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A SIMPLE PREPARATION OF BIS-ARENE-RUTHENIUM CATIONIC COMPLEXES, INCLUDING THOSE CONTAINING DIFFERENT ARENES

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Summary

Bis-η^6-arene-ruthenium(II) salts of general formula $[Ru(arene^1)(arene^2)]Y_2$ ($arene^1$ = benzene, mesitylene or hexamethylbenzene, $arene^2$ = a wide range of aromatic compounds and Y = BF_4 or PF_6) can be prepared in moderate to high yields by treatment of $[RuCl_2(\eta^6\text{-arene}^1)]_2$ in acetone successively with $AgBF_4$ or $AgPF_6$, acid (CF_3CO_2H, HBF_4 or HPF_6) and $arene^2$.

Introduction

Although η^6-benzene-η^6-biphenylchromium complexes $[Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5\text{-}C_6H_5)]^{n+}$ (n = 0, 1) are formed in the reaction between anhydrous chromium(III) chloride and phenylmagnesium bromide originally studied by Hein [1,2], there are few systematic methods for the synthesis of bis-arene-metal complexes containing different η^6-arenes. The Fischer—Hafner method is not suitable for this purpose and is in any case restricted to those aromatic molecules containing alkyl or aryl substituents which do not rearrange under Friedel—Crafts conditions. The cation $[Cr(\eta^6\text{-}C_6H_5CO_2H)(\eta^6\text{-}C_6H_5C_6H_5)]^+$ can be isolated in poor yield by carbonation of $CrCl_3/C_6H_5MgBr$ and subsequent hydrolysis and acidification [3]. Other mixed η^6-arene-chromium(0) complexes, such as $Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5COMe)$, have been made by metalation of dibenzenechromium and subsequent treatment with appropriate organic carbonyl compounds [4]. Recently, the metal atom technique has been used to make hitherto unobtainable bis-arene-metal complexes, including unsymmetrical species such as $Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_6)$ [5,6].

We report here a simple route to cationic, mixed arene complexes of ruthenium(II) of general formula $[Ru(\eta^6\text{-arene}^1)(\eta^6\text{-arene}^2)]^{2+}$.

Results and discussion

The species formed in situ by treatment of $[RuCl_2(\eta^6\text{-arene}^1)]_2$ ($arene^1$ = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6) [7,8] with $AgBF_4$ or $AgPF_6$ in acetone react on warming with a wide range of arenes (arene^2) in the presence of acid (CF_3CO_2H. HPF_6 or HBF_4) to form colourless or pale yellow, air-stable salts $[Ru(\eta^6\text{-arene}^1)(\eta^6\text{-arene}^2)]Y_2$ (Y = BF_4, PF_6; arene^2 = benzene, mesitylene, hexamethylbenzene, naphthalene, anthracene, biphenyl, anisole, chlorobenzene, acetophenone, *N*,*N*-dimethylaniline, methyl benzoate, benzoic acid, phenol, and trifluoromethylbenzene). Yields range from 20% to almost quantitative, usually being dependent on the arene in $[RuCl_2(\eta^6\text{-arene})]_2$ in the order $C_6Me_6 > 1,3,5\text{-}C_6H_3Me_3 > C_6H_6$. The presence of acid is not absolutely essential to the success of many of the preparations, but in its absence longer reaction times are required and yields are lower. Complexes of benzoic acid and of anthracene could only be obtained analytically pure if acid (preferably trifluoroacetic acid) was used in the preparation. We have shown [9] that the triacetone cations $[Ru(\eta^6\text{-arene})(OCMe_2)_3]^{2+}$ initially formed from $[RuCl_2(\eta^6\text{-arene})]_2$ and $AgBF_4$ or $AgPF_6$ in acetone rapidly undergo further reactions which depend on the counter-anion. In the case of BF_4^-, aldol condensation of coordinated acetone affords complexes containing bidentate diacetone alcohol, $[Ru(\eta^6\text{-arene})\{Me_2C(OH)CH_2COCH_3\}(OCMe_2)](BF_4)_2$, whereas in the case of PF_6^- the anion is partially solvolysed to give tri-μ-difluorophosphato complexes $[Ru_2(\mu\text{-}O_2PF_2)_3(\eta^6\text{-arene})_2]PF_6$ analogous to those isolated by solvolysis of the isoelectronic species $[M(\eta^5\text{-}C_5Me_5)(OCMe_2)_3](PF_6)_2$ (M = Rh, Ir) [10,11]. Since both the diacetone alcohol and the tri-μ-difluorophosphato complexes react with arenes in the presence of acid to give bis-arene-ruthenium salts, it is likely that the acid in the in situ preparation serves to remove these two ligands by protonation.

Bis-arene complexes could not be isolated for arene^2 = hexafluorobenzene, nitrobenzene, s-collidine, aniline or thiophene, although the *p*-cymene tetramethylthiophene salt $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta^5\text{-}C_4Me_4S)](PF_6)_2$ has recently been made [12] using essentially the method described here. For the complexes containing identical arenes, $[Ru(arene)_2]^{2+}$ (arene = C_6H_6, $1,3,5\text{-}C_6H_3Me_4$, C_6Me_6), the yields and convenience of the present method are superior to those of the previously employed Fischer—Hafner synthesis [13—15].

The bis-arene-ruthenium(II) salts behave as 2/1 electrolytes in nitromethane, and their ^1H NMR spectra show a small upfield shift of the aromatic proton resonances relative to those in the free arene. In contrast with the isoelectronic cations $[M(\eta^5\text{-}C_5Me_5)(arene)]^{2+}$ (M = Rh, Ir) [16,17], the coordinated arenes are not readily replaced by other ligands. The only solvent in which all the complexes are reasonably soluble is dimethyl sulphoxide, the solutions being stable for long periods. The anthracene complexes are exceptional since they rapidly change from red to yellow in dimethyl sulphoxide, giving $[Ru(\eta^6\text{-arene})(DMSO)_3]^{2+}$ and free anthracene. The η^6-chlorobenzene complexes are quantitatively converted into the corresponding anisole complexes on addition of methanol. A similar but much slower reaction occurs when $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ is heated with methanolic sodium methoxide [18,19]. Undoubtedly the positive charge on the ruthenium complexes assists nucleophilic substitution.

The η^6-phenol salt $[Ru(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_5OH)](BF_4)_2$ is readily deprotonated in the presence of base to give a pale yellow, crystalline η^6-phenoxo salt $[Ru(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_5O)]BF_4$. Some deprotonation also takes place if acid (HBF_4 or CF_3CO_2H) is not added during the preparation of the η^6-phenol complex. The η^6-phenoxo (or η^5-oxocyclohexadienyl) salt is a 1/1 electrolyte in nitromethane and shows an intense ν(C—O) band at 1625 cm^{-1} in its IR spectrum. Bands in the region 1580—1630 cm^{-1} have been reported for other η^6-phenoxo-complexes of ruthenium(II), rhodium(III) and iridium(III) [20,21].

Preliminary work indicates that the bis-arene-ruthenium(II) salts described herein can be reduced by alkali metals to give zerovalent bis-arene-ruthenium(0) complexes similar to the known complex Ru(η^6-C_6Me_6)(η^4-C_6Me_6) [15] but containing different arenes. Recently, complexes of this type have been isolated from photochemically promoted cyclotrimerization of acetylenic compounds in the presence of the cyclohexa-1,3-diene complex Ru(η^6-C_6H_6)(η^4-C_6H_8) [22].

Experimental

Elemental analyses were carried out by the Microanalytical Department of this University (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates). ^{1}H NMR spectra were recorded at 34°C on a Jeolco MH-100 spectrometer. Conductivities were measured at ca. 25°C using a Philips GM4144 bridge and PW9510 cell. The complexes [$RuCl_2(C_6H_6)]_2$ and [$RuCl_2(C_6H_3Me_3)]_2$ were prepared by literature procedures [8]; the complexes [$RuCl_2(C_6Me_6)]_2$, [Ru($C_6H_3Me_3$){$Me_2C(OH)CH_2COMe$}($OCMe_2$)](BF_4)$_2$ and [$Ru_2(\mu$-$PO_2F_2)_3$($C_6H_3Me_3$)$_2$]PF_6 will be described elsewhere [9,23]. Yields, analyses and ^{1}H NMR data for the complexes [Ru(arene^1)(arene^2)](BF_4)$_2$ are in Table 1.

All the complexes in Table 1 were prepared essentially by the typical procedures outlined in (i)—(iii) below, yields being generally higher if acid (CF_3CO_2H, HBF_4 or HPF_6) was present. The chlorobenzene complexes were recrystallized from DMSO/ether rather than from DMSO/methanol/ether owing to their rapid conversion into anisole complexes in the latter medium. The anthracene complexes could not be recrystallized from DMSO owing to their rapid decomposition in this solvent. They were isolated by cautious addition of ether to the acid solution in which they had been generated.

(i) Bis(η^6-hexamethylbenzene)ruthenium(II) bis(tetrafluoroborate)

To [$RuCl_2(C_6Me_6)]_2$ (0.200 g, 0.03 mmol) in acetone (5 ml) was added silver tetrafluoroborate (0.233 g, 1.2 mmol) and the mixture was stirred vigorously at room temperature for 15 min. Precipitated silver chloride was filtered off and the yellow solution was evaporated to dryness under reduced pressure. The residue was treated with an excess of hexamethylbenzene (0.2—0.3 g) and trifluoroacetic acid (5 ml) and the solution was heated at 90°C for 5 min. Solvent was removed in vacuo and the oily residue was triturated with a few ml of diethyl ether. The resulting off-white solid, which represented an almost quantitative yield of product, was washed with ether and recrystallised from DMSO/methanol/ether to give white crystals of [$Ru(C_6Me_6)_2$](BF_4)$_2$ (0.272 g, 76%).

(ii) (η^6-Benzene)(η^6-mesitylene)ruthenium(II) salts

(a) Using HBF_4. An acetone solution prepared as under (i) from [$RuCl_2(\eta^6$-$C_6H_3Me_3)]_2$ (0.085 g, 0.15 mmol) and silver tetrafluoroborate (0.113 g, 0.6 mmol) was evaporated to dryness under reduced pressure, treated with benzene (2 ml) and 40% aqueous HBF_4/propionic anhydride (2 ml), and heated at

Cont. on p. 92.

TABLE 1

YIELDS, ANALYSES AND ^{1}H NMR SPECTROSCOPIC DATA FOR COMPLEXES [Ru(arene^1)(arene^2)](BF$_4$)$_2$ ^{a}

Arene^1	Arene^2	Yield (%)	Analysis (found (calcd.) (%))			^{1}H NMR (δ) ^{b}
			C	H	N	
C_6H_6	C_6H_6	58	33.6 (33.3)	3.0 (2.8)		6.87 (s, C_6H_6) ^{c}
1,3,5-$C_6H_3Me_3$ ^{d}	1,3,5-$C_6H_3Me_3$	72	42.1 (41.9)	4.8 (4.7)		2.27 (s, 9 H, Me), 6.78 (s, 3 H, $C_6\mathit{H}_3Me_3$)
C_6Me_6	C_6Me_6	76	48.0 (48.0)	6.2 (6.0)		2.09 (s, Me) ^{e}
C_6H_6 ^{f}	C_6Me_6	36	42.0 (41.9)	4.9 (4.7)		2.45 (s, 18 H, Me), 6.70 (s, 6 H, $C_6\mathit{H}_6$)
C_6Me_6	C_6H_6	75	41.8 (41.9)	4.7 (4.7)		2.45 (s, 18 H, Me), 6.70 (s, 6 H, $C_6\mathit{H}_6$)
C_6H_6	1,3,5-$C_6H_3Me_3$	46	37.7 (38.0)	4.1 (3.8)		2.36(s, 9 H, Me), 6.84 (s, 6 H, $C_6\mathit{H}_6$) 6.91 (s, 3 H, $C_6\mathit{H}_3Me_3$)
1,3,5-$C_6H_3Me_3$	C_6H_6	68	38.4 (38.0)	4.2 (3.8)		2.36 (s, 9 H, Me), 6.84 (s, 6 H, $C_6\mathit{H}_6$) 6.91 (s, 3 H, $C_6\mathit{H}_3Me_3$)
1,3,5-$C_6H_3Me_3$	C_6Me_6	54	45.3 (45.2)	5.3 (5.4)		2.18 (s, 9 H, $C_6H_3\mathit{Me}_3$) 2.34 (s, 18 H, $C_6\mathit{Me}_6$), 6.61 (s, 3 H, $C_6\mathit{H}_3Me_3$)
C_6Me_6	1,3,5-$C_6H_3Me_3$	54	45.1 (45.2)	5.3 (5.4)		2.18 (s, 9 H, $C_6H_3\mathit{Me}_3$) 2.34 (s, 18 H, $C_6\mathit{Me}_6$), 6.61 (s, 3 H, $C_6\mathit{H}_3Me_3$)
1,3,5-$C_6H_3Me_3$	$C_{10}H_8$	60	43.9 (43.5)	4.1 (3.8)		2.05 (s, 9 H, Me), 6.47 (s, 3 H, $C_6\mathit{H}_3Me_3$), 7.01, 7.75, 7.95, 8.15, (each m, 2 H, $C_{10}\mathit{H}_8$)
C_6Me_6 ^{g}	$C_{10}H_8$	64	46.7 (46.6)	4.7 (4.6)		2.07 (s, 18H, $C_6\mathit{Me}_6$), 6.93, 7.53, 7.87, 8.19 (each m, 2 H, $C_{10}\mathit{H}_8$)
1,3,5-$C_6H_3Me_3$	$C_{14}H_{10}$	50	48.1 (48.2)	3.7 (3.8)		^{h}
C_6H_6	$C_6H_5C_6H_5$	21	42.7 (42.6)	3.2 (3.2)		6.88 (s, 6 H, $C_6\mathit{H}_6$), 7.09 (3 H), 7.60 (5 H), 7.96 (2 H) (each m, $C_{12}\mathit{H}_{10}$)
1,3,5-$C_6H_3Me_3$	$C_6H_5C_6H_5$	66	46.2 (45.9)	4.2 (4.0)		2.10 (s, 9 H, Me), 6.86 (s, 3 H, $C_6\mathit{H}_3Me_3$), 7.00 (3 H), 7.66 (5 H), 8.04 (2 H) (each m, $C_{12}\mathit{H}_{10}$)
C_6H_6	C_6H_5OMe	35	34.4 (33.8)	3.6 (3.0)		3.97 (s, 3 H, OMe), 6.80 (m, 5 H, $C_6\mathit{H}_5OMe$), 6.88 (s, 6 H, $C_6\mathit{H}_6$)
1,3,5-$C_6H_3Me_3$	C_6H_5OMe	65	38.7 (38.1)	4.4 (4.0)		2.33 (s, 9 H, $C_6H_3\mathit{Me}_3$), 3.99 (s, 3 H, OMe), 6.90 (m, 5 H, $C_6\mathit{H}_5OMe$), 6.95 (m, 3 H, $C_6\mathit{H}_3Me_3$)
C_6Me_6	C_6H_5OMe	63	42.3 (41.8)	5.2 (4.8)		2.38 (s, 18 H, $C_6\mathit{Me}_6$), 3.89 (s, 3 H, OMe), 6.74 (m, 5 H, $C_6\mathit{H}_5OMe$)
C_6H_6	C_6H_5Cl	65	30.0 (30.9)	2.3 (2.4)		7.02 (s, 6 H, $C_6\mathit{H}_6$), 7.01 (3 H), 7.54 (2 H) (each m, $C_6\mathit{H}_5Cl$)

TABLE 1 (continued)

Arene^1	Arene^2	Yield (%)	Analysis (found (calcd.) (%))			^{1}H NMR (δ) [b]
			C	H	N	
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5Cl}$	72	35.6 (35.4)	3.5 (3.3)		2.35 (s, 9 H, Me), 7.01 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$), 7.01 (3 H), 7.42 (2 H), each m, $\mathrm{C_6}H_5\mathrm{Cl}$)
$\mathrm{C_6Me_6}$	$\mathrm{C_6H_5Cl}$	97	39.5 (39.2)	4.2 (4.2)		2.42 (s, 18 H, Me), 6.95 (3 H), 7.32 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{Cl}$)
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5NMe_2}$	42	39.8 (39.5)	4.7 (4.5)	2.5 (2.7)	2.33 (s, 9 H, $\mathrm{C_6H_3}Me_3$), 3.13 (s, 6 H, $\mathrm{N}Me_2$), 6.24 (2 H), 6.49 (3 H) (each m, $\mathrm{C_6}H_5\mathrm{NMe_2}$), 6.82 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$)
$\mathrm{C_6Me_6}$	$\mathrm{C_6H_5NMe_2}$	34	42.9 (42.9)	5.1 (5.2)	2.2 (2.5)	2.41 (s, 18 H, $\mathrm{C_6}Me_6$), 3.14 (s, 6 H, $\mathrm{N}Me_2$), 6.12 (2 H), 6.40 (3 H) (each m, $\mathrm{C_6}H_5\mathrm{NMe_2}$)
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5OH}$	81	37.0 (36.8)	4.3 (3.7)		2.26 (s, 9 H, Me), 5.66 (2 H), 6.31 (3 H) (each m, $\mathrm{C_6}H_5\mathrm{OH}$), 6.66 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$)
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5O}$ [i]	77	44.7 (44.9)	4.3 (4.2)		2.26 (s, 9 H, Me), 5.36 (2 H), 6.16 (3 H) (each m, $\mathrm{C_6}H_5\mathrm{O}$), 6.55 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$)
$\mathrm{C_6H_6}$	$\mathrm{C_6H_5COMe}$	28	35.1 (35.4)	3.2 (3.0)		2.66 (s, 3 H, Me), 6.96 (s, 6 H, $\mathrm{C_6}H_6$), 7.09 (3 H), 7.34 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{COMe}$)
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5COMe}$ [j]	24	40.2 (39.5)	4.2 (3.9)		2.30 (s, 9 H, $\mathrm{C_6H_3}Me_3$), 2.69 (s, 3 H, $\mathrm{CO}Me$), 7.02 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$), 7.06 (3 H), 7.40 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{COMe}$)
$\mathrm{C_6Me_6}$	$\mathrm{C_6H_5COMe}$	31	43.4 (43.0)	5.1 (4.7)		2.39 (s, 18 H, $\mathrm{C_6}Me_6$), 2.65 (s, 3 H, $\mathrm{CO}Me$), 7.02 (3 H), 7.24 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{COMe}$)
$\mathrm{C_6H_6}$	$\mathrm{C_6H_5CO_2Me}$	28	34.1 (34.3)	3.4 (2.9)		3.87 (s, 3 H, $\mathrm{CO_2}Me$), 6.82 (s, 6 H, $\mathrm{C_6}H_6$), 6.90 (3 H), 7.22 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{CO_2Me}$)
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5CO_2Me}$ [k]	44	38.7 (38.4)	3.7 (3.8)		2.24 (s, 9 H, $\mathrm{C_6H_3}Me_3$), 3.91 (s, 3 H, $\mathrm{CO_2}Me$) 6.87 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$), 6.93 (3 H), 7.23 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{CO_2Me}$)
$\mathrm{C_6Me_6}$	$\mathrm{C_6H_5CO_2Me}$	51	42.0 (41.9)	4.9 (4.5)		2.35 (s, 18 H, $\mathrm{C_6}Me_6$), 4.02 (s, 3 H, $\mathrm{CO_2}Me$), 6.97 (3 H), 7.20 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{CO_2Me}$)
1,3,5-$\mathrm{C_6H_3Me_3}$	$\mathrm{C_6H_5CO_2H}$ [l]	75	37.5 (37.1)	3.8 (3.5)		3.31 (s, 9 H, Me), 6.93 (s, 3 H, $\mathrm{C_6}H_3\mathrm{Me_3}$), 6.93 (3 H), 7.28 (2 H) (each m, $\mathrm{C_6}H_5\mathrm{CO_2H}$)

TABLE I (continued)

Arene[1]	Arene[2]	Yield (%)	Analysis (found (calcd.) (%))			^1H NMR (δ) [b]
			C	H	N	
1,3,5-$C_6H_3Me_3$	$C_6H_5CF_3$	17	35.9 (35.5)	3.6 (3.1)		2.39 (s, 9 H, Me), 7.14 (s, 3 H, $C_6H_3Me_3$), 7.17 (3 H), 7.62 (2 H) (each m, $C_6H_5CF_3$)

[a] Prepared from $[RuCl_2(\eta^6\text{-arene}^1)]_2$, $AgBF_4$ and arene^2. [b] In DMSO-d_6, using Me_4Si as internal reference. [c] Literature value [15]: δ 6.9 (in DMSO-d_6). [d] Λ_M ($MeNO_2$, 1.09×10^{-3} M): 191 ohm^{-1} cm^2 mol^{-1} cf. quoted range for 2/1 electrolytes in $MeNO_2$: 150—180 ohm^{-1} cm^2 mol^{-1} [24]. [e] Literature value [15]: δ 2.35 (in acetone-d_6). [f] Λ_M ($MeNO_2$, 1.01×10^{-3} M): 176 ohm^{-1} cm^2 mol^{-1}. [g] Λ_M ($MeNO_2$, 1.12×10^{-3} M): 174 ohm^{-1} cm^2 mol^{-1}. [h] Could not be recorded owing to displacement of anthracene by DMSO-d_6. [i] Formula $[Ru(1,3,5\text{-}C_6H_3Me_3)(C_6H_5O)]BF_4$. Λ_M ($MeNO_2$, 1.24×10^{-3} M) 89 ohm^{-1} cm^2 mol^{-1} cf. quoted range for 1/1 electrolytes in $MeNO_2$: 75—95 ohm^{-1} cm^2 mol^{-1} [24]. [j] IR (cm^{-1}, Nujol) 1715s [$\nu(C{=}O)$]. Independent of arene^1. [k] IR (cm^{-1}, Nujol) 1748s [$\nu(C{=}O)$]. Independent of arene^1. [l] IR (cm^{-1}, Nujol) 1750s, 1720s [$\nu(C{=}O)$].

80°C for 10 min. The resulting colourless solution was worked up as under (i) to give white crystals of $[Ru(C_6H_6)(C_6H_3Me_3)](BF_4)_2$ (0.106 g, 68%).

(b) Without acid. An acetone solution prepared as under (i) from $[RuCl_2(C_6H_3Me_3)]_2$ (0.200 g, 0.34 mmol) and silver tetrafluoroborate (0.266 g, 1.4 mmol) was filtered and the filtrate was treated with an excess of benzene (2 ml). After heating under reflux for 2.5 h, the colourless crystals of $[Ru(C_6H_6)(C_6H_3Me_3)](BF_4)_2$ were filtered off and dried in vacuo to give 0.211 g (66%) of product.

(c) Using HPF_6. An acetone solution prepared as under (i) from $[RuCl_2(C_6H_3Me_3)]_2$ (0.100 g, 0.17 mmol) and silver hexafluorophosphate (0.173 g, 0.7 mmol) was evaporated to dryness under reduced pressure, treated with benzene (2 ml) and 60% aqueous HPF_6 (2 ml) and heated at 80°C for 10 min. Work up as under (i) gave white crystals of $[Ru(C_6H_6)(C_6H_3Me_3)](PF_6)_2$ (0.127 g, 78%). Anal. Found: C, 31.4; H, 3.4. $C_{15}H_{18}F_{12}P_2Ru$ calcd.: C, 30.6; H, 3.1%.

(d) From the diacetone alcohol acetone salt $[Ru(C_6H_3Me_3)\{Me_2C(OH)CH_2COMe\}(OCMe_2)](BF_4)_2$. A mixture of this salt (0.080 g, 0.14 mmol), trifluoroacetic acid (5 ml) and benzene (1 ml) was heated at 90°C for 5 min. The clear yellow solution became colourless and on work-up as above gave white crystalline $[Ru(C_6H_6)(C_6H_3Me_3)](BF_4)_2$ (0.050 g, 75%). Anal. Found: C, 38.1; H, 4.0; $C_{15}H_{18}B_2F_8Ru$ calcd.: C, 38.0; H, 3.8%.

(e) From the tris(μ-difluorophosphato)complex $[Ru_2(\mu\text{-}PO_2F_2)_3(C_6H_3Me_3)_2]PF_6$. A mixture of this salt (0.100 g, 0.11 mmol), benzene (2 ml) and 40% fluoroboric acid in acetic anhydride (2 ml) was heated at 80°C for 10 min. Work-up as above gave $[Ru(C_6H_6)(C_6H_3Me_3)](BF_4)_2$ (0.075 g, 71%). The corresponding PF_6 salt was prepared similarly using HPF_6.

(iii) (η^6-Mesitylene)(η^6-phenol)ruthenium(II)bis(tetrafluoroborate)

An acetone solution prepared as under (i) from $[RuCl_2(C_6H_3Me_3)]_2$ (0.200 g, 0.34 mmol) and silver tetrafluoroborate (0.266 g, 1.4 mmol) was treated with an excess of phenol (0.3 g) and 40% aqueous HBF_4/acetic anhydride (2 ml).

The solution was heated at 90°C for 1 h and allowed to cool to room temperature. Careful addition of ether gave white microcrystals of $[Ru(C_6H_3Me_3)(C_6H_5OH)](BF_4)_2$ (0.272 g, (81%). IR (cm^{-1}, Nujol) 1550s [ν(C=C)].

(iv) Preparation of (η^6-mesitylene)(η^6-phenoxo)ruthenium(II) tetrafluoroborate

The phenol complex $[Ru(C_6H_3Me_3)(C_6H_5OH)](BF_4)_2$ (0.080 g, 0.16 mmol) was dissolved in acetone (10 ml), ethyldiisopropylamine (1 ml) was added, and the solution was allowed to stand at room temperature for 1.5 h. After removal of the solvent in vacuo, the residue was recrystallized from acetone/ether to give pale yellow crystalline $[Ru(C_6H_3Me_3)(C_6H_5O)]BF_4$ (0.061 g, 77%). IR (cm^{-1}, Nujol) 1625s [ν(C=O)], 1585s [ν(C=C)].

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