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Low Oxidation States Ruthenium Chemistry. II*. Synthesis and Reactions of Arylazo and Aryldi-imine Derivatives of Ruthenium

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Arylazo derivatives of ruthenium (A), $[Ru(N_2C_6H_4R\text{-p})(CO)_2L_2]^+(X^-)$ (L = PPh_3, R = NO_2, F, H, OMe, X = BF_4; L = PPh_3, R = F, NMe_2, X = BPh_4; L = $PPh_2(C_6H_4Me\text{-p})$, R = OMe, X = BF_4) and $[Ru(N_2C_6H_3R_2\text{-}2,6)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (R = Me, Cl), have been prepared by reacting diazonium salts with the complexes $Ru(CO)_3L_2$. Their reactions with HX (X = BF_4, Cl, I) or LiCl gave the aryldi-imine derivatives (B), $[Ru(N_2HC_6H_4R\text{-p})(CO)_2L_2]^{++}(BF_4^-)_2$, $[RuI(N_2HC_6H_4F\text{-p})(CO)_2(PPh_3)_2]^+(I_3^-)$ and $RuCl_2(N_2HC_6H_4R\text{-p})(CO)(PPh_3)_2$ (R = F, OMe). Deprotonation reactions with organic or inorganic bases of some of compounds (B) regenerated the starting arylazo complexes (A).

The unusual spectroscopic properties of the new compounds are reported and discussed, and it has been shown that the interaction with carbon dioxide of the arylazo complexes (A) when in solution is in part responsible for the anomalous i.r. absorptions observed in the carbonyl stretching frequencies region.

A comparison with the properties of the homologous, already known iron arylazo complexes has shown that the only reactions in which they behave analogously are the reactions with $NaBH_4$, which gave the hydrides cis-$MH_2(CO)_2(PPh_3)_2$ and with LiOEt, which gave the very reactive zerovalent complexes, $M(CO)_2(PPh_3)_3$ (M = Fe, Ru).

Introduction

Many interesting aspects of the chemistry of diazonium salts towards complexes of transition metals have stimulated a considerable number of researches in this field [1]. Among the most recent results, particularly significant is the structural characterization of a rhodium complex having the arylazo ligand coordinated in a doubly-bent arrangement [2a]. We report here on the synthesis and reactivity of cationic arylazo complexes of ruthenium, where the arylazo ligand displays different spectral properties depending on the reaction conditions employed in the synthesis of these compounds. A preliminary report on this work has been published [3]. While this final report was in preparation, a paper partially overlapping with our work has appeared [2b].

Results and Discussion

Synthesis of Ruthenium Arylazo Complexes

As already briefly reported [3], by reaction in dry benzene of the zerovalent complexes $Ru(CO)_3L_2$ with an equimolar quantity of a diazonium salt, a series of cationic arylazo derivatives of ruthenium (A), insoluble in the reaction medium, has been isolated (compounds Ia, II, IVa, V, VI, VII, VIII and IX, Table I):

$$Ru(CO)_3L_2 + ArN_2^+X^- \xrightarrow{\text{benzene}} [Ru(N_2Ar)(CO)_2L_2]^+X^- + CO \quad (1)$$

(L = PPh_3, $PPh_2(C_6H_4Me\text{-}p)$; Ar = $p\text{-}RC_6H_4$, 2,6-$R'_2C_6H_3$; X = BF_4, BPh_4). Compound (III) (Ar = $p\text{-}FC_6H_4$; X = BPh_4) could be more readily obtained by the anion exchange reaction between compound (II) (Ar = $p\text{-}FC_6H_4$; X = BF_4) and $NaBPh_4$.

When reaction (1) was carried out in the presence of LiCl (L = PPh_3, R = OMe) a yellow compound analyzing as *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ has been obtained. This compound appears to be the third possible isomer having this stoichiometry and with the CO molecules in a *cis* configuration (see experimental) [4].

In some cases compounds (A) have been obtained with benzene clathrated in the lattice. This has been confirmed by using dry toluene as solvent in the reaction (L = PPh_3; R = OMe, F); the signals due to the solvent have been detected in the ^1H n.m.r. spectra of the products (τ_{Me} *ca.* 7.6) and the methyl resonance was in a one to one ratio with the resonance due to the methoxy group (IVb, R = OMe). In the other cases, elemental analyses not always clearly distinguish between solvated and unsolvated forms (Table I). However compounds (A) generally

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*Part I: S. Cenini, A. Mantovani, A. Fusi and M. Keubler, *Gazzetta, 105,* 255 (1975).

TABLE I. Analytical Data for Compounds (A) of Formula $[Ru(N_2Ar)(CO)_2L_2]^+(X^-)\cdot$Solvent.[a]

	Ar	X	Solvent	Colour	M.P. (°C)	Λ_M[b]	C	H	N	C	H	N
							(calculated)			(found)		
(Ia)	$C_6H_4NO_2$-*p*	BF_4	–	Orange	187	20	57.61	3.70	4.57	58.07	4.01	4.00
(Ia)	$C_6H_4NO_2$-*p*	BF_4	C_6H_6				60.24	4.02	4.21			
(Ib)	$C_6H_4NO_2$-*p*	BF_4	Et_2O				58.06	4.43	4.23	57.23	3.74	4.36
(II)	C_6H_4F-*p*	BF_4	–	Yellow	195	23.1	59.26	3.82	3.14	60.61	3.88	3.05
(II)	C_6H_4F-*p*	BF_4	C_6H_6				61.92	4.13	2.89			
(III)	C_6H_4F-*p*	BPh_4	–	Yellow	141	13.5	72.68	4.83	2.50	71.99	4.20	2.62
(IVa)	C_6H_4OMe-*p*	BF_4	–	Yellow	149	20.6	59.80	4.09	3.10	62.1	4.19	3.03
(IVa)	C_6H_4OMe-*p*	BF_4	C_6H_6				62.39	4.38	2.86			
(IVb)	C_6H_4OMe-*p*	BF_4	C_6H_5Me				62.71	4.52	2.82	61.06	4.44	2.90
(IVc)	C_6H_4OMe-*p*	BF_4	½ Me_2CO				59.61	4.29	3.00	59.54	3.9	2.81
(IVd)	C_6H_4OMe-*p*	BF_4	$CHCl_3$				53.99	3.72	2.74	53.94	3.45	2.48
(IVe)	C_6H_4OMe-*p*	BF_4	Et_2O				60.10	4.81	2.86	61.09	4.57	3.04
(V)[a]	C_6H_4OMe-*p*	BF_4	–	Yellow	–	–	60.58	4.40	3.01	61.33	4.86	3.12
(V)[a]	C_6H_4OMe-*p*	BF_4	C_6H_6				63.03	4.66	2.80			
(VI)	C_6H_5	BF_4	–	Yellow	193–95	19.5	60.48	4.03	3.20	62.53	4.27	2.74
(VI)	C_6H_5	BF_4	C_6H_6				63.00	4.30	2.94			
(VII)	$C_6H_4NMe_2$-*p*	BPh_4	–	Orange	133	13.45	73.18	5.23	3.60	75.89	5.78	3.20
(VII)[c]	$C_6H_4NMe_2$-*p*	BPh_4	C_6H_6				74.50	5.40	3.40			
(VIII)	$C_6H_3Me_2$-2,6	BF_4	–	Yellow	178–80	–	61.27	4.33	3.12	61.97	4.98	2.97
(VIII)	$C_6H_3Me_2$-2,6	BF_4	C_6H_6				63.60	4.60	2.86			
(IX)	$C_6H_3Cl_2$-2,6	BF_4	–	Yellow–orange	161–62	20.8	56.06	3.48	2.96	55.79	3.33	2.58
(IX)	$C_6H_3Cl_2$-2,6	BF_4	C_6H_6				58.7	3.82	2.74			

[a] L = PPh_3, except for compound (V) for which L = $PPh_2(C_6H_4Me$-*p*). [b] In nitrobenzene. [c] Oxygen, found(calcd.): 2.9(2.6).

show in the i.r. spectrum a band at *ca.* 680–670 cm^{-1}, which is indicative of the presence of benzene in the complex. By crystallisation from solvents such as chloroform or acetone compound (IV) (L = PPh_3, R = OMe) was recovered with half a mol of acetone (IVc; $\nu_{C=O}$ = 1710 cm^{-1}; τ_{Me} = 7.83) or one mol of chloroform trapped in the lattice (IVd). These solvents are slowly lost by the complex even in the solid state, as shown by elemental analyses and by the disappearance in the spectra of the absorptions due to acetone. For this reason we were unable to obtain crystals suitable for X-ray structural determinations.

In order to confirm by ^1H n.m.r. the correct ratio between the ligand L and the arylazo group without any complication due to clathrated solvents, we have also synthesised compound (V) (L = $PPh_2(C_6H_4Me$-*p*); R = OMe); the resonances of the methyl and methoxy groups were in the expected two to one ratio. Moreover oxygen analysis for the tetraphenylborate derivative (VII) has confirmed the presence of only two carbonyl groups in this compound.

Compounds (VIII) and (IX) (Ar = 2,6-$Me_2C_6H_3$; 2,6-$Cl_2C_6H_3$) have been synthesised in order to have derivatives where the *ortho* positions of the arylazo ligand are blocked by the two substituents. It is known that for some iridium arylazo derivatives, *ortho*-metallation at the phenyl group of the arylazo ligand readily occurs to give a five-membered metallocycle [5]. The reactivity of these derivatives will be reported elsewhere [6].

Reactions of Ruthenium and Iron Arylazo Complexes

As already reported [3], the arylazo derivatives (A) can be readily protonated with tetrafluoroboric acid in a suspension of ethyl ether, to give the corresponding aryldi-imine derivatives (B) (compounds X, XI, XIII, XIV, IV, XV, Table II):

$$\underset{(A)}{[Ru(N_2Ar)(CO)_2L_2]^+(BF_4^-)} \underset{\text{base}}{\overset{HBF_4}{\rightleftharpoons}} \underset{(B)}{[Ru(N_2HAr)(CO)_2L_2]^{++}(BF_4^-)_2} \quad (2)$$

The i.r. spectra (broad absorptions at *ca.* 3550 and 3450 cm^{-1}) and the elemental analyses (Table II), have shown that these compounds invariably contain water.

Moreover in the ^1H n.m.r. spectrum broad signals were observed at *ca.* 4.7 τ, corresponding to one mol of water per mol of complex. These signals disap-

TABLE II. Analytical Data (required values in parentheses) for aryldi-imine Derivatives of Ruthenium.

Compound		Colour	M.P. (°C)	Λ_M[a]	C	H	N
(X)	$[Ru(N_2HC_6H_4NO_2\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2 \cdot H_2O$	Brown-yellow	>200	22.5	50.10 (51.56)	3.65 (3.61)	3.82 (4.10)
(XI)	$[Ru(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2 \cdot H_2O$	White	174	28.7	52.38 (52.96)	3.72 (3.71)	2.75 (2.81)
(XII)	$[Ru(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^{++}(CF_3COO^-)_2 \cdot Et_2O$	White	133	27.8	55.17 (56.47)	3.82 (4.07)	2.61 (2.53)
(XIII)	$[Ru(N_2HC_6H_4OMe\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2 \cdot H_2O$	Pale Yellow	144	29.4	52.40 (53.51)	4.21 (3.96)	2.72 (2.77)
(XIV)	$[Ru(N_2HC_6H_5)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2 \cdot H_2O$	White	165	22.9	54.93 (53.93)	3.95 (3.88)	2.90 (2.86)
(XV)	$[Ru(N_2HC_6H_4NMe_2\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2 \cdot H_2O$	Orange	145	29.6	54.39 (54.01)	4.29 (4.20)	3.74 (4.10)
(XVI)	$[RuI(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^{+}(I_3^-)$[b]	Dark Yellow	170–171	20.3	40.85 (40.20)	2.38 (2.66)	2.13 (2.14)
(XVII)	$RuCl_2(N_2HC_6H_4F\text{-}p)(CO)(PPh_3)_2$	Yellow	169	–	61.39 (61.00)	4.28 (4.13)	2.87 (3.30)
(XVIII)	$RuCl_2(N_2HC_6H_4OMe\text{-}p)(CO)(PPh_3)_2 \cdot \frac{1}{2}Me_2CO$	Pale Yellow	93–95	c	59.80 (61.50)	4.38 (4.51)	2.91 (3.15)

[a] In nitrobenzene. [b] Iodine, found(calcd.): 35.4(38.69). [c] M.w., found(calcd.): 890(889) in chloroform.

peared by treatment with D_2O, but their integrated areas were not consistent with a resonance due to the hydrogens of the aryldi-imine ligands.

The water molecule is probably associated with the tetrafluoroborate ion, since it was absent in the aryldi-imine derivative obtained by using CF_3COOH as the protonating agent (compound XII, Table II):

$$[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-) + 2CF_3COOH \longrightarrow [Ru(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^{++}(CF_3COO^-)_2 + HBF_4 \quad (3)$$

In this case one mol of ether was present in the complex instead of water, as indicated by the ^1H n.m.r. spectrum (τ_{CH_2} = 6.5, quartet; τ_{CH_3} = 8.8, triplet). Compounds (B) generally showed Λ_M higher than those observed for compounds (A), as expected. The protonation reaction is reversible and in some cases, as for instance for compounds (XI) (Ar = p-FC_6H_4), prolonged washings of the products with water and ethyl ether gave a mixture of compounds (A) and (B).

By reaction of compounds (B) with bases such as $NaHCO_3$, NEt_3, *etc.* in a suspension of ethyl ether the arylazo complexes (A) can be readily obtained. However different solvated forms have been isolated, depending on the base employed. With $NaHCO_3$, one to one adducts of the complexes with the ether were isolated (compounds (Ib) and (IVe), Table I). The presence of the ether was confirmed by the ^1H n.m.r. spectrum (τ_{CH_2} = 6.5, quartet; τ_{CH_3} = 8.8, triplet), in a one to one ratio with the signal of the methoxy group in compound (IVe). However, even this solvent is rapidly lost by the arylazo derivatives. More complex products were obtained with the organic bases, since in these cases not only the ether but also the amines were sometimes present in the products, as clearly indicated by the i.r. and ^1H n.m.r. spectra.

We have also studied the reactions of the ruthenium arylazo derivatives with other reagents. The arylazo complexes (A) can also be protonated with acids such as HX (X = Cl, I). However with these acids nucleophilic attack of the anion to the metal also occurs, generally giving a mixture of products. Only in two cases, $[RuI(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(I_3^-)$ (XVI) and $RuCl_2(N_2HC_6H_4F\text{-}p)(CO)(PPh_3)_2$ (XVII) (Table II), were we able to isolate the pure products.

Similarly, the anion exchange reactions of compounds (A) with the salts LiX (X = Cl, I) lead to a mixture of products, and only the aryldi-imine derivative $RuCl_2(N_2HC_6H_4OMe\text{-}p)(CO)(PPh_3)_2 \cdot 1/2Me_2CO$, (XVIII), could be isolated in a pure form. Complexes analogous to (XVII) and (XVIII) have been previously reported [7], and the formation of an aryldi-imine derivative from the exchange reaction of an arylazo cationic complex with excess of LiCl has been already observed [8].

When we attempted a deprotonation reaction with $NaHCO_3$ or an ion exchange with $NaBF_4$ on $[RuI(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(I_3^-)$ (XVI), we isolated only the yellow *cis*-$Ru(CO)_2(PPh_3)_2I_2$ (see Experimental), but no stable arylazo products could be obtained.

By comparison we have also studied the protonation reactions of the iron arylazo complexes $[Fe(N_2Ar)(CO)_2(PPh_3)_2]^+(BF_4^-)$, reported by other authors [9]. While no reaction was observed with HBF_4 in a suspension of ethyl ether, aqueous HI gave $[Fe(N_2Ar)(CO)_2(PPh_3)_2]^+(I^-)$ (Ar = p-FC_6H_4, see Experimental), but again we did not observe the formation of aryldi-imine derivatives of iron. Both the iron and ruthenium arylazo complexes $[M(N_2Ar)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (M = Fe; Ar = p-FC_6H_4; M = Ru, Ar = p-FC_6H_4, p-$OMeC_6H_4$) react with a reducing agent such as $NaBH_4$ in ethanol.

From these reactions we obtained the hydrides *cis*-$MH_2(CO)_2(PPh_3)_2$ (M = Fe, Ru) in good yields. A similar reaction has been reported to occur with the homologous arylazo derivative of osmium [2b]. The ruthenium hydride has been previously obtained from the reaction of $Ru(CO)_3(PPh_3)_2$ with hydrogen at high temperature and pressure [10].

Analytical and spectroscopic data (τ_{Ru-H} = 16.5, triplet; J_{P-H} = 23.5 Hz, in C_6D_6; ν_{CO} = 2015(s)–1970(s); ν_{Ru-H} = 1870(m)–1820(m), δ_{Ru-H} = 810 cm^{-1} nujol mull), are practically coincident with those already reported [10], in accordance with a structure having both the CO molecules and the hydridic ligands in a *cis*-configuration.

The iron hydride has an i.r. spectrum very similar to that of its ruthenium homologue (ν_{CO} = 1980(s)–1940(s), ν_{Fe-H} = 1880(m)–1855(m), δ_{Fe-H} = 795 cm^{-1}, nujol mull). Although we were unable to confirm by ^1H n.m.r. the configuration of the hydridic hydrogens in the iron derivative, these two complexes are probably isostructural.

By reaction of $[Ru(N_2C_6H_4R\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (R = F, OMe) with LiOEt in ethanol, a mixture of at least two products was obtained. The insoluble portion in acetone was shown to be the yellow $Ru(CO)_2(PPh_3)_3$ [11], by its elemental analyses, by the absence of hydridic hydrogens in the ^1H n.m.r. spectrum and by its i.r. spectrum (ν_{CO} = 1895 cm^{-1}, nujol mull). The soluble by-product was too unstable to be characterised. The amount of $Ru(CO)_2(PPh_3)_3$ formed in the reaction did not increase even in the presence of free triphenylphosphine. However, further support to its formulation came from the reaction with fumaronitrile in a suspension of ethyl ether, which readily gave $Ru(CO)_2(PPh_3)_2(NCCH{=}CHCN)$ [12]. This ruthenium olefin derivative can also be obtained by reacting $Ru(CO)_3(PPh_3)_2$ with fumaronitrile, but the reaction requires a prolonged refluxing in benzene [12]. Moreover a similar reaction has been reported to occur between $[Fe(N_2C_6H_4Me\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ and methoxide ion, giving $Fe(CO)_2(PPh_3)_3$ [13]. We have also obtained the zerovalent iron complex and in good yields, by reducing $[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ with LiOEt and in the presence of excess phosphine. Finally the ruthenium arylazo derivatives (A) did not react in a clean way with molecules such as CO and H_2, even after many hours of reaction with these reagents and in solvents such as acetone or chloroform.

Spectral Properties

The arylazo derivatives (A) show in the i.r. spectra recorded in nujol mull two ν_{CO} of equal intensities (Table III), indicative of a *cis*-arrangement of the carbonyl groups. These stretching frequencies are sensitive to the electron withdrawing capacity of the *para* substituent R of the arylazo ligand, and they significantly decrease on going from R = NO_2 to R = NMe_2, as expected. In the 1600 cm^{-1} region more absorptions are observed in the nujol mull spectra. The two bands reported in Table III for compounds (I), (IV), (V) and (VI) dramatically change their relative intensities depending on the reaction conditions employed for the synthesis of these arylazo complexes, or in some cases but to a lesser extent even for different batches of the compounds prepared in the same manner.

When the arylazo derivatives (I) and (IV) are obtained by deprotonation with organic or inorganic bases of the corresponding aryldi-imine derivatives (eq. 2) they show the band at higher frequency as the more intense. These bands disappear in the corresponding aryldi-imine derivatives (B) and are associated with the vibration of the azo group, as has been demonstrated by ^{15}N labelling [2b]. On the basis of this, one could propose the existence of isomers of derivatives (A) with the arylazo ligands in a singly or doubly bent arrangement, as recently suggested by other authors [2b]. The existence of different solvated forms seems to play a relevant role in determining the structure and the i.r. absorptions of the arylazo ligand in these complexes.

The i.r. spectra of compounds (A) showed another peculiarity, when recorded in solution. In a solvent such as chloroform four carbonyl stretching frequencies were observed (Table III), two of which close to those observed in nujol mull. The vibrations due to the azo group were of too low intensity to be clearly detected in solution. The other two carbonyl absorptions observed in chloroform lie at higher frequencies and are close to those detected in the corresponding aryldi-imine derivatives (B) (Table III).

The increase of the ν_{CO} in compounds (B) is expected, a doubly charged cation being formed. Moreover a band at 2340 cm^{-1} was detected together with the four carbonyl bands. The band at 2340 cm^{-1} was also observed in solvents such as acetone or

TABLE III. I.r. and ^{1}H N.m.r. Data for Arylazo and Aryldi-imine Derivatives of Iron and Ruthenium.

Complex		ν_{CO} [a]	ν_{CO} [b]	$\nu_{-N=N-}$ [a]	ν_{NH} [a]	$\tau_{p\text{-}RC_6H_4}$ [c]	τ_{H_2O} and/or τ_{NH} [c]
(Ia)	$[Ru(N_2C_6H_4NO_2\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$	2080–1980	–	1670(m)–1550(m)	–	–	–
(Ib)	$[Ru(N_2C_6H_4NO_2\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)\cdot Et_2O$	2065–2005	–	1675(s)–1555(w)	–	–	–
(II)	$[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$	2060–1990	2070–2060–2020–1990	– 1565	–	–	–
(IVa)	$[Ru(N_2C_6H_4OMe\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$	2040–1970	2070–2045–2010–1985	1690(w)–1550(s)	–	6.1	–
(IVe)	$[Ru(N_2C_6H_4OMe\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)\cdot Et_2O$	2040–1970	–	1690(s)–1550(w)	–	6.15	–
(V)	$[Ru(N_2C_6H_4OMe\text{-}p)(CO)_2\{PPh_2(C_6H_4Me\text{-}p)\}_2]^+(BF_4^-)$	2040–1970	–	1690(w)–1550(s)	–	6.1–7.65[d]	–
(VI)	$[Ru(N_2C_6H_5)(CO)_2(PPh_3)_2]^+(BF_4^-)$	2060–1970	–	1680(m)–1550(w)	–	–	–
(VII)	$[Ru(N_2C_6H_4NMe_2\text{-}p)(CO)_2(PPh_3)_2]^+(BPh_4^-)$	2020–1955	2040–1980	– 1530	–	7.1	–
(VIII)	$[Ru(N_2C_6H_3Me_2\text{-}2,6)(CO)_2(PPh_3)_2]^+(BF_4^-)$	2050–1990	–	– 1545	–	7.82–8.26[e]	–
(IX)	$[Ru(N_2C_6H_3Cl_2\text{-}2,6)(CO)_2(PPh_3)_2]^+(BF_4^-)$	2060–1990	2080–2055–2025–1990	– 1570	–	–	–
(X)	$[Ru(N_2HC_6H_4NO_2\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2\cdot H_2O$	2100–2050	2080–2040	–	3120	–	4.7
(XI)	$[Ru(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2\cdot H_2O$	2095–2045	2075–2025	1505	3140	–	–
(XII)	$[Ru(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^{++}(CF_3COO^-)_2\cdot Et_2O$[f]	2090–2020	2080–2030	1505	3130	–	–3.65
(XIII)	$[Ru(N_2HC_6H_4OMe\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2\cdot H_2O$	2090–2040	2070–2020	1500	3120	6.1	4.7
(XIV)	$[Ru(N_2HC_6H_5)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2\cdot H_2O$	2090–2040	–	1505	3120	–	–
(XV)	$[Ru(N_2HC_6H_4NMe_2\text{-}p)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2\cdot H_2O$	2070–2020	–	–	3160	6.8	4.8; –2.2
(XVI)	$[RuI(N_2HC_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(I_3^-)$	2080–2040	2070–2020	1500	3140	–	–
(XVII)	$RuCl_2(N_2HC_6H_4F\text{-}p)(CO)(PPh_3)_2$	1970–1960	1970	1500	–	–	–2.7
(XVIII)	$RuCl_2(N_2HC_6H_4OMe\text{-}p)(CO)(PPh_3)_2\cdot \tfrac{1}{2}Me_2CO$[g]	1950	1970	1500	–	6.2	–

[a] Nujol or hexachlorobutadiene mull. [b] In $CHCl_3$. [c] In $CDCl_3$. [d] $\tau_{PPh_2(C_6H_4Me\text{-}p)}$. [e] Broad and complex absorptions. [f] $\nu_{CF_3COO^-} = 1675\ cm^{-1}$. [g] $\nu_{C=O} = 1700\ cm^{-1}$; $\tau_{Me_2CO} = 7.82$.

deuterochloroform, and thus it was not attributable to an interaction with the solvent. On the other hand it was absent in the i.r. spectra recorded in a nitrogen or oxygen atmosphere (IVa), which showed only the two ν_{CO} at lower frequencies. In a carbon dioxide atmosphere the band at 2340 cm^{-1} and the ν_{CO} at higher frequencies increased. All these facts support a reversible interaction in solution of compounds (A) with carbon dioxide adsorbed from the atmosphere. However, with time another transformation occurs in solution, since even in a nitrogen atmosphere new bands began to appear.

For the aryldi-imine derivatives (B) a band at *ca.* 1500 cm^{-1} in the i.r. spectra was tentatively assigned to $\nu_{NH=N}$ (Table III), by comparison with the spectra recorded in hexachlorobutadiene mull of the corresponding arylazo derivatives (A) and of the uncomplexed diazonium salts. For some of these derivatives, ν_{NH} (*ca.* 3120 cm^{-1}) and τ_{NH} (negative values with respect to TMS) could be also observed. For all the compounds here reported, the ^1H n.m.r. resonances of the *para* substituent of the arylazo or aryldi-imino ligands were always detected in the expected positions (Table III).

Fresh solutions in $CHCl_3$ of compounds (Ia), (II) (IVa) and (IVd) showed in the electronic spectra a band at *ca.* λ_1 = 340–380 nm ($\epsilon = 10^3$ for compound (IVa)) followed by a stronger absorption in the u.v. region at about λ_2 = 305 nm. Only compound (VII) showed an absorption at 450 nm, well separated from the u.v. band and in accordance with its colour. These data compare with those reported for the related iron arylazo derivative [9]. The band at lower energy can be tentatively assigned to a $n \rightarrow \pi^*$ transition of the arylazo ligand [1, 9, 14]. However some transformation occurs with time in solution, as evidenced for compound (IVa) by the presence of an isosbestic point in the electronic spectrum, with a shift of λ_1 to a slightly lower energy.

Experimental

All the reactions were carried out under nitrogen at room temperature with stirring, but the work-up of the reaction mixtures was carried out in air. The syntheses of the ruthenium arylazo complexes were accomplished in the dark. Dry benzene was distilled over sodium and under nitrogen immediately before use. Ethyl ether was purified from peroxides and dried over sodium.

$Fe(CO)_3(PPh_3)_2$ [15] and $Ru(CO)_3(PPh_3)_2$ [16] were prepared as described in the literature. The pale yellow $Ru(CO)_3\{PPh_2(C_6H_4Me\text{-}p)\}_2$ was obtained in an analytical pure form, by using a procedure similar to that described for $Ru(CO)_3(PPh_3)_2$ [16]. However a longer reaction time was necessary (2.5–3 hr at reflux of the solution of the reactants), and the product was obtained in lower yields (*ca.* 35%).

I.R. spectra were recorded with a Perkin-Elmer 457 instrument. ^1H n.m.r. spectra were recorded with a Varian NV-14 instrument operating at 60 MHz, with TMS as internal standard.

Melting points were determined on a Leitz Heiztischmikroskop, and are not corrected. Elemental analyses were carried out by the Analytical Laboratories of Milan University. Molecular weights were obtained using a Mechrolab osmometer. Conductivity data were obtained with a Philips PR 9500 conductivity bridge.

Arylazo Derivatives

$[Ru(N_2Ar)(CO)_2L_2]^+(X^-)\cdot C_6H_6$, *(Ia), (II), (IVa), (V), (VI), (VII), (VIII), (IX)*

These compounds have been obtained by reacting $Ru(CO)_3L_2$ [L = PPh_3, $PPh_2(C_6H_4Me\text{-}p)$] (0.2–0.3 g) in benzene (15–20 ml) with an equimolar quantity of the corresponding diazonium salts, $(ArN_2^+)(X^-)$. The reaction time was normally of 16–18 hr. However for compounds (Ia) (Ar = $p\text{-}NO_2C_6H_4$) and (VII) (Ar = $p\text{-}NMe_2C_6H_4$) the reaction was completed in about 6 hr. The compounds were filtered off, washed with fresh benzene and n-hexane and dried *in vacuo*. The yields vary from 75 to 95%.

$[Ru(N_2Ar)(CO)_2(PPh_3)_2]^+(BF_4^-)\cdot Et_2O$, *(Ib), (IVe)*

To a suspension of the aryldi-imine derivative $[Ru(N_2HAr)(CO)_2(PPh_3)_2]^{++}(BF_4^-)_2X\cdot H_2O$ (see later), (X) or (XIII) (0.1 g) in ethyl ether (15 ml), a solution of $NaHCO_3$ (0.085 g) in water (5 ml) was added dropwise. After 1 hr the compounds were filtered off, washed repeatedly with water, then with ethyl ether and n-hexane.

$[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BPh_4^-)$, *(III)*

$[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (II) (0.1 g) was dissolved in the minimum required of acetone. A solution of $NaBPh_4$ (0.384 g) in the minimum required of ethanol was added dropwise. The acetone was then allowed to evaporate in a slow flux of nitrogen (0.30 hr). By adding ethanol and by scratching the reaction vessel a yellow compound precipitated. It was left under stirring for 1 hr. The compound was filtered off, washed with ethanol and n-hexane, and dried *in vacuo* for 3 days.

$[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$

This compound was prepared under experimental conditions slightly different from those reported in the literature [9]. To a solution of $Fe(CO)_3(PPh_3)_2$ (1.328 g) in benzene (40 ml), a solution of $(p\text{-}FC_6H_4N_2^+)(BF_4^-)$ (0.42 g) in acetone (1 ml) was added. A reddish suspension was immediately formed. After 3 hr the brick-red precipitate was filtered off and washed with benzene and n-hexane.

It was crystallised from acetone–ethyl ether and dried *in vacuo*. The compound melts at 203 °C; $\Lambda_M = 23.8$ (in nitrobenzene); ν_{CO} = 2040(s)–1975(s) cm^{-1} (in nujol); ν_{CO} = 2030(s)–1960(s) cm^{-1} (in $CHCl_3$); $\nu_{N=N}$ = 1710 cm^{-1} (in nujol). *Anal.*, calcd. (found): C, 62.4(61.86); H, 4.02(4.01); N, 3.3 (3.22)%.

$[Fe(N_2C_6H_4F\text{-p})(CO)_2(PPh_3)_2]^+I^-$

To a suspension of $[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (0.277 g) in ethyl ether (20 ml), HI (2.5 ml of a 57% solution in water) was added. A brown suspension was immediately formed. After 16 hr the yellow-orange compound was filtered off, washed with water, ethyl ether and n-hexane, and dried *in vacuo*. With acids such as HBF_4 and CF_3COOH no reaction was observed under these experimental conditions. The compound melts at 157 °C; $\Lambda_M = 21.9$ (in nitrobenzene); ν_{CO} = 2040(s) –1960(s) cm^{-1}; $\nu_{N=N}$ = 1720 cm^{-1} (nujol mull). *Anal.*, calcd.(found): C, 59 5(58.82); H, 3.85(3.73); N, 3.16(3.10)%.

Aryldi-imine Derivatives

$[Ru(N_2HAr)(CO)_2L_2]^{2+}(BF_4^-)_2\cdot H_2O$, (X), (XI), (XIII), (XIV), (XV)

To a suspension of the arylazo complex (0.2–0.3 g) in ethyl ether (15–20 ml), HBF_4 (1 ml of a 40% solution in water) was added. A solution was initially formed. The ether was allowed to evaporate in a slow flux of nitrogen. After *ca.* 3–4 hr the precipitate was filtered off, washed with a little water, ethyl ether, n-hexane and dried *in vacuo*. Compound (XV) was the most difficult to isolate by this procedure. The yields vary from 50 to 70%.

$[Ru(N_2HC_6H_4F\text{-p})(CO)_2(PPh_3)_2]^{2+}(CF_3COO^-)_2\cdot Et_2O$, (XII)

To a suspension of the yellow $[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (II) (0.192 g) in ethyl ether (15 ml), CF_3COOH (1 ml) was added. The suspension turned white in a few minutes. After 0.5 hr the white precipitate was filtered off, washed with water, ethyl ether, n-hexane and dried *in vacuo*.

$[RuI(N_2HC_6H_4F\text{-p})(CO)_2(PPh_3)_2]^+(I_3^-)$, (XVI)

To a suspension of $[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (II) (0.36 g) in ethyl ether (20 ml), HI (2.5 ml of a 57% solution in water) was added. The brown suspension was left under stirring for 2.5 hr. The dark yellow precipitate was filtered off, washed repeatedly with water and then with ethyl ether and n-hexane and dried *in vacuo*. By adding water to the mother liquor of the reaction, a further portion of oily product was obtained; it was solidified by decanting the solution and washing the precipitate with water, a little ethyl ether and n-hexane.

$RuCl_2(N_2HC_6H_4F\text{-p})(CO)(PPh_3)_2$, (XVII)

$[Ru(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (II) (0.3 g) was added to ethyl ether (60 ml) where gaseous HCl was previously bubbled through for 10 minutes. Gaseous HCl was bubbled for a further 10 minutes. The suspension was then left for 1 hr under stirring. The yellow precipitate was filtered off under nitrogen, washed with water, ethyl ether and n-hexane. The yellow material was then dissolved under nitrogen in $CHCl_3$; by adding n-hexane a pale yellow compound precipitated, which was filtered off. It was shown to be a mixture, possibly containing $Ru(CO)_2(PPh_3)_2Cl_2$, from its i.r. spectrum. The resulting solution was evaporated to dryness. The yellow residue was washed with n-hexane and crystallized from benzene–ethanol, giving the pure product.

$RuCl_2(N_2HC_6H_4OMe\text{-p})(CO)(PPh_3)_2\cdot\frac{1}{2}Me_2CO$, (XVIII)

To a suspension of $[Ru(N_2C_6H_4OMe\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (IVa) in dry ethanol (20 ml), LiCl (0.09 g) was added. After 20 hr the lemon-yellow precipitate was filtered off. The compound was crystallized from acetone-n-hexane, by filtering off an acetone-insoluble residue.

Other Products

Reaction between $Ru(CO)_3(PPh_3)_2$ and $(p\text{-}OMeC_6H_4N_2^+)(BF_4^-)$ in the Presence of LiCl. Synthesis of cis-$Ru(CO)_2(PPh_3)_2Cl_2$ (Yellow Isomer)

Solid LiCl (0.037 g) and $(p\text{-}OMeC_6H_4N_2^+)(BF_4^-)$ (0.099 g) were mixed in commercial ethanol (5 ml). After 15 min $Ru(CO)_3(PPh_3)_2$ (0.2 g) and benzene (10 ml) were added. After 24 hr the dark yellow precipitate was filtered off, washed with n-hexane, water and n-hexane. The product was crystallised from tetrahydrofuran–n-hexane. Melting point > 240 °C; ν_{CO} = 2065(s)–1990(s), ν_{Ru-Cl} = 310(w)–290(w) cm^{-1} (in nujol). *Anal.*, calcd.(found): C, 61.00(61.44); H, 4.00(4.10); N, nil; m.w. 752(720–852) in chloroform.

The two already known ruthenium complexes having this stoichiometry and a *cis* arrangement of the carbonyl groups are white [4], thus the compound here reported appears to be the third possible isomer.

Reaction between $[RuI(N_2HC_6H_4F\text{-p})(CO)_2(PPh_3)_2]^+(I_3^-)$ (XVI) and $NaBF_4$ or $NaHCO_3$. Synthesis of cis-$Ru(CO)_2(PPh_3)_2I_2$

a) To a suspension of compound (XVI) (0.05 g) in ethanol (10 ml), $NaBF_4$ (0.01 g) was added. After 6 hr the ochre-yellow precipitate was filtered off, washed with water and n-hexane, and dried *in vacuo*.

b) To a suspension of compound (XVI) (0.08 g) in ethyl ether (15 ml) a solution of $NaHCO_3$ (0.05 g) in water (5 ml) was added. After 48 hr the orange–yellow precipitate was filtered off, washed with water and n-hexane and dried *in vacuo*. Melting point > 240 °C; ν_{CO} = 2060(s)–1990(s) cm^{-1} (in $CHCl_3$). *Anal.*, calcd.(found): C, 48.7(48.2); H, 3.5(3.2); N, nil. In some preparations the product was in mixture with a compound showing a sharp band at *ca.* 1900 cm^{-1}.

Reaction between $[Ru(N_2Ar)(CO)_2(PPh_3)_2]^+(BF_4^-)$ *and* $NaBH_4$. *Synthesis of* cis-$RuH_2(CO)_2(PPh_3)_2$

To compounds (II) or (IVa) (0.35 g) a solution of $NaBH_4$ (0.29 g) in dry ethanol (15 ml) was added. A fast reaction occurred giving a brown suspension. After 1.5 hr the colourless product was filtered off, washed with ethanol, n-hexane and dried *in vacuo* (65% yield). The compound melts at 166–167 °C. It was characterized by its i.r. and ^1H n.m.r. spectra (see text). *Anal.*, calcd.(found): C, 66.8(66.44); H, 4.7(4.4); N, nil.

Reaction between $[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ *and* $NaBH_4$. *Synthesis of* cis-$FeH_2(CO)_2(PPh_3)_2$.

To $[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (0.27 g) a solution of $NaBH_4$(0.236 g) in ethanol (15 ml) was added. A fast reaction occurred with gas evolution, giving a brown suspension. After 1 hr the light brown product was filtered off, washed with ethanol, n-hexane and dried *in vacuo*. It was crystallised from benzene–n-hexane, by filtering off a benzene-insoluble residue. The compound slowly decomposes in air, even in the solid state. It was characterized by its i.r. spectrum (see text). *Anal.*, calcd.(found): C, 71.9(73.3); H, 5.0(4.7); N, nil.

Reaction between $[Ru(N_2C_6H_4OMe\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ *(IVa) and LiOEt. Synthesis of* $Ru(CO)_2(PPh_3)_3$

To compound (IVa) (0.369 g) and PPh_3 (0.338 g) a solution of LiOEt in ethanol (obtained by dissolving in a nitrogen atmosphere lithium metal (0.057 g) in dry ethanol (15–20 ml)) was added. A brown suspension was rapidly formed. After 24 hr the brown–yellow precipitate was filtered off, washed with ethanol, water, ethanol and n-hexane. By further washing this material with acetone, a brown by-product was eliminated and the pure yellow product, only slightly soluble in acetone, was isolated (*ca.* 30–40% yield). The compound was dried *in vacuo* and stored under nitrogen. It melts at 130 °C. *Anal.*, calcd.(found): C, 71.6(70.9); H, 4.77(4.42); N, nil.

Reaction between $[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ *and LiOEt. Synthesis of* $Fe(CO)_2(PPh_3)_3$

To $[Fe(N_2C_6H_4F\text{-}p)(CO)_2(PPh_3)_2]^+(BF_4^-)$ (1.154 g) and PPh_3 (1.42 g) a solution of LiOEt in ethanol (obtained by dissolving in a nitrogen atmosphere lithium metal (0.236 g) in dry ethanol (60 ml)) was added. After 24 hr the red precipitate was filtered off, washed with ethanol, water, ethanol, n-hexane, and dried *in vacuo* (70–80% yield). The compound was stored under nitrogen. It melts at 127 °C; ν_{CO} = 1900(m)–1840(s) cm^{-1} (in nujol). *Anal.*, calcd.(found): C, 75.00(74.4); H, 5.0(4.9); N, nil.

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