CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000387

Synthetic Design of Heterometallic Cluster Compounds with Site-Selective and Stepwise Substitution of Bridging Carboxylates

Atsushi Ikegami, Masaaki Abe,* Atsushi Inatomi, and Yoshio Hisaeda*[a]

Heterometallic complexes and clusters have attracted considerable attention recently not only due to their biological significance in metalloenzyme active-sites[1] but also to the widespread interest in synthetic coordination chemistry, intramolecular electronic and magnetic interactions, and catalysis.[2] Nonequivalence of metal centers in such systems also facilitates site-selective reactions based on disparate metal centers. This distinctive character is, in principle, extended to synthesize new compounds incorporating differentiated ligands at distinct metal sites through coordination. Such site-selectivity is well documented by solution kinetic studies in many heterometallic systems,[3,4] but its the usefulness and applications to synthetic aspects remain little explored to date.

Oxo-centered, acetato-bridged trinuclear complexes $[Ru^{III}{}_2M^{II}(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]$, where M = the first-row transition-metal divalent ions and Mg^{II} and py = pyridine, constitute a rare but crucial class of heterometallic compounds, in which two distinct metal centers with remarkably different degrees of substitution-lability are incorporated.[5–8] This feature has been solely demonstrated by kinetic studies for the substitution of *monodentate* ancillary ligands.[6,7] Here we report that this site-selectivity is extended to the substitution of the *bridging carboxylates* in this class of compounds, through which more diverse, synthetic derivatization of the heterometallic clusters should be amenable. We show that the acetato ligands at the hetrometallic Ru···Mg sites are selectively substituted in the $\{Ru_2MgO(CH_3COO)_6\}$ core in a stepwise manner, and the individual substituted products thus formed have been successfully separated and characterized. The substitution-lability-dependent synthetic strategy described here will lead to a new generation of "multi-chromophore" compounds, in which the functional subunits are immobilized in the molecular framework in well-defined number and geometrical location.

Compounds **1**–**4** prepared in this work are shown in Scheme 1:

$[Ru_2MgO(CH_3COO)_5(C_2H_5COO)(py)_2(H_2O)]$ **1**

$[Ru_2MgO(CH_3COO)_4(C_2H_5COO)_2(py)_2(H_2O)]$ **2**

$[Ru_2MgO(CH_3COO)_3(C_2H_5COO)_3(py)_2(H_2O)]$ **3**

$[Ru_2MgO(CH_3COO)_2(C_2H_5COO)_4(py)_2(H_2O)]$ **4**

Complex **2** is isolated as a mixture of three coordination position isomers with respect to the location of two propionato and two acetato ligands spanning the Mg···Ru sites in the Ru_2MgO core.

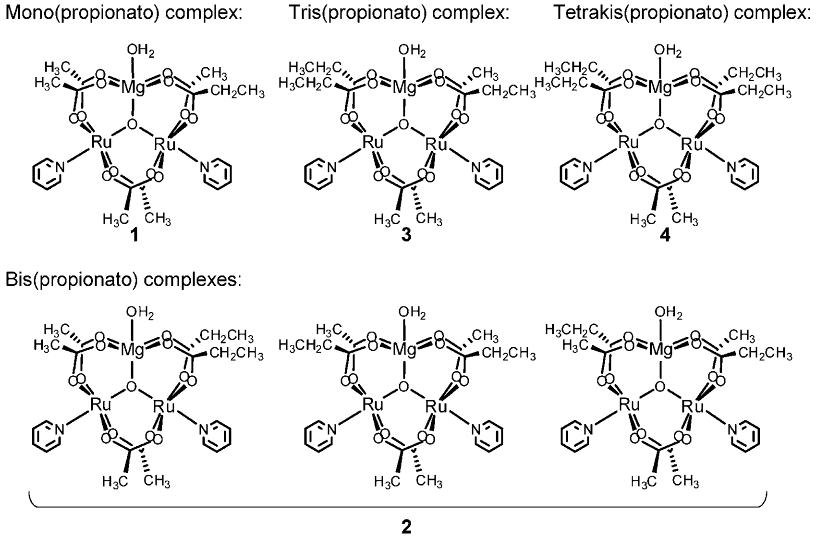
Through **1** to **4**, one, two, three, and four propionate ions replace the corresponding number of acetato bridges in the $\{Ru_2MgO(CH_3COO)_6\}$ core. Compounds **1**–**4** were prepared in a one-pot manner by the reaction of $[Ru_2MgO(CH_3COO)_6(py)_3]$[5] with a large excess of C_2H_5COONa in an acetone–water mixture (10:1, v/v) for 24 h at room temperature, followed by separation of the substituted products with column chromatography, in which compounds with the increasing number of propionato ligands were eluted faster.[9] The compounds have been identified by several spectroscopic and electrochemical methods, and satisfactory elemental analysis, along with an X-ray diffraction study on a derivative of **4**. In all the cases, an aqua ligand is found to occupy the sixth coordination site of the Mg center. Synthetic yields of **1**, **2**, **3**, and **4** were 6.9, 12.4, 29.2, and 36.1 %, respectively.

Electrospray ionization (ESI) mass spectra of **1**, **2**, **3**, and **4** clearly show the corresponding parent peaks at *m/z* of 770, 784, 798, and 814, respectively, indicating the formation of $[Ru_2MgO(CH_3COO)_{6-n}(C_2H_5COO)_n(py)_2]$ with $n = 1$ through 4, where the loss of the aqua ligand on Mg is ob-

---

[a] A. Ikegami, Prof. Dr. M. Abe, A. Inatomi, Prof. Dr. Y. Hisaeda
Department of Applied Chemistry
Graduate School of Engineering
Kyushu University, Nishi-ku, Fukuoka 819-0395 (Japan)
Fax: (+81) 92-803-2827
E-mail: mabe@mail.cstm.kyushu-u.ac.jp
yhisatcm@mail.cstm.kyushu-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000387.



Scheme 1. Chemical structures of **1**–**4**.

served upon ionization. No other products such as pentakis- and hexakis(propionato) complexes were detected.

Single crystals suitable for X-ray diffraction study were obtained from a CH_2Cl_2/*n*-hexane/pyridine mixed solution of **4**. This solvent system afforded crystals with the formula $[Ru_2MgO(CH_3COO)_2(C_2H_5COO)_4(py)_3]\cdot py$ (**4'**·py), in which pyridine occupies the Mg center as a result of ligand replacement during crystallization.[10] The molecular structure, shown in Figure 1, clearly reveals site-selective substitution on the Ru_2MgO core, where four propionato ligands bridge the Mg···Ru edges, while two acetato ligands still remain on the Ru···Ru edge. The triangular framework is best described as an equilateral triangle with longer Mg···Ru distances (3.396(4) and 3.434(4) Å) as compared to the Ru···Ru (3.301(3) Å) distance, which is an outcome of the significant difference in the metal–(μ_3-O) distances; Mg–(μ_3-O) 2.052(7), Ru–(μ_3-O) 1.879(7) and 1.918(6) Å.

Compounds **1**–**4**, which contain a $Ru_2^{III,III}Mg^{II}O$ core, are all diamagnetic and the structural confirmation has been further substantiated by ^1H NMR spectra measured in $CDCl_3$, which show resonances due to aromatic protons on the ancillary pyridyl rings, methyl groups of acetato ligands, and ethyl groups of the propionato ligands being consistent with the expected numbers and intensity ratio for the respective compounds.[9] As already shown in Scheme 1, complex **2** turned out to be a mixture of three "coordination position isomers" with respect to the location of two acetato and two proponato ligands on the Mg···Ru bridging sites. Separation and isolation of these isomers remain yet to be achieved.

We note that such substitution reactions to form "mixed carboxylate" hetero-trimetallic complexes is unprecedented in the literature, although site-selectivity for some homometallic systems such as dinuclear and metal-metal bonded cluster compounds have been reported.[11,12]

A carboxylate substituent effect is not apparent in the absorption spectra, but it is observed in the redox potential shift in the cyclic voltammograms (CVs).[9] The reference compound $[Ru_2MgO(CH_3COO)_6(py)_2(H_2O)]$[8] in CH_2Cl_2 containing 0.1 M nBu_4NPF_6 as a supporting electrolyte exhibits two reversible processes at $E_{1/2} = 0.00$ and $+1.07$ V versus Fc/Fc^+, which are assigned to Ru-based, successive one-electron transfers, $Ru_2^{III,III}/Ru_2^{III,IV}$ and $Ru_2^{III,IV}/Ru_2^{IV,IV}$, respectively, and also gives an irreversible peak at $E_{pc} = -1.75$ V ascribed to a one-electron reduction of $Ru_2^{III,III}$ to $Ru_2^{II,III}$.[8] We find a small but

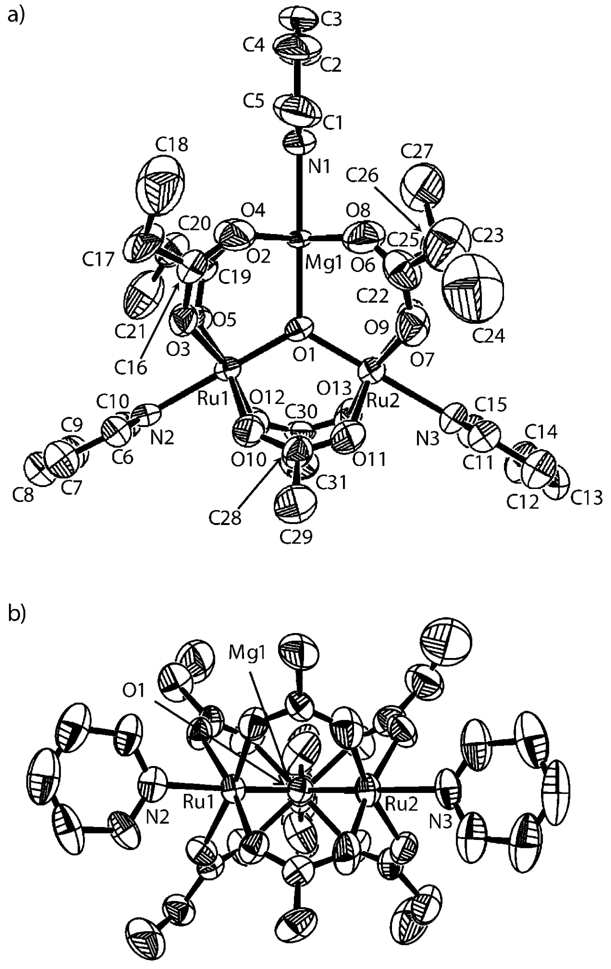
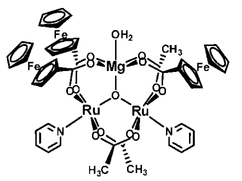


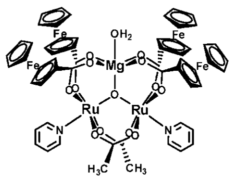
Figure 1. ORTEP drawings of **4'**·py viewed from two different directions, (a) and (b), with thermal ellipsoids at a 50 % probability level. A solvated pyridine molecule and hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: Mg1···Ru1 3.396(4), Mg1···Ru2 3.434(4), Ru1···Ru2 3.301(3), Mg1–O1 2.052(7), Ru1–O1 1.879(7), Ru2–O1 1.918(6), Mg1–N1 2.199(10), Ru1–N2 2.147(9), Ru2–N3 2.159(10); Mg1-O1-Ru1 119.4(3), Mg1-O1-Ru2 119.8(3), Ru1-O1-Ru2 120.8(3).

significant shift in $E_{1/2}$ and E_{pc} values to a negative side upon increasing the number of propionato bridges due apparently to the electron-donating ability of the ethyl group in the propionato ligand.[13]

With the site selectivity for carboxylato ligands in hand, it is possible to immobilize various chemical functionalities on the Ru_2MgO motif with the well-defined number and location. To investigate this feasibility, we set out to attach ferrocenylcarboxylate anions ($FcCOO^-$) to the Ru_2MgO core to yield new redox-active heterometallic compounds. The ferrocenylcarboxylate has been well utilized for the synthesis of multiferrocene assemblies.[14] Also, relevant to molecular quantum cellular automata,[15] the synthesis of compounds incorporating four identical redox-active groups is highly sought. Thus, the reaction of $[Ru_2MgO(CH_3COO)_6(py)_2(H_2O)]$ with four equivalents of sodium ferrocenylcarboxylate (FcCOONa) in CH_2Cl_2–CH_3OH for three days at room temperature afforded substituted products from which, after workup, compounds containing three and four ferrocenyl groups, $[Ru_2MgO(CH_3COO)_3(FcCOO)_3(py)_2(H_2O)]$ (**5**) and $[Ru_2MgO(CH_3COO)_2(FcCOO)_4(py)_2(H_2O)]$ (**6**), have been successfully isolated in reasonable yields.



5



6

We have found that the Fc groups attached to the Ru_2MgO core through the metal–carboxylate coordination mutually interact in the electrochemical oxidation process. Cyclic voltammograms of **5** and **6** (Figure 2) dissolved in CH_2Cl_2–CH_3OH (10:1, v/v) containing 0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte revealed three fully reversible processes in the potential region between −0.40 and +1.20 V versus Fc/Fc$^+$.[16]

For **6** (Figure 2a), the first process, labeled as I ($E_{1/2} = -0.07$ V), is readily assigned to a Ru-based, reversible one-electron transfer, $Ru_2^{III,III}/Ru_2^{III,IV}$.[8] This $E_{1/2}$ value is found to be more negative than that of the parent hexakis(acetato) complex $[Ru_2MgO(CH_3COO)_6(py)_2(H_2O)]$ under the same conditions ($E_{1/2} = 0.00$ V), reflecting the larger electron-donating effect of the Fc group. The second and third reversible processes, labeled as II ($E_{1/2} = +0.15$ V) and III ($E_{1/2} = +0.44$ V), respectively, are ascribed to stepwise oxidations of the Fc groups to yield ferricinium (Fc$^+$) ions. The intensity ratio of these Fc-based waves suggests that three of the four Fc groups in **6** are first oxidized at very similar potentials (process II) and then the remaining single Fc group is oxidized in the more positive potential (process III).[17] The comproportionation constant (K_{com})[18] for the mixed-valent $\{Fc^+\}_3\{Fc\}$ state is remarkably large (8.0×10^4 at 298 K), suggesting the occurrence of intramolecular electronic communication among the multiple Fc and Fc$^+$ centers through the Ru_2MgO core. A similar trend is seen for **5** (Figure 2b), where the mixed-valent $\{Fc^+\}_2\{Fc\}$ state is observed. In these systems, an electrostatic contribution to split the redox waves seems unlikely because of a large separation among the redox-active sites within the molecule.[19] We note that the reversibility of those Ru-based and Fc-based redox waves was found to decrease when strongly donating DMF was employed as a solvent.[9]

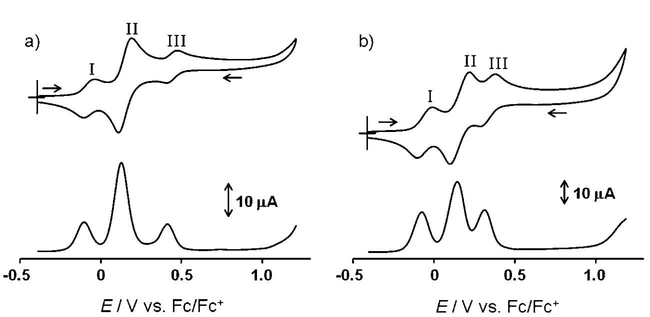


Figure 2. Cyclic voltammograms and differential-pulse voltammograms (DPVs) for a) **6** (0.3 mM) and b) **5** (1.0 mM) in CH_2Cl_2–CH_3OH (10:1, v/v) containing 0.1 M nBu$_4$NPF$_6$. Scan rates: 0.10 V s^{-1} for CVs and 0.05 V s^{-1} for DPVs.

In conclusion, the substitution-lability difference of distinct metal centers has been successfully extended for the first time to the synthesis of new types of mixed-carboxylato compounds in which the number and location of the different carboxylato groups are immobilized in a well-defined manner. This synthetic methodology is useful for the facile immobilization of redox-ative groups onto the trinuclear framework through which they are able to be mutually interactive. Owing to the availability of versatile carboxylato ligands,[20] the synthetic route developed in this work will be readily applied to various “multi-chromophore” architectures where different subunits are linked together in one molecule through coordination; studies in this direction are in progress.

Experimental Section

Synthesis of complexes 1–4: To a solution of $[Ru_2MgO(CH_3COO)_6(py)_3]\cdot CH_2Cl_2$ (200 mg, 0.218 mmol) in acetone (100 mL) was added an aqueous solution (10 mL) of sodium propionate (1150 mg, 12.0 mmol) with stirring. The resulting solution was allowed to react for 24 h at room temperature. Evaporation of the solvent gave a purple solid residue, which was dissolved in CH_2Cl_2 (200 mL). The solution was washed with water (3 × 100 mL) to extract the unreacted sodium propionate, and dried over $MgSO_4$ overnight. After filtration, the solvent was evaporated. The solid residue thus obtained was separated by chromatography on a silica gel column (ϕ 5 × 40 cm). Elution with 3% CH_3OH–CH_2Cl_2 gave four purple bands. On the basis of the following analytical and spectroscopic data, the first, second, third, and fourth bands were assigned to be **4**, **3**, **2**, and **1**, respectively. Analytically pure compounds were obtained as purple solids by recrystallization from CH_2Cl_2/n-hexane at room temperature. Yield: **1**: 11.8 mg (6.9%); **2**: 21.7 mg (12.4%); **3**: 51.9 mg (29.2%); **4**: 65.2 mg (36.1%).

Synthesis of complexes 5 and 6: To a solution of $[Ru_2MgO(CH_3COO)_6(py)_3]\cdot CH_2Cl_2$ (50 mg, 0.055 mmol) in CH_2Cl_2 (20 mL) was added a solution of sodium ferrocenylcarboxylate (55.9 mg, 0.22 mmol) in CH_3OH (3 mL) with stirring. The solution was allowed to react for three days at room temperature. Evaporation of the solvent gave a solid residue, which was dissolved in CH_2Cl_2 (100 mL). The solution was washed with water (3×100 mL) to remove unreacted sodium ferrocenylcarboxylate, and then dried over $MgSO_4$ overnight. After filtration, the solvent was evaporated, and the solid residue was separated by chromatography on a silica gel column (ϕ 2.5×30 cm). Elution with 5% CH_3OH–C_6H_6 gave three bands and a minor adsorbed species remained on the column. Due to a sample limitation, only the first and second bands were studied. Complex **5** was obtained as a purple solid from the first band by evaporating the solvent followed by recrystallization of the residue from CH_2Cl_2/*n*-hexane. Yield: 19.0 mg (23.6%). Complex **6** was obtained as a purple solid from the second band similarly. Yield: 24.1 mg (34.0%).

Characterization data of **1**–**6** as well as experimental details are provided in the Supporting Information.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Area of “Chemistry of Concerto Catalysis” (No. 18065018), “Chemistry of Coordination Space” (No. 17036002), Grant-in-Aid for Scientific Research (A) (No. 21245016), Grant-in-Aid for Scientific Research (B) (No. 20350029), and the Global COE Program, “Science for Future Molecular Systems”, from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Keywords: carboxylates · cluster compounds · coordination chemistry · ruthenium · substitution reactions

---

[1] a) A. Volbeda, E. Garcin, C. Piras, A. L. de Lacey, V. M. Fernandez, E. C. Hatchikian, M. Frey, J. C. Fontecilla-Camps, *J. Am. Chem. Soc.* **1996**, *118*, 12989–12996; b) J. C. Fontecilla-Camps, P. Amara, C. Cavazza, Y. Nicolet, A. Volbeda, *Nature* **2009**, *460*, 814–822; c) D. J. Evans, C. J. Pickett, *Chem. Soc. Rev.* **2003**, *32*, 268–275; d) B. E. Barton, C. M. Whaley, T. B. Rauchfuss, D. L. Gray, *J. Am. Chem. Soc.* **2009**, *131*, 6942–6943; e) C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245–2274; f) S. E. McGlynn, D. W. Mulder, E. Spepard, J. B. Broderick, J. W. Peters, *J. Chem. Soc. Dalton Trans.* **2009**, 4274–4285.

[2] a) R. D. Cannon, R. P. White, *Prog. Inorg. Chem.* **1988**, *36*, 195–298; b) J. A. Stride, S. K. Bollen, N. Chai Sa-Ard, G. J. Kearley, U. A. Jayasooriya, R. D. Cannon, *J. Am. Chem. Soc.* **1993**, *115*, 7778–7782; c) M. Abe, Y. Sasaki, Y. Yamada, K. Tsukahara, S. Yano, T. Yamaguchi, M. Tominaga, I. Taniguchi, T. Ito, *Inorg. Chem.* **1996**, *35*, 6724–6734; d) A. B. Blake, E. Sinn, A. Yavari, K. S. Murray, B. Moubaraki, *J. Chem. Soc. Dalton Trans.* **1998**, 45–49; e) B. Singh, J. R. Long, F. F. de Biani, D. Gatteschi, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 7030–7047; f) R. D. Adams, B. Captain, *Angew. Chem.* **2008**, *120*, 258–263; *Angew. Chem. Int. Ed.* **2008**, *47*, 252–257.

[3] G. Novitchi, F. Riblet, R. Scopelliti, L. Helm, A. Gulea, A. E. Merbach, *Inorg. Chem.* **2008**, *47*, 10587–10599.

[4] a) K. Nakata, A. Nagasawa, N. Soyama, Y. Sasaki, T. Ito, *Inorg. Chem.* **1991**, *30*, 1575–1579; b) Y. Sasaki, A. Tokiwa, T. Ito, *J. Am. Chem. Soc.* **1987**, *109*, 6341–6347; c) Y. Sasaki, A. Nagasawa, A. Tokiwa-Yamamoto, T. Ito, *Inorg. Chim. Acta* **1993**, *212*, 175–182.

[5] A. Ohto, Y. Sasaki, T. Ito, *Inorg. Chem.* **1994**, *33*, 1245–1246.

[6] M. Abe, M. Tanaka, K. Umakoshi, Y. Sasaki, *Inorg. Chem.* **1999**, *38*, 4146–4148.

[7] a) Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, T. Ochi, T. Ito, *Inorg. Chem.* **1991**, *30*, 4903–4908; b) M. Abe, A. Mitani, A. Ohsawa, M. Herai, M. Tanaka, Y. Sasaki, *Inorg. Chim. Acta* **2002**, *331*, 158–167.

[8] M. Tanaka, N. Kariya, M. Abe, Y. Sasaki, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 192–194.

[9] See the Supporting Information for details.

[10] Crystal data for **4′**·py: $C_{31}H_{41}MgN_3O_{13}Ru_2{\cdot}C_5H_5N$, $M=969.22$, monoclinic, space group $P2_1/n$, $a=13.057(14)$, $b=15.261(16)$, $c=21.43(2)$ Å, $\beta=91.44(2)°$, $V=4269(8)$ Å^3, $Z=4$, $T=223(2)$ K, $\rho_{calcd}=1.508$ g cm^{-3}, $\mu=0.786$ mm^{-1}, 18573 reflections collected, 6271 independent reflections ($R_{int}=0.0926$), final R indices [$I>2\sigma(I)$]: $R_1=0.0750$, $wR_2=0.1747$, GOF=1.124 [$I>2\sigma(I)$]. For more details, see the Supporting Information. CCDC-754952 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] T. Yamaguchi, Y. Sasaki, A. Nagasawa, T. Ito, N. Koga, K. Morokuma, *Inorg. Chem.* **1989**, *28*, 4311–4312.

[12] a) M. Ohashi, A. Yagyu, Q. Xu, K. Mashima, *Chem. Lett.* **2006**, *35*, 954–955; b) M. Ohashi, A. Yagyu, T. Yamagata, K. Mashima, *Chem. Commun.* **2007**, 3103–3105.

[13] A. Inatomi, M. Abe, Y. Hisaeda, *Eur. J. Inorg. Chem.* **2009**, 4830–4836.

[14] a) N. Prokopuk, D. F. Shriver, *Inorg. Chem.* **1997**, *36*, 5609–5613; b) J. H. K. Yip, J. Wu, K.-Y. Wong, K. P. Ho, C. S.-N. Pun, J. J. Vittal, *Organometallics* **2002**, *21*, 5292–5300; c) M. W. Cooke, T. S. Cameron, K. N. Robertson, J. C. Swarts, M. A. S. Aquino, *Organometallics* **2002**, *21*, 5962–5971; d) Q.-H. Wei, L.-X. Zhang, L.-X. Shi, Z.-N. Chen, *Inorg. Chem. Commun.* **2004**, *7*, 286–288; e) G.-L. Zheng, J.-F. Ma, Z.-M. Su, L.-K. Yan, J. Yang, Y.-Y. Li, J.-F. Liu, *Angew. Chem.* **2004**, *116*, 2463–2465; *Angew. Chem. Int. Ed.* **2004**, *43*, 2409–2411; f) A. Albinati, F. F. de Biani, P. Leoni, L. Marchetti, M. Pasquali, S. Rizzato, P. Zanello, *Angew. Chem.* **2005**, *117*, 5847–5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5701–5705.

[15] a) J. Jiao, G. J. Long, L. Rebbouh, F. Grandjean, A. M. Beatty, T. P. Fehlner, *J. Am. Chem. Soc.* **2005**, *127*, 17819–17831; b) J. Jiao, G. J. Long, F. Grandjean, A. M. Beatty, T. P. Fehlner, *J. Am. Chem. Soc.* **2003**, *125*, 7522–7523.

[16] Due to low solubility of **6** in CH_2Cl_2, a small amount of CH_3OH was required to prepare the solution for the electrochemical measurements.

[17] The second Ru-based process $Ru_2^{III,IV}/Ru_2^{IV,IV}$ which occurs at $E_{1/2}=1.04$ V versus Fc/Fc$^+$ for **4** in 0.1 M nBu$_4$NPF$_6$/CH$_2$Cl$_2$, was not observed for **5** and **6** in the potential region studied and may be shifted beyond the potential window due to the highly positive charge (+5) of the electrochemically generated species.

[18] a) D. E. Richardson, H. Taube, *Coord. Chem. Rev.* **1984**, *60*, 107–129; b) Y. Sasaki, M. Abe, *Chem. Rec.* **2004**, *4*, 279–290.

[19] V. Mereacre, M. Nakano, J. Gmez-Segura, I. Imaz, C. Sporer, K. Wurst, J. Veciana, C. Turta, D. Ruiz-Molina, P. Jaitner, *Inorg. Chem.* **2006**, *45*, 10443–10445.

[20] For example, see: M. W. Cooke, G. S. Hanan, F. Loiseau, S. Campagna, M. Watanabe, Y. Tanaka, *Angew. Chem.* **2005**, *117*, 4959–4962; *Angew. Chem. Int. Ed.* **2005**, *44*, 4881–4884.

Received: February 13, 2010