opens to 99.6 (1.3)° in complex 3, which is higher than that for complexes 1 and 2 and also larger than that for the Schiff base analogue. In that case the Tc–O(phenol) distance (2.01 (1) Å) appears to be slightly longer than that observed here (1.99 (1) Å).

The least-squares planes (supplementary material) show the Tc atom to be approximately 0.1 Å out of the plane defined by the coordinated atoms of the tetradentate ligand toward the terminal oxygen atoms. The chloroform molecules present in all three crystal structures are not especially close to any of the Tc complex atoms (closest contacts: compound 1, O1–C18 = 3.15 Å, O1–C19 = 3.19 Å; compound 2, O1–C20 = 3.16 Å, O2–C20 = 3.21 Å; compound 3, O1–C20 = 3.12 Å, O2–C20 = 3.27 Å). Within the dimers, the aromatic rings bend away from the terminal oxygen atoms. This results in rather close contact between portions of these rings (e.g.: in compound 1, C14---C14′ = 3.19 Å, C13---C13′ = 3.31 Å; in compound 2, C13---C14 = 3.18 Å, C12---C14 = 3.36a; in compound 3, C14---C15′ = 3.42 Å, C14′---C15 = 3.49 Å).

The behavior of the complexes of the ^{99m}Tc isomer has also been investigated.[13] These complexes are formed in very dilute solutions in greater than 95% yield, are stable in vitro, and are readily extracted into CHCl$_3$ or 1-octanol. These observations suggest that derivatives of these ligands as bifunctional chelating agents for technetium might be useful for protein labeling. Studies of the biodistribution in rats of the ^{99m}Tc complexes[11] showed a very slow clearance from the blood. Further studies showed that white blood cells could be labeled in 30–70% yield after 30-min reaction with the complex. However, radioactivity was released from the cells at 37 °C at a rate of ~30%/h. Because of this high rate of release, the complexes described in this work are probably not directly suited for cell labeling, but it may be possible to prepare derivatives with higher retention.

Contribution from the Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan, Faculty of Pharmaceutical Sciences, Kanazawa University, Takaramachi, Kanazawa 920, Japan, and Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Indole Nitrogen–Palladium(II) Bonding. Chemical and Structural Characterization of Palladium(II) Complexes of Alkylindoles and Intermediacy of the 3H-Indole Ring

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The first palladium(II) complexes of alkylindoles (2-methylindole (MI) and 2,5-dimethylindole (DMI)) coordinating through the nitrogen atom in the 3H-indole form have been isolated and characterized by X-ray crystal structure analysis and spectroscopic methods. The complexes [Pd(MI)$_2$Cl$_2$] (1) and [Pd(DMI)$_2$Cl$_2$] (2) were obtained as pale brown crystals from methanol solutions. Both complexes crystallized in the monoclinic space group $P2_1/c$ with $Z = 2$. They have a square-planar structure with two indole molecules coordinating to Pd(II) in the trans geometry with two chloride ions occupying the remaining positions. The indole ring is bound to Pd(II) through the sp^2 nitrogen atom (N(1)) and is nearly perpendicular to the Pd(II) coordination plane. The N(1)–C(2) bond length (1.305 (12) Å) in 1 is much shorter than that found for 2,3-diphenylindole (1.392 (2) Å), and the C(2)–C(3) (1.516 (12) Å) and C(3)–C(3a) (1.469 (15) Å) bonds are nearly equal to single bonds, indicating that the indole ring assumes the 3H-indole form. The ^{1}H NMR spectra of 1 in CDCl$_3$ exhibited CH$_2$ signals at ~3.9 ppm but no C(3) and N(1) proton signals observed for MI, which is in accord with the 3H-indole structure. The ^{13}C NMR spectra in solution and in the solid state further confirmed that the 3H-indole structure with the sp^3-like C(3) is maintained under both conditions. The results establish the coordination of the indole ring through the "pyridine-like" nitrogen and the intermediacy of the 3H-indole structure in the course of reactions catalyzed, e.g., by metal ions having strong affinity toward nitrogen donors.

Introduction

Indole is an electron-rich aromatic ring showing characteristic chemical reactivities and serving as an important constituent of tryptophan and ergot alkaloids and other pharmacologically active natural compounds.[2] It has the greatest hydrophobicity among amino acid side chains,[3] which is suitable for constituting a hydrophobic environment in proteins. Some oligopeptides with a tryptophyl residue recognize apurinic sites in DNA or intercalate into the base pairs by this residue.[4] Because of the enamine nature of the indole ring, 3H-indole forms are often assumed as intermediates in the reactions with electrophiles.[2] While alkali-metal and Grignard derivatives are known to involve essentially ionic metal–nitrogen bonds,[5] the bonding with transition-metal ions is usually achieved by side-chain donor groups such as the amino and carboxylate groups of tryptophan typically exemplified by the structure of a ternary copper(II) complex [Cu(phen)(L-Trp)]$^+$ (phen = 1,10-phenanthroline; Trp = tryptophan).[6] A bidentate bonding with Pd(II) through the nitrogen (N(1)) and carbon (C(2)) has been reported for binuclear complexes with N,C-bridging indole or 3-methylindole, where the N(1)–C(2) double bond with protonation at C(3) has been concluded from ^{1}H NMR spectra.[7] In the course of the studies on the aromatic ring stacking

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and possible metal ion-aromatic ring π-type interactions in ternary Cu(II) and Pd(II) complexes containing aromatic amino acids and diamines, we observed that stabilization of the ternary complexes mainly due to stacking is greatest with tryptophan and its analogues.[8] With these points in mind, we initiated investigations on possible direct Pd(II)–indole ring interactions and their effects on the properties of indoles. We present here the first chemical and structural evidence that alkyl indoles (2-methylindole (MI) and 2,5-dimethylindole (DMI)) reversibly coordinate to Pd(II) through the nitrogen in the 3H-indole form, demonstrating the intermediacy of the 3H-indole ring in the systems involving metal ions with a high affinity for nitrogens.

Experimental Section

Materials. 2-Methylindole (MI) and 2,5-dimethylindole (DMI) were purchased from Aldrich and recrystallized from hexane. Palladium(II) was used as Na_2PdCl_4 obtained from Higuchi.

Synthesis of Pd(II) Complexes. [Pd(MI)$_2$Cl$_2$] (1). MI (0.53 g, 4 mmol) dissolved in methanol was mixed with Na_2PdCl_4 (0.59 g, 2 mmol) in methanol, and the mixture was stirred overnight at room temperature. Pale brown crystals, which separated from the solution, were recrystallized from $CHCl_3$–CH_3OH. Anal. Calcd for $C_{18}H_{18}N_2Cl_2Pd$: C, 49.17; H, 4.12; N, 6.37. Found: C, 48.48; H, 4.02; N, 6.17.

The C(3)-deutero form of **1** was prepared in the same manner in CD_3OD.

[Pd(DMI)$_2$Cl$_2$] (2). This complex was prepared in the manner described above from DMI (0.14 g, 0.96 mmol) and Na_2PdCl_4 (0.14 g, 0.48 mmol) as pale brown crystals, which were recrystallized from $CHCl_3$–CH_3OH. Elemental analysis indicated the presence of one H_2O per complex. Anal. Calcd for $C_{20}H_{22}N_2Cl_2Pd\cdot H_2O$: C, 49.45; H, 4.98; N, 5.77. Found: C, 49.44; H, 4.91; N, 5.64.

Reaction of 1 with Pyridine. To a solution of **1** (0.22 g, 0.5 mmol) in methanol was added pyridine (py) (0.08 g, 1 mmol), and the mixture was stirred for 4 days. Yellow crystals, which separated from the solution, were recrystallized from $CHCl_3$–CH_3OH to give $Pd(py)_2Cl_2$.

Measurements of Spectra. Absorption spectra were recorded for MI, DMI, **1**, and **2** in $CHCl_3$ in the range 245–505 nm with a Union Giken SM-401 recording spectrophotometer. Reflectance spectra were measured for **1** and **2** with a Hitachi 3401 recording spectrophotometer. ^1H NMR spectra were measured for solutions of the complexes and ligands in $CDCl_3$, CD_3OD, or dimethyl-d_6 sulfoxide (DMSO) at 100 and 400 MHz with a JEOL FX-100 or a GX-400 NMR spectrometer, respectively, with TMS as internal standard. The temperature dependence of the spectrum of **1** in $CDCl_3$ was measured at 25–60 °C. ^{13}C NMR spectra were recorded at 100.4 MHz for the solution of **2** in $CDCl_3$ with a JEOL GX-400 NMR spectrometer with TMS as internal standard. ^{13}C-CP/MAS NMR spectra were measured at 67.8 MHz for the crystals of **1** with a JNM-GSH27T NMR spectrometer equipped with a CP/MAS accessory and referenced to external TMS.

X-ray Diffraction Analyses. Crystal data for **1**: $C_{18}H_{18}N_2Cl_2Pd$, M = 439.68, monoclinic, space group $P2_1/c$, a = 8.418 (1) Å, b = 9.310 (1) Å, c = 11.836 (2) Å, β = 97.38 (1)°, V = 919.9 Å^3, Z = 2, D_c = 1.587 g cm^{-3}, λ = 0.71073 Å, μ(Mo Kα) = 11.92 cm^{-1}, crystal dimensions 0.2 × 0.2 × 0.3 mm. Crystal data for **2**: $C_{20}H_{22}N_2Cl_2Pd$, M = 467.74, monoclinic, space group $P2_1/c$, a = 5.803 (3) Å, b = 10.954 (3) Å, c = 15.769 (7) Å, β = 99.62 (4)°, V = 988.3 Å^3, Z = 2, D_c = 1.565 g cm^{-3}, λ = 1.54178 Å, μ(Cu Kα) = 102.4 cm^{-1}, crystal dimensions 0.01 × 0.01 × 0.02 mm. Both diffraction intensities were measured on a Rigaku AFC-5R diffractometer. The intensity data in the ranges 2θ < 60° for **1** and 2θ < 120° for **2** were collected in the ω–2θ scan mode with a 1.2 scan range and a scan rate of 4 min^{-1} for both crystals. In the course of the data collection, three reflections were monitored for every 56 reflections. The intensity data were converted to F_o data in the usual manner. Absorption corrections were applied for both crystals. The standard deviations, $\sigma(F_o)$, were estimated by counting statistics. A total of 1869 and 747 independent reflections for **1** and **2**, respectively, with F_o > $3\sigma(F_o)$ were retained as observed and were used in solving and refining the structures.

The structures were solved by the heavy-atom method. The complete structures were elucidated through the iterative synthesis of Fourier maps and were refined by the full-matrix least-squares method. Several cycles of the refinement including anisotropic thermal parameters were carried out with the weighting scheme w^{-1} = ($\sigma^2(F_o)$ + $(0.023F_o)^2$). Atomic

Table I. Atomic Parameters for Non-Hydrogen Atoms in Pd(MI)$_2$Cl$_2$ (1) with the Estimated Standard Deviations in Parentheses

atom	x	y	z	$B_{eq}/Å^2$
Pd	0.0	0.0	0.0	3.27
Cl	0.0971 (3)	-0.2300 (3)	0.0081 (2)	5.05
N(1)	0.1200 (8)	0.0359 (8)	0.1568 (6)	3.68
C(2)	0.0663 (11)	0.0117 (12)	0.2537 (7)	4.23
C(3)	0.1929 (12)	0.0528 (12)	0.3512 (7)	4.83
C(3a)	0.3242 (12)	0.1049 (11)	0.2914 (7)	4.49
C(4)	0.4742 (14)	0.1600 (13)	0.3283 (9)	5.91
C(5)	0.5701 (13)	0.1982 (14)	0.2493 (11)	6.87
C(6)	0.5233 (14)	0.1814 (16)	0.1330 (11)	6.91
C(7)	0.3725 (12)	0.1286 (13)	0.0952 (9)	5.33
C(7a)	0.2775 (10)	0.0911 (10)	0.1748 (7)	4.00
C(2m)	-0.0910 (13)	-0.0451 (14)	0.2661 (9)	5.87

Table II. Atomic Parameters for Non-Hydrogen Atoms in Pd(DMI)$_2$Cl$_2$ (2) with the Estimated Standard Deviations in Parentheses

atom	x	y	z	$B_{eq}/Å^2$
Pd	0.0	0.5	0.5	3.1
Cl	-0.133 (3)	0.678 (1)	0.5490 (7)	4.6
N(1)	0.017 (6)	0.428 (4)	0.619 (2)	2.6
C(2)	-0.098 (7)	0.348 (5)	0.647 (2)	3.0
C(3)	-0.022 (9)	0.323 (5)	0.745 (3)	4.2
C(3a)	0.190 (8)	0.405 (5)	0.760 (3)	3.3
C(4)	0.352 (8)	0.413 (5)	0.833 (3)	3.5
C(5)	0.525 (8)	0.501 (5)	0.835 (3)	5.3
C(6)	0.561 (9)	0.563 (6)	0.759 (4)	5.6
C(7)	0.393 (9)	0.548 (5)	0.685 (3)	4.3
C(7a)	0.205 (7)	0.464 (4)	0.693 (3)	3.2
C(2m)	-0.298 (9)	0.304 (5)	0.592 (3)	4.8
C(5m)	0.722 (8)	0.530 (3)	0.912 (2)	2.4
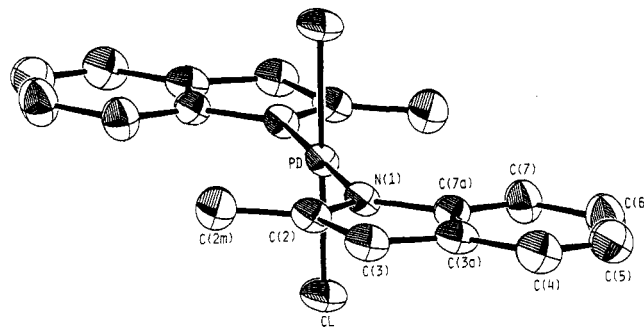
Figure 1. Computer-drawing model for [Pd(MI)$_2$Cl$_2$] (1) showing the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms have been omitted.

scattering factors and anomalous dispersion terms were taken from ref 9. The hydrogen atoms were included as being isotropic in the last cycle; their positions for **1** were obtained from the difference Fourier synthesis and those for **2** were introduced in the calculated positions (C–H = 1.09 Å). The final R and R_w values were 0.068 and 0.076 for **1** and 0.123 and 0.167 for **2**, respectively. The final difference Fourier maps for both crystals did not show any significant feature, with most of the largest peak occurring around the palladium atom. All calculations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY.[10] The final positional and isotropic temperature factors of the non-hydrogen atoms are listed in Tables I and II for **1** and **2**, respectively.

Results and Discussion

Isolation and Structural Determination of 1 and 2. In the absence of strong coordinating groups, the alkylindoles MI and DMI, respectively, reacted with $PdCl_4^{2-}$ to give **1** and **2**, whose compositions indicated that the indoles are bound to Pd(II) as monodentate neutral ligands. The indole NH group is depro-

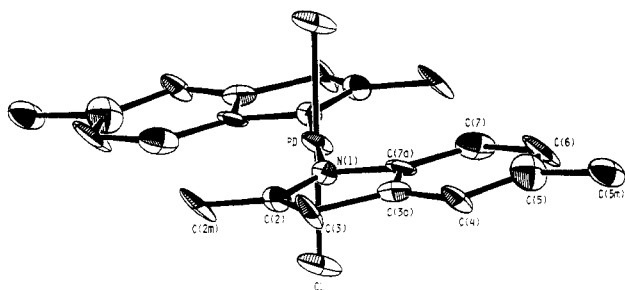(7) Robson, R. *Inorg. Chim. Acta* **1982**, *57*, 71–77.
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Table III. Bond Lengths (Å) and Angles (deg) for Pd(MI)₂Cl₂ (1) with the Estimated Standard Deviations in Parentheses

Bond Lengths			
Pd–Cl	2.290 (3)	Pd–N(1)	2.024 (7)
C(2)–C(3)	1.516 (12)	C(2)–C(2m)	1.451 (15)
C(2)–N(1)	1.305 (12)	C(3)–C(3a)	1.469 (14)
C(3a)–C(4)	1.381 (15)	C(3a)–C(7a)	1.392 (11)
C(4)–C(5)	1.359 (18)	C(5)–C(6)	1.391 (18)
C(6)–C(7)	1.381 (16)	C(7)–C(7a)	1.357 (14)
C(7a)–N(1)	1.412 (11)		

Bond Angles			
Cl–Pd–N(1)	89.0 (2)	C(3)–C(2)–C(2m)	125.2 (8)
C(3)–C(2)–N(1)	109.7 (8)	C(2m)–C(2)–N(1)	125.1 (8)
C(2)–C(3)–C(3a)	102.4 (7)	C(3)–C(3a)–C(4)	133.2 (8)
C(3)–C(3a)–C(7a)	108.2 (8)	C(4)–C(3a)–C(7a)	118.6 (9)
C(3a)–C(4)–C(5)	118.7 (10)	C(4)–C(5)–C(6)	122.3 (11)
C(5)–C(6)–C(7)	119.5 (12)	C(6)–C(7)–C(7a)	117.8 (10)
C(3a)–C(7a)–C(7)	123.2 (8)	C(3a)–C(7a)–N(1)	108.9 (8)
C(7)–C(7a)–N(1)	127.9 (8)	Pd–N(1)–C(2)	126.1 (6)
Pd–N(1)–C(7a)	123.1 (6)	C(2)–N(1)–C(7a)	110.8 (7)

Table IV. Bond Lengths (Å) and Angles (deg) for Pd(DMI)₂Cl₂ (2) with the Estimated Standard Deviations in Parentheses

Bond Lengths			
Pd–Cl	2.28 (1)	Pd–N(1)	2.02 (3)
C(2)–C(3)	1.57 (6)	C(2)–C(2m)	1.41 (6)
C(2)–N(1)	1.22 (6)	C(3)–C(3a)	1.51 (7)
C(3a)–C(4)	1.36 (6)	C(3a)–C(7a)	1.26 (6)
C(4)–C(5)	1.39 (8)	C(5)–C(6)	1.42 (8)
C(5)–C(5m)	1.56 (6)	C(6)–C(7)	1.41 (7)
C(7)–C(7a)	1.45 (7)	C(7a)–N(1)	1.51 (5)

Bond Angles			
Cl–Pd–N(1)	89 (1)	C(3)–C(2)–C(2m)	128 (4)
C(3)–C(2)–N(1)	113 (4)	C(2m)–C(2)–N(1)	118 (4)
C(2)–C(3)–C(3a)	98 (4)	C(3)–C(3a)–C(4)	127 (4)
C(3)–C(3a)–C(7a)	110 (4)	C(4)–C(3a)–C(7a)	123 (5)
C(3a)–C(4)–C(5)	118 (4)	C(4)–C(5)–C(6)	121 (4)

Figure 2. Computer-drawing model for [Pd(DMI)₂Cl₂] (2) showing the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms have been omitted.

Table V. ¹H NMR Spectral Data (400 MHz) for MI and [Pd(MI)₂Cl₂] (1) in CDCl₃

	δ/ppm^a		
proton	MI	[Pd(MI)₂Cl₂]	$\Delta\delta^b/ppm$
NH	7.83 (br)		
CH₃	2.44 (d, J = 1)	3.22 (s)	0.78
		3.29 (s)	0.85
3-H	6.22 (q, J = 1)	3.88	
		3.89	
4-H	7.51 (d, J = 8)	7.39 (d, J = 8)	−0.12
5-H	7.06 (t, d, J = 7, 1)	7.34 (t, J = 7)	0.28
6-H	7.11 (t, d, J = 7, 1)	7.54 (t, J = 8)	0.43
		7.59 (t, J = 7)	0.48
7-H	7.28 (d, d, J = 8, 1)	8.65 (d, J = 8)	1.37
		8.77 (d, J = 8)	1.49

^{a}br = broad; s = singlet; d = doublet; t = triplet; q = quartet. J in Hz. $^b\Delta\delta = \delta_{[Pd(MI)_2Cl_2]} - \delta_{MI}$.

Table VI. Comparison of the ¹³C Chemical Shifts for [Pd(DMI)₂Cl₂] (2) in CDCl₃ at 100.4 MHz and [Pd(MI)₂Cl₂] (1) in the Solid State at 67.8 MHz

δ/ppm		tentative
[Pd(DMI)Cl₂]	[Pd(MI)₂Cl₂]	assignt^a
21.50	21.73	C(2m)
21.63		
30.93		C(5m)
45.57	46.50	C(3)
120.44	119.05	⎫
120.59		⎪
123.45	123.13	⎬ C(4), C(5), C(6), C(7)
126.77	⎫	⎪
126.82	⎬ 128.19	⎪
128.21	⎪	⎭
128.32	⎭	
132.98	134.60	C(3a)
133.04		
152.74	152.86	C(7a)
185.02	188.50	C(2)
185.21		

^{a}Based on refs 17b, 18, and 19.

tonated to form ionic bonds with alkali metals and Grignard reagents[5] but not with transition metals, so that isolation of **1** and **2** suggested possible coordination of the indole nitrogen in the 3*H*-indole form. X-ray crystal structure determinations were carried out for **1** and **2**, and a satisfactory refinement has been attained for **1** with a final *R* factor of 0.068. Because of the small crystal size, the *R* value for **2** was less satisfactory (0.123). The crystal water molecules indicated by the elemental analysis for **2** were not detected by the X-ray analysis.

Structures of Complexes. The molecular structure of **1** is shown in Figure 1 together with the atomic numbering scheme. It reveals that two molecules of MI coordinate to Pd(II) in the trans geometry with two chloride ions occupying the remaining coordination sites to complete the square-planar structure. Each indole ring is bound to Pd(II) through the N(1) atom and is nearly perpendicular to the PdN₂Cl₂ coordination plane. Selected bond lengths and angles are presented in Table III. The Pd(II)–N(1) and Pd(II)–Cl bond lengths, 2.024 (7) and 2.290 (3) Å, respectively, are comparable, e.g., with those of 6,6′-disubstituted 2,2′-bipyridine complexes (2.02–2.06 and 2.28–2.30 Å, respectively).[11] The former is in the range generally observed for Pd(II) complexes with nitrogen ligands (1.95–2.10 Å)[12] and the latter is close to the values 2.25–2.29 Å reported for Pd(II)–Cl bonds.[13] The structure is similar to that revealed for *trans*-bis(2-aminopyridine)dichloropalladium(II) with the same Pd(II)–N bond length (2.024 (4) Å).[14] The angles around N(1) indicate that the bonding is of the sp² type with no proton on N(1). Most interestingly the N(1)–C(2) bond (1.305 (12) Å) is shorter than

the N(1)–C(7a) bond (1.412 (11) Å), and the C(2)–C(3) (1.516 (12) Å) and C(3)–C(3a) (1.469 (15) Å) bonds are nearly equal to single bonds. This is evident from comparison with the bond distances reported for 2,3-diphenylindole,[15] i.e., 1.392 (2), 1.375 (3), 1.438 (3), and 1.373 (2) Å for N(1)–C(2), C(2)–C(3), C(3)–C(3a), and N(1)–C(7a) bonds, respectively. Two protons were detected at the C(3) atom in the difference Fourier map, further substantiating that the indole ring assumes the 3*H*-indole form. The N(1) and C(3) atoms are each slightly displaced (0.02 Å) to the opposite sides from the mean plane including the 2-methyl group. As the ring is calculated to be planar to within 0.01 Å when these atoms are excluded, the geometry around C(3)

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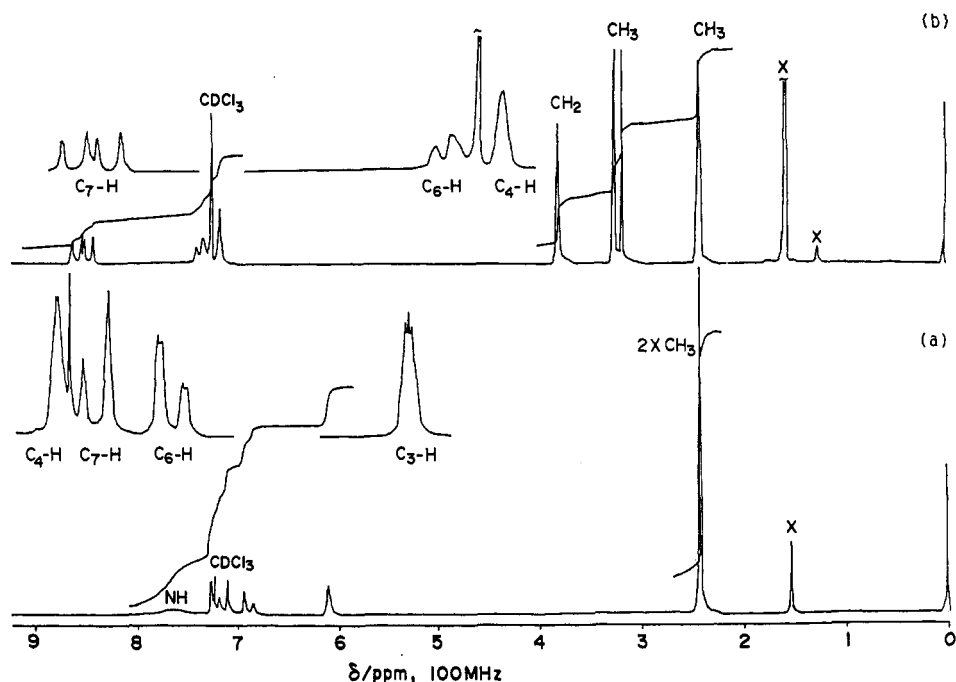(15) Schmelter, B.; Bradaczek, H.; Luger, P. *Acta Crystallogr.* **1973**, *B29*, 971–976.

Figure 3. ¹H NMR spectra (100 MHz) of DMI (a) and 2 (b) in CDCl₃. Measured with a JEOL FX-100 NMR spectrometer with TMS as an internal standard.

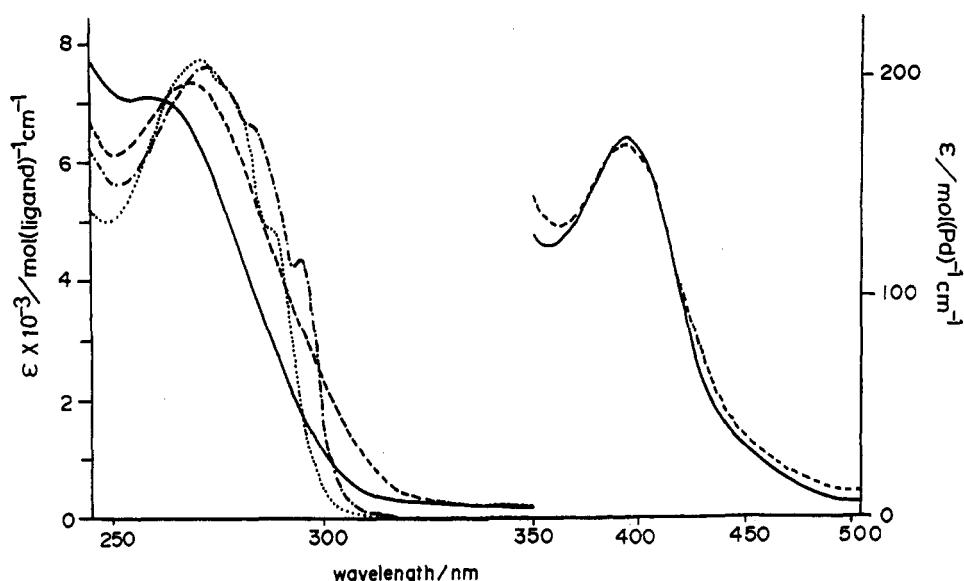**Figure 4.** Absorption spectra of MI (···), 1 (—), DMI (–·–), and 2 (--) in CHCl₃.

may be considered to be tetrahedral.

The molecular structure of 2 is depicted in Figure 2 with the atomic numbering scheme. Although the R value for 2 was not improved further and detailed discussions on the structure may not be appropriate, the structure obtained at this level establishes that the indole ring coordinates to Pd(II) through N(1) and not C(3) whose bonding could otherwise be suspected because of its high electron density.[16] Bond lengths and angles for this complex are comparable with those for 1 (Table IV).

Spectroscopic Characterization. In perfect agreement with the structure in the solid state, complex 1 dissolved in CDCl₃ exhibited a ¹H NMR spectrum with CH_2 signals at 3.88 and 3.89 ppm (2 H). These are assigned to the C(3) protons because no signals are observed at ~6.2 and ~7.8 ppm corresponding to the C(3) and the N(1) proton of MI, respectively. The spectral data and assignments based on the literature[17] are given in Table V.

Appearance of a new C(3) proton signal upon N,C-bridging to Pd(II) has been observed previously.[7] The signal due to the CH_3 group shifted downfield from 2.44 ppm to 3.22 and 3.29 ppm upon coordination. This is obvious in the spectrum for 2 shown in Figure 3, where the 2-methyl signal only is shifted from 2.42 ppm to 3.17 and 3.24 ppm. Two signals each for the CH_2 and CH_3 protons, two triplets at 7.54–7.59 ppm for the C(6) proton, and two doublets at 8.65–8.77 ppm (Table V) suggest that the two coordinated MI molecules are under slightly different conditions, which could result from restricted rotation around the Pd(II)–N bonds or from buckling at the C(3) atom. The signals were independent of temperature in the range 25–60 °C. The ¹³C NMR spectral data for 2 in CDCl₃ and 1 in the solid state (Table VI) show an excellent correspondence with each other, indicating that the structures in both states are the same. Spectral assignment based on recent papers[17b,18] and our data[19] reveals that C(2) (188.5 ppm)

(16) Coulson, C. A.; Streitwieser, Jr., A.; Poole, M. D.; Braumann, J. K. *Dictionary of π-Electron Calculation*; W. H. Freeman: San Francisco, CA, 1965.

(17) (a) Black, P. J.; Heffernan, M. L. *Aust. J. Chem.* **1965**, *18*, 353–361. (b) Joseph-Nathan, P.; del Rio, R. E.; Morales-Rios, M. S. *Heterocycles* **1988**, *27*, 377–383.

is analogous to an imine carbon and more importantly that C(3) (~47 ppm) is an sp³-like carbon, which is different from that in a normal indole ring showing signals at ~100 ppm.[17b,18]

The spectrum of **1** isolated from CD₃OD exhibited almost no CH₂ signal (0.3 H), implying that the C(3) position is deuterated probably during the indole ⇌ 3H-indole interconversion with proton migration. Addition of pyridine to a methanol solution of **1** gave Pd(py)₂Cl₂ as crystals, whereas with added dimethyl-d_6 sulfoxide the NMR spectrum of **1** in CDCl₃ changed to that of free MI in 24 h. The results indicate that the Pd(II)–indole bond is weak and that MI resumes its normal indole structure upon dissociation as shown below:
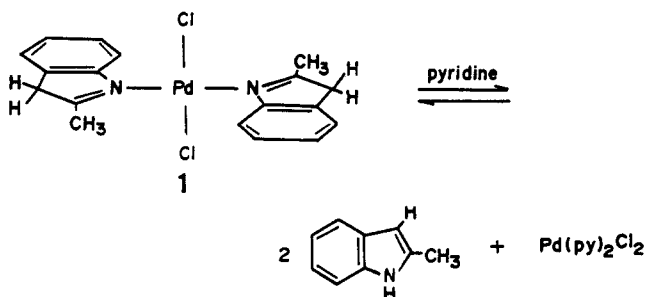
Transformation of the indole ring is also supported by the ultraviolet absorption spectra of **1** and **2** in CHCl₃ (Figure 4), where the indole peaks at ~270 and 280–295 nm are replaced with a broad band centered at a shorter wavelength without the

characteristic shoulder peaks.[20] They exhibited a peak assignable to the d–d transition at 395 nm (ϵ = 170 M⁻¹ cm⁻¹), which corresponds with the reflectance spectra of **1** and **2** showing maxima at 395 and 456–458 nm.

Concluding Remarks. The present findings offer evidence for the weak coordinating ability of the indole nitrogen and the intermediacy of the 3H-indole ring probably formed in the metal ion catalyzed reactions, and may explain the reactivities of indoles in such reactions.[2] In hydrophobic environments where the Lewis acidity of metal ions is stronger than in aqueous media, metal ions such as Cu(II) having a high affinity for nitrogens may be able to interact with the indole nitrogen in the manner observed for Pd(II), and this could be a possibility in biological systems.

(18) Morales-Rios, M. S.; Espineira, J.; Joseph-Nathan, P. *Magn. Reson. Chem.* **1987**, *25*, 377–395.

(19) The assignment of the indole ring (C(2), C(3a), and C(7a)) and methyl (C(2m)) signals was further supported by the ¹³C NMR spectrum obtained by the dipolar dephasing method.

(20) The ternary system containing Pd(II), L-glutamate, and tryptamine at pH 5.8 exhibited strong absorption peaks at 325 and 393 nm with ϵ = 2400 and 1920 M(Pd)⁻¹ cm⁻¹, respectively, and unusually intense circular dichroism peaks at 415 nm ($\Delta\epsilon$ = 4.55 M(Pd)⁻¹ cm⁻¹) and at 280 nm ($\Delta\epsilon$ = –5.33 M(Pd)⁻¹ cm⁻¹) corresponding to the indole ring absorption. A similar anomaly was also observed for 3-indoleacetate (unpublished results). Both could be related to the process of 3H-indole formation, its deprotonation, and/or metal binding at C(3) in 3H-indole.

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Spectroelectrochemical Characterization of Nitridochromium(V) Porphyrins and Their Reactivity with Substituted Acetic Anhydrides

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The redox reactivity of a variety of nitridochromium(V) porphyrins was investigated by cyclic and differential pulse voltammetry as well as electronic and EPR spectroelectrochemical techniques. Each complex investigated underwent two single-electron reversible oxidation and two single-electron reversible reduction reactions at a Pt electrode in several nonaqueous solvents on the cyclic voltammetric time scale. The site of each electron-transfer reaction was centered on the porphyrin ring. This compares with the previously documented redox behavior of nitridomanganese(V) porphyrins but contrasts with the general redox behavior of chromium porphyrins. The reaction of nitridochromium(V) porphyrins with substituted acetic anhydrides produced (acylimido)chromium porphyrins at rates at least 1 order of magnitude faster than the corresponding nitridomanganese porphyrins. However, the subsequent transfer of the acylimido group from the Cr center to olefins was not observed for the complexes and olefins investigated herein. A spectroelectrochemical investigation revealed that the (acylimido)chromium porphyrins are best described as Cr(IV) cation radicals. This is in contrast to the corresponding (acylimido)manganese porphyrin complexes, which possess Mn(V) centers, and may account for the unreactivity of the (acylimido)chromium porphyrins with olefins.

In recent reports, we[1–3] and others[4–14] have detailed the unusual redox and functionalized nitrogen atom transfer reactivity of

nitridomanganese porphyrins. Original interest in nitridomanganese porphyrins was spawned from the observation[4] that while high-valent manganese porphyrins are capable of oxidizing water, the high-valent nitridomanganese porphyrins are readily

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