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Kinetics and Mechanism of Reactions of Water-Soluble Ferriporphyrins. 2. Reduction by Ascorbic Acid

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Kinetics of the ascorbic acid reduction of a water-soluble ferriporphyrin, $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphineiron(III), $Fe^{III}P$, have been studied by UV–vis spectrophotometry. At 25.0 °C, $\mu = 0.10$ (NaCl), and pH ranging from 4.00–7.00, the reduction of $Fe^{III}P$ follows a pseudo-second-order rate expression in excess ascorbic acid. The pseudo-second-order rate constants are pH dependent, obtaining limiting values at high relative concentrations of reductant, and are related to the concentration of ascorbic acid in accordance with the following expression: $k_{obsd} = k_x'k_d'[\text{ascorbic acid}](k_m' + k_x'[\text{ascorbic acid}])^{-1}$, where k_x', k_d', and k_m' represent $[H^+]$-dependent rate constants for electron transfer, ferriporphyrin dimer formation, and ferriporphyrin dimer dissociation, respectively. Rate constants for dimer formation are observed to decrease with increasing $[H^+]$, while rate constants for electron transfer increase with increasing $[H^+]$. Results are interpreted in terms of a mechanism involving the formation of ferriporphyrin dimeric forms as precursors to electron transfer. The $[H^+]$ dependence of k_m' and k_d' indicate that dimer formation occurs through interaction of conjugate base forms of the ferriporphyrin: $2Fe(por)OH \rightarrow$ dimer, with a rate constant of $(2.06 \pm 0.16) \times 10^5\ M^{-1}\ s^{-1}$. The rate constant for transfer of electrons from the free acid form of the reductant (H_2A) to the ferriporphyrin dimer is observed to be $283 \pm 6\ M^{-1}\ s^{-1}$.

Introduction

The importance of iron porphyrins as prosthetic groups in heme proteins has stimulated numerous studies of the mechanisms of electron transfer in metalloporphyrins. Heretofore, the majority of such studies[1] have employed one-electron, inorganic reductants such as Cr(II), V(II), and Eu(II). Whereas significant inferences may be drawn from studies involving such powerful reductants, there remains a paucity of information pertaining to the reduction of metalloporphyrins by relatively mild, multielectron reducing agents. For example, studies of the latter type employing ascorbic acid[2] and catechol[3] have been proven useful in the elucidation of the mechanisms of electron-transfer reactions of cytochrome *c*, but experiments designed to probe the mechanisms of reduction of relatively simple metalloporphyrins by multielectron reductants have not received similar attention.

This report describes the results of a study designed to explore pathways for electron transfer from ascorbic acid to a water-soluble ferriporphyrin, $\alpha,\beta,\gamma,\delta$-tetra(4-*N*-methylpyridyl)porphineiron(III), abbreviated herein as $Fe^{III}P$.[4] Two striking features have emerged in the course of the present study: (1) the reduction of $Fe^{III}P$ follows a pseudo-second-order rate expression in the presence of excess reductant, and (2) the observed pH-dependent rate constants for electron transfer attain limiting values at high relative reductant concentrations. In the following discussion, these results will be interpreted in terms of electron-transfer pathways involving dimeric forms of the ferriporphyrin.

Experimental Section

$\alpha,\beta,\gamma,\delta$-Tetra(4-*N*-methylpyridyl)porphineiron(III) pentaperchlorate, $Fe^{III}P$, was prepared and purified as described previously.[4] *Caution*! A small sample of this compound exploded when scraped with a metal spatula on a glass frit. All experiments were conducted in buffered media (0.010 M phosphate, phthalate, or Tris, adjusted to the desired pH with 0.100 M NaOH or 0.100 M HCl) at $\mu = 0.100$ (NaCl). $[H^+]$ was computed from pH using a value of 0.83 ($\mu = 0.10$)[5] for the activity coefficient of H^+. Deionized (>1 MΩ) or doubly quartz distilled water was used exclusively.

Reductant solutions were prepared by dissolving weighed quantities of L-ascorbic acid (Sigma) in appropriate buffer and adjusting to the desired pH with 0.100 M NaOH or HCl as above. Dissolution of ascorbic acid and subsequent pH adjustment were carried out in a Cr^{2+}-scrubbed Ar atmosphere. Gel filtration chromatography of ascorbate solutions was found to have no effect on kinetics parameters, and most runs used ascorbate solutions which were not so purified. Solutions were discarded after 4 h.

Kinetics studies were carried out in the following manner. Aliquots of buffered $Fe^{III}P$ were deaerated with Cr^{2+}-scrubbed Ar for 30 min in 2.000-cm cylindrical spectrophotometer cells equipped with 7-mm Teflon-coated stirbars. The cells were housed in the thermally regulated cell compartment of a Cary 14 spectrophotometer. Reductant was introduced via the standard syringe technique after 15 min of thermal equilibration. Stirring was accomplished magnetically. Iron(II) porphyrin solutions are extremely air sensitive, exposure to O_2 resulting in oxidation of the porphyrin ring and disappearance of the Soret band.[6]

Absorbance vs. time data were recorded at 450 nm ($\Delta A/\Delta t > 0$, corresponding to the appearance of $Fe^{II}P$) or at 420 nm ($\Delta A/\Delta t < 0$, corresponding to the disappearance of $Fe^{III}P$). Values of $\epsilon_{Fe^{II}P} - \epsilon_{Fe^{III}P}$ at 450 nm or $\epsilon_{Fe^{III}P} - \epsilon_{Fe^{II}P}$ at 420 nm were obtained from scans of iron porphyrin spectra before and after reduction with ascorbate. $[Fe]_{total}$ in these solutions was obtained by both iron atomic absorption (Instrumentation Laboratories Model 121, air–acetylene flame) and spectrophotometry ($\epsilon_{Fe^{III}P,422\ nm} = 8.99 \times 10^4\ M^{-1}\ cm^{-1}$).[4] Results from both methods agreed within 1.3% in all cases.

A series of reactions between $Fe^{III}P$ and ascorbate were carried out in deaerated vials at 25 °C in the presence of acrylonitrile (5% v/v). Initial concentrations of $Fe^{III}P$ and ascorbate ranged from ca. 10^{-6}–10^{-3} and 10^{-3}–10^{-1} M, respectively, at pH 5. Such a test has been used to demonstrate the existence of a free-radical intermediate in the oxidation of ascorbic acid by V(V).[7] No evidence of polymerization was observed in any case, even after 48 h. The spectrum of the resultant solutions exhibited the characteristic 445 nm Soret band of the iron(II) porphyrin species. While these experiments do not serve to unequivocally rule out a free-radical intermediate in the electron-transfer process, in concert with the kinetic results outlined below, they are suggestive of the absence of substantial contributions by terms involving such species to the overall rate of electron transfer.

Results and Discussion

A series of experiments designed to examine possible pathways for electron transfer from ascorbic acid to the ferriporphyrin $Fe^{III}P$ was carried out at 25.0 °C. In order to maintain pseudo-zero-order kinetics in [ascorbate] in each run, the concentration of ascorbic acid was maintained at high levels in all experiments, ranging from a stoichiometric excess of 70-fold at minimum concentration to an excess of 3400-fold at the highest concentration. The effects of $[H^+]$ were studied over the pH range 4.00–7.00. The course of the reaction between $Fe^{III}P$ and ascorbate is characterized by the disappearance of the $Fe^{III}P$ Soret band ($\epsilon_{422} = 8.99 \times 10^4\ M^{-1}\ cm^{-1}$, pH 7.00) with concomitant appearance of a longer wavelength Soret band ($\epsilon_{445} = 1.06 \times 10^5\ M^{-1}\ cm^{-1}$, pH 7.00). The results

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Table I. Kinetic Data for the Reduction of $Fe^{III}P$ by Ascorbic Acid (25.0 °C, $\mu = 0.10$ (NaCl))

pH	10^4 [ascorbic acid]$_{total}$, M	$10^{-3}k_{obsd}$,[a] $M^{-1}\ s^{-1}$	$10^{-3}k_{calcd}$,[b] $M^{-1}\ s^{-1}$
4.00	3.93	2.26 ± 0.02	2.25
	7.51	3.35 ± 0.04	3.35
	13.8	4.28 ± 0.05	4.42
	17.2	4.78 ± 0.05	4.79
	27.5	5.56 ± 0.09	5.48
	97.3	6.57 ± 0.23	6.61
	125	6.73 ± 0.19	6.73
	151	7.01 ± 0.12	6.81
5.00	1.54	3.45 ± 0.04	3.45
	3.74	8.01 ± 0.10	7.95
	8.41	16.5 ± 0.10	16.1
	10.8	19.4 ± 0.20	19.8
	17.1	26.1 ± 0.20	27.8
	40.0	49.3 ± 0.60	46.3
7.00	1.55	14.1 ± 0.70	14.0
	3.01	24.7 ± 1.50	22.5
	7.74	57.3 ± 3.00	54.7
	15.5	83.1 ± 2.50	86.0
	38.7	127 ± 5.00	131
	77.4	172 ± 8.00	159

[a] Each entry represents the mean of at least three runs. Errors are standard deviations. Initial concentration of $Fe^{III}P$ ranged from 1.10×10^{-6} to 4.40×10^{-6} M in these experiments. [b] Calculated from the slope and intercept obtained from least-squares analysis of k_{obsd}^{-1} vs. [ascorbic acid]$_{total}^{-1}$.

of the kinetics experiments appear in Table I. In spite of the large excess [ascorbate], linear kinetics plots of $-\ln (A_\infty - A_t)$ vs. time[8] were never obtained. Rather, plots of $(A_\infty - A_t)^{-1}$ vs. time were always linear (for at least 90% reaction), implying a rate law with a second-order dependence on $Fe^{III}P$, the reactant in limiting concentration. For such a system the rate expression is $-d(Fe^{III}P)/dt = +d(Fe^{II}P)dt = k_{obsd}[Fe^{III}P]^2$, in which k_{obsd}[9] is some function of [ascorbate] and $[H^+]$, and k_{obsd} is a pseudo-second-order rate constant. Such behavior suggests participation of a pair of ferriporphyrin species in the rate-determining step for electron transfer. Furthermore, plots of k_{obsd} vs. [ascorbate] are also observed to be nonlinear, exhibiting instead a saturation of the pseudo-second-order rate constant with increasing [ascorbate]. For example, at pH 4.00, k_{obsd} increased by a factor of only 3.1 for a corresponding 38-fold increase in [ascorbate]. This result is consistent with a rate law for which the observed rate constant can be expressed as (1), in which a, b, and c represent composite kinetics

$$k_{obsd} = \frac{ab[R]}{c + a[R]} \qquad (1)$$

parameters characteristic of the system and [R] represents reductant concentration.

Scheme I

$$H_2O + PFeOH_2 \rightleftharpoons PFeOH + H_3O^+ \qquad K_{am} = 10^{-4.58} \text{ (rapid)}$$

$$2PFeOH \underset{k_m}{\overset{k_d}{\rightleftharpoons}} PFeOHFeP + OH^- \qquad K_d = k_d/k_m \text{ (rate determining)}$$

$$OH^- + PFeOHFeP \rightleftharpoons PFeOFeP + H_2O \qquad K = K_{ad}/K_w \text{ (rapid)}$$

Interpretation of the observed kinetic behavior must take into account not only the observation of pseudo-second-order behavior but also the saturation of the observed rate constant at high reductant concentration. Such an interpretation is aided by the previously demonstrated formation of equilibrium concentrations of μ-hydroxo- and μ-oxo-bridged dimers in iron(III) porphyrin solutions.[4,10] One mechanism which is consistent with the observed behavior consists of initial formation of small concentrations of $(Fe^{III}P)_2$ dimeric species to which subsequent transfer of electrons from the reductant occurs:

$$2M \underset{k_m'}{\overset{k_d'}{\rightleftharpoons}} D \qquad K_D = k_d'/k_m'$$

$$H_2A + D \xrightarrow{k_x'} P$$

k_d', k_m', and k_x' represent the pH-dependent rate constants for dimerization (bimolecular), dissociation (unimolecular), and electron transfer (bimolecular). Since the electron-transfer experiments were conducted under conditions designed to minimize concentrations of dimeric species ($[Fe^{III}P]_{total} = 4.4 \times 10^{-6}$ M, at most),[4] concentrations of dimer can not be expected to attain high levels, allowing application of the usual steady-state treatment:

$$dD/dt = k_d'[M]^2 - k_m'[D] - k_x'[D][R] \cong 0$$

for which

$$[D] = \frac{k_d'[M]^2}{k_m' + k_x'[R]}$$

leading to

$$dP/dt = k_x'[D][R] = \frac{k_x'k_d'[R][M]^2}{k_m' + k_x'[R]}$$

for which

$$k_{obsd} = \frac{k_x'k_d'[R]}{k_m' + k_x'[R]}$$

corresponding to the empirical rate expression (vide supra) for which $a = k_x'$, $b = k_d'$, and $c = k_m'$. The slope and intercept of each plot of k_{obsd}^{-1} vs. [ascorbic acid]$^{-1}$ at the specified pH are presented in Table II. Values of k_d', (intercept)$^{-1}$, of each plot also appear in Table II. Values of k_x' at each pH, calculated as $k_x' = k_m'$(intercept)(slope)$^{-1}$, where k_m' at each pH has been obtained from ref 4, also appear in Table II.

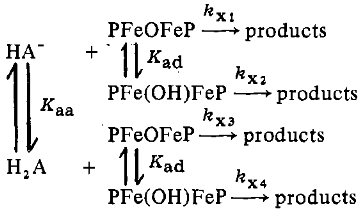
Without exception, the calculated values of rate constants k_m', k_d', and k_x' are dependent upon $[H^+]$. The values of k_d' and k_m' can be considered independently of k_x' since they reflect only the monomer–dimer equilibrium. The bimolecular rate constant for dimer formation, k_d', is seen to increase with decreasing $[H^+]$. This is consistent with a mechanism of dimerization involving interaction of conjugate base forms of the metalloporphyrin (e.g., see Scheme I). Monomerization has been shown to proceed via a μ-hydroxo-bridged intermediate and microscopic reversibility considerations dictate

Table II. Kinetics Parameters for Electron Transfer between Ascorbic Acid and $Fe^{III}P$

pH	$10^8 \times$ slope[a]	$10^6 \times$ intercept[a]	k_m', s^{-1} [b]	$10^{-3}k_d'$, $M^{-1}\ s^{-1}$	k_x', $M^{-1}\ s^{-1}$	$10^{-5}k_d$, $M^{-1}\ s^{-1}$
4.00	12.0 ± 0.2	139 ± 2	0.153	7.20 ± 0.10	177	2.24
5.00	4.29 ± 0.31	10.9 ± 0.9	0.140	91.9 ± 7.7	35.5	1.95
7.00	1.02 ± 0.02	5.10 ± 0.57	1.29×10^{-2}	196 ± 5	6.46	1.98
						Av 2.06 ± 0.16

[a] Slope and intercept of plots of k_{obsd}^{-1} vs. [ascorbic acid]$^{-1}$; see text. [b] Data obtained from ref 4.

Scheme II



that dimerization must also occur via a μ-hydroxo intermediate.[4] Values of dimer and monomer acid dissociation constants, K_{ad} and K_{am}, respectively, have been reported previously.[4] In this scheme the observed conditional rate constants for dimerization, k_d', are related to the pH-independent rate constant k_d via

$$\frac{d[\text{dimer}]}{dt} = k_d[\text{PFeOH}]^2 = k_d(1 + [\text{H}^+]/K_{am})^{-2}[\text{monomer}]_{\text{total}}^2$$

for which $k_d = k_d'(1 + [\text{H}^+]/K_{am})^2$. Values of k_d, calculated as $k_d'(1 + [\text{H}^+]/K_{am})^2$ at each pH, also appear in Table II. In spite of the wide pH range (4.00–7.00) over which data were gathered, a relatively constant value of $(2.06 \pm 0.16) \times 10^5$ $\text{M}^{-1}\ \text{s}^{-1}$ is obtained for k_d. If other reacting monomer pairs are chosen, e.g., $\text{PFeOH}_2 + \text{PFeOH}_2$ or $\text{PFeOH} + \text{PFeOH}_2$, constant values of k_d are not obtained, strongly suggesting that dimerization of $\text{Fe}^{\text{III}}\text{P}$ proceeds via interaction of a pair of conjugate base forms of the monomeric ferriporphyrin.

The calculated rate constants for electron transfer are also hydrogen ion dependent, increasing with increasing acidity. Since both ascorbic acid and $\text{Fe}^{\text{III}}\text{P}$ can engage in protolytic equilibria with conjugate base pairs, Scheme II for electron transfer was considered, where vertical interactions are proton-transfer processes and are assumed to occur rapidly compared to electron-transfer processes which appear as k_{x1}–k_{x4}, and comprise all possible pathways for electron transfer via dimeric $\text{Fe}^{\text{III}}\text{P}$. K_{aa} and K_{ad} are proton dissociation constants of ascorbic acid ($K_a = 10^{-4.14}$)[11] and the μ-hydroxo dimer ($K_a = 10^{-5.9}$).[4] Protons are omitted for clarity. Products represent the ferroporphyrin and dehydroascorbic acid. For a scheme of this type, the observed rate constants for electron transfer may be represented as

$$\frac{d[\text{Fe}^{\text{II}}\text{P}]}{dt} = k_x[\text{dimer}]_{\text{total}}[\text{R}]_{\text{total}}$$

where $[\text{dimer}]_{\text{total}} = [\text{PFeOFeP}] + [\text{PFe(OH)FeP}]$, $[\text{R}]_{\text{total}} = [\text{HA}^-] + [\text{H}_2\text{A}]$, and k_x, the apparent rate constant for electron transfer, can be represented as[12] (2). Rearrangement and

$$k_x = \frac{k_{x1}K_{aa}K_{ad} + (k_{x2}K_{aa} + k_{x3}K_{ad})[\text{H}^+] + k_{x4}[\text{H}^+]^2}{K_{aa}K_{ad} + (K_{aa} + K_{ad})[\text{H}^+] + [\text{H}^+]^2} \tag{2}$$

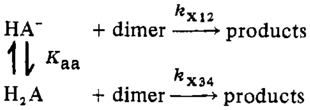
solution of the set of three resultant simultaneous equations give values of 6.24×10^{-10} M s^{-1}, 4.37×10^{-4} s^{-1}, and 283.9 $\text{M}^{-1}\ \text{s}^{-1}$ for $k_{x1}K_{aa}K_{ad}$, $k_{x2}K_{aa} + k_{x3}K_{ad}$, and k_{x4}, respectively. If $k_{x2}K_{aa} \gg k_{x3}K_{ad}$, the value of k_{x2} so obtained is found to be 6.03 $\text{M}^{-1}\ \text{s}^{-1}$. In the alternate limiting case, the value of k_{x3} is found to be 329 $\text{M}^{-1}\ \text{s}^{-1}$. An unambiguous value of k_{x1} = 6.47 $\text{M}^{-1}\ \text{s}^{-1}$ is also obtained from the $k_{x1}K_{ad}K_{aa}$ term.

In spite of the apparent complexity of the rate law for electron transfer, a reasonably simple portrait of the mechanism of the electron transfer emerges from this study. Both μ-hydroxo- and μ-oxo-bridged $\text{Fe}^{\text{III}}\text{P}$ dimeric forms are capable of accepting electrons from ascorbic acid. The rate of electron transfer is insensitive to the nature of the bridging ligand since $k_{x1} \approx k_{x2}$ and $k_{x3} \approx k_{x4}$. On the other hand, ascorbic acid appears to reduce either dimeric form almost fifty times more rapidly than does ascorbate. Indeed, ignoring the protolytic equilibria of $\text{Fe}^{\text{III}}\text{P}$ dimers allows simplification of the rate expression (see Scheme III), giving

$$k_x = \frac{k_{x12}K_{aa} + k_{x34}[\text{H}^+]}{K_{aa} + [\text{H}^+]}$$

for which least-squares analysis of $k_x(K_{aa} + [\text{H}^+])$ vs. $[\text{H}^+]$ yields values of $k_{x34} = 283 \pm 6$ $\text{M}^{-1}\ \text{s}^{-1}$ and $k_{x12} = 4 \pm 2$ $\text{M}^{-1}\ \text{s}^{-1}$ for the H_2A and HA^- terms, respectively. Indeed, the small magnitude and large standard deviation observed for the k_{x12} path obtained via this analysis leads us to consider only the k_{x34} (i.e., H_2A) pathway in the following discussion.

Scheme III



The absence of significant terms arising from involvement of ascorbate radical species is clear both from the observed saturation pseudo-second-order electron-transfer kinetics and from the failure to observe acrylonitrile polymerization in the free-radical trapping experiments. We conclude that either: (1) $\text{Fe}^{\text{III}}\text{P}$ monomers are simply not capable of one-electron oxidation of ascorbic acid to ascorbate radical or (2) ascorbate radicals, if any are formed via such a monomer reaction, disappear via reversible reduction by $\text{Fe}^{\text{II}}\text{P}$ or by disproportionation[2] more rapidly than initiation of acrylonitrile polymerization. It is interesting to note that the ascorbic acid reduction of ferricytochrome *c* exhibits a rate law which contains terms which are first order in both ferriprotein and reductant. It has been shown that electron transfer proceeds predominantly via one-electron ascorbate reduction (eq 3), followed by disproportionation of the radical produced[2] (eq 4).

$$\text{Cyt } c(\text{III}) + \text{HA}^- \rightarrow \text{Cyt } c(\text{II}) + \text{A}^{-}\cdot + \text{H}^+ \tag{3}$$

$$2\text{A}^{-}\cdot + \text{H}^+ \rightarrow \text{A} + \text{HA}^- \quad (\text{rapid}) \tag{4}$$

On the other hand, the reduction of ferricytochrome *c* by catechol (a weaker reductant by ca. 0.3 V)[13] exhibits a rate law containing $[\text{Cyt } c(\text{III})]^2$, suggesting that a mechanism involving a pair of electron acceptors becomes necessary when the driving force for electron transfer from a multielectron donor becomes too small for free-radical production.[3] It appears that the ascorbic acid reduction of $\text{Fe}^{\text{III}}\text{P}$ falls into this latter category, the formation of $\text{Fe}^{\text{III}}\text{P}$ dimers providing a low energy pathway for two-electron transfer. In light of the positive charge of the porphyrin periphery, it is surprising that ascorbic acid reduces the dimeric system more rapidly than does the ascorbate anion. Comparisons to other systems cannot be made, however, since very few two-electron mechanisms for the ascorbate system have been observed.[14] Further study in this area is clearly required.

Determination of the exact site of electron transfer cannot be made from the results of the present study. Some inferences may be drawn, however. The implication that the nature of the bridging ligand has little effect on the rate of electron transfer and consideration of the reductant's limited access to that bridging ligand strongly suggest that the site of electron transfer lies elsewhere. If the accessible nonbridging axial positions provide the electron-acceptor sites, transfer of one electron takes place through the bridge. On the other hand, porphyrin edge attack has been recognized as a viable mechanism for electon transfer in metalloprotein systems.[3] Experiments designed to probe the mechanism of electron transfer to porphyrins with hindered axial accessibility are in progress in this laboratory.

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Registry No. $Fe^{III}P$ (monomer), 64364-99-4; $Fe^{III}P$ (dimer), 64365-02-2; ascorbic acid, 50-81-7.

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Dimethyl Compounds of Platinum(II). 2. Reactions Involving Carbon–, Silicon–, and Germanium–Halogen Bonds

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Reactions of GeR_nX_{4-n} (X = Cl, R = Me, n = 1, 2, 3; X = Cl, R = Ph, n = 2, 3; X = Br, R = Me, Ph, n = 3) with $PtMe_2(N\text{-}N)$ (N-N = bipyridine, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) afforded the new compounds $[PtMe_2X(GeR_nX_{3-n})(N\text{-}N)]$. The compounds were stable to H_2O, alcohol (except for n = 3), pyridine, and PPh_3. Compounds with formula $[PtMe_2X(GeR_3)(bpy)]$ (R = Me, Ph; X = Cl) were not stable in solution and decomposed to $PtMe_2Cl(CH_2Cl)(bpy)$. Exchange reactions of $[PtMe_2Cl(MR_nCl_{3-n})(bpy)]$ with $M'R_mCl_{4-m}$ (M, M′ = Ge, Sn, Pb) were studied. Reactions with $[GeR_3Br]$ resulted in bromine exchange. In the presence of moisture SiR_nCl_{4-n} (R = Ph, Me; n = 0, 1, 2) reacted with $PtMe_2(bpy)$ in CH_2Cl_2 to give PtMeCl(bpy). Reactions of CR_nCl_{4-n} gave the following results (R = Ph, Me; n = 0, 1, 2, 3): Trans oxidative addition occurred with CCl_4 and $CPhCl_3$. With CPh_2Cl_2 and CPh_3Cl the compound $PtMe_2Cl_2(bpy)$ was obtained. With $CMeCl_3$ trans addition and further reaction to the vinyl compound $[PtMe_2Cl(CH_2CCl)(bpy)]$ occurred. No reaction was observed with CMe_3Cl. Reactions of CH_nCl_{4-n} (n = 0, 2, 3) proceeded via trans oxidative addition to $[PtMe_2Cl(CH_nCl_{3-n})(bpy)]$, except in the case of CH_2Cl_2 when also cis addition was observed. The rate of the conversion cis → trans was enhanced by added $SiPh_3Cl$.

Introduction

In a previous paper oxidative-addition reactions with square-planar d^8 compounds involving tin– and lead–halogen bonds were reported.[1] It was shown that reactions of $PtMe_2(N\text{-}N)$ (N-N = bipyridine, phenanthroline) with tin and lead compounds of general formula MR_nCl_{4-n} (M = Sn, R = Me, Ph, n = 0, 1, 2, 3; M = Pb, n = 2, 3) proceeded via a trans addition and the new compounds $[PtMe_2Cl(MR_nCl_{3-n})(N\text{-}N)]$ were obtained in high yield. It was shown that the stability of the products was critically dependent upon the nature of the (MR_nCl_{3-n}) group. Since several isostructural compounds of divalent platinum were known with Si, Ge, Sn, or Pb,[2-7] it was of interest to investigate the reactions of $PtMe_2(N\text{-}N)$ with analogous MR_nCl_{3-n} compounds in which M = C, Si, or Ge. In addition reactions of CH_nCl_{4-n} with $PtMe_2(bpy)$ were also studied.

Experimental Section

General Information. Although the compounds prepared in this study were stable in air, several of the starting materials were susceptible to atmospheric moisture. Therefore all preparations were carried out in a dry nitrogen atmosphere. The abbreviations bpy = 2,2′-bipyridine and Ph_2Me_2phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline are used in the text.

Chemicals. Carbon, silicon, and germanium alkyl or aryl chlorides were commercially available and were distilled prior to use. Reagent grade solvents were dried with P_2O_5 and distilled. ^1H NMR spectra in CH_2Cl_2 (ppm relative to CH_2Cl_2) or $CDCl_3$ (ppm relative to Me_4Si) were recorded on a Varian HA100 NMR spectrometer. Elemental analyses were performed by Childers Laboratories, Milford, N.J., and by Chemical Analytical Services, Berkeley, and are summarized in Table I.

Preparation of $[PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)]$. $GeMe_2Cl_2$ was added slowly in small drops with the aid of a syringe to a stirred solution of $PtMe_2(Ph_2Me_2phen)$[1] (0.33 mmol) in CH_2Cl_2 (~2 mL). As soon as the solution had turned yellow, further addition of $GeMe_2Cl_2$ was stopped (a slight excess was used). Subsequently hexane was added until the solution started to cloud (5–10 mL). At −20 °C bright yellow crystals were obtained in 65% yield. The compound $[PtMe_2Cl(GeMeCl_2)(Ph_2Me_2phen)]$ was obtained by a similar procedure.

Preparation of $[PtMe_2Cl(SnMe_2Cl)(Ph_2Me_2phen)]$. This compound was prepared similarly to $[PtMe_2Cl(GeMe_2Cl)(Ph_2Me_2phen)]$ in 90% yield.

Preparation of $[PtMe_2Cl(GeMeCl_2)(bpy)]$. $PtMe_2(bpy)$ (0.5 mmol) was dissolved in a minimum amount of CH_2Cl_2 (~3 mL) and subsequently $GeMeCl_3$ was added in small drops with a syringe until the solution turned yellow. Then ether (3 mL) was added to the reaction mixture in which crystallization was already observed. After 10 min at 0 °C the crystals were collected on a filter with the aid of a pipet and washed with ether/CH_2Cl_2 and ether. Light yellow crystals of $[PtMe_2Cl(GeMeCl_2)(bpy)]$ were obtained in 75% yield. Similar yields were obtained for $[PtMe_2Cl(GeMe_2Cl)(bpy)]$ and $[PtMe_2Cl(GePh_2Cl)(bpy)]$. $[PtMe_2Cl(GePh_3)(bpy)]$ was prepared similarly in 90% yield with a threefold excess of $GePh_3Cl$ added at once to the $PtMe_2(bpy)$ solution. In the case of $[PtMe_2Br(GePh_3)(bpy)]$ a twofold excess was used and the yield was also 90%. $[PtMe_2Cl(GePh_3)(bpy)]$ was unstable in CH_2Cl_2 solution and decomposed slowly to $[PtMe_2Cl(CH_2Cl)(bpy)]$.

Preparation of $[PtMe_2Cl(GeMe_3)(bpy)]$. $PtMe_2(bpy)$ (0.5 mmol) was dissolved in a minimum amount of CH_2Cl_2 (~3 mL). Immediately after the solution was cooled with an ice bath, excess

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