

## 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*-MeC<sub>6</sub>H<sub>4</sub> or *p*-MeOC<sub>6</sub>H<sub>4</sub>) 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 ArNH<sub>2</sub> and NH<sub>3</sub>, 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  $[\text{Rh}(\text{PPh}_3)_2\text{HCl}]$ ,<sup>1</sup> 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  $[\text{Ir}(\text{PPh}_3)_3\text{H}_3]$ ,<sup>3</sup> or a hydrazine complex, *e.g.*  $[\text{Rh}(\text{NH}_2\text{NAr})(\text{PPh}_3)_2\text{Cl}_2]$  from  $[\text{Rh}(\text{PPh}_3)_2\text{H}_2\text{Cl}]$ .<sup>3</sup> 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.*  $1700\text{ cm}^{-1}$  which is assigned to  $\nu_{\text{NN}}$  of the co-ordinated  $\text{ArN}_2$  groups. Chlorination of the bis-arylazo-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  $\text{ArN}_2$  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 tetrazeno ligand system was formed;<sup>4</sup> the latter exhibited no  $\nu_{\text{NN}}$ , and, on chlorination, would not be expected to form diazonium salts.

The bis-arylazo-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  $[\text{Pt}(\text{NH}=\text{NAr})(\text{PEt}_3)_2\text{Cl}]^+$ .<sup>2</sup>

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,  $[\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_2\text{Ar})][\text{BF}_4]$ .

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

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<sup>2</sup> G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133, and 1967, **89**, 1822.

<sup>3</sup> L. Toniolo and R. Eisenberg, *Chem. Comm.*, 1971, 455.

<sup>4</sup> F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1971, **93**, 1826.