ortho-Metallation of Azobenzenes: Mechanistic Results

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Summary *ortho*-Metallation of azobenzenes can proceed by two different routes, which depend on the nature of the metal and associated ligands; results consistent with palladation occurring by electrophilic substitution of the aryl group, and with $MeMn(CO)_5$ reacting *via* a nucleophilic mechanism, are described.

IT has been generally accepted[1,2] that palladation of azobenzene and related ligands, to form chelate complexes containing metal–carbon σ bonds (the *ortho*-metallation reaction), occurs by electrophilic attack on the aromatic ring by the metal. This mechanism seems unlikely for related reactions involving low-valent electron-rich metal complexes, *e.g.* $MeMn(CO)_5$.[3] It has been suggested[1,4] that the metal may act as a nucleophile towards P-donor ligands, although metallation reactions of N-donor ligands are considered to differ from those of P-donor ligands in several respects.[1] A study of substituent effects on these reactions has conclusively shown that two different mechanisms operate in the *ortho*-metallation of azobenzenes.

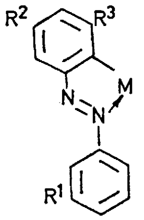
We have used *meta*-substituted azobenzenes, because the substituent will be *ortho* or *para* to the metal atom if metallation occurs in the substituted ring, and hence any effects may be more directly related to the reaction than in the *para*-substituted compounds studied hitherto.[1,2] The (π-cyclopentadienyl)palladium[5] and tetracarbonylmanganese[3] derivatives of m-$XC_6H_4N{:}NPh$ (I; $X = F, CF_3, CO_2Et$, Me or OMe) have been prepared. The former complexes, chosen for their solubility and simple ^1H n.m.r. spectra, were formed from the chloro-complex (obtained directly from $PdCl_2$ and the azobenzene) and thallium cyclopentadienide. There are three possible isomers of each complex, and the configuration, ratio, and number of isomers in each case have been determined using ^1H and ^{19}F n.m.r. spectroscopy.

TABLE. *Isomers formed in metallation reactions of* m-$FC_6H_4N{=}NPh$

Complex	M	^{19}F Chemical shift (p.p.m.)[a]	Yield (%)
(A)	$Pd(\pi\text{-}C_5H_5)$	109·8	80
	$Mn(CO)_4$	108·7	20
	H	110·1	
(B)	$Pd(\pi\text{-}C_5H_5)$	117·4	20
	$Mn(CO)_4$	—	—
(C)	$Pd(\pi\text{-}C_5H_5)$	90·5	<1
	$Mn(CO)_4$	86·2	80

[a] Relative to CCl_3F (0·0 p.p.m.).

The results obtained using (I; $X = F$) are illustrative, and are detailed in the Table, together with their characteristic ^{19}F chemical shifts. Our observations are consistent with the accepted electrophilic mechanism for palladation, in that 80% of the resulting mixture is metallated in the non-fluorinated ring (A). Further, where palladation has occurred in the substituted ring (B), reaction occurs *para* to fluorine, *i.e.* the position most favoured for electrophilic attack. Using $MeMn(CO)_5$, the major isomer obtained (C) is that substituted *ortho* to fluorine, a result consistent with nucleophilic attack on a carbon atom powerfully activated by the inductive effect of fluorine. The formation of the other isomers in these reactions is accounted for by (i) co-ordination to either nitrogen (their donor power being little affected by the *meta* substitutent) occurring before metallation,[3] resulting in two competitive metallation reactions, and (ii) the presence of the electron-withdrawing arylazo-function in each ring.



A; $R^1 = F, R^2 = H, R^3 = H$
B; $R^1 = H, R^2 = F, R^3 = H$
C; $R^1 = H, R^2 = H, R^3 = F$

Results obtained with the other substituted azobenzenes are also consistent with these two reaction mechanisms, although in some cases the effects of steric factors on the course of the reaction, and hence on the isomer ratios, have also to be considered. This work demonstrates for the first time that both electrophilic and nucleophilic reaction paths may be followed in the course of internal metallations of the same ligand; which route predominates depends on the nature of the metal and associated ligands.

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