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Supplementary Material Available: Listings of anisotropic temperature factors for non-hydrogen atoms, isotropic temperature factors and atom coordinates for hydrogen atoms, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Dealkylation of *N*-Methyl-5,10,15,20-tetraphenylporphine by Palladium(II) in Acetonitrile, Dimethyl Sulfoxide, and Dimethylformamide

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Kinetics data for the dealkylation of *N*-methyl-5,10,15,20-tetraphenylporphyrin by palladium(II) have been obtained in acetonitrile, dimethyl sulfoxide, and dimethylformamide solutions. The data are consistent with a general mechanism involving ion-dipole association of a solvated Pd(II) complex with the free base *N*-methylporphyrin followed by a series of ligand dissociation and bond formation equilibria and a terminal step involving nucleophilic displacement of the *N*-methyl group. The rate-determining step and the ability of the solvent itself to act as the nucleophile, however, differ in these three solvents. In acetonitrile, rapid formation of an *N*-methylporphyrin complex of Pd(II) ($Pd(N\text{-}CH_3TPP)^+$) is indicated by visible absorption spectroscopy. The overall formation of (tetraphenylporphinato)palladium(II) (PdTPP) is only affected slightly by the concentration of Pd(II) and is first order in the concentration of added nucleophile, di-*n*-butylamine. At [Pd(II)] = 0.010 M, $\Delta H^\ddagger = 14.0 \bullet 0.4$ kcal/mol and $\Delta S^\ddagger = -23.2 \pm 1.2$ cal/(mol K). In Me_2SO, an intermediate that does not correspond spectrally to $Pd(N\text{-}CH_3TPP)^+$ is $\Delta S^\ddagger$ 2 orders of magnitude faster than the formation of PdTPP. The activation parameters for the second process are $\Delta H^\ddagger = 19.1 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -12.3 \pm 0.4$ cal/(mol K). In contrast for the reactions in CH_3CN and Me_2SO, in DMF isosbestic points indicated conversion of $N\text{-}CH_3HTPP$ to PdTPP without appreciable accumulation of any intermediate. Both Me_2SO and DMF act as nucleophiles in the dealkylation of $N\text{-}CH_3HTPP$ in the presence of Pd(II).

Introduction

In this report we discuss the formation of (tetraphenylporphinato)palladium(II) from *N*-methyl-5,10,15,20-tetraphenylporphine (Figure 1) and Pd(II) in acetonitrile, dimethyl sulfoxide, and dimethylformamide. These dealkylation reactions are of interest for several reasons. Several years ago Fawwaz and co-workers found that the rejection of transplanted tissue in small animals could be controlled by administration of ^{109}Pd hematoporphyrin IX,[1] but experimentation with larger animals was prevented because the traditional route for the preparation of Pd(II) complexes of porphyrins[2] is too time consuming and only about 15% of the initial activity of the ^{109}Pd is present in the product. We have shown that ^{109}Pd hematoporphyrin IX can be synthesized with about 80% retention of activity in a simple, rapid procedure using *N*-methylhematoporphyrin IX as starting material.[3] Since this reaction takes place in dimethyl sulfoxide, we were interested in elucidating its mechanism. In addition, we have investigated dealkylation reactions involving Cu(II), Ni(II), Mn(II), and Zn(II) in acetonitrile and concluded that the stability of the final dealkylated porphyrin complex rather than the size or Lewis acidity of the metal ion determines the relative rate of dealkylation.[4] The dealkylation reaction with Pd(II), a relatively large ion that forms very stable porphyrin complex,[5] would be a good test of this conclusion. The third solvent, dimethylformamide, was chosen because it is one of the few solvents in which kinetic studies for the formation of porphyrin complexes with a significant number of metal ions show second-order behavior.[6,7] If formation of the *N*-methylporphyrin complex of Pd(II) were to be rate determining in the dealkylation reaction, the formation rate could be compared with those of other metal ions.[7]

Experimental Section

N-Methyl-5,10,15,20-tetraphenylporphine was prepared as previously described,[8] with the exception that methyl trifluoromethanesulfonate was substituted for the methyl fluoromethanesulfonate, which is reported to be more toxic. It was chromatographed on alumina, recrystallized, and showed appropriate spectral properties.[8] Acetonitrile was stirred overnight with 4-Å molecular sieves (Davison) and CaH_2 and filtered. After being stirred overnight with P_2O_5, it was refluxed for 1 h, distilled, and stored over molecular sieves. Dimethylformamide was stirred with BaO for 2 h under N_2 and distilled from BaO into a receiver containing 4-Å molecular sieves. No dimethylamine or formic acid was evident in the ^{1}H NMR spectrum of the distillate. Dimethyl sulfoxide was stirred with BaO for 30 min, distilled under vacuum, and stored over molecular sieves. Di-*n*-butylamine was stored over KOH pellets and CaH_2 for 2 dys, filtered, and fractionally distilled into a receiver containing molecular sieves. The 2,6-lutidine and 2,6-di-*tert*-butylpyridine were refluxed with BaO and distilled. The 2,2,6,6-tetramethylpiperidine was used as received from Aldrich Chemical Co.

The Pd(II) stock solutions were prepared by dissolving $Pd(NO_3)_2 \cdot xH_2O$ (Alfa Ventron) in the appropriate solvent, filtering through

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Table I. Kinetic Results for the Formation of (Tetraphenylporphinato)palladium(II) from Pd(II) and *N*-Methyltetraphenylporphyrin in Acetonitrile

[amine],[a] M	10^3[Pd(II)], M	10^5[*N*-CH_3HTPP]$_0$, M	10^3k_{obsd}, s^{-1}	10^3k_{obsd}/[amine], M^{-1} s^{-1}	*T*, °C
1.00	10.0	2.67	2.04	2.04	25.0
0.80	10.0	2.89	1.70	2.12	25.0
0.600	10.0	3.10	1.39	2.31	25.0
0.600[b]	10.0	3.23	1.38	2.30	25.0
0.373[b]	10.0	3.59	0.88	2.36	25.0
0.200	10.0	0.296	0.517	2.59	25.0
0.100[c]	10.0	0.304	0.294 ± 0.011	0.294 ± 0.011	25.0
0.100	10.00	0.527	0.300	3.00	25.0
0.100	10.0	0.166	0.306	3.06	25.0
0.0500	10.0	0.296	0.137 ± 0.001	2.74 ± 0.02	25.0
0.0500	10.0	0.166	0.143	2.86	25.0
0.400	1.00	0.166	1.21	3.02	25.0
0.400	1.00	0.130	1.23	3.06	25.0
0.400	1.00	0.332	1.20	3.00	25.0
0.200	1.00	0.296	0.633	3.16	25.0
0.100	1.00	0.296	0.367	3.67	25.0
0.0500[d]	1.00	0.296	0.205 ± 0.004	4.10 ± 0.08	25.0
0.0250[d]	1.00	0.206	0.099 ± 0.001	3.98 ± 0.06	25.0
0.0200[d]	10.0	0.296	1.21 ± 0.02	6.05 ± 0.10	37.0
0.100[d]	10.0	0.304	0.73 ± 0.04	7.28 ± 0.43	37.0
0.050[d]	10.0	0.296	0.324 ± 0.004	6.48 ± 0.08	37.0
0.0250[d]	1.00	0.296	0.290 ± 0.001	11.6 ± 0.1	37.0
0.200	10.0	0.296	3.49	17.4	50.0
0.200	5.00	0.296	3.70	18.5	50.0
0.200	1.00	0.296	4.20 ± 0.02	21.0 ± 0.1	50.0
0.100	1.00	0.296	2.52 ± 0.07	25.2 ± 0.7	50.0
0.050	1.00	0.296	1.34 ± 0.01	26.7 ± 0.1	50.0
0.0250	1.00	0.296	0.758 ± 0.004	30.4 ± 0.2	50.0

[a] Di-*n*-butylamine. [b] 2,6-Lutidine was added first (concentration 0.200 M), and later, the given amount of amine was added. [c] Average of four runs with average deviation given. [d] Average of two runs with average deviation given.

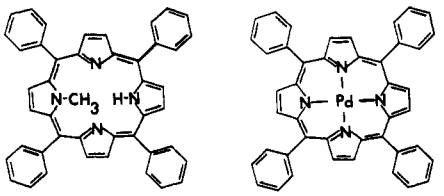

Figure 1. Structures of *N*-methyl-5,10,15,20-tetraphenylporphine, *N*-CH_3HTPP (left), and (5,10,15,20-tetraphenylporphinato)palladium(II), PdTPP (right).

a sintered-glass funnel, and dilution in a volumetric flask. The Pd(II) concentration of each stock solution was determined by an indirect EDTA titration.[9] In this method, Pd(II) displaces Ni(II) from $[Ni(CN)_4]^{2+}$ (prepared by the method of Fernelius[10]), the Ni(II) is complexed by EDTA, and the excess EDTA is determined with Mn(II). The Mn(II) stock solutions were standardized with use of Eriochrome Black T indicator.[11]

Kinetics Measurements

Three spectrophotometers, each with thermoregulated cuvette holders and digital thermocouple thermometers that monitor the temperature adjacent to the cuvette, were employed: a Cary 14 with a Lauda K4/R bath, a Varian 635 D with Fisher Model 90 bath, and a Beckman DU-8 with a Peltier thermoelectric heater/cooler. Prior to each run, spectra were taken of reactant solutions to verify concentrations and the solutions were allowed to equilibrate to the appropriate temperature for at least $^1/_2$ h. For each solvent, some runs were made by overlaying successive spectra. Most data were obtained by monitoring absorbance changes at a single wavelength. Typically, data were taken for at least 6 half-lives. In all cases, pseudo-first-order conditions with Pd(II) and amine or noncoordinating base in large excess were used. Data treatment was performed by using the statistical programs available in the PROPHET computer system.[12]

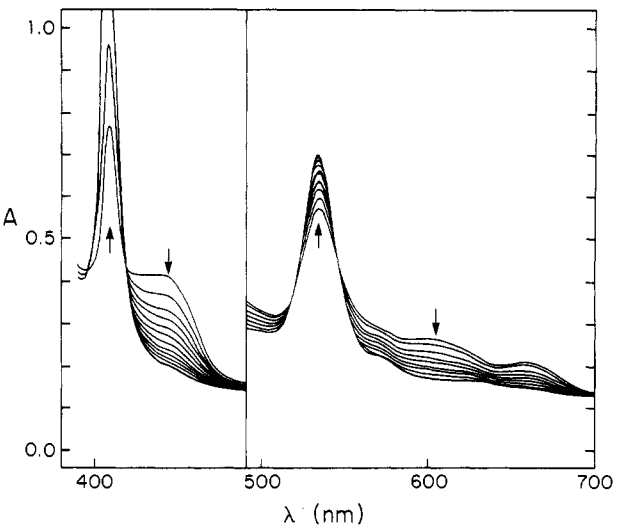

Figure 2. Visible absorption spectra of the formation of (5,10,15,20-tetraphenylporphinato)palladium(II) in acetonitrile at 25 °C. Conditions were as follows: $[Pd(NO_3)_2]_0 = 1.00 \times 10^{-2}$ M, [*N*-CH_3HTPP]$_0 = 3.23 \times 10^{-5}$ M, [2,6-lutidine] = 0.200 M, [di-*n*-butylamine] = 0.600 M, scan interval about 6 min. A 10-mm cuvette was used in the region of 480–700 nm and a 1.0-mm cuvette in the region of 380–480 nm.

Results

The data for reactions of Pd(II) with *N*-methyl-5,10,15,20-tetraphenylporphine in acetonitrile using di-*n*-butylamine as nucleophile are given in Table I. The amine concentration was varied over a 40-fold range: from 0.0250 to 1.00 M. At a Pd(II) concentration of 1.00×10^{-2} M, the

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(11) Reference 9, p 434.
(12) The PROPHET computing system is a multisite network, the CBIS system of the NIH, which includes a wide array of statistics and structural simulation software. We are grateful to the NIH for the installation of the Hunter College facility.

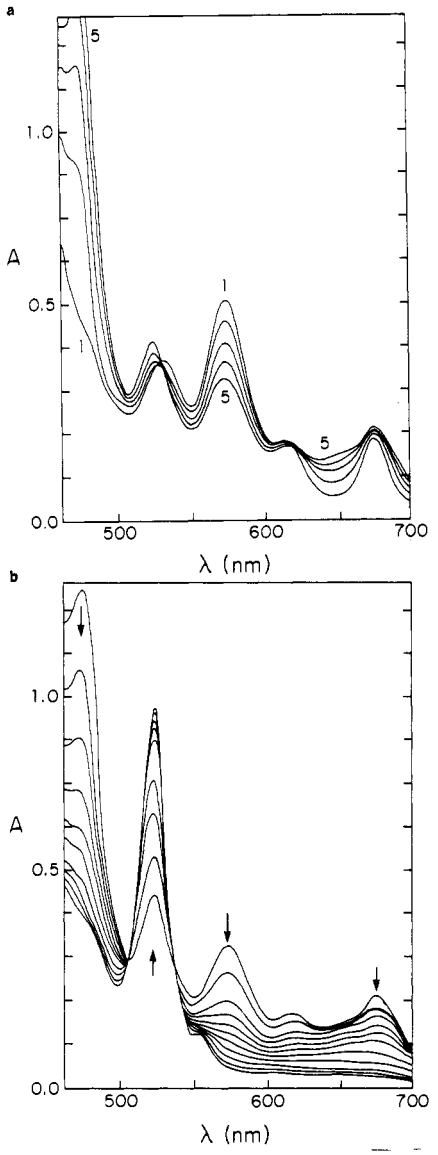

Figure 3. Visible absorption spectra of the formation (5,10,15,20-tetraphenylporphinato)palladium(II) in dimethyl sulfoxide at 50 °C. Conditions were as follows: $[Pd(NO_3)_2]_0 = 1.86 \times 10^{-2}$ M, $[N\text{-}CH_3HTPP]_0 = 7.0 \times 10^{-5}$ M, [2,2,6,6-tetramethylpiperdine] = 0.200 M. Spectra a (upper) are the initial spectra leading to the formation of an intermediate, scan interval of about 4 min, and spectra b (lower) are from the continuation of the reaction leading to the PdTPP product, scan interval of about 16 min.

rate constant for the rate law $d(\ln [PdTPP])/dt = k[\text{amine}]$ was found to be $(2.45 \pm 0.34) \times 10^{-3}$ M^{-1} s^{-1} at 25.0 °C, and with a Pd(II) concentration of 1.00×10^{-3}M, it was found to be $(3.59 \pm 0.48) \times 10^{-3}$ M^{-1} s^{-1}. Four different stock solutions were used to obtain these data. Figure 2 shows a kinetic run by spectral overlay. The initial spectrum obtained after mixing the Pd(II) and *N*-methylporphyrin solution indicates rapid formation of the (*N*-methyltetraphenylporphinato)palladium-(II) ($Pd(N\text{-}CH_3TPP)^+$) complex. The complexes of *N*-methyltetraphenylporphyrin with 2+ transition-metal ions generally show similar absorption spectra that are quite distinct from the spectrum of the free ligand.[13] The peaks at 536 and 410 nm are due to PdTPP.[14] Isosbestic points at 544 and 521 nm indicate that the intermediate complex proceeds directly to the planar PdTPP product without a significant accumulation of any intermediate. From the linear Eyring plot of the rate constants for runs with $[Pd(II)] = 1.0 \times 10^{-2}$ M, the activation parameters were determined to be $\Delta H^{\ddagger} = 14.0 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -23.3 \pm 1.2$ cal/(mol K). From the rate constants obtained for runs with $[Pd(II)] = 1.0 \times 10^{-3}$ M, $\Delta H^{\ddagger} = 14.8 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -19.7 \pm 0.7$ cal/(mol K).

Spectra taken during a reaction of Pd(II) with *N*-methyltetraphenylporphyrin in dimethyl sulfoxide (in the presence of a noncoordinating base, 2,2,6,6-tetramethylpiperidine, required to prevent protonation of the free porphyrin) are shown in Figure 3. It is evident that two processes occur that affect the absorption spectrum of the porphyrin. The initial spectrum is essentially that of the free base *N*-methylporphyrin.

The spectral change associated with the first process is a decrease in the major peak at 572 nm, an increase in absorbance above 620 nm, and development of a very prominent peak at 475 nm. The second process results in the spectrum of PdTPP. Data for the two processes are given in Tables II and III. The spectrum of the apparent intermediate being formed in the first process is not one characteristic of an *N*-methyltetraphenylporphyrin complex.[13] Experiments were also performed with use of 2,6-lutidine as the noncoordinating base. These runs, which were typically 1 order of magnitude slower than those with 2,2,6,6-tetramethylpiperidine under comparable conditions, did not fit the first-order function as well (correlation coefficients of 0.9759–0.9967 vs. better than 0.999). In addition, a distinct color change in the Pd(II) stock

Table II. Kinetic Results for the Initial Reaction Involving Pd(II) and *N*-Methyltetraphenylporphyrin in Dimethyl Sulfoxide[a]

$[Pd(NO_3)_2]$, M	$10^3 k_{obsd}$, s^{-1}	*T*, °C
0.0186	7.11	15.0
0.0093	6.07	15.0
0.00465	6.70	15.0
0.0186	16.2	25.0
0.0093	12.2	25.0
0.00465	15.7	25.0
0.00232	19.2	25.0
0.0186[b]	8.46 ± 1.18	25.0
0.0093[b]	5.00 ± 0.75	25.0
0.0186	10.9 ± 1.0	37.5

[a] $[N\text{-}CH_3HTPP]_0 = 6.96 \times 10^{-5}$ M; [2,2,6,6-tetramethylpiperidine] = 0.200 M. [b] Average of two runs with average deviation given.

Table III. Kinetic Results for the Second Reaction Involving Pd(II) and *N*-Methyltetraphenylporphyrin in Dimethyl Sulfoxide[a]

$[Pd(NO_3)_2]$, M	$10^3 k_{obsd}$, s^{-1}	*T*, °C
0.0093	0.0483	15.0
0.00465	0.0347	15.0
0.0186[b]	0.144 ± 0.023	25.0
0.0093[b]	0.121 ± 0.001	25.0
0.186[c]	0.553 ± 0.019	37.5
0.0093	0.447	37.5
0.00465	0.423	37.5
0.00232	0.432	37.5
0.0186	0.690	37.5
0.0186[d]	0.599	37.5
0.00465[e]	0.426	37.5
0.00465	0.502	37.5
0.0186	2.22	50.0
0.0093[b]	1.69 ± 0.07	50.0
0.0186[c]	14.9 ± 0.9	75.0
0.0186[d]	14.16	75.0

[a] $[N\text{-}CH_3HTPP]_0 = 6.96 \times 10^{-5}$ M; [2,2,6,6-tetramethylpiperidine] = 0.200 M unless otherwise specified. [b] Average of two runs with average deviation given. [c] Average of three runs with average deviation given. [d] $[N\text{-}CH_3HTPP]_0 = 3.48 \times 10^{-5}$ M; [2,2,6,6-tetramethylpiperidine] = 0.200 M. [e] $[N\text{-}CH_3HTPP]_0 = 3.48 \times 10^{-5}$ M; [2,2,6,6-tetramethylpiperidine] = 0.100 M. [f] $[N\text{-}CH_3HTPP]_0 = 3.48 \times 10^{-5}$ M; [2,2,6,6-tetramethylpiperidine] = 0.050 M.

(13) Lavallee, D. K. *Bioinorg. Chem.* **1976**, *6*, 219.
(14) Thomas, D. W.; Martell, A. E. *J. Am. Chem. Soc.* **1956**, *78*, 1338.

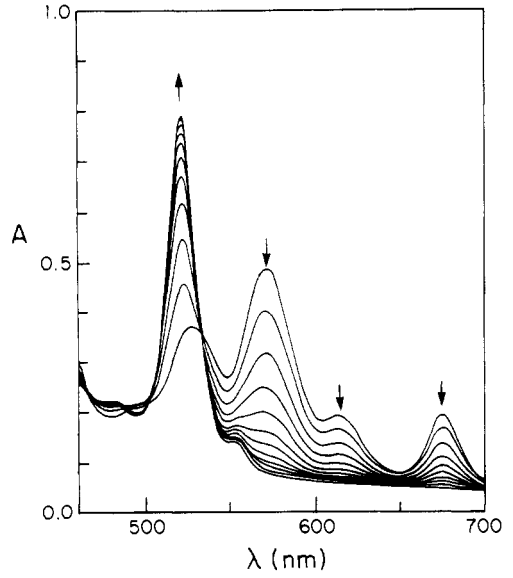

Figure 4. Visible absorption spectra of the formation of (5,10,15,20-tetraphenylporphinato)palladium(II) in dimethylformamide at 25 °C. Conditions were as follows: $[Pd(NO_3)_2]_0 = 2.21 \times 10^{-3}$ M, $[N\text{-}CH_3HTPP]_0 = 3.5 \times 10^{-5}$ M, [di-*n*-butylamine] = 2.5×10^{-3} M, scan interval about 4 min.

solution occurred on addition of the 2,6-lutidine.

Spectra taken during a reaction of Pd(II) with *N*-methyltetraphenylporphyrin in dimethylformamide are shown in Figure 4. Isosbestic points are observed at 533, 502, and 465 nm. The initial spectrum is that of the free base *N*-methyltetraphenylporphyrin, and the final spectrum is that of PdTPP. Thus, there is no indication of appreciable quantities of any intermediate, including $Pd(N\text{-}CH_3TPP)^+$. Kinetic data for the reactions in dimethylformamide, with and without added di-*n*-butylamine, are shown in Table IV.

Discussion

The reactions of complexes of *N*-alkylporphyrins are currently of interest with respect to the formation of *N*-alkylporphyrins from the cytochrome P-450 prosthetic group.[15] It is of interest to determine what conditions favor the formation of *N*-alkylporphyrins from metalloporphyrins and under what conditions dealkylation or demetalation occur.[16] The reaction of a Pd(II) *N*-methylporphyrin complex has been used to make a therapeutic agent, but its reaction kinetics and mechanism have not been studied.[3] In addition, results have been obtained for dealkylation reactions of a number of first-row transition-metal ions, but none have been obtained for the heavier elements.

Of the three solvents chosen for study, acetonitrile provides the results that are most straightforward to interpret. From the spectral changes that occur as the reaction proceeds, it is evident that the $Pd(N\text{-}CH_3TPP)^+$ complex is formed relatively rapidly compared with the dealkylation reaction. The three isosbestic points in the spectral region from 400 to 700 nm indicate that $Pd(N\text{-}CH_3TPP)^+$ formation is essentially complete when the initial data for the dealkylation reaction are obtained. The rate law for the formation of PdTPP from Pd(II) and $N\text{-}CH_3HTPP$ in acetonitrile is $d[Pd(II)]/dt = k[N\text{-}CH_3HTPP][\text{di-}n\text{-butylamine}]$. Although the rate is not totally independent of the concentration of Pd(II), it shows only a slight dependence (a decrease of 18% in the observed rate constant for a factor of 10 in Pd(II) concentration, which is consistent with a decrease in the available amine concentration due to complexation by Pd(II)). As shown in Table V, the activation parameters for the reaction of Pd(II) fit the general pattern that has been observed for the nucleophilic displacement dealkylation reactions of *N*-methyltetraphenylporphyrin complexes:[4a] the more stable the metalloporphyrin product, the lower the activation energy. This result leads to the prediction that high-spin iron and manganese and other out-of-plane metalloporphyrins should show relatively slow dealkylation reactions, as has been observed.[4b,16] The Pd(II) ion is the largest and "softest" we have studied, but it shows the most rapid dealkylation, supporting the contention that Lewis acidity, and consequent attraction of the $N\text{-}CH_3$

Table IV. Kinetic Results for the Formation of (Tetraphenylporphinato)palladium(II) from Pd(II) and *N*-Methyltetraphenylporphyrin in Dimethylformamide

$10^3 \times$ [Pd(II)], M	$10^5 \times$ [$N\text{-}CH_3H(TPP)$], M	[amine],[a] M	$10^3 k_{obsd}$, s^{-1}	*T*, °C
23.9	4.08	0.100[b]	1.81[c]	25.0
11.9	4.08	0.100[b]	1.41[c]	25.0
3.32[d]	1.75	0.300	0.474 ± 0.006	25.0
3.32[d]	1.75	0.100	0.547 ± 0.001	25.0
2.21	4.08	0.300	0.530	25.0
2.21	4.00	0.200	0.532	25.0
2.21	4.08	0.050	0.578	25.0
2.21	3.93	0.100	0.620	25.0
2.21	2.91	0.300	0.391	25.0
2.21	2.04	0.100	0.254	25.0
1.66	3.93	0.600	0.292[c]	25.0
1.66[d]	3.93	0.300	0.380 ± 0.007	25.0
1.21	4.09	0.097	0.413	25.0
1.11	0.408	0.100	0.198	25.0
1.11	0.205	0.100	0.224	25.0
2.21[d]	4.08	0.200	0.375 ± 0.025	37.5
2.21[c,d]	4.08	0.200	0.225 ± 0.017	37.5
2.21[d]	4.08	0.200	2.60 ± 0.26	50.0
3.91[e]	4.08	0.100	2.25	25.2
3.91[e]	1.02	0.100	1.01	25.2
2.21[e]	4.08	0.200	1.39	25.0
2.21[e]	4.08	0.100	1.20	25.0
2.21[e]	4.08	0.050	1.37	25.0
1.96[e]	4.08	0.200	1.02	25.2
1.11[d,e]	3.93	0.300	0.304 ± 0.008	25.0
2.21[d,e]	4.08	0.200	4.40 ± 0.77	37.5
2.21[e]	4.08	0.200	4.66	50.0
2.21	4.08		0.803	25.0
2.21	4.08		0.454[c]	25.0
2.21	3.93		0.872	25.3
0.96	4.37		0.262[c]	58.0
0.96	4.37		0.361	62.7
2.21[e]	4.08		5.94[c]	25.0
2.21[e]	4.08		14.7[c]	25.0
1.11[c]	3.93		0.489[c]	25.0
0.74	4.08		0.202	25.0

[a] Di-*n*-butylamine. [b] Attempts to use higher concentrations of amine (e.g. 0.200 M) resulted in dark opaque mixtures. [c] Poorer correlation coefficients (0.987–0.997) and nonrandom deviations were found. [d] Average of two runs with average deviation given. [e] Different stock solution of $Pd(NO_3)_2$ in DMF.

Table V. Activation Parameters for the Demethylation of Metalated *N*-Methyltetraphenylporphyrin Complexes by Di-*n*-butylamine in Acetonitrile[a]

metal ion	$\Delta H^{\ddagger}$, kcal/mol	ΔS (318 K), eu	$\Delta G^{\ddagger}$, kcal/mol
Pd(II)	14.4 ± 0.6	−21.5 ± 1.6	20.8
Cu(II)[b]	16.9 ± 1.0	−13.1 ± 2.9	21
Ni(II)[b]	18.0 ± 1.0	−14.0 ± 3.0	23
Zn(II)[b]	41.6 ± 2.0	54.6 ± 6.2	26
Mn(II)[b]	>51	>65	

[a] Error limits are the standard deviations from the calculated least-squares fit of ln (k/T) vs. $1/T$. Eyring activation parameters are specified. [b] Data taken from ref 4b.

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bonding electrons, is not the most important factor in determining the dealkylation rate. From the observed rate law and from the compensation effect seen for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values in Table V, it appears that the reaction of Pd(II) with N-CH_3HTPP in acetonitrile proceeds by the same mechanism as the reactions of the Cu(II), Ni(II), Zn(II), and also the Mn(II)[4b] complexes. This proposed mechanism is a bimolecular nucleophilic displacment of the methyl group with concomitant formation of the corresponding non-N-methylated metalloporphyrin. In contrast to this mechanism of dealkylation, N-methylporphyrin complexes of Co(I) and Rh(I) undergo dealkylation by oxidative addition.[17-19] Although some complexes of Pd(II) undergo oxidative-addition reactions,[20] it appears that nucleophilic displacement is preferred under our reaction conditions.

From the spectra taken during the reaction of Pd(II) with N-CH_3HTPP in dimethyl sulfoxide (Figure 3), two reactions are indicated. The first reaction begins with the free base N-CH_3HTPP, and an intermediate is formed that does not correspond spectrally to the Pd(II) complex of N-CH_3HTPP. The absorbance changes for this reaction are first order with respect to the N-methylporphyrin concentration and appear to be independent of [Pd(II)]. The first-order rate constants show no discernible temperature dependence either (Table II). Pasternack and co-workers have recently shown that an outer-sphere ion-dipole type interaction occurs between Cu(II) and H_2TPP in dimethyl sulfoxide prior to the formation of CuTPP.[21] The ion-dipole interaction does not appear to significantly change the spectrum of H_2TPP, but the effect of the ion-dipole formation is evident from the reaction kinetics. It is quite possible that with the less planar and more polar N-CH_3TPP molecule, ion-dipole formation could lead to greater spectral changes than in the case of H_2TPP. Indeed, Burnham and Zuckerman have shown that ion pairs involving different anionic metal complexes with the same diacid porphyrin cation show small but significant spectral differences in the visible region.[22] The lack of a large temperature dependence for the initial reaction of Pd(II) with N-CH_3HTPP is consistent with ion-dipole formation.[21,23] Two observations that seem inconsistent with ion-dipole formation, however, are the lack of a dependence of the rate constant on the Pd(II) concentration and the slowness of the process (i.e. $t_{1/2}$ values of 1–2 min at 25 °C). In addition, in the study of the formation of N-CH_3HTPP complexes with Cu(II), Zn(II), Co(II), and Mn(II) in dimethylformamide, the rate laws were all first order with respect to metal ion at concentrations comparable to those of Pd(II) in this study,[7] and the complexation of porphyrins by chloride salts of a number of metal ions have been found by Longo and co-workers to be first order in metal ion. Dimethyl sulfoxide has a higher dielectric constant than dimethylformamide (47 vs. 37). If ion-dipole association were to affect the dependence of the rate of formation of N-methylporphyrin complexes in Me_2SO on the metal ion concentration, it should be evident for reactions in DMF as well.

Another possible rationalization of the initial process in dimethyl sulfoxide is the formation of a covalently bound complex between Pd(II) and the N-methylporphyrin in which the hydrogen atom bound to the pyrrolic nitrogen in the free base remains bound; i.e. a "sitting-atop" complex. Such a complex has been isolated by Theophanides and co-workers.[24] Although other proposed "sitting-atop" complexes have generally been demonstrated to be ion pairs rather than covalently bound complexes,[22,25,26] Theophanides has compiled evidence from infrared and UV–visible spectroscopy,[24] Raman spectroscopy,[27] and X-ray photoelectron spectroscopy[28] to demonstrate the existence of the *cis*-Pt(H_2hematoporphyrin)Cl_2 complex in which the two N–H bonds of the free base porphyrin are retained. If such a complex were formed in this case, the spectral changes and the relative slowness of the process could be explained. The lack of a dependence of this reaction on the concentration of Pd(II) could be accounted for if the rate of formation of the intermediate is determined by the formation of the second covalent bond between Pd(II) and the N-methylporphyrin (to form a structure analogous to that proposed for Pt(H_2hematoporphyrin)Cl_2 by Theophanides[24]). To be independent of [Pd(II)], the formation of the first Pd(II)–N bond must be favorable so that an increase in [Pd(II)] would have little effect. The idea that formation of the second bond to the N-methylporphyrin is important to the overall complexation rate is consistent with the data obtained by Hambright et al. for the acid-catalyzed solvolysis of (N-methyletioporphinato)zinc(II), which follows the rate law[29]

$$k_{obsd} = k_b[HCl]_0^2/(\rho + [HCl]_0)$$

Since there are three strong Zn–N bonds in a Zn(II) complex of an N-methylporphyrin[30] and two of the nitrogens must be protonated in the rate-determining step, a species with only one strong Zn–N bond readily dissociates. In the case of non-N-methylated (etioporphinato)zinc, Hambright et al. found the rate law[29]

$$k_{obsd} = k_a[HCl]^2/(\rho + [HCl]_0)$$

also indicating the relative lability of a single Zn–N bond.

The intermediate formed in the first process in dimethyl sulfoxide is converted to planar PdTPP without the accumulation of significant concentrations of any further intermediates such as Pd(N-CH_3TPP)$^+$ is indicated by the isosbestic points at 506 and 536 nm (Figure 3b). The activation parameters for the second process ($\Delta H^{\ddagger}$ = 19.1 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ = −12.3 ± 0.4 cal/(mol K), $\Delta G^{\ddagger}$ = 22.8 kcal/mol) are consistent with those for dealkylation reactions in which the bimolecular nucleophilic displacement step is rate determining (Table V), but they may also be consistent for the formation of Pd(N-CH_3TPP)$^+$ from the intermediate. Of course, from the spectral evidence, the Pd(N-CH_3TPP)$^+$ would have to then react rapidly to form PdTPP. The only activation parameters available for the formation of M(N-CH_3TPP)$^+$ complexes relate to their formation from M(DMF)$_6^{2+}$ complexes with no spectroscopically detectable intermediates.[7]

The spectra for the reaction of Pd(II) with N-CH_3HTPP in dimethylformamide (Figure 4) indicate no perceptible accumulation of any porphyrin complexes as reaction intermediates. From the data in Table IV, it is apparent that the

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formation of PdTPP occurs in dimethylformamide without the addition of di-*n*-butylamine at a rate comparable to that found in the presence of amine. In some cases, however, the spectral changes for these reactions could not be fit to any reasonable reaction order and they were less reproducible than those in the presence of amine. Overall, the observed first-order rate constants do not correlate well with Pd(II) concentration (a genereally positive but not well-defined effect) nor with the concentration of amine (a generally negative but again poorly defined effect). The values for the rate constants are inconsistent with respect to temperature changes and even vary considerably from one stock solution of Pd(II) to another. All of the rate constants at 25 °C with amine present do fall within a reasonably narrow range (0.19×10^{-3} to 3.5×10^{-3} s^{-1}). With such data at hand, any mechanistic interpretation is highly speculative. Our interpretation is that the most important factor determining overall conversion of *N*-CH_3HTPP to the complex PdTPP is the formation of the Pd(*N*-CH_3TPP)$^+$ intermediate, which can really alkylate DMF itself. The reactivity of the Pd(II) may be highly dependent on the ligands in the first coordination sphere, which may vary under the conditions used to study the reaction. The proposal that dealkylation of Pd(*N*-CH_3TPP)$^+$ could be fast relative to the rate of its formation in dimethylformamide is reasonable in view of the fact that the rate of dealkylation of Ni(*N*-CH_3TPP)$^+$ is competitive with the complexation rate[7] and that the dealkylation rate of Pd(*N*-CH_3TPP)$^+$ is faster than that of Ni(*N*-CH_3TPP)$^+$ under comparable conditions (3.0×10^{-3} and 2.8×10^{-4} M^{-1} s^{-1},[4b] respectively, at 25 °C in acetonitrile with di-*n*-butylamine as nucleophile).

The overall mechanism for formation of PdTPP from Pd(II) and *N*-CH_3HTPP in several solvents appears to be as in eq 1-5.

$$Pd^{II}L_4^{2+} + N\text{-}CH_3HTPP \rightarrow L_4Pd{:}N\text{-}CH_3HTPP^{2+} \quad (1)$$

$$L_4Pd{:}N\text{-}CH_3HTPP^{2+} \rightarrow L_3Pd(N\text{-}CH_3HTPP)^{2+} + L \quad (2)$$

$$L_3Pd(N\text{-}CH_3TPP)^{2+} \rightarrow L_2Pd(N\text{-}CH_3HTPP)^{2+} + L \quad (3)$$

$$L_2Pd(N\text{-}CH_3HTPP)^{2+} \rightarrow LPd(N\text{-}CH_3TPP)^{+} + H^{+} + L \quad (4)$$

$$LPd(N\text{-}CH_3TPP)^{+} + nu \rightarrow PdTPP + CH_3nu^{+} + L \quad (5)$$

In all cases, ion-dipole formation (step 1) can be considered rapid. In acetonitrile all steps principally involving loss of ligands from Pd(II) (2-4) are rapid, and step 5, the nucleophilic displacement of PdTPP from the methyl group, is rate determining. If the formation of LPd(*N*-CH_3TPP)$^+$ is highly favorable, as is typical for *N*-methylporphyrin complexes in the absence of acid, [Pd] $\gg$ [*N*-CH_3HTPP], and equilibria 1-4 are established rapidly; the overall reaction rate should be dependent on the amine concentration but not the palladium(II) concentration. In dimethyl sulfoxide, it appears that steps 3 and 4 are relatively slow. They are distinguishable, with step 3 occurring about 2 orders of magnitude faster than step 4. Once the Pd(*N*-CH_3TPP)$^+$ complex is formed in dimethyl sulfoxide, it is rapidly dealkylated (step 5). Typical half-lives for the overall reaction at 25 °C are 5 min in acetonitrile (1 M di-*n*-butylamine), 100 min in dimethyl sulfoxide, and 20 min in dimethylformamide. Both the formation of an *N*-methylporphyrin complex (1-4) and the dealkylation reaction (5) are expected to be slower in solvents that form better complexes and have higher dielectric constants, the former because complexation rates tend to parallel ligand exchange rates[7,31] and the latter because better solvation of the reactants retards bimolecular nucleophilic displacement reactions, including the dealkylation of *N*-methylporphyrins.[32] Thus, the order of rates in the solvents studied CH_3CN > DMF > Me_2SO, appears reasonable.

The nature of the rate-determining step as well as the overall rate of formation of a non-N-methylated palladium(II) porphyrin complex from Pd(II) and an *N*-methylporphyrin depends on the solvent medium. In strongly complexing solvent media, which are nucleophilic with respect to alkyl groups, dealkylation can occur rapidly with respect to complexation. Rates of complexation are more rapid in poorly complexing solvents.

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Effect of pH and Acetate on the Rate of Hydrolysis of the Chromium-Carbon Bond in (α-Hydroxyalkyl)chromium(III) Complexes

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The kinetics of the hydrolysis of $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$ in the pH range 0.0-5.6 are reported. The results indicate that the hydrolysis reaction is faster for $[(H_2O)_{5-n}(OH)_nCrC(CH_3)_2OH]^{2-n}$. Furthermore, the rate of hydrolysis of $[(H_2O)_5CrCR_1R_2OH]^{2+}$ is accelerated by acetate anions. The mechanistic implications of these results are discussed in detail.

Introduction

The mechanism of metal-carbon bond cleavage in alkylchromium(III) and (substituted alkyl)chromium(III) complexes in aqueous solutions has been recently studied extensively.[1,2] The interest in this mechanism arose as it serves as a model system for the behavior of metal-carbon σ bonds in aqueous solutions and as these complexes are relatively easily attainable.[1,3] Two mechanisms of decomposition of CrR^{2+}

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