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Ru(η^6-1,3,5-cyclooctatriene)(η^2-dimethyl fumarate)$_2$: a novel, versatile zerovalent ruthenium complex with electron-deficient olefinic ligands

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Abstract

The reactivity of a novel zerovalent ruthenium complex, Ru(η^6-cot)(η^2-dmfm)$_2$ (cot = 1,3,5-cyclooctatriene, dmfm, =dimethyl fumarate), which is readily prepared from Ru(η^4-cod)(η^6-cot) (cod = 1,5-cyclooctadiene) and dmfm was examined. The reaction with monodentate phosphine or amine ligands gave Ru(η^6-cot)(dmfm)(L) (L = ligand) via dissociation of dmfm. Among bidentate phosphines, dppm (dppm = bis(diphenylphosphino)methane) reacted to give Ru(η^4-cot)(dmfm)(dppm) along with releasing a dmfm ligand. In the case of dppe (dppe = 1,2-bis(diphenylphosphino)ethane), two types of complexes were obtained depending on the reaction conditions, Ru(dmfm)(dppe)$_2$ and an alkyl alkenyl complex; in the formation of the latter complex, sp^2 C–H bond activation of dmfm occurred. Ru(η^4-cot)(dmfm)(N⌒N) and Ru(dmfm)$_2$ (N⌒N⌒N) were formed by reacting with bidentate and tridentate nitrogen ligands. The reactions with arenes gave π-coordinated complexes, Ru(η^6-arene)(dmfm)$_2$. *p*-Quinones and a *p*-biqunone reacted to give Ru(η^6-cot)(*p*-quinone) and {Ru(η^6-cot)}$_2$(*p*-biquinone), respectively, along with the dissociation of two dmfm ligands. It was found that low-valent ruthenium complexes preferably bear both electron-donating and accepting ligands simultaneously to be thermodynamically stable.

Keywords: Zerovalent ruthenium complexes; Dimethyl fumarate; Cyclooctatriene; Ligand displacement

1. Introduction

A variety of synthetic organic reactions catalyzed by ruthenium complexes have been rapidly developed in the past three decades taking advantage of the various reactivities [1,2]. Especially, low-valent ruthenium complexes have an electron-rich metal center which is favorable for a metal-oxidation step such as oxidative addition and cyclization reactions. In addition, since ruthenium has relatively many coordination sites compared with group 9 or 10 metals such as rhodium and palladium, proper tuning and matching of the ligands for each reaction is critically important to achieve high catalytic activity. At the same time, it also makes the designing of novel complexes attractive because of a wide selection of the combination of ligands, leading to versatility of the catalysis.

Among low-valent ruthenium complexes, zerovalent complexes are very interesting in terms of high reactivity as mentioned above. Especially, extensive efforts have been made towards the synthesis and elucidation of the reactivity of a versatile zerovalent complex, Ru(η^4-cod)(η^6-cot) (**1**) (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) and its derivatives, to date [3–20]. During the course of a specific C–C bond forming reaction involving **1** as a precatalyst (Eq. (1)), we found that the unique dimerization of 2,5-nor-

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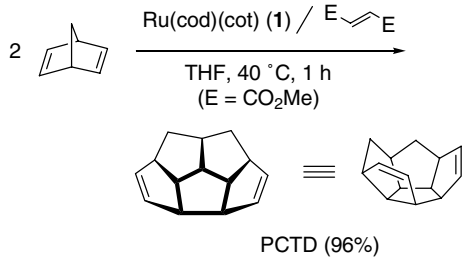
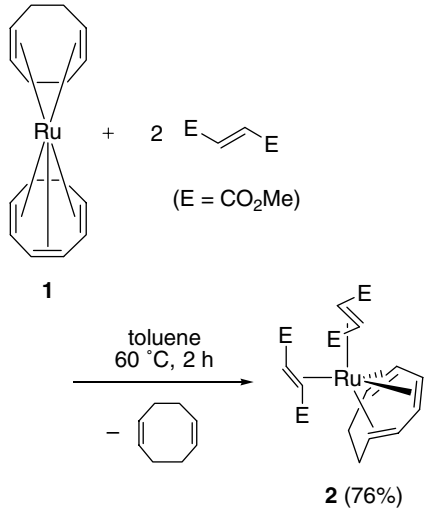
bornadiene to give pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-di- ene (PCTD) involving C–C bond cleavage and reconstruction catalyzed by **1** required dimethyl fumarate as additive [21].



(1)

A stoichiometric reaction between **1** and dimethyl fumarate performed with the aim to trap the active species gave the new zerovalent ruthenium complex Ru(η^6-cot)(η^2-dmfm)$_2$ (**2**) (dmfm = dimethyl fumarate) in high yield via the ligand displacement between cod and 2 equiv. of dmfm (Eq. (2)) [21b]. Complex **2** itself was also found to work as an effective catalyst in the dimerization of 2,5-norbornadiene without additives, where the dimethyl fumarate ligand on ruthenium would play an essential role as an olefinic π-acceptor. These findings prompted us to explore further the chemistry of complex **2**, whose representative reactions toward phosphorus and nitrogen ligands, arenes and *p*-quinones are reviewed here (Scheme 1).



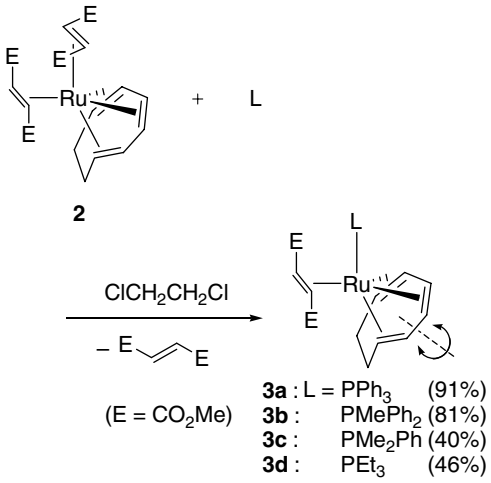
(2)

2. Reactivity of Ru(cot)(dmfm)$_2$

2.1. Reactions with phosphorus ligands

2.1.1. Monodentate phosphorus ligands

Complex **2** readily reacts with monodentate phosphine ligands (L) in 1,2-dichloroethane at room temperature to give novel zerovalent ruthenium complexes, Ru(η^6-cot)(dmfm)(L) (L = PPh_3 (**3a**), PMePh2 (**3b**), PMe_2Ph (**3c**), PEt_3 (**3d**)), in good to high yields by substitution of one of the dimethyl fumarates with L (Eq. (3), Fig. 1) [22].

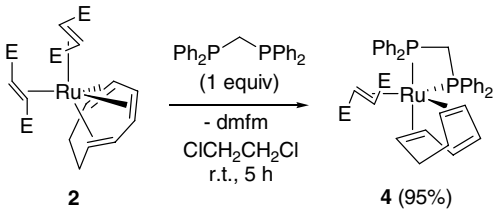


(3)

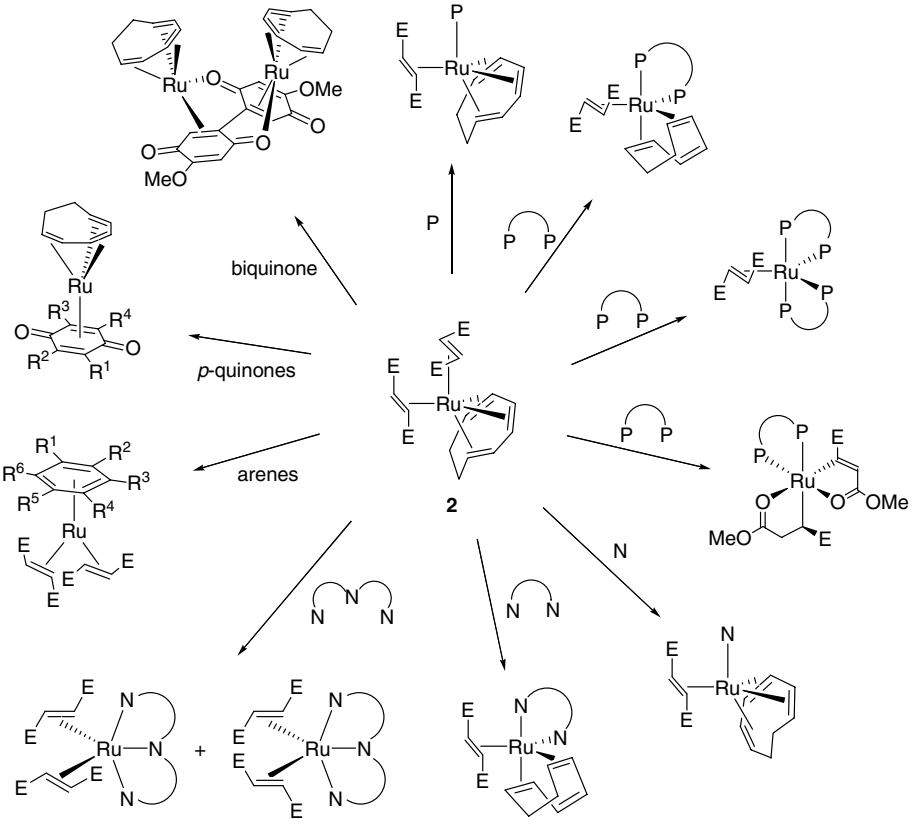
The molecular structures of **3b–d**, which were determined by X-ray diffraction, are roughly similar. However, a close look at each structure reveals three slightly different coordination modes, **A**, **C** and **D**, for the cyclooctatriene ligand (Scheme 2). The structures of **A**, **C** and **D** correspond to the solid-state structure of **3b**, **3d** and **3c**, respectively. In solution, complexes **3a–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 the π-back bonding to both the phosphorus ligand and the dimethyl fumarate from the ruthenium center [22].

2.1.2. Bidentate phosphorus ligands

Reactions of **2** with bidentate phosphines vary depending on the phosphines and reaction conditions. Ru(1-2:5-6-η-1,3,5-cyclooctatriene)(dmfm)(dppm) (**4**) was obtained by the reaction of **2** with bis(diphenylphosphino)methane (dppm) in 1,2-dichloroethane (Eq. (4), Fig. 2) [23]. The first step of the formation of **4** is probably the same as that of monodentate phosphine complexes **3**, i.e., the dissociation of dmfm followed by the coordination of dppm in a monodentate manner. Partial dissociation of the cot ligand from η^6 to η^4-coordination, and subsequent chelation by dppm leads to the formation of **4**. Complex **4** was apparently very stable and further ligand exchange reactions did not proceed.



(4)



Scheme 1. Reactivity of Ru(η^6-cot)(dmfm)$_2$ (**2**) toward various substrates.

On the other hand, the reaction of **2** with 2 equiv. of 1,2-bis(diphenylphosphino)ethane (dppe) in toluene at 50 °C for 6 h afforded not an analogue of **4** but a new complex, Ru(dmfm)(dppe)$_2$ (**5**), in 66% yield (Eq. (5)) [22]. In complex **5**, dimethyl fumarate occupies an equatorial position, and the two phosphorus atoms of a dppe ligand occupy an axial and an equatorial position, respectively, and the other dppe coordinates in the same way. Complex **5** is formed via substitution of the cyclooctatriene and one of the dimethyl fumarate ligands in **2** by two molecules of dppe.

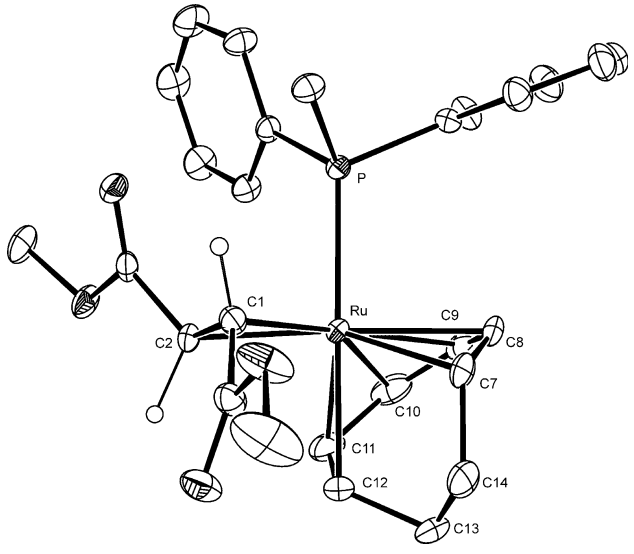
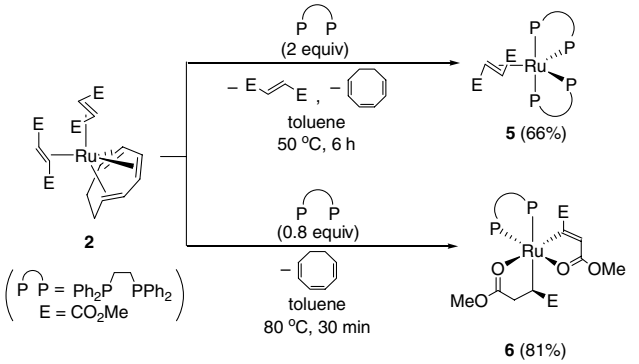
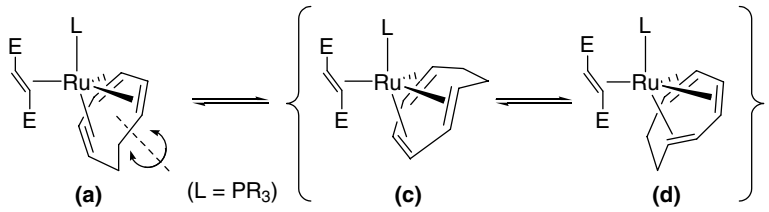


Fig. 1. ORTEP drawing of **3b**.



(5)

The treatment of **2** with 0.8 equiv. of dppe in toluene at 80 °C for 30 min gave a novel alkyl alkenyl complex **6** in 81% yield [22]. Complex **6** has β-methoxycarbonylalkenyl and β-methoxycarbonylalkyl chelate



Scheme 2. A possible mechanism for the isomerization of **3a**–**d**.

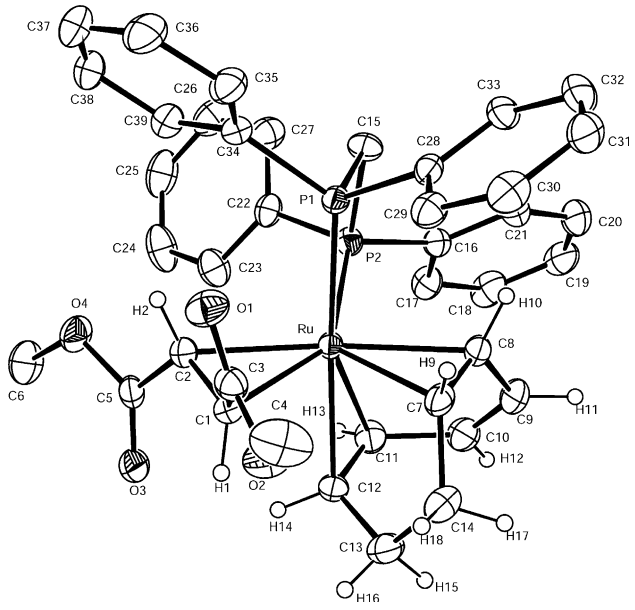
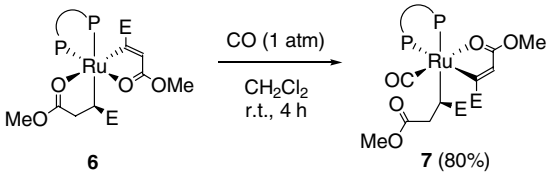


Fig. 2. ORTEP drawing of **4**.

ligands. A plausible mechanism of the formation of **6** is shown in Scheme 3. The dimethyl fumarate ligand and one of the olefinic bonds of cyclooctatriene in **2** dissociate, and then dppe coordinates with both phosphorus atoms to generate an intermediate similar to dppm complex **4**. Then the cyclooctatriene ligand dissociates and the removed dimethyl fumarate coordinates again. The activation of the sp^2 C–H bond of the dimethyl fumarate ligand occurs followed by the insertion of the other dimethyl fumarate into the formed Ru–H bond to give **6**.

Reactions of **2** with other bidentate phosphines such as 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb) were attempted but no isolable complex was intercepted.

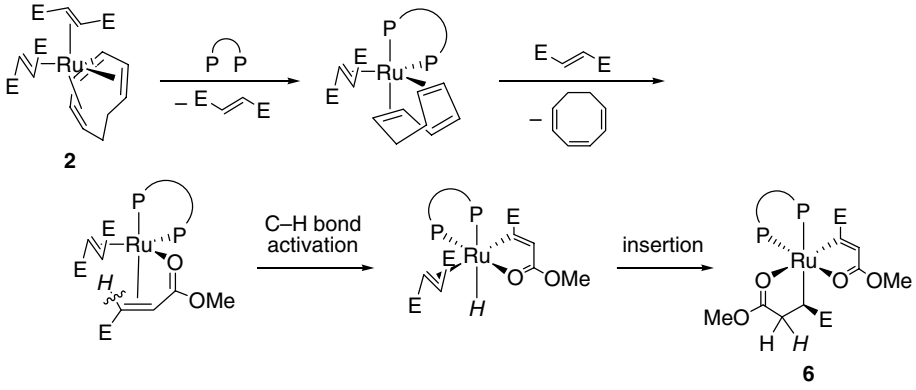
Complex **6** readily reacts with 1 atm of carbon monoxide in CH_2Cl_2 at room temperature to give complex **7** (Eq. (6)) [22]. The reductive elimination to afford the dimer of dimethyl fumarate did not occur under these conditions.



(6)

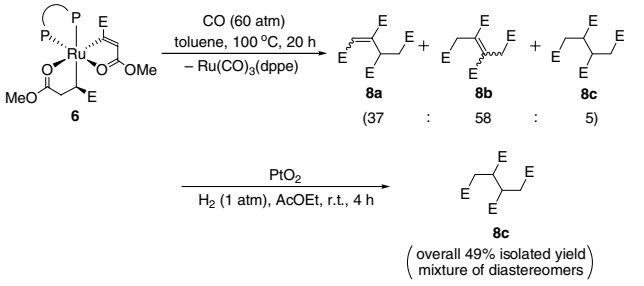
The reaction appears to be a simple substitution reaction of the coordinated methoxy carbonyl group with carbon monoxide; however, the reaction was not simple. The product **7** was not the complex derived via simple substitution of **6**. In **7**, the alkenyl group is located at the *trans* position of one of the phosphorus atoms of dppe, showing a rearrangement occurred during the reaction.

Complex **6** was treated under 60 atm of carbon monoxide at 100 °C to give dimers of dimethyl fumarate **8a**–**c** (**8a**:**8b**:**8c** = 37:58:5) and $Ru(CO)_3$(dppe) [24] via reductive elimination (Eq. (7)) [22]. Hydrogenation of



Scheme 3. A plausible mechanism of the formation of **6**.

the mixture of **8a**–**c** by the PtO_2 catalyst afforded **8c** in 49% yield based on **6**. Although the hydrodimerization of dialkyl fumarate has been performed by an electrolytic reduction [25], the present reactions are the first example of the stepwise dimerization of dimethyl fumarate mediated by a transition metal, and can be regarded as a model of catalytic dimerization of an olefinic compound.

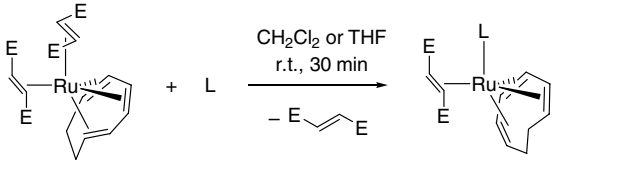


(7)

2.2. Reactions with nitrogen ligands

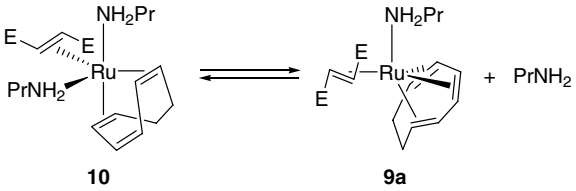
2.2.1. Monodentate nitrogen ligands

Complex **2** readily reacted with monodentate amines or pyridine in CH_2Cl_2 or THF at room temperature to give Ru(η^6-cot)(dmfm)(L) (**9**) similar to phosphine-coordinated complexes **3**, in high yields (Eq. (8)) [26]. Complexes **9** are the first examples of mononuclear zerovalent ruthenium complexes coordinated by a monodentate amine or pyridine ligand which were isolated purely and are well characterized. In contrast to **3**, the cot ligand of **9** does not rotate even at over 50 °C. This fixation of cot is explained by the strong π-back bonding from Ru to cot, which was strengthened by the coordinated nitrogen ligand.



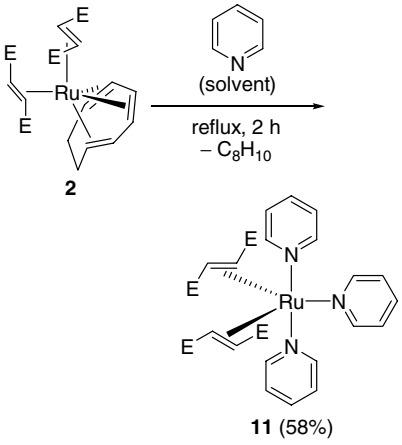
(8)

Although the reaction of **2** with *n*-propylamine affords Ru(η^6-cot)(dmfm)(*n*-$PrNH_2$) (**9a**), the crystallization of **9a** in the presence of an excess of *n*-propylamine gave Ru(η^4-cot)(dmfm)(*n*-$PrNH_2$)$_2$ (**10**), whose structure was determined by X-ray crystallography [26]. The solid state ^{13}C (CP-MAS) NMR spectrum of **10** was consistent with the result of X-ray analysis. However, when complex **10** was dissolved in CD_2Cl_2, the ^1H and ^{13}C NMR spectra showed the signals of **9a** and free *n*-propylamine. These results indicate the existence of equilibrium between **10** and **9a**, where **10** is predominant in a solid state, whereas the complete conversion from **10** to **9a** occurs in solution along with the dissociation of *n*-propylamine,



(9)

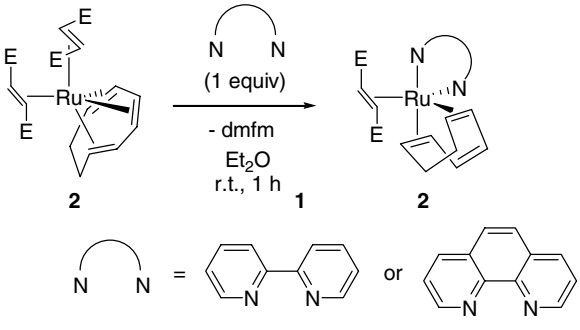
A pyridine solution of **2** was refluxed for 2 h to give Ru(dmfm)$_2$(pyridine)$_3$ (**11**) in 58% yield via the dissociation of the cot ligand in **2** by the coordination of three pyridine molecules [27],



(10)

2.2.2. Bidentate nitrogen ligands

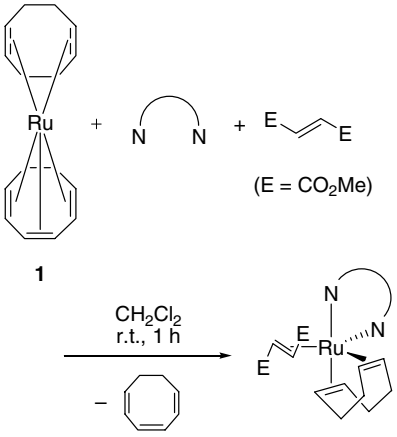
The reaction of **2** with 2,2′-bipyridyl in diethyl ether at room temperature gave orange crystals of Ru(η^4-cot)(dmfm)(bipy) (**12a**) in quantitative yield (Eq. (11)) [28]. Complex **12** is the first example of a mononuclear zerovalent ruthenium complex coordinated by bidentate pyridyl ligands. The formation mechanism of **12** would be similar to that of **4**.



(11)

On the other hand, in the presence of 2,2′-bipyridyl or 1,10-phenanthroline, the reaction of complex **1** with 1 equiv. of dimethyl fumarate in CH_2Cl_2 at room temperature generated Ru(cod)(dmfm)(N⌒N) (**13**) in high

yields (Eq. (12)), whereas complex **1** itself does not react with N⌒N [28]. Notably, complexes **12** and **13** are stable enough to be kept in air for several days due to the strong coordination of each ligand powered by the combination of electron-donor and acceptor, although most zerovalent complexes readily decompose under the same conditions.



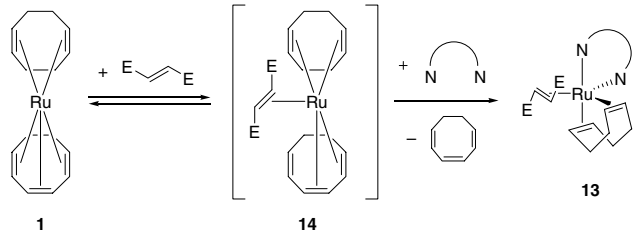
13a: 83%
13b: 79%

(12)

A possible mechanism for the formation of **13** is shown in Scheme 4. Complex **1** would react with 1 equiv. of dmfm to give Ru(cod)(η^4-cot)(dmfm) (**14**) reversibly. In the presence of the bidentate nitrogen ligands (N⌒N), the cot ligand of the intermediate **14** would be replaced by N⌒N to give **13**.

2.2.3. Tridentate nitrogen ligands

A tridentate nitrogen ligand, 2,2′:6′,2″-terpyridine (terpy), was reacted with **2** in acetone under reflux for 2 h to afford a mixture of stereoisomers of a novel ruthenium(0) complex, Ru(dmfm)$_2$(terpy) (**15**) in 36% yield via the substitution between the cot ligand and terpy (Eq. (13), Fig. 3) [27]. In this reaction, complex **2** was consumed completely; however, the ^{1}H NMR spectrum of the reaction mixture revealed that the selective formation of **15** was not successful and the products were a mixture of various complexes. The obtained complexes were revealed to be a mixture of two diastereomers, **15a** and **15b** (2.5:1) based on the ^{1}H NMR spectra. In **15a**, two dmfm ligands coordinate with (*re*, *re*) and (*si*, *si*) enantiofaces, respectively, while in **15b**, both of the dmfm ligands coordinate with the same enantiofaces,



Scheme 4. A possible mechanism for the formation of **13**.

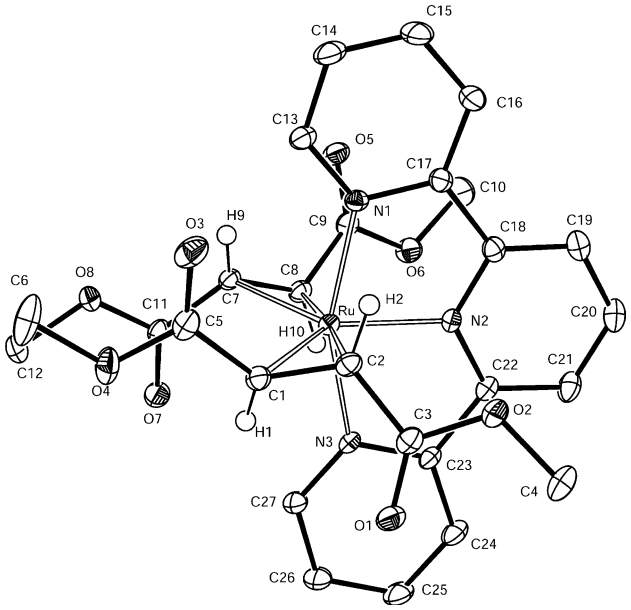
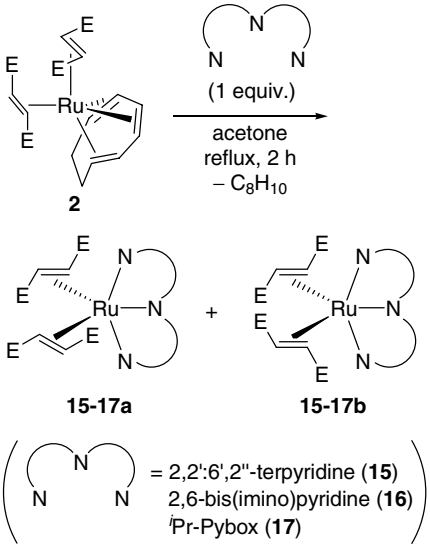


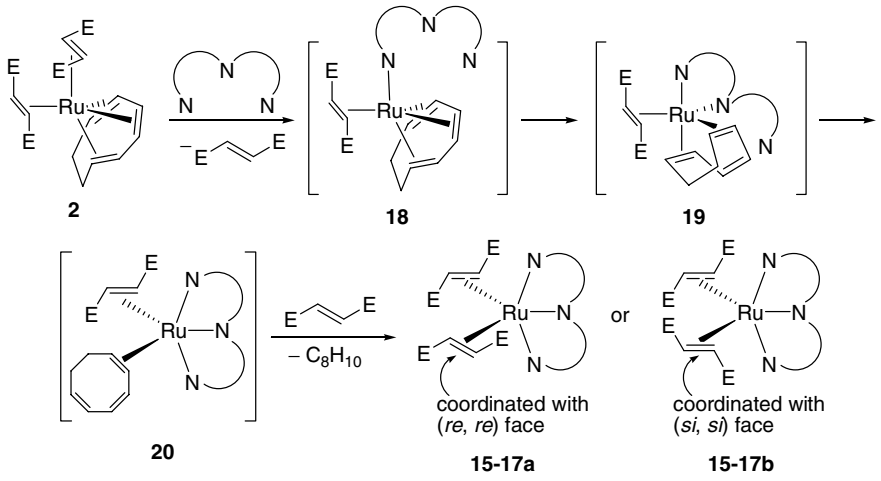
Fig. 3. ORTEP drawing of **15b**.

(*si*, *si*) and (*si*, *si*) [or (*re*, *re*) and (*re*, *re*) in the enantiomer]. Thus, **15a** has a mirror plane containing all the nitrogen atoms and the Ru center like **11**, while complex **15b** has a C_2 symmetry axis involving the Ru–N(central) bond. The reaction with 2,6-bis(imino)pyridine and 2,6-bis(oxazolinyl)pyridine (Pybox) also gave the analogous complexes **16** and **17**, respectively. Complexes **15**–**17** are the first example of isolable mononuclear zerovalent ruthenium complexes with a tridentate nitrogen ligand.



(13)

Switching the coordinative enantioface of one of the dmfm ligands through this reaction suggests that the reaction would begin with the dissociation of the dmfm ligand (Scheme 5). The generated vacant site would be occupied by one of the terminal nitrogen atoms of a tridentate ligand to give an intermediate **18**. Then the dissociation of the central olefinic group of the cot ligand is followed by the coordination of the central pyridyl group

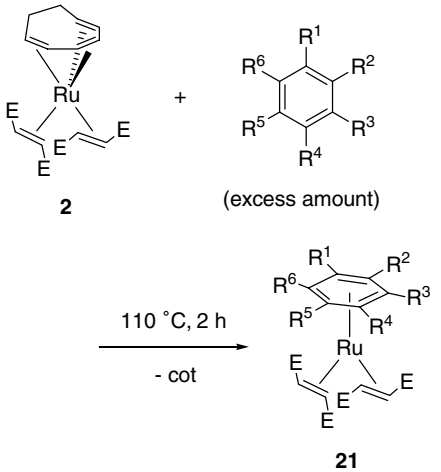


Scheme 5. Possible mechanism for the formation of complexes **15**–**17**.

of the tridentate ligand to afford an intermediate **19**, according to the reaction pathway to form ruthenium(0) complexes having bidentate nitrogen ligands [28]. The dissociation of the second olefinic group of cot and the coordination of the last nitrogen moiety formed the Ru(N⁀N⁀N) species **20**. Finally, the dissociated dmfm recoordinates in place of the complete dissociation of the cot ligand with the (*si*, *si*) or (*re*, *re*) enantioface, which would produce stereoisomers such as **15**–**17a** and **15**–**17b** in Scheme 5. Thus, the cot ligand is not directly substituted by a tridentate nitrogen ligand.

2.3. Reactions with arenes

Complex **2** reacted with various aromatic compounds to give a series of novel zerovalent ruthenium η^6-arene complexes Ru(η^6-arene)(dmfm)$_2$ (**21**) in good yields by ligand exchange between the tridentate ligands, 1,3,-5-cyclooctatriene and arene (Eq. (14)) [29]. Benzene, alkyl-substituted arenes, anisole, *N*,*N*-dimethylaniline, biphenyl and naphthalene were efficiently reacted. The molecular structure of Ru(η^6-anisole)(dmfm)$_2$ is shown in Fig. 4.



(14)

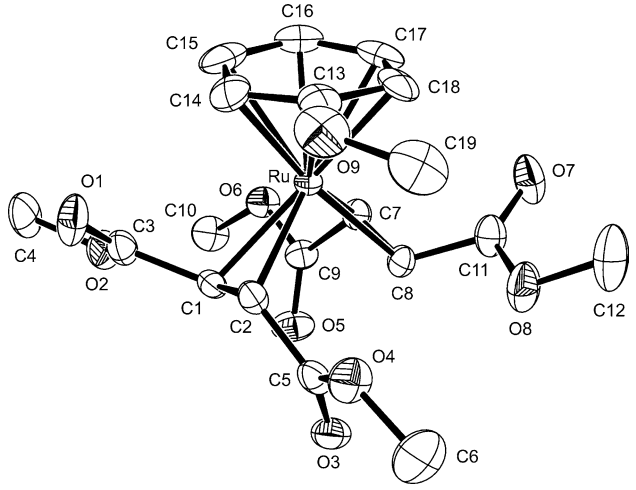
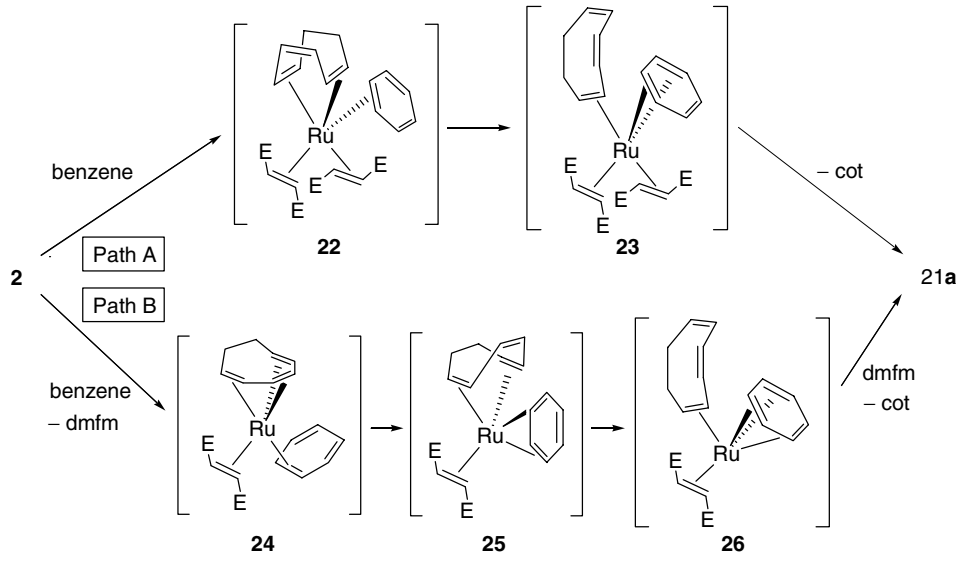


Fig. 4. ORTEP drawing of Ru(η^6-anisole)(dmfm)$_2$.

As a displacement mechanism, two pathways can be considered (Scheme 6). *Path A* shows a straightforward exchange mechanism between cyclooctatriene and arene without dissociation of dimethyl fumarate. On the other hand, in *Path B*, the release of a dimethyl fumarate ligand is followed by displacement of the cyclooctatriene ligand with arene and the recoordination of dimethyl fumarate to give complex **21**. While the intermediates **22**–**26** have not yet been detected, complexes **3** and **9** as analogues of **24**, and, **4** and **12** as analogues of **25** have been known as described above. *Path B* is similar to the formation mechanism of tridentate nitrogen ligand coordinated complexes **15**–**17** in Scheme 5. It was revealed that the addition of dimethyl fumarate decelerated the displacement of 1,3,5-cyclooctatriene by toluene-d_8. In the reaction of **2** with toluene-d_8 This result also strongly supports *Path B*, which involves the dissociation step of a dimethyl fumarate ligand.



Scheme 6. Possible mechanism for the formation of **21a** from 2.

2.4. Reactions with quinones

As shown in Eq. (15), the reactions of **2** with *p*-quinones were performed. The selective ligand exchange between π-acceptors, dimethyl fumarate and *p*-quinone, smoothly occurred to afford Ru(η^6-cot)(*p*-quinone) (**27**) in good to high yield, which are the first example of *zero-valent* ruthenium *p*-quinone complexes [30]. Several kinds of *p*-quinones with an electron-donating group or an electron-withdrawing group were found to be suitable for this substitution reaction including *p*-naphthoquinone. The molecular structure of Ru(η^6-cot)(2,6-dimethoxy-*p*-benzoquinone) was confirmed by X-ray crystallography (Fig. 5). Noteworthy is that in the formation of **27**, complete dissociation of two dmfm ligands in the starting complex **2** occurred, whereas all the complexes described above have at least one dmfm or related ligand. This is probably due to the strong π-acidity of *p*-quinones similar to dmfm and in order to balance the proper electron density around ruthenium, two dmfm ligands were driven out by the added *p*-quinones.

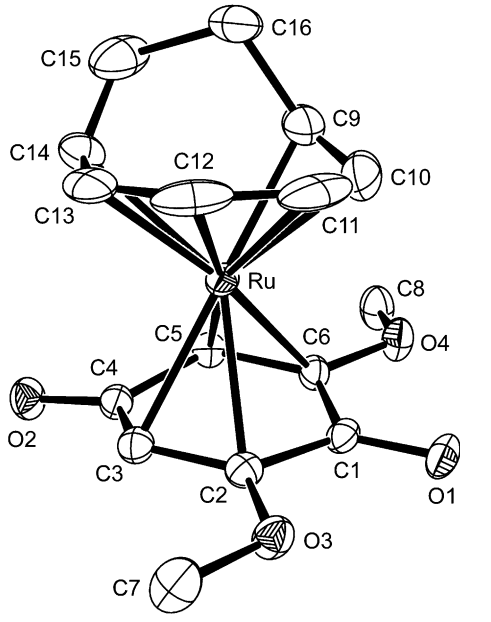
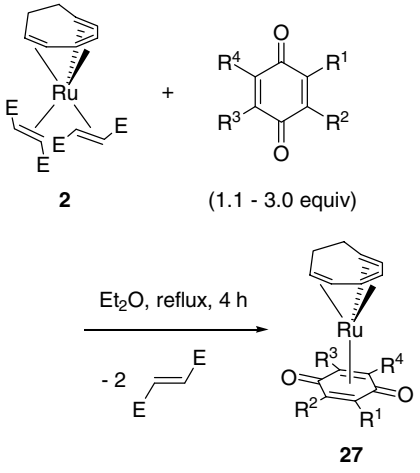


Fig. 5. ORTEP drawing of Ru(η^6-cot)(2,6-dimethoxy-*p*-benzoquinone).



(15)

The reaction of **2** with a 0.5 equiv. of a *p*-biquinone in place of *p*-quinones gave a novel Ru(0) bimetallic complex **28** under very mild conditions as illustrated in Eq. (16) [30]. η^4-Coordinated monometallic or bimetallic complexes which are similar to complexes **27** did not form at all in this reaction. The ORTEP drawing of **28** is shown in Fig. 6.

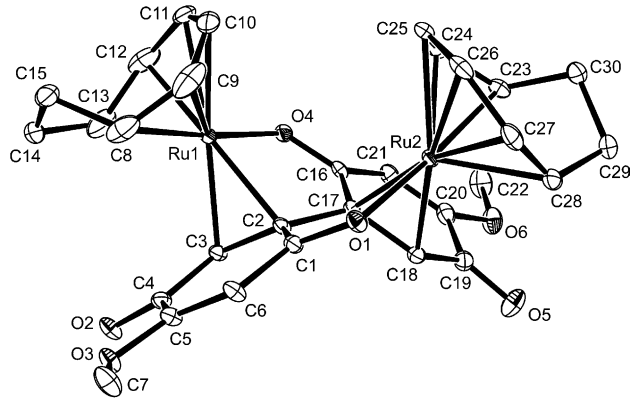
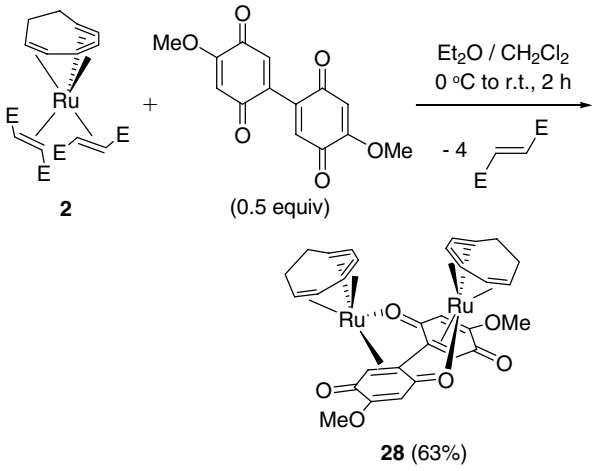


Fig. 6. ORTEP drawing of **28**.



(16)

In complex **28**, one of the two olefinic parts and an oxygen atom of the carbonyl group of each *p*-quinone moiety coordinate to each ruthenium atom to form stable chelate rings. Thus, **28** is a C_2-symmetric compound and the symmetry axis penetrates the center of *p*-biquinone vertically. The distance between two ruthenium atoms is 4.12 Å and no metal–metal bond exists. The ruthenium atoms withdraw the electrons from the carbonyl oxygens and give d-electrons to the electron-deficient olefinic moieties of *p*-quinone. Such a cooperative electron push–pull system and the stable chelation strengthens the binding of the *p*-quinone ligands to the ruthenium atoms.

3. Conclusion

A number of novel zero- and divalent complexes were generated from the prototype complex **2**. Such complexes are seen to accommodate both strong electron donors and acceptors within their coordination sphere, thus resulting in thermodynamic stabilization as a whole. The mechanistic aspects of these reactions were also clarified by relating the obtained several findings. The complexes prepared from **2** are electron-rich and bear various ligands; therefore, versatile catalytic functions are expected to be derived from their individual characters. Further investigations are now focused on the development of novel catalytic reactions using these complexes.

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