Complexes of the Platinum Metals. Part III.[1] Arylazo and Aryldi-imine Derivatives

By **Kerry R. Laing, Stephen D. Robinson,*** and **Michael F. Uttley,** Department of Chemistry, King's College, Strand, London WC2R 2LS

Arylazo derivatives $RuX_3(N_2Ar)(PPh_3)_2$, $OsBr_3(N_2Ar)(PPh_3)_2$, and $RhX_2(N_2Ar)(PPh_3)_2$ have been prepared by reacting diazonium tetrafluoroborates with the preformed metal phosphine complexes $RuX_2(PPh_3)_3$, $OsBr_2(PPh_3)_3$, and $RhX(PPh_3)_3$ respectively then adding the appropriate lithium halide to the reaction mixture. The ruthenium and rhodium arylazo complexes are also conveniently prepared by a single step procedure involving addition of the appropriate metal trihalide and 1,3-diaryltriazene to an ethanolic solution of a triarylphosphine. These latter reactions are thought to involve diazonium cations generated *in situ* by acidolysis of 1,3-diaryltriazene. Products obtained on reacting $RhHCl_2(PPh_3)_3$ with diazonium tetrafluoroborates and lithium chloride, and previously formulated by other workers as solvated arylazo derivatives $RhCl_2(N_2Ar)(PPh_3)_2(sol)_x$ ($x = \frac{1}{2}$—1; sol = CH_2Cl_2 or $CHCl_3$), are reformulated as aryldi-imine derivatives $RhCl_3(NH{=}NAr)(PPh_3)_2$. Similar reactions of the hydrides $MHCl(CO)(PPh_3)_3$ and $MH_2(CO)(PPh_3)_3$ (M = Ru or Os) with diazonium salts afford new aryldi-imine derivatives of ruthenium and osmium. The interconversion of arylazo and aryldi-imine complexes is reported and the carbonylation and hydrogenation of some of these products are described. The structure of the aryldi-imine ligands is confirmed by ^1H n.m.r. spectroscopy using ^{15}N labelled ligands. Structural and spectroscopic analogies between isoelectronic arylazo and nitrosyl complexes are discussed.

CURRENT interest in the mode of co-ordination of nitrosyl[2] and dinitrogen ligands,[3] and in the reduction of co-ordinated dinitrogen has focussed attention on the closely related arylazo (NNAr) ligands and their reduction products. The arylazo group (·NNAr) is of particular interest since it is isoelectronic with nitric oxide (·NO), and may reasonably be expected to adopt modes of co-ordination analogous to those found for the latter ligand.[2] Furthermore, recent studies have confirmed the role of transition metal ions in biological nitrogen fixation,[3] and have given rise to speculation that arylazo complexes, capable of being reduced at nitrogen, might serve as model systems for nitrogenase.[4,5]

Synthetic studies, stimulated by these observations, have centred on reactions between diazonium salts $ArN_2^+BF_4^-$ and transition-metal phosphine complexes, and have yielded a variety of products containing arylazo and related nitrogen ligands. These include arylazo derivatives of molybdenum,[4,6-10] tungsten,[7,9,11,12] rhenium,[13] ruthenium,[12] rhodium,[14] iridium,[15,16] and platinum,[4,17,18] together with aryldi-imine (NH = NAr) derivatives of ruthenium,[19] iridium,[5,16,20,21] and platinum[4,17] and tetrazene complexes of iridium.[22] Much of this work was reported while our study on these systems was in progress.

In this paper we describe convenient routes to the most extensive series of arylazo and aryldi-imine complexes yet reported, and discuss their structures, reactivities, and spectroscopic properties. A preliminary report on this work has been published.[23]

The efficiency of *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (MNTS) as a source of nitrosyl ligands in the single step synthesis of platinum-metal nitrosyl complexes[24,25] encouraged us to seek similar convenient reagents for use in the synthesis of isoelectronic arylazo derivatives of the platinum metals. The arylazo analogues of MNTS, p-$MeC_6H_4SO_2N(Me)N_2Ar$, and the closely related reagents p-$MeC_6H_4SO_2N_2Ar$ were both investigated and found to yield intractable mixtures containing sulphinate and sulphonylazo complexes in addition to the required arylazo derivatives. However, 1,3-diaryltriazenes, ArHN–N=NAr and 1-methyl-1,3-diaryltriazenes, Ar(Me)N–N=NAr, which are known to cleave readily in acid solution forming the corresponding amines and diazonium cations, were found to be effective reagents for the single step synthesis of arylazo complexes. Thus successive addition of ethanolic solutions containing

---

[1] Part II, S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912.

[2] N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.

[3] J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1972, **1**, 121.

[4] G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822.

[5] A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *Nature*, 1972, **235**, 42.

[6] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1966, **5**, 300.

[7] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675.

[8] S. Trofimenko, *J. Amer. Chem. Soc.*, 1970, **92**, 5118.

[9] D. Cashman and F. J. Lalor, *J. Organometallic Chem.*, 1970, **24**, C29; 1971, **32**, 351.

[10] F. J. Lalor and P. L. Pauson, *J. Organometallic Chem.*, 1970, **25**, C51.

[11] A. N. Nesmeyanov, Y. A. Chapovskii, N. A. Ustynyuk, and L. G. Makarova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 449.

[12] J. A. McCleverty and R. N. Whiteley, *Chem. Comm.*, 1971, 1159.

[13] V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1970, 1083.

[14] L. Toniolo, *Inorg. Chim. Acta*, 1972, **6**, 660.

[15] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128; B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972,223.

[16] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1972, **94**, 645.

[17] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133.

[18] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 3441.

[19] D. F. Gill, B. E. Mann, and B. L. Shaw, *J.C.S. Dalton*, 1973, 311.

[20] L. Toniolo and R. Eisenberg, *Chem. Comm.*, 1971, 455.

[21] G. Caglio and M. Angoletta, *Gazzetta*, 1972, **102**, 462.

[22] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, 1971, **93**, 1826.

[23] K. R. Laing, S. D. Robinson, and M. F. Uttley, *Chem. Comm.*, 1973, 176.

[24] S. D. Robinson and M. F. Uttley, *J. Chem. Soc.* (*A*), 1971, 1254.

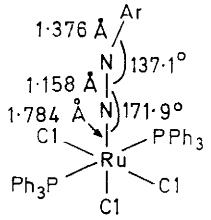
[25] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1972, 1.

$RuCl_3$ or $RhCl_3$ and a 1,3-diaryltriazene to a solution of triphenylphosphine in hot ethanol readily afforded the arylazo derivatives $RuCl_3(N_2Ar)(PPh_3)_2$ and $RhCl_2(N_2Ar)(PPh_3)_2$ respectively. Presumably the acidity of these reaction solutions is sufficient to cleave the 1,3-diaryltriazene thus generating *in situ* diazonium cations, the effective source of the arylazo ligands. Attempts to prepare the related iridium and osmium derivatives by a similar technique either failed or gave very poor yields. We therefore employed the more conventional reactions of phosphine metal halide complexes with diazonium salts and lithium halides to prepare arylazo derivatives of ruthenium, osmium, and rhodium. Thus the complexes $RuX_2(PPh_3)_3$, $OsBr_2(PPh_3)_3$, and $RhX(PPh_3)_3$ reacted with diazonium tetrafluoroborates in the presence of lithium halides LiX (X = Cl or Br) to afford arylazo derivatives $RuX_3(N_2Ar)(PPh_3)_2$, $OsBr_3(N_2Ar)(PPh_3)_2$, and $RhX_2(N_2Ar)(PPh_3)_2$ respectively. Attempts to obtain the corresponding iridium derivatives $IrX_2(N_2Ar)(PPh_3)_2$ from $IrCl(PPh_3)_3$ and aryldiazonium tetrafluoroborates were frustrated by side reactions and the instability of the products. Other workers have recently shown that the complexes, $RuHCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, and $RhCl(PPh_3)_3$, react with aryldiazonium tetrafluoroborates in the absence of lithium halides to yield charged species formulated as $[RuCl(N_2Ar)_2(PPh_3)_2]BF_4$, $\{[RuCl_2(N_2Ar)(PPh_3)_2]BF_4\}_n$ (n probably = 2),[12] and $[RhCl(N_2Ar)(PPh_3)_3]BF_4$.[26] Chlorination of the salts $[RuCl(N_2Ar)_2(PPh_3)_2]BF_4$ to afford the neutral complexes $RuCl_3(N_2Ar)(PPh_3)_2$ was also reported.[12]

The ruthenium and osmium arylazo complexes, $MX_3(N_2Ar)(PPh_3)_2$ are sparingly soluble, air-stable microcrystalline solids, and, unlike their rhodium and iridium analogues (see below), are resistant to protonation or hydrogenation under mild conditions. They are characterised by the presence of very strong broad i.r. bands in the range 1850—1900 cm^{-1} attributable to $\nu(N{=}NAr)$. A reduction of the $\nu(N{=}NAr)$ frequency by *ca.* 25—30 cm^{-1} in complexes containing the labelled ($^{15}N{=}NAr$) arylazo ligands verifies this assignment. These frequencies are, by a considerable margin, the highest yet reported for any metal arylazo complex, and are remarkably similar to the values of $\nu(NO)$ found for the analogous nitrosyl complexes $MX_3(NO)(PPh_3)_2$.[25] We suggest that this close agreement between the values of $\nu(NO)$ and $\nu(N{=}NAr)$ in the complexes $MX_3(NO)(PPh_3)_2$ and $MX_3(N{=}NAr)(PPh_3)_2$ respectively is probably indicative of an analogous mode of bonding for the nitrosyl and arylazo ligands in these systems. The structures of the nitrosyls $MX_3(NO)(PPh_3)_2$ are unknown, however, on the basis of i.r. data they are generally thought to be formal ruthenium(II) and osmium(II) derivatives containing linearly co-ordinated NO^+ ligands.[25] Our suggestion, that the corresponding arylazo complexes are best formulated in a similar manner, has recently received some confirmation. Single crystal *X*-ray diffraction studies on the complexes $RuCl_3(N_2C_6H_4\text{-}p\text{-}Me)(PPh_3)_2,CH_2Cl_2$[27] and $RuCl_3(N_2C_6H_4\text{-}p\text{-}Me)(PPh_3)_2,Me_2CO$[28] reveal octahedral co-ordination about the ruthenium, and an essentially linear Ru–N–NAr linkage (I).

The new rhodium arylazo complexes $RhX_2(N_2Ar)(PPh_3)_2$ are air-stable microcrystalline brown or red-brown solids. Unlike their ruthenium and osmium analogues they dissolve in organic solvents to yield unstable solutions which react either by eliminating dinitrogen or, where appropriate, by abstraction of hydrogen chloride from the solvent (see below). The contrasting reactivities of the rhodium and ruthenium (or osmium) arylazo derivatives suggest that the nature and mode of co-ordination of the arylazo ligands may be substantially different in these two series of complexes. This suggestion receives some support from a comparison of the i.r. data recorded for the ruthenium and rhodium arylazo complexes, whereas the former show a single band at *ca.* 1850—1900 cm^{-1} attributable to $\nu(N{=}NAr)$ the latter show two bands at much lower frequencies (*ca.* 1550—1615 cm^{-1}). The $\nu(N{=}NAr)$ frequencies observed for the rhodium arylazo complexes are in the same region as, but slightly lower than, those reported for the corresponding nitrosyls $RhX_2(NO)(PPh_3)_2$.[24] The latter have been formulated as NO^- derivatives of rhodium(III) on the basis of i.r. evidence[24] and, by analogy, we tentatively formulate our arylazo complexes as $N_2Ar^-{-}Rh^{III}$ species. This formulation implies the probable presence of a non-linear Rh–N–NAr linkage; and confirmatory evidence is therefore being sought by *X*-ray diffraction studies.

(I)



The appearance of two bands in the spectra of the rhodium arylazo complexes was unexpected and was therefore investigated further. Spectra taken using isotopically labelled ($^{15}N{=}NAr$) ligands confirmed that both vibrations are associated with the arylazo moiety; however the magnitudes of the isotopic shifts observed (*ca.* 5—15 cm^{-1} for each band) are less than expected for pure N=NAr stretching vibrations (compare with values of 25—30 cm^{-1} for the isotopic shift in the corresponding ^{15}N labelled ruthenium arylazo derivatives). The presence of the second band is not attributable to solid state effects since both bands appear in the spectra of freshly prepared solutions and decay simultaneously over a period of *ca.* 30 min as the complexes decompose. However if our speculation concerning the non-linear nature of the arylazo ligand in the rhodium complexes is correct, then it is conceivable that the appearance of two bands associated with $\nu(N{=}NAr)$ could indicate the

---

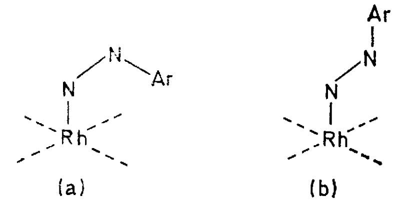
[26] M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 865

[27] B. Haymore and J. A. Ibers, personal communication.

[28] J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 1676.

presence of *cis*- and *trans*-forms of the arylazo ligand (IIa,b). Small variations in the relative intensities of these bands, observed for different batches of the same compound, lend support to this suggestion.*

(II)



Other workers have studied the reactions of diazonium salts with $\mathrm{RhHCl_2(PPh_3)_3}$ [or with $\mathrm{RhCl(PPh_3)_3}$ in the presence of HCl] in chlorinated hydrocarbon solvents and have isolated stable orange-yellow products which they formulated as solvated rhodium arylazo derivatives $\mathrm{RhCl_2(N_2Ar)(PPh_3)_2,(sol)}_x$ ($x = \frac{1}{2}$ or 1; sol = $\mathrm{CH_2Cl_2}$ or $\mathrm{CHCl_3}$).[26] These complexes were reported to show very weak i.r.[26] and very strong Raman bands[29] in the region 1470—1530 cm^{-1} which were attributed to ν(N=NAr). Since these latter complexes obviously differed fundamentally from the rhodium arylazo derivatives obtained in the present work, their formation was reinvestigated and a comparative study of both series of compounds was instituted. Our observations, described below, lead us to the conclusion that the products, previously formulated as solvated arylazo complexes,[26,29] are aryldi-imine derivatives of rhodium(III) $\mathrm{RhCl_3(NH{=}NAr)(PPh_3)_2}$. Formation of these products can be attributed either to 'insertion' of arylazo moieties into the rhodium–hydrogen bonds or to protonation of co-ordinated arylazo ligands.

TABLE 1

N.m.r. data [a] for aryldi-imine complexes

Complex [b]	τ(Me)	τ(OMe)	τ(NH)	$J(^{15}$NH)/Hz	τ(MH)	J(PH)/Hz
$\mathrm{RhCl_3(NH{:}NR)(PPh_3)_2}$	7·65		−1·89	68		
$\mathrm{RhCl_3(NH{:}NR^1)(PPh_3)_2}$		6·17	−1·60	65		
$\mathrm{IrCl_3(NH{:}NR)(PPh_3)_2}$	7·70		−3·12			
$\mathrm{[IrCl_2(NH{:}NR)(PPh_3)_3]BF_4}$	7·49, 7·68		−3·98, −3·90			
$\mathrm{RuCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2}$	7·70		−3·10			
$\mathrm{RuCl(FBF_3)(NH{:}NR^1)(CO)(PPh_3)_2}$		6·19	−2·68			
$\mathrm{OsCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2}$	7·72		−3·78	69·3		
$\mathrm{OsCl(FBF_3)(NH{:}NR^1)(CO)(PPh_3)_2}$		6·16	−3·47			
$\mathrm{RuCl_2(NH{:}NR)(CO)(PPh_3)_2}$ [c]	7·70		−2·60			
$\mathrm{OsCl_2(NH{:}NR)(CO)(PPh_3)_2}$ [c]	7·74		−3·50	67		
$\mathrm{[RuCl(NH{:}NR)(CO)(PPh_3)_2]BF_4}$	7·54		−1·66			
$\mathrm{[OsCl(NH{:}NR)(CO)(PPh_3)_2]BF_4}$	7·54		−1·76			
$\mathrm{[RuH(NH{:}NR)(CO)(PPh_3)_3]BF_4}$	7·62		−2·05		17·8	88·5 (*trans*) 26·0 (*cis*)
$\mathrm{[OsH(NH{:}NR)(CO)(PPh_3)_3]BF_4}$	7·64		−2·28		18·15	72·5 (*trans*) 26·5 (*cis*)
$\mathrm{[RuH(NH{:}NR)(CO)_2(PPh_3)_2]BF_4}$	7·72		−2·70		14·4	17·7
$\mathrm{RuHCl(NH{:}NR)(CO)(PPh_3)_2}$	7·72		−2·97		23·8	24
	7·72		−2·62		19·6	22

[a] Spectra recorded at 90 MHz in $\mathrm{CDCl_3}$ solution and referenced to internal tetramethylsilane. [b] R = p-$\mathrm{C_6H_4Me}$; $\mathrm{R^1}$ = p-$\mathrm{C_6H_4OMe}$. [c] Isomers (Va) and (Vb) give identical n.m.r. spectra.

The reformulated complexes, $\mathrm{RhCl_3(NH{=}NAr)(PPh_3)_2}$, were obtained by reacting diazonium tetrafluoroborates with $\mathrm{RhCl(PPh_3)_3}$ in the presence of an excess of hydrogen chloride. The reaction of $\mathrm{RhHCl_2(PPh_3)_3}$ with diazonium tetrafluoroborates in the absence of hydrogen chloride is thought to give the salts $\mathrm{[RhCl_2(NH{=}NAr)(PPh_3)_3]BF_4}$. Our attempts to purify and fully characterise these salts have been unsuccessful; however, addition of chloride anions to the crude products in solution affords an alternative route to the required neutral complexes $\mathrm{RhCl_3(NH{=}NAr)(PPh_3)_2}$. The corresponding iridium aryldi-imine complexes $\mathrm{[IrCl_2(NH{=}NAr)(PPh_3)_3]BF_4}$ and $\mathrm{IrCl_3(NH{=}NAr)(PPh_3)_2}$ were similarly prepared from $\mathrm{IrHCl_2(PPh_3)_3}$. The salts were characterised by i.r. ($\mathrm{BF_4}$-bands) and n.m.r. spectroscopy (NH *ca.* τ −3·9) but were not obtained in an analytically pure form.

The arylazo complexes, $\mathrm{RhCl_2(N_2Ar)(PPh_3)_2}$ and the aryldi-imine derivatives $\mathrm{RhCl_3(NH{=}NAr)(PPh_3)_2}$ were found to be monomeric and diamagnetic. The far-i.r. spectra of the arylazo complexes show a single strong band at *ca.* 340 cm^{-1} attributable to ν(RhCl) and comparable with the single band at *ca.* 340 cm^{-1} observed[30] for the isoelectronic nitrosyl $\mathrm{RhCl_2(NO)(PPh_3)_2}$. This observation may indicate that the rhodium arylazo complexes possess a tetragonal pyramidal structure (III), analogous to that found for $\mathrm{IrCl_2(NO)(PPh_3)_2}$[31] with *trans* chloride ligands and an apical arylazo group. In

---

* Crystals of the complex $\mathrm{\{Rh[PhP(CH_2CH_2CH_2PPh_2)_2]Cl(N_2Ph)\}\{PF_6\}}$, which also show two i.r. bands (1627 and 1561 cm^{-1}) associated with the azo function of the arylazo ligands, have now been shown by an X-ray diffraction study to contain only arylazo ligands with the doubly bent *trans*-configuration [as in (IIb)]. (B. L. Haymore, personal communication). We therefore conclude that the doubly bent arylazo ligands give rise to two i.r. active vibrations involving the azo moiety, neither of which is a pure ν(N=NAr) vibration, and that the occurrence of these bands is not indicative of the presence of arylazo ligands in *cis* and *trans* configurations. This structure provides the first authenticated example of a non-linear M–N–NAr linkage, and supports our conclusion that this arrangement prevails in the closely related rhodium complexes $\mathrm{RhX_2(N_2Ar)(PPh_3)_2}$.

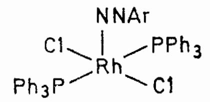
[29] G. W. Rayner-Canham and D. Sutton, *Canad. J. Chem.*, 1971, **49**, 3994.

[30] G. R. Crooks and B. F. G. Johnson, *J. Chem. Soc.* (*A*), 1970, 1662.

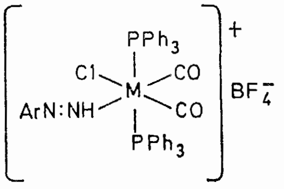
[31] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

contrast the aryldi-imine complexes $RhCl_3(NH{=}NAr)(PPh_3)_2$ show three i.r. bands at *ca.* 350, 330, and 320 cm^{-1} similar to those reported [32] for *mer*-$RhCl_3(CO)(PPh_3)_2$ and presumably have a similar configuration. It is difficult to detect and identify aryldi-imine complexes by i.r. spectroscopy since the bands associated with ν(NH=NAr) and ν(NH) are usually weak, and frequently obscured by aromatic C=C and C–H vibrations respectively. The presence and the structure of the aryldi-imine ligands were therefore confirmed by ^1H n.m.r. studies using labelled ($^{15}NH{=}NAr$) and unlabelled complexes. The ^{15}N isotope was introduced using labelled diazonium salts $[ArN{=}^{15}N]BF_4$ prepared from $Na^{15}NO_2$ (95% enriched) and arylamines $ArNH_2$. Previous workers have shown that ^{15}N labelling performed in this manner is specific and that the specificity is retained during complex formation.[4,33] Therefore measurement of ^{15}NH coupling constants for the aryldi-imine complexes provides a reliable means of detecting and locating the protonated nitrogen site. The unlabelled complexes each show a weak resonance (*ca.* τ −2·0) broadened by the quadrupole moment of the adjacent ^{14}N atom, and attributable to the nitrogen-bound proton of an NH=NAr moiety. In the ^{15}N labelled complexes this broad signal is replaced by a sharp doublet with a coupling constant, $J(^{15}NH)$ 65—70 Hz. The appearance of a corresponding doublet in the ^{15}N n.m.r. spectrum of one aryldi-imine complex confirms assignment. The $^{15}N^1H$ coupling is consistent with the presence of a proton directly bound to ^{15}N,[4] and taken in conjunction with the chemical and analytical evidence, confirms the structure NH=NAr for the aryldi-imine ligands. A coupling $^1J(^{15}NH)$ of similar magnitude has previously been reported for some closely related platinum(II) aryldi-imine complexes.[4]

(III)



(IV)



Final confirmation of the relationship between the arylazo $RhCl_2(N_2Ar)(PPh_3)_2$ and aryldi-imine $RhCl_3(NH{=}NAr)(PPh_3)_2$ complexes was provided by their interconversion:

$$RhCl_2(N_2Ar)(PPh_3)_2 \underset{-HCl}{\overset{HCl}{\rightleftharpoons}} RhCl_3(NH{=}NAr)(PPh_3)_2$$

Dichloromethane solutions of the arylazo complexes rapidly lightened in colour on treatment with dry gaseous hydrogen chloride, and afforded orange crystals of the aryldi-imine derivatives. The arylazo complexes also abstract the elements of hydrogen chloride from chloroform thus achieving the same conversion in the absence of the free acid. This hydrogen chloride abstraction reaction accounts for the formation of arylhydrazine and aryldi-imine derivatives respectively when the arylazo complexes $RhCl_2(N_2Ar)(PPh_3)_2$ are hydrogenated or merely allowed to decompose in chlorinated hydrocarbon solvents (see below). Triethylamine readily removes hydrogen chloride from the aryldi-imine complexes thus regenerating the arylazo derivatives. These reactions with hydrogen chloride and triethylamine are analogous to the reversible hydrogen transfer processes previously reported for the isoelectronic nitrosyl ligand,[34] *i.e.*

$$OsCl(CO)(NO)(PPh_3)_2 \underset{-HCl}{\overset{HCl}{\rightleftharpoons}} OsCl_2(CO)(NH{=}O)(PPh_3)_2$$

A related process involving interconversion of methyleneamido and alkylimido complexes has also recently been reported.[35]

$$ReCl_2(N{=}CH_2)(py)(PPh_2R)_2 \underset{\substack{-HCl\\+py}}{\overset{HCl}{\rightleftharpoons}} ReCl_3(NMe)(PPh_2R)_2$$

Treatment of the iridium aryldi-imine complexes $IrCl_3(NH{=}NAr)(PPh_3)_2$ with triethylamine gave an unstable brown complex, tentatively identified as the arylazo derivative $IrCl_2(N{=}NAr)(PPh_3)_2$. This product reacts with gaseous hydrogen chloride to regenerate the parent aryldi-imine complex. The iridium ' arylazo ' derivative like its rhodium analogues, shows two i.r. bands (1470 and 1430 cm^{-1}) attributable to ν(N=NAr) however both are partially obscured by triphenylphosphine bands and this assignment must therefore be subject to some reservations. The i.r. spectrum of the related complex $IrCl_2(CO)(N_2Ar)(PPh_3)_2$ shows a similar band at 1460 cm^{-1}.

The rhodium aryldi-imine complexes $RhCl_3(NH{=}NAr)(PPh_3)_2$ undergo carbonylation in benzene to form $RhCl_3(CO)(PPh_3)_2$ [ν(CO) 2108 cm^{-1}] in excellent yield; under similar conditions the arylazo derivatives $RhCl_2(N_2Ar)(PPh_3)_2$ afforded a mixture of $RhCl_3(CO)(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$ [ν(CO) 1960 cm^{-1}] by reduction and chloride ion redistribution.

Passage of dihydrogen through warm chloroform or benzene solutions of the complexes $RhCl_3(NH{=}NAr)(PPh_3)_2$ or $RhCl(N_2Ar)(PPh_3)_2$ affords a common series of products formulated as arylhydrazine derivatives $[RhCl_3(NH_2NHAr)(PPh_3)]_2$ on the basis of analytical data and the presence of i.r. bands (3150—3250 cm^{-1}) attributable to ν(NH). The very low solubility of these complexes in common organic solvents precluded the taking of molecular weight or n.m.r. measurements. Hydrazine complexes of this general formula have previously been

---

[32] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

[33] A. K. Bose and I. Kugajevsky, *J. Amer. Chem. Soc.*, 1966, **88**, 2325.

[34] K. R. Grundy, C. A. Reed, and W. R. Roper, *Chem. Comm.*, 1970, 1501.

[35] J. Chatt, R. J. Dosser, and G. J. Leigh, *Chem. Comm.*, 1972, 1243.

obtained by reacting $RhH_2Cl(PPh_3)_3$ with a diazonium salt and dihydrogen in chloroform–methanol.[14,20]

The hydrogenation of $RhCl_2(N_2Ar)(PPh_3)_2$ to $[RhCl_3(NH_2NHAr)(PPh_3)]_2$ in warm chloroform solution presumably proceeds *via* a hydrogen chloride abstraction reaction; the corresponding conversions performed in benzene solution give only a small yield of product and probably involve a ligand redistribution step. This hydrogenation reaction closely parallels the previously reported hydrogenation of azobenzene to aniline[36] and the reduction of diazonium salts to arenes,[37] both of which employ homogeneous rhodium catalysts.

The formation of aryldi-imine complexes by reaction of diazonium tetrafluoroborates with metal hydrides does not require the presence of free acid, the hydrogen chloride employed serves essentially as a source of chloride ions and may be replaced by lithium chloride. It therefore appears probable that, in the absence of free acid at least, the formation of aryldi-imine derivatives involves 'insertion' of aryldiazonium cations into metal–hydrogen bonds rather than direct protonation of co-ordinated arylazo ligands. To further test the scope of this process as a route to aryldi-imine complexes we investigated reactions of the hydrides $MHCl(CO)(PPh_3)_3$ and $MH_2(CO)(PPh_3)_3$ ($M = Ru$ or Os) with diazonium salts. The hydride complexes $MHCl(CO)(PPh_3)_3$ react with diazonium tetrafluoroborates to afford complexes of stoicheiometry $MCl(BF_4)(NH{=}NAr)(CO)(PPh_3)_2$; the presence of only two phosphine ligands in these products is unexpected and implies either five-co-ordination or the presence of co-ordinated tetrafluoroborate ligands. I.r. spectra (Nujol mulls) do not permit an unambiguous distinction between ionic and co-ordinated BF_4^- groups in the present instance but favour the latter arrangement. However the perchlorate analogue $OsCl(OClO_3)(NH{=}NAr)(CO)(PPh_3)_2$ ($Ar = p$-tolyl) clearly shows i.r. bands at 1130 and 1070 cm^{-1} attributable to co-ordinated perchlorate ligands.[38] In contrast the complexes behave as 1 : 1 electrolytes in polar solvents (nitrobenzene, acetonitrile) and presumably exist under these conditions as tetrafluoroborate or perchlorate salts of the solvated cations $[MCl(NH{=}NAr)(CO)(PPh_3)_2(sol)]^+$. These observations imply the presence of a solvent dependent equilibrium:

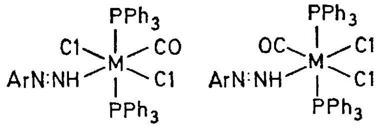
$$MCl(FBF_3)(NH{=}NAr)(CO)(PPh_3)_2 + sol \rightleftharpoons [MCl(NH{=}NAr)(CO)(PPh_3)_2(sol)]^+BF_4^-$$

Complexes containing weakly co-ordinated tetrafluoroborate[39] or perchlorate[38,39] ligands have previously been reported, and an equilibrium of the form given above seems entirely feasible. Acetone solutions of the aryldi-imine complexes '$MCl(FBF_3)(NH{=}NAr)(CO)(PPh_3)_2$' readily undergo carbonylation to afford *cis*-dicarbonyl salts $[MCl(NH{=}NAr)(CO)_2(PPh_3)_2]BF_4$ (IV) characterised by two strong bands at 2050, 1980 (Os) or 2070, 2010 (Ru) cm^{-1} attributable to ν(CO) and strong absorption at *ca.* 1060 cm^{-1} indicative of ionic tetrafluoroborate groups. On treatment with lithium chloride the monocarbonyl complexes $MCl(FBF_3)(NH{=}NAr)(CO)(PPh_3)_2$ yield neutral dichlorides $MCl_2(NH{=}NAr)(CO)(PPh_3)_2$; under similar conditions the dicarbonyl salts $[MCl(NH{=}NAr)(CO)_2(PPh_3)_2]BF_4$ afford mixtures of $MCl_2(NH{=}NAr)(CO)(PPh_3)_2$ and *cis*-$MCl_2(CO)_2(PPh_3)_2$ [identified by i.r. spectroscopy, ν(CO) 2040, 1975 (Os) or 2050, 1990 (Ru) cm^{-1}].

The complexes $MCl_2(NH{=}NAr)(CO)(PPh_3)_2$ are also obtained by reacting the hydrides $MHCl(CO)(PPh_3)_3$ with 1,3-diaryltriazenes in benzene–ethanol solution containing a small amount of hydrogen chloride. This reaction probably involves diazonium cations formed by acidolysis of the 1,3-diaryltriazenes; analogous syntheses performed in the absence of acid have previously been shown to afford 1,3-diaryltriazene derivatives.[40]

The neutral dichloro-complexes $MCl_2(CO)(NH{=}NAr)(PPh_3)_2$ ($Ar = p$-tolyl) each exist in two isomeric forms (Va and Vb). Isomer (Va) [ν(CO) 1975 cm^{-1}, (Ru); 1948 cm^{-1}, (Os)], which initially precipitates out of solution when lithium chloride is added to solutions containing $MCl(FBF_3)(NH{=}NAr)(CO)(PPh_3)_2$, is converted to isomer (Vb) [ν(CO) 1957 cm^{-1}, (Ru); 1934 cm^{-1} (Os)] by slow crystallisation. Isomer (Vb) is also the product obtained on reacting the complexes $MHCl(CO)(PPh_3)_3$ with 1,3-diaryltriazenes in the presence of hydrogen chloride, and is thought to be the thermodynamically preferred isomer corresponding to the *cis-cis*-dichlorodicarbonyl complexes $MCl_2(CO)_2(PPh_3)_2$.[41] Recrystallisation of the aryldi-imine complexes $MCl_2(NH{=}NAr)(CO)(PPh_3)_2$ (both isomers) in the presence of dichloromethane, acetone, or benzene leads to the formation of solvates, the stoicheiometry of these products was established by analysis and confirmed by i.r. or ^1H n.m.r. spectroscopy. The aryldi-imine ligands present in these complexes are resistant to mild hydrogenation under the conditions successfully employed to reduce the analogous rhodium aryldi-imine derivatives, but are readily displaced by carbon monoxide. Thus passage of a stream of carbon monoxide through a boiling solution of the aryldi-imine complex (either isomer) in benzene (ruthenium) or toluene (osmium) affords the well-known *cis-cis*-dichlorodicarbonyl derivatives $MCl_2(CO)_2(PPh_3)_2$.[41]

(V)



(a) (b)

The dihydrido-complexes $MH_2(CO)(PPh_3)_3$ react rapidly with diazonium tetrafluoroborates to yield the ionic

---

[36] I. Jardine and F. J. McQuillin, *Chem. Comm.*, 1970, 626.

[37] G. S. Marx, *J. Org. Chem.*, 1971, **36**, 1725.

[38] A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404.

[39] A. A. G. Tomlinson, M. Bonamico, G. Dessy, V. Fares, and L. L. Scaramuzza, *J.C.S. Dalton*, 1972, 1671 and references therein.

[40] S. D. Robinson and M. F. Uttley, *Chem. Comm.*, 1972, 184.

[41] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

TABLE 2

M.p., i.r., analytical, and conductivity data for arylazo and aryldi-imine complexes of the platinum metals

Complex	R	M.p./°C [a]	ν(N=NR) [b,c]	ν(C=O) [b]	Analytical data [d]				Conductivity [e]
					C	H	N	Cl	
$RuCl_3(N_2R)(PPh_3)_2$	Ph	185—186	1881		60·0 (60·2)	4·3 (4·2)	3·6 (3·3)		
$RuCl_3(N_2R)(PPh_3)_2,C_6H_6$	*p*-C_6H_4Me	175—177	1895 (1868)		63·8 (63·3)	4·6 (4·6)			
$RuCl_3(N_2R)(PPh_3)_2,0{\cdot}5CH_2Cl_2$	*p*-C_6H_4Me	(187—189)			58·3 (58·5)	4·5 (4·3)	3·7 (3·15)	15·9 (15·9)	
$RuCl_3(N_2R)(PPh_3)_2$	*p*-C_6H_4OMe	193—195	1884 (1858)		59·5 (59·6)	4·6 (4·3)	3·2 (3·2)		
$RuCl_3(N_2R)(PPh_3)_2,CH_2Cl_2$	*p*-C_6H_4Cl	187—189	1859		54·2 (54·0)	3·8 (3·8)	3·1 (2·9)		
$RuCl_3(N_2R)(PPh_3)_2,CH_2Cl_2$	*p*-$C_6H_4NO_2$	(177—181)	1858 (1830)		53·25 (53·4)	3·7 (3·65)	4·35 (4·35)		
$RuCl_3(N_2R)[P(p\text{-}C_6H_4Me)_3]_2$	*p*-C_6H_4Me	206—207	1856		62·7 (62·9)	5·2 (5·3)	2·9 (3·0)		
$RuCl_3(N_2R)[P(p\text{-}C_6H_4Cl)_3]_2$	*p*-C_6H_4Me	212—214	1886		48·6 (48·8)	3·2 (3·0)	2·5 (2·7)		
$RuCl_3(N_2R)[P(p\text{-}C_6H_4Cl)_3]_2$	*p*-C_6H_4Cl	208—209	1871		47·1 (46·8)	3·0 (2·6)		33·4 (32·9)	
$RuBr_3(N_2R)(PPh_3)_2$	*p*-C_6H_4Me	(182—185)	1895		52·3 (52·45)	4·1 (3·8)	2·55 (2·85)		
$OsBr_3(N_2R)(PPh_3)_2$	*p*-C_6H_4Me	(211—214)	1855		48·7 (48·1)	3·4 (3·5)	2·75 (2·6)		
$RhCl_2(N_2R)(PPh_3)_2$	Ph	189—193	1610 1545		62·8 (62·8)	4·6 (4·4)	3·3 (3·5)		
$RhCl_2(N_2R)(PPh_3)_2$	*p*-C_6H_4Me	230—232	1615 (1610) 1557 (1544)		63·2 (63·2)	4·5 (4·6)	3·6 (3·4)	8·4 (8·7)	
$RhCl_2(N_2R)(PPh_3)_2$	*p*-C_6H_4OMe	218—221	[f] (1605) 1558 (1545)		61·8 (62·0)	4·8 (4·5)	3·3 (3·4)		
$RhCl_2(N_2R)(PPh_3)_2$	*p*-C_6H_4Cl	204—207	1605 1560		60·5 (60·2)	4·1 (4·1)	3·1 (3·3)		
$RhCl_2(N_2R)(PPh_3)_2$	*p*-$C_6H_4NO_2$	(142—144)	1610 (1605) 1553 (1538)		59·6 (59·45)	4·45 (4·05)	4·55 (4·95)		
$RhBr_2(N_2R)(PPh_3)_2$	*p*-C_6H_4Me	(157—160)	1620 1565		57·1 (57·0)	3·95 (4·1)	2·85 (3·1)		
$RhCl_3(NH{:}NR)(PPh_3)_2,0{\cdot}5CH_2Cl_2$	*p*-C_6H_4Me	(175—178)			58·2 (58·25)	4·5 (4·4)	3·2 (3·15)	16·6 (15·9)	
$RhCl_3(NH{:}NR)(PPh_3)_2,0{\cdot}5CH_2Cl_2$	*p*-C_6H_4OMe	(161—164)			57·65 (57·3)	4·35 (4·30)	2·80 (3·10)	14·5 (15·5)	
$IrCl_3(NH{:}NR)(PPh_3)_2$	*p*-C_6H_4Me	(202—205)			54·7 (54·75)	4·25 (4·05)	2·85 (2·95)	11·45 (11·3)	
$[IrCl_2(NH{:}NR)(PPh_3)_3]BF_4$	*p*-C_6H_4Me								24·0
$[RhCl_3(NH_2{\cdot}NHR)(PPh_3)]_2$	*p*-C_6H_4Me	(>350)			49·5 (50·3)	4·15 (4·25)	4·5 (4·7)		
$[RhCl_3(NH_2{\cdot}NHR)(PPh_3)]_2$	*p*-C_6H_4Cl	(>350)			46·35 (46·95)	3·65 (3·6)	4·25 (4·55)	22·6 (23·05)	
$RuCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2$	*p*-C_6H_4Me	156—158		1970	58·9 (59·0)	4·3 (4·3)	2·9 (2·8)	3·9 (3·9)	16·35
$RuCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2,H_2O$	*p*-C_6H_4OMe	(152—156)		1968	56·7 (56·8)	4·5 (4·35)	2·85 (3·0)		20·0
$RuCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2,H_2O$	*p*-C_6H_4Cl	155—156		1971	56·1 (56·3)	4·0 (3·9)	2·8 (3·1)		16·8
$OsCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2$	*p*-C_6H_4Me	178—180		1951	52·9 (53·6)	4·2 (3·9)	2·2 (2·8)		16·6
$OsCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2$	*p*-C_6H_4OMe	174—175		1953	52·4 (52·8)	4·0 (3·8)	2·7 (2·8)		16·0
$OsCl(FBF_3)(NH{:}NR)(CO)(PPh_3)_2$	*p*-C_6H_4Cl	198—200		1954	52·0 (51·8)	4·0 (3·8)		6·6 (6·9)	17·2
$OsCl(OClO_3)(NH{:}NR)(CO)(PPh_3)_2$	*p*-C_6H_4Me	(158—160)		1947	52·85 (52·75)	4·15 (3·8)	2·3 (2·3)		16·2
$[RuCl(NH{:}NR)(CO)_2(PPh_3)_2]BF_4$	*p*-C_6H_4Me	(130—133)		2070, 2010	58·0 (58·5)	4·2 (4·15)	2·3 (3·0)		20·7
$[RuCl(NH{:}NR)(CO)_2(PPh_3)_2]BF_4$	*p*-C_6H_4OMe	(160—164)		2060, 2005	57·45 (57·5)	4·2 (4·05)	2·0 (3·0)		18·6
$[OsCl(NH{:}NR)(CO)_2(PPh_3)_2]BF_4$	*p*-C_6H_4Me	(153—156)		2050, 1975	53·4 (53·35)	3·95 (3·8)	2·0 (2·75)		19·3
$[OsCl(NH{:}NR)(CO)_2(PPh_3)_2]BF_4$	*p*-C_6H_4OMe	(200—205)		2050, 1980	51·95 (52·55)	3·7 (3·7)	2·45 (2·7)		22·1

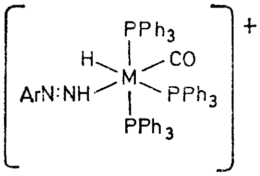
Table 2 (*Continued*)

Complex	R	M.p./°C [a]	ν(C=O) [b]	Analytical data [d] C	H	N	Cl	Conductivity [e]
$RuCl_2(NH{:}NR)(CO)(PPh_3)_2$,-$Me_2CO$	p-C_6H_4Me	189—190	1975	62·6 (62·5)	4·6 (4·7)	3·0 (3·1)	8·0 (7·85)	0·85
$RuCl_2(NH{:}NR)(CO)(PPh_3)_2$,-$CH_2Cl_2$	p-C_6H_4Me	(155—157)	1957	58·6 (58·6)	4·25 (4·35)	3·05 (3·0)	14·7 (15·2)	
$OsCl_2(NH{:}NR)(CO)(PPh_3)_2$	p-C_6H_4Me	(220—222)	1948	55·9 (56·6)	4·25 (4·3)	2·95 (3·0)	7·95 (7·6)	
$OsCl_2(NH{:}NR)(CO)(PPh_3)_2$,-$CH_2Cl_2$	p-C_6H_4Me	243—246	1934	54·1 (53·5)	4·1 (3·95)	2·7 (2·75)	14·6 (13·9)	
$RuHCl(NH{:}NR)(CO)(PPh_3)_2$,-$CH_2Cl_2$	p-C_6H_4Me	(147—150)	1920, 1910	60·75 (60·3)	4·8 (4·6)	3·05 (3·15)	11·15 (11·8)	
$[OsH(NH{:}NR)(CO)(PPh_3)_3]BF_4$	p-C_6H_4Me	(177—180)	1943	60·25 (60·4)	4·65 (4·4)	1·95 (2·25)		24·6
$[RuH(NH{:}NR)(CO)_2(PPh_3)_2]BF_4$,-EtOH	p-C_6H_4Me	(169—172)	2070, 1980	60·1 (60·35)	4·55 (4·85)	2·85 (3·0)		24·3

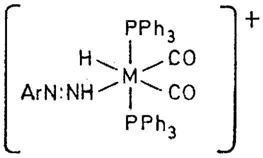
[a] M.p.s in parentheses taken on a Kofler hot-stage, others taken sealed under nitrogen using Buchi m.p. apparatus. [b] I.r. spectra taken for Nujol mulls. [c] Values for labelled (^{15}N=NR) derivatives in parentheses. [d] Theoretical values in parentheses. [e] Measured for *ca.* 10^{-3}M solutions in nitrobenzene, in Ω^{-1} cm^2 mol^{-1}. [f] Obscured by ligand absorptions.

derivatives $[MH(NH{=}NAr)(CO)(PPh_3)_3]BF_4$ (cation configuration VI). The orange-red crystalline osmium complex (Ar = p-tolyl) is characterised by i.r. bands at 2030w and 1943s cm^{-1} assigned to ν(OsH) and ν(CO) respectively, together with a high field n.m.r. pattern comprising a doublet of triplets. The corresponding ruthenium complex was too unstable to isolate and was characterised by its high field n.m.r. spectrum (doublet of triplets). Carbon monoxide failed to displace a triphenylphosphine ligand from the osmium complex, but reacted with the ruthenium analogue to form a *cis*-dicarbonyl salt $[RuH(NH{=}NAr)(CO)_2(PPh_3)_2]BF_4$ (cation configuration VII). The salts $[MH(NH{=}NAr)(CO)(PPh_3)_3]BF_4$ react with lithium chloride in boiling acetone–ethanol to afford the dichlorides $MCl_2(NH{=}NAr)(CO)(PPh_3)_2$; however, using cold concentrated solutions of the ruthenium salt the hydride complex $RuHCl(NH{=}NAr)(CO)(PPh_3)_2$ may be obtained.

(VI)



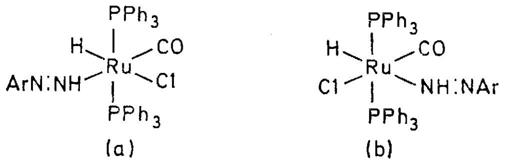
(VII)



This latter complex apparently exists as a mixture of two isomers (VII a and b) both of which were detected by proton n.m.r. spectra (see Table 1). However separation of these isomers was not possible since attempted recrystallisation or purification led to rapid formation of $RuCl_2(NH{=}NAr)(CO)(PPh_3)_2$ (isomer Vb).

It was hoped that a number of the aryldi-imine complexes of ruthenium and osmium described above would undergo deprotonation or dehydrochlorination reactions to afford arylazo derivatives isoelectronic with a number of known nitrosyl complexes. Although observed colour changes suggested that several of these reactions were successful, no stable arylazo products could be isolated.

(VIII)



The reactions of diazonium tetrafluoroborates with a number of other hydride complexes including $RhH(PPh_3)_4$, $MH(CO)(PPh_3)_3$ (M = Rh, Ir), $RuH_2(PPh_3)_4$, and $OsH_4(PPh_3)_3$ were investigated. Reaction was immediate in all cases but the products decomposed spontaneously with evolution of nitrogen and were therefore not investigated further.

EXPERIMENTAL

I.r. spectra were recorded as Nujol or hexachlorobutadiene mulls on Perkin-Elmer 457 or 621 spectrometers and were calibrated with polystyrene. ^1H N.m.r. spectra were recorded on a Bruker 90 MHz spectrometer. M.p.s were measured on a Kofler hot-stage or in sealed capillary tubes under nitrogen. Conductivities were measured using a Radiometer type CDM2e conductivity meter. Platinum metal salts were purchased from Johnson Matthey and 95% enriched $Na^{15}NO_2$ from Prochem. Diaryltriazenes, aryldiazonium salts, and platinum-metal phosphine complexes were prepared by literature methods. All reactions were performed under a nitrogen atmosphere but subsequent handling was under open conditions. Analyses by Dr. Strauss, Oxford, and the microanalytical laboratory, University College, London.

Several of the complexes described below formed solvates when recrystallised in the presence of dichloromethane, acetone, or benzene; for details of the nature and stoicheiometry of these solvates see Table 2.

Arylazo Complexes. Preparations involving 1,3-*Diaryltriazenes*.— *Trichloro*(*phenylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II). Warm solutions of ruthenium trichloride (0·13 g) in ethanol (10 ml) and 1,3-diphenyltriazene (0·2 g) in ethanol (10 ml) were added successively to a stirred, boiling solution of triphenylphosphine (0·54 g) in ethanol (10 ml) and the mixture was heated under reflux for 5 min. After cooling the product was filtered off as a brown precipitate and recrystallised from dichloromethane–methanol as brown crystals (25%).

The following were similarly prepared: *trichloro*(p-*tolylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II)*dichloromethane solvate* as golden-brown crystals (46%); recrystallisation from benzene–ethanol gave a benzene solvate; *trichloro*(p-*methoxyphenylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II) as brown crystals (56%); *trichloro*(p-*chlorophenylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II)*dichloromethane solvate* as green-brown crystals (62%); *trichloro*(p-*chlorophenylazo*)-*bis*(*tri*-p-*chlorophenylphosphine*)*ruthenium*(II) as green-brown crystals (62%).

Dichloro(*phenylazo*)*bis*(*triphenylphosphine*)*rhodium*(III). Solutions of rhodium trichloride (0·13 g) in ethanol (10 ml) and 1,3-diphenyltriazene (0·2 g) in ethanol (10 ml) were added to a solution of triphenylphosphine (0·54 g) in ethanol (10 ml), maintained at 40°, and the mixture was stirred for 10 min. After cooling the product was filtered off and recrystallised rapidly from dichloromethane–ethanol as brown crystals (83%).

The following were similarly prepared: *dichloro*(p-*tolylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) as brown crystals (43%); *dichloro*(p-*chlorophenylazo*)*bis*(*triphenylphosphine*)-*rhodium*(III) as brown crystals (62%).

Some syntheses were more effectively achieved using 1-methyl-1,3-di-*p*-tolyltriazene (except that in the formation of the rhodium complex the reaction mixture was also boiled under reflux for 1—2 min) and the following were thus prepared: *trichloro*(p-*tolylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II)*dichloromethane solvate* as golden-brown crystals (82%); *trichloro*(p-*tolylazo*)*bis*(*tri*-p-*tolylphosphine*)*ruthenium*(II) as brown crystals (32%); *trichloro*(p-*tolylazo*)*bis*(*tri*-p-*chlorophenylphosphine*)*ruthenium*(II) as green-brown crystals (81%); *dichloro*(p-*tolylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) as brown crystals (91%).

Arylazo complexes.—Preparations involving Diazonium Tetrafluoroborates.— Trichloro(p-*chlorophenylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II) *dichloromethane solvate.* A suspension of dichlorotris(triphenylphosphine)ruthenium (0·5 g) and *p*-chlorophenyldiazonium tetrafluoroborate (0·15 g) in acetone (10 ml) was stirred until complete dissolution occurred. The red-brown solution was treated with lithium chloride (0·15 g) in ethanol (10 ml) and then stirred for a further 5 min. The product, which precipitated during this time was filtered off, washed successively with water, ethanol, and n-hexane, and then recrystallised from dichloromethane–ethanol as green-brown crystals (81%).

The following were similarly prepared using the appropriate diazonium tetrafluoroborate and lithium halide: *trichloro*(p-*tolylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II) *dichloromethane solvate* as golden-brown crystals (85%); *trichloro*(p-*methoxyphenylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II) as brown crystals (85%); *trichloro*(p-*nitrophenylazo*)-*bis*(*triphenylphosphine*)*ruthenium*(II) *dichloromethane solvate* as orange-brown crystals (90%); *tribromo*(p-*tolylazo*)*bis*(*triphenylphosphine*)*ruthenium*(II) from dibromotris(triphenylphosphine)ruthenium as golden-brown crystals (77%); *tribromo*(p-*tolylazo*)*bis*(*triphenylphosphine*)*osmium*(II) from dibromotris(triphenylphosphine)osmium as golden crystals (70%).

Dichloro(*phenylazo*)*bis*(*triphenylphosphine*)*rhodium*(III). Chlorotris(triphenylphosphine)rhodium (0·5 g) and phenyldiazonium tetrafluoroborate (0·12 g) were mixed in acetone (5 ml) to give a dark green solution. Lithium chloride (0·15 g) in ethanol (5 ml) was added and the mixture was stirred for 3 min during which time the product crystallised out. The product was filtered off, washed successively with water, ethanol, and hexane then dried *in vacuo* as brown crystals (72%). Similarly prepared were: *dichloro*(p-*tolylazo*)*bis*-(*triphenylphosphine*)*rhodium*(III) as brown crysyals (78%); *dichloro*(p-*methoxyphenylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) as brown crystals (75%); *dichloro*(p-*chlorophenylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) as orange-brown crystals (91%); *dichloro*(p-*nitrophenylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) as orange-brown crystals (82%); *dibromo*(p-*tolylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) from bromotris(triphenylphosphine)rhodium and lithium bromide as brown crystals (80%).

Aryldi-imine Complexes.—Trichloro(p-*tolyldi-imine*)*bis*(*triphenylphosphine*)*rhodium*(III). A solution of chlorotris(triphenylphosphine)rhodium (0·4 g) in dichloromethane (5 ml) was treated with dry hydrogen chloride until light orange in colour. *p*-Tolyldiazonium tetrafluoroborate (0·15 g) and ethanol (10 ml) were added, and the mixture heated under reflux for 3 min then cooled. The precipitated product was filtered off, washed with ethanol, then hexane and dried *in vacuo* as golden-orange crystals (76%). Recrystallisation from dichloromethane–ethanol gave a dichloromethane solvate.

Similarly prepared was *trichloro*(p-*methoxyphenyldi-imine*)*bis*(*triphenylphosphine*)*rhodium*(III) as golden-orange crystals (83%), recrystallised from dichloromethane–ethanol as a dichloromethane solvate.

Dichloro(p-*tolyldi-imine*)*tris*(*triphenylphosphine*)*iridium*(III) *tetrafluoroborate.* Dichlorohydridotris(triphenylphosphine)iridium (0·3 g) and *p*-tolyldiazonium tetrafluoroborate (0·12 g) in dichloromethane (10 ml) and diethyl ether (15 ml) were boiled under reflux for 10 min. After cooling and standing yellow crystals of the required product were filtered off, washed with diethyl ether and dried *in vacuo* (36%).

Trichloro(p-*tolyldi-imine*)*bis*(*triphenylphosphine*)*iridium*(III).—Dichlorohydridotris(triphenylphosphine)iridium (0·3 g) and *p*-tolyldiazonium tetrafluoroborate (0·12 g) were stirred together in cold acetone (15 ml) for 3 h. Lithium chloride (0·1 g) in ethanol (15 ml) was added and the solution was evaporated on a steam-bath until the product crystallised. These yellow-orange crystals (73%) were filtered off, washed with ethanol then hexane and dried *in vacuo.*

Interconversion of Arylazo and Aryldi-imine Complexes.—Dry hydrogen chloride was bubbled through a solution of dichloro(*p*-tolylazo)bis(triphenylphosphine)rhodium (0·2 g) in dichloromethane (10 ml) whereupon the colour of the solution rapidly changed from red-brown to light orange. Ethanol (10 ml) was added and the solution evaporated under reduced pressure to give golden-orange crystals (90%) of *trichloro*(p-*tolyldi-imine*)*bis*(*triphenylphosphine*)*rhodium*(III) identified by comparison with an authentic sample.

Triethylamine (2 drops) were added to a solution of trichloro(*p*-tolyldi-imine)bis(triphenylphosphine)rhodium(III) (0·25 g) in dichloromethane (10 ml). The colour of the solution rapidly darkened, n-hexane (10 ml) was added and the solution evaporated under reduced pressure to give *dichloro*(p-*tolylazo*)*bis*(*triphenylphosphine*)*rhodium*(III) as a brown precipitate (60%) identical with an authentic sample.

Similar interconversion of the analogous iridium arylazo and aryldi-imine complexes was achieved; however the iridium arylazo complexes were unstable and difficult to characterise.

Tetrachloro-μ-dichloro-bis(triphenylphosphine)bis(p-*tolylhydrazine*)*dirhodium*(III).— Dichloro(*p*-tolylazo)bis(triphenylphosphine)rhodium or trichloro(*p*-tolyldi-imine)bis(triphenylphosphine)rhodium (0·25 g) was suspended in a mixture of chloroform (12·5 ml) and methanol (12·5 ml). Dry dihydrogen was bubbled through the boiling mixture for 1 h, the solution was then cooled and stored at 0 °C overnight. The resultant orange crystals (35%) of tetrachloro-μ-dichlorobis(triphenylphosphine)bis(*p*-tolylhydrazine)dirhodium were filtered off, washed with methanol and dried *in vacuo*. Similarly prepared was *tetrachloro-μ-dichlorobis*(p-*chlorophenylhydrazine*)*bis*(*triphenylphosphine*)*dirhodium*(III) as orange crystals (43%).

Chloro(*tetrafluoroborato*)(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II). Chlorohydrido(carbonyl)tris(triphenylphosphine)ruthenium (0·4 g) and *p*-tolyldiazonium tetrafluoroborate (0·15 g) were stirred together in cold acetone (15 ml) for 3 h. The solution was evaporated under reduced pressure to yield an oil which crystallised on addition of methanol (5 ml). The yellow crystals of required product (50%) were filtered off, washed with a small volume of cold methanol and dried *in vacuo.*

Similarly prepared were: *chloro*(*tetrafluoroborato*)(p-*methoxyphenyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II) *hydrate* as green crystals (43%); *chloro*(*tetrafluoroborato*)(p-*chlorophenyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II) as lime green crystals (37%). The following were similarly prepared using chlorohydrido(carbonyl)tris(triphenylphosphine)osmium: *chloro*(*tetrafluoroborato*)(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (64%); *chloro*(*tetrafluoroborato*)(p-*methoxyphenyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (63%); *chloro*(*tetrafluoroborato*)(p-*chlorophenyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (34%); *chloro*(*perchlorato*)(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) as yellow crystals (54%) [perchloric acid (0·3 ml, 65% aq.) was added after the reactants had completely dissolved].

Chloro(p-*tolyldi-imine*)(*dicarbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II) *tetrafluoroborate.*—Carbon monoxide was bubbled through a solution of chloro(tetrafluoroborato)(p-tolyldi-imine)(carbonyl)bis(triphenylphosphine)ruthenium [prepared from chlorohydrido(carbonyl)tris(triphenylphosphine)ruthenium (0·4 g) in acetone (15 ml), as described above] for 2 h. Tetrafluoroboric acid (0·5 ml, 40% aq.) in ethanol (10 ml) was added and the solution was evaporated under reduced pressure to small volume. The concentrated solution was covered with a layer of n-hexane (20 ml) and set aside to crystallise. The product was filtered off, washed with ethanol, then hexane and dried *in vacuo* as yellow-green crystals (56%). Similarly prepared were: *chloro*(p-*methoxyphenyldi-imine*)*di*(*carbonyl*)*bis*(*triphenylphosphine*) *ruthenium*(II) *tetrafluoroborate* as yellow-green crystals (63%); and using chlorohydrido(carbonyl)tris(triphenylphosphine)osmium with the appropriate diazonium salt, *chloro*(p-*tolyldi-imine*)*di*(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) *tetrafluoroborate* as yellow crystals (74%); *chloro*(p-*methoxyphenyldi-imine*)(*dicarbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) *tetrafluoroborate* as orange crystals (67%).

Dichloro(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II) [*isomers* (Va) and Vb)].—(a) Lithium chloride (0·15 g) in ethanol (10 ml) was added to an acetone solution of chloro(tetrafluoroborato)(*p*-tolyldi-imine)(carbonyl)bis(triphenylphosphine)ruthenium prepared from chlorohydrido(carbonyl)tris(triphenylphosphine)ruthenium (0·4 g) as described above, and the solution was stirred for 10 min. The product, which precipitated during this time was filtered off, washed with water, ethanol then hexane and dried *in vacuo* as yellow crystals (74%) of the acetone solvate $RuCl_2(NH{=}NC_6H_4\text{-}p\text{-}Me)(CO)(PPh_3)_2,Me_2CO$ [isomer (Va); ν(CO) 1975 cm^{-1}]. Recrystallisation of this product gave the second isomer [configuration (Vb); ν(CO) 1957 cm^{-1}] either as solvent-free crystals (from benzene–ethanol) or as a dichloromethane adduct $RuCl_2(NH{=}NC_6H_4\text{-}p\text{-}Me)(CO)(PPh_3)_2,CH_2Cl_2$ (from dichloromethane–ethanol).

(b) Lithium chloride (0·15 g) in ethanol (10 ml) was added to an acetone solution of hydrido(*p*-tolyldi-imine)(carbonyl)tris(triphenylphosphine)ruthenium tetrafluoroborate [prepared from dihydrido(carbonyl)tris(triphenylphosphine)ruthenium (0·4 g) as described below] and the mixture was boiled under reflux for 30 min. Crystals (80%) of the required product [isomer (Va)] solvated with one mole of acetone were obtained from the cooled mixture.

(c) Dry hydrogen chloride was bubbled through a suspension of chlorohydrido(carbonyl)tris(triphenylphosphine)ruthenium (0·3 g) in benzene (15 ml) for a brief period; 1,3-di-*p*-tolyltriazene (0·2 g) in ethanol (15 ml) was added and the mixture was heated under reflux for 30 min. After cooling and the addition of methanol (15 ml) yellow crystals (68%) of the required unsolvated product [isomer (Vb)] were filtered off, washed with n-hexane and dried *in vacuo.*

Similarly prepared by method (a) from an acetone solution of chloro(tetrafluoroborato)(p-tolyldi-imine)(carbonyl)bis(triphenylphosphine)osmium was *dichloro*(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) [isomer (Va); ν(CO) 1948 cm^{-1}] as yellow-orange crystals (83%).

Similarly prepared by method (c) from chlorohydrido(carbonyl)tris(triphenylphosphine)osmium, and recrystallised from dichloromethane–ethanol was *dichloro*(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*osmium*(II) *dichloromethane solvate* [isomer (Vb); ν(CO) 1934 cm^{-1}] as yellow-orange crystals (73%).

Hydrido(p-*tolyldi-imine*)(*carbonyl*)*tris*(*triphenylphosphine*)*osmium*(II) *tetrafluoroborate.* Dihydrido(carbonyl)tris(triphenylphosphine)osmium (0·4 g) and *p*-tolyldiazonium tetrafluoroborate (0·15 g) were mixed together in acetone (10 ml) to form an orange-red solution.

Tetrafluoroboric acid (0·5 ml, 40% aq.) in ethanol (10 ml) was added and the solution evaporated to small volume, then covered with a layer of n-hexane and set aside to crystallise. The product was filtered, washed with ethanol, then hexane and dried *in vacuo* as orange-red crystals (80%). The analogous ruthenium complex was similarly prepared, and identified in solution by n.m.r. spectroscopy.

Hydrido(p-*tolyldi-imine*)*di*(*carbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II) *tetrafluoroborate.*—Carbon monoxide was passed for 30 min through an acetone solution of hydrido(*p*-tolyldi-imine)(carbonyl)tris(triphenylphosphine)ruthenium tetrafluoroborate, prepared *in situ* by the same method as the osmium analogue. The solution was treated as above and the product, which deposited was collected as reddish-pink crystals (64%).

Chlorohydrido(p-*tolyldi-imine*)(*carbonyl*)*bis*(*triphenylphosphine*)*ruthenium*(II) *dichloromethane solvate* [*isomers* (VIIIa) and (VIIIb)]. Lithium chloride (0·05 g) in ethanol (10 ml) was added to a stirred acetone solution of hydrido(*p*-tolyldi-imine)(carbonyl)tris(triphenylphosphine)ruthenium tetrafluoroborate prepared as described above. The product, which immediately deposited as yellow micro-crystals (64%) was filtered off before further reaction could occur, washed successively with water, ethanol, and n-hexane then dried *in vacuo*. Further purification was achieved by dissolving the complex in cold dichloromethane and immediately precipitating with methanol. Prolonged exposure of the complex to dichloromethane leads to formation of dichloro(*p*-tolyldi-imine)(carbonyl)bis(triphenylphosphine)ruthenium.

We thank the S.R.C., the Royal Society, and the University of London Central Research Fund for financial support.

[3/1168 *Received*, 6*th June*, 1973]