons of rings II and IV (positions 3, 4, 7, and 8). The next two coupling constants are attributed to the 1- and 5-methyl groups. *T* = 129 K: The solvent is frozen (crystalline). The  $\beta$  protons are no longer detected but the methyl groups are still observed because of continued free rotation.<sup>1-5,11</sup> *T* = 183 K: The solvent is fluid. Spectra are well resolved; note the nitrogen line at low field (*a<sub>N</sub>* = 1.08 G).<sup>13</sup> *T* = 163 K: Solvent becomes glassy. The methyl groups do not change but the relative intensities of the protons do, and additional lines appear.<sup>16</sup> *T* = 153 K: The solvent is a glassy matrix. The methyl groups remain unchanged, and the additional lines are still visible.<sup>16</sup> They are attributed to various conformations of the flexible rings II and IV induced by the matrix. Analogous variations in the saturated rings, induced by different packing modes, have been observed in X-ray structures of single crystals of methyl bacteriopheophorbides a and d.<sup>17</sup>

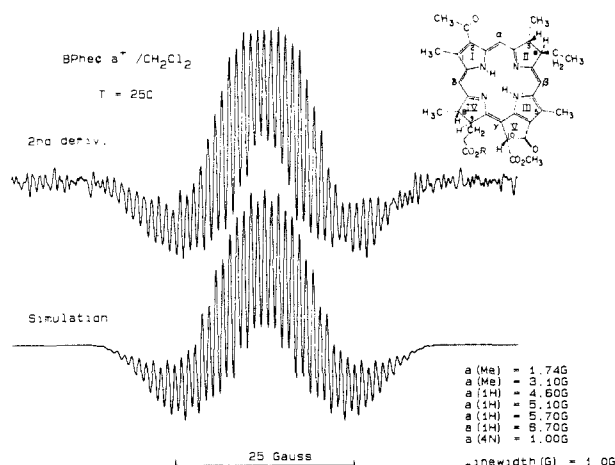
calculations, and analogy with model studies.<sup>1-5,10,11,14</sup> The results may be summarized as follows:

- (1) In CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> solutions, in which the Mg is complexed and the oxygen functions of the macrocycles are hydrogen-bonded by the methanol,<sup>15</sup> ENDOR results are comparable for BChl a<sup>+</sup> and BPheo a<sup>+</sup> (Table I). The differences that do exist in the  $\beta$ -proton coupling constants are also observed in synthetic bacteriochlorins and are predicted theoretically.<sup>14</sup>
- (2) In "nonbonding" CH<sub>2</sub>Cl<sub>2</sub> solutions, the coupling constants

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**Figure 2.** (Top) Second-derivative ESR spectrum of BPheo  $a^+$  in  $\text{CH}_2\text{Cl}_2$  at 25 °C obtained by computer averaging.<sup>13</sup> (Bottom) Simulation that demonstrates that two methyl groups, four large protons, and four nitrogens determine the spectral pattern observed.

of BPheo  $a^+$  agree within 2% with those observed in the alcoholic solvent, indicating that hydrogen bonding has little effect on the spin distributions of the radicals (Table I). (Comparison of BChl  $a^+$  in  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  is complicated by the formation of aggregates in  $\text{CH}_2\text{Cl}_2$ ).

The combination of (1) and (2) suggests therefore that oxygen ligation of the Mg in BChls and/or hydrogen bonding of the oxygen peripheral groups do not significantly alter the spin profiles of BChl  $a^+$  in vitro and, by extrapolation, the profiles of the primary donors P870<sup>+</sup> and P960<sup>+</sup> in vivo.

(3) Computer signal averaging yields<sup>3</sup> a partially resolved solution ESR spectrum of BPheo  $a^+$  with 40 or more lines (Figure 2). This spectrum provides a sensitive test for the assignments of the ENDOR coupling constants. A satisfactory facsimile of the experimental BPheo  $a^+$  spectrum is obtained with a computer simulation (Figure 2) that assumes two methyl groups with  $a_{\text{H}} = 1.74$  (1- $\text{CH}_3$ ) and 3.10 G (5- $\text{CH}_3$ ), four protons with  $a_{\text{H}} = 4.6$ , 5.1, 5.7, and 6.7 G ( $\beta$  protons on rings II and IV), and four nitrogens with  $a_{\text{N}} = 1.0$  G (approximated from the sole N splitting that is resolved).<sup>13</sup> These results thus support the ENDOR assignments and the similar spin profiles predicted by MO calculations for the BPheo and BChl cations.<sup>3,4,10,14</sup>

(4) Changes in the coupling constants of BPheo  $a^+$  can be induced near the "freezing" point of  $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$  mixtures (Figure 1,  $T = 153$ – $163$  K). However, only the  $\beta$  protons of rings II and IV are significantly affected. The effect observed is attributable to conformational changes<sup>4,11</sup> (twisting) of the flexible saturated rings<sup>17</sup> induced by the glassy matrix. Analogous variations in rings IV or II have been observed in X-ray structures of single crystals of methyl bacteriopheophorbides a and d.<sup>17</sup> Similar conformational effects could be induced by packing and protein interactions in vivo and may explain some of the ESR and ENDOR variations observed in different photosynthetic bacteria.<sup>1-5</sup> It is intriguing to speculate further that some conformational rearrangements accompany electron transfer<sup>18</sup> and alter both the distances and the relative orientations of BChl donors and acceptors in vivo and thereby help to regulate forward and back electron flow.<sup>19</sup>

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**Registry No.** BPheo $a^+$ , 60686-68-2.

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## First Realization of Threefold Fluxionality in Polycyclic Conjugated Hydrocarbon-Metal Complexes: Synthesis and Dynamic NMR Study of $[\text{Pd}(\eta^3\text{-phenalenyl})(\text{tmeda})]^+\text{PF}_6^-$ and Its Methyl Derivative

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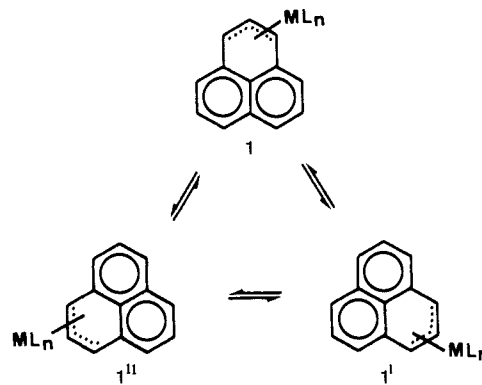
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A major goal of current research in the area of dynamic behaviors in organometallic chemistry is the synthesis of new metal complexes that exhibit migration of an  $\text{ML}_n$  unit from one ring to another in a polycyclic conjugated hydrocarbon ligand.<sup>1-3</sup> A case in point would be the phenalenyl- $\text{ML}_n$  system.<sup>4-7</sup> If the  $\text{ML}_n$  unit in an  $\eta^3$ -phenalenyl complex **1** migrates around the phenalenyl skeleton through the pathway of  $1 \rightleftharpoons 1' \rightleftharpoons 1''$ , such a stereo-



chemical nonrigid behavior provides a novel example of a 3-fold fluxionality in the metal complexes of polycyclic conjugated hydrocarbon.<sup>8,9</sup> We now report the first realization of such a

(1) Much experimental information for this type of process is confined to simple cyclic polyene complexes. (a) Cotton, F. A. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 10. (b) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. (c) Deganello, G. "Transition Metal Complexes of Cyclic Polyolefins"; Academic Press: New York, 1979. (d) Fedorov, L. A. *Russ. Chem. Rev.* **1973**, *42*, 678.

(2) For a leading review and theoretical treatment of the interring migration of an  $\text{ML}_n$  unit in polycyclic hydrocarbon-metal complexes, see: Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lilly, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396 and references cited therein. **Note Added In Proof.** After submission of this paper Silvestra and Albright (*J. Am. Chem. Soc.* **1985**, *107*, 6829) have reported some aspects of the haptotropic shift in phenalenium- $\text{ML}_2$  complex.

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(8) For attempts to detect such a behavior, see ref 5 and 6.