CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CINCINNATI, CINCINNATI, OHIO 45221

Ligand Lability of Ethylene–Platinum(II) Complexes. Studies with Anilines and Cyclohexylamines

BY THOMAS A. WEIL, PAUL J. SCHMIDT, AND MILTON ORCHIN

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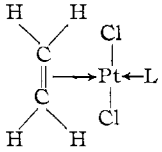
The ligand lability of L in the complexes *trans*-$(PtCl_2)(C_2H_4)(L)$, **1**, where L may be aniline, cyclohexylamine, or their N-methyl derivatives, has been studied by nmr spectroscopy and in particular by measuring the temperature at which Pt–N, CH_3 coupling occurs. The relative labilities of the ligands L depend upon the base strength of L, its steric requirements and the solvent. The ethylene is much less susceptible to exchange than L since coupling with ^{195}Pt was observed at all temperatures studied.

Introduction

It is known, principally as a result of nmr studies,[1-4] that both the olefin and pyridine ligands of complexes of structure **1** (L = pyridine series) undergo ligand exchange with solvent molecules, pyridines exchanging much more rapidly than ethylene or other olefins. The exchange also occurs when Zeise's salt (**1**, L = Cl) is dissolved in water.[5,6] Infrared studies of the *trans*-carbonyl complexes $(PtCl_2)(CO)(L)$ have shown[7] that acetone and acetonitrile can partially or even completely replace L when L is pyridine, pyridine N-oxide, aniline, or derivatives of these bases. These studies have made it possible to determine[1a] the relative order in which unsaturated ligands are able to labilize the group *trans* to them; such ordering has been very difficult to ascertain by kinetic experiments.[1b]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The use of amines as the L in **1** was expected to lead to particularly instructive results with respect to the study of ligand lability. The nmr spectra of methylamines such as N-methylaniline and N-methylcyclohexylamine in neutral solvents show an unsplit methyl signal; no coupling with the N–H proton occurs because of rapid intermolecular proton exchange.[8-14] On protonation, however, the methyl signal appears as a triplet.[8,10,12] In contrast to the unsplit methyl signal observed with N-methylaniline, the less basic and more hindered 2,4-dinitro-, and 2,4,6-trinitro-N-methylanilines show a doublet.[13,15] Because metalation formally resembles protonation, a study of CH_3–N–H and ^{195}Pt–N–CH_3 couplings[16] in the nmr spectra of complexes **1** should give useful information on the lability of L and its steric requirements for complexation.

Results and Discussion

A. Effect of Structure on Coupling Temperature.—The methyl proton region of the nmr spectrum of **1** ($L = C_6H_5NHCH_3$) in $DCCl_3$ at three temperatures is shown in Figure 1. Only at −39° do coupling of the N-methyl protons to ^{195}Pt (J = 34.6 cps)[17-22] and H–N–CH_3 coupling (J = 5.9 cps) occur.[23] The observed H–N–CH_3 coupling constants agree with prior related observations.[14,18] At higher temperatures, exchange of this amine with solvent occurs rapidly on the nmr time scale. Although N,N-dimethylaniline is a stronger base than N-methylaniline, the nmr spectrum of its complex **1** [$L = C_6H_5N(CH_3)_2$] shows no Pt–N–CH_3 coupling even at −58°, although some broadening of the methyl peak is observed. Obviously, the steric factors involved reduce the interaction of this amine with the platinum atom and facilitate its displacement by solvent. Aniline is a weaker base than either the methyl or the dimethyl homolog, but its steric requirements are the smallest in the series. Examination of the nmr spectrum of **1**

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[1] (a) P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Am. Chem. Soc.*, **89**, 4537 (1967). For a recent and complete review see M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.*, **2**, 123 (1968); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1967, have an excellent review of the *trans* effect in square-planar complexes.

[2] A. R. Brause, M. Rycheck, and M. Orchin, *J. Am. Chem. Soc.*, **89**, 6500 (1967).

[3] P. D. Kaplan, P. Schmidt, A. Brause, and M. Orchin, *ibid.*, **91**, 85 (1969).

[4] H. P. Fritz and D. Sellmann, *Z. Naturforsch.*, **22b**, 610 (1967).

[5] S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

[6] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

[7] T. A. Weil, P. Schmidt, M. Rycheck, and M. Orchin, *Inorg. Chem.*, **8**, 1002 (1969).

[8] M. Freifelder, R. W. Mattoon, and R. W. Kriese, *J. Org. Chem.*, **31**, 1196 (1966).

[9] M. Freifelder, R. W. Mattoon, and R. W. Kriese, *J. Phys. Chem.*, **69**, 3645 (1965).

[10] H. Booth, N. C. Franklin, and G. C. Gidley, *Tetrahedron*, **21**, 1077 (1965).

[11] I. Yamaguchi, *Bull. Chem. Soc. Japan.*, **34**, 1606 (1961).

[12] J. C. N. Ma and E. W. Warnhoff, *Can. J. Chem.*, **43**, 1849 (1965).

[13] B. Lamm, *Acta Chem. Scand.*, **19**, 2316 (1965).

[14] W. F. Reynolds and T. Schaefer, *Can. J. Chem.*, **41**, 2339 (1963).

[15] J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

[16] When rapid exchange (on the nmr time scale) of L occurs in compounds of structure **1**, coupling of the amine ligand to the ^{195}Pt (spin $^1/_2$ and natural abundance of about 34%) is lost.[3]

[17] Coupling of the type ^{195}Pt–N–CH_3 has been reported in other systems with J values from 25 to 60 cps.[1-3,18-22]

[18] P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **90**, 2293 (1968).

[19] L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *ibid.*, **90**, 6371 (1968).

[20] A. C. Cope and E. C. Freidrich, *ibid.*, **90**, 909 (1968).

[21] H. P. Fritz, I. R. Gordon, K. E. Schwarzhans, and L. M. Venanzi, *J. Chem. Soc.*, 5210 (1965).

[22] D. B. Powell and N. Sheppard, *ibid.*, 791 (1959).

[23] The ^{195}Pt–N–H coupling could not be resolved because this proton signal occurred as a broad, low-intensity peak.

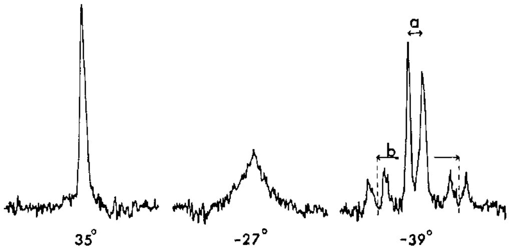

Figure 1.—The nmr spectra of methyl protons in $PtCl_2(C_2H_4)(CH_3NHC_6H_5)$: (a) J_{H-N-CH_3} = 5.9 cps; (b) $J_{Pt-N-CH_3}$ = 34.6 cps.

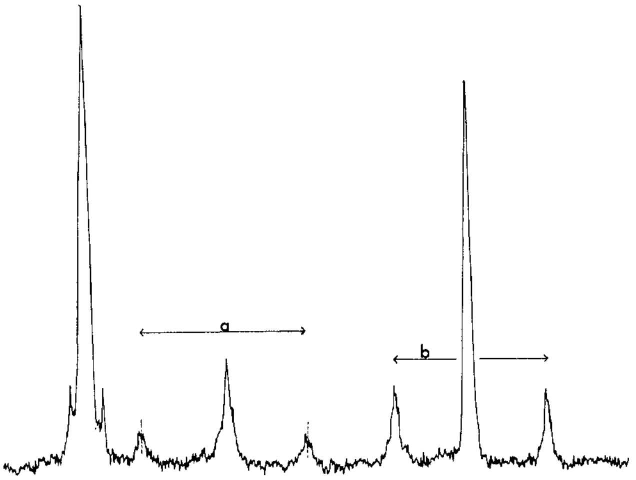

Figure 2.—Nmr spectrum of $PtCl_2(C_2H_4)(NH_2C_6H_5)$ at −50°: (a) J_{Pt-N-H} = 66.6 cps; (b) $J_{Pt-C_2H_4}$ = 62.2 cps.

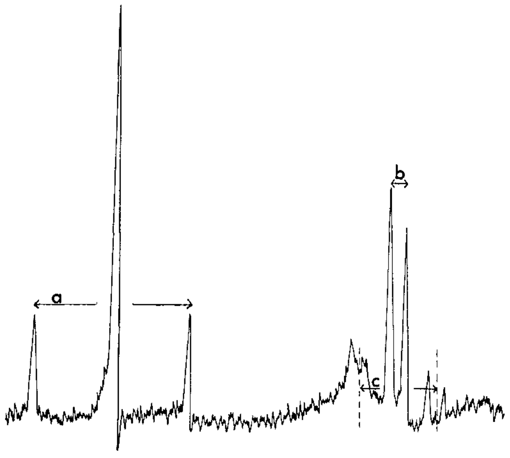

Figure 3.—Nmr spectrum of $PtCl_2(C_2H_4)(CH_3NHC_6H_{11})$ at 35°: (a) $J_{Pt-C_2H_4}$ = 60.6 cps; (b) J_{H-N-CH_3} = 5.9 cps; (c) $J_{Pt-N-CH_3}$ = 30.0 cps; the higher intensity of the downfield doublet is probably due to overlap with the signal due to the no. 1 ring proton.

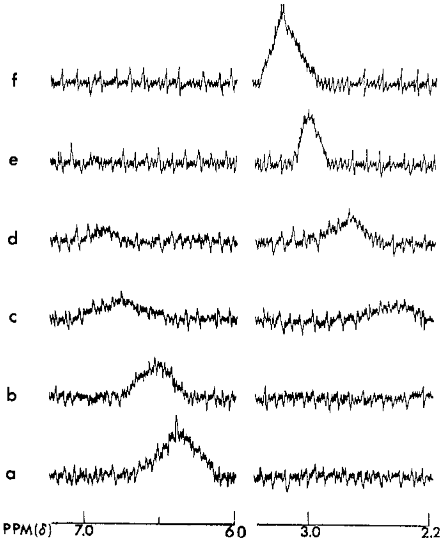

Figure 4.—Effect of acetone on the NH protons in the nmr spectrum of $PtCl_2(C_2H_4)(NH_2C_6H_5)$: (a) 10% w/w in $DCCl_3$; (b) 1 mol of acetone-d_6 added/mol of complex; (c) 4 mol of acetone/mol of complex; (d) 10 mol of acetone/mol of complex; (e) 38 mol of acetone/mol of complex; (f) 10% w/w in acetone-d_6.

(L = $C_6H_5NH_2$), Figure 2, shows, not unexpectedly, that, in order to observe Pt–N–H coupling, cooling to −50° is required (J = 66.6 cps);[24] this temperature is intermediate between that required for coupling with the methyl and that required for the dimethyl derivatives.

Because of the greater base strength of N-methylcyclohexylamine as compared with its aromatic analog, it might be expected that the Pt–N bonding would be stronger in the complex with the saturated amine. That this is indeed the case is shown by Figure 3, where now Pt–N–CH_3 and H–N–CH_3 coupling in the complex 1 (L = $C_6H_{11}NHCH_3$) occurs at room temperature (instrument temperature ~35°). Both coupling constants are essentially identical with those of the corresponding aromatic amine.[25]

The complexes 1 [L = $C_6H_{11}N(CH_3)_2$ and L = $C_6H_{11}NH_2$] were also prepared, but their nmr spectra were difficult to interpret because of peak overlap. However, the values for ethylene coupling with ^{195}Pt were determined (*vide infra*).

B. Chemical Shift of Ligand Protons.—The chemical shifts of the methyl protons in free, protonated, and metalated amines used in this study are shown in Table I. There is the expected downfield shift on protonation and metalation. It is of special interest to note, for example, that at 35°, a temperature at which Pt–N–CH_3 coupling cannot be detected in 1 (L = $C_6H_5NHCH_3$), the methyl protons show a signal at 3.23 ppm compared to the signal in the free amine at 2.66 ppm, whereas at −39° where coupling is observed, there is only a further 0.03-ppm downfield shift. Obviously, at room temperature where exchange with solvent is rapid, the equilibrium between free and complexed amine is very strongly in favor of the complexed amine. Examination of the data shows this situation to be generally true; even though exchange can be quite rapid on the nmr time scale, most of the amine is complexed to the metal at any particular time.[26]

C. Solvent Effects.—The effect of adding incremental amounts of acetone-d_6 to a $DCCl_3$ solution of complex 1 (L = $C_6H_5NH_2$) is readily followed by nmr, Figure 4. The signal at 6.35 ppm, assigned to com-

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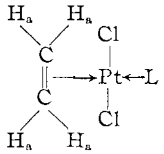
[24] G. W. Parshall, *J. Am. Chem. Soc.*, **89**, 1822 (1967), has reported two-bond coupling to ^{195}Pt through nitrogen in another system with $J_{^{195}Pt-N-H}$ = 80 cps.

[25] The coupling constants for the N-methylcyclohexylamine complex remain unchanged as the temperature is lowered to −40°.

[26] J. P. Fackler, Jr., J. A. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **91**, 1217 (1969), reported similar observations in some platinum–phosphine complexes.

Table I

Nmr Spectra of



L	pK_a	Temp, °C	Chemical shifts of methyl protons of free, protonated, and metalated amines, δ, ppm			J_{Pt-H_a}, cps
			L in $DCCl_3$	L in CF_3COOH	Complex in $DCCl_3$	
$C_6H_5NH_2$	4.60[a]	35	3.45[c]		6.35[c]	62.3
		−50			6.48[c]	62.2
$C_6H_5NHCH_3$	4.85[a]	35	2.66[b]	3.17,[b] 3.25[b]	3.23	63.1
		−39			3.26[d]	63.2
$C_6H_5N(CH_3)_2$	5.12[a]	35	2.85[b]	3.46[b]	3.41	66.5
		−58			3.38	67.2
$C_6H_{11}NH_2$	10.79[e]	35				60.6
		−14.5				60.0
$C_6H_{11}NHCH_3$		35	2.41[b]	2.86,[b] 2.70 (in HCl)[f]	2.76[d]	60.6
		−40.5			2.75[d]	60.4
$C_6H_{11}N(CH_3)_2$	8.81[g]	35				61.6
	8.17[h]	−50.5				61.0

[a] R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2685 (1954). [b] See ref 12. [c] Value for N–H protons. [d] Center of multiplet. [e] H. K. Hall, Jr., *J. Phys. Chem.*, **60,** 63 (1956). [f] See ref 8. [g] C. W. Bird and R. C. Cookson, *Chem. Ind.* (London), 1479 (1955). [h] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73,** 5030 (1951).

plexed N–H protons, shifts downfield slightly[27] and decreases in intensity as more acetone is added until it finally disappears. Concomitantly, a new peak at 2.41 ppm develops which increases in intensity and also shifts downfield[27] as the concentration of acetone increases, until it reaches the value of 3.07 ppm. (The NH_2 protons of pure aniline have a chemical shift of ~3.8 ppm in acetone and 3.45 ppm in chloroform.) When acetone is added to a chloroform solution of the complex **1** (L = $C_6H_5NH_2$) in an amount only equal to the molar quantity of complex, exactly the same effect occurs on standing for about 18 hr. This behavior clearly indicates that acetone is very effective in displacing aniline form the complex.

D. Lability of Ethylene.—Although the above data all show that the ligands L in **1** can be displaced under mild conditions, the ethylene appears to be firmly fixed on the metal. Coupling of the ethylene protons with ^{195}Pt is observed at room temperature for all complexes (Table I). Under certain conditions, however, exchange of ethylene does occur,[4] and it should be pointed out that because of the high values of the coupling constants, the rate of exchange for ethylene can be considerably greater than for L without losing the ethylene coupling.[1a] It is interesting to note that, as has been observed previously,[1a] the coupling constants are the highest when the ligand is most labile.

Experimental Section

Nmr Spectra.—Spectra were obtained on a Varian Associates A-60 spectrometer at room temperature (instrument temperature 34–35°) unless otherwise noted. Tetramethylsilane was employed as an internal standard with calibration achieved by means of the audiooscillation side-band technique. Methanol was used for low-temperature calibration in the standard procedure. All chemical shift values are in δ (ppm); all coupling constants are in cps.

New Complexes: 1,3-Dichloro-2-ethylene-4-(L)-platinum(II), 1. L = Aniline.—To 200 mg of Zeise's salt dissolved in 5 ml of water and cooled to 0–5° was added slowly a solution of 0.05 ml of aniline dissolved in 10 ml of water. The yellow solid which precipitated was washed with water and with pentane and dried *in vacuo* at room temperature; mp 122–125° dec. *Anal.* Calcd for $C_8H_{11}NPtCl_2$: C, 24.81; H, 2.86. Found: C, 25.08; H, 3.01.

L = Cyclohexylamine.—The same amounts and procedure as above were employed; mp 120–122° dec. *Anal.* Calcd for $C_8H_{17}NPtCl_2$: C, 24.48; H, 4.36. Found: C, 24.69; H, 4.50.

L = N-Methylaniline.—N-Methylaniline (0.05 ml) was added to 10 ml of water and just sufficient dilute HCl was added to dissolve the amine completely. This solution was cooled and added slowly with stirring to a cold solution made from 200 mg of Zeise's salt in 10 ml of H_2O. The yellow solid which precipitated was washed with water and then with pentane and dried; mp 119–121° dec. *Anal.* Calcd for $C_9H_{13}NPtCl_2$: C, 26.94; H, 3.26. Found: C, 27.03; H, 3.30.

L = N-Methylcyclohexylamine.—The above procedure was repeated with N-methylcyclohexylamine; mp 91–93°. *Anal.* Calcd for $C_9H_{19}NPtCl_2$: C, 26.45; H, 5.02. Found: C, 26.44; H, 4.80.

L = N,N-Dimethylaniline.—To a cold solution of 0.06 ml of N,N-dimethylaniline in 10 ml of water containing dilute HCl was added 200 mg of Zeise's salt in water at 0–5°. The resulting yellow solution was kept at 0–5° and stirred for 10 min whereupon a yellow crystalline solid precipitated. This was collected and dissolved in chloroform and the mixture was filtered. The complex was then reprecipitated from the chloroform filtrate by slow addition of pentane with cooling. The product was collected and air dried but was found to be quite unstable and could not be stored for long; mp 103–104° dec. *Anal.* Calcd for $C_{10}H_{15}NPtCl_2$: C, 28.92; H, 3.64. Found: C, 26.92; H, 3.70.

L = N,N-Dimethylcyclohexylamine.—To 200 mg of Zeise's salt in 5 ml of cold water was added excess N,N-dimethylcyclohexylamine (~0.2 ml) dissolved in dilute HCl. After stirring this solution at 0–5° for 1 hr a yellow-white solid precipitated. (Additional dilute base may be added to initiate precipitation.) The solid was collected, dissolved in chloroform, reprecipitated

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[27] Similar shifts in the nmr spectrum of free aniline have been observed and attributed to solvent effects and hydrogen bonding.[11]

with pentane, and air dried; mp 63–65°. *Anal.* Calcd for $C_{10}H_{21}NPtCl_2$: C, 28.51; H, 5.02. Found: C, 27.70; H, 4.98.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HOWARD UNIVERSITY, WASHINGTON, D. C. 20001

Stability Constants and Proton Magnetic Resonance Studies of Zinc α,β,γ,δ-Tetraphenylporphin and Substituted Pyridines

BY CARL H. KIRKSEY,[1a] PETER HAMBRIGHT,[1b] AND CARLYLE B. STORM

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The equilibrium constants of ten substituted pyridine derivatives with zinc α,β,γ,δ-tetraphenylporphin have been measured in benzene at 25°. Only 1:1 complexes are observed. In contrast to iron(II) and magnesium(II) porphyrins, the stability constants parallel the ligand basicity. A linear log K–pK correlation and a Hammett plot with $\rho = +1.50$ was obtained. Proton magnetic resonance studies indicated that the exchange between the coordinated and uncoordinated pyridine was rapid at −60° and that the structures of the zinc(II) and magnesium(II) monopyridinates are similar.

Introduction

The stability constants of reactions between metalloporphyrins (MP) and nitrogenous bases (L) have

$$MP + nL \longrightarrow L_nMP \qquad (1)$$

received considerable attention. With respect to metal ions in reaction 1, Cu(II),[2] VO(II),[3,4] Hg(II),[5] Zn(II),[4] and Cd(II)[5] have $n = 1$, whereas Ni(II)[2,6,7] and Fe(II)[8] show $n = 2$ with no evidence for LMP species. In contrast, magnesium(II) porphyrins normally form LMP and L_2MP complexes.[9] Several studies have focused attention on stability constants of the same metal ion with different types of porphyrins. Using a series of substituted deuteroporphyrins, nickel(II)–pyridine systems[6,7] give linear Hammett plots, whereas magnesium(II)–pyridine systems do not.[9] Work has also been reported on the variation of the stability constants with ligand basicity. Magnesium(II) porphyrins and some Fe(II) derivatives show stability constants that decrease as the ligand basicity increases.[10] Proton magnetic resonance (pmr) studies have been done on magnesium porphyrin–pyridine reactions.[9,11]

We report the stability constants of the reactions between zinc α,β,γ,δ-tetraphenylporphin[12] and ten substituted pyridine derivatives in benzene at 25°. A pmr study of the zinc porphyrin–pyridine system is also included.

Experimental Section

Tetraphenylporphrin[13] and its zinc complex[14] were synthesized by literature methods. The molar extinction coefficient of the zinc complex in benzene at 550 mμ was 2.27 × 10⁴, the same as that obtained by other workers.[15] Substituted pyridines from various sources were in all cases purified before use.[9]

The stability constants were measured in benzene at 25.0 ± 0.1° by a spectrophotometric titration method using the equations derived by Miller and Dorough.[5] Figure 1 shows a typical titration, in this case of the zinc porphyrin with 4-aminopyridine, and the four isosbestic points were observed. The concentration of the zinc porphyrin was usually in the range of 2×10^{-5} M.

It has been shown[5] that the equilibrium constant, K, for an $n = 1$ process in eq 1 is given by the expression

$$K = \left[\frac{(\mathrm{LMP})}{(\mathrm{MP})}\right]\left[\frac{1}{(\mathrm{L})}\right] = \left[\frac{F_c}{1 - F_c}\right]\left[\frac{1}{B}\right] \qquad (2)$$

F_c is the fraction of the total porphyrin complexed with pyridine and is equal to X/A; $X = D_m - D_u$, and $A = D_u - D_c$, where, at a given wavelength, D_u and D_m are the optical densities of the uncomplexed and fully complexed porphyrin, respectively. D_m is the optical density at a given pyridine concentration. The equilibrium pyridine concentration, B, is equal to the total pyridine concentration, $B_0 - F_cC_t$, with C_t equal to the total porphyrin concentration. Table I shows a typical calculation of K for 4-aminopyridine and the zinc porphyrin using the 550-mμ wavelength in Figure 1.

The reported constants are averages of at least two determinations and are those calculated from the 550-mμ peak. It was found that such constants calculated from the longer wavelength peaks had standard deviations within a run usually of 20–30%, even though good isobestic points were obtained. The spectra

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(1) (a) Abstracted in part from the Ph.D. dissertation of C. H. K., Howard University, 1969. (b) Author to whom further communications should be addressed.

(2) E. W. Baker, M. S. Brookhart, and A. H. Corwin, *J. Am. Chem. Soc.*, **86**, 4587 (1964).

(3) J. G. Erdman, V. G. Ramsey, N. W. Kalenda, and W. E. Hanson, *ibid.*, **78**, 5844 (1956).

(4) P. Hambright, *Chem. Commun.*, 470 (1967).

(5) J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).

(6) E. W. Baker and A. H. Corwin, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., 1965, p 12R.

(7) B. D. McLees and W. S. Caughey, *Biochemistry*, **7**, 642 (1968).

(8) M. B. Lowe and J. N. Phillips in "Porphyrins and Metalloporphyrins," J. E. Falk, Ed., Elsevier Publishing Co., Amsterdam, 1964, p 50.

(9) C. B. Storm, A. H. Corwin, R. A. Arellano, M. Martz, and R. Weintraub, *J. Am. Chem. Soc.*, **88**, 2525 (1966).

(10) J. E. Falk, J. N. Phillips, and E. A. Magnusson, *Nature*, **212**, 1531 (1966).

(11) C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

(12) Henceforth called tetraphenylporphin or TPP.

(13) A. D. Adler, F. R. Longo, F. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 475 (1968).

(14) P. Hambright, A. N. Thorpe, and C. C. Alexander, *J. Inorg. Nucl. Chem.*, **30**, 3139 (1968).

(15) G. D. Dorough, R. J. Miller, and F. M. Huennekins, *J. Am. Chem. Soc.*, **73**, 431 (1951).