Journal of Organometallic Chemistry, 263 (1984) 375–384
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND REACTIONS OF SOME TRIPLE ALKOXO- AND THIOATO-BRIDGED ARENERUTHENIUM(II) COMPLEXES. X-RAY STRUCTURE DETERMINATION OF $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$

R.O. GOULD, T.A. STEPHENSON* and D.A. TOCHER

Department of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ (Great Britain)

(Received October 10th, 1983)

Summary

Reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$) with $NaNH_2$ in CH_3CN gives a dark oil which upon treatment with $ROH/NaBPh_4$ (R = Me, Et) gives the triple bridged complexes $[Ru_2(\eta\text{-arene})_2(OR)_3]$ $[BPh_4]$. The structure of the benzene complex (R = Me) has been verified by X-ray analysis. The crystals are monoclinic, space group $P2_1/n$ with *a* 11.725(4), *b* 15.573(5), *c* 18.739(2) Å; *β* 103.29(2)°. These complexes undergo reactions with tertiary phosphines and hydrogen halides. There is also spectroscopic evidence for intermolecular exchange of the bridging alkoxo ligands on mixing pure solutions of the $[M_2(arene)_2(OR)_3]^+$ cations (M = Ru, Os). Reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with $Pb(SEt)_2$ in CH_3CN gives the analogous $[Ru_2(arene)_2(SEt)_3]^+$ cations.

Recently [1] we reported the preparation of a variety of complexes of the type $[M_2(\eta\text{-arene})_2(OR)_3]X$ (M = Ru, arene = C_6H_6, R = Me, Et, X = BPh_4, PF_6; arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6, R = Me, X = BPh_4; arene = C_6H_6, R = Ph, X = BPh_4: M = Os, arene = C_6H_6, R = Me, X = BPh_4) by two routes: (a) treatment of the corresponding hydroxo complex with alcohol under reflux and (b) reaction of the dimers $[\{M(\eta\text{-arene})Cl_2\}_2]$ with a "freshly prepared solution of NaOR in ROH". Unfortunately, both these synthetic methods given rise to an inseparable mixture of products when arene = *p*-cymene, R = Me, Et, and for arene = 1,3,5-$C_6H_3Me_3$ and R = Et [2]. In this paper we now report another route for the preparation of these triple alkoxo bridged complexes, together with a successful synthesis of their sulphur analogues and an X-ray structural analysis of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$.

Results and discussion

If $[\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ is shaken in CH_3CN containing "80–90% $NaNH_2$" a dark yellow-brown solution is obtained. If after filtering through celite, to remove NaCl and excess $NaNH_2$, the solvent is evaporated off and the residual

0022-328X/84/$03.00

TABLE 1

HYDROGEN-1 NMR DATA FOR SOME RUTHENIUM(II) COMPLEXES AT 298 K (J in Hz)

Compound	Solvent	δ (ppm) [a,b]	
		η-arene	others
$[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$	$(CD_3)_2CO$	5.48(s)	4.42(s,O*Me*)
$[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$	$(CD_3)_2SO$	5.43(s)	4.50(q,CH_2) 1.35(t,CH_3, $^3J(CH_2CH_3)$ 7.0)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OMe)_3][BPh_4]$	CD_3NO_2	5.24(ΔH_AH_B 18 Hz; J 7.0) 2.82(sp C*H*Me_2);2.20(s,CH_3) 1.32(d, CH_3 of $CHMe_2$ J 7.0)	4.49(s,OMe)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OEt)_3][BPh_4]$	CD_3NO_2	5.21(ΔH_AH_B 26 Hz; J 6.0) 2.79(sp C*H*Me_2); 2.18(s,CH_3) 1.31(d,CH_3 of $CHMe_2$ J 7.0)	4.60(q,CH_2) 1.50(t,CH_3,$^3J(CH_2CH_3)$ 7.0)
$[Ru_2(\eta\text{-}C_6H_6)_2(SEt)_3][BPh_4]MeOH$	$(CD_3)_2SO$	5.69(s)	2.35 (q,CH_2) 1.30(t,CH_3, $^3J(CH_2CH_3)$ 7.4)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(SEt)_3][BPh_4]$	$CDCl_3$	4.74(ΔH_AH_B 21 Hz; J 7.0) 2.55(sp C*H*Me_2)1.93(s,CH_3) 1.21(d, CH_3 of C*H*Me_2 J 7.0)	4.37(q,CH_2) 1.35(t,CH_3,$^3J(CH_2CH_3)$ 7.4)
$[Ru_2(\eta\text{-}C_6H_6)_2(i\text{-}BuO)_3][BPh_4]$	CD_3NO_2	5.36(s)	1.12(d,CH_3, J 7.0) 4.27(d,CH_2) 2.28(m,CH)
$[Ru_2(\eta\text{-}C_6H_6)_2(i\text{-}PrO)_3][BPh_4]$	CD_3NO_2	5.46(s)	4.89(sp,CH) 1.48(d,CH_3,$^3J(CH(CH_3)_2$ 7.0)
$[OsRu(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ [c]	CD_3NO_2	6.01(s, C_6H_6-Os) 5.43(s,C_6H_6-Ru)	4.47(s,OMe)

[a] Reference standard internal TMS lock. [b] Where appropriate $[BPh_4]^-$ multiplets observed between δ 6.8–7.6 ppm. [c] NMR parameters determined from spectrum of mixture.

oil treated with a methanolic solution of Na[BPh$_4$], a yellow crystalline solid is slowly deposited. The infrared spectrum of this product contains no bands attributable to ν(Ru–Cl) but exhibits a strong ν(C–O) vibration at ca. 1050 cm^{-1}. Its ^{1}H NMR spectrum in CD$_3$NO$_2$ (Table 1) reveals the usual [BPh$_4$]$^-$ multiplets (δ 6.8–7.5 ppm), an AB pattern, centred at δ 5.24, a septet, at δ 2.82, a singlet at δ 2.20 and doublet at δ 1.32 ppm, (all from the *p*-cymene ring) and a sharp singlet at δ 4.49 ppm, (assigned to the OMe groups). Integration of this spectrum indicates a ratio of [BPh$_4$]$^-$/OMe/*p*-cymene groups of 1/3/2 respectively, suggesting the formulation [Ru$_2$(η-1,4-MeC$_6$H$_4$CHMe$_2$)$_2$(OMe)$_3$][BPh$_4$]. Micro-analytical data and conductivity measurements in CH$_3$NO$_2$ over a concentration range (Table 2) support this formulation. If the oil remaining after removal of solvent is treated with an ethanolic solution of Na[BPh$_4$[then [Ru$_2$(η-1,4-MeC$_6$H$_4$CHMe$_2$)$_2$(OEt)$_3$][BPh$_4$] is obtained in high yield.

The compounds [Ru$_2$(η-C$_6$H$_6$)$_2$(OR)$_3$][BPh$_4$] (R = Me, Et) were also prepared by this new synthetic route (see Experimental). In view of the recent discovery that the compounds previously formulated as [M$_2$(η-C$_6$H$_6$)$_2$(OH)$_3$][BPh$_4$]·Me$_2$CO are in fact [M$_4$(η-C$_6$H$_6$)$_4$(μ_2-OH)$_4$(μ_4-O)][BPh$_4$]$_2$·2Me$_2$CO (M = Ru, Os) [3], unequivocal characterisation of the structure of these alkoxo complexes was very desirable and therefore an X-ray structural analysis on [Ru$_2$(η-C$_6$H$_6$)$_2$(OMe)$_3$]BPh$_4$ was undertaken. This confirmed the authenticity of this binuclear, tri-methoxo-bridged structure. (see Fig. 1 and Table 3 for selected intramolecular distances and angles). The Ru ··· Ru distance of 3.005(2) Å is of similar magnitude to that found for the hydroxo-bridged compounds [3], (c.f. 3.283 Å in [Ru$_2$(η-1,4-MeC$_6$H$_4$-CHMe$_2$)$_2$Cl$_3$]BPh$_4$·MeOH [4]). The Ru–O distances lie between 2.044 and 2.080 Å

TABLE 2

MICROANALYTICAL AND CONDUCTIVITY DATA FOR SOME RUTHENIUM(II) COMPLEXES

Compound	Analyses (Found (calcd.) (%))		Λ_M [a]
	C	H	
[Ru$_2$(η-C$_6$H$_6$)$_2$(OMe)$_3$][BPh$_4$]	60.5 (60.8)	5.3 (5.3)	68
[Ru$_2$(η-C$_6$H$_6$)$_2$(OEt)$_3$][BPh$_4$]	61.9 (62.1)	5.8 (5.8)	50
[Ru$_2$(η-1,4-MeC$_6$H$_4$CHMe$_2$)$_2$(OMe)$_3$][BPh$_4$]	63.1 (63.9)	6.2 (6.5)	56
[Ru$_2$(η-1,4-MeC$_6$H$_4$CHMe$_2$)$_2$(OEt)$_3$][BPh$_4$]	64.1 (64.9)	6.7 (6.9)	–
[Ru$_2$(η-C$_6$H$_6$)$_2$(SEt)$_3$][BPh$_4$]MeOH	56.9 (57.8)	5.6 (5.8)	48
[Ru$_2$(η-1,4-MeC$_6$H$_4$CHMe$_2$)$_2$(SEt)$_3$][BPh$_4$]	60.3 (61.7)	6.3 (6.5)	48
[Ru$_2$(η-C$_6$H$_6$)$_2$(i-BuO)$_3$][BPh$_4$]	64.4 (64.2)	6.6 (6.6)	54
[Ru$_2$(η-C$_6$H$_6$)$_2$(i-PrO)$_3$][BPh$_4$]	63.4 (63.2)	6.4 (6.3)	52
[Ru(η-C$_6$H$_6$)(PEtPh$_2$)$_3$][PF$_6$]$_2$	52.1 (51.8)	4.6 (4.4)	119

[a] Molar conductivities (S cm^2 mol^{-1}) measured in CH$_3$NO$_2$ at 10^{-3} dm^{-3} concentration.

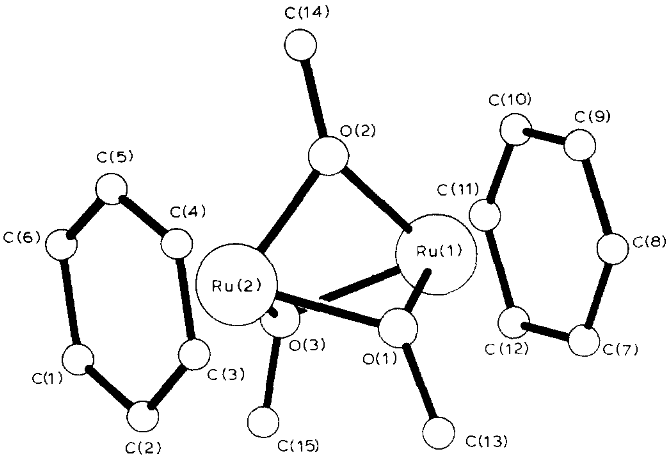

Fig. 1. The molecular structure of the cation $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$.

and have an average value of 2.060(8) Å. Although bonds to O(3) are longer, the difference does not appear to be significant. The Ru–C distances for the two rings are 2.155(14) and 2.158(13) Å while the distance from the metal to the ring centroids are 1.643 and 1.646 Å respectively. The two benzene rings are partially disordered

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR THE COMPOUND $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ (With standard deviations in parentheses)

Ru(1)–Ru(2)	3.005(2)	Ru(2)–C(4)	2.162(13)
Ru(1)–O(1)	2.056(7)	Ru(2)–C(5)	2.167(13)
Ru(1)–O(2)	2.046(8)	Ru(2)–C(6)	2.163(13)
Ru(1)–O(3)	2.078(7)	O(1)–C(13)	1.432(18)
Ru(1)–C(7)	2.133(14)	O(2)–C(14)	1.407(18)
Ru(1)–C(8)	2.142(14)		
Ru(1)–C(9)	2.164(14)		
Ru(1)–C(10)	2.177(14)		
Ru(1)–C(11)	2.168(14)		
Ru(1)–C(12)	2.146(14)		
Ru(2)–O(1)	2.057(7)	O(3)–C(15)	1.419(11)
Ru(2)–O(2)	2.044(8)	B(1)–C(16)	1.691(13)
Ru(2)–O(3)	2.080(7)	B(1)–C(22)	1.698(14)
Ru(2)–C(1)	2.154(13)	B(1)–C(28)	1.702(13)
Ru(2)–C(2)	2.149(13)	B(1)–C(34)	1.709(14)
Ru(2)–C(3)	2.153(13)		
Ru(1)–O(1)–Ru(2)	93.9(3)	O(2)–Ru(2)–O(3)	71.4(3)
Ru(1)–O(2)–Ru(2)	94.6(3)	Ru(1)–O(1)–C(13)	125.7(8)
Ru(1)–O(3)–Ru(2)	92.6(3)	Ru(1)–O(2)–C(14)	132.1(8)
O(1)–Ru(1)–O(2)	71.5(3)	Ru(1)–O(3)–C(15)	121.7(8)
O(1)–Ru(1)–O(3)	74.9(3)	Ru(2)–O(1)–C(13)	124.7(8)
O(2)–Ru(1)–O(3)	71.4(3)	Ru(2)–O(2)–C(14)	130.5(8)
O(1)–Ru(2)–O(2)	71.5(3)	Ru(2)–O(3)–C(15)	119.3(7)
O(1)–Ru(2)–O(3)	74.9(3)		

over two positions (see Experimental). The major sites (80% occupancy) are twisted 26° with respect to one another, giving an almost staggered conformation. The Ru–O–Ru angles lie in the range 92.6 to 94.6° and the O–Ru–O angles between 71.4–74.9°. These values are very similar to those found in both $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl \cdot 3H_2O$ and $[Ru_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)][BPh_4]_2 \cdot 2Me_2CO$ [3].

Our earlier attempts to synthesise longer chain alkoxides such as i-PrO or n-BuO using either the $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$/ROH or $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$/NaOR/ROH routes were unsuccessful since extensive decomposition occurred and no ruthenium complexes could be isolated from the reaction mixture [1]. However, the reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ [1] with isopropanol under mild conditions (40°C, 10–15 min) produces a microcrystalline yellow precipitate. The infrared spectrum of this product contains no bands attributable to aqua or hydroxo ligands but an intense band at 1050 cm^{-1} can be assigned to a ν(C–O) vibration. The ^1H NMR spectrum in CD_3NO_2 shows a singlet at δ 5.46 ppm, due to η-benzene, and a doublet and septet, at δ 1.48 and 4.89 ppm respectively, ascribed to isopropoxo ligands, in addition to the usual $[BPh_4]^-$ multiplets. The relative intensity of these signals indicate that the ratio of C_6H_6/i-PrO/$[BPh_4]^-$ groups is 2/3/1. The $^{13}C\{^1H\}$ spectrum in CD_3NO_2 consists of three signals, (in addition to $[BPh_4]^-$ signals at 120–140 ppm), at δ 78.8, 33.8 and 19.7 ppm. The resonance at δ 78.8 ppm is readily assigned to η-C_6H_6, while the proton coupled spectrum indicates that the signal at δ 33.8 ppm arises from $O\mathit{C}H(CH_3)_2$ and the signal at δ 19.7 ppm from $OCH(\mathit{C}H_3)_2$. The analytical data and conductivity measurements in CH_3NO_2 (Table 2) also fit the formulation $[Ru_2(\eta\text{-}C_6H_6)_2(i\text{-}PrO)_3][BPh_4]$. The complex $[Ru_2(\eta\text{-}C_6H_6)_2(i\text{-}BuO)_3][BPh_4]$ was prepared similarly from $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ and isobutanol.

In an attempt to extend the range of triple bridged areneruthenium(II) complexes, we have examined the reaction of a variety of compounds with ethanethiol and its salts. When "$[Ru_2(\eta\text{-arene})_2(OH)_3][BPh_4]$" is refluxed in EtSH for periods of up to 6 h no reaction is observed and only starting materials are recovered on work-up. Reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with a "freshly prepared solution of Na[SEt] in EtSH" results in rapid decomposition and no ruthenium complexes could be isolated. However, treatment of a CH_3CN solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with an excess of $Pb(SEt)_2$ results in the formation of a dark brown solution. After filtering, the solvent was removed and the residue treated with $Na[BPh_4]$. The infrared spectrum of the resultant yellow precipitate contains no bands due to ν(Ru–Cl) vibrations. Bands at 605, 809, and 840 cm^{-1} are characteristic of π-bonded benzene and a weak band at 610 cm^{-1} is ascribed to ν(S–C) vibrations. The ^1H NMR spectrum in CD_3NO_2 contains a singlet at δ 5.69 (η-C_6H_6), multiplets at δ 6.8–7.6 (BPh_4^-) and a triplet and quartet, at δ 1.30 and 2.35 ppm respectively, due to the ethanethiolato ligands. Integration of the ^1H NMR spectrum suggests the formulation $[Ru_2(\eta\text{-}C_6H_6)_2(SEt)_3][BPh_4]$ with a structure analogous to that of the alkoxides. The $^{13}C\ \{^1H\}$ spectrum contains signals at δ 84.5 (η-C_6H_6), 32.8 (CH_2), 17.0 (CH_3) and 120–140 ppm ($[BPh_4]^-$). The *p*-cymene complex $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(SEt)_3][BPh_4]$ was prepared similarly.

Reactions of alkoxo-bridged complexes

The inertness of hydroxo-bridged complexes towards neutral Lewis bases has been demonstrated by their resistance to cleavage [1] under conditions in which halide bridges are normally broken [5]. This lack of reactivity might in the case of triple hydroxo-bridged complexes be due to the presence of substantial intramolecular hydrogen bonding interactions. If this assumption is correct then the analogous $[Ru_2(\eta\text{-arene})_2(OR)_3]^+$ cations, in which such interactions are not possible, would be expected to cleave readily. However, our preliminary investigations show that $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][PF_6]$ does not react with nitrogen donor ligands such as pyridine, 2,2'-bipyridyl, 1,10-phenanthroline even under reflux conditions. No reaction was observed with PPh_3 but the complex does react with $PEtPh_2$ to give a low yield (< 5%) of $[Ru(\eta\text{-}C_6H_6)(PEtPh_2)_3][PF_6]_2$. High yield syntheses of these types of compound have already been published [6].

We have recently demonstrated that a variety of hydroxo-bridged complexes react with hydrogen halides to give both cationic, $[Ru_2(\eta\text{-arene})_2X_3]^+$, and neutral, $[\{Ru(\eta\text{-arene})X_2\}_2]$, products [3]. Similarly, $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ reacts with anhydrous HCl to give both $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$ and $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ while reaction with HX (X = Br, I) gives only $[\{Ru(\eta\text{-}C_6H_6)X_2\}_2]$.

Previously it has been shown that mixing equimolar amounts of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BF_4]$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3][BF_4]$ in $(CD_3)_2CO$ at ambient temperature led to the formation of the mixed halide-bridged complexes $[Ru_2(\eta\text{-}C_6H_6)_2Cl_2Br][BF_4]$ and $[Ru_2(\eta\text{-}C_6H_6)_2ClBr_2][BF_4]$, which were present as part of an inseparable statistical mixture of the four compounds [7]. This type of reaction was extended to the formation of heterobridged, heteroarene and heteronuclear triple halide-bridged arene complexes of ruthenium(II) and osmium(II) [7].

Related studies on alkoxo-bridged complexes have now produced similar results. Thus, the ^1H NMR spectrum in $(CD_3)_2SO$ of an aged solution of an equimolar mixture of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ and $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$ shows four distinct sets of resonances. Two of these sets are due to unchanged $[Ru_2(\eta\text{-}C_6H_6)_2(OR)_3][BPh_4]$ (R = Me, Et). Two additional singlets, in the η-benzene range, at δ 5.40 and 5.37 ppm, two singlets, in the OMe region, at δ 4.30 and 4.26 ppm, and additional quartets, at δ 4.41 and 4.10 ppm, and triplets, at δ 1.06 and 0.90 ppm, can be assigned to the hetero-bridged cations $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_2(OEt)]^+$ and $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)(OEt)_2]^+$. The mixed metal complex $[(\eta\text{-}C_6H_6)Os(OMe)_3Ru(\eta\text{-}C_6H_6)][BPh_4]$ can be prepared by mixing CD_3NO_2 solutions of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ and $[Os_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$. The ^1H NMR spectrum of the aged solution contains signals due to both starting materials and, in addition, resonances at δ 6.01, 5.43 and 4.47 ppm, assigned to the heterometallic complex, $[(\eta\text{-}C_6H_6)Ru(OMe)_3Os(\eta\text{-}C_6H_6)][BPh_4]$. The mechanism previously postulated for exchange of the halide-bridged cations (see Fig. 2 in ref. 7) is equally applicable to the processes described here.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the range 250–4000 cm^{-1} on a Perkin–Elmer 577 grating spectrometer using Nujol mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on Bruker WP 80 and WP 200 spectrometers. Carbon-13 NMR spectra were recorded on a Varian CFT 20 spectrometer operating at 20 MHz (chemical shifts quoted to high frequency of TMS). Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Plots of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ gave a straight line whose gradient is a function of the ionic charges [8]. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials

$Pb(SEt)_2$ was prepared from lead tetraacetate and ethanethiol [9] and anhydrous hydrogen halides by standard literature methods [10]. All other reagents were purchased from normal commercial suppliers.

All reactions were carried out in degassed solvents under nitrogen. Hydrogen-1 NMR data are presented in Table 1 and analytical and conductivity data in Table 2.

Tri-μ-methoxobis[(η-benzene)ruthenium(II)] tetraphenylborate

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.10 g, 0.20 mmol) was added to a suspension of "80–90% $NaNH_2$" (0.12 g, 3.0 mmol) in CH_3CN (25 cm^3). This mixture was shaken for 24 h and then precipitated NaCl and excess "$NaNH_2$" were removed by filtration through celite. The resulting yellow/brown solution was evaporated to dryness on a rotary evaporator. Treatment of the residue with a methanol (5 cm^3) solution of $Na[BPh_4]$ (0.14 g, 0.40 mmol) precipitated a yellow microcrystalline solid which was washed with methanol and air dried (Yield 90 mg, 58%) m.p. 198°C (decomp.) (ν(CO) 1050 cm^{-1}; δ(Ru–O–C) 1145 cm^{-1}; ν(RuO) 550 cm^{-1} (mull)]. Similarly prepared was *Tri-methoxobis[(η-p-cymene)ruthenium(II)] tetraphenylborate* from $[\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.12 g, 0.20 mmol) and $NaNH_2/CH_3CN$ (70 mg, 40%) m.p. 151°C (ν(CO) 1045 cm^{-1}; ν(RuO) 510 cm^{-1} (mull)]; slope of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ plot in $CH_3NO_2 = 136$.

Tri-μ-ethoxobis[(η-benzene)ruthenium(II)] tetraphenylborate

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.10 g, 0.20 mmol) was added to a suspension of "80–90% $NaNH_2$" (0.12 g, 3.0 mmol) in CH_3CN (30 cm^3). This mixture was shaken for 24 h and then the precipitated NaCl and excess "$NaNH_2$" removed by filtration through celite. The resulting solution was evaporated to dryness and treatment of the residue with an ethanol (3 cm^3) solution of $Na[BPh_4[$ (0.07 g, 0.20 mmol) precipitated an orange crystalline solid which was washed with ethanol and dried under vacuo (110 mg, 67%) m.p. 220°C (decomp.) ν(CO) 1050 cm^{-1}; ν(RuO) 570 cm^{-1} (mull)). Similarly prepared was *Tri-μ-ethoxobis[(η-p-cymene)ruthenium(II)] tetraphenylborate* from $[\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.12 g, 0.20 mmol) and $NaNH_2/CH_3CN$ (75 mg, 41%) m.p. 188°C (ν(CO) 1055 cm^{-1}; ν(RuO) 500 cm^{-1} (mull)).

Tri-μ-isobutoxobis[(η-benzene)ruthenium(II)] tetraphenylborate

The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ (0.20 g, 0.27 mmol) was warmed gently in isobutanol (30 cm^3) for 15 min. The microcrystalline golden precipitate was filtered off, washed with diethyl ether and air dried (180 mg, 75%) m.p. 201–203°C (decomp.) (ν(CO) 1050 cm^{-1}; ν(RuO) 510 cm^{-1} (mull)). Similarly prepared was *Tri-μ-isopropoxobis[(η-benzene)ruthenium(II)] tetraphenylborate* from reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ (0.22 g, 0.30 mmol) in isopropanol (240 mg, 95%) m.p. 148–150°C (decomp.) (ν(CO) 960 cm^{-1}; ν(RuO) 485 cm^{-1} (mull)).

^{13}C $\{^1H\}$ NMR spectrum in CD_3NO_2 (298 K): δ 78.8 (s), (C_6H_6), 33.8 and 19.7, ($OCH(CH_3)_2$), 121–136 ppm $[BPh_4]^-$.

Tri-μ-ethanethiolatobis[(η-benzene)ruthenium(II)] tetraphenylborate

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.10 g, 0.20 mmol) was shaken with $Pb(SEt)_2$ (0.30 g, 0.90 mmol) in CH_3CN (25 cm^3) for 48 h. The precipitated $PbCl_2$ was removed by filtration through celite. The resulting yellow/brown solution was evaporated to dryness and the residue dissolved in methanol (5 cm^3) and treated with $Na[BPh_4]$ (0.14 g, 0.40 mmol) to give a yellow precipitate. This was filtered off, washed with methanol and diethyl ether and dried in vacuo at 56°C (90 mg, 52%) m.p. 219–223°C (decomp.) (ν(SC) 610 cm^{-1}; ν(RuS) 365 cm^{-1} (mull)).

^{13}C $\{^1H\}$ NMR spectrum in CD_3NO_2 (298 K): δ 84.5(s) ($\eta\text{-}C_6H_6$), 121–136 $[BPh_4]^-$, 32.8 and 17.0 ppm (SEt).

Similarly prepared was *Tri-μ-ethanethiolatobis[(η-p-cymene)ruthenium(II)] tetraphenylborate* from $[\{Ru(\eta\text{-}1{,}4\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.12 g, 0.20 mmol) and $Pb(SEt)_2$ in CH_3CN. (110 mg, 57%) m.p. 181°C (ν(SC) 650 cm^{-1}; ν(RuS) 370 cm^{-1} (mull)).

[(η-Benzene)tris(ethyldiphenylphosphine)ruthenium(II)] hexafluorophosphate

The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][PF_6]$ (0.20 g, 0.33 mmol) was refluxed in methanol (30 cm^3) with $PEtPh_2$ (0.30 g, 1.40 mmol) for 4 h. The solvent was removed and the gummy residue redissolved in a little methanol (5 cm^3). Diethyl ether (5 cm^3) was added and the solution left at 0°C for 48 h. The orange crystalline deposit was filtered off, washed with diethyl ether and dried under vacuo at 56°C (30 mg, 4%) m.p. 208°C.

Tri-μ-chlorobis[(η-benzene)ruthenium(II)] tetraphenylborate

The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ (0.10 g, 0.13 mmol) was dissolved in CH_3NO_2 (10 cm^3) and anhydrous HCl gas passed through the stirred solution for 20 min. The red solid formed was filtered off, washed with diethyl ether and air dried. This product was identified as *di-μ-chlorobis[chloro(η-benzene)ruthenium(II)]* (39 mg, 29%). The remaining solution was evaporated to dryness and the residue dissolved in methanol (5 cm^3). Addition of $Na[BPh_4]$ (0.20 g) gave an orange precipitate which was filtered off, washed with methanol and air dried (40 mg, 61%).

Di-μ-bromobis[bromo(η-benzene)ruthenium(II)]

The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ (0.10 g, 0.13 mmol) was dissolved in CH_3NO_2 (10 cm^3) and HBr passed through the solution for 20 min. The dark precipitate was filtered off, washed with diethyl ether and air dried (75 mg, 86%).

Di-μ-iodobis[iodo(η-benzene)ruthenium(II)] was similarly prepared from the methoxo-bridged compound and HI (90 mg, 80%).

Crystal structure determination of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$

Crystals suitable for X-ray analysis were obtained by the slow cooling to 273 K for 24 h of a methanolic solution of the complex. A yellow needle-shaped crystal (0.2 × 0.1 × 0.1 mm) was mounted along the needle axis and the data collected in the ω-2θ scan mode using a CAD-4 diffractometer with monochromated Mo-K_α radiation for θ out to 25°.

Crystal data. $C_{39}H_{41}BO_3Ru_2$, $M = 771$, monoclinic a 11.725(4), b 15.573(5), c 18.739(2) Å; β 103.29(2)°, D_m 1.51, D_c 1.53 g cm^{-3}; $Z = 4$, μ(Mo-K_α) 9.15 cm^{-1}, space group is $P2_1/n$.

TABLE 4

FRACTIONAL COORDINATES FOR $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$

Cation	*x*	*y*	*z*
Ru(1)	0.44249(8)	0.64469(6)	0.57108(4)
Ru(2)	0.33189(7)	0.74695(6)	0.43696(4)
O(1)	0.3412(6)	0.7534(4)	0.5478(3)
O(2)	0.4971(6)	0.7125(6)	0.4915(4)
O(3)	0.3282(7)	0.6199(4)	0.4708(3)
C(1)	0.2034(14)	0.7337(6)	0.3350(7)
C(2)	0.1610(14)	0.7904(6)	0.3804(7)
C(3)	0.2278(14)	0.8614(6)	0.4102(7)
C(4)	0.3370(14)	0.8756(6)	0.3946(7)
C(5)	0.3793(14)	0.8189(6)	0.3491(7)
C(6)	0.3125(14)	0.7480(6)	0.3193(7)
C(7)	0.4107(11)	0.6096(9)	0.6748(7)
C(8)	0.5063(11)	0.6653(9)	0.6864(7)
C(9)	0.6020(11)	0.6467(9)	0.6565(7)
C(10)	0.6020(11)	0.5723(9)	0.6150(7)
C(11)	0.5064(11)	0.5166(9)	0.6034(7)
C(12)	0.4107(11)	0.5352(9)	0.6333(7)
C(13)	0.2458(16)	0.7761(10)	0.5797(8)
C(14)	0.6026(15)	0.7125(11)	0.4686(8)
C(15)	0.2179(14)	0.5787(9)	0.4661(8)
Tetraphenylborate			
B(1)	0.0732(11)	0.5149(7)	0.7541(6)
C(16)	0.0427(6)	0.6135(3)	0.7168(3)
C(17)	−0.0471(6)	0.6241(3)	0.6542(3)
C(18)	−0.0725(6)	0.7056(3)	0.6238(3)
C(19)	−0.0082(6)	0.7765(3)	0.6561(3)
C(20)	0.0816(6)	0.7660(3)	0.7188(3)
C(21)	0.1070(6)	0.6844(3)	0.7491(3)
C(22)	0.1972(5)	0.5211(4)	0.8213(3)
C(23)	0.1918(5)	0.5558(4)	0.8892(3)
C(24)	0.2948(5)	0.5720(4)	0.9417(3)
C(25)	0.4032(5)	0.5537(4)	0.9264(3)
C(26)	0.4086(5)	0.5191(4)	0.8586(3)
C(27)	0.3056(5)	0.5028(4)	0.8061(3)
C(28)	0.0935(6)	0.4414(4)	0.6908(3)
C(29)	0.0925(6)	0.4643(4)	0.6187(3)
C(30)	0.1073(6)	0.4016(4)	0.5684(3)
C(31)	0.1232(6)	0.3159(4)	0.5903(3)
C(32)	0.1241(6)	0.2930(4)	0.6624(3)
C(33)	0.1093(6)	0.3558(4)	0.7126(3)
C(34)	−0.0368(5)	0.4744(4)	0.7902(4)
C(35)	−0.1535(5)	0.4935(4)	0.7580(4)
C(36)	−0.2431(5)	0.4578(4)	0.7861(4)
C(37)	−0.2160(5)	0.4030(4)	0.8465(4)
C(38)	−0.0993(5)	0.3839(4)	0.8788(4)
C(39)	−0.0097(5)	0.4196(4)	0.8507(4)

Intensities were measured for 4349 independent reflections of which 2546 had $I > 2.5\sigma(I)$. No crystal decay was observed and no absorption correction was applied. The two ruthenium atoms were located from a Patterson synthesis, and all remaining non-hydrogen atoms were found from subsequent Fourier maps. The ruthenium and oxygen atoms were refined anisotropically. In the refinement, both the benzene rings and the phenyl groups of the tetraphenylborate were constrained to be regular hexagons. The benzene rings were disordered over two positions. In the refinement each set of six carbon atoms were given individual site occupancy factors and thermal parameters. In the latter stages of refinement hydrogen atoms were included in fixed positions to give C–H 1.10 Å, with a fixed common temperature factor of U 0.08 Å^2. The hydrogen atoms of the methoxo ligands were located from the Fourier map and refined with a common temperature factor. The weighting scheme applied was $W = 1/\sigma^2(F_o) + 0.0014F_o^2$ and the final R factor was $R = 0.052$, $R_w = 0.064$. A final difference map showed only one peak above 0.5 e Å^{-3} (about 0.75 e Å^{-3}); it was near Ru(2). Final fractional coordinates are given in Table 4. Tables of observed and calculated structure factors and a full list of positional and thermal parameters may be obtained on request from the authors. Most crystallographic calculations used the SHELX program [11].

Acknowledgement

We thank Johnson Matthey plc for loans of ruthenium trichloride and the SERC (D.A.T.) for financial support.

References

1 T. Arthur, D.R. Robertson, D.A. Tocher and T.A. Stephenson, J. Organomet. Chem., 208 (1981) 389.
2 T. Arthur, PhD Thesis, University of Edinburgh, 1980.
3 R.O. Gould, C.L. Jones, T.A. Stephenson and D.A. Tocher, J Organomet. Chem., 264 (1984) 365.
4 D.A. Tocher and M.D. Walkinshaw, Acta Cryst B38, (1982) 3083.
5 See D.R. Robertson, T.A., Stephenson and T. Arthur, J. Organomet. Chem., 162 (1978) 121 and references therein.
6 H. Werner and R. Werner J. Organomet. Chem., 210 (1981) C11.
7 T. Arthur and T.A. Stephenson J. Organomet. Chem., 208 (1981) 369.
8 R.D. Feltham and R.G. Hayter, J. Chem. Soc., (1964)4587.
9 P. Borgstrom, L.M. Ellis and E.E. Reid, J. Am. Chem. Soc., 51 (1929) 3649.
10 G. Brauer, Handbook of Preparative Inorganic Chemistry Volume 1, p. 280–289, Academic Press, 1963, 2nd Edition.
11 G.M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Göttingen.