

# Electron-deficient linear tetranuclear ruthenium(I) carboxylate chains



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## ABSTRACT

The reaction of carboxylic acids RCOOH (R = <sup>t</sup>Bu, Ph, Fc) with [Ru<sub>3</sub>(CO)<sub>12</sub>] in refluxing acetonitrile afforded dark purple/red solids. These reacted with phosphines in a 2:1 (Ru:P) ratio to form phosphine-substituted derivatives of the electron-deficient tetra ruthenium chains, viz., [Ru<sub>4</sub>(CO)<sub>8</sub>(μ-OOCR)<sub>4</sub>(PR'<sub>3</sub>)<sub>2</sub>] (where R' = Ph or OMe).

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## 1. Introduction

The reaction of [Ru<sub>3</sub>(CO)<sub>12</sub>] (**1**) with carboxylic acids (**2**) have been reported to give polymeric, tetranuclear or dinuclear species made up of diruthenium [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCR)<sub>2</sub>] units, depending on the identity of the acid and the reaction conditions used [1–16]. Polymeric complexes [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCR)<sub>2</sub>]<sub>∞</sub> were first reported by Lewis et al. [12]. These comprised dinuclear [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCR)<sub>2</sub>] sawhorse units linked together by two Ru–O bonds, between an Ru atom of one unit and an O atom of the carboxylate bridge of the other unit [5,7,8]. They dissolved reversibly in coordinating solvents (S), such as, acetonitrile, tetrahydrofuran or pyridine, to form dinuclear complexes. These were proposed to have the formulation [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCR)<sub>2</sub>(S)<sub>2</sub>], on the basis of their reactions with phosphines (PR'<sub>3</sub>) to form the dinuclear derivatives [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCR)<sub>2</sub>(PR'<sub>3</sub>)<sub>2</sub>] [4,12]; a single crystal X-ray structural determination on [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OOCAd)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] confirmed it to comprise a sawhorse diruthenium unit, with the two PPh<sub>3</sub> ligands occupying the axial positions [3].

Interestingly, reaction of the polymer with a phosphine in a 2:1 (Ru:P) ratio afforded the tetra ruthenium species [Ru<sub>4</sub>(CO)<sub>8</sub>(μ-OOCR)<sub>4</sub>(PR'<sub>3</sub>)<sub>2</sub>]. These can be regarded as “dimer of dimers” with two dinuclear units linked via either Ru–O interactions, or an unsupported Ru–Ru bond (Fig. 1) [10,11]. Analogues with a carboxylic

acid in place of the phosphines have also been isolated from some of the reactions of [Ru<sub>3</sub>(CO)<sub>12</sub>] with carboxylic acids [5–7,9]. Only two examples of the “dimer of dimers” containing an unsupported Ru–Ru bond have been reported, however, that with R = C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub> and CO ligands in the axial positions reported by the group of Petrukhina [6], and that with R = 1-adamantyl (Ad) and PPh<sub>3</sub> ligands in the axial positions reported by us [3]. These two tetra ruthenium complexes are interesting because they are electron-deficient, with a total valence electron count of 64 compared to the 66 required by the EAN rule. We now believe that these “dimer of dimers” containing an unsupported Ru–Ru bond may not be at all uncommon; our findings on this point are reported here.

## 2. Results and discussion

We have examined the products of the reaction of **1** with four different carboxylic acids **2**, and their reactivity; some of the chemistry for R = Ad (**a**) and <sup>t</sup>Bu (**b**) have already been reported [3,2]. Our results are summarised in Scheme 1.

The reaction of **1** and **2** in refluxing acetonitrile gave yellow solutions which, upon the removal of volatiles, gave either dark purple (**3a** and **3b**) or dark red (**3c** and **3d**) solids. These solids dissolved in various solvents to give orange-yellow solutions but reverted to their original colours upon removal of the solvent. Further characterisation of **3c** and **3d** other than by IR spectroscopy was hampered by their tendency to form an orange solid. For example, **3c** gradually turned orange when left in air and more readily so when heated (80 °C) under vacuum. The IR

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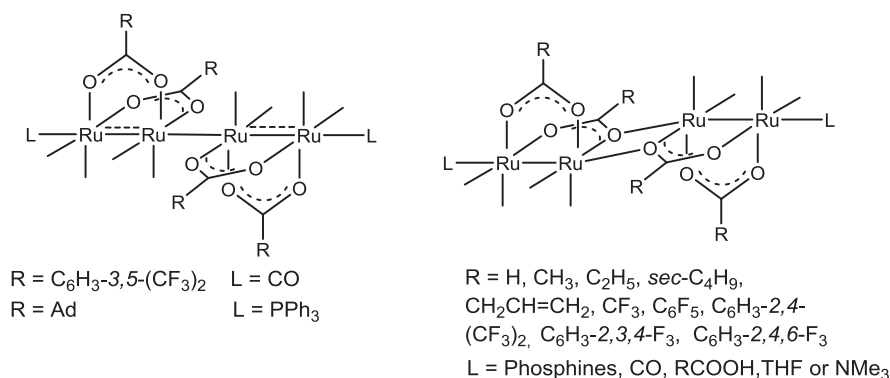
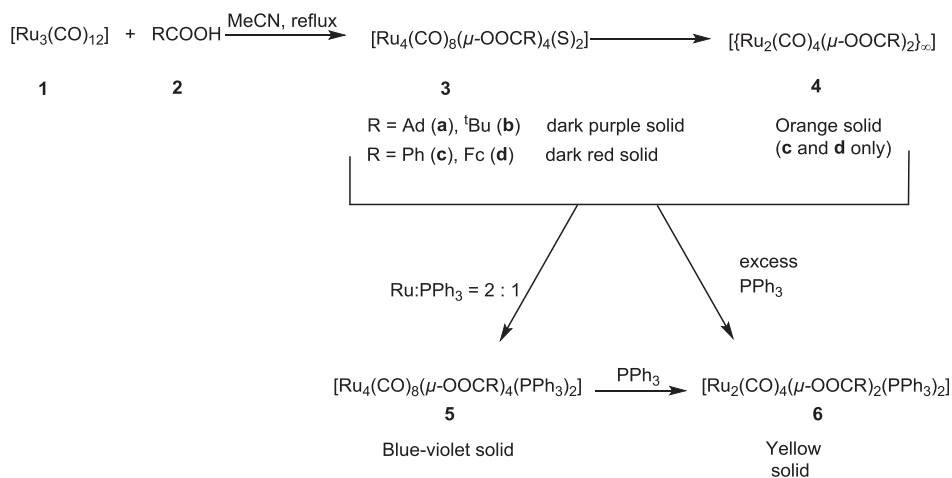


Fig. 1. Ru–Ru vs Ru–O interactions found in tetraruthenium chain complexes [1,3,5–7,9–11,13–16].



Scheme 1.

characteristics of the orange solid **4c** are similar to that for the previously reported benzoate polymer  $\{[\text{Ru}_2(\text{CO})_4(\mu\text{-OOCPh})_2]_\infty\}$  and hence, we believe that it is also polymeric [9]. A dichloromethane solution of **3d** similarly afforded an orange precipitate **4d** on standing. Although the IR spectrum is identical to that for dark red **3d**, we believe that **4d** is also a polymer. In contrast, both **3a** and **3b** remained purple upon heating in vacuum and showed no precipitation when left standing in a dichloromethane solution. Their mass spectra shows ions corresponding to both diruthenium and tetraruthenium fragments but not higher nuclearities such as a hexaruthenium.

It had been assumed earlier that the complexes **3a** and **3b** were polymeric [3,2]. The  $^1\text{H}$  NMR spectrum of **3b**, however, exhibits a resonance at 1.25 ppm, which can be assigned to a bound pivalic acid similar to that reported for the diruthenium species  $[\text{Ru}_2(\text{CO})_4(\mu\text{-OOC}^t\text{Bu})_2(^t\text{BuCOOH})_2]$  [9]; weak IR bands at  $\sim 1600\text{--}1700\text{ cm}^{-1}$  can also be attributed to the carbonyl stretches of the bound pivalic acid group. Complex **3b** thus probably has the formulation  $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOC}^t\text{Bu})_4(^t\text{BuCOOH})_2]$ . The mass spectrum of an acetonitrile solution, on the other hand, shows fragments corresponding to substitution of the acid ligands by acetonitrile. We therefore believe that all the solids **3** are tetraruthenium species with the formulation  $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCR})_4(\text{S})_2]$ ; the intense purple/red colours are due to the presence of an unsupported, electron-deficient Ru–Ru bond, and they are weakly coordinated in the axial positions by a solvent molecule (like acetonitrile or dichloromethane [17]), or a carboxylic acid. They are probably mixtures of solvent- and acid-coordinated species,

depending on the synthetic methodology and the work-up procedure.

That **3a** and **3b** are more stable in the tetranuclear form may possibly be due to steric crowding; it has been reported that pivalate complexes resist polymerization because of steric crowding at the  $\alpha$  position of the acid [9]. A longer Ru–Ru chain is also presumed to be less favoured as that will require even more electron-deficiency. Interestingly, for  $R = \text{C}_6\text{H}_3\text{-}3,5\text{-(CF}_3)_2$ , it has been reported that both a tetranuclear species containing an unsupported Ru–Ru bond, and a polymeric species containing Ru–O interactions, could be formed [6]. Taken together, we believe that these suggest that polymeric **4** containing Ru–O linkages is the more favoured form but a sterically bulky R group can disfavor this.

The reaction of polymeric **4** with phosphines has been described as a depolymerization reaction, in which the diruthenium species was first formed, whatever the Ru:P ratio [10,11]. Irrespective of the true nature of **3** and **4**, we have observed that both undergo a similar depolymerization reaction with  $\text{PPh}_3$ , except that when the Ru:P ratio was 2:1, the linear tetranuclear chains  $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCR})_4(\text{PPh}_3)_2]$  (**5**) were obtained as dark blue/violet solids beside the diruthenium species  $[\text{Ru}_2(\text{CO})_4(\mu\text{-OOC}^t\text{Bu})_2(\text{PPh}_3)_2]$  (**6**). With an excess of the phosphine, only **6** was formed. The  $\text{P}(\text{OMe})_3$  analogue  $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOC}^t\text{Bu})_4(\text{P}(\text{OMe})_3)_2]$  (**5b'**) has also been similarly synthesised from **3b**. We have observed (by spot TLC) that **6** was first formed, and over a longer reaction time, the tetraruthenium species **5** resulted, with a concomitant decrease in the amount of **6**.

The electronic spectra of solid **5b-d** all showed a strong

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