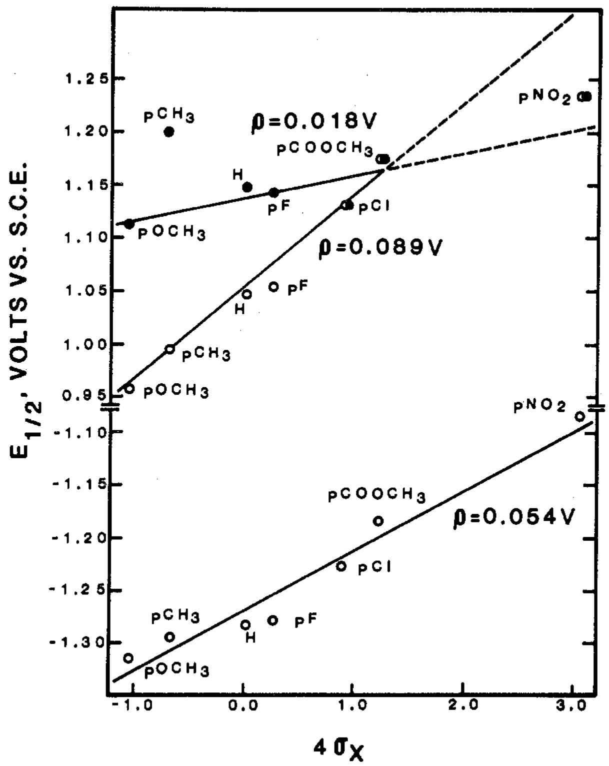

Figure 2. Plot of $E_{1/2}$ vs. 4σ for the redox reactions of Ni(p-X)TPP in 0.1 M TBAP, CH_2Cl_2: ○, first oxidation peak or first reduction peak to yield anion or cation radical; ●, second oxidation peak to yield nickel(III) cation radical.

pound, $[Ni^{II}(p\text{-}X)TPP]^+$ the cation radical of nickel(II), and $[Ni^{III}(p\text{-}X)TPP]^{2+}$ the cation radical of nickel(III). This agrees with the data of Dolphin et al.[17] which show the initial single-electron oxidation of NiTPP in CH_2Cl_2 yields a stable species whose optical spectrum resembles those of $MgTPP^+$ and $ZnTPP^+$. Oxidation of nickel octaethylporphyrin, NiOEP, by ferric perchlorate also yields optical and ESR spectra characteristic of ring oxidation.[18]

The electrochemical ρ of 0.018 V obtained for reaction 3 is consistent with a reduced interaction of the central nickel $d\pi$ electrons and the π electrons of the porphyrin ring. It has been shown that transmission of electronic effects from the periphery of the porphyrin ring is along the plane of the porphyrin to the central nitrogens where a cis and trans effect may be observed.[19] A "normal" pattern of substituent effects is noted for ligand addition to nickel(II) for a series of neutral metalloporphyrins containing substituents at either the porphyrin ring[20] or the four phenyl groups of tetraphenylporphyrin.[15] The ρ of 0.089 V for reaction 2 is close to the ρ of 0.085 V for the ring oxidation of $Co^{III}(p\text{-}X)TPP$[12] and fits into the range observed for other transition metal tetraphenylporphyrins, 0.068 ± 0.021 V. Of special note is the fact that the metal reaction apparently occurs after the formation of the cation radical for the compounds containing electron-donating substituents. This role may be reversed for electron-withdrawing substituents (as indicated by slope of Hammett plot for reaction 2). Studies are now in progress which show that, through the judicious placement of electron-donating or -withdrawing substituents on a porphyrin ring, the reactivities of metalloporphyrins can be drastically altered, and in certain cases, reversals may be observed in the order of ring vs. metal reaction.

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Registry No. Ni(p-OCH_3)TPP, 39828-57-4; Ni(p-CH_3)TPP, 58188-46-8; Ni(p-H)TPP, 14172-92-0; Ni(p-F)TPP, 58188-47-9; Ni(p-Cl)TPP, 57774-14-8; Ni(p-$COOCH_3$)TPP, 58188-48-0; Ni(p-NO_2)TPP, 58188-49-1.

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Preparation and Some Reactions of Diethylenetriaminepalladium(II)-Solvento Complexes

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Complexes in which solvents are present as ligands are of interest for several reasons. They are potential intermediates in reactions carried out in solution. Many solvents form relatively weak bonds to metal ions so that solvento complexes are highly reactive starting materials. Solvento complexes may show unusual and interesting reactions such as that of $[Pt(dien)H_2O](ClO_4)_2$[3] with sodium tetraphenylboron to yield $[Pt(dien)Ph]BPh_4$.[4] Here we describe the preparation of aquo, hydroxide, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile complexes of palladium(II), together with the reaction of the aquo complex with sodium tetraphenylboron and the hydroxy complex with carbon monoxide.

Experimental Section

$[Pd(dien)I]I$,[5] $[Pd(dien)H_2O](ClO_4)_2$,[5] and $[Pd(dien)Cl]Cl$[6] were prepared as described previously. Methanol, acetone, and acetonitrile were dried as in the literature.[7] Tetrahydrofuran was stored over sodium wire (48 h) and then fractionally distilled under oxygen-free

Table I. Analytical and Spectroscopic Properties of the Complexes

Complex	Solvent used in prepn	Anal,[h] %			Electronic spectra[a]		Proton NMR spectra[b]			^{13}C NMR spectra of dien carbon atoms[c]	
		C	H	N	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	Solvent	τ,[d] ppm	Assignment	Chem shift, ppm	Δ,[e] ppm
$[Pd(dien)DMSO](ClO_4)_2$	DMSO	14.66	3.89	8.59	260	6406	D_2O	6.7 (4)	CH_2	54.38	6.88
		14.80	3.94	8.63				6.9 (10)	$CH_2 + CH_3$[f]	47.50	
$[Pd(dien)DMF](ClO_4)_2$	DMF	17.01	4.12	11.84	313	773	D_2O	6.7 (8)	CH_2	54.38	6.93
		17.44	4.19	11.63				6.9 (6)	CH_3-N	47.45	
								1.8 (1)	CHO		
$[Pd(dien)MeCN](ClO_4)_2$	MeCN	15.68	3.51	12.28	302	627	D_2O	6.6 (8)	CH_2	54.47	6.56
		16.01	3.59	12.57				7.5 (3)	CH_3	47.91	
$[Pd(dien)H_2O](ClO_4)_2$	H_2O	10.82	3.25	9.67	316	545	D_2O	6.7	CH_2	53.61	6.78
		11.27	3.55	9.85						46.83	
$[Pd(dien)H_2O](ClO_4)_2$	Me_2CO	11.77	3.55	9.87			D_2O	6.7 (sharp)	CH_2		
		11.27	3.55	9.85			C_2D_6CO	6.7 (broad)	CH_2		
$[Pd(dien)H_2O](ClO_4)_2$	THF	11.56	3.55	9.95	316	545	D_2O	6.6 (sharp)	CH_2		
		11.27	3.55	9.85			C_2D_6CO	6.6 (broad)	CH_2		
$[Pd(dien)OH]ClO_4$[g]	MeOH	15.35	3.51	12.07	315	434	D_2O	6.7	CH_2	54.48	6.64
		14.75	4.32	12.90						47.84	
$[Pd(dien)I]I$	H_2O	10.45	2.79	9.04	372	605				53.13	2.66
		10.37	2.83	9.07						50.47	
$[Pd(dien)Cl]Cl$	H_2O	17.21	4.62	15.03						53.94	5.28
		17.13	4.66	14.99						48.66	

[a] Recorded in water except for the DMSO, DMF, and MeCN complexes which were recorded in their own solvents. [b] Recorded on a Perkin-Elmer R12 60-MHz spectrometer. [c] Chemical shifts, which are to low field of TMS, were determined in D_2O using 1,4-dioxane as an internal reference (assumed to lie 66.50 ppm to low field of TMS[8] at +33 °C using a Varian XL-100 spectrometer operating in the Fourier transform Mode at a frequency of 25.2 MHz with proton noise decoupling. [d] τ values are relative to TMS = 10.0 ppm; the integrated number of protons is shown in parentheses. [e] Δ is the difference between the chemical shifts of the two inequivalent methylene carbon atoms. [f] See text. [g] Containing a small amount of $[Pd(dien)H_2O](ClO_4)_2$–see text. [h] Top values are found; bottom values are calculated.

nitrogen.

Preparation of Solvento Complexes $[Pd(dien)S](ClO_4)_2$. Equivalent amounts of anhydrous silver perchlorate (dried over calcium sulfate) and $[Pd(dien)I]I$ were stirred in the appropriate solvent at room temperature in the dark for 24 h before filtering off the precipitated silver iodide.

In the case of low-boiling solvents (acetone, acetonitrile, methanol, and tetrahydrofuran) the excess solvent was pumped off at room temperature until an oily residue was obtained (care was required to avoid taking the solution to dryness since this led to decomposition). The oily residue was vigorously stirred with dichloromethane to obtain pale yellow crystals. The products were characterized by elemental analysis, uv–visible, infrared, and ^1H and ^{13}C NMR spectroscopy, and molar conductance and shown to be $[Pd(dien)MeCN](ClO_4)_2$ from acetonitrile, $[Pd(dien)H_2O](ClO_4)_2$ from acetone and tetrahydrofuran, and $[Pd(dien)OH]ClO_4$ together with a little $[Pd(dien)H_2O](ClO_4)_2$ from methanol (see Table I).

In the case of high-boiling solvents (DMF and DMSO) the excess solvent was removed by solvent extraction (2:1 diethyl ether–petroleum ether, then diethyl ether alone for DMF; 2:1 benzene–petroleum ether, then benzene alone for DMSO). Traces of the extracting solvent were removed from the yellow complex-containing layer by treatment in vacuo. For the DMF complex addition of dichloromethane to the yellow solution yielded an oily material which solidified on addition of diethyl ether. For the DMSO complex the yellow solution was treated with diethyl ether with vigorous stirring and then frozen, and the liquid diethyl ether layer was poured off. The frozen material was then warmed gradually and dichloromethane was added slowly with stirring to yield pale yellow crystals which were well washed with dichloromethane and dried in vacuo at room temperature.

Preparation of $[Pd(dien)Ph]BPh_4$. An aqueous solution of $[Pd(dien)H_2O](ClO_4)_2$ (0.290 g, 0.68 mmol) was treated with sodium tetraphenylboron (0.465 g, 1.36 mmol). A pale yellow fluffy precipitate was initially formed but this gradually turned off-white. All attempts to isolate the pale yellow material, which was probably $[Pd(dien)H_2O](BPh_4)_2$, failed. The mixture was stirred for 2 h at room temperature to ensure completeness of reaction before filtering off the precipitate, washing it with cold water, and drying it over phosphorus pentoxide. The dried product was extracted with benzene to remove triphenylboron before further drying in vacuo to give an off-white crystalline product (0.377 g; 91.5% yield). Anal. Calcd for $[Pd(dien)Ph]BPh_4$: C, 67.44; H, 6.28; N, 6.94. Found: C, 67.14; H, 6.36; N, 6.87.

The product was soluble in acetone and acetonitrile, in which it spontaneously decomposed to palladium metal, and slightly soluble in 1,4-dioxane (λ_{max} 254 nm). In the infrared spectrum bands at about 3500 and 1630 cm^{-1} that would have indicated the presence of water were absent and bands were observed at 1430, 1340, 1280, 1140, and 750 cm^{-1} consistent with the presence of phenyl groups. The tetraphenylboron counterion was replaced by nitrate using cesium nitrate. The 60-MHz ^1H NMR spectrum[9] of $[Pd(dien)Ph]NO_3$ showed bands at τ 2.75 (1 H), 3.30 (2 H), 3.70 (2 H), and 7.00 ppm (8 H) that were assigned to the para, meta, and ortho phenyl and dien methylene protons, respectively.

Reaction of $[Pd(dien)OH]ClO_4$ with Carbon Monoxide. A solution of $[Pd(dien)H_2O](ClO_4)_2$ (0.043 g, 0.1 mmol) and carbon dioxide free potassium hydroxide (0.202 g, 3.6 mmol) in water (36 ml) was flushed with dry nitrogen gas for 2 h. No carbon dioxide could then be detected[10] in the gas stream. Carbon monoxide was then bubbled through the solution, whereupon the detector showed the presence of carbon dioxide. The initially colorless reaction mixture gradually darkened due to the formation of palladium metal.

Molar Conductance. The molar conductances[11] of $[Pd(dien)OH]ClO_4$ and $[Pd(dien)H_2O](ClO_4)_2$ (79.0 and 142.8 ohm^{-1} cm^2 M^{-1}, respectively) are consistent with their formulation as 1:1 and 2:1 electrolytes.[12]

Estimation of the pK_a Value of $[Pd(dien)H_2O](ClO_4)_2$. A series of solutions (10 ml) containing $[Pd(dien)H_2O](ClO_4)_2$ (1.00×10^{-3} M) and various amounts of sodium hydroxide and sodium perchlorate (to give a final ionic strength of 0.10 M) were studied spectrophotometrically[13] and potentiometrically.[14] The final pK_a (7.1) was obtained as the mean result from both techniques.

Results and Discussion

The solvento complexes prepared in water, acetonitrile, DMF, and DMSO are straightforward. The aquo ligand is deprotonated in basic solution, the pK_a being about 7.1 which is rather higher than that found previously in the analogous platinum(II) complex (6.13).[4] This would suggest that the metal–oxygen interaction in $[M(dien)H_2O]^{2+}$ is stronger when M = Pt than when M = Pd. The infrared spectra suggested that acetonitrile is N bonded,[15] DMF is O bonded,[16,17] and DMSO is S bonded.[18]

The 60-MHz proton NMR spectra (see Table I) of the aquo, acetonitrile, and DMF complexes were as expected. In contrast the DMSO complex showed absorptions at 6.7 and 6.9 ppm which at first sight appeared to arise from the dien methylene and DMSO methyl protons, respectively. However the absorptions were in the ratio of 4:10 rather than 8:6. When the 100-MHz spectrum[19] was recorded, it showed that the larger peak was made up of two peaks, one due to the dien methylene protons and the other due to the DMSO methyl protons. This is the only complex we have found in which the dien methylene protons are split into two groups. While several explanations based on either steric or electronic effects can be offered, it seems perhaps more likely that the steric bulk of the S-bonded DMSO restricts the conformational freedom of the dien ligand so that the methylene protons, which in all other Pd^{II}–dien complexes absorb at the same frequency, are split. With this explanation in mind we examined the ^{13}C NMR chemical shifts of the methylene carbon atoms to see if those in the DMSO complex were in any way unusual. It is apparent from Table I that while the methylene carbons give rise to two signals,[20] as expected from two chemically inequivalent carbon atoms, the chemical shifts and the frequency difference between them in the DMSO complex are in no way unusual for complexes of the type $[Pd(dien)L](ClO_4)_2$. Both methylene resonances in the complexes are largely independent of the nature of the other ligand and of the charge on the complex, although that at about 47 ppm is rather more variable than that at about 54 ppm. The band at about 54 ppm is assigned to the methylene carbon atom next to the secondary amino nitrogen and that at about 47 ppm to the other carbon on the basis of literature data for $CH_3NHCH_2CH_2NHCH_3$ (52.0 ppm[21]) and $NH_2CH_2CH_2NH_2$ (45.8 ppm[22]).

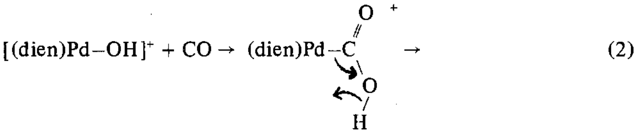
All attempts to prepare the acetone and tetrahydrofuran complexes led solely to the aquo complexes in spite of rigorous precautions being used in drying the solvents. The discovery that all attempts to prepare $[Pd(dien)MeOH](ClO_4)_2$ led to $[Pd(dien)OH]ClO_4$ was unexpected. The identity of the product was confirmed by comparison with authentic $[Pd(dien)OH]ClO_4$ using spectroscopy (e.g., ν(OH) 3500 cm^{-1}; λ_{max} 315 nm, ϵ 434 M^{-1} cm^{-1}) and molar conductance [in dry methanol it is possible that OH^-–OMe^- exchange occurs, but the product is still a 1:1 electrolyte]. In connection with the formation of this hydroxy complex it should be noted, first, that any methanol complex formed should readily undergo deprotonation to yield the methoxy complex and, second, that the methoxy complex $[(Ph_2PCH_2CH_2PPh_2)Pt(C_6H_9)OMe]$ is known to be very sensitive to moisture yielding the corresponding hydroxy complex.[23]

It was of interest to study the reaction of the palladium(II)–aquo complex with tetraphenylboron anions.[4,24] The product was $[Pd(dien)Ph]BPh_4$ formed by reaction 1. This

$$[Pd(dien)H_2O]^{2+} + 2BPh_4^- \rightarrow [Pd(dien)Ph]BPh_4 + H_2O + BPh_3 \quad (1)$$

was confirmed by (i) isolating the triphenylboron formed and confirming both its identity and the fact that it was formed in equivalent amount to the amount of palladium(II) present, (ii) chemical analysis of $[Pd(dien)Ph]BPh_4$, and (iii) the fact that the infrared spectrum showed no bands around 3500 or 1630 cm^{-1} that would have been expected in an aquo complex but did show bands consistent with the presence of a phenyl group. When a bulky anion is added to a solution containing a bulky cation, an immediate precipitate is normally formed within the time of mixing. Accordingly one might expect to observe the precipitation of $[Pd(dien)H_2O](BPh_4)_2$ and indeed an initial pale yellow material was always observed. However all attempts to isolate this material were frustrated because it rapidly turned to the off-white color of $[Pd(dien)Ph]BPh_4$.

Although carbon monoxide insertion into metal–carbon σ bonds has been widely reported, similar insertions into metal–oxygen σ bonds are rare. However a number of reactions involving nucleophilic attack (e.g., by RO^-) on carbon monoxide ligands have been reported.[25] Accordingly $[Pd(dien)OH]ClO_4$ was treated with carbon monoxide to see (i) whether reaction occurred and (ii) whether the product was stable by analogy to Bennett's Pt–COOH complex[26] or whether carbon dioxide was eliminated. Carbon dioxide was eliminated and palladium metal deposited. We are currently investigating the mechanism of this reaction to determine whether it involves insertion (as in eq 2 and 3) or whether a



$$[(dien)Pd{-}OH]^+ + CO \rightarrow [(dien)Pd{-}C({=}O)OH]^+ \rightarrow \quad (2)$$

$$[(dien)Pd{-}H]^+ + CO_2$$

$$[(dien)PdH]^+ \rightarrow Pd^0 + dien + H^+ \quad (3)$$

carbonyl complex is first formed followed by nucleophilic attack by hydroxide ion on the coordinated CO.[27,28]

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Registry No. $[Pd(dien)DMSO](ClO_4)_2$, 58324-76-8; $[Pd(dien)DMF](ClO_4)_2$, 58298-24-1; $[Pd(dien)MeCN](ClO_4)_2$, 58298-26-3; $[Pd(dien)H_2O](ClO_4)_2$, 53773-88-9; $[Pd(dien)OH]ClO_4$, 58298-28-5; [Pd(dien)I]I, 53798-18-8; [Pd(dien)Cl]Cl, 23041-96-5; $[Pd(dien)Ph]BPh_4$, 58298-30-9; $[Pd(dien)Ph]NO_3$, 58298-31-0; sodium tetraphenylboron, 143-66-8; carbon monoxide, 630-08-0.

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