Stepwise Elongation of a Trinuclear Ruthenium Unit in Pyrazine-Bridged Linear Oligomers with Use of [Ru3(μ_3-O)(μ-CH3COO)6(pyridine)(CO)(H2O)]

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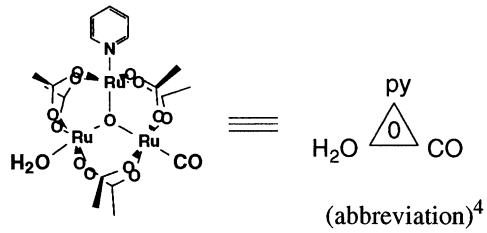
The synthetic method for the stepwise Ru3 unit elongation of pyrazine-bridged linear oligomer of trinuclear ruthenium complex with the Ru3(μ3-O)(μ-CH3COO)6 core has been developed, using a newly designed [Ru3(μ3-O)(μ-CH3COO)6(py)(CO)-(H2O)] (py = pyridine) with labile and photoactive sites.

Chemistry of redox active multi-metal-centered complexes or metal complex assemblies with highly ordered structure have attracted much attention.[1] Designing of the synthetic method is important for the construction of such structures, for the control of the properties and for the development of the functionality. One way to form such a multi-metal system is to oligomerize polynuclear metal complexes.[2] In this paper, we report a systematic linear-oligomerization of the trinuclear ruthenium complex with the Ru3(μ3-O)(μ-CH3COO)6 core by use of a newly designed complex [Ru3(μ3-O)(μ-CH3COO)6(py)(CO)-(H2O)] (**1**) which has two labilized sites with different nature in reactivity. The trinuclear ruthenium complex and its pyrazine(pz)-bridged dimer and trimer are of particular interest with the strong Ru(dπ)-oxo(pπ) interactions manifested by their redox behavior and their strong visible absorption.[3]

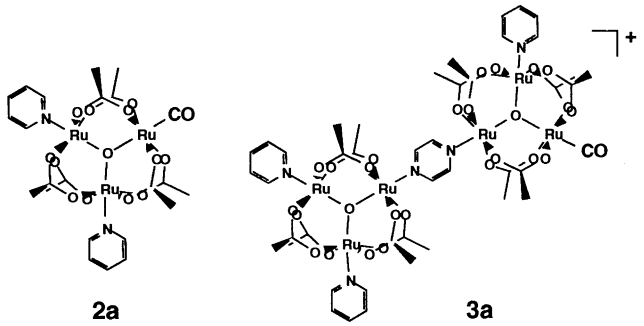


1 (abbreviation)[4]

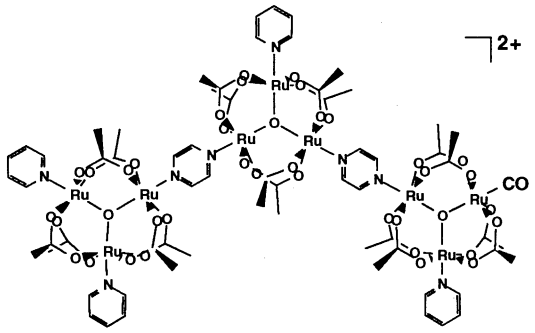
Compound **1** is a key Ru3 monomer for the one by one unit elongation in this study, and has three different ligands at the terminal positions.[5] It is known for this type of Ru3 complex that solvent ligands are labile and readily replaced by pyridyl ligands,[6] while the carbonyl site is inert but undergoes the photoelimination of the carbonyl group to pick up a solvent molecule or coexisting ligands.[7] Compound **1** has both the ligands as "reactive head" (H2O) and "protected tail" (CO) together with the inert "residual" ligand (py).[8]

Scheme 1[4,9] shows procedures for the stepwise Ru3 unit elongation, from carbonyl monomer **2a** to dimer **3a** and to trimer **4a**. The procedures for one unit elongation consist of three steps : (i) photo-decarbonylation of **2a** or **3a** to give solvent complexes **2b** or **3b**;[10] (ii) introduction of pz ligand to the resulting solvent site, giving pz-complexes **2c** or **3c**; (iii) introduction of **1** to the free nitrogen of the coordinated pyrazine, giving a one unit longer oligomer, **3a** or **4a**. The two reactive sites in the key monomer **1** are used sequentially. The solvent site (reactive head) is used in step (iii) to accept pyrazine complex **2c** or **3c**. The carbonyl site (protected tail) is used in step (i) of one unit elongated species **3a**.

Procedures for three step reaction leading monomer **2a** to dimer **3a** are roughly as follows. (i) A solution of **2a** (79 mg) in CH2Cl2 (90 cm3) was irradiated for 2 h with a high pressure Hg lamp. An excess of NH4PF6 (89 mg) in CH3OH was added.



2a **3a**

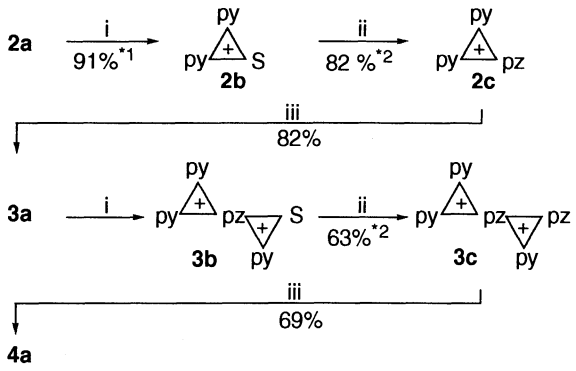


4a

The resulting solution was stirred for 29 min. and evaporated to dryness to give after workup **2b**PF6. (ii) The residue was again dissolved in CH2Cl2 (20 cm3) and pyrazine (37 equiv.) was added. The solution was stirred for 27 h and concentrated to ca. 3 cm3. The greenish-blue powder precipitating upon addition of n-hexane (100 cm3) was filtered and washed thoroughly with n-hexane. The solid was dissolved in CH2Cl2, and NH4PF6 was removed by filtration. Silica gel chromatography (Wakogel C-200, eluate: 0.4% CH3OH in CH2Cl2) yielded **2c**PF6 (71 mg, 73% yield from **2a**). (iii) The equimolar mixture of **2c**PF6 (490 mg) and **1** (375 mg) in CH2Cl2 (100 cm3) was stirred for 19 h and subjected to chromatography (0.7% in CH3OH in CH2Cl2) to yield **3a**PF6 (703 mg). Dimer **3a** has a carbonyl group at the elongated unit. The same three step reaction can be apply to the carbonyl site of **3a** to afford trimer **4a**, which has again carbonyl group at the end unit. Compounds **2b**, **2c**, **3a**, **3b**, **3c**, and **4a**

were isolated as PF_6^- salts and characterized by means of elemental analyses, ^1H NMR,[11] FAB mass, and cyclic voltammetry.

We emphasize the meanings and the potentiality of the method: (a) This series of processes can increase the number of the Ru3 unit in the oligomer one by one and afford the oligomer which has the same end unit structure as that of the precursor. Accordingly, this method should be applicable to the preparation of higher order oligomer, e.g., tetramer and pentamer, in a similar way. (b) Compounds in Scheme 1 could be precursors for functional supramolecules. Solvent sites in **1**, **2b**, and **3b** should behave as a Lewis acid site to accept the coordination of complexed ligand, e.g., photosensitizer such as 5-pyridyl-10,15,20-triphenylporphine,[12] or redox active ligand. The free nitrogen center of the coodinated pyrazine in **2c** and **3c** is a Lewis base site and the compounds should act as a redox active complexed ligand. (c) Substituted pyridines such as 4-cyano- or 4-dimethylamino-pyridine can be used as "residual ligand" in place of pyridine in **1**. Such derivaives of **1** have definitely different redox potentials depending on the substituents.[13] By using a derivative of **1** as the key monomer in the stepwise elongation in an appropriate sequence, oligomer with the redox potential slope along the chain can be prepared.[14]



Scheme 1.[4] i : hν/CH_2Cl_2, ii : pz(excess)/CH_2Cl_2, iii : **1**/CH_2Cl_2.
*1 yield for single step from **2a** to **2b**.
*2 total yield for i and ii without isolation of **2b** or **3b**.

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References and Notes

1 G. Denti, S. Campagna, S. Serron, M. Ciano, and V. Balzani, *J. Am. Chem. Soc.*, **114**, 2944 (1992). S. Campagna, G. Denti, S. Serron, M. Ciano, A. Juris, and V. Balzani, *Inorg. Chem.*, **31**, 2982 (1992) and references cited therein.

2 Recently, we prepared linear and branched Ru3 tetramers of the type of this study. T. Ito, H. Nagino, Y. Noguchi, and H. Kido, presented at 1995 International Chemical Congress of Pacific Basin Societies (Honolulu, December 1995). Abstract 698.

3 a) J. A. Baumann, D. J. Salmon, S. T. Wilson, and T. J. Meyer, *Inorg. Chem.*, **17**, 3342 (1978). b) J. A. Baumann, D. J. Salmon, S. T. Wilson, and T. J. Meyer, *Inorg. Chem.*, **18**, 2472 (1979). c) J. A. Baumann, S. T. Wilson, D. J. Salmon, S. P. Hood, and T. J. Meyer, *J. Am. Chem. Soc.*, **101**, 2916 (1979).

4 Triangle represents the $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$ core. Formal charge of the core is indicated inside the triangle, where 0 and + (see Scheme 1) correspond to the formal oxidation states $Ru_3^{III,III,II}$ and $Ru_3^{III,III,III}$, respectively. Terminal ligands are abbreviated : py = pyridine, pz = pyrazine, S = H_2O or CH_3OH.

5 Compound **1** was synthesized as follows. $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)(CH_3OH)_2)]$[3c] (395 mg or 0.0517 mmol) was dissolved in CH_2Cl_2-CH_3OH (1:1, 100 cm^3) containing pyridine (0.8 equiv). The solution was stirred for 2 d at room temperature and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (ca 20 cm^3) and insoluble materials were removed by filtration. The filtrate was chromatographed over silica gel (Wacogel C-200) and eluted with 2% CH_3OH in CH_2Cl_2. The blue-purple solution from the main band (2nd fraction) was evaporated to dryness to give powdery solid of **1**. Yield, 184 mg (45%). Anal. Found: C, 27.27; H, 3.36; N, 1.69%. Calcd for **1** (=$Ru_3C_{19}H_{27}O_{15}N$): C, 27.07; H, 3.16; N, 1.75%. FABMS: *m/z* : 754 [calcd M-CO-H_2O = 752]. ^1H NMR (270 MHz) in D_2O : δ = 9.62 (2H, d, *o*-py), 8.61 (1H, t, *p*-py), 8.27 (2H, m, *m*-py), 1.99 (6H, s, CH_3)), 1.97 (6H, s, CH_3)), 1.76 (6H, s, CH_3)).

6 Y. Sasaki, A. Nagasawa, A. Tokiwa, and T. Ito, *Inorg. Chim. Acta*, **212**, 175 (1993). M. Abe, Y. Sasaki, A. Nagasawa, and T. Ito, *Bull. Chem. Soc. Jpn.*, **65**, 1411 (1992).

7 H. Kido, T. Matsumoto, H. Nagino, D. Akashi, M. Abe, Y. Sasaki, and T. Ito, pressented at XXXth ICCC (Kyoto, July 1994). Abstracts p.172.

8 This ligand is irrelevant to bridging and locates outside as the residual group when the core is incorporated into oligomers.

9 Compounds **2a**, **2b**, and **2c** are known,[3a] but the synthetic methods and routes are new. **2a** was obtained together with **1** as the first band of the chromatography described in Refs. and Notes 5.

10 Photo-decarbonylation in CH_2Cl_2 in step (i) makes the electric charge of the resulting compound increased by +1.

11 All the compounds except for **2a** in Scheme 1 are paramagnetic, however, trinuclear units with the CO ligand show sharp ^1H NMR signals at normal positions as if they are diamagnetic. Non carbonyl trinuclear units also show relatively sharp ^1H NMR signals except for protons in the close proximity of paramagnetic ruthenium centers. Most of them are assignable, although their chemical shifts are far shifted from the normal positions.

12 M. Hata, Y. Ishida, H. Kido, and T. Ito, presented at XXIX ICCC (Lausanne, July 1992), Abstract P 421. T. Sakuma and H. Kido, to be presented at XXXIst ICCC (Vancouver, August 1996).

13 H. E. Toma, C. J. Cunha, and C. Cipriano, *Inorg. Chim. Acta*, **154**, 63 (1988). M. Abe, Y. Sasaki, T. Yamaguchi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **65**, 1585 (1992).

14 Recently, such a compound, $[\{Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(4\text{-cyanopyridine})_2\}\text{-pz-}\{Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)\}\text{-pz-}\{Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(4\text{-dimethylaminopyridine})_2\}](PF_6)_3$ was preliminarily isolated in our laboratories.