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Reaction of 2-(Phenylazo)aniline with Na_2PdCl_4: Formation of a 2-(Phenylazo)imino Complex of Bivalent Palladium

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Transition-metal chelates incorporating azo ligands have drawn much attention in recent years. Among these, complexes of arylazooximes,[1] arylazophenols,[2] arylazoimines,[3] alkylthioazobenzenes,[4] and sulfenylazobenzenes[5] are some notable examples. Interesting coordination modes and molecular structures, C−H bond activation, potential sites of facile electron transfer, and interesting electronic structure due to the presence of low-lying π^* orbitals are some of the important properties exhibited by these. Herein we scrutinize the synthesis and structure of 2-(phenylazo)aniline (H_2L) and bis chelate $Pd^{II}(HL)_2$, wherein the ligand displays predominant azoimine character due to delocalization.

Experimental Section

The solvents used in the reactions were of reagent grade obtained from E. Merck, Calcutta, India, and were dried by reported procedures.[6] *o*-Phenylenediamine was recrystallized from ethanol−water (2/1 v/v) before use. Palladium chloride was purchased from Arrora Matthey, Calcutta, India. Disodium tetrachloropalladate was prepared by a reported procedure.[6] Microanalyses (C, H, N) were done on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Perkin-Elmer 783 spectrometer with the sample prepared as KBr pellets. Electronic spectra were recorded on a Hitachi U-2001 spectrophotometer. ^1H NMR data were collected from Bruker AC-200 and Bruker Avance DPX 300 NMR spectrometers in $CDCl_3$. $SiMe_4$ was used as the internal standard.

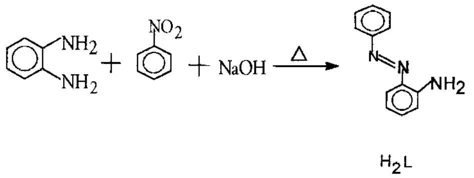
2-(Phenylazo)aniline (H_2L). *o*-Phenylenediamine (2 g, 18.5 mmol), nitrobenzene (2.28 g, 18.5 mmol), and sodium hydroxide (0.74 g, 18.5 mmol) were mixed and triturated followed by heating at 70 °C with constant scratching for 20 min. The dark pasty mass thus obtained was cooled to room temperature and extracted with benzene. The benzene-soluble part was subjected to column chromatography on a silica gel (60−120 mesh) column (2 cm × 45 cm). The first band that was eluted by a benzene−petroleum ether mixture (5/95 v/v) was collected, and upon evaporation of solvent, the pure 2-(phenylazo)aniline (H_2L) was obtained: yield 1.824 g (50%). ^1H NMR ($CDCl_3$): δ 5.9 (s, NH_2); 6.7 (d, C6−H); 6.8 (t, C4−H); 7.2 (t, C5−H); 7.4 (t, C10−H); 7.5 (t, C9−H and C11−H); 7.8 (d, C8−H, C12−H and C3−H). IR (KBr; cm^{-1}): 3456, 3382 (ν_{NH_2}); 1592 ($\nu_{C=C}$); 1461 ($\nu_{N=N}$); 1230 (ν_{C-N}). UV−vis (CH_2Cl_2; λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$)): 416 (8963), 313 (14 455), 243 (14 791). Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.09; H, 5.58; N, 21.32. Found: C, 73.19; H, 5.52; N, 21.42.

[$Pd^{II}(HL)_2$]. To an aqueous solution of Na_2PdCl_4 (0.374 g, 1.27 mmol) in a beaker was added a benzene solution of H_2L (0.5 g, 2.54 mmol). The mixture was stirred for 3 h. The organic layer gradually turned green. The green benzene solution was separated from the aqueous layer and subjected to column chromatography on a silica gel (60−120 mesh) column. A green band was eluted with benzene, and upon evaporation of the solvent, pure $Pd^{II}(HL)_2$ was obtained: yield 0.949 g (75%). ^1H NMR ($CDCl_3$): δ 4.9 (s, N−H); 6.0 (d, C6−H); 6.3 (t, C4−H); 6.9 (t, C5−H). IR (KBr; cm^{-1}): 3332 (ν_{NH}); 1602 ($\nu_{C=N}$); 1342 ($\nu_{N=N}$). UV−vis (CH_2Cl_2; λ_{max}, nm; (ϵ, $M^{-1}cm^{-1}$)): 628 (9327), 387 (9826), 333 (24 101), 262 (94 695). Anal. Calcd for $PdC_{24}H_{20}N_6$: C, 57.78; H, 4.01; N, 16.85. Found: C, 57.83; H, 4.08; N, 16.88.

X-ray Crystallography. Crystals of $Pd^{II}(HL)_2$ were grown by diffusion of hexane into benzene solution at 25 °C. The size of the crystal suitable for X-ray studies was 0.48 × 0.32 × 0.20 mm^3. The cell parameters were determined by least-squares fits of 25 machine-centered reflections ($2\theta = 15-25°$). Data were collected by the ω-scan technique on a Enraf-Nonius CAMX-3 diffractometer with Mo Kα radiation monochromated by a graphite crystal. No absorption correction was performed. Crystal data were collected in Table 1. The structure solution was carried out by direct methods with the SHELXS-90 program. Full-matrix least-squares refinements were performed using the SHELX-97 program (PC version). All non-hydrogen atoms were refined anisotropically using reflections with $I > 2\sigma(I)$. Hydrogen atoms were included at the calculated position.

Results and Discussion

Synthesis and Characterization. An equimolar mixture of *o*-phenylenediamine, nitrobenzene, and sodium hydroxide was titurated and heated. Workup of the reaction mixture afforded orange-red 2-(phenylazo)aniline (H_2L; eq 1).



H_2L

(1)

The diamagnetic bis complex $Pd^{II}(HL)_2$ was isolated by reacting H_2L and Na_2PdCl_4 in a 2/1 ratio in a benzene−water mixture. The green complex shows an absorption at 630 nm for the MLCT transition. On coordination the ligand undergoes deprotonation to HL^-, as is consistent with IR and ^1H NMR data.

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Table 1. Crystallographic Data for Pd^{II}(HL)$_2$

chem formula	$C_{24}H_{20}N_6Pd$	Z	2
fw	498.86	T, °C	20
space group	$P2_1/n$	λ, Å	0.710 73
a, Å	6.2220(11)	ρ_{calcd}, Mg/m^3	1.626
b, Å	14.8034(19)	μ, mm^{-1}	0.935
c, Å	11.1229(15)	R,^{a} %	2.43
β, deg	95.877(13)	R_w,^{b} %	6.50
V, Å^3	1019.1(3)	GOF^c	1.095

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]$; $w^{-1} = \sigma^2(|F_o| + g|F_o|)^2$. ^{c} The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$ where n_o and n_v denote the numbers of data and variables, respectively.

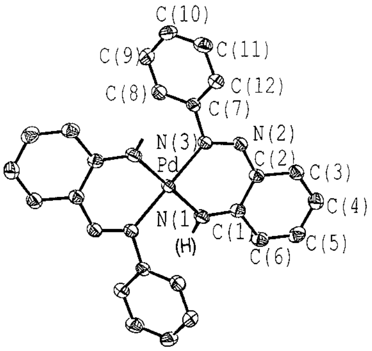

Figure 1. ORTEP plot of Pd^{II}(HL)$_2$ with atom-numbering scheme. Hydrogen atoms, except that on N1, are omitted for clarity.

The free H_2L ligand display symmetric and asymmetric ν_{NH_2} bands at 3450 and 3370 cm^{-1}. In contrast, Pd^{II}(HL)$_2$ shows a sharp single stretch at 3330 cm^{-1} characteristic of the NH function.[1a] $\nu_{N=N}$ of Pd^{II}(HL)$_2$ is shifted to lower frequency (1340 cm^{-1}) compared to $\nu_{N=N}$ of H_2L (1460 cm^{-1}). In Pd^{II}(HL)$_2$, a strong band is observed at 1600 cm^{-1} which is absent in H_2L. This is assigned to $\nu_{C=N}$, consistent with crystallographic results (vide infra).

In the ^{1}H NMR spectrum of H_2L the relatively broad band of the amino proton occurs at 5.9 ppm. On the other hand, in Pd^{II}(HL)$_2$ the signal is shifted to 4.9 ppm and its integration corresponds to two protons of the equivalent NH groups.

X-ray Structure. The X-ray structure of Pd^{II}(HL)$_2$ was determined. A perspective view of the molecule and the atom-numbering scheme are shown in Figure 1. Selected bond parameters are collected in Table 2. The 2-(phenylazo)aniline ligand binds in a bidentate (N,N) fashion. One ligand is symmetry equivalent to the other, held in a trans position. Palladium occupies a special position on a 2-fold axis of symmetry, and the PdN_4 coordination sphere is planar, consistent with metal bivalency and monoionized nature of the ligands. The chelate ring is, however, not planar. The fragment containing N2, C2, C3, C4, C5, C6, and C1 is satisfactorily planar (mean deviation 0.05 Å), and its dihedral angle with the PdN_4 plane is 24.5°. The dihedral angle between the pendant phenyl ring and the PdN_4 plane is 62.61°.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Pd^{II}(HL)$_2$

Distances			
Pd−N(1)	1.984(2)	C(1)−C(2)	1.438(3)
Pd−N(3)	2.0272(19)	C(1)−C(6)	1.435(3)
N(1)−C(1)	1.322(3)	C(2)−C(3)	1.423(4)
N(2)−N(3)	1.286(3)	C(3)−C(4)	1.360(4)
N(2)−C(2)	1.358(3)	C(4)−C(5)	1.410(4)
N(3)−C(7)	1.440(3)	C(5)−C(6)	1.350(4)

Angles			
N(1)−Pd−N(3)#1	93.69(8)	C(1)−N(1)−Pd	127.45(17)
N(1)−Pd−N(3)	86.31(8)	N(2)−N(3)−Pd	128.96(16)
N(3)#1−Pd−N(3)	180.0	N(2)−C(2)−C(1)	126.10(2)

In the six-membered chelate ring, the N1−C1 length (1.322(3) Å) is considerably shorter than the C−N single bond (N3−C7 = 1.440(3) Å) in the same molecule and is similar to the typical N-coordinated C═N (1.323(19) Å).[7] The N−N distance of azo nitrogens in the chelate ring (1.286(3) Å) is within the range of coordinated azo lengths.[1] Thus, it is reasonable to infer that Pd^{II}(HL)$_2$ is an azoimine bis chelate obtained from an azoaniline ligand precursor. Though the C2−N2 length (1.358(3) Å) is not as short as the imine C−N length, it is considerably shorter than the C−N single bond in the same molecule (vide supra), suggesting a bond order between a single and a double bond. The coordination mode of HL$^-$ is similar to one of the coordination modes of arylazophenols,[8] but unlike arylazophenols the phenyl ring which is adjacent to the chelate ring is distorted with two short (∼1.355 Å) and four long (∼1.427 Å) C−C lengths. This type of distortion in the phenyl ring as a consequence of delocalization due to formation of chelates has been reported in the cases of *o*-arylenedimines[9] and *o*-arylenedioxolenes,[10] where the chelate rings are five-membered,[9,10] unlike the present six-membered chelate.

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Supporting Information Available: ^{1}H NMR and IR spectra of H_2L and Pd^{II}(HL)$_2$ and X-ray crystallographic files in CIF format for the structure determination of Pd^{II}(HL)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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