

Figure 2.—Hammett plots for Zn(II), Cd(II), and Hg(II) TPP with substituted pyridines.

relatively higher stability of HgTPP with 4-cyanopyridine as compared to its normal behavior with Zn- and CdTPP could argue for some back-bonding of Hg(II) to pyridine. While the case for HgTPP donation simply rests on one observation, similar phenomena have been observed with Pt(II)–styrene complexes.¹⁷

Figure 2 shows that the equilibrium data fit a Hammett correlation of the form

$$-\log K_t^o / K_t^o = \rho\sigma \quad (3)$$

where K_t^o is for $M^{II}TPP$ –pyridine, K_t^o is for $M^{II}TPP$ –substituted pyridines, and σ is the Hammett substituent constant.¹⁸ The ρ values observed were +1.5 for ZnTPP, +2.2 for CdTPP, and +3.1 for HgTPP. The positive ρ values indicate that the reaction is favored by electron-donating substituents, or ligand to metal σ -bonding influences. In general terms, the ρ values show the HgTPP reactions to be more sensitive to substituent effects than those of ZnTPP. This can be interpreted on the following basis.¹⁹ The higher ρ value of HgTPP compared to ZnTPP indicates that in the complex the pyridine nitrogen on HgTPP has a higher formal positive charge than that on the nitrogen in the Zn(II) adduct. Thus a given electron-donating group on pyridine will have more effect (greater sensitivity) in stabilizing the higher positive charge on the nitrogen adjacent to Hg(II) than in the corresponding Zn(II) species. The higher positive charge on the pyridine nitrogen in HgTPP results from the Hg(II) accepting relatively more of the electron pair from nitrogen than did Zn(II). In other words, the Hg(II) is a better σ polarizer than Zn(II), a conclusion reached earlier on the basis of the a values.

(17) J. R. Roy and M. Orchin, *J. Amer. Chem. Soc.*, **81**, 308 (1959).

(18) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(19) C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, **73**, 2813 (1951).

Hence the cation polarizing tendencies of metal ions in metalloporphyrins are in the order Zn(II) < Cd(II) < Hg(II). A quantitative order on the basis of ρ or a values is *ca.* 1:1.4:2. These tendencies, as expected, parallel the ionic size and electronegativity²⁰ of the divalent ions. The observed order is also in agreement with predictions of the order of class b character for these three cations.¹⁴

It has been shown that the magnitudes of these equilibrium constants found in solution parallel the temperatures at which pyridine type ligands are liberated from the pyridine–metalloporphyrins in the solid state.²¹ For tetraphenylporphyrin complexes, the liberation temperatures increase with ligand basicity, and decrease with increasing metal ion size (Mg > Zn > Cd > Hg).

Attempts were made to measure the formation constants of the Cu(II), Pd(II), Ni(II), and VO(II) tetraphenylporphyrin–pyridine adducts to extend the order of metal ions. However, the absorption spectral changes between the complexed and uncomplexed metalloporphyrins were too small to allow the equilibria to be observed.

(20) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

(21) R. Lee and P. Hambright, *ibid.*, in press.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
EAST CAROLINA UNIVERSITY,
GREENVILLE, NORTH CAROLINA 27834,
AND THE CHEMISTRY AND LIFE SCIENCES LABORATORY,
RESEARCH TRIANGLE INSTITUTE,
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

The Rearrangement of Some Bis(diphenylphosphino)amines upon Chloramination

BY DONALD F. CLEMENS,^{1a} MYRON L. CASPAR,^{1a}
DAVID ROSENTHAL,^{1b} AND ROBERT PELUSO^{1a}

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We now have evidence that the structure that we previously postulated² for the chloramination products of bis(diphenylphosphino)amines should be modified. In the course of extending this work³ we have had occasion to reexamine the chloramination of bis(diphenylphosphino)methylamine. While chloramination takes place on the phosphorus atoms, as previously demonstrated,^{4,5} we find that during the course of the reaction an apparent nitrogen to nitrogen methyl migration has occurred to yield compound III which is expected to be strongly resonance stabilized.

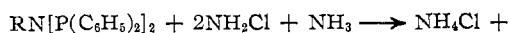
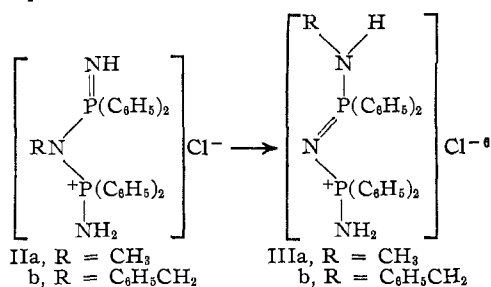
(1) (a) East Carolina University. (b) Research Triangle Institute.

(2) D. F. Clemens and H. H. Sisler, *Inorg. Chem.*, **4**, 1222 (1965).

(3) D. F. Clemens, W. Woodford, E. Dellinger, and Z. Tyndall, *ibid.*, **8**, 998 (1969).

(4) R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).

(5) W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964).

Ia, R = CH₃b, R = C₆H₅CH₂

Experimental Section

Materials.—Solvents used were dried over calcium hydride. The anhydrous amines were obtained from Eastman Kodak Co. and The Matheson Co. and were used as received. Diphenylchlorophosphine was provided by the Victor Chemical Works.

Analyses.—Elemental analyses were done by Galbraith Micro-analytical Laboratories. Melting points were obtained in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Apparatus.—Infrared spectra of new compounds were recorded on a Beckman Model IR-12. The infrared spectral data are presented in Table I. The nuclear magnetic resonance data

TABLE I^a
INFRARED DATA IN KBr PELLETS

Compound IIIb
313 bw, 368 vw, 419 m, 439 m, 465 w, 513 s, 521 m, 538 vs, 550 s, 588 m, 618 vw, 674 sh, 695 vs, 718 s, 735 s, 748 sh, 754 m, 758 sh, 778 vw, 799 vw, 850 w, 887 m, 915 w, 934 bw, 965 m, 991 sh, 998 m, 1010 w, 1025 m, 1073 m, 1103 sh, 1119 vs, 1155 w, 1165 w, 1181 m, 1189 sh, 1197 sh, 1244 sh, 1269 vw, 1316 sh, 1360 w, 1441 s, 1451 m, 1488 w, 1496 w, 1571 m, 1591 w, 1604 vw, 1687 bw, 1789 bw, 1832 bw, 1910 bw, 1944 bw, 2040 bw, 2250 bw, 2349 bw, 2550 bw, 2678 bw, 2810 sh, 2840 m, 2859 m, 2890 w, 3060 vs, 3160 s

C ₆ H ₅ CH ₂ N[P(C ₆ H ₅) ₂] ₂
318 wb, 344 m, 377 vw, 395 vw, 421 vw, 449 s, 461 m, 485 s, 499 s, 520 w, 581 w, 618 w, 646 m, 669 sh, 674 sh, 696 vs, 700 sh, 731 vs, 745 vs, 793 vs, 815 s, 834 vs, 850 m, 904 s, 914 w, 996 w, 972 w, 996 m, 1010 m, 1027 s, 1054 s, 1071 m, 1085 s, 1092 s, 1097 sh, 1129 w, 1160 m, 1180 m, 1194 m, 1261 m, 1283 mb, 1303 m, 1311 m, 1332 m, 1355 m, 1434 vs, 1449 s, 1480 s, 1496 s, 1574 w, 1585 m, 1604 wb, 1668 wb, 1765 wb, 1821 wb, 1890 wb, 1959 wb, 2840 w, 2882 w, 2920 w, 3009 w, 3032 w, 3053 w, 3072 w, 3090 sh

^a Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad.

were obtained with a Perkin-Elmer Model R-20 spectrometer. The proton spectra were obtained using tetramethylsilane as an internal reference and the ³¹P spectra were obtained using H₃PO₄ as an external reference. In Table II are reported the nmr spectral parameters for the compounds studied.

Mass Spectral Data.—Mass spectra are reproduced in Table III. The spectra were originally produced on an AEI MS-902 double-focusing mass spectrometer. The samples were introduced *via* direct probe. Defocusing was accomplished, semi-automatically, by tuning the instrument at the desired daughter peak at 4 kV, and then linearly scanning the accelerating voltage from 3.9 to *ca.* 7 kV.⁷

(6) The same tautomerism has previously been observed for the chloramination product when the parent compound was HN[P(C₆H₅)₂]₂. (See ref 2.)

(7) K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davis, Ed., United Trade Press, London, 1967.

TABLE II

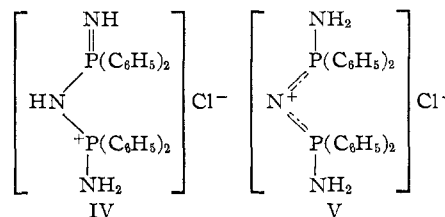
Compd	NMR SPECTRAL DATA		δ ³¹ P
	τ _{CH₃N}	τ _{CH₂N}	
IIIa	7.68 dd (14.6 Hz, 5.3 Hz)		-17, -20 2 ppm broad
IIIa after addn of D ₂ O	7.68 d (14.6 Hz)		
Ia	7.58 t (3.1 Hz)		-71
IIIb		6.27 d (7 Hz, 12 Hz)	-19, -22 2 ppm broad
IIIb after addn of D ₂ O		6.27 d (11.8 Hz)	
Ib		5.52 t (10.4 Hz)	-59

Synthetic Procedures.⁸—The procedure used to synthesize bis(diphenylphosphino)benzylamine was essentially the same as that for bis(diphenylphosphino)methylamine which has been reported previously.⁹ The procedure outlined by Hart and Sisler⁵ was used in the chloramination reactions. The effluent gas from the chloramine generator yielded about 0.1 mol of chloramine/hr. *Anal.* Calcd for C₆H₅CH₂N[P(C₆H₅)₂]₂: C, 78.30; H, 5.72; N, 2.95; P, 13.03. Found: C, 78.22; H, 5.75; N, 2.95; P, 12.98. The product had a melting range of 150–152°; yield 70.0%. *Anal.* Calcd for structure IIIb: C, 68.70; H, 5.58; N, 7.76; P, 11.43; Cl, 6.54. Found: C, 68.30; H, 5.59; N, 7.86; P, 11.30; Cl, 6.81. Product IIIb had a melting range of 210–214°; yield 67.1%.

The methyl- and benzylphosphonium salts discussed in this paper are not hydrolyzed by base but acid hydrolysis results in the cleavage of all the PN bonds.

Discussion

In an earlier paper² we pointed out that when bis(diphenylphosphino)amine, HN[P(C₆H₅)₂]₂, was allowed to react with chloramine and ammonia the product was not that expected from the postulated reaction sequence, *viz.*, IV, but was the rearranged tautomer



V.^{10,11} While this tautomerization was to be expected, we did not perform any experiments to detect the analogous migrations of an alkyl group on the nitrogen atom.² We wish to examine the question of whether the originally reported structures II do not, in fact, have the rearranged structures III. This question was decided from nmr and mass spectral studies.

The nmr spectrum of bis(diphenylphosphino)methylamine, compound Ia, shows a triplet for the methyl protons due to coupling with two equivalent phosphorus atoms as shown in Figure 1a. The nmr spec-

(8) George Crain and George Locko helped with some of the early experiments on this project.

(9) G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.*, 1543 (1964).

(10) I. I. Bezman and J. H. Smalley, *Chem. Ind. (London)*, 839 (1960).

(11) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, 1, 84 (1962).

TABLE III
 MASS SPECTRAL DATA

Methyl chloramination product <i>m/e</i>	Rel intens	Benzyl chloramination product <i>m/e</i>	Rel intens
430.0000	13.00	506.0000	6.80
429.0000	48.00	505.0000	21.00
428.0000	83.00	504.0000	34.00
402.0000	4.40	429.0000	2.30
401.0000	26.00	428.0000	13.00
400.0000	100.00	415.0000	2.30
399.0000	26.00	414.0000	4.50
353.0000	9.00	402.0000	2.30
352.0000	35.00	401.0000	27.00
338.0000	4.40	400.0000	100.00
337.0000	9.00	399.0000	21.00
325.0000	9.00	386.0000	2.30
324.0000	39.00	385.0000	0.10
323.0000	83.00	338.0000	2.30
321.0000	4.40	325.0000	2.30
277.0000	4.40	324.0000	17.00
276.0000	13.00	323.0000	64.00
247.0000	4.40	321.0000	2.30
245.0000	9.00	308.0000	2.30
201.0000	9.00	276.0000	2.30
200.0000	26.00	262.0000	2.30
199.0000	9.00	245.0000	4.50
198.0000	9.00	201.0000	4.50
185.0000	13.00	200.5000	2.30
184.0000	4.40	200.0000	23.00
183.0000	26.00	199.0000	2.30
161.0000	13.00	198.0000	4.50
124.0000	13.00	192.5000	2.30
122.0000	26.00	191.5000	2.30
109.0000	17.00	186.0000	2.30
108.0000	4.40	185.0000	5.70
107.0000	4.40	184.0000	2.30
97.0000	4.40	183.0000	11.00
95.0000	4.40	161.0000	4.50
93.0000	4.40	124.0000	9.00
91.0000	4.40	123.0000	2.30
85.0000	4.40	122.0000	16.00
83.0000	4.40	91.0000	5.70
81.0000	4.40	78.0000	3.40
78.0000	9.00	77.0000	5.70
77.0000	13.00	69.0000	3.40
71.0000	6.50	57.0000	4.50
69.0000	9.00	55.0000	3.40
60.0000	6.50	46.0000	5.70
57.0000	11.00		
55.0000	9.00		
51.0000	4.50		
46.0000	11.00		

trum of the chloramination product of this compound, which was at first assumed to have structure IIa, exhibits a pair of doublets for the methyl protons, $J = 5.3$ and 14.6 Hz (Figure 1b), which collapses to a doublet, $J = 14.6$ Hz, upon the addition of D_2O or DCl (Figure 1c). Structure IIa is not compatible with this nmr evidence because the methyl group would be coupled to both phosphorus atoms and there is no reasonable explanation for the transformation of the pair of doublets into a single doublet. Structure III is, however, compatible with the nmr evidence since the second phosphorus atom is five bonds away from the methyl protons and $^5J_{PH}$ is approximately zero.¹² Under the conditions of the experiment the

(12) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

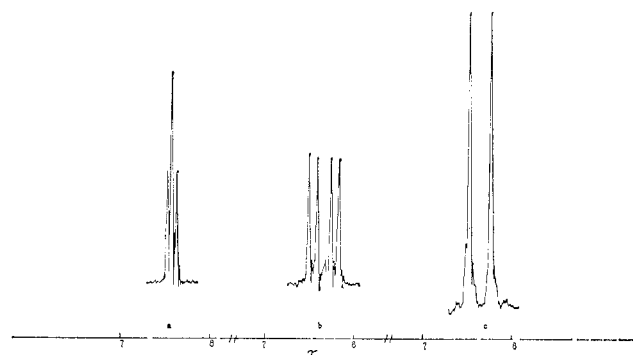


Figure 1.—The 1H nmr spectra of: (a) bis(diphenylphosphino)methylamine (Ia); (b) chloramination product of Ia; (c) chloramination product of Ia with added D_2O .

protons bonded to nitrogen would be exchanged with deuterons and the methyl protons would thus be coupled to just one phosphorus atom. The nmr spectrum of the chloramination product of bis(diphenylphosphino)benzylamine, $C_6H_5CH_2N[P(C_6H_5)_2]_2$, shows the same effect as that described above and can be interpreted in an identical fashion.

These results strongly suggest that the chloramination products possess the rearranged structures III in which the alkyl group is attached to one of the terminal nitrogen atoms rather than to the bridging nitrogen atom. This hypothesis was further confirmed by mass spectral studies.

Neither of the phosphonium salts showed a peak for the undissociated molecular ion, nevertheless peaks of significant intensity were observed at m/e 430 and 506. (In this discussion, the mention of two masses refer to the entirely analogous fragmentation products of the methyl and the benzyl salts IIIa and IIIb, respectively.) These peaks must represent $M - Cl$ (the molecular ion minus a chlorine atom) fragments, being too intense to be interpreted as isotope peaks of the intense species $M - HCl$ (429,505) which were also observed, thus implying that at least some of the molecules are ionized or predissociated without decomposition or thermal dehydrochlorination prior to ionization (source temperature 280°). In addition, strong peaks were observed for the key fragment, m/e 400, which was observed in both compounds IIIa and IIIb (as the base peak). The elemental composition of this fragment was the same in both compounds and was shown to be $C_{24}H_{22}N_2P_2$ (calcd: 400.1258; found: 400.1286, 400.1282). This composition corresponds to the loss of CH_3NH- (30) and $C_6H_5CH_2NH-$ (106) from the $M - Cl$ peaks or to the loss of one hydrogen atom less from the $M - HCl$ peaks. In either event this fragmentation would be much more readily explained as arising from structures III than from structures II since no peak was observed at m/e 415 for loss of just a methyl or benzyl group.

The above fragmentation processes were fully confirmed by metastable decompositions using defocusing techniques. The 400 peak in the methylphosphonium salt is the daughter ion associated with a broad meta-

stable band (relative intensity (ri) = 0.022). The calculated mass of the parent ion was 428.6. In the benzyl compound, a similar strong transition was observed (ri = 0.055) for which the parent ion was calculated to be 504.2. The resolution of our instrument in this procedure did not allow the identification of the parent ion mass to better than about 1–2 mass units; however, there can be no doubt about the specific loss of methylamine and benzylamine, respectively, as structural units plus or minus a single proton.

The demonstration of the exceedingly facile loss of the alkylamine group in the mass spectrometer provides strong evidence in favor of structures III, since cleavage of the two N–P bonds with the subsequent re-formation of a P–P bond is highly unlikely. This was further confirmed by the observation that in the mass spectra of the parent amines, Ia and Ib, no significant M – RN or M – RNH peaks were observed. The possibility that the observed transition corresponds to a rearrangement in the molecular ion prior to fragmentation also appears remote, especially in view of the fact that *no other* metastable decomposition to mass 400 involving the separate losses of the R group and the nitrogen atom were observed. Further discussion of the mass spectra of these compounds will be reported elsewhere.

Migration of an alkyl group may occur either by breaking an R–N bond in a base-catalyzed reaction formally analogous to the Stevens rearrangement or by breaking an N–P bond *via* an intramolecular SN2 type rearrangement. Investigations are under way to determine the stage in this multistep reaction sequence at which rearrangement occurs and to determine the mechanism of this rearrangement.

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CONTRIBUTION FROM THE ANALYTICAL CHEMISTRY LABORATORY,
FACULTY OF ENGINEERING,
HOKKAIDO UNIVERSITY, SAPPORO, JAPAN

The Mechanism of Oxygenation of Ferrous Ion in Neutral Solution

BY KATSUMI GOTO, HIROKI TAMURA, AND MASAICHI NAGAYAMA

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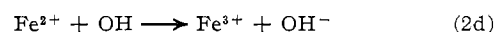
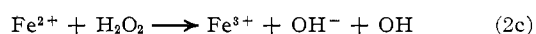
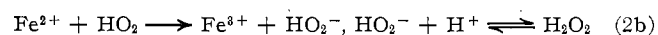
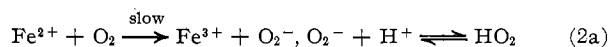
As early as 1906, Just¹ had shown that the rate of oxidation of ferrous ion by dissolved oxygen in neutral solutions is expressed by

$$-\frac{d[\text{Fe(II)}]}{dt} = k_0[\text{Fe(II)}][\text{O}_2][\text{OH}^-]^2 \quad (1)$$

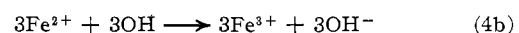
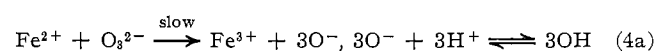
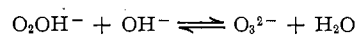
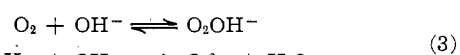
(1) G. Just, *Z. Physik. Chem.*, **68**, 385 (1908).

More recently, Stumm and Lee² and Schenck and Weber³ ascertained the validity of eq 1 from measurements under more carefully controlled conditions. The value of k_0 determined by the authors at 20° was $5.7 \times 10^{13} M^{-3} \text{sec}^{-1}$.

Weiss⁴ proposed the following radical mechanism to explain the first-order dependence of the rate both on dissolved oxygen and on ferrous ion



However, since this does not explain the second-order dependence of the rate on hydroxyl ion concentration, Abel⁵ proposed a somewhat different model



The important assumption in his mechanism was that the O_3^{2-} ion which he named "peroxide-like oxygen" existed in the solution in equilibrium with the O_2 molecule and OH^- ion. He considered that the O_3^{2-} ion is much more reactive toward Fe(II) than is the ordinary O_2 molecule. This leads to the rate equation

$$-\frac{d[\text{Fe(II)}]}{dt} = 4k\beta_{\text{O}_3^{2-}}[\text{Fe}^{2+}][\text{O}_2][\text{OH}^-]^2 \quad (5)$$

where $\beta_{\text{O}_3^{2-}}$ designates the overall stability constant of O_3^{2-} . The value of k in eq 5 is considered to be smaller than $1.4 \times 10^{11} M^{-1} \text{sec}^{-1}$, the rate constant⁶ of the reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$. Considering that $k_0 = 5.7 \times 10^{13}$ is equal to $4k\beta_{\text{O}_3^{2-}}$ and the value of k is smaller than 1.4×10^{11} , the value of $\beta_{\text{O}_3^{2-}}$ should be larger than 1.0×10^2 . However, this seems unlikely when the solubility of oxygen is taken into consideration. If $\beta_{\text{O}_3^{2-}} = [\text{O}_3^{2-}]/[\text{O}_2][\text{OH}^-]^2 = 1.0 \times 10^2$ is the case, the equilibrium concentration of O_3^{2-} would be equal to that of the ordinary oxygen molecule O_2 at a pH of about 13. This means that the $[\text{O}_3^{2-}]$, hence the total concentration of oxygen $[\text{O}_2] + [\text{O}_2\text{OH}^-] + [\text{O}_3^{2-}]$, will change remarkably around this pH. Since the value of $\beta_{\text{O}_3^{2-}}$ given above is the maximum possible value, the change of the solubility of oxygen should occur around a lower pH value. This conflicts with the experimental fact that there is no appreciable change in the solubility of oxygen over a wide range of pH's from strongly acidic to strongly alkaline.⁷ It is therefore clear that the assumption adopted in Abel's mechanism is inadequate.

(2) W. Stumm and G. F. Lee, *Ind. Eng. Chem.*, **53**, 143 (1961).

(3) J. E. Schenck and W. J. Weber, Jr., *J. Am. Water Works Assoc.*, **60**, 199 (1968).

(4) J. Weiss, *Naturwissenschaften*, **23**, 64 (1935).

(5) E. Abel, *Z. Elektrochem.*, **59**, 903 (1955).

(6) M. Eigen and L. DeMaeyer, *ibid.*, **59**, 986 (1955).

(7) F. Linke, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 2, 4th ed, American Chemical Society, Washington, D. C., 1965, p 1220.