Review

Chemistry of a novel zerovalent ruthenium π-acidic alkene complex, Ru(η^6-1,3,5-cyclooctatriene)(η^2-dimethyl fumarate)$_2$

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Abstract: A novel zerovalent ruthenium complex with a π-acidic ligand, Ru(η^6-cyclooctatriene)(η^2-dimethyl fumarate)$_2$ (**1**), was prepared from Ru(η^4-cyclooctadiene)(η^6-cyclooctatriene) [Ru(cod)(cot)]. Complex **1** or Ru(cod)(cot) catalyzes various new carbon-carbon bond-forming reactions that include the [2 + 2] cycloaddition of alkenes and alkynes via ruthenacycles, the creation of a new hydrocarbon, pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene [PCTD], by dimerization of 2,5-norbornadiene via C-C bond cleavage, and the codimerization of alkynes and/or alkenes. Complex **1** was shown to be an excellent mother complex for various zerovalent ruthenium complexes. Complex **1** reacts with amines, phosphines or water to give new zerovalent ruthenium complexes with the ligands. The resulting aqua complexes have a water ligand with an oxygen atom that is a chiral center, i.e., ruthenium complexes with a 'chiral water' ligand were prepared and fully characterized.

Keywords: zerovalent ruthenium complex, [2 + 2] cycloaddition, ruthenacycle, codimerization, aqua complex, chiral water

Introduction

Ruthenium complexes have been shown to have very characteristic catalytic performance in organic synthesis.[1] The most significant organic reactions catalyzed by ruthenium complexes are the alkene metathesis developed by Grubbs *et al.*[2] and the selective asymmetric hydrogenation described by Noyori *et al.*[3] Both reactions have attracted much attention because they provide powerful tools in organic synthesis and are effective for use in industrial chemistry. As a result of their contributions, both Grubbs and Noyori received Nobel Prizes. However, the characteristic features of ruthenium complex catalysts are not limited to these reactions.[1] Some other examples include carbon-carbon bond-forming reactions catalyzed by low valent ruthenium complexes, including C-H bond activation,[4] C-C bond activation or reactions via

ruthenacycles.[1d)–1j),11)] As for low valent ruthenium complexes, Ru$_3$(CO)$_{12}$, RuH$_2$(PPh$_3$)$_4$, RuH$_2$(CO)(PPh$_3$)$_3$, RuHCl(CO)(PPh$_3$)$_3$, RuCl$_2$(PPh$_3$)$_3$, Cp*RuCl(cod) [Cp* = pentamethylcyclopentadienyl, cod = η^4-1,5-cyclooctadiene], Ru(cod)(cot) [cot = η^6-1,3,5-cyclooctatriene] etc. have been investigated.[1] Among them, Ru(cod)(cot) is a zerovalent complex without halogen, carbonyl or phosphine ligands,[5] which could provide versatile catalytic systems in combination with appropriate ligands. Since 1979, when we found that Ru(cod)(cot) could act as a catalyst for carbon-carbon bond-forming reactions[6] considerable effort has been devoted to elucidating the catalytic activity of the complex[1g),7)–12)] as well as the stoichiometric reactivity of Ru(cod)(cot).[13)–15)] In 1999, Ru(cot)(dmfm)$_2$ (**1**) [dmfm = η^2-dimethyl fumarate] was synthesized from Ru(cod)(cot)[16] and the significant features of Ru(cot)(dmfm)$_2$ as a catalyst have been revealed.[16)–20)] For example, organic synthesis that includes a catalytic reaction via C-C bond cleavage has been explored.[16] Further, in studies on the stoichiometric reaction of Ru(cot)(dmfm)$_2$[21)–30)] the door to the novel chemistry of complexes with a

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'chiral water' ligand is being opened.[26), 27)] This paper reviews the novel chemistry of $Ru(cot)(dmfm)_2$ as well as the catalytic features of the precursor $Ru(cod)(cot)$ in carbon-carbon bond-forming reactions mainly developed by the authors.

Synthesis of $Ru(cot)(dmfm)_2$ from $Ru(cod)(cot)$

$Ru(cot)(dmfm)_2$ was prepared in high yield reacting $Ru(cod)(cot)$ with dimethyl fumarate or dimethyl maleate (eq. 1).[16)] The structure of $Ru(cot)(dmfm)_2$ was determined by X-ray crystallography.
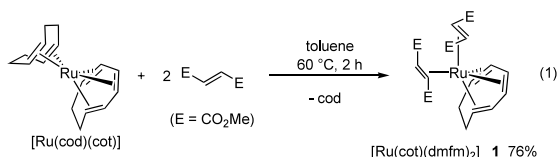
$Ru(cod)(cot)$ and $Ru(cot)(dmfm)_2$ are yellow-orange solids that are thermally stable under an inert gas atmosphere, and they can be easily treated in air for several hours when the complexes are micro crystals.

Catalytic activities of $Ru(cot)(dmfm)_2$ and $Ru(cod)(cot)$ in carbon-carbon bond-forming reactions

$Ru(cod)(cot)$ was considered a hydrogenation catalyst until 1979,[7)] when we found that $Ru(cod)(cot)$ also acts as an efficient catalyst for a carbon-carbon bond-forming reaction, i.e. the [2 + 2] cycloaddition of alkenes and alkynes.[6a)] Since then, various carbon-carbon bond-forming reactions catalyzed by $Ru(cod)(cot)$ have been explored.[7)−12)] In the course of our study on the catalytic activity of a [Ru(cod)(cot)/π-acidic ligand] system, $Ru(cot)(dmfm)_2$ was prepared and found to be a highly efficient catalyst for these reactions. This section describes $Ru(cod)(cot)$- and $Ru(cot)(dmfm)_2$-catalyzed carbon-carbon bond-forming reactions mainly found by the authors.

Codimerization of alkenes and alkynes. Catalytic selective codimerization of alkenes with alkynes and that of different alkenes are very attractive synthetic methods[1)] as well as the homodimerization[31)] of unsaturated compounds. To perform a selective codimerization reaction, the competing homodimerization should be completely suppressed. When low valent ruthenium complexes are used as catalysts, several useful codimerizations of alkenes
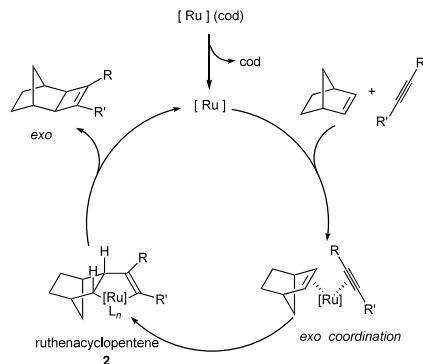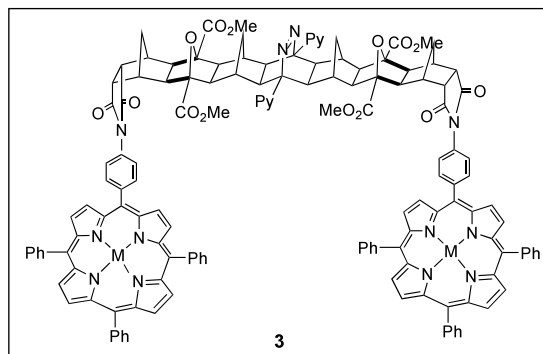
Scheme 1.　Mechanism of the [2 + 2] cycloaddition.

Fig. 1.　A molecule prepared by the ruthenium complex-catalyzed [2 + 2] cycloaddition.

and/or alkynes can be realized.

[2 + 2] Cycloaddition of 2-norbornenes with alkynes. Low valent ruthenium complexes catalyze the [2 + 2] cycloaddition of 2-norbornenes with alkynes to give tricyclo[4.2.1.0^{2,5}]non-3-ene derivatives (eq. 2).[6), 7)] The combination of $Ru(cod)(cot)$ with trialkylphosphines showed high catalytic activity.[7)] The reaction mechanism can be explained by a catalytic cycle via a ruthenacyclopentene intermediate **2** (Scheme 1).[6)]
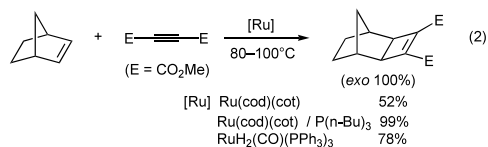
The ruthenium-catalyzed [2 + 2] cycloaddition was further developed using several ruthenium complexes and is widely used to construct various pseudoladder structures[7), 32), 33)] such as **3**[32c)] in Fig. 1. The carbon-carbon bonds depicted by bold bonds are formed by the present reaction.

The [2 + 2] cycloaddition reaction reported by the present authors is the starting point for the codimerization of different alkenes and alkynes catalyzed by mononuclear low valent ruthenium complexes.[6]

Linear codimerization of alkynes with 1,3-dienes and/or alkenes. Ru(cod)(cot)-trialkylphoshines efficiently catalyze the codimerization of terminal alkynes and 1,3-dienes, which represents an efficient method for the synthesis of enynes (eq. 3).[9]
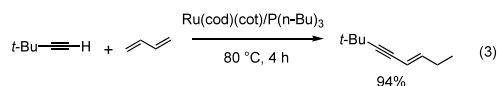
These reactions are atom-economic and characteristic for the ruthenium complex catalyst.[34] When a rhodium complex such as RhCl(PPh$_3$)$_3$ is used, homodimerization of terminal alkynes proceeds selectively and no codimerization occurs.

The catalytic codimerization of internal alkynes with alkenes was also performed using Ru(cod)(cot) with appropriate ligands. For example, diphenylacetylene and methyl acrylate react in the presence of Ru(cod)(cot) catalyst in pyridine to give a linear codimer selectively (eq. 4).[10]
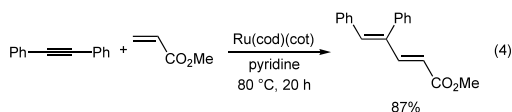
Selective codimerization of different alkenes. The catalytic and selective codimerization of different alkenes is a powerful and atom-economical method for synthesizing unsaturated carbon skeletons in one step.

Recently, Ru(cot)(dmfm)$_2$ was shown to be an excellent active catalyst for the selective codimerization of different alkenes. A typical reaction is the regio- and stereoselective codimerization of 2,3-dihydrofurans and α,β-unsaturated carboxylic esters to provide a novel route to 2-(1-alkoxycarbonyl)-alkylidenetetrahydrofurans, which are building blocks for natural products such as macrotetrolide antibiotics. For example, 2,3-dihydrofuran reacts with ethyl acrylate in the presence of Ru(cot)(dmfm)$_2$ catalyst (3 mol %) in N,N-dimethylacetamide (DMA) at 160 °C for 20 h to give (E)-2-(1-ethoxycarbonyl)ethylidenetetrahydrofuran in 70% yield (eq. 5).[17]
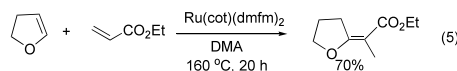
Another example of the selective codimerization of different alkenes is the cross-dimerization of N-vinylamides with acrylates to give enamides (eq. 6).[35]
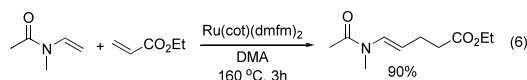
When an excess amount of acrylates is used, further codimerization occurs to give a 1:2 adduct (eq. 7).[35]
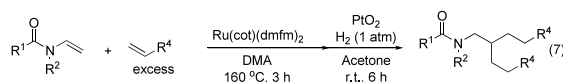
Based on an experiment using deuterated dimethyl fumarate, a mechanism involving a ruthenium hydride complex formed via C-H activation on a zerovalent ruthenium complex has been proposed. The successive insertion of different alkenes and β-hydride elimination gives the product with the regeneration of a catalytically active ruthenium species.

These reactions provide a novel tool for the preparation of enamides, which are useful building blocks for the synthesis of natural products.

**Dimerization of 2,5-norbornadiene to PCTD via carbon-carbon bond cleavage.** The dimerization of 2,5-norbornadiene via carbon-carbon bond cleavage was first performed using the Ru(cod)(cot)/π-acidic ligand catalyst system.[16] For example, 2,5-norbornadiene dimerizes in the presence of Ru(cod)(cot)/N,N-dimethylacrylamide or dimethyl fumarate to give a novel hydrocarbon, pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene [PCTD], in high yields together with a small amount of a known dimer, heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane [HCTD], as a byproduct. Ru(cot)(dmfm)$_2$ in toluene or THF showed excellent high catalytic activity without an induction period, which was observed in the Ru(cod)(cot)/N,N-dimethylacrylamide-catalyzed reaction (eq. 8).[16]
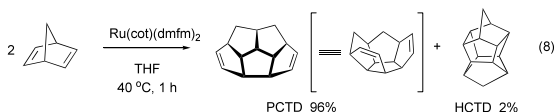
During the formation of PCTD from two molecules of 2,5-norbornadiene, carbon-carbon bond cleavage occurs twice. The structure of PCTD is very unique. It
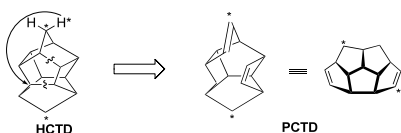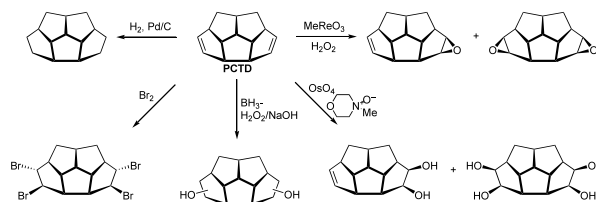
Scheme 2.   Structual relation between HCTD and PCTD.
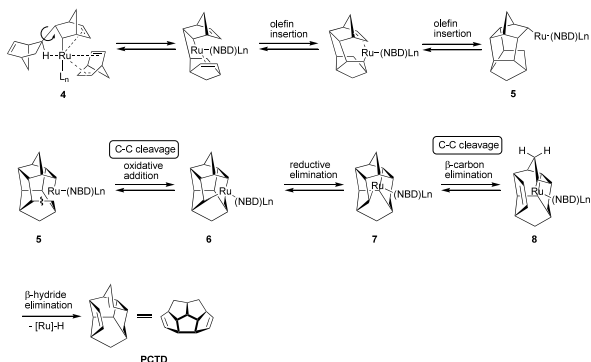
Scheme 3.   A possible mechanism of the formation of PCTD.

Scheme 4.   Derivatives of PCTD.

has five five-membered carbon rings and two olefinic groups on both sides of the molecule and also has Cs symmetry. The selectivity of the products in the dimerization could be controlled by the reaction conditions. In DMSO, for example, the main product was HCTD.

The relation between the structures of PCTD and HCTD was considered. In the molecular model of HCTD, the *endo-endo* dimer of 2,5-norbornadiene, when the two carbon-carbon bonds of the model are cleaved and a hydrogen atom is transferred as shown in Scheme 2, PCTD is formed. This consideration shows that PCTD is an isomer of the *endo-endo* dimer of 2,5-norbornadiene and the dimerization of a 7-substituted 2,5-norbornadiene gives 4,9-disubstituted PCTD. Indeed, 7-*t*-butoxy-2,5-norbornadiene dimerizes under these reaction conditions to give a mixture of *endo-* and *exo*-4,9-di-*t*-butoxy-PCTD in good yield.

Although the mechanism of the dimerization to PCTD is not yet clear, a hypothetical mechanism is as follows (Scheme 3). One 2,5-norbornadiene molecule inserts into a hydrido-ruthenium bond, which could be easily formed by the activation of a C-H bond of the ligands. Successive insertion of another 2,5-norbornadiene between the carbon-ruthenium bond would give intermediate complex **4**. A similar complex in which Ln = Cl has been isolated in the reaction of a hydridochlororuthenium com-

plex with 2,5-norbornadiene.[36] Further intramolecular insertion of the olefinic part of the ligand in complex **4** between the carbon-ruthenium bond gives complex **5**, in which an *endo-endo* dimer of 2,5-norbornadiene is bound to the ruthenium center with a σ-carbon-ruthenium bond. Oxidative addition of the carbon-carbon bond to the ruthenium complex gives Ru(IV) complex **6**, and reductive elimination gives **7**. β-Carbon elimination of **7** gives complex **8** and β-hydride elimination gives the product PCTD irreversibly. Dimethyl fumarate or N,N-dimethylacrylamide may be a source of the hydride and also acts as a ligand that controls the electronic density of the ruthenium catalytic center. Especially, reductive elimination would be accelerated by the π-acidic ligand.

Starting from PCTD, a series of unique derivatives can be prepared (Scheme 4).[16), 37), 38] These compounds could be useful as starting materials for polymers with specified structures as well as for interesting compounds in the field of physical organic chemistry, such as peristylane and oxaperistylane.[38]

### Stoichiometric reactions of Ru(cot)(dmfm)$_2$

The stoichiometric reactivity of Ru(cot)(dmfm)$_2$ should be elucidated to better understand the mechanisms of the catalytic reactions and to develop new catalytic performance. In this section, novel stoichiometric reactions of Ru(cot)(dmfm)$_2$ are discussed.[20]

Reactions of Ru(cot)(dmfm)$_2$ with amines and phosphines. Ru(cot)(dmfm)$_2$ reacts with a stoichiometric amount of monodentate amines to give monoamine complexes, Ru(cot)(dmfm)(amine), with the dissociation of one dmfm ligand (eq. 9).[21] These complexes are the first examples of mononuclear zerovalent ruthenium amine complexes that are thermally stable at ambient temperature. The stability of the complexes is due to the balance between the electron-donating nature of amines and the π-acidity of dimethyl
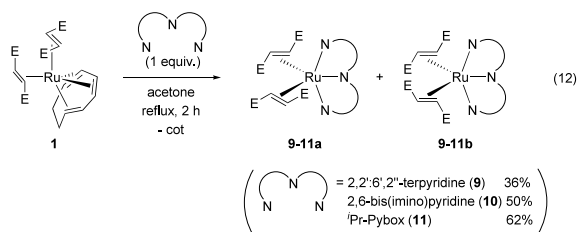
fumarate.

(9)

L = PrNH₂ (87%)
PhCH₂NH₂ (79%)
Me₂NH (70%)
morpholine (81%)
pyridine (85%)
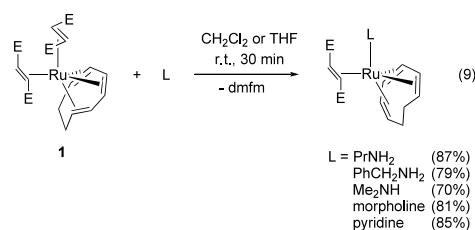
A pyridine solution (excess) of Ru(cot)(dmfm)₂ (**1**) was refluxed for 2 h to give Ru(dmfm)₂(pyridine)₃ in 58% yield via dissociation of the cot ligand in **1** by the coordination of three pyridine molecules (eq. 10).[22]


(10)

58%
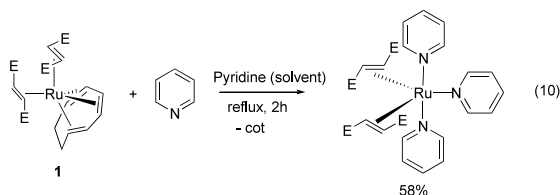
The reaction of Ru(cot)(dmfm)₂ with bidentate nitrogen ligands such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (1,10-phen) in diethyl ether at room temperature gave Ru(η^4-cot)(dmfm)(bipy) and Ru(η^4-cot)(dmfm)(1,10-phen), respectively, in excellent yields (eq. 11).[23]

(11)

(2,2′-bipyridyl) 99%
(1,10-phenanthroline) 96%
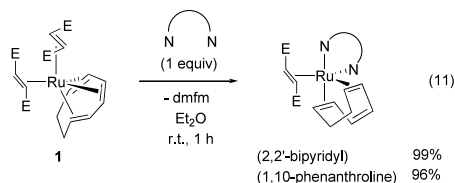
In contrast, the reaction of Ru(cot)(dmfm)₂ with a tridentate nitrogen ligand, terpy [terpy = 2,2′:6′,2″-terpyridine], in acetone under reflux for 2 h gave a diastereomeric mixture of Ru(η^2-dmfm)₂(terpy) (**9a** : **9b** = 2.5 : 1) in 36% yield (eq. 12).[22] In **9a**, two dmfm ligands coordinate with the (re, re) and (si, si) enantiofaces, respectively, while in **9b**, both of the dmfm ligands coordinate with the same enantiofaces, (si, si) and (si, si) [or (re, re) and (re, re) in the enantiomer]. Thus, **9a** has a mirror plane that contains all of the nitrogen atoms and the Ru center, while complex **9b** has an axis of C_2 symmetry that involves the Ru–N(central) bond. The reaction with 2,6-bis(1-phenyliminoethyl)pyridine [2,6-bis(imino)pyridine] and 2,6-bis[(4S)-(-)-isopropyl-2-oxazolin-2-yl]pyridine (i-Pr-Pybox) also gave analogous complexes **10** and **11**, respectively (eq. 12).


(12)

9-11a   9-11b

$\widehat{N}$ $\widehat{N}$ = 2,2′:6′,2″-terpyridine (**9**) 36%
2,6-bis(imino)pyridine (**10**) 50%
^{i}Pr-Pybox (**11**) 62%

Ru(η^6-cot)(dmfm)₂ (**1**) readily reacts with monodentate phosphine ligands (L) in 1,2-dichloroethane at room temperature to give novel zerovalent ruthenium phosphine complexes, Ru(η^6-cot)(η^2-dmfm)(L) (L = PPh₃ (**12a**), PMePh₂ (**12b**), PMe₂Ph (**12c**), PEt₃ (**12d**)), in good to high yields by substitution of one of the dmfm ligands with L (eq. 13).[24]

(13)

L = PPh₃ **12a** (91%)
PMePh₂ **12b** (81%)
PMe₂Ph **12c** (40%)
PEt₃ **12d** (46%)
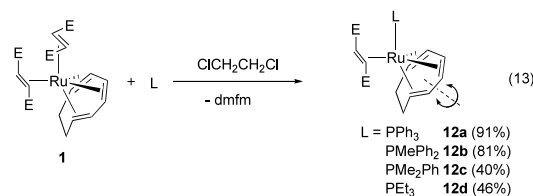
The molecular structures of **12b-d**, which were determined by X-ray crystallography, are roughly similar. In solution, complexes **12a-d** are fluxional and exhibit a reversible temperature-dependent conformational isomerization, which was observed by NMR and appears to be due to the weakness of the bond between Ru and cot attributed to π-back-bonding to both phosphines and dimethyl fumarate from the ruthenium center.

The reactions of Ru(cot)(dmfm)₂ (**1**) with bidentate phosphines depend on the phosphines and the reaction conditions. The reaction of **1** with dppm [dppm = bis(diphenylphosphino)methane] in 1,2-dichloroethane (eq. 14) gives Ru(1-2:5-6-η-1,3,5-cyclooctatriene)(dmfm)(dppm) (**13**).[25] The first step in the formation of **13** is probably the same as that of monodentate phosphine complexes **12**, i.e., the dissociation of dmfm followed by the coordination of dppm in a monodentate manner. The partial dissociation of the cot ligand from η^6 to η^4-coordination, and subsequent chelation by dppm leads to the formation of **13**.

(14)

13
95%
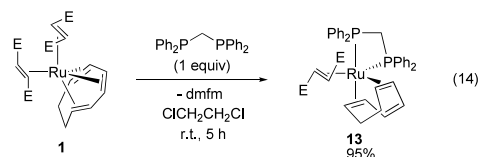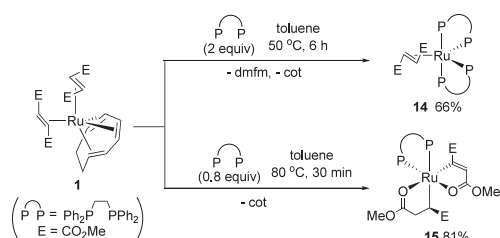
Scheme 5.   Reactions of **1** with dppe.
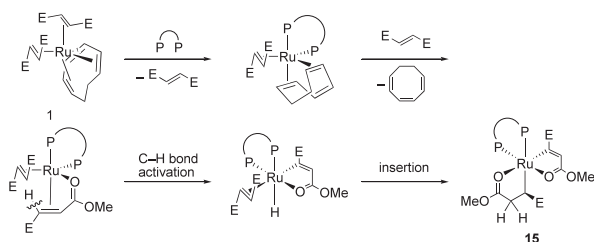
Scheme 6.   A plausible mechanism of the formation of **15**.
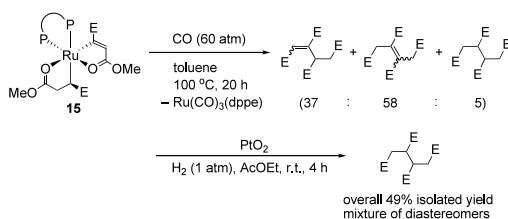

Scheme 7.   Reductive elimination of **15**.

In contrast, the reaction of $Ru(cot)(dmfm)_2$ (**1**) with 2 equiv of dppe [dppe = 1,2-bis(diphenylphosphino)ethane] in toluene at $50\,^{\circ}C$ for 6 h did not give an analogue of **13**, but rather a new complex, $Ru(\eta^2\text{-dmfm})(dppe)_2$ (**14**), in 66% yield, while treatment of **1** with 0.8 equiv of dppe in toluene at $80\,^{\circ}C$ for 30 min gave an alkyl alkenyl complex **15** in 81% yield (Scheme 5).[25]

A plausible mechanism for the formation of **15** is shown in Scheme 6. The dmfm ligand and one of the olefinic bonds of cot in **1** dissociate, and then dppe coordinates with both phosphorus atoms to generate an intermediate similar to dppm complex **13**. The cot ligand then dissociates and the liberated dmfm coordinates again. Activation of the sp^2 C–H bond of the dimethyl fumarate ligand occurs, followed by insertion of the other dmfm into the formed Ru–H bond to give **15**.

The coupling reaction of the alkyl and alkenyl groups occurs under 60 atm of CO to give a mix-

ture of the dimers of dimethyl fumarate (Scheme 7). This reaction seems to be a model reaction for the dimerization of alkenes.

Reactions with water: complexes with a 'chiral water' ligand mononuclear zerovalent ruthenium aqua complex. The behavior of a water molecule in organometallic aqua complexes is of great interest since it represents fundamental information that could be useful for metal complex-catalyzed organic synthesis in aqueous media or reactions using H_2O as a reagent. We recently reported the synthesis of a racemic zerovalent ruthenium aqua complex, $Ru(dppe)(\eta^2\text{-dmfm})_2(H_2O)$ (**16a** + **16b**), in a total yield of 55% by the reaction of the racemic form of **1** with H_2O in the presence of dppe (eq. 15).[25]
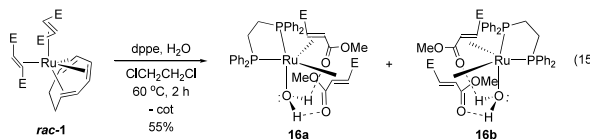
In a further study, the spontaneous resolution of *rac*-**16**, which occurred during recrystallization from chlorobenzene/pentane, enabled each enantiomer **16a** and **16b** to be isolated in pure form.[26] The solid-state structures of **16a** and **16b** determined by X-ray crystallography are shown in Fig. 2; their absolute configurations were confirmed by the values of the Flack parameters, 0.00(4) for **16a** and 0.03(4) for **16b**, as refined by least-squares techniques. The water protons (H1, H2) could be found based on Fourier maps. As is clearly shown, the oxygen atom of H_2O (O1) is bound to ruthenium, and the two hydrogen atoms are located close to the carbonyl oxygen atoms of the dmfm ligands (O2, O3). The distances of O1···O2 (2.652(5) Å) and O1···O3 (2.643(5) Å) for **16a** and O1···O2 (2.657(6) Å) and O1···O3 (2.627(6) Å) for **16b** reflect the existence of intramolecular hydrogen bonds, H1···O2 and H2···O3. The coordinative directions of the two dmfm ligands differ from each other; the dmfm ligands coordinate to ruthenium by the (*re*, *re*)-enantioface in **16a** and by the (*si*, *si*)-enantioface in **16b**. Thus, the water protons H1 and H2 are fixed in different chemical environments, and *a chiral center is generated on O1* in each enantiomer (Fig. 3). Optical resolution of **16a** and **16b** by HPLC equipped with a chiral column was also successful and gave **16a** in 98%ee and **16b** in 92%ee. The
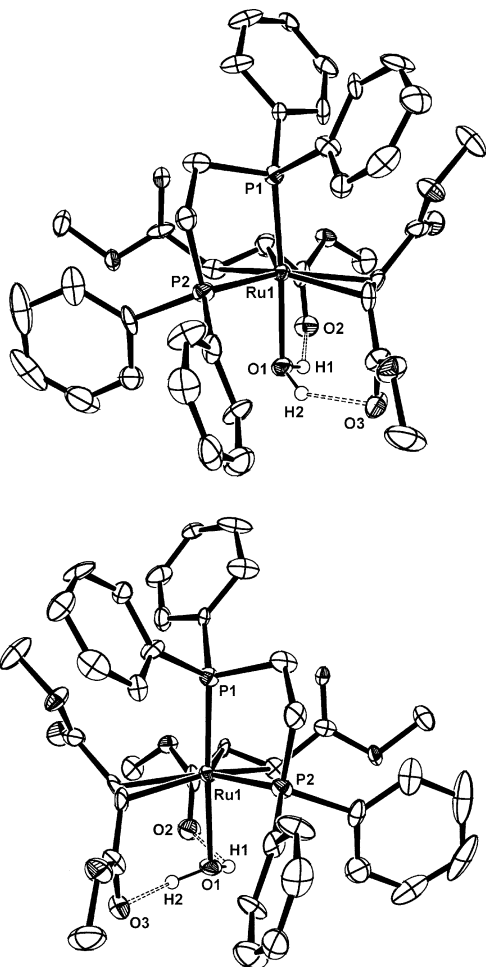
Fig. 2. Molecular structures of **16a** (top) and **16b** (bottom). Thermal ellipsoids are set at 50% probability. Solvents and all hydrogen atoms except water are omitted for clarity. Dashed bonds between water protons (H1, H2) and oxygen atoms of dimethyl fumarates (O2, O3) exhibit hydrogen bonds.
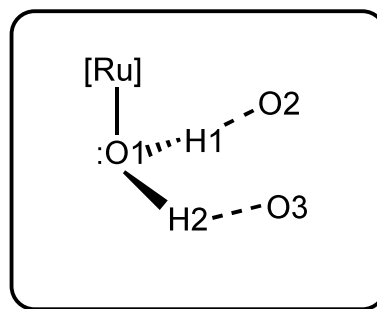

Fig. 3. Generation of chirality on O1 when O2 and O3 are nonequivalent.
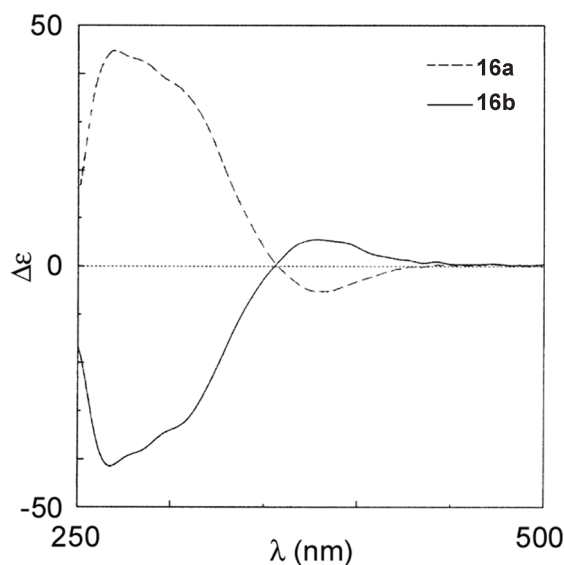
Fig. 4. CD spectra of **16a** ($c = 2.5 \times 10^{-5}$ M) and **16b** ($c = 3.7 \times 10^{-5}$ M) in CHCl$_3$. For **16a**: λ_{max} 270 nm ($\Delta\varepsilon + 45$), 381 (-5). For **16b**: λ 268 nm ($\Delta\varepsilon - 41$), 378 ($+5$).

CD spectra of these separated complexes measured in CHCl$_3$ clearly showed their enantiomeric relationship (Fig. 4).

The behavior of H$_2$O in **16** in solution was examined by variable-temperature ^{1}H NMR spectroscopic analysis in CD$_2$Cl$_2$ (Fig. 5, left). The signal for the water protons appears as a broad singlet at 4.68 ppm at 25 °C. As the temperature was lowered, the broad singlet gradually sharpened (0 °C ~ -40 °C) with the appearance of a small shoulder peak at a slightly lower magnetic field, and the top of the signal began to split into two peaks at -70 °C. Further splitting was observed by cooling to -80 °C, with peaks at 4.64 and 4.52 ppm. In addition, the ^{1}H-^{1}H COSY spectra showed the relationship between these peaks. The nonequivalent geminal protons of the coordinated H$_2$O are clearly observed in these spectra, and their positional exchange is slowed by a decrease in temperature.

By a DFT calculation, the positional exchange of the geminal protons strongly suggests the involvement of the rotation and inversion of H$_2$O; rotation has a higher energy barrier (ca. 13.6 kcal mol^{-1}) than inversion, which proceeds with nearly no barrier. The value 13.6 kcal mol^{-1} was somewhat consistent with that of the activated enthalpy obtained experimentally (10.8 kcal mol^{-1}). The information obtained here may contribute to understanding the behavior of water molecules in general metal aqua

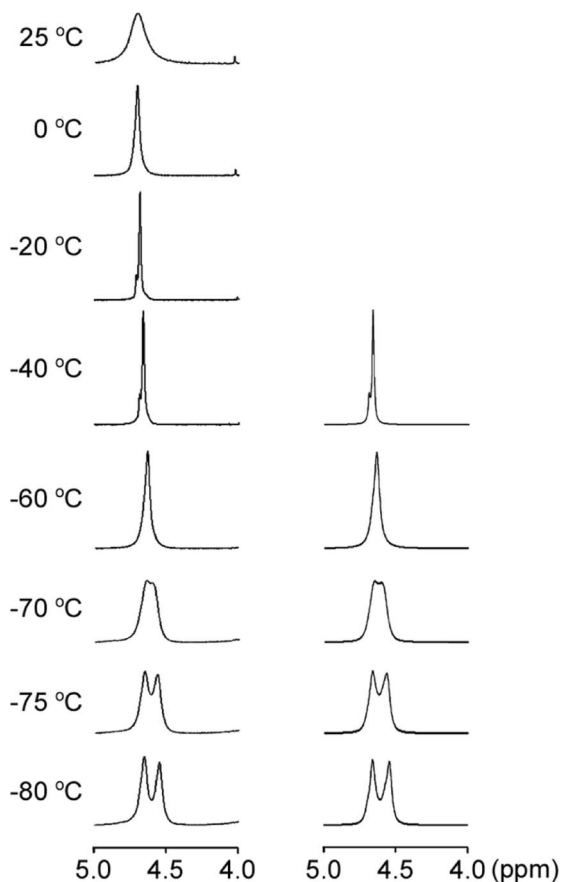Fig. 5. Experimental ^{1}H NMR spectra of **16** (left) in CD$_2$Cl$_2$ at temperatures of 25 °C ∼ −80 °C, and simulated ^{1}H NMR spectra of **16** (right) at −40 °C ∼ −80 °C. Chemical shifts are referenced to internal solvent resonances and reported relative to SiMe$_4$.

complexes, which could lead to developments in the chemistry of water and related fields.

The water molecule could be substituted with other small polar molecules such as NH$_3$. A zerovalent ammonia complex **17** could be isolated, and the structure was determined by X-ray crystallography (eq. 16).[26]
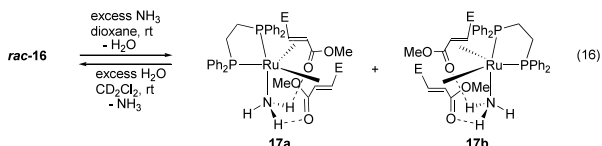
Chiral centers are generated on the nitrogen atoms of the coordinated NH$_3$ in **17a** and **17b** in the solid state. In solution, even at −90 °C, splitting of the ammonia proton signal in ^{1}H NMR was not observed.
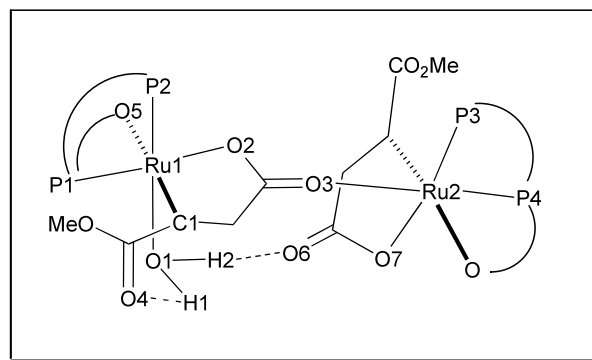

Fig. 6. Atom numbering of **18** and **19**.

Dinuclear ruthenium aqua complexes. When dppe derivatives with methoxy-substituted groups are used in place of dppe, they act as facial tridentate ligands to give very unique binuclear aqua complexes via an unexpected bond cleavage of dimethyl fumarate.[27]

The reaction of the racemic form of Ru(cot)(dmfm)$_2$ (**1**) in dichloromethane/H$_2$O with the phosphine ligand (S,S)-DIPAMP or o-MeO-dppe at 60 °C gave **18** and **19** in respective yields of 26% and 59% (eq. 17). The structures of these complexes were confirmed by X-ray crystallography.

Complex **18** is a binuclear Ru(II) aqua complex in which (S,S)-DIPAMP ligands coordinate to the ruthenium centers in a facial tridentate manner. Notably, oxaruthenacycle structures are formed via the apparent cleavage of an O–CH$_3$ bond in dimethyl fumarate.
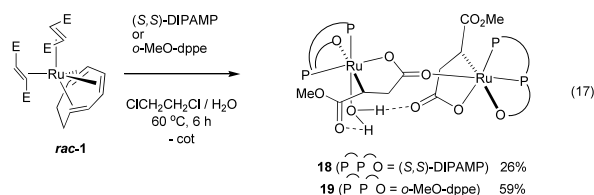
In the component of **18** shown on the left-hand side of the structure in Fig. 6, the water oxygen atom O1 is located at a *trans* position relative to the phosphorus atom P2, and the sp^3 carbon atom C1 in the oxametallacycle moiety is *trans* to O5. On the other hand, in the component on the right-hand side, while (S,S)-DIPAMP coordinates in the same manner, the position of the oxametallacycle relative to the (S,S)-DIPAMP ligand is different from that in the component on the left side; i.e., in the right-hand

Fig. 7.   Structures of (S,S)-DIPAMP and o-MeO-dppe.
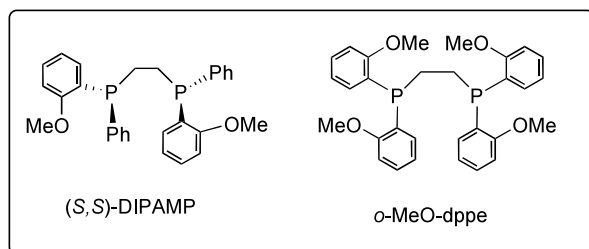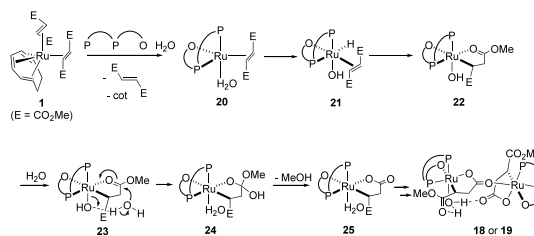

Scheme 8.   Mechanism of the fomation of **18** or **19**.

Scheme 9.   Reaction of **19** with H_2O or NH_3.

component, the oxygen atom of the oxaruthenacycle O7 is located *trans* to the phosphorus atom P3, to give a noncoordinated methoxyphenyl group. The carbonyl oxygen atom O3 is bound to Ru2, and the coordinated water molecule is connected to two different carbonyl oxygen atoms O4 and O6. The distances O1···O4 and O1···O6 are 2.820(11) and 2.701(11) Å, which indicates the presence of hydrogen bonds between H1···O4 and H2···O6, respectively. Overall, the aggregation of the two P-P-O ligated oxaruthenacycle moieties is stabilized by coordination of the carbonyl oxygen and the hydrogen bond H2···O6. The oxygen atom of the water molecule O1 can be considered a chiral center in the solid state, since it has four different groups, i.e. ruthenium, an unshared electron pair, and two protons with different hydrogen bonds, as was observed in complexes **16**.[26]

A possible pathway to **18** and **19** based on our previous investigation of the reactivity of Ru(cot)(dmfm)$_2$ (**1**) is proposed in Scheme 8. The reaction of **1** with a P-P-O ligand and H_2O would give the Ru(0) aqua complex **20** via Ru(η^4-cot)(dmfm)(η^2-P-P-O) and Ru(η^2-cot)(dmfm)(η^3-P-P-O). The structure of **20** is partially similar to that of **16**, but the ruthenium center is more electron-rich, and thus oxidative addition of the coordinated H_2O would proceed and subsequent insertion of dimethyl fumarate into the formed Ru-H bond would give alkyl hydroxo intermediate **22**. From **22**, nucleophilic attack of H_2O toward the carbonyl carbon with the assistance of ruthenium, which acts as a Lewis acid, and the loss of MeOH would give the oxaruthenacycle aqua complex **25**, corresponding to the left-hand component of **18**. Liberation of H_2O from **25** and migration of the oxaruthenacycle moiety would give the coordinatively unsaturated 16-electron moiety of the right-hand component of **18**, which finally combines with **25** to afford **18**.
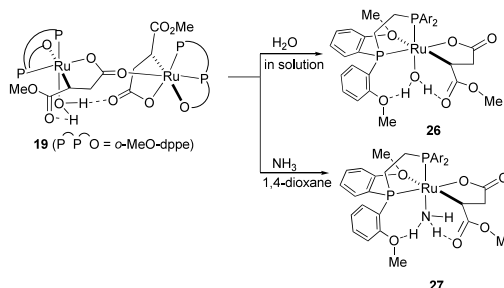
In solution, complex **18** maintains a binuclear form, while complex **19** dissociates to a mononuclear form.[27] Complex **19** was further reacted with an excess amount of NH_3 in 1,4-dioxane to give the mononuclear ammonia complex **27** (Scheme 9), the solid-state structure of which was determined by X-ray crystallography.[27]

Other reactions of Ru(cot)(dmfm)$_2$ to give zerovalent arene and p-quinone complexes. Complex Ru(cot)(dmfm)$_2$ (**1**) reacted with various aromatic compounds to give a series of novel zerovalent ruthenium η^6-arene complexes, Ru(η^6-arene)(η^2-dmfm)$_2$, in good yields by ligand exchange between cot and arenes,[28] while in the reactions of **1** with p-quinones, selective ligand exchange between dmfm and p-quinone proceeded smoothly to give Ru(cot)(p-quinone) complexes in high yields.[29]

Conclusion

Zero valent ruthenium complexes Ru(cot) (dmfm)$_2$ and Ru(cod)(cot) have been shown to be very versatile catalysts for carbon-carbon bond-forming reactions and carbon-carbon bond-cleaving reactions which are characteristic of ruthenium. Completely new hydrocarbons and their derivatives are synthesized by this method and they should serve as new starting compounds for functional materi-

als. Further, Ru(cot)(dmfm)$_2$ is a versatile mother complex for a series of new low valent ruthenium complexes, including entirely novel aqua complexes in which a chiral center is generated on the water molecule coordinated to the ruthenium center. Such coordinated water is called 'chiral water' and this phenomenon may not be limited to organometallic chemistry. Generally, the concept of 'chiral water' can be applied widely, even in biochemistry. It is possible that 'chiral water' may control the enantioselective reaction on the active center of enzymes. The novel concept of 'chiral water' should open the door to a new field of chemistry.

Acknowledgement

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