Simple Reduction of the Diazonium Functional Group

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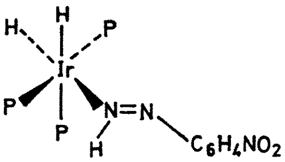
Summary Aryldiazonium cations react with polyhydrido-complexes *mer*-$IrH_3(PPh_3)_3$ and $RhH_2Cl(PPh_3)_2(S)$ (S = solvent) to yield simple insertion products in the former case and hydrazine derivatives in the latter.

IN 1967, Parshall[1] reported on an analogue for nitrogen reductase in which a metal hydride complex was shown to activate the N≡N triple bond of a diazonium group. We report a series of related reactions between diazonium cations and metal hydride complexes in which the diazonium group, in at least one case, is easily reduced to the corresponding hydrazine derivative without the use of additional catalyst. The present hydride activator complexes either possess an additional molecule of hydrogen in an activated or dissociated form[2] or can function as the necessary centre for promoting the hydrogenation step.

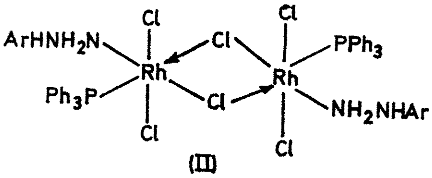
In reactions involving a hydride activator complex of the first type, equimolar amounts of *mer*-$IrH_3(PPh_3)_3$[3] and the BF_4^- salt of the aryldiazonium cation were mixed in either benzene or tetrahydrofuran–acetone (*ca.* 5 : 1) solution from which a microcrystalline product having properties different from those of the partially insoluble diazonium salt separated out. *p*-Nitro-, *p*-cyano-, and *p*-acetyl-diazonium cations were used in these reactions. In all cases, the product was the insertion complex $[IrH_2(NH{=}NAr)(PPh_3)_3][BF_4]$ which gave satisfactory elemental analyses. The i.r. spectra of these complexes indicate the presence of Ir–H bonds and the BF_4^- anion in each system. The presence of the proton bonded to the co-ordinated nitrogen atom was confirmed by the ^1H n.m.r. spectrum of the *p*-nitro-system (CH_2Cl_2 solution) which shows a broad resonance at τ − 3·5 indicating an acidic proton bonded to nitrogen (*cf.* τ −5·1 observed for the initial insertion product obtained by Parshall[1]). In none of the i.r. spectra could ν(N=N) be unequivocally assigned.

Preliminary *X*-ray results for the insertion product $[IrH_2(NH{=}NC_6H_4NO_2)(PPh_3)_3](BF_4)$[4] show it to have structure (I), demonstrating that insertion of the diazonium group occurs *trans* to a second hydrido-ligand. This structure is also assigned to the other insertion products on the basis of their similar chemical and physical properties. Despite the fact that each insertion product possesses an additional molecule of hydrogen in its activated form, attempts failed to reduce the di-imide group to the hydrazine in ethanol under 1—3 atm of H_2 and at 50—80 °C.



(I)

A second series of reactions was carried out between various diazonium cations and the hydride activator complex $RhH_2Cl(PPh_3)_2(S)$. For each reaction, the di-hydrido-complex was formed by shaking or stirring the Rh^I complex $RhCl(PPh_3)_3$[2a] under H_2 (1—3 atm) in the appropriate solvent. All reactions were carried out under H_2. In $CHCl_3$, the yellow dihydride solution quickly turned dark green upon the addition of a stoicheiometric amount of the diazonium cation salt *p*-$XC_6H_4N_2^+BF_4^-$ (X = H, F, or Me) dissolved in MeOH, and then red-brown within 15 min. When solutions were set aside, an orange microcrystalline product precipitated out in all cases. Elemental analyses of the orange products indicate their molecular formulae to be $C_{24}H_{22}Cl_3N_2PRhX$, and i.r. spectra show bands assignable as ν(N–H), the absence of the BF_4^- anion, and several bands in the low-frequency region (350—200 cm^{-1}) which may be attributed to ν(Rh–Cl). The reaction with the *p*-fluorophenyldiazonium cation also gave *p*-fluorophenylhydrazine. On the basis of these results, we suggest (II) as a possible structure for the orange products.



(II)

Reactions in $CHCl_3$ suggested that HCl was being abstracted, presumably from the solvent. It was subsequently observed that a mixture of $RhCl(PPh_3)_3$ and phenylhydrazine is able to extract HCl from chloroform solvent, and that the reaction of the dihydrido-complex and the diazonium salt in benzene solution produces a similar series of colour changes as the reaction in $CHCl_3$, but no hydrochloride is precipitated until anhydrous HCl is introduced.

These results support Parshall's theory.[1] On insertion the diazonium group undergoes a two-electron reduction with consequent rehybridization and bond-order lowering, making it susceptible to further reduction. If the activating complex is also able to function as a promotion centre for the hydrogenation of the co-ordinated di-imide, a simple reduction of diazonium cations to the corresponding hydrazine derivatives can be achieved.

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