EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe

DOI:10.1002/ejic.201403156

Complexation of Tetrakis(acetato)chloridodiruthenium with Naphthyridine-2,7-dicarboxylate – Characterization and Catalytic Activity

Chia-Han Lee,[a] Cai-Ling Wu,[a] Shao-An Hua,[a] Yi-Hung Liu,[a] Shie-Ming Peng,[a] and Shiuh-Tzung Liu*[a]

Keywords: Dimetallic complexes / Ruthenium / Carboxylate ligands / Cleavage reactions

The reaction of calcium naphthyridine-2,7-dicarboxylate (Cadcnp) with $Ru_2(OAc)_4Cl$ in water resulted in the formation of $Ca[Ru_2(dcnp)(OAc)_3]_2$ (**3**). X-ray crystal structural analysis of **3** confirmed its molecular structure and showed that the calcium ion binds to the lateral carboxylate groups of four neighboring anionic units of $[Ru_2(dcnp)(\mu\text{-}OAc)_3]$ and two acetone molecules to form a two-dimensional framework. The Ru^{II}–Ru^{II} valence state of the diruthenium core was supported by superconducting quantum interference device (SQUID) magnetometry [μ_{eff} (300 K) = 2.77 μ_B]. Complex **3** appears to be an efficient catalyst for the oxidative cleavage of olefins in aqueous media under mild conditions. Typically, the reaction of pulegone with $NaIO_4$ in water catalyzed by **3** (1 mol-%) at 45 °C afforded 3-methyladipic acid quantitatively.

Introduction

Owing to unique metal–metal interactions between the mixed-valence ruthenium ions, tetrakis(acetato)chloridodiruthenium, $Ru_2(OAc)_4Cl$,[1] and related coordination compounds represent an important class of dimetallic complexes, which have drawn much attention in many aspects including coordination studies[2–4] and biological,[5] materials,[6] and catalysis applications.[7] The diruthenium centers of $Ru_2(OAc)_4Cl$ are coordinated to four carboxylate groups to form a paddle-wheel shape and are linked by the axial chloride ligand into a polymeric chain. Thus, the axial ligands dramatically affect the electronic, spectroscopic, electrochemical, and magnetic properties.[1–9] Furthermore, there are many reports concerning the electronic structures of the diruthenium cores, including "Ru_2^{4+}" in the neutral species $[Ru_2(O_2CR)_4]^0$ and "Ru_2^{5+}" in the cationic species $[Ru_2(O_2CR)_4]^+$ with two and three unpaired electrons, respectively.[9]

The replacement of the bridging carboxylate ligands with other multidentate ligands to modify the properties of the resulting complexes is another interesting subject in this area of research. Among various bridging ligands, 1,8-naphthyridine-based donors are considered as "masked carboxylates", as the nitrogen donor atoms can bind to two metal ions in a *syn,syn* mode, similarly to a carboxylate group. Few diruthenium complexes with bridging naphthyridinyl ligands have been reported.[8] Among them, Sauvage and co-workers reported that sodium 1,8-naphthyridine-2,7-dicarboxylate (Na_2dcnp) reacted with $Ru_2(OAc)_4Cl$ under an argon atmosphere to yield a neutral species, $[Ru_2(dcnp)(OAc)_3]$ (**1**), in which the diruthenium core was revealed to be a "Ru_2^{5+}" species.[8b]

In this work, we reinvestigated the complexation of $Ru_2(OAc)_4Cl$ with the calcium salt of dcnp to yield $Ca[Ru_2(dcnp)(OAc)_3]_2$ (**3**), which is an ionic species, in contrast to the neutral nature of **1**. Complex **3** was fully characterized by spectroscopic, X-ray crystallographic, and superconducting quantum interference device (SQUID) analyses. In addition, the catalytic activity of the diruthenium complex in the oxidative cleavage of olefinic substrates in aqueous media was explored.

Results and Discussion

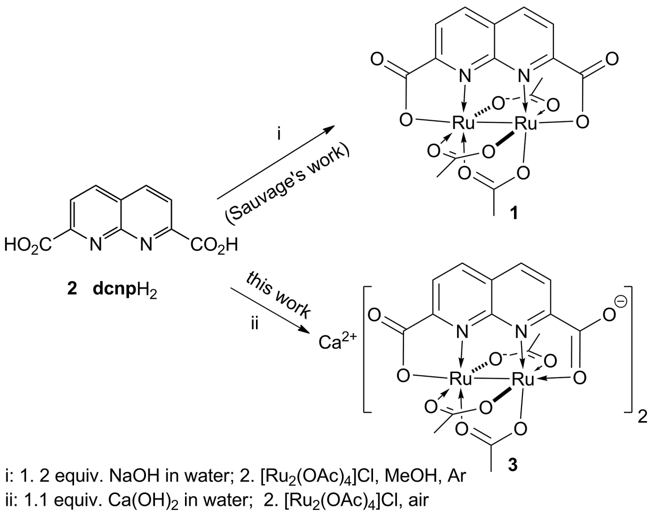
Preparation and Characterization of Ruthenium Complexes

The desired ligand, 1,8-naphthyridine-2,7-dicarboxylic acid [$dcnpH_2$] (**2**), was prepared according to the method reported previously.[10] The deprotonation of **2** with $Ca(OH)_2$ was performed at ambient temperature in aqueous medium for 12 h. The treatment of the calcium salt with $Ru_2(OAc)_4Cl$ in air resulted in the formation of deep purple crystalline solid **3**. The synthetic procedure for **3** is different from that for **1** (Scheme 1). The obtained complex **3** is stable in air and soluble in water, methanol, and other highly polar solvents. The electronic absorption spectrum of **3** in water shows intensive bands at λ = 207 (log ε = 4.6) and 269 nm (log ε = 4.03), attributed to the π–π* transitions

---

[a] Department of Chemistry, National Taiwan University,
1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106
E-mail: stliu@ntu.edu.tw
http://www.ch.ntu.edu.tw/

of the ligand, and λ = 716 nm (logε = 3.32) owing to metal-to-ligand charge transfer (MLCT). In addition, a weak absorption at λ = 891 nm is due to a δ–δ* transition in the "Ru_2^{4+}" paddle-wheel structure.[8d] The absorptions of **3** are essentially similar to those of **1**, the MLCT band of which appears at λ =710 nm (logε = 3.22).



Scheme 1. Preparation of ruthenium complexes **1** and **3**.

Table 1. Selected bond lengths [Å] and angles [°] for **3**.

Bond lengths		Bond angles	
Ru(1)–Ru(2)	2.2706(3)	O(1)–Ru(1)–Ru(2)	165.25(5)
Ru(1)–N(1)	2.022(2)	N(1)–Ru(1)–O(7)	179.11(8)
Ru(1)–O(1)	2.287(2)	O(5)–Ru(1)–O(9)	177.68(7)
Ru(2)–N(2)	2.015(2)	N(1)–Ru(1)–O(1)	75.41(8)
Ru(2)–O(3)	2.251 (2)	O(3)–Ru(2)–Ru(1)	166.39(5)
Ca(1)–O(11)$_{(acetone)}$	2.379(2)	N(2)–Ru(2)–O(8)	178.64(8)
Ca(1)–O(2)$^{\#}$	2.313(2)	O(6)–Ru(2)–O(10)	177.74(8)
Ca(1)–O(4)	2.275(2)	N(2)–Ru(2)–O(3)	75.76(8)
Ru(1)–O(7)	2.074(2)	N(1)–Ru(1)–O(7)	179.11(8)

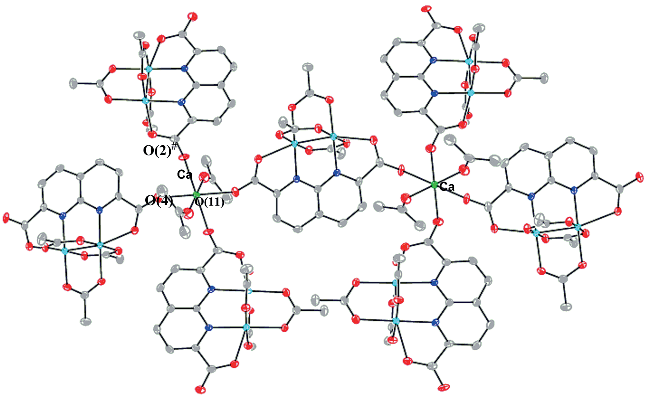


Figure 1. ORTEP plot of **3**.

The ESI-MS spectra of the complex in negative-ion mode showed the highest mass peak at m/z = 596.8658, which corresponds to the mass of the anion $[C_{16}H_{13}N_2O_{10}Ru_2]^-$ with two ruthenium ions, three acetato ligands, and the dcnp ligand. To unambiguously characterize this compound, the crystal structure of **3** was determined.

The solid-state structure of **3**, crystallized from water, tetrahydrofuran (THF), and acetone, was determined by X-ray crystallography. The detailed structure is discussed with its structural features, and the selected bond lengths and angles are presented in Table 1. The coordination characteristics of **3** are depicted in Figure 1. Complex **3** shows a continuous interaction throughout the crystal lattice, wherein the calcium ion binds to the lateral carboxylate groups of four different neighboring [Ru$_2$(dcnp)(μ-OAc)$_3$] units and two acetone molecules. The calcium ion is hexacoordinate with two acetone molecules in a *trans* arrangement. The terminal carboxylate groups of [Ru$_2$(dcnp)(μ-OAc)$_3$] adopt a bridging mode and connect the Ca^{II} centers to construct a two-dimensional framework. The bond lengths between the calcium ion and the carboxylate O atoms, Ca–O(4) and Ca–O(2)$^{\#}$, are 2.313(2) and 2.275(2) Å, respectively, whereas the bond length between the calcium ion and the acetone O atom is 2.379(2) Å. The O(4)–Ca(1)–O(2)$^{\#}$ and O(4)–Ca(1)–O(2)$^{\#2}$ angles are 84.96(7) and 95.04(8)°, respectively; presumably, the deviation from 90° is due to the crystal packing.

The diruthenium portion in **3** is shown in Figure 2 and reveals a dimetallic core bridged by the dcnp ligand and three acetato ligands; this structure is consistent with the ESI-MS observations. This part of the structure is quite similar to the previously reported crystal structure of **1**, which is a "Ru_2^{5+}" complex.[8b] Each Ru ion in **3** exhibits an octahedral coordination sphere with a metal–metal bond [2.2706(3) Å]. A comparison of some structural parameters of **1** and **3** is shown in Scheme 2. Compared with a Ru–Ru bond length of 2.273(4) Å in **1**, the metal–metal distance in **3** is slightly shorter by ca. 0.002 Å. All other bond lengths and angles in **3** are in the normal range and comparable to those in **1**, except for the C–O bond length of the dcnp ligand. The coordination of the Ca^{II} ion to the carbonyl

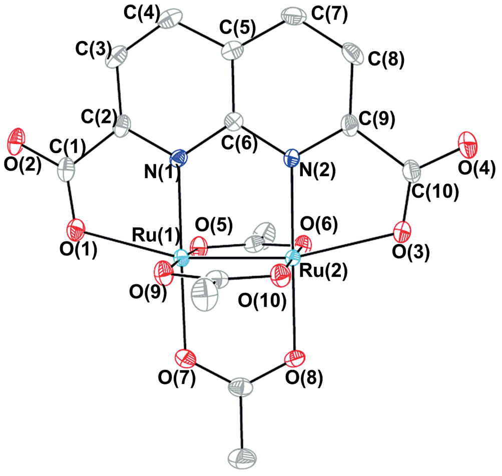
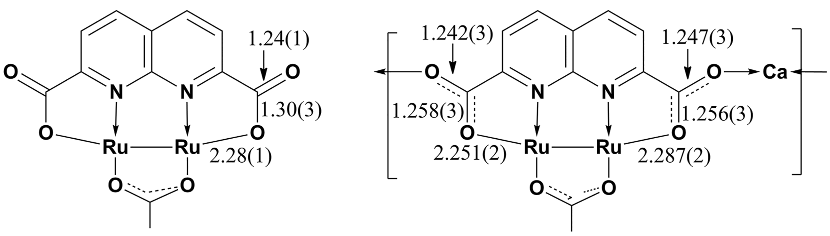


Figure 2. ORTEP plot of the diruthenium portion in **3** (30% probability level).



Formula: $Ru_2C_{16}H_{13}O_{10}N_2\,(H_2O)_2$ $C_{22}H_{25}Ca_{0.50}N_2O_{12}Ru_2$

Space group: *Pnam* *P*2(1)/*n*

Scheme 2. Comparison of bond lengths [Å] in **1** and **3**.

moieties does not affect the lengths of the C=O bonds. There is no significant difference between the C(10)–O(4) and C(10)–O(3) bond lengths in **3**, but a difference (ca. 0.05 Å) appears between these two bonds in **1**.

Crystallographic analysis shows the empirical formula of **3** to be $Ca_{0.5}[C_{22}H_{25}N_2O_{12}Ru_2]$. On the basis of charge balance, the $[Ru_2(dcnp)(\mu\text{-}OAc)_3]$ fragment should be a "–1" ion, which implies that the diruthenium core is a "Ru^{II}–Ru^{II}" species. This is supported by magnetism measurements. The temperature dependence of the magnetization has been measured for **3** with a SQUID magnetometer. The temperature-dependent data were transformed to the effective magnetic moment. The effective magnetic moment (μ_{eff}) of **3** at room temperature is ca. 2.77 μ_B (Figure 3), which is consistent with the theoretical value of 2.83 μ_B for a "Ru_2^{4+}" species with two unpaired electrons. This observation is consistent with the structure revealed by crystallography. According to the zero-field-splitting (ZFS) model,[9b] the *D* value of $^3A_{2g}$ splitting was estimated to be 226 cm^{-1}.

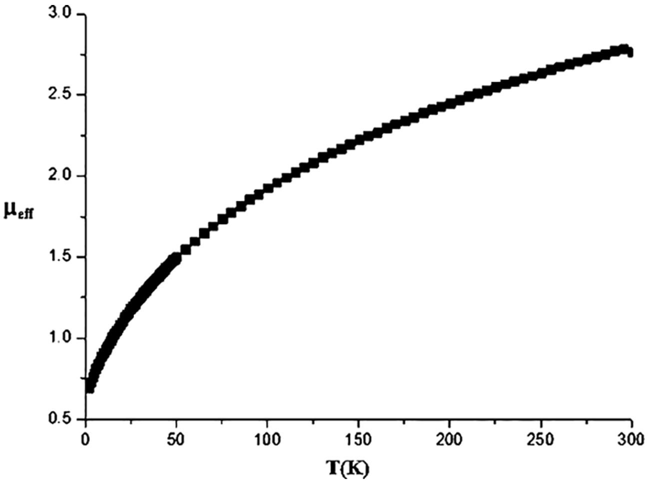


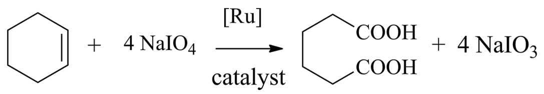
Figure 3. SQUID data for **3**.

The potentials of the $Ru^{III}_2/Ru^{III}Ru^{II}$ and $Ru^{III}Ru^{II}/Ru^{II}_2$ redox couples of **1** are +0.33 V and –1.11 V, respectively. The redox behavior of **3** in anhydrous *N*,*N*-dimethylformamide (DMF) has been studied by cyclic voltammetry. The cyclic voltammogram of **3** consists of two reversible one-electron oxidation processes [$Ru^{III}Ru^{II}/Ru^{II}_2$ = 0.51 V and $Ru^{II}_2/Ru^{II}Ru^{I}$ = –1.01 V], which are quite different from those of **1**. The cyclic voltammogram of **3** in a 5% water/DMF solution is essentially similar to that in anhydrous DMF; therefore, the substitution of the acetato ligands by water proceeds very slowly at ambient temperature.[12c]

Catalytic Oxidative Cleavage of Alkenes

The oxidative cleavage of C=C bonds is an important methodology for the conversion of olefinic substrates into carboxylic acids and ketones, and various methods have been developed.[11] Diruthenium carboxylate complexes are potential catalysts for the oxidation of several organic substrates.[7,12] To minimize the environmental impact of the use of organic solvents, aqueous reactions are required in the development of new catalytic reactions. It occurred to us that the water-soluble nature of **3** should make it possible to cleave carbon–carbon double bonds in an aqueous system.

To obtain information on the catalytic system, we first examined the oxidation of cyclohexene catalyzed by **3** in the presence of various oxidants. The standardized protocol was performed with cyclohexene (0.25 mmol), $NaIO_4$ (1 mmol), and **3** (2.5×10^{-3} mmol) in water (1 mL) at ambient temperature for 16 h (Scheme 3). In this reaction, adipic acid was obtained as the product, as determined by NMR spectroscopic analysis. The optimization results are summarized in Table 2.



Scheme 3. Oxidative cleavage of cyclohexene.

Among the various oxidants used in this study, most gave poor results, except $NaIO_4$ and $PhI(OAc)_2$. The use of $NaIO_4$ provided the best yield of the desired product (Table 2, Entry 1). The reaction proceeded more quickly at an elevated reaction temperature (Table 2, Entries 2 and 3). In addition to the above factors, we investigated the solvent

Table 2. Oxidative cleavage of cyclohexene catalyzed by **3** under various conditions.[a]

Entry	Solvent	Oxidant (*c*, mmol)	*T* [°C]	Yield [%][b]
1	H_2O	$NaIO_4$ (1)	30	72
2	H_2O	$NaIO_4$ (1)	45	85
3	H_2O	$NaIO_4$ (1)	60	86
4	H_2O	H_2O_2 (2.5)	30	trace
5	H_2O	*t*BuO_2H (1)	30	10
6	H_2O	oxone (1)	30	8
7	H_2O	$PhI(OAc)_2$ (1)	30	58
8	H_2O	benzoquinone (1)	30	trace
9	H_2O	NaClO (1)	30	trace
10	H_2O	NaClO (1)/$NaIO_4$ (0.05)	30	trace
11	H_2O/acetone (1:1)	$NaIO_4$ (1)	30	25
12	H_2O/THF (1:1)	$NaIO_4$ (1)	30	–[c]
13	H_2O/CH_3CN (1:1)	$NaIO_4$ (1)	30	71
14	H_2O/CH_3CN(3:1)	$NaIO_4$ (1)	30	56
15	H_2O/CH_3CN (4:1)	$NaIO_4$ (1)	30	24

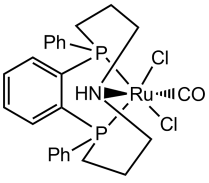
[a] Reaction conditions: cyclohexene (0.25 mmol), oxidant, and Ru complex (2.5×10^{-3} mmol) in solvent (1 mL) for 16 h. [b] Yield determined by NMR spectroscopy. [c] A complex mixture of products.

effect on the catalysis. As shown in the Table 2, the activity of the catalyst was remarkably influenced by the solvent. Water appears to be the best choice of solvent for **3** as the catalyst; therefore, the process meets the environmental criterion. Complex **3** loses its catalytic selectivity in a mixture of water/THF (Table 2, Entry 12), in which a complex mixture of products was produced. We cannot fully interpret the differences in various solvents, but it seems clear that ligand **2** is a good choice for water-soluble catalyst design.

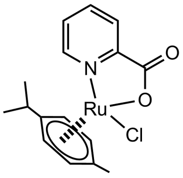
A series of experiments was performed to evaluate the suitability of various ruthenium sources for the oxidation process (Table 3). Clearly, complex **3** has the best activity for this oxidation. The other ruthenium complexes tested as catalyst precursors exhibited some activity (Table 3, Entries 2–6) but were not as active as **3**. It is quite clear that the ligand plays an important role in the catalysis. To validate the ligand effect on the catalysis, the oxidative cleavage of norbornene catalyzed by **3**, **5**, and $Ru_2(OAc)_4Cl$ was monitored by NMR spectroscopy, and the yields of the desired products are plotted in Figure 4. The oxidation of norbornene catalyzed by diruthenium complex **3** proceeded smoothly, and the yield of cyclopentanedicarboxylic acid reached 62% within 1 h. A moderate yield was achieved when $Ru_2(OAc)_4Cl$ was employed as the catalyst, but the diminished activity after ca. 50 min indicates the effect of the ligand on the stabilization of the active metal species. Complex **5**, a mononuclear species stabilized by a pyridinecarboxylato ligand, showed a similar initial rate as that for **3**, but the activity decreased gradually. These observations demonstrate the advantage of diruthenium complex **3** in the catalytic reaction.

Table 3. Oxidation of cyclohexene catalyzed by various Ru complexes.[a]

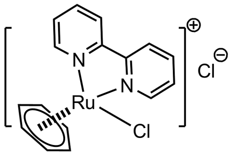
Entry	Ru complex	Amount of catalyst [mmol]	Yield [%][b]
1	Complex **3**	2.5×10^{-3} (1 mol-%)	72
2	$Ru_2(OAc)_4Cl$	5×10^{-3} (2 mol-%)	52
3	Complex **4**	0.01 (4 mol-%)	45
4	Complex **5**	0.01 (4 mol-%)	42
5	Complex **6**	0.01 (4 mol-%)	36
6	$RuCl_3·3H_2O$	0.01 (4 mol-%)	38



4



5



6

[a] Reaction conditions: cyclohexene (0.25 mmol), $NaIO_4$ (1 mmol), and Ru complex in H_2O (1 mL) at 30 °C for 16 h. [b] Yields determined by NMR spectroscopy.

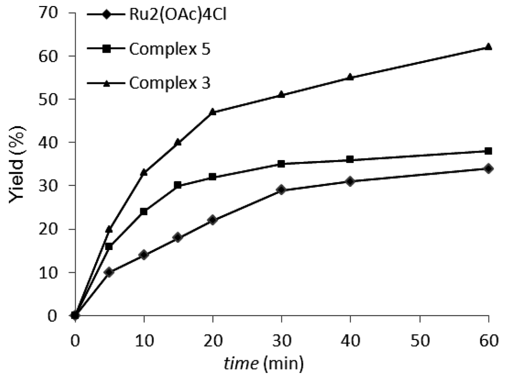
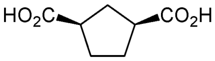
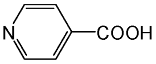
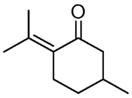
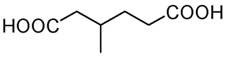


Figure 4. Oxidation of norbornene with several catalysts.

With the optimized conditions in hand, the generality of the oxidative cleavage of C=C bonds catalyzed by **3** was investigated (Table 4). We performed the reactions with a variety of cycloalkenes and styrene derivatives. All cycloalkenes underwent oxidative cleavage to afford the respective dicarboxylic acids in good-to-excellent yields. The oxidation of norbornene proceeded smoothly under the optimized conditions to yield *cis*-cyclopentanedicarboxylic acid in 80%. However, the yield was improved to 99% by the addition of acetone to the reaction mixture as the cosolvent owing to the poor solubility of the substrate in water. Vinylbenzene derivatives were also reactive under the oxidation conditions and afforded the corresponding benzoic acids in high yields even for 4-vinylpyridine and *trans*-stilbene. Moreover, the oxidation of cinnamates was accomplished in excellent yields (Table 4, Entries 12, and 13). This system was successfully applied to the oxidation of pulegone to quantitatively provide 3-methyladipic acid. However, the oxidative cleavage of cyclohexenone led to the production of pentanedioic acid (33%), presumably via the α-dicarbonyl intermediate followed by decarboxylation.

Table 4. Oxidative cleavage of olefins catalyzed by **3**.[a]

Entry	Substrate	Product	Yield[b]
1	cyclohexene	$HO_2C(CH_2)_4CO_2H$	86%
2	cyclopentene	$HO_2C(CH_2)_3CO_2H$	69%
3	cyclooctene	$HO_2C(CH_2)_6CO_2H$	95%
4	1,5-cyclooctadiene	$HO_2C(CH_2)_2CO_2H$	50%
5	norbornene		80% (99%)[c]
6	$C_6H_5CH=CH_2$	C_6H_5COOH	70%
7	*p*-$ClC_6H_4CH=CH_2$	*p*-ClC_6H_4COOH	76%
8[c]	*p*-$BrC_6H_4CH=CH_2$	*p*-BrC_6H_4COOH	90%
9[c]	4-vinylpyridine		57%
10[c]	*trans*-$C_6H_5CH=CHC_6H_5$	C_6H_5COOH	83%
11	$C_6H_5CH_2CH=CH_2$	$C_6H_5CH_2COOH$	83%
12[c]	$C_6H_5CH=CHCOOCH_3$	C_6H_5COOH	99%
13[c]	*p*-$NO_2C_6H_5CH=CHCO_2{}^nBu$	*p*-$NO_2C_6H_4COOH$	99%
14[c]			99%[d]
15	cyclohex-2-enone	$HO_2C(CH_2)_3CO_2H$	33%

[a] Reaction conditions: olefin (0.25 mmol), $NaIO_4$ (1 mmol), H_2O (1 mL), and Ru complex **3** (2.5 × 10–3 mmol) at 45 °C for 16 h. [b] Isolated yield. [c] Cosolvent (water/acetone 3:1). [d] Acetone as the side product.

Conclusions

We have prepared and characterized the diruthenium complex $Ca[Ru_2(dcnp)(OAc)_3]_2$ (**3**), in which the diruthenium core is a "Ru^{II}–Ru^{II}" species. The crystal structure of **3** clearly shows that the anionic unit of $[Ru_2(dcnp)(\mu\text{-}OAc)_3]^-$ coordinates to the Ca^{2+} ion to form a two-dimensional framework. The utilization of the diruthenium complex **3** as the catalyst for the oxidative cleavage of alkenes in water led to the corresponding carboxylic acids. Complex **3** is an excellent catalyst for the oxidation of olefins to carboxylic acids under mild conditions. More catalytic activity studies involving **3** for other transformations are in progress.

Experimental Section

General Information: Chemicals and solvents of analytical grade were used without further purification. Nuclear magnetic resonance spectra were recorded with a 400 MHz spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR spectroscopy. Infrared spectra were recorded with samples as KBr pallets. The ligand $dcnpH_2$,[10] dicarbonyl{(*P,P′,N*-1,9-diphenyl-2,3,4,5,6,7,8,9-octahydro-1*H*-5,1,9-benzazadiphosphacycloundecine)}chlororuthenium (**4**),[13] (*N,O*-2-pyridinecarboxylato)(η^6-*p*-cymene)chlororuthenium (**5**),[14] and (*N,N*-bipyridine)(η^6-benzene)chlororuthenium chloride (**6**)[15] were prepared according to the reported methods. Cyclic voltammetry measurements were performed with a CH instruments 750A potentiostat with a graphite working electrode and Pt wire auxiliary electrode at ambient temperature. The potentials were measured versus the saturated sodium chloride calomel electrode (SSCE). Complex **3** in DMF [0.1 M *tert*-butylammonium perchlorate (TBAP]) was determined at a scan rate of 100 mV/s.

Complex 3: To a mixture of H_2dcnp (100 mg, 0.46 mmol) and $Ca(OH)_2$ (34 mg, 0.46 mmol) in a 25 mL flask was added water (10 mL), and the mixture was stirred at ambient temperature for 12 h. $Ru_2(OAc)_4Cl$ (196 mg, 0.46 mmol) was then added to the above solution, and the resulting mixture was heated at 60 °C for 5 h. After removal of the water, the residue was dissolved in methanol (20 mL), and the solution was filtered to remove salts. After concentration, the desired complex was obtained as a deep purple solid (191 mg, 68 %). Recrystallization from water/THF/acetone gave **1** as a deep purple crystalline solid, suitable for X-ray crystallography. HRMS (ESI–): calcd. for $C_{16}H_{13}N_2O_{10}Ru_2$ $[Ru_2(dcnp)(\mu\text{-}OAc)_3]^-$ 596.8669; found 596.8658.

Complex 5:[14] A mixture of 2-picolinic acid (100 mg, 0.81 mmol) and $[RuCl(p\text{-cymene})]_2$ (248.9 mg, 0.41 mmol) in isopropyl alcohol (5 mL) was stirred at ambient temperature for 48 h. The solution slowly turned bright orange. Filtration of the mixture gave an orange solid, which was washed with water, methanol, and ether. The desired complex was obtained as an orange solid (212.8 mg, 60 %): ^1H NMR (400 MHz, $CDCl_3$): δ = 8.94 (m, 1 H, Py-H), 8.00 (d, J = 7.6 Hz, 1 H, Py-H), 7.91 (t, J = 7.6 Hz, 1 H, Py-H), 7.55 (m, 1 H, Py-H), 5.60 (d, J = 6 Hz, 1 H, Ar-H), 5.57 (d, J = 6 Hz, 1 H, Ar-H), 5.45 (d, J = 5.2 Hz, 1 H, Ar-H), 5.36 (d, J = 5.2 Hz, 1 H, *p*-Ar-H), 2.85 (m, J = 6.8 Hz, 1 H, CH), 2.27 (s, 3 H, CH_3), 1.20 [d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (100 MHz): δ = 171.3, 152.8, 150.9, 139.3, 128.3, 126.7, 102.5, 98.9, 83.0, 82.7, 81.6, 80.9, 77.5, 77.2, 76.9, 31.3, 22.6, 22.5, 19.1 ppm.

Typical Procedure for Oxidative Cleavage of Olefins: An olefinic substrate (0.25 mmol), Ru complex (1 mol-%), and $NaIO_4$ (1.025 mmol) in water (1 mL) were loaded in a reaction vessel with a stirring bar. The mixture was heated at 45 °C for 16 h. After the completion of the reaction, brine (4 mL) was added to the reaction mixture, which was then extracted with diethyl ether (5 mL × 3). The combined organic extracts were dried and concentrated. The residue was analyzed by NMR spectroscopy. Recrystallization provided the desired compounds in pure form. The spectroscopic data of the organic products are essentially identical to those reported previously.

Adipic Acid: ^1H NMR {400 Hz, $[D_6]$dimethyl sulfoxide ($[D_6]$DMSO)}: δ = 1.47 (m, 4 H), 2.17 (m, 4 H), 11.97 (br, 2 H, CO_2H) ppm. ^{13}C NMR (100 Hz): δ = 174.4, 33.4, 24.1 ppm.

Glutaric Acid: ^1H NMR (400 Hz, $[D_3]$acetonitrile): δ = 1.81 (m, J = 7.4 Hz, 2 H), 2.33 (t, J = 7.4 Hz, 4 H) ppm. ^{13}C NMR (100 Hz): δ = 175.4, 33.7, 21.3 ppm.

Octanedioic Acid: ^1H NMR (400 Hz, $[D_6]$DMSO): δ = 1.26 (m, 4 H), 1.48 (m, 4 H), 2.18 (m, 4 H), 11.95 (br, 2 H, CO_2H) ppm. ^{13}C NMR (100 Hz): δ = 174.2, 38.9, 28.3, 24.4 ppm.

Succinic Acid: ^{1}H NMR (400 Hz, [D$_6$]DMSO): δ = 2.40 (s, 4 H), 11.6–13.4 (br, 2 H) ppm. ^{13}C NMR (100 Hz): δ = 173.7, 28.8 ppm.

***cis*-Cyclopentane-1,3-dicarboxylic Acid:** ^{1}H NMR (400 Hz, [D$_6$]-DMSO): δ = 1.72–1.88 (m, 5 H), 2.06–2.11 (m, 1 H), 3.39 (br, 2 H), 12.08 (br, 2 H, CO_2H) ppm. ^{13}C NMR (100 Hz): δ = 176.4, 43.4, 33.0, 29.2 ppm.

Benzoic Acid: ^{1}H NMR (400 Hz, [D$_6$]DMSO): δ = 7.50 (dd, *J* = 8, 4 Hz, 2 H, Ar-H), 7.62 (t, *J* = 8 Hz, 1 H, Ar-H), 7.94 (d, *J* = 4 Hz, 2 H, Ar-H), 12.94 (br, 1 H, CO_2H) ppm. ^{13}C NMR (100 Hz): δ = 167.3, 132.9, 130.8, 129.3, 128.6 ppm.

4-Chlorobenzoic Acid: ^{1}H NMR (400 Hz, [D$_6$]DMSO): δ = 7.54 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 13.0 (br, 1 H, CO_2H) ppm. ^{13}C NMR (100 Hz): δ = 166.2, 137.6, 131.0, 129.4, 128.6 ppm.

4-Bromorobenzoic Acid: ^{1}H NMR (400 Hz, [D$_6$]acetone): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.69 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 Hz): δ = 166.6, 132.5, 132.1, 130.5, 128.0 ppm.

4-Picolinic Acid: ^{1}H NMR (400 Hz, D_2O): δ = 8.59 (d, *J* = 4.2 Hz, 2 H), 7.72 (d, *J* = 4.2 Hz, 2 H) ppm. ^{13}C NMR (100 Hz): δ = 173.2, 149.1, 145.2, 123.1 ppm.

2-Phenylacetic Acid: ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.29–7.36 (m, 5 H, Ar), 3.67 (s, 2 H, CH_2) ppm. ^{13}C NMR (100 Hz): δ = 178.2, 133.3, 129.4, 128.7, 127.4, 41.3 ppm.

3-Methylhexanedioic Acid: ^{1}H NMR (400 Hz, $CDCl_3$): δ = 0.98 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.50–1.58 (m, 1 H), 1.71–1.75 (m, 1 H), 1.98–2.03 (m, 1 H), 2.18–2.23 (m, 1 H), 2.30–2.43 (m, 3 H) ppm. ^{13}C NMR (100 Hz): δ = 180.0, 179.3, 41.4, 31.8, 31.3, 29.8, 19.5 ppm.

Crystallography: Crystals of **3** suitable for X-ray structure determination were obtained by recrystallization from a solution of water, THF, and acetone. The cell parameters were determined with a Siemens SMART CCD diffractometer. Crystal data of **3**: $C_{22}H_{25}Ca_{0.50}N_2O_{12}Ru_2$, M_w = 731.62, monoclinic, space group $P2_1/n$; a = 8.2264(2) Å, b = 18.0498(5) Å, c = 17.5389(5) Å, α = 90°, β = 92.405(2)°, γ = 90°; V = 2601.97(12) Å^3; Z = 4; $\rho_{calcd.}$ = 1.868 Mg m^{-3}; $F(000)$ = 1460; crystal size: 0.20 × 0.15 × 0.10 mm; reflections collected: 15966; independent reflections: 5795 [R(int) = 0.0311]; θ range 2.92 to 27.50°; goodness-of-fit on F_2 0.999; final R indices [$I > 2\sigma(I)$] R_1 = 0.0283, wR_2 = 0.0616; R indices (all data) R_1 = 0.0400, wR_2 = 0.0665. The structure was solved with the SHELXS-97 program[16] and refined with the SHELXL-97 program[17] by full-matrix least-squares techniques on F^2 values. CCDC-1036945 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.

Acknowledgments

The authors thank the National Science Council, Taiwan for financial support (grant number MOST103-2113-M-002 -002-MY3).

---

[1] M. J. Bennett, K. G. Caulton, F. A. Cotton, *Inorg. Chem.* **1969**, *8*, 1–6.

[2] a) P. Angaridis, J. F. Berry, F. A. Cotton, C. A. Murillo, X. Wang, *J. Am. Chem. Soc.* **2003**, *125*, 10327–10334; b) Y. Liao, W. W. Shum, J. S. Miller, *J. Am. Chem. Soc.* **2002**, *124*, 9336–9337; c) M. Manowong, B. Han, T. R. McAloon, J. Shao, I. A. Guzei, S. Ngubane, E. Van Caemelbecke, J. L. Bear, K. M. Kadish, *Inorg. Chem.* **2014**, *53*, 7416–7428; d) D. A. Boyd, Z. Cao, Y. Song, T.-W. Wang, P. E. Fanwick, R. J. Crutchley, T. Ren, *Inorg. Chem.* **2010**, *49*, 11525–11531; e) J. S. Pap, J. L. Snyder, P. M. B. Piccoli, J. F. Berry, *Inorg. Chem.* **2009**, *48*, 9846–9852; f) K. M. Kadish, R. Garcia, T. Phan, J. Wellhoff, E. Van Caemelbecke, J. L. Bear, *Inorg. Chem.* **2008**, *47*, 11423–11428; g) H. Miyasaka, T. Izawa, K. Sugiura, M. Yamashita, *Inorg. Chem.* **2003**, *42*, 7683–7690; h) R. Lee, Y. Yang, G. K. Tan, C.-H. Tan, K.-W. Huang, *Dalton Trans.* **2010**, *39*, 723–725; i) S. Ngubane, K. M. Kadish, J. L. Bear, E. Van Caemelbecke, A. Thuriere, K. P. Ramirez, *Dalton Trans.* **2013**, *42*, 3571–3580; j) R. Gracia, H. Adams, N. J. Patmore, *Dalton Trans.* **2009**, 259–261; k) L.-Y. Zhang, J.-L. Chen, L.-X. Shi, Z.-N. Chen, *Organometallics* **2002**, *21*, 5919–5925; l) M. A. S. Aquino, *Coord. Chem. Rev.* **2004**, *248*, 1025–1045.

[3] a) G. M. Chiarella, F. A. Cotton, C. A. Murillo, M. D. Young, Q. Zhao, *Inorg. Chem.* **2010**, *49*, 3051–3056; b) D. A. Boyd, R. J. Crutchley, P. E. Fanwick, T. Ren, *Inorg. Chem.* **2010**, *49*, 1322–1324; c) L. Zhang, B. Xi, I. Po-Chun Liu, M. M. R. Choudhuri, R. J. Crutchley, J. B. Updegraff, J. D. Protasiewicz, T. Ren, *Inorg. Chem.* **2009**, *48*, 5187–5194; d) W.-Z. Chen, T. Ren, *Organometallics* **2005**, *24*, 2660–2669; e) W.-Z. Chen, T. Ren, *Organometallics* **2004**, *23*, 3766–3768; f) J. Savchenko, P. E. Fanwick, H. Hope, Y. Gao, C. K. Yerneni, T. Ren, *Inorg. Chim. Acta* **2013**, *396*, 144–148.

[4] a) P. Delgado-Martínez, R. González-Prieto, C. J. Gómez-García, R. Jiménez-Aparicio, J. L. Priego, M. R. Torres, *Dalton Trans.* **2014**, *43*, 3227–3237; b) P. Delgado, R. González-Prieto, R. Jiménez-Aparicio, J. Perles, J. L. Priego, R. M. Torres, *Dalton Trans.* **2012**, *41*, 11866–11874; c) B. R. Groves, D. I. Arbuckle, E. Essoun, T. L. Lundrigan, R. Wang, M. A. S. Aquino, *Inorg. Chem.* **2013**, *52*, 11563–11572; d) M. W. Cooke, T. S. Cameron, K. N. Robertson, J. C. Swarts, M. A. S. Aquino, *Organometallics* **2002**, *21*, 5962–5971.

[5] a) R. L. S. R. Santos, R. van Eldik, D. de Oliveira Silva, *Inorg. Chem.* **2012**, *51*, 6615–6625; b) L. Messori, T. Marzo, R. N. F. Sanches, Hanif-Ur-Rehman, D. de Oliveira Silva, A. Merlino, *Angew. Chem. Int. Ed.* **2014**, *53*, 6172–6175; *Angew. Chem.* **2014**, *126*, 6286–6289; c) R. W.-Y. Sun, M. F.-Y. Ng, E. L.-M. Wong, J. Zhang, S. S.-Y. Chui, L. Shek, T.-C. Lau, C.-M. Che, *Dalton Trans.* **2009**, 10712–10716.

[6] a) R. Kuwahara, S. Fujikawa, K. Kuroiwa, N. Kimizuka, *J. Am. Chem. Soc.* **2012**, *134*, 1192–1199; b) T. E. Vos, Y. Liao, W. W. Shum, J.-H. Her, P. W. Stephens, W. M. Reiff, J. S. Miller, *J. Am. Chem. Soc.* **2004**, *126*, 11630–11639.

[7] a) M. E. Harvey, D. G. Musaev, J. Du Bois, *J. Am. Chem. Soc.* **2011**, *133*, 17207–17216; b) L. Villalobos, J. E. Barker Paredes, Z. Cao, T. Ren, *Inorg. Chem.* **2013**, *52*, 12545–12552; c) J. E. Barker, T. Ren, *Inorg. Chem.* **2008**, *47*, 2264–2266; d) L. Villalobos, Z. Cao, P. E. Fanwick, T. Ren, *Dalton Trans.* **2012**, *41*, 644–650.

[8] a) J. K. Bera, N. Sadhukhan, M. Majumdar, *Eur. J. Inorg. Chem.* **2009**, 4023–4038; b) J. P. Collin, A. Jouaiti, J. P. Sauvage, W. C. Kaska, M. A. McLoughlin, N. L. Keder, W. T. A. Harrison, G. D. Stucky, *Inorg. Chem.* **1990**, *29*, 2238–2241; c) A. Petitjean, F. Puntoriero, S. Campagna, A. Juris, J.-M. Lehn, *Eur. J. Inorg. Chem.* **2006**, 3878–3892; d) E. Binamira-Soriaga, N. L. Keder, W. C. Kaska, *Inorg. Chem.* **1990**, *29*, 3167–3171.

[9] a) M. H. Chisholm, G. Christou, K. Folting, J. C. Huffman, C. A. James, J. A. Samuels, J. L. Wesemann, W. H. Woodruff, *Inorg. Chem.* **1996**, *35*, 3643–3658; b) F. A. Cotton, V. M. Miskowski, B. Zhong, *J. Am. Chem. Soc.* **1989**, *111*, 6177–6182; c) F. A. Cotton, Y. Kim, T. Ren, *Polyhedron* **1993**, *12*, 607–611; d) J. Telser, R. S. Drago, *Inorg. Chem.* **1984**, *23*, 3114–3120.

[10] C. Vu, D. Walker, J. Wells, S. Fox, *J. Heterocycl. Chem.* **2002**, *39*, 829–832.

[11] a) F. E. Kuehn, R. W. Fischer, W. A. Herrmann, T. Weskamp, *Transition Metals in Organic Synthesis* 2nd ed., Wiley-VCH, Weinheim, Germany, **2004**, vol. 2, p. 427–436; b) D. G. Lee, T. Chen, *Cleavage Reactions*, in: *Comprehensive Organic Synthesis*, vol. 7, *Oxidation* (Eds.: B. M. Trost, I. Fleming), 1st ed.,

Pergamon Press, Oxford, UK, **1991**, p. 541–591; c) B. R. Travis, R. S. Narayan, B. Borhan, *J. Am. Chem. Soc.* **2002**, *124*, 3824–3825, and references cited therein.
[12] a) R. K. Das, B. Saha, S. M. W. Rahaman, J. K. Bera, *Chem. Eur. J.* **2010**, *16*, 14459–14468; b) H. B. Lee, T. Ren, *Inorg. Chim. Acta* **2009**, *362*, 1467–1470; c) C. D. Giovanni, A. Poater, J. Benet-Buchholz, L. Cavallo, M. Solà, A. Llobet, *Chem. Eur. J.* **2014**, *20*, 3898–3902.
[13] C.-C. Lee, H.-C. Huang, S.-T. Liu, Y.-H. Liu, S.-M. Peng, J.-T. Chen, *Polyhedron* **2013**, *52*, 1024–1029.
[14] O. Dayan, N. Ozdemir, Z. Serbetci, M. Dincer, B. Cetinkaya, O. Buyukgungor, *Inorg. Chim. Acta* **2012**, *392*, 246–253.
[15] D. A. Freedman, J. K. Evju, M. K. Pomije, K. R. Mann, *Inorg. Chem.* **2001**, *40*, 5711–5715.
[16] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 467–473.
[17] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

Received: December 4, 2014