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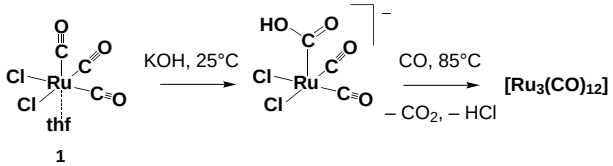
Novel Polymeric Carbonylhaloruthenium(I) Polyanions: Rational Design and Self-Reorganization in the Presence of CO_2 and H_2O**

Luc Maurette, Bruno Donnadieu, and Guy Lavigne*

Dedicated to Professor René Poilblanc on the occasion of his 65th birthday

We recently reported that Ru^{II} is readily reduced to Ru^0 by simple treatment of $[Ru(CO)_3Cl_2(thf)]$ (**1**) with KOH followed by thermally induced decarboxylation of the incipient hydroxy-carbonyl adduct at 85 °C under CO (1 atm) to produce $[Ru_3(CO)_{12}]$ (Scheme 1).[1] The reaction is understood in terms of a reductive elimination of HCl[2, 3] from an unstable "acid"[4] hydrido intermediate. Though elusive, the latter is prone to insertion reactions in the presence of olefins or alkynes.[1, 5, 6] Upon simply replacing KOH by $[NEt_4][OH]$ with the aim to obtain highly concentrated solutions of the hydroxy-carbonyl adduct for a ^{13}C NMR investigation, we were surprised to observe that CO_2 evolution was becoming significant at room temperature, and occurred at rates apparently depending both on the nature of the counterion and the concentration.



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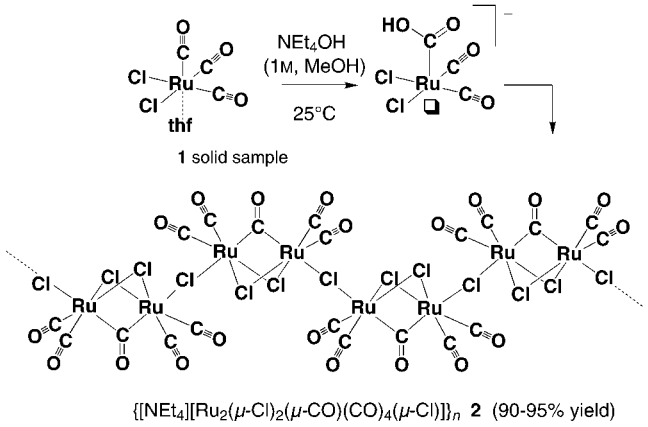
Scheme 1. Reaction of **1** with KOH.

Typically, when one equivalent of a concentrated methanolic solution of $[NEt_4][OH]$ (1 mL, 1.5 M) was added to a solid sample of **1** (500 mg, 1.5 mmol) at 25 °C, rapid dissolution of the complex was observed within seconds along with gas evolution (strong $\nu(CO_2)$ IR absorption at 2338 cm^{-1}) and development of an intense red color. This was rapidly followed by nearly quantitative precipitation of a red-orange microcrystalline product. High-quality homogeneous single crystals of this product were obtained from slightly modified experiments where **1** was dissolved in a minimum amount of ethanol or methanol (1 – 2 mL) prior to the addition of the hydroxide. This complex, recovered in 90 – 95 % yield, was formulated as **2** (Scheme 2) on the basis of an X-ray structure analysis revealing its polymeric nature (Figure 1).[7]



Scheme 2. Synthesis of the polymeric polyanion **2**. The square represents a vacant coordiation site.

The structure of **2** is based on the discrete association of identical monoanionic dimeric units. The basic motive is a face-sharing bioctahedron in which two ruthenium centers are connected through two bridging halides and one bridging carbonyl group. Each ruthenium atom bears two terminal carbonyl groups in a *fac* arrangement with the bridging one. The third halide (*trans* to the bridging CO) serves as a symmetric bridge between neighboring units of the polymeric chain. Though the metal – metal separation within the dimer is 2.964(1) Å, an electron count reveals that, formally, there is no metal – metal bond.

Complex **2** appears to be the first representative of the family of binary halo-carbonyl Ru^I species. Indeed, the relevant edge double-bridged Ru^I prototype $[Ru_2X_2(CO)_6]$ recently identified by Fachinetti, Funaioli et al.[8] for X = trifluoroacetate, is still unknown for X = halide,[9] though a number of phosphane-substituted derivatives have been prepared from other precursors.[10, 11]

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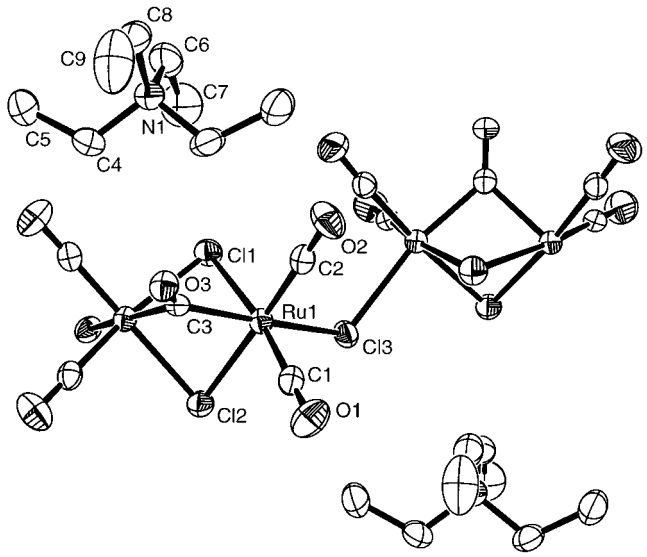
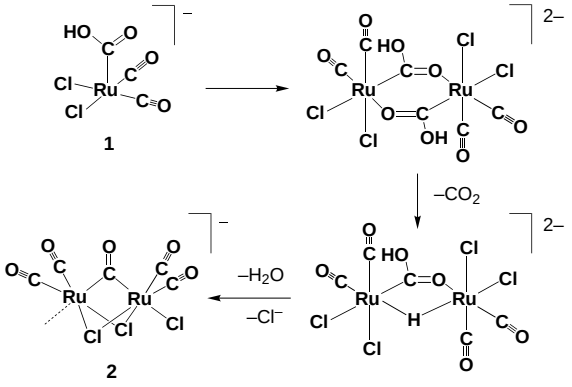


Figure 1. Perspective view of two consecutive units of the polymeric polyanion **2**. Selected interatomic distances [Å] and angles [°]: Ru1–Ru1* 2.964(1), Ru1–C1 1.842(6), Ru1–C2 1.838(6), Ru1–C3 2.031(6), Ru1–Cl1 2.499(2), Ru1–Cl2 2.489(2), Ru1–Cl3 2.614(2); Ru1-Cl3-Ru1* 113.24(8), Cl1-Ru1-Cl2 84.81(6), Cl1-Ru1-Cl3 88.64(6), Cl2-Ru1-Cl3 87.30(4), C1-Ru1-C2 87.9(2), C1-Ru1-C3 93.5(3), C2-Ru1-C3 90.7(2).

Why do we get Ru^{I} here? Indeed, reductive elimination of HCl from a Ru^{I} precursor should normally give Ru^{0}, as previously observed[1] when the decarboxylation of K[Ru{C(O)OH}$Cl_2(CO)_2$] is thermally induced under CO atmosphere (Scheme 1). We propose that both the high concentration and the absence of a strongly coordinating solvent favor intermolecular association of the incipient unsaturated mononuclear hydroxy-carbonyl adduct as a dimer involving either bridging hydroxy-carbonyl groups[12] or bridging halides (Scheme 3).



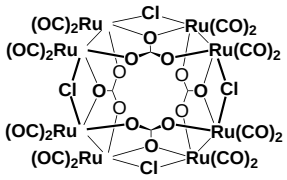
Scheme 3. Proposed mechanism for the formation of **2**.

At room temperature, the molecule loses only one CO_2 per dimeric unit to form a transient bimetallic hydrido-hydroxy-carbonyl complex. Intramolecular neutralization between the "acid" hydride and the OH^- of the remaining hydroxy-carbonyl group will lead directly to the unsaturated building block of the polymer [Eq. (1)].

$$2n[Ru(CO)_3Cl_2(thf)] + 2n NEt_4OH \longrightarrow \{[NEt_4][Ru_2(CO)_5Cl_3]\}_n + n CO_2 + n H_2O + n NEt_4Cl \quad (1)$$

On several occasions, beautiful yellow crystals of a minor species exhibiting an IR absorption at 1532 cm^{-1} were obtained from the filtrate of the reaction in Equation (1) after a few days. Their electrospray mass spectrum revealed a puzzling pattern, consisting of three multiplets at high m/z, namely, 1816.3, 1757.4, and 1651.1. A single-crystal X-ray analysis provided the clue to this phenomenon (see the Experimental Section) and allowed unambiguous formulation of the compound as the tetraanionic cluster **3** containing carbonate ligands (Scheme 4, Figure 2).[7b, 13]

$[NEt_4]Na_2[Ru_8(\mu\text{-}CO_3)_4(\mu\text{-}Cl)_4(CO)_{16}]$ **3**



Scheme 4. The tetraanionic unit of the carbonato cluster **3**.

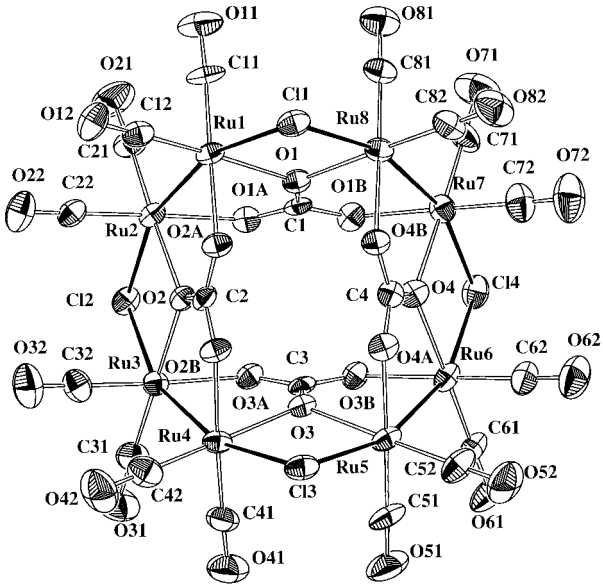


Figure 2. Perspective view of one of the two identical independent tetraanionic units of the carbonato cluster complex **3**. Selected interatomic distances [Å]: Ru1–Ru2 2.648(1), Ru3–Ru4 2.645(1), Ru5–Ru6 2.637(1), Ru7–Ru8 2.639(1), Ru1–O1 2.138(5), Ru8–O1 2.130(5), Ru1–Cl1 2.552(2), Ru8–Cl1 2.526(2), Ru1–O2A 2.108(5), Ru8–O4B 2.120(5), C1–O1 1.32(1), C1–O1A 1.26(1), C1–O1B 1.262(9), Ru1–C11 1.811(8), Ru1–C12 1.804(9), C11–O11 1.16(1), C12–O12 1.16(1).

The tetraanionic ensemble is based on the fusion of four identical metal–metal-bonded dimeric units "$Ru_2(CO)_4$" assembled together into a ring by four bridging halides and four bridging carbonate moieties. The carbonate groups are the principal building blocks responsible for the observed annulation: Each one holds two consecutive Ru dimers by acting 1) as a bridging ligand connecting these dimers through a μ_2-oxygen atom spanning the same open Ru···Ru edge as the μ-halide, and 2) as a doubly chelating ligand supporting the two Ru–Ru-bonded edges. Though carbonate ligands are rarely seen in ruthenium carbonyl complexes, there is some precedent with other metals.[14] A close examination of the

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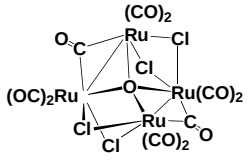
packing[7b] reveals that the sodium cations are located on both sides of the crown, along its virtual fourfold symmetry axis, and in close contact with the carbonate oxygen atoms.

Let us confess that the source of sodium ions in the original preparation giving the first crystals of **3** was incidental: We believe they came from our glassware which had been cleaned by immersion into an ethanolic NaOH bath and might have been insufficiently rinsed. It is amazing that such traces of sodium ions were selectively removed from the solution by the multiply charged anion just acting as a crown ether.

Of course, the carbonate ligand originates from the reaction products, namely, CO_2 and H_2O. Evidence for this dual origin could be obtained by simple modifications of the experimental conditions: First, when the released CO_2 was evacuated under reduced pressure, the minor product obtained in addition to **2** was no longer **3**, but the known oxo species **4** (Scheme 5),[15, 16] the oxygen atom of which comes from the water released in the reaction [see Eq. (1)]. The oxo compound even became the major product when more water was added. Second, we found that improved yields of **3** can be obtained when the reaction is carried out in the presence of $NaHCO_3$ (see the Experimental Section).

$[NEt_4]_2[Ru_4(\mu\text{-}O)(\mu\text{-}Cl)_4(CO)_{10}]$ **4**



Scheme 5. The dianionic unit of the oxo cluster **4**.

Thus, the addition of $[NEt_4][OH]$ to **1** at 25 °C in concentrated solution appears to be a simple, rapid, and mild procedure to generate unsaturated ruthenium carbonyl halide fragments in a low oxidation state. Such fragments are prone to either polymerization in the absence of donor ligand or capturing any potentially coordinating molecule (including those produced in situ, as observed here). Consequently, we should be able to quench the polymerization process by any incoming donor ligand.[17] Effectively, if we saturate the solution and the atmosphere of the Schlenk flask with CO prior to the addition of $[NEt_4][OH]$ to **1** at 25 °C, we do not generate the polymer **2**. Instead, a 1/1 mixture of $[Ru_3(CO)_{12}]$ and $[NEt_4][Ru(CO)_3Cl_3]$ is recovered after a few hours. A glance at the basic unit of **2** allows an understanding of this phenomenon: The relative oxidation states of the two metal centers within the dimeric unit depend formally on how the bridging halides share their three electrons. Thus, the Ru^I–Ru^I dimer can be alternatively viewed as a Ru^0–Ru^{II} dimer in which we can even visualize the preformed ligand environment of the Ru^{II} center, "$[Ru(CO)_3Cl_3]^-$". Disruption of the chain by CO leads to a net differentiation between Ru^0 and Ru^{II} centers.

The present observation is reminiscent of the CO-induced disproportionation of $[Ru_2X_2(CO)_6]$ ($X = CF_3COO$) in the presence of an excess of X^-.[8] Our concordant findings, probably generalizable to a range of other anionic nucleophiles, demonstrate the ability of halides or pseudohalides to mediate an interplay between low oxidation states of ruthenium, with possible relevance for their role as promoters in many catalytic systems.[6, 18]

We have recently observed that treatment of **1** with $[NEt_4][OH]$ at 25 °C in the presence of various unsaturated incoming substrates (e.g., olefins, alkynes, formate esters) does not yield the polymer **2**, but new trappable adducts between these substrates and the unsaturated fragments thus generated.

Experimental Section

2: A solid sample of **1**[1] (500 mg, 1.5 mmol) was dissolved in ethanol (ca. 1–2 mL) and stirred in a small Schlenk flask under nitrogen. A 1.5 M solution of NEt_4OH in methanol (1 mL) was added dropwise. Magnetic stirring was stopped after 2 min. Homogeneous large crystals of **2** suitable for X-ray diffraction were obtained within 2 h. The mother liquor was then cannulated into another tube and kept separately. Slower crystallization of the minor product **3** was then observed after a few days; a direct synthesis of **3** was also devised (see below). Crystals of **2** were washed with dichloromethane and alcohol, and isolated (420 mg, 95% yield). IR (KBr pellets from single crystals): $\tilde{\nu} = 2052$(s), 2043(s), 2021(s), 1984(s), 1962(s), 1944(sh), 1928(sh), 1728(s), 1723(s) cm^{-1} (ν(CO)). The crystals are only soluble in CH_3CN, which, however, causes disruption of the polymer as indicated by 1) the disappearance of the absorption for the bridging CO group (IR (CH_3CN): $\tilde{\nu} = 2047$(s), 2021(s), 1982(s), 1964(s) cm) and 2) the detection of the ion $[Ru_2(CO)_4Cl_3]^-$ (m/z 422.6) in the electrospray mass spectrum.

3: Complex **1** (500 mg, 1.5 mmol) and $NaHCO_3$ (126 mg, 1.5 mmol) were dissolved in ethanol (10 mL). After addition of a 1.5 M solution of NEt_4OH in methanol (1 mL), the solution was heated at 85 °C for 5 min, during which the orange color intensified. After addition of acetone (2 mL), the solution was allowed to crystallize at room temperature.[13] Crystals of **3** suitable for X-ray diffraction appeared on the walls of the glassware over a period of 5 d. They were isolated by filtration and washed with ethanol (70 mg, 19% yield). IR (KBr pellets from single crystals): $\tilde{\nu} = 2028$(vs), 1953(m), 2021(s), 1948(s, br), 1910(m) (ν(CO)), 1532(s) cm^{-1} (ν(OCO)). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) $\delta = 204.8$, 204.6 (CO), 169.5 (CO_3), 52.5 ($N(CH_2CH_3)_4^+$), 14 ($N(CH_2CH_3)_4^+$); ES-MS (CH_3CN): m/z: 843 ($[Na_2(Ru_8(CO_3)_4Cl_4(CO)_{16})]^{2-}$), 1816 ($[Na_2(NEt_4)(Ru_8(CO_3)_4Cl_4(CO)_{16})]^-$), 1758 ($[Na(NEt_4)(Ru_8(CO_3)_4Cl_3(CO)_{16})]^-$), 1651 ($[Na_2(Ru_8(CO_3)_4Cl_3(CO)_{16})]^-$).

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Keywords: carbonyl complexes · cluster compounds · halogens · polyanions · ruthenium

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[7] a) Crystallographic data for **2**: orthorhombic, space group *Cmca*; $a = 11.721(2)$, $b = 19.580(2)$, $c = 17.686(2)$ Å; $V = 4058.9(9)$ Å^3; $R = 0.026$, $Rw = 0.057$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-133106 (**2**) and 133107 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[13] The first crystals of **3** were obtained from methanol/ethanol in a systematically twinned crystalline form (orthorhombic, space group *Immm*, $a = 14.919(1)$, $b = 20.006(2)$, $c = 22.279(3)$ Å). Acetone/ethanol mixtures gave single crystals of a different form, albeit containing solvent molecules: $[NEt_4]_2Na_2[Ru_8(\mu\text{-}CO_3)_4(\mu\text{-}Cl)_4(CO)_{16}] \cdot 2\,EtOH \cdot 0.5\,(CH_3)_2CO \cdot 1.5\,H_2O$: triclinic, space group *P*1, $a = 16.405(3)$, $b = 19.109(4)$, $c = 23.073(8)$ Å; $\alpha = 85.26(3)$, $\beta = 85.64(3)$, $\gamma = 72.97(2)$; $V = 6882(3)$ Å^3; $R = 0.035$, $Rw = 0.079$ (refinement on F^2).[7b]
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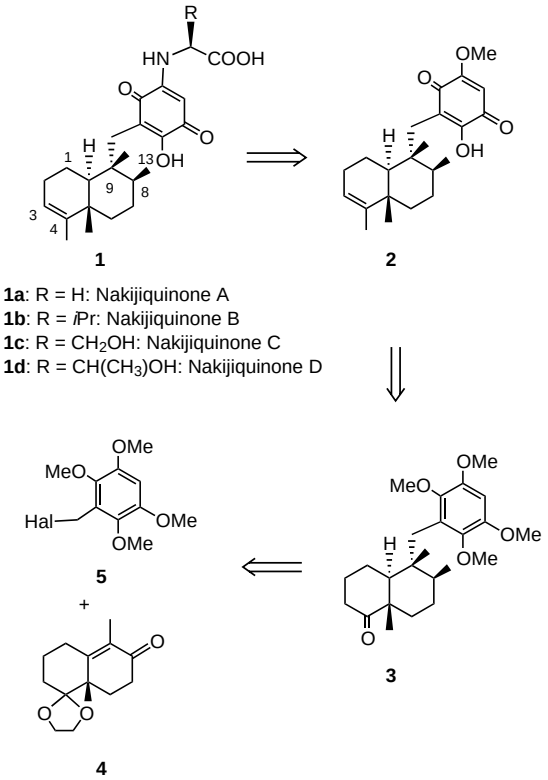
Asymmetric Synthesis of the Nakijiquinones—Selective Inhibitors of the Her-2/Neu Protooncogene**

Petra Stahl and Herbert Waldmann*

Extracellular growth-promoting signals are recognized in many cases by transmembrane receptors with tyrosine kinase activity. These proteins trigger numerous intracellular signalling cascades by which cell growth, proliferation, and other genetic programs are regulated.[1] Dysregulation of these signal sequences may contribute to or cause many diseases. For instance, enhanced activity of receptor tyrosine kinases can promote tumor growth and has been implicated in carcinogenesis.[2] A particularly relevant example is the Her-2/Neu-protooncogene (also called erbB-2). This receptor is vastly overexpressed in about 30% of primary breast, ovary, and gastric carcinomas.[1, 3, 4] Amplification is closely correlated with the clinical behavior of these neoplasms, such that tumors with Her-2 amplification are more agressive and associated with reduced patient survival. Therefore, compounds that can selectively block Her-2 activity are of paramount importance for the development of new anticancer drugs;[1, 2, 5] a monoclonal antibody against Her-2 has already been introduced by Genentech into the clinic as a new revolutionary treatment for breast cancer. In addition, such drugs are likely to be useful in dissecting signalling pathways.[2, 6, 7] Until today only a few natural products with intrinsic tyrosine kinase inhibiting activity per se were isolated and, in particular, a natural product that inhibits Her-2 has not been synthesized.[2, 6] Recently, however, the nakijiquinones **1a – d** (see Scheme 1) were identified as selective inhibitors of the Her-2/Neu kinase, displaying pronounced cytotoxicity against L 1210 murine leukemia cells and KB human epidermoid carcinoma cells.[8] We now disclose the first enantioselective total synthesis of the nakijiquinones.

The nakijiquinones embody three basic structural elements, an amino acid, a central *p*-quinoid unit, and a diterpenoid system. To reach a high degree of convergency, the nakijiquinones were first, dissected in a retrosynthetic sense into isospongiaquinone (**2**), an interesting natural product in its own right[9] and an amino acid that can be introduced in the last step by conjugate addition to the vinylogous methyl ester present[8] (Scheme 1). It was further planned to generate the selectively functionalized quinoid system by oxidation of a tetramethoxy-substituted aromatic precursor **3** to a 1,4-dicarbonyl compound and subsequent selective saponification



Scheme 1. Retrosynthetic analysis of the nakijiquinones **1**.

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