

Formation of hydride complexes of ruthenium from diruthenium(II,III) carboxylate compounds

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Abstract

The reactions of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me, Et, Ph, cyclo-C}_6\text{H}_{11}, o\text{-HO-C}_6\text{H}_4$) with PPh_3 in boiling 2-methoxyethanol have been studied. In all cases, the cleavage of the ruthenium–ruthenium bonds and the abstraction of hydride and carbonyl ligands from the solvent are observed. In these reactions $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ and $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ have been isolated and the hydride complexes, $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$, have been detected in the reaction mixtures by NMR.

Introduction

The reactivity of diruthenium(II,III) complexes towards phosphines has attracted considerable interest for several years [1–19]. For instance, all attempts to obtain adducts of the type $[\text{Ru}_2(\mu\text{-L})_4(\text{PPh}_3)_2]^n$ ($n = 0, +1$; $\text{L} = \text{carboxylate or amidate ligands}$) have been unsuccessful, giving oxotrimer-compounds [2, 5], transposition reactions [8, 9] or disproportionation processes [17, 18].

Although it has been described that the reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CCH}_3)_4$ with triphenylphosphine in methanol at room temperature leads to the formation of an insoluble compound formulated as $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ [6], the prolonged reflux of this reaction mixture has shown that carbonyl complexes were formed. Thus, $\text{Ru}(\text{Cl})(\text{O}_2\text{CPh})(\text{CO})(\text{PPh}_3)_2$ is obtained from $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CPh})_4$ and PPh_3 in methanol at reflux [9]. Also, the reactions of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me, Ph}$) with PPh_3 , using several alcohols as solvent, have been briefly described [19].

In this paper we report a study of the reactions of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me, Et, Ph, cyclo-C}_6\text{H}_{11}$ (Cy), $o\text{-HOC}_6\text{H}_4$) with PPh_3 in 2-methoxyethanol.

Experimental

^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded with a Varian VXR-300 spectrometer, using CDCl_3 as

solvent. ^1H NMR chemical shifts are reported in ppm relative to TMS; ^{31}P NMR chemical shifts are reported in ppm relative to external 85% H_3PO_4 . IR spectra were recorded on a Philips PU 9712 infrared spectrophotometer. Elemental analyses for C and H were performed with a Perkin-Elmer 240 B microanalyser.

All reactions were carried out in an inert atmosphere using standard Schlenk techniques. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Engelhard), $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ (Fluka), *cyclo-C*₆*H*₁₁*CO*₂*H* (Merck), *C*₆*H*₅*CO*₂*H* (Probus), *o*-*HOC*₆*H*₄*CO*₂*H* (Probus), PPh_3 (Merck), LiCl (Probus) were purchased from commercial sources. Solvents (Fluka or Panreac) were used without previous purification. The complexes $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me}$ [6], Ph [20], Cy [21], *o*-*HOC*₆*H*₄ [21]), $\text{Ru}_2\text{O}(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ [18], $\text{Ru}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3) \cdot \text{toluene}$ [18] and $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ ($\text{R} = \text{Me, Et, Ph, } o\text{-OHC}_6\text{H}_4$) [22] were prepared according to published methods.

Since the used procedure in the reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me, Et, Cy, Ph, } o\text{-OHC}_6\text{H}_4$) with PPh_3 was similar in all cases, a detailed reaction is given only for the case of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CEt})_4$.

Reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CEt})_4$ with PPh_3

$\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CEt})_4$ (0.13 g, 0.25 mmol) in 2-methoxyethanol (17 ml) was treated with an excess of PPh_3 (0.50 g, 1.92 mmol). The reaction mixture was heated at reflux for 4 h. In a few minutes the colour turns from dark-brown to purple and then changes to pale yellow. On cooling, a yellow precipitate of

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$\text{Ru}(\text{H})(\text{O}_2\text{CEt})(\text{CO})(\text{PPh}_3)_2$ appeared. This yellow precipitate was separated by filtration, washed with a mixture of diethylether/petroleum ether (30–60°) (1:2) and dried in vacuum. The analysis, IR, and ^1H NMR spectra are in agreement with those reported in the literature for this compound [22].

The mother liquid was concentrated and pale yellow crystals of $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ appeared. These crystals were separated by filtration, washed with diethyl ether/petroleum ether (30–60°) (1:2) and dried *in vacuo*. The analysis, ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR data are in agreement with those reported in the literature for this compound [23].

In another experiment, the reaction mixture was pumped to dryness. The high field ^1H NMR of this mixture shows three groups of signals: -7.16 (dt, $J(\text{P}-\text{H})_{\text{cis}} = 24.1$ Hz, $J(\text{P}-\text{H})_{\text{trans}} = 100.5$ Hz); -16.4 (t, $J(\text{P}-\text{H}) = 20$ Hz); and -18.7 (q, $J(\text{P}-\text{H}) = 27$ Hz), assigned to $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ [23], $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ [22] and $\text{Ru}(\text{H})(\text{O}_2\text{CEt})(\text{PPh}_3)_3$ [24], respectively.

The results obtained for the other carboxylates were very similar; the only differences were found in the solubility of the compounds. Thus, when $\text{R} = \text{Me}$ and Ph , the corresponding $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ were precipitated when the hot reaction mixture was allowed to stand at room temperature; $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ can be isolated if the remaining solution is concentrated to vacuum. However, when $\text{R} = \text{Cy}$ and *o*- HOC_6H_4 , the compounds $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ are very soluble in 2-methoxyethanol and $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ was obtained in the first place; the corresponding $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ were obtained when the concentrate mother liquor was allowed to stand in N_2 atmosphere for several days. In all cases, in the residual solution, $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ was detected by NMR.

Reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{Cy}, o\text{-HOC}_6\text{H}_4$) with PPh_3 in the presence of LiCl

The reaction was carried out by the same procedure as that described above: $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$, PPh_3 and LiCl were refluxed in 2-methoxyethanol for 4 h. The reaction mixture was concentrated to vacuum and only $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ was obtained.

Reaction of $\text{Ru}_2\text{O}(\text{O}_2\text{CMe})_4(\text{PPh}_3)_2$ with PPh_3

$\text{Ru}_2\text{O}(\text{O}_2\text{CMe})_4(\text{PPh}_3)_2$ (0.1 g, 0.10 mmol) in 2-methoxyethanol (10 ml) was treated with an excess of PPh_3 (0.16 g, 0.61 mmol). The reaction mixture was heated at reflux for 2 h. In a few minutes, the colour changed from purple to pale yellow. The mixture was pumped to dryness and only $\text{Ru}(\text{H})(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2$ was obtained.

Reaction of $\text{Ru}_2\text{O}(\text{O}_2\text{CMe})_4(\text{PPh}_3)_2$ with PPh_3 in the presence of LiCl

$\text{Ru}_2\text{O}(\text{O}_2\text{CMe})_4(\text{PPh}_3)_2$ (0.1 g, 0.10 mmol) in 2-methoxyethanol (10 ml) was treated with an excess of PPh_3 (0.16 g, 0.61 mmol) in the presence of LiCl (0.04 g, 1.02 mmol). The reaction mixture was heated at reflux for 2 h. In a few minutes, the colour of the mixture changed from purple to pale yellow. The mixture was pumped to dryness and only $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ was obtained.

Reaction of $\text{Ru}(\text{O}_2\text{CMe})_2(\text{PPh}_3) \cdot \text{toluene}$ with PPh_3

$\text{Ru}(\text{O}_2\text{CMe})_2(\text{PPh}_3) \cdot \text{toluene}$ (0.1 g, 0.21 mmol) in 2-methoxyethanol (12 ml) was treated with an excess of PPh_3 (0.16 g, 0.62 mmol). The reaction mixture was heated at reflux for 2 h. In a few minutes, the colour changed from yellow to orange and then to pale yellow. The mixture was pumped to dryness giving an oil. The ^1H NMR spectrum of this oil did not show any hydride signal corresponding to the hydrides described above.

Synthesis of $\text{Ru}(\text{H})(\text{O}_2\text{CCy})(\text{PPh}_3)_3$

This compound was prepared by the method described by Robinson and Uttley [22]. *Anal.* Found: C, 72.16; H, 5.59. Calc.: C, 72.11; H, 5.65%. IR (KBr): $\nu(\text{Ru}-\text{H})$ 1990 cm^{-1} . ^1H NMR (δ , ppm): -18.93 (q, 1H; $J(\text{P}-\text{H}) = 27.83$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , ppm): 97.38 (t, 2P; $J(\text{P}-\text{P}') = 28$ Hz), 64.10 (d, 1P; $J(\text{P}'-\text{P}) = 28$ Hz).

Results and discussion

The reactions of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{Cy}, o\text{-HOC}_6\text{H}_4$) with PPh_3 in boiling 2-methoxyethanol lead to the formation of a mixture of products; from these mixtures, the hydrides $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ have been isolated, whereas the compounds $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ have been detected by NMR. In these reactions PPh_3 causes the rupture of the metal-metal bond and the reduction of the ruthenium(II, III) compound giving ruthenium(II) complexes. Carbon monoxide and hydride ligands are abstracted from the solvent to give the aforementioned species. The R group of the carboxylate ligand has some influence on the solubility of the products formed, but not on the nature of it, because, in all cases, analogous compounds are obtained.

In the high field ^1H NMR spectra of the crude reaction mixture, three groups of signals are observed: a triplet around -16 ppm due to $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$; a doublet of triplets centered at -7.16 ppm due to $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$; and a quartet around -18 ppm due to $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$. In

all cases $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ is formed in approximately 50% yield, whereas the ratio between $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ (deduced from the integral in the ^1H NMR of the reaction mixture) depends on the nature of R, although $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ is formed in small quantities. The yield obtained for $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ indicates that all chloro ligands present in the starting material are used in the formation of this hydride compound. The greater tendency for the formation of this compound is shown when the reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ with PPh_3 is carried out in the presence of LiCl ; under these conditions only $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ is produced in a nearly quantitative yield.

The formation of $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$, $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ and $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ in these reactions, carried out in 2-methoxyethanol, contrasts with the observed behaviour for the reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CR})_4$ (R = Me, Ph) with PPh_3 in other alcoholic media, $\text{R}'\text{CH}_2\text{OH}$ (R' = H, Me, Pr), which leads to the formation of $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{Cl})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ [19].

The analysis and spectroscopic data for the hydrides $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ and $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ are in agreement with those previously described in the literature [22, 24, 25]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ displays only a single resonance in each case, indicating a *trans* disposition of the phosphine ligand (Table 1).

For a complete identification of the compounds responsible for the quartet observed in the ^1H NMR of the reaction mixture, we have independently prepared the hydrides $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ following the general procedure described by Robinson and Uttley [22]. Effectively, the ^1H NMR spectrum of each compound of this series shows one quartet identical to those observed in the corresponding reaction mixture. All data obtained for these compounds are essentially in agreement with those previously reported [22, 23, 26].

In accordance with that observed by Hoffman and Caulton [27] for $\text{Ru}(\text{H})(\text{O}_2\text{CMe})(\text{PPh}_3)_3$, the quartet

TABLE 1. $^{31}\text{P}\{^1\text{H}\}$ NMR data for the hydrides $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_3$

Compound	δ (ppm)
$\text{Ru}(\text{H})(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2^*$	44.50 s
$\text{Ru}(\text{H})(\text{O}_2\text{CEt})(\text{CO})(\text{PPh}_3)_2$	45.25 s
$\text{Ru}(\text{H})(\text{O}_2\text{CCy})(\text{CO})(\text{PPh}_3)_2$	42.07 s
$\text{Ru}(\text{H})(\text{O}_2\text{CPh})(\text{CO})(\text{PPh}_3)_2$	35.72 s
$\text{Ru}(\text{H})[\text{O}_2\text{C}(o\text{-OHC}_6\text{H}_4)](\text{CO})(\text{PPh}_3)_2$	44.05 s

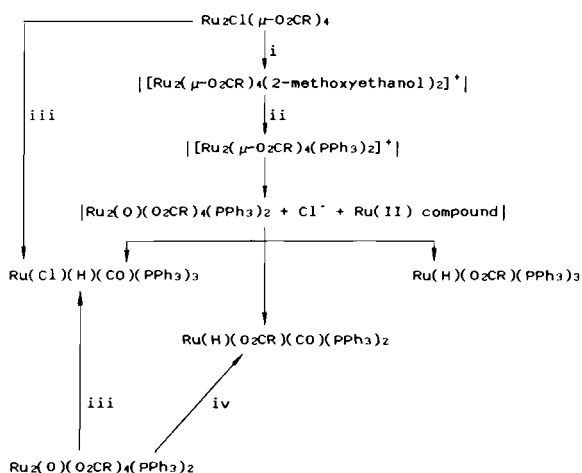
*See ref. 22.

observed for $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{PPh}_3)_3$ is better described as a doublet of triplets with very similar $J(\text{P-H})$ values. This is also consistent with the pattern observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the new compound $\text{Ru}(\text{H})(\text{O}_2\text{CCy})(\text{PPh}_3)_3$. This $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two signals, a doublet at 64.10 ppm and a triplet at 97.38 ppm, indicating that this hydride is a rigid six-coordinate complex in solution. The unequivalence of the phosphine ligands for $\text{Ru}(\text{H})(\text{O}_2\text{CMe})(\text{PPh}_3)_3$ in the solid state has been described previously [28].

In order to gain some insight into the reactions of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CCH}_3)_4$ with PPh_3 in 2-methoxyethanol, we have chosen to study the reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CCH}_3)_4$ in more detail.

When $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CCH}_3)_4$ is dissolved in 2-methoxyethanol, the polymer structure of this compound is broken and the species $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(2\text{-methoxyethanol})_2]^+$ should be formed; the addition of PPh_3 to the solution produces the substitution of the axial solvent molecules by PPh_3 , giving $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{PPh}_3)_2]^+$. This compound is unstable, leading to the formation of the aforementioned hydrides. The instability of this compound was previously observed; thus, in the reaction of $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{thf})_2]\text{BF}_4$ with PPh_3 , in thf or toluene, a permanent deep purple solution was formed and $\text{Ru}_2\text{O}(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ (violet) and $\text{Ru}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)\cdot\text{toluene}$ (yellow) were obtained [17, 18]. In the reaction carried out in 2-methoxyethanol, a transient purple colour appears, indicating that the violet oxo-compound could be an intermediate in the formation of the hydride complexes. This was confirmed carrying out the reaction of $\text{Ru}_2\text{O}(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ with PPh_3 in boiling 2-methoxyethanol; in the course of the reaction, the violet colour disappears and the hydride $\text{Ru}(\text{H})(\text{O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$ was formed. When the reaction of $\text{Ru}_2\text{O}(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ and PPh_3 in boiling 2-methoxyethanol is carried out in the presence of LiCl , only the hydride $\text{Ru}(\text{Cl})(\text{H})(\text{CO})(\text{PPh}_3)_3$ was obtained. These reactions confirm that the $\text{Ru}_2\text{O}(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ compound is an intermediate in this process, being active in the decarbonylation process of the solvent. These results contrast with those obtained in the reactions carried out in methanol in which the oxodimer is unactive [19]. The ease of oxidation of the 2-methoxyethanol could explain the differences in reactivity observed in this solvent with respect to those reported in other alcoholic media [19].

On the other hand, the reaction of the yellow $\text{Ru}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)\cdot\text{toluene}$ with PPh_3 , in boiling 2-methoxyethanol, does not lead to any of the hydrides obtained in the reaction of $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CCH}_3)_4$ with PPh_3 in 2-methoxyethanol, so that the postulate



Scheme 1. (i) 2-Methoxyethanol at reflux; (ii) PPh_3 ; (iii) PPh_3 and LiCl in 2-methoxyethanol at reflux; (iv) PPh_3 in 2-methoxyethanol at reflux.

disproportionation of $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{PPh}_3)_2]^+$ in 2-methoxyethanol must lead to $\text{Ru}_2\text{O}(\text{O}_2\text{CR})_4(\text{PPh}_3)_2$ and some Ru(II) compound, different to that observed in toluene. The reactions carried out and the proposed intermediates are shown in Scheme 1.

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