

Silver and Palladium Complexes of Some Aromatic Azo and Azoxy Compounds.

John J. Porter, Joel Luke Murray, and Kenneth B. Takvorian

Department of Textiles, Clemson University, Clemson, South Carolina 29631

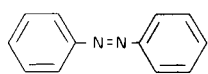
Received September 21, 1972

The complexing ability of derivatives of azobenzene (I) is well known (1) and responsible for the production of a wide variety of dyestuffs and analytical chemicals. While the azo group generally participates in the coordination, the determination of the degree of its interaction is complicated by other functional groups which are also coordinated with the transition metal. In a previous publication (2), we reported the preparation of the silver and palladium complexes of benzo[*c*]cinnoline (II) and proposed that these results might be used to explain the electron donor properties of azobenzene. We are now reporting the preparation of some additional complexes with ligands containing the azo group.

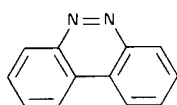
The silver and palladium complexes of pyridazine (III), phthalazine (IV), dibenzo[*c,g*]-1,2-diazocine (V), 2,7-dimethyl-4,5,9,10-tetraazapyrene (VI) were prepared and the analytical data for these compounds are shown in Table I. Also shown are the data for II and 3,8-dimethyl-dipyrido[3,2-*b*:2',3'-*d*]pyridazine (VIII) from a previous communication and the data for some *N*-oxide derivatives of the above azo compounds.

It is apparent from the data obtained with I, II, III, IV, V, VII that the ease of the complex formation of the ligand is a function of its basic character. Since the planar benzo[*c*]cinnoline (II) coordinates readily with silver and palladium and the essentially planar (3) *trans*-azobenzene (I) does not, resonance stabilization of the coordinated ligand must be the major factor accounting for the observed difference in metal interaction and absence of any rearrangement to carbon-metal bond compounds (4). The importance of this type of stabilization has been shown for the protonation of *cis* and *trans*-azobenzene derivatives by Collins and Jaffe (3). In agreement with this interpretation III and IV gave rapid, well-defined reactions with both metals.

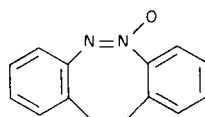
The results reported by Popp and coworkers (5) with dibenzo[*c,f*]-1,2-diazepine (VII) are included in Table I.



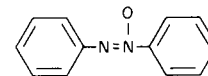
I



II



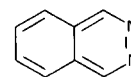
V



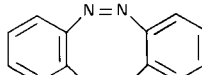
XII



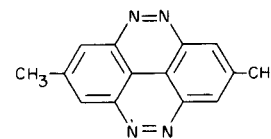
III



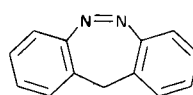
IV



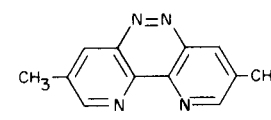
V



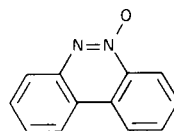
VI



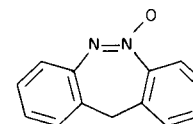
VII



VIII



IX



X

TABLE I
Analytical Data for Silver and Palladium Complexes

Organic Ligand	pK _a	Metal Salt	Color	M.p., °C	Ligand to Metal Ratio	Analysis Calculated			Analysis Found						
						H	N	Metal	C	H	N	Metal			
I. Azobenzene	-1.6 <i>cis</i> (a) -2.9 <i>trans</i> (a)	AgNO ₃ PdCl ₂	No Reaction (b) No Reaction (b)												
II. Benzo[<i>c</i>]cinnoline	1.8 (a)	AgNO ₃ PdCl ₂	Yellow Yellow	320 dec. 320 dec.	1:1 2:1	41.25 53.60	2.29 2.98	12.02 10.42	30.62 19.80	13.20	41.95 54.69	2.26 2.98	11.61 10.40	30.57 19.18	11.98
III. Pyridazine	2.33 (c)	AgNO ₃ PdCl ₂	L. Yellow L. Yellow	202 dec. 320 dec.	1:1 2:1	19.30 28.44	1.60 2.34	16.70 16.50	43.10 31.70	21.02	19.49 28.64	1.75 2.49	16.35 16.15	41.07 31.75	21.09
IV. Phthalazine	3.47 (c)	AgNO ₃ PdCl ₂	L. Yellow L. Yellow	210 dec. 320 dec.	1:1 1:1	32.00 31.26	2.00 1.95	14.00 9.14			32.06 29.80	2.29 2.26	13.81 8.72		
V. Dibenzol[<i>c,g</i>] [1,2] diazocine	-3.1 (d)	AgNO ₃ PdCl ₂	No Reaction (b) Yellow	320	3:2	52.98	3.97	9.39			51.81	3.97	8.81		
VI. 2,7-Dimethyl-4,5,9,10-tetraazapyrene		AgNO ₃ PdCl ₂	Orange Orange	320 dec. 320	1:1 1:1	29.26 40.77	1.74 2.43	14.63 13.59	37.6		29.23 41.25	1.72 2.28	14.84 14.56		
VII. Dibenzol[<i>c,f</i>] [1,2] diazepine (e)		AgNO ₃ Pd(NO ₃) ₂		245 274	1:1 2:1										
VIII. 3,8-Dimethyldipyrido[3,2- <i>b</i> :2',3'- <i>d</i>]pyridazine		AgNO ₃ Pd(NO ₃) ₂	Yellow Yellow	320 320	4:3 1:1	42.64 37.16	2.96 2.58	19.70 14.46	24.02 27.46	18.33	42.93 37.61	3.14 2.77	19.22 14.76	24.06 26.70	15.75
IX. Benzo[<i>c</i>]cinnoline <i>N</i> -oxide		AgNO ₃ Pd(NO ₃) ₂	L. Yellow Yellow	195 295 dec.	2:1 2:1	51.33 50.61	2.85 2.81	12.47 9.84	19.09 18.63		51.09 51.73	2.97 3.41	12.27 9.94	19.39 19.12	
X. 11- <i>H</i> -Dibenzo[<i>c,f</i>] [1,2] diazepine <i>N</i> -oxide		AgNO ₃ PdCl ₂	No Reaction No Reaction												
XI. Dibenzo[<i>c,g</i>] [1,2] diazocine <i>N</i> -oxide		AgNO ₃ PdCl ₂	No Reaction (b) L. Yellow	293 dec.	3:2	49.12	3.50	8.18	20.66	13.84	50.94	3.71	8.37	20.92	13.44
XII. Azoxybenzene	6.45 (f)	AgNO ₃ PdCl ₂	No Reaction (b) No Reaction (b)												

(a) G. E. Lewis, *J. Org. Chem.*, **25**, 2193 (1960). (b) No significant reaction was observed in eight hours when methanol, ethanol, or dilute hydrochloric acid were used as solvents. (c) H. C. Brown, D. H. McDaniel, O. Haflinger, E. A. Braude, and F. C. Machod, "Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, pp. 594, 634. (d) F. Gerson, E. Heilbronner, A. van Veen, and B. M. Wepster, *Helv. Chimica Acta*, **43**, 1889 (1960). (e) See reference 5. (f) See reference 6.

The diazepine VII readily forms compounds with silver and palladium. When an ethylene bridge is placed between the *ortho* positions of the two benzene rings as is the case with dibenzo[*c,g*]-1,2-diazocine (V), no complex is isolated with silver nitrate and palladium chloride coordinated only after several hours. This indicates that I and V are comparable as electron pair donors which is in agreement with the pK_a values reported for the two compounds in Table I. In support of this, the ir spectra of all of the complexes were very similar to that of the ligand. Sharp and coworkers (6) have reported that the ir spectra of the silver perchlorate complex of *trans*-azobenzene, which they were able to form in ether, was very similar to that of the ligand. If much interaction was occurring with the aromatic system we would expect major changes to appear in the visible and ir spectra. This has been observed by Cope and Sickman (4) who, after allowing palladium chloride and azobenzene to react for several days in water-dioxane, isolated a maroon complex with different spectral properties from that of the ligand. In their case, the palladium was later shown to be σ -bonded (7) to one of the aromatic rings in addition to the azo group. Our results coincide more with those obtained by Sharp where coordination compounds were isolated with the azo group acting as the electron pair donor.

A different aromatic system, 3,8-dimethyldipyrido-[3,2-*b*:2',3'-*d*]pyridazine reported previously (2) readily formed complexes with palladium and silver salts. The ligand VIII gave the same results with silver nitrate in neutral solution. The absence of any color change or reaction of VIII with common transition metals was surprising in view of the similarity of its structure to 1,10-phenanthroline. The palladium complex of VIII was insoluble in boiling dimethyl formamide and nitrobenzene. This fact and the metal to ligand ratio (which was reproducible) would be expected of a polymeric complex of the bidentate ligand. The insolubility, in such solvents as hot dimethylformamide, of practically all complexes reported prevented further investigation for additional structure information.

In the cases presented in this paper, better coordination occurred when the nonbonding electrons were in a *cis* configuration. This would naturally favor simultaneous interaction of the metal with both *p*-orbitals and has been proposed to account for the increased basicity of *cis* over *trans*-azobenzene (6). In spite of this attempts to prepare complexes of *cis*-azobenzene were unsuccessful. When the rate of complex formation is slow the *cis*-azobenzene can rearrange to give the known *trans* complex (6) or react further to give more complex aromatic substitution products (7).

N-Oxide Complexes.

The ir and visible spectra of the azoxy metal complexes were comparable to that of the ligand. For this reason it seems logical that simple coordination compounds were formed. In this case, however, two different possibilities exist for coordination with the metal. The oxygen atom and one nitrogen atom both have unpaired electrons. In a related case involving the acid-base equilibria of azoxybenzene protonation has been proposed to occur on the oxygen atom (8). The argument seems valid and even more applicable to the larger metal ions. Thus the main criterion determining the ease of coordination of IX is the basic character of the unpaired electrons on oxygen and not the interaction of the metal with the π electrons of the aromatic system.

EXPERIMENTAL

General.

Analytical reagents were used for all preparations. Ir spectra were measured on a Perkin-Elmer Model 337 Infracord Spectrophotometer and nmr spectra on a Varian A-60 spectrometer. Melting points, uncorrected, were determined with a Fisher-Johns Melting Point Apparatus. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee and Alfred Bernhardt Laboratories, Max-Planck-Institute, West Germany.

Silver Complex Preparation.

In all cases except for VI, the following procedure was used for complex preparation. A solution (30 ml.) of the ligand (0.2 to 0.5 g.) was mixed with a nitric acid (5-10%) solution (30 ml.) of the metal ion at or near ambient temperature. The mixture was stirred for approximately two hours and filtered. The precipitates were washed first with dilute nitric acid and then with a small portion (50 ml.) of ethanol. The solid was dried in a desiccator and stored in the dark.

For compound VI, glacial acetic acid was used for dissolving both the ligand and silver nitrate. A warm solution (40°) of the ligand, VI, and salt were mixed, yielding a yellow precipitate. The precipitate was filtered, washed with warm glacial acetic acid and dried under high vacuum.

Palladium Complex Preparation.

Essentially the same procedure was followed as described for the silver complex preparation except hydrochloric acid (5-10%) was used as the solvent medium for the ligand and palladium(II) chloride. Solutions of the ligand and salt were mixed at room temperature, stirred for approximately two hours, filtered, and washed with 10% hydrochloric acid followed with ethanol (50 ml.).

For compound VI, concentrated hydrochloric acid (10 ml.) was required to dissolve the ligand and was mixed with a concentrated hydrochloric acid (10 ml.) solution of palladium chloride. After stirring the solution a few minutes, water (40 ml.) was slowly added causing a yellow precipitate to form. The precipitate was filtered, washed with water and absolute ethanol.

Preparation of Ligands.

Azobenzene (I), azoxybenzene (XII), and benzo[*c*]cinnoline

(II) were purchased from commercial suppliers and recrystallized when melting points indicated the need.

Phthalazine (IV) was prepared by the method of Gabriel and Muller (9).

Dibenzo[*c,g*]-1,2-diazocine (VII) was prepared by the method of Lowrie (10) and after recrystallization from petroleum ether had a melting point of 111°.

Dibenzo[*c,g*]-1,2-diazocine *N*-oxide (XI) was prepared from the diazocine (2.08 g.) by oxidation with a 40% aqueous solution of peracetic acid (30 ml.). The mixture was stirred for 4 hours at room temperature, poured into cold water (150 ml.) and recrystallized from acetic acid (70%). The *N*-oxide obtained melted at 154°.

Anal. Calcd. for C₁₄H₈N₂O: C, 75.00; H, 5.35; N, 12.50. Found: C, 74.89; H, 5.58; N, 12.37.

Benzo[*c*]cinnoline *N*-oxide (IX) was prepared from benzo[*c*]cinnoline (II) by the standard oxidation (11) with peracetic acid which was described above for XI. The product had a melting point of 139° (lit. (12) 139°).

2,7-Dimethyl-4,5,9,10-tetraazapyrene (VI) was prepared by first coupling 1-chloro-4-methyl-2,6-dinitrobenzene (20 g.) with activated copper powder (20 g.) in dimethyl formamide (30 ml.) which had been dried over anhydrous magnesium sulfate, at 150° for four hours. The chlorobenzene derivative was added to the dimethyl formamide and the solution heated to 150°. Copper powder was added over a 30 minute period and the mixture maintained at 150° for four hours total time. Dimethyl formamide (75 ml.) was then added and the mixture was filtered hot to remove copper and the filtrate was poured over ice (300 g.) and concentrated ammonium hydroxide (100 ml.). The solid product was dissolved in a hot mixture of ethanol (270 ml.) and dimethyl formamide (30 ml.), treated with activated carbon and cooled to yield 7.5 g. of yellow crystals melting at 260-262° and shown to be the tetranitro compound.

Anal. Calcd. for C₁₄H₁₀N₄O₈: C, 46.42; H, 2.78; N, 15.47. Found: C, 46.28; H, 3.11; N, 15.52.

The nmr spectra showed two peaks having absorption at 504 and 152 cps (τ 1.60 and 7.46) respectively. The area ratio obtained from integration was 1 (504):1.5 (152).

The 4,4'-dimethyl-2,6,2',6'-tetranitro-1,1'-biphenyl (5.2 g.) isolated in the above reaction was reduced with hydrogen by a method described by Stetter and Schwartz (13) using a palladium on carbon (0.4 g.) catalyst in absolute ethanol (75 ml.) containing sodium hydroxide (0.4 g.). The hydrogen (2600 ml.) was added at

room temperature and the solution cooled to 0° and filtered. The solid residue was extracted with boiling dimethylsulfoxide (50 ml.) and the extract poured over ice (200 g.) yielding a brownish product. The product was sublimed at 350° to give orange crystals which had a decomposition point of 275°.

Anal. Calcd. for C₁₄H₁₀N₄: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.74; H, 4.54; N, 23.90.

The low solubility of the compound in available solvents prevented nmr analysis.

Acknowledgement.

We wish to express our thanks to the Faculty Basic Research Committee for partial support of this work. Thanks are also due to Dr. J. C. Fanning for helpful discussions while preparing the manuscript.

REFERENCES

- (1) H. Baumann and H. R. Hensel, *Fortschr. Chem. Forsch.*, **7**, 643 (1967).
- (2) J. J. Porter and J. L. Murray, *J. Am. Chem. Soc.*, **87**, 1628 (1965).
- (3) J. H. Collins and H. H. Jaffe, *ibid.*, **84**, 4708 (1962).
- (4) A. C. Cope and R. W. Sickman, *ibid.*, **87**, 3272 (1965); G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).
- (5) R. J. Dubois, J. Hagymasy, A. C. Noble, and F. D. Popp, *J. Heterocyclic Chem.*, **3**, 377 (1966).
- (6) R. H. Nuttall, E. R. Roberts, and D. W. A. Sharp, *J. Chem. Soc.*, 2854 (1962).
- (7) P. E. Baikie and O. S. Mills, *Chem. Commun.*, 707 (1966).
- (8) Chi-Sun Hahn and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 949 (1962).
- (9) S. Gabriel and F. Muller, *Ber.*, **26**, 2210 (1893).
- (10) H. Lowrie, U. S. Patent, 3,170,929, issued February 23, 1965.
- (11) A. Angeli, *Atti. Accad. Lincei*, **191**, 793 (1910).
- (12) F. Ullmann and P. Dieterle, *Ber.*, **37**, 24 (1904).
- (13) H. Stetter and M. S. Schwartz, *Chem. Ber.*, **90**, 1349 (1957).