CHEMISTRY LETTERS, pp. 789 - 792, 1984. © The Chemical Society of Japan 1984

PREPARATION AND SPECTROSCOPY OF THE FIRST Ru(IV) METHYL COMPLEXES, Ru(CH$_3$)$_2$(1-3:6-7:10-12-η-C$_{12}$H$_{18}$) and Ru(CH$_3$)I(1-3:6-7:10-12-η-C$_{12}$H$_{18}$)

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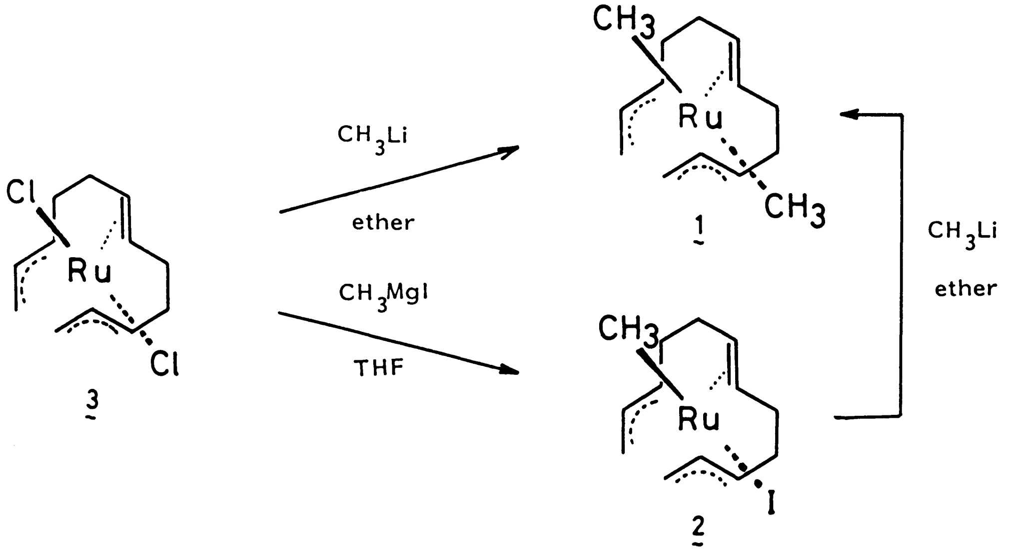
The first Ru(IV) methyl complexes, Ru(CH$_3$)$_2$(1-3:6-7:10-12-η-C$_{12}$H$_{18}$) and Ru(CH$_3$)I(1-3:6-7:10-12-η-C$_{12}$H$_{18}$), are prepared by organometallic methylation of RuCl$_2$(1-3:6-7:10-12-η-C$_{12}$H$_{18}$).

Current extensive studies on the properties and reactivity of transition metal alkyl complexes have provided much information on the role of metal-alkyl bonds in various transition metal catalyzed carbon-carbon bond forming reactions.[1-3] Alkyl complexes of early transition metals or later side elements of Group VIII transition metals have received much attention, especially related to the Grignard coupling reaction[4] and olefin metathesis reaction;[5] however, studies on the ruthenium complexes have not been undertaken in full detail. Several di-valent ruthenium alkyl complexes, stabilized by cyclopentadienyl or phosphine ligands, have been prepared by organometallic alkylation of Ru(II) halide complexes[6] or oxidative addition of organic halides to Ru(0) complexes.[7] However, alkyl complexes bearing other oxidation states are almost unknown despite of the potential possibility to synthesize Ru(I) to Ru(VIII) alkyl complexes. In this paper, we wish to report preparation and spectroscopy of Ru(CH$_3$)$_2$(1-3:6-7:10-12-η-C$_{12}$H$_{18}$) (1) and Ru(CH$_3$)I(1-3:6-7:10-12-η-C$_{12}$H$_{18}$) (2), which are the first methyl complexes of quadrivalent ruthenium.



The novel methyl complexes, **1** and **2**, were prepared by methylation of $RuCl_2$-(1-3:6-7:10-12-η-$C_{12}H_{18}$) (**3**).$^{8)}$ The dimethylation of **3** was accomplished with CH_3Li in ether at -40 °C under nitrogen atmosphere. After the work-up and purification by column chromatography (Al_2O_3; pentane) below -40 °C, **1** was obtained as pale yellow crystals in 50-60% yields. This complex is sensitive either thermally or to oxygen; decomposition occurred above -30 °C in solution or around 0 °C in solid states even under an inert gas atmosphere. Exposure to air instantly promoted the precipitation of ruthenium black.

In contrast to the instability of **1**, monomethyl complex **2** was isolated as air and thermally stable crystals by the reaction of **3** with CH_3MgI. Addition of an etherial solution of CH_3MgI to a THF solution of **3** at -40 °C under nitrogen atmosphere afforded a yellow homogeneous solution containing **2**. After the aqueous work-up and chromatographic purification (silica-gel, hexane-ether, and then Al_2O_3, hexane-ether), **2** was obtained in around 60% yields as yellow crystals. [mp 90-100 °C, decomp ; Found: C, 38.53; H, 5.23%. Calcd for $C_{13}H_{21}RuI$: C, 38.53; H, 5.22%] As a by-product, a small amount of **1** was formed, which was decomposed during the work-up to ruthenium black and a mixture of hydrocarbons. The hydrocarbons were easily removed by the chromatography. In the above procedure, control of the temperature is important, and at lower temperature, RuI_2(1-3:6-7:10-12-η-$C_{12}H_{18}$) (**4**) was formed as another by-product.

Careful treatment of **3** with one equivalent of CH_3Li in THF afforded the corresponding monomethyl complex, $Ru(CH_3)Cl$(1-3:6-7:10-12-η-$C_{12}H_{18}$) (**5**). However, **5** was hardly separated from the by-products concomitantly formed. In contrast, further methylation of **2** was accomplished with CH_3Li in ether to give **1** in 80% yield.

^1H- and ^{13}C-NMR spectra of **1**, **2**, **3**, and **4** are summarized in Table 1 and Fig. 1. X-Ray analysis showed that **3** had pseudo-trigonal bi-pyramidal structure bearing <u>trans</u>-dichloro ligands and a C_2-axis in the molecule.$^{8)}$ Due to the C_2-symmetry, spectral data of **3** as well as **4** are simple, and typically, ^{13}C-NMR spectra of **3** and **4** shows only six signals for $C_{12}H_{18}$ ligand. Noteworthily, ^{13}C-NMR spectrum of **1** affords six peaks for $C_{12}H_{18}$ ligand, accompanied by a signal at 14.9 ppm due to Ru-CH_3 (J_{CH}=125 Hz). The ^1H-NMR spectrum of **1** is also simple, and a new peak at -0.5 ppm for Ru-CH_3 and comparable signals to $C_{12}H_{18}$ ligand of **3** appear.$^{9)}$ These spectral data strongly suggest that **1** also has an intramolecular C_2-axis and probably similar structure to **3**.

Spectral data of **2** are rather complicated. ^{13}C-NMR spectrum of **2** affords a peak at 11.5 ppm assigned to Ru-CH_3 (J_{CH}=130 Hz) and twelve peaks for $C_{12}H_{18}$ ligand. This result indicates a loss of C_2-symmetry. Final assignments were carried out by ^1H-NMR (400 MHz) and ^{13}C-NMR (22.5 MHz) spectra including their selective irradiation studies. These data suggest the existence of two sets of a π-allyl moiety and olefinic carbon. The spectral data as well as the finding that **2** underwent methylation with CH_3Li to form **1** implicate that **2** has a similar structure to **1**, **3**, and **4**, namely, the one obtained by substitution of one halogen atom of **4** to the methyl group.

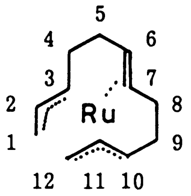
The significant view of above results is unusual stability of the Ru(IV)

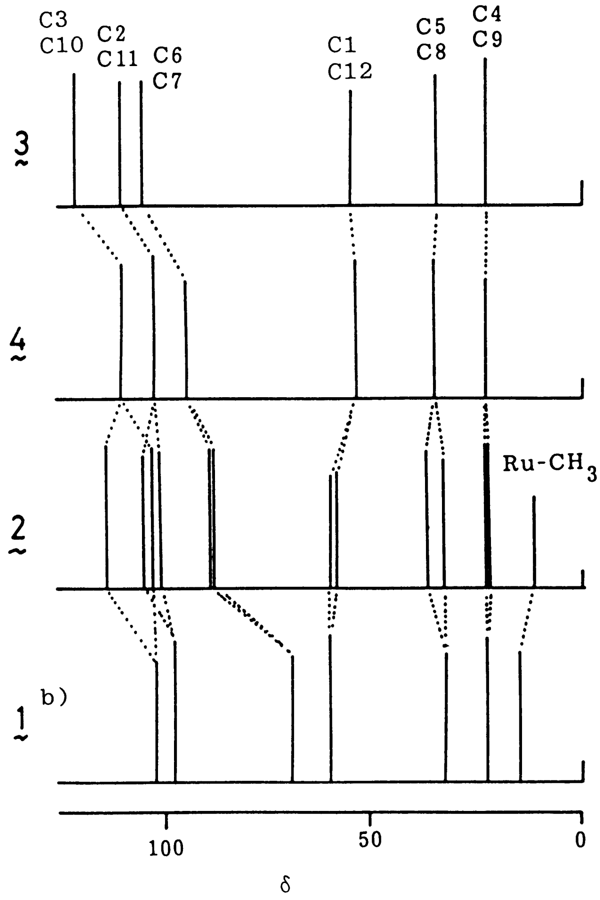
Table 1. ^{1}H-NMR spectra of 1, 2, 3, and 4 $^{a)}$

	1$^{b,d)}$	2$^{c)}$	3$^{d)}$	4$^{d)}$
Ru-CH_3	-1.01 (s)	-0.34 (s)	-	-
H4,H9	1.14-2.05 (m)	1.90-2.20 (m)	2.90-3.50 (m)	2.00-2.30 (m)
H5,H8	2.14-2.80 (m)	2.4-2.7,3.1-3.2,3.6-3.7 (m)	2.90-3.50 (m)	2.90-3.80 (m)
H1'	1.89	2.11 (d, J=11.2 Hz)	3.77	4.60
H12'	(d, J=10.1 Hz)	4.37 (d, J=11.2 Hz)	(d, J=11.7 Hz)	(d, J=10.8 Hz)
H1	3.54	4.53 (d, J=7.3 Hz)	4.89	4.68
H12	(d, J=6.98 Hz)	4.04 (d, J=7.3 Hz)	(d, J=7.7 Hz)	(d, J=7.7 Hz)
H3	2.89-3.25 (m)	3.10-3.20 (m)	4.90-5.20 (m)	5.61 (dt,
H10		5.90-6.00 (m)		J=6.4, 12.8 Hz)
H6	3.09 (s)	3.76 (br.d, J=13.7 Hz)	5.50 (br.s)	5.40 (br.s)
H7		5.53 (br.d, J=13.7 Hz)		
H2	3.89	6.50 (dt, J=7.8,11.7 Hz)	5.60	5.94 (ddd, J=
H11	(dt, J=7,10 Hz)	3.80 (dt, J=7.8,11.7 Hz)	(dt, J=8,10 Hz)	7.7,10.8,12.8 Hz)

a) All spectra were taken in $CDCl_3$. Chemical shifts (δ) are represented as ppm downfield from tetramethylsilane. b) Measured at -40 °C. c) Taken at 400 MHz. d) Taken at 90 MHz. e) Taken at 22.5 MHz.

Fig. 1. ^{13}C-NMR spectra of 1, 2, 3, and 4$^{a,e)}$





methyl complexes, especially 2, in spite of the structure having the methyl group and the π-allyl moiety in cis-orientation.$^{9)}$ Although the cis-orientation might lead to facile reductive elimination of the methyl group and the π-allyl moiety, GC-MS analysis of hydrocarbons obtained by thermal decomposition of 1 or 2 showed that products were a complicated mixture of olefinic compounds consisting of twelve or thirteen carbons.$^{10)}$

Among Group VIII transition metals, alkyl complexes without phosphine and other donor ligands are not very common except platinum.$^{11)}$ In contrast, a number of stable complexes, known as homo- and heteroleptic compounds, of early transition metals have been isolated.$^{2)}$ The present work is of interest as a rare successful example of homo- and heteroleptic-type complexes of late transition metals.

Experimental assistance by Mr. Hiroyuki Katsumi is acknowledged. The authors are greatly indebted to Assistant Professor Hidemasa Takaya, Institute for Molecular Science, for his stimulating discussion. The authors also thank to the Research Center of Chemometrics, Toyohashi University of Technology, for measurement of FX-90Q NMR spectrometer, and to Institute for Molecular Science for taking 400 MHz NMR spectra and GC-MS spectra. One of the authors (K. I.) are grateful to the Ministry of Education, Science, and Culture for a Grant-in-aid for Special Project Research (58210014).

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9) In a similar fashion, we attempted the preparation of Ru(IV) ethyl complexes. Treatment of **3** with excess C_2H_5MgBr at -78 °C and successive work-up below -60 °C afforded an unstable solid, ^{1}H-NMR of which suggests the structure, $Ru(C_2H_5)_2(1\text{-}3{:}6\text{-}7{:}10\text{-}12\text{-}\eta\text{-}C_{12}H_{18})$ [δ -0.35 ppm, q, 4H, Ru-CH_2]. However, in both solution and solid states, this compound decomposed above -60 °C, and detailed spectroscopic studies were not successful. Attempted isolation of the monoethyl complexes failed.
10) The main products of the thermal decomposition of **1** and **2** were tridecatrienes and dodecatrienes, respectively. Further studies on the reductive elimination are described in a subsequent paper.
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(Received March 7, 1984)