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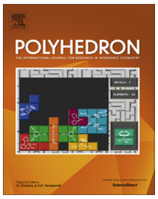

Dynamic behaviour in nicotinate-bridged binuclear ruthenium(IV) complexes

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ABSTRACT

The isonicotinic acid adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(p\text{-}NC_5H_4CO_2H)]$ **1** and nicotinate and isonicotinate bridged binuclear complexes $[Ru_2(\eta^3:\eta^3\text{-}C_{10}H_{16})_2Cl_3(\mu\text{-}\kappa N,O,O'\text{-}NC_5H_4CO_2)]$ **2** and **3** are reported. Complexes **2** and **3** exist as mixtures of diastereoisomers and are dynamic in water saturated chloroform solution with complexes involving bidentate chelating carboxylate ligands in equilibrium with unidente carboxylate aquo complexes $[Ru_2(\eta^3:\eta^3\text{-}C_{10}H_{16})_2Cl_3(OH_2)(\mu\text{-}\kappa N,O\text{-}NC_5H_4CO_2)]$.

1. Introduction

Bis(allyl) ruthenium(IV) complexes are of ongoing interest as catalysts and catalyst precursors in a range of processes such as carbonyl reduction [1], alkene oligomerization and polymerization [2–5], transfer hydrogenation [6], photo-initiated ring-opening metathesis polymerization [7], S–S and C–S bond cleavage [8] and as guanidinate precursors [9]. Of particular interest are reactions either involving water or occurring in aqueous solution such as the hydrolysis of nitriles to amides [10–12] and redox isomerization of allylic alcohols [13,14]. Bis(allyl) ruthenium(IV) complexes are also of interest in catalysis related chemistry such as transmetallation [15], and as precursors to novel ruthenium(II) systems via reductive elimination [16]. Carboxylate complexes of bis(allyl) ruthenium(IV) species in particular are active catalysts and catalyst precursors [17–19] and the field has been reviewed [20]. The simple acetate chelate complex [21] of 2,7-dimethylocta-2,6-diene-1,8-diyl ruthenium(IV) $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ possesses significant catalytic activity and surprisingly is soluble in both water and in ionic liquids despite its neutral, relatively hydrophobic structure [17,19]. Previous work has shown that complexes of this organometallic fragment with more electron withdrawing carboxylates (acid pK_a of 2.9 or below) are in equilibrium with aquo species bearing a unidentate carboxylate ligand of type $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(OH_2)(O_2CR)]$ where R = CH_2Cl, CH_2F [21]. Such a process may promote both catalytic activity (by creation of a vacant site) and water solubility. In this work we report the formation of bis(allyl) ruthenium(IV) complexes of nicotinic and isonicotinic acids. Both species have comparable pK_a to acetic acid (4.75, 4.96 and 4.75, respectively [22]) but offer the possibility of bridged coordination via the pyridyl nitrogen atom as well as the carboxylate group. In addition, nicotinato analogues of the pyrazine-bridged ruthenium-containing Creutz-Taubé ion display an extensive electrochemistry [23]. The unsymmetrical nature of nicotinic acids suggests that it may be possible to generate mononuclear compounds bound *via* the pyridyl nitrogen atom before deprotonation of the carboxylate functionality in the presence of a second metal complex to give an unsymmetrically bridged compound. Such an unsymmetrical system would complement previous work on more symmetrical binuclear ruthenium(IV) complexes [24–29].

2. Results and discussion

In contrast to the case of the mononuclear pyrazene adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(N_2C_4H_4)]$ [26], reaction of the chloro-bridged precursor $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)\}_2]$ [30] with two molar equivalents of isonicotinic acid ($p\text{-}NC_5H_4CO_2H$) results in the clean formation of the adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(p\text{-}NC_5H_4CO_2H)]$ **1** in 80% yield. This is consistent with results reported by Creutz [23] in which isonicotinate and isonicotinamidate bridged analogues of the Creutz–Taubé ion are readily prepared from mononuclear precursors. The ^1H NMR spectrum of **1** is consistent with its

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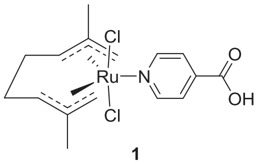
formulation as an equatorial adduct, with the only noteworthy feature being the surprisingly similar chemical shifts of the two terminal allyl signals (δ 4.62 and 4.46 ppm). The infrared spectrum of the complex shows a strong ν_{asymm}(OCO) at 1732 cm^{-1} and ν_{symm}(OCO) 1414 and 1369 cm^{-1}, similar to the values for free carboxylic acids and implying the complex to be N-bound [31]. If the reaction is carried out with a single mole equivalent of nicotinic (m-$NC_5H_4CO_2H$) or isonicotinic acid in the presence of excess Na_2CO_3 an equally smooth reaction occurs to give the unsymmetrical binuclear complexes $[Ru_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})_2Cl_3(\mu\text{-}m\text{-}NC_5H_4CO_2)]$ **2** and $[Ru_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})_2Cl_3(\mu\text{-}p\text{-}NC_5H_4CO_2)]$ **3** respectively in *ca.* 70% yield. Unlike **1**, the infrared spectra of **2** and **3** no longer display a band at *ca.* 1700 cm^{-1}, instead two new bands at lower wavenumber, assignable to ν_{asymm}(OCO) are apparent [1607 and 1509 cm^{-1} in **2** and 1509 and 1496 cm^{-1} in **3**]. Bands assignable to ν_{symm}(OCO) also occur in both complexes [1444 and 1381 (**2**) and 1429 and 1383 cm^{-1} (**3**)]. The difference in frequency between ν_{asymm} and ν_{symm}, $\Delta\nu$ is ambiguous, and hence from this data the coordination mode of the carboxylato functionalities is uncertain, although the chelate mode is suspected based on previous related examples and the requirement to complete the metal coordination sphere [32]. The binuclear nature of **2** was confirmed by a FAB mass spectrum which exhibited a clear molecular ion peak centred on m/z 703 with isotope distribution characteristic of two ruthenium and three chlorine atoms along with a fragmentation peak corresponding to loss of chloride m/z 668.



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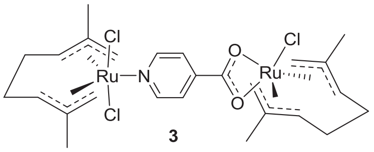


3

The ^1H NMR spectra of **2** and **3** strongly reflect the asymmetric, binuclear nature of the compounds. In the spectrum of **2** for example, the N-bound "$Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$" fragment demonstrates sharp resonances similar to the N-bound adduct **1**, the terminal allyl resonances again occurring at similar chemical shifts to one another. In common with other binuclear complexes containing the chiral "$Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$" moiety, **2** is expected to exist as two diastereoisomers [21,26,27]. The linkage between the two metal atoms is long however (six atoms), and thus only small chemical shift differences are anticipated in the ^1H NMR resonances for the two forms. In reality the diastereoisomers are resolved on only one of the terminal allyl signals for the N-bound side of the molecule: δ 4.60 and 4.59 ppm. The other two terminal allyl signals are coincident, δ 4.41 ppm. In contrast to the N-bound side of the molecule, the O-bound "$Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$" fragment exhibits four terminal allyl signals at room temperature, δ 5.61, 4.73, 4.70 and 3.75 ppm, all of which are broad implying a fluxional process that apparently has most effect on the O-bound end of the molecule. The remainder of the spectrum of the O-bound fragment resembles strongly that of carboxylato complexes such as the chelate acetate $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(O_2CMe)]$ [21].

At −20 °C all the resonances in the spectrum of **2** are sharp (Fig. 1) and consistent with the proposed formulation with signals for individual diastereoisomers resolved on some of the resonances due to the terminal allylic protons on the O-bound end of the molecule. Interestingly, a number of additional resonances of very low intensity (*ca.* 5% of the total sample) are observed, including a broad signal at δ 6.46 ppm. It seems likely that this second species contains a unidentate carboxylato group with the vacant coordination site at the carboxylate bound metal centre occupied by a water molecule. An ^1H NMR spectrum exhibiting similar features is observed for **3** and it would thus appear that the carboxylatopyridines exhibit behaviour related to that of the fluoro- and chloroacetato complexes $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl(OH_2)(O_2CR)]$ [21], with chelating compounds in equilibrium with aqua species containing unidentate carboxylato ligands (Scheme 1). This behaviour is surprising given the chelate nature of the analogous acetate complex and the higher pK_a values of nicotinic and isonicotinic acid compared to chloro- and fluoroacetic acid. While the coordination of the second ruthenium(IV) fragment may enhance the electron withdrawing nature of the nicotinate and isonicotinate pyridyl substituent, it implies that exchange between bidentate carboxylates and unidentate aqua species may be widespread and may contribute to the water solubility of the parent acetate complex.

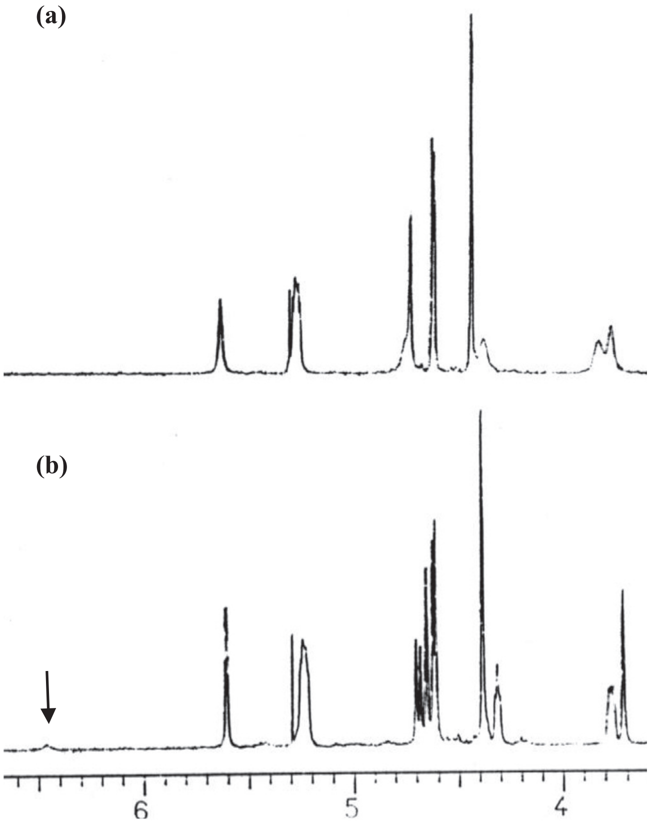
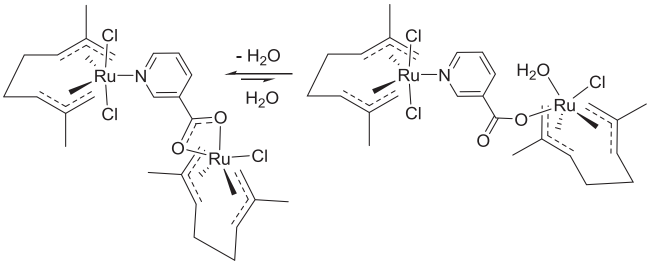


Fig. 1. partial ^1H NMR spectrum of the binuclear compound. $[Ru_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})_2Cl_3(\mu\text{-}m\text{-}NC_5H_4CO_2)]$ **2** (a) recorded at +20 °C; (b) −20 °C in water-saturated $CDCl_3$ solution. The arrow indicates the resonance at δ 6.46 ppm assigned to coordinated water.



Scheme 1. Fluxionality in the nicotinato bridged. Compound $[Ru_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})_2Cl_3(\mu\text{-}NC_5H_4CO_2)]$ **2**.