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Stoichiometric and Catalytic Dimerization of Conjugated Dienes with $(C_5R_5)Ru(diene)^+$

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When $Cp^*Ru(\eta^4\text{-butadiene})X$ ($Cp^* = \eta^5\text{-}C_5Me_5$; **1a**, X = Cl; **1b**, X = Br) was treated with excess butadiene in the presence of silver trifluoromethanesulfonate (AgOTf) followed by carbon monoxide (1 atm), 1,5-cyclooctadiene complex $[Cp^*Ru(\eta^2{:}\eta^2\text{-}C_8H_{12})(CO)]OTf$ (**2**) was isolated in 79% yield. Similar [4 + 4] cycloaddition occurred in the reaction of $Cp^*Ru(\eta^4\text{-isoprene})Cl$ (**1c**) with isoprene, AgOTf, and CO to give $[Cp^*Ru(\eta^2{:}\eta^2$-*cis*-3,7-dimethyl-1,5-cyclooctadiene)(CO)]OTf (**4a**) at ambient temperature. Similar reaction of $Cp^*Ru(\eta^4$-1,3-pentadiene)Cl (**1d**) with 1,3-pentadiene, however, furnished [Cp*Ru(4-methyl-(1,3-η^3:6–8-η^3)-nonadienediyl)]OTf (**5**) in the presence of AgOTf as result of regiospecific linear dimerization. This stoichiometric regioselective dimerization was extended to catalytic formation of 1,5-cyclooctadiene, dimethylcyclooctadienes, and 6-methyl-2,4,7-nonatriene from butadiene, isoprene, or 1,3-pentadiene, respectively, with a catalytic amount of **1b**, **1c**, or **1d** and AgOTf. Alternatively, treatment of butadiene with $CpRu(\eta^4\text{-butadiene})Br$ ($Cp = \eta^5\text{-}C_5H_5$) and AgOTf induced linear dimerization of butadiene, and $[CpRu(\eta^4{:}\eta^2$-1,3,7-octatriene)]OTf (**6**) was obtained in 98% yield by way of single-step C–C bond formation.

Introduction

A wide range of transition metal complexes have been reported to be efficient catalysts for oligomerizations and cooligomerizations of several conjugated dienes.[1] In particular, homogeneous nickel(0) catalysis was extensively investigated by Wilke and co-workers and opened methodology to obtain four-, six-, eight-, or 12-membered carbocyclic skeletons in short steps from conjugated dienes. It has been widely accepted that bis(allyl)nickel intermediates played the most important roles in such catalysis.[2] The judicious choice of auxiliary phosphorus ligands was essential for selective formation of one of these cyclic oligomers. Commercial production of cyclododecatriene has been performed by means of a Ziegler-type catalyst based on Wilke's pioneering observation that the first-row transition metals were quite effective in the formation of cycloaddition products from conjugated dienes in many cases.[1–3]

Alternatively, several transition metal complexes of the second-row elements, in particular, palladium catalysts, have been known to provide linear oligomers, cooligomers, or telomers of conjugated dienes.[1,4] The larger atomic size and the conformational rigidity of allylic intermediates in the second-row elements have been thought to keep the two metal–carbon bonds too far away to induce the second-stage C–C bond formation from key bis(allyl) intermediates. As a consequence, facile elimination of metal hydride takes place spontaneously from the key bis(allyl) intermediates to result in predominant formation of linear coupling products from conjugated dienes.

In the last decade, however, transition metal mediated coupling has been designed as a type of *intramolecular* process, and such devices make catalytic cycloaddition useful in cyclization methods in organic synthesis.[5] In such intramolecular cycloadditions, the choice of transition

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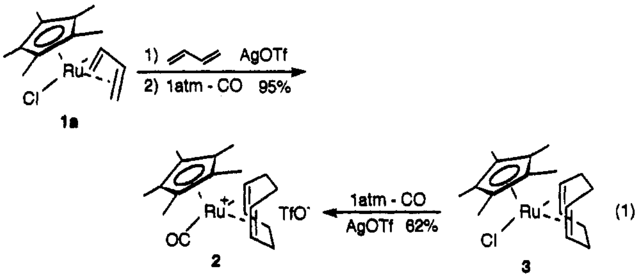
metal elements has broadened presumably because the particular stereochemical bias of substrates may accelerate the second-stage C–C bond forming reductive elimination from metallacycle intermediates.

In the organoruthenium chemistry of conjugated dienes, Shaw and his co-workers reported many years ago a bis(η^3-allyl)dichlororuthenium(IV) complex, $RuCl_2((1-3-\eta^3:6-7-\eta^2:10-12-\eta^3)-C_{12}H_{18})$, involving a butadiene trimer framework as an eight-electron ligand.[6] Allegra *et al.* revealed the formation of a bis(η^3-allyl)ruthenium(IV) complex, $[RuCl_2((1-3-\eta^3:6-8-\eta^3)-C_{10}H_{16})]_2$, which was formed by tail-to-tail dimerization of two isoprene molecules.[7] Their structures were determined unequivocally by X-ray determinations and indicate definitely that direct cyclization by way of reductive elimination to carbocyclic ligands did not take place at all. It was reported that a methylruthenium(IV) iodide derivative of Shaw's compound, $RuI(CH_3)((1-3-\eta^3:6-7-\eta^2:10-12-\eta^3)-C_{12}H_{18})$, induced reductive elimination between an internal carbon of one of the two allylic moieties of the particular C_{12} ligand and the apical methyl group.[8] It is important that reductive elimination between the two allylic terminal carbons did not occur to give cyclododecatriene, which was one of the typical trimer products of butadiene in nickel or titanium catalysis.

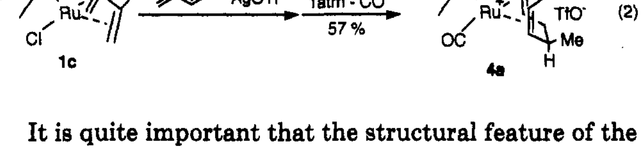
Several years ago, we found ruthenium(0)-mediated [6 + 2] cycloadditions between coordinated cyclic 1,3,5-trienes and 1-alkynes to yield bicyclo trienes.[9] The author reported preliminary results on another thermally forbidden [4 + 4] cycloaddition, in which $[Cp^*Ru(\eta^4\text{-butadiene})]^+$ furnished selectively 1,5-cyclooctadiene on reaction with the second butadiene molecule, although the less bulky cyclopentadienyl analogue, $[CpRu(\eta^4\text{-butadiene})]^+$, gave the linear dimerization product $[CpRu(\eta^4:\eta^2\text{-1,3,7-octatriene})]^+$.[10] We also claimed that $[Cp(\text{or } Cp^*)Ru(\eta^4\text{-diene})]^+$ reacted with alkynes to give $[Cp(\text{or } Cp^*)Ru(\eta^6\text{-arene})]^+$ and related products via ruthenium-mediated [4 + 2] cycloadditions.[11] More recently, Trost *et al.* reported CpRu-catalyzed [2 + 2 + 2] cycloaddition between 1,5-cyclooctadiene and alkynes to result in the formation of a new tricyclodecene skeleton.[12] These examples suggest to us that even simple *intermolecular* cycloadditions to carbocyclic products are not limited to the first-row transition elements but the judicious selection of auxiliary ligands and ligand fields of the second-row metals can induce efficient cycloadditions. In this article, we report full details of stoichiometric and catalytic C–C bond formation of butadiene, isoprene, and 1,3-pentadiene induced by $[Cp^*Ru(\eta^4\text{-diene})]^+$ and $[CpRu(\eta^4\text{-diene})]^+$ and mechanistic aspects of such dimerization processes.[13]

Results and Discussion

Stoichiometric Reaction of $Cp^*Ru(\eta^4\text{-diene})^+$ with Conjugated Dienes (Diene = Butadiene, Isoprene, and 1,3-Pentadiene). When $Cp^*Ru(\eta^4\text{-butadiene})X$ (**1a**, X = Cl; **1b**, X = Br) in dichloromethane was treated with an acetone solution of equimolar silver trifluoromethanesulfonate (AgOTf) in the presence of excess butadiene at ambient temperatures, followed by allowing the mixture to react with carbon monoxide (1 atm), a cationic 1,5-cyclooctadiene carbonyl complex, $[Cp^*Ru(\eta^2:\eta^2\text{-1,5-}C_8H_{12})(CO)]OTf$ (**2**), was isolated in 95% yield (eq 1). The ^1H and ^{13}C NMR spectra of isolated **2** were identical to those of an authentic sample prepared from $Cp^*Ru(\eta^2:\eta^2\text{-1,5-cyclooctadiene})Cl$[14] (**3**) and carbon monoxide (1 atm) in the presence of equimolar AgOTf. It is notable that the formal [4 + 4] cycloaddition proceeds between the coordinated butadiene and the second butadiene molecule with high periselectivity in the presence of carbon monoxide.



Similar reaction of $Cp^*Ru(\eta^4\text{-isoprene})Cl$ (**1c**) with excess isoprene in the presence of AgOTf, followed by carbon monoxide (1 atm), gave $[Cp^*Ru(\eta^2:\eta^2\text{-}cis\text{-3,7-dimethyl-1,5-cyclooctadiene})(CO)]OTf$ (**4a**) in 57% yield with high regioselectivity (heat–tail), periselectivity ([4 + 4]), and stereoselectivity (two methyl groups in cis geometry) (eq 2). The structure of **4a** was elucidated on the basis of ^1H and ^{13}C NMR spectral data, and their comparison with those of **2**, since suitable single crystals of **2** and **4a** for X-ray analysis have not been obtained. In the ^1H NMR spectrum of **4a**, the *cis*-3,7-dimethyl-1,5-cyclooctadiene ligand shows two nonequivalent sets of signals due to the $CH(CH_3)CH{=}CH$ framework; δ 1.20 (d) and 1.22 (d) for methyl groups, δ 2.88 and 3.19 for methyne multiplets, δ 4.04 (dd) and 4.12 (dd), as well as δ 4.39 (td) and 3.80 (td) for two kinds of vinyl protons. In addition, two methylene protons appeared as two multiplet signals at δ 1.66 and 2.44. These assignments were confirmed unequivocally by careful ^1H–^1H decoupling experiments.



It is quite important that the structural feature of the *cis*-3,7-dimethyl-1,5-cyclooctadiene ligand of **4a** is not identical to the known 1,5-dimethyl-1,5-cyclooctadiene ligand formed by direct [4 + 4] cyclodimerization of isoprene under nickel catalysis. These two C_{10} ligands

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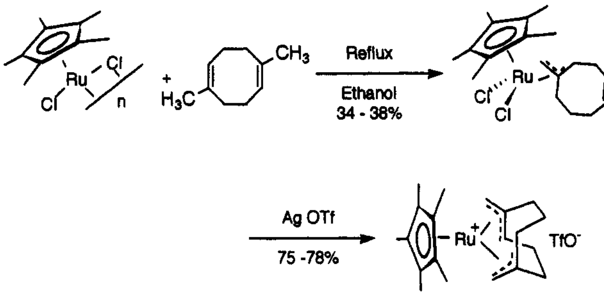
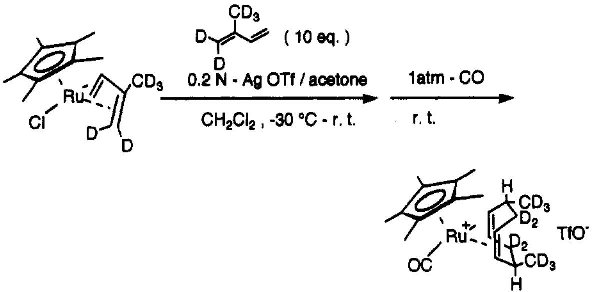
are double-bond isomers of each other, and mechanistic aspects for formation of **4a** will be discussed later in more detail.

In this context, we recently reported that $[Cp^*RuCl_2]_2$ and excess 1,5-dimethyl-1,5-cyclooctadene gave a bis(π-allyl)ruthenium(IV) complex by way of sequential C–H bond activation of exocyclic methyl groups (eq 3),[15] although the reaction of $[Cp^*RuCl_2]_2$ with 1,5-cyclooctadiene itself gave $Cp^*Ru(\eta^2{:}\eta^2$-1,5-cyclooctadiene)Cl (**3**) readily.[14] This difference suggests that it is difficult for the bulky Cp^*Ru^+ fragment to accept 1,5-dimethyl-1,5-cyclooctadiene in the usual $\eta^2{:}\eta^2$-mode in its coordination sphere.



(3)

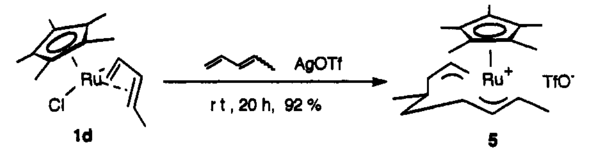
In order to understand the hydrogen migration process a deuterium-labeled experiment was undertaken by means of 2-(trideuteriomethyl)-1,1-dideuterio-1,3-butadiene. Isolated complex **4b** is a single isomer in which no deuterium atom migration takes place at all (eq 4), indicating that the 1,3-migration only occurs at the allylic positions located at the original 3,4-position of the isoprene molecule. The hydrogen migration process is closely related to the mechanism of C–C bond formation from an acyclic precursor; discussion on the mechanistic aspects will be provided in the last part.



(4)

4b

When $Cp^*Ru(\eta^4$-1,3-pentadiene)Cl (**1d**) was treated with excess 1,3-pentadiene in the presence of AgOTf at ambient temperatures, bis(π-allyl)ruthenium(IV) complex [Cp*Ru-(4-methyl-(1–3-η^3:6–8-η^3)-nonadienediyl)]OTf (**5**) was isolated as a single product, by regioselective tail–head dimerization (eq 5).



(5)

1d **5**

Table 1. Crystal Data for 5 and 8

	5	**8**
composition	$RuSF_3O_3C_{21}H_{31}$	$RuSF_3O_3C_{19}H_{27}$
fw	521.61	493.55
cryst color	yellow, plate	brown, plate
cryst dimens (mm)	0.40 × 0.40 × 0.30	0.30 × 0.25 × 0.10
cryst syst	orthorhombic	orthorhombic
space group	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)
cell const		
a (Å)	17.579(8)	18.903(5)
b (Å)	14.431(5)	8.872(2)
c (Å)	8.833(4)	12.211(3)
V (Å^3)	2240(2)	2047(1)
Z	4	4
diffractometer	Rigaku AFC5	Rigaku AFC7R
μ (cm^{-1})	8.17	9.10
radiation (Å)	Mo Kα av = 0.710 69	Mo Kα av = 0.710 69
2θ limits (deg)	5.0–50.0	4.0–55.0
no. of collected reflns	2277	2698
no. of unique rflns	1963 ($F_o \geq 3\sigma(F_o)$)	1079 ($F_o \geq 3\sigma(F_o)$)
R^a	0.0312	0.069
R'^b	0.0316	0.059
S^c	1.324	5.03

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R' = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [c] $S = [\sum w(|F_o| - F_c|)^2/(m - n)]^{1/2}$.

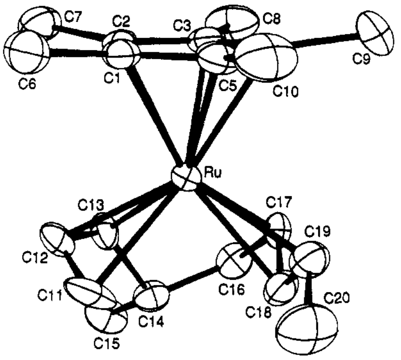


Figure 1. ORTEP view of **5** with ellipsoids drawn at the 30% probability level. All hydrogen atoms and the anion moiety are omitted.

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 5

Ru–C11	2.267(6)	Ru–C12	2.178(7)
Ru–C13	2.225(5)	Ru–C17	2.186(7)
Ru–C18	2.184(7)	Ru–C19	2.269(8)
C11–C12	1.44(1)	C12–C13	1.38(1)
C13–C14	1.51(1)	C14–C15	1.546(9)
C14–C16	1.52(1)	C16–C17	1.53(1)
C17–C18	1.39(1)	C18–C19	1.38(1)
C19–C20	1.52(1)		

C11–C12–C13	122.6(7)
C12–C13–C14	129.0(7)
C13–C14–C15	111.0(6)
C13–C14–C16	106.7(6)
C15–C14–C16	112.7(6)
C14–C16–C17	107.8(6)
C16–C17–C18	117.5(6)
C17–C18–C19	121.6(6)
C18–C19–C20	122.5(7)
Ru–C11–C12	67.8(5)
Ru–C13–C12	69.9(5)
Ru–C12–C11	74.5(5)
Ru–C12–C13	73.6(5)
Ru–C17–C18	71.4(4)
Ru–C19–C18	68.7(4)
Ru–C18–C17	71.6(4)
Ru–C18–C19	75.4(4)

We achieved an X-ray structure determination of **5**, and its crystal data are summarized in Table 1. The molecular structure is depicted in Figure 1, and selected bond lengths and bond angles are shown in Table 2. During our X-ray structure determination of **5**, at the final stage of refinement Chaudret *et al.* reported preliminary results on the formation of **5** from $[Cp^*Ru(OMe)]_4$ and 1,4-hexadiene

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[15] Itoh, K.; Masuda, K.; Ikeda, H. *Organometallics* **1993**, *12*, 2752.

Table 3. Catalytic Cyclodimerization of Butadiene with Cp*Ru$^{+\,a}$

entry	catalyst^b	solvent	temp (°C)	time (h)	yield (%)	products
1	**1b** + AgOTf	THF	70	10	89	1,5-COD
2	**1b** + AgOTf	CD_3COCD_3	80	7	59	1,5-COD^c
3	**1b** + AgOTf	CD_3COCD_3	60	48	73	1,5-COD^c
4	**1b** + AgOTf	CH_2Cl_2	80	7	13	1,5-COD
5	**1b** + AgOTf	none	60	1	2	1,5-COD^d

[a] Standard conditions: butadiene (2.0 mL, 24 mmol), **1b** (102 mg, 0.24 mmol), AgOTf (0.15 N diethyl ether solution, 2.0 mL, 0.30 mmol), solvent (5 mL). [b] Catalyst was prepared by the reaction of **1b** with AgOTf in situ. [c] Trace amounts of mesityl oxide and diacetone alcohol were confirmed as byproducts. [d] A small amount of chain C_8 was detected as a byproduct.

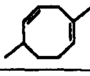
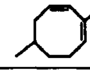
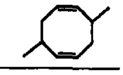
in 33% yield.[16] The ^1H and ^{13}C spectral data of **5** were fully consistent with Chaudret's results. It is evident from Figure 1 that the two allylic moieities are present in an endo–exo configuration relative to the Cp* ligand. Furthermore, one of the allylic parts, C11–C12–C13, contains an anti allylic C13–C14 bond, while the other, C17–C18–C19 contains two syn C–C bonds (C16 and C20 = CH_3).

The configuration of the $C_{10}H_{16}$ ligand strongly suggests that the originally coordinated cisoid 1,3-pentadiene ligand (C11–C15) formed a C–C bond (C14–C16) with the entering transoid 1,3-pentadiene (C16–C20) which had at first interacted with the less substituted vinyl moiety (C16–C17) in η^2-fashion. The entering transoid 1,3-pentadiene approaches in such a way that the methyl substituent (C20) is as remote as possible from the methyl group (C15) of the previously coordinated cisoid η^4-1,3-pentadiene ligand. This explanation accounts for the regioselectivity in the C–C bond formation between C14 and C16, as well as the endo–exo arrangement of the two allylic entities. It is important that bis(π-allyl) complex **5** did never convert into a ruthenium(II) cyclic diene complex related to **2** or **4** on treatment with carbon monoxide (1 atm). This suggests that [4 + 4] cyclic dimers are not always formed directly from the bis(π-allyl)ruthenium(IV) intermediates.

Furthermore, it becomes apparent that the formation of **5** depends largely on the stereochemistry of the 1,3-pentadiene employed. When a trans and cis mixture (1.6:1) of 1,3-pentadiene was employed in an excess amount, **5** was obtained in 95% yield as a single product. The same results were obtained with *trans*-1,3-pentadiene as a starting diene. On the contrary, the formation of **5** was completely inhibited in the case where *cis*-1,3-pentadiene was treated with **1d** and AgOTf at ambient temperatures. Therefore, the formation of **5** is initiated by stereoselective complexation of the *trans*-1,3-pentadiene.

Catalytic Dimerization of Conjugated Dienes. Above stoichiometric Cp*Ru$^+$-mediated dimerizations of butadiene, isoprene, and 1,3-pentadiene are found to proceed under catalytic conditions at higher temperatures. For instance, catalytic [4 + 4] cycloaddition of butadiene also takes place periselectively at 70 °C for 10 h in a THF–ether (5:2 volume ratio) mixed solvent by means of **1b** and AgOTf (each 1 mol %) as catalyst, and 1,5-cyclooctadiene was obtained in 89% yield based on charged butadiene (Table 3, entry 1). When acetone was present in the catalytic system, the yield of the cyclic diene was decreased to 59% (Table 3, entry 2). In such cases diacetone alcohol and mesityl oxide were formed as byproducts, indicative of the Cp*Ru$^+$ species being also an active catalyst to aldol condensation of acetone.

Table 4. Catalytic Cyclodimerization of Isoprene with Cp*Ru$^{+\,a}$

entry	temp (°C)	time (h)	yield (%)	isomer ratio (%) 	 	 
1	rt^b	2	7	67	0	33
2	rt	60	17	86	0	14
3	50	24	49	31	46	23
4	60	1		46	3	51
5	60	24	81	0	60	40
6	60	48	>95	0	48	52
7	70	25	>95	0	44	56
8	80	12	93	0	33	67
9	90	24	>95	0	21	79

[a] Standard conditions: 1,3-pentadiene (4.8 mL, 48 mmol), **1c** (87.2 mg, 0.24 mmol), AgOTf (0.15 N diethyl ether solution, 2.0 mL, 0.30 mmol), THF (5 mL). Trace amounts of 1,5-dimethyl-1,5-cyclooctadiene and 1,5-dimethyl-1,3-cyclooctadiene were confirmed as byproducts. [b] Room temperature.

In the case of isoprene, the peri- and regioselectivity of the cyclodimerization was maintained even under catalytic conditions (0.5 mol % of Cp*Ru$^+$ to the charged isoprene). Several double-bond isomers, however, were formed in a variety of ratios depending on reaction temperatures (Table 4). For example, the catalytic reaction at room temperature gave a mixture (67:33) of 2,6-dimethyl-1,4-cyclooctadiene and 3,7-dimethyl-1,5-cyclooctadiene (Table 4, entries, 1, 2; although these products were obtained in much lower yields). At elevated temperatures above 70 °C, 3,7-dimethyl-1,5-cyclooctadiene becomes the predominant product together with substantial amounts of a conjugated diene isomer, 2,6-dimethyl-1,3-cyclooctadiene (Table 4, entries 6–9). In addition, 1,5-dimethyl-1,5-cyclooctadiene and 1,5-dimethyl-1,3-cyclooctadiene were detected as byproducts in extremely small quantities in every case.

When one compares product ratios at 60 °C (Table 4, entries 4, 6), it is reasonable to conclude that initially produced 2,6-dimethyl-1,4-cyclooctadiene has isomerized to the more thermodynamically stable conjugated diene, 2,6-dimethyl-1,3-cyclooctadiene, by subsequent Cp*Ru$^+$-catalyzed hydrogen migrations. Consequently, the former 1,4-diene is definitely formed only under conditions of kinetic control. At elevated temperatures and for longer reaction times, the dimer mixture is composed of two thermodynamic products, 2,6-dimethyl-1,3-cyclooctadiene and 3,7-dimethyl-1,5-cyclooctadiene, in which the latter dimer is most stable under thermodynamic control and is identical to the cyclic dimer ligand in **4a** formed by stoichiometric reactions (eq 2).

Catalytic dimerization of 1,3-pentadiene (trans/cis = 1.6) took place in the presence of a catalyst composed of **1d** and AgOTf (0.5 mol %) in THF as shown in Table 5. It is important that a linear dimer, 6-methyl-2,4,7-nonatriene, was obtained selectively at 80 °C (Table 5, entry 2), whereas a complex mixture of linear dimer isomers was obtained in lower yield below 60 °C (Table 5, entry 1). It is surprising that stereochemically pure *cis*-1,3-pentadiene also furnished the same nonatriene in 78% yield (Table 5, entry 3), while *cis*-1,3-pentadiene has not proved to induce C–C bond formation to form **5** under stoichiometric conditions at lower temperatures as discussed previously. This difference is explained in terms of catalytic cis–trans isomerization of 1,3-pentadiene

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[16] Carreno, R.; Chaudret, B.; Labroue, D.; Sabo-Etienne, S. *Organometallics* **1993**, *12*, 13.

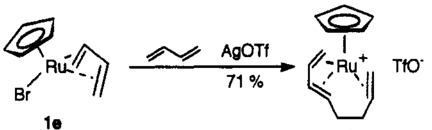
Table 5. Catalytic Linear Dimerization of 1,3-Pentadiene with Cp*Ru$^+$ [a]

entry	substrate	temp (°C)	time (h)	yield (%)	products
1	trans/cis = 1.6	60	96	61	mixture of linear C_{10} dimers
2	trans/cis = 1.6	80	48	95	6-methyl-2,4,7-nonatriene
3	cis	80	48	78	6-methyl-2,4,7-nonatriene

[a] Standard conditions: 1,3-pentadiene (4.8 mL, 48 mmol), **1c** (87.2 mg, 0.24 mmol), AgOTf (0.15 N diethyl ether solution, 2.0 mL, 0.30 mmol), THF (5 mL).

taking place at 80 °C under Cp*Ru$^+$ catalysis. Such isomerization of 1,3-pentadiene was observed by Crocker and co-workers, and they explained it to proceed through an (η^3-allyl)hydridoruthenium intermediate.[17]

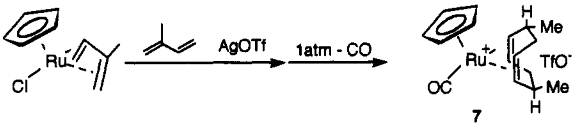
Stoichiometric and Catalytic Reaction of CpRu(η^4-diene)$^+$ with Conjugated Dienes (Diene = Butadiene, Isoprene, and 1,3-Pentadiene). In order to elucidate the role of the auxiliary ligand in the stoichiometric and catalytic dimerization of conjugated dienes, a less bulky and less electron-donating ligand, η^5-C_5H_5 (Cp), was employed. Treatment of CpRu(η^4-butadiene)Br (**1e**) and butadiene in the presence of AgOTf afforded selectively [CpRu(η^4:η^2-1,3,7-octatriene)]OTf (**6**) composed of two butadiene molecules (eq 6). In the presence of carbon monoxide, complex **6** did not give the 1,5-cyclooctadiene ligand at all. This is quite different from the formation of **2** in the case of the Cp*Ru$^+$ system. Such a difference is considered to be reasonable if the stereochemistry of the C_8 ligand of **6** is different from that of the corresponding octatriene intermediate in the case of the Cp* homologue. The geometrical difference of the C3–C4 double bond in the 1,3,7-octatriene ligands complexed to CpRu$^+$ (*trans* in **6**) and the Cp*Ru$^+$ (*cis* in **8**) fragments will be discussed in the following part on the dimerization mechanism.



1e **6**

(6)

Alternatively, when isoprene was used in the CpRu$^+$ system, a complex mixture of several cationic ruthenium compounds was obtained, and its carbonylation gave [CpRu(η^2:η^2-*cis*-3,7-dimethyl-1,5-cyclooctadiene)(CO)]-OTf (**7**) as the main product in 55% yield (eq 7). The structure of **7** can be readily elucidated by comparing its ^{1}H NMR spectra with that of **4a**. The cyclic diene ligand is identical to the previously discussed **4a**. The reaction of CpRu(η^4-1,3-pentadiene)Br (**1g**) with 1,3-pentadiene was quite nonselective and produced a mixture composed of several intractable products, the structures of which could not be determined.



7

(7)

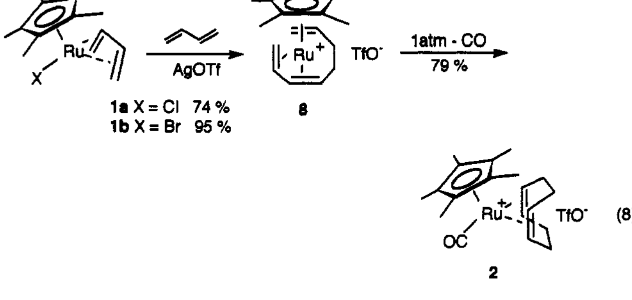
The catalytic potential of **6** as a CpRu$^+$ equivalent was assessed in the catalytic oligomerization of butadiene, isoprene, and 1,3-pentadiene. Results are summarized in Table 6. It is important that catalytic oligomerization of butadiene gave a mixture of C_{12} linear products by means of **6** as catalyst (1 mol %), as well as small amounts of C_8 and C_{16} oligomers. Isolated C_{12} trimers were identified to be 1,5,7,11-dodecatetraene and 1,3,7,11-dodecatetraene on the basis of their ^{1}H and ^{13}C NMR spectra.

Alternatively, CpRu$^+$-catalyzed oligomerization of isoprene affords 2,7-dimethyl-2,4,6-octatriene as a linear dimer of tail–tail coupling and 3,7-dimethyl-1,3-cyclooctadiene in the ratio of 13:87 at 50 °C (Table 6, run 4). At higher temperatures, regioisomeric 3,6-dimethyl-1,3-cyclooctadiene appeared as a minor tail–tail cyclic dimer (Table 6, run 5). It is worthwhile to note that the main product of the CpRu$^+$ system, 3,7-dimethyl-1,3-cyclooctadiene, was a minor product in the case of the Cp*Ru$^+$ system under thermodynamic control (Table 4, runs 8, 9).

It is also important that both 3,6-dimethyl-1,5-cyclooctadiene and 2,7-dimethyl-2,4,6-octatriene, produced in CpRu$^+$-catalyzed dimerization of isoprene, were tail–tail dimers. Thus the regioselectivity of the CpRu$^+$ catalyst is much worse than that of Cp*Ru$^+$, which furnished head–tail isomers with complete regioselectivity as shown in Table 4. We can conclude that the Cp* ligand is superior to the Cp one because of the extremely high regio- and periselectivity of catalytic [4 + 4] cyclodimerization of the former. This regioselectivity is contrary to Allegra's finding tht the stoichiometric formation of tail–tail linear dimerization took place by means of a "$RuCl_2$" species generated from alcoholic $RuCl_3$ with isoprene.[7] These comparisons suggest that the regioselectivity of cyclodimerization may be controlled by selecting auxiliary ligands in isoprene oligomerizations. Cp or Cp* ligands can make the simplest intermolecular [4 + 4] cycloaddition possible by means of a second-row ruthenium catalyst.

In the case of 1,3-pentadiene, the products were 4-methyl-1,5,7-nonatriene and 4-methyl-1,3,7-nonatriene in a 24:76 ratio at 50 °C for 42 h. Both C_{10} trienes were regioselective head–tail coupling products of 1,3-pentadiene, although the positions of the double bonds were different from those in the products with Cp*Ru$^+$ at 90 °C. In this context, Trost *et al.* reported recently a catalytic cross linear dimerization between 1-alkenes and 1-alkynes by means of CpRu(COD)Cl as catalyst at 100 °C.[18]

Dimerization Mechanism of Conjugated Dienes. When the reaction of Cp*Ru(η^4-butadiene)Cl (**1a**) with butadiene (eq 1) was not terminated by carbon monoxide, a quite labile octatriene complex, [Cp*Ru(η^4:η^2-1,3,7-octatriene)]OTf (**8**), was isolated in 74% yield (eq 8). This labile octatriene complex (**8**) was characterized by ^{1}H and ^{13}C NMR and elemental analysis. In solution **8** was quite



1a X = Cl 74 %
1b X = Br 95 %
8
2

(8)

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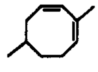
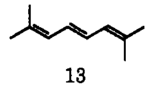
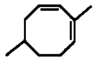
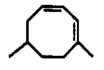
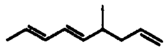
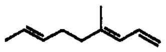
[17] Crocker, M.; Green, M.; Morton, C. E.; Nagle, K. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 2145. Crocker, M.; Green, M.; Nagle, K. R.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 2571. The other process, an "envelope flip" mechanism, on the CpMo complex has been reported: Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858.

[18] Trost, B. M.; Indolese, A. *J. Am. Chem. Soc.* **1993**, *115*, 4361.

Table 6. Catalytic Dimerization of Conjugated Dienes by Means of CpRu$^+$ [a]

entry	diene	temp (°C)	time	solvent	yield (%)	product
1	butadiene	60	4 d	CH_2Cl_2	92	C_8, C_{12}, and C_{16} mixtures[b]
2	butadiene	60	10 h	CH_2Cl_2	32	C_8, C_{12}, and C_{16} mixtures[b]
3	butadiene	40	3 d	CH_2Cl_2	16	C_8, C_{12}, and C_{16} mixtures[b]
4	isoprene	50	42 h	THF	95	  87 : 13
5	isoprene	90	15 h	THF	95	  65 : 35
6	1,3-pentadiene	50	42 h	THF	97	  24 : 76

[a] Entries 1–3 employed 1 mol % of **6** as catalyst, and entries 4–6 employed 0.5 mol % of [CpRu(diene)]OTf complex prepared from the corresponding diene complex and AgOTf in situ. [b] C_{12} tetraenes are major products with small amounts of C_8 and C_{16} linear oligomers.

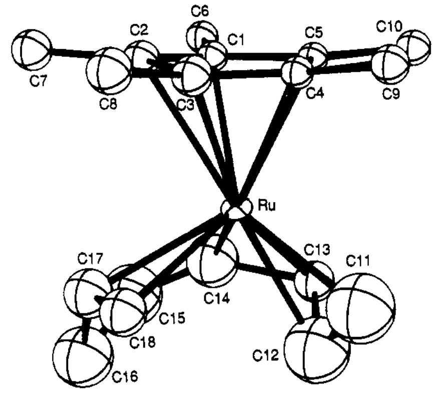


Figure 2. ORTEP view of **8** with ellipsoids drawn at the 30% probability level. The anion moiety is omitted.

Table 7. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 8

Ru–C11	2.19(6)	Ru–C12	2.23(6)
Ru–C13	2.24(3)	Ru–C14	2.27(5)
Ru–C17	2.29(4)	Ru–C18	2.18(3)
C11–C12	1.44(7)	C12–C13	1.51(7)
C13–C14	1.54(6)	C14–C15	1.34(6)
C14–C16	1.45(7)	C16–C17	1.57(6)
C17–C18	1.36(5)		

C11–C12–C13	115(5)
C12–C13–C14	109(4)
C13–C14–C15	147(5)
C14–C15–C16	112(5)
C15–C16–C17	100(3)
C16–C17–C18	133(4)
Ru–C11–C12	72(3)
Ru–C12–C11	69(3)
Ru–C12–C13	70(2)
Ru–C13–C12	69(2)
Ru–C13–C14	71(2)
Ru–C14–C13	68(2)
Ru–C17–C18	76(2)
Ru–C18–C17	67(2)

unstable (completely decomposed in chloroform within 20 h at 22 °C). Comparison of the coupling constants of the diene part in the Cp*Ru(η^4:η^2-octatriene) complex (**8**) with those in the Cp analogue (**6**) indicates a substantial difference in stereochemistry at the C3–C4 position of 1,3,7-octatriene ligands. In Cp*Ru(η^4:η^2-octatriene) (**8**) the configuration of C3–C4 double bond is concluded to be cis, while in the Cp analogue (**6**) the configuration is trans on the basis of J(H3–H4) coupling constants; J(H3–H4) for **8** (δ 5.01) was measured to be 8.5 Hz, while that for **6** (δ 6.07) was 11.6 Hz. Accordingly, it is reasonable to assume that the two terminal carbon atoms, C1 and C8, in the *cis*-1,3,7-octatriene ligand of **8** can be quite close to each other in the Cp* case. Such proximity in **8** is responsible for the selective cyclization to the eight-membered ring.

In addition, we have attempted X-ray analyses of [Cp(η^4:η^2-octatriene)]OTf (**6**) and [Cp*Ru(η^4:η^2-octatriene)]OTf (**8**) several times. Regretfully, all attempts to solve the structure of [Cp(η^4:η^2-octatriene)]OTf (**6**) have been unsuccessful because a high degree of disorder was present for both the triflate anion and the Cp ligand in **6**. On the other hand, instability of [Cp*Ru(η^4:η^2-octatriene)]OTf (**8**) in solution causes serious problems in recrystallization to obtain good crystals for X-ray structure determination, since the crystallization competes every time with rapid decomposition. Although collection of enough data points was difficult because of poor crystallinity, we finally obtained the molecular structure of **8** as depicted in Figure 2 and Tables 1 and 7.

The structure of the (3,4-*cis*-octatriene)ruthenium(II) complex **8** indicates that the main structural features of the second transoid diene (C11–C14; Figure 2) are maintained. The octatriene complex **8** is considered to be formed by way of hydrogen migration from carbon 4 (C14) to the internal carbon 6 (C16) from its bis(π-allyl)ruthenium(IV) precursor. An excellent model of the bis(π-allyl)ruthenium(IV) precursor is the previously discussed complex **5**. The structure of **5**, shown in Figure 1, suggests unequivocally that the carbon–carbon bond formation took place between the initially coordinated cisoid *exo*-diene and the second 1,2-η^2-diene having transoid geometry with retention of original coordination geometry.

Formation of cyclic dimers or trimers with low-valent transition metal complexes has long been interpreted in terms of C–C bond forming reductive elimination directly from key bis-allylic intermediates since elegant investigation on bis(allyl)nickel complexes by Wilke and his coworkers.[2] Although this mechanism is definitely operative particularly in the case of homogeneous catalysis consisting of the first-row transition elements, present results suggest another mechanistic possibility, that the second-stage C–C bond formation to furnish cyclic products can take place from a transition metal mediated electrocyclization of a low-valent η^6-triene complex which is formed by 1,3-

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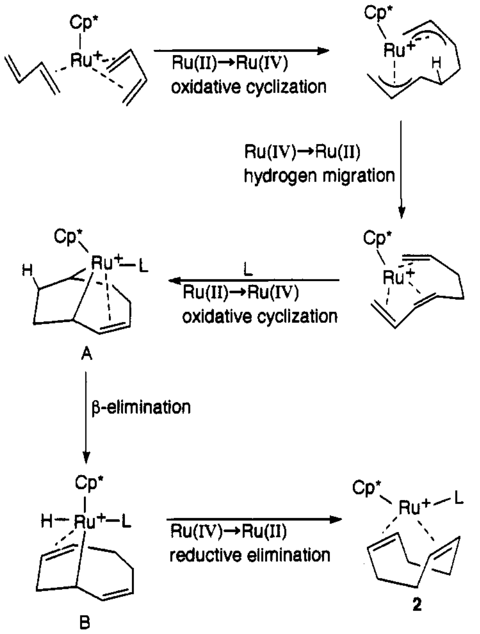
(19) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

Scheme 1



hydrogen migration (C4 → C6) from a bis(π-allyl)ruthenium(IV) complex similar to **5**.

In the case of the butadiene–Cp*Ru$^+$ system, the most probable pathway for cyclic products is intramolecular metallacycle formation (oxidative cyclization) as exemplified in Scheme 1. Coupling of the C1 and C8 terminal carbon atoms gives rise to 9-ruthenal(IV)bicyclo[4.2.1]-2-nonene (**A**), which induces β-elimination of the C6–H bond to give a cationic (diene)hydridoruthenium(IV) species (**B**). Spontaneous C–H-bond-forming reductive elimination at the C4 position may furnish the observed (1,5-cyclooctadiene)carbonylruthenium(II) product (**2**; L = CO).

All steps of the previously discussed deuterium-labeled experiment in the case of isoprene dimerization (eq 4) are reasonably explained by a similar mechanism depicted in Scheme 2. First-stage C–C bond formation between η^4-*exo*-isoprene and the entering η^2-transoid diene results in the formation of an *endo,exo*-bis(η^3-allyl) intermediate in regioselective fashion (head–tail coupling), from which a hydrogen atom at the C4 position migrates to the C6 carbon via ruthenium(IV) hydride. At this point, the generated 1,3,7-octatriene ligand is forced to adopt a cis configuration at the C3–C4 bond, since room for the octatriene ligand is quite limited by steric congestion caused by five methyl substituents on the Cp* ligand.

Second-stage C–C bond formation thus occurs between terminal carbon atoms in a manner analogous to the butadiene dimerization (Scheme 1). The final ligand structure, 3,7-dimethyl-1,5-cyclooctadiene, was formed by hydrogen migration through a (3-η^1:6-η^1:1,2-η^2)-cyclooctadiene intermediate by the sequence of steps shown. As every migration of hydrogen atoms takes place at the front side of the metal center, the final hydrocarbon ligand should have stereospecific *cis*-dimethyl substituents in the final dimethylcyclooctadiene ligand.

In the catalytic reaction of isoprene, formation of the tail–head dimer products, 3,7-dimethyl-1,5-cyclooctadiene, 2,6-dimethyl-1,4-cyclooctadiene, and 2,6-dimethyl-1,3-cyclooctadiene, was explained in terms of the above metallacycle intermediate complex as a key intermediate (Scheme 3). 1,5-Diene, 1,4-diene, and 1,3-diene were formed from activation of C1-hydrogen, C2-hydrogen, and C3-hydrogen, respectively. At lower temperatures, 1,4-diene was kinetically dominant, since a more crowded C–H bond (C3) was activated. At higher temperatures, the thermodynamically less stable 1,4-diene was coordinated again, and repeated hydrogen migrations by way of the key metallacycle intermediate gave more stable 1,3- and 1,5-dienes as isomerization products. Finally at 90 °C, the most thermodynamically stable 1,5-diene became the dominant product. In summary, the 1,4-diene was the kinetic product, whereas the 1,5-diene was the thermodynamic one.

In the case of 1,3-pentadiene, hydrogen migration does not occur from bis(allyl)ruthenium(IV) complex **5** even by the assistance of CO at ambient temperature, because of enhanced conformational rigidity due to the presence of two methyl substituents on the 4-methylnona-(1-3-η^3:6-8-η^3)-bis(enyl) ligand. Under catalytic conditions at higher temperatures, one of the dienylic C–H bonds is simply activated more readily than cyclization, which is substantially blocked by a methyl group present at the coupling position, to finalize as a linear dimer, 6-methyl-2,4,7-nonatriene.

Experimental Section

General Remarks. All reactions were carried out under a dinitrogen stream. Ruthenium trichloride hydrate was purchased from NE Chemcat Corp. Trans and cis mixtures of 1,3-pentadiene and silver trifluoromethanesulfonate were purchased from Aldrich Chemical Company, Inc., and isoprene and *cis*-1,3-pentadiene were purchased from Tokyo Kasei Co., LTD. Butadiene and carbon monoxide were supplied from Seitetsu Kagaku and Nippon Sanso, respectively. Dichloromethane was dried over phosphorus pentoxide and stored under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-270 spectrometer. Elemental analyses were achieved at the Microanalysis Center of Kyoto University or determined by a YANAKO CHN Corder. IR spectra were measured with a JASCO A-3 spectrometer. Deuterated isoprene was prepared by the reaction of acetone-d_6 with vinyl Grignard reagent followed by sulfuric acid, which was a modification of a reported method.[20] Cp*Ru(diene)X and CpRu(diene)Br (**1a–g**) were made by our reported method.[10,11]

Synthesis of [Cp*Ru(η^2:η^2-1,5-cyclooctadiene)(CO)]OTf (2). Compound **1a** (110 mg, 0.316 mmol) was placed in a 30-mL round-bottomed flask with a stirring bar under an argon atmosphere. Dichloromethane (20 mL) was added, and the flask was cooled to −25 °C. An acetone solution (0.2 N) of silver triflate (2.2 mL, 0.440 mmol) and liquid butadiene (2 mL, 24 mmol) was added with magnetic stirring. The reaction temperature was raised to room temperature for 60 min, and the atmosphere was changed to carbon monoxide (1 atm). After being stirred overnight, the reaction mixture was concentrated under reduced pressure. The residue was washed with Et$_2$O and dissolved with dichloromethane. This solution was filtered with Celite. The filtrate was concentrated under reduced pressure to give the title complex as pale yellow powder in quantitative yield (159.7 mg).

The other procedure to prepare this complex is described below. To a stirred solution of Cp*Ru(1,5-cyclooctadiene)Cl (**3**, 30 mg, 0.0791 mmol) in dichloromethane (3 mL) was added an acetone solution (0.2 N) of silver triflate (0.475 mL, 0.0949 mmol), and the atmosphere was changed to carbon monoxide (1 atm). The reaction mixture was treated with a procedure similar to that described above, and complex **2** was obtained in 61.9% yield.

^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ 1.91 (15H, s, Me of Cp*), 2.25 (4H, m, =CHCH_2), 2.46 (4H, m, =CHCH_2), 4.14 (2H, m,

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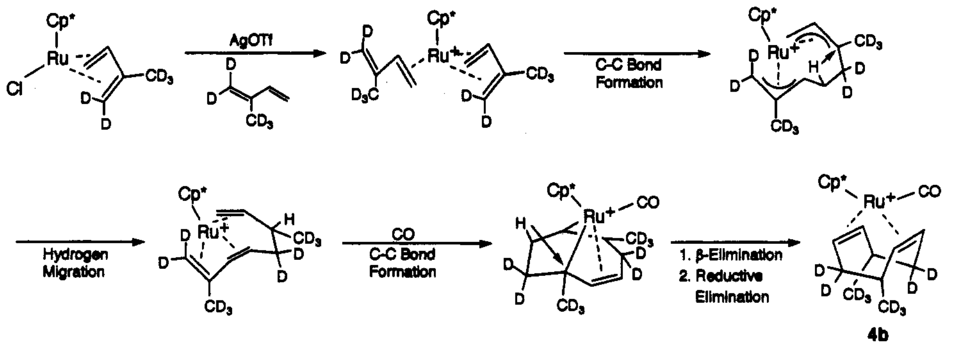
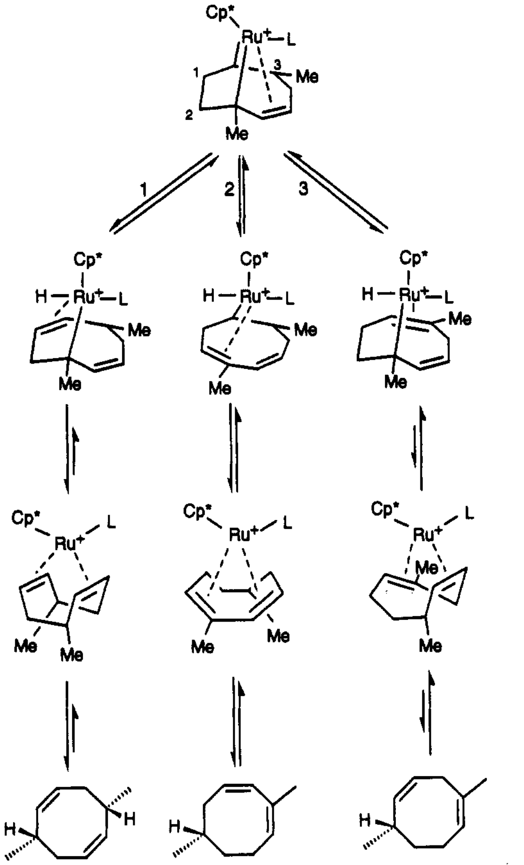
(20) Oliver, G.; Becker, E. I. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. IV, pp 771.

Scheme 2



Scheme 3



C*H*=CH), 4.34 (2H, m, C*H*=CH). ^{13}C NMR (67.8 MHz, CDCl$_3$): δ 9.9 (Me of Cp*), 28.6 (=CH*C*H$_2$), 29.5 (=CH*C*H$_2$), 87.3 (*C*H=CH), 91.9 (*C*H=CH), 99.5 (Cp* ring), 209.8 (CO). IR: 1980, 1450, 1265, 1132, 1018, 625 cm^{-1}. Anal. Calcd for $C_{20}H_{27}O_4SF_3Ru$: C, 46.06; H, 5.22. Found: C, 45.96; H, 5.34. Mp: 205.5–206 °C dec.

Synthesis of [Cp*Ru(η^2:η^2-3,7-dimethyl-1,5-cyclooctadiene)(CO)]OTf (4). The procedure was similar to that described above for the synthesis of **2**. The reaction was performed using Cp*Ru(isoprene)Cl (**1b**, 141.7 mg, 0.391 mmol), silver triflate (1.2 equiv), and isoprene (0.39 mL, 3.91 mmol) in dichloromethane (4 mL) for 25 min, −30 °C to room temperature. Carbon monoxide (1 atm) was introduced to the reaction mixture for 15 min. Removal of solvent gave the title complex (**4a**, 121.5 mg, 56.6% yield) as pale yellow powder.

^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ 1.20 (3H, d, *J* = 1.71 Hz, =CHCH(*Me*)), 1.22 (3H, d, *J* = 1.71 Hz, =CHCH(*Me*)), 1.66 (2H, m, =CH$_2$C*H*$_2$), 1.88 (15H, s, Cp*), 2.44 (2H, m, =CH$_2$C*H*$_2$), 2.88 (1H, m, =CHC*H*(Me)), 3.19 (1H, m, =CHC*H*(Me)), 3.80 (1H, td, *J* = 6.35, 9.28 Hz, C*H*=CHCH(Me)), 4.04 (1H, dd, *J* = 5.13, 9.28 Hz, CH=C*H*CH(Me)), 4.12 (1H, dd, *J* = 5.13, 9.28 Hz, CH=C*H*CH(Me)), 4.39 (1H, td, *J* = 6.35, 9.28 Hz, C*H*=CHCH(Me)). ^{13}C NMR (67.8 MHz, CDCl$_3$): δ 9.5 (q, *J* = 129 Hz, Cp*), 19.9 (q, *J* = 129 Hz, =CHCH(*Me*)), 20.3 (q, *J* = 129 Hz, =CHCH(*Me*)), 31.0 (t, *J* = 132 Hz, =CH$_2$*C*H$_2$), 31.8 (t, *J* = 132 Hz, =CH$_2$*C*H$_2$), 40.8 (d, *J* = 134 Hz, =CH*C*H(Me)), 42.2 (d, *J* = 129 Hz, =CH*C*H(Me)), 85.8 (d, *J* = 178 Hz, *C*H=CH), 88.2 (d, *J* = 183 Hz, *C*H=CH), 88.8 (d, *J* = 164 Hz, *C*H=CH), 96.9 (d, *J* = 156 Hz, *C*H=CH), 99.1 (s, Cp*), 209.8 (s, CO). IR: 1995, 1270, 1140, 1030, 635 cm^{-1}. Anal. Calcd for $C_{22}H_{31}O_4SF_3Ru$: C, 48.08; H, 5.69. Found: C, 47.81; H, 5.52. Mp: 210.5–218 °C dec.

The procedure for Cp*Ru(isoprene-*d*$_5$)Cl and deuterated isoprene was similar to that described above. The reaction was performed using Cp*Ru(isoprene-*d*$_5$)Cl (101 mg, 0.294 mmol), silver triflate (0.353 mmol), and isoprene-*d*$_5$ (2.94 mmol) in dichloromethane (15 mL), followed by carbon monoxide (1 atm). Complex **4b** was isolated in 71.2% yield.

^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ 1.66 (2H, m, =CH$_2$C*H*$_2$), 1.88 (15H, s, Cp*), 2.88 (1H, m, =CHC*H*(Me)), 3.19 (1H, m, =CHC*H*(Me)), 3.80 (1H, td, *J* = 6.35 Hz, 9.28 Hz, C*H*=CHCH(Me)), 4.04 (1H, dd, *J* = 5.13 Hz, 9.28 Hz, CH=C*H*(Me)), 4.12 (1H, dd, *J* = 5.13, 9.28 Hz, CH=C*H*CH(Me)), 4.39 (1H, td, *J* = 6.35, 9.28 Hz, C*H*=CHCH(Me)); ^{2}H NMR (41.3 MHz, CHCl$_3$): broad peaks appeared at 1.20–1.22, 1.66, and 2.44 ppm corresponding to ^{1}H NMR of **4a**.

Synthesis of [Cp*Ru(4-methyl-(1–3-η^3:6-8-η^3)-nonadienyl)]OTf (5). To a stirred solution of Cp*Ru(1,3-pentadiene)Cl (**1d**, 20 mg, 0.054 mmol) in 5 mL of dichloromethane at −30 °C was added an acetone solution (0.2 N) of silver triflate (0.75 mL, 0.15 mmol). After stirring for 15 min, the disappearance of the starting complex was confirmed by way of TLC. Then the reaction temperature was raised to 0 °C, 1,3-pentadiene (0.027 mL, 0.27 mmol) was added to this reaction mixture, and the mixture was stirred for 15 min at 0 °C. The mixture was stirred further at room temperature for 22 h. The solvent was removed under reduced pressure. The residue was washed with ether and filtered with Celite to remove silver chloride. Recrystallization (CH$_2$Cl$_2$–ether) gave **5** (26 mg, 91.7% yield).

^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ 1.16 (3H, d, *J* = 5.86 Hz, CH(*Me*)), 1.51 (1H, m, =CC*H*(Me)C=), 1.71 (15H, s, Cp*), 1.96 (3H, d, *J* = 5.86 Hz, =CH=CH(*Me*)), 2.35 (1H, m, CH(Me)C*H*H′CH=), 2.45 (1H, d, *J* = 12.21 Hz, =CH=C*H*$_{\text{anit}}$H), 2.74 (1H, dd, *J* = 4.88, 15.13 Hz, CH(Me)CH*H*′CH=), 2.99 (1H, m, CH=C*H*(Me)), 3.01 (1H, d, *J* = 5.86 Hz, =CH=CH*H*$_{\text{syn}}$), 3.18 (2H, m, CH$_2$C*H*=CH=, CH=C*H*=CH$_2$), 3.60 (1H, t, *J* = 10.26 Hz, CH=C*H*=CH(Me)), 3.94 (1H, t, *J* = 8.79 Hz, CH(Me)C*H*=CH=). ^{13}C NMR (67.8 MHz, CDCl$_3$): δ 9.1 (q, *J* = 129 Hz, Me of Cp*), 18.4 (q, *J* = 129 Hz, CH(*Me*)), 21.4 (d, *J* = 125 Hz, =CH=CH(*Me*)), 35.0 (d, *J* = 131 Hz, *C*H(Me)), 45.9 (t, *J* = 125 Hz, CH(Me)*C*H$_2$CH=), 57.9 (t, *J* = 161 Hz, CH=CH=*C*H$_2$), 74.1 (d, *J* = 151 Hz, *C*H=CH=), 90.3 (d, *J* = 162 Hz, CH=CH=*C*H(Me)), 93.4 (d, *J* = 141 Hz, CH=*C*H=), 98.5 (d, *J* = 155 Hz, CH=*C*H=), 102.4 (s) and one allyl inert terminal (*C*H=CH=) was buried solvent peaks. IR: 1257, 1164, 1030 cm^{-1}. Anal. Calcd for $C_{21}H_{31}O_3SF_3Ru$: C, 48.36; H, 5.99. Found: C, 47.89; H, 5.88. Mp: 221 − 224 °C dec.

Synthesis of [CpRu(η^4:η^2-1,3,7-octatriene)]OTf (6). In a 20-mL round-bottomed flask were placed the butadiene–bromoruthenium complex (**1e**, 28.6 mg, 0.093 mmol) and dichlo-

Table 8. Chemical Shift Values for the Oligomers

	^{1}H NMR (ppm)			
oligomer	CH_3	CH_2	CH	=CH
1,5-cyclooctadiene		2.40 (8H)		5.55 (4H)
3,7-dimethyl-1,5-cyclooctadiene	1.01 (6H, d)	2.09–2.10 (2H, m), 2.27–2.33 (2H, m)	2.93 (2H, m)	5.30 (2H, m), 5.48 (2H, m)
2,6-dimethyl-1,4-cyclooctadiene	1.00 (3H, d), 1.72 (3H, s)	1.48 (2H, m), 1.94 (2H, m), 2.49–2.75 (2H, m)	2.82 (1H, m)	5.06 (1H, t), 5.21 (1H, t), 5.64 (1H, m)
2,6-dimethyl-1,3-cyclooctadiene	1.02 (3H, d), 1.76 (3H, s)	1.25 (2H, m), 1.46–1.66 (2H, m), 1.98–2.24 (2H, m)	−2.24 (1H, m)	5.26 (1H, t), 5.63 (1H, d), 5.69 (1H, t)
1,5-dimethyl-1,5-cyclooctadiene	1.67 (3H, s)	2.28–2.34 (8H, m)		5.34 (2H, t)
1,5-dimethyl-1,3-cyclooctadiene	1.01 (3H, d), 1.75 (3H, s)	2.10 (4H, m), 2.21 (2H, m)	2.92 (1H, m)	5.46 (1H, d), 5.52 (1H, d), 5.80 (1H, m)
6-methyl-2,4,7-nonatriene	1.0 (3H, d), 1.6 (3H, d), 1.7 (3H, d)		2.8 (1H, m)	5.4 (2H, m), 5.5 (1H, dd), 5.6 (1H, dd), 5.9–6.0 (2H, m)
2,7-dimethyl-2,4,6-octatriene	1.74 (6H, s), 1.76 (6H, s)			5.86 (2H, d), 6.27 (2H, dd)
1,6-dimethyl-1,3-cyclooctadiene	0.90 (3H, d), 1.72 (3H, s)	1.2–1.4 (1H, m), 1.8–2.0 (2H, m), 2.0–2.2 (2H, m), 2.2–2.4 (1H, m)	1.6–1.7 (1H, m)	5.42 (1H, dd), 5.63 (1H, dd), 5.72 (1H, d)
4-methyl-1,3,7-nonatriene	1.62 (3H, s), 1.71 (3H, d)	2.06–2.19 (4H, m)		5.38 (1H, m), 5.40 (2H, m), 5.57 (1H, m), 5.97 (1H, dd), 6.32 (1H, dd)
4-methyl-1,5,7-nonatriene	1.00, 1.71	1.97=2.12 (2H, m)	2.15–2.33 (1H, m)	4.98 (2H, m), 5.38 (1H, m), 5.54 (1H, q), 5.75 (1H, m), 5.96 (1H, q), 6.29 (1H, dd)

romethane (9.0 mL). The flask was put into an acetone–dry ice bath kept at −30 °C. To this solution was added a diethyl ether solution (0.15 N) of silver triflate (0.76 mL, 0.114 mmol). The mixture was stirred for 10 min at this temperature. The reaction mixture was concentrated under reduced pressure at −10 °C or below. The residue was washed with diethyl ether (5 mL, three times). Concentration of the filtrate combined with a washing solution under reduced pressure gave CpRu(butadiene)OTf (32 mg, 90.9%). In a 20-mL round-bottomed flask were placed this butadiene–ruthenium triflate complex (8.5 mg, 0.023 mmol) and acetone (5.0 mL). The flask was put in an acetone–dry ice bath and cooled to −25 °C. In this solution was dissolved a 1,3-butadiene (0.86 mL at 25 °C, 0.035 mmol). The mixture was stirred for 1 h, and the temperature was slowly raised to ambient temperature. The reaction mixture was filtered through a Celite band. Removal of the solvent under reduced pressure gave the title complex (**6**, 9.5 mg, 97.8%) as yellow crystals.

^{1}H NMR (270 MHz, CD_3COCD_3): δ 1.39 (1H, m, CH_2=CH-C*H*H′), 2.04 (1H, m, CH_2=CHCH*H′*), 2.53 (1H, d, *J* = 12.9 Hz, CH_2CH=CHH_{anti}), 2.64–2.78 (1H, m, CH=CHCH*H′*), 2.86–2.99 (1H, m, CH=CHC*H*H′), 2.95 (1H, dd, *J* = 7.9, 11.6 Hz, =CH-C*H*=C), 3.92 (1H, d, *J* = 11.2 Hz, CH_{anti}H=CC=), 4.01 (1H, d, CH_{syn}H=CHCH_2), 4.05 (1H, d, *J* = 6.5 Hz, CH_{syn}H=CC=), 4.71 (1H, m, CH_2=C*H*CH=), 5.29 (1H, m, CH_2=C*H*C), 5.70 (5H, s, Cp), 6.07 (1H, m, CH_2=CHCH=C*H*). ^{13}C NMR (67.8 MHz, CD_3COCD_3): δ 29.7 (C6), 40.8 (C5), 50.3 (C1), 56.6 (C8), 81.6 (C2), 83.6 (C7), 85.5 (C4), 91.5 (Cp), 98.1 (C3). IR: 1265, 1150, 1018, 625 cm^{-1}. Anal. Calcd for $C_{14}H_{17}O_3SF_3Ru$: C, 39.71; H, 4.05. Found: C, 38.96; H, 3.91. Mp: 152–153 °C dec.

Synthesis of [Cp*Ru(η^4:η^2-1,3,7-octatriene)]OTf (8). The procedure for the reaction was similar to that described above. Cp*Ru(butadiene)Cl (**1a**, 50 mg, 0.133 mmol), silver triflate (1.2 equiv), and liquid butadiene (2 mL, 24 mmol) in dichloromethane gave the octatriene complex in 73.5% yield. Alternatively, when Cp*Ru(butadiene)Br (**1b**) was used, the octatriene complex was obtained in better yield (96.4%).

^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 1.77 (15H, s, Cp*), 2.01 (2H, m, CH_{anti}H=CC=, CH_2CH=CHH_{anti}), 2.52 (1H, d, *J* = 8.30 Hz, CH_{syn}H=CHCH_2), 2.71 (1H, m, CH_2=CHC*H*H′), 3.01 (2H, m, CH=CHCH_2), 3.30 (1H, t, *J* = 8.30 Hz, CH_2=CHC*H*=C), 3.33 (1H, m, CH_2=C*H*CH=), 3.85 (1H, m, CH_2=CHCH*H′*), 4.26 (1H, m, CH_2=C*H*CH_2), 4.27 (1H, d, *J* = 6.35 Hz, CH_{syn}H=CC=), 5.01 (1H, m, CH_2=CHCH=C*H*). ^{13}C NMR (67.8 MHz, CD_3COCD_3, 0 °C): δ 9.2 (q, *J* = 128 Hz, Me of Cp*), 36.9 (t, *J* = 130 Hz, C5), 38.1 (t, *J* = 130 Hz, C6), 62.2 (t, *J* = 156 Hz, C8), 67.4 (t, *J* = 164 Hz, C1), 89.7 (d, *J* = 153 Hz, C2), 90.1 (d, *J* = 156 Hz, C7), 97.7 (d, *J* = 164 Hz, C3), 101.6 (s, ring of Cp*), 104.7 (d, *J* = 144 Hz, C4). IR: 1270, 1145, 1030, 635 cm^{-1}. Anal. Calcd for $C_{19}H_{27}O_3SF_3Ru$: C, 46.24; H, 5.51. Found: C, 45.24; H, 5.29.

Catalytic Oligomerization. As a representative example, the linear dimerization of 1,3-pentadiene is described, using Cp*Ru$^+$ at 60 °C for 1 day.

A 50-mL pressure bottle containing a Teflon-coated magnetic stirring bar was charged with 87.2 mg (0.24 mmol) of 1,3-pentadiene complex **1d** and converted to an argon atmosphere. To this bottle was added 5 mL of THF, 2.0 mL (0.30 mmol) of a diethyl ether solution (0.15 N) of silver triflate, and 4.8 mL (48 mmol) of 1,3-pentadiene. At this point **1d** was changed to an active Cp*Ru$^+$ species. This reaction mixture was heated to 60 °C in an oil bath for 1 day. The color of the solution changed to yellow from red-brown. After the reaction mixture was cooled to room temperature, it was filtered with Celite to remove silver chloride, and the filtrate was passed through a silica gel column with pentane. The eluents were evaporated, and the residue was analyzed by gas chromatography and ^{1}H NMR. All oligomers were also confirmed by mass spectrometry.

^{1}H NMR spectra for the oligomers are summarized in Table 8.

X-ray Crystallographic Analysis. Crystals of **5** grown from acetone and hexane solutions were found suitable for X-ray crystal structure determination. A single crystal was sealed on a glass fiber and mounted on a Rigaku AFC-5 automated four-circle diffractometer for data collection. The orthorhombic *Pna*2$_1$ unit cell dimensions were determined and refined by a least-squares fit of 24 independent reflections with 20° ≤ 2θ < 25°. Intensity data were measured by the ω-2θ scan technique (scan range: 5° < 2θ < 50°, scan speed 8 deg/min) with Mo Kα radiation (λ = 0.710 68 Å) from a graphite monochromator. If $\sigma(F)/F$ was more than 0.1, a scan was repeated, up to three scans, and the results were added to the first scan. Three standard reflections were monitored every 150 measurements. For the reduction data, Lorentz and polarization corrections were made but no absorption correction. The position of the Ru atom was revealed by the inspection of a Patterson map. Subsequent difference Fourier maps revealed the positions of all other non-hydrogen atoms with 1963 unique data ($F > 3\sigma(F)$). Ru, S, F, O, and C atoms were refined anisotropically with full-matrix least-squares refinements by minimizing the fraction $\sum w(|F_0| - |F_c|)^2$, where $w = 1/[\sigma(F_o)^2 + p(F_o)^2]$, the parameter *p* being automatically optimized. Hydrogen atoms were introduced in ideal positions and fixed with the isotropic temperature factors (B_{eq} = 9 Å^2). The final cycle of least-squares refinement of the structure converged

Table 9. Atomic Coordinates with Estimated Standard Deviations in Parentheses for 5

atom	*x/a*	*y/b*	*z/c*
Ru	0.3799(0)	0.2191(0)	0.7770(2)
S	0.1040(1)	0.2602(1)	0.2664(4)
O1	0.0294(3)	0.2185(5)	0.302(1)
O2	0.1134(4)	0.2905(4)	0.1187(7)
O3	0.1327(5)	0.3183(4)	0.382(1)
F1	0.1430(3)	0.0927(3)	0.1902(6)
F2	0.1633(3)	0.1259(4)	0.4224(6)
F3	0.2351(2)	0.1779(4)	0.252(1)
C1	0.3472(4)	0.1634(5)	0.5464(7)
C2	0.3268(3)	0.2602(5)	0.5515(7)
C3	0.2731(4)	0.2715(5)	0.6671(7)
C4	0.2587(3)	0.1807(5)	0.7295(7)
C5	0.3054(4)	0.1158(5)	0.6539(9)
C6	0.3996(4)	0.1224(7)	0.427(1)
C7	0.3517(5)	0.3327(6)	0.442(1)
C8	0.2291(5)	0.3577(6)	0.708(1)
C9	0.1942(4)	0.1572(8)	0.840(1)
C10	0.3002(5)	0.0124(6)	0.674(1)
C11	0.5060(3)	0.1872(5)	0.764(2)
C12	0.4874(3)	0.2745(6)	0.6943(9)
C13	0.4523(3)	0.3456(4)	0.773(1)
C14	0.4679(4)	0.3805(4)	0.9302(8)
C15	0.5068(5)	0.4766(5)	0.926(1)
C16	0.3919(4)	0.3821(5)	1.0126(9)
C17	0.3547(4)	0.2875(5)	0.9920(9)
C18	0.3988(4)	0.2099(5)	1.0208(8)
C19	0.3754(4)	0.1225(5)	0.9794(9)
C20	0.4259(6)	0.0379(6)	0.996(1)
C21	0.1632(4)	0.1585(5)	0.285(1)

at $R = 0.031$. Neutral scattering factors were obtained from ref 21. The final fractional atomic coordinates are listed in Table 9. An ORTEP plot of 5 is shown Figure 1.

Crystals of 8 grown from dichloromethane and hexane solutions at −20 °C were found suitable for X-ray crystal structure determination. A single crystal was sealed on a glass fiber and mounted on a Rigaku AFC-7R automated four-circle diffractometer from data collection. The orthorhombic $Pna2_1$ unit cell dimensions were determined and refined by a least-squares fit of 25 independent reflections with $30° < 2\theta < 40°$. Intensity data were measured by the ω–2θ scan technique (scan range: $4° < 2\theta < 55°$, scan speed 32 deg/min) with Mo Kα radiation (λ = 0.710 68 Å) from a graphite monochromator. If $\sigma(F)/F$ was more than 0.1, a scan was repeated, up to three scans, and the results were added to the first scan. Three standard reflections were monitored every 150 measurements. For the reduction data, Lorentz and polarization corrections were made but no absorption correction. The position of the Ru atom was revealed by the inspection of a Patterson map. Subsequent difference Fourier maps revealed the positions of all other non-hydrogen atoms with 1079 unique data ($F > 3\sigma(F)$). Ru was refined anisotropically, and S, F, O, and C atoms were refined isotropically because of limits of poor crystallinity. Full-matrix least-squares refinements minimized the fraction $[\Sigma w|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$, the parameter p being automatically optimized. Hydrogen atoms were not introduced. The final cycle of least-squares refinement of the structure converged at $R = 0.069$. Neutral scattering factors were obtained from ref 21. The final fractional atomic coordinates are listed in Table 10. An ORTEP plot of 8 is shown in Figure 2.

Table 10. Atomic Coordinates with Estimated Standard Deviations in Parentheses for 8

atom	*x/a*	*y/b*	*z/c*
Ru	0.1220(1)	0.2475(3)	0.0000
S	0.5849(4)	0.1895(8)	0.491(2)
F1	0.666(1)	0.398(3)	0.404(2)
F2	0.640(1)	0.433(2)	0.586(2)
F3	0.7186(9)	0.258(3)	0.523(3)
O1	0.588(2)	0.124(4)	0.388(3)
O2	0.5237(9)	0.285(2)	0.525(3)
O3	0.602(1)	0.091(3)	0.589(2)
C1	0.160(2)	0.467(4)	0.073(3)
C2	0.205(2)	0.373(5)	0.109(3)
C3	0.238(1)	0.294(3)	0.006(6)
C4	0.213(2)	0.358(5)	−0.084(3)
C5	0.158(2)	0.484(4)	−0.046(3)
C6	0.118(3)	0.578(6)	0.140(4)
C7	0.223(2)	0.341(5)	0.226(3)
C8	0.300(1)	0.185(3)	0.030(3)
C9	0.241(2)	0.337(4)	−0.202(3)
C10	0.117(2)	0.591(5)	−0.126(3)
C11	0.088(3)	0.151(7)	−0.156(5)
C12	0.029(3)	0.143(7)	−0.083(6)
C13	0.007(2)	0.291(4)	−0.032(3)
C14	0.020(2)	0.286(6)	0.093(4)
C15	0.007(3)	0.216(7)	0.189(5)
C16	0.032(3)	0.061(6)	0.190(5)
C17	0.108(2)	0.083(5)	0.142(4)
C18	0.143(2)	0.019(4)	0.057(3)
C19	0.660(2)	0.346(4)	0.489(7)

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Supplementary Material Available: Tables of positional parameters, bond distances and angles, and temperature factors for 5 and 8 (12 pages). Ordering information is given on any current masthead page.

OM9306279

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