Characterisation of the Air- and Water-stable Organometallic Ruthenium(IV) Complex $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})RuCl(H_2O)][BF_4]$

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The reaction of $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})RuCl_2]$ with $Ag[BF_4]$ (1 : 1 mole ratio) in water–acetone gives an air-stable aqueous solution of $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})RuCl(H_2O)][BF_4]$; the isolated complex has been characterised by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography.

At the present time there is considerable interest in water-soluble organometallic compounds for a variety of catalytic reactions[1] and in organometallic compounds with high formal oxidation states,[2] although the two features rarely appear concurrently. In many cases water-solubility is conferred on the metal complex by the use of ligands which are themselves water-soluble *e.g.* $(m\text{-}NaSO_3C_6H_4)_3P$,[3] although in other instances genuine aquo complexes must be the important intermediates in the catalytic cycle.

The ruthenium(IV) compound $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})RuCl_2]$ **1** was first prepared and characterised[4] by Shaw and Truter in the 1960s. The compound is diamagnetic and the geometry about the metal centre is best described as approximately pentagonal bipyramidal. There are several reports of catalytic applications[5] of **1** but only a single study of its chemistry.[6] We now report a new reaction of **1** giving rise to an air- and moisture-stable organometallic ruthenium(IV) compound which also contains a strongly bonded water ligand.

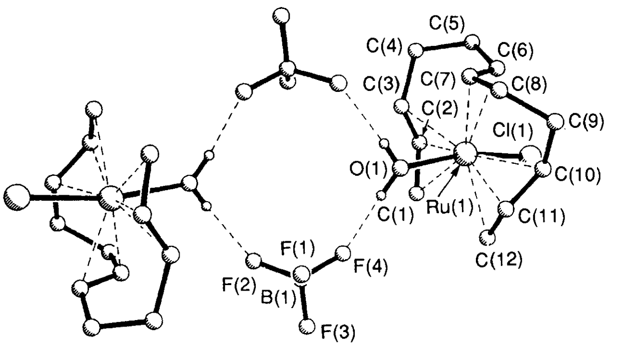

Fig. 1 The crystal and molecular structure of $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})\text{-}RuCl(H_2O)][BF_4]$ showing the atom numbering scheme adopted. Selected bond lengths (Å) and angles (°): Ru(1)–Cl(1) 2.396(2), Ru(1)–C(1) 2.196(6), Ru(1)–C(2) 2.207(6), Ru(1)–C(3) 2.282(6), Ru(1)–C(6) 2.314(5), Ru(1)–C(7) 2.291(5), Ru(1)–C(10) 2.320(5), Ru(1)–C(11) 2.210(6), Ru(1)–C(12) 2.214, Ru(1)–O(1) 2.165(5), O(1)···F(4) 2.74(3), O(1A)···F(2) 2.68(3); O(1)–Ru(1)–Cl(1) 169.0(1), C(2)–Ru(1)–C(11) 150.5(2).

The reaction of **1** with one molar equivalent of $Ag[BF_4]$ in acetone–water (1 : 1 v/v) gives a straw-brown solution from which brown crystals of $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})RuCl(H_2O)][BF_4]$ **2** are deposited.† The ^1H NMR spectrum‡ of diamagnetic compound **2** is substantially more complicated than that of **1** and is generally similar to that previously reported for $[(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})RuI(CH_3)]$[6] indicating that the two axial sites of the pentagonal bipyramidal complex are inequivalent. This is confirmed by the $^{13}C\{H\}$ NMR spectrum‡ which exhibits twelve resonances for the dodeca-2,6,10-triene-1,12-diyl ligand rather than the six observed for **1**. The presence of a water molecule is indicated by the appearance of a broad singlet in the ^1H NMR spectrum, at δ 2.21, integrating for two protons, and ν(OH) bands in the infrared spectrum at 3369 and 3169 cm^{-1}. The structure has been confirmed by X-ray crystallography.§

The crystal and molecular structure of **2**, together with the atom numbering scheme adopted, is shown in Fig. 1. For reasons which have been discussed in detail previously[4] the geometry about the ruthenium(IV) centre is best described as a distorted pentagonal bipyramid. A chloride ion and a water molecule occupy the two axial sites. The bonds to these ligands [Ru(1)–Cl(1) 2.396(2), Ru(1)–O(1) 2.165(5) Å] are not collinear but subtend an angle of 169.0(1)° at the metal ion. The six carbon atoms of the two η^3-allyl functionalities are not equidistant from the metal but form two distinct sets [av. Ru(1)–C(1), C(2), C(11), C(12) 2.206(6), av. Ru(1)–C(3), C(10) 2.301(5) Å] indicative of an imbalance between the steric requirements of the metal and that of the ligand. The distortions in the organic ligand which arise on coordination to this metal centre also result in long bonds to the alkenic functionality [Ru(1)–C(6) 2.314, Ru(1)–C(7) 2.291(5) Å]. This situation can be contrasted with that observed in related bis-allyl compounds of ruthenium(IV), containing the ligand $\eta^3:\eta^3\text{-}C_{10}H_{16}$, in which the six ruthenium carbon bond lengths are invariably statistically indistinguishable.[7] Examination of Fig. 1 clearly explains the reason behind the complexity of the NMR spectra. While the proton on C(2) is pseudo-eclipsed with the chloride ligand, that on C(11) has a similar orientation with respect to the coordinated water molecule, hence all the protons and carbon atoms of the organic ligand are unique. In the crystalline solid pairs of cations are hydrogen-bonded together *via* bridging tetrafluoroborate anions. Each tetrafluoroborate anion forms two relatively short hydrogen bonds [av. O···F 2.71(3) Å] to coordinated water molecules.

Compound **2** is readily redissolved in aqueous solution and these solutions are stable in air for periods of up to five days. This observation is virtually without precedent in π-allyl chemistry, only one other recently reported compound, $[(\eta^3:\eta^3\text{-}C_{10}H_{12})RuCl(CH_5N_3O)]Cl$,[8] having similar properties. The existence of **2** offers the potential for the development of water-based organometallic compounds with the metal in a non-traditional oxidation state. Indeed it is not at all unlikely that related species may exist in aqueous solutions of ruthenium trichloride containing unsaturated organic molecules. Studies on the reactions and possible catalytic activity of **2** are planned.

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† Satisfactory elemental analysis (C, H, Cl) has been obtained.

‡ *^1H NMR data* (400 MHz, $CDCl_3$): $\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18}$; δ 2.45 (m, 2H), 2.63 (m, 2H), 2.82 (m, 1H), 3.16 (m, 1H), 3.19 (m, 2H), 3.39 (d, $^3J_{HH}$ 12 Hz, 1H), 3.87 (d, $^3J_{HH}$ 12 Hz, 1H), 4.40 (m, 1H), 5.15 (dd, $^2J_{HH}$ 2, $^3J_{HH}$ 8 Hz, 1H), 5.26 (m, 2H), 5.30 (m, 1H), 5.68 (m, 1H), 5.78 (d, $^3J_{HH}$ 13 Hz, 1H), 5.93 (dd, $^3J_{HH}$ 13 and 4.5 Hz, 1H); H_2O, δ 2.21 (s, 2H). $^{13}C\{^1H\}$ NMR data (100.6 MHz, CD_3CN): $\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18}$; δ 24.2, 24.6, 36.3, 37.0, 63.2, 66.4, 108.5, 109.0, 113.2, 118.0, 122.2, 128.6.

§ *Crystal data*: $C_{12}H_{20}BClF_4ORu$, brown needles, M = 403.65, monoclinic, space group $P2_1/n$, a = 7.366(1), b = 14.132(3), c = 14.510(3) Å, β = 101.22(2)°, U = 1482 Å^3, Z = 4, D_c = 1.81 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 12.5 cm^{-1}. A total of 2915 reflections were measured in the range 5° ≤ 2θ ≤ 50° on a Nicolet R3mV diffractometer. Data corrected for Lorentz and polarisation effects and an empirical absorption correction applied. The 1803 unique data with $I \geq 3\sigma(I)$ were used to solve (Patterson method) and refine (full-matrix least-squares) the structure. All non-hydrogen atoms were refined anisotropically, the hydrogens on the water molecule were located and their coordinates refined, while the remaining hydrogens were placed in idealised positions (C–H 0.96 Å). The fluorines of the $[BF_4]^-$ ions were disordered over two positions (occupancy refined to 50%). At the conclusion of refinement R = 0.0323, R_w = 0.0372, and the largest shift/esd was 0.02. Calculations were performed on a Microvax II computer using the SHELXTL PLUS program package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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