

Arylazo and Aryldi-imine Derivatives of the Platinum Metals

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Summary Convenient routes to some arylazo and aryldi-imine derivatives of ruthenium, osmium, and rhodium are described; the reported complexes 'RhCl₂(N₂Ar)(PPh₃)₂, ½CH₂Cl₂' are reformulated as aryldi-imine derivatives RhCl₃(NH=NAr)(PPh₃)₂.

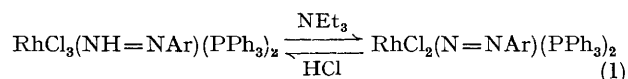
CURRENT interest in the chemistry of arylazo and aryldi-imine derivatives of the transition metals prompts this report on the convenient synthesis of these complexes, and the reformulation of some previously reported examples.

Arylazo-derivatives of ruthenium [RuX₃(N₂Ar)(PPh₃)₂], osmium [OsX₃(N₂Ar)(PPh₃)₂], and rhodium [RhX₂(N₂Ar)(PPh₃)₂] are readily obtained by the successive addition of diazonium tetrafluoroborate and lithium halide to suspensions of RuX₂(PPh₃)₃, OsX₂(PPh₃)₃, and RhX(PPh₃)₃ (X = Cl, Br) respectively in cold acetone. The ruthenium and rhodium derivatives may also be prepared by a single-stage process involving the addition of 1,3-diaryltriazenes, ArN=N-NHAr, and RuCl₃ or RhCl₃ to a solution of PPh₃ in boiling EtOH. Under the acid conditions prevailing in these solutions the triazene is presumably cleaved generating a diazonium cation, the effective source of the arylazo-ligand. The very inert ruthenium and osmium complexes MX₃(N₂Ar)(PPh₃)₂ show strong i.r. bands, attributable to ν(N=NAr) in the region 1850—1900 cm⁻¹. These frequencies are, by a considerable margin, the highest yet reported for arylazo-derivatives and are very close to those recorded for the corresponding nitrosyl complexes, MX₃(NO)(PPh₃)₂.¹ By analogy with these latter complexes, our products are formulated as ruthenium(II) and osmium(II) derivatives containing linearly co-ordinated (N=NAr)⁺ groups. The structure of RuCl₃(N₂-*p*-tolyl)(PPh₃)₂, determined by X-ray crystallography, confirms the stoichiometry and the presence of an essentially linear Ru-N-NAr linkage; bond angles are 172 and 137° for ∠Ru-N-NAr and ∠RuN-N-Ar respectively.†

The rhodium complexes, RhX₂(N₂Ar)(PPh₃)₂ show two i.r. bands, at *ca.* 1620 and 1560 cm⁻¹, associated with the N=Ar group. Both bands persist in solution (CHCl₃)

and both are shifted to lower frequencies by 10—15 cm⁻¹ in the labelled complexes RhX₂(¹⁵N=NAr)(PPh₃)₂. These values of ν(N=NAr) are close to but lower than those found for ν(NO) in the corresponding nitrosyls RhX₂(NO)(PPh₃)₂² and this suggests that the arylazo-complexes are probably best formulated as rhodium(III) derivatives of (N=NAr⁻).

Other workers previously synthesised^{3,4} complexes which they formulated as solvated rhodium arylazo-derivatives, *e.g.* RhCl₂(N₂Ar)(PPh₃)₂, ½CH₂Cl₂. These complexes show no i.r. bands attributable to ν(N=NAr) but do give rise to a Raman absorption⁴ at *ca.* 1500—1530 cm⁻¹. We have re-examined these products and find them to be aryldi-imine derivatives of rhodium(III), RhCl₃(NH=NAr)(PPh₃)₂. This conclusion is based on analytical data, ¹H n.m.r. measurements (see below) and the successful interconversion with genuine arylazo derivatives [reaction (1)]. The rhodium



arylazo-derivatives, RhCl₂(N₂Ar)(PPh₃)₂, are more reactive than their ruthenium and osmium analogues and readily abstract HCl from chlorinated solvents, thereby forming aryldi-imine complexes. Thus mild hydrogenation (1 atm., 60°) of RhCl₂(N₂Ar)(PPh₃)₂ or RhCl₃(NH=NAr)(PPh₃)₂ in chloroform affords a common product, identified as the known dimeric arylhydrazine complex [RhCl₃(NH₂-NHAr)(PPh₃)₂].⁵

We also find that the ruthenium and osmium hydrido-complexes MH₂(CO)(PPh₃)₃ and MHCl(CO)(PPh₃)₃ react with ArN₂⁺BF₄⁻ to afford a variety of stable aryldi-imine-derivatives.⁶ These, like the reformulated rhodium aryldi-imine-complexes do not show a ν(NH) band in their i.r. spectra. However, their identity may be readily ascertained by ¹H n.m.r. spectroscopy; the NH group of each complex gives rise to a broad singlet at τ -4.0 to -1.5 which is split into a sharp doublet [*J*(¹⁵NH) 65—70 Hz] for

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derivatives containing labelled ($^{15}\text{N}=\text{NAr}$) ligands. These observations highlight the deficiencies of i.r. spectroscopy as a means of distinguishing between arylazo and arylidimine ligands.

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