Oxidative coupling reactions at ruthenium(0) and their applications to catalytic homo- and cross-dimerizations

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Graphical Abstract

Abstract

Aspects of the chemistry of zero-valent ruthenium complexes having a cyclic diene ligand, and their use for homo- and cross-dimerizations are reviewed. The naphthalene ligand in $[\text{Ru}(\eta^6\text{-naphthalene})(\eta^4\text{-1,5-COD})]$ is readily removed to generate a formal 12e species, “ $\text{Ru}(\eta^4\text{-1,5-COD})$ ”, having 6e coordination sites. These 6e coordination sites can be divided into 4e and 2e sites, and a conjugated compound and substituted alkene therefore selectively coordinate to them to satisfy the 18e rule. The zero-valent ruthenium center is highly Lewis basic and the oxidative coupling reaction readily occurs to form a ruthenacycle. The ruthenium(0) complexes catalyze homo- and cross-dimerizations by the oxidative coupling mechanism and some of the solid evidence in support of the mechanism is summarized. The coordination of substrates is prochiral-selective and when a chiral cyclic diene is incorporated in the catalyst, the first enantioselective cross-dimerizations are achieved.

1. Introduction: the homo- and cross-dimerizations using substituted alkenes by transition-metal complexes

Carbon-carbon bond formation is undoubtedly at the heart of organic chemistry and is indispensable for making a wide range of organic molecules. However, development of more efficient, straightforward process having higher atom- and step-economy is urgently needed. The catalytic dimerization using substituted alkenes is a promising candidate. For example, adipic acid is a world-wide commodity chemical that is used particularly for the use in Nylon-6,6 production and urethanes, the annual world production being more than 1.8 million tons [1]. The conventional process normally involves oxidation of cyclohexanone/cyclohexanol by nitric acid, which evolves a large amount of nitrous oxide, whose global warming potential is 310, *i.e.* 310 times higher than CO_2 per molecule [2]. In contrast, there would be no emission of greenhouse gases comes from the reaction itself if the product were formed by the tail-to-tail dimerization of acrylic acid or acrylates. This is one of the motivations behind this chemistry.

The dimerization of substituted alkenes is generally proposed to proceed by one of three different catalytic cycles, namely, the hydride insertion mechanism, the carbon-hydrogen bond activation mechanism and the oxidative coupling mechanism. We would like to start from the classifications of transition-metal catalyzed dimerizations between alkenes, and

between conjugated diene and alkenes, from the mechanistic point of view. Understanding of the mechanism would provide the basis and impetus of the catalysis, by which new reactions will be discovered and invented.

1.1. Hydride insertion mechanism

The first example is a hydride insertion mechanism, which starts from a hydride species to which a 1,2-insertion of an alkene occurs to give an alkyl complex and then a second alkene inserts into the resulting metal-carbon bond by a 2,1-insertion. Finally β -hydride elimination from the alkyl group releases the tail-to-tail dimer with recovery of the hydride complex (Scheme 1).

Scheme 1. Hydride insertion mechanism.

It is worth noting that the metal valency does not change throughout the catalytic cycle. This mechanism has been proposed for catalyses promoted by $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{PCy}_3)(\text{OEt}_2)][\text{BAR}^{\text{F}}_4]$ [3], $[\text{RhCp}^*(\text{C}_2\text{H}_4)_2]/\text{HBAR}^{\text{F}}_4(\text{Et}_2\text{O})_2$ [4], and $[\text{RuH}_2(\text{PPh}_3)_4]/\text{CF}_3\text{SO}_3\text{H}$ [5] for dimerization of methyl acrylate, and $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]/\text{H}_2$ [6] and $[\text{RuCl}_2(\text{DMSO})_4]/\text{EtCO}_2\text{Na}/\text{DMSO}/\text{carboxylic acid}$ [7] for dimerization of acrylonitrile. In support of this mechanism, alkyl complexes of Pd(II) [3], Rh(III) and Ir(III) [4] that mimic the proposed intermediates have been isolated. Probably this is the most well-established mechanism for dimerization of substituted alkenes.

Kondo, Ura and coworkers documented the catalysis of the cross-dimerization of *N*-vinyl acetamide with diethyl fumarate and with ethyl acrylate by a zero-valent ruthenium complex, $[\text{Ru}(\eta^6\text{-1,3,5-COT})(\eta^2\text{-dimethyl fumarate})_2]$, for which they proposed the hydride insertion mechanism because *N*-vinyl caprolactam did not react with the coordinated dimethyl fumarate in $[\text{Ru}(\eta^6\text{-1,3,5-COT})(\eta^2\text{-dimethyl fumarate})_2]$ [8].

The first examples of transition-metal catalyzed cross-dimerizations between conjugated diene and substituted alkenes appeared in a very brief report by Wittenberg [9]. The catalysts were brown solutions in hydrocarbons or ether formed by reducing cobalt compounds with metal alkyls in the presence of 1,3-dienes. For example, butadiene alone gave, as the main products, a mixture of 3-methyl-1,3,6-heptatriene and 1,3,6-octatriene; butadiene with ethylene gave 1,3-hexadiene and with acrylic esters produced 4,6-heptadienoic esters. Wilke and co-workers showed that $[\text{CoH}(\eta^4\text{-1,5-COD})_2]$, which is in tautomeric equilibrium with $[\text{Co}(\eta^1\text{:}\eta^2\text{-cyclooct-4-ene-1-yl})(\eta^4\text{-1,5-COD})]$, effectively catalyzed the reaction between butadiene and methyl acrylate to give methyl (2*E*,5*Z*)-hepta-2,5-dienoate and methyl (*E*)-hepta-4,6-dienoate [10]. Ziegler type catalysts such as $[\text{Fe}(\text{acac})_3]/\text{AlEt}_3$ [11] and $[\text{Co}(\text{acac})_3]/\text{AlEt}_3$ [12,13] are also effective for the cross-dimerization between conjugated dienes and alkenes. Although the detailed mechanism for these processes is not entirely clear, the hydride insertion mechanism is the most probable. Mitsudo and co-workers documented the cross-dimerization between butadienes and methyl acrylates by $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ to give methyl (3*E*, 5*Z*)-hepta-2,5-dienoate and methyl (2*E*, 5*Z*)-hepta-2,5-dienoate [14]. Although $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ is a zero-valent ruthenium complex, it readily gives a hydridoruthenium(II) species [15,16,17]. They also provided some evidence for a hydride insertion mechanism.

1.2. C–H bond activation mechanism

The second mechanism is the so-called C–H bond activation mechanism. By the oxidative addition of a C–H bond in a substituted alkene, an (alkenyl)(hydrido)metal species is produced, into the metal-hydride bond of which a second alkene inserts. Reductive elimination from the resulting alkyl produces the tail-to-tail dimer (Scheme 2).

Scheme 2. Carbon-hydrogen bond activation mechanism.

This mechanism generally requires low-valent metal species for the initial C–H bond activation step, and a few examples of alkene dimerization by this mechanism have been reported. This mechanism has been proposed for the catalytic dimerizations promoted by $\text{RuCl}_3/\text{Zn}/\text{MeOH}$ [18], $[\text{Cp}^*\text{Ni}(\mu\text{-CO})\text{MoCp}(\text{CO})_2]$ [19], $[\text{RuH}_2(\text{PPh}_3)_4]$ and $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ [20] in the case of methyl acrylate, by $[\text{Ru}(\eta^6\text{-benzene})(\eta^4\text{-1,5-COD})]$ [21] for acrolein, and by $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ [22] for acrylonitrile.

The cross-dimerizations between conjugated carbonyls and vinylsilanes catalyzed by $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ in refluxing toluene were reported by Trost [23] and Murai [24]. Because the catalyst and the substrates are exactly same as used for the Murai reaction [25], this reaction must proceed by the C–H bond activation mechanism. A mimic stoichiometric reaction for the C–H bond oxidative addition of butyl methacrylate to $[\text{RuH}_2(\text{PPh}_3)_4]$ has also been reported [26]. Recently, Darses documented the cross-dimerization between conjugated carbonyl compounds and vinylsilanes promoted by $[\text{RuCl}_2(p\text{-cymene})]_2$ [27]. This and related complexes are known to be effective catalysts for the C–H bond activation [28,29], and they also proposed the C–H bond activation mechanism.

To our knowledge, there is no report of a catalyzed cross-dimerization between conjugated dienes and alkenes that occurs by this mechanism.

1.3. Oxidative coupling mechanism

Before describing the third mechanism, we should mention an elementary reaction in organometallic chemistry. Many transition-metal complexes induce a coupling reaction of two coordinating alkenes to form a metallacyclopentane (Eq. (1)). This is widely referred to as an oxidative coupling reaction because the formal metal valency increases by 2 units in

this reaction [30]. In some cases this reaction is reversible and, consistent with the term oxidative coupling, the backward reaction is called reductive fragmentation.

The catalytic dimerization of substituted alkenes based on this elementary reaction is shown in Scheme 3, where two substituted alkenes coordinate to the metal center at the same time and the oxidative coupling reaction occurs to give a metallacyclopentane. The coupling product is released by subsequent β -hydride elimination and C–H reductive elimination.

Scheme 3. Oxidative coupling mechanism.

Although the coupling in this catalytic cycle is widely accepted as proceeding by an *oxidative coupling mechanism*, there are some arguments about the name. Some organic chemists prefer to call this mechanism *oxidative cyclization* or *reductive coupling* [31]. We believe that the term “oxidative coupling mechanism” is very reasonable because both mechanisms shown in Schemes 1 and 2 are named on the basis of the characteristic key elementary reaction in the catalytic cycles, and the term for the present key step is the oxidative coupling reaction (Eq. (1)). The term *reductive coupling* is based on the alkenes but the elementary reactions of metal complexes should be referred to the metal atom itself so as to maintain consistency with other terms in organometallic chemistry such as oxidative addition or reductive elimination.

Although this mechanism has been proposed for some coupling reactions between substituted alkenes, *e.g.* for dimerization of methyl acrylate by Pd(II) complexes such as $[\text{Pd}(\text{acac})_2]$ [32] and $[\text{Pd}(\text{acac})(\text{BIM})_2]\text{BF}_4$ [33], no direct supporting evidence has been reported. Ogoshi *et al.* also suggested a similar mechanism for cross-dimerizations of conjugated carbonyl compounds with alkenes catalyzed by $[\text{Ni}(\eta^4\text{-1,5-COD})_2]/\text{PCy}_3$ [34]. The complexes $[\text{CoBr}_2(\text{dppe})]$, $[\text{CoBr}_2(\text{dppb})]$ and $[\text{CoBr}_2(\text{SchmalzPos})]$ are reported to

catalyze the linear cross-dimerization between some conjugated dienes with mono-substituted alkenes in the presence of Zn/ZnI₂ [35]. Although the mechanism was not discussed, a concerted pathway such as oxidative coupling mechanism may also operate in this case. Linear cross-dimerization of conjugated diene with styrene was also achieved by in situ reduction of FeCl₂/iminopyridine with activated magnesium [36]. Kondo reported linear homo-dimerization of styrene and cross-dimerization between styrene and ethylene by [Ru(η⁶-1,3,5-COT)(η²-dimethyl fumarate)₂] in alcohol [37]. This complex also catalyzes selective trimerization of ethylene to isohexenes [38]. Ruthenium(II) complexes bearing a cyclopentadienyl or pentamethylcyclopentadienyl ligand, such as [RuCp(NCMe)₃][PF₆] and [RuCp*Cl(η⁴-1,5-COD)] catalyze the coupling reaction between conjugated dienes and electron rich alkenes through a putative Ru(IV) intermediate; this reaction is favored over the corresponding couplings with a wide variety of alkenes in which alkynes, allenes, and ketenes are the other partner [39]. Note that these Ru(II) complexes cannot catalyze the homo- and cross-dimerizations between alkenes. Mitsudo *et al* also reported cross-dimerization between alkynes and alkenes by [Ru(η⁴-1,5-COD)(η⁶-1,3,5-COT)]/pyridine [40]. These reactions are proposed to proceed by the oxidative coupling mechanism.

In contrast to these homo- and cross-dimerizations of substituted alkenes, there are many direct and indirect supporting evidence of oxidative coupling mechanism for oligomerization of conjugated dienes, which is extending back to the pioneering discovery by Wilke's group [41]. There are numerous examples of stoichiometric coupling of 1,3-diene units at a transition metal center [42,43,44,45,46,47,48]. Stoichiometric coupling of 1,3-dienes at ruthenium centers seems to be particularly favorable, both in low and high oxidation states. For example, heating the 1,3-cyclohexadiene complex [Ru(η⁴-1,3-C₆H₈)(CO)₃] with an excess 1,3-cyclohexadiene gave the coupled product, [Ru(η³:η³-C₆H₈C₆H₈)(CO)₂] [49]. Addition of CO to [Ru(η⁴-*cisoid*-2,3-dimethylbutadiene)₂(CO)] induced diene coupling to give the 2,3,6,7-tetramethyl-2,6-diene-1,8-diyl complexes [Ru(η³:η³-C₁₂H₂₀)(CO)₂] [50]. The analogous mono-substitution products [Ru(η³:η³-C₁₂H₂₀)(CO){P(OMe)₃}] and [Ru(η⁴-C₁₂H₂₀)(CO){P(OMe)₃}₂] were obtained when [Ru(η⁴-*cisoid*-2,3-dimethylbutadiene)₂(CO)] was heated with trimethylphosphite (Scheme 4) [51].

Scheme 4. Reaction of $[\text{Ru}(\eta^4\text{-1,3-dimethylbutadiene})_2(\text{CO})]$ with $\text{P}(\text{OMe})_3$.

Treatment of hydrated RuCl_3 with an excess of isoprene in refluxing ethanol gave the dimeric $\text{Ru}(\text{IV})$ complex, $[\text{Ru}(\eta^3\text{:}\eta^3\text{-2,7-dimethyl-2,6-octadiene-1,8-diyl})(\mu\text{-Cl})\text{Cl}]_2$ (Eq. (2)) [52,53].

In spite of these pioneering studies, the mechanism of dimerization of conjugated dienes at a transition metal center, and the factors that control the stereo- and regio-selectivity in the C–C bond-forming step, are still largely unknown.

1.4. Aspects of present review

This review focuses on aspects of our past and current studies on the chemistry of ruthenium(0) complexes having a cyclic diene ligand, and their use for homo- and cross-dimerizations of substituted alkenes. Although pioneering works in this field have been published, we have succeeded in isolating several intermediates and in using them as catalysts for homo- and cross-dimerizations, thus clearly supporting the oxidative coupling mechanism for the dimerizations. We have also extensively developed the first enantioselective dimerizations by the oxidative coupling mechanism.

The key compound used in this chemistry is $[\text{Ru}(\eta^6\text{-naphthalene})(\eta^4\text{-1,5-COD})]$ (**1a**), which was originally prepared by replacement of 1,3,5-COT in this compound by naphthalene under an atmosphere of H_2 [54]. Although **1a** was also prepared by the reduction of $[\text{RuCl}_2(\eta^4\text{-1,5-COD})]_n$ with lithium naphthalene, the product yield remained poor (10-20%) [55]. This is probably owing to the low solubility of $[\text{RuCl}_2(\eta^4\text{-1,5-COD})]_n$ in the reaction medium. The most reliable and convenient method for the preparation of **1a** on a multigram scale, developed by Bennett and coworkers, is the reduction of $[\text{Ru}(\text{acac})_2(\eta^4\text{-1,5-COD})]$ (**2a**) with sodium naphthalene [56].

Naphthalene is a 10π aromatic compound which coordinates as a 6π donor to the “ $\text{Ru}(\eta^4\text{-1,5-COD})$ ” moiety, thus satisfying the 18-electron rule. In this complex, the uncoordinated ring in the naphthalene ligand is thus forced to become a 4π ring, entailing a loss of the

aromaticity [57]. In order to recover the aromaticity, the naphthalene ligand can undergo a η^6 -to- η^4 -transformation and is thus more labile than a monocyclic arene (Eq. (3)). The transformation can be assisted by a weakly binding ligand such as acetonitrile [58].

Note that such slipping from an η^6 - to η^4 -naphthalene is similar to the so-called indenyl effect [59].

Once the naphthalene ligand is removed from the ruthenium center, a formal coordinatively unsaturated zero-valent ruthenium species is generated. Such species must have high Lewis basicity with 6-coordinate sites suitable for the oxidative coupling reactions of unsaturated compounds. Moreover, the η^4 -1,5-COD ligand in **1a** acts as a spectator ligand in most of the reactions. Therefore, similar cyclic chiral diene ligands can be expected to work as chiral scaffolds in certain reactions. This is visionary working-hypothesis of our study and we describe the details in this review.

2. Oxidative coupling reaction of conjugated carbonyls at ruthenium(0) and the application to linear dimerizations

2.1. Stoichiometric oxidative coupling reactions

Pertici and Bennett et al. originally reported the tail-to-tail dimerization of methyl acrylate catalyzed by $[\text{Ru}(\eta^6\text{-naphthalene})(\eta^4\text{-1,5-COD})]$ (**1a**) in the presence of acetonitrile under very harsh conditions (140 °C) [60]. Although they suggested several possibilities, they were unable to establish the mechanism conclusively. They also noted the presence of acetonitrile being indispensable for the formation of the tail-to-tail dimer in reasonable yield.

When we treated **1a** with a slight excess of methyl acrylate (4.2 equiv) in freshly distilled hexane at room temperature, an off-yellow solid immediately deposited from the solution. Recrystallization of the extremely air-sensitive powder from cold THF gave single crystals of a dinuclear ruthenacyclopentane **2** in 67% yield based on the Ru atom (Scheme 5) [61].

Scheme 5. Formation of ruthenacyclopentanes.

Fig. 1. Molecular structure of ruthenacyclopentane dimer 2.

The molecular structure of **2** is depicted in Fig. 1. The two methoxycarbonyl groups in each ruthenacyclopentane unit are located in a mutually *trans*-arrangement at the 2- and 5-positions. One of the CO₂Me groups is terminal to one Ru and the other CO₂Me bridges to the second Ru center, thus satisfying the 18-electron rule. The identification of a ruthenacyclopentane intermediate clearly shows that an oxidative coupling has taken place at the Ru(0). During the formation of **2**, dimethyl (*E*)-2-hexenedioate (**4**) was also produced in 88% yield.

Fig.3. Molecular structure of **7**.

By treatment of **1a** with MMA in the presence of PMe_3 at 50 °C in benzene, a new Ru(0) complex, $[\text{Ru}(\kappa^4\text{-cisoid-methyl methacrylate})(\eta^2\text{-cisoid-methyl methacrylate})(\text{PMe}_3)_2]$ (**8**) was formed in 32% yield (Fig.4). Although the ancillary 1,5-COD ligand is displaced by PMe_3 ligands, this is one of the pieces of evidence in support of κ^4 - and η^2 -coordination of MMA to the Ru(0) center.

Fig.4. Molecular structure of **8**.

2.2.Catalytic linear dimerizations

Because the dinuclear ruthenacyclopentane **2** is extremely air-sensitive, it was difficult to handle for the catalysis. When the isolated ruthenacyclopentane **3** was used as the catalyst, methyl acrylate was converted in 40 min at 140 °C into **4** in 52% yield (Eq. (5)).

Although the yield was not particularly high, this result provides the first solid evidence for the oxidative coupling mechanism for dimerization of substituted alkenes.

These results are consistent with the catalytic cycle shown in Scheme 6. In the first step, methyl acrylate initiates facile displacement of the naphthalene ligand in **1a**. The Lewis basic Ru(0) center can be expected to have a high affinity for electron-deficient methyl acrylate. In the resulting intermediate **A**, two methyl acrylate molecules preferentially coordinate by the same prostereogenic faces. This stereochemistry, which accounts for the *trans* configuration of **2** and **3**, is probably favored by steric repulsion between the two methoxycarbonyl groups. Then, the oxidative coupling reaction produces a ruthenacyclopentane intermediate **B**. After successive β -hydride elimination and reductive elimination, **4** is released. The isolated complexes **2** and **3** are probably present as resting states, which easily give intermediate **B**.

Scheme 6. Proposed catalytic cycle for dimerization of methyl acrylate by **1a**.

According to a textbook explanation [64], the hydrogen atoms at the β -carbon in a metallacyclopentane are held away from the metal center and so are not readily available for β -hydride elimination. This is probably one of the reasons why the present reaction needs such harsh conditions.

Though the tail-to-tail dimerization of methyl acrylate is documented in many papers, the reaction using MMA is generally difficult. Before our first publication [62], only a handful of examples had been reported for dimerization of MMA by transition metal-based catalysts, and their catalytic activities were generally low. For example, the dimerization of MMA is promoted by $[\text{Pd}(\text{NCMe})_4][\text{PF}_6]/\text{LiBF}_4$ at 25 °C for 3 days in 63% total yield [65], by $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(1,5\text{-COD})][\text{BF}_4]/\text{PR}_3$ in 12% yield at 80 °C [66], by in situ formed Ni(II) to give the dimer in 26% yield at room temperature for 20 h [67], and by $[\text{PdCl}_2(p\text{-nonylC}_6\text{H}_4\text{CN})_2]/\text{LiBF}_4$

to give the dimer in 50% conversion at 20-50 °C [68]. After our publication had appeared, some organocatalysts were also reported to be effective catalysts for dimerization of MMA [69,70].

Complex **1a** effectively catalyzed the tail-to-tail dimerization of MMA at 70 °C in 78% yield along with the trimers in 14% yield (Eq. (6)). However, the isolated complexes **7** and **8** were almost inactive toward the tail-to-tail dimerization of MMA.

3. Oxidative coupling reactions of conjugated dienes at ruthenium(0) and the application to linear dimerizations

3.1. Stoichiometric oxidative coupling reactions

On exposure of a benzene solution of **1a** to excess butadiene for 30 min at room temperature, a bis(η^3 -allylic)ruthenium(II) complex, *supine,prone*-[Ru(η^3 : η^3 -C₈H₁₂)(η^4 -1,5-COD)](**10**) was formed as the exclusive product; its molecular structure was revealed by X-ray structural analysis (Scheme 7 and Fig.5) [71,72].

Scheme 7. Reactions of naphthalene complex **1a** with conjugated dienes.

Fig. 5. Molecular structure of *supine, prone*-**10**.

Isoprene reacted similarly with **1a** to give *supine, prone*-**11**. Interestingly, treatment of **1a** with (*E*)-1,3-pentadiene gave the *anti-supine, syn-prone*-**12**, where one of the C=C bonds in (*E*)-

1,3-pentadiene must rotate during the reaction. Similarly, reaction of (*Z*)-1,3-pentadiene with **1a** produced *anti-supine,anti-prone-12*, suggesting that the original *E/Z*-stereochemistry must be retained for the *prone* allylic moiety. During the reaction of **1a** with butadiene, we observed a (*cisoid*- η^4 -diene)(*transoid*- η^2 -diene)ruthenium(0) intermediate **13** in toluene-*d*₈ at $-60\text{ }^\circ\text{C}$, which then underwent C–C coupling to give *supine,prone-10*.

Scheme 8. Observation of an intermediate **13**.

When (*E*)-1,3-pentadiene was used for this reaction, the corresponding intermediate **14** was shown to contain *Z/E* mixtures of *cisoid*- η^4 -1,3-pentadiene, the ratio being 60/40 ratio at $-60\text{ }^\circ\text{C}$ (Eq.(7)).

EXCY analysis of this mixture **14** at $-50\text{ }^\circ\text{C}$ revealed exclusive rotation of the C(3)=C(4) double bond, while the C(1)=C(2) double bond remained intact (Table 1).

Table 1.

Exchanging protons in (*Z*)-**14** and (*E*)-**14** by EXCY at $-50\text{ }^\circ\text{C}$

 (<i>Z</i>)- 14	$\rightleftharpoons$	 (<i>E</i>)- 14
<i>endo</i> -1-CH (δ -1.24, d)	$\longleftrightarrow$	<i>endo</i> -1-CH (δ 0.14, d)
<i>exo</i> -1-CH (δ 0.77, d)	$\longleftrightarrow$	<i>exo</i> -1-CH (δ 1.69, d)
<i>exo</i> -4-CH (δ 0.68, qui)	$\longleftrightarrow$	<i>endo</i> -4-CH (δ 0.46, qui)
<i>endo</i> -5-Me (δ 0.95, d)	$\longleftrightarrow$	<i>exo</i> -5-Me (δ 0.60, d)

All these observations are consistent with a process of oxidative coupling reaction between the *cisoid*- η^4 -diene and *transoid*- η^2 -diene at Ru(0) to give the *supine,prone*-bis(η^3 -allylic)ruthenium(II) complex. For 1,3-pentadiene, there is *E/Z* isomerization of the *cisoid*- η^4 -diene fragment, while the *transoid*- η^2 -diene does not isomerize, and only the *cisoid*-(*Z*)- η^4 -diene fragment can undergo the oxidative coupling reaction, probably for steric reasons.

3.2. Synthesis of conjugated diene complexes

Although the naphthalene complex **1a** rapidly reacts with conjugated dienes to give the bis(η^3 -allylic)ruthenium(II) complexes, η^4 -diene complexes of ruthenium(0) are formed in the presence of acetonitrile. A series of conjugated diene complexes of ruthenium(0) **15-20** are easily prepared in moderate to high yields by the reaction of the naphthalene complex **1a** with conjugated diene in the presence of acetonitrile at room temperature [73,74]. The crystallographic analysis clearly shows a *cisoid*- η^4 -coordination of the 1,3-diene ligand at ruthenium, which is approximately square pyramid with the nitrile ligand in the axial position (Eq.(8) and Fig. 6).

Fig. 6. The molecular structure of **16a**.

As for all 1,3-diene compounds, an ene-diyl extreme resonance contribution can be considered but the spectroscopic data indicate the diene extreme to be the dominant contributor, hence these compounds are best regarded as derivatives of zero-valent ruthenium(Eq.(9)) [75].

An interesting feature of the *cisoid*- η^4 -diene complex, (*Z*)-**18a** is the fluxionality of the (*Z*)-1,3-pentadiene fragment. While the 3-CH resonance remained a sharp triplet at room temperature in the ^1H NMR spectrum, all the other resonances due to the diene fragment broadened at room temperature. This feature can be explained by assuming that the 3-CH proton lies on a center of symmetry of the dynamic behavior. Based on EXCY analysis of *Z*-**18a**, this hydrogen shift arises from a [1,5]-sigmatropic rearrangement between the *endo*-1-methylene and the *endo*-5-methyl protons (Table 2). Similar behavior of the *cisoid*- η^4 -(*Z*)-1,3-pentadiene fragment has been reported for $[\text{RuCp}(\textit{cisoid}\text{-}\eta^4\text{-(Z)-1,3-pentadiene})(\text{CO})][\text{BF}_4]$ [76].

Table 2.

Exchanging protons in the (Z)-1,3-pentadiene ligand in (Z)-**18a** in acetonitrile-*d*₃ as observed by EXCY at -40 °C

The 3-CH proton is always observed as a sharp triplet at δ 4.68.

3.3. Stoichiometric reactions using conjugated diene complexes

When the butadiene complex **15a** was treated with a conjugated carbonyl compound, a series of new ruthenium(0) complexes containing a coupled dienylcarboxylate ligand was obtained (Scheme 9) [77,78]. These processes involve a C–C bond-forming step between 1,3-butadiene and conjugated carbonyl compound, and subsequent migration steps of the hydrogen atoms. A 1,2-disubstituted conjugated carbonyl can be used in this reaction to give **25a**. Vinyl acetate gave a thermally unstable coupling product **26**. This $\eta^1:\eta^3:\kappa^1$ -O-ruthenacycle can be regarded as the initial coupling product trapped by coordination of the carbonyl group so that further hydrogen migration is inhibited. This fact strongly suggests that cross-dimerization between conjugated dienes and substituted alkenes also takes place by the oxidative coupling mechanism.

Scheme 9. Reactions of butadiene complex **15a** with conjugated carbonyl compounds and vinyl acetate.

In order to understand the reaction mechanism, we have tried to prepare the butadiene- d_4 complex **15a- d_4** by the treatment of naphthalene complex **1a** with [1,1,4,4- d_4]-1,3-butadiene (>98 atom % D) in the presence of acetonitrile. Unexpectedly, however, the deuterium atoms in **15a- d_4** were found to be randomly distributed (50 atom % D) over eight sites, *i.e.*, four at the terminal carbon atoms of butadiene and four at the *endo*-methylene sites of 1,5-COD ligand, as shown in Scheme 10 [78].

Scheme 10. Reaction of **1a** with butadiene- d_4 .

A likely intermediate in this scrambling process is a 16-electron Ru(II) species $[\text{Ru}(\eta^3\text{-buteny})(\eta^5\text{-cyclooctadienyl})]$, which could be generated by reversible C–H bond cleavage

reaction of 1,5-COD. Treatment of **15a-d₄** with methyl acrylate gave **21a-d₄** (50 atom % D), where deuterium atoms are located exclusively at the 4- and 5-methine carbon (50 atom% D) and 7-methyl carbon (33 atom % D) positions in the methyl 2,4-heptadienoate fragment, in addition to *endo*-methylene sites in the 1,5-COD ligand (50 atom % D). This deuterium distribution can be accounted for as shown in Scheme 11. Methyl acrylate replaces the weakly bound acetonitrile ligand and then undergoes oxidative coupling to give **A**, which in turn undergoes successive β -hydrogen elimination and reductive elimination to give **B**. Then, C–H bond oxidative addition of the alkenyl proton at the 5-position forms **C**. Notably, no incorporation of deuterium occurred at the 6-position during the formation of **21a-d₄**, suggesting selective migration of a deuterium atom from the 4- to 5-position in the methyl heptadienoate fragment. This process may occur via the carbene intermediate **D**, although similar isomerizations from alkenyls to carbenes is generally achieved by protonation [79].

Scheme 11. Possible mechanism for the formation of **21a-d₄**. Deuterium atoms in the 1,5-COD ligand are omitted for clarity.

A series of diene complexes also readily reacted with conjugated carbonyl compounds to give the corresponding ruthenium(0) complexes having a coupled ligand (Scheme 12). When 2,3-dimethylbutadiene complex **16a** was used in this reaction, the original diene moiety remained as the conjugated diene fragment probably to give the most stable isomer at ruthenium(0). In the case of the isoprene complex, the conjugated carbonyl compounds reacts with the less hindered terminal carbon in isoprene to give **31a-33a**. However, when the 1,3-pentadiene complex was employed, the branched coupling products **34a-39a** dominated in all cases. Treatment of 2,5-dimethylhexa-1,3-diene with methyl acrylate exclusively produced the

branched product **40a**. A possible explanation for this regioselectivity, which is supported by DFT calculations, is that the entering alkene attacks the HOMO of the coordinating diene.

Scheme 12. Reactions of a series of diene complexes with conjugated carbonyls.

The conjugated diene complexes of ruthenium(0) also reacted with other conjugated dienes. The *cisoid*- η^4 -butadiene complex **15a** reacted with added butadiene at room temperature to give *supine,prone*-**10** in 95% yield (Scheme 13). Treatment of *cisoid*-(*E*)- η^4 -1,3-pentadiene complex **17a** with (*E*)-1,3-pentadiene gave *anti-supine,syn-prone*-**12** in high yield. This stereochemistry is consistent with the direct reaction of **1a** with (*E*)-1,3-pentadiene.

Scheme 13. Stoichiometric homo-dimerization between conjugated dienes at a Ru(0) center.

Similarly, the *cisoid*- η^4 -2,3-dimethylbutadiene complex **16a** reacted with a series of conjugated dienes to give the bis(η^3 -allyl)ruthenium(II) complexes **41-42** (Scheme 14). This experiment clearly shows that the *cisoid*- η^4 -2,3-dimethylbutadiene fragment is converted into the *supine*- η^3 -allyl fragment, and the added diene which must have the *transoid* structure as the stable conformer, is transformed to the *prone*- η^3 -allyl fragment in the product. The molecular structure of *supine, prone*-**41** is depicted in Fig. 7.

Scheme 14. Stoichiometric cross-dimerizations between conjugated dienes at a Ru(0) center.

Fig. 7. Molecular structure of *supine, prone-41*.

The catalyzed reactions of 1,3-dienes with 1,2-dienes (allenes) are also interesting from the synthetic point of view. Early examples involve formations of η^3 -allylic Pd(II) complexes from 1,2-dienes [80]. Ru(II) complexes having a Cp* or Cp ligand are particularly promising catalysts for transformations of 1,2-dienes. Examples include internal [2+2] cycloaddition, formation of alkylidenebicyclo[3.1.0]hexane by [2+2] addition with diazoalkane by [RuCp*Cl(η^4 -1,5-COD)] [81], pentacyclic compounds via successive [2+2] cyclizations by [RuCp*Cl(η^4 -1,5-COD)] [82], intermolecular coupling between 1,2-diene and alkynes by [RuCp*Cl(η^4 -1,5-COD)] or [RuCp*Cl(PPh₃)₂] [83], and the intermolecular coupling reaction between 1,2-dienes and enones to give 1,3-dienes by [RuCpCl(η^4 -1,5-COD)] [84]. In most of these reactions, ruthenacyclopentenes are postulated in the carbon-carbon bond forming step [85]. In addition, internal [4+3], [4+2] and [2+2] cycloadditions of allenyl-tethered 1,3-dienes have been reported to be catalyzed by Au(I) [86], Ni(0) [87], Pd(II) [88], Pt(II) [89], Rh(I) [87], Ru(IV) [90], and Os(IV) [91]. Although intermolecular coupling (Diels-Alder reaction) between 1,3-dienes and 1,2-dienes is known [92], the possible influence of transition metal complexes has not been explored.

Treatment of **15a** with ethyl buta-2,3-dienoate gave a bis(η^3 -allylic)ruthenium(II) complex, *supine,anti-prone*-**43** in 78% yield as a single diastereomer, whose molecular structure is depicted in Fig. 8 [93].

Scheme 15. Reactions of [Ru(η^4 -diene)(η^4 -1,5-COD)(NCMe)] with 1,2-dienes.

Fig. 8. Molecular structure of *supine, anti-prone-44*.

All 1,2-dienes employed form a new C–C bond through their central, electron-deficient carbon atom with the terminal carbon atom of the coordinated 1,3-diene, and the primary coupling products have the same stereochemistry regardless of the electronic properties of the reactants, as shown in Scheme 15. In the products, the η^3 -allylic fragments derived from 1,3-diene and 1,2-diene always adopt *supine*- and *prone*-conformations, respectively. This provides evidence for prior coordination of the 1,2-diene to Ru(0)[94]. Evidently, despite their high reactivity, 1,2-dienes cannot react with the coordinated 1,3-dienes directly from the *exo* side. Since we have selectively obtained a single diastereomer in this reaction, the regioselectivity and prostereogenic face selectivity of the 1,2-diene are carefully controlled by the Ru(0) center before the carbon-carbon bond formation. Among four potential coordination modes of the 1,2-diene, the Ru(0) favors the less sterically congested face of 1,2-dienes. The central carbon atom in 1,2-dienes is generally electron deficient and is susceptible to nucleophilic attack; in this case, the nucleophile is the coordinated 1,3-diene.

Ketenes comprise another group of reactive cumulenes. When diphenylketene was allowed to react with $[\text{Ru}(\eta^4\text{-1,3-diene})(\eta^4\text{-1,5-COD})(\text{NCMe})]$, zero-valent ruthenium dienylketone complexes are formed (Scheme 16 and Fig. 9) [95]. This is the first example for the formation of dienylketone by the coupling of 1,3-diene with ketene. Although $[\text{Ru}(\eta^4\text{-1,3-diene})(\eta^4\text{-1,5-COD})(\text{NCMe})]$ did react with CO_2 , isocyanates, and carbodiimides, very complicated mixtures were obtained.

Scheme 16. Reactions of $[\text{Ru}(\eta^4\text{-diene})(\eta^4\text{-1,5-diene})(\text{NCMe})]$ with diphenylketene.

Fig. 9. Molecular structure of **49a**.

3.4. Catalytic cross-dimerizations using conjugated diene complexes

The coupling reaction between different unsaturated compounds is known as cross-dimerization. Although some prefer to use the term *cross-coupling*, this term, in the context of transition metal catalysis, normally includes three steps: (i) oxidative addition of an organic halide, (ii) alkylation (or arylation) so called “transmetallation” to replace the halogen ligand to give the diorganometal species, and (iii) reductive elimination between the organic groups [96,97,98]. Because not all the reactions dealt with in the following section follow this protocol, we prefer to use the term *cross-dimerization*.

One of the problems for catalytic cross-dimerizations is how to avoid homo-dimerizations and further reactions of the products. A reasonable strategy to overcome this serious problem is to use substrates that differ widely in their properties. From this point of view, the most well-established cross-dimerizations are the reactions of conjugated dienes with (i) alkenes, such as the reactions between conjugated dienes with acrylates catalyzed by Co(diene) complex [9], $[\text{Co}(\eta^1:\eta^2\text{-cyclooct-4-ene-1-yl})(\eta^4\text{-1,5-COD})]$, [10], $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ [14], $[\text{Fe}(\text{acac})_3]/\text{AlEt}_3$ [11], and $[\text{PdCl}_2(\text{DMA})_2]/\text{AgBF}_4/\text{P}(\text{C}_8\text{H}_{17})_3$ [99], (ii) with non-conjugated dienes by $[\text{RhCl}_3\cdot\text{H}_2\text{O}]/\text{EtOH}$ [100], (iii) with vinyl acetate by $[\text{RuCp}^*\text{Cl}(\eta^5\text{-COD})]$ [101], (iv) with styrene by $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2/\text{BF}_3\cdot\text{PPh}_3$ [102], $[\text{CoBr}_2(\text{SchmalzPos})]/\text{ZnI}_2/\text{Zn}^*$ [103], and $\text{FeCl}_2/\text{iminopyridine}/\text{Mg}^*$ [35], (v) with vinyltrimethylsilane by $[\text{Ni}(\eta^2\text{-1,5-COD})]/\text{AlEt}_3/\text{PPh}(\text{OMe})_2$ [104,105]. In relation to this aspect, Davis and coworkers have reported the use of the cross-dimer between butadiene and methyl acrylate for production of methyl hepta-2,5-diene in one step to replace a conventional five-step process for production of the biologically active compound sperabillin [106].

A second strategy for successful cross-dimerization is to use a highly active alkene such as styrene or a vinylarene, as one of the coupling partners. Examples of this approach are the cross-dimerization of styrene with methyl acrylate by $[\text{PdCl}_2(\text{NCPh})_2]$ [107], that of styrene with vinyltrimethoxysilane or allylbenzene catalyzed by $[\text{YH}(\text{indenyl})_2]_2$ [108], and that between *N*-acetylarylamine and acrylate [109].

The cross-dimerizations of conjugated dienes with conjugated carbonyl compounds catalyzed by Ru(0)-diene complexes are shown in Scheme 17. The 2,3-dimethylbutadiene complex **16a** effectively catalyzed the formation of cross-dimers between 2,3-dimethylbutadiene and methyl acrylate, although the regioselectivity of the C=C bond was not very high. Catalytic reactions of 1,3-pentadiene also gave mainly the branched cross-dimer **53**, as expected on the basis of the stoichiometric reaction. This is consistent with the

stoichiometric reaction. Notably a natural terpene, myrcene, reacted with methyl acrylate quantitatively. Such transformations of myrcene are still limited [110,111].

Scheme 17. Catalytic cross-dimerizations between conjugated diene and methyl acrylate.

In contrast to the catalytic cross-dimerizations between 1,3-diene and alkenes, catalytic reactions between 1,3-dienes, between 1,3-dienes and 1,2-dienes, or between 1,3-dienes and ketenes were not observed, probably due to the high stability of the coupling product at Ru center.

4. Synthesis of and enantioselective cross-dimerizations by new ruthenium(0) complexes having a cyclic diene ligand

In all the reactions mentioned, the 1,5-COD in **1a** acted as an unchanged spectator ligand, apart from the scrambling between its *endo*-methylene protons and the terminal protons of the coordinated 1,3-diene. We expect that the reactivity of the naphthalene complex could be modified by replacing 1,5-COD by another cyclic diene. In particular, introduction of a chiral cyclic diene offers the possibility of enantioselective reactions. Over a decade ago, Hayashi and coworkers introduced a chiral cyclic diene ligand into transition metal mediated

asymmetric catalysis [112], and Carriera and coworkers also developed a very efficient synthesis of chiral diene ligands from a commercially natural product [113]. However, these catalysts are limited to conjugated additions or kinetic resolutions with use mainly of Group 9 metal catalysts, and Ru-catalyzed processes of this type are unknown.

4.1. Synthesis of new ruthenium(0) complexes having a cyclic diene ligand

As noted above, the best preparation method for the naphthalene complex **1a** is reduction of $[\text{Ru}(\text{acac})_2(\eta^4\text{-1,5-COD})]$ (**56a**) with 2 equiv of sodium naphthalene [56], and **56a** can easily be derived from $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ and 1,5-COD in two steps [114,115]. Although the preparation and limited spectroscopic data of a compound formulated as the norbornadiene analogue $[\text{Ru}(\eta^6\text{-naphthalene})(\eta^4\text{-norbornadiene})]$ (**1g**) were reported [55], this assignment appears to be incorrect. Bennett, Neumann and our group, have prepared **1g** from $[\text{Ru}(\text{acac})_2(\eta^4\text{-norbornadiene})]$ (**56g**) as a thermally unstable and air-sensitive yellow-brown solid in 23% yield [116]. Its instability is probably a consequence of steric strain arising from the narrow bite angle of norbornadiene (*ca.* 71 °) [117] relative to that of 1,5-COD (*ca.* 85 °) [118]. Because $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ has very poor reactivity with other cyclic diene ligands we have tried, a new preparation method of $[\text{Ru}(\text{acac})_2(\text{diene})]$ is needed. A breakthrough methodology to overcome this problem is to use $[\text{Ru}(\text{acac})_3]$ (**57**) as the starting material [119]. We have prepared a series of naphthalene complexes having cyclic diene or phosphine-alkene ligands **1b-j** (Scheme 18) [120,121].

Scheme 18. Synthesis of $\text{Ru}(\text{naphthalene})\text{L}$ complexes.

Fig. 10. Some naphthalene-diene complexes of ruthenium(0).

The molecular structures of **1a**, **1b**, **1c**, **1d** and **1f** were revealed, as determined by X-ray crystallography, were similar. In order to understand the electronic property of these cyclic diene ligands, some of these naphthalene complexes were converted into the corresponding monocarbonyl adduct (Fig. 11), whose CO stretching frequency reflects the π -back-bonding ability of the diene ligand.

Fig. 11. The stretching vibration of the carbonyl complexes of ruthenium(0) having a cyclic diene ligand.

The stretching vibration of the carbonyl group in **58f** (L = dibenzocyclooctatetraene) is shifted by about 20 cm⁻¹ to the higher frequency (1984 cm⁻¹) compared with those in **58a** (L = 1,5-COD) and **58b** (L = bicyclononadiene). This feature corresponds to reduction in the basicity of the Ru(0) center. Therefore, dibenzocyclooctatetraene can be regarded as the most electron-withdrawing ligand in the series.

The results of cross-dimerization of MMA with 2,5-dihydrofuran under Ru(0)-diene catalysis are listed in Table 3. The naphthalene complex **1a** catalyzed the cross-dimerization between MMA and 2,5-dihydrofuran to give *rac*-(2*S*)-3-[(3*R*)-2,3-dihydrofuran-3-yl]-2-methylpropionate (**59**), along with small amount of minor isomers (entry 1). The diastereoselectivity of **59** was at least 99%. This is the first diastereoselective cross-dimerization between substituted alkenes [122]. The bicyclononadiene complex **1b** was the most active catalyst among the catalysts used (entry 2).

Table 3.
Cross-dimerization between MMA and 2,5-dihydrofuran

entry	cat.	/mol%	temp /°C	time /h	Yield /% (59/60/E-61/Z-61)
1	1a	5	0	24	87 (92/6/2/0)
2	<i>rac</i> - 1b	1	0	4	85 (7/17/52/24)
3	<i>rac</i> - 1c	5	50	24	37 (3/3/90/6)
4	<i>rac</i> - 1d	5	50	24	2 (0/0/100/0)
5	<i>rac</i> - 1e	1	0	24	74 (79/18/2/1)
6	1f	5	50	24	18 (49/0/0/51)

As already discussed, the reaction probably proceeds by the oxidative coupling mechanism and the most important mechanistic information given by this reaction is control of the orientation and the prostereogenic face of the coordinating alkenes.

In contrast with its 2,5-isomer, 2,3-dihydrofuran did not react with MMA in the presence of **1a**; the only isolated product was the tail-to-tail dimers of MMA. The reaction of ethyl acrylate with 2,5-dihydrofuran catalyzed by **1a** (5 mol%) at 30 °C produced ethyl 3-(2,3-dihydrofuran-3-yl)propionate (**62**) in modest yield (24%) without any formation of the other cross-dimers. Although the yield is rather poor, the product is completely different from 2-(1-ethoxycarbonyl)ethylidenetetrahydrofuran (**63**), which is formed from cross-dimerization of ethyl acrylate and 2,5-dihydrofuran catalyzed by [Ru(η^4 -1,5-COD)(η^6 -1,3,5-COT)]/DMA (Scheme 19) [123]. On the basis of a labeling experiment, the authors of this pioneering study proposed a hydride-insertion mechanism. We suggest that these products arising from the use of different Ru(0)-based catalysts may be a consequence of the different mechanisms in operation.

Scheme 19. Reaction of ethyl acrylate with 2,5-dihydrofuran catalyzed by **1a** or [Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)].

The naphthalene complex **1a** also catalyzed the reaction between MMA and norbornene to give the *exo*-cross-dimers **64** and **65** (Table 4). Complex **1b** was, however, the most active catalyst for this reaction.

Table 4.
Cross-dimerization between MMA and norbornene

entry	cat.	temp		time	Yield
		/mol%	/°C		
				/h	% (<i>E</i> - 64 / <i>Z</i> - 64 / 65)
1	1a	5	30	5	83 (70/27/3)
2	<i>rac</i> - 1b	2	30	2	95 (97/2/1)
3	<i>rac</i> - 1c	5	50	24	56 (89/5/6)
4	<i>rac</i> - 1d	5	50	24	3 (44/45/11)
5	<i>rac</i> - 1e	5	30	2	90 (92/6/2)

These complexes also catalyzed the cross-dimerization between MMA and vinyl(trimethoxy)silane (Table 5).

Table 5.
Cross-dimerization between MMA and vinyl(trimethoxy)silane

entry	cat.	temp		time	Yield
		/mol%	/°C		
				/h	% (<i>E</i> - 66 / <i>Z</i> - 66 / 67)
1	1a	5	30	24	75 (15/37/48)
2	<i>rac</i> - 1b	2	30	4	91 (87/5/8)
3	<i>rac</i> - 1c	5	50	24	15 (48/45/7)
4	<i>rac</i> - 1d	5	50	24	3 (70/21/9)
5	<i>rac</i> - 1e	5	30	8	70 (50/25/25)

These Ru(0) catalysts were evaluated for the cross-dimerization of (*E*)-1,3-pentadiene with methyl acrylate (Table 6). Without exception, the branched cross-dimer **68** is the main product. In contrast to the cross-dimerization between methyl methacrylate and alkenes, the bicyclononadiene complex **1b** is not an effective catalyst for this reaction (entry 2). The dibenzocyclooctatetraene complex **1f** very effectively catalyzes the reaction (entries 6 and 7).

Table 6.

Cross-dimerization of (*E*)-1,3-pentadiene with methyl acrylate

entry	cat.	temp		time	yield
		/mol%	/°C		
				/h	/% (68/69)
1	1a	1	50	1	48 (84/16)
2	<i>rac</i> - 1b	5	70	2	27 (90/10)
3	<i>rac</i> - 1c	5	70	2	55 (84/16)
4	<i>rac</i> - 1d	5	70	8	56 (86/14)
5	<i>rac</i> - 1e	5	70	1	25 (85/15)
6	1f	1	50	1	99 (77/23)
7	1f	0.5	50	8	90 (77/23)
8	1h	1	50	4	6 (82/18)
9	1i	5	70	4	44 (87/13)
10	1j	1	50	4	83 (87/13)

Actually complex **1f** is also a very active catalyst for the cross-dimerization between various conjugated dienes with acrylates. As one of the typical examples, reaction of 3,4-dimethyl-2,4-hexadiene with methyl acrylate is depicted in Eq. 10.

As a summary of this section, the cross-dimerizations between conjugated carbonyl compounds and alkenes seem to be promoted by the catalyst bearing an electron donating cyclic diene ligand, and the reaction between conjugated dienes and alkenes would be promoted by the electron withdrawing cyclic diene ligand, although we do not have

conclusive evidence yet. This consequence is probably arising from electron rich and deficient nature of conjugated carbonyl compounds and conjugated dienes, respectively.

4.2. Enantioselective cross-dimerizations

One of the ultimate goals for the cross-dimerization is enantioselective reaction. To achieve enantioselective reactions in cross-dimerizations of substituted alkenes, we have three major hurdles to overcome (Scheme 14). The first one is the chemoselective (or substrate-selective) coordination of two different compounds to the catalyst. The second is prochiral selective coordination of the substrates. The third is that the rotation of two substrates must be fixed at the stage of oxidative coupling. Therefore, this process is required to control many issues and seems to be more difficult than asymmetric hydrogenations.

Scheme 14. Construction of a chiral center by oxidative coupling between substituted alkenes.

Because of these difficulties, enantioselective cross-dimerizations between substituted alkenes were unprecedented before our report. Although the related enantioselective hydrovinylation reaction has been documented as an extension of enantioselective allylation reactions, this reaction must use ethylene (ethene) as one of the coupling partners [124,125,126]. Therefore, our methodology is much more divergent than hydrovinylation.

We have prepared a series of chiral bicyclo[3.3.1]nona-2,6-diene derivatives from dimethyl malonate with formaldehyde followed by the kinetic resolution of the diketone intermediate. Because 2,6-dimethylbicyclononadiene having C_2 symmetry showed only low

catalytic activity, we newly prepared the C_1 -symmetric analogue, (*S,S*)-2-methylbicyclo[3.3.1]nona-2,6-diene (L3). The chiral bicyclo[2.2.2]octa-1,4-diene derivatives were easily prepared using a natural product, carvone. The 2-methylbicyclononadiene complex (*S,S*)-**1c** catalyzed the cross-dimerization between MMA and 2,5-dihydrofuran to give **61** in 74% yield with up to 80% ee (Eq.(11)).

The absolute configuration of **61** prepared by (*S,S*)-**1c** was found to be *R*. Similarly, the bicyclononadiene complex (*S,R,R*)-**1i** catalyzed the enantioselective cross-dimerizations between 3,4-dimethylhexa-2,4-diene and acrylate in moderate yields and enantiomeric excess (Eq. (12)).

The overall mechanism for the enantioselective cross-dimerization between MMA and 2,5-dihydrofuran catalyzed by (*S,S*)-**1c** is depicted in Scheme 15. The naphthalene ligand in (*S,S*)-**1c** is readily removed by MMA and 2,5-dihydrofuran to give **A**, where MMA and 2,5-dihydrofuran coordinate as 4e and 2e donors, respectively, to the 6e vacant site. This hapticity of the substrates is the key for chemoselectivity in the present reaction. The prostereogenic face selectivity of MMA is one of the key factors for the enantioselectivity. DFT calculations suggest that MMA favors coordination by the *si*-face to the Ru[(*S,S*)-2-methylbicyclo[3.3.1]nona-2,6-diene] fragment (F1 in Fig. 12).

Scheme 15. Enantioselective cross-dimerization between MMA and 2,5-dihydrofuran.

Fig. 12. Relative stabilities of conformers among $[\text{Ru}(\kappa^4\text{-MMA})(\eta^4\text{-2-methylbicyclononadiene})\text{L}]$ ($\text{L} = \text{MeCN}$).

2,5-Dihydrofuran is not a prochiral alkene but it has two stable rotamers, *anti*-**F1** and *eclipsed*-**F1**, and each rotamer will give different enantiomers of the final product as shown in Scheme 16.

Scheme 16. Absolute configurations of product **61** from the possible intermediates.

The *anti*rotamer is 7.8 kJ mol⁻¹ more stable than the *eclipsed* one probably due to the steric repulsion between the 2,5-dihydrofuran and the bicyclononadiene ligand. If we postulate the reaction to proceed from the stable intermediate *anti*-F1 followed by the oxidative coupling reaction and subsequent β -hydride elimination from the *axial* methylene proton/reductive elimination, (R)-(E)-**61** would be produced, which is consistent with the experimental result.

5. Conclusion and outlook

Many transition-metal complexes are known to catalyze the formation of C–C bonds by oxidative coupling. However, the work in the field of Ru(0) catalysts described herein is just beginning of much more to come. Although homo-dimerization of substituted alkenes is well investigated, the finding of evidence for the oxidative coupling mechanism in a stoichiometric organometallic reaction is a breakthrough. We have isolated a ruthenacyclopentane as an active key intermediate in the catalytic dimerization of methyl acrylate. This was the starting point of present work and these mechanistic studies opened a further stage of the cross-dimerization. In fact, an ultimate goal of this chemistry is undoubtedly the enantioselective cross-dimerization and we have developed the first of these reactions between conjugated alkene and substituted alkene, and between conjugated diene and substituted alkenes. These enantioselective cross-dimerizations provide a more powerful method with high atom- and step-economy.

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Abbreviations: COD = cyclooctadiene, COT = cyclooctatriene, MMA = methyl methacrylate, DMA = *N,N*-dimethylacrylamide, dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,4-bis(diphenylphosphino)butane, SchmalzPos = $\text{PPh}_2[\text{C}_6\text{H}_3(3\text{-Ph})\{2\text{-O}(\text{PC}_{31}\text{H}_{28}\text{O}_4)\}]$

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