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In Situ Routes to Catalytically Active Ru(0) Species by Reduction of Readily Available, Air-Stable Precursors

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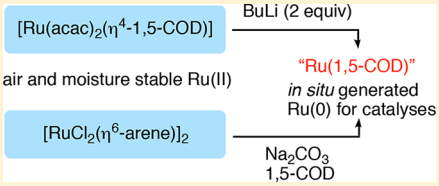
Supporting Information

ABSTRACT: Cross-dimerization of a conjugated diene with a substituted alkene catalyzed by in situ reduction of an air-stable Ru(II) catalyst precursor has been achieved. Reaction of 2,3-dimethylbutadiene with styrene is catalyzed by [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) (5 mol %) with BuLi (10 mol %) at 50 °C for 6 h in hexane, giving the cross-dimers in 99% yield ((*E*)-4,5-dimethyl-1-phenylhexa-1,4-diene (**3a**)/(*E*)-4,5-dimethyl-1-phenylhexa-2,4-diene (**3b**)/isomers = 84/9/7). Because neither **2a** nor BuLi separately catalyzes the cross-dimerization and reduction of **2a** with BuLi in the presence of naphthalene produces [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**), the active species in this catalysis is considered to be a Ru(0) compound. Interestingly, this in situ reduction method of Ru(II) using BuLi can be applied to the cross-dimerization using an ester such as methyl acrylate. Alternatively, an air-stable Ru(II) complex having a labile arene ligand such as [RuCl$_2$(η^6-anisole)]$_2$ (**5c**) (5 mol %) with Na$_2$CO$_3$ (40 mol %) in the presence of 1,5-COD (20 mol %) at 100 °C for 6 h in 2-butanol also catalyzes the same cross-dimerization in 62% yield. These protocols provide facile methods for production of unsaturated linear compounds by the cross-dimerization using air-stable Ru(II) catalyst precursors.



INTRODUCTION

Catalytic cross-dimerization between conjugated dienes and substituted alkenes is a reliable and promising method for production of linear organic molecules with high atom and step economy. Following the first brief report by Wittenberg of Co-catalyzed cross-dimerizations of dienes,[1] various catalytic systems based on transition metal compounds from groups 10 to 8 have been reported (Table 1).[2−15] We have documented regio- and enantioselective cross-dimerizations between conjugated dienes and substituted alkenes catalyzed by [Ru(η^6-naphthalene)(η^4-cyclic diene)] (**1**),[16] where the cyclic diene ligand acts as an important ancillary ligand for the activity and selectivity. Typical examples are the cross-dimerization of 1,3-dienes with acrylates,[17] the tail-to-tail dimerization of acrylates,[18] and the chemo- and stereoselective cross-dimerization of methyl methacrylate or methacrylamide with unsaturated five-membered-ring compounds.[19]

Table 1. Selected Groups 10 to 8 Catalyst Systems for Cross-Dimerization using Conjugated Dienes/Related Compounds

catalyst system	ref
[Ni(η^4-1,5-COD)$_2$]/AlEt$_3$/PPh(OMe)$_2$	2
[PdCl$_2$(DMA)$_2$]/AgBF$_4$/P(C$_8$H$_{17}$)$_3$	3
[PdCl(η^3-C$_3$H$_5$)]$_2$/BF$_3$·PPh$_3$	4
[Co(η^1:η^2-cyclooct-4-en-1-yl)(η^4-1,5-COD)]	5
[CoBr$_2$(SchmalzPhos)]/ZnI$_2$/activated Zn	6, 7
[CoBr$_2$(diphosphine)]/NaBARF/Zn	8
RhCl$_3$·H$_2$O/EtOH	9
[Fe(acac)$_3$]/AlEt$_3$	10
[Ru(η^4-1,5-COD)(η^6-1,3,5-COT)]	11
[RuCp*Cl(η^4-1,5-COD)]	12
FeCl$_2$/iminopyridine/activated Mg	13
RuCl$_3$·3H$_2$O/Zn-Cu/EtOH/CO	14
[RuCl$_2$(η^6-*p*-cymene)]$_2$/HCO$_2$Na/PCyPh$_2$	15

The detailed mechanism of operation of this catalytic system has been established by isolation/observation of the intermediates, kinetic studies, and DFT calculations.[20] These reactions are initiated by displacement of the labile η^6-naphthalene ligand to generate a formal "Ru(cyclic diene)" (**A**) with a 6e vacant site, to which a η^4-conjugated compound (4π) and η^2-unsaturated compound (2π) selectively coordinate, and the subsequent C−C coupling proceeds by an oxidative coupling mechanism. Scheme 1 outlines the mechanism for the cross-dimerization catalyzed by [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**).

Although this is a potentially useful catalytic system for the cross-dimerization, one must first prepare the thermally unstable and air-sensitive naphthalene complex **1a**. For the practical use of this catalysis, it would be desirable to generate in situ catalytically active Ru(0) species **A** by reduction of readily available, air-stable precursors such as [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) and [RuCl$_2$(η^6-arene)]$_2$ (**5**) (Scheme 1). In this paper, we report two different methods for the facile

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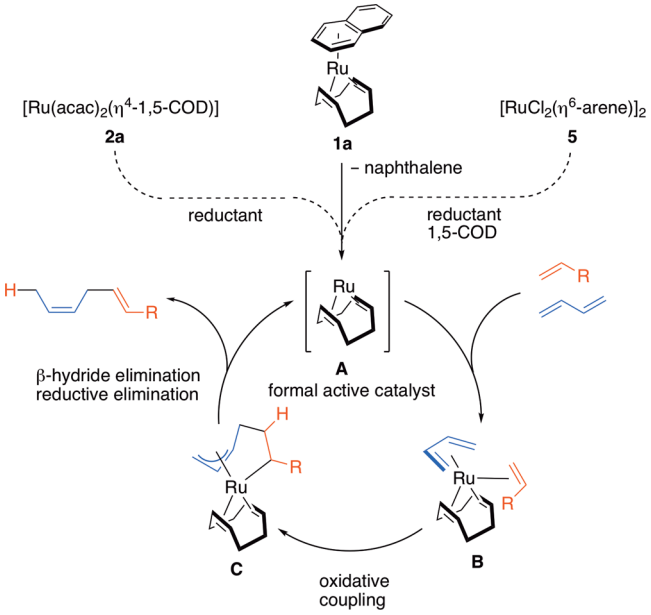
Scheme 1. Outline of Catalytic Linear Cross-Dimerization of Diene with Alkene



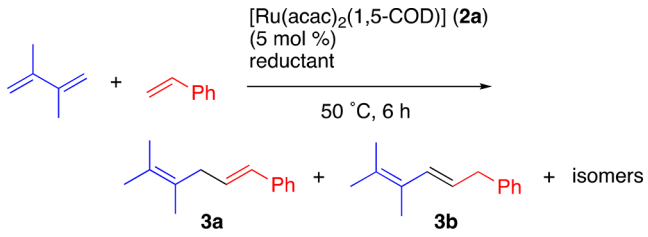
generation of the "Ru(1,5-COD)" and related "Ru(cyclic diene)" species by in situ reduction of ruthenium(II) compounds.

RESULTS AND DISCUSSION

In Situ Reduction of [Ru(acac)$_2$(η^4-1,5-COD)] (2a) as the Catalyst Precursor. A series of [Ru(acac)$_2$(η^4-cyclic diene)] (**2**) complexes is readily prepared by treatment of [Ru(acac)$_3$] with cyclic dienes in the presence of Zn in wet THF.[21] We focused on the air- and moisture-stable compound [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) as a catalyst precursor for the present cross-dimerization. We employed the cross-dimerization of 2,3-dimethylbutadiene with styrene as a model reaction, because this reaction is catalyzed by the Ru(0) complex [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**) and the reaction mechanism is well-established.[20a] Table 2 illustrates the results of screening of several reductants for **2a**. In this catalysis, the major and primary minor products were (*E*)-**3a** and (*E*)-**3b**, respectively. We also detected several minor isomers having the same molecular weight as **3** by GC/GC-MS analyses, but their detailed structures are still unclear. The divalent Ru complex **2a** precursor alone showed no catalytic activity (entry 1).

A reductant was therefore required to generate a Ru(0) species, but Mg metal did not work at all (Table 2, entry 2). More active metal powders, prepared by a reduction of the corresponding anhydrous metal chloride with an alkali metal such as K, Na, and Li, are known as Rieke metals.[22] However, both Rieke Mg (Mg*) and Rieke Zn (Zn*) were very inefficient (entries 3 and 4). Sodium/naphthalene and lithium/naphthalene yielded the cross-dimers in moderate yields (entries 5 and 6). Among the hydride reagents screened, $LiAlH_4$ gave the desired cross-dimers in promising yield (entry 8), although $NaBH_4$ was almost ineffective (entry 7). Alkylmetal reagents such as MeLi and BuLi furnished the cross-dimers in good yields (entries 12 and 13). We focused on BuLi, as a mild reductant with low nucleophilicity, for reduction of **2a**.

Table 2. Screening of Reductants for [Ru(acac)$_2$(η^4-1,5-COD)] (2a)[a]



	reductant		cross-dimers	
entry		amt (mol %)	yield (%)	**3a**/**3b**/isomers
1	none		0	
2	Mg	10	0	
3[b]	Mg*	10	21	80/10/10
4[c]	Zn*	10	1	100/0/0
5[d]	Na/naphthalene	10	57	72/14/14
6[d]	Li/naphthalene	10	32	78/13/9
7	$NaBH_4$	10	1	100/0/0
8	$LiAlH_4$	10	76	72/11/17
9	NaH	64	46	67/20/13
10	MeMgBr	10	26	81/11/8
11[e]	Et_2Zn	10	0	
12	MeLi	10	75	74/11/15
13	BuLi	10	73	82/8/10
14[f]	BuLi	4	14	86/14/0
15[g]	BuLi	10	13	85/15/0
16[h]	BuLi	10	0	

[a]Typical conditions: **2a** (0.05 mmol), 2,3-dimethylbutadiene (1.0 mmol), styrene (1.0 mmol), hexane (1.5 mL), 50 °C, 6 h. Yields and ratios of the cross-dimers were determined by GLC analysis. [b]Rieke Mg. [c]Rieke Zn. [d]Metal/naphthalene was prepared in another vessel and was transferred into the catalytic system by a cannula tube. [e][2,3-dimethylbutadiene]/[styrene] = 2/1. [f]**2a** (2 mol %). [g]Temperature 30 °C. [h]In the absence of **2a**.

The optimized conditions for the cross-dimerization of 2,3-dimethylbutadiene with styrene catalyzed by **2a** (5 mol %) and BuLi were established; the results are given in Table 3. The optimal BuLi/**2a** ratio was found to be 2/1, which gave cross-dimers in 87% yield. The yield was reduced slightly, to 81%, by use of a BuLi/**2a** ratio of 4/1, but use of a large excess of BuLi (8 equiv) stopped the reaction completely (entry 4), probably because of competing anionic polymerization of 2,3-dimethylbutadiene and/or styrene. Finally, a slight excess of 2,3-dimethylbutadiene over styrene, with 10 mol % BuLi, furnished the cross-dimers almost quantitatively (entry 9).

Because the yield and distribution of the products by this catalysis (Table 3, entry 7) are similar to those observed in the Ru(0)-catalyzed reaction (entry 9), the **2a**/BuLi system is likely to act by the same mechanism as **1a**.

The GLC analysis for reduction of **2a** with 2 equiv of BuLi in hexane showed evolution of butane (17.6%), 1-butene (5.0%), (*E*)-2-butene (1.8%), and octane (6.9%), and (*Z*)-2-butene was not observed. This observation supports formation of a Ru(0) species by the in situ reduction. Although the present data suggest that this system reduces a limited amount of Ru(II) species, further addition of BuLi does not improve the catalysis (Table 3). In another effort to obtain evidence for generation of a Ru(0) species by this in situ reduction, we performed the stoichiometric reaction of **2a** with 2 equiv of BuLi in the presence of naphthalene. The Ru(0) complex [Ru(η^6-

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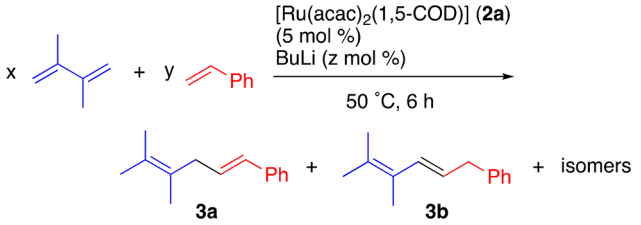
Table 3. Optimizations for Reaction of 2,3-Dimethylbutadiene with Styrene[a]

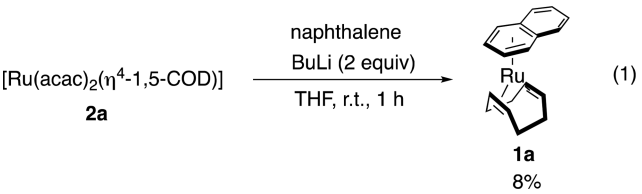


3a 3b

	amt (mol %)		cross-dimers	
entry	*x*/*y*	*z*	yield (%)	**3a**/**3b**/isomers
1	2/1	5	80	84/9/7
2	2/1	10	87	83/10/7
3	2/1	20	81	80/9/11
4	2/1	40	0	
5	1/3	10	81	62/31/7
6	1/2	10	82	65/26/9
7	1/1	10	73	82/8/10
8	3/1	10	99	84/9/7
9[b]	1.2/1	0	84	79/13/8

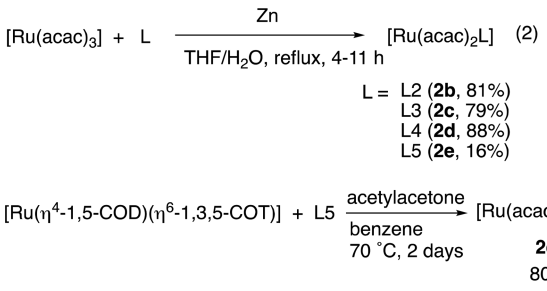
[a]Conditions unless specified otherwise: **2a** (0.05 mmol), 2,3-dimethylbutadiene (1.04−2.99 mmol), styrene (1.04−2.96 mmol), in BuLi (0.049−0.396 mmol), hexane (1.5 mL), temperature 50 °C, time 6 h. Yields and product ratios were determined by GLC analysis. [b]Conditions: **1a** (0.03 mmol), 2,3-dimethylbutadiene (1.77 mmol), styrene (1.48 mmol), temperature 50 °C, time 5 h.

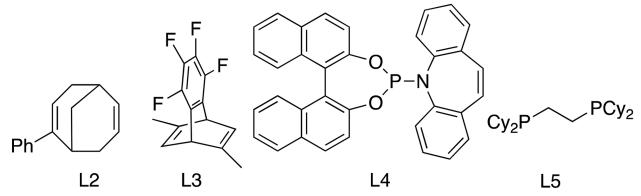
naphthalene)(η^4-1,5-COD)] (**1a**) was certainly produced, although it was obtained in only 8% yield (eq 1) and the



other products were not well characterized. We know little about the course of reaction. However, **2a** was almost completely consumed and very broad resonances were observed in the aliphatic region in the ^{1}H NMR spectrum. It appears that a ruthenium(0) species was formed under the reaction conditions, among other unidentified products.

Synthesis of and Cross-Dimerization by [Ru(acac)$_2$L] (2) as the Catalyst Precursor. With the optimized conditions for reduction of **2a** in hand, we explored the scope of the catalyst [Ru(acac)$_2$L] (**2**) (5 mol %) in the presence of BuLi (10 mol %). A series of new [Ru(acac)$_2$L] complexes (L = 2-phenylbicyclo[3.3.1]nona-2,6-diene (L2), 2,5-dimethyl-7,8-(tetrafluorobenzo)bicyclo[2.2.2]octatriene (L3), (3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)-iminostilbene (L4)) was prepared from [Ru(acac)$_3$] according to our previous method (eq 2).[21] Oligomeric complexes [Ru(acac)$_2$(μ_2,κ^1*P*-L)$_2$]$_n$ are formed initially in the case of L = dppe, dppp under these conditions, and heating to 140 °C is required to convert them into monomeric *cis*-[Ru(acac)$_2$L].[21b,23] However, [Ru(acac)$_3$] in the presence of Zn reacted with dcype in refluxing THF to give *cis*-[Ru(acac)$_2$(dcype)] (**2e**) directly, although in only moderate yield (16%). More efficient access to **2e** (80% yield) was





L2 L3 L4 L5

provided by the treatment of [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] with dcype and acetylacetone at 70 °C (eq 3).

Single crystals suitable for X-ray analysis were obtained by recrystallization from acetone/hexane for **2b** and from THF/hexane for **2c**,**d**, respectively (Figure 1). Although complexes **2** bearing an unsymmetrical bidentate ligand potentially produce a diastereomeric mixture arising from the Δ and Λ forms of the two chelating acac ligands, the single crystals of **2b**−**d** were obtained as single diastereomers of *rac*-Λ-**2b**, *rac*-Δ-**2c**, and *rac*-Δ-**2d**. Knowing the X-ray structures, we could determine the diastereomer ratios of the original samples of **2b**−**d** from the NMR data to be *rac*-Δ-**2b**/*rac*-Λ-**2b** = 62/38, *rac*-Δ-**2c**/*rac*-Λ-**2c** = 85/15, and *rac*-Δ-(*S*)-**2d**/*rac*-Λ-(*S*)-**2d** = 79/21, respectively.

Under the optimized conditions, cross-dimerization between 2,3-dimethylbutadiene and styrene was catalyzed by the in situ reduction of **2**/BuLi (Table 4), the process being most efficient for **2a**. The cross-dimerization was also catalyzed by **2b**/BuLi and **2c**/BuLi in moderate yields (entries 2 and 3), but the product yield was much lower in the case of **2d**/BuLi (entry 4), while the system [Ru(acac)$_2$(dcype)] (**2e**) gave no cross-dimer at all. Note that although [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**)[24] is readily obtained by treatment of [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) with 2 equiv of sodium naphthalene,[24a] all attempts to prepare the corresponding [Ru(η^6-naphthalene)L] complexes from **2b** (L = 2-phenylbicyclo[3.3.1]nona-2,6-diene (L2)), **2c** (L = 2,5-dimethyl-7,8-(tetrafluorobenzo)-bicyclo[2.2.2]octatriene (L3)), and **2d** (L = (3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)-iminostilbenzene (L4)) failed even at low temperature; thus, their catalytic behavior could not be examined.

No cross-dimers were obtained when BuLi was added to a mixture of 2,3-dimethylbutadiene and methyl acrylate in hexane containing the catalyst precursor **2a** (Table 5, entry 1), probably owing to the undesirable competing reaction of BuLi with methyl acrylate. However, when 2,3-dimethylbutadiene and methyl acrylate were added after pretreatment of **2a** (5 mol %) with BuLi (10 mol %) for 1 h at room temperature, the result was more promising, the cross-dimers being obtained in 35% yield (entry 2). In THF, under the same conditions with the pretreatment, the cross-dimers were obtained almost quantitatively (entry 4).

The results obtained with a range of catalyst precursors under optimized conditions are shown in Table 6. In this

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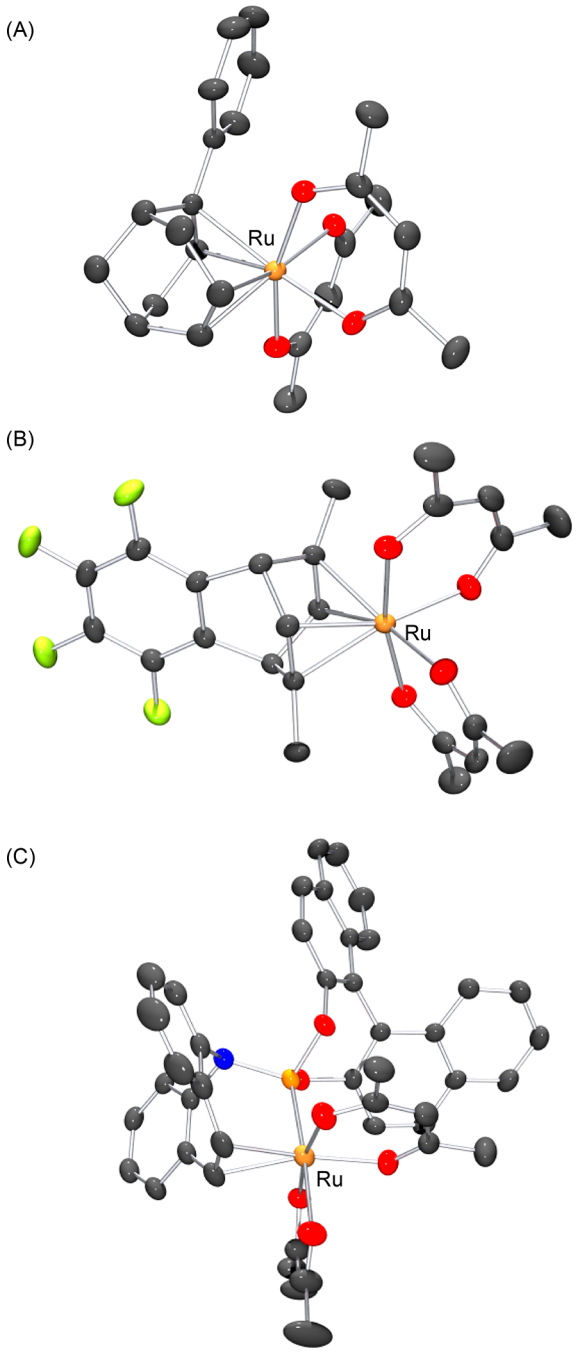
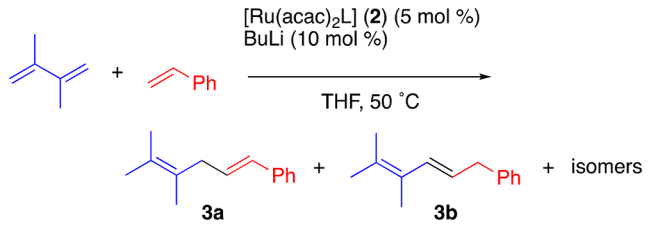


Figure 1. Molecular structures determined by single-crystal X-ray diffraction for Λ-**2b** (A), Δ-**2c** (B), and Δ-**2d** (C). All hydrogen atoms and incorporated molecules are omitted for clarity. Ellipsoids represent 50% probability.

reaction, the major product was (*E*)-**4a** along with (*Z*)-**4a** and **4b** as the prime minor products. The GC/GC-MS analyses also suggested formation of isomers having the same molecular weight as **4**, but their detailed structures are unknown. When a slight excess of methyl acrylate was used, the reaction occurred in excellent yield (entry 1), but an increase in the amount of 2,3-dimethylbutadiene decreased the product yield (entry 2). As in the 2,3-dimethylbutadiene/styrene cross-dimerization, complex **2a** showed the highest activity of these precursors.

Synthesis of and Cross-Dimerization by [Ru(η^6-arene)(η^4-1,5-COD)] (1). We examined initially the catalytic ability of

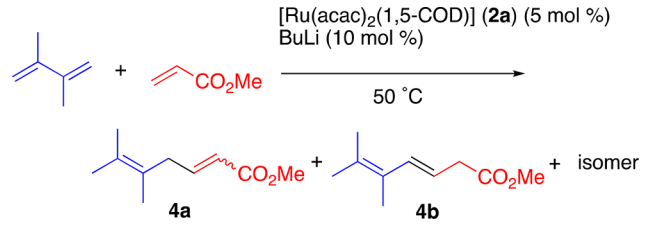
Table 4. Cross-Dimerization of 2,3-Dimethylbutadiene with Styrene Catalyzed by [Ru(acac)$_2$L]/BuLi[a]



			cross-dimers	
entry	catalyst precursor	time (h)	yield (%)	**3a**/**3b**/isomers
1	**2a**	6	99	84/9/7
2	**2b**	2	77	73/13/14
3	**2c**	2	66	74/14/12
4	**2d**	15	22	73/9/18
5	**2e**	6	0	

[a]Conditions: **2a**–**e** (0.0398–0.0500 mmol), BuLi (0.10 mmol), 2,3-dimethylbutadiene (1.49–2.11 mmol), styrene (1.00–1.04 mmol), THF (1.5 mL).

Table 5. Cross-Dimerization of 2,3-Dimethylbutadiene with Methyl Acrylate Catalyzed by [Ru(acac)$_2$(1,5-COD)] (2a)/BuLi[a]



				cross-dimers	
entry	solvent	pretreatment (h)	time (h)	yield (%)	*E*-**4a**/*Z*-**4a**/**4b**/isomers
1	hexane	0	6	0	
2[b]	hexane	1	6	35	74/20/6/0
3	THF	0	6	65	67/9/22/2
4[b]	THF	1	4	97	69/8/21/2
5[b]	toluene	1	10	41	68/17/12/3
6[b]	benzene	1	10	57	75/14/9/2

[a]Conditions: **2a** (0.0498–0.0506 mmol), BuLi (0.093–0.10 mmol), 2,3-dimethylbutadiene (1.05 mmol), methyl acrylate (1.56 mmol), temperature 50 °C. Yields and product ratios were determined by GLC analysis. [b]The substrates were added after pretreatment of **2a** with BuLi for 1 h at room temperature.

a series of [Ru(η^6-arene)(η^4-1,5-COD)] complexes, analogous to the naphthalene compound, which, if the arene is sufficiently labile, are potential precursors to a coordinatively unsaturated "Ru(η^4-1,5-COD)" species.[24] If the [RuCl$_2$(η^6-arene)]$_2$ complex is readily available starting from RuCl$_3$, it can be converted into [Ru(η^6-arene)(η^4-1,5-COD)] by treatment with 1,5-COD in 2-propanol or ethanol in the presence of anhydrous Na$_2$CO$_3$. This procedure has been used for the C$_6$Me$_6$,[25,26] *p*-cymene,[27,28] and benzene[28] complexes. More versatile procedures employ labile ruthenium(0) systems as starting materials: e.g. [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] with an arene in the presence of hydrogen[29] or [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**) with an arene in the presence of acetonitrile.[24] We used the second method to make the complexes of benzene (**1b**), anisole (**1c**), dimethylaniline (**1d**), acetophenone (**1e**)

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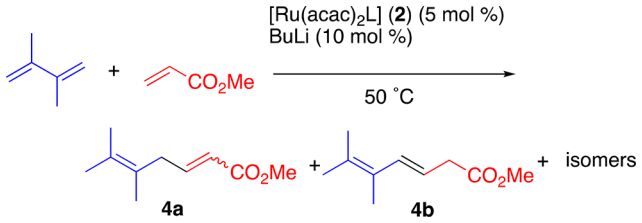
Table 6. Cross-Dimerization of 2,3-Dimethylbutadiene with Methyl Acrylate Catalyzed by [Ru(acac)$_2$(L)] (2)/BuLi in THF[a]

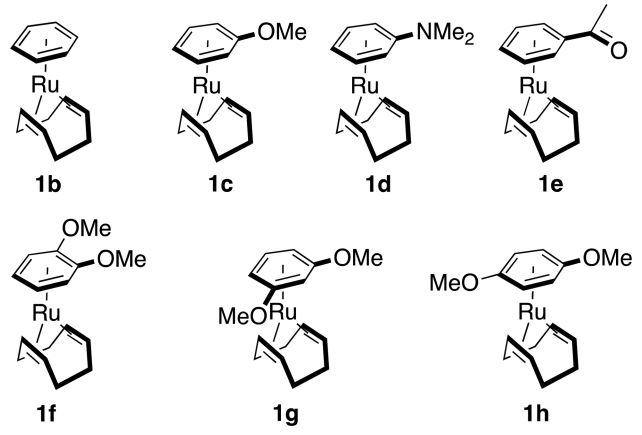


entry	catalyst precursor	time (h)	cross-dimers yield (%)	*E*-**4a**/*Z*-**4a**/**4b**/isomers
1[b]	**2a**	4	97	69/8/21/2
2	**2a**	4	63	81/3/14/2
3	**2b**	6	10	90/0/10/0
4	**2c**	3	46	78/4/18/0
5	**2d**	4	49	74/18/8/0

[a]Conditions: **2** (0.0487−0.0506 mmol), BuLi (0.10 mmol), pretreatment 1 h at room temperature, 2,3-dimethylbutadiene (2.02−2.11 mmol), methyl acrylate (1.00 mmol), temperature 50 °C.Yields and product ratios were determined by GLC. [b]2,3-Dimethylbutadiene (1.05 mmol) and methyl acrylate (1.56 mmol) were used for the catalysis.

and 1,2-, 1,3-, and 1,4-dimethoxybenzene (**1f−h**, respectively); complexes **1b,c** had already been made by the first method (Chart 1).[29] They were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis and by X-ray analyses for **1d,g,h**.

Chart 1



The molecular structures of **1d,g,h** determined by X-ray analysis are depicted in Figure 2, and the Ru−C(arene) distances are given in Table 7. In the reported structure of **1b**, the Ru−C(arene) distances fall in the range 2.199(7)−2.261(7) Å.[30] Similar Ru−C(arene) distances to the unsaturated carbon atoms are observed in **1d,g,h**, but some of the Ru−C(ipso) distances in **1g,h** are slightly above this range (Ru−C(3) in **1g** 2.304(6) Å; Ru−C(4) in **1h** 2.310(4) Å), while in **1d** the Ru−C(1) distance of 2.385(3) Å to the ipso carbon atom bearing the strongly electron-donating substituent NMe_2 is well above the range.

The catalytic activities of [Ru(η^6-arene)(η^4-1,5-COD)] (**1**) for cross-dimerization between 2,3-dimethylbutadiene with methyl acrylate were tested; the results are shown in Table 8.

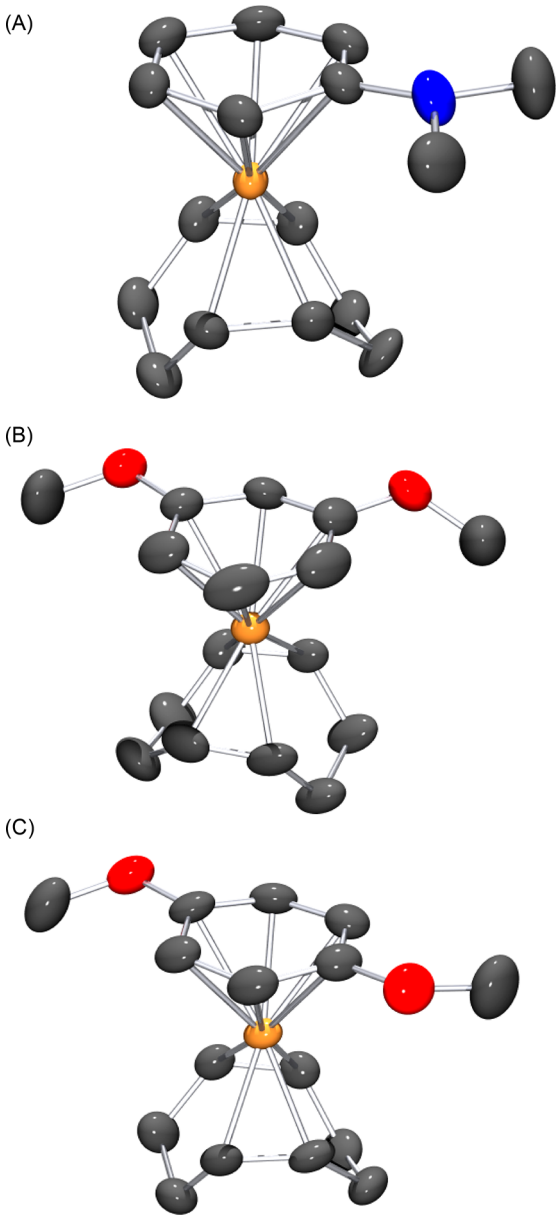


Figure 2. Molecular structures by single-crystal X-ray diffration for **1d** (A), **1g** (B), and **1h** (C). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

In addition to the naphthalene complex, several of the [Ru(η^6-arene)(η^4-1,5-COD)] compounds containing electron-donating substituents catalyzed the formation of cross-dimers in moderate to high yield (entries 1−5). The acetophenone complex **1e** was completely inactive (entry 6), probably because the electron-withdrawing COMe substituent stabilizes η^6 coordination, thus disfavoring arene dissociation. It is worth noting that the 1,3-dimethoxybenzene complex **1g** produced cross-dimers in 74% yield after 14 h at 50 °C (entry 9), whereas the 1,2- and 1,4-analogues (**1f,h**) were much less active under similar conditions; the reasons for this difference remain unclear. As noted above, the *N,N*-dimethylaniline complex **1d** contains one remarkably long Ru−C(arene) bond, indicating that the arene in this case might be fairly weakly bound, but **1d** is nevertheless not the most active catalyst. Finally, we note that the isomeric ratio **4a**/**4b** of the cross-dimers catalyzed by the anisole complex **1c** at 100 °C for 4 h is strongly in favor of **4b**

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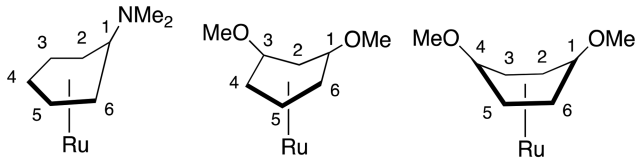
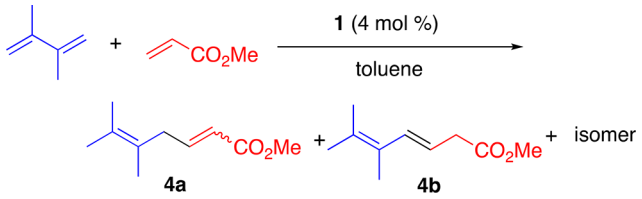
Table 7. Distortions of the Aromatic Fragment in 1d,f.g and Selected Bond Distances between Ruthenium and the Aromatic Carbons (Å)



1d **1g** **1h**

	1d	1g	1h
Ru−C(1)	2.385(3)	2.279(4)	2.297(4)
Ru−C(2)	2.210(3)	2.200(4)	2.185(4)
Ru−C(3)	2.264(3)	2.304(6)	2.258(4)
Ru−C(4)	2.284(4)	2.279(5)	2.310(4)
Ru−C(5)	2.204(3)	2.189(4)	2.205(4)
Ru−C(6)	2.275(3)	2.274(4)	2.259(4)

Table 8. Cross-Dimerization of 2,3-Dimethylbutadiene with Methyl Acrylate Catalyzed by [Ru(η^6-arene)(η^4-1,5-COD)] (1)[a]



4a **4b**

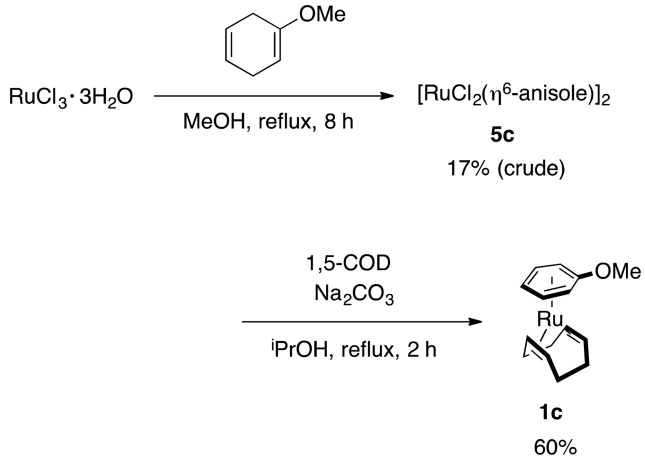
				cross-dimers	
entry	catalyst	temp (°C)	time (h)	yield (%)	*E*-**4a**/*Z*-**4a**/**4b**/isomers
1	**1a**	30	2	98	63/4/30/3
2	**1b**	100	10	54	20/6/57/17
3	**1c**	100	4	85	3/6/81/9
4	**1c**	80	4	25	49/7/25/20
5	**1d**	70	8	26	46/12/35/18
6	**1e**	50	4	trace	
7	**1f**	50	14	8	58/9/33/0
8	**1g**	50	14	74	47/22/30/1
9	**1h**	50	13	trace	

[a]Conditions: **1** (0.029−0.030 mmol), 2,3-dimethylbutadiene (0.89 mmol), methyl acrylate (0.70 mmol). Yields and product ratios were determined by GLC.

(entry 3), in marked contrast with the results reported in Table 5. This apparent reversal in regioselectivity is probably caused by thermal, Ru-catalyzed isomerization of initially formed **4a** as the kinetic product of the coupling. In agreement, the isomeric ratio of the cross-dimerization product after 4 h at 80 °C using **1c** as catalyst favors **4a** over **4b**. The occurrence of the isomerization of cross-dimer **3a** to **3b** has been demonstrated.[20a]

Synthesis of [$RuCl_2(\eta^6$-anisole)]$_2$ (5c). These promising results with cross-dimerization using the Ru(η^4-1,5-COD) complexes of anisole (**1c**) and 1,3-dimethoxybenzene (**1g**) as catalysts prompted us to examine the $Ru^{II}Cl_2$ complexes of these aromatics, **5c**,**g**, respectively, as possible precursors. A product formulated as [$RuCl_2(\eta^6$-anisole)]$_2$ (**5c**) was first reported briefly by Bennett and Smith in 1974 as a brown solid, obtained from the reaction of hydrated $RuCl_3$ with 1-methoxycyclohexa-1,4-diene, the Birch reduction product of anisole, in refluxing methanol in 25% yield.[31] The formulation was based on elemental analysis and ^{1}H NMR data, though it was noted that the product contained about 10% of the benzene complex [$RuCl_2(\eta^6$-benzene)]$_2$ (**5b**), arising from competing demethoxylation of anisole. Soleimannejad and White also re-examined and reported on this chemistry.[32] We attempted to prepare **5c** from methanolic $RuCl_3$ and 1-methoxycyclohexa-1,4-diene (Scheme 2: method A). The

Scheme 2



initially formed, poorly soluble green-brown solid was Soxhlet-extracted with hot chloroform to give a brown solution, from which a green-brown solid was obtained after evaporation of the solvent. The ^{1}H NMR spectrum in DMSO-d_6 indicated it to be a mixture of the anisole complex **5c** (89%) and the benzene complex **5b** (11%), but the estimated yield remained generally in the range of only 10−17%. Note that Iwata and Ogata[33] reported that these compounds also contain [$RuCl_2(\eta^6$-arene)]$_n$[$RuCl_2$]$_m$ (m/n = 0.1−0.2 for arene = benzene; m/n = 0.4−0.5 for arene = mesitylene; m/n = 1−2 for arene = 1,3,5-triphenylbenzene), rather than the previously assumed [$RuCl_2(\eta^6$-arene)]$_2$. Our elemental analyses are fairly consistent with the empirical formula [$RuCl_2(\eta^6$-anisole)]-[$RuCl_2$]$_{0.22}$, and the chemical reactions of this product with PMe_3 are also consistent with this composition (see the Supporting Information).

Following the procedure of Vitulli et al.,[29] we prepared an analytically pure sample of **5c** as an orange powder in 83% yield based on Ru by treatment of [Ru(η^6-anisole)(η^4-1,5-COD)] with hydrochloric acid (method B). Except for the absence of peaks due to **5b**, the ^{1}H NMR spectrum of this solid in DMSO-d_6 was identical with that of the green-brown solid made by method A.

Similar attempts to prepare [$RuCl_2(\eta^6$-1,3-dimethoxybenzene)]$_2$ (**5f**) by heating 1,3-dimethoxy-1,4-cyclohexadiene with methanolic $RuCl_3$ at 50 °C for 2 days failed, the only product isolated being 3-methoxy-2-cyclohexenone.

Catalytic Cross-Dimerization by [$RuCl_2(\eta^6$-anisole)]$_2$ (5c) as the Catalyst Precursor. Using **5c** with a reductant and 1,5-COD, a catalytic cross-dimerization between 2,3-dimethylbutadiene with styrene was performed (Table 9).

In a typical experiment, a suspension of **5c** (5 mol %), 1,5-COD (20 mol %), and Na_2CO_3 (20 mol %) was heated in a Schlenk tube in ^{i}PrOH at 100 °C for 1 h, and after the reaction mixture was cooled to room temperature, 2,3-dimethylbutadiene and styrene were added. After 6 h at 100 °C, the cross-dimers were obtained in 8% yield (Table 9, entry 1). The

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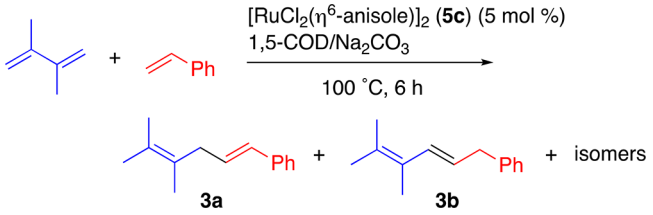
Table 9. Catalytic Cross-Dimerization between 2,3-Dimethylbutadiene with Styrene Catalyzed by [$RuCl_2(\eta^6$-anisole)]$_2$ (5c) with 1,5-COD in the Presence of Na_2CO_3[a]



	amt (mol %)			cross-dimers	
entry	1,5-COD	Na_2CO_3	solvent	yield (%)	3a/3b/isomers
1	20	20	^{i}PrOH	8	12/50/38
2[b,c]	20	20	^{i}PrOH	47	21/43/36
3[b,c]	20	40	^{i}PrOH	55	19/26/10
4[b,c]	40	40	^{i}PrOH	44	20/39/41
5	20	40	DMSO	1	
6	20	40	1-BuOH	1	
7	20	40	2-BuOH	62	24/40/36
8	0	40	2-BuOH	0	
9[b,d]	20	40	^{i}PrOH	45	18/44/38

[a]In all reactions, 2,3-dimethylbutadiene and styrene were added after pretreatment of **5c** with 1,5-COD and Na_2CO_3 at 100 °C (oil bath temperature) for 1 h: 2,3-dimethylbutadiene (0.88 mmol), styrene (0.75 mmol). [b]This reaction was carried out in an autoclave. [c]Time 10 h. [d][$Ru(OAc)_2(\eta^6$-anisole)] (prepared by treatment of **5c** with an excess of AgOAc) was used for the catalyst precursor.

reaction in an autoclave improved the product yield (47% yield), probably by preventing the loss of 2,3-dimethylbutadiene. When the relative amount of Na_2CO_3 was increased to 40 mol %, there was a small increase in the yield of the cross-dimers (55% yield). With 2-butanol, the product yield increased to 62% but the reaction using 1-butanol significantly decreased the product yield (entries 6 and 7). The high efficiency of secondary alcohols suggests that the reduction of **5c** occurs via β-hydride elimination from an alkoxoruthenium species. The cross-dimerization did not occur in the absence of 1,5-COD (entry 8).

CONCLUDING REMARKS

We have shown that a catalytically active species for the one-pot C−C coupling between 2,3-dimethylbutadiene and styrene or methyl acrylate can be generated in situ by reduction of [$Ru(acac)_2(\eta^4$-cyclic diene)] (**2**) with BuLi or of [$RuCl_2(\eta^6$-arene)] (**5**)/1,5-COD with Na_2CO_3. With these procedures, it is not necessary to isolate the air-sensitive Ru(0) species which is the actual catalyst precursor. This is a clear advantage over the corresponding Ru(0) naphthalene system **1a**, although the latter is probably catalytically more active. Moreover, the present methods could generate a catalytically active Ru(0) species, even if [$Ru(\eta^6$-naphthalene)L] cannot survive during the reduction using sodium naphthalene. Of the two present procedures starting from Ru(II) complexes, in situ reduction of [$Ru(acac)_2$L] with 2 equiv of BuLi is probably the more facile, reliable, and practical protocol for generating an active Ru(0) species that is capable of catalyzing the cross-dimerization of conjugated dienes and substituted alkenes. With this amount, BuLi probably cannot reduce the Ru(II) species completely. However, further addition of BuLi causes undesirable polymerization of substrates. This is probably why the present system is catalytically less active than **1a**. However, presumably one needs only a minor amount of a Ru(0) species for the catalysis to be effective. Controls of the regioselective formation of the C═C bond and enantioselective cross-dimerizations remain the challenges in the future for the preparative-scale catalysis.

EXPERIMENTAL SECTION

General Procedures. All manipulations and reactions were performed under dry nitrogen with use of standard Schlenk and vacuum line techniques. Diethyl ether, THF, benzene, toluene, and hexane were dried and deoxygenated with a Glass Contour Ultimate Solvent System. The following starting materials were prepared according to literature methods: Rieke Mg[13] and Rieke Zn,[22] [$Ru(acac)_3$],[34] [$Ru(\eta^4$-1,5-COD)(η^6-1,3,5-COT)],[35] [$Ru(acac)_2(\eta^4$-1,5-COD)],[36] [$Ru(\eta^6$-naphthalene)(η^4-1,5-COD)] (**1a**),[24] and [$Ru(\eta^6$-benzene)(η^4-1,5-COD)] (**1b**).[26] The known complexes [$Ru(\eta^6$-arene)(η^4-1,5-COD)] (arene = anisole, acetophenone)[29] were made from **1a** and the arene in the presence of acetonitrile by use of the literature procedure.[24] [$RuCl_2(\eta^6$-anisole)] (**5c**) was also prepared by the literature method.[31] 2-Phenylbicyclo[3.3.1]nona-2,6-diene was prepared according to the modification of the reported procedure.[19b] Solutions of BuLi (1.003 M) were standardized by titration with 1,10-phenanthroline/*sec*-BuOH (1.003 M) prior to use. 2,5-Dimethyl-7,8-(tetrafluorobenzo)bicyclo[2.2.2]octatriene[37] and (3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalen-4-yl)iminostilbene[38] were prepared by literature methods. dcype was prepared according to literature methods.[39] All other reagents were obtained from commercial suppliers and used as received. Chromatographic separation was carried out on Al_2O_3 (Merck, Activity I, 250 mesh). ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded on JEOL ECX-400P (400 MHz for ^{1}H) and JEOL Lambda-300 (300 MHz for ^{1}H) instruments. Benzene-d_6 was distilled over sodium wire and stored under vacuum. Chemical shifts (δ) are given in ppm, relative to internal TMS for ^{1}H and ^{13}C. All coupling constants are given in Hz. Most elemental analyses were carried out on a PerkinElmer 2400 series II CHN analyzer; some C, H, Cl analyses on **5c** were done at the Center for Organic Elemental Microanalysis, Department of Pharmaceutical Sciences, Kyoto University, and at the Campbell Microanalytical Laboratory, the University of Otago, Otago, New Zealand. IR spectra were recorded on a JASCO FT/IR-4100 instrument with use of KBr disks. GLC analysis was performed on a Shimadzu GC-14B instrument with a FID detector equipped with a ZB-WAX plus column (0.25 mm i.d. × 30 m). The GC-MS analyses were performed on a Shimadzu QP2010 instrument.

Preparations of [Ru(acac)$_2$(2-phenylbicyclo[3.3.1]nona-2,6-diene)] (2b). Complex **2b** was prepared according to our previous report[21c] using [$Ru(acac)_3$] (1.5427 g, 3.8723 mmol) with 2-phenylbicyclo[3.3.1]nona-2,6-diene (795.6 mg, 4.053 mmol) and Zn dust (2.5 g, 39 mmol) in THF (39 mL) and water (1 mL). Crystallization of the resulting oil from cold (−20 °C) hexane (10 mL) gave orange plates of **2b** (57% yield, 1.0916 g, 2.2027 mmol, *rac*-Δ-(*S*,*S*)-**2b**/*rac*-Λ-(*S*,*S*)-**2b** = 62/38). From the mother liquor, **2b** was obtained (24% yield, 488.0 mg, 0.9847 mmol, *rac*-Δ-(*S*,*S*)-**2b**/*rac*-Λ-(*S*,*S*)-**2b** = 93/7). Data for *rac*-Δ-(*S*,*S*)-**2b** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58 (br s, 2H, CH_2), 1.73 (s, 3H, *Me*), 1.81 (s, 3H, *Me*), 1.85 (s, 3H, *Me*), 2.15 (s, 3H, *Me*), 2.3−2.6 (m, 5H, CH_2 and *CH*), 2.65 (br s, 1H, bridge head), 4.09 (dd, $^3J_{H-H}$ = 7.8, 5.2 Hz, 1H, ═*CH*), 4.32 (dd, $^3J_{H-H}$ = 7.8, 4.0 Hz, 1H, ═*CH*), 5.16 (d, $^3J_{H-H}$ = 2.9 Hz, 1H, ═*CH*), 5.29 (s, 1H, *CH* in acac), 5.38 (s, 1H, *CH* in acac), 7.04−7.16 (m, 5H, *Ph*). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ 27.03, 27.29, 28.30, 28.39, 29.51, 34.37, 35.62, 38.59, 38.94, 78.17, 86.32, 92.49, 93.15, 98.37, 98.82, 125.57, 126.21 (2C), 126.25 (2C), 143.54, 184.37, 186.15 (2C), 186.25. IR (KBr, cm^{-1}): 3086 (w), 3016 (w), 2966 (w), 2910 (m), 2836 (m), 1576 (vs), 1519 (vs), 1401 (vs), 1271 (m), 1196 (m), 1184 (m), 1017 (s), 933 (m), 764 (s), 691 (m), 611 (m), 436 (m). Anal. Calcd for $C_{25}H_{30}O_4Ru$: C, 60.59; H, 6.10. Found: 60.57; H, 5.98. Data for *rac*-Λ-(*S*,*S*)-**2b** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 3H, *Me*), 1.65 (br s, overlapped, 2H, CH_2), 1.81 (s, 3H, *Me*), 1.82 (s, 3H, *Me*), 2.13 (s, 3H, *Me*), 2.3−

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2.5 (m, 3H, CH_2 and CH), 2.65 (br s, 1H, bridge head), 3.18 (dt, $^3J_{H-H}$ = 14.3, 4.0 Hz, 1H, CH_2), 3.23 (dt, $^3J_{H-H}$ = 14.3, 4.0 Hz, 1H, CH_2), 3.65 (dd, $^3J_{H-H}$ = 8.3, 5.2 Hz, 1H, =CH_2), 4.30 (dd, $^3J_{H-H}$ = 8.3, 4.3 Hz, 1H, =CH_2), 4.47 (s, 1H, CH in acac), 5.15 (s, 1H, CH in acac), 5.39 (d, $^3J_{H-H}$ = 4.0 Hz, 1H, =CH), 6.97−7.02 (m, 3H, *Ph*), 7.04−7.16 (m, 2H, *Ph*). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 26.89 (s), 26.97 (s), 28.40 (s), 28.88 (s), 29.72 (s), 35.06 (s), 25.81 (s), 37.10 (s), 37.40 (s), 81.90 (s), 85.53 (s), 89.29 (s), 91.66 (s), 97.61 (s), 98.19 (s), 125.31 (s, 2C), 125.53 (s), 126.74 (s, 2C), 143.08 (s), 185.07 (s), 185.32 (s), 185.81 (s), 186.79 (s).

[Ru(acac)$_2$(2,5-dimethyl-7,8-(tetrafluorobenzo)bicyclo-[2.2.2]octatriene)] (2c). **2c** was prepared from [Ru(acac)$_3$] (410.4 mg, 1.030 mmol) with 2,5-dimethyl-7,8-(tetrafluorobenzo)-bicyclo[2.2.2]octatriene (275.8 mg, 1.085 mmol) and Zn dust (0.7 g, 11 mmol) (79% yield, 448.0 mg, 0.8094 mmol, *rac*-Δ-(*S*,*S*)-**2c**/*rac*-Λ-(*S*,*S*)-**2c** = 85/15). Data for *rac*-Δ-(*S*,*S*)-**2c** are as follows. ^1H NMR (400 MHz, $CDCl_3$): δ 1.48 (s, 6H, *Me*), 1.86 (s, 6H, *Me* in acac), 2.25 (s, 6H, *Me* in acac), 3.69 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, =CH), 4.79 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, CH in bridge head), 5.35 (s, 2H, CH in acac). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 17.47 (*Me*), 27.14 (*Me* in acac), 28.36 (*Me* in acac), 47.51 (bridge head), 69.24 (=CH), 84.13 (=C<), 99.30 (*acac*), 127.1−127.4 (m, *aromatic*), 186.57 (CO), 187.10 (CO). IR (KBr, cm^{-1}): 2975 (w), 2896 (m), 1594 (vs), 1580 (vs), 1519 (vs), 1489 (vs), 1368 (m), 1297 (s), 1269 (s), 1200 (m), 1175 (m), 1135 (m), 1106 (m), 1085 (m), 1024 (s), 998 (m), 930 (s), 772 (s), 699 (w), 617 (m), 437 (m). Anal. Calcd for $C_{24}H_{24}F_4O_4Ru$: C, 52.08; H, 4.37. Found: C, 51.81; H, 4.54. Data for *rac*-Λ-(*S*,*S*)-**2c** are as follows. ^1H NMR (400 MHz, $CDCl_3$): δ 1.21 (s, 6H, *Me*), 1.88 (s, 6H, *Me* in acac), 2.28 (s, 6H, *Me* in acac), 4.13 (d, $^3J_{H-H}$ = 5.2 Hz, 2H, =CH), 4.97 (d, $^3J_{H-H}$ = 5.2 Hz, CH in bridge head), 5.34 (s, 2H, CH in acac). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 18.35 (s, *Me*), 27.18 (s, *Me* in acac), 28.30 (s, *Me* in acac), 47.39 (s, bridge head), 71.59 (s, =CH), 85.18 (s, =CH), 98.74 (s, CH in acac), 127.1−127.4 (m, *aromatic*), 186.40 (s, CO), 187.41 (s, CO).

[Ru(acac)$_2$(3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]-dinaphthalen-4-yl)iminostilbene] (2d). **2d** was prepared from [Ru(acac)$_3$] (651.5 mg, 1.635 mmol) with (3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalene-4-yl)iminostilbene (870.3 mg, 1.715 mmol) and Zn dust (1.0 g, 15 mmol) as an analytically pure pale yellow powder (88% yield, 1.3208 g, 1.5028 mmol, *rac*-Δ-(*S*)-**2d**/*rac*-Λ-(*S*)-**2d** = 79/21). Data for *rac*-Δ-(*S*)-**2d** are as follows. ^1H NMR (400 MHz, $CDCl_3$): δ 0.60 (s, 3H, *Me*), 1.59 (s, 3H, *Me*), 2.04 (s, 3H, *Me*), 2.08 (s, 3H, *Me*), 4.67 (s, 1H, CH in acac), 4.90 (d, $^3J_{H-H}$ = 10.0 Hz, 1H, =CH), 5.33 (d, $^3J_{H-H}$ = 10.0 Hz, 1H, =CH), 5.46 (s, 1H, CH in acac), 7.01 (d, $^3J_{H-H}$ = 8.6 Hz, 1H, aromatic), 7.1−7.2 (m, 5H, *aromatic*), 7.2−7.25 (m, 2H, *aromatic*), 7.3−7.35 (m, 3H, *aromatic*), 7.4 (m, 2H, *aromatic*), 7.43 (m, 1H, *aromatic*), 7.58 (d, $^3J_{H-H}$ = 9.2 Hz, 1H, *aromatic*), 7.62 (d, $^3J_{H-H}$ = 7.5 Hz, 1H, *aromatic*), 7.79 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, *aromatic*), 7.92 (d, $^3J_{H-H}$ = 8.6 Hz, 1H, *aromatic*), 7.93 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, *aromatic*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 25.30 (s), 27.68 (s), 28.53 (s), (d, $^2J_{C-P}$ = 8.6 Hz), 28.77 (s), 80.38 (s), 83.88 (s), 98.53 (s), 98.97 (s), 121.83 (s), 122.16 (s), 122.83 (s), 124.55 (s), 124.86 (s), 125.52 (s), 125.93 (s), 126.51 (s), 126.70 (s), 126.93 (s), 127.06 (s), 127.43 (s), 127.50 (s), 127.93 (s), 128.15 (s), 129.19 (s), 129.28 (s), 129.43 (s), 129.78 (s), 130.31 (s), 131.06 (s), 131.28 (s), 131.63 (s), 132.07 (s), 132.75 (s), 141.63 (s), 131.86 (s), 141.91 (s), 142.91 (d, $^2J_{C-P}$ = 6.7 Hz), 142.73 (d, $^2J_{C-P}$ = 5.8 Hz), 147.77 (s), 149.07 (s), 185.75 (s), 185.87 (s), 187.41 (s), 187.46 (s). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 192.10 (s). Data for *rac*-Λ-(*S*)-**2d** are as follows. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 3H, *Me*), 1.82 (s, 3H, *Me*), 1.95 (s, 3H, *Me*), 2.05 (s, 3H, *Me*), 5.12 (d, $^3J_{H-H}$ = 9.7 Hz, 1H, =CH), 5.28 (s, 1H, CH in acac), 5.31 (s, 1H, CH in acac), 5.52 (d, $^3J_{H-H}$ = 9.7 Hz, 1H, =CH), 6.8−7.7 (m, overlapped, 20H, *aromatic*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 192.24 (s). **2d**: Anal. Calcd for $C_{48}H_{44}NO_7PRu$: C, 65.59; H, 5.05; N, 1.59. Found: C, 65.10; H, 4.78; N, 1.54.

[Ru(acac)$_2$(1,2-bis(dicyclohexylphosphino)ethane)] (2e). Complex **2e** was prepared from [Ru(acac)$_3$] (199.6 mg, 0.5010 mmol) with 1,2-bis(dicyclohexylphosphino)ethane (222.1 mg, 0.5255 mmol) and Zn (327.1 mg, 5.003 mmol) in refluxing THF/H_2O for 11 h in 16% yield. A higher yield of **2e** was obtained as follows: [Ru(η^4-1,5-COD)(η^6-1,3,5-COT)] (546 mg, 1.73 mmol) and 1,2-bis-(dicyclohexylphosphino)ethane (756 mg, 1.80 mmol) in benzene (7 mL) were treated with acetylacetone (541 μL, 5.2 mmol) at room temperature. After 48 h, the initially orange solution had turned red. After evaporation of all volatile material under reduced pressure, an orange oil remained, which on recrystallization from cold hexane gave analytically pure orange crystals of **2e** (80% yield, 1.00 g, 1.39 mmol). ^1H NMR (300 MHz, C_6D_6): δ 1.14−2.68 (m, 48H, P*Cy* and PC_2H_4P), 1.82 (s, 6H, *Me* in acac), 2.01 (s, 6H, *Me* in acac), 5.41 (s, 2H, CH in acac). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 88.2 (s). Anal. Calcd for $C_{36}H_{62}O_4P_2Ru$: C, 59.90; H, 8.66. Found: C, 60.21; H, 8.69.

Catalytic Cross-Dimerization of 2,3-Dimethylbutadiene with Styrene in the Presence of [Ru(acac)$_2$(η^4-1,5-COD)] (2a) with/without Reductant. [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) (20.63 mg, 0.0506 mmol) and dibenzyl as an internal standard (36.6 mg, 0.201 mmol) were placed in a 25 mL Schlenk tube, into which hexane (1.5 mL), styrene (120 μL, 1.04 mmol), 2,3-dimethylbutadiene (120 μL, 1.05 mmol), and BuLi (40 μL, 2.33 M, 0.093 mmol) were placed from a hypodermic syringe. The reaction mixture was warmed to 50 °C for 6 h, and the product yields were estimated by GLC (73% total yield, **3a**/**3b**/isomers = 82/8/10). The other evaluations of reductants are summarized in the Supporting Information.

Effect of Amount of BuLi to [Ru(acac)$_2$(η^4-1,5-COD)] (2a) on Cross-Dimerization of 2,3-Dimethylbutadiene with Styrene. Similar to the standard reaction of 2,3-dimethylbutadiene with styrene catalyzed by **2a**/BuLi described above, the following experiments were performed. **2a** (20.49 mg, 0.0502 mmol), hexane (1.5 mL), styrene (120 μL, 1.04 mmol), 2,3-dimethylbutadiene (240 μL, 2.11 mmol), BuLi (21 μL, 2.3 M, 0.049 mmol): 80% total yield, **3a**/**3b**/isomers = 84/9/7. The other screening data for the amount of BuLi are summarized in the Supporting Information.

Effect of Diene/Styrene Ratio on [Ru(acac)$_2$(η^4-1,5-COD)] (2a)-Catalyzed Cross-Dimerization of 2,3-Dimethylbutadiene with Styrene. Similar to the standard reaction of 2,3-dimethylbutadiene with styrene catalyzed by **2a**/BuLi described above, the following experiments were performed. **2a** (20.44 mg, 0.0501 mmol), hexane (1.5 mL), styrene (340 μL, 2.96 mmol), 2,3-dimethylbutadiene (120 μL, 1.05 mmol), BuLi (43 μL, 2.3 M, 0.10 mmol): 81% total yield, **3a**/**3b**/isomers = 62/31/7. The other screening data for the diene/styrene ratio are summarized in the Supporting Information.

Effect of [Ru(acac)$_2$L] (2) on Cross-Dimerization of 2,3-Dimethylbutadiene with Styrene in the Presence of BuLi. Similar to the standard reaction of 2,3-dimethylbutadiene with styrene catalyzed by **2a**/BuLi described above, the following experiments were performed. [Ru(acac)$_2$(2-phenylbicyclo[3.3.1]nona-2,6-diene)] (**2b**) (24.72 mg, 0.0498 mmol), THF (1.5 mL), styrene (115 μL, 1.00 mmol), 2,3-dimethylbutadiene (240 μL, 2.11 mmol), BuLi (43 μL, 2.3 M, 0.10 mmol): 77% total yield, **3a**/**3b**/isomers = 73/13/14. The other screening of [Ru(acac)$_2$L] are summarized in the Supporting Information.

Cross-Dimerization of 2,3-Dimethylbutadiene with Methyl Acrylate. [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) (20.66 mg, 0.0506 mmol) and dibenzyl as an internal standard (35.71 mg, 0.196 mmol) were placed in a 25 mL Schlenk tube, into which hexane (1.5 mL), 2,3-dimethylbutadiene (120 μL, 1.05 mmol), methyl acrylate (140 μL, 1.56 mmol), and BuLi (40 μL, 2.3 M, 0.093 mmol) were placed by a hypodermic syringe. The reaction mixture was warmed to 50 °C for 6 h, and the product yields were estimated by GLC. The total yield of cross-dimers was 0%. A similar reaction was carried out in THF with **2a** (20.33 mg, 0.0498 mmol), THF (1.5 mL), BuLi (40 μL, 0.093 mmol), 2,3-dimethylbutadiene (120 μL, 1.05 mmol), and methyl acrylate (140 μL, 1.56 mmol), and the product yields were measured by GLC: 65% total yield, *E*-**4a**/*Z*-**4a**/**4b**/isomers = 67/9/22/2. The other screenings of the catalysis are summarized in the Supporting Information.

Effect of [Ru(acac)$_2$L] (2) on Cross-Dimerization of 2,3-Dimethylbutadiene with Methyl Acrylate in the Presence of BuLi. Similar to the standard reaction of 2,3-dimethylbutadiene with methyl acrylate catalyzed by **2a** with pretreatment of the catalyst

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precursor with BuLi, the following experiments were performed. [Ru(acac)$_2$(1,5-COD)] (**2a**) (20.63 mg, 0.0506 mmol), THF (1.5 mL), BuLi (43 μL, 0.10 mmol), 2,3-dimethylbutadiene (230 μL, 2.02 mmol), methyl acrylate (90 μL, 1.00 mmol): 63% total yield, *E*-**4a**/*Z*-**4a**/**4b**/isomers = 81/3/14/2. The other screening data of the catalyst are summarized in the Supporting Information.

Reaction of [Ru(acac)$_2$(η^4-1,5-COD)] (2a) with 2 equiv of BuLi. [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) (20.3 mg, 0.0500 mmol) was dissolved in hexane (1.5 mL), and BuLi (2.49 M, 40.0 μL, 0.996 mmol) was added to the solution under reduced pressure by a hypodermic syringe. Then, methane (99.8 μL, 1019 hPa, 10 °C) was added to the system as an internal standard. An orange suspension formed immediately. The system was stirred at 0 °C for 5 min, and the GC analysis (Unicarbon column, 1 m × 3 mmϕ) suggests generation of butane (17.6%), 1-hexene (5.0%), and (*E*)-2-butene (1.8%). (*Z*)-2-Butene was not observed. Then, cyclooctane (2.0 μL, 0.015 mmol) was added to the system as an internal standard. The GLC analysis (OV-1 column, 30 m × 0.25 mm i.d.) indicated formation of octane (6.9%).

Reaction of [Ru(acac)$_2$(η^4-1,5-COD)] (2a) with 2 equiv of BuLi in the Presence of Naphthalene. [Ru(acac)$_2$(η^4-1,5-COD)] (**2a**) (20.44 mg, 0.0501 mmol) and naphthalene (12.90 mg, 0.1008 mmol) were dissolved in THF (1.5 mL), and BuLi (43 μL, 0.10 mmol) was added to the solution. After removal of volatile materials, triphenylmethane (5.54 mg, 0.022 mmol) was added as an internal standard. **1a**: 0.004 mmol, 8% yield.

[Ru(η^6-*N*,*N*-dimethylaniline)(η^4-1,5-COD)] (1d). [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**) (203.8 mg, 0.604 mmol) was treated with MeCN (1 mL, 20 mmol) and *N*,*N*-dimethylaniline (1 mL, 8 mmol) in THF (10 mL) at room temperature for 17 h. After concentration of the solution, the product was purified by alumina chromatography using hexane and all volatile matter was removed under reduced pressure. Recrystallization of the resulting solid from cold hexane produced yellow plates of **1d** (54% yield, 107.8 mg, 0.326 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 2.29 (s, 6H, N*Me*), 2.35−2.48 (m, 8H, CH_2 in COD), 3.43 (d, $^3J_{H-H}$ = 9.2 Hz, 4H, =C*H* in COD), 4.46 (d, $^3J_{H-H}$ = 5.7 Hz, 2H, 2-C*H* in aromatic ring), 4.71−4.77 (m, 2H, 3-C*H* in aromatic ring), 5.06 (t, $^3J_{H-H}$ = 5.7 Hz, 1H, 4-C*H* in aromatic ring). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 34.69 (s, CH_2 in COD), 29.88 (s, *Me*), 58.78 (s, = C*H* in COD), 69.60 (s, *arene*), 82.22 (s, *arene*), 90.14 (s, *arene*), 130.16 (s, *arene*). Satisfactory elemental analysis data were not obtained, and this compound was characterized by spectroscopic methods.

[Ru(η^6-1,2-dimethoxybenzene)(η^4-1,5-COD)] (1f). Similar to the case for **1d**, **1f** was prepared by the reaction of **1a** (203.2 mg, 0.602 mmol), MeCN (1 mL, 20 mmol), and 1,2-dimethoxybenzene (600 μL, 4.69 mmol) in THF (16 mL) at room temperature for 4 days. **1f** was obtained as yellow plates (25% yield, 53.1 mg, 0.153 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 2.37−2.39 (m, 8H, CH_2 in COD), 3.35 (s, 6H, O*Me*), 3.43 (m, 4H, =C*H* in COD), 4.46 (s, 2H, *aromatic*), 4.95 (s, 2H, *aromatic*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 34.57 (s, CH_2 in COD), 57.40 (s, O*Me*), 61.43 (s, =CH in COD), 72.88 (s, *arene*), 83.35 (s, *arene*), 126.0 (s, *arene*). Anal. Calcd for $C_{16}H_{22}O_2Ru$: C, 55.31; H, 6.38. Found: C, 55.31; H, 6.59.

[Ru(η^6-1,3-dimethoxybenzene)(η^4-1,5-COD)] (1g). Similar to the case for **1d**, **1g** was prepared by the reaction of **1a** (106.2 mg, 0.315 mmol), MeCN (1 mL, 20 mmol), and 1,3-dimethoxybenzene (150 μL, 1.00 mmol) in THF (10 mL) at room temperature for 42 h. **1g** was obtained as yellow plates (25% yield, 51.4 mg, 0.148 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 2.37 (m, 8H, CH_2 in COD), 3.23 (s, 6H, O*Me*), 3.40 (m, 4H, =C*H* in COD), 4.03 (t, $^3J_{H-H}$ = 5.6 Hz, 1H, *aromatic*), 4.82 (d, $^3J_{H-H}$ = 5.6 Hz, 2H, *aromatic*), 4.96 (s, 1H, *aromatic*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 34.64 (s, CH_2 in COD), 55.95 (s, O*Me*), 62.25 (s, =CH in COD), 67.54 (s, *arene*), 73.51 (s, *arene*), 74.36 (s, *arene*), 136.19 (s, *arene*). Anal. Calcd for $C_{16}H_{22}O_2Ru$: C, 55.31; H, 6.38. Found: C, 55.39; H, 6.28.

[Ru(η^6-1,4-dimethoxybenzene)(η^4-1,5-COD)] (1h). Similar to the case for **1d**, **1h** was prepared by the reaction of **1a** (199.2 mg, 0.590 mmol), MeCN (2 mL, 40 mmol), and 1,4-dimethoxybenzene (297.5 μL, 2.153 mmol) in THF (15 mL) at room temperature for 2 days. **1h** was obtained as yellow plates (67% yield, 136.5 mg, 0.392 mmol). ^{1}H NMR (400 MHz, C_6D_6): δ 2.37−2.42 (m, 8H, CH_2 in COD), 3.25 (s, 6H, O*Me*), 3.35 (m, 4H, =C*H* in COD), 4.62 (s, 4H, *aromatic*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 34.86 (s, CH_2 in COD), 55.50 (s, O*Me*), 63.55 (s, =CH in COD), 70.08 (s, *arene*), 136.62 (s, *arene*). Satisfactory elemental analysis data were not obtained, and this compound was characterized by spectroscopic methods.

Synthesis of [RuCl$_2$(η^6-anisole)]$_2$ (5c). *Method A.* According to the literature method,[31] $RuCl_3{\cdot}3H_2O$ (2.054 g, 7.8955 mmol) was dissolved in methanol (80 mL) and 1-methoxy-1,4-cyclohexadiene (5.4 mL, 39.59 mmol) was added. The reaction mixture was refluxed for 24 h to give a brown precipitate. The product was obtained by extraction with a Soxhlet extraction apparatus with hot chloroform of the initially formed, poorly soluble green-brown solid and isolated as a green-brown solid by evaporation of the chloroform in 17% crude yield (378 mg, 0.65 mmol). The ^{1}H NMR spectrum of the obtained green-brown solid in DMSO-d_6 indicated it to be a mixture of **5c** (89%) and **5b** (11%). Data for **5c** are as follows. ^{1}H NMR (400 MHz, 22.2 °C, DMSO-d_6): δ 3.90 (s, 6H, O*Me*), 5.36 (t, $^3J_{H-H}$ = 4.3 Hz, 2H, arene), 5.53 (d, $^3J_{H-H}$ = 5.2 Hz, 4H, arene), 6.15 (t, $^3J_{H-H}$ = 4.9 Hz, 4H, arene). Typical analytical data of two different batches of this compound made in Kyoto and Canberra are as follows Found: C, 26.99, 27.03; H, 2.50, 2.68; N, 0, <0.3; Cl, 28.18, 27.86. A sample of the solid that had not been extracted with chloroform but only dried in vacuo was analyzed as follows. Found: C, 25.59; H, 2.53; Cl, 28.28. Calcd for $C_7H_8Cl_2ORu$: C, 30.02; H, 2.88; N, 0; Cl, 25.31. Calcd for $C_7H_8Cl_2ORu{\cdot}0.22RuCl_2$: C, 26.44; H, 2.54; Cl, 27.21.

Method B. According to the literature method,[24] [Ru(η^6-anisole)(η^4-1,5-COD)] (**1c**) was prepared by the reaction of [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1a**) (264.2 mg, 0.7839 mmol) with excess anisole (4.6041 g, 42.63 mmol) in the presence of MeCN (60 μL, 0.952 mmol) at room temperature for 2 days (96% yield, 239.5 mg, 0.756 mmol). Following the procedure of ref 29, this was dissolved in acetone (5 mL) and HCl (36 M, 0.20 mL, 7.2 mmol) was added to the solution at room temperature. An orange-brown precipitate deposited immediately. The dark red supernatant was removed by cannula, and the resulting orange powder was washed twice with acetone (2 mL) and dried under vacuum (83% yield based on Ru, 175.1 mg, 0.3127 mmol). ^{1}H NMR (400 MHz, 22.3 °C, DMSO-d_6): δ 3.29 (s, O*Me*), 5.38 (t, $^3J_{H-H}$ = 5.4 Hz, 1H, *Ph*), 5.54 (d, $^3J_{H-H}$ = 5.7 Hz, 2H, *Ph*), 6.17 (t, $^3J_{H-H}$ = 5.7 Hz, 2H, *Ph*). Anal. Calcd for $C_7H_8Cl_2ORu$: C, 30.02; H, 2.88; N, 0. Found: C, 30.38; H, 2.61; N, 0.22.

Synthesis of [Ru(η^6-anisole)(η^4-1,5-COD)] (1c) by Use of 5c. A crude mixture of **5c** and **5b** (91 mg, 0.15 mmol, **5c**/**5b** = 89/11) and Na_2CO_3 (160 mg, 1.52 mmol) was dissolved in 2-propanol (10 mL), and 1,5-COD (1 mL, 8 mmol) was added to the solution. After the solution was heated to 100 °C for 30 min, it was concentrated and purified by alumina column chromatography with THF. The yellow fraction was evaporated under reduced pressure to give a brown oil (72 mg). The ^{1}H NMR analysis suggested formation of **1c** (60% yield) as an inseparable mixture with **1b** (8% yield).

Cross-Dimerization of 2,3-Dimethylbutadiene with Styrene Catalyzed by [RuCl$_2$(η^6-anisole)]$_2$ (5c). Complex **5c** (21.07 mg, 0.376 mmol), Na_2CO_3 (32.04 mg, 0.302 mmol), and dibenzyl (45.07 mg, 0.251 mmol) as an internal standard were dissolved in 2-butanol (2 mL), and 1,5-COD (20 μL, 0.15 mmol) was added to the solution. After the mixture was heated to 100 °C for 1 h, to the solution at room temperature were added 2,3-dimethylbutadiene (100 μL, 0.88 mmol) and styrene (86 μL, 0.75 mmol) in an autoclave. The reaction mixture was heated at 100 °C for 6 h, during which the reaction course was monitored by GLC: 62% total yield, **3a**/**3b**/isomers = 24/40/36. Similar experiments were performed. **5c** (21.2 mg, 0.0378 mmol), Na_2CO_3 (16.1 mg, 0.152 mmol) 2-propanol (2 mL), 1,5-COD (20 μL, 0.152 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in Schlenk tube: 8% total yield, **3a**/**3b**/isomers = 12/50/38. **5c** (20.8 mg, 0.0371 mmol), Na_2CO_3 (16.0 mg, 0.151 mmol), 2-propanol (2 mL), 1,5-COD (20 μL, 0.152 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75

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mmol) in autoclave: 47% total yield, **3a**/**3b**/isomers = 21/43/36. **5c** (21.1 mg, 0.0377 mmol), Na_2CO_3 (32.0 mg, 0.302 mmol), 2-propanol (2 mL), 1,5-COD (20 μL, 0.15 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in autoclave: 55% total yield, **3a**/**3b**/isomers = 16/47/36. **5c** (20.9 mg, 0.0373 mmol), Na_2CO_3 (31.9 mg, 0.301 mmol), 2-propanol (2 mL), 1,5-COD (40 μL, 0.30 mmol), 2,3-dimethylbutadiene (31.7 mg, 0.299 mmol), DMSO (2 mL), 1,5-COD (20 μL, 0.15 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in a Schlenk tube: 1% yield. **5c** (20.9 mg, 0.0373 mmol), Na_2CO_3 (30.2 mg, 0.289 mmol), 1-butanol (2 mL), 1,5-COD (20 μL, 0.15 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in a Schlenk tube: 1% yield. **5c** (21.1 mg, 0.0376 mmol), Na_2CO_3 (32.0 mg, 0.302 mmol), 2-butanol (2 mL), 1,5-COD (20 μL, 0.15 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in a Schlenk tube: 62% total yield, **3a**/**3b**/isomers = 24/40/36. **5c** (21.0 mg, 0.0375 mmol), Na_2CO_3 (31.8 mg, 0.300 mmol), 2-butanol (2 mL), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in a Schlenk tube: 0% yield. **6c** (21.5 mg, 0.00656 mmol), Na_2CO_3 (31.9 mg, 0.301 mmol), 2-propyl alcohol (2 mL), 1,5-COD (20 μL, 0.15 mmol), 2,3-dimethylbutadiene (100 μL, 0.88 mmol), and styrene (86 μL, 0.75 mmol) in autoclave: 45% total yield, **3a**/**3b**/isomers = 18/44/38.

X-ray Analyses. A single crystal was selected using a polarized microscope and was mounted on a glass capillary by use of Paratone-N oil. A Rigaku AFC-7R Mercury II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) was used for data collection. The collected data were solved by direct methods and refined by a full-matrix least-squares procedure using the CrystalStructure program (ver. 4.2).[40,41] All hydrogen atoms were treated as a riding model. The optimized structures are depicted by use of the POV-Ray program (ver. 3.6.2).[42] Incorporation of THF and 5*H*-dibenzo[*b*,*f*]azepine molecules were observed in a unit cell of **2d**. CCDC 1567421, 1567423, 1567422, 1567420, 1567419, and 1567438 contain the supplementary crystallographic data for **1d**,**g**,**h** and **2b**−**d**, respectively.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00882.

Screening data of the catalysts and catalyses, NMR data of new complexes **1d**,**f**−**h**, and **2b**−**d**, and crystallographic data for **1d**,**g**,**h** and **2b**−**d** (PDF)

Accession Codes

CCDC 1567419−1567423 and 1567438 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

COD,cyclooctadiene (C_8H_{12}); COT,cyclooctatriene (C_8H_{10}); DMA,dimethylacetamide (C_4H_9ON); acac,acetylacetonate ($C_5H_7O_2$); Cp*,pentamethylcyclopentadienyl ($C_{10}H_{15}$); THF,tetrahydrofuran (C_4H_8O); dcype,1,2-bis(dicyclohexylphosphino)ethane ($C_{26}H_{48}P_2$); DMSO,dimethyl sulfoxide (C_3H_6OS); Schmalzphos,(3a*R*,8a*R*)-6-((3-(diphenylphosphaneyl)[1,1′-biphenyl]-2-yl)oxy)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]-dioxaphosphepine ($C_{55}H_{46}O_5P_2$)

■ REFERENCES

(1) Wittenberg, D. *Angew. Chem.* **1963**, *75*, 1124.

(2) Cros, P.; Triantaphylides, C.; Buono, G. *J. Org. Chem.* **1988**, *53*, 185−187.

(3) Hattori, S.; Tatsuoka, K. Ger. Pat. DE2104626, 1971

(4) Ito, T.; Takahashi, K.; Takami, Y. *Tetrahedron Lett.* **1973**, *14*, 5049−5050.

(5) (a) Bönnemann, H.; Grard, C.; Kopp, W.; Pump, W.; Tanaka, K.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 964−975. (b) Bönnemann, H.; Grard, C.; Kopp, W.; Wilke, G. *Int. Congr. Pure Appl. Chem.* **1971**, *6*, 265.

(6) (a) Auvinet, A.-L.; Harrity, J. P. A.; Hilt, G. *J. Org. Chem.* **2010**, *75*, 3893−3896.

(7) Hilt, G.; Danz, M. *Synthesis* **2008**, *2008*, 2257−2263.

(8) Jing, S. M.; Balasanthiran, V.; Pagar, V.; Gallucci, J. C.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2017**, *139*, 18034−18043.

(9) Bochmann, M.; Thomas, M. *J. Mol. Catal.* **1984**, *26*, 79−88.

(10) Misono, A.; Uchida, Y.; Saito, T.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1889−1893.

(11) (a) Mitsudo, T.; Zhang, S.-W.; Kondo, T.; Watanabe, Y. *Tetrahedron Lett.* **1992**, *33*, 341−344. Related selected papers: (b) Ura, Y.; Tsujita, H.; Wada, K.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **2005**, *70*, 6623−6628. Tsujita, H.; Ura, Y.; Wada, K.; Kondo, T.; Mitsudo, T. *Chem. Commun.* **2005**, 5100−5102. (d) Tsujita, H.; Ura, Y.; Matsuki, S.; Wada, K.; Mitsudo, T.; Kondo, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 5160−5163. (e) Kondo, T.; Takagi, D.; Tsujita, H.; Ura, Y.; Wada, K.; Mitsudo, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 5958−5961.

(12) Fujiwhara, M.; Nishikawa, T.; Hori, Y. *Org. Lett.* **1999**, *1*, 1635−1637.

(13) Moreau, B.; Wu, J. Y.; Ritter, T. *Org. Lett.* **2009**, *11*, 337−339.

(14) Fukuzawa, H.; Aoyagi, N.; Sato, R.; Kataoka, Y.; Ura, Y. *Organometallics* **2017**, *36*, 3931−3939.

(15) Simon, M.-O.; Darses, S. *J. Org. Chem.* **2013**, *78*, 9981−9985.

(16) Hirano, M.; Komiya, S. *Coord. Chem. Rev.* **2016**, *314*, 182−200.

(17) Hirano, M.; Arai, Y.; Hamamura, Y.; Komine, N.; Komiya, S. *Organometallics* **2012**, *31*, 4006−4019.

(18) (a) Pertici, P.; Ballantini, V.; Salvadori, P.; Bennett, M. A. *Organometallics* **1995**, *14*, 2565−2569. (b) Hirano, M.; Sakate, Y.; Komine, N.; Komiya, S.; Bennett, M. A. *Organometallics* **2009**, *28*,

DOI: 10.1021/acs.organomet.7b00882
Organometallics XXXX, XXX, XXX−XXX

4902−4905. (c) Hirano, M.; Hiroi, Y.; Komine, N.; Komiya, S. *Organometallics* **2010**, *29*, 3690−3693.
(19) (a) Hiroi, Y.; Komine, N.; Hirano, M.; Komiya, S. *Organometallics* **2011**, *30*, 1307−1310. (b) Hiroi, Y.; Komine, N.; Komiya, S.; Hirano, M. *Org. Lett.* **2013**, *15*, 2486−2489. (c) Hirano, M.; Moritake, M.; Murakami, T.; Komine, N. *Chem. Lett.* **2017**, *46*, 1522−1524.
(20) (a) Hirano, M.; Ueda, T.; Komine, N.; Komiya, S.; Nakamura, S.; Deguchi, H.; Kawauchi, S. *J. Organomet. Chem.* **2015**, *797*, 174−184. (b) Hirano, M.; Sakate, Y.; Komine, N.; Komiya, S.; Wang, X.-Q.; Bennett, M. A. *Organometallics* **2011**, *30*, 768−777.
(21) (a) Bennett, M. A.; Byrnes, M. J.; Willis, A. C. *Organometallics* **2003**, *22*, 1018−1028. (b) Bennett, M. A.; Byrnes, M. J.; Kovácik, I. *J. Organomet. Chem.* **2004**, *689*, 4463−4474. (c) Hiroi, Y.; Komine, N.; Komiya, S.; Hirano, M. *Organometallics* **2014**, *33*, 6604−6613.
(22) Rieke, R. D. *Science* **1989**, *246*, 1260−1264.
(23) Bennett, M. A.; Chung, G.; Hockless, D. C. R.; Neumann, H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1999**, 3451−3462.
(24) (a) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X.-Q.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3237−3245. Vitulli, G.; Pertici, P.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2255−2257.
(25) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127−138.
(26) (a) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1978**, *153*, C25−27. (b) One can refer to the detailed description of the following procedure for the [Ru(C_6Me_6)L] analogues: Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **2007**, *21*, 74−78.
(27) Katayama, H.; Nagao, M.; Ozawa, F. *Organometallics* **2003**, *22*, 586−593.
(28) Pertici, P.; Bertozzi, S.; Lazzaroni, R.; Vitulli, G.; Bennett, M. A. *J. Organomet. Chem.* **1988**, *354*, 117−122.
(29) Pertici, P.; Vitulli, G.; Lazzaroni, R.; Salvadori, P.; Barili, P. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1019−1022.
(30) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 132−138.
(31) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233−241.
(32) Soleimannejad, J.; White, C. *Organometallics* **2005**, *24*, 2538−2541.
(33) Iwata, R.; Ogata, I. *Tetrahedron* **1973**, *29*, 2753−2758.
(34) Knowles, T. S.; Howells, M. E.; Howlin, B. J.; Smith, G. W.; Amodio, C. A. *Polyhedron* **1994**, *13*, 2197−2203.
(35) Itoh, K.; Nagashima, H.; Ohshima, T.; Oshima, N.; Nishiyama, N. *J. Organomet. Chem.* **1984**, *272*, 179−188.
(36) Powell, P. *J. Organomet. Chem.* **1974**, *65*, 89−92.
(37) Callander, D. D.; Coe, P. L.; Tatlow, J. C.; Uff, A. J. *Tetrahedron* **1969**, *25*, 25−35.
(38) Roggen, M.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5568−5571.
(39) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203−206.
(40) *Crystalstructure ver.4.2*; Rigaku Corporation, Tokyo, Japan, 2015.
(41) Sheldrick, G. M. *SHELXL97*; University of Göttingen, Göttingen, Germany, 1997.
(42) *POV-Ray for windows ver. 3.6.2*; Persistence of Vision Ray Tracer Pty, Ltd.

DOI: 10.1021/acs.organomet.7b00882
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