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Synthesis and copolymerization of a ruthenium(II) complex with the deprotonated form of 2-(acetoacetoxy)ethylmetacrylate

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Abstract

The new polymerizable complex $Ru(PPh_3)_2(AAEMA)_2$ was obtained by reaction of $RuCl_2(PPh_3)_3$ with the anion of 2-(acetoacetoxy)ethylmethacrylate (AAEMA⁻). The complex was characterized by NMR, IR, UV–Vis, mass spectrometry and cyclic voltammetry techniques. In order to obtain a supported metal complex suitable for catalytic applications, $Ru(PPh_3)_2(AAEMA)_2$ was copolymerized with *N*,*N*-dimethylacrylamide as comonomer and *N*,*N*'-methylenebisacrylamide as cross-linker. The obtained insoluble resin [Ru-pol] was characterized by elemental analyses, IR, UV–Vis and CP/MAS ³¹P{¹H} NMR techniques. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Supported complexes; Polymerizable complexes; Hydrogenation

1. Introduction

The ease of separation and potential recyclability of a supported metal complex are among the most important reasons for the widespread interest devoted to this topic by the scientific community [1]. The materials for catalytic applications obtained by supporting a soluble metal complex onto an organic polymer are often referred to as 'hybrid' due to the fact that they preserve the features of the homogeneous catalyst in terms of activity and selectivity and gain the advantages of heterogeneous systems, namely their robustness and recyclability. Very recent works on the topic of ruthenium supported metal complexes include the use of ruthenium(II) cationic complexes bearing a sulphonated pendant chain supported by hydrogen bonding on silica [2], RuCl₂(PPh₃)₃ supported on Merrifield resin [3], polymer-anchored complexes of Ru(III) with Schiff's bases [4], sol-gel entrapped ruthenium chiral catalysts

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[5] and optically active BINOL-BINAP supported complexes [6].

We have recently studied the synthesis [7] and use in catalysis [8] of several hybrid catalysts based on Group VIII–X metal complexes with the anion of 2-(acetoacetoxy)ethyl methacrylate (AAEMA⁻). This paper deals with the synthesis of the new polymerizable ruthenium complex Ru(PPh₃)₂(AAEMA)₂, which was copolymerized with a suitable comonomer [N,N-dimethylacrylamide (DMAA)] and cross-linker [N,N'-methylenebisacrylamide (MBAA)] to obtain a supported ruthenium(II) complex.

2. Results and discussion

Our first attempt to synthesise a polymerizable ruthenium species was aimed at the preparation of the homoleptic complex $Ru(AAEMA)_3$. The reaction of $RuCl_3$ with KAAEMA in ethanol, a procedure successfully used for the synthesis of $Fe(AAEMA)_3$ [7b], did not afford the expected $Ru(AAEMA)_3$. Neutralization by KOH or NaHCO₃ of a Ru(III) acidic solution and subsequent reaction at room temperature with

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Scheme 1. Synthesis of Ru(PPh₃)₂(AAEMA)₂.

HAAEMA was then tried, adapting the known synthesis of $Ru(acac)_3$ [9,10] to our aim. Unfortunately these tests resulted in the obtainment of complex mixtures of oily products, from which the isolation of well-defined compounds was hampered.

The synthesis of a polymerizable ruthenium complex was achieved by reacting $RuCl_2(PPh_3)_3$ with AAEMA⁻ in ethanol, leading to $Ru(PPh_3)_2(AAEMA)_2$ as a yellow powder in a 68% yield (Scheme 1).

This compound is air-stable in the solid state but rapidly decomposes in non-deoxygenated solvents. $Ru(PPh_3)_2(AAEMA)_2$ is fairly soluble in THF, dimethylformamide and acetonitrile, slightly soluble in methanol, ethanol, diethylether and light petroleum ether and insoluble in water. It decomposes in acetone, aromatic and chlorinated solvents, giving deep green solutions.

Its UV-Vis spectrum exhibits absorptions at $\lambda_{max} =$ 219 nm [$\varepsilon = 52940 \ 1 \ \text{mol}^{-1} \ \text{cm}^{-1}$], 260 nm [$\varepsilon = 18400 \ 1$ $mol^{-1} cm^{-1}$], 310 nm [$\varepsilon = 7900$ l mol⁻¹ cm⁻¹] and is consistent with a Ru(II) involved in an octahedral coordination [11]. Comparison between the IR spectrum of Ru(PPh₃)₂(AAEMA)₂ and that of RuCl₂(PPh₃)₃ shows the disappearence of the Ru-Cl stretching at 319 cm^{-1} , and the appearance of the strong combination bands of the β -ketoesterate ring at 1609 and 1504 cm⁻¹; the β -ketoesterate ring out of plane bending appears at 772 cm^{-1} . The presence of a strong absorption at 1717 cm^{-1} is ascribable to the uncoordinated methacrylate carbonyl stretching while bands for the coordinated phosphine appear at 740, 695 and 523 cm⁻¹. The ¹H NMR spectrum recorded in CD₃OD shows the methacrylate olefinic protons of the AAEMA⁻ at δ 5.60 and δ 6.05. The methynic proton appears at δ 4.58 and the methyl protons of the β ketoesterate and of the methacrylate moieties fall at δ 1.72 and δ 1.90 respectively.

The coupling constant between the phosphorus atoms provides information on the geometry of the phosphine ligands around the metal, being the values of ${}^{2}J_{PP}$ for *trans*-phosphines sensibly higher than those for *cis*-phosphines. The value of ${}^{2}J_{PP}$ can be accessed by studying the resonance of the *ipso*-carbons of the phenyl rings in the 13 C NMR spectrum [12].

In the hypothesis of two chemically equivalent coordinated phosphines the appearance of such resonances has been studied by Nelson et al. [13] who simulated different AXX' spin systems (A: ${}^{13}C_{ipso}$; X, X' = ${}^{31}P$), varying the $J_{XX'}$ coupling constant. Depending on the relative value of $J_{XX'}$ and J_{AX} the spectrum was demonstrated to contain three ($J_{XX'} = 20 J_{AX}$) or five

lines $(J_{XX'}$ comparable with J_{AX}). In the case of Ru(PPh₃)₂(AAEMA)₂, the signal attributable to the ipso-carbons of the phenyl rings consists of six lines and can in no way be interpreted in terms of an AXX' spin system. However, by admitting a chemical inequivalency between the two phosphorus atoms that would result in the occurence of an AXY spin system (A: ${}^{13}C_{ipso}$; X, Y = ${}^{31}P$), six lines are predictable for the A part of the spectrum. A good agreement between simulated and experimental spectrum (Fig. 1(a)) was obtained using the following parameters: $\delta(P_X)$ 53.616, $\delta(P_Y)$ 53.584, $J_{AX} = 39.8$ Hz, $J_{AY} = 1.3$ Hz, $J_{XY} = 41.0$ Hz. Due to the very small difference in chemical shift necessary to fit the Cipso signal, both simulated and experimental ³¹P{¹H} NMR spectrum of Ru(P-Ph₃)₂(AAEMA)₂ consists of a singlet at δ 53.6 (Fig. **1**(b)).

The obtained J_{XY} (41.0 Hz) allows to assign a *cis*geometry for the two coordinated phosphines and rules out structures **d** and **e** among the five possible isomers of Ru(PPh₃)₂(AAEMA)₂ shown in Fig. 2.

Moreover, the inequivalency between the two P atoms seems to indicate structure \mathbf{b} as the most probable.

The electrochemical behaviour of $Ru(P-Ph_3)_2(AAEMA)_2$ was submitted to investigation by cyclic voltammetry in CH₃CN under inert gas (nitrogen) atmosphere (Fig. 3).

The proximity of the anodic peak $(+60 \text{ mV} \text{ with} \text{ respect to Ag/AgNO}_3)$ to the cathodic peak $(-85 \text{ mV} \text{ with} \text{ respect to Ag/AgNO}_3)$ potential and the comparable anodic and cathodic area indicate the quasi-reversibility of the first electrochemical process:

 $[Ru(II)(PPh_3)_2(AAEMA)_2] \rightarrow$ $[Ru(III)(PPh_3)_2(AAEMA)_2]^+ + e^{-it}$

At an anodic potential of 845 mV, a peak attributable to the following process was observed:

$$[Ru(III)(PPh_3)_2(AAEMA)_2]^+ \rightarrow$$
$$[Ru(IV)(PPh_3)_2(AAEMA)_2]^{2+} + e^{-1}$$

The corresponding reduction peak was observed at 726 mV. Also this process appears to be quasi-reversible.

The complex Ru(PPh₃)₂(AAEMA)₂ was submitted to MS analysis by MALDI TOF and LC-MS. MALDI TOF analysis did not return the expected molecular weight of the complex: choosing 9-nitroantracene as matrix and C₆₀/C₇₀ as reference, the highest mass peak observed was at m/z = 1059, seven m/z units higher than the calculated (1052 Da). Noteworthy, a peak attributable to the loss of PPh₃ at m/z = 794 was observed [expected value of $[M-262]^+$: 790 Da].

LC MS analysis performed by direct injection of a methanol solution of the complex gave the expected $[M+H^+]$ peak at m/z = 1053.2 (Fig. 4) and a satisfactory match with the calculated isotope pattern.





Fig. 1. (a) Experimental (top trace) and simulated (bottom trace) spectrum for the ${}^{13}C_{ipso}$ in Ru(PPh₃)₂(AAEMA)₂. (b) Experimental (top trace) and simulated (bottom trace) spectrum for the ${}^{31}P$ signal in Ru(PPh₃)₂(AAEMA)₂.

Complex $Ru(PPh_3)_2(AAEMA)_2$ was submitted to copolymerization with DMAA and MBAA (Fig. 5), at 60 °C in dimethylformamide (DMF) in the presence of 2,2-azobisisobutyronitrile (AIBN) as radical initiator, obtaining a yellow-orange powder referred to in the following as Ru-pol.

The copolymer is insoluble in all common organic solvents, swells in halogenated and polar solvents and shrinks in hexane or diethyl ether. Elemental analysis showed a ruthenium content of 1.85%. The comparison of IR and UV–Vis spectra of the copolymer with those of the precursor complex indicates that the polymeriza-

tion preserves the ruthenium(II) chemical environment. In particular, the appearance of the two combination bands in the IR of Ru-pol at 1610 and 1505 cm⁻¹ proves that the Ru(II) centre is present in the polymer as a β -ketoesterate. Moreover, peaks attributable to the coordinated triphenylphosphine appear at 745, 697 and 523 cm⁻¹ appear in the IR of Ru-pol.

Solid state CP/MAS ³¹P{¹H} NMR spectra of the obtained resin showed a broad signal at δ 53.0, in accordance with the signal observed for Ru(P-Ph₃)₂(AAEMA)₂ in CD₃OD [δ ³¹P{¹H} 53.6 ppm]. It can be thus assumed that the coordination mode of



Fig. 2. Possible isomers for the complex Ru(PPh₃)₂(AAEMA)₂.



Fig. 3. Cyclic voltammogram for a 0.01 M Ru(PPh₃)₂(AAEMA)₂ in acetonitrile containing 0.1 M TEAP.

triphenylphosphine is unchanged in the monomeric complex and in its heterogeneous analogue.

In order to check for catalytic activity of Ru(P-Ph₃)₂(AAEMA)₂ and of its heterogeneous analogue, 1heptene was submitted to hydrogenation at 65 °C in methanol at P(H₂) = 20 bar. The first results show that both Ru(PPh₃)₂(AAEMA)₂ and Ru-pol act as moderately active hydrogenation catalyst with TOF of 8 and 16 h⁻¹, respectively. Work is in progress in order to confirm the higher activity of Ru-pol respect to Ru(P-Ph₃)₂(AAEMA)₂ and to verify if the catalyst can be recycled and used in the hydrogenation of other organic substrates.

3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques.

HAAEMA was purchased from Polyscience, RuCl₃ was purchased from Johnson Matthey UK. Reagents were used as received. RuCl₂(PPh₃)₃ was prepared by literature methods [14]. UV–Vis spectra were recorded on a Uvikon 942 spectrophotometer. IR spectra were recorded on a Bruker Vector 22. NMR spectra were

recorded on a Bruker AM 500 or on a Bruker Avance DRX500 spectrometer; frequencies are referenced to Me₄Si (¹H and ¹³C) and 85% H₃PO₄ (³¹P). The high resolution ³¹P solid state NMR spectra were performed on a JEOL GSE 270 (6.34 T) operating at 109.4 MHz under conditions of ${}^{1}\text{H} \rightarrow {}^{31}\text{P}$ cross-polarization, high power proton decoupling and magic angle spinning. The 90° pulse was 6.0 µs and the contact pulse was 5 ms. The spectra of the complexes were collected after 1000 transients and a relaxation delay of 10 s. The line broadening was set to 100 Hz. H₃PO₄ 85% was used as a reference ($\delta = 0$). Cylindrical 6 mm o.d. zirconia rotors with sample volume of 120 µl were employed with spinning speed of 6.5 KHz. The magic angle was adjusted from the ⁷⁹Br MAS spectrum of KBr by minimizing the linewidth of the spinning side band satellite transitions.

GC-MS analyses were acquired on a HP 5973 instrument. Conversions and yields were calculated by GLC analysis using the internal standard method. MALDI-TOF mass spectrometry was performed on a Voyager-DE Biospectrometry Workstation (PerSpective Biosystems Inc., Framingham, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was set to linear mode at an accelerating voltage in the range 23 000-25 000 V. External calibration was performed using C_{60}/C_{70} . The detecting system was composed of a linear detector and a digitising oscilloscope (frequency: 500 MHz). The sample was prepared with an approximate concentration of 30 mg ml^{-1} in THF. The chosen matrix was 9-nitroantracene in THF. A 0.2- μ l sample of the solution and 0.2 μ l of the matrix solution were mixed, placed on a golden target and then analysed after solvent evaporation. LC-MS analyses were performed on a Agilent HPLC system equipped with DAD and MS systems (Agilent 1100 LC MS). The LC-MS system was controlled by Agilent Chemstation software, which allowed full instrument control, simultaneous mass spectrometry and UV-Vis spectrum data acquisition and data analysis. UV-Vis detection was carried out at a wavelength of 254 nm.



Fig. 4. LC MS spectrum of Ru(PPh₃)₂(AAEMA)₂.



Fig. 5. Synthesis of the heterogeneous analogue of $Ru(PPh_3)_2(AAEMA)_2$.

APCI conditions were: positive ion mode, solvent methanol, flow rate 0.5 ml/min, nitrogen as nebulizing and drying gas, nebulizer pressure 60 psig, drying gas flow 3 1 min⁻¹ at 325 °C, vaporizer temperature 325 °C, capillary voltage 4000 V, corona current 4 μ A, fragmentor voltage 150 V. Mass spectrometry data were acquired in the scan mode (mass range m/z 50– 1500). C and H elemental analyses were carried out on a Carlo Erba EA 1108. Ruthenium elemental analyses were carried out on a Perkin Elmer Optima 3000 ICP-AES instrument equipped with a diode array detector. The ICP torch uses Argon as feed gas and nitrogen for the elimination of oxygen traces in the plasma. The electromagnetic induction power was set to 1300 W. The readings were taken at $\lambda = 240.272$ nm.

The cyclic voltammograms were recorded with a potentiostat–galvanostat PAR 273 EG&G (Princeton Applied Research) coupled with an HP 1070 X–Y–t recorder and a conventional three electrode system (counter electrode: Pt plate; reference electrode Ag/AgNO₃, working electrode Pt plate). The solution was

prepared under nitrogen, in degassed CH₃CN containing 0.1 M tetraethylammonium perchlorate (TEAP) and 0.01 M in Ru(PPh₃)₂(AAEMA)₂. The scan rate was 50 mV s⁻¹.

3.1. Synthesis of $Ru(PPh_3)_2(AAEMA)_2$

RuCl₂(PPh₃)₃ (1g, 1.04 mmol) was dissolved in 150 ml ethanol. Under vigorous stirring, 0.725 ml (3.75 mmol) of HAAEMA and 0.524 ml (3.75 mmol) of triethylamine was added dropwise to the metal complex solution, and reacted, for 32 h at room temperature (r.t.). The solution colour slowly turned from dark red to dark yellow. The solvent mixture was evaporated to 15 ml and a light yellow solid precipitated. The remaining solution was removed and the solid washed with 3×15 ml of ethanol, 2×15 ml of degassed water and eventually with 15 ml of ethanol. After drying in vacuo, 0.750 g of the pure product was obtained as yellow powder (yield 68%).

Elemental analysis: Anal. Calc. for C₅₆H₅₆O₁₀P₂Ru: C, 63.93; H, 5.36; P, 5.89 Ru, 9.61. Found: C, 63.37; H, 5.43; P, 6.0; Ru, 9.4%. M.p.: 112–120 °C (dec). ¹H NMR (CD₃OD, 500 MHz, 293 K): [ppm] $\delta = 1.72$ (s, 3H, C(O)CH₃), 1.90 (dd, $J_{trans} = 1.0$ Hz, $J_{cis} = 1.5$ Hz, 3H, methacrylate CH₃), 3.46–3.50 (m, 2H, O–CH₂), 4.01-4.04 (m, 2H, O-CH₂), 4.58 (s, 1H, C(O)CHC(O)), 5.59-5.60 (m, 1H, cis vinyl proton), 6.046-6.05 (m, 1H, trans vinyl proton), 7.05-7.08 (m, 12H, Phortho), 7.22-7.25 (m, 18H, Ph_{meta}, Ph_{para}); ¹³C{¹H} NMR (THF-d₈, 125 MHz, 293 K): [ppm] $\delta = 18.45$ (s, methacrylate CH₃), 27.87 (O-C(O)CHC(O)CH₃), 62.30, (CH₂-CH₂), 63.67 (CH₂-CH₂), 83.91 (O-C(O)CHC(O)CH₃), 125.30 (s, O-C(O)C=C), 127.76 (m, Ph_{meta}), 129.34 (s, Ph_{para}), 135.36 (m, Ph_{ortho}), 136.62 (m, Ph_{ipso}), 137.48 (s, O-C(O)C=C), 166.95 (s, O-C(O)C=C), 169.62 (s, O-C(O)C=C) C(O)CHC(O)CH₃), 188.87 (s, O-C(O)CHC(O)CH₃). ³¹P{¹H} NMR (CD₃OD, 202 MHz, 293K) $\delta = 53.6$ (s). IR (nujol, CsI pellets): $[cm^{-1}] v = 1717 vs$ (methacrylate C = O), 1609 vs, 1504 vs (β -ketoesterate combination bands), 1259 vs, 1161 vs, 1087 s, 982 m, 772 m (βketoesterate ring out of plane bending), 740 m, 723 m, 695 s, 543 m, 523 s, 280 w, 254 w, 226 m; UV–Vis [ethanol, 6.27×10^{-5} mol 1^{-1}]: 219 nm [ε = 52940 1 $mol^{-1} cm^{-1}$], 260 nm [$\varepsilon = 18400 \ 1 \ mol^{-1} cm^{-1}$], 310 nm [$\varepsilon = 7900$ 1 mol⁻¹ cm⁻¹].

3.2. Copolymerization of $Ru(PPh_3)_2(AAEMA)_2$

A solution containing 0.715 g of Ru(P-Ph₃)₂(AAEMA)₂ (0.68 mmol), 0.119 g of MBAA (0.78 mmol), 2.21 g of DMAA (22.3 mmol) and 3.0 mg of AIBN (18 μ mol) in 2 ml of DMF was heated under vigorous stirring at 60 °C. After 5 min the stirring stopped because of the formation of a gelatinous polymer and, after cooling at r.t., 20 ml of diethyl ether was added. The solid was filtered off, washed with methyl alcohol, diethyl ether and dried under vacuum.

Yield: 3.0 g of yellow solid. Elemental analysis: C, 60.1; H, 8.7; N, 10.4; P, 1.11; Ru, 1.85%. IR (KBr): $[\text{cm}^{-1}] v = 3480 \text{ vs vb}, 1719 \text{ s}, 1610 \text{ w}, 1618 \text{ vs}, 1505 \text{ w}, 1495 \text{ s}, 1402 \text{ s}, 1257 \text{ m}, 1149 \text{ s}, 1055 \text{ m}, 745 \text{ w}, 697 \text{ w}, 523 \text{ m}. UV-Vis [nujol]: 187, 281, 316 \text{ nm}. {}^{31}\text{P}\{{}^{1}\text{H}\} \text{ CP MAS NMR: } \delta = 53.0 \text{ ppm}.$

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