

Insertion reactions of acrylonitrile with hydridocarbonylbis(triphenylphosphine)ruthenium(II) carboxylates

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Abstract

Reactions between $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ and carboxylic acid in 2-methoxyethanol give white crystalline carboxylate complexes of the type $[\text{RuH}(\text{CO})(\text{OCOR})(\text{PPh}_3)_2]$, where $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_6\text{H}_5, p\text{-OCH}_3\text{C}_6\text{H}_4$ or $p\text{-CH}_3\text{C}_6\text{H}_4$. In these octahedral complexes the carboxylate species is O–O chelated to the metal. Acrylonitrile inserts into the Ru–H bond in the carboxylates to give Ru–C σ -bonded insertion products of the formula $[\text{Ru}(\text{CO})(\text{OCOR})(\text{PPh}_3)_2(\text{CH}_3\text{CHCN})]$. These complexes have been characterised by elemental analyses, IR, ^1H NMR and ^{31}P NMR spectral studies. The large values for ^{31}P – ^{31}P coupling constants suggest that the two phosphine ligands are *trans* to each other, as in $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})]$.

Introduction

An extensive range of carboxylato complexes of platinum group metals have been synthesised by Robinson et al. [1]. Insertions of acetylenes into the Ru–H bond of the hydrido complex $[\text{RuH}(\text{CO})(\text{OCOCF}_3)(\text{PPh}_3)_2]$ give vinylic derivatives [2]. There is no report in the literature on insertions of activated olefins into hydridoruthenium(II) carboxylates of the type $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})]$.

In continuation of our work on Ru–C σ -bonded complexes [3–6], we describe below the synthesis of products of insertion of acrylonitrile into hydridoruthenium carboxylates.

Experimental

All reactions were carried out under dry, oxygen-free nitrogen. Solvents were dried and freshly distilled [7]. The complexes $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ [8] and

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$\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})$ [1] ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, p\text{-OCH}_3\text{C}_6\text{H}_4, p\text{-CH}_3\text{C}_6\text{H}_4$) were prepared by published procedures.

The IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer as either KBr pellets or Nujol mulls. The ^1H and ^{31}P NMR spectra were recorded on a Bruker 90 spectrometer and Bruker MSL 300 spectrometer, respectively. The chemical shifts were determined relative to internal tetramethylsilane for ^1H and to external 85% phosphoric acid for ^{31}P , with a positive value indicating a shift to lower field.

Preparation of $\text{RuH}(\text{CO})[\text{OCO}(\text{CH}_2)_2\text{CH}_3](\text{PPh}_3)_2$

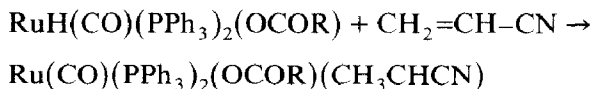
$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (0.91 g, 1 mmol) was suspended in 2-methoxyethanol (15 ml) and refluxed. To the boiling suspension was added butyric acid (1 ml), and the refluxing was continued for 15 min during which the mixture became clear, and subsequently precipitation commenced. Methanol (20 ml) was added and after cooling of the solution the product separated out was filtered off, washed successively with methanol, water, and methanol, and dried in vacuo. The white crystals obtained weighed 0.43 g (62% of theory).

Preparation of $\text{Ru}(\text{CO})[\text{OCO}(\text{CH}_2)_2\text{CH}_3](\text{CH}_3\text{CHCN})(\text{PPh}_3)_2$

To a solution of $\text{RuH}(\text{CO})[\text{OCO}(\text{CH}_2)_2\text{CH}_3)_2$ (0.37 g, 0.5 mmol) in benzene (50 ml) was added acrylonitrile (1.5 ml). The mixture was stirred at room temperature for 24 h and the clear yellow solution was then concentrated to one third volume and set aside. The yellow microcrystals that separated were washed with hexane and dried in vacuo. Yield 0.22 g (55% of theory).

Results and discussion

The complex $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ reacts with carboxylic acids in boiling 2-methoxyethanol to give carboxylate derivatives of the type $\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})$ as white crystalline solids (Table 1). The complexes are non-electrolytes, soluble in benzene and chloroform, and insoluble in hexane. Acrylonitrile inserts into the Ru–H bond in these carboxylates to give cyanoethylruthenium(II) complexes of the type $[\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})(\text{CH}_3\text{CHCN})]$:



The complexes listed in Table 1 are microcrystalline pale yellow solids, stable in an inert atmosphere and soluble in benzene, methylene chloride, and chloroform. On exposure to air for 2 h they become grey. In chlorinated solvents the colour of the solution changes from pale to dark brown on prolonged storage, suggesting decomposition.

The infrared spectra of the hydridoruthenium(II) carboxylates (Table 2) show bands at ~ 2000 and 1925 cm^{-1} attributable to $\nu(\text{Ru}-\text{H})$ and terminal $\nu(\text{C}\equiv\text{O})$ respectively. A band between $1500\text{--}1530\text{ cm}^{-1}$ is due to $\nu_{\text{as}}(\text{C}=\text{O})$ of the chelated carboxylate. The $\nu_s(\text{C}=\text{O})$ is discernible at $\sim 1440\text{ cm}^{-1}$.

The ^1H NMR spectra of the complexes show an upfield shift of resonances due to CH , CH_3 , C_2H_5 , C_3H_7 and OCH_3 protons of the carboxylic acid residue

Table 1

Melting points and analytical data for carboxylate complexes of ruthenium(II)

Compound	M.p. (°C)	Analysis (found (calc.) (%))		
		C	H	P
RuH(CO)(CO ₂ CH ₃)(PPh ₃) ₂ (1)	190	65.82 (65.60)	4.52 (4.76)	8.63 (8.69)
RuH(CO)(CO ₂ CH ₂ CH ₃)(PPh ₃) ₂ (2)	188	65.74 (65.98)	4.67 (4.94)	8.64 (8.52)
RuH(CO)(CO ₂ H)(PPh ₃) ₂ (3)	172	64.98 (65.16)	4.38 (4.57)	8.71 (8.86)
RuH(CO)(CO ₂ (CH ₂) ₂ CH ₃)(PPh ₃) ₂ (4)	179	66.26 (66.45)	5.05 (4.99)	8.19 (8.37)
RuH(CO)(CO ₂ C ₆ H ₅)(PPh ₃) ₂ (5)	203	68.34 (68.09)	4.59 (4.64)	7.81 (7.99)
RuH(CO)(CO ₂ C ₆ H ₅ CH ₃)(PPh ₃) ₂ (6)	217	68.36 (68.40)	4.65 (4.81)	7.99 (7.85)
RuH(CO)(CO ₂ C ₆ H ₅ OCH ₃)(PPh ₃) ₂ (7)	201	66.93 (67.04)	4.62 (4.71)	7.34 (7.69)
Ru(CO)(CO ₂ CH ₃)(CH ₃ CHCN)(PPh ₃) ₂ (8)	185	65.55 (65.76)	4.44 (4.82)	7.74 (8.08)
Ru(CO)(CO ₂ CH ₂ CH ₃)(CH ₃ CHCN)(PPh ₃) ₂ (9)	222	66.43 (66.12)	4.57 (4.99)	7.72 (7.94)
Ru(CO)(CO ₂ H)(CH ₃ CHCN)(PPh ₃) ₂ (10)	184	65.08 (65.36)	4.70 (4.64)	7.99 (8.23)
Ru(CO)(CO ₂ (CH ₂) ₂ CH ₃)(CH ₃ CHCN)(PPh ₃) ₂ (11)	168	66.78 (66.54)	5.01 (5.04)	7.49 (7.81)
Ru(CO)(CO ₂ C ₆ H ₅)(CH ₃ CHCN)(PPh ₃) ₂ (12)	177	68.05 (68.25)	4.46 (4.70)	7.56 (7.48)
Ru(CO)(CO ₂ C ₆ H ₅ CH ₃)(CH ₃ CHCN)(PPh ₃) ₂ (13)	152	68.24 (68.37)	4.96 (4.86)	7.10 (7.36)
Ru(CO)(CO ₂ C ₆ H ₅ OCH ₃)(CH ₃ CHCN)(PPh ₃) ₂ (14)	179	66.86 (67.10)	4.41 (4.77)	7.49 (7.22)

compared to those for the corresponding free acids. The high field part of the ¹H NMR spectra contain a triplet at $\sim \delta -16.20$ ppm with $^2J(\text{PH})_{\text{cis}} \sim 20$ Hz indicating that the two equivalent phosphine ligands are *trans* to each other. Proton-decoupled ³¹P NMR spectra consist of a singlet at $\sim \delta 45$ ppm, confirming the *trans* disposition of the phosphine ligands.

The insertion products Ru(CO)(PPh₃)₂(OCOR)(CH₃CHCN) show $\nu(\text{C}\equiv\text{N})$ at 2200 cm⁻¹. In the acrylonitrile the $\nu(\text{C}\equiv\text{N})$ band is observed at 2230 cm⁻¹. This reduction in the carbon–nitrogen bond order may be attributed to the increased electronic charge on the nitrile carbon of the 1-cyanoethyl group, which is *trans* to the chelated carboxylate ligand in the hexacoordinated ruthenium(II) complex. The $\nu_{\text{as}}(\text{OCO})$ band in the complex shifts to lower frequency region at ~ 1500 cm⁻¹ owing to the effect of the strongly chelated carboxylic group. In the far IR region there is a medium band at ~ 300 cm⁻¹ due to Ru(OCOR) in which the carboxylic group is bidentate [9].

The ¹H NMR spectra exhibit a doublet centered at $\delta 0.8$ ppm ($^3J(\text{HH})$ 8 Hz) due to methyl protons and a multiplet at $\delta 2.2$ assignable to $>\text{CH}$ proton of the 1-cyanoethyl group. These resonances due to carboxylate alkyl protons are shifted

Table 2

IR, ^1H and ^{31}P NMR data for hydrido, ruthenium(II) carboxylates and their acrylonitrile insertion products

Compound	IR ν in cm^{-1}				Aliphatic protons	NMR δ in ppm	
	$\text{C}\equiv\text{O}$	$\text{Ru-H}/\text{C}\equiv\text{N}$	$\nu_{\text{as}}(\text{CO}_2)$	$\nu_{\text{s}}(\text{CO}_2)$		Ru-H^b CH_3CHCN^c protons	^{31}P
1	1925	2005	1530	1460	0.62(CH_3)	-16.25t	44.50s
2	1925	1995	1530	1445	0.18(CH_3), 0.85(CH_2)	-16.20t	45.43s
3	1925	2015	1555	1460	^a	-16.65t	—
4	1925, 1950	1990	1535	1445	0.32(CH_3), 0.59, 0.81	-16.42t	45.07s
5	1925	2010	1520	1435	—	-16.20t	45.23s
6	1930	2020	1500	1435	2.25(CH_3)	-16.20t	45.11s
7	1925	2010	1500	1440	3.75(OCH_3)	-16.26t	45.14s
8	1915	2180	1510	1440	0.30(CH_3)	0.8d, 2.30	38.51d 41.87d
9	1925	2200	1510	1450	0.05(CH_3), 0.55(CH_2), ^a	0.8d, 2.35	38.14 41.36d
10	1930	2210	1520	1440	—	0.8d, 2.20	— —
11	1930, 1960	2200	1510	1450	0.28(CH_3), 0.39, 0.45	0.8d, 2.20	37.95d 41.07d
12	1925	2200	1500	1445	—	0.9d, 2.20	38.22d 41.67d
13	1930, 1970	2210	1485	1455	2.15(CH_3)	0.88d, 2.24	37.99d 41.49d
14	1925, 1970	2200	1490	1445	3.62(OCH_3)	0.9d, 2.20	38.05d 41.46d

^a Resonates in the aromatic region. ^b Ru-H, 1-7. ^c CH_3CHCN , 8-14.

to higher fields, possibly owing to diamagnetic shielding by the phenyl rings of the phosphine in the sterically hindered complex.

^{31}P NMR spectra exhibit two close doublets in the form of an AB quartet, as shown in Fig. 1 at $\sim \delta$ 38 and δ 41.5 ppm with a coupling constant of $^2J(\text{PP}) \sim 316$

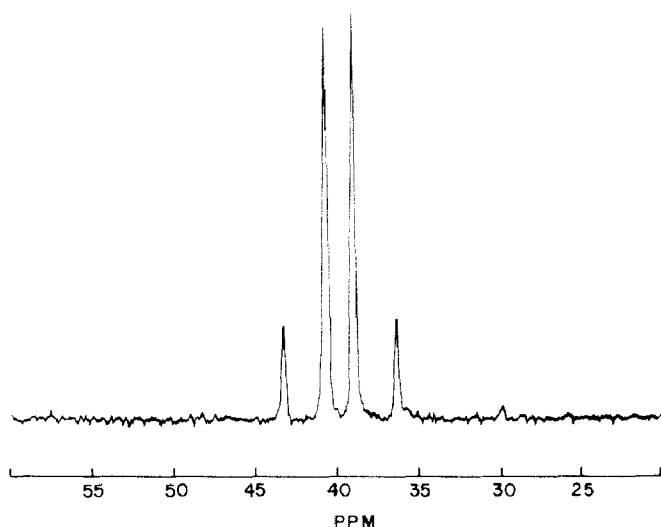


Fig. 1. ^{31}P NMR spectrum of $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})(\text{CH}_3\text{CHCN})$.

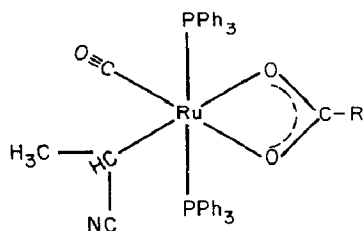


Fig. 2. Stereochemistry of $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{OCOR})(\text{CH}_3\text{CHCN})$.

Hz due to the presence of two magnetically non-equivalent phosphorus atoms. The high values of the coupling constants suggest that the phosphines are *trans* to each other. It has been observed [10] that in a variety of systems the ^{31}P – ^{31}P coupling constants of *trans* oriented ^{31}P nuclei are large and the *cis* coupling constants small. Restricted rotation of the ligands attached to ruthenium due to the presence of relatively bulky 1-cyanoethyl group in place of the hydride ion in $\text{RuH}(\text{CO})-(\text{OCOR})(\text{PPh}_3)_2$ may be the main cause of the non-equivalency of the phosphines. Model studies support this view. The high field shift of the ^{31}P resonances in these insertion complexes compared to those for the hydrido derivatives is attributed to an increased electron density at phosphorus atom as a result of Ru–C bond formation. Thus ^1H and ^{31}P NMR data are consistent with the stereochemistry of the complex $[\text{Ru}(\text{CO})(\text{OCOR})(\text{PPh}_3)_2(\text{CH}_3\text{CHCN})]$ shown in Fig. 2.

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