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Interconversion between $(C_5R_5)Ru^{IV}$(allyl) and $(C_5R_5)Ru^{II}$(diene) complexes

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Abstract

When CpRu(η^3-crotyl)Cl_2 complex (**1a**; Cp = η^5-C_5H_5) was eluted with a silica-gel column, a methyl C–H bond of **1a** was activated to give CpRu(η^4-butadiene)Cl (**2**). Similar activation occurred for CpRu(η^3-prenyl)Cl_2 (**1b**) and Cp*Ru(η^3-crotyl)Cl_2 (**1c**; Cp* = η^3-C_5Me_5) to give the corresponding diene Ru^{II} complexes. This conversion depends on retention time on a silica-gel column, and character of supports. However, the reaction of $[Cp^*RuCl_2]_2$ with prenyl chloride did not give the expected prenyl complex, but instead gave Cp*Ru(*syn*-1-chloromethyl-η^3-methallyl)Cl_2 (**3a**). Another 1-chloromethyl-methallyl *anti*-stereoisomer (**4a**) was obtained by treatment of $[Cp^*RuCl_3]_2$ with isoprene. The structures of these two isomeric 1-chloromethyl-methallyl Ru^{IV} complexes were determined by X-ray diffraction studies. The analogous 1-chloromethyl-allyl complex (**4b**) was also obtained by treatment of $[Cp^*RuCl_3]_2$ with butadiene. In these complexes, irreversible isomerization from the *anti*-into the more stable *syn* isomer took place via η^1-allyl intermediates.

Key words: Ruthenium; Bond activation; Interconversion

1. Introduction

Allyl complex has been postulated as reactive intermediates in the various catalytic reactions. Wilke and coworkers reported that bis(allyl)Ni complexes were key intermediates [1] in the dimerization of conjugated diene by means of nickel catalysts. A number of palladium catalyses have been reported to proceed with η^3-allyl complexes as key intermediates [2,3]. Allyl ruthenium species have recently attracted much attention [4,5]. In our previous study on the dimerization of conjugated dienes by use of the $Ru^{II} \Leftrightarrow Ru^{IV}$ redox channel, allyl Ru^{IV} intermediates played important roles in the catalysis [6]. Thus, it is appropriate to make more detailed study on the synthesis and reactivity of allyl ruthenium complexes with a wide range of auxiliary ligands. We have already reported synthetic routes of allylruthenium(IV) complexes, $(C_5R_5)Ru(allyl)X_2$ (R = H, Me), the structure of which was determined unequivocally to have an *endo*-allyl fragment [7]. In the Ru^{II} oxidation state, the configuration of allyl or methallyl ligands attached to a CpRu fragment was reported to exist both in *endo* and *exo* form [8,9]. Lehmkuhl and coworkers reported the reaction of a $CpRu(PPh_3)_2(\eta^1$-vinyl) complex and ethylene, or $CpRu(PPh_3)_2(\eta^1$-4-bute-1-nyl) to give a $CpRu(PPh_3)$-(η^3-crotyl) complex [9]. In addition, we recently reported that silver-ion-promoted reaction of CpRu-(allyl)Cl_2 with propene or 2-butene induced selective allylic C–H bond activation to give bis(η^3-allyl)Ru^{IV} complexes [10]. We report here the new interconversion process between the η^3-allyl Ru^{IV} and the η^4-diene Ru^{II} complexes.

2. Results and discussion

2.1. Chromatographic conversion of Ru^{IV} methylallyl into Ru^{II} diene complexes.

When CpRu(η^3-crotyl)Cl_2 (**1a**; Cp = η^5-C_5H_5) was subjected to silica-gel chromatography, a C–H bond of the methyl group in the crotyl ligand was activated unexpectedly, and the corresponding CpRu(η^4-butadiene)Cl (**2a**) was obtained (eqn. (1)). Formally, this transformation is the elimination of a hydrogen

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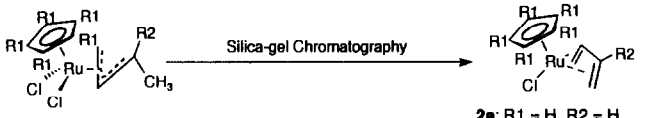
chloride molecule from **2a**. The activation depends on retention times on silica-gel (run 1–3, Table 1), and eluting solvents (run 4 and 5), as summarized in Table 1. This transformation was considered to be induced by the silanol group on silica-gel. In fact, when silanised or modified silica-gel with water was employed, the transformation was suppressed completely or partially (run 6 and 7). We also observed similar HCl elimination from $CpRu(\eta^3\text{-prenyl})Cl_2$ (**1b**) and $Cp^*Ru(\eta^3\text{-crotyl})Cl_2$ (**1c**) to yield $CpRu(\eta^4\text{-isoprene})Cl$ (**2b**) and $Cp^*Ru(\eta^4\text{-butadiene})Cl$ (**2c**), respectively. In this context, a more complicated transformation of ruthenium allyl complex on silica-gel was reported by Eisenstadt and Efraty, that $CpRu(CO)(\eta^3\text{-allyl})$ was converted into a $\mu\text{-}\eta^1,\eta^3$-allylidene diruthenium complex [11].



1a; R1 = H, R2 = H
1b; R1 = H, R2 = Me
1c; R1 = Me, R2 = H

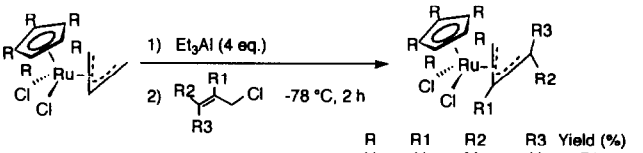
2a; R1 = H, R2 = H
2b; R1 = H, R2 = Me
2c; R1 = Me, R2 = H

(1)

2.2. *Preparation of Ru^{IV} allyl complexes by allyl group exchange*

The above-mentioned reaction caused a serious problem for our previous synthetic method for substituted allyl Ru^{IV} complexes such as $CpRu(\eta^3\text{-crotyl})Cl_2$ (**1a**) and $CpRu(\eta^3\text{-prenyl})Cl_2$ (**1b**) from $CpRuCl(PPh_3)_2$ and allylic halides [7], because its final step required the conversion of the allyl phosphonium ruthenate salt, $[Ph_3P\text{-}CH_2CH{=}CHR]_2[CpRuCl_3]$ into **1a** and **1b** by way of silica-gel chromatography. Thus, we had to develop a new synthetic route towards substituted allyl ruthenium(IV) complexes.

The alternative method is an allyl group exchange route, and $CpRu(C_3H_5)X_2$ or $Cp^*Ru(C_3H_5)Cl_2$, readily available in bulk quantities, were employed as starting materials. These parent Ru^{IV} allyl complxes were treated with an excess of triethylaluminium at low temperature, followed *in situ* by oxidative addition of substituted allylic halides at low temperature (eqn. (2)).



	R	R1	R2	R3	Yield (%)
1a	H	H	Me	H	71
	H	H	H	Me	20
1b	H	H	Me	Me	53
1c	Me	H	Me	H	91
4a	Me	Me	CH_2Cl	H	78

(2)

$CpRu(\eta^3\text{-crotyl})Cl_2$ (**1a**), prepared by this allyl exchange method, contains two configurational isomers (78:22). The ^1H NMR of the predominant product indicates a double double doublet signal at δ 4.75 (J = 5.9, 9.8, 10.7 Hz) assignable to the proton attached at allyl center carbon (C2). The proton coupling constant of J = 10.7 Hz for $CH_2{=}\mathit{CH}{-}\mathit{CH}{-}Me$ suggests that the geometry around the C2–C3 bond has a *syn* configuration. In contrast, the ^1H NMR spectra of the minor product showed a double triplet signal of proton attached to the allyl center carbon at δ 4.86 (J = 6.8, 11.2 Hz). This coupling constant of J = 6.8 Hz for $CH_2{=}\mathit{CH}{-}\mathit{CH}{-}Me$ suggests the methyl group at an allyl fragment in the minor product takes the *anti* configuration around the C2–C3 bond. It is notable

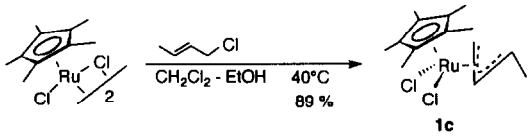
TABLE 1. Chromatographic conversion of allyldichlororuthenium(IV) into chloro(diene)ruthenium(II) complexes

run	Stationary Phase [a]	Coumn length (mm) [b]	Eluting solvent (Vol. ratio)	Relative ratio (mol%)	
				allyl	diene
1	Silica-gel	60	CH_2Cl_2/MeOH(100/1)	56	44
2	Silica-gel	120	CH_2Cl_2/MeOH(100/1)	24	76
3	Silica-gel	240	CH_2Cl_2/MeOH(100/1)	11	89
4	Silica-gel	60	CH_2Cl_2/MeOH(300/1)	32	68
5	Silica-gel	60	THF	94	6
6	Modified Silica-gel [c]	60	CH_2Cl_2	73	27
7	Silanised Silica-gel	60	CH_2Cl_2/MeOH(100/1)	100	0
8	Alumina	60	CH_2Cl_2/MeOH(100/1)	– [d]	

[a] Silica-gel; Merck Art. 7734, Silanised Silica-gel; Merck Art. 7719, Alumina; Merck Art. 1097.
[b] Column ∅ = 10 mm.
[c] This silica-gel was stirred in water and dried at 80°C for 24 h.
[d] Decomposition took place.

that the *anti* isomer (*anti*-**1a**) never isomerized into the corresponding diene complex, not even after silica-gel chromatography. Accordingly, the dienylic C–H activation only took place selectively for the *syn* isomer of **1a**.

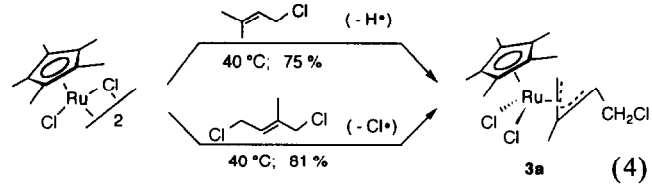
Similarly, CpRu(η^3-prenyl)Cl_2 (**1b**) and Cp*Ru(η^3-crotyl)Cl_2 (**1c**) were prepared successfully from the allyl exchange methodology. Complex **1c** was also prepared from $[Cp^*RuCl_2]_2$ and crotyl chloride (eqn. (3)). In both methods, complex **1c** was the sole product identified to be a *syn* isomer on the basis of coupling constants in ^{1}H-NMR; δ 5.03 (allyl central proton, J = 5.9, 9.3, 10.8 Hz).



(3)

2.3. 1-Chloromethylallyl complexes of Cp^*Ru^{IV}

However, Cp*Ru(η^3-prenyl)Cl_2 (**1d**) could not be prepared by either methods. The reaction of $[Cp^*RuCl_2]_2$ with prenyl chloride gave an allyl complex, with the composition of Cp*Ru(C_5H_9Cl)Cl_2 (**3a**) in 75% yield (eqn. (4)). The same complex was also prepared by the oxidative addition of $[Cp^*RuCl_2]_2$ with 1,4-dichloro-2-methyl-2-butene (eqn. (4)).



(4)

The structure of **3a** in the solid state has been determined by a single crystal X-ray diffraction study, and its ORTEP plot is shown in Fig. 1. Crystal data and selected bond lengths and angle parameters of **3a** are listed in Tables 2 and 3. The chloromethyl substituent of **3a** unequivocally takes the *syn* position. It is noteworthy that in the reaction with prenyl chloride the carbon–chlorine bond was not oxidatively added but one of the allylic C–H bond of the *trans* oriented methyl group of prenyl chloride was activated. This behavior is in contrast to our previous findings that allylic halides selectively induce oxidative addition to give Ru^{IV} allyl complexes in the reaction with $[Cp^*RuCl_2]_2$ [7,12]. However, the reaction of $[Cp^*RuCl_2]_2$ with 1,4-dichloro-2-butene is consistent with the oxidative addition of a carbon–chlorine bond, and gave

TABLE 2. Crystal data for **3a** and **4a**

	3a	**4a**
Composition	$C_{15}H_{23}Cl_3Ru$	$C_{15}H_{23}Cl_3Ru$
FW	410.28	410.28
Crystal color	yellow	dark brown
Crystal dimens. (mm)	0.05 × 0.15 × 0.20	0.30 × 0.30 × 0.30
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (No. 61)	$P2_1/a$ (No. 14)
Cell constant		
a (Å)	14.691(6)	12.226(2)
b (Å)	26.531(4)	11.194(1)
c (Å)	8.640(6)	12.724(4)
β (°)		104.22(2)
V (Å^3)	3367(2)	1688.0(6)
Z	8	4
Diffractometer	Rigaku AFC7R	Rigaku AFC7R
μ (cm^{-1})	13.80	13.77
Radiation (Å)	Mo Kα Av. = 0.71069	Mo Kα Av. = 0.71069
2θ Max (°)	50.0	55.0
Collected reflections	2857	4265
Unique reflections	1067 ($I \geq 3\sigma(I)$)	2893 ($I \geq 3\sigma(I)$)
R [a]	0.056	0.035
R' [b]	0.048	0.044
S [c]	1.65	1.66

[a] $R = \Sigma w \| F_o \| - \| F_c \| / \Sigma | F_o |$.
[b] $R' = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$.
[c] $S = [\Sigma (w \| F_o \| - \| F_c \|)^2 / (N_o - N_p)]^{1/2}$.

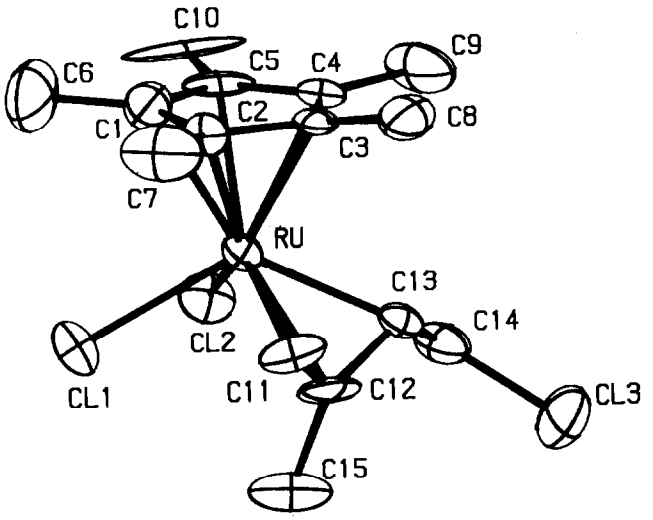


Fig. 1. ORTEP view of Cp*Ru(*syn*-chloromethyl-methallyl)Cl_2 (**3a**) with ellipsoids drawn 30% probability. All hydrogen atoms are omitted.

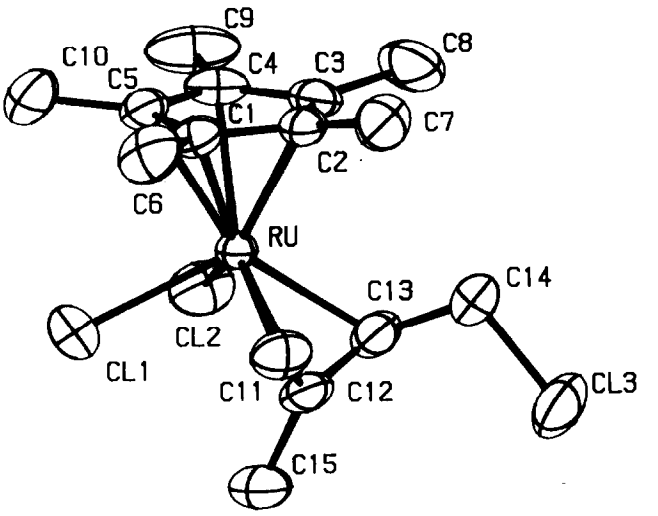
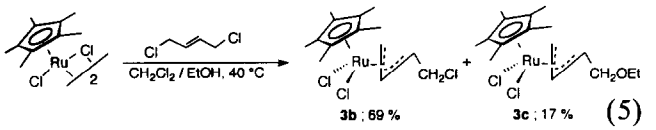


Fig. 2. ORTEP view of Cp*Ru(*anti*-chloromethyl-methallyl)Cl_2 (**4a**) with ellipsoids drawn 40% probability. All hydrogen atoms are omitted.

Cp*Ru{1-(*syn*-chloromethyl)allyl}Cl_2 (**3b**) as the major product (69%), as well as Cp*Ru{1-(*syn*-ethoxymethyl)-allyl}Cl_2 (**3c**) (17%) (eqn. (5)).



(5)

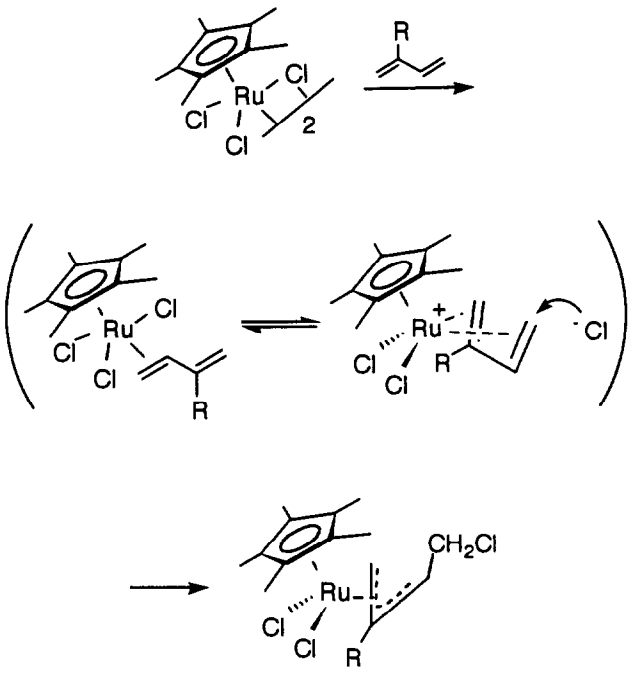
On the other hand, the reaction of $[Cp^*RuCl_3]_2$ with isoprene gave another Cp*Ru(C_5H_9Cl)Cl_2 stereo-isomer (**4a**) (eqn. (6)). Its ^{1}H-NMR spectra was not identical with the *syn*-chloromethyl substituted allyl complex (**3a**) mentioned above. Its structure has also been determined by a single crystal X-ray diffraction study, and its ORTEP view is shown in Fig. 2. Crystal data and selected bond lengths and angles were summarized in Tables 2 and 4. The structure of **4a** clearly shows a 1-chloromethyl substituent being present at the *anti*-position of the allyl fragment. This *anti* isomer was considered to be generated by way of formal insertion of isoprene into the ruthenium–chlorine bond. A plausible mechanism for formation of **4a** is shown in Scheme 1, and involves attack of the chloride anion to the coordinated diene ligand of a

TABLE 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for *syn*

Ru–Cl1	2.441(5)	Ru–Cl2	2.418(6)
Ru–C11	2.22(2)	Ru–C12	2.16(2)
Ru–C13	2.25(2)		
C11–C12	1.40(3)	C12–C13	1.45(3)
C13–C14	1.47(2)	C12–C15	1.50(2)
C14–Cl3	1.83(2)		
Cl1–Ru–Cl2	82.9(2)		
C11–Ru–C13	65.7(6)		
C11–C12–C13	116 (1)		
C12–C13–C14	123 (1)		
C13–C14–Cl3	108 (1)		
C11–C12–C15	122 (2)		
C13–C12–C15	120 (2)		
Ru–C11–C12	68 (1)		
Ru–C12–C11	73 (1)		
Ru–C12–C13	74 (1)		
Ru–C13–C12	67 (1)		

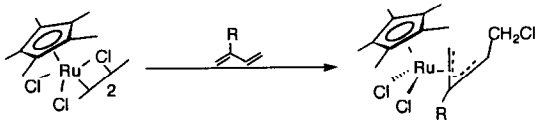
TABLE 4. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for *anti*

Ru–Cl1	2.419(1)	Ru–Cl2	2.417(1)
Ru–C11	2.185(5)	Ru–C12	2.157(4)
Ru–C13	2.227(5)		
C11–C12	1.412(7)	C12–C13	1.416(7)
C13–C14	1.481(7)	C12–C15	1.501(7)
C14–Cl3	1.820(5)		
Cl1–Ru–Cl2	83.32(6)		
C11–Ru–C13	65.9(2)		
C11–C12–C13	116.1(4)		
C12–C13–C14	121.7(5)		
C13–C14–Cl3	108.2(4)		
C11–C12–C15	123.0(5)		
C13–C12–C15	120.7(5)		
Ru–C11–C12	69.9(3)		
Ru–C12–C11	72.1(3)		
Ru–C12–C13	73.9(3)		
Ru–C13–C12	68.5(3)		



Scheme 1.

cationic *endo*-η^4-isoprene intermediate. Similarly, the reaction of $[Cp^*RuCl_3]_2$ with butadiene gave $Cp^*Ru(C_4H_6Cl)Cl_2$ (**4b**), which had a chloromethyl substituent at the *anti*-position of the allyl fragment (eqn. (6)). These observations were similar to those of reactions of (η^4-diene)tricarbonyliron with hydride or other nucleophiles to give (*anti*-crotyl) iron complexes [13]. Tolman reported the insertion of butadiene into the nickel–hydrogen bond to give an *anti*-crotyl intermediate [14]. Consequently, formation of *anti*-substituted allyl species is considered to be a common feature to give a *cisoid* η^4-diene ligand of metal complexes.



4a; R = Me 98 %
4b; R = H 96 %

(6)

The *anti*-1-chloromethyl-allyl complex (**4**) is found to isomerize into the more thermodynamically stable *syn* isomer **3** by heating or UV irradiation in solution. During the whole process of the isomerization, the ^{1}H-NMR spectra showed only two components which were identified to be unequivocally *anti*- and *syn*-chloromethyl complexes (**3** and **4**), indicative of selective isomerization taking place. The relationship of ln[**4a**] and ln[**4b**] *vs.* time, based on ^{1}H-NMR, in these *anti* into *syn* isomerizations, is shown in Figs. 3 and 4, respectively. This process follows first-order kinetics, and calculated rate constants under various conditions are listed in Table 5. One can now assume that the *anti–syn* isomerization proceeds by way of a σ-allyl intermediate (eqn. (7)), although it is difficult to explain why the difference in rates between **4a** and **4b** is

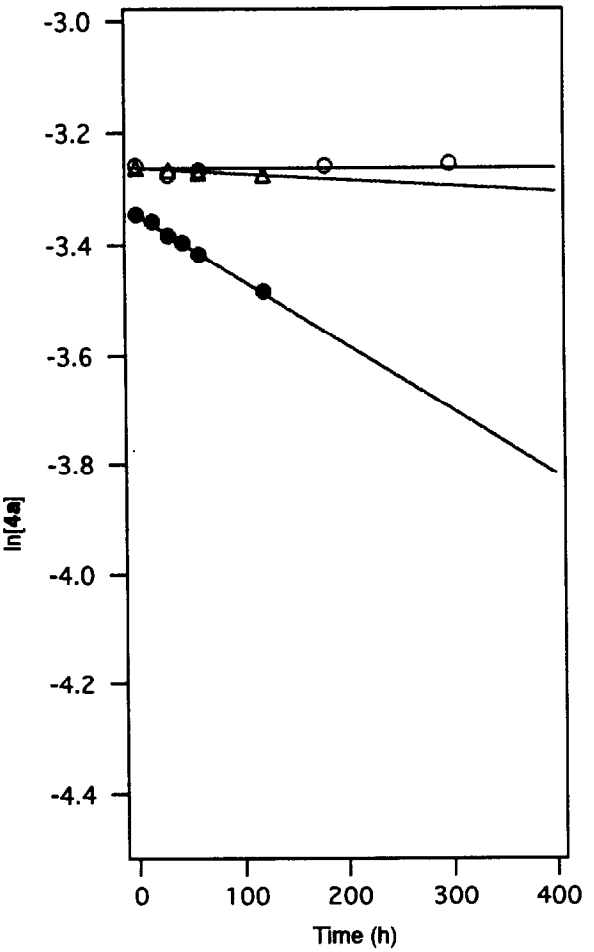


Fig. 3. Plot of ln[**4a**] *vs.* time (h) for the isomerization of **4a** into **3a**.

TABLE 5. Calculated rate constants for the isomerization of **3** to **4**

Reaction	Condition	Rate constant (s^{-1})
4a → **3a**	25.5°C	3.78×10^{-8}
4a → **3a**	33°C	1.68×10^{-6}
4a → **3a**	UV (r.t.)	1.95×10^{-5}
4b → **3b**	25.5°C	2.92×10^{-5}
4b → **3b**	33°C	7.25×10^{-5}
4b → **3b**	40°C	1.64×10^{-4}
4b → **3b**	UV (r.t.)	8.03×10^{-5}

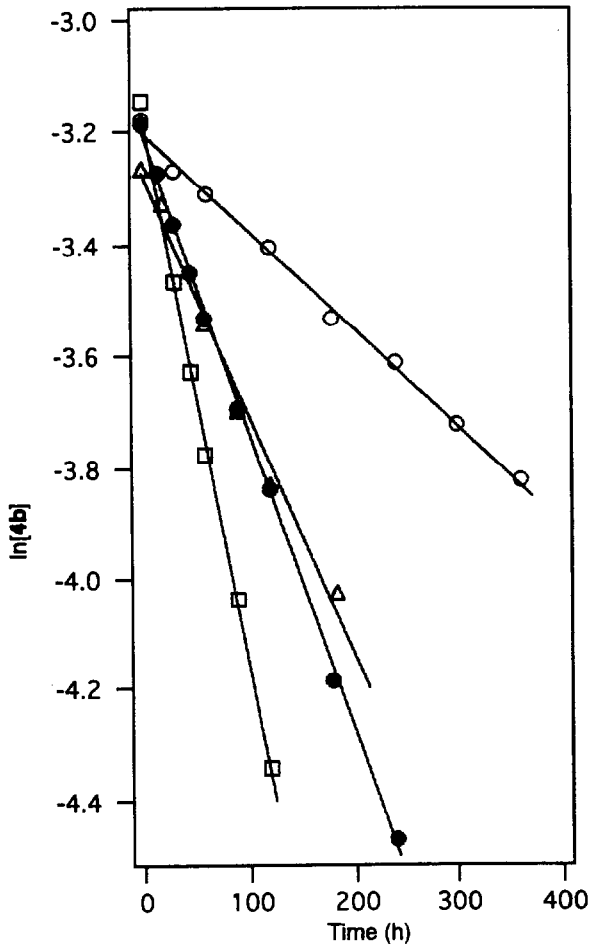
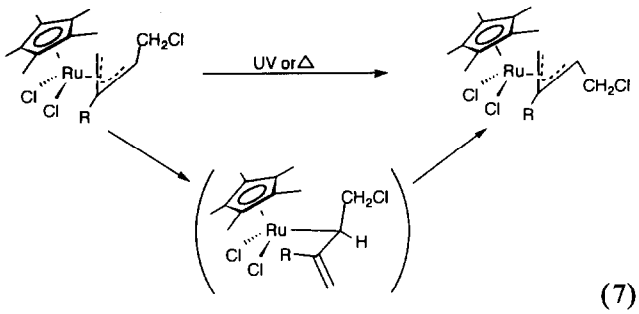


Fig. 4. Plot of ln[**4b**] *vs.* time (h) for the isosmerization of **4b** into **3b**.

much larger under thermal conditions than that under photochemical conditions.



(7)

3. Experimental details

3.1. General remarks

All reactions were carried out under dinitrogen stream. Ruthenium trichloride hydrate was purchased from NE Chemcat Corp. Isoprene was purchased from Tokyou Kasei Co., Ltd.. Gaseous butadiene and carbon monoxide were obtained from Seitetsu kagaku and Nippon Sanso, respectively. Dichloromethane was dried over phosphorus pentoxide, and stored under argon. Silica-gel and silanised silica-gel employed Merck 7734 and Merck 7719, respectively. ^1H and ^{13}C NMR spectra were recorded on a Jeol GX-270 spectrometer. Elemental analyses were performed at the Microanalysis Center of Kyoto University or determined by a Yanako CHN Corder. IR spectra were measured with a Jasco A-3 spectrometer. 1,4-Dichloro-2-methyl-2-butene and 1,4-Dichloro-2-butene were obtained by reported method [15]. $[Cp^*RuCl_2]_2$ and $[Cp^*RuCl_3]_2$ were prepared according to the reported methods [16,17]. Authentic Cp- and Cp*Ru(diene) complexes (**2a–c**) were prepared by our reported methods [6,18].

3.2. Synthesis of CpRu(crotyl)Cl_2 (1a)

A dichloromethane (10 ml) solution of $CpRuBr_2$-(C_3H_5) (401.8 mg, 1.45 mmol) was cooled at −78°C. A hexane solution of triethylaluminium (6.35 ml of 0.91 N solution, 5.78 mmol) was added with stirring for 30 min. After disappearance of starting complex (TLC), crotyl chloride (1.42 ml, 14.5 mmol) was added. The mixture was reacted at this temperature for 2 h. After remaining triethylaluminium was decomposed by saturated aqueous ammonum chloride solution, the organic layer was dried over magnesium sulfate. Drying agent was filtered off with a column filled with Celite under dinitrogen, and the liquid phase was concentrated under reduced pressure. Chromatographic purification of the residue (silanised silica-gel/CH_2Cl_2) gave the mixture of two complexes (*syn*- and *anti*-isomer) as yellow powder (382.3 mg, 1.31 mmol, 91%). ^1H-NMR analysis indicated that the relative ratio of *syn*-**1a** and *anti*-**1a** was 78:22.

3.2.1. syn-1a

Mp. 225°C (dec.). ^1H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.76 (3H, d, Me, $J = 6.4$ Hz), 3.57 (1H, d, $CH_{anti}H$=CH, $J = 9.8$ Hz), 4.46 (1H, d, $CH_{syn}H$=CH, $J = 5.9$ Hz), 4.57 (1H, m, MeC*H*=CH), 4.75 (1H, ddd, allyl center, $J = 5.9$, 9.8, 10.7 Hz), 5.58 (5H, s, Cp); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 18.7 (Me), 61.8 (CH_2=CH), 85.4(Me*C*H=CH), 94.2 (Cp), 100.0 (allyl center); IR (KBr), 3000 cm^{-1} (m), 1400 (s), 970 (m), 825 (s), 560 (w), 370 (w).

3.2.2. anti-1a

^1H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.30 (3H, d, Me, $J = 6.8$ Hz), 4.11 (1H, d, $CH_{anti}H$=CH, $J = 11.2$ Hz), 4.48 (1H, dd, $CH_{syn}H$=CH, $J = 6.8$ Hz), 4.86 (1H, dt, allyl center, $J = 6.8$, 11.2 Hz), 5.46 (5H, s, Cp), 5.58 (1H, m, MeC*H*=CH).

Anal. Calcd for $C_9H_{12}Cl_2Ru$ for the mixture of *syn*- and *anti*- form: C, 47.00; H, 4.14. Found: C, 47.88; H, 4.08.

3.3. Synthesis of CpRu(prenyl)Cl_2 (1b)

The procedure for the reaction was similar to that described above. The reaction was performed from CpRu(allyl)Cl_2 (30.4 mg, 0.108 mmol), triethylaluminium (4 equiv.), and prenyl chloride (0.12 ml, 1.08 mmol) in dichloromethane (10 ml). The title complex was formed in 53% yield (17.4 mg, 0.057 mmol).

^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.47 (3H, s, Me*Me*(*anti*)C=C), 1.75 (3H, s, Me*Me*(*syn*)C=CH), 4.14 (1H, d, CH_{syn}H=CH, 4.80–4.69 (2H, m, CH_{anti}H=CH, allyl center), 5.43 (5H, s, Cp).

3.4. Synthesis of Cp*Ru(crotyl)Cl_2 (1c)

The procedure for the reaction was similar to that described above; Cp*Ru(allyl)Cl_2 (32.9 mg, 0.095 mmol), triethylaluminium (1.2 equiv.), and crotyl chloride (0.09 ml, 0.95 mmol) in dichloromethane (10 ml). The title complex was formed in 91% yield (32.2 mg, 0.086 mmol).

Alternative procedure was undertaken by modification of our previously reported method [3]. The reaction was performed from $[Cp^*RuCl_2]_2$ (60.8 mg, 0.198 mmol), and crotyl chloride (0.19 ml, 1.98 mmol) in dichloromethane (10 ml) and ethanol (2.5 ml). The reaction mixture was heated to 40°C for 2 h, and was concentrated at reduced pressure. Chromatographic purification of the residue (silanised silica-gel/CH_2Cl_2) gave the title complex (64.1 mg, 0.177 mmol, 89%). Mp. 230°C (dec.).

^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.50 (3H, d, =CH-*Me*, J = 6.36), 1.59 (15H, s, Cp*), 2.29 (1H, d, CH=CHH_{anti}, J = 9.28 Hz), 3.06 (1H, m, =C*Hanti*-Me, J = 9.96), 4.11 (1H, d, CH=CHH_{syn}, J = 6.35 Hz), 5.03 (1H, ddd, allyl center, J = 6.35, 9.28, 10.75); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 9.3 (q, Me of Cp*, J = 129.1 Hz), 17.1 (t, =CH-*Me*, J = 129.1 Hz), 64.7 (t, CH=CH_2, J = 166.3 Hz), 85.5 (d, CH=*C*H-Me, J = 154.6 Hz), 98.1 (d, allyl center, J = 178.0 Hz), 103.4 (s, ring of Cp*). Anal. Calcd for $C_{14}H_{22}Cl_2Ru$: C, 46.41; H, 6.12. Found: C, 46.31; H, 6.13. IR (KBr), 2840 cm^{-1} (w), 1435 (s), 1410 (s), 1360 (s), 1005 (s).

3.5. Synthesis of Cp*Ru{1-(syn-chloromethyl)-methallyl}Cl_2 (3a)

Procedure was modification of our previously reported method [7].

3.5.1. Reaction of $[Cp^*RuCl_2]_2$ and prenyl chloride

$[Cp^*RuCl_2]_2$ (2.03 g, 6.62 mmol) was dissolved in dichloromethane (200 ml) and ethanol (50 ml) in a 300-ml round bottomed flask fitted with a magnetic stirrer under an argon atmosphere. Prenyl chloride (3.70 ml, 33.1 mmol) was added by syringe with stirring at 40°C for 24 h. The reaction mixture was concentrated by rotary evaporator to dryness. Chromatographic purification of the residue (silica-gel/CH_2Cl_2) gave the title complex (2.04 g, 4.96 mmol, 75%).

3.5.2. Reaction of $[Cp^*RuCl_2]_2$ and 1,4-dichloro-2-methyl-2-butene

The procedure for the reaction was similar to that described above. The reaction was performed from $[Cp^*RuCl_2]_2$ (951 mg, 3.10 mmol), and 1,4-dichloro-2-methyl-2-butene (2.0 ml) in dichloromethane (80 ml) and ethanol (20 ml). The title complex was formed in 81% yield (999 mg, 2.52 mmol).

3.5.3. Reaction of $[Cp^*RuCl_2]_2$ and 1,4-dichloro-2-methyl-2-butene by the allyl exchanged method

The procedure for the reaction was similar to that described above. The reaction was performed with Cp*Ru(allyl)Cl_2 (45.6 mg, 0.131 mmol), triethylaluminium (1.2 equiv.), and 1,4-dichloro-2-methyl-2-butene (0.18 ml) in dichloromethane (10 ml). Chromatographic purification of the residue (silica-gel/CH_2Cl_2) gave the title complex (42.2 mg, 0.103 mmol, 78%).

Mp 217°C (dec.). ^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.60 (15H, s, Cp*), 2.31 (1H, s CH=CHH_{anti}), 2.33 (3H, s, Me), 2.68 (1H, dd, =CH-CH_2-Cl, J = 3.90, 11.23 Hz), 3.50 (1H, dd, =CH-CH_2-Cl, J = 3.90, 12.20 Hz), 3.83 (1H, s, CH=CHH_{syn}), 4.44 (1H, dd, CH=CH_{anti}-CH_2, J = 11.23, 12.20 Hz); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 9.4 (q, Me of Cp*, J = 129.1 Hz), 14.3 (q, CH_2=C(*Me*)=CH, J = 135.0 Hz), 42.6 (t, =CH-*C*H_2-Cl, J = 158.5 Hz), 65.4 (t, CH=*C*H_2, J = 164.5 Hz), 71.5 (d, CH=*C*H-CH_2, J = 156.5 Hz), 105.0 (s, ring of Cp*), 108.9 (s, CH_2=*C*(Me)=CH). Anal. Calcd for $C_{15}H_{23}Cl_3Ru$: C, 43.85; H, 5.60. Found: C, 43.72; H, 5.67. IR (KBr), 2900 cm^{-1} (m), 1420 (s), 1370 (s), 1230 (m), 1010 (m), 670 (m), 580 (m), 470 (m).

3.6. Synthesis of Cp*Ru{1-(syn-chloromethyl)-allyl}Cl_2 (3b)

The procedure for the reaction was similar to that described above. The reaction was performed from $[Cp^*RuCl_2]_2$ (96.1 mg, 0.313 mmol), and 1,4-dichloro-2-butene (0.33 ml, 3.13 mmol) in dichloromethane (80 ml) and ethanol (20 ml) at 40°C for 4 h. The title complex (**3b**) was formed in 69% yield (85.9 mg, 0.217 mmol), and Cp*Ru{1-(*syn*-ethoxymethyl)-allyl}Cl_2 (**3c**) was formed in 17% yield (21.2 mg, 0.054 mmol) as by-product.

3.6.1. 3b

^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.63 (15H, s, Cp*), 2.37 (1H, d, CH=CHH_{anti}, J = 9.27), 2.80 (1H, dt, CH=CH_{anti}-CH_2, J = 2.93, 10.01 Hz), 3.64 (1H, dd, =CH-CH_2-Cl, J = 2.93, 12.20 Hz), 4.14 (1H, d, CH=CHH_{syn}, J = 6.35 Hz), 4.30 (1H, dd, =CH-CH_2-Cl, J = 10.01, 12.20 Hz), 5.22 (1H, m, allyl center); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 9.5 (q, Me of Cp*, J = 129.1 Hz), 45.4 (t, =CH-CH_2-Cl, J = 156.5 Hz), 66.0 (t, CH=CH_2, J = 166.3 Hz), 78.0 (d, CH=C H-CH_2, J = 162.4 Hz), 97.1 (d, allyl center, J = 174.1 Hz), 105.2 (s, ring of Cp*). Anal. Calcd for $C_{14}H_{21}Cl_3Ru$: C, 42.37; H, 5.30. Found: C, 42.31; H, 5.30. IR (KBr), 1440 cm^{-1} (s), 1370 (s), 1230 (m), 1010 (m), 670 (s), 465 (s). decomposition at 212°C.

3.6.2. 3c

^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.22 (3H, t, Me, J = 6.84 Hz), 1.62 (15H, s, Cp*), 2.34 (1H, d, CH=CHH_{anti}, J = 9.77 Hz), 2.83 (1H, ddd, CH=CH_{anti}-CH_2, J = 2.93, 9.28, 12.69 Hz), 3.47–3.63 (2H, dq, O-CH_2-CH_3, J = 6.84 Hz), 3.68 (1H, dd, =CH-CH_2-O, J = 2.93, 12.20 Hz), 3.95 (1H, dd, =CH-CH_2-O, J = 12.20, 12.69 Hz), 4.15 (1H, d, CH=CHH_{syn}, J = 5.86 Hz), 5.18 (1H, m, allyl center). Anal. Calcd for $C_{16}H_{26}Cl_2Ru$: C, 47.29; H, 6.40. Found: C, 46.68; H, 6.45. IR (KBr), 2850 cm^{-1} (m), 1430 (s), 1360 (s), 1340 (m), 1080 (vs), 1010 (s), 860 (w), 610 (w), 500 (w).

*3.7. Synthesis of Cp*Ru{1(anti-chloromethyl)-methallyl}Cl_2 (4a)*

$[Cp^*RuCl_3]_2$ (88.4 mg, 0.258 mmol) was dissolved in dichloromethane (10 ml) in a 20-ml round bottomed flask fitted with a magnetic stirrer bar under an argon atmosphere. Isoprene (0.26 ml, 2.58 mmol) was added by syringe with stirring at room temperature for 3 h. The liquid was concentrated, and chromatographic purification of the residue (silanised silica-gel/CH_2Cl_2) gave the title complex (103.3 mg, 0.252 mmol, 98% yield). Mp 90°C (dec.).

^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.67 (15H, s, Cp*), 2.40 (3H, s, Me), 2.98 (1H, dd, =CH-CH_2-Cl, J = 3.42, 12.70 Hz), 3.01 (1H, d, CH=CHH_{anti}), 3.71 (1H, s, CH=CHH_{syn}), 3.74 (1H, dd, =CH-CH_2-Cl, J = 3.42, 9.28 Hz), 4.80 (1H, m, CH=CH_{syn}-CH_2); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 10.4 (q, Me of Cp*, J = 129.1 Hz), 20.3 (q, CH_2=C(*Me*)=CH, J = 129.1 Hz), 45.9 (t, =CH-CH_2-Cl, J = 154.6 Hz), 58.3 (t, CH=CH_2, J = 162.4 Hz), 73.4 (d, CH=C H-CH_2, J = 158.5 Hz), 106.0 (s, ring of Cp*), 110.0 (s, CH_2=C(Me) = CH). Anal. Calcd for $C_{15}H_{23}Cl_3Ru$: C, 43.85; H, 5.60. Found: C, 44.88; H, 5.80. IR (KBr), 2840 cm^{-1} (m), 1350 (s), 1240 (s), 990 (s), 640 (w), 580 (w).

*3.8. Synthesis of Cp*Ru {1-(anti-chloromethyl)-allyl}Cl_2 (4b)*

The procedure for the reaction was similar to that described above. The reaction was performed from $[Cp^*RuCl_3]_2$ (54.3 mg, 0.159 mmol) in dichloromethane (10 ml), and butadiene (1 atm) was introduced at ambient temperature for 15 min. The title complex was formed in 96% yield (60.1 mg, 0.152 mmol). Mp 210°C (dec.).

^{1}H-NMR (270 MHz, $CDCl_3$, TMS), δ 1.69 (15H, s, Cp*), 3.00 (1H, dd, =CH-CH_2-Cl, J = 9.76, 11.23 Hz), 3.04 (1H, d, CH=CHH_{anti}, J = 9.77 Hz), 3.61 (1H, dd, =CH-CH_2-Cl, J = 3.42, 9.76 Hz), 4.17 (1H, dd, CH=CHH_{syn}, J = 1.96, 6.35 Hz), 5.34–5.50 (2H, m, CH=CH_{syn}-CH_2Cl, and allyl center); ^{13}C-NMR (67.8 MHz, $CDCl_3$), δ 10.3 (q, Me of Cp*, J = 129.1 Hz), 43.1 (t, =CH-CH_2-Cl, J = 156.5 Hz), 61.6 (t, CH=CH_2, J = 162.3 Hz), 80.5 (d, CH=C H-CH_2, J = 176.1 Hz), 96.0 (d, allyl center, J = 178.0 Hz), 106.0 (s, ring of Cp*). Anal. Calcd for $C_{14}H_{21}Cl_3Ru$: C, 42.37; H, 5.30. Found: C, 42.21; H, 5.27. IR (KBr), 2870 cm^{-1} (w), 1460 (s), 1410 (s), 1360 (s), 1240 (m), 1200 (m), 1060 (w), 1000 (s), 900 (w), 780 (w) 720 (m), 650 (m), 520 (w), 420 (m), 380 (m).

3.9. X-ray crystallographic analysis

Crystals of **3a** were grown from dichloromethane and pentane solutions, and crystals of **4a** from dichloromethane and hexane. For **4a** and **3a**, a single crystal was mounted on a glass fiber. All measurements were made on a Rigaku AFC-7R automated four-circle

TABLE 6. Atomic coordinates with estimated standard deviations in parentheses for *syn*

Atom	x	y	z
Ru	0.0511(1)	0.37114(5)	0.6455(2)
Cl1	−0.0668(3)	0.3581(2)	0.8405(6)
Cl2	0.1517(4)	0.3552(2)	0.8616(7)
Cl3	0.2550(4)	0.5156(2)	0.6466(8)
C1	0.014(2)	0.2928(8)	0.559(3)
C2	−0.026(1)	0.3319(8)	0.469(2)
C3	0.050(2)	0.3574(6)	0.398(2)
C4	0.130(2)	0.3367(8)	0.450(3)
C5	0.108(2)	0.2972(8)	0.549(2)
C6	−0.037(2)	0.2534(9)	0.642(3)
C7	−0.124(1)	0.3375(9)	0.436(3)
C8	0.041(2)	0.3933(6)	0.262(2)
C9	0.223(1)	0.3514(9)	0.396(3)
C10	0.174(2)	0.2611(8)	0.631(3)
C11	−0.033(1)	0.4390(7)	0.599(2)
C12	0.045(2)	0.4514(6)	0.683(2)
C13	0.131(1)	0.4421(7)	0.608(2)
C14	0.220(1)	0.4505(7)	0.682(2)
C15	0.041(2)	0.4697(7)	0.847(3)

diffractometer with graphite-monocromater Mo Kα radiation ($\lambda = 0.71069$ Å) and a 18 kW rotating anode generator. The cell dimensions were determined by a least-squares fit of 20 independent reflections with $14° < 2\theta < 31°$ for **3a** and 25 independent reflections with $45° < 2\theta < 48°$ for **4a**. Crystal data along with refinement are listed in Table II. Intensity data were measured by the ω–2θ scan technique (scan speed 16 deg/min). 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. The intensity data were corrected for Lorentz and polarization corrections but no adsorption correction because of their small crystal sizes and small linear absorption coefficients. The position of the Ru atom was revealed by the inspection of a Patterson map. Subsequent difference Fourrier maps revealed the positions of all other non-hydrogen atoms with 1067 unique data ($I > 3\sigma(I)$) for **3a** and 2893 for **4a**. Ru, Cl, and C atoms were refined anisotropically with full-matrix least-squares refinements by minimizing the fraction $\Sigma w(|F_o| - |F_c|)^2$, 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 ($B = 1.2\ B_{eq}$ Å^2 of the corresponding bonded atoms). The final cycle of least-squares refinements of the structure converged at $R = 0.056$ for **3a** and $R = 0.035$ for **4a**. Neutral-atomic scattering factors were used with Ru corrected for anomalous dispersion [19]. Computations were carried out using the TEXSAN software package [20]. The final fractional atomic coordinates for **3a** and **4a** are listed in Tables 6 and 7, respectively.

TABLE 7. Atomic coordinates with estimated standard deviations in parentheses for *anti*

Atom	x	y	z
Ru	0.11114(3)	0.07709(3)	−0.23671(3)
Cl1	0.0062(1)	0.1686(1)	−0.1197(1)
Cl2	−0.0499(1)	0.1373(1)	−0.3785(1)
Cl3	0.0975(1)	−0.3341(1)	−0.3370(1)
C1	0.2670(4)	0.1542(4)	−0.1379(4)
C2	0.2984(3)	0.0658(4)	−0.2060(4)
C3	0.2557(4)	0.1033(4)	−0.3166(4)
C4	0.2043(4)	0.2169(5)	−0.3150(4)
C5	0.2110(4)	0.2493(4)	−0.2064(4)
C6	0.3041(5)	0.1572(5)	−0.0168(4)
C7	0.3829(4)	−0.0317(5)	−0.1655(5)
C8	0.2817(6)	0.0479(6)	−0.4145(5)
C9	0.1576(5)	0.2942(7)	−0.4107(5)
C10	0.1760(5)	0.3663(5)	−0.1690(6)
C11	0.1177(4)	−0.0697(4)	−0.1220(4)
C12	0.0303(4)	−0.0895(4)	−0.2160(4)
C13	0.0637(4)	−0.0999(4)	−0.3147(4)
C14	0.1541(5)	−0.1830(4)	−0.3265(4)
C15	−0.0922(5)	−0.0925(5)	−0.2150(6)

4. Supplementary material available

Tables of positional parameters, bond distances and angles, temperature factors, and an $F_o - F_c$ table for **3a** and **4a** can be obtained from the authors.

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