Arylazo, Aryldi-imide, and some Isocyanide Complexes of Ruthenium

By **Jon A. McCleverty,* Duncan Seddon, and R. (Bob) N. Whiteley,** Department of Chemistry, The University, Sheffield S3 7HF

Reaction of $[RuHCl(PPh_3)_3]$ and $[RuCl_2(PPh_3)_3]$ with $[ArN_2]X$ afforded $[RuCl(N_2Ar)_2(PPh_3)_2]X$ (Ar = *p*-MeC_6H_4, *o*-, *m*-, or *p*-$MeOC_6H_4$; X = BF_4 or PF_6) and $[RuCl_2(N_2Ar)(PPh_3)_2]_n[X]_n$ (Ar = *p*-MeC_6H_4, *o*- or *m*-$MeOC_6H_4$; X = BF_4 or PF_6), respectively. The species $[Ru_2Cl_3\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_3][PF_6]$ was also obtained from $[RuCl_2(PPh_3)_3]$. Chlorination of $[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2][BF_4]$ afforded $[RuCl_3\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]$. Addition of $[ArN_2][PF_6]$ and of CNR to $[RuHCl(CO)(PPh_3)_3]$ gave the aryldi-imide species $[RuCl(NCMe)(NH{=}NAr)(PPh_3)_2][PF_6]$ (Ar = *o*-, *m*-, or *p*-$MeOC_6H_4$) and $[RuHCl(CO)(CNR)(PPh_3)_2]$ (R = Pr^i, Bu^t, or *p*-ClC_6H_4), respectively. Reaction of $[RuHCl(CO)(PPh_3)_2]$ with HCl gas in ethanol gave $[RuCl_2(CO)_2(PPh_3)_2]$ and $[Ru_2Cl_4(CO)_2(PPh_3)_3]$, and with nitrous acid, $[RuCl_3(NO)(PPh_3)_2]$.

ARENEDIAZONIUM ions, $[ArN_2]^+$, are electronically equivalent to the nitrosonium ion, $[NO]^+$, and as such may be regarded as two-electron donors towards transition-metal atoms. Many transition-metal complexes react with $[NO]^+$ forming cationic and neutral (with concomitant uptake of halide ion) nitrosyl complexes,[1,2] and arylazo-complexes can often be prepared similarly.[2,3] It is known that arylazo or aryldi-imide complexes of rhodium, iridium, or platinum can be prepared by addition of $[ArN_2]^+$ to the appropriate transition-metal hydrides. Aryldi-imide complexes, formed in the reaction $L_nMH + [ArN_2]^+ \longrightarrow [L_nM(NH{=}NAr)]^+$, may be readily deprotonated[4] affording the corresponding arylazo-compounds. Thus, we attempted to prepare arylazo-complexes of ruthenium *via* the co-ordinatively unsaturated species $[RuHCl(PPh_3)_3]$ and $[RuCl_2(PPh_3)_2]$, and also using $[RuH_4(PPh_3)_4]$, $[RuHCl(CO)(PPh_3)_3]$, and $[RuH_2(N_2)(PPh_3)_3]$. Our preliminary results have been reported,[5] and since then Robinson and his co-workers described extensive complementary studies[6] of ruthenium arylazo and related complexes.

EXPERIMENTAL

The arenediazonium salts $[ArN_2]^+$ (Ar = *p*-MeC_6H_4, *o*-, *m*-, or *p*-$MeOC_6H_4$) were obtained by standard procedures using HBF_4 or HPF_6. The complexes $[RuCl_2(PPh_3)_3]$, $[RuHCl(PPh_3)]$, and $[RuHCl(CO)(PPh_3)_3]$ were prepared by literature methods. All reactions were carried out under nitrogen, and all solvents was degassed prior to their use.

Conductivity measurements were made at room temperature with a Phillips conductivity meter. The i.r. and n.m.r. spectra were obtained using PE 457 and 180 spectrophotometers and a Varian HA 100 instrument, respectively.

$[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2][BF_4]\cdot0\cdot3CH_2Cl_2$.—A mixture of $[RuCl_2(PPh_3)_3]$ (2·3 g), sodium borohydride (0·5 g), water (5·0 ml), and benzene (350 ml) was refluxed for 3 h under nitrogen. After cooling to room temperature, the deep red benzene solution was separated from the aqueous layer. The benzene was removed *in vacuo* to give crude *trans*-$[RuClH(PPh_3)_3]$ as a reddish purple solid. The crude hydride was suspended in acetone (100 ml) and cooled in an ice-bath. Toluene-*p*-diazonium tetrafluoroborate (1·2 g, 2·4 mmol) was added, and the mixture was stirred for 1 h to give an orange-yellow solution. The volume of this solution was reduced *in vacuo* to *ca.* 20 ml, ether (30 ml) was added, and the mixture was set aside at room temperature for 15 min. A yellow solid formed and was collected by centrifuging. After drying *in vacuo* the solid was redissolved in dichloromethane (50 ml) and chromatographed on silica gel using acetone as eluant. The deep reddish yellow band was collected, reduced to *ca.* 20 ml *in vacuo*, ether (150 ml) was added, and the mixture stored at −20 °C for 15 h. The small yellow crystals which formed were filtered off and recrystallised from dichloromethane–ether.

$[RuCl\{N_2(MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$.— $[RuClH(PPh_3)_3]$ (0·5 g) In degassed methanol (50 ml) was stirred with an excess of methoxybenzenediazonium hexafluorophosphate for 1·5 h. A precipitate of $[RuCl\{N_2(MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$ was formed and filtered off, washed with ether, and dried *in vacuo*. The products were sufficiently pure for analysis. However, $[RuCl\{N_2(o\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$ was further purified by chromatography on alumina using acetone as eluant, with a final recrystallisation from acetone–light petroleum (b.p. 60—80 °C). The yields of the complexes were 80% (*o*-$MeOC_6H_4$), 60% (*m*-$MeOC_6H_4$), and 80% (*p*-$MeOC_6H_4$).

$[RuCl_2\{N_2(p\text{-}MeC_6H_4)(PPh_3)_2\}]_n[BF_4]_n$.—A mixture of $[RuCl_2(PPh_3)_3]$ (1·0 g), acetone (30 ml), and dichloromethane (30 ml) was cooled in an ice-bath. Toluene-*p*-diazonium tetrafluoroborate (0·4 g) was added and the mixture stirred for 20 min. The yellow solution which formed was reduced to 30 ml *in vacuo* and treated with light petroleum (b.p. 60—80 °C), and after 20 min an orange-yellow solid had precipitated. This mixture was centrifuged, the supernatant liquid discarded, and the residue dissolved in dichloromethane (30 ml); the solution was filtered and toluene (20 ml) added to it. After 5 min the

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

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

[6] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Chem. Comm.*, 1973, 176; *J.C.S. Dalton*, 1973, 2713.

mixture was treated with light petroleum (b.p. 60—80 °C; 50 ml) and after 20 min at −20 °C, orange-red crystals had separated. These were filtered off, and recrystallised from dichloromethane–light petroleum.

$[RuCl_2\{N_2(MeOC_6H_4)\}(PPh_3)]_n[PF_6]_n$.— $[RuCl_2(PPh_3)_3]$ (1·0 g) Was stirred in acetone (50 ml) for 1 h with an excess of the appropriate methoxybenzenediazonium hexafluorophosphate. The solvent was then evaporated *in vacuo* and the residue washed with ethanol. The combined residue and washings were filtered, and the residue was identified as $[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$ when $[p\text{-}MeOC_6H_4N_2][PF_6]$ was used. The filtrate was gradually evaporated affording the orange-yellow $[RuCl_2\{N_2(MeOC_6H_4)\}(PPh_3)_2]_n[PF_6]_n$ which was recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C). The yields were 30% (o-$MeOC_6H_4$) and 15% (m-$MeOC_6H_4$); no product of this type was obtained using $[p\text{-}MeOC_6H_4N_2][PF_6]$.

$[Ru_2Cl_3\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_3][PF_6]$.—An acetone mixture (50 ml) of $[RuCl_2(PPh_3)_3]$ (1·0 g) and $[p\text{-}MeOC_6H_4N_2][PF_6]$ (1·0 g) were stirred at 0 °C for 1 h. The mixture was then chromatographed on a 6-ft column packed with silica gel using acetone as eluant. The first brown band was collected, the solvent removed *in vacuo*, and the residue recrystallised from acetone–light petroleum (b.p. 60—80 °C) giving brown crystals of the product (10%). A second red band was eluted and on evaporation of the solvent afforded an uncharacterisable red oil.

Reaction of $[RuCl_2(PPh_3)_3]$ *with* $[p\text{-}MeOC_6H_4N_2][PF_6]$ *in Acetonitrile*.—$[RuCl_2(PPh_3)_3]$ (1·0 g) Was stirred under N_2 in acetonitrile (30 ml) until a clear yellow solution had formed (15 min). To this was added methoxybenzene-p-diazonium hexafluorophosphate (1·0 g) and the mixture was stirred for a further 3 h. The solvent was then removed *in vacuo* and the residue extracted with ethanol. Partial evaporation of the ethanol extract afforded $[Ru_2(NCMe)_3Cl_2\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_4][PF_6]_2$ as brown crystals.

$[RuCl_3\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]\cdot 1\cdot 1CH_2Cl_2$.—An acetone solution (100 ml) of $[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2]^+$ (0·6 g) was treated with a slow stream of chlorine gas for *ca.* 5 min. During this time the solution became warm, and unless care was taken, might boil explosively. The colour of the solution changed from orange to yellow and yellow crystals formed, and after standing in air for 5 min the solvent was removed *in vacuo*. The residue was partly dissolved in dichloromethane (25 ml) and chromatographed on a silica-gel column using dichloromethane–acetone (50 : 50 v/v) as eluant. The red band was collected, the solvent removed *in vacuo*, and the residue recrystallised from dichloromethane–light petroleum (b.p. 60—80 °C). The yellow plates which were obtained were rechromatographed on Kieselguhr using dichloromethane as eluant. The yellow band was separated, and the solvent reduced to *ca.* 25 ml *in vacuo*. Light petroleum (b.p. 40—60 °C; 30 ml) was added and the mixture set aside for 30 min. The yellow plates which formed were filtered off, washed with light petroleum, and dried *in vacuo*.

$[Ru(NCMe)(CO)Cl\{NH{:}N(MeOC_6H_4)\}(PPh_3)_2][PF_6]$.— A mixture of $[Ru(CO)ClH(PPh_3)_3]$ (1·0 g) and an excess of $[MeOC_6H_4N_2][PF_6]$ was stirred in acetonitrile (50 ml) under N_2 until a clear yellow solution was obtained. The solution was filtered and an equal volume of propan-2-ol was added, the bulk of the solution being evaporated *in vacuo* until crystallisation began. On the further addition of propan-2-ol, and cooling of the mixture at −10 °C for 18 h, the complexes $[Ru(NCMe)(CO)Cl\{N_2(MeOC_6H_4)\}(PPh_3)_2][PF_6]$ crystallised (o-, m-, and p-isomers). The products were filtered off, washed with ether, and dried *in vacuo* (yields *ca.* 80%).

$[RuClH(CO)(CNR)(PPh_3)_2]$ ($R = Pr^i$, Bu^t, p-ClC_6H_4).—A mixture of $[RuClH(CO)(PPh_3)_3]$ (0·5 g) and an excess of CNR was stirred in degassed methanol under N_2 for 48 h. After that time, the white precipitate of the product was filtered off, washed with light petroleum (b.p. 40—60 °C), and dried *in vacuo*. No further purification was necessary (yields *ca.* 80%).

RESULTS

Synthetic Studies and Spectral Characterisation.—Reaction of $[RuHCl(PPh_3)_3]$ with $[ArN_2]X$ ($Ar = p\text{-}MeC_6H_4$, o-, m-, or p-$MeOC_6H_4$; $X = BF_4$ or PF_6) afforded $[RuCl(N_2Ar)_2(PPh_3)_2]X$. When these reactions were carried out in dichloromethane ($X = BF_4$) solvent of crystallisation was incorporated in the isolated solids. This was retained even when the compound was recrystallised from acetone–ether. When the syntheses were carried out in acetone or methanol ($X = PF_6$), however, no solvent of crystallisation was found in the isolated complexes. The amount of dichloromethane incorporated in the tetrafluoroborates, and in other species described in this work, was readily established by elemental analyses and ^1H n.m.r. spectral studies (Tables 1 and 2).

The bis-arylazo-complexes were 1 : 1 electrolytes in acetone, and were stable for a few hours in air and in solution. Attempts to recrystallise them from chloroform led to decomposition, and on one occasion to $[RuCl_3(N_2Ar)(PPh_3)_2]$. Their ^1H n.m.r. spectra provided no useful structural information, but confirmed their overall stoicheiometry. The i.r. spectra of the complexes (Table 3) in the region 1850—1550 cm^{-1} were characteristic of these species, and served to distinguish them from the other arylazo-complexes prepared. Thus, in KBr discs, two strong bands occurred at *ca.* 1740 and 1600 cm^{-1}, and are tentatively assigned to stretching modes associated with the two ArN=N groups.

Reaction of $[RuH_4(PPh_3)_3]$ or $[RuH_2(N_2)(PPh_3)_3]$ with arenediazonium salts, either in the presence or absence of H_2, afforded ill-defined and uncharacterisable solids. No evidence could be obtained for $[Ru(N_2Ar)_2(PPh_3)_2]$, and this species could not be prepared by reduction of $[RuCl(N_2Ar)_2(PPh_3)_2]^+$ (*vide infra*).

When $[RuCl_2(PPh_3)_3]$ was treated with $[ArN_2]^+$, the nature of the product was dependent on the solvent used for the reaction. In dichloromethane, either with or without added acetone, the mono-arylazo-species $[RuCl_2(N_2Ar)(PPh_3)_2]_nX_n$ ($Ar = p\text{-}MeC_6H_4$, o- or m-$MeOC_6H_4$; $X = BF_4$ or PF_6) was formed. When $Ar = p\text{-}MeOC_6H_4$, however, the only product we could isolate was $[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$. While the ^1H n.m.r. spectra of these complexes were consistent with their empirical formulae, and their i.r. spectra were distinct from those of $[RuCl(N_2Ar)_2(PPh_3)_2]^+$, having one broad NN stretching frequency at *ca.* 1870 cm^{-1}, they did not indicate the value of n. From conductivity studies, it seems possible that $n = 2$, but this cannot be definitely confirmed.

In acetonitrile, $[RuCl_2(PPh_3)_3]$ dissolved to give, presumably, the reactive $[RuCl_2(NCMe)_2(PPh_3)_2]$.[7] When

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[7] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 1749.

treated with $[p\text{-}MeOC_6H_4N_2][PF_6]$, the product, which could be obtained occasionally but not reproducibly, had an analysis consistent with its formulation as $[RuCl\{N_2(p\text{-}MeOC_6H_4)\}(PPh_3)]_2[PF_6]_2\cdot3MeCN$. The i.r. and ^1H n.m.r. spectral data indicated that this species was different to the other arylazo-complexes described herein. Three methyl resonances, associated with the acetonitrile, were observed in addition to the $MeOC_6H_4$ signals, in the ^1H n.m.r. spectrum of the complex. However, in view of the limited data, no meaningful structure can be proposed.

TABLE 1

Analytical, molecular-weight, and conductivity data

	Elemental analyses (%)									
	Calc.				Found					
Compound	C	H	N	Cl	C	H	N	Cl	M [a]	Λ [b]
$[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2][BF_4]\cdot0\cdot3CH_2Cl_2$	59·7	4·4	5·5	5·6	59·6	4·6	5·7	5·4		95·9
$[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][BF_4]\cdot0\cdot7CH_2Cl_2$	56·5	4·3	5·2	7·9	56·3	4·3	5·2	7·6		92·1
$[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$	55·8	4·1	5·2	3·3	56·1	4·4	5·3	3·3		138
					56·0 [c]	4·5 [c]	5·1 [c]			123 [c]
$[RuCl\{N_2(o\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$	55·8	4·1	5·2	3·3	54·6	4·5	5·6			161
$[RuCl\{N_2(m\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$	55·8	4·1	5·2	3·3	55·4	4·2	5·0	3·2		111
$[RuCl_2\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]_n[BF_4]_n$	57·2	4·1	3·2	7·9	56·8	4·5	3·3	7·9		94·3
$[RuCl_2\{N_2(o\text{-}MeOC_6H_4)\}(PPh_3)_2]_n[PF_6]_n$	52·9	3·8	2·9	7·3	53·2	4·3	3·0	6·9		170
$[RuCl_2\{N_2(m\text{-}MeOC_6H_4)\}(PPh_3)_2]_n[PF_6]_n$	52·9	3·8	2·9	7·3	53·0	4·2	2·8	7·2		
$[RuCl_3\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]\cdot1\cdot1CH_2Cl_2$	56·1	4·2	3·0	19·6	56·0	4·4	3·2	19·8		1·5
$[RuCl\{N_2(p\text{-}MeOC_6H_4)\}(PPh_3)_2]_2[PF_6]_2\cdot3MeCN$	55·1	4·1	4·9	3·5	55·3	4·5	4·8	4·5		244
$[Ru_2Cl_3\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_3][PF_6]$	54·1	3·9	3·7	7·1	54·3	4·3	3·5	7·0		137
$[RuCl(NCMe)\{NH{:}N(p\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2][PF_6]$	54·6	3·8	4·3	3·5	54·6	4·6	4·2	2·9		162
$[RuCl(NCMe)\{NH{:}N(o\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2][PF_6]$	54·6	3·8	4·3	3·5	55·5	4·2	4·1	3·1		145
$[RuCl(NCMe)\{NH{:}N(m\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2][PF_6]$	54·6	3·8	4·3	3·5	55·2	4·4	3·9			149
$[RuClH(CO)\{CN(p\text{-}ClC_6H_4)\}(PPh_3)_2]$	63·9	4·1	1·7	8·6	63·9	4·5	1·7	8·7	698 (826)	
$[RuClH(CO)(CNPr^i)(PPh_3)_2]$	64·9	4·9	1·8	4·7	64·9	5·2	1·8	5·3	792 (758)	
$[RuClH(CO)(CNBu^t)(PPh_3)_2]$	65·3	5·1	1·8	4·6	65·7	5·1	1·9	4·3	708 (772)	
$[Ru_2(CO)_2(PPh_3)_3Cl_4]$	56·7	3·8		12·0	57·0	4·4		11·7	1140 (1186)	2·5

[a] Obtained osmometrically in chloroform. [b] In Ω^{-1} cm^2 mol^{-1} in 10^{-3}M $(CH_3)_2CO$ solutions. [c] As prepared from $[RuCl_2(PPh_3)_3]$.

TABLE 2

^1H N.m.r. spectral data obtained from ruthenium complexes

		Resonances (100 MHz)		
Complexes	Solvent	Aryl protons [a]	Methyl [b] protons	Other protons
$[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2][BF_4]\cdot0\cdot3CH_2Cl_2$	$CDCl_3$	2·3—3·5 (19)	7·63s (3)	4·72s (0·3) [c]
$[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][BF_4]\cdot0\cdot7CH_2Cl_2$	$CDCl_3$	2·3—3·3 (19)	6·11s (3)	4·69s (0·7) [c]
$[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$	$(CD_3)_2CO/$ $(CD_3)_2SO$	2·51—3·04 (19)	6·12s (3)	
$[RuCl\{N_2(m\text{-}OC_6H_4)\}_2(PPh_3)_2][PF_6]$	$CDCl_3$	2·60—3·70 (20)	6·24s (3)	
$[RuCl_2\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]_n[BF_4]_n$	$CDCl_3$	2·0—3·5 (34)	7·65s (3)	
$[RuCl_2\{N_2(m\text{-}OC_6H_4)\}(PPh_3)_2]_n[PF_6]_n$	$CDCl_3$	2·0—3·0 (34)	6·35 (3)	
$[RuCl_2\{N_2(o\text{-}MeOC_6H_4)\}(PPh_3)_2]_n[PF_6]_n$	$CDCl_3$	2·0—3·4 (34)	6·26 (3)	
$[Ru_2Cl_3\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2][PF_6]$	$CDCl_3$	2·0—3·4 (50)	$\left.\begin{matrix}6{\cdot}15s\\6{\cdot}20s\end{matrix}\right\}6$	
$[Ru_2Cl_4\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_4][PF_6]_2\cdot3MeCN$	$CDCl_3$	2·0—3·3 (34)	6·18s (3)	$\left.\begin{matrix}8{\cdot}00s\\8{\cdot}12s\\8{\cdot}42s\end{matrix}\right\}2{\cdot}5$ [d]
$[RuCl(NCMe)\{NH{:}N(p\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2][PF_6]$	$(CD_3)_2CO$	1·9—3·2 (34)	6·08s (3)	7·63s (3) [d] −2·10s (1) [d]
$[RuCl(NCMe)\{NH{:}N(m\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2][PF_6]$	$(CD_3)_2CO$	2·0—3·8 (34)	6·18s (3)	7·73s (3) [e] −2·65s (1) [e]
$[RuCl(NCMe)\{NH{:}N(o\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2][PF_6]$	$(CD_3)_2CO$	2·1—3·9 (34)	6·46s (3) −3·96s (1) [e]	7·58s (3) [d]

[a] Complex multiplet, intensity in parentheses. [b] p-Me or p-MeO Protons, intensity in parentheses. [c] Dichloromethane of crystallisation. [d] Acetonitrile. [e] NH Proton, absent in $(CD_3)_2CO$–D_2O mixtures.

When $[RuCl_2(PPh_3)_3]$ was treated with $[p\text{-}MeOC_6H_4N_2][PF_6]$ in acetone, a brown mixture was formed which, upon chromatographic separation, afforded brown $[Ru_2Cl_3\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_3][PF_6]$. The species was a 1 : 1 electrolyte and exhibited ν_{NN} at 1882 and 1860 cm^{-1}; the ^1H n.m.r. spectrum was consistent with the formulation and revealed inequivalent p-methoxyphenyl groups. Attempts to obtain a similar complex by reaction of $[ArN_2][PF_6]$ with $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ afforded only the $[PF_6]^-$ salt of the latter.

It has been reported that arenediazonium salts react with ruthenium hydrido-complexes giving metal-stabilised di-imide groups, $\{Ru(NH{=}NAr)\}$.[6] Such intermediates are probably important in the stepwise reduction of metal-co-ordinated arylazo-groups to hydrazines and amines. Indeed, such a path has been implicated in the reduction of $[ArN_2]^+$ *via* Pt^{II} and Rh^{III} complexes.[4,8] Treatment of $[RuHCl(CO)(PPh_3)_3]$ with $[ArN_2][PF_6]$ (Ar = *o*-, *m*-, or *p*-$MeOC_6H_4$) afforded the aryldi-imide species $[RuCl(NCMe)(NH{=}NAr)(CO)(PPh_3)_2][PF_6]$. These complexes were 1 : 1 electrolytes in acetone, and in their i.r. spectra ν_{CO} was strong, but bands due to ν_{NH} or ν_{CN} could not be detected. The presence of the acetonitrile and the imido-proton was clearly established, however, by ^1H n.m.r. spectral studies. The resonance due to the latter occurred at low fields ($\tau = -2{\cdot}1$ to $-4{\cdot}0$) and disappeared when solutions containing the complexes were treated with D_2O.

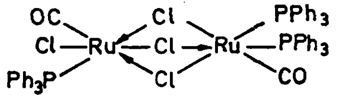
TABLE 3

I.r. spectral data obtained from ruthenium complexes

Complex	Medium	ν_{NN}/cm^{-1}	Other frequencies/cm^{-1}
$[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2]^+$	$CHCl_3$ [a]	1714s	
$[RuCl\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_2]^+$	$CHCl_3$ [a]	1710s	
	$CHCl_3$ [b]	1712s	
	KBr	1755s, 1710s	
$[RuCl\{N_2(m\text{-}MeOC_6H_4)\}_2(PPh_3)_2]^+$	$CHCl_3$ [a]	1712s	
	KBr [b]	1735s, 1694s	
$[RuCl_2\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]^{n+}$	CH_2Cl_2 [a]	1861s	
	$CHCl_3$ [b]	1860s, 1882sh	
	KBr [b]	1860s, 1880sh	
$[RuCl_2\{N_2(m\text{-}MeOC_6H_4)\}(PPh_3)_2]^{n+}$	$CHCl_3$ [b]	1870s, 1836sh	
	KBr [b]	1875s, 1850sh	
$[RuCl_3\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]$	CH_2Cl_2	1890s	
$[RuCl_3\{N_2(p\text{-}MeOC_6H_4)\}(PPh_3)_2]$	KBr	1890s	
$[Ru_2Cl_3\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_3]^+$	KBr [b]	1882s, 1860sh	
$[RuCl(NCMe)\{NH{:}N(p\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2]^+$	KBr [b]		2004s (ν_{CO})
$[RuCl(NCMe)\{NH{:}N(m\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2]^+$	KBr [b]		2008s (ν_{CO})
$[RuCl(NCMe)\{NH{:}N(o\text{-}MeOC_6H_4)\}(CO)(PPh_3)_2]^+$	KBr [b]		2002s (ν_{CO})
$[RuHCl(CO)(CNBu^t)(PPh_3)_2]$	$CHCl_3$		2155s (ν_{CO}), 2060w (ν_{RuH}?), 1952s (ν_{CO})
	KBr		2160s (ν_{CN}), 2050w (ν_{RuH}?), 1940s (ν_{CN})
$[RuHCl(CO)(CNPr^i)(PPh_3)_2]$	$CHCl_3$		2160s (ν_{CN}), 1952s (ν_{CO})
	KBr		2168s (ν_{CN}), 1952s (ν_{CO})
$[RuHCl(CO)\{CN(p\text{-}ClC_6H_4)\}(PPh_3)_2]$	KBr		2138s (ν_{CN}), 1950sh, 1930 (ν_{CO})
	$CHCl_3$		2127 (ν_{CN}), 2102 (ν_{RuH}?), 1957vs, 1930wsh (ν_{CO})
$[Ru_2Cl_4(CO)_2(PPh_3)_3]$	KBr		1970 (ν_{CO})

[a] As $[BF_4]^-$ salt. [b] As $[PF_6]^-$ salt.

Attempts were made to prepare arylazo-complexes by *in situ* reactions between $[RuHCl(CO)(PPh_3)_3]$ and $ArNH_2$ in the presence of HNO_2. The nitrous acid was generated by reaction of $NaNO_2$ or pentyl nitrite with gaseous HCl. From these reactions only the known $[RuCl_3(NO)(PPh_3)_2]$ [9] was obtained, together with other, minor, uncharacterisable by-products. If the nitrites were omitted from the reaction, a yellow solution was obtained which afforded, after chromatography, *trans*-$[RuCl_2(CO)_2(PPh_3)_2]$ and $[RuCl_4(CO)_2(PPh_3)_3]$ [possible structure (I)]. Compounds similar



(I)

to the latter have been obtained from reactions of $[RuHCl(PPh_3)_3]$ with CS_2.[10]

The observations that arenediazonium groups can be 'inserted' into Ru–H bonds, giving aryldi-imide complexes, prompted our investigation of the behaviour of other unsaturated substrates with $[RuHCl(CO)(PPh_3)_2]$. No reaction occurred between this hydride and either PhC≡CPh or PhC≡CH under mild conditions. However, with CNR, the species $[RuHCl(CO)(CNR)(PPh_3)_2]$ (R = Pr^i, Bu^t, or *p*-ClC_6H_4) was formed. These isocyanide complexes were insufficiently soluble for effective ^1H n.m.r. studies, but molecular-weight measurements confirmed their monomeric nature. The metal hydride stretching frequency could not be conclusively identified in the i.r. spectra of the compounds, since it is probably weak and occurred close to or under ν_{CN}. There was no evidence for species containing the group {Ru–CH=NR}. In the light of the strong *trans* weakening effect of hydride ligand, and the protonation of $[Ru(CO)_2(CNR)(PPh_3)_2]$ [11] and $[Ir(CNR)_3(PPh_3)_2]^+$ [12] *trans* to an isocyanide group, we would expect that the species $[RuHCl(CO)(CNR)(PPh_3)_2]$ would contain a *trans* H–Ru–CNR arrangement.

Reactions of the Arylazo-complexes.—Chlorination of $[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2][PF_6]$ in acetone under carefully controlled conditions gave $[RuCl_3\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]$. If, after precipitation of the complex, the remaining solution was evaporated, the i.r. spectrum of the residue so obtained exhibited a weak band at *ca.* 2300 cm^{-1} which may be attributed to $[p\text{-}MeC_6H_4N_2]Cl$. Attempts to isolate this diazonium salt failed, and chlorination experiments in other solvents, *e.g.* dichloromethane

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[8] L. Toniolo and R. Eisenberg, *Chem. Comm.*, 1971, 455; L. Toniolo, *Inorg. Chim. Acta*, 1972, **6**, 660.

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

[10] T. A. Stephenson, E. S. Switkes, and P. W. Armit, *J.C.S. Dalton*, 1974, 1134.

[11] D. F. Christian and W. R. Roper, *Chem. Comm.*, 1971, 1271.

[12] J. W. Dart, M. K. Lloyd, J. A. McCleverty, and R. Mason, *J.C.S. Dalton*, 1973, 2046.

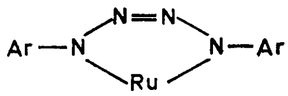
or chloroform, led to intractable tars. Similar trichloro(arylazo) complexes were obtained occasionally during attempts to recrystallise either $[RuCl(N_2Ar)_2(PPh_3)_2]^+$ or $[RuCl_2(N_2Ar)(PPh_3)_2]_n^{n+}$ salts from dichloromethane or chloroform. The source of extra Cl^- may arise from HCl in these solvents, and, indeed, it has been shown[13] that Cl^- addition to reactions designed to produce these ruthenium arylazo-cations afforded $[RuCl_3(N_2Ar)(PPh_3)_2]$ (Ar = p-MeC_6H_4).

The bis-arylazo-complexes could be reduced by an excess of sodium amalgam in ethanol. After addition of water to the reaction mixture obtained by such treatment of $[RuCl\{N_2(p\text{-}MeC_6H_4)\}_2(PPh_3)_2]^+$, it was possible to distil out ammonia and p-$MeC_6H_4NH_2$. By similar reduction of the corresponding p-$MeOC_6H_4N_2$ complex, ammonia and p-$MeOC_6H_4NH_2$ were formed, the latter being identified by diazotisation and tests for $[ArN_2]^+$. The nature of the ruthenium residues of these reactions could not be established.

Reaction of $[RuCl_2(N_2Ar)(PPh_3)_2]_n^{n+}$ with PPh_3 resulted in the formation of small amounts of $[RuCl_2(PPh_3)_3]$, but no identifiable products could be obtained with other Lewis bases. On heating with dimethylformamide, a mixture of carbonyl species, not containing $[ArN_2]^+$, was formed, but these have not been fully characterised.

DISCUSSION

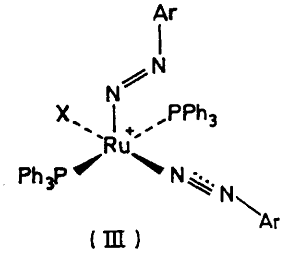
The complexes $[RuCl(N_2Ar)_2(PPh_3)_2]^+$ are the first in which two separate arylazo-groups are bound to one metal. It is conceivable, of course, that the ArN_2 groups are not present as such, but have coupled to give a metal-tetrazene system, (II). Such a structure has been identified crystallographically in the species $[Ir\{N_2(p\text{-}FC_6H_4)_2\}_2(CO)(PPh_3)_2][BF_4]\cdot C_6H_6$, obtained[14] by treating Vaska's compound with $[p\text{-}FC_6H_4N_2][BF_4]$ in benzene.



(II)

Two pieces of evidence suggest that the ruthenium complexes described here contain separate arenediazo-groups. Firstly, the compounds exhibit *two* i.r. active bands in the region 1600—1700 cm^{-1}, whereas the iridium complex apparently does not. These bands may be assigned to $\nu_{N\equiv N}$ of co-ordinated arylazo-groups but not $\nu_{N=N}$ of a metalloheterocycle, and a species containing two *cis*-co-ordinated arylazo-groups would be expected to exhibit two ν_{NN}. Secondly, the bis-tolylazo-complex can be oxidised to $[RuCl_3\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2]$ with the apparent loss of $[p\text{-}MeC_6H_4N_2]Cl$. This reaction is easily understood if the tolylazo-groups are present as discrete entities bound to the metal, and in view of the known chemistry of substituted tetrazoles[15] it seems rather unlikely that chlorination of a system like (I) would lead to the elimination of $[ArN_2]Cl$.

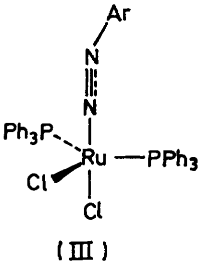
These bis-arylazo-complexes are electronically equivalent to $[RuX(NO)_2(PPh_3)_2]^+$ (X = Cl or OH), in which there is one linear and one bent Ru–N–O group.[16] Such a structure is possible for $[RuCl(N_2Ar)_2(PPh_3)_2]^+$, where the overall geometry would probably be square-pyramidal (III). The complexes were insufficiently soluble in suitable solvents to permit low-temperature ^1H n.m.r. studies, and we have so far failed to obtain crystals suitable for *X*-ray work. While this structural proposal must remain tentative, a bent arylazo-group has been discovered in $[RhCl(N_2Ph)\{PhP[(CH_2)_3PPh_2]_2\}][PF_6]$.[2]



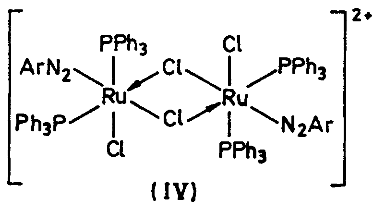
(III)

The formation of the bis-arylazo-complexes from $[RuHCl(PPh_3)_3]$ may involve prior addition of $[ArN_2]^+$ to give $[RuHCl(N_2Ar)(PPh_3)_n]^+$ (n = 2 or 3) followed by migration of H to the $[ArN_2]$ group, affording $[RuCl(NH{:}NAr)(PPh_3)_3]^+$. Dissociation of PPh_3 together with deprotonation (elimination of Ph_3PH^+?) would afford the co-ordinatively unsaturated $[RuCl(N_2Ar)(PPh_3)_2]$ (analogous to $[RuCl(NO)(PPh_3)_2]$[17]) which could then accept a further $[ArN_2]^+$ giving $[RuCl(N_2Ar)_2(PPh_3)_2]^+$.

There is no reliable direct evidence for the value of n in $[RuCl_2(N_2Ar)(PPh_3)_2]_n^{n+}$. There is no solvent of crystallisation in some of the species isolated, so the compound could be five-co-ordinate (n = 1) with a trigonal bipyramidal structure containing a linear Ru–NN group (16-electron configuration at the metal), (III), or six-co-ordinate with a weakly bound BF_4



(III)
(or isomers)



(IV)

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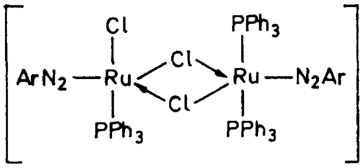
group, *e.g.* Ru···F–BF$_3$. Weakly co-ordinated BF$_4$ has been proposed[6] in [RuCl(FBF$_3$)(NH=NAr)(CO)(PPh$_3$)$_2$] which, on carbonylation, afforded [RuCl(NH=NAr)(CO)$_2$(PPh$_3$)$_2$][BF$_4$]. Attempts to prepare [RuCl$_2$(N$_2$Ar)(CO)(PPh$_3$)$_2$]$^+$ by carbonylation of the [RuCl$_2$(N$_2$Ar)(PPh$_3$)$_2$]$_n^{n+}$ were unsuccessful and treatment with PPh$_3$ gave only [RuCl$_2$(PPh$_3$)$_3$]. It is possible that $n = 2$, (IV), so that each metal atom is six-co-ordinate by virtue of chloride bridging (18-electron configuration at the metal). There is no analogue of (III) or (IV) in ruthenium nitrosyl chemistry.

The product of chlorination of [RuCl(N$_2$Ar)$_2$(PPh$_3$)$_2$]$^+$, or of Cl$^-$ addition to [RuCl$_2$(N$_2$Ar)(PPh$_3$)$_2$]$_n^{n+}$, is [RuCl$_3$(N$_2$Ar)(PPh$_3$)$_2$] which is, of course, entirely analogous to [RuCl$_3$(NO)(PPh$_3$)$_2$]. The arylazo-complex has a linear Ru–NN bond arrangement.[13]

The species [Ru$_2$Cl$_3${N$_2$(*p*-MeOC$_6$H$_4$)}$_2$(PPh$_3$)$_3$][PF$_6$], which contains two inequivalent *p*-methoxyphenyl groups, may have the dichloride bridged structure (V), in which each metal is five-co-ordinate. In this structure one Ru atom has a 16- and the other an 18-electron configuration (unless the latter was co-ordinated by a bent ArN$_2$ group).



(V)

(or isomers)

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