Mono- and Bi-dentate Carboxylato Complexes of Ruthenium(IV)†

Brian Kavanagh, Jonathan W. Steed and Derek A. Tocher*
Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, UK

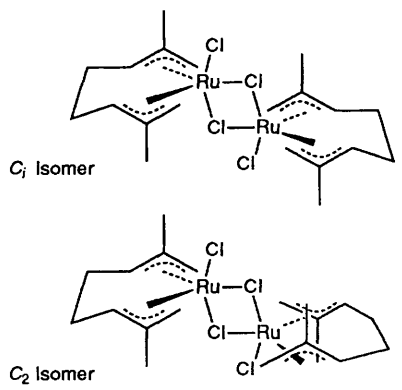
Treatment of the ruthenium(IV) chloro-bridged dimer $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **1** with sodium acetate or silver acetate at room temperature in acetone gives the chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ **2**. Refluxing **1** in trifluoroacetic acid, or reaction of **1** at room temperature with $Ag[CF_3CO_2]$ gives the monodentate, dicarboxylate species $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(OH_2)]$ **3**, which contains a tightly bound water ligand. A range of chloro and fluoro substituted carboxylato complexes has been prepared (**5**–**9**) and the 'cross-over' point between mono- and bi-dentate co-ordination determined. The hexafluoro β-diketonate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{F_3CC(O)CHC(O)CF_3\}]$ **10**, exhibits the expected bidentate mode of co-ordination. Reaction of **1** with thioacetic acid over short reaction times yields the adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\{SC(OH)Me\}]$ **11**. The corresponding chelate species $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(SOCMe)]$ **12**, is formed over longer reaction times. Analogous reactions with thiopivalic and thiobenzoic acids result only in the isolation of the chelate products $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(SOCR)]$ (R = Bu^t **13** or Ph **14**). The structures of complexes **2** and **3** have been verified by X-ray crystallography.

The bis(allyl) ruthenium(IV) complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ **1**[1,2] is clearly related to the well known family of ruthenium(II) chloro-bridged dimer compounds $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6 *etc.*).[3,4] In contrast to the intensely studied[5–10] arene analogues however, the chemistry of **1** has remained relatively neglected. Compound **1** offers a facile gateway into the higher oxidation state organometallic chemistry of ruthenium, and that fact, coupled with the unusual steric requirements of the bis(allyl) 2,7-dimethylocta-2,6-diene-1,8-diyl ligand have recently brought about a strong surge of interest in its reactivity.[11–18]

Compound **1** has been shown[13] to exist as two diastereoisomers, referred to as the C_i (*meso*) and C_2 (*rac*) forms, arising as a consequence of the chirality of the $(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru$ unit. These isomers are readily distinguished by ^1H NMR spectroscopy, giving rise to a characteristic 'doubling' of the number of resonances expected for a single compound. Thus in **1** there are eight singlet resonances arising from the terminal allyl protons of the bis(allyl) ligand and four from the methyl groups. Non-diastereomeric (though still chiral), mononuclear complexes derived from **1** display half this number of resonances if the axial sites of the approximately trigonal-bipyramidal ruthenium ion are different from one another. More symmetric equatorial, adducts such as $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(CO)]$,[19] give rise to only two terminal allyl and a single methyl signal.

In previous reports[20,21] we have examined the reactions of areneruthenium(II) complexes with a wide range of carboxylate and α-hydroxypyridinate ligands while, more recently, we have investigated the formation of binuclear, carboxylato-bridged complexes, such as the oxalato derivative $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\}_2(\mu\text{-}C_2O_4)]$.[22] We now describe our investigations into the reactions of **1** with a range of carboxylato ligands to form mononuclear complexes containing mono- and bi-dentate carboxylates. Our studies on the reactions of **1** with α-hydroxypyridinate ligands are reported elsewhere.[23] A preliminary report of part of this work has already been published.[24]

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



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Experimental

Infrared spectra were recorded on a PE983 grating spectrometer between 4000 and 180 cm^{-1} as either KBr discs or Nujol mulls on CsI plates, NMR spectra on Varian XL200 and VXR400 spectrometers. Microanalyses were carried out by the departmental service at University College London. Mass spectra were run by the University of London Intercollegiate Research Service at the School of Pharmacy. 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.

The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ was prepared by published literature methods.[1,13,15] Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by dissolution in water and boiling to dryness. Sodium carboxylates were prepared by reaction of sodium metal with solutions of the acids in dry tetrahydrofuran (thf), or alternatively with the neat acid, for those that are liquids. Silver salts were prepared by the reaction of the aqueous acid with Ag_2O.[25] All other reagents and materials were obtained from the usual commercial sources.

Preparations.—$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ **2**. (*a*) The

compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.040 g, 0.065 mmol) was suspended in acetone (5 cm^3), $Ag[MeCO_2]$ (0.022 g, 0.133 mmol) was added and the mixture stirred for 1 h. The resulting orange-red solution was filtered through Celite to remove the precipitate of AgCl and the solvent removed *in vacuo* to give an orange oil which was recrystallised from diethyl ether. Yield: 0.026 g, 0.078 mmol, 60% (Found: C, 43.65; H, 5.85. Calc. for $C_{12}H_{19}ClO_2Ru$: C, 43.45; H, 5.75%).

(*b*) The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.200 g, 0.324 mmol) was suspended in acetone (5 cm^3), $Na[MeCO_2]$ (0.05 g, excess) was added and the mixture stirred for 24 h. The resulting product was recovered in a similar manner to (*a*). Yield: 0.185 g, 0.559 mmol, 86%.

(*c*) Attempts to prepare **2** by refluxing **1** in acetic acid resulted in the formation of a dark brown colouration over a period of *ca.* 4 h. However no product could be isolated probably due to high solubility in this reaction mixture.

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(OH)_2]$ **3**. (*a*) The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.096 g, 0.156 mmol) was suspended in 'wet' acetone (5 cm^3). Silver trifluoroacetate (0.127 g, 0.574 mmol) was added and the mixture stirred for 1 h. The resulting orange solution was filtered through Celite to remove the precipitate of AgCl and the volume reduced to *ca.* one quarter resulting in the precipitation of the orange product which was isolated by filtration, washed with acetone and diethyl ether and air dried. Yield: 0.096 g, 0.200 mmol, 64% (Found: C, 35.10; H, 3.75. Calc. for $C_{14}H_{18}F_6O_5Ru$: C, 34.95; H, 3.75%).

(*b*) The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.195 g, 0.316 mmol) was refluxed in trifluoroacetic acid (15 cm^3) in the presence of trifluoroacetic anhydride (3 cm^3) for 4 h. The resulting red-brown solution was filtered through Celite to remove particulate matter, evaporated to *ca.* half volume and layered with hexane. The product separated out as large, orange crystals after standing for 48 h at 250 K. Yield: 0.215 g, 0.446 mmol, 71%.

(*c*) The product may also be prepared in near-quantitative yield by refluxing of the acetate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ **2** in neat CF_3CO_2H, followed by work-up in a similar manner as described in (*b*).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(N_2C_4H_4)]$ **4**. To $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(OH_2)]$ (0.079 g, 0.165 mmol) was added pyrazine (0.017 g, 0.212 mmol) and the mixture stirred in CH_2Cl_2 (5 cm^3) for 72 h. The resulting orange solution was evaporated to *ca.* one quarter volume and hexane added to precipitate the product as an orange, microcrystalline solid which was isolated by filtration, washed with diethyl ether and air dried. Yield: 0.068 g, 0.126 mmol, 76% (Found: C, 39.55; H, 3.60; N, 5.15. Calc. for $C_{18}H_{20}F_6N_2O_4Ru$: C, 39.80; H, 3.70; N, 5.15%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCCl_3)_2(OH_2)]$ **5**. To a solution of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.120 g, 0.195 mmol) in CH_2Cl_2 (4 cm^3) was added an acetone (4 cm^3) suspension of $Na[CCl_3CO_2]$ (0.181 g, 0.979 mmol). The mixture was stirred for 12 h at room temperature. The resulting brown-orange solution was filtered through Celite to remove the precipitate of NaCl and the solvents removed *in vacuo* to give a dark solid. Recrystallisation from chloroform–diethyl ether (1:1 v/v) yielded bright yellow crystals which were isolated by filtration and air dried. Yield: 0.102 g, 0.176 mmol, 45% (Found: C, 28.75; H, 3.25; Cl, 37.45. Calc. for $C_{14}H_{18}Cl_6O_5Ru$: C, 29.00; H, 3.15; Cl, 36.65%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCHCl_2)_2(OH_2)]$ **6**. A similar procedure to that employed for **5** was followed using $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.120 g, 0.195 mmol) and $Na[CHCl_2CO_2]$ (0.146 g, 0.967 mmol). Yield: 0.100 g, 0.196 mmol, 50% (Found: C, 32.80; H, 4.00; Cl, 27.75. Calc. for $C_{14}H_{20}Cl_4O_5Ru$: C, 32.90; H, 3.90; Cl, 28.50%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCHF_2)_2(OH_2)]$ **7**. A similar procedure to that employed for **5** was followed using $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.060 g, 0.097 mmol) and $Na[CHF_2CO_2]$ (0.058 g, 0.492 mmol). The product was purified by dry flash column chromatography and recrystallised from CH_2Cl_2–diethyl ether (1:1 v/v). Yield: 0.020 g, 0.045 mmol, 23% (Found: C, 37.80; H, 4.75. Calc. for $C_{14}H_{20}F_4O_5Ru$: C, 37.75; H, 4.55%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_2Cl)]$ **8a** *and* $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCH_2Cl)_2(OH_2)]$ **8b**. To a solution of $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.120 g, 0.195 mmol) in CH_2Cl_2 (4 cm^3) was added $Na[CH_2ClCO_2]$ (0.116 g, 0.996 mmol) in acetone (4 cm^3). The mixture was stirred at room temperature for 12 h. Removal of the solvents *in vacuo* gave a yellow oily product which was recrystallised from diethyl ether–hexane (1:4 v/v) to give 0.055 g of orange-yellow crystals which were shown by ^1H NMR spectroscopy to be a mixture of **8a**, **8b** and unreacted starting material. Pure samples of **8a** and **8b** were isolated by dry flash column chromatography (Found: C, 39.75; H, 5.25. Calc. for $C_{12}H_{18}Cl_2O_2Ru$, **8a**: C, 39.35; H, 4.95%. Found: C, 36.80; H, 5.20. Calc. for $C_{14}H_{22}Cl_2O_5Ru$, **8b**: C, 38.00; H, 5.00%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_2F)]$ **9a** *and* $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCH_2F)_2(OH_2)]$ **9b**. A similar procedure to that adopted for **8a** and **8b** was employed using $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.120 g, 0.195 mmol) and $Na[CH_2FCO_2]$ (0.100 g, 0.998 mmol) to give 0.017 g of a yellow material shown by ^1H NMR to be a mixture of **9a** and **9b**. The products were separated by dry flash column chromatography (Found: C, 40.40; H, 5.55. Calc. for $C_{12}H_{18}ClF_2O_2Ru$, **9a**: C, 41.20; H, 5.20%. Found: C, 39.85; H, 5.70. Calc. for $C_{14}H_{22}F_2O_5Ru$, **9b**: C, 41.05; H, 5.40%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{F_3CC(O)CHC(O)CF_3\}]$ **10**. (*a*) The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.043 g, 0.070 mmol) was suspended in acetone (5 cm^3), $Ag[CF_3C(O)CHC(O)CF_3]$ (0.1 g, excess) was added and the mixture stirred for 24 h. The resulting pale orange solution was filtered through Celite to remove the precipitate of AgCl and unreacted starting material and the solvent removed *in vacuo* to give an orange oil which was recrystallised from diethyl ether. Yield: 0.015 g, 0.031 mmol, 22% (Found: C, 36.90; H, 3.50. Calc. for $C_{15}H_{17}ClF_6O_2Ru$: C, 37.55; H, 3.55%). Some difficulty was noted in the separation of the product from the excess of silver hexafluoroacetylacetonate.

(*b*) The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.053 g, 0.086 mmol) was suspended in acetone (5 cm^3), $Na[CF_3C(O)CHC(O)CF_3]$ (0.040 g, 0.194 mmol) was added and the mixture stirred at room temperature for 2 weeks. The product was isolated as in (*a*). Yield: 0.028 g, 0.059 mmol, 34%.

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\{SC(OH)CH_3\})]$ **11**. The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.072 g, 0.117 mmol) was stirred in acetone (5 cm^3) containing a small excess of thioacetic acid (0.2 cm^3) for 15 min during which time the solution became bright orange. The solvent was removed *in vacuo* to give an orange oil from which the product was deposited as orange crystals. These were filtered off and washed with *n*-hexane, then air dried. Yield: 0.074 g, 0.193 mmol, 82% (Found: C, 37.60; H, 5.50. Calc. for $C_{12}H_{20}Cl_2ORuS$: C, 37.50; H, 5.25%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(SOCMe)]$ **12a**, **12b**. The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.111 g, 0.180 mmol) was stirred in CH_2Cl_2 (5 cm^3) with a small excess of thioacetic acid (0.2 cm^3) for 24 h during which time the bright orange colouration initially formed darkened to a deep brown. The reaction mixture was evaporated to *ca.* one quarter volume and diethyl ether added to precipitate the product as a red-brown solid which was isolated by filtration and air dried. Yield: 0.08 g, 0.196 mmol, 54% (Found: C, 42.40; H, 5.55. Calc. for $C_{12}H_{19}ClORuS$: C, 41.45; H, 5.50%).

$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(SOCBu^t)]$ **13a**, **13b**. The compound $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ (0.057 g, 0.093 mmol) was stirred in acetone (5 cm^3) with a small excess of thiopivalic acid (0.2 cm^3) for 1 h during which time a deep orange solution formed. The reaction mixture was evaporated to an orange oil which yielded an orange precipitate on trituration with methanol–hexane (1:2 v/v). The product was isolated by filtration and air dried. Yield: 0.064 g, 0.164 mmol, 88% (Found: C, 47.15; H, 6.90. Calc. for $C_{15}H_{25}ClORuS$: C, 46.20; H, 6.45%).

Table 1 Atomic coordinates ($\times 10^4$) for [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CMe)] **2**

Atom	x	y	z
Ru	872(1)	1555(1)	1185(1)
Cl	−870(2)	1787(2)	630(2)
O(1)	1494(5)	1150(5)	−168(4)
O(2)	2468(5)	1226(4)	1051(4)
C(1)	563(7)	−1(6)	1231(6)
C(2)	278(7)	389(6)	2076(6)
C(3)	1106(7)	884(6)	2506(6)
C(4)	962(8)	1473(7)	3374(6)
C(5)	315(9)	2375(8)	3184(7)
C(6)	411(7)	2646(6)	2175(6)
C(7)	1358(8)	2936(6)	1752(7)
C(8)	1283(8)	3016(7)	798(7)
C(9)	−832(8)	383(7)	2417(7)
C(10)	2392(8)	3025(8)	2240(7)
C(11)	2376(8)	1045(6)	192(6)
C(12)	3283(7)	682(8)	−350(8)

Table 2 Atomic coordinates ($\times 10^4$) for [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$(OH_2)] **3**

Atom	x	y	z
Ru	5000	6634(1)	2500
O(1)	5000	5394(2)	2500
O(2)	6282(3)	6578(2)	1373(3)
O(3)	5630(4)	5654(3)	−281(5)
C(1)	6375(4)	6081(3)	448(6)
C(2)	7505(5)	6075(4)	70(8)
C(3)	3488(4)	6436(3)	560(5)
C(4)	3918(3)	7167(3)	388(4)
C(5)	3996(3)	7676(2)	1587(4)
C(6)	4586(5)	8456(3)	1728(6)
C(7)	4383(4)	7351(3)	−924(5)
F(1)	7778(17)	6749(7)	−321(32)
F(2)	8283(15)	5875(20)	1143(22)
F(3)	7538(15)	5640(15)	−1008(27)
F(1A)	7424(17)	6353(22)	−1238(24)
F(2A)	8337(13)	6396(16)	1007(25)
F(3A)	7893(15)	5360(9)	−25(41)

[Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOCPh)] **14a**,**14b**. The compound [{Ru(η^3:η^3-$C_{10}H_{16}$)Cl(μ-Cl)}$_2$] (0.01 g, 0.116 mmol) was stirred in acetone (5 cm^3) with a small excess of thiobenzoic acid (0.1 cm^3) for 1 h resulting in the formation of a bright orange solution. The solvent was removed *in vacuo* and the residue dissolved in diethyl ether (1 cm^3) and layered with hexane resulting in the formation of a deep red crystalline product over a period of *ca.* 12 h. This product was collected by filtration and air dried. Yield: 0.057 g, 0.139 mmol, 60% (Found: C, 49.65; H, 5.00. Calc. for $C_{17}H_{21}ClORuS$: C, 49.80; H, 5.15%).

Crystallography.—*Crystal data.* $C_{12}H_{19}ClO_2Ru$ **2**, M = 331.80, orthorhombic, space group *Pbca*, a = 12.742(6), b = 14.082(6), c = 14.614(6) Å, U = 2622 $Å^3$ (by least-squares refinement of diffractometer angles for 30 automatically centred reflections in the range $10 \leqslant 2\theta \leqslant 23°$, λ = 0.710 73 Å), Z = 8, $F(000)$ = 1344, D_c = 1.68 g cm^{-3}, μ(Mo-Kα) = 13.63 cm^{-1}. Pink plate, 0.4 × 0.3 × 0.05 mm.

$C_{14}H_{18}O_5F_6Ru$ **3**, M = 481.39, monoclinic, space group $C2/c$, a = 12.191(3), b = 17.318(5), c = 9.314(2) Å, β = 105.14(2)°, U = 1898 $Å^3$ (by least-squares refinement diffractometer angles for 46 automatically centred reflections in the range $15 \leqslant 2\theta \leqslant 30°$, λ = 0.710 73 Å), Z = 4, $F(000)$ = 960, D_c = 1.68 g cm^{-3}, μ(Mo-Kα) = 8.80 cm^{-1}. Orange wedge, 0.6 × 0.25 × 0.2 mm.

Data collection and processing. The ω–2θ technique was used to collect 2576 (compound **2**, 2270 unique) and 2116 (compound **3**, 1675 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 either 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 1381 (**3**) and 1568 (**3**) observed data which were employed in the analysis.

Table 3 Selected bond lengths (Å) and angles (°) for [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CMe)] **2**

Ru–Cl	2.385(3)	Ru–O(1)	2.205(6)
Ru–O(2)	2.095(6)	Ru–C(1)	2.227(8)
Ru–C(2)	2.227(9)	Ru–C(3)	2.169(9)
Ru–C(6)	2.191(9)	Ru–C(7)	2.203(9)
Ru–C(8)	2.197(10)	O(1)–C(11)	1.249(11)
O(2)–C(11)	1.287(10)	C(11)–C(12)	1.491(14)
Cl–Ru–O(1)	93.7(2)	Cl–Ru–O(2)	154.4(2)
O(1)–Ru–O(2)	60.7(2)	O(1)–C(11)–O(2)	118.0(8)

Table 4 Selected bond lengths (Å) and angles (°) for [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$(OH_2)] **3**

Ru–O(1)	2.146(4)	Ru–O(2)	2.100(3)
Ru–C(3)	2.245(4)	Ru–C(4)	2.260(4)
Ru–C(5)	2.221(4)	O(2)–C(1)	1.244(6)
O(3)–C(1)	1.229(6)	C(1)–C(2)	1.509(9)
O(1)–Ru–O(2)	87.4(1)	O(2)–Ru–O(2A)	174.8(1)
Ru–O(2)–C(1)	126.3(3)	O(2)–C(1)–O(3)	127.7(5)

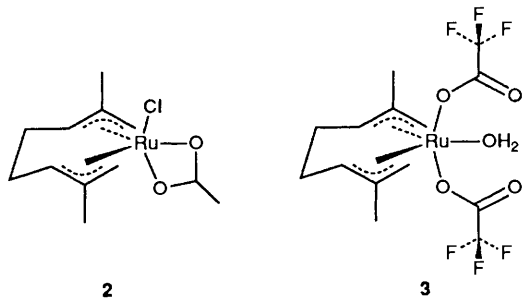
Atoms labelled A generated by two-fold rotation about $\frac{1}{2}$, y, $\frac{1}{4}$.

Structure analysis and refinement. The structures were solved by a combination of conventional direct methods (**2**), Patterson methods (**3**) and Fourier difference synthesis. The asymmetric unit for **2** contained one complete molecule, while for **3** it was one half of the molecule, which sits on a crystallographic two-fold axis. In both cases 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 $Å^2$). For compound **2** the final cycle of least-squares refinement included 145 parameters [weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,338F^2$] and did not shift any parameter by more than 0.002 times its standard deviation (R = 0.0447, R' = 0.0458). The largest residual peak was 0.523 e $Å^{-3}$.

In the case of compound **3** the final cycle included 146 parameters [weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,350F^2$] and gave R = 0.0384, R' = 0.0395. The fluorine atoms of the CF_3 groups were found to be disordered and were each modelled as having two positions, each of 50% occupancy. The largest shift to error ratio was 0.116 (associated with a thermal parameter for one of the disordered fluorine atoms) and the largest residual peak was 0.81 e $Å^{-3}$. Intermolecular short contacts of 2.70 Å were observed between oxygen atoms of the co-ordinated water molecules and the unco-ordinated oxygen atoms of trifluoroacetate ligands in adjacent molecules (see Discussion). Attempts to refine the structure of **3** in the non-centrosymmetric space group *Cc* (in which disorder need not be present) were unsuccessful.

All calculations were carried out using the SHELXTL PLUS program package [26] on a MicroVax II computer. Final fractional atomic coordinates are given in Tables 1 and 2 and selected bond lengths and angles in Tables 3 and 4 for compounds **2** and **3** respectively.

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



2 3

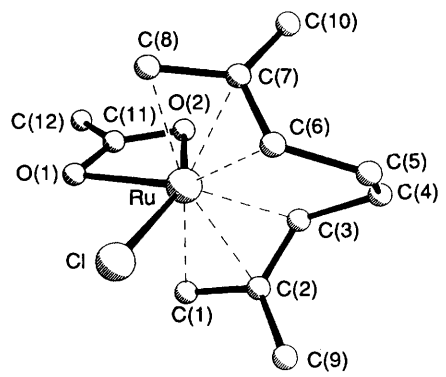


Fig. 1 Crystal structure of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ **2** showing the atom numbering scheme adopted

Results and Discussion

In our previous work [20] we demonstrated that areneruthenium(II) carboxylato complexes may be synthesised by one or more of three general methods: (*i*) reflux of the appropriate areneruthenium(II) chloro-bridged dimer in a mixture of the neat acid and the acid anhydride; (*ii*) treatment of $[\{Ru(arene)Cl(\mu\text{-}Cl)\}_2]$ with two mole equivalents of silver carboxylate in acetone or benzene; or (*iii*) reaction of $[\{Ru(arene)Cl(\mu\text{-}Cl)\}_2]$ with an excess of sodium carboxylate in acetone.

The greater solubility of complexes derived from **1**, in comparison to their areneruthenium(II) analogues, makes method (*i*) unsuitable for all but the most insoluble products and it is found that, in general, reaction of **1** with silver- or sodium-carboxylates is most likely to lead to the formation and isolation of the desired products.

The reaction of **1** with $Ag[MeCO_2]$ proceeds rapidly at room temperature in acetone to give a red solution from which the chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ **2**, analogous to the areneruthenium(II) complexes previously synthesised,[20] may be isolated in good yield. The reaction also proceeds, albeit more slowly, with sodium acetate but we were unable to recover any complexes from the direct interaction of **1** with refluxing acetic acid because of the high solubility of the products in this medium. The solid-state infrared spectrum of **2** (Table 5) displays two strong bands at 1517 and 1461 cm^{-1}, assignable respectively to $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ [27] {*cf.* 1510, 1470 cm^{-1} for $[Ru(\eta^6\text{-}C_6H_6)Cl(O_2CMe)]$ [20]}. A $\Delta\nu$ ($=\nu_{asym} - \nu_{sym}$) value of 56 cm^{-1} clearly indicates a chelate mode of co-ordination for the carboxylate ligand.[27] Medium intensity bands at 345 and 273 cm^{-1} are assigned to ν(RuO) and ν(RuCl) respectively. An electron impact mass spectrum (^{102}Ru, ^{35}Cl) of this material displayed peaks centred on *m/z* 317 $\{[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2C)]^+\}$, 297 $\{[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CMe)]^+\}$ and 235 $\{[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})]^+\}$ with isotope distribution patterns consistent with the presence of one ruthenium atom. The ^1H NMR spectrum of **2** (Table 6) displays a pattern of $\eta^3:\eta^3\text{-}C_{10}H_{16}$ resonances closely analogous to those already reported for the chelate benzothiazole-2-thiolate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(SNC_7H_4SH\text{-}2)]$ [15] and the 2,2′-bipyridine (bipy) complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(bipy)][BF_4]$.[18] The terminal allylic protons of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand give rise to four singlet signals (δ 5.51, 4.65, 4.63 and 3.56, $^2J_{syn\text{-}anti}$ not observed) while the methyl substituents resonate at δ 2.29 and 2.12, a spectrum consistent with inequivalent axial sites on the trigonal-bipyramidal ruthenium ion. A further singlet resonance, observed at δ 1.85, is due to the acetate methyl group. The formulation and structure of **2** was unequivocally confirmed by a single-crystal X-ray structure determination, Fig. 1.

The formation of **2** contrasts sharply with the much more insoluble deep orange trifluoroacetate product $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(OH_2)]$ **3**,* readily obtained by methods (*i*) and (*ii*) above. We have however, been unable to isolate the corresponding 1:1 chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCF_3)]$ since the interaction of **1** with only two mole equivalents of $Ag[CF_3CO_2]$ gives a low yield of **3** along with a large quantity of unreacted starting material. This observation contrasts with that made in the area of areneruthenium(II) chemistry where the compounds $[Ru(\eta^6\text{-arene})Cl(O_2CCF_3)]$ (arene = C_6H_6 or C_6Me_6) can be readily synthesised by methods (*i*) and (*ii*).[20] Interestingly the reaction of the bis(acetato) complexes $[Ru(\eta^6\text{-arene})(O_2CMe)_2]$ with trifluoroacetic acid gives bis(trifluoroacetato) complexes, tentatively formulated as $[Ru(\eta^6\text{-arene})(O_2CCF_3)_2]\cdot H_2O$, which crystallise as monohydrates.[20] The water of crystallisation in these complexes occurs as a broad resonance at δ *ca.* 6 in the ^1H NMR spectrum and is thought to be only loosely associated with the metal atom.

The ^1H NMR spectrum of **3**, in $CDCl_3$, displays only half the number of $\eta^3:\eta^3\text{-}C_{10}H_{16}$ resonances of **2**, *viz* two terminal allyl singlets (δ 5.68 and 4.23) and a single methyl resonance (δ 2.12) indicative of equivalent axial sites on the trigonal-bipyramidal ruthenium atom and inconsistent with a compound containing both mono- and bi-dentate carboxylate ligands. The water ligand occurs as a sharp singlet resonance at δ 7.11, broadening somewhat in $[^2H_3]$nitromethane solution. The ^{19}F NMR spectrum displays a single singlet resonance at δ −76.50 (relative to $CFCl_3$), close to the value observed for the free acid (δ −76.41) but somewhat upfield of the corresponding resonance in the fluxional arene complex $[Ru(\eta^6\text{-}C_6H_6)(O_2CCF_3)_2]\cdot H_2O$ (δ −74.71).[20] This latter signal represents an average between mono- and bi-dentate co-ordination. In the infrared spectrum, **3** displays a strong, broad band at 3362 cm^{-1} assignable to ν(OH) and indicative of hydrogen bonding in the solid state. The trifluoroacetate ligands give ν(CF) bands at 1196 and 1143 cm^{-1}, $\nu_{asym}(OCO)$ at 1703 and 1670 cm^{-1} and $\nu_{sym}(OCO)$ at 1421 cm^{-1}. The much larger value of Δν (249–282 cm^{-1}) is suggestive of a monodentate mode of co-ordination.

Compound **3** will sublime intact at *ca.* 100 °C under reduced pressure with no trace of displacement of the water molecule and similarly refluxing **3** in dry dichloromethane containing anhydrous magnesium sulfate results in the recovery of the unchanged material. These observations suggest that the water molecule in **3** is strongly bound and actually forms part of the co-ordination sphere of the metal ion with the two trifluoroacetate ligands bonding in a monodentate mode at the axial sites, consistent with the ^1H NMR data. This contention is further supported by the low substitutional lability of the water ligand which is slowly displaced by pyrazine over a period of days at room temperature, to give the adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2(N_2C_4H_4)]$ **4** along with a quantity of residual **3**.

The formulation of **3** was confirmed by a single-crystal X-ray structure determination. Fig. 2 shows the water molecule to occupy one of the equatorial co-ordination sites of the trigonal-bipyramidal ruthenium ion while the two trifluoroacetato

* A trifluoroacetato bridged complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCF_3)_2\}_2]$ has been reported [28] to be formed from the reaction of thallium trifluoroacetate with **1** although no spectroscopic data were quoted and we find no evidence for the existence of this material.

Table 5 Selected infrared data for new complexes[a]

Compound	Infrared absorption/cm^{-1} ν_{asym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$	ν(OH$_2$)	ν(RuCl)	Other
2 [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CMe)]	1517s	1461s	56	—	273m	345m ν(RuO)
3 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$(OH_2)]	1703vs, 1670vs	1421m	249–282	3362s (br)	—	1196s, 1143s ν(CF)
5 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCCl_3)$_2$(OH_2)]	1702vs, 1680vs	1323s	379–357	3390s (br)	—	844s, 831s ν(CCl)
6 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCHCl_2)$_2$(OH_2)]	1671s, 1629s	1359s, 1341s	270–330	3372s	—	814s, 787s ν(CCl)
7 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCHF_2)$_2$(OH_2)]	1660s, 1625s	1436	189–224	3317s	—	1117s, 1064s ν(CF)
8a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2Cl)]	1526s, 1519s	1452s, 1441s	67–85	—	*b*	790m ν(CCl)
8b [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCH_2Cl)$_2$(OH_2)]	1612s	1374s	238	3326s	—	784m ν(CCl)
9a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2F)]	1556s, 1536s	1466s, 1454s	70–102	—	*b*	1076s, 1066s ν(CF)
9b [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCH_2F)$_2$(OH_2)]	1617s	1419s	198	3328s	—	1085s ν(CF)
10 [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{$F_3CC(O)CHC(O)CF_3$}]	1655m, 1623s[c]	—	—	—	317s	1258s (br), 1205s (br), 1143s (br) ν(CF)

[a] Spectra run in Nujol mulls or as KBr disc. Abbreviations: s = strong, m = medium, w = weak, v = very, br = broad. [b] Impossible to assign unambiguously. [c] ν(CO).

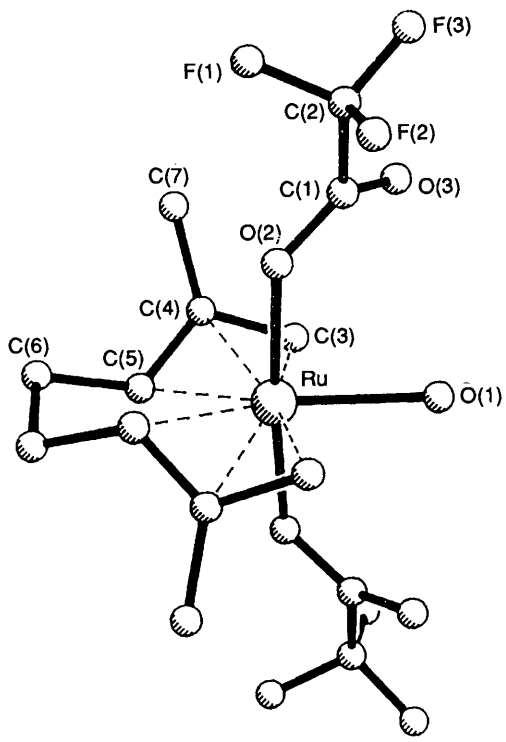


Fig. 2 Crystal structure of [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$(OH_2)] **3** showing the atom numbering scheme adopted

ligands are bound in a monodentate fashion in the axial positions. The Ru–OH_2 distance, 2.146(4) Å, is only slightly longer than the Ru–O bond lengths to the axial trifluoroacetate ligands, 2.100(3) Å, and is very similar to other Ru–L_{eq} distances (L = acetate, pyrazine[14] or 2,2′:6′,2″-terpyridine[18]) and suggests clearly that the water molecule is relatively strongly bound to the metal centre. A similar Ru^{IV}–OH_2 distance [2.165(5) Å] has been observed by us in the related complex [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl(OH_2)][BF_4].[29] Similarly, the cycloocta-1,5-diene (cod) complex [Ru(cod)(OH_2)$_4$][$O_3SC_6H_4$-Me-4]$_2$[30] exhibits Ru–OH_2 distances of 2.158(1) Å *trans* to cod and 2.095(2) Å *trans* to water, while the Fe^{II}–OH_2 distance in the 2,6-diacetylpyridine bis(semicarbazone) (L) complex [FeL(H_2O)$_2$]$^{2+}$ is 2.214 Å.[31]

In solution the aqua ligand is presumably intramolecularly hydrogen bonded to the trifluoroacetato ligands. In the solid state however, an infinite intermolecular hydrogen bonded lattice exists (Fig. 3) with short contacts O(1)···O(3′) of 2.70 Å, implying relatively strong[32] interactions.

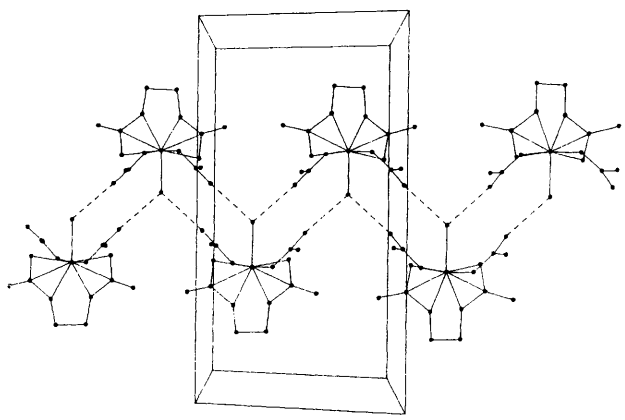


Fig. 3 Crystal packing diagram of [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$(OH_2)] **3**, viewed down the *a* axis (fluorine atoms omitted for clarity)

'Cross-over' between Mono- and Bi-dentate Co-ordination.— The differences in the reactivity of **1** towards acetate and trifluoroacetate ligands is presumably a consequence of the differing electronic properties of the $-CH_3$ and $-CF_3$ substituents. These electronic properties may be quantified, either (*i*) simply by consideration of the pK_a of the neutral acid (a parameter which contains both inductive and resonance components), or (*ii*) by examination of substituent polarity parameters such as the $\mathcal{F}$ parameter of Swain and Lupton[33] (a wide variety of $\mathcal{F}$ values are available, derived from the Hammett constants σ_m and σ_p[34]) which deals solely with the field (*i.e.* inductive as opposed to resonance) effects of substituent groups [$\mathcal{F}(CF_3) = 0.38$, $\mathcal{F}(CH_3) = -0.052$[35]]. Logically there must be a certain value of $\mathcal{F}$ (or pK_a) where the cross-over from mono- to bi-dentate co-ordination occurs. With this in mind, a range of simple chloro- and fluoro-carboxylates has been examined in the hope determining that point and perhaps of finding a ligand exhibiting both types of co-ordination.

We find that interaction of **1** with an excess of the sodium salts of trichloro-, dichloro- and difluoro-acetic acids ($\mathcal{F}_{acid\ substituent}$ = 0.31, 0.17, 0.27;[35] acid pK_a = 0.52, 1.35 and 1.34[36]) gives the complexes [Ru(η^3:η^3-$C_{10}H_{16}$)($O_2CCH_{3-n}X_n$)$_2$(OH_2)] (X = Cl, *n* = 3 **5**; X = Cl, *n* = 2 **6**; X = F, *n* = 2 **7**) which are structurally related to **3**. The ^{1}H NMR spectra of these complexes are all consistent with a geometry incorporating equivalent axial sites. In addition complex **6** displays a single, singlet resonance at δ 5.45 assigned to the $CHCl_2$– group, while the corresponding CHF_2– resonance in **7** appears as a triplet (δ 5.34, $^2J_{H-F}$ = 54.8 Hz).

In analogous reactions involving the sodium salts of chloro- and fluoro-acetic acids mixtures of two complexes are formed, namely [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2X)] (X = Cl **8a** or F **9a**)

Table 6 Proton NMR data for new complexes[a]

Compound	δ (J_{H-H}/Hz) Terminal allyl	Internal allyl	Ethylinic	Me	Ligand
2 [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CMe)]	5.51 (s,1 H), 4.65 (s, 1 H) 4.63 (s, 1 H), 3.56 (s, 1 H)	4.20 (m, 1 H) 3.49 (m, 1 H)	2.53 (m, 4 H)	2.29 (s, 3 H) 2.12 (s, 3 H)	1.85 (s, 3 H, CH_3)
3 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$(OH_2)]	5.68 (s, 2 H), 4.23 (s, 2 H)	4.42 (m, 2 H)	3.07 (m, 2 H) 2.47 (m, 2 H)	2.12 (s, 6 H)	7.11 (s, 2 H, OH_2)
4 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCF_3)$_2$($N_2C_4H_4$)]	5.22 (s, 2 H), 4.16 (s, 2 H)	6.17 (m, 2 H)	3.47 (m, 2 H) 2.71 (m, 2 H)	2.15 (s, 6 H)	8.72, 8.44 (AB, 4 H, ^3J = 3.2, $N_2C_4H_4$)
5 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCCl_3)$_2$(OH_2)]	5.77 (s, 2 H), 4.29 (s, 2 H)	4.56 (m, 2 H)	3.11 (m, 2 H) 2.50 (m, 2 H)	2.23 (s, 6 H)	7.13 (s, 2 H, OH_2)
6 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCHCl_2)$_2$(OH_2)]	5.67 (s, 2 H), 4.29 (s, 2 H)	4.52 (m, 2 H)	3.09 (m, 2 H) 2.48 (m, 2 H)	2.17 (s, 6 H)	7.52 (s, 2 H, OH_2) 5.45 (s, 2 H, $CHCl_2$)
7 [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCHF_2)$_2$(OH_2)]	5.65 (s, 2 H), 4.22 (s, 2 H)	4.38 (m, 2 H)	3.08 (m, 2 H) 2.48 (m, 2 H)	2.15 (s, 6 H)	7.68 (s, br, 2 H, OH_2) 5.34 (t, 2 H, $^2J_{H-F}$ = 54.8, CHF_2)
8a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2Cl)] (*i*) 20 °C (average between **8a** and **8c**)	5.59 (s, 1 H), 4.74 (s, br, 1 H) 4.70 (s, 1 H), 3.69 (s, br, 1 H)	4.31 (m, br, 1 H) 3.71 (m, br, 1 H)	2.58 (m, 4 H)	2.30 (s, 3 H) 2.15 (s, 3 H)	3.80, 3.74 (AB, 2 H, ^2J = 14.3, CH_2Cl)
(*ii*) −50 °C	5.61 (s, 1 H), 4.75 (s, 1 H) 4.66 (s, 1 H), 3.71 (s, 1 H)	4.29 (m, 1 H) 3.73 (m, 1 H)	2.58 (m, 4 H)	2.30 (s, 3 H) 2.17 (s, 3 H)	3.80, 3.74 (AB, 2 H, ^2J = 14.3, CH_2Cl)
8b [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCH_2Cl)$_2$(OH_2)]	5.56 (s, 2 H), 4.16 (s, 2 H)	4.28 (m, br, 2 H)	3.02 (m, br, 2 H) 2.48 (m, br, 2 H)	2.12 (s, 6 H)	8.10 (s, br, 2 H, OH_2) 3.64 (s, br, 2 H, CH_2Cl)
8c [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2Cl)(OH_2)][b]	5.46 (s, 1 H), 5.34 (s, 1 H) 4.87 (s, 1 H), 4.10 (s, 1 H)	4.98 (m, 1 H) 4.32 (m, 1 H)	2.92 (m, 4 H)	2.39 (s, 3 H) 2.06 (s, 3 H)	6.39 (s, br, 2 H, OH_2) 3.78 (s, 2 H, CH_2Cl)
9a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2F)] (*i*) 20 °C (average between **9a** and **9c**)	5.56 (s, br, 1 H), 4.89 (s, br, 1 H) 4.75 (s, 1 H), 3.86 (s, br, 1 H)	4.46 (m, br, 1 H) 3.86 (m, br, 1 H)	2.50 (m, br, 4 H)	2.32 (s, 3 H) 2.13 (s, 3 H)	4.58 (d, br, $^2J_{H-F}$ = 47.1, CH_2F)
(*ii*) −50 °C	5.63 (s, 1 H), 4.83 (s, 1 H) 4.69 (s, 1 H), 3.80 (s, 1 H)	4.42 (m, 1 H) 3.79 (m, 1 H)	2.50 (m, 4 H)	2.30 (s, 3 H) 2.17 (s, 3 H)	4.61, 4.55 (dAB, $^2J_{H-H}$ = 8.2, $^2J_{H-F}$ = 47.1, CH_2F)
9b [Ru(η^3:η^3-$C_{10}H_{16}$)(O_2CCH_2F)$_2$(OH_2)]	5.58 (s, 2 H), 4.21 (s, 2 H)	4.37 (m, 2 H)	3.01 (m, 2 H) 2.50 (m, 2 H)	2.10 (s, 6 H)	8.18 (s, br, 2 H, OH_2) 4.32 (d, 2 H, $^2J_{H-F}$ = 48.3, CH_2F)
9c [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(O_2CCH_2F)(OH_2)][b]	5.47 (s, 1 H), 5.37 (s, 1 H) 4.79 (s, 1 H), 4.13 (s, 1 H)	5.00 (m, 1 H) 4.59 (m, 1 H)	2.90 (m, 4 H)	2.41 (s, 3 H) 2.05 (s, 3 H)	6.52 (s, br, 2 H, OH_2) 4.30 (m, br, 2 H, CH_2F)
10 [Ru(η^3:η^3-$C_{10}H_{16}$)Cl{$F_3CC(O)CHC(O)CF_3$}]	6.08 (s, 1 H), 4.92 (s, 1 H) 4.89 (s, 1 H), 3.50 (s, 1 H)	5.19 (m, 1 H) 4.44 (m, 1 H)	3.04 (m, 2 H) 2.43 (m, 2 H)	2.45 (s, 3 H) 1.99 (s, 3 H)	4.96 (s, 1 H, $CF_3COCHCOCF_3$)[c]
11 [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2{$SC(OH)CH_3$}]	4.76 (s, 2 H), 4.00 (s, 2 H)[d]	5.08 (m, 2 H)	3.26 (m, 2 H) 2.57 (m, 2 H)	2.30 (s, 6 H)	13.99 (s, 1 H, OH) 2.69 (s, 3 H, CH_3)
12a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOMe)] (*S equatorial*)	5.28 (s, 1 H), 4.24 (s, 1 H) 4.06 (s, 1 H), 2.61 (s, 1 H)	4.31 (m, 1 H) 3.30 (m, 1 H)	2.83 (m, 4 H)	2.32 (s, 3 H) 2.07 (s, 3 H)	1.66 (s, 3 H, CH_3)
12b [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOMe)] (*S axial*)	5.28 (s, 1 H), 4.68 (s, 1 H) 4.36 (s, 1 H), 3.52 (s, 1 H)	4.41 (m, 1 H) 3.67 (m, 1 H)	2.65 (m, 4 H)	2.21 (s, 3 H) 2.13 (s, 3 H)	1.68 (s, 3 H, CH_3)
13a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOBu^t)] (*S equatorial*)	5.27 (s, 1 H), 4.05 (s, 1 H) 4.04 (s, 1 H), 2.36 (s, 1 H)	4.32 (m, 1 H) 3.27 (m, 1 H)	2.88 (m, 4 H)	2.36 (s, 3 H) 2.09 (s, 3 H)	1.05 [s, 9 H, $C(CH_3)_3$]
13b [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOBu^t)] (*S axial*)	5.21 (s, 1 H), 4.66 (s, 1 H) 4.18 (s, 1 H), 3.20 (s, 1 H)	4.43 (m, 1 H) 3.63 (m, 1 H)	2.69 (m, 4 H)	2.44 (s, 3 H) 2.19 (s, 3 H)	1.14 [s, 9 H, $C(CH_3)_3$]
14a [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOPh)] (*S equatorial*)	5.33 (s, 1 H), 4.28 (s, 1 H) 4.11 (s, 1 H), 2.69 (s, 1 H)	4.30 (m, 1 H) 3.50 (m, 1 H)	2.93 (m, 4 H)	2.39 (s, 3 H) 2.17 (s, 3 H)	7.84 (dd, 2 H, ^3J = 8.4, ^4J = 1.2, *o*-C_6H_5) 7.54 (dt, 1 H, ^3J = 7.5, ^4J = 1.2, *p*-C_6H_5) 7.37 (t, 2 H, ^3J = 7.9, *m*-C_6H_5)
14b [Ru(η^3:η^3-$C_{10}H_{16}$)Cl(SOPh)] (*S axial*)	5.33 (s, 1 H), 4.69 (s, 1 H) 4.38 (s, 1 H), 3.45 (s, 1 H)	4.51 (m, 1 H) 3.79 (m, 1 H)	2.44 (m, 4 H)	2.48 (s, 3 H) 2.26 (s, 3 H)	7.96 (dd, 2 H, ^3J = 7.8, ^4J = 0.6, *o*-C_6H_5) 7.55 (dt, 1 H, ^3J = 7.6, ^4J = 1.3, *p*-C_6H_5) 7.42 (t, 2 H, ^3J = 7.5, *m*-C_6H_5)

[a] Recorded at 298 K unless otherwise stated. s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, AB = AB pattern, dAB = doublet of AB patterns, m = multiplet and br = broad. [b] At −50 °C. [c] Unambiguous assignment of this resonance is not possible since it occurs at a very similar chemical shift to two other 1 H singlet signals arising from the bis(allyl) ligand. [d] Signals noticeably broader than the corresponding resonances for the other half of the bis(allyl) ligand.

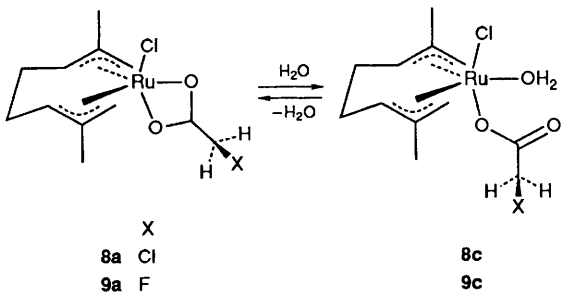
and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(O_2CCH_2X)_2(OH_2)]$ **8b**, **9b**. In both cases the complex with chelating ligands (**8a**, **9a**) forms the bulk of the isolated yields [product ratios: 7:1 (**8a**:**8b**), 6:1 (**9a**:**9b**)]. The ^1H NMR spectra of **8a** and **9a** exhibit the expected four singlet resonances for the terminal allylic protons of the dimethyloctadienyl ligand and two signals for the methyl groups, indicative of inequivalent axial sites. At 20 °C two of the terminal allyl resonances in each spectrum are broad whilst the other two are much sharper, implying a fluxional process may be occurring in which the major changes take place on only one side of the molecule. This process is slightly slower in the case of **9a** than **8a** as indicated by an increased peak width. In both cases raising the temperature to 50 °C results in sharp, four-line patterns for the terminal allyl protons, consistent with inequivalent axial sites, even in a rapid-exchange regime. Lowering the temperature results in a gradual broadening of all the lines in the spectrum until, at −20 °C, they are significantly flattened into the baseline. At −50 °C eight sharp singlet resonances are observed in the allylic region of the spectrum, half of them four times the intensity of the other four. Similarly, four methyl signals can now be observed. In addition broad peaks are also observed at δ 6.39 and 6.52 respectively [close to the value of δ *ca.* 6 for the exchanging water of crystallisation in the areneruthenium(II) carboxylato compounds[20]]. Other new resonances corresponding to the carboxylates and the remainder of the bis(allyl) ligands are also apparent. Complete NMR data for these processes are given in Table 6.

These temperature-dependent NMR spectra are interpreted in terms of an equilibrium involving mono- and bi-dentate co-ordination of the $[CH_2XCO_2]^-$ ligands analogous to that observed in the trisphosphine complex *fac*-$[RuCl(O_2CMe)\{PPh[C_3H_6P(C_6H_{11})_2]_2\}]$,[37] and activated by means of residual water in the deuteriated chloroform solvent. Thus we believe complexes **8a** and **9a** are each in equilibrium with further aqua complexes, $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_2X)(OH_2)]$ **8c**, **9c** each of which also possesses inequivalent axial sites, Scheme 1. The equilibrium constant at −50 °C for this process (K = [*N*a]/[*N*c]) is *ca.* 5 in both cases.

The NMR spectra of the bis(carboxylato) aqua complexes **8b** and **9b** also display evidence of fluxionality. Raising the temperature to 50 °C results in a gradual broadening of all the resonances in the spectra, most notably those corresponding to the water ligands. At 0 °C however, all the resonances are sharp, as in the case of **3**. Further lowering of the temperature produces no further changes in the spectra. These observations are consistent with a simple exchange of co-ordinated water with that in the bulk solvent.

The ^1H NMR spectrum of **8a** at room temperature displays a closely spaced AB pattern (δ 3.80 and 3.74, $^2J_{H-H}$ = 14.3 Hz) assigned to the protons of the chloroacetate ligand. These protons are diastereotopic and the presence of the chiral metal centre results in the splitting of the expected singlet into the observed AB pattern. The analogous protons in **9a** give rise to an eight-line pattern because of additional coupling to fluorine ($^2J_{H-F}$ = 47.1 Hz). The effect is analogous to that observed in the ^{19}F NMR spectrum of the adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(Me_2NPF_2)]$ where the diastereotopic fluorine atoms* give rise to an eight-line pattern due to coupling to phosphorus.

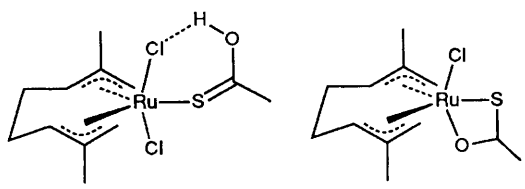
In summary, the more electron withdrawing carboxylates favour the formation of complexes with monodentate ligands and equatorially co-ordinated water molecules. Increasing the electron releasing properties of the substituent group on the carboxylate leads to fluxional behaviour involving mono- and bi-dentate co-ordinated ligands. In the limiting case (R = Me **2**) the second carboxylate oxygen atom is a sufficiently good donor to bind more rigidly to the metal centre resulting in the formation of the 1:1 chelate complex. It would thus appear that the 'cross-over' between these two bonding modes occurs gradually over acid pK_a values of *ca.* 1.3–2.9; $\bar{F}$ of *ca.* 0.1–0.27.



X
8a Cl
9a F

8c
9c

Scheme 1 Fluxional behaviour of the halogenoacetato complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_2X)]$ (X = F or Cl)



11 **12a**

In a further attempt to observe aqua complexes we have also investigated the reaction of **1** with other electron-withdrawing ligands such as the hexafluoroacetylacetonate anion, $[CF_3C(O)CHC(O)CF_3]^-$. We find that in this case a chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{F_3CC(O)CHC(O)CF_3\}]$ **10** is formed, analogous to the ruthenium(II) complex $[Ru(\eta^6\text{-}C_6H_6)Cl(acac)]$[38] (Hacac = acetylacetone). The less strained nature of the six-membered heterocyclic ring no doubt stabilises the bidentate co-ordination mode.

Reactions with Thiocarboxylic Acids.—Reaction of **1** with a small excess of thioacetic acid in acetone rapidly produces a bright orange solution from which may be isolated a complex of formula $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2\{SC(OH)Me\}]$ **11**, containing a neutral co-ordinated thioacetic acid molecule. The infrared spectrum of this molecule shows two broad bands of medium intensity at surprisingly low wavenumber (2606, 2458 cm^{-1}) which fall in the region expected for ν(SH) or for hydrogen-bonded carboxylic acid dimers.[39] No bands assignable to co-ordinated C=O in the region[21] of 1600 cm^{-1} were observed however, instead the complex exhibits two strong bands at 1437 and 1347 cm^{-1} assignable to ν(O–C=S) in addition to the usual weaker bands arising from the bis(allyl) ligand. The far infrared spectrum contains two strong ν(RuCl) absorptions at 310 and 239 cm^{-1}. The ^1H NMR spectrum of **11** displays two resonances arising from the terminal allyl protons of the dimethyloctadienediyl ligand, δ 4.76 and 4.00, the latter signal being noticeably broader than the former at room temperature, perhaps indicating a hydrogen-bonding interaction involving one of the axial chloride ligands. In addition, an extremely sharp singlet resonance is observed at δ 13.99 assignable to a strongly hydrogen bonded acidic proton. This evidence leads us to suggest that the thioacetic acid molecule is S-bound with the hydroxyl proton involved in a strong hydrogen-bonding interaction with one of the axial chloride ligands both in the solid state and in solution, giving rise to ν(O ••• H ••• Cl) at an anomalously low wavenumber.

Reaction of **1** with thioacetic acid over longer reaction times, up to 24 h, gives the chelate complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(OSCMe)]$ **12**, analogous to **2**. Because of the asymmetry of the thioacetate ligand the existence of axial and/or equatorial isomers arises. In this case **12** is found to exist as both

* At the time this inequivalence was thought to be a consequence of restricted rotation about the Ru–P bond. The phenomenon has since been reinterpreted by Cox and Roulet[13] however.

geometrical isomers **12a** and **12b** (distinguished by their ^1H NMR spectra) in a ratio of approximately 4:1. It is unclear whether the major isomer has the sulfur atom equatorially or axially bound but it seems likely that the more bulky donor atom occupies an equatorial position in order to minimise unfavourable axial ligand–methyl substituent steric interactions. A number of examples of the related 2-hydroxypyridinate complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4O)]$ exhibit analogous isomerism, and have been studied by us in some detail.[23]

The two-step mechanism of co-ordination of thioacids, initially proceeding *via* adducts such as **11**, is analogous to the reaction of **1** with pyridine-2-thiol [15] which proceeds initially *via* the monoadduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(NC_5H_4SH)]$ before base-induced deprotonation occurs to form the chelate compound $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4S)]$. In contrast, in the reaction of **1** with 2-hydroxypyridine only the complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(NC_5H_4O)]$ are isolated.[23]

Reaction of **1** with thiopivalic and thiobenzoic acids also gives chelate species $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(OSCR)]$ (R = Bu^t **13** or Ph **14**), although in these cases we have been unable to observe the formation of simple adduct intermediates related to **11**. We infer that the chelation step in these instances is more rapid than in the former case. Also the high solubility of the complexes makes it difficult to isolate them quickly and chelation may well occur during the recrystallisation procedure. As with **12**, complexes **13** and **14** exist as *axial* and *equatorial* isomers, each possessing similar, but distinct, ^1H NMR spectra (Table 6). Isolated isomer ratios were 25:1 and 6:1 for **13** and **14** respectively. In the absence of competing interactions the major isomers are again assigned S-equatorial structures for reasons outlined above.

X-Ray Crystal Structure Determinations.—The X-ray crystal structures of complexes **2** and **3** are shown in Figs. 1 and 2 respectively. Fractional atomic coordinates are listed in Tables 1 and 2 and selected bond lengths and angles in Tables 3 and 4. In both compounds the geometry about the ruthenium atom may be loosely described as approximately trigonal bipyramidal with the bis(allyl) ligands occupying two of the equatorial co-ordination sites and possessing the usual local C_2 symmetry.[2,11,12,14–18] No significant variation is observed in the Ru–C bond lengths. The bonds to the two axial oxygen atoms [O(2)] are virtually identical in length in the two complexes (2.10 Å) and are somewhat shorter than the corresponding distances in the fluxional ruthenium(II) complex *fac*-$[RuCl(O_2CMe)\{PPh[C_3H_6P(C_6H_{11})_2]_2\}]$ (2.21–2.23 Å).[37] In complex **3**, the equatorial Ru–OH_2 bond, 2.146(4) Å, is actually somewhat shorter than the Ru–O(1) distance in **2**, 2.205(6) Å. This arises as a consequence of the strained nature of the four-membered heterocyclic ring which is evinced in the characteristically small bite angle, O(1)–Ru–O(2) 60.7(2)°, comparable to the value observed in *fac*-$[RuCl(O_2CMe)\{PPh[C_3H_6P(C_6H_{11})_2]_2\}]$,[37] 58.9(1)°, and in the 6-chloro-2-hydroxypyridinate compound $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl\{NC_5H_3(O)Cl\text{-}6\}]$,[23] 61.9(4)°. The large Cl–Ru–O(1) angle in complex **2**, 93.7(2)°, is also indicative of the strained nature of the chelate ring. The angles between axial and equatorial ligands normally fall in the region of *ca.* 85°[2,14–16] although a value of only 80.3(1)° has been observed by us for the thiocyanato-bridged complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}SCN)\}_2]$.[17] The analogous unstrained angle in complex **3** is 87.4(1)°. Similarly, the endocyclic, O(1)–C(11)–O(2), angle is 118.0(8)° whereas the corresponding parameter in complex **3** is 127.7(5)°, again indicative of the fact that the acetate ligand is distorting significantly in order to chelate the small ruthenium(IV) centre.

This lengthening of the equatorial Ru–O bond in the chelate complex as a result of strain in the heterocyclic ring is almost certainly a contributory factor in the formation of aqua complexes as the donor ability of the carboxylato ligand decreases. The small size of the ruthenium(IV) centre exacerbates the effect, thus resulting in the observed differences in reactivity, compared to the analogous carboxylates of ruthenium(II).[20]

Conclusion

It has been demonstrated that the small size of the ruthenium(IV) centre, coupled with the inherently strained nature of four-membered heterocyclic rings acts to destabilise the formation of bidentate carboxylates containing the '$(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru$' moiety, resulting in fluxionality and, ultimately, the formation of aqua species beyond a threshold in the electron withdrawing properties of the carboxylate substituent group. Notwithstanding this however the electron withdrawing ligand hexafluoroacetylacetonate forms a more stable six-membered chelate ring and shows no propensity for a monodentate mode of co-ordination, or fluxional behaviour in solution. The apparent strength and stability of the Ru^{IV}–OH_2 bond augers well for the potential synthesis of oxo species derived from aqua complexes[40–43] of ruthenium(IV) which may, given the unusual stereochemical requirements of the dimethyloctadienyl ligand, exhibit interesting selectivity in organic oxidations, and in the oxidative cleavage of DNA.[29]

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References

1 L. Porri, M. C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett.*, 1965, **47**, 4187.
2 A. Colombo and G. Allegra, *Acta Crystallogr., Sect. B*, 1971, **27**, 1653.
3 G. Winkhaus and H. Singer, *J. Organomet. Chem.*, 1967, **7**, 487.
4 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.
5 H. LeBozec, D. Touchard and P. H. Dixneuf, *Adv. Organomet. Chem.*, 1989, **29**, 163.
6 R. A. Zelonka and M. C. Baird, *J. Organomet. Chem.*, 1972, **44**, 383.
7 M. A. Bennett, G. B. Robertson and A. K. Smith, *J. Organomet. Chem.*, 1972, **43**, C41.
8 R. O. Gould, T. A. Stephenson and D. A. Tocher, *J. Organomet. Chem.*, 1984, **263**, 375.
9 R. Aronson, M. R. J. Elsegood, J. W. Steed and D. A. Tocher, *Polyhedron*, 1991, **10**, 1727.
10 S. K. Mandal, A. R. Chakravarty, *J. Organomet. Chem.*, 1991, **417**, C59.
11 D. N. Cox, R. W. H. Small and R. Roulet, *J. Chem. Soc., Dalton Trans.*, 1991, 2013.
12 S. O. Sommerer and G. J. Palenik, *Organometallics*, 1991, **10**, 12203.
13 D. N. Cox and R. Roulet, *Inorg. Chem.*, 1990, **29**, 1360.
14 J. W. Steed and D. A. Tocher, *J. Organomet. Chem.*, 1991, **412**, C34.
15 J. G. Toerien and P. H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, 1991, 1563.
16 J. G. Toerien and P. H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, 1991, 2693.
17 J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1992, 459.
18 J. W. Steed and D. A. Tocher, *Inorg. Chim. Acta*, 1992, **191**, 29.
19 R. A. Head, J. F. Nixon, J. R. Swain and C. M. Woodard, *J. Organomet. Chem.*, 1974, **76**, 393.
20 D. A. Tocher, R. O. Gould, T. A. Stephenson, M. A. Bennett, J. P. Ennett, T. W. Matheson, L. Sawyer and V. K. Shah, *J. Chem. Soc., Dalton Trans.*, 1983, 1571.
21 E. C. Morrison, C. A. Palmer and D. A. Tocher, *J. Organomet. Chem.*, 1988, **349**, 405.
22 J. W. Steed and D. A. Tocher, *Polyhedron*, 1992, **11**, 1849.
23 J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1992, 2765.
24 J. W. Steed and D. A. Tocher, *Inorg. Chim. Acta*, 1991, **189**, 135.
25 A. C. Cope and E. R. Trumbull, in *Organic Reactions*, ed. A. C. Cope, Wiley, New York, 1960, vol. 11, ch. 5.
26 G. M. Sheldrick, SHELXTL PLUS, an integrated system for refining and displaying crystal structures from diffraction data, University of Göttingen, 1986.
27 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.

28 L. Porri, R. Rossi, P. Diversi and A. Lucherini, *Makromol. Chem.*, 1974, **175**, 3097.
29 J. W. Steed and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1991, 1609.
30 U. Kölle, G. Flunkert, R. Görissen, M. U. Schmidt and U. Englert, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 440.
31 S. O. Sommerer, J. D. Baker, M. C. Zerner and G. J. Palenik, *Inorg. Chem.*, 1992, **31**, 563.
32 W. Frank and B. Bertsch-Frank, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 436.
33 C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, 1968, **90**, 4328.
34 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 2nd edn., Harper and Row, New York, 1981 and refs. therein.
35 C. Hansch and A. J. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley, New York, 1979.
36 E. P. Serjeant and B. Dempsey (Editors), *Ionisation Constants of Organic Acids in Aqueous Solution*, IUPAC, London, 1979.
37 G. Jia, A. L. Rheingold, B. S. Haggerty and D. W. Meek, *Inorg. Chem.*, 1992, **31**, 900.
38 M. R. Stevens, PhD Thesis, Australian National University, 1981.
39 C. J. Pouchert (Editor), *Aldrich Library of Infrared Spectra*, 3rd edn., 1981.
40 W. P. Griffith, *Transition Met. Chem.*, 1990, **15**, 251.
41 C.-K. Li, C.-M. Che, W.-F. Tong and T.-F. Lai, *J. Chem. Soc., Dalton Trans.*, 1992, 813.
42 C.-M. Che, W.-T. Tang, K.-Y. Wong and C.-K. Li, *J. Chem. Soc., Dalton Trans.*, 1991, 3277.
43 H. Nagao, M. Shibayama, Y. Kitanaka, F. S. Howell, K. Shimizu, M. Mukaida and H. Kakihana, *Inorg. Chim. Acta*, 1991, **185**, 75.

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