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Organometallic complexes of ruthenium(IV) with bidentate oxygen and nitrogen donor ligands

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Abstract

Reaction of the dichloride dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**3**) with β-diketones or their sodium salts results in the formation of the neutral chelate complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(R\cdot CO\cdot CH\cdot CO\cdot R')]$ ($R=R'=CH_3$ (**7**); $R=CH_3$, $R'=CF_3$ (**8**)). The equatorial (most abundant) isomer of **8** (**8a**) has been characterised by X-ray crystallography. Attempts to remove the chloride ligand in compounds such as **7** (via Ag^+) to form cationic aqua species were unsuccessful. However, analogous reactions with the cationic chelate complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(L\text{-}L)][BF_4]$ (L-L = 2,2′-bipyridyl (**4**); 1,10-phenanthroline (**5**)) resulted in the isolation of the aqua compounds $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(L\text{-}L)(OH_2)][BF_4]_2$ (**10** and **11**) in good yields. Attempts to generate oxo species derived from **10** and **11** by both electrochemical and chemical means were unsuccessful.

Key words: Ruthenium complexes; Bidentate ligand complexes; Organometallic complexes; Crystal structures

Introduction

There exists significant current interest in redox reactions of metal aqua compounds of the form:

$$[M\text{-}OH_2]^{n+} \rightleftharpoons [M{=}O]^{n+} + 2H^+ + 2e$$

In particular, work by Thorp and co-workers [1–4] has shown that complexes related to the ruthenium(II) aqua dication $[Ru(terpy)(bipy)(OH_2)]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine, bipy = 2,2′-bipyridine) (readily reversibly oxidised to the $Ru^{(III)}$–OH and $Ru^{(IV)}{=}O$ forms) are effective agents for the cleavage of DNA, and (in the presence of a suitable co-oxidant) similar compounds also function as catalytic reagents for organic oxidations [5–7].

Recent work has demonstrated that a number of organometallic allyl compounds of ruthenium(IV) (e.g. $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(OH_2)]$ (**1**) $[Ru(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})Cl(OH_2)]^+$ (**2**)) show a high affinity for water and, in some cases, significant solubility in aqueous media, an important pre-requisite for *in vivo* application of DNA cleavage agents [8–11]. Furthermore the geometry about the Ru(IV) centre in these compounds takes the form of a distorted trigonal (or pentagonal) bipyramid [12, 13] in contrast to the octahedral Ru(II) complexes. These observations have led us to embark upon a programme of synthesis of further aqua Ru(IV) complexes in the presence of various ancillary ligands in the hope that these materials may also exhibit electrochemical activity given a suitable choice of spectator groups (cf. the recent observation that the Ru(IV) thiolate complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}SEt)\}_2]$ may be oxidised to Ru(V) with a significant degree of reversibility [14]). Ultimately, it is anticipated that given their unusual geometry, these compounds may exhibit unusual selectivity in organic oxidations or in oxidative cleavage of DNA.

In this contribution we report the synthesis of β-diketonate complexes derived from the bis(allyl)-ruthenium(IV) chloro-bridged binuclear compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (**3**) and subsequent attempts to synthesise aqua, and hence oxo complexes with β-diketonate and other bidentate ancillary ligands.

Results and discussion

β-Diketonate compounds

Preliminary work by ourselves [8] has shown that aqua complexes of Ru(IV) may conveniently be generated by abstraction of chloride with Ag^+ in 'wet', weakly coordinating solvents such as acetone. Previously we have reported the synthesis of the chloro complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(L\text{-}L)][BF_4]$ (L-L = bipy (**4**); 1,10-

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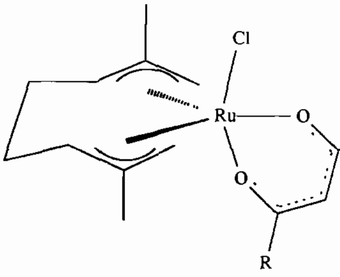
phenanthroline (**5**)) [10]. Further studies [9] show that reaction of **3** with hexafluoroacetylacetonate (as the silver or sodium salt) results in the formation of a related neutral chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(F_3C\cdot CO\cdot CH\cdot CO\cdot CF_3)]$ (**6**) in 20–30% yield, in which there is no evidence for the incorporation of water in the inner coordination sphere, in contrast to observations made in the presence of other electron withdrawing ligands such as trifluoroacetate.



$R = R' = CF_3$ **6**

$R = R' = CH_3$ **7**

$R = CH_3, R' = CF_3$ **8a**

$R = CF_3, R' = CH_3$ **8b**

We find that reaction of **3** with acetylacetone (acacH) and trifluoroacetylacetone (or their sodium salts) also results in the formation of chloro complexes with chelating β-diketonate ligands of the form $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(H_3C\cdot CO\cdot CH\cdot CO\cdot R)]$ ($R = CH_3$, (**7**); CF_3 (**8**)). Isolated yields were found to increase with the donor properties of the β-diketonate ligand whilst reaction times decreased. Hence the yield of the trifluoro complex **8** was 33% obtained after a reaction time of 72 h as against a yield of 20–30% for **6** after 1–2 weeks. Compound **7** was obtained in 52% yield after only 1 h. This trend is attributed to the poor nucleophilicity of the highly fluorinated β-diketonates. Compounds **7** and **8** were characterised by mass spectrometry (M^+ 372 (**7**); 426 (**8**)—based on ^{102}Ru and ^{35}Cl), by IR spectroscopy and by their distinctive ^1H NMR spectra (Table 1), which displayed the typical four terminal allyl and two methyl resonances arising from the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand, characteristic of a mononuclear compound with inequivalent axial sites on the trigonal bipyramidal Ru(IV) ion. Resonances for both the γ-proton of the β-diketonate ligand and the terminal allyl protons of the bis(allyl) ligand were observed to move downfield by approximately similar amounts with increasing fluorination of the ligand. The ^1H NMR spectrum of the trifluoroacetylacetonato complex **8** clearly demonstrated that this material exists as two isomers (**8a**, **8b**), present in the ratio of *c*. 3:1. By analogy with earlier reports on compounds containing unsymmetrical bidentate ligands (e.g. $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(OSCCH_3)]$ [9], $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4O)]$ [15]) this isomerism is likely to be of the axial/equatorial type with the trifluoromethyl substituent occupying a position adjacent to either an axial or equatorial coordination site. Previous work [15] has shown that the equatorial coordination site is the least sterically crowded and hence the relatively bulky CF_3 substituent would be expected to occupy an equatorial position in the most abundant isomer, **8a**. To confirm this a single crystal X-ray structure determination was undertaken. Isomerically pure crystals of **8** were prepared by hexane/diethyl ether vapour diffusion and were shown by ^1H NMR spectroscopy to consist solely of the more abundant isomer **8a**. Figure 1 shows the results of the structure determination and demonstrates the expected geometry incorporating a six-membered heterocyclic chelate ring containing the Ru(IV) centre (which exhibits the usual approximately trigonal bipyramidal coordination geometry [9, 10, 15, 16]) and the trifluoroacetylacetonato ligand with the oxygen atom on the carbon containing the CF_3 substituent occupying an equatorial coordination site. Unlike the crystal structure of the related acetate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ (**9**), the chelate ring is relatively unstrained with the axial and equatorial Ru–O bond distances approximately equal (Ru–O(1) 2.099(3), Ru–O(2) 2.117(3) Å, cf. compound **9**: $Ru\text{–}O_{axial}$ 2.095(6), $Ru\text{–}O_{equatorial}$ 2.205(6) Å). Similarly, the O(1)–Ru–O(2) angle is very close to the ideal value of 90° (actually 89.2(1)°) unlike comparable angles in most other compounds containing the '$Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})$' moiety, in which values of 85° or less are the norm [9, 10, 15, 16]. For comparison in the compound $[Ru(acac)_3]$ the bidentate ligands exhibit a bite angle of 93.7(9)° [17].

Aqua complexes

Action of AgX ($X = BF_4$, PF_6) upon the benzothiazole-2-thiolate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(mcbt)]$ in acetonitrile has been shown to result in the formation of the cationic solvate $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(mcbt)(MeCN)]X$ [18]. Similarly reaction of **7** with one mole equivalent of $Ag[BF_4]$ in undried acetone results in the formation of a white precipitate of AgCl along with a brown solution. Unfortunately it proved impossible to isolate any solid product from this reaction mixture, apparently because of the very high solubility of the products in the reaction medium. Similar problems have been encountered by us in attempting to synthesise a number of related solvento complexes. Analogous reaction of $Ag[BF_4]$ with the bipyridyl and phenanthroline compounds **4** and **5** [10] proved to be more successful however, possibly because of the more insoluble nature of the dicationic products, namely $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(N\text{-}N)(OH_2)][BF_4]_2$ (N-N = bipy (**10**); phen (**11**)) which were formed cleanly as greenish-yellow crystals in yields of 60–75%. No evidence was found for the incorporation

TABLE 1. ^1H NMR data for new compounds[a]

Compound	δ				
	Terminal allyl	Internal allyl	Ethylenic	Me	Ligand
$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(CF_3\cdot CO\cdot CH\cdot CO\cdot CF_3)]$ (**6**)[b]	6.08 (s, 1H) 4.92 (s, 1H) 4.89 (s, 1H) 3.50 (s, 1H)	5.19 (m, 1H) 4.44 (m, 1H)	3.04 (m, 2H) 2.43 (m, 2H)	2.45 (s, 3H) 1.99 (s, 3H)	4.96 (s, 1H, $F_3CCOC\mathit{H}COCF_3$)[c]
$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(CH_3\cdot CO\cdot CH\cdot CO\cdot CH_3)]$ (**7**)	5.29 (s, 1H) 4.65 (s, 1H) 4.62 (s, 1H) 3.30 (s, 1H)	4.97 (m, 1H) 4.21 (m, 1H)	2.99 (m, 2H) 2.41 (m, 2H)	2.42 (s, 3H) 1.90 (s, 3H)	4.73 (s, 1H, $H_3CCOC\mathit{H}COCH_3$)[c], 2.13 (s, 3H, $\mathit{H}_3CCOCHCOCH_3$), 1.73 (s, 3H, $H_3CCOCHCOC\mathit{H}_3$)
eq-$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(CH_3\cdot CO\cdot CH\cdot CO\cdot CF_3)]$ (**8a**)	5.72 (s, 1H) 4.84 (s, 1H) 4.79 (s, 1H) 3.44 (s, 1H)	5.10 (m, 1H) 4.39 (m, 1H)	3.11 (m, 2H) 2.45 (m, 2H)	2.47 (s, 3H) 1.95 (s, 3H)	4.84 (s, 1H, $H_3CCOC\mathit{H}COCH_3$)[c], 1.94 (s, 3H, $F_3CCOCHCOC\mathit{H}_3$)
ax-$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(CH_3\cdot CO\cdot CH\cdot CO\cdot CF_3)]$ (**8b**)	5.74 (s, 1H) 4.86 (s, 1H) 4.77 (s, 1H) 3.41 (s, 1H)	5.10 (m, 1H) 4.35 (m, 1H)	3.11 (m, 2H) 2.45 (m, 2H)	2.46 (s, 3H) 1.98 (s, 3H)	4.84 (s, 1H, $H_3CCOC\mathit{H}COCH_3$)[c], 2.33 (s, 3H, $F_3CCOCHCOC\mathit{H}_3$)
$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(N_2C_{10}H_8)(OH_2)][BF_4]_2$ (**10**)[d]	4.77 (s, 1H) 4.04 (s, 1H) 3.89 (s, 1H) 2.92 (s, 1H)	5.08 (m, 2H)	3.84 (m, 2H) 3.09 (m, 2H)	2.46 (m, 3H) 1.93 (m, 3H)	8.79 (d, 1H, $^3J=5.7$), 8.64 (d, 1H, $^3J=8.4$), 8.42 (m, 2H), 8.32 (d, 1H, $^3J=5.8$), 8.18 (t, 1H, $^3J=8.1$), 7.98 (t. 1H, $^3J=6.2$), 7.68 (t, 1H, $^3J=6.2$), 4.36 (s, 2H, $O\mathit{H}_2$)
$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(N_2C_{12}H_8)(OH_2)][BF_4]_2$ (**11**)[d]	4.77 (s, 1H) 4.22 (s, 1H) 3.94 (s, 1H) 3.57 (s, 1H)	5.28 (dd, 1H, $^3J=11.5$ and 4.6) 5.17 (dd, 1H, $^3J=11.1$ and 3.8)	3.94 (m, 2H) 3.12 (m, 2H)	2.49 (s, 3H) 1.84 (s, 3H)	9.21 (d, 1H, $^3J=5.3$), 9.00 (d, 1H, $^3J=8.2$), 8.74 (d, 1H, $^3J=8.2$) 8.71 (d, 1H, $^3J=5.6$), 8.36 (d, 1H, $^3J=8.9$), 8.31 (dd, 1H, $^3J=8.2$ and 5.4), 8.23 (d, 1H, $^3J=8.9$), 7.99 (dd, 1H, $^3J=8.2$ and 5.7), 3.92 (s, 2H, $O\mathit{H}_2$)

[a] δ in ppm, J(H–H) in Hz, 400 MHz, 20 °C, solvent $CDCl_3$ unless otherwise stated, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, se = septet, m = multiplet, br = broad. [b] Taken from ref. 10. [c] Uncertain assignment because of the proximity of the signal to the resonances arising from the terminal allyl protons. [d] Solvent nitromethane-d_3.

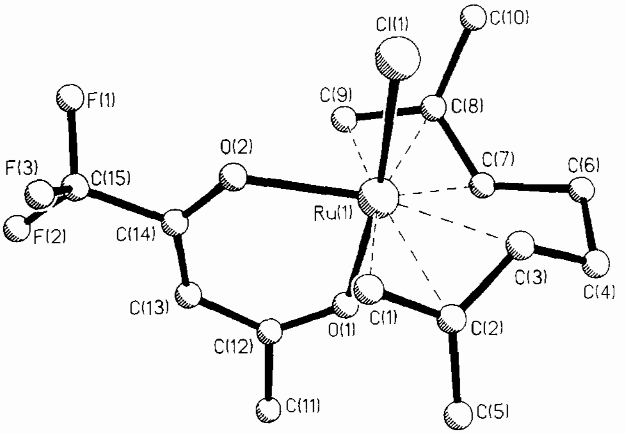
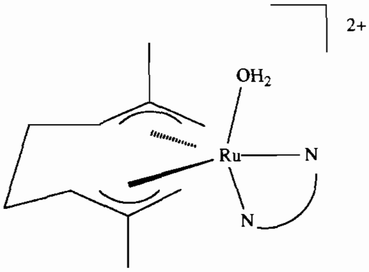


Fig. 1. Crystal structure of *equatorial*-[Ru(η^3:η^3-$C_{10}H_{16}$)-Cl(CH_3 CO·CH·CO·CF_3)] (**8a**) showing the atom numbering scheme adopted.

of acetone in these compounds but the presence of the water molecule in each complex was clearly indicated by the observation of reproducible sharp, singlet resonances integrating for two protons in each compounds' ^{1}H NMR spectra (δ 4.26 (**10**) and 3.92 (**11**) ppm). Similarly bands attributable to $\nu(OH_2)$ were observed in the respective IR spectra (e.g. 3390 cm^{-1} in **10**; in the closely related neutral compounds [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CR)$_2$(OH_2)] these bands are observed in the range 3310–3390 cm^{-1} [9]).



N-N = 2,2'-bipyridyl **10**
N-N = 1,10-phenanthroline **11**

Attempted oxidations

As a precursor to chemical oxidation the phenanthroline compound **11** was examined by cyclic voltammetry. Unfortunately the cyclic voltammogram ([^{n}Bu$_4$N][BF_4]/CH_2Cl_2, scan rate 100 mV s^{-1}) was essentially featureless in the region 0 to +1.5 V (versus Ag/AgCl) and the only observable wave was a single, irreversible reduction at *c.* −1.7 V possibly associated with the phenanthroline or more likely with loss of the bis(allyl) ligand, as is commonly observed in compounds containing the 'Ru(η^3:η^3-$C_{10}H_{16}$)' moiety [10].

Consistent with these results, attempts to chemically generate oxo species derived from **10** and **11** using oxidants such as 4-methylmorpholine-*N*-oxide, ceric ammonium nitrate and PhIO, or by deprotonation using strong bases such as KBu^{t}O, resulted either in recovery of unchanged starting material or extensive decomposition, and no oxidised products were isolated. Similar attempts were made to oxidise solutions presumed to contain [Ru(η^3:η^3-$C_{10}H_{16}$)(OH_2)$_3$][BF_4]$_2$ or [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)(OH_2)$_2$][BF_4]$_2$, generated by action of excess Ag[BF_4] upon the corresponding chloro complexes **3** [12, 19] and [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] [13, 20, 21] in undried acetone, again with no useful results.

Conclusions

The Ru(IV) ion in compounds related to **3** readily binds water as a ligand in preference to acetone in a similar way to *trans*,*mer*-[$MCl_2(H_2O)(PMe_2Ph)_3$]X (M = Rh, Ir; X = PF_6, ClO_4) [22]. The resulting aqua species are often highly soluble in polar media. The related arene Ru(II) [23] and pentamethylcyclopentadienyl Rh(III) complexes [24] are known to coordinate both acetone and water as ligands. Higher oxidation state (+5, +6) organometallic oxo species have not been observed either electrochemically or chemically and it seems likely that such materials derived from complexes of this type are not accessible using the methodologies employed herein.

We are currently carrying out an extensive investigation of the reactions of **3** with simple alkyl and aryl thiols which, in contrast to the results reported herein, do display some reversible oxidation chemistry in their cyclic voltammograms [14].

Experimental

Instrumental

IR spectra were recorded on a PE983 spectrometer between 4000 and 180 cm^{-1} as either KBr disks or nujol mulls on CsI plates. NMR spectra were recorded on a Varian VXR400 spectrometer at University College London. Microanalyses were carried out by the departmental service and mass spectra were recorded by the University of London Intercolliegate Research Service at the School of Pharmacy. Cyclic voltammetric measurements were performed using a Metrohm E506 potentiostat interfaced with a Metrohm E612 VA scanner and a Hewlett Packard 7035B XY recorder. Electrolyte solutions were 0.2 molar in tetra-n-butyl ammonium tetrafluoroborate in CH_2Cl_2. Deaeration of the solution was performed before the experiment and a stream of nitrogen passed throughout. The working electrode was a platinum wire (Metrohm EA285). A platinum wire was used as a pseudo-reference electrode and potentials were corrected relative to the ferrocene/ferrocinium couple (ferrocene was added at the end of each experiment). A massive platinum wire was used as the auxiliary electrode. All potentials are reported with respect to the Ag/AgCl couple against which ferrocene is oxidised at a potential of +0.60 V. All manipulations were carried out under nitrogen with degassed solvents using conventional Schlenk line techniques although no significant air sensitivity of the products was noted.

Materials

$[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(L\text{-}L)][BF_4]$ were prepared by published literature methods [10, 18, 19]. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by repeated dissolution in water and boiling to dryness. Sodium salts were obtained by the reaction of the β-diketone with a molar amount of sodium metal in anhydrous thf. Both salts and free ligands were used successfully in the reactions. All other reagents and materials were obtained from the usual commercial sources.

Preparations

$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(CH_3\cdot CO\cdot CH\cdot CO\cdot CH_3)]$ *(7)*

Compound **3** (0.21 g, 0.35 mmol) was suspended in acetone (15 cm^3). Sodium acetylacetonate (0.10 g, 0.85 mmol) was added and the purple suspension was stirred for 1 h at room temperature under a nitrogen atmosphere. The resulting brown solution was filtered through Celite to remove precipitated NaCl and the solvent removed *in vacuo*. The remaining brown oil was dissolved in the minimum volume of refluxing hexane under a nitrogen atmosphere and allowed to stand at *c.* −20 °C overnight, resulting in the separation of the product as a brown precipitate which was isolated by filtration and air dried. Yield: 0.13 g, 0.36 mmol, 52%. *Anal.* Found: C, 48.50; H, 6.20; Cl, 9.35. Calc. for $C_{15}H_{23}ClO_2Ru$: C, 48.45; H, 6.25; Cl, 9.35%.

$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(CF_3\cdot CO\cdot CH\cdot CO\cdot CH_3)]$ *(8)*

Treatment of **3** (0.10 g, 0.16 mmol) with $Na[CF_3\cdot CO\cdot CH\cdot CO\cdot CH_3)]$ (0.069 g, 0.45 mmol) in a similar way to that outlined above for the preparation of **7** over a period of 72 h, gave, after work-up, the product as a brown powder. Yield: 0.023 g, 0.054 mmol, 33%. *Anal.* Found: C, 41.70; H, 4.85. Calc. for $C_{15}H_{20}ClF_3O_2Ru$: C, 42.35; H, 4.75%.

$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(N_2C_{10}H_8)(OH_2)][BF_4]_2$ *(10)*

$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(N_2C_{10}H_8)][BF_4]$ (0.06 g, 0.12 mmol) was dissolved in undried acetone (5 cm^3) and stirred with $Ag[BF_4]$ (0.03 g, 0.16 mmol) for 1 h. The resulting orange solution was filtered through Celite and the filtrate added to diethyl ether (20 cm^3) resulting in the formation of the product as a hygroscopic yellow precipitate which was recovered by filtration and dried *in vacuo*. Yield: 0.04 g, 0.07 mmol, 58%. *Anal.* Found: C, 40.85; H, 4.45; N, 4.70. Calc. for $C_{20}H_{26}B_2F_8N_2ORu$: C, 41.05; H, 4.50; N, 4.80%. The product was also prepared more cleanly in comparable yield, by the analogous reaction in anhydrous thf followed by recrystallisation from 'wet' CH_2Cl_2.

$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(N_2C_{12}H_8)(OH_2)][BF_4]_2$ *(11)*

$[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(N_2C_{12}H_8)][BF_4]$ (0.39 g, 0.72 mmol) was dissolved in undried acetone (5 cm^3) and stirred with $Ag[BF_4]$ (0.15 g, 0.77 mmol) for 1 h. The resulting orange solution was filtered through Celite and the volume reduced to *c.* 1 cm^3 resulting in the formation of the product as yellow–green microcrystals which were recovered by filtration, washed sparingly with acetone and diethyl ether and air dried. Yield: 0.33 g, 0.54 mmol, 75%. *Anal.* Found: C, 43.40; H, 4.30; N, 4.95. Calc. for $C_{22}H_{26}B_2F_8N_2ORu$: C, 43.40; H, 4.30; N, 4.60%.

Crystallography

Crystal data

8: $C_{15}H_{20}ClF_3O_2Ru$, $M = 425.84$ g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 7.377(1)$, $b = 16.054(3)$, $c = 14.662(3)$, $\beta = 104.59(2)°$, $U = 1680$ Å^3 (by least-squares refinement of diffractometer angles for 45 automatically centred reflections in the range $16 \leqslant 2\theta \leqslant 30°$, $\lambda = 0.71073$ Å), $Z = 4$, $F(000) = 856$, $D_c = 1.68$ g cm^{-3}, μ(Mo Kα) = 11.06 cm^{-1}. Red block 0.60×0.55×0.35 mm.

Data collection and processing

The ω-2θ technique was used to collect 4318 (3875 unique) data in the range $5 \leqslant 2\theta \leqslant 50°$ on a Nicolet R3mV diffractometer equipped with graphite monochromated Mo Kα radiation. Three standards monitored every 97 reflections showed no appreciable change in intensity throughout the data collection. Data were corrected for Lorentz and polarisation effects and for absorption based on additional azimuthal scan data. Omission of intensities of $I \leqslant 3\sigma(I)$ gave 3011 observed data which were employed in the analysis.

Structure analysis and refinement

The structure was solved by a combination of conventional Patterson methods and difference-Fourier synthesis. The asymmetric unit contained one complete molecule. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in idealised positions and allowed to ride on the atoms to which they were attached (C–H 0.96 Å, U_{iso} 0.08 Å^2). The final cycle of least-squares refinement included 199 parameters (weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.000333F^2$) and did not shift any parameter by more than 0.006 times its standard deviation. The final residuals were $R = 0.0368$ and $R_w = 0.0394$. The largest peak in the final electron density difference map was 0.60 e Å^{-3}.

All calculations were carried out using the SHELXTL PLUS program package [25] on a Micro Vax II computer. Final fractional atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for *equatorial*-[Ru(η^3·η^3-$C_{10}H_{16}$)Cl(CH_3·CO·CH CO CF_3)] (**8a**)

	x	*y*	*z*	U_{eq}
Ru(1)	1501(1)	1760(1)	3022(1)	38(1)
Cl(1)	1602(2)	2536(1)	1645(1)	64(1)
O(1)	1307(4)	1235(2)	4306(2)	51(1)
O(2)	306(4)	2871(2)	3388(2)	56(2)
C(11)	948(9)	1130(3)	5853(3)	79(2)
C(12)	687(6)	1599(3)	4931(3)	52(1)
C(13)	−153(6)	2393(3)	4863(3)	54(2)
C(14)	−286(6)	2937(3)	4121(3)	50(1)
C(15)	−1259(7)	3777(3)	4149(3)	59(2)
F(3)	−73(4)	4403(2)	4189(2)	78(1)
F(2)	−1997(7)	3864(2)	4871(3)	123(2)
F(1)	−2621(5)	3901(2)	3375(3)	102(1)
C(1)	4170(6)	2430(3)	3696(3)	61(2)
C(2)	4597(6)	1588(3)	3710(3)	52(1)
C(3)	4128(6)	1172(3)	2826(3)	57(2)
C(4)	4201(7)	219(3)	2746(4)	75(2)
C(5)	5278(8)	1123(4)	4608(3)	77(2)
C(6)	2309(7)	−28(3)	2150(4)	67(2)
C(7)	895(6)	440(3)	2550(3)	53(1)
C(8)	−565(6)	926(3)	2006(3)	54(1)
C(9)	−1506(6)	1427(3)	2516(4)	64(2)
C(10)	−961(8)	995(4)	945(3)	77(2)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3 Selected bond lengths (Å) and angles (°) for *equatorial*-[Ru(η^3:η^3-$C_{10}H_{16}$)Cl(CH_3 CO·CH CO·CF_3)] (**8a**)

Bond lengths			
Ru–Cl(1)	2.390(1)	Ru–O(1)	2.099(3)
Ru–O(2)	2.117(3)	Ru–C(1)	2.243(4)
Ru–C(2)	2.269(4)	Ru–C(3)	2.238(4)
Ru–C(7)	2.240(4)	Ru–C(8)	2.279(4)
Ru–C(9)	2.220(4)	O(1)–C(12)	1.266(6)
O(2)–C(14)	1 262(6)	C(11)–C(12)	1.517(7)
C(12)–C(13)	1.410(6)	C(13)–C(14)	1.379(6)
C(14)–C(15)	1.533(6)	C(15)–F(1)	1.328(6)
C(15)–F(2)	1 314(7)	C(15)–F(3)	1 324(6)
C(1)–C(2)	1.386(6)	C(2)–C(3)	1.421(6)
C(2)–C(5)	1.486(7)	C(3)–C(4)	1.537(7)
C(4)–C(6)	1.501(7)	C(6)–C(7)	1.517(7)
C(7)–C(8)	1.405(6)	C(8)–C(9)	1.397(7)
C(8)–C(10)	1.513(6)		
Bond angles			
Cl(1)–Ru–O(1)	172 0(1)	Cl(1)–Ru–O(2)	83 0(1)
O(1)–Ru–O(2)	89.1(1)	Cl(1)–Ru–C(2)	101.3(1)
O(1)–Ru–C(2)	80.9(1)	O(2)–Ru–C(2)	115.2(1)
O(1)–C(12)–C(13)	126.8(4)	C(12)–C(13)–C(14)	124 8(4)
O(2)–C(14)–C(13)	130.4(4)		

Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises H atom coordinates, thermal parameters and remaining bond lengths and angles.

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