Areneruthenium(II) Carboxylates: Reactions with Ligands and the *X*-Ray Structure of the *p*-Cymene Pyrazine Complex $[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2]PF_6$ †

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The preparation of monomeric areneruthenium(II) acetates and trifluoroacetates $[Ru(\eta\text{-arene})X(O_2CR)]$ and $[Ru(\eta\text{-arene})(O_2CR)_2]$ (X = Cl or Br; R = Me or CF_3; arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$, $C_6H_3Me_3$-1,3,5, $C_6H_2Me_4$-1,2,4,5, or C_6Me_6) (not all possible combinations) from the corresponding dihalides $[\{Ru(\eta\text{-arene})X_2\}_2]$ is described. Infrared spectra suggest that the complexes $[Ru(\eta\text{-arene})X(O_2CR)]$ contain a bidentate carboxylate group and that $[Ru(\eta\text{-arene})(O_2CR)_2]$ contain one bi- and one uni-dentate carboxylate group, which are apparently equivalent on the n.m.r. time-scale at room temperature. Reaction of trifluoroacetic acid with $[\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2]$ gives a complex of empirical formula $Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)\cdot CF_3CO_2H$ which may be a salt $[(\eta\text{-}C_6Me_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}O_2CCF_3)Ru(\eta\text{-}C_6Me_6)][H(O_2CCF_3)_2]\cdot CF_3CO_2H$. Triphenylphosphine converts $[Ru(\eta\text{-}C_6Me_6)(O_2CR)_2]$ (R = Me or CF_3) into $[Ru(\eta\text{-}C_6Me_6)(O_2CR)_2(PPh_3)]$ in which both carboxylate groups are unidentate. The trifluoroacetate group is completely displaced from $[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ by pyridine (py) or ethyldiphenylphosphine to give $[Ru(\eta\text{-}C_6H_6)ClL_2]^+$ (L = py or $PEtPh_2$), isolated as PF_6^- or BPh_4^- salts. The potentially binucleating ligands pyrazine (pyz), 4,4′-bipyridyl, and 1,3-dithiane react either with $[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ or with $[\{M(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (M = Ru or Os) in the presence of NH_4PF_6 or $NaBPh_4$ in methanol to give $[M(\eta\text{-arene})ClL_2]^+$ salts in which only one donor atom of the ligand is co-ordinated, but pyz and $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ react in dry tetrahydrofuran to give the pyrazine-bridged species $\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2(\mu\text{-pyz})$. The structure of the complex $[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2]PF_6$ has been verified by *X*-ray analysis. The crystals are triclinic, space group $P\bar{1}$, with a = 9.265(2), b = 9.684(4), c = 12.969(2) Å, α = 86.51(2), β = 72.89(2), and γ = 85.59(2)°.

Carboxylato-complexes of the platinum-group metals are useful synthetic precursors owing to the lability of the carboxylate ligands, which allows, for example, the generation of hydrido-complexes under mild conditions.[1,2] Here we report jointly the results obtained by our groups on the synthesis and some reactions of a range of areneruthenium(II) carboxylates. While our work was in progress, some hexamethylbenzeneruthenium(II) carboxylato-derivatives were described independently: *viz.* $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]\cdot H_2O$ [3] and $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PMe_3)]$ [4] obtained by reaction of silver acetate with $[\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2]$ and $[Ru(\eta\text{-}C_6Me_6)Cl_2(PMe_3)]$ respectively; the salt $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)(PMe_3)]PF_6$ [4] derived from $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PMe_3)]$ and KPF_6; and the trifluoroacetato-complexes $[Ru(\eta\text{-}C_6Me_6)Me(O_2CCF_3)(PR_3)]$ and $[Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PR_3)]$ (PR_3 = PMe_3, $PMePh_2$, or PPh_3) [5] formed by stepwise cleavage of the metal–carbon σ bonds of $[Ru(\eta\text{-}C_6Me_6)Me_2(PR_3)]$ with trifluoroacetic acid.

Results and Discussion

Orange or red-brown microcrystalline complexes of general formula $[Ru(\eta\text{-arene})Cl(O_2CR)]$ can be prepared in yields of *ca.* 50—80% by three general methods.

(*a*) Heating the arenedihalogenoruthenium(II) dimer $[\{Ru(\eta\text{-arene})X_2\}_2]$ with a mixture of the carboxylic acid (RCO_2H) and the acid anhydride $[(RCO)_2O]$ (arene = C_6H_6 or $p\text{-}MeC_6H_4CHMe_2$, X = Cl, R = Me; arene = C_6H_6, X = Cl, Br, or I, R = CF_3).

(*b*) Treatment of $[\{Ru(\eta\text{-arene})X_2\}_2]$ in benzene with 2 mol of silver carboxylate per mol of dimer (arene = C_6Me_6, X = Cl, R = Me; arene = C_6Me_6, $C_6H_3Me_3$-1,3,5, X = Cl, R = CF_3; arene = C_6Me_6, $C_6H_2Me_4$-1,2,4,5, $C_6H_3Me_3$-1,3,5, or $p\text{-}MeC_6H_4CHMe_2$, X = Br, R = Me).

(*c*) Reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with an excess of sodium acetate in acetone at room temperature (arene = $p\text{-}MeC_6H_4CHMe_2$, $C_6H_3Me_3$-1,3,5, $C_6H_2Me_4$-1,2,4,5, or C_6Me_6).

In method (*a*) it is important to use $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ which has been prepared from ruthenium trichloride, activated by repeated evaporation of its aqueous solution to dryness on a water-bath.[6] If this is not done, the reaction of the $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ is very slow and the yield of $[Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)]$ is poor (<10%). This difficulty can also be circumvented by use of the more soluble 2,4-pentanedionato-complex $[Ru(\eta\text{-}C_6H_6)Cl(acac)]$ [7] in place of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$, although the reaction with acetic acid–acetic anhydride is still slow; the yield of $[Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)]$ is 95% after heating under reflux for 5 d. Method (*b*) works well for the complexes specified but is not satisfactory for the chloro(carboxylato)-complexes of benzene and mesitylene. Although method (*c*) gives good yields of the chloro(acetato)-complexes for the arenes cited, it cannot be used to make $[Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)]$ in a pure state, owing to the difficulty of separating this compound from excess of sodium acetate. We have also been unable to make bromo(acetato)-complexes $[Ru(\eta\text{-arene})Br(O_2CMe)]$ or chloro(trifluoroacetato)-complexes by method (*c*).

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† Chloro(1—6-η-*p*-cymene)bis(pyrazine)ruthenium(II) hexafluorophosphate.

Supplementary data available (No. SUP 23629, 17 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical data for areneruthenium(II) carboxylates and related complexes of ruthenium and osmium [a]

Complex	Analysis/% C	H	Other
$[Ru(\eta-C_6H_6)Cl(O_2CMe)]$	35.4 (35.1)	3.5 (3.3)	13.3 (13.0) (Cl) [b]
$[Ru(\eta-C_6H_6)Cl(O_2CCF_3)]$	29.5 (29.3)	2.0 (1.9)	10.8 (10.8) (Cl)
$[Ru(\eta-C_6H_6)Br(O_2CCF_3)]$	25.2 (25.8)	1.9 (1.6)	
$[Ru(\eta-p-MeC_6H_4CHMe_2)Cl(O_2CMe)]$	43.6 (43.7)	5.2 (5.2)	11.0 (10.8) (Cl) [c]
$[Ru(\eta-p-MeC_6H_4CHMe_2)Br(O_2CMe)]$	38.6 (38.5)	4.4 (4.55)	21.8 (21.4) (Br)
$[Ru(\eta-C_6H_3Me_3-1,3,5)Cl(O_2CMe)]$	41.5 (41.8)	4.8 (4.75)	11.4 (11.25) (Cl) [d]
$[Ru(\eta-C_6H_3Me_3-1,3,5)Br(O_2CMe)]$	36.6 (36.7)	4.2 (4.2)	22.1 (22.2) (Br)
$[Ru(\eta-C_6H_3Me_3-1,3,5)Cl(O_2CCF_3)]$	35.5 (35.7)	3.4 (3.25)	9.9 (9.6) (Cl) 15.2 (15.4) (F)
$[Ru(\eta-C_6H_2Me_4-1,2,4,5)Cl(O_2CMe)]$	43.8 (43.7)	5.2 (5.2)	10.7 (10.8) (Cl)
$[Ru(\eta-C_6H_2Me_4-1,2,4,5)Br(O_2CMe)]$	38.3 (38.5)	4.6 (4.55)	22.0 (21.4) (Br)
$[Ru(\eta-C_6Me_6)Cl(O_2CMe)]$	47.0 (47.0)	6.0 (5.9)	10.1 (9.9) (Cl) [e]
$[Ru(\eta-C_6Me_6)Br(O_2CMe)]$	41.9 (41.8)	5.3 (5.2)	20.05 (19.9) (Br)
$[Ru(\eta-C_6Me_6)Cl(O_2CCF_3)]$	40.8 (40.8)	4.6 (4.4)	7.6 (8.6) (Cl) 14.3 (13.9) (F)
$[Ru(\eta-C_6Me_6)Cl(O_2CCF_3)]\cdot CF_3CO_2H$	37.0 (36.5)	3.7 (3.6)	7.3 (6.7) (Cl) [f] 21.6 (21.7) (F)
$[Ru(\eta-C_6H_6)(O_2CMe)_2]$	38.8 (40.3)	4.2 (4.0)	20.3 (21.4) (O)
$[Ru(\eta-C_6H_6)(O_2CCF_3)_2]\cdot H_2O$	28.4 (28.4)	1.9 (1.9)	26.8 (26.95) (F)
$[Ru(\eta-p-MeC_6H_4CHMe_2)(O_2CMe)_2]$	48.0 (47.6)	5.8 (5.7)	17.9 (18.1) (O) [g] 28.5 (28.6) (Ru)
$[Ru(\eta-p-MeC_6H_4CHMe_2)(O_2CCF_3)_2]\cdot H_2O$	35.1 (35.1)	3.4 (3.3)	23.7 (23.8) (F)
$[Ru(\eta-C_6H_3Me_3-1,3,5)(O_2CMe)_2]$	46.15 (46.0)	5.4 (5.3)	18.1 (18.9) (O)
$[Ru(\eta-C_6H_3Me_3-1,3,5)(O_2CCF_3)_2]\cdot H_2O$	33.7 (33.55)	3.0 (3.0)	23.7 (24.5) (F) 30.3 (29.8) (Ru)
$[Ru(\eta-C_6H_2Me_4-1,2,4,5)(O_2CMe)_2]\cdot H_2O$	45.4 (45.3)	6.0 (5.9)	21.7 (21.6) (O)
$[Ru(\eta-C_6H_2Me_4-1,2,4,5)(O_2CCF_3)_2]\cdot H_2O$	35.4 (35.1)	3.5 (3.3)	22.9 (23.8) (F)
$[Ru(\eta-C_6Me_6)(O_2CMe)_2]\cdot H_2O$	48.1 (48.1)	6.6 (6.5)	20.0 (20.05) (O) [h] 25.0 (25.3) (Ru)
$[Ru(\eta-C_6Me_6)(O_2CCF_3)_2]\cdot H_2O$	37.45 (37.9)	4.0 (3.9)	21.5 (22.4) (F) [i]
$[Ru(\eta-C_6Me_6)(O_2CMe)_2(PPh_3)]$	63.5 (63.45)	6.1 (6.1)	5.1 (4.8) (P)
$[Ru(\eta-C_6Me_6)(O_2CCF_3)_2(PPh_3)]$	54.3 (54.3)	4.5 (4.4)	4.1 (4.1) (P) 14.8 (15.2) (F)
$[Ru(\eta-C_6H_6)Cl(pyz)_2]BPh_4$	64.4 (65.7)	5.1 (5.0)	7.7 (8.0) (N) 5.0 (5.1) (Cl)
$[Ru(\eta-C_6H_6)Cl(pyz)_2]PF_6$	32.6 (32.4)	2.9 (2.7)	10.5 (10.8) (N)
$[Ru(\eta-C_6H_6)Cl(4,4'-bipy)_2]BPh_4$	69.8 (70.4)	5.1 (5.0)	6.3 (6.6) (N) 4.3 (4.2) (Cl)
$[Ru(\eta-C_6H_6)Cl(1,3-S_2C_4H_8)_2]PF_6$	28.2 (28.0)	3.8 (3.7)	
$[Ru(\eta-C_6Me_6)Cl(1,3-S_2C_4H_8)_2]BPh_4$	60.3 (61.5)	6.4 (6.3)	
$[Os(\eta-p-MeC_6H_4CHMe_2)Cl(pyz)_2]PF_6$	32.5 (32.5)	3.3 (3.3)	8.1 (8.4) (N)
$[Os(\eta-p-MeC_6H_4CHMe_2)Cl(1,3-S_2C_4H_8)_2]BPh_4$	53.9 (54.9)	5.6 (5.5)	
$\{Ru(\eta-p-MeC_6H_4CHMe_2)Cl_2\}_2(\mu-pyz)$	40.6 (41.6)	4.5 (4.7)	4.1 (4.1) (N) 20.7 (20.5) (Cl)
$[Ru(\eta-p-MeC_6H_4CHMe_2)Cl(pyz)_2]PF_6$	37.4 (37.5)	4.0 (3.9)	9.6 (9.7) (N)
$[Ru(\eta-p-MeC_6H_4CHMe_2)Cl(4,4'-bipy)_2]BPh_4$	70.6 (71.8)	5.6 (5.6)	6.4 (6.2) (N)

[a] Calculated values in parentheses. [b] *M* (acetone, 45 °C) 283 (calc. 274). [c] *M* (acetone, 45 °C) 345 (330). [d] *M* (CH_2Cl_2, 25 °C) 341 (315). [e] *M* (CH_2Cl_2, 25 °C) 360 (357). [f] *M* (CH_2Cl_2, 25 °C) 1 047 (1 051, dimer). [g] *M* (CH_2Cl_2, 25 °C) 371 (353). [h] *M* (CH_2Cl_2, 25 °C) 407 (399). [i] *M* (CH_2Cl_2, 25 °C) 503 (507).

The acetato-complexes are readily soluble in water, alcohols, and acetone. Those containing methyl-substituted benzenes are also readily soluble in dichloromethane and chloroform, but the benzene complex $[Ru(\eta-C_6H_6)Cl(O_2CMe)]$ is less soluble in these solvents. The trifluoroacetates are less soluble than the acetates in all organic solvents and $[Ru(\eta-C_6H_6)Cl(O_2CCF_3)]$ dissolves readily only in nitromethane. Molecular-weight determinations by osmometry on selected compounds show that, with the exception of some of the chloro(trifluoroacetato)-complexes discussed below, they are monomeric (Table 1). The i.r. spectra of the acetates show a strong band due to $\nu_{asym.}(OCO)$ at 1 500—1 515 cm^{-1} and strong bands at 1 470 and 1 410—1 420 cm^{-1}, both of which are in the region expected for $\nu_{sym.}(OCO)$ (Table 2).[8,9] Irrespective of the correct assignment of the latter vibration, the value of $\Delta\nu$ [$\nu_{asym.}(OCO) - \nu_{sym.}(OCO)$] is less than 200 cm^{-1}, consistent with the presence of bidentate acetate [structure (1)]. The corresponding bands in the i.r. spectra of the trifluoroacetates are at *ca.* 1 690—1 720 and 1 420 cm^{-1} respectively. The ^1H n.m.r. spectra of the acetato-complexes show sharp singlets due to the acetate methyl groups and the expected resonances due to the η-arenes (Table 3).

In solvents such as nitromethane and methanol there is evidence for some ionic dissociation [equation (i)]. Thus, the

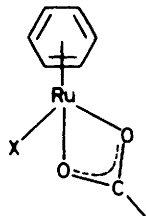
$$[Ru(\eta\text{-arene})Cl(O_2CR)] \rightleftharpoons [Ru(\eta\text{-arene})Cl(solvent)_2]^+ + RCO_2^- \quad (i)$$

singlet due to bound O_2CCF_3 at δ − 75.95 p.p.m. relative to $CFCl_3$ in the ^{19}F n.m.r. spectrum of a freshly prepared solu-

Table 2. Selected i.r. bands (cm^{-1}) of areneruthenium(II) carboxylates *

Compound	$\nu_{asym.}$(OCO)	$\nu_{sym.}$(OCO)	$\Delta\nu$
[Ru(η-C_5H_6)Cl(O_2CMe)]	1 510s,br	1 470s, 1 410s	40—100
[Ru(η-p-$MeC_6H_4CHMe_2$)Cl(O_2CMe)]	1 512s	1 465vs, 1 382s	50—130
[Ru(η-p-$MeC_6H_4CHMe_2$)Br(O_2CMe)]	1 515vs	1 470vs, 1 450s (sh), 1 387s	45—130
[Ru(η-$C_6H_3Me_3$-1,3,5)Cl(O_2CMe)]	1 510vs	1 475vs, 1 410s, 1 387vs	35—130
[Ru(η-$C_6H_3Me_3$-1,3,5)Br(O_2CMe)]	1 525m (sh), 1 505s	1 475vs, 1 412s	50—110
[Ru(η-$C_6H_2Me_4$-1,2,4,5)Cl(O_2CMe)]	1 515vs	1 460vs, 1 410m, 1 385m	55—130
[Ru(η-$C_6H_2Me_4$-1,2,4,5)Br(O_2CMe)]	1 518s	1 475vs, 1 380m	45—140
[Ru(η-C_6Me_6)Cl(O_2CMe)]	1 515s	1 470vs, 1 420s, 1 385s	45—130
[Ru(η-C_6Me_6)Br(O_2CMe)]	1 510s	1 465vs, 1 410vs, 1 380s	45—130
[Ru(η-C_6H_6)Cl(O_2CCF_3)]	1 720 (sh), 1 685vs	1 418m	267
[Ru(η-C_6H_6)Br(O_2CCF_3)]	1 720 (sh), 1 685vs	1 415w	270
[Ru(η-C_6H_6)I(O_2CCF_3)]	1 720 (sh), 1 690vs,br	1 410w	280
[Ru(η-$C_6H_3Me_3$-1,3,5)Cl(O_2CCF_3)]	1 712vs, 1 685vs, 1 580m, 1 530s	1 440m, 1 402vs	–
[Ru(η-C_6Me_6)Cl(O_2CCF_3)]	1 690vs, 1 655vs	1 450m, br, 1 400vs, 1 388vs	–
Ru(η-C_6Me_6)Cl(O_2CCF_3)·CF_3CO_2H	1 782s, 1 720m, 1 648vs	1 445m, 1 385m	–
[Ru(η-C_6H_6)(O_2CMe)$_2$]	1 625s, 1 565s, 1 538s	1 475vs, 1 435vs, 1 370vs, 1 315vs	60—100 (bd) 310 (ud)
[Ru(η-p-$MeC_6H_4CHMe_2$)(O_2CMe)$_2$]	1 630vs, 1 585m (sh), 1 517s	1 475vs, 1 380vs 1 362vs, 1 310vs	40—155 (bd) 310 (ud)
[Ru(η-$C_6H_3Me_3$-1,3,5)(O_2CMe)$_2$]	1 620vs, 1 570m, 1 510m	1 470vs, 1 312vs	40—115 (bd) 310 (ud)
[Ru(η-$C_6H_2Me_4$-1,2,4,5)(O_2CMe)$_2$]·H_2O	1 565vs, 1 515vs	1 470vs, 1 445vs, 1 340vs	45—100 (bd) 225 (ud)
[Ru(η-C_6Me_6)(O_2CMe)$_2$]·H_2O	1 565s	1 470 (sh), 1 410 (sh), 1 395vs, 1 342s	– 223 (ud)
[Ru(η-C_6H_6)(O_2CCF_3)$_2$]·H_2O	1 675vs, 1 580w	1 440s, 1 430s	–
[Ru(η-p-$MeC_6H_4CHMe_2$)(O_2CCF_3)$_2$]·H_2O	1 675vs, 1 580w	1 475m, 1 430s	–
[Ru(η-$C_6H_3Me_3$-1,3,5)(O_2CCF_3)$_2$]·H_2O	1 670vs, 1 530w	1 442s, 1 380s	–
[Ru(η-$C_6H_2Me_4$-1,2,4,5)(O_2CCF_3)$_2$]·H_2O	1 685vs, 1 590w (sh)	1 445vs, 1 432vs, 1 382s	–
[Ru(η-C_6Me_6)(O_2CCF_3)$_2$]·H_2O	1 685vs, 1 612s, 1 565vs	1 438s, 1 385s	–
[Ru(η-C_6Me_6)(O_2CMe)$_2$(PPh_3)]	1 640m, 1 610m	1 360s	250—280 (ud)
[Ru(η-C_6Me_6)(O_2CCF_3)$_2$(PPh_3)]	1 710vs, 1 690vs	1 390m	300—320 (ud)

* Spectra run in Nujol and hexachlorobutadiene mulls. Abbreviations: v = very; s = strong; m = medium; w = weak; sh = shoulder; br = broad; ud = unidentate; and bd = bidentate.



(1) X = Cl or Br, R = Me or CF_3

tion of [Ru(η-C_6H_6)Cl(O_2CCF_3)] in nitromethane is partially replaced on standing by a signal at δ – 77.48 p.p.m. which is ascribed to free [CF_3CO_2]$^-$ (relative intensity *ca.* 7 : 1 respectively). Also, the conductivity of a *ca.* 10^{-3} mol dm^{-3} solution of [Ru(η-C_6H_6)Cl(O_2CCF_3)] in nitromethane at 25 °C increases from 4.5 S cm^2 mol^{-1} to a steady value of 13 S cm^3 mol^{-1} over a 6 h period (*ca.* 15% dissociation since Λ_M for a 1 : 1 electrolyte in nitromethane is in the range 60—115 S cm^2 mol^{-1}).[10] Similarly, the ^{1}H n.m.r. spectrum of [Ru(η-C_6H_6)Cl(O_2CMe)] in CD_3NO_2 initially shows sharp singlets at δ 5.70 and 1.56 p.p.m. due to the η-C_6H_6 and acetate methyl groups respectively, but after 48 h there is an additional peak at δ 2.02 p.p.m. due to free acetate and the benzene resonance is broadened. The conductivity rises to a steady value of 10 S cm^2 mol^{-1} over the same period (*ca.* 10% dissociated).

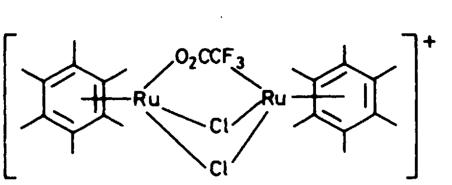
The hexamethylbenzene complex [{Ru(η-C_6Me_6)Cl_2}$_2$] behaves differently from its benzene analogue on reaction with trifluoroacetic acid. The product is a yellow, microcrystalline solid of empirical formula Ru(η-C_6Me_6)Cl(O_2CCF_3)·CF_3CO_2H; the same compound is obtained from [Ru(η-C_6Me_6)Cl(O_2CMe)] and trifluoroacetic acid. The compound is dimeric in dichloromethane but dilute solutions are appreciably conducting and in nitromethane solutions (1×10^{-3}—1.25×10^{-4} mol dm^{-3}) the equivalent conductivity (based on a dimeric formulation) varies between 76 and 106 S cm^2 equiv.$^{-1}$. The individual values are apparently consistent with the presence of a 1 : 1 electrolyte,[10] but the curvature of the Λ *vs.* $c^{\frac{1}{2}}$ plot suggests the presence either of a higher electrolyte type and/or extensive ion pairing. The i.r. spectrum shows a strong band at 1 782 cm^{-1} assignable to [H(O_2CCF_3)$_2$]$^-$ {*cf.* K[H(O_2CCF_3)$_2$] 1 792 cm^{-1},[11] CF_3CO_2H 1 819 cm^{-1} [12]}, in addition to bands at lower frequency arising from co-ordinated trifluoroacetate (Table 2). The ^{19}F n.m.r. spectrum contains a sharp singlet at δ –76.28 p.p.m. and a very broad resonance at δ *ca.* –75.6 p.p.m. (relative to $CFCl_3$) in an intensity ratio of about 1 : 2 which can be assigned to co-ordinated and hydrogen bonded trifluoroacetate groups respectively, but there is no signal in the range δ 0—20 p.p.m. in which an acidic proton might be expected to appear. Salts isolated by addition of $NaPF_6$ or $NaBPh_4$ to the compound did not give completely satisfactory elemental analyses and sometimes showed two C_6Me_6 resonances in their ^{1}H n.m.r. spectra. However, the ^{19}F n.m.r. spectrum of the PF_6 salt

Table 3. Proton n.m.r. data for areneruthenium(II) carboxylates and derived complexes

Compound	Solvent	δ [a]		
		η-Arene	Acetate	Other
$[Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)]$	$CDCl_3$	5.76 (s, C_6H_6)	1.87	
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl(O_2CMe)]$	$CDCl_3$	5.63, 5.44 (AB pattern, C_6H_4, *J* 6), 2.94 (sp, C*H*Me_2), 2.31 (s, Me), 1.37 (d, CH*Me*$_2$, *J* 7)	1.82	
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Br(O_2CMe)]$	$CDCl_3$	5.41, 5.61 (AB pattern, C_6H_4, *J* 6), 2.93 (m, C*H*Me_2), 2.31 (s, Me), 1.39 (d, CH*Me*$_2$, *J* 7)	1.80	
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl(O_2CMe)]$	$CDCl_3$	5.0 (s, C_6H_3), 2.25 (s, C_6Me_3)	1.83	
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Br(O_2CMe)]$	$CDCl_3$	5.0 (s, C_6H_3), 2.27 (s, C_6Me_3)	1.81	
$[Ru(\eta\text{-}C_6H_2Me_4\text{-}1,2,4,5)Cl(O_2CMe)]$	$CDCl_3$	5.23 (s, C_6H_2), 2.18 (s, C_6Me_4)	1.83	
$[Ru(\eta\text{-}C_6H_2Me_4\text{-}1,2,4,5)Br(O_2CMe)]$	$CDCl_3$	5.29 (s, C_6H_2), 2.20 (s, C_6Me_4)	1.85	
$[Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)]$	$CDCl_3$	2.17 (s, C_6Me_6)	1.79	
$[Ru(\eta\text{-}C_6Me_6)Br(O_2CMe)]$	$CDCl_3$	2.15 (s, C_6Me_6)	1.77	
$[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$	CD_3NO_2	5.88 (s, C_6H_6)		
$[Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)]$	$CDCl_3$	2.0 (s, C_6Me_6)		
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)\cdot CF_3CO_2H$	$CDCl_3$	2.02 (s, C_6Me_6)		
$[Ru(\eta\text{-}C_6H_6)(O_2CMe)_2]$	$CDCl_3$	5.80 (s, C_6H_6)	1.92	
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(O_2CMe)_2]$	$CDCl_3$	5.79, 5.57 (AB pattern, C_6H_4, *J* 6), 2.85 (sp, C*H*Me_2), 2.23 (s, Me), 1.33 (d, CH*Me*$_2$, *J* 7)	1.90	
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(O_2CMe)_2]$	$CDCl_3$	5.09 (s, C_6H_3), 2.26 (s, C_6Me_3)	1.90	
$[Ru(\eta\text{-}C_6H_2Me_4\text{-}1,2,4,5)(O_2CMe)_2]\cdot H_2O$	$CDCl_3$	5.39 (s, C_6H_2), 2.14 (s, C_6Me_4)	1.93	4.3 (H_2O)
$[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]\cdot H_2O$	$CDCl_3$	2.13 (s, C_6Me_6)	1.95	6.74 (H_2O)
$[Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2]\cdot H_2O$	$(CD_3)_2SO$	6.15 (s, C_6H_6)		5.91 (H_2O)
	CD_3CN	5.68 (s, C_6H_6)		5.77 (H_2O)
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(O_2CCF_3)_2]\cdot H_2O$	$CDCl_3$	5.63, 5.44 (AB pattern, C_6H_4 *J* 6), 2.90 (sp, C*H*Me_2), 2.21 (s, Me), 1.36 (d, CH*Me*$_2$, *J* 7)		
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(O_2CCF_3)_2]\cdot H_2O$	$CDCl_3$	5.03 (s, C_6H_3), 2.13 (s, C_6Me_3)		
$[Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2]\cdot H_2O$	$CDCl_3$	2.08 (s, C_6Me_6)		6.40 (H_2O)
$[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PPh_3)]$	$CDCl_3$	2.17 (s, C_6Me_6)	1.93 [b]	7.33 (PPh_3)
$[Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PPh_3)]$	CD_2Cl_2	1.79 (s, C_6Me_6)		7.4 (PPh_3)

[a] Chemical shifts in p.p.m. relative to internal $SiMe_4$, *J* values in Hz; sp = septet. Chemical shifts measured in CD_3NO_2 (δ 4.33), $(CD_3)_2SO$ (δ 2.62), and CD_3CN (δ 2.00 p.p.m.) were referenced to the residual proton resonances of the respective solvents. [b] An additional peak at δ 1.98 p.p.m. of unknown origin was also present.

showed only the singlet due to bound CF_3CO_2 at δ −76.22 p.p.m. in addition to the usual PF_6 doublet, the broad resonance at δ −75.6 p.p.m. having disappeared. We suggest tentatively that the compound is a salt, $[(\eta\text{-}C_6Me_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}O_2CCF_3)Ru(\eta\text{-}C_6Me_6)][H(O_2CCF_3)_2]\cdot CF_3CO_2H$ in which the cation contains three bridging ligands [structure (2)]. The ' unsolvated ' compound $[Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)]$ can be made by treatment of $[\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2]$ with the stoicheiometric quantity of silver trifluoroacetate.



(2)

Unexpectedly the apparent molecular weight of this compound in CH_2Cl_2 is about 50% higher than expected for the monomer and is concentration dependent [Found: 611 (0.009), 619 (0.014), 645 (0.019), and 685 (0.036 mol dm^{-3}). Calc. for monomer: 412]. The ^{19}F n.m.r. spectrum in CD_2Cl_2 shows two very closely spaced, equally intense peaks at δ −75.2 and −75.8 p.p.m. (relative to $CFCl_3$) and the molar conductivity in CH_2Cl_2 varies from 24.4 to 32.0 S cm^2 mol^{-1} in the concentration range 1×10^{-3}—1.25×10^{-4} mol dm^{-3} (Λ_M for a 1 : 1 electrolyte in CH_2Cl_2 is in the range 40—50 S cm^2 mol^{-1}). Hence this suggests that at least in solution this complex should be formulated as $[(\eta\text{-}C_6Me_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}O_2CCF_3)Ru(\eta\text{-}C_6Me_6)]O_2CCF_3$ (2).

Treatment of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with ⩾4 mol of silver acetate per mol of dimer in benzene at room temperature gives orange, microcrystalline bis(acetato)-complexes $[Ru(\eta\text{-arene})(O_2CMe)_2]$ in 70—80% yield, which are monomeric in dichloromethane. The durene (1,2,4,5-tetramethylbenzene) and hexamethylbenzene complexes crystallize as monohydrates, as shown by a complete elemental analysis of the latter and by the presence of a peak at δ 4.03 p.p.m. due to water in the ^1H n.m.r. spectrum of the former in CD_2Cl_2. Maitlis and co-workers [3] record a water peak at δ 2.70 p.p.m. in the ^1H n.m.r. spectrum of the hexamethylbenzene complex in $(CD_3)_2CO$, and at 301 K we observe this broad peak in CD_2Cl_2 at δ 6.74 p.p.m. In contrast, the benzene, *p*-cymene, and mesitylene complexes appear to be anhydrous. The i.r. spectra show bands attributable to both unidentate and bidentate functions (Table 2), *e.g.* for $[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(O_2CMe)_2]$, 1 620 [$\nu_{asym.}$(OCO)(unidentate)], 1 570 [$\nu_{asym.}$(OCO)(bidentate)], 1 470 [$\nu_{sym.}$(OCO)(bidentate)], and 1 310—1 365 cm^{-1} [$\nu_{sym.}$(OCO)(unidentate)], and are thus consistent with structure (3). The hexamethylbenzene and durene complexes probably also have this structure, although the highest frequency due to $\nu_{asym.}$(OCO) in these cases is only 1 565 cm^{-1}, perhaps as a consequence of hydrogen bonding of water to the unidentate acetate group. A band at *ca.* 390 cm^{-1} in the i.r. spectra of

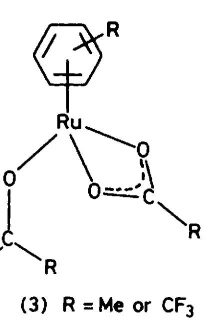
Table 4. Infrared spectra (400—150 cm^{-1}) of areneruthenium(II) carboxylates [a]

$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl(O_2CMe)]$	308vs,[b] 297vs,[c] 269w, 228m, 209 (sh), 203s, 179s
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Br(O_2CMe)]$	302s,[b] 270w,br, 203m,br, 163m
$[Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)]$	309vs,[b] 295 (sh),[c] 237s, 225s, 193m, 168m,br
$[Ru(\eta\text{-}C_6Me_6)Br(O_2CMe)]$	302s,[b] 270w, 223s, 188m,br, 158m,br
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl(O_2CCF_3)]$	395w,br, 320—310w,br, 290—280m,br, 220w
$[Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)]$	384w, 280s, 270 (sh), 208s, 193 (sh),164m,br
$[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(O_2CMe)_2]$	395w,br,[d] 307vs,[b] 289s, 270 (sh), 227m, 220—200m,br, 183s
$[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]\cdot H_2O$	384s,[d] 308vs,br,[b] 294vs,br, 272s, 242m, 210m, 164s

[a] Spectra run as Polythene discs. [b] ν(Ru–OCOMe)(bidentate). [c] ν(Ru–Cl). [d] ν(Ru–OCOMe)(unidentate).

$[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]\cdot H_2O$ and $[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(O_2CMe)_2]$ can be assigned tentatively to ν(Ru–OCOMe)(unidentate) since it is absent from the spectra of the corresponding chloro- and bromo-acetates (Table 4). Both the mono- and bis-(acetato)-complexes show strong absorption at *ca.* 300 cm^{-1} which may be due to ν(Ru–OCOMe)(bidentate); in the case of the chloro(acetates) this overlaps the strong band due to ν(Ru–Cl)(terminal). We have been unable to assign with certainty the corresponding ν(Ru–Br) absorption owing to the presence of strong interfering bands in the region 170—250 cm^{-1} in the spectra of all the complexes studied.

The bis(acetato)-complexes react with trifluoroacetic acid to give the corresponding bis(trifluoroacetates), isolated as monohydrates $[Ru(\eta\text{-arene})(O_2CCF_3)_2]\cdot H_2O$. The benzene complex has also been made by reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with an excess of silver trifluoroacetate, but generally this method gives less pure products. Although the ν(OCO) bands in the i.r. spectra cannot be assigned unambiguously to unidentate and bidentate trifluoroacetate ligands (Table 2), the compounds probably have structure (3), the water molecule being hydrogen-bonded to one of the trifluoroacetate groups. A broad peak at δ *ca.* 6 p.p.m. in the ^1H n.m.r. spectra is assigned to the water protons (Table 3).



(3) R = Me or CF_3

In the complexes $[Ru(\eta\text{-}C_6H_6)(S\text{–}S)_2]$ [S–S = S_2PMe_2, S_2PPh_2, or $S_2P(OEt)_2$] the unidentate and bidentate dithioacid ligands do not undergo rapid intramolecular exchange on the n.m.r. time-scale at room temperature, although the closely related complexes $[Rh(\eta\text{-}C_5Me_5)(S\text{–}S)_2]$ [S–S = S_2PMe_2, S_2PPh_2, S_2CNMe_2, or S_2COEt] do so above room temperature.[13] The ^1H n.m.r. spectra of the bis(acetato)-complexes show only one acetate methyl resonance at room temperature, but the behaviour of the spectrum of $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]\cdot H_2O$ in $CDCl_3$ between 25 and −65 °C suggests that another process must be occurring instead of, or in addition to, intramolecular scrambling of the acetate groups. On cooling, the peaks at δ 2.00 and 2.18 p.p.m. due respectively to acetate and arene methyl groups broaden and apparently coalesce at *ca.* −50 °C. At still lower temperature two new peaks grow on either side of the C_6Me_6 resonance. The broad peak at δ 6.74 p.p.m. sharpens and shifts to δ *ca.* 9 p.p.m. on lowering the temperature. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum shows three peaks at room temperature [δ(p.p.m.) 88.30, $C_6(CH_3)_6$; 15.71, $C_6(CH_3)_6$; 24.30, O_2CCH_3] but at −65 °C additional peaks at δ 87.46, 16.18, and 23.88 p.p.m. are now present. These effects are ascribed to a temperature-dependent equilibrium similar to that discussed above for the chloro(acetates), involving either the solvent or water of hydration, *e.g.* equations (ii) and (iii).

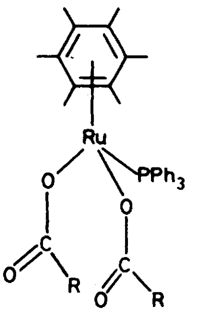
$$[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]\cdot H_2O \rightleftharpoons [Ru(\eta\text{-}C_6Me_6)(O_2CMe)(\text{solvent})]^+ + [O_2CMe]^- \quad \text{(ii)}$$

$$[Ru(\eta\text{-}C_6Me_6)(\sigma\text{-}O_2CMe)(\eta^2\text{-}O_2CMe)]\cdot H_2O \rightleftharpoons [Ru(\eta\text{-}C_6Me_6)(\sigma\text{-}O_2CMe)_2(H_2O)] \quad \text{(iii)}$$

The ^{19}F n.m.r. spectrum of $[Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2]\cdot H_2O$ in CD_3CN shows a sharp singlet at δ −74.71 p.p.m. due to trifluoroacetate groups which are equivalent on the n.m.r. time-scale; there are two other weak peaks which may be due to free $CF_3CO_2^-$ and $[Ru(\eta\text{-}C_6H_6)(O_2CCF_3)(CD_3CN)]^+$. Further work on the behaviour of these complexes in various solvents is in progress.

The lability of the co-ordinated carboxylate groups in the areneruthenium(II) complexes makes them useful synthetic precursors. Reaction of $[Ru(\eta\text{-arene})Cl(O_2CR)]$ or $[Ru(\eta\text{-arene})(O_2CR)_2]$ with sodium methoxide or ethoxide gives yellow solutions from which the known tri-μ-alkoxo-salts $[Ru_2(\eta\text{-arene})_2(OR')_3]BPh_4$ (R′ = Me or Et)[14] can be precipitated by addition of $NaBPh_4$. The carboxylates also readily form μ-hydrido-complexes on heating with propan-2-ol, probably *via* thermally unstable propan-2-oxides.[15]

Reaction of $[Ru(\eta\text{-}C_6Me_6)(O_2CR)_2]$ (R = Me or CF_3) with triphenylphosphine gives yellow 1 : 1 adducts. The i.r. spectrum of the bis(acetato)-complex shows medium-intensity bands at 1 640 and 1 610 cm^{-1} assigned to $\nu_{asym.}$(OCO) and a strong band at 1 360 cm^{-1} due to $\nu_{sym.}$(OCO), the value of Δν (250—280 cm^{-1}) being consistent with the presence of unidentate carboxylate groups [structure (4)]. Attempts to isolate the corresponding chloro(carboxylato)-compounds $[Ru(\eta\text{-}C_6Me_6)Cl(O_2CR)(PPh_3)]$ from $[Ru(\eta\text{-}C_6Me_6)Cl(O_2CR)]$ gave only small amounts of $[Ru(\eta\text{-}C_6Me_6)Cl_2(PPh_3)]$, ap-



(4) R = Me or CF_3

Table 5. Proton n.m.r., ν(Ru–Cl), and conductivity data for arene-ruthenium(II) and -osmium(II) complexes

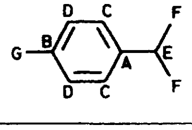
Compound	Solvent	δ η-Arene	δ Other	ν(Ru–Cl)/ cm^{-1}	Λ/ S cm^2 mol^{-1}
[Ru(η-C_6H_6)Cl(pyz)$_2$]PF_6	CD_3NO_2	6.10 (s, C_6H_6)	8.72m (pyz)	299	75
[Ru(η-C_6H_6)Cl(4,4′-bipy)$_2$]BPh_4	CD_3NO_2	5.93 (s, C_6H_6)	8.67m, 7.61m (bipy) [a]	285br	49
[Ru(η-C_6H_6)Cl(1,3-$S_2C_4H_8$)$_2$]PF_6	CD_3NO_2	6.07 (s, C_6H_6)	3.25m, 2.92m 2.33m (1,3-$S_2C_4H_8$)	330	86
{$RuCl_2$(η-*p*-$MeC_6H_4CHMe_2$)}$_2$(μ-pyz)	CD_3NO_2	5.66, 5.40 (AB pattern, C_6H_4, *J* 8), 3.05 (sp, C*H*Me_2), 2.21 (s, Me), 1.35 (d, CH*Me*$_2$, *J* 7)	9.10s (pyz)	290	0
[Ru(η-*p*-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6	CD_3NO_2	6.05, 5.78 (AB pattern, C_6H_4, *J* 10), 2.79 (sp, C*H*Me_2), 1.88 (s, Me), 1.15 (d, CH*Me*$_2$, *J* 7)	8.82m (pyz)	296	85
[Os(η-*p*-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6	CD_3NO_2	6.28, 6.08 (AB pattern, C_6H_4, *J* 9), 1.93 (s, Me), 1.19 (d, CH*Me*$_2$, *J* 7) [c]	8.67m (pyz) [b]	298	79
[Os(η-*p*-$MeC_6H_4CHMe_2$)Cl(1,3-$S_2C_4H_8$)$_2$]BPh_4	CD_3NO_2	6.05 (s, C_6H_4), 2.28 (s, Me), 1.31 (d, CH*Me*$_2$, *J* 7)	3.28m, 2.86m (1,3-$S_2C_4H_8$)	292	48

[a] Overlapping with peaks due to BPh_4^- at δ 6.8—7.7 p.p.m. [b] Overlapping AB patterns. [c] Septet due to C*H*Me_2 not observed.

Table 6. ^{13}C-{^{1}H} N.m.r. data [a] at 301 K for selected compounds in CD_3NO_2

Compound	η-Arene	Other
[Ru(η-C_6Me_6)(O_2CMe)$_2$]·H_2O [b–d]	88.30 (*C*$_6Me_6$), 15.71 [C_6(*C*H_3)$_6$]	24.30 (O_2C*C*H_3), 182.77 (O_2*C*CH_3)
[Ru(η-C_6H_6)Cl(pyz)$_2$]PF_6 [b]	86.4	147.84, 146.50
[Os(η-*p*-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6 [e,h]	95.44 (A), 92.91 (B), 79.90 (C), 73.98 (D), 29.71 (E), 20.16 (F), 15.38 (G)	147.32, 147.09
[Os(η-*p*-$MeC_6H_4CHMe_2$)Cl(1,3-$S_2C_4H_8$)$_2$]BPh_4 [f,h]	105.17 (A), 96.75 (B), 82.00 (C), 78.47 (D), 32.08 (E), 22.55 (F), 18.35 (G)	30.07, 29.30 (166.64, 137.26, 127.19, 123.30) [g]
[Ru(η-*p*-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6 [e,h]	104.54 (A), 101.65 (B), 87.14 (C), 82.51 (D), 29.86 (E), 20.37 (F), 15.83 (G)	147.54, 146.56

[a] Chemical shifts quoted to high frequency of $SiMe_4$. [b] Recorded on XL-100A. [c] Spectrum recorded in $CDCl_3$. [d] At 208 K peaks shift to 88.72, 15.13, and 25.51 p.p.m. respectively. [e] Recorded on WH360. [f] Recorded on CFT20. [g] Due to carbons of BPh_4^-. [h] Labelling of *p*-cymene signal is shown below.

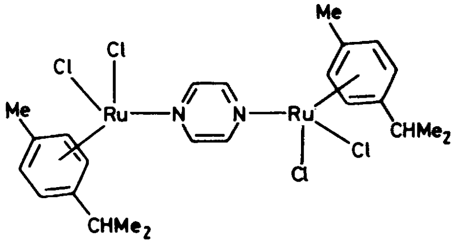


parently arising from rapid disproportionation of the desired complex.

The trifluoroacetate ligand of [Ru(η-C_6H_6)Cl(O_2CCF_3)] is completely displaced by reaction with ligands such as neat pyridine (py), neat ethyldiphenylphosphine, or 2,2′-bipyridyl (bipy) in methanol, and addition of NH_4PF_6 or $NaBPh_4$ gives salts containing the known cations [Ru(η-C_6H_6)ClL$_2$]$^+$ (L = py, $PEtPh_2$, or ½bipy).[6,16,17] A similar reaction occurs with the potentially binucleating ligands pyrazine (pyz), 4,4′-bipyridyl, and 1,3-dithiane. The i.r. spectra of the yellow pyrazine salts [Ru(η-C_6H_6)Cl(pyz)$_2$]Y (Y = PF_6 or BPh_4) lack bands due to bound [CF_3CO_2]$^-$ but do show bands at 845 and 610 cm^{-1} characteristic of η-benzene and bands at 1 582, 1 418, 1 151, 1 120, and 1 054 cm^{-1} arising from vibrations associated with the pyrazine rings; a band at 300 cm^{-1} is clearly due to ν(Ru–Cl)(terminal) and a broad absorption at 368 cm^{-1} is assigned tentatively to ν(Ru–pyz). The salts are 1 : 1 electrolytes in nitromethane and their ^{1}H n.m.r. spectra (Table 5) agree with the formulation, the pyrazine resonances appearing as a complex multiplet at δ 8.72 p.p.m.

Analogous complexes containing *p*-cymene have been prepared by direct reaction of [{M(η-*p*-$MeC_6H_4CHMe_2$)Cl_2}$_2$] (M = Ru or Os) with an excess of various ligands in methanol and subsequent precipitation with NH_4PF_6 or $NaBPh_4$. For reasons which are not clear, the ^{1}H n.m.r. signals of the ligands in the benzene and *p*-cymene complexes containing 1,3-dithiane or 4,4′-bipyridyl are very broad and several of these compounds have therefore been characterized by their ^{13}C n.m.r. spectra (Table 6). Attempts to prepare mixed-metal complexes using the unco-ordinated nitrogen atoms of [Ru(η-*p*-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6 have been unsuccessful so far. The single-crystal *X*-ray structure of this compound (see below) shows that the free nitrogen atoms are too far apart for bidentate co-ordination to one metal atom.

Interestingly, direct reaction of pyrazine with [{Ru(η-*p*-$MeC_6H_4CHMe_2$)Cl_2}$_2$] in dry tetrahydrofuran (thf) gives a



(5)

brown, microcrystalline solid of empirical formula {Ru(η-p-$MeC_6H_4CHMe_2$)Cl_2}$_2$pyz, which is non-conducting in nitromethane. The ^1H n.m.r. spectrum in CD_3NO_2 shows a sharp singlet at δ 9.10 p.p.m. due to the pyrazine protons in addition to the usual arene signals, and integration confirms the stoicheiometry indicated by the microanalytical data. The i.r. spectrum shows a broad band due to ν(RuCl)(terminal) at 290 cm^{-1}. The most reasonable structure, (5), is one in which pyrazine bridges two Ru(η-arene)Cl_2 moieties in a manner well established in other areas of ruthenium chemistry.[18]

Crystal Structure of [Ru(η-p-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6.—Details of the solution of the structure are given in the Experimental section. Final atomic parameters are in Table 7 and bond distances and angles in Figure 1. This shows a tetrahedral arrangement around the ruthenium atom with the η-arene ring and three other ligands adopting a ' piano-stool ' configuration. The complex has a similar arrangement to that of [Ru(η-p-$MeC_6H_4CHMe_2$)Cl_2($PMePh_2$)] [19] with the Ru–C distances to the p-cymene not significantly different. There is also good agreement with the Ru–Cl distance. However, the p-cymene ring here shows no significant deviation from planarity. The root-mean-square (r.m.s.) deviation of the six atoms in the plane is 0.006 Å with no atom being further than 0.008 Å. The ring-to-metal distance is 1.68 Å which is slightly further than that found in the [{Os(η-p-$MeC_6H_4CHMe_2$)Cl_2}$_2$] complex recently reported by Watkins and Fronczek [20] but is in agreement with the ruthenium–arene distance found by Bennett *et al.*[19] The methyl and isopropyl substituents are bent towards the Ru by 3.0 and 1.2° respectively and thus the distortion is similar to that found in the osmium complex. Also, the atoms C(71) and C(70) are displaced by similar amounts (1.40 Å away and 0.99 Å towards the Ru) to those observed in both ruthenium and osmium complexes.

The pyrazine molecules are both planar, the r.m.s. deviations being 0.009 and 0.007 Å for the N(1) and N(1′) rings respectively. The Ru atom is 0.13 and 0.12 Å out of the ring planes and the distances, Ru–N, of 2.15 and 2.18 Å are slightly longer than those reported for the octahedral complexes of Ru^{II} and Ru^{III} by Gress *et al.*[21] The angle between the normals to the pyrazine ring planes is 87°. The explanation for the inability of the complex to bind further metals through the distal ring nitrogens can be seen immediately from Figure 2. The separation is 6.89 Å which is much too great when compared with the 2.91 Å between the two bound atoms N(1) and N(1′). Figure 3 shows the crystal packing.

Finally, the PF_6^- anion is octahedrally co-ordinated and does not appear to be disordered although the thermal parameters for F(1)—F(6) are higher than those for the rest of the non-hydrogen atoms.

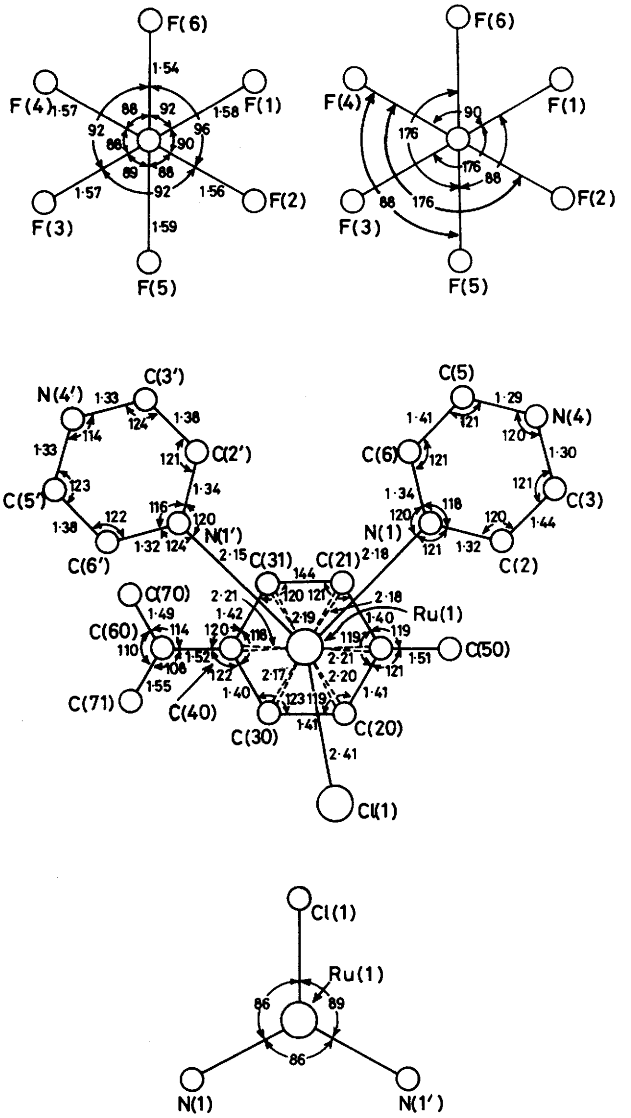


Figure 1. The molecular structure of [Ru(η-p-$MeC_6H_4CHMe_2$)-Cl(pyz)$_2$]PF_6. The e.s.d.s in bond length are all less than 0.02 Å and and in bond angle are generally less than 1.0°

Experimental

Instrumental.—The following instrumentation was employed: i.r. spectra, PE 447, 4 000—250 cm^{-1} (Edinburgh), PE 683, 4 000—200 cm^{-1} (Canberra), Nujol and hexachlorobutadiene mulls, KBr and CsI plates; Hitachi FIS 3, 400—33 cm^{-1} (Canberra), Polythene discs; ^1H n.m.r. spectra, Varian HA-100 and EM-360 (Edinburgh), Varian HA-100, JEOL PMX-60 (Canberra); ^{13}C n.m.r. spectra, Varian CFT20, XL100 and Bruker WH360 (Edinburgh); ^{19}F n.m.r. spectra, Varian XL100 (Edinburgh), Bruker CXP200 (Canberra); conductivity, Portland Electronics model 310 (Edinburgh), WTW LFD 550 (Canberra).

Microanalyses were by Butterworths Micro Analytical Consultancy, the University of Edinburgh Chemistry Department, and the Microanalytical Unit of the Australian National University. Molecular weights were determined in acetone at 45 °C on a Perkin-Elmer–Hitachi model 115 osmometer calibrated with benzil (Edinburgh), and in dichloromethane at 25 °C on a Knauer osmometer (Canberra). Starting materials were obtained from normal commercial suppliers.

Complexes.—The complexes [{Ru(η-arene)Cl_2}$_2$] (η-arene = C_6H_6, p-$MeC_6H_4CHMe_2$, or $C_6H_3Me_3$-1,3,5) were pre-

Table 7. Atomic co-ordinates (fractional × 10^4) with estimated standard deviations (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	8 183(1)	−1 969(09)	−2 963(07)	F(3)	4 899(13)	−3 763(12)	2 320(9)
Cl(1)	10 254(3)	−2 153(3)	−4 593(2)	F(6)	7 093(16)	−2 829(15)	3 125(12)
N(4)	11 876(16)	−941(11)	−1 146(14)	F(5)	6 061(12)	−5 218(11)	1 047(8)
C(5)	11 889(19)	−344(7)	−2 065(13)	F(4)	6 897(12)	−5 042(11)	2 447(9)
C(6)	10 851(14)	−652(13)	−2 606(10)	H(5)	12 685(19)	439(17)	−2 044(13)
N(1)	9 831(10)	−1 590(9)	−2 182(7)	H(6)	10 833(14)	−150(13)	−3 378(10)
C(2)	9 791(15)	−2 174(13)	−1 230(10)	H(2)	8 948(15)	−2 906(13)	−857(10)
C(3)	10 870(17)	−1 835(16)	−702(13)	H(3)	10 853(17)	−2 139(16)	74(13)
N(4′)	8 988(12)	−6 961(11)	−2 042(9)	H(5′)	10 785(16)	−6 959(15)	−3 443(11)
C(5′)	9 888(16)	−6 335(15)	−2 912(11)	H(6′)	10 522(14)	−4 488(13)	−3 863(10)
C(6′)	9 722(14)	−4 937(13)	−3 165(10)	H(2′)	6 791(14)	−4 107(13)	−1 166(10)
N(1′)	8 610(9)	−4 124(8)	−2 573(7)	H(3′)	7 099(16)	−6 584(15)	−752(11)
C(2′)	7 691(14)	−4 732(13)	−1 694(10)	H(21)	5 499(12)	−2 119(11)	−1 026(9)
C(3′)	7 887(16)	−6 130(15)	−1 456(11)	H(31)	5 238(11)	−3 292(10)	−2 638(8)
C(10)	6 639(12)	−395(11)	−1 956(9)	H(30)	7 610(12)	−50(11)	−4 691(9)
C(21)	5 936(12)	−1 654(11)	−1 825(9)	H(20)	7 817(12)	1 144(12)	−3 115(9)
C(31)	5 803(11)	−2 336(10)	−2 745(8)	H(51)	7 897(14)	713(13)	−1 326(10)
C(40)	6 402(12)	−1 743(11)	−3 795(9)	H(52)	6 792(14)	−227(13)	−200(10)
C(30)	7 130(12)	−502(11)	−3 893(9)	H(53)	5 917(14)	1 049(13)	−886(10)
C(20)	7 256(12)	185(12)	−3 002(9)	H(701)	7 838(15)	−4 261(13)	−4 741(11)
C(50)	6 825(14)	254(13)	−980(10)	H(702)	6 530(15)	−4 351(13)	−5 482(11)
C(70)	6 687(15)	−4 002(13)	−4 749(11)	H(703)	5 920(15)	−4 351(13)	−4 060(11)
C(60)	6 314(13)	−2 476(12)	−4 780(9)	H(60)	6 794(13)	−1 891(12)	−5 523(9)
C(71)	4 690(18)	−2 191(18)	−4 875(14)	H(711)	4 185(18)	−1 153(18)	−4 725(14)
P(1)	6 572(5)	−3 968(5)	1 573(3)	H(712)	3 972(18)	−2 920(18)	−4 337(14)
F(1)	8 236(12)	−4 276(11)	822(9)	H(713)	4 814(18)	−2 427(18)	−5 701(14)
F(2)	6 215(13)	−2 997(12)	659(10)				

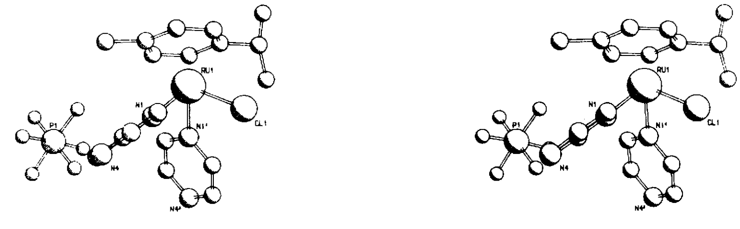


Figure 2. Stereodiagram of the molecular structure of [Ru(η-*p*-$MeC_6H_4CHMe_2$)Cl(pyz)$_2$]PF_6

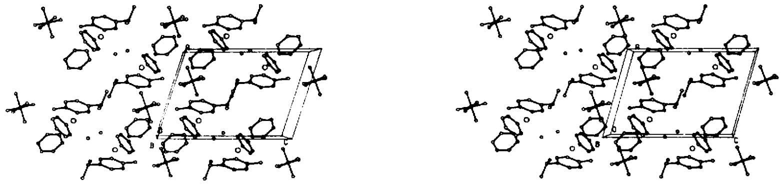


Figure 3. Stereodiagram showing the crystal packing

pared from ethanolic hydrated $RuCl_3$ and the appropriate dihydroarene; [22,23] in the case of the benzene complex it was preferable to activate the $RuCl_3$ by repeated evaporation of its aqueous solution on a steam-bath.[6] The hexamethylbenzene and durene complexes [{Ru(η-arene)X_2}$_2$] (η-arene = C_6Me_6 and $C_6H_2Me_4$-1,2,4,5; X = Cl or Br) were obtained by heating the *p*-cymene complex with a large excess of molten arene at *ca.* 180 °C (arene = C_6Me_6) or 210 °C (arene = $C_6H_2Me_4$-1,2,4,5).[24] The complexes [{Ru(η-C_6H_6)X_2}$_2$] (X = Br or I) were prepared by reaction of [{Ru(η-C_6H_6)Cl_2}$_2$] with the appropriate lithium halide in water.[19,22] Reaction of α-phellandrene (*p*-mentha-1,5-diene) with ethanolic $RuBr_3$ gave [{Ru(η-*p*-$MeC_6H_4CHMe_2$)Br_2}$_2$] [24] and with ethanolic Na_2[Os-Cl_6] gave [{Os(η-*p*-$MeC_6H_4CHMe_2$)Cl_2}$_2$].[6] The complex [Ru(η-C_6H_6)Cl(acac)] was made from [{Ru(η-C_6H_6)Cl_2}$_2$] and thallium(I) acetylacetonate.[7]

All reactions were carried out under dry nitrogen using degassed solvents, although the isolated complexes were air-stable.

Acetato(η-benzene)chlororuthenium(II), [Ru(η-C_6H_6)Cl(O_2-CMe)]. (*a*) A suspension of [{Ru(η-C_6H_6)Cl_2}$_2$] (160 mg, 0.32 mmol) in acetic acid (10 cm^3) and acetic anhydride (2 cm^3) was heated under reflux for periods of 6 h to 5 d (depending on the quality of the starting material) to give a dark red-brown solution. This was filtered whilst hot to remove a brown solid. On cooling the filtrate deposited the product as a dark red-brown crystalline solid (90 mg, 52%), m.p. 208 °C (decomp.).

(*b*) A suspension of [Ru(η-C_6H_6)Cl(acac)] (240 mg, 0.93

mmol) in acetic acid (35 cm^3) and acetic anhydride (25 cm^3) was stirred at 75 °C for 5 d. Solvents were removed *in vacuo* and the residue triturated with diethyl ether to give the orange, microcrystalline product (160 mg, 59%).

Acetato(chloro)(η-p-cymene)ruthenium(II), [Ru(η-MeC$_6$H$_4$CHMe$_2$)Cl(O$_2$CMe)]. A solution of [{Ru(η-MeC$_6$H$_4$CHMe$_2$)Cl$_2$}$_2$] (160 mg, 0.26 mmol) in acetic acid (20 cm^3) and acetic anhydride (5 cm^3) was heated under reflux for 3 h. The mixture was evaporated to *ca.* half-volume, diethyl ether and n-heptane were added, and the solution was set aside at 0 °C for 24 h. The red-brown crystalline solid was filtered off, washed with a few cm^3 of ether, and air-dried. Yield 180 mg (56%), m.p. 172—173 °C.

(*η-Benzene*)*chloro*(*trifluoroacetato*)*ruthenium*(II), [Ru(η-C$_6$H$_6$)Cl(O$_2$CCF$_3$)]. The complex [{Ru(η-C$_6$H$_6$)Cl$_2$}$_2$] (200 mg, 0.40 mmol) was added to a mixture of trifluoroacetic acid (15 cm^3) and trifluoroacetic anhydride (1 cm^3) and refluxed for 2.5 h. The solution was then filtered whilst hot to remove any undissolved starting material. The orange filtrate was evaporated under reduced pressure to *ca.* half-volume and the product precipitated as an orange powder by addition of diethyl ether. After filtration, washing with ether, and air-drying the yield was 150 mg (55%), m.p. 232—235 °C (decomp.).

The corresponding bromo- and iodo-complexes [Ru(η-C$_6$H$_6$)X(O$_2$CCF$_3$)] (X = Br or I) were prepared similarly, although both were too insoluble for their n.m.r. spectra to be recorded and the latter was not analytically pure.

Acetato(*chloro*)(*η-hexamethylbenzene*)*ruthenium*(II), [Ru(η-C$_6$Me$_6$)Cl(O$_2$CMe)]. (*a*) A mixture of [{Ru(η-C$_6$Me$_6$)Cl$_2$}$_2$] (200 mg, 0.3 mmol) and anhydrous sodium acetate (300 mg, 3.66 mmol) was stirred in acetone (50 cm^3) at room temperature for 22 h. After centrifuging, the supernatant liquid was evaporated to dryness under reduced pressure and the residue was recrystallized from dichloromethane–n-hexane (1 : 1 v/v) to give the product as bright orange microcrystals (120 mg, 56%).

(*b*) A mixture of [{Ru(η-C$_6$Me$_6$)Cl$_2$}$_2$] (200 mg, 0.3 mmol) and silver acetate (100 mg, 0.6 mmol) in benzene (25 cm^3) was stirred at room temperature for 2.5 h. Work-up as in (*a*) gave the product (120 mg, 56%), m.p. 209—212 °C (decomp.).

Acetato(*bromo*)(*η-1,2,4,5-tetramethylbenzene*)*ruthenium*(II), [Ru(η-C$_6$H$_2$Me$_4$-1,2,4,5)Br(O$_2$CMe)]. A mixture of [{Ru(η-C$_6$H$_2$Me$_4$-1,2,4,5)Br$_2$}$_2$] (395 mg, 0.5 mmol) and silver acetate (167 mg, 1.0 mmol) was stirred in benzene (60 cm^3) at room temperature for 5 h. Centrifugation gave a red-violet solution. Solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane–n-hexane (1 : 1 v/v) to give orange-red crystals of the product (240 mg, 63%).

Chloro(*η-hexamethylbenzene*)(*trifluoroacetato*)*ruthenium*(II), [Ru(η-C$_6$Me$_6$)Cl(O$_2$CCF$_3$)]. A mixture of [{Ru(η-C$_6$Me$_6$)Cl$_2$}$_2$] (200 mg, 0.3 mmol) and silver trifluoroacetate (132 mg, 0.6 mmol) in benzene (45 cm^3) was stirred for 6 h at room temperature. The orange-red solution obtained after removal of AgCl was evaporated to dryness under reduced pressure and the residue was recrystallized from dichloromethane–n-hexane (1 : 1 v/v) to give bright orange microcrystals (123 mg, 50%).

Reaction of [{Ru(η-C$_6$Me$_6$)Cl$_2$}$_2$] *with trifluoroacetic acid.* The complex [{Ru(η-C$_6$Me$_6$)Cl$_2$}$_2$] (100 mg, 0.3 mmol) was added to trifluoroacetic acid (3 cm^3) and the mixture stirred at 75 °C for 5 h to give a dark red solution. The acid was removed *in vacuo* leaving a yellow-brown oil which gave an orange solid on addition of diethyl ether. Recrystallization from dichloromethane–n-hexane (1 : 1 v/v) gave pale yellow, micro-crystalline Ru(η-C$_6$Me$_6$)Cl(O$_2$CCF$_3$)·CF$_3$CO$_2$H (122 mg, 45% yield).

The same product was obtained from the reaction of [Ru(η-C$_6$Me$_6$)Cl(O$_2$CMe)] (90 mg, 0.25 mmol) and trifluoroacetic acid (2 cm^3) at 46 °C for 10 min. Yield 98 mg (74%).

Bis(*acetato*)(*η-hexamethylbenzene*)*ruthenium*(II) *monohydrate*, [Ru(η-C$_6$Me$_6$)(O$_2$CMe)$_2$]·H$_2$O. A mixture of [{Ru(η-C$_6$Me$_6$)Cl$_2$}$_2$] (400 mg, 0.6 mmol) and silver acetate (434 mg, 2.6 mmol) in benzene (30 cm^3) was stirred at room temperature for 12 h. The solution was either centrifuged or filtered through Celite to remove AgCl and was evaporated to dryness under reduced pressure. The residue was recrystallized from diethyl ether–n-hexane (1 : 1 v/v) and dried *in vacuo* to give yellow needles of the product (365 mg, 80%), m.p. 162—165 °C (decomp.).

The other areneruthenium bis(acetates) were prepared similarly and were recrystallized from dichloromethane–n-hexane (1 : 1 v/v). The durene complex tenaciously retains dichloromethane and was therefore recrystallized from diethyl ether–n-hexane (1 : 1 v/v).

(*η-Hexamethylbenzene*)*bis*(*trifluoroacetato*)*ruthenium*(II) *monohydrate*, [Ru(η-C$_6$Me$_6$)(O$_2$CCF$_3$)$_2$]·H$_2$O. A mixture of [Ru(η-C$_6$Me$_6$)(O$_2$CMe)$_2$]·H$_2$O (100 mg, 0.25 mmol) and trifluoroacetic acid (2 cm^3) was stirred at 45 °C for 20 min to give a deep red solution. The acid was removed *in vacuo* to give a wine-red oil which dissolved in diethyl ether (15 cm^3) to form a pale yellow solution. The volume was reduced to *ca.* 3 cm^3 and the solution was cooled to 0 °C affording fine yellow crystals of the product (80 mg, 63%).

The other areneruthenium bis(trifluoroacetates) were obtained similarly, although the method given below could also be used.

(*η-Benzene*)*bis*(*trifluoroacetato*)*ruthenium*(II) *monohydrate*, [Ru(η-C$_6$H$_6$)(O$_2$CCF$_3$)$_2$]·H$_2$O. The complex [{Ru(η-C$_6$H$_6$)Cl$_2$}$_2$] (200 mg, 0.4 mmol) was treated with silver trifluoroacetate (350 mg, 1.58 mmol) for 6 h at room temperature. The usual work-up gave the product as an orange-yellow powder (150 mg, 44%), m.p. 128—130 °C.

Reactions of [Ru(η-C$_6$H$_6$)Cl(O$_2$CCF$_3$)] *with ligands.* (*a*) *Pyridine.* A solution of the complex (0.15 g, 0.45 mmol) in pyridine (5 cm^3) was stirred for 1 h at room temperature. Pyridine was evaporated *in vacuo* and the resulting dark oil was dissolved in methanol to give a yellow solution. This was filtered and added to a solution containing NH$_4$PF$_6$ (0.3 g) in methanol (8 cm^3). The yellow solid product which precipitated was filtered off in air, washed with diethyl ether and methanol, and dried *in vacuo* at 54 °C (0.18 g, 76%), m.p. 227 °C. Its spectroscopic properties were identical with those previously reported for [Ru(η-C$_6$H$_6$)Cl(py)$_2$]PF$_6$.[6,16]

(*b*) *Ethyldiphenylphosphine.* The complex (0.1 g, 0.3 mmol) was stirred in the neat ligand (1.5 cm^3) for 4 h to give a red solution. Excess of ligand was pumped off and the residue redissolved in methanol to which NaBPh$_4$ (0.4 g) was added. After several minutes a bright yellow precipitate of [Ru(η-C$_6$H$_6$)Cl(PEtPh$_2$)$_2$]BPh$_4$ formed. This was filtered off, washed with diethyl ether and methanol, and dried *in vacuo* (0.27 g, 91%), m.p. 186—188 °C (decomp.).

(*c*) 2,2′-*Bipyridyl.* A suspension of the complex (0.15 g, 0.45 mmol) in degassed methanol (30 cm^3) containing an excess of 2,2′-bipyridyl was refluxed for 3 h. The solid which precipitated on addition of NH$_4$PF$_6$ (0.3 g) was filtered off, washed with methanol, and dried *in vacuo* (0.14 g, 59%), m.p. 275 °C (decomp.). Its spectroscopic properties were identical with those previously reported for [Ru(η-C$_6$H$_6$)Cl(2,2′-bipy)]PF$_6$.[17]

(*d*) *Alkoxides.* A suspension of Na$_2$CO$_3$ (0.3 g) in methanol (15 cm^3) was treated with the complex (0.1 g, 0.3 mmol) and stirred for 1 h to give a yellow solution. This was filtered and NaBPh$_4$ (0.3 g) was added to give a yellow precipitate. After filtration, washing with methanol, and drying *in vacuo* the yield of product, m.p. 198 °C (decomp.), was 70 mg (30%). It was identified as [Ru$_2$(η-C$_6$H$_6$)$_2$(OMe)$_3$]BPh$_4$ by comparison of its ^{1}H n.m.r. spectrum with that of an authentic sample.[14]

The same complex was obtained in 65% yield from the reaction of $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(O_2CCF_3)]$ (0.1 g) with a solution of sodium methoxide prepared from sodium (0.3 g) and methanol (15 cm^3). Likewise, reaction of $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(O_2CCF_3)]$ with ethanolic sodium ethoxide gave $[\mathrm{Ru}_2(\eta\text{-}C_6H_6)_2(\mathrm{OEt})_3]\mathrm{PF}_6$, m.p. 191 °C (decomp.), yield 45%.[14]

(*e*) *Pyrazine.* A suspension of $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(O_2CCF_3)]$ (0.15 g, 0.45 mmol) in degassed methanol (20 cm^3) was treated with an excess of pyrazine (0.5 g) and the mixture was shaken for 2 h. Addition of NaBPh_4 (0.35 g) to the orange solution gave $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(\mathrm{pyz})_2]\mathrm{BPh}_4$, m.p. 185—187 °C, as a microcrystalline, golden-yellow solid which was filtered off, washed with methanol and diethyl ether, and dried *in vacuo* (0.26 g, 82%). The corresponding PF_6 salt was obtained similarly using $\mathrm{NH_4PF_6}$ in place of NaBPh_4.

(*f*) 4,4′-*Bipyridyl.* A suspension of $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(O_2CCF_3)]$ (0.12 g, 0.36 mmol) in methanol (20 cm^3) was shaken with an excess of 4,4′-bipyridyl for 2 d to give a red solution. Addition of NaBPh_4 (0.2 g) gave a yellow-brown solid $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(4,4'\text{-bipy})_2]\mathrm{BPh}_4$, m.p. 173—174 °C (decomp.), which was filtered off, washed with methanol, and air-dried. Yield 0.22 g (71%).

(*g*) 1,3-*Dithiane.* A reaction carried out as above, using 1,3-dithiane and $\mathrm{NH_4PF_6}$, gave $[\mathrm{Ru}(\eta\text{-}C_6H_6)\mathrm{Cl}(1,3\text{-}S_2C_4H_8)_2]\mathrm{PF}_6$, m.p. 210—212 °C, in 67% yield.

Reactions of $[\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)(O_2CR)_2]$ *with ligands.* (*a*) *Alkoxides.* To a solution of sodium methoxide freshly prepared from sodium (0.4 g) and methanol (10 cm^3) was added $[\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)(O_2C\mathrm{Me})_2]\cdot H_2O$ (0.1 g, 0.25 mmol). The mixture was stirred for 1.5 h to give a yellow solution. This was filtered and treated with NaBPh_4 (0.3 g) to give a yellow precipitate. After filtration, washing with methanol, and drying in air this was identified as $[\mathrm{Ru}_2(\eta\text{-}C_6\mathrm{Me}_6)_2(\mathrm{OMe})_3]\mathrm{BPh}_4$, m.p. 169—173 °C (decomp.), yield 90 mg (38%), by ^{1}H n.m.r. spectroscopy.[14]

(*b*) *Triphenylphosphine.* A mixture of $[\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)(O_2CCF_3)_2]\cdot H_2O$ (100 mg, 0.20 mmol) and triphenylphosphine (57.6 mg, 0.22 mmol) in benzene (25 cm^3) was stirred at room temperature for 3.5 h. Solvent was evaporated under reduced pressure and the product $[\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)(O_2CCF_3)_2(\mathrm{PPh}_3)]$ was precipitated by addition of n-hexane (30 cm^3). After washing with two 30-cm^3 portions of n-hexane and drying *in vacuo*, the yield of orange-yellow crystals was 90 mg (61%).

The corresponding bis(acetate) was prepared similarly from $[\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)(O_2C\mathrm{Me})_2]\cdot H_2O$.

Complexes formed from potentially binucleating ligands with $[\{\mathrm{M}(\eta\text{-arene})\mathrm{Cl}_2\}_2]$ (M = Ru, arene = *p*-$\mathrm{MeC_6H_4CHMe_2}$ *or* $C_6\mathrm{Me}_6$; M = Os, arene = *p*-$\mathrm{MeC_6H_4CHMe_2}$). (*a*) $[\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)\mathrm{Cl}(1,3\text{-}S_2C_4H_8)_2]\mathrm{BPh}_4$. A suspension of $[\{\mathrm{Ru}(\eta\text{-}C_6\mathrm{Me}_6)\mathrm{Cl}_2\}_2]$ (0.12 g, 0.18 mmol) in methanol containing an excess of 1,3-dithiane (0.23 g) was shaken for 4 h to give a yellow solution. After filtration to remove unreacted starting material, addition to methanolic NaBPh_4 gave the product as a bright yellow precipitate. This was filtered off, washed with water, methanol, and diethyl ether, and dried *in vacuo* at 54 °C. Yield 0.13 g (42%), m.p. 108 °C.

(*b*) $[\mathrm{Os}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}(\mathrm{pyz})_2]\mathrm{PF}_6$. The complex $[\{\mathrm{Os}(\eta\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}_2\}_2]$ (0.1 g, 0.13 mmol) was shaken in methanol (20 cm^3) containing an excess of pyrazine (0.3 g) for 3 h. The resulting solution was filtered directly into a methanolic solution of $\mathrm{NH_4PF_6}$. After 3 d at 0 °C the yellow-brown solid product which had deposited was filtered off and air-dried. Yield 0.16 g (67%), m.p. 178—184 °C.

Similarly prepared in 68% yield from $[\{\mathrm{Os}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}_2\}_2]$ and 1,3-dithiane in methanol was $[\mathrm{Os}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}(1,3\text{-}S_2C_4H_8)_2]\mathrm{BPh}_4$, m.p. 168—170 °C, and in 77% yield from $[\{\mathrm{Ru}(\eta\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}_2\}_2]$ and pyrazine in methanol yellow-brown needles of $[\mathrm{Ru}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}(\mathrm{pyz})_2]\mathrm{PF}_6$, m.p. 185—188 °C.

(*c*) $[\mathrm{Ru}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}(4,4'\text{-bipy})_2]\mathrm{BPh}_4$. The complex $[\{\mathrm{Ru}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}_2\}_2]$ (0.2 g, 0.16 mmol) was shaken with a solution of 4,4′-bipyridyl (0.3 g) in methanol (25 cm^3) for 9 h. The mixture was filtered and NaBPh_4 was added. The creamy brown precipitate was filtered off, washed with methanol, and dried *in vacuo*. Yield 0.29 g (95%), m.p. 122—125 °C (decomp.).

(*d*) $\{\mathrm{Ru}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}_2\}_2(\mu\text{-pyz})$. To a solution of $[\{\mathrm{Ru}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}_2\}_2]$ (0.2 g, 0.16 mmol) in dry thf (25 cm^3) was added pyrazine (30 mg, 0.38 mmol). The mixture was heated under reflux for 1 h and the brown microcrystalline solid which deposited was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.14 g (66%), m.p. 232 °C.

Crystal Structure Determination of $[\mathrm{Ru}(\eta\text{-}p\text{-}\mathrm{MeC_6H_4CHMe_2})\mathrm{Cl}(\mathrm{pyz})_2]\mathrm{PF}_6$.—Crystals suitable for *X*-ray analysis were prepared by the method given. A brown, elongated crystal (0.2 × 0.4 × 0.6 mm) was chosen and precession photographs indicated a triclinic space group. Accurate cell dimensions were obtained by least-squares refinement of 18 reflections measured on a Nonius CAD4 diffractometer with monochromatized Mo-K_α radiation.

Crystal data. $C_8H_{22}ClF_6N_4PRu$, $M = 573.83$, $a = 9.265(2)$, $b = 9.684(4)$, $c = 12.969(2)$ Å, $\alpha = 86.51(2)$, $\beta = 72.89(2)$, $\gamma = 85.59(2)^\circ$, $U = 1\,107.9$ Å^3, $D_c = 1.73$ g cm^{-3}, $Z = 2$, $D_m = 1.72$ g cm^{-3} (by flotation), $F(000) = 576$, $\mu(\text{Mo-}K_\alpha) = 9.54$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å. There is one molecule in the asymmetric unit assuming space group $P\bar{1}$.

Intensity data were collected by an ω—2θ scan of $1.5(0.8 + 0.35 \tan\theta)^\circ$ for varying times up to a maximum of 60 s such that where possible $I > 3\sigma(I)$. A standard reflection was monitored regularly throughout data collection but no decay was observed. After correction for Lorentz polarization effects, 2 030 out of the 3 866 reflections measured to a $\theta_{\text{max.}} = 25^\circ$ had $I > 3\sigma(I)$. No absorption correction was applied.

Structure solution and refinement. The structure was solved by the conventional Patterson and difference-Fourier technique. A Patterson map revealed the Ru–Ru vector and the remaining atoms were obtained from Fourier-difference syntheses. Refinement of the structure by least squares reduced *R* from 0.295 to 0.063 in three cycles with the Ru, Cl, and P atoms refined anisotropically. The hydrogen atoms were placed in their predicted positions and allowed to ride on the atoms to which they were attached, for a further cycle of least squares. A weighting scheme of the form $w = 0.818/[\sigma^2(F) + 0.001F^2]$ was applied for a final cycle and gave $R = 0.059$ ($R' = 0.070$). The maximum shift-to-error ratio at this stage was 0.014 and no significant residual electron density was observed in the final Fourier-difference map. No extinction correction was applied but two reflections (232) and ($\bar{2}$42) were omitted because of likely extinction. The atomic scattering factor for Ru was taken from ref. 25.

No corrections were made for riding motion, and no short intermolecular contacts were observed.

All calculations were performed on the ICL 2972 at the Edinburgh Regional Computing Centre, except the mean planes which were determined on the Napier College PRIME 750. The SHELX program[26] was used for the crystallographic calculations and the stereodiagrams were produced by PLUTO.[27]

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