

Cationic Bis-arylazo, and Related, Complexes of Ruthenium

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Summary Reaction of $[\text{Ru}(\text{PPh}_3)_3\text{HCl}]$ with $[\text{ArN}_2][\text{BF}_4]$ (Ar = *p*-MeC₆H₄ or *p*-MeOC₆H₄) gave $[\text{Ru}(\text{N}_2\text{Ar})_2(\text{PPh}_3)_2\text{Cl}][\text{BF}_4]$, reduction with sodium amalgam in ethanol affords ArNH₂ and NH₃, oxidation with chlorine gives $[\text{Ru}(\text{N}_2\text{Ar})(\text{PPh}_3)_2\text{Cl}_2]$, and with $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$, $[\text{ArN}_2][\text{BF}_4]$ affords $[\text{Ru}(\text{N}_2\text{Ar})(\text{PPh}_3)_2\text{Cl}_2]_2 [\text{BF}_4]_2$

THE addition of aryldiazonium salts to transition-metal phosphine hydride complexes appears to proceed either with the formation of an arylazo-complex, with concomitant elimination of the hydrido-group, *e.g.* $[\text{Rh}(\text{N}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2\text{Cl}_2]$ from $[\text{Rh}(\text{PPh}_3)_2\text{HCl}_2]$,¹ or with partial or complete reduction of the diazonium group, and formation of a metal di-imide, *e.g.* $[\text{Pt}(\text{NH}=\text{NAr})(\text{PEt}_3)_2\text{Cl}]^+$ from $[\text{Pt}(\text{PEt}_3)_2\text{HCl}]_2$ or $[\text{Ir}(\text{NH}=\text{NAr})(\text{PPh}_3)_3\text{H}_2]$ from $[\text{Ir}(\text{PPh}_3)_3\text{H}_3]$,³ or a hydrazine complex, *e.g.* $[\text{Rh}(\text{NH}_2\text{-NHAr})(\text{PPh}_3)_2\text{Cl}_2]$ from $[\text{Rh}(\text{PPh}_3)_2\text{H}_2\text{Cl}]$.³ We have found, however, that addition of diazonium salts to $[\text{Ru}(\text{PPh}_3)_3\text{-HCl}]$ affords the first transition-metal complexes containing *two* arylazo-groups bonded to the same metal.

Reaction of $[\text{ArN}_2][\text{BF}_4]$ ($\text{Ar} = p\text{-MeC}_6\text{H}_4$ or $p\text{-MeOC}_6\text{H}_4$) with $[\text{Ru}(\text{PPh}_3)_3\text{HCl}]$ in cold acetone affords the yellow, crystalline, 1:1 electrolyte $[\text{Ru}(\text{N}_2\text{Ar})_2(\text{PPh}_3)_2\text{Cl}][\text{BF}_4]$. These complexes are stable towards air and light, and, when recrystallised from dichloromethane, contain solvent of crystallisation.† The complexes exhibit an i.r. band at *ca.* 1700 cm^{-1} which is assigned to ν_{NN} of the co-ordinated ArN_2 groups. Chlorination of the bis-aryldiazonium cations in acetone affords $[\text{Ru}(\text{N}_2\text{Ar})(\text{PPh}_3)_2\text{Cl}_3]$ and $[\text{ArN}_2]^+$. These data suggest strongly that the ArN_2 groups are co-ordinated as separate entities, and are not coupled as occurs in the

reaction of $[\text{ArN}_2]^+$ with $[\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$, in which a metal-co-ordinated tetrazene ligand system was formed;⁴ the latter exhibited no ν_{NN} , and, on chlorination, would not be expected to form diazonium salts.

The bis-aryldiazonium cations are reduced by stirring in ethanol with an excess of sodium amalgam, and the organic products were identified as ammonia and either *p*-toluidine or *p*-anisidine. Parshall obtained similar products after prolonged reaction of hydrogen with $[\text{Pt}(\text{NH}=\text{NAr})(\text{PEt}_3)_2\text{Cl}]^+$.²

Reaction of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ with $[\text{ArN}_2][\text{BF}_4]$ affords, in acetone-dichloromethane mixtures, orange yellow complexes of empirical formula $\{[\text{Ru}(\text{N}_2\text{Ar})(\text{PPh}_3)_2\text{Cl}_2][\text{BF}_4]\}_n$. These compounds are diamagnetic, and if they obey the 18-electron rule, are presumably dimeric ($n = 2$).

The formation of arylazo-cations, with elimination of hydrido-ligands from metal hydrido-complexes, is not confined to the noble metals. Thus, treatment of $[(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2]$ with $[\text{ArN}_2][\text{BF}_4]$ afforded, in low yields, $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_2\text{Ar})][\text{BF}_4]$.

We thank the S.R.C. for financial support.

(Received, August 6th, 1971; Com. 1368.)

† All complexes were characterised satisfactorily by elemental analyses, i.r. and n.m.r. spectroscopy.

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