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LETTER

Synthesis of cationic ruthenium(IV) allyl compounds containing chelating N-donor ligands: X-ray crystal structure of $[(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru(N_3C_{15}H_{11})][BF_4]_2\cdot CH_3NO_2$

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The chemistry of the ruthenium(IV) chloro bridged dimer $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ (**1**) has been surprisingly neglected in spite of the fact that it has been known since 1965 [1, 2]. Recent interest, however, in the chemistry of organometallic compounds in high formal oxidation states [3, 4], especially those possessing the property of water solubility [5], has renewed interest into the reactions of **1** by virtue of its ready preparation and versatile chemistry.

Previous reports [6, 7] have described **1** as existing as two diastereoisomers of C_2 and C_i symmetry, the latter having been characterised by X-ray crystallography [2].

Compound **1** is known to react with neutral, monodentate ligands L (L = PF_3, PPh_3, pyridine, CO etc.) to form simple adducts $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2L]$. **1** will also react with bidentate chelating ligands such as benzothiazole-2-thiolate [7] and semicarbazide [5]. These complexes are diastereotopic (due to inequivalent axial sites) and characteristically exhibit two singlet resonances due to magnetically inequivalent methyl groups and four resonances due to the terminal allylic protons of the $\eta^3:\eta^3\text{-}C_{10}H_{16}$ ligand. In alcoholic solvents the reaction of **1** with $Ag[BF_4]$ has been shown to produce solvated Ru^{2+} cations [8]. We now report preliminary results on some reactions of **1** with the chelating ligands 2,2′:6,2″-terpyridine (terpy), 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) via pretreatment with silver tetrafluoroborate in the non-reducing solvent, acetone.

In common with the analogous ruthenium(II) arene complexes [9], we find that, in acetone, treatment of **1** with $Ag[BF_4]$ leads to monocationic and dicationic solvate species which readily react with Lewis bases. Treatment of **1** with four equivalents of $Ag[BF_4]$ in acetone proceeds smoothly to generate an orange solution of the tris solvate complex. Stirring the filtered solution with two equivalents of 2,2′:6′,2″-terpyridine over several hours gives a yellow precipitate of $[(\eta^3,\eta^3\text{-}C_{10}H_{16})Ru(terpy)][BF_4]_2$ (**3**) (C, H, N analysis). The ^1H NMR spectrum of this material shows a single set of resonances for the allyl moiety (i.e. two terminal allyl singlets at δ 3.94, 2.94 ppm and one methyl singlet resonance at δ 2.11 ppm) and a further six signals due to the terpyridine ligand. This spectrum is consistent with a mononuclear complex ion with the two axial pyridyl rings equivalent [6].

The X-ray crystal structure of **3** (Fig. 1) shows the allyl ligand to have the usual C_2 symmetry [2, 5, 7, 10]. The geometry about the metal ion is best described as a distorted trigonal bipyramid with the terminal pyridyl rings occupying the axial sites, $r(Ru\text{–}N_{ax})$ 2.16(1) Å. The two $Ru\text{–}N_{ax}$ bonds are not collinear (N(1)–Ru(1)–N(3) 154.5(4)°). Although much of the distortion is due to the chelating nature of the polypyridine ligand (cf. a corresponding angle of 156.4°

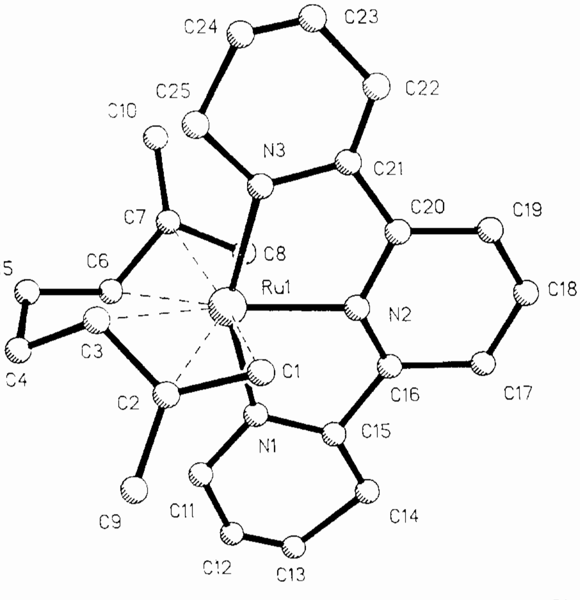

Fig. 1. View of the structure of one of the $[(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru(N_3C_{15}H_{11})]$ cations (the other is essentially identical) showing the atom labelling adopted. Selected bond lengths (Å): Ru(1)–N(1) 2.172(10), Ru(1)–N(2) 2.018(10), Ru(1)–N(3) 2.147(9), Ru(1)–C(1) 2.283(18), Ru(1)–C(2) 2.241(15), Ru(1)–C(3) 2.423(18), Ru(1)–C(6) 2.281(15), Ru(1)–C(7) 2.294(12), Ru(1)–C(8) 2.203(15). Selected interbond angles (°): N(1)–Ru(1)–N(2) 77.1(4), N(1)–Ru(1)–N(3) 154.5(4), N(2)–Ru(1)–N(3) 77.5(4), N(1)–Ru(1)–C(2) 88.1(5), N(1)–Ru(1)–C(7) 103.4(4), N(3)–Ru(1)–C(2) 104.7(5), N(3)–Ru(1)–C(7) 84.7(4), C(2)–Ru(1)–C(7) 131.7(4), N(2)–Ru(1)–C(2) 114.5(5), N(2)–Ru(1)–C(7) 113.8(4).

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in the benzothiazole-2-thiolate complex $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(SNC_7H_4S\text{-}2)$ [7]) it should be noted that even in $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}N_2C_4H_4)]$ the angle between the axial ligands is reduced to 170° [11]. The $Ru\text{–}N_{eq}$ distance is 2.02(1) Å, a value rather shorter than that observed in the equatorial adduct $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}N_2C_4H_4)]$, 2.19 Å. This difference is attributed to the distortions of the terpyridine ligand which occur on coordination to a metal centre and are often observed in polypyridyl chemistry [12].

The single most remarkable feature of this compound is the combination of its stability and water solubility. As has been commented upon very recently [5] this observation has important implications for the nature of aqueous solutions of ruthenium trichloride with unsaturated organic molecules and indicates an area of water-based organometallic chemistry and catalysis which had previously gone unrecognised.

Using a 2:1:1 mole ratio of $Ag[BF_4]$:1:L_2 an analogous synthetic procedure gives the monocationic species $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(L_2)][BF_4]$ (2) (L_2 = 2,2'-bipyridyl or 1,10-phenanthroline) which have been characterised by microanalysis and ^{1}H NMR spectroscopy. In contrast to the ^{1}H NMR spectrum of 3, these compounds show twice as many resonances for the dimethyloctadienediyl ligands (e.g. terminal CH_2 δ 4.35, 4.02, 3.69, 2.49 ppm, CH_3 δ 2.45, 1.77 ppm, L_2 = bipy; terminal CH_2 δ 4.36, 4.00, 3.47, 2.44 ppm, CH_3 δ 2.50, 1.76 ppm, L_2 = phen) and eight resonances for the bipy and phen ligands. This type of pattern is consistent with inequivalent axial sites on the trigonal bipyramidal ruthenium(IV) ion, and closely mimics the pattern of resonances observed with other complexes containing chelating ligands [7].

Experimental

Crystal data for $C_{26}H_{30}N_4O_2F_8B_2Ru$

M = 705.23, a = 7.121(2), b = 31.412(8), c = 13.373(3) Å, β = 101.13(2)°, monoclinic, space group Pc, V = 2935 Å^3, Z = 4, D_{calc} = 1.60 g cm^{-1}, $F(000)$ = 1424, μ(Mo Kα) = 6.03 cm^{-1}, the asymmetric unit contains two enantiomeric cations, four tetrafluoroborate anions and two molecules of nitromethane of crystallisation.

Structure determination

A yellow crystal of dimensions 0.4 × 0.4 × 0.6 mm was used to collect 5518 unique data in the range $5 \leqslant 2\theta \leqslant 50°$ on a Nicolet R3mV diffractometer equipped with graphite monochromated Mo Kα radiation. The data were corrected for Lorentz and polarisation effects and for crystal decay (c. 30%). An empirical absorption correction was applied. The space group was identified from the systematic absences as either $P2/c$ or Pc. The 3689 reflections with $I \geqslant 3\sigma(I)$ were used to solve (direct methods) and refine (blocked least-squares) the structure in the space group Pc. We were very aware that problems are frequently encountered when the choice of space group is Pc or $P2/c$, however although the coordinates of the cations appear to be symmetry related the fact that only *one* of the four $[BF_4]^-$ anions, in the asymmetric unit in the Pc refinement, is disordered, is sufficient to lower the symmetry and establish Pc as the correct space group. Metal atoms were refined anisotropically but an isotropic model was used for the remaining light atoms due to the lack of data. Hydrogen atoms were placed in their predicted positions and allowed to ride on the atoms to which they were attached, r(CH) 0.96 Å, and were assigned a common isotropic temperature factor, U_{iso} 0.08 Å^2. One of the tetrafluoroborate anions was disordered and was fixed as an idealised tetrahedron. At the end of refinement (353 parameters) R = 0.0640, R_w = 0.0717 ($w^{-1} = \sigma^2(F) + 0.000682F^2$). All calculations were carried out on a Micro Vax II computer using SHELXTL PLUS software [13].

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