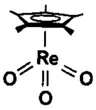

theoretical abundancies as the only prominent feature, with m/z values (theoretical percent in parentheses): 368 [56% (58.5%), ^{185}Re], 369 [8% (6.7%)], 370 [100% (100%), ^{187}Re], 371 [12.5% (11.5%)]. The IR spectrum (KBr) had bands at 910 (s) cm^{-1} [$\nu_{sym}(ReO_3)$] and 881 (vs) cm^{-1} [$\nu_{asym}(ReO_3)$], and the ^{1}H NMR ($CDCl_3$) had only a single resonance for the C_5Me_5 group at δ 2.16. It sublimes readily at 40 °C and 10^{-2} torr and is insoluble in hexane but soluble in common organic solvents (ether, THF, C_6H_6, MeOH, CH_2Cl_2), and the solutions are air stable. Although optically excellent crystals can be grown readily from, e.g., CH_2Cl_2–hexane, all thus far examined have been twinned and no X-ray structure is yet available.

In all of the reactions giving 1 (above) where THF is the solvent, organic oxidation products are observed, identified by a characteristic IR having prominent absorptions at 1776 (vs) and 1726 (m) cm^{-1} plus associated shoulders. These separate from 1 by elution in hexane, and GC/MS shows there to be at least five components, not all yet identified. The major one is γ-butyrolactone (ν(CO) 1776 cm^{-1}; m/z 86). These oxidation products were not formed when pure THF was pressurized with O_2 at 450 psi for 1 day alone or in the presence of 1.

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Registry No. 1, 90695-83-3; (η^5-C_5Me_5)Re(CO)$_2$(THF), 90695-84-4.

Preparation of Novel Ruthenium(IV) Complexes (η^5-$C_5(CH_3)_5$)Ru(η^3-allyl)X_2 and (η^5-C_5H_5)Ru(η^3-allyl)X_2 by Oxidative Addition of Allylic Halides to Ruthenium(II) Precursors

Hideo Nagashima, Katsunori Mukai, and Kenji Itoh*

School of Materials Science
Toyohashi University of Technology
Tempaku-cho, Toyohashi, Aichi 440, Japan

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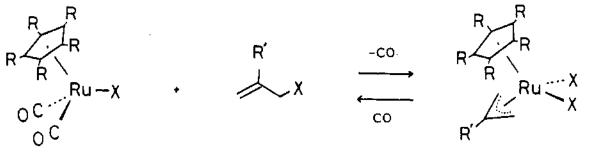
Summary: Oxidative addition of allylic halides to ruthenium(II) carbonyl complexes Cp′Ru(CO)$_2$X and CpRu(CO)$_2$X [Cp′ = η^5-$C_5(CH_3)_5$; Cp = η^5-C_5H_5; X = Br, Cl] resulted in the formation of novel Ru(IV) complexes Cp′Ru(η^3-allyl)X_2 and CpRu(η^3-allyl)X_2. Reaction of the resulting ruthenium(IV) allyl complexes with CO did not lead to incorporation of CO into the allylic moiety but gave rise to reductive elimination of the allylic halides from the Ru(IV) metal center to afford the ruthenium(II) carbonyl complexes Cp′- and CpRu(CO)$_2$X.

The chemistry of late transition metals in their higher oxidation states requires further investigation.[1-3] Recent studies by Maitlis[2] and Bergman[3] have resulted in the successful preparation of several d^4 complexes of Rh(V) and Ir(V). In this context, the isoelectronic Ru(IV) complexes are an attractive target for us, only a few organometallic complexes of Ru(IV) having been reported.[4-7] In this paper, we wish to report a simple preparation of novel ruthenium(IV) π-allyl complexes by oxidative addition of allylic halides to ruthenium(II) carbonyl precursors. The resulting Ru(IV) complexes undergo smooth reductive elimination of the allylic halides by reaction with CO (Scheme I).

Scheme I



R = CH_3, H, R′ = Ph, CH_3, H, X = Br, Cl

Some Ru(IV) complexes have been prepared by oxidative addition of hydrogen,[4] halogens,[5] or quinones[6] to several Ru(II) complexes. Alternatively, oxidative cyclization of 1,3-dienes on Ru(II) species generated in situ in an alcoholic solution of $RuCl_3$ affords some ruthenium(IV) bis(π-allyl) complexes.[7] Organic halides are potentially applicable as the addenda of oxidative addition to Ru(II) precursors, but few studies have been undertaken. We have found that ruthenium(II) carbonyl complexes Cp′Ru(CO)$_2$Br (1) reacted with allyl bromide at 100–140 °C to give a new Ru(IV) complex, Cp′Ru(η^3-allyl)Br$_2$ (**5a**), in higher than 90% yields. In a typical example, a solution of 1 (372 mg, 1 mmol) in decane (10 mL) containing allyl bromide (0.17 mL, 2 mmol) was heated at 140 °C for 10 h under nitrogen. Brown crystals that precipitated from the solution were collected and were recrystallized from dichloromethane–ether to give **5a**[8] as thermally air-stable crystals. Oxidative addition of allylic halides to Cp′Ru(CO)$_2$Br (1), Cp′Ru(CO)$_2$Cl (2), CpRu(CO)$_2$Br (3), and CpRu(CO)$_2$Cl (4) can be generally used for the preparation of the ruthenium(IV) η^3-allyl complexes **5b–h** with similar procedures to that described above. The results are summarized in Table I.[9]

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[1] Organometallic compounds of Pt(IV) are well-known examples of this issue; Hartley, F. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 471.

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(8) Spectral data of **5a**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.74 (s, 15 H, Cp′), 2.25 (d, J = 9.91 Hz, 2 H, syn proton on terminal carbon of π-allyl), 4.25 (d, J = 6.08 Hz, 2 H, anti proton on terminal carbon of π-allyl), 5.20 (m, 1 H, proton on central carbon of π-allyl); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 9.6 (q), 64.8 (d), 96.2 (d), 103.7 (s); mp 200–205 °C dec. Anal. Calcd for $C_{13}H_{20}Br_2Ru$: C, 35.72; H, 4.61. Found: C, 35.53; H, 4.56. The Ru(IV) complexes **5b–h** had satisfactory spectral data and elementary analysis. The data are given in the supplementary material.

(9) Ruthenium(II) phosphine complexes CpRu(PPh$_3$)$_2$Cl and Cp′Ru(CO)(PPh$_3$)Br also underwent the oxidative addition of allylic halides to form the corresponding ruthenium(IV) η^3-allyl complexes 5 but in 40–50% yields.

Table I. Oxidative Addition of Allylic Halides to Ruthenium(II) Carbonyl Complexes[a]

entry	Ru(II) complex[b]	allylic halide	product	yield,[c] %
1	$Cp'Ru(CO)_2Br$ (**1**)	allyl bromide	**5a**, $R^1 = CH_3$, $R^2 = H$, $X = Br$	96
2	$Cp'Ru(CO)_2Cl$ (**2**)	allyl chloride	**5b**, $R^1 = CH_3$, $R^2 = H$, $X = Cl$	90
3	$Cp'Ru(CO)_2Cl$ (**2**)	methallyl chloride	**5c**, $R^1 = CH_3$, $R^2 = CH_3$, $X = Cl$	94
4	$Cp'Ru(CO)_2Br$ (**1**)	1-bromo-2-phenyl-1-propene	**5d**, $R^1 = CH_3$, $R^2 = Ph$, $X = Br$	96
5	$CpRu(CO)_2Br$ (**3**)	allyl bromide	**5e**, $R^1 = H$, $R^2 = H$, $X = Br$	92
6	$CpRu(CO)_2Cl$ (**4**)	allyl chloride	**5f**, $R^1 = H$, $R^2 = H$, $X = Cl$	92
7	$CpRu(CO)_2Cl$ (**4**)	methallyl chloride	**5g**, $R^1 = H$, $R^2 = CH_3$, $X = Cl$	94
8	$CpRu(CO)_2Br$ (**3**)	1-bromo-2-phenyl-1-propene	**5h**, $R^1 = H$, $R^2 = Ph$, $X = Br$	82

[a] All reactions were carried out in *n*-decane at 140 °C for 3-12 h. [b] $Cp = \eta^5\text{-}C_5H_5$; $Cp' = \eta^5\text{-}C_5(CH_3)_5$. [c] The reactions were accompanied by the recovery of a small amount of the starting Ru(II) complex (~10%). The yields listed are those taking into account the recovery of starting complex and are not optimized. [d] **1** and **2** were prepared by the same procedure as **3** and **4**. [e] Haines, R. J.; du Preez, A. L.; *J. Chem. Soc., Dalton Trans.* **1972**, 944. [f] Blackmore, T.; Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2931.

Oxidative addition of some organic halides to Ru(0) complexes $Ru_3(CO)_{12}$[10] and $RuCl(NO)(PPh_3)_3$[11] have been reported. On the other hand, group 6 d^6 complexes, $Mo(CO)_6$,[12] $W(CO)_6$,[13] and their derivatives and bis(arene) complexes of Mo and W[14] are known to undergo oxidative addition of allylic halides to give the corresponding divalent η^3 complexes. The present work is the first example of the oxidative addition of organic halides to d^6 Ru(II) complexes, which are isoelectronic to Mo(0) complexes[12,14] to our knowledge.

Reaction of Ru(IV) complexes **5** with CO resulted in reductive elimination of the allylic halides from the metal center to give ruthenium(II) halogeno carbonyl complexes **1**–**4**. This result implies that reversal of the above described oxidative addition is easily induced by coordination of CO. Typically, a diglyme solution of **5h** was heated at 140 °C for 0.5 h under an atmosphere of CO to give the Ru(II) complex **3** and 1-bromo-2-phenyl-1-propene in 80 and 73% yields, respectively. In the absence of CO, **5h** was completely recovered under the same conditions. We recently found that a ruthenium(IV) methyl complex, $Ru(CH_3)I(1\text{–}3,6,7,10\text{–}12\text{-}\eta\text{-}C_{12}H_{18})$, underwent smooth reductive coupling of the methyl moiety with one of the π-allyl moieties under CO atmosphere.[15] It was proven that reduction of electron density on the metal center was crucial in reductive elimination of alkanes from dialkylnickel complexes.[16] It is reasonable that coordination of CO to the Ru(IV) metal center of **5h** reduces the electron density on the metal, facilitating the reductive elimination of allylic halides. Other Ru(IV) complexes **5a** and **5d** also underwent reductive elimination under conditions similar to those above to give **1** (70–80%) and the corresponding allylic halides (50–70% yields).

Attempted carbonylation of the coordinated allylic moiety was unsuccessful; heating a diglyme solution of **5h** at 120–140 °C under 30 atm of CO pressure results in no incorporation of CO into the allylic moiety but only simple reductive elimination of the allylic halides.[17]

High-valent organometallic complexes of late transition metals are of interest because they have comparable numbers of d electrons to those of early transition metals and would be expected to have properties that differ from those found for the more commonly encountered transition-metal complexes. Chemistry stemming from the Ru(IV) complexes described in this paper is under active study.

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Supplementary Material Available: Tables of ^{1}H NMR and analytical data for **5a–h** (2 pages). Ordering information is given on any current masthead page.

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(17) As found in the carbonylation studies on the palladium η^3-allyl complexes, CO may be incorporated into the allylic moiety via the (alkoxycarbonyl)palladium species formed by nucleophilic attack of alkoxide on the coordinated CO rather than by the direct insertion of CO in the Pd–allyl linkage.[18] In fact, carbonylation of palladium η^3-allyl complexes proceeded more smoothly in alcoholic media under basic conditions, where the nucleophilic attack of alkoxide to the coordinated CO is enhanced.[18c] We attempted the carbonylation of **5h** in ethanol at 100–140 °C under 30–50 atm of CO pressure. However, no carbonyl compounds was formed in either the presence or absence of K_2CO_3. These results indicate that the reductive elimination of allylic halides from ruthenium(IV) η^3-allyl complexes predominates over either the direct insertion of CO in the Ru–allyl linkage or formation of alkoxycarbonyl complex of Ru(IV) by nucleophilic attack of alkoxide on the Ru–CO group.

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Solvated Triorganotin Cations. Structure and Use as Catalysts for Diels–Alder Additions to Furan

William A. Nugent,* Ronald J. McKinney, and
R. L. Harlow

E. I. du Pont de Nemours and Company
Central Research and Development Department
Experimental Station, Wilmington, Delaware 19898

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Summary: The title compounds, $R_3SnL_2{}^+X^-$, where L is acetonitrile and X is a non-coordinating anion (e.g. $SbF_6{}^-$), have been prepared and characterized. They are effective Lewis acid catalysts for the Diels–Alder addition of α,β-unsaturated nitriles to furan.

Uncharged group 3B derivatives ($AlEtCl_2$, BF_3, BPh_3, etc.) constitute a broadly useful class of Lewis acid cata-