A Convenient Route to Ruthenium(IV)–Allyl Complexes $(C_5Me_5)RuX_2(\eta^3\text{-allyl})$ from $[(C_5Me_5)RuCl_2]_n$

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Summary: Ruthenium(IV)–allyl complexes $(C_5Me_5)RuCl_2(\eta^3\text{-allyl})$ are easily prepared from a Ru(III) complex, $[(C_5Me_5)RuCl_2]_n$, by treatment with allylic halides, alcohol, ethers, acetate, or sulfides. Treatment of the resulting dichlororuthenium(IV) complex with aqueous HBr or HI solution resulted in smooth halogen-exchange reactions.

In a previous paper we have reported a preparation of ruthenium(IV)–allyl complexes $(C_5R_5)RuX_2(\eta^3\text{-allyl})$ (R = H, Me; X = Cl, Br) by oxidative addition of allylic halides to several Ru(II) precursors.[3] Although these allyl complexes are attractive starting points for exploring the chemical properties of high-valent ruthenium species, the procedure starting with Ru(II) frequently requires the use of an excess of allylic substrate at elevated temperature to attain high yields of the ruthenium(IV)–allyl complex. Thermally labile allylic halides such as 1-bromo-2-phenyl-2-propene often decompose, and the formation of the Ru(IV) complexes is compromised. We report here a solution to this problem, namely, an extremely mild and convenient route to Ru(IV) complexes having the C_5Me_5 ligand from a Ru(III) precursor.

A CH_2Cl_2 solution containing $[(C_5Me_5)RuCl_2]_n$ (1)[4] (1 mmol), allyl chloride (2 mmol), and 95% ethanol (50 mmol) was stirred at 40 °C for 2 h under nitrogen to give a clear brown solution. After concentration, the residue was purified by chromatography (silica gel, hexane–ethyl acetate) to provide $(C_5Me_5)RuCl_2(\eta^3\text{-}C_3H_5)$ (**2a**) as orange crystals. As shown in Table I, Ru(IV) complexes having various η^3-allyl ligands were efficiently prepared by similar treatment of **1** with methallyl chloride, 1,2-dichloro-2-propene, or 1-chloro-2-phenyl-2-propene. The overall equation should be expressed as eq 1.[5]

Treatment of **1** with allyl alcohol, allyl acetate, allyl benzyl ether, allyl phenyl ether, or allylamine resulted in C–O or C–N bond cleavage and oxidation of alcohol solvent to provide *another preparative route to the dichlororuthenium(IV)–allyl complex* ***2a*** although the reaction was slower than that with the allylic chlorides. Allyl phenyl sulfide also was a source of the allylic component to **1**. The reaction was rapid and afforded **2a** or **2b** in quantitative yield even at 0 °C within 1 h in the absence of an alcohol component, with dimerization of the PhS moiety to give PhSSPh (eq 2). All results are summarized in Table I.

Table I

entry	R	X	temp, °C	time, h	product	yield, %
1	H	Cl	40	1.5	**2a**	94
2	H	Cl	20	3	**2a**	92
3	CH_3	Cl	40	3.5	**2b**	86
4	C_6H_5	Cl	40	6	**2c**	84
5	Cl	Cl	40	7	**2d**	91
6	H	OH	40	7	**2a**	80
7	CH_3	OH	40	48	**2b**	80
8	H	OAc	40	7	**2a**	88
9	H	OCH_2Ph	40	26	**2a**	83
10	H	OPh	40	26	**2a**	79
11	H	NH_2	40	16	**2a**	42
12[b]	H	SPh	0	1	**2a**	100
13[b]	CH_3	SPh	0	1	**2b**	100

[a] All reactions were carried out as described in the text. [b] An equimolar amount of the sulfide to 1 was used.

$$[(C_5Me_5)RuCl_2]_n + CH_2{=}CH(R)CH_2X + {}^1/_2R'_2CHOH \rightarrow (C_5Me_5)RuCl_2(\eta^3\text{-}CH_2CH(R)CH_2) + {}^1/_2R'_2C{=}O + HX \quad (1)$$

(**1** → **2**)

X = Cl, OH, OAc, OCH_2Ph, OPh, NH_2; R = H, Me, Ph, Cl

$$[(C_5Me_5)RuCl_2]_n + CH_2{=}CH(R)CH_2SPh \rightarrow (C_5Me_5)RuCl_2(\eta^3\text{-}CH_2CH(R)CH_2) + PhSSPh \quad (2)$$

(**1** → **2**)

The reaction of **1** with allyl bromide proceeded as rapidly as that with allyl phenyl sulfide to give **2a** and its halogen-exchange products $(C_5Me_5)RuBrCl(\eta^3\text{-}C_3H_5)$ (**3**) and $(C_5Me_5)RuBr_2(\eta^3\text{-}C_3H_5)$ (**4**) (eq 3). Monitoring the reaction by TLC indicated that **2a** was initially formed. The content of **3** and **4** slowly increased with reaction time. We have found that HBr, which should be produced in forming **2a** according to the overall equation, resulted in the halogen exchange of **2a** to **3** and **4**. In fact, **2a** was treated with aqueous 47% HBr in CH_2Cl_2 at 40 °C to afford **3** and **4**. With a 6 M excess of aqueous HBr heating the solution for 5 h provided selective formation of **4**. Similarly, treatment of **2a** with aqueous HI gave the diiodo complex **5** (eq 4).

$$1 + CH_2{=}CHCH_2Br \rightarrow \mathbf{2a} + (C_5Me_5)RuBrCl(\eta^3\text{-}C_3H_5) + (C_5Me_5)RuBr_2(\eta^3\text{-}C_3H_5) \quad (3)$$

(**1** → **3**, **4**)

	% yield **2a**, **3**, **4**
at −78 °C, 10 h	13, 0, 0
at −40 °C, 10 h	25, 7, 0
at 0 °, 1.5 h	42, 6, 3
at 40 °C, 1 h	46, 33, 12

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(5) Aqueous ethanol acts as hydrogen donor. Other primary or secondary alcohols such as methanol, isopropyl alcohol, and cyclohexanol could be used instead of ethanol. Aqueous alcohol gave **2** in somewhat higher yields than anhydrous alcohol. It was confirmed from the experiments using 4-*tert*-butylcyclohexanol as the hydrogen donor that an approximately half-molar amount of the alcohol was oxidized to 4-*tert*-butylcyclohexanone. Treatment of **1** with allyl chloride (2 equiv) and 4-*tert*-butylcyclohexanol (1 equiv) in CH_2Cl_2 at 40 °C for 2 h resulted in formation of **2a** in 73% yield. From the reaction medium, 4-*tert*-butylcyclohexanone was isolated in 31% yield by chromatographic purification. Since the alcohol is a two hydrogen donor per mole, the oxidation of Ru(III) to Ru(IV) approximately accompanies the oxidation of one hydrogen of the alcohol. Use of allyl acetate instead of allyl chloride gave **2a** and 4-*tert*-butylcyclohexanone in 72 and 36% yields, respectively. In the absence of alcohol, **2** was formed lower than 50% yield using either allyl chloride or allyl acetate as the allylation reagent. In these cases, a considerable amount of intractable materials was also obtained.

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$$\mathbf{2a} + HX \xrightarrow[1\text{–}1.5\ h]{40\ ^\circ C} \underset{90\text{–}95\%}{(C_5Me_5)RuX_2(\eta^3\text{-}C_3H_5)} \qquad (4)$$

X = Br, I

The above results show that the Ru(IV) complexes **2** can be conveniently prepared from **1** by treatment with several allylic substrates. Furthermore, facile halogen exchange of **2** with HBr or HI provides a convenient preparation of **4** and **5**, which contain more reactive leaving groups and are useful in the syntheses of alkyl derivatives.[6] Since the starting Ru(III) complex **1** can be prepared simply by treating hydrated $RuCl_3$ with C_5Me_5H,[4] the present procedure has established a highly convenient and economical preparation of these ruthenium(IV)–allyl complexes.

The present reaction also generates keen mechanistic questions regarding the cleavage of C–Cl, C–Br, C–O, C–N, and C–S bonds by a Ru(III) precursor. As previously reported, the Ru(III) complex **1** undergoes reduction by alcohols in the presence of several phosphines or dienes to give Ru(II) complexes $(C_5Me_5)RuL_2Cl$ (**6**).[4] Furthermore, we have already found that **6** (L = CO, PPh_3) reacts with allylic chlorides to give **2**.[3] One explanation for the present route from **1** to **2** is the reduction of **1** to Ru(II) species by the alcohol, followed by the oxidative addition of the allylic compounds to the Ru(II) center. However, there are no known examples of oxidative addition of allylic alcohol derivatives, allylamine, or allyl sulfide to Ru(II) complexes. In all cases where C–O, C–N, and C–S bond cleavage occurs, *Ru–O, Ru–N, or Ru–S bond formation never was observed.* In the reaction with allyl bromide, the dichloro complex was **2a** formed mainly at the early stages of the reaction at lower temperature and the halogen exchange to **3** and **4** seemed the secondary reaction. The reaction with allyl phenyl sulfide was not accompanied by any oxidation of alcohol solvents; the reaction proceeded smoothly even in anhydrous CH_2Cl_2 and a quantitative formation of PhSSPh. All of these findings indicate an alternative mechanism that the reaction of **1** to **2** takes place with retention of the Ru(III) framework "$(C_5Me_5)RuCl_2$", which abstracts the allylic component homolytically from the allylic compounds. The resulting halo, hydroxy, thiyl, etc. radicals will abstract hydrogen from the alcohol solvent or will undergo dimerization. We are seeking experimental support for this homolytic pathway.[7]

Registry No. **1**, 96503-27-4; **2a**, 91083-13-5; **2b**, 91083-14-6; **2c**, 96503-23-0; **2d**, 96503-24-1; **3**, 96503-25-2; **4**, 91083-12-4; **5**, 96503-26-3; $H_2C{=}CHCH_2Cl$, 107-05-1; $H_2C{=}C(CH_3)CH_2Cl$, 563-47-3; $H_2C{=}C(C_6H_5)CH_2Cl$, 3360-52-9; $H_2C{=}CClCH_2Cl$, 78-88-6; $H_2C{=}CHCH_2OH$, 107-18-6; $H_2C{=}C(CH_3)CH_2OH$, 513-42-8; $H_2C{=}CHCH_2OAc$, 591-87-7; $H_2C{=}CHCH_2OCH_2Ph$, 14593-43-2; $H_2C{=}CHCH_2OPh$, 1746-13-0; $H_2C{=}CHCH_2NH_2$, 107-11-9; $H_2C{=}CHCH_2SPh$, 5296-64-0; $H_2C{=}C(CH_3)CH_2SPh$, 702-00-1; PhSSPh, 882-33-7; $H_2C{=}CHCH_2Br$, 106-95-6; 4-*tert*-butylcyclohexanol, 98-52-2; 4-*tert*-butylcyclohexanone, 98-53-3.

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(7) According to this homolytic mechanism, **1** formally abstracts an allyl radical from the allylic compound. In other words, allylic compounds undergo homolytic substitution by **1** in releasing halo, hydroxy, or thiyl radicals. The transition metal–alkyl bond formation with an overall one-electron oxidation of the metal is usually initiated by halogen abstraction by the metal from organic halides, and the resulting alkyl radical was captured by another metal species to produce the metal–alkyl bond. The present oxidative allylation of **1** may be an unusual example involving the S_H pathway. For the leading references, see: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 229–232. Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978. Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.

Supplementary Material Available: Melting points, ^1H NMR data, and analyses for compounds **2c**, **2d**, **3**, and **5** (2 pages). Ordering information is given on any current masthead page.

Structure and Reactivity of $[CpFeS_2]_2$

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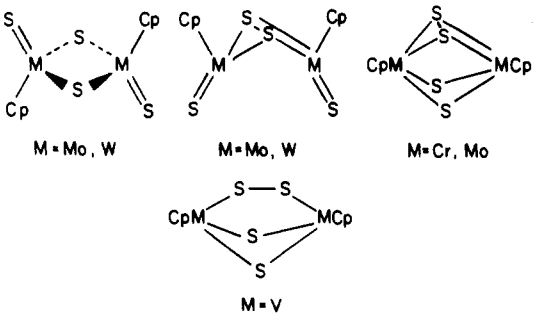
Summary: The complex $[CpFeS_2]_2$, IA (Cp = C_5H_5), which is the reported product of the photolytic reaction of elemental sulfur with $[CpFe(CO)_2]_2$, has been characterized by an X-ray diffraction study. The complex crystallizes in space group *Pbca* with a = 7.286 (1) Å, b = 17.468 (5) Å, and c = 19.472 (6) Å. The metal ions in IA are bridged by two mutually perpendicular disulfide ligands. In solution, IA is in equilibrium with a second isomer. The equilibrium mixture reacts with electrophiles such as methyl iodide and hexafluorobutyne. The reaction with the latter reagent results in two products, $(CpFeS)_2S_2C_2(CF_3)_2$, III, and $(CpFe)_2(S_2C_2(CF_3)_2)_2$, IV. Single crystals of IV crystallize in space group *C*2/*c* with a = 16.429 (3) Å, b = 10.134 (2) Å, c = 14.591 (2) Å, and β = 114.67 (2)°. Each butenedithiolate ligand in IV is bidentate with one bridging and one terminally coordinated sulfur donor.

Molybdenum dimers of oxidation states, V, IV, and III, which have in common the $Cp_2M_2S_4$ core, have been found to display unusual sulfur ligand-based reactivity.[2-4] Both the structure and reactivity of the M_2S_4 unit have been found to vary as a function of molybdenum ion oxidation state.[5] A variation in metal ion is an alternate way of changing the electronic and structural characteristics of the dimers. A comparison of the known complexes of chromium, molybdenum, tungsten, and vanadium with the $Cp_2M_2S_4$ formulation[6-8] (where Cp = $R_nC_5H_{5-n}$, n = 0, 1, or 5) reveal four different structural types in which the reactivities of the sulfur ligands vary significantly.



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