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Synthesis and Spectroscopic Characterization of Dinuclear Mono(μ-hydrido) Arene Complexes of Divalent Ruthenium

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Dinuclear mono(μ-hydrido) arene complexes $\{RuX(\eta\text{-arene})\}_2(\mu\text{-H})(\mu\text{-X})$ (X = Cl, Br, arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$; X = Cl, arene = C_6H_4-1-Me-4-$CHMe_2$, C_6H_6) containing one bridging and two terminal halide groups are formed from the reaction of $[RuX_2(\eta\text{-arene})]_2$ with hydrogen (4 atm) at room temperature in the presence of triethylamine. The tendency for one chloride ion to dissociate in nitromethane is enhanced by increasing the degree of alkyl substitution on the arene, the hexamethylbenzene chloro complex being a 1:1 electrolyte in this solvent. The cations $[\{Ru(\eta\text{-arene})\}_2(\mu\text{-H})(\mu\text{-X})_2]^+$ containing two bridging halide groups can be isolated as PF_6 salts. Heating of acetato complexes $Ru(O_2CMe)_2(\eta\text{-arene})$ with 2-propanol gives mono(μ-hydrido) bis(μ-acetato) complexes containing the cations $[\{Ru(\eta\text{-arene})\}_2(\mu\text{-H})(\mu\text{-}O_2CMe)_2]^+$, which can be isolated as solid hydrogenbis(acetate) salts for arene = C_6Me_6 or 1,2,4,5-$C_6H_2Me_4$ and as PF_6 salts for all the arenes studied. The corresponding trifluoroacetato complexes could not be isolated in a pure state but were identified spectroscopically. Reaction of $Ru(O_2CR)X(\eta\text{-arene})$ with hot 2-propanol gives hydrido complexes of empirical formula $\{Ru(\eta\text{-arene})\}_2H(O_2CR)X_2$ (X = Cl, Br; R = CH_3, CF_3) except when arene = C_6H_6; in this case $\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$ is formed. These complexes readily give PF_6 salts of the cations $[\{Ru(\eta\text{-arene})\}_2(\mu\text{-H})(\mu\text{-}O_2CR)(\mu\text{-X})]^+$ that have three different bridging groups. In solution, the parent compounds (arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$) behave as the halide salts of these cations but when arene = *p*-cymene (C_6H_4-1-Me-4-$CHMe_2$) and R = CH_3, the halide salt and a neutral dimer $\{RuX(\eta\text{-arene})\}_2(\mu\text{-H})(\mu\text{-}O_2CR)$ coexist. Complexes of *p*-cymene in which three different groups are attached to ruthenium exhibit diastereotopic aromatic protons and isopropyl methyl groups in their ^1H NMR spectra; those of durene (1,2,4,5-$C_6H_2Me_4$) have diastereotopic methyl groups. The hydride protons of all the carboxylato complexes become progressively more shielded with increasing alkyl substitution on the arene. The formation and structure of the hydrido(arene)ruthenium(II) complexes are compared with those of the corresponding (η-pentamethylcyclopentadienyl)rhodium(III) and -iridium(III) compounds.

Introduction

The chemistry of $[RuCl_2(\eta\text{-arene})]_2$ complexes, especially that of the hexamethylbenzene derivative, is similar in many respects to that of the isoelectronic (η^5-pentamethylcyclopentadienyl)rhodium(III) and -iridium(III) compounds $[MCl_2(\eta\text{-}C_5Me_5)]_2$ (M = Rh, Ir) which has been developed largely by Maitlis and co-workers.[1] Although arene is more readily displaced from the coordination sphere of a metal than C_5Me_5, the (arene)ruthenium complexes offer the advantage of a readily accessible range of substituents and substituent patterns. Derived from $[MCl_2(\eta\text{-}C_5Me_5)]_2$ is a series of dinuclear mono-, bis-, and tris(μ-hydrido) complexes (Figure 1) in which the additional bridging ligands may be halide, acetate, or trifluoroacetate.[2-5] Many of these complexes are very active homogeneous catalysts for olefin hydrogenation. We have been interested to see whether analogous dinuclear (arene)ruthenium hydrides can be made and to examine their catalytic activity. It has been known for some time that suspensions or solutions of $[RuCl_2(\eta\text{-}C_6H_6)]_2$ and of other (arene)ruthenium(II) chlorides in various organic solvents in the presence of organic bases will catalyze olefin hydrogenation and η-arene hydrido complexes have been implicated as intermediates.[6-8] We[9] reported in a preliminary communication that when $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ is heated in 2-propanol in the presence of sodium carbonate a purple, dinuclear bis(μ-hydrido) complex formulated as $[\{Ru(\eta\text{-}C_6Me_6)\}_2(\mu\text{-H})_2(\mu\text{-Cl})]Cl$ is formed which catalyzes olefin and arene hydrogenation, but unfortunately this result has proved to be irreproducible. A red mono(μ-hydrido) complex $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$ can be isolated from this reaction,[10a] but prolonged heating tends to give inseparable mixtures of hydrido complexes. In this paper we describe the reproducible synthesis of a range of mono(μ-hydrido)ruthenium(II) complexes containing benzene and various alkyl-substituted arenes.

Experimental Section

^1H NMR spectra were measured on Varian HA 100, JEOL PMX 60, JEOL FX 200, and Bruker CXP 200 instruments, $(CH_3)_4Si$ being the internal reference. The Bruker CXP 200 was also used to measure ^{19}F NMR spectra that are reported in parts per million relative to $CFCl_3$. IR spectra were measured in the range 4000–200 cm^{-1} as Nujol and hexachlorobutadiene mulls on CsI and KBr plates, respectively, by means of a Perkin-Elmer 683 spectrophotometer. Conductivities were measured on a WTW

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(10) (a) Bennett, M. A.; Ennett, J. P.; Gell, K. I. *J. Organomet. Chem.* **1982**, *233*, C17–C20. (b) A few of the elemental analyses reported in Table I are below the normally accepted level of agreement with calculated values. Some of the complexes, especially those of hexamethylbenzene and durene, hold variable amounts of chloroform or dichloromethane used in the workup. These solvents are not completely removed on pumping, but they are lost slowly on standing, so the composition of the sample may vary somewhat with time. In the case of $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$, contamination by a small amount of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ cannot be ruled out. We have also experienced difficulty in obtaining satisfactory fluorine analyses on some of the trifluoroacetates and PF_6 salts. Nevertheless, the analyses taken with the spectroscopic data leave little doubt about the formulation of the compounds.

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Table I. Analytical Data for (Arene)ruthenium(II) Hydrido Complexes

	calcd			found		
	C	H	other	C	H	other
$\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$	45.5	5.9	16.8 (Cl)	44.4	5.8	15.7 (Cl)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_2]PF_6$	38.8	5.0	9.5 (Cl)	39.0	5.1	9.0 (Cl)
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_3$	41.5	5.0	18.4 (Cl)	40.8	5.0	18.3 (Cl)
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_2]PF_6$	35.0	4.2	10.3 (Cl) 4.5 (P)	36.5	4.5	11.9 (Cl) 4.9 (P)
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HBr_3$	33.8	4.1	33.75 (Br)	34.1	4.3	34.6 (Br)
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2HCl_3$	39.3	4.55	19.4 (Cl)	39.2	4.65	20.2 (Cl)
$\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_3$	41.5	5.0	18.4 (Cl)	40.9	5.1	18.4 (Cl)
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_2]PF_6$	35.0	4.2	4.5 (P)	35.0	4.3	4.8 (P)
$\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$	30.9	2.8	22.9 (Cl)	29.9	2.9	22.8 (Cl)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ (1)	49.1	6.65	18.4 (O) 25.8 (Ru)	48.8	6.6	17.6 (O) 26.1 (Ru)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]PF_6$ (2)	42.5	5.4	3.9 (P)	42.5	5.6	4.1 (P)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)_2]H(O_2CCF_3)_2\cdot H_2O$	38.5	4.0	22.8 (F)	38.6	4.2	21.0 (F)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)_2]PF_6$	37.4	4.1	25.4 (F)	37.2	4.2	23.25 (F)
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O\cdot 0.5CH_2Cl_2$	44.4	5.85	18.7 (O)	44.6	6.1	18.0 (O)
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]PF_6\cdot 0.5CH_2Cl_2$	38.7	4.6	4.0 (P)	37.8	4.8	4.3 (P)
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]PF_6$	37.4	4.4	4.4 (P)	38.1	4.9	5.4 (P)
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)_2]PF_6$	39.2	4.8	4.2 (P)	37.7	5.0	4.8 (P)
$[\{Ru(\eta\text{-}C_6H_6)\}_2H(O_2CMe)_2]PF_6$	30.9	3.05	5.0 (P)	32.2	3.65	5.1 (P)
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl_2\cdot H_2O$	46.2	6.2	10.5 (Cl) 7.1 (O)	45.6	6.7	10.4 (Cl) 7.3 (O)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl]PF_6$	40.7	5.1	4.6 (Cl) 4.0 (P)	40.45	5.2	4.7 (Cl) 4.1 (P)
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Br_2$	41.8	5.4	21.4 (Br)	41.05	5.5	21.0 (Br)
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$	40.7	4.6	8.6 (Cl) 13.8 (F)	40.5	4.6	8.8 (Cl) 12.95 (F)
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	41.4	5.65	11.1 (Cl) 10.0 (O)	43.4	5.8	10.1 (Cl) 10.5 (O)
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl]PF_6\cdot 0.2CH_2Cl_2$	36.7	4.5	6.5 (Cl)	36.25	4.5	6.55 (Cl)
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Br_2\cdot 0.5CH_2Cl_2$	36.9	4.5	4.4 (O)	36.3	4.5	4.9 (O)
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	39.4	5.25	11.7 (Cl) 10.5 (O)	39.5	4.9	12.05 (Cl) 10.3 (O)
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl]PF_6$	35.2	4.1	5.2 (Cl) 4.5 (P)	35.4	4.4	5.6 (Cl) 5.2 (P)
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Br_2$	36.25	4.2	24.2 (Br)	35.25	4.2	24.8 (Br)
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$	35.6	3.5	9.6 (Cl) 15.4 (F)	36.4	3.7	7.6 (Cl) 14.8 (F)
$\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)Cl_2\cdot H_2O$	42.6	5.5	11.5 (Cl) 7.75 (O)	42.3	5.25	11.0 (Cl) 8.2 (O)
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)Cl]PF_6$	37.2	4.5	5.0 (Cl)	36.7	4.4	5.3 (Cl)

Table II. Molecular Weights by Osmometry of Selected (Arene)ruthenium(II) Hydrido Complexes

	mol wt (calcd)	mol wt (CH_2Cl_2, 25 °C)	concn, M	mol wt (CH_3NO_2, 25 °C)	concn, M
$\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$	634	626	1.22×10^{-2}		
$\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_3$	578	558	1.95×10^{-2}	498	1.53×10^{-2}
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ (1)	782	508 625	1.35×10^{-2} 1.62×10^{-2}	404	9.90×10^{-3}
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]PF_6$ (2)	790	677–723[a]	1.90×10^{-2}	373	8.50×10^{-3}
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl_2\cdot H_2O$	675	542	2.11×10^{-2}	397	1.08×10^{-2}
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl]PF_6$	767	651	1.42×10^{-2}	390	9.90×10^{-3}
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	609	547	1.22×10^{-2}	347	1.25×10^{-2}

[a] Values increasing with time over 10-min period.

LFD 550 instrument. Microanalyses (Table I) and molecular weight determinations by osmometry (Table II)) were carried out by the Analytical Unit of this University (Miss Brenda Stevenson and associates). Selected conductivity, IR, and ^1H NMR data are given in Tables III, IV, and V, respectively.

All reactions were carried out under an atmosphere of argon or nitrogen with use of degassed solvents and standard Schlenk techniques, although the hydrido complexes, once isolated, seemed to be air stable as solids and in solution.[10b]

The (arene)ruthenium(II) chloro and carboxylato precursors were prepared by literature methods.[10–13] The durene complexes

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Table III. Molar Conductivities Λ_M (s cm^2 mol^{-1}) of Selected (Arene)ruthenium(II) Hydrido Complexes[a]

complex	Λ_M CH$_3$NO$_2$	Λ_M CH$_2$Cl$_2$
$\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$	62-80[b]	6.5-10.5[b]
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_3$	20-32[b]	<1
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2HCl_3$	7-12[b]	<1
$\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_3$	8-18[b]	1-3[b]
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ (1)	63	
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]PF_6$ (2)	85-114[b]	56-81[b]
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	71-77[b,c]	
$\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)Cl_2\cdot H_2O$	18-30[b]	
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl]PF_6$	79-106[b]	60-88[b]

[a] Measured at ca. 20 °C for concentrations in the range 10^{-3} to 1.25×10^{-4} M. [b] Lower values refer to more concentrated solutions in the given range. [c] Slope of $\Lambda_0 - \Lambda_e$ vs. $C^{1/2}$ plot was 225, consistent with 1:1 electrolyte (Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587-4591).

Table IV. Selected Bands in the IR Spectra (cm^{-1}) of (Arene)ruthenium(II) Hydrido Carboxylato Complexes[a]

	ν_{asym}(OCO)	ν_{sym}(OCO)	other
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ (1)	1570 s	1470 m sp, 1410 vs br	3400 w, 1650 s br (H$_2$O)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]PF_6$ (2)	1570 s	1440 vs, 1387 m	842 s sp (PF$_6$)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)_2]H(O_2CCF_3)_2\cdot H_2O$	1740 w, 1670 vs	1440 s, 1385 s	1200-1150 vs (CF$_3$)
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)_2]PF_6$	1680 vs	1440 s, 1410 s, 1388 s	1200 vs, 1148 vs (CF$_3$), 835 vs, 560 s sp (PF$_6$)
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]PF_6$	1563 vs	1430 vs	835 vs, 555 vs sp (PF$_6$)
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$	1565 vs	1480 s, 1420 s br, 1380 s, 1360 s	3500-3100 w br, 1620 br (H$_2$O)
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]PF_6$	1540 s br	1430 s br, 1380 s sp	830 s, 560 s sp (PF$_6$)
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CCF_3)_2]PF_6$	1635 s sp	1455 s sp, 1380 s sp	1205 vs, 1165 vs (CF$_3$), 840 vs, 560 vs (PF$_6$)
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$	1550 s br	1415 w, 1385 w	
$[\{Ru(\eta\text{-}C_6H_6)\}_2H(O_2CMe)_2]PF_6$	1570 s, 1540 s	1430 s	1150 w br [ν(Ru-H-Ru)?]
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl_2\cdot H_2O$	1565 s, 1550 s	1428 s br, 1382 s sp	3600 br, 1715 s br (H$_2$O), 1120 w [ν(Ru-H-Ru)?]
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl]PF_6$	1555 vs	1430 s sp, 1385 m sp	840 vs, 560 s sp (PF$_6$)
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Br_2$	1540 vs	1432 s, 1380 s	
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$	1690 m, 1650 s sp	1450 s br, 1385 s	1202, 1182, 1150, 1138 (all vs) (CF$_3$)
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	1545 vs	1440 vs, 1385 s	3340 m br, 3270 vs (H$_2$O), 1162 w [ν(Ru-H-Ru)?]
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl]PF_6\cdot 0.2CH_2Cl_2$	1540 vs, 1518 vs	1435 vs, 1382 s	840 vs, 556 s sp (PF$_6$), 1165 w [ν(Ru-H-Ru)]
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Br_2\cdot 0.5CH_2Cl_2$	1540 vs	1432 s, 1380 s	
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	1535 s	1425 s, 1385 m	3600-3350 s br (H$_2$O)
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl]PF_6$	1552 s sp, 1522 m sp	1435 s br, 1380 s sp	1150 w br [ν(Ru-H-Ru)?], 837 vs sp, 558 s sp (PF$_6$)
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Br_2$	1530 s	1435 s, 1412 s	1160 w br [ν(Ru-H-Ru)?]
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$	1780 s, 1730 vs, 1690 s, 1680 sh, 1640 vs	1448 s, 1378 s	1200, 1187, 1148, 1135 (all vs) (CF$_3$)
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)Cl]PF_6$	1540 vs br	1430 vs, 1390 s sp	1170 w [ν(Ru-H-Ru)], 835 vs, 560 vs (PF$_6$)

[a] Measured as mulls in Nujol or hexachlorobutadiene. [b] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad; sp, sharp.

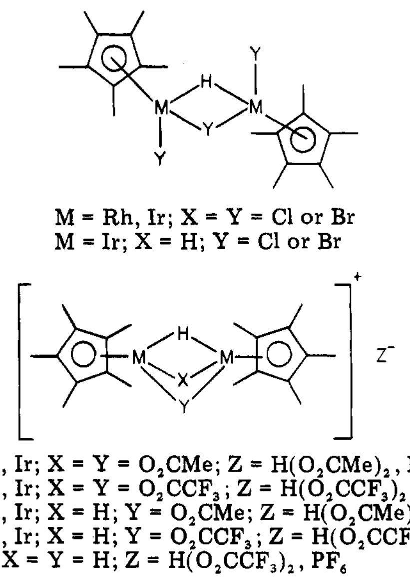
$[RuCl_2(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$ (X = Cl, Br) were prepared similarly to $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ by fusing the *p*-cymene complex $[RuCl_2(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)]_2$ with a large excess of durene.[14] The brown mesitylene complex $[RuCl_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$ that pre-

Table V. NMR Spectra (δ) of (Arene)ruthenium(II) Hydrido Complexes[a]

	arene	other	hydride
$\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$ [b]	2.06 (C_6Me_6)		−11.60
$[\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_2]PF_6$ [b]	2.24 (C_6Me_6)		−9.0
$\{Ru(\eta\text{-}C_6Me_6)\}_2HBr_3$	2.10 (C_6Me_6)		−11.45
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_3$	5.14 ($C_6\mathit{H}_2Me_4$), 2.35, 2.03 ($C_6H_2\mathit{Me}_4$)		−10.74
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_2]PF_6$ [c]	6.19 ($C_6\mathit{H}_2Me_4$); 2.16 ($C_6H_2\mathit{Me}_4$)		−7.09
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HBr_3$	5.24 ($C_6\mathit{H}_2Me_4$), 2.36, 2.14 ($C_6H_2\mathit{Me}_4$)		−11.48
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2HCl_3$	5.08 ($C_6\mathit{H}_3Me_3$), 2.21 ($C_6H_3\mathit{Me}_3$)		−10.84
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2HBr_3$	5.19 ($C_6\mathit{H}_3Me_3$), 2.13 ($C_6H_3\mathit{Me}_3$)	5.29 (CH_2Cl_2)	−11.85
$\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_3$	5.66, 4.88 (AB, J = 6 Hz), 5.54, 5.31 (AB, J = 6 Hz, C_6H_4), 3.03 (sp, $C\mathit{H}Me_2$), 2.30 (s, $C_6H_4\mathit{Me}$), 1.46 (d, J = 7 Hz), 1.43 (d, J = 7 Hz, $CH\mathit{Me}_2$)		−10.10
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_2]PF_6$ [b]	6.04, 5.69 (AB, J = 6 Hz, C_6H_4), 2.63 (sp, $C\mathit{H}Me_2$), 2.15 (s, $C_6H_4\mathit{Me}$), 1.26 (d, J = 7 Hz, $CH\mathit{Me}_2$)		−6.96
$\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$	5.7 (C_6H_6)		−9.48
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ (1)	2.12 (C_6Me_6)	2.16, 2.00 (O_2CMe)	−11.56
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]PF_6$ (2)	2.09 (C_6Me_6)	1.96 (O_2CMe)	−11.58
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$	6.50 ($C_6\mathit{H}_2Me_4$), 2.01 ($C_6H_2\mathit{Me}_4$)	2.15, 1.98 (O_2CMe)	−9.32
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]PF_6$	6.00 ($C_6\mathit{H}_2Me_4$), 1.98 ($C_6H_2\mathit{Me}_4$)	1.97 (O_2CMe)	−9.59
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$	5.68 ($C_6\mathit{H}_3Me_3$), 2.34 ($C_6H_3\mathit{Me}_3$)	1.95, 1.78 (O_2CMe)	−8.67
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]PF_6$	5.33 ($C_6\mathit{H}_3Me_3$), 2.28 ($C_6H_3\mathit{Me}_3$)	1.78 (O_2CMe)	−8.88
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ [b]	5.72, 5.50 (AB, J = 6 Hz), 2.80 (m, $C\mathit{H}Me_2$), 2.18 (s, $C_6H_4\mathit{Me}$), 1.30 (d, J = 7 Hz, $CH\mathit{Me}_2$)	1.83 (O_2CMe)	−8.58
$[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)_2]PF_6$	6.07, 5.81 (AB, J = 6 Hz), 2.6 (m, $C\mathit{H}Me_2$), 1.99 (s, $C_6H_4\mathit{Me}$), 1.21 (d, J = 7 Hz)	1.96 (O_2CMe)	−8.73
$[\{Ru(\eta\text{-}C_6H_6)\}_2H(O_2CMe)_2]PF_6$ [c]	5.94 (C_6H_6)	1.98 (O_2CMe)	−6.6
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl_2\cdot H_2O$	2.22 (C_6Me_6)	1.89 (O_2CMe) 3.5 (H_2O)	−10.2
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl]PF_6$	2.18 (C_6Me_6)	1.87 (O_2CMe)	−10.2
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Br_2$	2.24 (C_6Me_6)	1.98 (O_2CMe)	−10.1
$\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$ [b]	2.22 (C_6Me_6)	−74.84, −75.93 ($O_2C\mathit{CF}_3$)	−10.1
$[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)Cl]PF_6$	2.22 (C_6Me_6)	−74.77 ($O_2C\mathit{CF}_3$), −73.38 (d, J = 711 Hz, PF_6)	−10.08
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	6.60 ($C_6\mathit{H}_2Me_4$), 2.44, 1.88 ($C_6H_2\mathit{Me}_4$)	1.81 (O_2CMe)	−8.47
$[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl]PF_6\cdot 0.2CH_2Cl_2$	5.99 ($C_6\mathit{H}_2Me_4$), 2.36, 1.89 ($C_6H_2\mathit{Me}_4$)	1.83 (O_2CMe), 5.28 (CH_2Cl_2)	−8.62
$\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Br_2\cdot 0.5CH_2Cl_2$	6.59 ($C_6\mathit{H}_2Me_4$), 2.48, 1.91 ($C_6H_2\mathit{Me}_4$)	1.84 (O_2CMe), 5.28 (CH_2Cl_2)	−8.08
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2\cdot 2H_2O$	5.82 ($C_6\mathit{H}_3Me_3$), 2.36 ($C_6H_3\mathit{Me}_3$)	1.80 (O_2CMe), 2.7 (br, H_2O)	−8.52
$[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl]PF_6$ [c]	5.42 ($C_6\mathit{H}_3Me_3$), 2.34 ($C_6H_3\mathit{Me}_3$)	1.86 (O_2CMe)	−8.66
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Br_2$	5.75 ($C_6\mathit{H}_3Me_3$), 2.38 ($C_6H_3\mathit{Me}_3$)	1.83 (O_2CMe)	−8.13
$\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$	5.42 ($C_6\mathit{H}_3Me_3$), 2.20 ($C_6H_3\mathit{Me}_3$)	−75.9 (CF_3CO_2H), −74.8 ($O_2C\mathit{CF}_3$)	−8.64

{Ru(η-C_6H_4-1-Me-4-CHMe$_2$)}$_2$H(O_2CMe)Cl_2·H_2O	5.65, 5.32 (AB, J = 6 Hz), 5.56, 4.86 (AB, J = 6 Hz, C_6H_4 of IIe), 5.64, 5.42 (AB, J = 6 Hz), 5.44, 5.35 (AB, J = 6 Hz, C_6H_4 of Ib), 2.99 (m, CHMe$_2$), 2.62 (m, CHMe$_2$), 2.30 (s, C_6H_4Me of IIe), 1.95 (s, C_6H_4Me of Ib), 1.45 (d, J = 7 Hz), 1.38 (d, J = 7 Hz, CHMe$_2$ of Ia), 1.23 (d, J = 7 Hz), 1.21 (d, J = 7 Hz, CHMe$_2$ of IIe)	1.83 (O_2CMe), 1.68 (O_2CMe)	−7.26 (IIe), −10.17 (Ib)
[{Ru(η-C_6H_4-1-Me-4-CHMe$_2$)}$_2$H(O_2CMe)Cl]PF_6	6.47, 5.77 (AB, J = 6 Hz), 6.13, 5.42 (AB, J = 6 Hz, C_6H_4), 2.71 (m, CHMe$_2$), 2.10 (s, C_6H_4Me), 1.30 (d, J = 7 Hz), 1.28 (d, J = 7 Hz, CHMe$_2$)	1.74 (O_2CMe)	−7.32
{Ru(η-C_6H_4-1-Me-4-CHMe$_2$)}$_2$H(O_2CMe)Br_2	6.70, 5.71 (AB, J = 6 Hz), 6.18, 5.67 (AB, J = 6 Hz, C_6H_4 of IIe), 5.63, 5.39 (AB, J = 6 Hz), 5.57, 4.99 (AB, J = 6 Hz, C_6H_4 of Ib), 3.02 (m, CHMe$_2$ of Ib), 2.63 (m, CHMe$_2$ of IIe), 2.37 (s, C_6H_4Me of Ib), 2.06 (s, C_6H_4Me of IIe), 1.44 (d, J = 7 Hz), 1.38 (d, J = 7 Hz), CHMe$_2$ of Ib), 1.23 (d, J = 7 Hz), 1.22 (d, J = 7 Hz, CHMe$_2$ of IIe)	1.68 (O_2CMe)	−6.88 (IIe), −11.04 (Ib)

[a] Measured in $CDCl_3$, except where stated otherwise, containing $(CH_3)_4$Si as internal reference. [b] Measured in CD_2Cl_2. [c] Measured in acetone-d_6.



M = Rh, Ir; X = Y = Cl or Br
M = Ir; X = H; Y = Cl or Br

M = Rh, Ir; X = Y = O_2CMe; Z = H(O_2CMe)$_2$, PF_6
M = Rh, Ir; X = Y = O_2CCF_3; Z = H(O_2CCF_3)$_2$, PF_6
M = Rh, Ir; X = H; Y = O_2CMe; Z = H(O_2CMe)$_2$, PF_6
M = Rh, Ir; X = H; Y = O_2CCF_3; Z = H(O_2CCF_3)$_2$, PF_6
M = Ir; X = Y = H; Z = H(O_2CCF_3)$_2$, PF_6

Figure 1. Dinuclear (μ-hydrido)(η-pentamethylcyclopentadienyl)rhodium and iridium complexes.

cipitated after ethanolic ruthenium trichloride and 1,4-dihydromesitylene were heated for 20 h[11] was converted into the bis(acetate) by means of silver acetate.[13] This was treated with concentrated HCl to give a flesh-colored, microcrystalline form of [$RuCl_2$(η-1,3,5-$C_6H_3Me_3$)]$_2$. Although both the brown and red forms analyzed satisfactorily, the latter gave higher yields and less decomposition in the reactions described below.

Preparations. Dichloro(μ-chloro)(μ-hydrido)bis(η-hexamethylbenzene)diruthenium(II), {Ru(η-C_6Me_6)}$_2$$HCl_3$. Method 1.[15] A suspension of [$RuCl_2$(η-C_6Me_6)]$_2$ (0.45 g, 0.67 mmol) in dichloromethane (100 mL) containing triethylamine (0.2 mL, 1.5 mmol) was stirred at room temperature under hydrogen (4 atm) in a Fisher-Porter vessel for 48 h. The resulting dark red solution was concentrated under reduced pressure to ca. 50 mL volume, filtered to remove unreacted dimer, and then pumped to dryness. The residue was taken up in the minimum volume of chloroform and chromatographed on neutral alumina (Grade 2, ca. 50 g) at room temperature. The red band that eluted with chloroform/2-propanol (10:1) was collected and evaporated to dryness. The solid was recrystallized from methanol/ether (1:5) to give the product as bright red microcrystals in ca. 60% yield. Attempts to separate [Et_3NH]Cl from the product by vacuum sublimation instead of chromatography were unsuccessful.

Method 2. A suspension of [$RuCl_2$(η-C_6Me_6)]$_2$ (0.3 g, 0.45 mmol) in degassed 2-propanol in a 100-mL Schlenk flask fitted with a serum cap was stirred rapidly under nitrogen to 85 °C for 2.5 min and treated by means of a syringe with 0.8 mL of a degassed aqueous 1 M sodium carbonate solution over a 1.5-min period. After 5 min the solution was deep red. It was allowed to cool to room temperature, stirred rapidly for 10 min, and filtered to remove a yellow precipitate. The filtrate was evaporated to dryness; ^{1}H NMR analysis showed that {Ru(η-C_6Me_6)}$_2$$HCl_3$ (>70% yield) was the only hydride present. The product was purified by chromatography as in method 1.

Dichloro(μ-chloro)(μ-hydrido)bis(η-mesitylene)diruthenium(II), {Ru(η-1,3,5-$C_6H_3Me_3$)}$_2$$HCl_3$. A suspension of [$RuCl_2$($\eta$-1,3,5-$C_6H_3Me_3$)]$_2$ (150 mg, 0.26 mmol) in dichloromethane (80 mL) containing triethylamine (0.1 mL, 0.7 mmol) was stirred at room temperature under hydrogen (4 atm) in a Fisher-Porter vessel for 64 h. The resulting dark red solution was centrifuged and evaporated to dryness under reduced pressure. The residue was shaken with distilled water (80 mL) for about

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[13] Tocher, D. A.; Gould, R. O.; Stephenson, T. A.; Bennett, M. A.; Ennett, J. P.; Matheson, T. W.; Sawyer, L.; Shah, V. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1571–1581.

[14] Bennett, M. A.; Mitchell, T. R. B., to be submitted for publication.

[15] We thank Dr. Kerrie Gell for developing these two synthetic procedures.

a minute, and the mixture was filtered rapidly through filter aid. The aqueous extract containing $Et_3NH^+Cl^-$ was discarded. The solid was taken up in dichloromethane (ca. 20 mL), and the solution was separated from a small amount of residual aqueous extract. It was evaporated to ca. 3 mL under reduced pressure, and either *n*-hexane or ether was added. Cooling to −78 °C overnight gave the microcrystalline dark red product in 45–55% yield.

The durene and *p*-cymene analogues were prepared similarly in yields of 51% and 43%, respectively.

Dichloro(μ-chloro)(μ-hydrido)bis(η-benzene)diruthenium(II), $\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$. A suspension of $[RuCl_2(\eta\text{-}C_6H_6)]_2$ (250 mg, 0.5 mmol) in dichloromethane (70 mL) containing triethylamine (0.15 mL, 1.1 mmol) was stirred under hydrogen (3 atm) for 49 h at room temperature. The light red suspension gradually turned dark red, but most of the solid did not dissolve. It was allowed to settle, and the red solution was removed by decantation. The remaining dark red solid was washed with ether and dried in vacuo to give the analytically pure product. It is insoluble or almost insoluble in water, methanol, Me_2SO, and most common other organic solvents and only slightly soluble in chloroform.

The bromo complexes $\{Ru(\eta\text{-arene})\}_2HBr_3$ (arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, and 1,3,5-$C_6H_3Me_3$) were prepared similarly to their chloro analogues from $[RuBr_2(\eta\text{-arene})]_2$, triethylamine, and hydrogen. The durene complex was isolated and analyzed; the other two were identified by their ^1H NMR spectra.

Bis(μ-chloro)(μ-hydrido)bis(η-hexamethylbenzene)diruthenium(II) Hexafluorophosphate, $[\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_2]PF_6$. Addition of an excess of aqueous NH_4PF_6 to a solution of $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$ in 2-propanol/methanol (1:1) gave an immediate dark red-purple precipitate of the product.

The other $[\{Ru(\eta\text{-arene})\}_2HCl_2]PF_6$ salts were prepared by adding an excess of $NaPF_6$ to a solution of $\{Ru(\eta\text{-arene})\}_2HCl_3$ in acetone. Solvent was removed, and the residue was extracted with dichloromethane. The products crystallized on addition of ether in about 60% yield.

Bis(μ-acetato)(μ-hydrido)bis(η-hexamethylbenzene)diruthenium(II) Hydrogenbis(acetate) Monohydrate, $[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$, 1. A solution of $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)\cdot H_2O$ (480 mg, 1.20 mmol) in degassed 2-propanol (45 mL) was heated at 80 °C for 4 h. The initial orange color changed to wine red within 5 min although the product could not be detected by ^1H NMR spectroscopy at this stage. After 4 h the 2-propanol was pumped off, leaving a red-brown oil, which crystallized on addition of ether. Recrystallization from dichloromethane/*n*-hexane gave the dark red-brown microcrystalline product (370 mg, 79%).

The corresponding durene complex was prepared similarly in 45–50% yield. After recrystallization from dichloromethane/*n*-hexane, the product retained ca. 0.5 mol of CH_2Cl_2/mol of dimer. The oils obtained by reaction of the $Ru(O_2CMe)_2(\eta\text{-arene})$ complexes of mesitylene, *p*-cymene, and benzene with 2-propanol could not be crystallized. They were identified by their ^1H NMR spectra and by formation of PF_6 salts (see below).

Reaction of the trifluoroacetato complexes $Ru(O_2CCF_3)_2(\eta\text{-arene})\cdot H_2O$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$) with 2-propanol gave red-brown solids that were shown by ^1H and ^{19}F NMR spectroscopy (see text) to be mixtures in which the mono(μ-hydrido) complexes $[\{Ru(\eta\text{-arene})\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]H(O_2CCF_3)_2$ predominated.

Bis(μ-acetato)(μ-hydrido)bis(η-hexamethylbenzene)diruthenium(II) Hexafluorophosphate, $[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]PF_6$, 2. A solution of 1 (ca. 50 mg) in acetone (2 mL) was treated with 2 mL of a saturated aqueous solution of NH_4PF_6 to give an immediate orange-brown precipitate. After addition of water (15 mL) the product was separated by centrifugation and extracted with dichloromethane. Evaporation to ca. 2-mL volume and addition of *n*-hexane gave the product in 65% yield.

The complex can also be obtained in 50–55% yield by directly adding solid $NaPF_6$ or NH_4PF_6 either to an acetone solution of the oil formed after removal of 2-propanol from its reaction with $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)\cdot H_2O$ or to the 2-propanol solution itself after the reaction is complete (see below).

Bis(μ-acetato)(μ-hydrido)bis(η-mesitylene)diruthenium(II) Hexafluorophosphate, $[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]PF_6$. A solution of $Ru(O_2CMe)_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$ (100 mg, 0.29 mmol) in 2-propanol (60 mL) was heated at 80 °C for 2.5 h. The dark red solution was allowed to cool to room temperature and treated with $NaPF_6$ (0.5 g) to give a cloudy orange-brown suspension. After being stirred for 1 h, the solution was evaporated to dryness under reduced pressure. The residue was taken up in dichloromethane (25 mL), and the solution was centrifuged and evaporated to dryness to give a light brown solid. Recrystallization from dichloromethane/ether gave the orange-brown product (55 mg, 52%).

The durene, *p*-cymene, and benzene complexes were prepared similarly in yields of 50%, 83%, and 77%, respectively. The reaction of $Ru(O_2CMe)_2(\eta\text{-}C_6H_6)$ with 2-propanol was carried out at 60 °C for 3 h, since at 80 °C some decomposition ensued. The benzene complex is soluble in acetone, but, in contrast with its congeners, it is not very soluble in chloroform or dichloromethane. However, it can be recrystallized from a large volume of dichloromethane/ether (ca. 8 mL/80 mg of product).

(μ-Acetato)(μ-chloro)(μ-hydrido)bis(η-mesitylene)diruthenium(II) Chloride Dihydrate, $[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl\cdot 2H_2O$. A solution of $Ru(O_2CMe)Cl(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$ (70 mg, 0.22 mmol) in 2-propanol (30 mL) was heated at 75 °C for 4.5 h. The initial orange color changed to wine red within 5 min. Solvent was removed in vacuo, and the residual orange-red solid was recrystallized from dichloromethane (3 mL) and *n*-hexane (40 mL) to give the product as orange-red microcrystals (40 mg, 59%) that are soluble in water, acetone, and benzene.

The analogous durene complex (crystallized as a dihydrate) and the hexamethylbenzene and *p*-cymene complexes (monohydrates) were obtained similarly in yields of 88%, 73%, and 55–60%, respectively. The product obtained by heating $Ru(O_2CMe)Cl(\eta\text{-}C_6H_6)$ in 2-propanol showed no acetate bands in its IR spectrum, and its hydride chemical shift was the same as that of $\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$.

The corresponding PF_6 salts were obtained in the usual way by adding aqueous or solid NH_4PF_6 either to the isolated chloride salts or to the reaction solution in 2-propanol and recrystallizing the products from dichloromethane/ether.

Reaction of $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$ with Triphenylphosphine. Treatment of $\{Ru(\eta\text{-}C_6Me_6)_2\}HCl_3$ with slightly more than 1 mol of PPh_3/mol Ru in refluxing benzene for 2 h caused a lightening in color within 0.5 h and formation of a light red precipitate. The yellow-brown supernatant liquid was filtered off and evaporated to dryness. ^1H NMR examination of the precipitate and of the residue showed the presence in both of $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$[16] [$\delta$ (CD_2Cl_2) −8.99 (d, J = 52 Hz, RuH), 1.83 (s, C_6Me_6)] and of $RuCl_2(\eta\text{-}C_6Me_6)(PPh_3)$[17] [$\delta$ 1.71 (s, C_6Me_6)]. The latter predominated in the precipitate, and the former predominated in the supernatant liquid.

Results

The most general method for the preparation of mono(μ-hydrido) complexes of the general type $\{Ru(\eta\text{-arene})\}_2HX_3$ (X = Cl, Br) is to treat the parent dimer $[RuX_2(\eta\text{-arene})]_2$ in dichloromethane containing triethylamine with hydrogen (3–4 atm) at room temperature for 2–3 days (eq 1). This method requires heterolytic

$$[RuX_2(\eta\text{-arene})]_2 + H_2 + Et_3N \rightarrow \{Ru(\eta\text{-arene})\}_2HX_3 + Et_3NH^+X^- \quad (1)$$

arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$, C_6H_4-1-Me-4-$CHMe_2$, C_6H_6, X = Cl

arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$, X = Br

cleavage of hydrogen and is similar in principle to that used to make $RuHCl(PPh_3)_3$ from $RuCl_2(PPh_3)_3$.[18] However,

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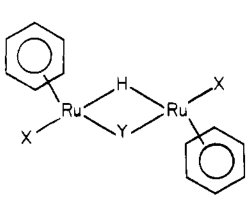
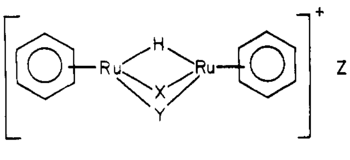
[16] Bennett, M. A.; Huang, T.-N.; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1978**, 582–583.

[17] Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1982**, *228*, 289–300.



Ia, X = Y = Cl or Br
b, X = Cl or Br; Y = O_2CMe



IIa, X = Y = Cl; Z = PF_6
b, X = Y = O_2CMe, Z = $H(O_2CMe)_2$, PF_6
c, X = Y = O_2CCF_3; Z = $H(O_2CCF_3)_2$
d, X = Cl or Br; Y = O_2CMe; Z = PF_6
e, X = Cl or Br; Y = O_2CMe; Z = Cl or Br
f, X = Cl, Y = O_2CCF_3; Z = Cl or $Cl\cdot CF_3CO_2H$

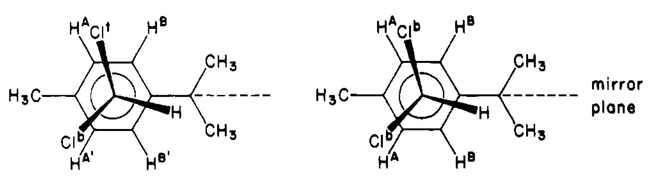
Figure 2. Proposed structures of dinuclear mono(μ-hydrido)(arene)ruthenium(II) complexes.

the latter reaction takes place even in the presence of a weakly basic solvent such as ethanol under 1 atm of hydrogen; this is not the case for the arene complexes.

The hydrido complexes containing durene (1,2,4,5-tetramethylbenzene), mesitylene, and *p*-cymene are readily separated from triethylammonium chloride by rapid extraction of the reaction product with water; these hydrides are insoluble in this solvent, at least for limited periods, although on prolonged contact they dissolve, presumably owing to aquation. In contrast, the hexamethylbenzene complexes are soluble in water and have to be purified by chromatography. The benzene complex $\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$ is insoluble in most organic solvents, including dichloromethane, and precipitates from the reaction mixture. All the other hydrido complexes in this series can be purified by recrystallization from dichloromethane/*n*-hexane, yields being generally 40–60%. They are deep red, air-stable solids which, with the exception of the benzene complex, are readily soluble in dichloromethane, chloroform, and acetone, less soluble in benzene, and insoluble in alkanes. The hexamethylbenzene and *p*-cymene complexes are dimeric in dichloromethane by osmometry (Table II), and the other members of the series are assumed to be similar.

The ^1H NMR spectra (Table V) show a singlet due to Ru–H in the range δ −7 to −11.6, the chemical shift of which depends on the nature of the halide and of the arene, though not in any obviously systematic way. Addition of $NaPF_6$ to the $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes gives salts $[\{Ru(\eta\text{-arene})\}_2HCl_2]PF_6$ that have hydride chemical shifts ca. 3 ppm to higher frequency than those of their precursors. The η-arene resonances of the two series also differ in the cases of the durene and *p*-cymene complexes. Thus, the aromatic methyl groups of $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_2]PF_6$ appear as one singlet, whereas those of $\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_3$ appear as two singlets of equal intensity. Similarly, both the AB pattern of the aromatic proton resonances and the isopropyl methyl doublets of η-*p*-cymene are doubled in passing from $[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_2]PF_6$ to $\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_3$.

These observations can be accounted for if we assume that the $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes have a dimeric structure Ia containing one bridging hydride and one bridging chloride, while the cation in the $[\{Ru(\eta\text{-arene})\}_2HCl_2]PF_6$ complexes has a dimeric structure IIa containing one bridging hydride and two bridging chloride ligands (Figure 2). Structure Ia corresponds to that of the (η^5-pentamethylcyclopentadienyl)rhodium(III) and -iridium(III) analogues $\{M(\eta\text{-}C_5Me_5)\}_2HCl_3$ (M = Rh, Ir), which have been established by single-crystal X-ray analysis.[19,20] Structure IIa resembles that of $[\{Rh(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$, which has been shown by X-ray study to contain two bridging hydride ligands and one bridging acetate.[5] In structure Ia, the three ligands forming the legs of the piano-stool arrangement are different (terminal chloride, bridging chloride, and bridging hydride), whereas in structure IIa two of these ligands are the same (bridging chloride).



Cl^t = terminal chlorine, Cl^b = bridging chlorine

Figure 3. Newman projections looking down the metal–arene bond of (η-*p*-cymene)ruthenium(II) hydrido complexes.

Figure 3 shows a Newman projection looking down the η-*p*-cymene-metal bond for the two cases. In principle, the $RuHCl_2$ fragment can take up various conformations with respect to the arene, but these will be averaged by rapid rotation about the arene–metal bond. We therefore choose one of the most symmetrical arrangements, in which the hydride ligand on the metal eclipses the isopropyl substituent on the arene. Clearly, in structure IIa, the two halves of the arene are related by a mirror plane, but in structure Ia, they are not. Thus the two pairs of aromatic protons and the isopropyl methyl groups in Ia are separately inequivalent, as is observed. A similar argument applied to durene coordination suggests that the opposite pairs of methyl groups should be inequivalent, although the aromatic protons are equivalent, in agreement with observation. No inequivalence is expected or observed for the aromatic protons or methyl groups of mesitylene, or for the benzene protons, in the ^1H NMR spectra of the respective $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes.

Although all the $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes are nonconducting in dichloromethane ($\Lambda_M < 2$ s cm^2 mol^{-1}), they do conduct appreciably in nitromethane (Table III). The molar conductivities of ca. 10^{-3} M solutions of the various complexes increase with the degree of alkyl substitution on the arene, and the value for $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$ suggests that this complex is a completely dissociated 1:1 electrolyte in nitromethane.[21] In view of the ready reaction of all the complexes with $NaPF_6$, the conductivity behavior probably can be attributed to reversible ionization of one of the chloride ligands (eq 2).

$$\{RuCl(\eta\text{-arene})\}_2(\mu\text{-}H)(\mu\text{-}Cl) \rightleftharpoons [\{Ru(\eta\text{-arene})\}_2(\mu\text{-}H)(\mu\text{-}Cl)_2]^+ + Cl^- \quad (2)$$

When the orange, mononuclear bis(acetato) complex $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)\cdot H_2O$ is heated in 2-propanol at 80 °C for 4 h, a wine red solution is formed from which a dark red-brown microcrystalline solid of empirical formula $Ru_2(O_2CMe)_4H_2(\eta\text{-}C_6Me_6)_2\cdot H_2O$ (1) can be isolated in 70–80% yield (eq 3). The ^1H NMR spectrum of 1 in

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(19) Churchill, M. R.; Wei-Yang Ni, S. *J. Am. Chem. Soc.* **1973**, *95*, 2150–2155.

(20) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1977**, *16*, 1488–1494.

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$$2Ru(O_2CMe)_2(\eta\text{-}C_6Me_6) + (CH_3)_2CHOH \rightarrow [\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)_2]H(O_2CMe)_2 + (CH_3)_2CO \quad (3)$$

$CDCl_3$ shows a singlet due to η-C_6Me_6 at δ 2.12, two acetate methyl singlets at δ 2.16 and 2.00, and a one-proton singlet at δ −11.56 due to a metal-bound hydride. In addition to bands at 3400 and 1650 cm^{-1} arising from lattice or coordinated water, the IR spectrum contains bands at 1570 cm^{-1} and in the 1410–1470 cm^{-1} region due to $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ modes, respectively, of coordinated acetate (Table IV). The value of $\nu_{asym}(OCO)$ is lower than that usually observed for monodentate acetate, e.g., 1620 cm^{-1} for the monodentate acetate in $Ru(O_2CMe)_2(\eta$-arene) complexes, although lower values are found in hydrated species, e.g., 1565 cm^{-1} for $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)\cdot H_2O$.[13] It has been suggested[22] that $\nu_{asym}(OCO)$ is greater for bridging than for bidentate acetates; e.g., for $Ru(O_2CMe)Cl(\eta$-arene) complexes, which contain only bidentate acetate, $\nu_{asym}(OCO)$ is at 1510–1520 cm^{-1}. Thus the IR data for **1** are consistent with, but do not unequivocally establish, the presence of bridging acetate groups. Addition of $NaPF_6$ converts **1** into a red-brown PF_6 salt of formula $[Ru_2H(O_2CMe)_2(\eta\text{-}C_6Me_6)_2]PF_6$ (**2**), which has similar hydride and arene resonances to those of **1** but shows only one acetate methyl resonance at δ 1.96. These data suggest that **1** and **2** are hydrogenbis(acetate) and PF_6 salts, respectively, of the dinuclear mono(μ-hydrido) cation $[\{Ru(\eta\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (structure IIb). The spectroscopic data are generally comparable with those for the corresponding η-C_5Me_5Rh and η-C_5Me_5Ir salts, though in contrast with the latter we could not locate the resonance due to the acid proton of $[H(O_2CMe)_2]^-$. The molar conductivity of **1** in nitromethane, 63 s cm^2 mol^{-1} at ca. 10^{-3} M concentration, falls in the range quoted for 1:1 electrolytes in this solvent.[21] Osmometric molecular weight determinations on **1** in dichloromethane at 25 °C (Table II) gave values of 508 and 625 at concentrations of 1.35×10^{-2} and 1.62×10^{-2} M, respectively, compared with a formula weight of 782; this behavior is consistent with the presence of an ion pair that dissociates to a small extent. In nitromethane, the molecular weight of **1** is 404 at 25 °C, indicative of complete dissociation in this solvent.

When the bis(acetato)ruthenium(II) complexes of durene, mesitylene, *p*-cymene, and benzene are heated with 2-propanol, similar color changes take place to those described above for hexamethylbenzene. A durene complex analogous to **1** can be isolated, but in the other cases only intractable oils were obtained. Their ^1H NMR spectra show that they probably are the expected $[\{Ru(\eta\text{-arene})\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2$ complexes and they can also be converted into solid PF_6 salts by addition of $NaPF_6$. In all cases, the hydride chemical shifts of corresponding $H(O_2CMe)_2$ and PF_6 salts are almost equal. These shifts vary from δ −11.6 (C_6Me_6) to −6.6 (C_6H_6), becoming progressively less shielded as the number of arene methyl groups is reduced. This may reflect an electronic effect in which the more electron-donating arenes induce greater electron density on the hydride ligand.

Reaction of $Ru(O_2CCF_3)_2(\eta\text{-}C_6Me_6)\cdot H_2O$ with 2-propanol gives a product that analyzes approximately for the expected mono(μ-hydrido) species $[\{Ru(\eta\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]H(O_2CCF_3)_2\cdot H_2O$, but the presence of four peaks due to C_6Me_6 in the region δ 2.0–2.3 shows that it is a mixture. The ^1H NMR spectrum shows a singlet hydride resonance at δ −11.3 that probably is due to the above-mentioned complex having structure IIc, but there are also less intense signals at δ −14.5 and −10.2 that may arise from bis(μ-hydrido) and mono(μ-hydrido) (μ-hydroxo) complexes. In agreement, the major hydride has peaks in the ^{19}F NMR spectrum at δ −74.5 and −75.9 relative to $CFCl_3$ assignable to bridging trifluoroacetate and $[H(O_2CCF_3)_2]^-$, respectively, but impurity peaks at δ −73.4 and −75.1 are also observed. The derived PF_6 salt also was not obtained pure, but, as expected, its ^{19}F NMR spectrum did not show the peak at δ −75.9. The IR spectra of both salts show an intense band at ca. 1680 cm^{-1} due to $\nu_{asym}(OCO)$ of bridging trifluoroacetate, and in the case of the $H(O_2CCF_3)_2$ salt there is an additional weak band at 1740 cm^{-1} that may arise from $\nu_{asym}(OCO)$ of the anion, cf. 1792 cm^{-1} (IR) and 1725 cm^{-1} (Raman) for $K[H(O_2CCF_3)_2]$.[23]

Reaction of $Ru(O_2CCF_3)_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$ with 2-propanol gives a complex that was not obtained analytically pure but showed a hydride resonance at δ −8.35 assignable to a (μ-hydrido) trifluoroacetato species.

We were unable to locate bands in the IR spectra of either the halo or carboxylato complexes that could be assigned with certainty to ν(Ru–H–Ru) although in some cases weak bands in the expected region (1100–1200 cm^{-1}) are observed. Attempts to prepare the corresponding deuterides by reaction of the bis(acetates) with 2-propanol-d_8 were unsuccessful.

Chloro and bromo carboxylato derivatives can also be used to generate new (μ-hydrido)(arene)ruthenium(II) complexes. When $Ru(O_2CMe)Cl(\eta$-arene) complexes are heated in 2-propanol for several hours, air-stable red solids of empirical formula $Ru_2H(O_2CMe)Cl_2(\eta\text{-arene})_2\cdot nH_2O$ (arene = C_6Me_6 or C_6H_4-1-Me-4-$CHMe_2$, n = 1; arene = 1,2,4,5-$C_6H_2Me_4$ or 1,3,5-$C_6H_3Me_3$, n = 2) are formed in 60–70% yield (eq 4). The bromo compounds made similarly from $Ru(O_2CMe)Br(\eta$-arene) and 2-propanol crystallize without water. Attempts to form a η-benzene complex of this class by heating $Ru(O_2CMe)Cl(\eta\text{-}C_6H_6)$ with 2-propanol gave only $\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$. When the chloro or bromo complexes are treated with NH_4PF_6, one of the halide groups is replaced to give $[Ru_2H(O_2CMe)Cl(\eta\text{-arene})_2]PF_6$. The IR spectra of all these compounds show bands due to $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ that are similar in position to those of the bis(acetato) hydrido complexes, and their ^1H NMR spectra show a singlet hydride resonance. In the case of the PF_6 salts, the hydride chemical shift varies from δ −10.2 (arene = C_6Me_6) to −6.7 (arene = C_6H_4-1-Me-4-$CHMe_2$). In the ^1H NMR spectrum of $[\{Ru(\eta\text{-}p\text{-cymene})\}_2H(O_2CMe)Cl]PF_6$ the isopropyl methyl protons appear as two doublets and the aromatic protons appear as two AB patterns. This behavior resembles that of the corresponding $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes discussed above and shows that the (arene)ruthenium(II) moiety is attached to three different groups, consistent with structure IId. The methyl protons of the durene complex also appear as a pair of equally intense singlets, as expected.

$$2Ru(O_2CMe)Cl(\eta\text{-arene}) + (CH_3)_2CHOH \rightarrow \{Ru(\eta\text{-arene})\}_2H(O_2CMe)Cl_2 + (CH_3)_2CO + MeCO_2H \quad (4)$$

The hydride chemical shifts of the parent complexes $\{Ru(\eta\text{-arene})\}_2H(O_2CMe)X_2$ (X = Cl, Br; arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$) are generally within 0.5 ppm of those of the derived halo PF_6 salts, whereas, as noted above, the hydride chemical shifts of the $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes are about 3 ppm to lower frequency

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than those of the derived PF_6 salts. The mesitylene complex $\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2$ is a 1:1 electrolyte in nitromethane, and the molecular weights of both this complex and its hexamethylbenzene analogue in nitromethane are approximately half the formula weight, as expected for complete ionization (eq 5).

$$\{Ru(\eta\text{-arene})\}_2H(O_2CMe)Cl_2 \rightarrow [\{Ru(\eta\text{-arene})\}_2H(O_2CMe)Cl]^+ + Cl^- \quad (5)$$

In dichloromethane, the molecular weights are about 80–90% of the formula weight, consistent either with partial dissociation of a neutral dimer or with extensive ion pairing. The compounds probably are best regarded as halide salts $[\{Ru(\eta\text{-arene})\}_2H(O_2CMe)X]X$ (X = Cl, Br), though the possibility of weak association of the halide ion with one of the ruthenium atoms in the solid state cannot be ruled out. Attempts are being made to grow X-ray quality single crystals of one of these compounds.

The ^1H NMR spectra of the *p*-cymene complexes $\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)X_2$ (X = Cl, Br) differ from those of the other members of the series in showing two hydride resonances and two acetate methyl resonances. In addition there are four isopropyl methyl doublets, two arene methyl singlets, and a set of overlapping peaks in the region δ 4.8–6.7 that can be dissected into four AB patterns due to the arene protons. We attribute these observations to the coexistence in solution of a neutral dimer Ib and a salt IIe formed by ionization of one of the terminal halide ligands. Consistent with this interpretation, the molar conductivity of the chloro compound in nitromethane is considerably less than that expected for a 1:1 electrolyte (Table III). Both species have three different groups bound to the (*p*-cymene)ruthenium unit, thus accounting for the NMR spectra. As expected, the hydride chemical shifts of the neutral dimers are in the region δ −10 to −11, similar to that of $\{Ru(\eta\text{-}p\text{-cymene})\}_2HCl_3$, and the hydride chemical shifts of the salts IIe are at δ −6 to −7, similar to those of $\{Ru(\eta\text{-}p\text{-cymene})\}_2H(O_2CMe)Cl]PF_6$ and $[\{Ru(\eta\text{-}p\text{-cymene})\}_2HCl_2]PF_6$. The proportions of the two species are solvent dependent, the relative intensities of the two hydride resonances of the bromo complex at δ −7.0 and −11.0 being about 1.3:1, 1.95:1, and 2.5:1 in $CDCl_3$, CD_3NO_2, and CD_3OD, respectively. Thus formation of the salt is favored in the more polar solvents, as expected.

The red-brown mono(μ-hydrido) trifluoroacetato complexes obtained in ca. 60% yield by heating $Ru(O_2CCF_3)Cl(\eta\text{-arene})$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$) with 2-propanol for 4 h crystallize as 1:1 adducts with trifluoroacetic acid $\{Ru(\eta\text{-arene})\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$. These show two ^{19}F NMR signals due to trifluoroacetate at δ −74.8 and −75.9 relative to $CFCl_3$ (Table V), hence the compounds are not simply hydrogenbis(trifluoroacetate) salts of the $[\{Ru(\eta\text{-arene})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]^+$ cations. We do not know whether they are neutral dimers, i.e., Ib with Y = O_2CCF_3, or chloride salts, i.e., IIf with X = Z = Cl and Y = O_2CCF_3, both containing trifluoroacetic acid of crystallization; the latter seems more likely. Treatment of $\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)Cl_2\cdot CF_3CO_2H$ with $NaPF_6$ gives a PF_6 salt that could not be obtained analytically pure but shows only one ^{19}F NMR signal due to trifluoroacetate at δ −74.8 (relative to $CFCl_3$). It is noteworthy that $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ or $Ru(O_2CMe)Cl(\eta\text{-}C_6Me_6)$ react with trifluoroacetic acid to give an adduct $Ru(O_2CCF_3)Cl(\eta\text{-}C_6Me_6)\cdot CF_3CO_2H$, which has been formulated tentatively as a salt, $[\{Ru(\eta\text{-}C_6Me_6)\}_2(\mu\text{-}O_2CCF_3)(\mu\text{-}Cl)_2]H(O_2CCF_3)_2$.[13] In the light of this work, a structure such as $[\{Ru(\eta\text{-}C_6Me_6)\}_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}Cl)]Cl\cdot CF_3CO_2H$ should also be considered.

Discussion

The dinuclear mono(μ-hydrido)(arene)ruthenium(II) complexes clearly resemble the corresponding (η-pentamethylcyclopentadienyl)rhodium(III) and -iridium(III) complexes, both in terms of structure and modes of formation. Both series show a propensity for forming a tris μ structure (II) from a bis μ structure (I) by loss of a terminal halide or carboxylate ligand. The tendency is most marked in the hydrides derived from $Ru(O_2CMe)_2(\eta\text{-arene})$, which all have a tris μ structure, and is least evident in those derived from $[RuCl_2(\eta\text{-arene})]_2$, with the halo carboxylato species being intermediate in behavior. The conductivities of the $\{Ru(\eta\text{-arene})\}_2HCl_3$ complexes in nitromethane and the balance between neutral bis μ and ionic tris μ structures in the $\{Ru(\eta\text{-arene})\}_2H(O_2CMe)X_2$ (X = Cl, Br) series provide clear evidence that saltlike tris μ structures are favored by increasing the degree of alkyl substitution on the arene. This is undoubtedly a reflection of the higher electron-donating ability of peralkylarenes combined with their greater steric bulk.[1]

Several observations suggest that (arene)ruthenium(II) complexes activate hydrogen less readily than do their (pentamethylcyclopentadienyl)rhodium(III) and -iridium(III) counterparts. Whereas $[RhCl_2(\eta\text{-}C_5Me_5)]_2$ is reported to react with hydrogen (1 atm) in the presence of triethylamine over a period of 1 h to give $\{Rh(\eta\text{-}C_5Me_5)\}_2HCl_3$,[2] the (arene)ruthenium(II) dichlorides react only very slowly and incompletely with hydrogen under the same conditions. Likewise, the bis(acetate) $Rh(O_2CMe)_2(\eta\text{-}C_5Me_5)$ reacts almost immediately, either with hydrogen (1 atm) or with 2-propanol on dissolution, to give $[\{Rh(\eta\text{-}C_5Me_5)\}_2H(O_2CMe)_2]H(O_2CMe)_2$, as shown by ^1H NMR spectroscopy.[2] In contrast, we find that several hours of heating is necessary to complete the reactions of $Ru(O_2CMe)_2(\eta\text{-arene})$ with 2-propanol. In these cases, there is a rapid color change from orange to red on heating, but this corresponds to the formation of only a very small amount of product, undetectable by ^1H NMR spectroscopy. Somewhat similar observations have been recorded for the reaction of $[\{Rh(\eta\text{-}C_5Me_5)\}_2(OH)_3]Cl$ with alcohols to form tri- and tetranuclear hydrido complexes.[5]

The reaction of $[RuCl_2(\eta\text{-arene})]_2$ with 2-propanol and base is not a satisfactory method for preparing the mono(μ-hydrido) complexes, except when arene = C_6Me_6. The reaction does not take place at room temperature, in contrast with the behavior of $[RhCl_2(\eta\text{-}C_5Me_5)]_2$.[2] On heating, a mixture of mono, bis and tris μ and other hydrido complexes is formed, and only when arene = C_6Me_6 can the reaction be controlled satisfactorily to give the mono(μ-hydrido) complex. Evidently the 2-propoxyruthenium(II) complexes that are the presumed precursors undergo β-elimination less readily than do the corresponding rhodium(III) compounds. This also follows from the fact that stable (arene)tris(μ-methoxy)- and tris(μ-ethoxy)ruthenium(II) complexes $[\{Ru(\eta\text{-arene})\}_2(OR)_3]BPh_4$ can be isolated,[24] whereas the analogous rhodium(III) and iridium(III) complexes are unknown.

The hydride chemical shifts of the mono(μ-hydrido)(arene)ruthenium(II) complexes remain essentially unchanged in good donor solvents such as acetonitrile and Me_2SO, indicating that these compounds, like their (pentamethylcyclopentadienyl)rhodium(III) and -iridium(III) counterparts, do not readily dissociate into mononuclear fragments. However, the complex $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$ reacts with triphenylphosphine on heating to give a mix-

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ture of $RuCl_2(\eta\text{-}C_6Me_6)(PPh_3)$ and $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$. Other reactions of this type with various dienes have been observed and will be reported in a later paper.

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Registry No. 1, 90720-51-7; 2, 90720-52-8; $\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_3$, 90720-53-9; $[\{Ru(\eta\text{-}C_6Me_6)\}_2HCl_2]PF_6$, 90720-55-1; $\{(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_3$, 90741-24-5; $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HCl_2]PF_6$, 90720-57-3; $\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2HBr_3$, 90720-58-4; $\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2HCl_3$, 90720-59-5; $\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_3$, 90720-60-8; $[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2HCl_2]PF6$, 90720-62-0; $\{Ru(\eta\text{-}C_6H_6)\}_2HCl_3$, 90720-63-1; $[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)_2]H(O_2CCF_3)_2$, 90741-25-6; $[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CCF_3)_2]PF_6$, 90720-65-3; $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6HzMe_4)\}_2H(O_2CMe)_2]H(O_2CMe)_2$, 90720-67-5; $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]PF_6$, 90720-68-6; $[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]PF6$, 90720-70-0; $[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)_2]PF_6$, 90720-72-2; $[\{Ru(\eta\text{-}C_6H_6)\}_2H(O_2CMe)_2]PF_6$, 90720-74-4; $\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl_2$, 90720-75-5; $[\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Cl]PF_6$, 90720-77-7; $\{Ru(\eta\text{-}C_6Me_6)\}_2H(O_2CMe)Br,2$, 90720-78-8; $\{Ru(\eta\text{-}C_6Me_6)\}_iH(O_2CCF_3)Cl_2{\cdot}CF_3CO_2H$, 90720-79-9; $\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl_2$, 90720-80-2; $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Cl]PF_6$, 90720-82-4; $\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)Br_i$, 90720-83-5; $\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl_2$, 90720-84-6; $[\{(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Cl]PF_6$, 90720-86-8; $\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)Br_2$, 90720-87-9; $\{Ru(\eta\text{-}1,3,5\text{-}H_3Me)\},2H(O_2CCF_3)Cl_2{\cdot}CF_3CO_2H$, 90720-88-0; $\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)Cl_2$, 90720-89-1; $[\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\},2H(O_2CMe)Cl]PF_6$, 90720-91-5; $\{Ru(\eta\text{-}C_6M_6)\}_2HBr_3$, 90720-92-6; $\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2HBr_3$, 90720-93-7; $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2H(O_2CMe)_2]H(O_2CMe)_2$, 90720-94-8; $[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2H(O_2CMe)_2]H(O_2CMe)_2$, 90720-95-9; $[\{Ru(\eta\text{-}C_lH_4\text{-}1\text{-}Me\text{-}4\text{-}ChMe_2)\}_2H(O_2CMe)_2]H(O_2CMe)_2$, 90720-96-0; $[\{Ru(\eta\text{-}C_6Me_6)\}_iH(O[2CCF_3)Cl]PF_6$, 90720-98-2; $\{Ru(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)\}_2H(O_2CMe)Br_2$, 90720-99-3; $[\{Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)\}_2(\mu\text{-}H)(\mu\text{-}O_iCCF_o)_2]H(O_2CCF_3)_2$, 90721-02-1; $RuHCl(\eta\text{-}C_6Me_6)(PPh_3)$, 75182-14-8; $RuCl_2(\eta\text{-}C_6Me_6)(PPh_3)$, 82498-46-2; $[RuCl(\eta\text{-}C_6Me_6)]_2$, 67421-02-7; $[RuCl_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$, 52462-31-4; $[RuCl_2(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$, 90721-03-2; $[RuCl_2(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)]_2$, 52462-29-0; $[RuCl_2(\eta\text{-}C_6H_6)]_2$, 37366-09-9; $[RuBr_2(\eta\text{-}C_6Me_6)]_2$, 90721-04-3; $[RuBr_2(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$, 88666-26-6; $[RuBr_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$, 90721-05-4; $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)$, 81062-49-9; $Ru(O_2CMe)_2(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)$, 90721-06-5; $Ru(O_2CMe)_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$, 90721-07-6; $Ru(O_2CMe)_2(\eta_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)$, 90721-08-7; $Ru(O_2CMe)_2(\eta\text{-}C_6H_6)$, 90721-09-8; $Ru(O_2CCF_3)_2(\eta\text{-}C_6Me_6)$, 90721-10-1; $Ru(O_2CCF_3)_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$, 90721-11-2; $Ru(O_2CMe)Cl(\eta\text{-}1,3,5\text{-}C_{H3}Me_o)$, 90721-12-3; $Ru(O_2CMe)Cl(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)$, 90721-13-4; $Ru(O_2CMe)Cl(\eta\text{-}C_6Me_6)$, 90721-14-5; $Ru(O_2CM))Cl(\eta\text{-}C_6H_4\text{-}1\text{-}Me\text{-}4\text{-}CHMe_2)$, 90721-15-6; $Ru(O_2CMe)Cl(\eta\text{-}C_6H_6)$, 90721-16-7.

Electrochemical Investigation of a Series of Organotriruthenium Clusters

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The reduction and oxidation behavior of a series of organotriruthenium clusters, namely, $HRu_3(CO)_9(\mu_3\text{-allenyl})$, $HRu_3(CO)_9(\mu_3\text{-allyl})$, and $HRu_3(CO)_9$ (μ_3-alkynyl) complexes, is investigated by voltammetric techniques at mercury and platinum microelectrodes. The relationships between the resulting electrode potentials and both ^{13}C NMR chemical shifts and $\nu(CO)$ frequencies are presented.

Introduction

The reactivity of carbonylmetal clusters with unsaturated hydrocarbons has been widely investigated, and a number of derivatives in which the organic substrate interacts with several metallic centers have been characterized.[1] Their interesting bonding features gave noticeable support to the view that organometal clusters can serve as useful models of chemisorbed molecules on a metallic surface.[2] In particular the triangular cluster $Ru_3(CO)_{12}$ reacts with alkynes[3] to afford three main types of organometallic complexes: $HRu_3(CO)_9(RC{=}C{=}CR'R'')$[4] (I), $HRu_3(CO)_9(RC{\cdots}CR'{\cdots}CR'')$[5] (II), and $HRu_3(CO)_9(C{\equiv}C{-}R)$[6] (III) (see Figure 1). Although their chemical reactivity has been investigated,[3] no report has been concerned with their redox behavior. The electrochemistry of carbonylmetal clusters is a matter of increasing interest,[7-13] since the redox properties should

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