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Formation of Ru^{II}-alkyl-butadiene complexes from dihalogeno-Ru^{IV}-allyl precursors by the reaction with $BrMg(CH_2)_4MgBr$: a novel decomposition pathway for ruthena(IV)cyclopentane intermediates

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Abstract

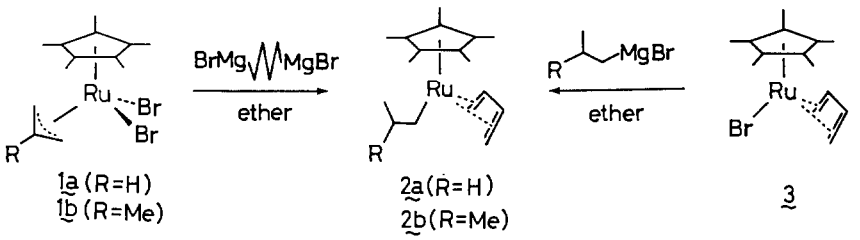
Treatment of $(C_5Me_5)RuBr_2(\eta^3\text{-}CH_2C(R)CH_2)$ [R = H (**1a**), Me (**1b**)] with $BrMg(CH_2)_4MgBr$ in ether afforded the Ru^{II}-alkyl-butadiene complexes, $(C_5Me_5)Ru(\eta^4\text{-}C_4H_6)(\eta^1\text{-}CH_2CHRCH_3)$ [R = H (**2a**), Me (**2b**)]. Labeling experiments have revealed a mechanism involving a double β-hydrogen elimination from ruthenacyclopentane intermediates and subsequent stepwise transfer of the hydrogen atoms to hydrogenate the η^3-allyl ligand.

Introduction

Chemistry of metallacyclopentanes has been extensively studied since they are intermediates of catalytic olefin oligomerization [1]. However, little is known on the preparation and the reactions of ruthenacyclopentanes except for three Ru^{II}-metallacyclic compounds reported by Lindner [2], Bennet [3], and Lucherini [4]. In the course of our studies on the chemistry of Ru^{IV}-alkyl-allyl complexes [5–7], we attempted to prepare ruthena(IV)cyclopentanes by the reaction of dihalogeno-Ru^{IV}-precursors, $(C_5R_5)RuX_2(\eta^3\text{-allyl})$ [R = H, Me; X = Cl, Br, I] with $BrMg(CH_2)_4MgBr$. In all the cases we examined, the desired ruthena^{IV}-cyclopentanes were not obtained. Instead, the unexpected novel products, $(C_5Me_5)Ru(\eta^4\text{-butadiene})(\eta^1\text{-alkyl})$, were isolated from the reaction mixture of $(C_5Me_5)RuBr_2(\eta^3\text{-allyl})$ with the di Grignard reagent as shown in Scheme 1. In this paper, we describe the preparation of these Ru^{II}-butadiene-alkyl complexes and discuss its mechanistic aspects.

Results and discussion

Treatment of $(C_5Me_5)RuBr_2(\eta^3\text{-}CH_2C(R)CH_2)$ [R = H (**1a**), R = Me (**1b**)] with $BrMg(CH_2)_4MgBr$ in ether at room temperature gave a two-layered reaction



1a (R=H)
1b (R=Me)

2a (R=H)
2b (R=Me)

3

Scheme 1

mixture consisting of a yellow solution and gray-white pastes, from which η^4-butadiene complexes, $(C_5Me_5)Ru(\eta^4\text{-}C_4H_6)(\eta^1\text{-}CH_2CH(R)CH_3)$ [R = H (**2a**); R = Me (**2b**)], were isolated as pale yellow metastable solids. Use of $Li(CH_2)_4Li$ as the alkylating reagent gave the butadiene complex in lower yields. Spectral features of the η^4-butadiene moiety in **2a** and **2b** are similar to those of $(C_5Me_5)RuBr(\eta^4\text{-}C_4H_6)$ (**3**), in which three proton signals with equal integral values, assigned to the *syn*, the *anti*, and the central protons of the butadiene ligand, appeared in the ^1H NMR spectrum (Table 1), whereas two peaks derived from its terminal and central carbons grew up in the ^{13}C NMR spectrum (see Experimental section), indicating the presence of C_s-symmetry in the molecules. Either the proton or carbon signals of the butadiene ligand in **2a** and **2b** showed up-field shifts in the NMR spectra compared with those in **3**, which indicate the strong σ-donor character of the η^1-alkyl ligands compared with that of the bromide. The butadiene complexes **2a** and **2b** were alternatively prepared by alkylation of **3** with either n-propyl or isobutyl-MgBr. We prepared **3** by thermolysis of $(C_5Me_5)RuBr(CH_3)(\eta^3\text{-}C_3H_5)$ in butadiene; a modified version of the procedure reported in ref. 7b. Recently, Fagan and coworkers reported alternative preparative routes to analogous compounds to **3** [8]. Attempted preparation of other butadiene complexes failed, when using $(C_5H_5)RuX_2(\eta^3\text{-allyl})$ as a precursor or when using other di Grignard reagents as alkylating reagents such as $BrMgCH_2(Me)CHCH_2CH_2MgBr$, $Me(BrMg)CHCH_2\text{-}CH_2CH_2MgBr$, and $BrMg(CH_2)_5MgBr$.

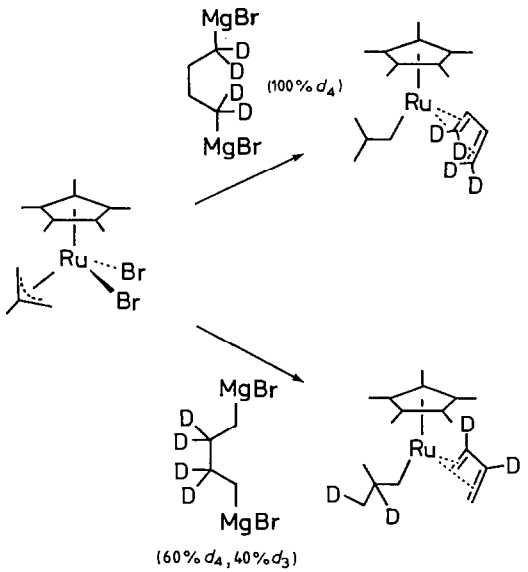
In order to clarify mechanisms of the butadiene complex formation, we carried out experiments with di Grignard reagents labeled by deuterium atoms. The results are summarized in Scheme 2. In the reaction of either **1a** or **1b** with $BrMgCD_2CH_2CH_2CD_2MgBr$, deuterium atoms were selectively located on terminal carbons of the η^4-butadiene ligand. In contrast, incorporation of deuterium atoms

Table 1

^1H NMR spectra of butadiene complexes **2a**, **2b**, and **3** [a]

Complex	Chemical shift (ppm)			Coupling constant (Hz)								
	ν_1 (ν_6)	ν_2 (ν_5)	ν_3 (ν_4)	J_{12} (J_{56})	J_{13} (J_{46})	J_{14} (J_{36})	J_{15} (J_{26})	J_{16}	J_{23} (J_{45})	J_{24} (J_{35})	J_{25}	J_{34}
2a [b]	−0.53	2.06	3.82	1.95	9.26	−1.70	0	0	7.24	0.82	0	4.52
2b [c]	−0.30	2.28	3.72	1.95	9.52	−1.75	0	0	7.37	0.70	0	4.78
3 [b]	1.62	3.14	4.37	1.95	10.58	−1.05	0	0	7.30	0.77	0	5.12

[a] Coupling constants were obtained by computer simulation. [b] NMR spectra were measured in $CDCl_3$. [c] NMR spectra were measured in C_6D_6.



Scheme 2

was observed on the internal carbon of the η^4-butadiene ligand and the 2,3-positions of η^1-isobutyl ligand in the reaction of **2b** with $BrMgCH_2CD_2CD_2CH_2MgBr$. As a representative, ^1H and ^2D NMR spectra of labeled and unlabeled **2b** are shown in Fig. 1.

It is known that organoruthenium compounds catalyze inter- or intramolecular hydrogen transfer reactions of organic substrates, realizing isomerization or hydrogenation of olefins, hydrogenation of ketones, and dehydrogenation of alcohols [9–11]. As a plausible explanation for these reactions, mechanisms through alkyl or alkoxy ruthenium intermediates are proposed as shown in Scheme 3, in which the β-hydrogen atom of these intermediates is transferred to the coordinated unsaturated ligands such as ketones and olefins by way of the corresponding Ru–H intermediate [12] or a direct hydrogen transfer pathway between the ligands [13].

Formation of η^4-butadiene complexes **2** could be attributed to intermediacy of ruthena(IV)cyclopentanes **4**, which readily undergo transfer of two hydrogen atoms from ruthenacyclopentanes to η^3-allyl ligand as shown in Scheme 4. This mechanism, in which the metallacycle acts as a hydrogen donor and the η^3-allyl ligand as an acceptor, is similar to the one proposed for the catalytic hydrogen transfer reactions shown in Scheme 3. It is apparent from the deuterium experiments described above that the initial step of the reaction is a β-hydrogen elimination from the metallacyclic ligand. General decomposition pathways for metallacyclopentanes are β-hydrogen elimination to form 1-butene, reductive elimination to give cyclobutene, or release of ethylene [1]. The formation of η^4-butadiene complexes from metallacyclopentane intermediates is rather unusual; and is probably involved in the catalytic oligomerization of ethylene by either zirconium [14] or tantalum [15] complexes; but no detailed studies, including labeling experiments were carried out.

The deuterium experiments also show that formation of the butadiene complexes **2a** or **2b** proceeds without scrambling of the hydrogens. The mechanism for catalytic

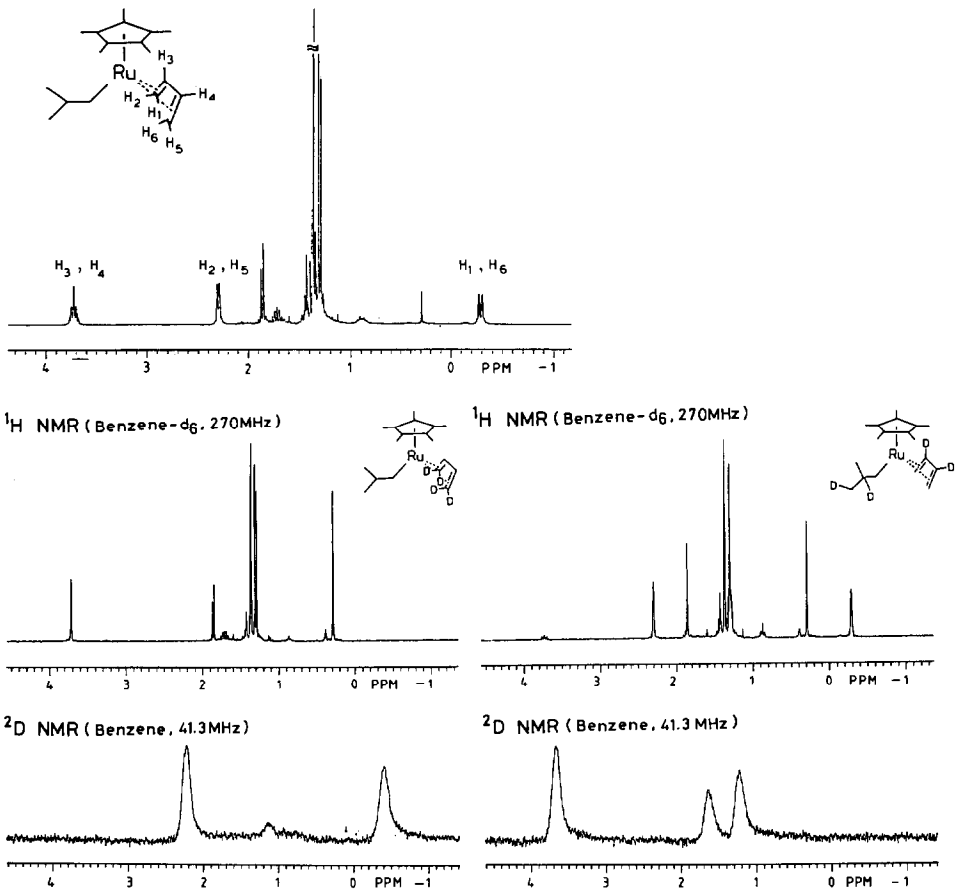
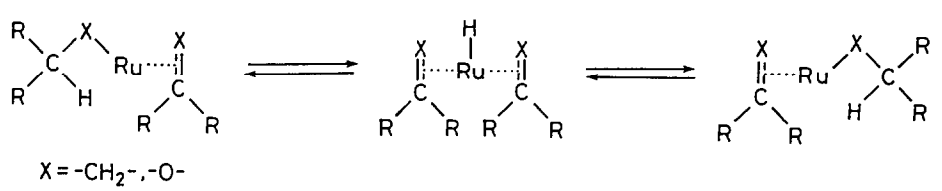
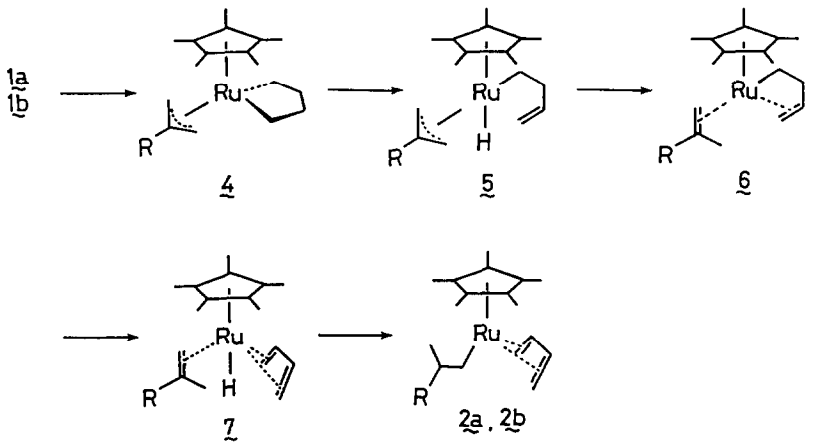


Fig. 1. ^{1}H NMR spectrum of **2b** (in benzene-d_6).

hydrogen transfer reactions shown in Scheme 3 is essentially in equilibrium. Similarly, it is probable that each step in Scheme 4 may be reversible. However, such reverse pathways could provide the scrambling of hydrogen atoms. For example, a process from **2a** or **2b** to **6** in Scheme 4 is achieved by hydrogen transfer from the η^1-alkyl ligand to the η^4-butadiene ligand. Thermal decomposition of **2a**, which actually occurred over 50 °C to give 1-butene and propylene, is likely to proceed via this process. However, isolation of a carbonyl complex, $(C_5Me_5)Ru(CO)(\eta^3\text{-}CH_2CHCHCH_3)$ [7b] when the decomposition was carried out under CO (Scheme 5) indicates that a hydrogen from η^1-propyl ligand subsequently



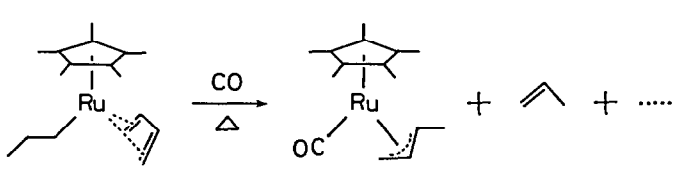
Scheme 3



Scheme 4

adds to a terminal carbon of the η^4-butadiene ligand to form $(C_5Me_5)Ru(\eta^2$-propylene$)(\eta^3$-$CH_2CHCHCH_3)$, which undergoes ligand exchange from propylene to CO. Thus, there is a reaction pathway in which hydrogen transfer does not provide the butenyl intermediate **6**. If this process involves that outlined in Scheme 4, scrambling of deuterium atoms should be observed in the deuterium experiments. Similarly, the microscopic reversibility consideration suggests that dual reverse pathways giving rise to scrambling of the deuterium atoms are possible in each step depicted in Scheme 4. Consequently, no scrambling of deuterium atoms suggests that the formation of **2a** or **2b** should proceed irreversibly.

Formation of the butadiene complex in the attempted synthesis of ruthena(IV)cyclopentanes suggests that facile intramolecular hydrogen transfer reactions occur in the dialkyl-allyl complexes of Ru^{IV}, when β-hydrogen elimination from η^1-alkyl ligand is possible. In fact, two methyl complexes, $(C_5R_5)RuMe_2(\eta^3$-allyl) [7b], and $(C_5R_5)RuMeX(\eta^3$-allyl) [7a], are stable up to 100 °C, above which they decompose by reductive elimination of the methyl and allyl ligands. In contrast, attempted preparation of their ethyl analogues only resulted in the formation of ethylene and propylene [14], which can be formed by the hydrogen transfer reaction from η^1-ethyl ligand to η^3-allyl ligand. It is of interest that the butadiene complexes, **2a** or **2b**, were successfully formed in the attempted synthesis of ruthena(IV)cyclopentanes, despite the number of possible decomposition pathways, for example, liberation of 1-butene. As shown in a recent, elegant study by Fagan and coworkers [8], halide, lithium salts, and alkyl complexes of Ru^{II}-complexes including framework of "$(C_5Me_5)Ru(\eta^4$-butadiene)" are stable enough to be isolated and characterized. Thus, high reactivity of the Ru^{IV}-dialkyl moieties to



Scheme 5

β-hydrogen elimination and high affinity of the η^4-butadiene ligand to $(C_5Me_5)Ru^{II}$ species may contribute to formation of **2a** and **2b** in high yields.

Conclusion

The attempted synthesis of ruthena(IV)cyclopentanes unexpectedly produces the novel Ru^{II} complexes, $(C_5Me_5)Ru(\eta^4$butadiene$)(\eta^1$-alkyl). The reaction probably proceeds via an irreversible double β-hydrogen elimination from ruthena(IV)cyclopentane intermediates. High reactivity toward β-hydrogen atom elimination is a characteristic property of Ru^{IV}allyl-alkyl complexes. The present data also reflect the high affinity of η^4-butadiene ligand to the $(C_5Me_5)Ru^{II}$ framework. We are currently investigating various reactions of η^4-butadiene ligands on this framework including catalytic oligomerization of butadiene.

Experimental

All manipulations were carried out using standard Schlenk techniques in anhydrous solvents under an inert-gas atmosphere. ^1H and ^{13}C NMR spectra were recorded with a JEOL GX-270 spectrometer. The Ru^{IV} complexes **1a** and **1b** were prepared by the methods reported previously [6]. $BrMg(CH_2)_4MgBr$ was prepared in ether from Mg and 1,4-dibromobutane before use. Elemental analyses were performed by the Elemental Analysis Center at Kyoto University. Melting points were measured in a sealed tube under a nitrogen atmosphere.

Preparation of $(C_5Me_5)Ru(\eta^1\text{-}C_3H_7)(\eta^4\text{-}C_4H_6)$ ***(2a).*** To a suspension of $(C_5Me_5)RuBr_2(\eta^3\text{-}C_3H_5)$ (**1a**) (500 mg, 1.14 mmol) in dry ether (15 ml) was added a slurry of $BrMg(CH_2)_4MgBr$ in ether (2 *N*, 2.3 ml) at 0 °C, and the mixture was stirred at 0 °C for 1 h. Pentane was added to the reaction mixture, and the solid formed was filtered. The filtrate was concentrated *in vacuo* and the residue was extracted by n-pentane. The extracts were concentrated and the residue was purified by alumina column, cooled by dry-ice/acetone at −78 °C, with pentane eluant. The pale-yellow band was collected and concentrated to give **2a** in 65% yield. Recrystallization from pentane gave the analytically pure sample. Mp. 60 °C (dec.). ^{13}C NMR ($CDCl_3$, 67.8 MHz) 9.5 ($C_5\mathit{Me}_5$), 22.0 (Me), 24.5 (Ru$\mathit{C}H_2$), 30.2 (Me$\mathit{C}H_2$), 44.1 ($\mathit{C}H_2$=CH), 83.7 (CH_2=CH), 93.0 (ring). Anal. Found: C, 61.37; H, 8.70. $C_{17}H_{28}Ru$ calcd.: C, 61.23; H, 8.46%.

Preparation of $(C_5Me_5)Ru(\eta^1\text{-}C_4H_9)(\eta^4\text{-}C_4H_6)$ ***(2b).*** This compound was prepared by the same procedure as the preparation of **2a**. **1b** (300 mg, 0.665 mmol) was treated with $BrMg(CH_2)_4MgBr$ (2 *N*, 1 ml) in ether at 0 °C for 1 h. The work-up followed by the chromatographic purification (alumina, pentane) in the same manner as in the preparation of **2a** afforded **2b** in 69% yield. Mp. 75–76 °C (dec.). ^{13}C NMR (C_6D_6, 67.8 MHz) 9.1 ($C_5\mathit{Me}_5$), 27.7 (CHMe), 30.2 (Ru$\mathit{C}H_2$), 31.9 ($\mathit{C}HMe_2$), 45.7 ($\mathit{C}H_2$=CH), 84.0 (CH_2=CH), 93.0 (ring). Anal. Found: C, 62.78; H, 8.91. $C_{18}H_{30}Ru$ calcd.: C, 62.21; H, 8.70%.

Preparation of 1,4-dibromobutane-1,1,4,4-d_4: To a suspension of $LiAlD_4$ (1 g, 23.8 mmol) in ether 20 ml was added dropwise a solution of dimethyl succinate (1.8 ml, 13.8 mmol) in ether (20 ml). The mixture was heated under reflux for 6 h, and then cooled to room temperature. Addition of NaF (4.0 g, 95 mmol) and water (1.7

ml, 95 mmol) was followed by filtration. The filtrate was dried over $MgSO_4$ and concentrated to give 1,4-butanediol-1,1,4,4-d_4 (799 mg, 62%) as a colorless oil, which was used for the next reaction without further purification. A mixture of this diol (519 mg, 5.5 mmol) with aqueous HBr (47%, 2.95 ml. 25.5 mmol) and conc. H_2SO_4 (0.3 ml) was heated under reflux for 6 h. The mixture was diluted with water and extracted with ether. The combined extracts were washed with water, aqueous Na_2CO_3, and dried over $MgSO_4$. After concentration, the residue was purified by distillation (95 °C/2 mmHg) to give 1,4-dibromobutane-1,1,4,4-d_4 (100%-d_4, 836 mg, 69%).

Preparation of 1,4-dibromobutane-2,2,3,3-d_4: Although preparation of 1,4-diiodobutane-2,2,3,3-d_4 was reported by Yang and Bergman [17], we preferred the procedure described below because of the easy access to tetradeuteriosuccinic acid. 1,4-Dibromobutane-2,2,3,3-d_4 was prepared from succinic acid-2,2,3,3-d_4 [18]. This acid (2.0 ml, 16.4 mmol) was esterified by treatment with $ClCO_2Me$ (2.5 ml, 32.8 mmol) and Et_3N (4.6 ml, 32.8 mmol) in CH_2Cl_2 (50 ml) at room temperature for 2 h. The mixture was poured into a cold, dilute, aqueous solution of HCl, and extracted with CH_2Cl_2. Distillation of the crude compound (80 °C/2 mmHg) gave dimethyl succinate-2,2,3,3-d_4 (1.67 g, 68%). This ester (1.30 g, 8.7 mmol) was treated with $LiAlH_4$ (659 mg, 17.3 mmol) in ether (10 ml) at 40 °C for 6 h. Addition of NaF (2.91 g, 69.4 mmol) and water (1.25 ml, 69.4 mmol) was followed by filtration. The filtrate was dried over $MgSO_4$ and concentrated to give 1,4-butanediol-2,2,3,3-d_4 (567 mg, 70%). Displacement of the hydroxy groups of this diol (400 mg, 4.26 mmol) in the same manner as described above gave 1,4-dibromobutane-2,2,3,3-d_4 (579 mg, 62%). The mass spectrum of this dibromide showed it to be contaminated with the d_3-isomer (ca. 40%).

Preparation of **2a** *and* **2b** *by the alkylation of* **3**: $(C_5Me_5)RuBr(\eta^4\text{-}C_4H_6)$ (**3**) (100 mg, 0.27 mmol) was treated with a solution of n-propyl magnesium bromide (1.8 *N*, 1.5 ml, 2.7 mmol) in ether at −5 °C for 4 h. Magnesium species precipitated by addition of n-pentane (9 ml) was filtered, and the filtrate was concentrated *in vacuo*. Chromatographic purification (alumina, pentane) afforded **2a** in 54% yield. A similar procedure with isobutyl magnesium bromode provided **2b** in 67% yield.

Preparation of $(C_5Me_5)RuBr(\eta^4\text{-}C_4H_6)$ *(3):* A series of the Ru^{II}-1,3-diene complexes, $(C_5R_5)Ru(\eta^4\text{-diene})X$ [R = H, Me; X = Cl, Br], can be prepared by the pyrolysis of $(C_5Me_5)RuBrMe(\eta^3\text{-}C_3H_5)$ [7b] in the presence of butadiene. $(C_5Me_5)RuBrMe(\eta^3\text{-}C_3H_5)$ (179 mg, 0.48 mmol) was heated with butadiene (34 ml) in a pyrex presssure bottle at 100 °C for 3 h. After removal of excess butadiene, the residue was washed with hexane and purified by silica-gel column. A yellow-brown band that was eluted with dichloromethane was collected and concentrated to give **4** in 65% yield (116 mg). Mp. 215–218 °C (dec). ^{13}C NMR (67.8 MHz) 9.7 ($C_5\mathit{Me}_5$), 51.7 ($\mathit{C}H_2$=CH–), 90.8 (CH_2=CH–), 94.8 (ring). Anal. Found: C, 45.63; H, 5.72. $C_{14}H_{21}BrRu$ calcd.: C, 45.41; H, 5.72%.

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