ELSEVIER Journal of Organometallic Chemistry 561 (1998) 175–179

Journal of Organo metallic Chemistry

Cyclovoltammetric studies on the reaction of dihydridotetrakis(triphenylphosphane)ruthenium(II) with methyl acrylate. CH-activation of methyl acrylate in the presence of $Ru(0)(MA)_2(PPh_3)_2$

Claudia Strehblow [a], Reiner Sustmann [a,*], Christian Amatore [b]

[a] *Institut für Organische Chemie der Universität Essen, D-45117 Essen, Germany*
[b] *Département de Chimie, Ecole Normale Supérieure, URA CNRS 1679, 24 rue Lhomond, 75231 Paris Cedex 05, France*

Received 20 January 1998

Abstract

Electrochemical studies on $RuH_2(PPh_3)_4$ (**1**) and $Ru(0)(MA)_2(PPh_3)_2$ (**2**), the complex that is generated when $RuH_2(PPh_3)_4$ is dissolved in methyl acrylate (MA), are carried out by cyclic voltammetry (CV). The combination of electrochemical with NMR spectroscopic measurements reveals that MA undergoes oxidative addition to $Ru(0)(MA)_2(PPh_3)_2$ via cleavage of a vinylic CH bond. The resulting hydridoruthenium(II) complex is not stable in MA and forms presumably a complex in which a further MA is inserted into the ruthenium–hydrogen bond. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cyclovoltammetry; Methyl acrylate

1. Introduction

Dihydridotetrakis(triphenylphosphane)ruthenium (**1**) can be used as a precatalyst for the dimerization of methyl acrylate (MA) [1]. It also reacts with other electron-deficient olefins such as alkyl methacrylates [2] and crotonic acid methyl ester [3]. In the case of alkyl methacrylates as reactants, 1 mol of the olefin is hydrogenated and complexes of the type $Ru(II)H(CH{=}C(Me)C(O)OR(PPh_3)_3$ with R = Me, Et, *n*-Bu and *i*-Pr are formed (eq. 1 below). The reaction of $RuH_2(PPh_3)_4$ with crotonic acid methyl ester leads to a η^3-allylcomplex. The product of an oxidative addition of crotonic acid methyl ester is assumed to be an intermediate in this reaction. Prior to the present electrochemical studies we reported that the reaction of $RuH_2(PPh_3)_4$ with MA produces $Ru(0)(MA)_2(PPh_3)_2$ (**2**) when dissolved in MA [4] (eq 2).

Here we describe a combination of electrochemical with NMR spectroscopic measurements on the reaction of MA with **1** and $Ru(0)(MA)_2(PPh_3)_2$ (**2**).

2. Experimental

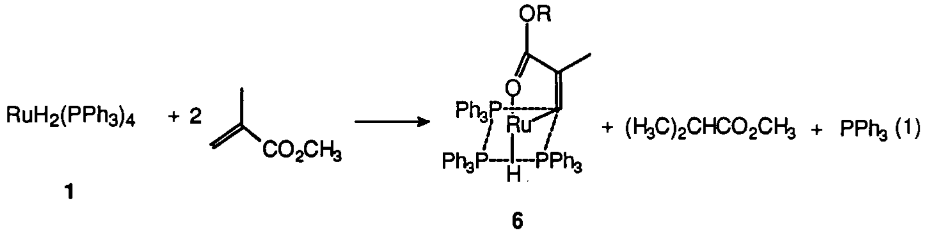
2.1. Materials

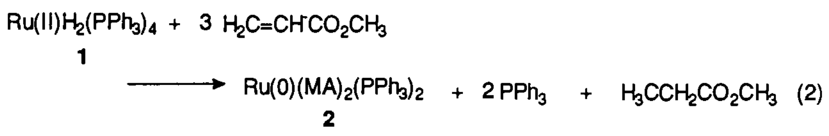
The solvents were thoroughly degassed and dried over sodium (toluene, methanol and *n*-hexane), CaH_2

---

* Corresponding author. Tel.: +49 201 1833097.

PII S0022-328X(98)00531-2





$$\underset{\mathbf{1}}{Ru(II)H_2(PPh_3)_4} + 3\ H_2C{=}CHCO_2CH_3 \longrightarrow \underset{\mathbf{2}}{Ru(0)(MA)_2(PPh_3)_2} + 2\,PPh_3 + H_3CCH_2CO_2CH_3 \quad (2)$$

(MA) and molecular sieve (deuterated solvents), respectively. Tetrabutylammonium hexafluorophosphate, used as the supporting electrolyte in the voltammetric studies, was obtained by Merck, used as-supplied by the manufacturer and kept under dry argon.

2.2. Preparation

$RuH_2(PPh_3)_4$ and $Ru(0)(MA)_2(PPh_3)_2$ were prepared according to literature procedures [4,5].

2.3. Instrumentation

^1H-, $^1H\{^{31}P\}$-, ^{31}P- and ^{13}C-NMR spectra were recorded on a Bruker AMX 300 instrument. ^{31}P-NMR chemical shifts were referenced against external 85% H_3PO_4. IR spectra were recorded on Perkin-Elmer FT-IR 1600. Cyclic voltammetry was performed on a modified polarograph E 310 (Bruker). Data acquisition was realized by a PC with the software package DigiS (GfS, Aachen) [6]. A platinum button was used as the working electrode, a platinum foil as auxiliary electrode. All potentials were measured against a saturated calomel electrode (Metrohm) using ferrocene as an internal standard [7]. The concentration of the supporting electrolyte tetrabutylammonium hexafluorophosphate (Merck) was 0.1 M. The potentials were obtained from measurements with a scan rate of 100 mV s^{-1}.

3. Results and discussion

Cyclovoltammetric studies on $RuH_2(PPh_3)_4$ (**1**) or $Ru(0)(MA)_2(PPh_3)_2$ (**2**) in neat MA show no reduction wave down to -2.5 V immediately after dissolving the complexes. Only one oxidation process at 0.55 V is observed for both complexes. Fig. 1 shows such a CV of $RuH_2(PPh_3)_4$ in MA immediately after dissolving the complex. The assignment of the oxidation peaks in Fig. 1 is as follows: O^1 is attributed to the oxidation of complex **2**. This was verified by recording a CV of **2** in MA where an oxidation wave was observed at identical potential with comparable current density. The second oxidation process in Fig. 1, labelled O^{TPP}, results from the oxidation of triphenylphosphane, as was demonstrated independently by recording a CV of triphenylphosphane in MA and also by the external addition of further phosphane to the solution of the complex, which results in an increase in the peak current of O^{TPP}.

Time-dependent CV investigations of **1** and **2** show that the current density of O^1 falls off with time. The decrease of O^1 is accompanied by the increase of a new oxidation process O^2 at 0.86 V. The voltammograms for **1** are shown in Fig. 2. A further oxidation wave (O^3) becomes apparent at 1.2 V, some time after dissolving **2**. This oxidation can hardly be recognized in the CV of **1** as it is hidden in the oxidation wave of triphenylphosphane, which is liberated from **1** but not

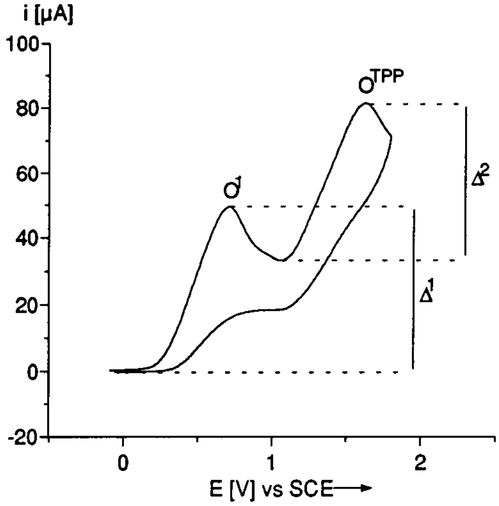


Fig. 1. Cyclic voltammogram of 1×10^{-3} M $RuH_2(PPh_3)_4$ in MA (0.1 M Bu_4NPF_6) at 0.6 mm Pt at a scan rate of 100 mV s^{-1}, immediately after dissolving the complex.

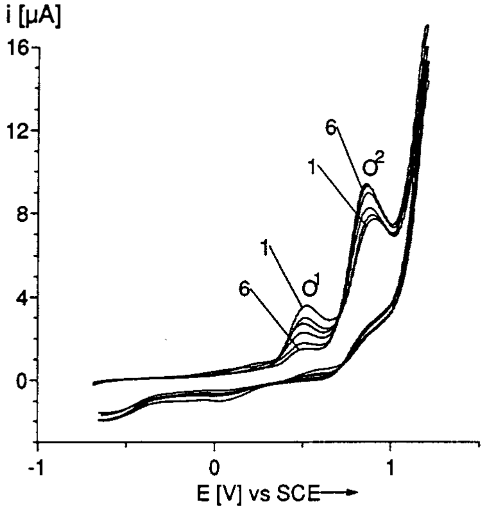


Fig. 2. Cyclic voltammograms of 1×10^{-3} M $RuH_2(PPh_3)_4$ in MA (0.1 M Bu_4NPF_6) at 0.6 mm Pt at scan rates of 100 mV s^{-1}. Curve (1) was recorded 9 min, and curve (6) 30 min after dissolving the complex.

from **2**. Another oxidation wave (O^4) is observed with a low current density at 1.5 V, which becomes visible after an induction period of 30 min and vanishes again after 5 h. The CV of **1** in Fig. 3 was recorded 2 h after dissolving $Ru(0)(MA)_2(PPh_3)_2$ in MA. It can be seen that not only O^1 disappears at the expense of O^3 but also O^2. After 22 h only O^3 is visible in the oxidative potential range.

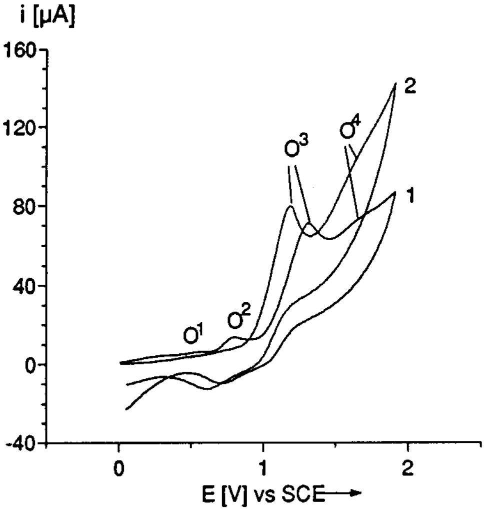


Fig. 3. Cyclic voltammograms of 1×10^{-3} M $Ru(0)(MA)_2(PPh_3)_2$ in MA (0.1 M Bu_4NPF_6) at 0.6 mm Pt at scan rates of 100 mV s^{-1}. Curve (1) was recorded 2 h and curve (2) 24 h after dissolving the complex.

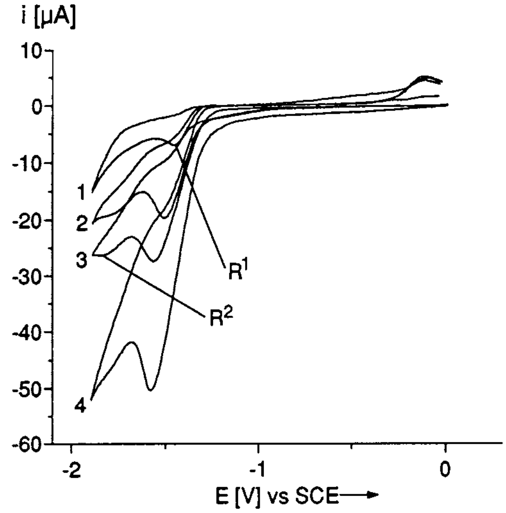


Fig. 4. Cyclic voltammograms of 1×10^{-3} M $RuH_2(PPh_3)_4$ in MA (0.1 M Bu_4NPF_6) at 0.6 mm Pt at scan rates of 100 mV s^{-1}. Curve (1) was recorded 2 min, (2) 30 min, (3) 4 h and (4) 30 h after dissolving the complex.

The reductive part of the CVs also changes with time. At the beginning, immediately after dissolving either $RuH_2(PPh_3)_4$ or $Ru(0)(MA)_2(PPh_3)_2$, there is no reduction wave down to potentials of -2.5 V. Recording a CV 1 min later produces a new reduction wave R^1. Its' current density increases with the same time constant as the current density of O^3. A second reduction peak R^2 is observed with a low current density at -1.7 V, which becomes visible after an induction period of 30 min and vanishes again after 5 h (Fig. 4). These changes indicate that $Ru(0)(MA)_2(PPh_3)_2$ reacts with MA because no other substance is present in solution. The reaction leads to a complex with an oxidation state higher than Ru(0) because the reaction product is reducible at -1.5 V.

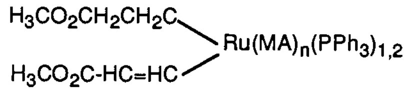
The time profile of the oxidation and reduction waves is shown in Fig. 5. The *y*-axis displays relative concentrations calculated from the peak current densities of each oxidation or reduction wave and which are normalized to the starting peak current density of O^1. During the first 30 min there is no oxidation or reduction process with a current density that matches the disappearance of O^1. Therefore, we postulate the existence of a compound **X** which shows no oxidation or reduction processes in the accessible potential window. Its concentration profile is calculated from the difference of the starting current density of O^1 minus the sum of all other oxidation and reduction waves occurring at that time. The markers display the normalized concentrations, whereas the lines are calculated by a kinetic simulation program. The values obtained for O^3 and O^4 are not depicted. They correspond to those of R^1 in case of O^3 and of R^2 in case of O^4. A reduction process with a concentration profile corresponding to that of O^2 was not observed. This might be due to the fact that its reduction occurs at more negative potentials beyond the accessible potential window. A kinetic model for the simulation of the time dependence of the concentration of the various complexes is illustrated in Scheme 1.

$Ru(II)H_2(PPh_3)_4$ **1**

$Ru(0)(MA)_2(PPh_3)_2$ **2**

$Ru(II)\mu\text{-}H(CH{=}CH\text{-}CO_2CH_3)(MA)_n(PPh_3)_{1,2}$ **3**

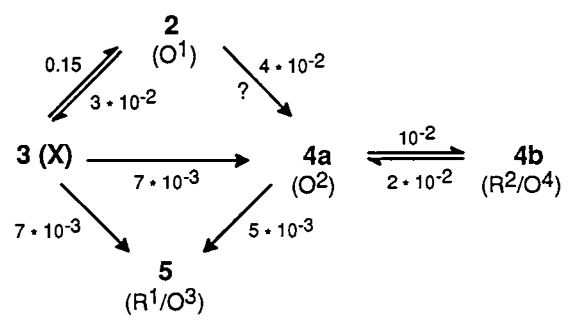
$Ru(II)H(CH{=}CH\text{-}CO_2CH_3)(MA)_n(PPh_3)_{1,2}$ **4a/b**



$(H_3CO_2CH_2CH_2C)(H_3CO_2C\text{-}HC{=}HC)Ru(MA)_n(PPh_3)_{1,2}$ **5**

Complex **2** (O^1) is in equilibrium with a complex **3** with the structural element [Ru(II)]μ-H(CH=CHCO$_2$Me) ([Ru(II)] corresponds to Ru(II)(MA)$_n$-(PPh$_3$)$_{1,2}$). The equilibrium is on the side of **3**. Both react to a complex [Ru(II)]H(CH=CHCO$_2$Me) (**4a**) that is oxidized in O^2. The latter complex and **3** form the product [Ru(II)](CH=CHCO$_2$Me)(CH$_2$CH$_2$CO$_2$Me) (**5**) that is oxidized in O^3 and reduced in R^1. Furthermore, there is an equilibrium between the compound oxidized in O^2 (**4a**) and a complex oxidized in O4 and reduced in R^2. The structural difference of **4a** and **4b**, which is oxidized in O^4 might consist in the number of phosphane ligands on the one hand, on the other hand it can differ in the arrangement of the hydrogen atoms at the double bond, i.e. either [Ru(II)]H(*cis*-CH=CHCO$_2$Me) or [Ru(II)]H-(*trans*-CH=CHCO$_2$Me).

Fig. 6 shows the time-dependent ^{31}P-NMR spectra of RuH$_2$(PPh$_3$)$_4$ in MA. Apart from the signals of free triphenylphosphane at −4.38 ppm and triphenylphosphaneoxide at 26.07 ppm, which are not shown in Fig. 6, there are four phosphor resonances. The first NMR spectrum which was recorded within 15 min after dissolving the complex, resembles that of Ru(0)(MA)$_2$(PPh$_3$)$_2$ in methylene chloride [4]. The NMR spectra recorded after 30, 150 and 300 min display a decrease of the four resonances and the appearance of a new signal at 47.27 ppm. The assignment of the signals is not possible. Previously [1] we assumed that the resonances were due to two isomers of the zero valent Ru(0)(MA)$_2$(PPh$_3$)$_2$. As the cyclovoltammetric results show that the bis(methylacrylate) complex **2** is converted within 15 min to new complexes, in which the oxidation state of ruthenium is higher than Ru(0), these signals must be due to other complexes. The comparison with the cyclovoltammetric results suggests that the new signal at 47.27 ppm should be attributed to the final product **5** of the reaction of MA with Ru(0)(MA)$_2$(PPh$_3$)$_2$, which is reduced in R^1 and oxidized in O^3.



Scheme 1. Illustration of a kinetic model for the simulation of the time dependence of the concentration of the various complexes.

A ^{1}H-NMR study in (not deuterated) MA [8] exhibits among a variety of other signals a broad triplett at −0.6 ppm (J(PH) ca. 30 Hz). This signal appears in the time scale postulated for the existence of the electro-inactive complex **3** (**X**). After more than 2 h it has disappeared. Further assignments could not be made. Taking into account the CV results that indicate the existence of a complex with an oxidation state greater than ruthenium(0), the oxidation and reduction processes O^1, O^2, O^3, O^4, R^1 and R^2 can be attributed to complexes with defined structural elements. The bis(methylacrylate) complex **2**, which is produced on dissolving RuH$_2$(PPh$_3$)$_4$ in MA, does not react to a hydridoruthenium complex, directly. A precursor **3** is formed. The broad triplett with a phosphorous coupling of 30 Hz at −0.6 ppm might result from an

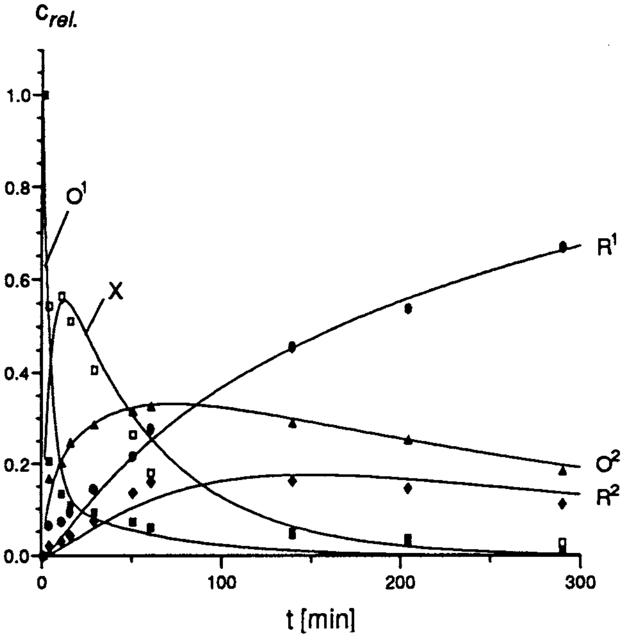


Fig. 5. Time dependency of the concentrations of the redoxactive species of a solution of Ru(0)(MA)$_2$(PPh$_3$)$_2$ in MA taken from the peak current densities of the oxidation and reduction processes. The symbols represent the experimental values (normalized by the initial concentration of O^1), and the line graphs correspond to the simulated values.

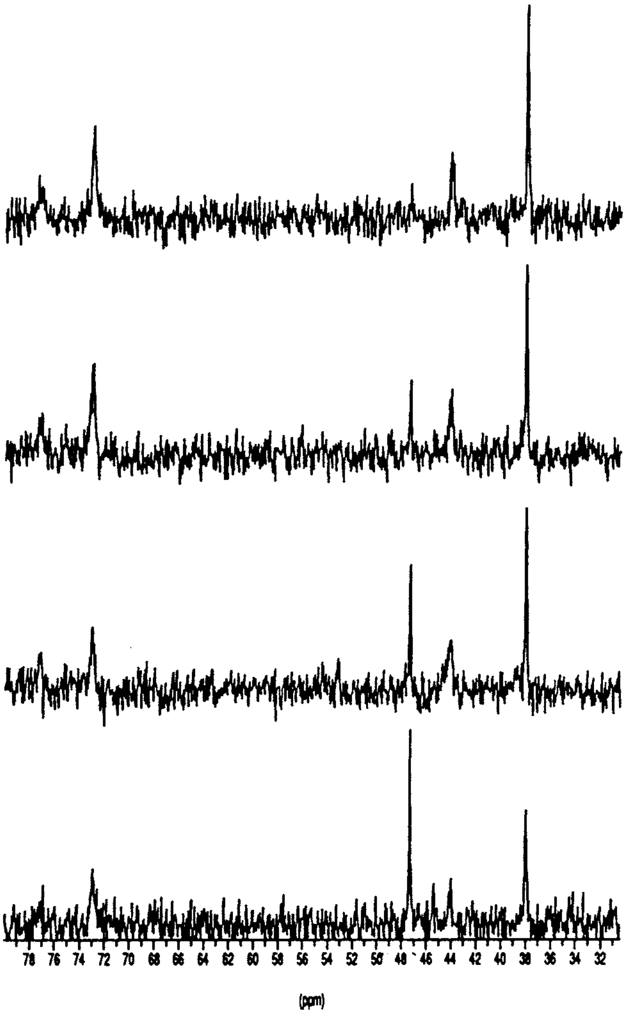


Fig. 6. Partial ^{31}P-NMR spectra of $RuH_2(PPh_3)_4$ in MA, spectrum (1) was recorded within 0–15 min, (2) 15–30 min, (3) 135–150 min and (4) 285–300 min after dissolving the complex.

agostic hydrogen atom. This complex should be the electro-inactive compound **X** in the potential window between -1.8 and $+1.8$ V. The products of the oxidative addition of MA to Ru(0) are complexes **4a** and **4b**, perhaps an isomer of **4a**. Complex **4a** is oxidized in O^2 and **4b** is oxidized in O^4 and reduced in R^2. The hydride signal of these complexes cannot be observed in their ^{1}H-NMR spectra. Note that the peak current density both of O^2, O^4 and R^2 are rather small compared with the initial concentration of the peak current density of O^1 that is attributed to the oxidation of the zero valent bis(methylacrylate) complex **2** and that of R^1, which is assigned to the reduction of the final reaction product **5**. This is formed after the oxidative addition step. We interpret the formation of this complex as the insertion of MA into the Ru–H bond of the complexes **4a** and **4b**.

4. Conclusion

The reaction of MA with $RuH_2(PPh_3)_4$ produces the bis(methlyacrylate) complex $Ru(0)(MA)_2(PPh_3)_2$ as reported before [4]. This zero valent complex is not stable in MA and undergoes further reactions with the electron deficient olefin. First, a precomplex is formed that reacts to give the hydrido species, a product of the oxidative addition of MA to $Ru(0)(MA)_2(PPh_3)_2$. As a following step, MA is presumably inserted into the Ru–H bond to give $[Ru(II)](CH{=}CHCO_2Me)(CH_2CH_2CO_2Me)$, the final product of the reaction of MA with either $RuH_2(PPh_3)_4$ or $Ru(0)(MA)_2(PPh_3)_2$. In this context we have shown that cyclovoltammetric studies in combination with conventional spectroscopic investigations are a useful tool in the examination of the reaction mechanism of transition metal complexes with organic compounds.

References

[1] B. Patzke, R. Sustmann, J. Organomet. Chem. 480 (1994) 65.
[2] S. Komiya, T. Ito, M. Cowie, A. Yamamoto, J.A. Ibers, J. Am. Chem. Soc. 98 (1976) 3874.
[3] S. Komiya, Y. Aoki, Y. Mizuho, N. Oyasato, J. Organomet. Chem. 463 (1993) 179.
[4] R. Sustmann, B. Patzke, R. Boese, J. Organomet Chem. 470 (1994) 191.
[5] R. Young, G. Wilkinson, S. Komiya, A. Yamamoto, Inorg. Synth. 17 (1977) 75.
[6] DigiS, User guide, GfS, Aachen 1992.
[7] R.R. Gagné, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854.
[8] In this NMR experiment, the resonance of the methoxy group of MA was saturated.