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SYNTHESIS AND CHARACTERISATION OF β-CARBOALKOXYRUTHENIUM(II) COMPLEXES *

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Summary

Methyl, ethyl, and butyl acrylates have been found to insert into the hydridoruthenium complex, $HRuClCO(PPh_3)_3$ under mild conditions to give Ru–C σ-bonded mononuclear complexes of the type $RuClCO(PPh_3)_2CH_2CH_2COOR$. The ruthenium atom is six coordinated in these complexes

Organoruthenium complexes are versatile catalysts for important reactions such as hydrogenation, polymerisation, homologation, carbonylation and oxidation. The Ru–C bond is usually formed by the halogen replacement in the metal halides using Grignard reagents, or alkyl- and aryl-alkali metals, but it can also be formed by the insertion of an activated olefin into a Ru–H bond ("hydroruthenation"). Our interest in the recent synthesis of thermodynamically stable mononuclear σ-bonded Ru–C complexes prompted us to prepare some functionally substituted ethyl derivatives of ruthenium by the insertion method. Hiraki et al. recently synthesised and studied some stable chloro-bridged binuclear (1-cyanoethyl)ruthenium(II) phosphine complexes [1].

Experimental

Reactions were performed under dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium hydride under nitrogen. Elemental microanalyses were carried out in the microanalytical section of this laboratory and the results are given in Table 1. Infrared spectra were recorded as Nujol mulls and chloroform solutions on a Perkin–Elmer 599 Grating Spectrophotometer. The proton NMR spectra were obtained at 80 MHz using a Varian FT-80A spectrometer in $CDCl_3$ solution. The complex $HRuClCO(PPh_3)_3$ was prepared as described in

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TABLE 1

β-CARBOALKOXYRUTHENIUM(II) COMPLEXES

Complex		M.p. (°C)	Analysis (Found (Calc.) (%))		
			C	H	P
$RuClCO(PPh_3)_2(CH_2CH_2COOCH_3)$	**(1)**	108	63.52 (63.44)	4.90 (4.80)	8.04 (7.97)
$RuClCO(PPh_3)_2(CH_2CH_2COOC_2H_5)$	**(2)**	109	63.74 (63.83)	4.91 (4.97)	7.81 (7.84)
$RuClCO(PPh_3)_2(CH_2CH_2COOC_4H_9)$	**(3)**	115	64.63 (64.58)	5.35 (5.30)	7.47 (7.56)

literature [2]. Methyl, ethyl and butyl acrylates were washed with water, dried over anhydrous magnesium sulphate, and vacuum distilled.

Reaction between methyl acrylate and $HRuClCO(PPh_3)_3$

Methyl acrylate (0.344 g, 4 mmol) was added to a suspension of $HRuClCO(PPh_3)_3$ (0.476 g, 0.5 mmol) in THF (50 ml) and the mixture was stirred for 28 h in nitrogen at room temperature. The resulting bottle-green solution was concentrated in vacuum to half its volume and than kept below −10°C in a refrigerator. The colourless microcrystalline product which separated was washed with hexane and dried in vacuum at 60°C (yield 0.272 g, 70%).

The related complexes were similarly prepared. In the case of the butyl ester the reaction required less time (10 h) for completion, and in this case the green colour of the solution gradually turned to brown if the reaction time was prolonged. The colourless micro-crystalline products were soluble in benzene and chloroform but insoluble in hexane. Their IR and ^1H NMR spectral data are given in Table 2.

Discussion

The IR spectra (in cm^{-1}) of methyl, ethyl and butyl acrylates show ester carbonyl stretching vibrations $\nu(C{=}O)$ at ca. 1720 cm^{-1} [3]. In methyl propionate the corresponding band is at 1738 cm^{-1}, and the corresponding band is observed at 1640 cm^{-1} in the ruthenium(II) complexes indicating coordination of an ester carbonyl group to ruthenium. Moreover, the $\nu(C{-}O)$ of the ester C–OR group ca. 1200 is shifted to higher frequency viz ca. 1230 cm^{-1}. This shift could be due to the involvement of the lone pair of electrons of the alkoxy group in coordination to Ru

TABLE 2

IR AND ^1H NMR SPECTRAL DATA FOR β-CARBOALKOXYRUTHENIUM(II) COMPLEXES

Complex	$\nu(C{\equiv}O)$ (cm^{-1})	$\nu(C{=}O)$ (cm^{-1})	$\nu(C{-}O)$ (cm^{-1})	Chemical shift δ(ppm)		
				α-CH_2	β-CH_2	OCH_3 or OCH_2
1	1915	1640	1230	1.85	3.70	3.00
2	1915	1640	1230	1.90	3.76	3.46
3	1915	1645	1225	1.87	3.70	3.30

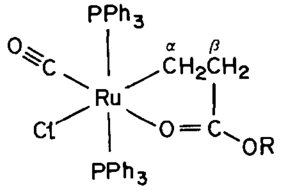

Fig. 1. $R = CH_3, C_2H_5, C_4H_9$

to give a C=O → Ru bond (cf. ref. 3–5). Since the carbonyl stretching frequency is unaffected by dilution (in chloroform) the coordination of the carbonyl group to ruthenium must be intramolecular. In the far IR region, ν(Ru–C) appears at 300 cm^{-1}, confirming metal–carbon bond formation. These results suggest that the metal is bonded to terminal carbon atom of the ester with simultaneous coordination of the ester carbonyl to Ru, and formation of a stable five-membered ring. The appearance of a strong band at 1915 cm^{-1} assignable to terminal carbonyl group, which is 15 cm^{-1} lower than that in the ruthenium hydrido complex, suggests a higher metal–carbon bond order. This is in agreement with the view that ester carbonyl is a better σ donor than the phosphine group but has practically no π-acceptor ability. The Ru–C≡O stretching frequency in the hydrido precursor at 590 cm^{-1} is shifted to 610 in the insertion complexes. Similarly a shift to the high frequency side is observed for ν(Ru–P), and ν(Ru–Cl) appears at 270 cm^{-1} in both starting material and products.

The ^1H NMR spectrum of $RuClCO(PPh_3)_2CH_2CH_2COOCH_3$ at room temperature shows well defined signals showing splitting for the methylene protons adjacent to ruthenium as a result of Ru–H coupling. The appearance of only two triplets and a singlet in the proton ratio 2/2/3, due to methylene and methyl protons, rules out the presence of stereoisomers. The methoxy protons resonate at δ 3.66 ppm in the case of methyl propionate, but the signal is shifted to δ 3.00 ppm, in the ruthenium complex. A shift in the opposite direction would have been expected on the basis of the electronic effects upon coordination of carbonyl to ruthenium, but model studies have shown that when the $CH_2CH_2COOCH_3$ group is bonded to ruthenium through carbon and carbonyl group to form a five-membered ring, the methoxy group comes into the neighbourhood of one of the phenyl groups of the phosphine and the ring current diamagnetism on the methoxy protons results in a shift to higher field as observed. The same feature is observed in the case of ethyl and butyl ester derivatives. The α- and β-methylene protons in all the three derivatives resonate at almost the same positions, namely δ 1.85 and 3.70 ppm, respectively.

From the IR and ^1H NMR spectra the structure of the new ruthenium complexes can be assigned as shown in Fig. 1.

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