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Preparation and spectroscopic characterization of (η^6-arene)-ruthenium(II) trifluoromethylsulfonates and of dinuclear di-μ- and tri-μ-hydrido (η^6-arene)ruthenium(II) complexes. Homogeneous hydrogenation of cyclohexene and 1-hexene catalysed by various (η^6-arene)ruthenium(II) complexes

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Abstract

Treatment of the hexamethylbenzene complex $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ in benzene or toluene with H_2 (50 bar) at 50 °C gives the dinuclear di-μ-hydrido cation $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]^+$ (**1**), which can be isolated as its red–violet PF_6 salt. The analogous mesitylene complex is obtained similarly, whereas under similar conditions the durene complex $Ru(O_2CMe)_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)$ gives the di-μ-hydrido complex in admixture with the mono-μ-hydrido complex $[\{Ru(\eta^6\text{-}C_6H_2Me_4\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$. The tri-$\mu$-hydrido complexes $[\{Ru(\eta^6\text{-}arene)\}_2(\mu\text{-}H)_3]CF_3SO_3$ (arene $= C_6Me_6$ (**2a**), $1,2,4,5\text{-}C_6H_2Me_4$ (**3a**)) are obtained by reaction of the (η^6-arene)-ruthenium(II) triflates $Ru(OSO_2CF_3)_2(\eta^6\text{-}arene)\cdot 2H_2O$ with 2-propanol and anhydrous Na_2CO_3, and can be converted into the corresponding PF_6 salts **2b**, **3b** by treatment with $NaPF_6$. The hydroxo complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}OH)_3]Cl\cdot 4H_2O$ reacts with 2-propanol to give $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]Cl\cdot 4H_2O$ (**2c**). The monomeric complexes $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)$ and $RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$ in various solvents at 50 °C/1 bar H_2 catalyse hydrogenation of cyclohexene to cyclohexane and 1-hexene to hexane much more effectively than the derived dinuclear μ-hydrido complexes. For $Ru(O_2CMe)_2(\eta^6\text{-}arene)$, the turnover numbers decrease in the order arene $= C_6Me_6 > 1,3,5\text{-}C_6H_3Me_3 > C_6H_6$ and solvent = 2-propanol > ethanol > benzene. It is suggested that monomeric, coordinatively unsaturated hydrido species such as $RuH(O_2CMe)(\eta^6\text{-}arene)$ and $RuH_2(\eta^6\text{-}arene)$ are involved both in catalysis of hydrogenation and in the formation of the dinuclear hydrides. In the case of 1-hexene there is competing isomerization to give predominantly *cis*-2-hexene; for this process $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$ is a better catalyst than $Ru(O_2\text{-}CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$.

Introduction

In an earlier paper [1] we reported the synthesis of a range of mono-μ-hydrido η^6-arene complexes of ruthenium(II) containing bridging halide or carboxylate groups by the reactions summarized in Scheme 1. We have been interested in extending this work to the preparation of the corresponding di- and tri-μ-hydrido compounds, especially because a reported synthesis of a di-μ-hydrido complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}Cl]Cl$ from the reaction of $[\{RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with 2-propanol and anhydrous sodium carbonate [2] has proved to be irreproducible [3]. It was thought that the presence of trifluoromethylsulfonate (triflate, CF_3SO_3), which is a better leaving group than either acetate or trifluoroacetate [4], might promote the formation of di- or tri-μ-hydrides in this series. Here we describe the preparation of arene ruthenium(II) triflates, the synthesis of arene ruthenium(II) di- and tri-μ-hydrido complexes from these and other precursors, and a preliminary investigation of the ability of various arene ruthenium(II) complexes to catalyse the hydrogenation of olefins. After our work was complete, reports dealing with closely related hydrido complexes of *p*-cymene- and mesitylene-osmium(II) appeared [5–8].

Experimental

All reactions were carried out in an atmosphere of argon or nitrogen with use of standard Schlenk techniques. Benzene and toluene were distilled from sodium benzophenone ketyl; dichloromethane and 2-propanol were distilled from calcium hydride. Cyclohexene and 1-hexene were passed through a column of neutral alumina.

Proton NMR measurements were made on Varian HA-100 (100 MHz, 30 °C), Jeol PMX60 (60 MHz, 25 °C) and Jeol FX 200 (200 MHz, 20 °C) spectrometers.

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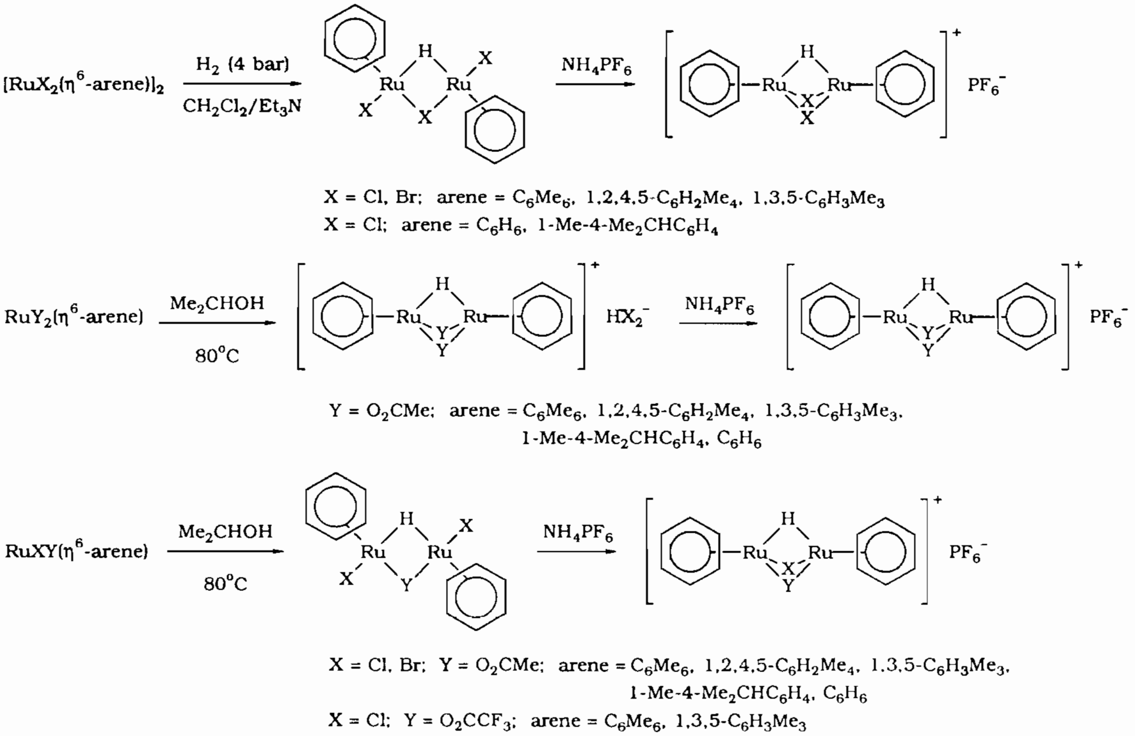


X = Cl, Br; arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$
X = Cl; arene = C_6H_6, 1-Me-4-$Me_2CHC_6H_4$

Y = O_2CMe; arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$,
1-Me-4-$Me_2CHC_6H_4$, C_6H_6

X = Cl, Br; Y = O_2CMe; arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$,
1-Me-4-$Me_2CHC_6H_4$, C_6H_6
X = Cl; Y = O_2CCF_3; arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$

Scheme 1.

TABLE 1. Analytical, selected IR and ^1H NMR data for (η^6-arene)ruthenium(II) triflates

	Analysis[a] (%)			IR (cm^{-1})[b, c]	^1H NMR (δ)[d]
	C	H	F		
$Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6Me_6)\cdot 2H_2O$	28.2(28.1)	4.0(3.7)	19.1(19.1)	3550–3050(vs, br), 1662(s, br) (H_2O) 1396(s, sp), 1320(s, sh), 1260(vs), 1235(vs), 1175(vs), 1163(vs), 1030(vs) (CF_3SO_3)	6.40 (H_2O) 2.18 (C_6Me_6)
$Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6H_2Me_4)\cdot 2H_2O$	24.8(25.3)	3.0(3.2)	19.6(20.0)	3550–3050(vs, br), 1655(m, br) (H_2O) 1391(s), 1310(s), 1252(s), 1228(s), 1168(s), 1042(s) (CF_3SO_3)	5.72 ($C_6\mathit{H}_2Me_4$), 2.16 ($C_6H_2\mathit{Me}_4$)[e]
$Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6H_3Me_3)\cdot 2H_2O$[f]				3300(vs, br), 1672(m, br) (H_2O) 1390(s, sp), 1270(s, br), 1228(s), 1166(vs), 1040–1020(s, br) (CF_3SO_3)	5.19 ($C_6\mathit{H}_3Me_3$), 2.21 ($C_6H_3\mathit{Me}_3$)[e]
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}Cl)_3]CF_3SO_3$	37.6(38.4)	4.5(4.6)	7.1(7.3)[g]	1382(w), 1275(s, sp), 1262(s, sp) 1222(w, sp), 1148(m, sp), 1135(m, sp) 1032(s, sp)	2.09 (C_6Me_6)

[a] Calculated values in parentheses. [b] Measured as Nujol and HCBD mulls. [c] Abbreviations: v = very, s = strong, m = medium, w = weak, sp = sharp, sh = shoulder, br = broad. [d] Measured in CD_2Cl_2. [e] Peak due to H_2O could not be located. [f] Not obtained analytically pure. [g] Cl: found, 14.9; calc., 13.6%.

IR spectra in the range 4000–250 cm^{-1} were measured on a Perkin-Elmer PE 683 instrument. Microanalyses were carried out in the Microanalytical Unit of the Research School of Chemistry and are collected in Tables 1 and 2. For several of the hydrido complexes, the agreement between calculated and found values for %C and %H is outside normally accepted limits. This problem also occurred with some of the mono-μ-hydrido complexes [1]. The spectroscopic data, however, leave little doubt about the formulations. Selected ^1H NMR and IR data for the triflate and hydrido complexes are in Tables 1 and 3, respectively.

TABLE 2. Analytical data for salts of (η^6-arene)ruthenium(II) hydrido cations[a]

Complex	C (%)	H (%)	Other (%)
$[Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$ (**1**)	42.5 (42.6)	5.8 (5.6)	4.0 (4.2) (P)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]CF_3SO_3$ (**2a**)	43.8 (44.2)	5.8 (5.8)	8.3 (8.4) (F)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]PF_6$ (**2b**)	41.5 (42.7)	5.7 (5.8)	4.7 (4.6) (P)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]Cl\cdot 4H_2O$ (**2c**)	43.0 (45.5)	6.15 (6.8)	5.6 (5.6) (Cl) 10.4 (10.1) (O)
$[\{Ru(\eta^6\text{-}C_6H_2Me_4)\}_2(\mu\text{-}H)_3]CF_3SO_3$ (**3a**)	39.8 (40.5)	5.0 (5.0)	8.4 (9.15) (F)
$[\{Ru(\eta^6\text{-}C_6H_2Me_4)\}_2(\mu\text{-}H)_3]PF_6$ (**3b**)	36.2 (38.8)	5.3 (5.05)	5.0 (5.0) (P)

[a]Calculated values in parentheses.

TABLE 3. Selected spectroscopic (^{1}H NMR, IR) data for cationic (η^6-arene)ruthenium(II) di-μ-hydrides and tri-μ-hydrides

Complex	^{1}H NMR			IR (cm^{-1})[a, b]	
	Solvent	δ_H	δ(arene)	ν(Ru–H–Ru)	Other bands
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$ (**1**)	CD_3OD	−14.44	2.28 (C_6Me_6)[c]	1190(s, br)	1550(m), 1445(s), 1388(s) (OCO), 837(vs), 555(s, sp) (PF_6)
$[\{Ru(\eta^6\text{-}C_6H_3Me_3)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$	acetone-d_6	−13.94	5.74 ($C_6\mathit{H}_3Me_3$), 2.44 ($C_6H_3\mathit{Me}_3$)	1218(s)	1558(m), 1525(s), 1440(vs), 1380(m)(OCO), 838(vs), 560(s, sp) (PF_6)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]CF_3SO_3$ (**2a**)	CD_2Cl_2	−16.09	2.30 (C_6Me_6)	1160(m)[d]	1450(m, br), 1390(m), 1270(vs), 1138(s, sp) (CF_3SO_3)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]PF_6$ (**2b**)	CD_2Cl_2	−16.09	2.31 (C_6Me_6)	1160(w, br)	837(s, sp), 556(s, sp) (PF_6)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]Cl\cdot 4H_2O$ (**2c**)	CD_2Cl_2	−15.92	2.30 (C_6Me_6)	[e]	3600–3100(s, br), 1630(m)(H_2O)
$[\{Ru(\eta^6\text{-}C_6H_2Me_4)\}_2(\mu\text{-}H)_3]CF_3SO_3$ (**3a**)	CD_2Cl_2	−15.57	5.60 ($C_6\mathit{H}_2Me_4$), 2.24 ($C_6H_2\mathit{Me}_4$)	1140(vs)[d]	1455(s, br), 1382(m), 1372(m), 1273(vs), 1220(m, sp), (CF_3SO_3)
$[\{Ru(\eta^6\text{-}C_6H_2Me_4)\}_2(\mu\text{-}H)_3]PF_6$ (**3b**)	CD_2Cl_2	−15.57	5.59 ($C_6\mathit{H}_2Me_4$), 2.24 ($C_6H_2\mathit{Me}_4$)	1160(m, br)	836(vs), 555(s, sp) (PF_6)

[a]Measured as Nujol and HCBD mulls. [b]Abbreviation: v = very, s = strong, m = medium, w = weak, sp = sharp, sh = shoulder, br = broad. [c]$\delta(O_2CMe)$ 2.12. [d]Overlaps band due to CF_3SO_3. [e]Could not be observed.

Hydrogenations under pressures of 1–5 bar were performed in a Fisher–Porter vessel, equipped with a magnetic stirrer, which could be heated in an oil-bath. Preparative reactions with ruthenium complexes in the pressure range 50–70 bar were done in a Berghof Laboratory Autoclave of 250 ml volume, having a Teflon lining and magnetic stirrer, in a thermostatically controlled heating mantle. Organic hydrogenation or isomerization products were identified by GLC on a Varian Aerograph series 1700 instrument with use of the following 4 m×3 mm columns: 20% Carbowax on Chromsorb W, 60–80 mesh, for cyclohexene/cyclohexane; 17% BMEA [bis(2-methoxyethyl)adipate] on Chromsorb P-AW, 60–80 mesh, for 1-hexene, 2-hexene and hexane.

Starting materials

The precursor arene ruthenium(II) halides [9–11], carboxylates [12] and hydroxides [13] were made by the appropriate literature procedures. Silver trifluoromethanesulfonate (triflate) was freshly prepared by adding triflic acid dropwise to a rapidly stirred slurry of silver carbonate in water or ether until the solution became clear and effervescence ceased. After being filtered through Celite, the solution was evaporated under reduced pressure on a steam bath to a white paste. Recrystallization from ether/CCl_4 gave silver triflate almost quantitatively as an off-white, extremely hygroscopic solid.

Preparations

Bis(trifluoromethylsulfonato)(η^6-hexamethylbenzene)ruthenium(II) dihydrate, $Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6Me_6)\cdot 2H_2O$

A suspension of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (167 mg, 0.25 mmol) in dichloromethane (50 ml) was stirred with anhydrous silver triflate (300 mg, 1.17 mmol) at room temperature. Within 15 min a gummy grey–green solid (impure AgCl) and a light orange solution had formed. After 24 h, the mixture was centrifuged, the supernatant liquid was evaporated to dryness in a vacuum, and the residue was stirred with ether (30 ml) for 5 min. The mixture was centrifuged again and the ether layer was discarded. The residue was recrystallized from dichloromethane (3 ml) and hexane (20 ml) to give orange, very hygroscopic microcrystals of the product (180 mg, *c.* 60%).

The durene complex was prepared similarly in 54% yield. Similar treatment of the mesitylene complex $[RuCl_2(\eta^6\text{-}C_6H_3Me_3)]_2$ with silver triflate gave the corresponding triflate complex as an impure, oily solid that was identified by IR and ^1H NMR spectroscopy.

Tri-μ-chlorobis(η⁶-hexamethylbenzene)diruthenium(II) triflate, $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6Me_6)_2]CF_3SO_3$

A suspension of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (167 mg, 0.25 mmol) in dichloromethane (45 ml) was stirred with sodium triflate (172 mg, 1 mmol) for 24 h at room temperature. The orange solution obtained after centrifugation was evaporated to dryness in a vacuum to give an orange solid. Work-up as described above gave the complex as yellow–orange microcrystals (165 mg, 85%) that were not hygroscopic.

μ-Acetato-di-μ-hydridobis(η⁶-hexamethylbenzene)diruthenium(II) hexafluorophosphate, $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$ *(1)*

An orange–yellow solution of $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ (200 mg, 0.50 mmol) in benzene (60 ml) was stirred under hydrogen (60 bar) for 40 h. The resulting dark red–violet solution was evaporated to dryness in a vacuum. The residue was dissolved in acetone (45 ml) and $NaPF_6$ (200 mg, 1.2 mmol) was added. The mixture was stirred for 1.5 h and acetone was pumped off. The residue was extracted with water (50 ml) to remove the excess of $NaPF_6$, centrifuged, and the aqueous extract discarded. The resulting oily solid was dried in a vacuum and recrystallized from methanol/ether to give small, dark red–violet needles of the product (**1**) (104 mg, 55%).

The mesitylene analogue was made similarly, but could not be obtained in a state of analytical purity.

Tri-μ-hydridobis(η⁶-hexamethylbenzene)diruthenium(II) triflate, $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]CF_3SO_3$ *(2a)*

A solution of $Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6Me_6)\cdot 2H_2O$ (70 mg, 0.16 mmol) in 2-propanol (35 ml) was treated with Na_2CO_3 (100 mg, 0.94 mmol) and the mixture was stirred at 70 °C for 4 h. The colour changed from orange to deep red–brown within 15 min. The solvent was pumped off and the residue was dissolved in dichloromethane. After centrifugation, the solvent was evaporated in a vacuum to leave a red–brown oil. Trituration with ether gave **2a** as light brown microcrystals (34 mg, 65%).

The durene analogue (**3a**) was made similarly in 62% yield.

Tri-μ-hydridobis(η⁶-hexamethylbenzene)diruthenium(II) hexafluorophosphate, $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]PF_6$ *(2b)*

A solution of **2a** (20 mg, 0.03 mmol) in acetone (20 ml) was stirred with $NaPF_6$ (60 mg, 0.36 mmol) for 1.5 h at room temperature. Solvent was removed from the red–brown mixture under reduced pressure and the residue was taken up in dichloromethane (20 ml). The extract was centrifuged and the volume of the solution was reduced to *c.* 4 ml in a vacuum. Addition of hexane (10 ml) gave **2b** as light brown microcrystals (15 mg, 77%).

The durene analogue was prepared similarly in *c.* 75% yield.

Tri-μ-hydridobis(η⁶-hexamethylbenzene)diruthenium(II) chloride tetrahydrate, $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]Cl\cdot 4H_2O$ *(2c)*

A yellow–green suspension of $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}OH)_3Cl\cdot 4H_2O$ (80 mg, 1.17 mmol) in 2-propanol (30 ml) was stirred at 65 °C for 2 h. The dark red–brown solution was evaporated to dryness under reduced pressure to give a dark, oily solid. Recrystallization from ether/hexane gave the dark brown, water-soluble **2c** (38 mg, 52%).

Catalytic hydrogenation

A typical procedure was as follows. To $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ (20 mg, 0.05 mmol) in a Fisher–Porter vessel under argon was added 2-propanol (15 ml) and cyclohexene (10 ml). The vessel was immersed in an oil-bath at 50 °C. After 5 min, the vessel was flushed with hydrogen and the pressure was adjusted to 1 bar. The solution was stirred vigorously during the reaction. At the end of the run, solvents were removed in a vacuum and collected in a dry-ice trap for GC analysis. The residue was examined by ^1H NMR spectroscopy.

Results

Arene ruthenium(II) triflates

Treatment of $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$) with an excess of silver triflate in dichloromethane at room temperature for 24 h gave hygroscopic, pale orange solids of empirical formula $Ru(OSO_2CF_3)_2(\eta^6\text{-arene})\cdot 2H_2O$. The mesitylene complex was obtained similarly as an oily solid that could not be purified. The ^1H NMR spectra of all three complexes show singlet resonances characteristic of the coordinated arene and a peak of δ 6.40 due to water. The presence of water is also evident from the appearance of broad IR absorptions at *c.* 3300 and *c.*

1640 cm^{-1}. The IR spectra of the C_6Me_6 and 1,2,4,5-$C_6H_2Me_4$ complexes show a strong band at 1260 cm^{-1} that appears to be characteristic of ionic triflate, although it is not clear whether it is due to a C–F or a S=O stretching frequency [4]. All three compounds show a pair of strong bands at *c.* 1390 and 1320 cm^{-1} assignable to ν(S=O) of coordinated triflate, but it is not possible to say whether the triflate is bridging or monodentate. There are many plausible formulations, both monomeric and dimeric, for these complexes; in the absence of definitive structural information, we shall refer to them as $Ru(OSO_2CF_3)_2(\eta^6\text{-arene})$.

Two alternative approaches to arene ruthenium(II) triflates were investigated, without success. Treatment of the bis(acetato) complex, $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)\cdot H_2O$ with triflic acid and subsequent removal of the excess of acid gave a red–brown oil that could not be recrystallized from ether or dichloromethane. Addition of benzene precipitated a white solid, which was identified as $[Ru(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_6H_6)]CF_3SO_3$ on the basis of its ^{1}H NMR spectrum in DMSO-d_6, which showed singlets at δ 2.48 (C_6Me_6) and 6.76 (C_6H_6) in a 3:1 intensity ratio, cf. $[Ru(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_6H_6)](BF_4)_2$ in DMSO-d_6: δ 2.45 (C_6Me_6), 6.70 (C_6H_6) [14]. The presence of free triflic acid is necessary for this reaction to proceed, because $Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6Me_6)$ alone does not react with benzene. Salts of $[M(\eta\text{-}C_5Me_5)(\eta^6\text{-arene})]^{2+}$ (M = Rh, Ir) have been made similarly from $M(\eta\text{-}C_5Me_5)(O_2CCF_3)_2\cdot H_2O$ and the arene in the presence of trifluoroacetic acid [15]. Treatment of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of sodium triflate in dichloromethane gave the triflate salt of $[Ru_2Cl_3(\eta^6\text{-}C_6Me_6)_2]^+$ [16], whose IR spectrum showed strong bands at 1275 and 1262 cm^{-1} characteristic of $[CF_3SO_3]^-$. In contrast, sodium acetate reacts with $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ to give monomeric $RuCl(O_2CMe)(\eta\text{-}C_6Me_6)$ [12].

Di-μ-hydrido arene ruthenium(II) complexes

The yellow–orange bis(acetato) complex $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ in benzene reacts with hydrogen (60 bar) at 50 °C over a period of 40 h to give, after removal of solvent, a violet–red oil. On treatment with $NaPF_6$, this forms the microcrystalline salt of the di-μ-hydrido cation, $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$ (**1**) in *c.* 50% yield. The oil probably contains the hydrogen bis(acetate) salt (eqn. (1)), but it was not characterized.

$$2Ru(O_2CMe)_2(\eta^6\text{-arene}) + 2H_2 \longrightarrow [\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]H(O_2CMe)_2 + MeCO_2H \qquad (1)$$

The reaction can be carried out at lower hydrogen pressure, e.g. 3–5 bar in benzene at 65 °C, although the isolated product is less pure. The corresponding dideuteride (**1a**) was prepared in this way, with use of deuterium gas (4 bar). The mono-μ-hydrido complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2$ can also be converted into **1** in benzene at 70 °C/3 bar H_2 (eqn. (2)), but the reaction is slower than that of eqn. (1)

$$[\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2 + H_2 \longrightarrow [\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]H(O_2CMe)_2 + MeCO_2H \qquad (2)$$

The spectroscopic data for **1** are consistent with the dinuclear structure **I** similar to that established by X-ray crystallography for the rhodium(III) complex $[\{Rh(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$ [17]. The ^{1}H NMR spectrum shows a singlet due to Ru–*H* at $\delta - 14.4$, i.e. about 3 ppm more shielded than the corresponding resonance in the mono-μ-hydride $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]PF_6$ [1]; the ^{2}H NMR spectrum of **1a** also contains a singlet due to Ru–*D* at $\delta - 14.4$. A similar difference in hydride chemical shifts between mono- and di-μ-hydrides is also evident in analogous $Rh(\eta^5\text{-}C_5Me_5)$ and $Ir(\eta^5\text{-}C_5Me_5)$ complexes [18]. There are also singlets at δ 2.28 and 2.12 due to C_6Me_6 and O_2CMe, respectively. The IR spectrum of **1** contains a band at 1550 cm^{-1} due to ν_{asym} (OCO) and a pair of bands at 1445 and 1388 cm^{-1} due to ν_{sym} (OCO). The derived value of $\Delta\nu(\nu_{asym} - \nu_{sym})$, 105–162 cm^{-1}, is consistent with the presence of bridging acetate. There is also a strong, broad absorption centred at *c.* 1190 cm^{-1} that is absent from the spectrum of **1a** and can, therefore, be assigned to ν(Ru–H–Ru). The corresponding ν(Ru–D–Ru) band could not be located with certainty in the spectrum of **1a**; it is probably partly masked by the strong band due to PF_6^- at *c.* 835 cm^{-1}.

Reactions of other $Ru(O_2CMe)_2(\eta^6\text{-arene})$ complexes in benzene with hydrogen (50 bar) at 50 °C were also investigated. The benzene complex underwent decomposition, but the mesitylene complex gave an oil which afforded a violet solid on treatment with $NaPF_6$. Although it could not be isolated analytically pure, its ^{1}H NMR and IR spectroscopic parameters [δ(Ru*H*), ν(Ru–H–Ru)] are similar to those of **1** and suggest that it is the corresponding mesitylene complex $[\{Ru(\eta^6\text{-}C_6H_3Me_3)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$. The durene complex $Ru(O_2CMe)_2(\eta^6\text{-}C_6H_2Me_4)\cdot H_2O$ gave a 2:1 mixture of mono- and di-μ-hydrido complexes that showed ^{1}H NMR hydride singlets at $\delta - 9.69$ and -13.98. Reaction of the bis(trifluoroacetate), $Ru(O_2CCF_3)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$, in benzene with hydrogen (5 bar) for 22 h also gave a di-μ-hydride, as judged by its hydride chemical shift, but this product also could not be obtained analytically pure.

The chloro(acetato) complex $RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$ also reacts with hydrogen (3 bar) in benzene to give a di-μ-hydrido complex, probably **1**, as the main product [δ(Ru–H) (CD_2Cl_2) −14.4], but some of the mono-μ-hydrido complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}Cl)]Cl \cdot H_2O$ [1] is also present.

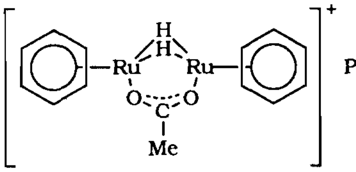
It is of interest that the di-μ-hydride **1** is only obtained exclusively under the conditions described above when benzene or toluene is used as solvent, and that no replacement of C_6Me_6 by these aromatic compounds is observed in the final product. In addition, significant amounts (5–10%) of cyclohexane or methylcyclohexane can be detected in the recovered solvents. Reaction of $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6) \cdot H_2O$ with hydrogen (3 bar) in 2-propanol at 65 °C in the presence of anhydrous Na_2CO_3 gave a mixture of mono- and di-μ-hydrido complexes in which the former predominated. A similar mixture resulted with use of dichloromethane at 40 °C for 2 days. The bis(acetate) appeared not to react with hydrogen (3 bar) in methanol over a period of 18 h at 55 °C, even in the presence of triethylamine, perhaps owing to the formation of the stable dinuclear cation $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}OMe)_3]^+$ [13]. In contrast, treatment of the bis(acetate) with hydrogen (3 bar) in THF caused the solution to darken rapidly, but no characterizable product could be isolated.

Tri-μ-hydrido arene ruthenium(II) complexes

Reaction of the hexamethylbenzene or durene complexes $Ru(OSO_2CF_3)_2(\eta^6\text{-arene}) \cdot 2H_2O$ with 2-propanol and anhydrous Na_2CO_3 at 70 °C for 3 h gives the brown tri-μ-hydrido triflate salts $[\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_3]CF_3SO_3$ (arene = C_6Me_6 (**2a**); 1,2,4,5-$C_6H_2Me_4$ (**3a**)) in *c.* 60% yield (eqn. (3)).

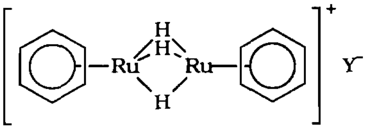
$$2Ru(OSO_2CF_3)_2(\eta^6\text{-arene}) + 3Me_2CHOH \longrightarrow [\{Ru(\eta^6\text{-arene})\}(\mu\text{-}H)_3]CF_3SO_3 + 3CF_3SO_3H + 3Me_2CO + 2H_2O \quad (3)$$

In the absence of Na_2CO_3, there is no reaction, in contrast to the behaviour of the corresponding bis(acetato) and chloro(acetato) complexes [1]. The mesitylene complex $Ru(OSO_2CF_3)_2(\eta^6\text{-}C_6H_3Me_3)$, prepared in crude form as described above, reacted with 2-propanol and Na_2CO_3 to give a mixture of hydrides, which was not investigated further. The corresponding PF_6 salts, $[\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_3]PF_6$ (arene = C_6Me_6 (**2b**), $C_6H_2Me_4$ (**3b**)) are obtained by addition of $NaPF_6$ to the triflate salts dissolved in acetone, removal of solvent, and extraction of the products with dichloromethane. The tri-μ-hydroxo complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}OH)_3]Cl \cdot 4H_2O$ reacts with 2-propanol at 65 °C for 2 h to give the corresponding tri-μ-hydrido complex as its brown–purple chloride salt $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]Cl \cdot 4H_2O$ (**2c**) in *c.* 50% yield; a similar procedure has been used to make $[\{Os(\eta^6\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)\}_2(\mu\text{-}H)_3]PF_6$ from the tri-μ-hydroxo *p*-cymene osmium PF_6 salt [7].



I

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



II

arene = C_6Me_6; Y = CF_3SO_3 (**2a**), PF_6 (**2b**), $Cl^- . 4H_2O$ (**2c**)

arene = 1,2,4,5-$C_6H_2Me_4$; Y = CF_3SO_3 (**3a**), PF_6 (**3b**)

The tri-μ-hydrido triflate and PF_6 salts are air-stable solids that are readily soluble in dichloromethane, acetone and methanol, and sparingly soluble in ether and water. In contrast, the chloride salt **2c** is also soluble in the last two solvents. The structure of the cation, **II**, is assigned on the basis of spectroscopic evidence and by analogy with the structure of the iso-electronic cation $[\{Ir(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}H)_3]^+$, whose BF_4 and ClO_4 salts have been structurally characterized by X-ray crystallography [19]; the ClO_4 salt has also been studied by neutron diffraction [20]. The hydride resonance in the ^1H NMR spectra of all the $[\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_3]^+$ salts appears as a singlet at δ *c.* −16.0, i.e. about 1.5–2.0 ppm more shielded than that in the di-μ-hydrides. The chemical shift is essentially independent of the counter-anion, whereas the hydride resonance of $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2HCl_3$ in *c.* 2.5 ppm more shielded than that of $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2HCl_2]PF_6$ [1]. This difference evidently arises because the chloride counter-anion in **2c** is unable to enter the coordination sphere by displacement of one of the bridging hydride ligands. The IR spectra of **2b** and **3b** show a weak to medium band at 1160 cm^{-1} assignable to ν(Ru–H–Ru), but in **2a** and **3a** this absorption is masked by triflate absorptions.

The tetraphenylborate salts $[\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}OH)_3]BPh_4$ (arene = 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$, 1-Me-4-$Me_2CHC_6H_4$) also react with refluxing 2-propanol, but more slowly than does the chloride salt

$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}OH)_3]Cl\cdot 4H_2O$. The crude durene and mesitylene products each show a single hydride resonance at $\delta -15.45$ and -15.28, respectively, attributable to the corresponding tri-μ-hydride cations. The *p*-cymene product shows hydride resonances at $\delta -15.19$ and -13.58, which suggests that it is a mixture of tri-μ- and di-μ-hydrido species. The nature of the hydrides formed in these reactions evidently depends on the arene, the counter-anion, and the reaction time. Maitlis and co-workers [6] have shown that $[\{Ru(\eta^6\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)\}_2(\mu\text{-}OH)_3]PF_6$ reacts with 2-propanol at 80 °C over 4 days to give a tetranuclear species $[\{Ru(\eta^6\text{-}1\text{-}Me\text{-}4\text{-}Me_2CHC_6H_4)\}_4(\mu\text{-}H)_4](PF_6)_2$.

Attempts to selectively cleave one of the Ru–H–Ru bonds in the tri-μ-hydrido cation to give $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}Cl)]Cl$ failed. Treatment of **2a** with aqueous HCl (2 mol per mol of dimer) in acetone at 60 °C for 2.5 h caused a colour change from deep red–brown to violet–red. The ^1H NMR spectrum in CD_2Cl_2 of the residue obtained after evaporation of solvents showed one hydride singlet at $\delta -8.7$, which we assign to the mono-μ-hydrido species $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}Cl)_2]CF_3SO_3$, cf. $\delta -9.0$ for the corresponding PF_6 salt [1]. There was no peak in the region of $\delta -14$ characteristic of di-μ-hydrides in this series of compounds. **3a** did not react with CF_3CO_2H (2 equiv.) in acetone at room temperature, but after refluxing for 2.5 h the main species present were a di-μ-hydride ($\delta -14.5$) and unchanged **3a**. The oil obtained after heating for 11 h and evaporation of the deep red solution *in vacuo* contained *c*. 90% of the di-μ-hydride, presumably $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CCF_3)]CF_3SO_3$; there was also a small amount of a mono-μ-hydride, $[\{Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]CF_3SO_3$ ($\delta -9.6$). The IR spectrum of the oil showed a band of medium intensity at 1650 cm^{-1} assigned to $\nu_{as}(OCO)$ of coordinated trifluoroacetate.

As in the isoelectronic $Rh(\eta^5\text{-}C_5Me_5)$ series, therefore, the $Ru(\eta^6\text{-arene})$ di-μ-hydrido complexes can apparently only be isolated when the third bridging ligand is carboxylate, not chloride. It is also worth noting that, whereas the $Ru(\eta^6\text{-arene})$ mono- and tri-μ-hydrides are stable in chloroform, the complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]PF_6$ (**1**) reacts slowly with $CDCl_3$ to give $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}Cl)]PF_6$ and $CHDCl_2$. Presumably $[\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_2(\mu\text{-}Cl)]Cl$ is unstable with respect to the corresponding mono-μ- and tri-μ-hydrido complexes.

Catalytic hydrogenation

Cyclohexene

The monomeric carboxylato complexes $Ru(O_2CMe)_2(\eta^6\text{-arene})\cdot nH_2O$ (arene = C_6Me_6, $n = 1$; arene = $1,3,5\text{-}C_6H_3Me_3$, C_6H_6, $n = 0$). $Ru(O_2CCF_3)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ and $RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$ in various solvents catalyse the hydrogenation of cyclohexene to cyclohexane at 50 °C/1 bar; the results are summarized in Table 4. The complex $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ is catalytically inactive at 20 °C, and the μ-hydrido complexes $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2$ [1] and $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)]_3CF_3SO_3$ (**2a**) are very poor catalysts, even at 50 °C. After the catalytic runs, the solutions are clear dark red or red–brown and contain no suspended solid. Catalytic activity depends both on solvent and on the coordinated arene. For $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ the order of efficacy of solvents is 2-propanol $\gg$ ethanol > benzene (Table 4, runs 1, 3, 4, 5 and 6) and the corresponding order for the η^6-arenes is $C_6Me_6 \gg 1,3,5\text{-}C_6H_3Me_3 > C_6H_6$ (runs 1, 7 and 8). Under the catalytic conditions specified in Table 4, $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ is converted into the mono-μ-hydrido complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ in 2-propanol and into a mixture of the mono- and di-μ-hydrido complexes in ethanol. Similarly, after 4.75 h at 50 °C/1 bar H_2, the less active mesitylene complex in 2-propanol is converted into a mixture of mono- and di-μ-hydrides, whereas after 4 h under the same conditions the C_6Me_6 complex gives only the mono-μ-hydride. The formation of the dinuclear hydrides probably accounts for the noticeable decrease in activity of $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ with time (compare runs 3 and 4, and, to a lesser extent, runs 5 and 6). The residue from run 8, in which the catalyst is $Ru(O_2CMe)_2(\eta^6\text{-}C_6H_6)$, showed a hydride resonance at $\delta -19.2$; this may be due to a polynuclear species such as $[\{Ru(\eta^6\text{-}C_6H_6)\}_4(\mu\text{-}H)_4]^+$, similar to the corresponding *p*-cymene complexes of ruthenium and osmium [6, 7, 21] and to $[\{M(\eta^5\text{-}C_5Me_5)\}_4(\mu\text{-}H)_4]^+$ (M = Rh, Ir) [6, 22].

In 2-propanol at 50 °C/1 bar H_2 the bis(trifluoroacetate) $Ru(O_2CCF_3)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ is catalytically much less active than the bis(acetate) (compare runs 1 and 9), but is more active than the mesitylene or benzene complexes $Ru(O_2CMe)_2(\eta^6\text{-arene})$ (runs 7 and 8). In contrast to $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$, the bis(trifluoroacetate) is converted into a di-μ-hydride under the reaction conditions. The chloro(acetato) complex $RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$ (run 10) is also much less active catalytically than $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$, but it too is more active than $Ru(O_2CMe)_2(\eta^6\text{-arene})$ (arene = mesitylene or benzene).

1-Hexene

Results for the hydrogenation of 1-hexene catalysed by various $Ru^{II}(\eta^6\text{-}C_6Me_6)$ precursors in 2-propanol are summarized in Table 5. In the presence of $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)$ and hydrogen (1 bar) hexane is readily formed, even at 20 °C; this reaction occurs even more rapidly at 50 °C, but at this temperature there is competing isomerization of 1-hexene to a

TABLE 4. Hydrogenation of cyclohexene catalysed by various (η^6-arene)ruthenium(II) complexes[a]

Run	Catalyst precursor	Solvent	Time (h)	Conversion[b] (%)	No. turnovers (min^{-1})	Residue[c]
1	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	Me_2CHOH	4	49	4.07	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ present (δ_H −11.6)
2	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	Me_2CHOH	6[d]	<1		no hydride detected
3	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	EtOH	3	5	0.55	not examined
4	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	EtOH	20	25	0.41	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (δ_H −11.6) and $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_2\text{-}(\mu\text{-}O_2CMe)]^+$ (δ_H −14.4) present
5	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	C_6H_6	4.25	3.7	0.29	not examined
6	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	C_6H_6	18	11.2	0.21	not examined
7	$Ru(O_2CMe)_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)$	Me_2CHOH	4.75	11.2	0.78	$[\{Ru(\eta^6\text{-}C_6H_3Me_3)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]^+$ (δ_H −13.9), small peak due to mono-μ-hydride (δ_H −8.7)
8	$Ru(O_2CMe)_2(\eta^6\text{-}C_6H_6)$	Me_2CHOH	1.8	3.0	0.55	singlet at δ −19.2 (see text)
9	$Ru(O_2CCF_3)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	Me_2CHOH	4	20	1.65	$[\{Ru(\eta^6\text{-}C_6Me_3)\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CCF_3)]^+$ (δ_H −14.1), small amount of mono-μ-hydride (δ_H −11.2)
10	$RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$	Me_2CHOH	20.5	64	1.02	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}O_2CMe)]^+$ (δ_H −10.2), small amount of di-μ-hydride (δ_H −13.9)
11	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)\text{-}(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2H_2O$[e]	Me_2CHOH	2.33	<1		unchanged precursor
12	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)_3]CF_3SO_3$[e]	Me_2CHOH	5.5	trace		not examined

[a]Conditions: catalyst precursor (0.05 mmol), cyclohexene (10 ml), solvent (15 ml), H_2 (1 bar), temperature of oil bath 60 °C (except where stated). [b]% Olefin converted into alkane. [c]Species detected by ^1H NMR spectroscopy after evaporation of solvents and dissolution of residue in CD_2Cl_2. [d]At 20 °C. [e]0.05 mmol Ru.

mixture of *cis*- and *trans*-2-hexene. Isomerization also takes place at 50 °C in the absence of hydrogen (run 4), and comparison with run 1 shows that this process occurs more rapidly under these conditions. As observed also for cyclohexene hydrogenation, the activity of the catalyst falls with time, e.g. the turnovers for hydrogenation of 1-hexene are 2.73 and 0.94 min^{-1} after 4.5 and 21 h, respectively. In contrast, the ratio of turnovers for hydrogenation and isomerization remains constant at *c.* 3:1 over time. In all the isomerizations, *cis*-2-hexene predominates over *trans*-2-hexene, presumably because it is the preferred kinetic product. This behaviour has also been observed in the isomerization of 1-olefins catalysed by other transition metal complexes [23–26].

The complex $Ru(O_2CMe)_2$ $(\eta^6\text{-}C_6Me_6)$ in 2-propanol does not catalyse the hydrogenation of 2-hexene to hexane at 50 °C/bar H_2, but does do so at 50 °C/60 bar H_2.

Comparison of runs 1 and 6 shows that $RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$ is a poorer catalyst for hydrogenation, but a better catalyst for isomerization, than $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$. Examination of the residues from both runs by ^1H NMR spectroscopy shows the presence of mono-μ-hydrido species, presumably $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}O_2CMe)]^+$ and $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$, respectively; the residue from the less active hydrogenation catalyst $RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$ also contains a di-μ-hydrido species (δ_H −14.4).

As in the case of cyclohexene hydrogenation, the mono-μ-hydrido complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(OAc)_2\cdot H_2O$ is less active than $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$ for hydrogenation of 1-hexene, but it is more active for isomerization (compare runs 1 and 7).

Discussion

This work, together with that described earlier [1], provides reliable syntheses of a series of dinuclear mono-, di-, and tri-μ-hydrido ruthernium(II) complexes containing η^6-alkylarenes. The proposed structures closely resemble those of the series of isoelectronic $Rh(\eta^5\text{-}C_5Me_5)$ and $Ir(\eta^5\text{-}C_5Me_5)$ complexes described

TABLE 5. Hydrogenation and isomerization of 1-hexene catalysed by various (η^6-arene)ruthenium(II) complexes[a]

Run	Catalyst precursor	Time (h)	Conversion to hexane[b] (%)	No. turnovers (min^{-1})	Conversion to 2-hexene[b] (%)	No. turnovers (min^{-1})	Residue[c]
1	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	4.5	46	2.73	15(66% *cis*, 34% *trans*)	0.90	not examined
2	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	21	74	0.94	25(79% *cis*, 21% *trans*)	0.32	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (δ_H −11.6) present
3	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	7[d]	19	0.73	none		mainly unchanged precursor, some $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (δ_H −11.6) present
4	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	24.5[e]	1.2		49(78% *cis*, 22% *trans*)	0.54	not examined
5	$Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)\cdot H_2O$	3[f]	0				not examined
6	$RuCl(O_2CMe)(\eta^6\text{-}C_6Me_6)$	18	54	0.80	35(70% *cis*, 30% *trans*)	0.52	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (δ_H −11.6), small amount of di-μ-hydride (δ_H −14.4) present
7	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2\cdot H_2O$[g]	2.8	5.7	0.54	11.7(72% *cis* 28% *trans*)	1.11	$[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]^+$ (δ_H −11.6), present

[a] Conditions: catalyst precursor (0.05 mmol), 1-hexene (10 ml), 2-propanol (15 ml), H_2 (1 bar), temperature of oil bath 50 °C (except where stated). [b] Based on total 1-hexene. [c] Species detected by ^1H NMR spectroscopy after evaporation of solvents and dissolution of residue in CD_2Cl_2. [d] At 20 °C. [e] In absence of H_2. [f] Commercial 2-hexene (16% *cis*, 84% *trans*) used in place of 1-hexene. [g] 0.05 mmol Ru.

by Maitlis and co-workers [15, 27]. As already noted [1], the $Ru(O_2CMe)_2$ (η^6-arene) complexes apparently activate H_2 less readily than do $M(O_2CMe)_2(\eta^5\text{-}C_5Me_5)$ (M = Rh, Ir). For example, the latter form di-μ-hydrido species on prolonged reaction with H_2 (1 bar), even at 20 °C, in 2-propanol or benzene, whereas the former require 50 °C/50 bar H_2, and use of an aromatic solvent (benzene or toluene) is essential.

We suggest that the precursors to the binuclear (η^6-arene)ruthenium(II) hydrides are coordinatively unsaturated, monomeric hydrido complexes (possibly solvated) that are generated by heterolytic activation of H_2 (eqns. (4) and (5)).

$$Ru(O_2CMe)_2(\eta^6\text{-arene}) + H_2 \xrightarrow{\text{solvent}} RuH(O_2CMe)(\eta^6\text{-arene})(\text{solvent}) + MeCO_2H \quad (4)$$

$$RuH(O_2CMe)(\eta^6\text{-arene})(\text{solvent}) + H_2 \longrightarrow RuH_2(\eta^6\text{-arene})(\text{solvent}) + MeCO_2H \quad (5)$$

The binuclear hydrides may be formed by condensation of these monomers, either with $Ru(O_2CMe)_2(\eta^6\text{-arene})$, or with each other (eqns. (6)–(8)))

$$RuH(O_2CMe)(\eta^6\text{-arene}) + Ru(O_2CMe)_2(\eta^6\text{-arene}) + MeCO_2H \longrightarrow [\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]H(O_2CMe)_2 \quad (6)$$

$$RuH_2(\eta^6\text{-arene}) + Ru(O_2CMe)_2(\eta^6\text{-arene}) + MeCO_2H \longrightarrow [\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]H(O_2CMe)_2 \quad (7)$$

$$2RuH(\eta^6\text{-arene})(O_2CMe) + MeCO_2H \longrightarrow [\{Ru(\eta^6\text{-arene})\}_2(\mu\text{-}H)_2(\mu\text{-}O_2CMe)]H(O_2CMe)_2 \quad (8)$$

The fact that benzene or toluene favour exclusive formation of the di-μ-hydrides from $Ru(O_2CMe)_2(\eta^6\text{-arene})$ suggests that these solvents may preferentially solvate the fragment $RuH_2(\eta^6\text{-arene})$, perhaps by formation of a *dihapto* complex. The formation of small amounts of cyclohexanes could then occur by competitive transfer of hydrogen to the η^2-arene to give cyclohexenes, which would be reduced even more readily than arenes under the reaction conditions. Most of the (η^6-arene) ruthenium(II) complexes, either with or without added base (triethylamine), catalyse hydrogenation of benzene to cyclohexane at 50 °C/50 bar H_2 [2], as does $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ in the presence of triethylamine [28], but under these conditions some or all of the coordinated arene may be displaced [29, 30]. This work will be described separately.

The mononuclear $Ru(O_2CMe)_2(\eta^6\text{-arene})$ complexes are better catalysts for olefin hydrogenation at 50 °C/1 bar H_2 than the dinuclear hydrido complexes. As in the $Rh(\eta^5\text{-}C_5\text{-}Me_5)$ and $Ir(\eta^5\text{-}C_5Me_5)$ series [31], the activity of the dinuclear hydrides decreases as the number of bridging hydride ligands increases, presumably reflecting the increasing difficulty of generating active monomeric fragments. Although detailed kinetic studies have not been made, the observations suggest that the active species in olefin hydrogenation are $RuH(O_2CMe)(\eta^6\text{-arene})$ and $RuH_2(\eta^6\text{-arene})$ (eqns. (4) and (5)). Similar species have been suggested to be responsible for olefin hydrogenation catalysed by dinuclear $Ir(\eta^5\text{-}C_5Me_5)$ complexes [31] and by $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ [32, 33].

The $Ru(O_2CMe)_2(\eta^6\text{-arene})$ complexes become more active hydrogenation catalysts for olefins as more methyl groups are introduced on the η^6-arene ring. This observation suggests that the vacant site at the metal atom required for olefin coordination in the catalytic cycle is generated by complete or by one-ended $(\eta^2 \leftrightarrows \eta^1)$ dissociation of the acetate ligand. We have noted previously [1] that in the dinuclear hydrido complexes $\{Ru(\eta^6\text{-arene})\}_2H(O_2CMe)X_2$ and $\{Ru(\eta^6\text{-arene})\}_2HX_3$ $(X = Cl, Br)$ the tendency of the halide ligand to ionize increases from C_6H_6 to C_6Me_6, i.e. with increasing electron-donating ability of the arene.

An important competing process in the hydrogenation of 1-hexene at 50 °C is isomerization to 2-hexene. The mononuclear complexes $RuX(O_2CMe)(\eta^6\text{-}C_6Me_6)$ $(X = O_2CMe, Cl)$ are better hydrogenation catalysts but poorer isomerization catalysts than is the dinuclear complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2]\text{-}H(O_2CMe)_2$. Although the mononuclear species $RuH(O_2CMe)(\eta^6\text{-}C_6Me_6)$ (eqn. (4)) is probably important in both processes for both mononuclear and dinuclear precursors, an active dinuclear (η^6-arene)ruthenium species may also be involved in olefin isomerization catalysed by the mono-μ-hydride.

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