Preparation and Reactions of η^3 -Allylcarboxylatoruthenium(II)

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Dedicated to Professor Dr. Dr. h. c. mult. Günther Wilke on the occasion of his 60th birthday

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Reactions of (1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium(0) with 3-butenic acid in the presence of tertiary phosphines, PR_3 , afford η^3 -allylcarboxylatoruthenium(II) complexes formulated as $(\text{PR}_3)_2\text{RuCH}_2\cdots\text{CH}\cdots\text{CHCOO}$ (**1** ($\text{PR}_3 = \text{PPh}_3$), **2** ($\text{PR}_3 = \text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3)_3$). The reaction of **1** with carbon monoxide gives the complex $(\text{PPh}_3)_2(\text{CO})\text{RuCH}_2\cdots\text{CH}\cdots\text{CHCOO}$ while reaction with Br_2 or I_2 leads to ring closure of the organic ligand to afford 2-butenolide.

Introduction

We have previously reported that $\text{Ni}(0)$ and $\text{Pd}(0)$ complexes react with α,β - or β,γ -unsaturated carboxylic acids, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{COOH}$ ($n = 0,1$), to give metal-containing cyclic esters (or lactones), $\text{L}_n\text{M}(\text{CH}_2)_{n+2}\text{COO}$ [1]. As an extension of this work, we have now investigated the reactions of the $\text{Ru}(0)$ complex $\text{Ru}(\text{cod})(\text{cot})$ [2] ($\text{cod} = 1,5$ -cyclooctadiene; $\text{cot} = 1,3,5$ -cyclooctatriene) with α,β - and β,γ -unsaturated carboxylic acids to explore whether similar reactions of unsaturated carboxylic acids with the ruthenium(0) complex give metallacyclic complexes.

The $\text{Ru}(0)$ in the starting material is complexed to hydrocarbon ligands which can be readily displaced and is considered to be ideally suited as a precursor to coordinatively unsaturated, reactive species whose reactivity can be controlled by addition of auxiliary ligands. However, only a few publications [3, 4] have appeared on the utilization of $\text{Ru}(\text{cod})(\text{cot})$ in the preparation of new organoruthenium complexes. We now report the results of the reactions of $\text{Ru}(\text{cod})(\text{cot})$ with 3-butenic acid in the presence of tertiary phosphines, characterization of the complexes obtained and some chemical reactions.

Results and Discussion

Preparation of the $\text{RuCH}_2\cdots\text{CH}\cdots\text{CHCOO}$ complexes

$\text{Ru}(\text{cod})(\text{cot})$ reacts with 3-butenic acid (1 mol/mol of $\text{Ru}(\text{cod})(\text{cot})$) in the presence of a tertiary phosphine

(PR_3) at room temperature to give the η^3 -allylcarboxylatoruthenium(II) complexes.

Addition of excess 3-butenic acid decreases the yields of the complexes. In the reaction solution we were able to detect the isomers of cyclooctadiene, but cyclooctene, a hydrogenation product of cod , was not present. The two hydrogen atoms consumed in reaction (1) are probably trapped by the cot ligand to give cyclooctadienes. The reaction presumably proceeds through

- (i) transfer of a proton from the 3-butenic acid to the cot ligand to give a cyclooctadienyl(3-butenato)ruthenium(II) complex,
 $\text{Ru}(\text{C}_8\text{H}_{11})(\text{OCOCH}_2\text{CH}=\text{CH}_2)\text{L}_n$,
 and
- (ii) abstraction of the allylic hydrogen in the 3-butenato ligand by the cyclooctadienyl ligand to give **1–3**.

Step 1 – The attack of a compound having active hydrogen (HA) on an olefin coordinated to a transition metal with formation of $\text{M}(\text{alkyl})(\text{A})$ type complexes (M = transition metal) – has precedence [5].

Use of 3-butenic acid- $^{13}\text{C}_1$ ($\text{CH}_2 = \text{CHCH}_2^{13}\text{COOH}$) in reaction (1) afforded **1**- $^{13}\text{C}_1$

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No isolable products were formed upon reaction of other α,β - or β,γ -unsaturated carboxylic acids such as acrylic acid, methacrylic acid, and 3-hexanoic acid or in the reaction with $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ and $\text{PPh}_2(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)$. Attempts to prepare **1** by oxidative addition of 2-butenolide to $\text{Ru}(\text{cod})(\text{cot})$ in the presence of PPh_3 were not successful.

Complex **1** is insoluble in most organic solvents, whereas **2** and **3** are soluble in polar solvents such as

THF, acetone, CHCl_3 and CH_2Cl_2 . The insoluble PPh_3 -coordinated complex **1** is converted into a soluble complex, **4**, by reaction with carbon monoxide.

The reaction of **3** with CO affords a similar complex, viz. $\text{RuCH}_2\text{---CH---CHCOO}(\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Cl})_3)_2(\text{CO})$, **5**. Reaction of **1**-¹³C₁ with CO affords **4**-¹³C₁. Complexes **1**–**5** are insensitive to air in the solid state, but decompose in solution.

Complex	IR ^a cm ⁻¹	¹ H-NMR ^b δ	¹³ C{ ¹ H}-NMR ^b ppm from TMS	³¹ P{ ¹ H}-NMR ^b ppm ^c
1	1535* 740 640	insoluble	insoluble	insoluble
2	1950 1545* 1500	^e	^e	38.5 (d, 31.2 Hz) 41.2 (d, 32.2 Hz) 58.8 (d, 31.2 Hz) 59.1 (d, 32.2 Hz)
3	1540* 1475 1090	^e	^e	–3.0 (free Phosph.) 44.2 (d, 31.3 Hz) 62.2 (d, 31.3 Hz)
4	1930 1670* 690	1.8 (1H, dddd, H ^a) 2.6 (1H, dddd, H ^b) 4.2 (1H, ddd, H ^c) 5.3 (1H, dddd, H ^d) 7.5–7.1 (H, m, Ph) $J(\text{H}^a\text{--H}^b) = 2 \text{ Hz}^d$ $J(\text{H}^a\text{--H}^c) = 2 \text{ Hz}^d$ $J(\text{H}^a\text{--H}^d) = 11.2 \text{ Hz}$ $J(\text{H}^a\text{--P}) = 7.0 \text{ Hz}$ $J(\text{H}^a\text{--P}') = 6.1 \text{ Hz}$ $J(\text{H}^b\text{--H}^c) = 2 \text{ Hz}^d$ $J(\text{H}^b\text{--H}^d) = 7.6 \text{ Hz}$ $J(\text{H}^b\text{--P}) = 3.0 \text{ Hz}$ $J(\text{H}^b\text{--P}') = 2 \text{ Hz}^d$ $J(\text{H}^c\text{--H}^d) = 7.6 \text{ Hz}$ $J(\text{H}^d\text{--P}) = 1.2 \text{ Hz}$	53.4 (dt, C ^{γ}) 76.0 (dd, C ^{α}) 101.2 (d, C ^{β}) 127.6–135.6 (m, Ph) 203.3 (t, Ru–CO) $J(\text{C}^{\gamma}\text{--H}) = 159.9 \text{ Hz}$ $J(\text{C}^{\alpha}\text{--H}) = 162.7 \text{ Hz}$ $J(\text{C}^{\beta}\text{--H}) = 161.2 \text{ Hz}$ $J(\text{C--P}) = 24.1 \text{ Hz}$ $J(\text{C--P}') = 21.1 \text{ Hz}$ $J(\text{C--P}) = 21.9 \text{ Hz}$ $J(\text{C--COO}) = 58.1 \text{ Hz}$ $J(\text{P--CO}) = 14.2 \text{ Hz}$	40.1 (d, 9.8 Hz) 35.4 (d, 9.8 Hz)
5	1950 1670* 1690	1.8–1.4 (1H, m, H ^a) 3.0–2.6 3.0–2.6 (1H, m, H ^b) 4.3–4.1 (1H, m, H ^c) 5.5–5.1 (1H, m, H ^d) 7.3–6.7 (24H, m, Ph)		
1 - ¹³ C	1500*			
4 - ¹³ C	1620–1630*			

Table I. IR and NMR Data for complexes **1**–**5**.

^a Strongest three peaks are shown. The absorption band with an asterisk is assigned to $\nu(\text{C=O})$ of the carboxylato ligand;

^b in CDCl_3 or $^{12}\text{CD}_2\text{Cl}_2$;

^c ppm from external PPh_3 ;

^d These coupling constants have about the same value, and a more accurate determination of their values was not possible;

^e full assignment was not possible since the peaks were very broad or overlapped with each other or with solvent peaks.

NMR and IR structural investigations

The IR spectra of complexes **1**, **2** and **3** show $\nu(\text{C}=\text{O})$ absorption bands for the carboxylato group at 1535, 1545 and 1540 cm^{-1} , respectively, whereas those for **4** and **5** appear at 1670 cm^{-1} . The IR spectrum of **1**- $^{13}\text{C}_1$ shows the expected low frequency shift of the $\nu(\text{C}=\text{O})$ absorption band to 1500 cm^{-1} . The IR spectra of **4** and **5** have bands at 1930 and 1950 cm^{-1} , respectively which are attributed to the terminal CO molecules.

Table I summarizes the ^1H , ^{13}C , and ^{31}P NMR data for **2**–**5**. The ^1H NMR spectra of the complexes are consistent with the proposed structures and have typical allylic H^a – H^d signals in the region 1.8–5.4 ppm. The coupling patterns of the H^a – H^d signals have been analyzed by homo-decoupling as well as by $^1\text{H}/^1\text{H}$ shift correlation in a two-dimensional NMR spectrum from which it can be clearly seen that H^d is coupled to H^a , H^b , and H^c .

In the ^{13}C – $\{^1\text{H}\}$ NMR spectrum of **4** (Fig. 1), the C^α and C^γ carbon atom resonances (but not C^β) couple to one of the two phosphorus nuclei (pre-

Fig. 1. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of **4** (lower spectrum) and **4**- $^{13}\text{C}_1$ (upper spectrum). In CD_2Cl_2 at room temperature.

sumably that trans to the carbon atoms). A ^1H -gated-decoupled ^{13}C NMR spectrum indicates that C^γ is bonded to two H atoms whereas both the C^α and C^β carbon atoms are bonded to one H atom. In the ^{13}C – $\{^1\text{H}\}$ NMR spectrum of the ^{13}C -enriched sample **4**- $^{13}\text{C}_1$, the C^α carbon atom couples to the ^{13}C - ^{13}C carbonyl carbon atom ($J^{13}\text{C}-^{13}\text{C} = 58.1 \text{ Hz}$) clearly indicating that the C^α signal arises from the carbon atom adjacent to the $^{13}\text{C}=\text{O}$ carbonyl group. The ^{13}C – $\{^1\text{H}\}$ NMR signal for **4** at 170.2 ppm is greatly enhanced in the spectrum of **4**-

$^{13}\text{C}_1$ which supports its assignment to the carbonyl carbon of the η^3 -allylcarboxylato group. The triplet at 203.3 ppm is also unequivocally assigned to the CO ligand and couples with two phosphorus nuclei ($^1J(^{13}\text{C}-^{31}\text{P}) = 14.2 \text{ Hz}$).

The $^1\text{H}/^{13}\text{C}$ shift correlation in a two-dimensional NMR spectrum further confirms the ^{13}C – ^1H couplings C^β – H^d and C^α – H^c . The values of $^1J(^{13}\text{C}-^1\text{H})$, derived from a gated decoupling experiment, are all in the region of 159.9–162.7 Hz (Table I) and are consistent with the sp^2 character of the three carbon atoms [6] in the η^3 -allylic group and exclude the possibility that **4** has a σ -allylic structure, *e.g.* **4'** or **4''**.

The ^{31}P – $\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2 consists of two sharp doublets, indicating that in solution **4** has a rigid structure (on the NMR time scale). The $^1\text{H}/^{31}\text{P}$ shift correlation in a two-dimensional NMR spectrum of **4** is shown in Fig. 2 and indicates a long distance correlation between H^a and the phosphorus

Fig. 2. Two dimensional NMR spectrum of **4** showing $^1\text{H}/^{31}\text{P}$ shift correlation. In CDCl_3 at room temperature.

atoms of the two PPh_3 ligands and is, to our knowledge, the first example of its kind. The other hydrogen atoms in the η^3 -allylcarboxylato ligand show no (or negligibly small) correlations with the ^{31}P absorptions. The strong correlation between H^a and the ^{31}P absorptions may be due to interaction of H^a with Ru which has been reported for some Ru complexes coordinated to hydrocarbon ligands [7]. The ^{31}P - $\{^1\text{H}\}$ NMR spectrum of **2** consists of complex absorptions patterns, suggesting a polynuclear structure formed through intermolecular coordination of the ester group to the Ru atom(s) of other molecule(s) or, alternatively, the presence of stereoisomers. In this respect it should be mentioned that Ni-containing cyclic ester and amide complexes (*e.g.*, $(\text{PR}_3)_n\text{NiCH}_2\text{CH}(\text{CH}_3)\text{CONH}$) [1] have been shown to have polynuclear structures in solution and in the solid [8], and their ^{31}P - $\{^1\text{H}\}$ NMR spectra also show complex absorption patterns. The ^{31}P - $\{^1\text{H}\}$ NMR spectrum of **3** shows the dissociation of one PPh_3 ligand in CD_2Cl_2 .

Chemical reactions

Treatment of compounds **1–5** with Br_2 at room temperature causes ring closure of the η^3 -allylcarboxylato ligand to produce the 5-membered unsaturated cyclic ester, 2-butenolide,

When the CO coordinated complexes, **4** and **5**, were reacted, yields of 2-butenolide were high (86% and 93%, respectively). However, reaction of **1**, **2**, and **3** gave only low yields (8–21%) of 2-butenolide. 2-Butenolide may be produced through a ruthenacyclic intermediate, similar to that postulated for **4'**. Treatment of **4** with I_2 (1 mol/mol of **4**) gave 2-butenolide in 21% yield. Formation of 2-butenolide in reaction (3) perhaps involves an initial Br_2 -instigated reductive coupling of the η^3 -allylcarboxylato group and could be regarded as the reverse of the oxidative addition of allylic carboxylates to transition metal complexes which has precedence [9]. Complexes **4** and **5** are inert to CO (20 atm), maleic anhydride, and S_8 which usually react with organometallic compounds. Attempts to hydrogenate the allylic moiety

over Pd/charcoal were unsuccessful and the starting material was recovered.

Experimental

Materials and manipulation of complexes

$\text{Ru}(\text{cod})(\text{cot})$ was prepared according to the literature [2]. Triphenylphosphine was used as purchased from Tokyo Kasei Co. Ltd., and other tertiary phosphines from Strem Chemicals, Inc. 3-Butenoic acid- $^{13}\text{C}_1$ was prepared by a reaction of $\text{CH}_2=\text{CHCH}_2\text{MgCl}$ with $^{13}\text{CO}_2$ (isotopic purity = 90%): $\nu(\text{C}=\text{O}) = 1680 \text{ cm}^{-1}$. Solvents were dried by the usual methods, distilled and stored under N_2 . Preparation, reactions and handling of the complexes were performed under an atmosphere of N_2 .

Preparation of complexes

1: $\text{Ru}(\text{cod})(\text{cot})$ (420 mg, 1.3 mmol), PPh_3 (700 mg, 2.7 mmol), and 3-butenic acid (0.10 cm^3 , 1.3 mmol) were dissolved in 5 cm^3 of THF. The solution was stirred for 1 d at room temperature to give a yellow precipitate, which was not soluble in the usual organic solvents. The yellow precipitate was washed repeatedly with hexane and dried under vacuum to give 0.66 g (70%) of **1**: m.p. 175–180 $^\circ\text{C}$ (decomp.).

Calcd	C 67.7	H 4.8,
Found	C 67.9	H 5.0.

Glc analysis of the solution used for preparation of **1** showed the presence of 1,3-, 1,4-, and 1,5-cyclooctadiene in approximately equal molar ratios.

2: $\text{Ru}(\text{cod})(\text{cot})$ (62 mg, 0.20 mmol), PPh_3 (140 mg, 0.53 mmol), and 3-butenic acid (0.017 cm^3 , 0.22 mmol) were dissolved in 2 cm^3 of THF. The solution was stirred for 1 d at room temperature to give a yellow homogeneous solution and microcrystals of **2**, which were separated by filtration, washed repeatedly with hexane, and dried under vacuum to yield 84 mg (48%) of **2**: m.p. 185–189 $^\circ\text{C}$ (decomp.).

Calcd	C 62.0	H 5.2,
Found	C 61.7	H 5.8.

3: $\text{Ru}(\text{cod})(\text{cot})$ (170 mg, 0.54 mmol), $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Cl})_3$ (400 mg, 1.1 mmol), and 3-butenic acid (0.047 cm^3 , 0.54 mmol) were dissolved in 5.4 cm^3 of THF. The solution was stirred for 1 d at room temperature to give a yellow homogeneous solution. Concentration of the solution gave a yellow solid, which was separated by filtration and washed repeatedly with hexane. The yellow solid was dissolved in THF and the THF solution was passed through an Al_2O_3 column. Evaporation of the THF

in a vacuum gave 210 mg (30%) of **3**: m.p. 105–110 °C.

Calcd C 54.3 H 3.1 Cl 23.6,
Found C 54.5 H 3.8 Cl 24.2.

4 and **5**: Stirring a heterogeneous mixture of **1** (100 mg, 0.14 mmol) and 5 cm³ of CH₂Cl₂ for 1 d at room temperature under an atmosphere of CO (1 atm) gave a yellow homogeneous solution. Concentration of the solution gave a yellow solid, which was separated by filtration, washed repeatedly with diethyl ether, and dried in a vacuum to yield 100 mg (96%) of **4**. The sample for elemental analysis was obtained by recrystallization from acetone: m.p. 135–140 °C.

Calcd C 66.8 H 4.6,
Found C 66.7 H 4.6.

Complex **5** was prepared analogously in 39% yield. Recrystallization from ether gave white crystals of **5**: m.p. 165–170 °C.

Calcd C 53.1 H 3.8 Cl 20.9,
Found C 52.9 H 3.8 Cl 21.3.

Reaction of Ru Complexes with Br₂ and I₂. Br₂ (0.010 cm³, 0.15 mmol) was added to a CH₂Cl₂

(1 cm³) solution of **4** (110 mg, 0.15 mmol) and the reaction mixture was stirred at room temperature. Glc analysis of the reaction mixture showed formation of 2-butenolide (86%). The retention time (glc) and fragmentation pattern of the product in a mass spectrum were identical with those of an authentic sample prepared according to the literature [10]. Similar reactions of **1**, **2**, **3**, and **5** with Br₂ (1 mol/mol of complex) afforded 2-butenolide in 21, 8, and 93% yield, respectively. Reaction of **4** with I₂ (1 mol/mol of **4**) in CH₂Cl₂ at room temperature gave 2-butenolide in 21% yield.

Analysis and Measurement of IR and NMR Spectra. Microanalysis of C and H was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. IR spectra were recorded on a Hitachi Model 295 spectrometer using KBr discs prepared under N₂. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Japan Electron Optics Lab. (JEOL) JNM-PS-100 and FX-100 spectrometers. ¹H/¹H, ¹H/¹³C, and ¹H/³¹P two dimensional NMR spectra and gated decouple ¹³C NMR spectrum were taken using a JEOL GX-400 spectrometer. Analysis of organic compounds was performed using a Shimadzu GC-5B gas chromatograph and a Hitachi mass spectrometer (GC-mass).

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