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Preliminary communication

X-RAY PHOTOELECTRON SPECTRA OF ARYLDIAZO DERIVATIVES OF TRANSITION METALS

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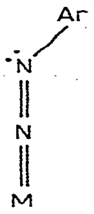
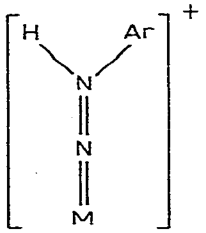
Summary

The X-ray photoelectron spectra of singly bent, doubly bent, and protonated doubly bent aryldiazonium complexes have been obtained and show that the RN_2 ligand is highly reduced. The correlation observed between binding energies and structure of the MN_2R moiety permit the assignment of the N(1s) photopeaks.

Aryldiazo* complexes were first prepared by King and Bisnette [1] in 1964. However, with the notable exception of Parshall's investigations of *trans*-[Pt(N_2-*p*-C_6H_4F)Cl(PPh_3)$_2$] [2—4], detailed studies of aryldiazo complexes have appeared only within the past five years [5—9]. These previous studies show that the coordinated aryldiazo ligand forms both singly bent and doubly bent M—N—N—Ar linkages (structures A and C) which have a wide range of N—N stretching frequencies (1920—1440 cm^{-1}), and can be protonated at either the *exo* [11] (structure B) [10, 11] or *endo* (structure D) [12] nitrogen atoms**.


(A)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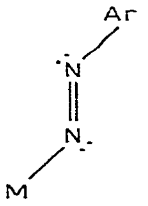
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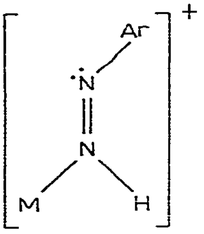
(D)

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*Complexes of the RN_2 ligand have been variously named as arylazo, aryldiazo, phenyldiimido and aryldiazenato. Although I.U.P.A.C. nomenclature may favor aryldiazenato, we have chosen to continue the common usage of aryldiazo. See ref. 5 for a more detailed discussion of this problem.

**In MNNR complexes, *endo* refers to the nitrogen atom attached to the metal and *exo* refers to the nitrogen atom attached to the R group.

TABLE 1

SPECTRAL AND STRUCTURAL PROPERTIES OF ARYLDIAZO COMPLEXES

Structural type	No.	Compound	N(1s) (eV)		ν(NN) (cm^{-1})	angle MNN (°)	angle NNAr (°)	Reference
			Endo	*Exo*				
Ar—N≡N$^+$	I	$(C_6H_5N_2)(BF_4)$	403.8	405.1^a	2260		177.5	19, 20
Ar—N=N—Ar	II	$(C_6H_5)_2N_2$	399.8(1.9)^b		1442		113	17, 18
M=N=N—Ar	III	$Ru(N_2\text{-}p\text{-}C_6H_4CH_3)Cl_3(C_6H_5)_3)_2$	401.7(1.7)	400.6(1.7)	1881	172	137	7, 21
	IV	$Os(N_2\text{-}p\text{-}C_6H_4F)Br_3[P(C_6H_5)_3]_2$	401.7(1.7)	400.5(1.7)	1850			21
	V	$[Fe(N_2\text{-}p\text{-}C_6H_4CH_3)(CO)_2\{P(C_6H_5)_3\}_2][PF_6]$	400.8(1.7)		1723	179	124	22, 23
	VI	$[Ru(N_2\text{-}p\text{-}C_6H_4F)(CO)_2\{P(C_6H_5)_3\}][BF_4]$	401.3(1.7)	399.6(1.7)	1650, 1555			24
	VII	$Mo(N_2C_6H_{11})I[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	400.0(1.6)	399.4(1.8)	1550	176	142	25
	VIII	$Mo(N_2CH_3)I[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	399.7(1.8)		1538			25
M—N=N—R	IX	$Ir(N_2\text{-}p\text{-}C_6H_4F)Cl_2(CO)[P(C_6H_5)_3]_2$	399.8(1.8)		1464			26
	X	$Pt(N_2\text{-}p\text{-}C_6H_4F)Cl[P(C_2H_5)_3]_2$	399.4(1.7)		1465	118	117	27, 28
M—N(H)=N—Ar	XI	$[Pt(NHN\text{-}p\text{-}C_6H_4F)Cl\{P(C_2H_5)_3\}_2][BF_4]$	401.0(1.7)	400.5(1.8)	1122	119	118	12, 27
	XII	$Rh(NHN\text{-}p\text{-}C_6H_4CH_3)Cl_3[P(C_6H_5)_3]_2$	400.4(1.7)					21

[a] *Endo* and *exo* are defined with respect to the coordinated metal. The binding energy of 405.1 eV is assigned by Finn and Jolly [19] to the nitrogen attached to the phenyl group, consistent with the assignments in this table. [b] FWHM in eV are listed in parentheses; all binding energies are standardized to C(1*s*), 285.0 eV.

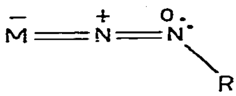
These important chemical and structural properties clearly reflect major redistribution of electron density between the metal and the aryldiazonium ion upon complex formation, but do not provide direct information about electron density at the individual nitrogen atoms. X-ray photoelectron spectroscopy (XPS) is one technique which can distinguish between individual atoms of a given type in different chemical environments. For this reason, we undertook the present study [13] of the N(1*s*) binding energies in aryldiazo complexes.

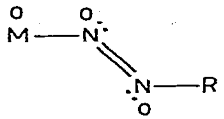
XPS data for compounds representative of structures A, C, and D are given in Table 1 along with their N—N stretching frequencies and MNN and NNR bond angles where available. The aryldiazo complexes were prepared according to the methods reported in the literature and are referenced separately in Table 1. Azobenzene was purchased from Matheson Co. and used without further purification. All compounds had satisfactory elemental analyses and were further characterized by their colors and IR spectra. The XPS data were obtained with a McPherson ESCA-36 spectrometer with a sample chamber temperature of ca. 35°C except for compounds I, VII, VIII and X which were measured at −100°C to eliminate sublimation or sample decomposition. In the N(1*s*) region, the spectra for compounds II, III, IV and VI consist of two peaks with area ratios of 1 : 1, while compounds I, V, and VII—XII exhibit a single peak. Compounds VII and XI have broad peaks (> 2.1 eV) which were resolved into two peaks with normal FWHM and area ratios of 1 : 1. No secondary structure was observed in any of the N(1*s*) spectra reported in Table 1.

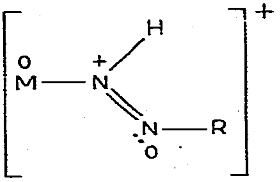
The most striking feature of the photoelectron spectra of the aryldiazo complexes is the presence of an N(1*s*) peak between 399.4 and 400.8 eV for each of the compounds III—XII. These N(1*s*) binding energies are among the lowest observed for nitrogen compounds [14], and correspond closely to the N(1*s*) binding energy of azobenzene (399.8 eV). Each of the compounds reported in Table 1 has a strongly bent RN_2 group with bond angles similar to those in azobenzene, $N{=}\dot{N}\diagdown_{R}$, and consequently, the N(1*s*) peaks at low binding energy near 400 eV were assigned to the nitrogen atom attached to the carbon atom. Complexes IX and X have strongly bent geometry at both nitrogen atoms of the RN_2 group and correspondingly each has only a single N(1*s*) peak at very low binding energy (399.4 and 399.9 eV respectively). Protonation of the doubly bent platinum complex *trans*-$Pt(N_2\text{-}p\text{-}C_6H_4F)Cl(PPh_3)_2$ (X) is known to take place at the *endo* nitrogen atom and results in a 1.6 eV increase of the N(1*s*) binding energy of the *endo* nitrogen atom from 399.4 eV (X) to 401.0 eV (XI). This increase in binding energy is similar to that observed (1.6—2.3 eV) upon protonation of trialkyl amines [14]. The binding energy of the *exo* nitrogen atom is also somewhat increased upon protonation of the *endo* nitrogen atom but still falls within the range found for the *exo* nitrogen atoms of the other aryldiazo complexes (399.4—400.8 eV). The remaining N(1*s*) peaks in the photoelectron spectra of complexes III—XII occur at binding energies equal to or greater than those of the *exo* nitrogen atom and must then be assigned to the *endo* nitrogen atoms.

The assignment of the N(1*s*) peaks at the lower binding energies to the *exo* nitrogen atom leads to a narrow range of binding energies for the *exo* nitrogen atom consistent with the relatively small structural variations in the $N{=}\dot{N}\diagdown_{R}$

group in these complexes. The assignments also lead to a wide range of binding energies (399.4—401.7 eV) for the *endo* nitrogen atom which are consistent with the diverse structural environments of the *endo* nitrogen atom represented by these complexes (linear, bent, and protonated-bent). These assignments also imply that the electron density on the *exo* nitrogen atom is approximately the same as or greater than that on the *endo* nitrogen atom. Although detailed calculations of the charge distribution within aryldiazo complexes would be desirable, the relative electron density at the *exo* and *endo* nitrogen atoms is consistent with the relative formal charges on the nitrogen atoms determined on the basis of the simple valence structures A, C, and D:







The highly variable N(1*s*) binding energies of the *endo* nitrogen atom in the singly bent complexes reflect the wide variation in σ and π acidities and basicities of the transition metals to which the aryldiazo ligand is coordinated. Comparison of the N(1*s*) binding energies of the aryldiazonium complexes with the N(1*s*) binding energies of the aryldiazonium ion shows that the electron density on both nitrogen atoms of the aryldiazonium ion is markedly increased upon coordination to transition metals, with the bulk of this excess electron density residing on the *exo* nitrogen atom in the singly bent complexes. The observation of a large flow of electron density from the metal to the ligand is in complete agreement with the conclusions reached by others from structural and IR studies [5, 25, 26].

Correlation of these XPS data with ^{15}N NMR studies which are underway [15] should assist in confirming the assignments made here and should provide information about the relative electron density on the *endo* and *exo* nitrogen atoms in compounds such as IX and X which have N(1*s*) peaks with XPS FWHM too large to be resolved. A more detailed discussion of the relationships between the XPS data for compounds VII and VIII and dinitrogen complexes will be found elsewhere [16].

Acknowledgments

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