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ARENE—RUTHENIUM COMPLEXES CONTAINING NITROGEN DONOR LIGANDS

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Summary

The complexes $[(\text{arene})RuCl_2]_2$ (arene = C_6H_6 or p-$MeC_6H_4CHMe_2$) react with hydrazine hydrate or 1,1-dimethylhydrazine in tetrahydrofuran or methanol to give $[(\text{arene})Ru(N_2H_4)_3]^{2+}$ or $[(\text{arene})Ru(NH_2NMe_2)_3]^{2+}$ and with ethylenediamine (= en) to give $[(\text{arene})RuCl(en)]^+$. Pyridine displaces only the hydrazine ligands from $[(\text{arene})Ru(N_2H_4)_3]^{2+}$ while the relatively more π-accepting PMe_2Ph replaces both these and the arene ligand.

Introduction

The dimers $[(\text{arene})RuCl_2]_2$ (I) (arene = C_6H_6, C_6H_5Me, p-$C_6H_4Me_2$, 1,3,5-$Me_3C_6H_3$, C_6H_5OMe or p-$MeC_6H_4CHMe_2$) have been shown to undergo bridge cleavage upon treatment with a ligand L (L = PR_3, $P(OR)_3$, AsR_3, pyridine; R = alkyl or aryl) to give the monomers $[(\text{arene})RuCl_2L]$ [1,2]. I (arene = C_6H_6) reacts with $AgBF_4$ in methyl cyanide to give $[(C_6H_6)Ru(MeCN)_3](BF_4)_2$ [2], with NaS_2PR_2 to give $[(C_6H_6)Ru(S_2PR_2)_2]$ (R = Me, Ph, OMe or OEt) [3], containing one mono- and one bi-dentate sulphur ligand, and with NH_2CHRCO_2K (R = H or Me) to give $[(\text{arene})RuCl(NH_2CHRCO_2)]$ [4]. Here we describe some further reactions of the complexes I (arene = C_6H_6 or p-$MeC_6H_4CHMe_2$).

Results and discussion

During our studies of the chemistry of arene—ruthenium complexes, we have found that I reacts with hydrazine hydrate or 1,1-dimethylhydrazine in tetrahydrofuran or methanol to give the complexes $[(\text{arene})RuL_3]^{2+}$ which were isolated as tetraphenylborate or hexafluorophosphate salts by the addition of

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$NaBPh_4$ or NH_4PF_6 as appropraite (eq. 1).

$$[(\text{arene})\text{RuCl}_2]_2 \xrightarrow[\text{(ii) } X^-]{\text{(i) } L} [(\text{arene})\text{RuL}_3]X_2 \qquad (1)$$

(I) (II—VII)

(II) arene = C_6H_6, L = N_2H_4, X = BPh_4
(III) arene = p-$MeC_6H_4CHMe_2$, L = N_2H_4, X = BPh_4
(IV) arene = C_6H_6, L = NH_2NMe_2, X = BPh_4
(V) arene = p-$MeC_6H_4CHMe_2$, L = NH_2NMe_2, X = BPh_4
(VI) arene = C_6H_6, L = NH_2NMe_2, X = PF_6
(VII) arene = p-$MeC_6H_4CHMe_2$, L = NH_2NMe_2, X = PF_6

These reactions are undoubtedly aided by the polar nature of the reaction medium, which facilitates the loss of chloride, and contrasts with the previously reported bridge cleavage reactions with phosphines, phosphites or pyridine. These were carried out in benzene, the neat phosphine or in pyridine and gave complexes of the type $[(\text{arene})\text{RuCl}_2\text{L}]$ [2].

The complexes II—VII are moderately air stable in the solid state but decompose quite rapidly in solution, even under an inert atmosphere (although more slowly in the latter case), thus necessitating fairly rapid recrystallisations. They behave as 2/1 electrolytes in acetonitrile solution (Table 1); the conductivity

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE ARENE—RUTHENIUM COMPLEXES

Complex	Colour	Yield (%)	Decomposition point (°C)	Conductivity [a] (ohm^{-1} cm^2 mol^{-1})	Analyses (found (calcd.) (%))			
					C	H	N	Cl
II · 2MeCN	Yellow	63	125	247	69.5	6.5	10.8	
					(69.9)	(6.5)	(11.3)	
III · N_2H_4	Yellow	79	126	240	69.5	7.1	10.8	
					(69.5)	(7.1)	(11.2)	
IV	Brown	69	132	236	72.6	6.8	8.4	
					(72.2)	(7.1)	(8.4)	
V · Me_2CO	Yellow	77	109	253	72.0	7.6	7.5	
					(72.3)	(7.6)	(7.5)	
VI	Buff	62	157	336	22.3	4.5	12.9	
					(22.2)	(4.7)	(12.9)	
VII	Yellow	37	114	320	26.8	5.2	10.9	
					(27.2)	(5.4)	(11.9)	
VIII · 2Me_2CO	Yellow	55	167	257	76.9	5.9	3.6	
					(76.9)	(6.3)	(3.6)	
IX	Yellow	60	154	230	78.5	6.4	4.1	
					(78.9)	(6.3)	(3.8)	
X	Yellow	60	108	231	79.0	6.5	3.7	
					(79.1)	(6.6)	(3.6)	
XI	Yellow	53	216	104	64.5	5.9	4.5	6.4
					(64.7)	(5.7)	(4.7)	(6.0)
XII	Yellow	75	180	102	66.3	6.5	4.4	6.2
					(66.5)	(6.5)	(4.3)	(5.5)

[a] In ca. 10^{-3} M MeCN solution; quoted ranges for 1/1 electrolytes: 120—160 and for 2/1 electrolytes: 220—300 ohm^{-1} cm^2 mol^{-1} [5].

values for complexes VI and VII are slightly higher than the quoted range (220—300 ohm^{-1} cm^2 mol^{-1}) but other examples are known [5].

The dimethylhydrazine complexes IV—VII show a moderately strong band in their infrared spectra at about 3200 cm^{-1} attributable to ν(NH) while the hydrazine complexes II and III show several bands in the region 3150—3350 cm^{-1}; all the complexes show a δ(NH) absorption at about 1600 cm^{-1} (Table 2). The ^{1}H NMR spectra (Table 2) of complexes II—VII all show resonances for the aromatic protons of the coordinated arenes characteristically shifted upfield

TABLE 2

IR AND ^{1}H NMR DATA FOR THE ARENE—RUTHENIUM COMPLEXES

Complex	IR (cm^{-1}) [a]		^{1}H NMR [b]	
	ν(NH)	δ(NH)	Arene	Other ligands
II - 2MeCN [c]	3325, 3255 3195 (br)	1605 s(br)	5.57, s	3.31 and 5.73, (br) N_2H_4
III - N_2H_4	3335, 3305(br) 3250, 3215	1600 s(br)	5.37 and 5.61, d(6), ArH 2.75, sp(6.6), ArCH 2.05, s, Me 1.18, d(6.6), $CH\underline{Me}_2$	3.42 and 5.78, (br) N_2H_4
IV	3160(br)	1615 ms(br)	5.86, s	6.64, (br) $N\underline{H}_2NMe_2$ 2.44, s, $NH_2N\underline{Me}_2$
V - Me_2CO [d]	3165 ms(br)	1605 w(br)	5.52 and 5.78, d(6), ArH 2.94, sp(6.6), ArCH 2.05, s, Me 1.19, d(6.6), $CH\underline{Me}_2$	6.39, (br) $N\underline{H}_2NMe_2$ 2.43, s, $NH_2N\underline{Me}_2$
VI	3215 ms	1618 ms	6.01, s	6.71 (br) $N\underline{H}_2NMe_2$ 2.49, s, $NH_2N\underline{Me}_2$
VII	3246 ms	1618(br)	5.77 and 5.95, d(6), ArH 2.89, sp(6.6), ArCH 2.23, s, Me 1.25, d(6.6), $CH\underline{Me}_2$	6.54 (br) $N\underline{H}_2NMe_2$ 2.52, s, $NH_2N\underline{Me}_2$
VIII - $2Me_2CO$ [e, f]			6.00, s	
IX [f]			5.74 and 5.96, d(6), ArH ~2.8 [g], ArCH 1.52, s, Me 0.98, d(6.6), $CH\underline{Me}_2$	
X [f]			5.65 and 5.87, d(6), ArH ~2.8 [g], ArCH 1.51, s, Me 0.97, d(6.6), $CH\underline{Me}_2$	2.39, s, $\underline{Me}C_5H_4N$
XI	3305, 3280 3238(br), 3108 w	1580 s(br)	5.64, s	2.10, (br) $(CH_2N\underline{H}_2)_2$ 2.26—2.48, m, $(C\underline{H}_2NH_2)_2$
XII	3300, 3288 3230, 3207 3125	1583 s(br)	5.34 and 5.52, d(6), ArH 2.66, sp(6.6), ArCH 2.08, s, Me 1.22, d(6.6), $CHMe_2$	2.20—2.44, m, $(C\underline{H}_2NH_2)_2$

[a] In nujol mulls, medium intensity bands unless otherwise stated; (br) broad, s strong, ms moderately strong, w weak. [b] In C^2H_3CN solution relative to TMS: reported as: position (δ, ppm) multiplicity (coupling constant [Hz]), assignment. Complexes containing acetone showed δ(Me) at 2.04 s; those containing acetonitrile showed δ(Me) at 1.87 s; those containing BPh_4 showed δ(Ph) at ca. 6.8—7.5. s singlet, d doublet, sp septet, m multiplet, (br) broad. [c] ν(CN) at 2295 w and 2260 cm^{-1}. [d] ν(CO) at 1695 s cm^{-1}. [e] ν(CO) at 1705 s cm^{-1}. [f] ^{1}H NMR spectrum showed resonances for the aromatic pyridine protons between δ 6.8 and 8.4. [g] Poorly resolved resonance due to low solubility of complex.

from those for the free arenes. The complexes IV—VII show a broad resonance at δ ca. 6.5 ppm, which disappears on addition of ^2H_2O and is thus assigned to the NH protons of the dimethylhydrazine ligands. The low field position of this resonance (cf. δ 2.8 ppm for NH_2NMe_2 in C^2H_3CN) suggests a considerable deshielding of the NH protons indicating bonding to the metal via the NH_2 nitrogen atom, a situation also favoured sterically. The complexes II and III both show two broad resonances for the NH protons of the hydrazines, one at δ ca. 5.5 ppm, which by comparison with the dimethylhydrazine complexes is assigned to the protons on the nitrogen atom bound to the metal, and the other at δ ca. 3.5 ppm. These two resonances are of approximately equal intensity for complex II, but for complex III the resonances at δ ca. 5.5 and ca. 3.5 ppm correspond to approximately 6 and 10 protons respectively, the higher intensity of the high field resonance being due to a molecule of hydrazine of crystallisation.

The complexes II and III react with pyridines to give $[(\text{arene})Ru(py)_3](BPh_4)_2$ as shown in eq. 2.

$$[(\text{arene})Ru(N_2H_4)_3](BPh_4)_2 \xrightarrow[Me_2CO]{py} [(\text{arene})Ru(py)_3](BPh_4)_2 \qquad (2)$$

(II or III) (VIII—X)

(VIII) arene = C_6H_6, py = C_5H_5N
(IX) arene = p-$MeC_6H_4CHMe_2$, py = C_5H_5N
(X) arene = p-$MeC_6H_4CHMe_2$, py = 4-MeC_5H_4N

The complexes VIII—X are yellow, air-stable crystalline solids which behave as 2/1 electrolytes in acetonitrile solution (Table 1).

Reaction of complexes II—VII with dimethylphenylphosphine gives products which do not contain coordinated arene and the exact nature of these compounds is still under investigation. This is in contrast to the reactions involving the relatively donor nitrogen ligands above and is a consequence of the greater π-acceptor properties of the PMe_2Ph ligand which upon coordination labilises the arene ligand by successfully competing for metal electron density. Similarly, refluxing I (arene = 1,3,5-$Me_3C_6H_3$ or p-$MeC_6H_4CHMe_2$) in pyridine leads to $[(\text{arene})RuCl_2(py)]$ whereas treatment of I with an excess of PMe_2Ph leads to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ [2]. Also, reaction of $[(C_6H_6)RuCl_3Ru(C_6H_6)]PF_6$ with pyridine in boiling ethanol leads to a mixture of $[(C_6H_6)RuCl(py)_2]PF_6$ and $[RuCl_2(py)_4]$ while reaction with PMe_2Ph gives only $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ [6].

Treatment of complexes I (arene = C_6H_6 or p-$MeC_6H_4CHMe_2$) with one equivalent of ethylenediamine (= en) in methanol followed by addition of $NaBPh_4$ gives the yellow, air-stable crystalline complexes $[(\text{arene})RuCl(en)]BPh_4$ (eq. 3) which are 1/1 electrolytes in acetonitrile solution (Table 1).

$$[(\text{arene})RuCl_2]_2 \xrightarrow[(ii)\ BPh_4^-]{(i)\ en} [(\text{arene})RuCl(en)]BPh_4 \qquad (3)$$

(I) (XI and XII)

(XI) arene = C_6H_6
(XII) arene = p-$MeC_6H_4CHMe_2$

The use of an excess of ethylenediamine in reaction 3 gives, in addition to the above products, small yields of the known [7] cation $[Ru(en)_3]^{2+}$; the mother liquor on standing slowly deposits yellow crystals of the salt $[Ru(en)_3](BPh_4)_2 \cdot 2MeOH$.

The complexes XI and XII show several bands in the region 3100—3310 cm^{-1} of their infrared spectra attributable to ν(NH) and a strong, broad band at ca. 1580 cm^{-1} for δ(NH) which also includes a component due to the BPh_4 anion (Table 2). The ^{1}H NMR spectrum of complex XI (Table 2) shows a broad resonance at δ 2.10 ppm which disappears on addition of ^2H_2O and is assigned to the NH protons of the (en) ligand, but a similar resonance was not detected for complex XII. The reasons for this are not at present clear.

Experimental

All manipulations were performed under dinitrogen using standard Schlenk techniques.

NMR spectra were run on a Perkin—Elmer R12A spectrometer and IR spectra on a Perkin—Elmer 257 grating spectrometer. Conductivity measurements were performed using a Philips PW9504/00 conductivity meter and a PW9510 conductivity cell. Melting points were determined on a Kofler hot-stage and analyses were performed by the Service de Microanalyse, C.N.R.S., Gif-sur-Yvette. $RuCl_3 \cdot 3H_2O$ was a generous loan from the Compagnie des Métaux Précieux.

$[(C_6H_6)Ru(N_2H_4)_3](BPh_4)_2 \cdot 2MeCN$ (II)

To a suspension of $[(C_6H_6)RuCl_2]_2$ [2] (0.2 g) in methanol (10 cm^3) was added hydrazine hydrate (0.5 cm^3) and the mixture stirred for 30 min. The resulting red solution was filtered and $NaBPh_4$ (0.8 g) added to precipitate a pale-yellow solid which was isolated by filtration, washed with water (2 × 10 cm^3) and recrystallised from CH_3CN/Et_2O to give yellow crystals (0.5 g, 65%).

$[(p\text{-}MeC_6H_4CHMe_2)Ru(N_2H_4)_3](BPh_4)_2 \cdot N_2H_4$ (III)

To a suspension of $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ [2] (0.25 g) in tetrahydrofuran (10 cm^3) was added hydrazine hydrate (0.5 cm^3) and the mixture stirred vigorously for 30 min during which time an orange oil separated. Addition of $NaBPh_4$ (0.8 g) resulted in dissolution of the oil to give a yellow solution. This was taken to dryness in vacuo and CH_2Cl_2 (10 cm^3) was added. The resulting yellow solid was filtered, washed with CH_2Cl_2 (5 cm^3), and water (2 × 10 cm^3) and recrystallised from CH_3CN/Et_2O to give yellow crystals (0.65 g, 79%).

$[(C_6H_6)Ru(NH_2NMe_2)_3](X)_2$ (IV, $X = BPh_4$; VI, $X = PF_6$)

To a suspension of $[(arene)RuCl_2]_2$ (0.2 g) in methanol (10 cm^3) was added NH_2NMe_2 (0.5 cm^3) and the mixture stirred for 30 min. The products were isolated by the addition of $NaBPh_4$ (0.8 g) or NH_4PF_6 (0.8 g) as appropriate. Yields, IV 69%; VI 62%.

$[(p\text{-}MeC_6H_4CHMe_2)Ru(NH_2NMe_2)_3](BPh_4)_2 \cdot Me_2CO$ (V)

To a suspension of $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ (0.25 g) in tetrahydrofuran (10 cm^3) was added NH_2NMe_2 (0.5 cm^3) and the mixture stirred for 1 h. $NaBPh_4$

(0.8 g) was added to the resulting orange solution and the mixture stirred for a further 30 min. This was then taken to dryness in vacuo and water (10 cm^3) added. The resulting yellow solid was filtered, washed with water (2 × 10 cm^3) and rapidly recrystallised from Me_2CO/Et_2O to give yellow crystals (0.7 g, 77%).

$[(p\text{-}MeC_6H_4CHMe_2)Ru(NH_2NMe_2)_3](PF_6)_2$ *(VII)*

To a suspension of $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ (0.25 g) in methanol (15 cm^3) was added NH_2NMe_2 (1.0 cm^3) and the mixture stirred for 30 min. NH_4PF_6 (1.0 g) was added to the resulting yellow solution and the mixture stirred for a further 30 min. The solution was reduced to ca. half-volume in vacuo and water added dropwise with stirring until the solution was faintly cloudy. On standing at —40°C for about 2 weeks, yellow crystals were deposited (0.24 g, 37%) which were filtered, washed with a little chilled water and dried in vacuo.

$[(Arene)Ru(py)_3](BPh_4)_2$ *(VIII—X)*

To a solution of $[(C_6H_6)Ru(N_2H_4)_3](BPh_4)_2 \cdot 2MeCN$ (0.2 g) in acetone (10 cm^3) was added pyridine (0.5 cm^3) and the solution stirred for 3 h. Reduction in volume of the solution in vacuo led to the deposition of yellow crystals of $[(C_6H_6)Ru(C_5H_5N)_3](BPh_4)_2 \cdot 2Me_2CO$ (VIII, 0.13 g, 55%).

The complex $[(p\text{-}MeC_6H_4CHMe_2)Ru(C_5H_5N)_3](BPh_4)_2$ (IX) was similarly prepared from $[(p\text{-}MeC_6H_4CHMe_2)Ru(N_2H_4)_3](BPh_4)_2 \cdot N_2H_4$ except that Et_2O (10 cm^3) was added after solvent volume reduction to precipitate the crude solid, which was recrystallised from CH_3CN/Et_2O to give yellow crystals in 60% yield.

The complex $[(p\text{-}MeC_6H_4CHMe_2)Ru(4\text{-}MeC_5H_4N)_3](BPh_4)_2$ (X) was simialrly prepared except that the reaction mixture was first taken to dryness. MeCN (5 cm^3), Et_2O (5 cm^3) and EtOH (5 cm^3) were added and slow solvent removal in vacuo gave the complex as a yellow microcrystalline solid in 60% yield.

$[(Arene)RuCl(en)]BPh_4$ *(XI and XII)*

To a suspension of $[(C_6H_6)RuCl_2]_2$ (0.2 g) in methanol (10 cm^3) was added ethylenediamine (0.05 cm^3; one equiv.) and the mixture stirred for 1 h. The mixture was filtered and $NaBPh_4$ (0.3 g) added to the resulting yellow-green solution to give $[(C_6H_6)RuCl(en)]BPh_4$ (XI) as a yellow microcrystalline solid (0.25 g, 53%) which was filtered, washed with chilled water (5 cm^3) and chilled methanol (5 cm^3) and dried in vacuo.

The complex $[(p\text{-}MeC_6H_4CHMe_2)RuCl(en)]BPh_4$ (XII) was similarly prepared from $[(p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ as yellow crystals in 75% yield.

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