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SOLID-PHASE SUPPORTED CHIRAL TRICARBONYL-CHROMIUM COMPLEXES

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Se prezintă sinteza unor polimeri organometalici conținând complecşi tricarbonil-crom-aromatici. S-au utilizat mai multe abordări, cum ar fi schimbul de liganzi şi grefarea prin substituție electrofilă aromatică utilizând carbocationi benzilici stabilizați de gruparea tricarbonilcrom. Polimerii sintetizați pot fi utilizați drept catalizatori chirali fixați pe fază solidă.

We disclose the synthesis of some organometallic polymers containing arene-tricarbonyl-chromium complexes. Several approaches were used for this purpose, such as ligand exchange and grafting by electrophilic aromatic substitution with benzylic carbocations stabilized by tricarbonylchromium groups. These polymers can be used as chiral solid-phase supported catalysts.

Keywords: solid-phase supported catalysts, tricarbonylchromium complexes

1. Introduction

Transition-metal arene complexes are well-known catalysts for many organic transformations [1]. Solid-phase supported catalysts offer some advantages over soluble ones, such as ease of separation from reaction mixtures, and the possibility of recycling the catalyst [2, 3].

The (arene)chromium complexes have some characteristic properties due to the electron-withdrawing ability and steric bulkyness of the tricarbonyl-chromium fragment. Benzylic anions and cations are stabilized due to the overlapping between a d orbital of chromium and a p-orbital of the benzylic carbon.

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Moreover, the (arene)chromium complexes can exist as two enantiomeric forms due to the planar chirality arising when the arene ring has different substituents at *ortho-* and *meta-* positions. Chiral complexes can also be synthesized starting from optically active arenes posessing a stereocenter.

We report the preparation of several polymer-bound (arene)tricarbonylchromium complexes having the structures presented in Fig. 1.

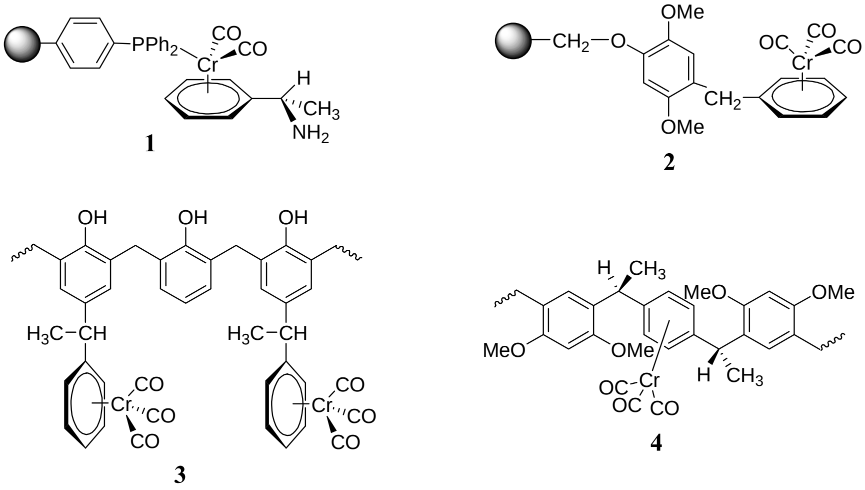


Fig. 1.

2. Experimental

All tricarbonylchromium complexes were prepared from arenes and $Cr(CO)_6$ in diglyme/THF following established procedures [4]. For the compounds 1-16 see scheme 1-4.

^1H and ^{13}C NMR data were obtained on Varian Unity 300 and 400 MHz spectrometers or Bruker Avance 400 MHz spectrometer. FT-IR spectra were recorded using a Bruker Vertex 70 spectrometer with a single reflection diamond ATR accesory (μ-ATR).

2.1. Synthesis of polymer 1. 96 mg (0.37 mmol) of (α-methylbenzylamine)$Cr(CO)_3$ were disolved in a mixture of 3.4 mL (26 mmol) *cis*-cyclooctene and 20 mL toluene. The mixture was deoxygenated with argon and irradiated for 30 min at 0 °C in a photochemical reactor using a 150 W medium pressure mercury lamp. After the irradiation, argon was bubbled in the reaction mixture for another 20 min and the content of the photochemical reactor vas transfered by cannulation in a fritted reaction vessel which contained 62.5 mg (equivalent to 0.185 mmol PPh_3) resin swollen in 5 mL toluene. The reaction vessel was shaken for 24 h at room temperature under argon. The resin was filtered and washed with toluene (3 x 10 mL) and THF (3 x 10 mL) and dried under vacuum.

Product **1** was isolated as yellow beads.

IR (µATR), (cm^{-1}): 1823, 1873 (ν_{CO}).

2.2. Reaction of (benzyl acetate)Cr(CO)$_3$ with 12. To 0.1 g (0.35 mmol) of (benzyl acetate)Cr(CO)$_3$ disolved in 2 mL chloroform were added 90 mg (0.37 mmol) (2,5-dimethoxyphenyl)benzyl ether and 50 µL of boron trifluoride diethyl etherate as catalyst. After stirring at room temperature for 4 h, 1 mL water was added and the reaction mixture was extracted with ether (3 x 5 mL). The organic layer was evaporated and the residue was chromatographed on alumina using petroleum ether and diethyl ether as eluents. The product was recovered after solvent removal from the diethyl ether fraction.

^{1}H-NMR (CDCl$_3$), δ (ppm): 3.69, s, 3H and 3.85, s, 3H (O-CH_3); 6.53, s, 1H (H^6); 6.80, s, 1H (H^3); 7.30 - 7.44, m, 5H (C$_6H_5$); 5.18 - 5.32, m, 5H (C$_6H_5$Cr(CO)$_3$)

2.3. Reaction of Merrifield resin with 10. 0.51 g (3.3 mmol) 2,5-dimethoxyphenol were disolved in 5 mL dimethyl sulphoxide and 0.16 g (3.8 mmol) NaOH were added. The mixture was heated under argon at 90 °C for 1 h and transfered in a fritted reaction vessel containing 250 mg (1.1 mmol Cl) Merrifiel resin swollen in 5 mL dimethyl sulphoxide. The reaction vessel was shaked at 90 °C for 8 h. The resin was filtered and washed succesively with water (3 x 10 mL), THF (3 x 25 mL) and diethyl ether (3 x 25 mL) and dried under vacuum.

2.4. Reaction of resin 15 with (benzyl acetate)Cr(CO)$_3$. 250 mg resin 15 (corresponding to 0.72 mmol of 2,5-dimethoxyphenol units) were swollen in 2 mL chloroform and 200 mg (0.7 mmol) (benzyl acetate)Cr(CO)$_3$ followed by adding 75 µL of boron trifluoride diethyl etherate under argon atmosphere. The reaction vessel was shaked at room temperature for 4 h and afterwards the reaction mixture was quenched with 1 mL water, filtered and washed with THF (3 x 5 mL) and ether (3 x 5 mL) and dried under vacuum.

IR (µATR), (cm^{-1}): 1873, 1957 (ν_{CO})

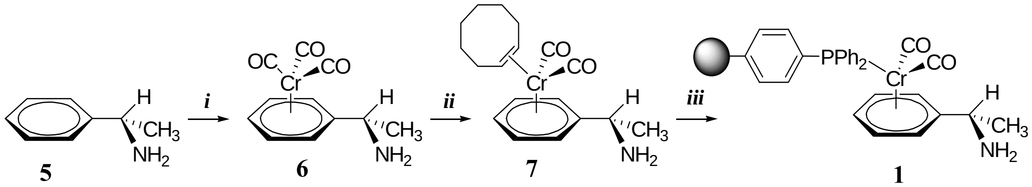
2.5. Synthesis of all-*ortho* novolak. To a solution of phenoxymagnesium bromide in benzene, prepared from 9.4 g (100 mmol) phenol were added 2.7 g (90 mmol) paraformaldehyde. The reaction mixture was refluxed under argon for 12 h. The product was recovered after adding water to the reaction mixture and evaporating under vacuum to dryness.

^{13}C-NMR: (CD_3OD), δ (ppm): 32.1 (CH_2); 128.8, 121.3 (C^3, C^4, C^5); 130.7 (C^2, C^6); 156.2 (C^1).
IR (μATR), (cm^{-1}): 3100 - 3500 ($\nu_{O\text{-}H}$); 2870 ($\nu_{CH2\ sym}$); 2929 ($\nu_{CH2\ asym}$); 1235 ($\nu_{Car\text{-}O\ asym}$); 1037 ($\nu_{Car\text{-}O\ sym}$)

2.6. Reaction of (α-methyl-benzylether)Cr(CO)$_3$ with all-*ortho*-novolak. 200 mg all-*ortho*-novolak (coresponding to 1.88 mmol phenolic units) were disolved in 20 mL dichloromethane and 125 mg (0.46 mmol) (α-methyl-benzylether)Cr(CO)$_3$ were added under argon, followed by 50 μL boron trifluoride diethyl etherate. The reaction mixture was stirred at room temperature for 2 h. The product was recovered after precipitation with hexane and dried under vacuum.
IR (μATR), (cm^{-1}): 1857, 1954 (ν_{CO}).

3. Results and discussion

Polystyrene-supported chiral arene chromium complex **1** was prepared from polystyrene-bound triphenylphosphine and complex **6** having an asymmetric benzylic carbon via ligand exchange with the intermediate complex **7** (Scheme 1). The (arene)Cr(CO)$_2$(cyclooctene) complex was prepared by photochemical ligand exchange, from optically active (α-methylbenzylamine)Cr(CO)$_3$ and *cis*-cyclooctene in toluene, at 0 °C [6]. A large excess of cyclooctene was used in order to avoid subsequent decomposition of the complex and side product formation during the loading step on the resin [7].



i: Cr(CO)$_3$, diglyme, 150 °C, 4 h; *ii*: cyclooctene, toluene, hν, 0 °C, 30 min; *iii*: polymer-bound triphenylphosphine, toluene, rt, 24 h.
Scheme 1.

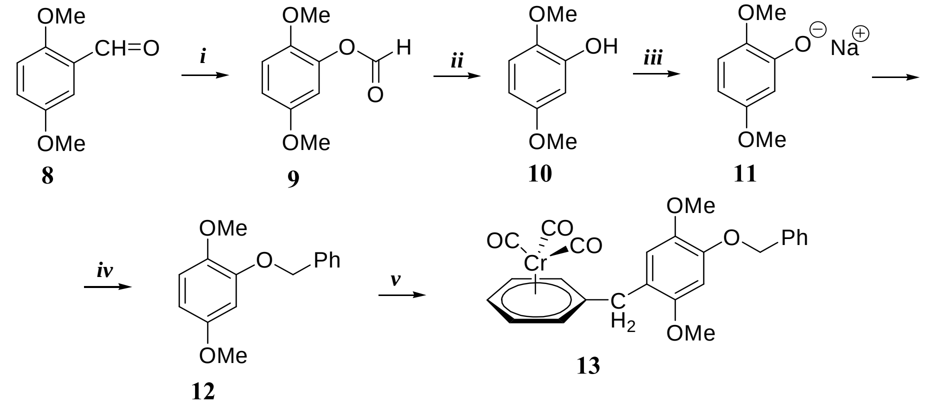
Product **1** was isolated as yellow beads after filtration, washing with THF and drying. The presence of the (arene)Cr(CO)$_2$(PPh$_3$) fragment was confirmed by IR spectroscopy. The IR spectrum showed two intense bands at 1823 and 1873 cm^{-1}.

Another method for preparing resin-bound π-arene chromium complexes is the reaction of stablized benzylic carbocations with activated arenes, extensively studied in the authors' laboratory [8].

In order to investigate the effectiveness of this reaction, we have chosen model compound **12**, obtained by reacting 2,5-dimethoxyphenol, **10,** with benzyl chloride. 2,5-Dimethoxyphenol was prepared from 2,5-dimethoxybenzaldehyde by a Baeyer-Villiger oxidation followed by saponification of the phenolic ester **9** (Scheme 2)[5].

In the presence of Lewis acids such as boron trifluoride diethyl etherate, (benzyl acetate)Cr(CO)$_3$ generates stable benzyl carbocations capable of acting as electrophiles in aromatic substitution reactions.

By comparing the aromatic proton region in the NMR spectra of (2,5-dimethoxyphenyl)benzyl ether, **12,** before and after the reaction with (benzyl acetate)Cr(CO)$_3$ (Figure 2), we can see the disapearance of the resonance at 6.42 ppm and the decoupling of the signals at 6.53 and 6.82 ppm. Thus, the electrophilic substitution of the model compound took place exclusively at the most activated position, *i.e. ortho* vs. one of the methoxy groups and *para* vs. the benzyloxy group.



i: *m*-chloroperbenzoic acid, DCM, reflux, 14 h; ***ii***: NaOH, MeOH, rt, 4 h; ***iii***: NaOH, DMSO, 1 h, 90 °C; ***iv***: $C_6H_5CH_2Cl$, DMSO, 90 °C, 1 h; ***v***: (benzyl acetate)Cr(CO)$_3$, $BF_3 \cdot Et_2O$, $CHCl_3$, rt, 4 h.
Scheme 2.

By analogy with the reaction involving model compound **12**, 2,5-dimethoxyphenol was used as linker and was attached to Merrifield's resin **14** by chlorine substitution with phenoxide ion **11** (Scheme 3). The reaction was monitored by gel-phase ^{13}C-NMR spectroscopy [9].

The spectrum recorded using intact resin beads of resin **15** swollen in deuterated chloroform, displays the signals corresponding to the 2,5-dimethoxy phenoxy unit (Figure 2A), which were attributed by comparison with the spectrum of 2,5-dimethoxyphenol in solution (Figure 2B).

Next, the π-arene chromium complex was attached by reacting (benzyl acetate)$Cr(CO)_3$ with resin **15**.

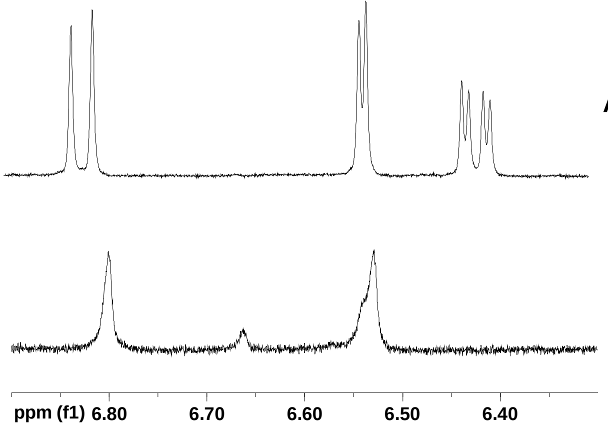
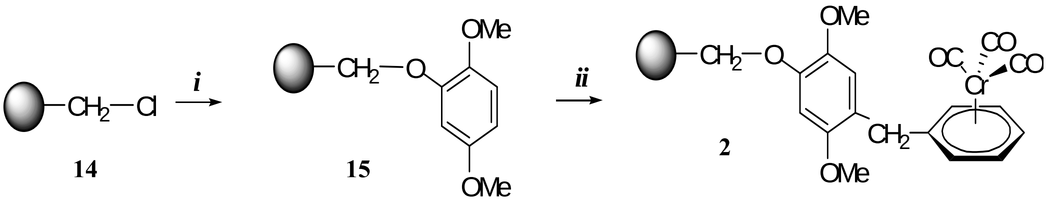


Fig. 2. The region of the aromatic protons in the 1H-NMR spectrum of (2,5-dimethoxy)benzyl ether before (A) and after (B) the reaction with (benzyl acetate)$Cr(CO)_3$

The structure assigned to resin **2** was consistent with the IR spectrum (Figure 4), which showed two C=O stretching bands at 1873 and 1957 cm^{-1}.



i: **11**, DMSO, 90 °C, 8 h; *ii*: (benzyl acetate)$Cr(CO)_3$, $BF_3 \cdot Et_2O$, $CHCl_3$, rt, 4 h.
Scheme 3.

The third method for grafting arene chromium complexes onto polymers also involves the electrophilic substitution reaction previously discussed. In this case, the activated arene is part of the main-chain instead of side-chain of the polymer. We have found novolak-type resins very suitable for functionalization.

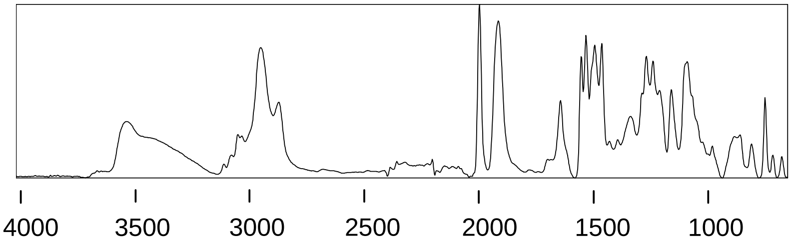
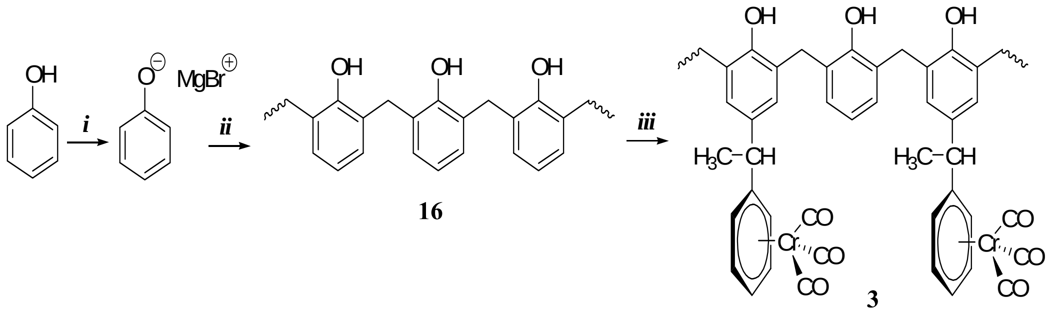


Fig. 3. FTIR spectra of resin **15** after tratment with (benzyl acetate)$Cr(CO)_3$

In order to have a final product with a well-defined structure, a linear novolak-type resin ("all-*ortho*" novolak) was prepared according to the procedure developed by Dradi *et al.* [10]. This involves the reaction of phenoxymagnesium bromide with paraformaldehyde (Scheme 4). The polymer was purified by reprecipitation from acetone and characterized by IR, ^{13}C-NMR spectroscopy and gel permeation chromatography (weight-average molecular weight 6000, polydispersity index 2,6).



i: EtMgBr, ether, rt; ***ii***: paraformaldehyde, benzene, reflux, 12 h; ***iii***: (α-methylbenzylether)$Cr(CO)_3$, DCM, rt, $BF_3{\cdot}Et_2O$, 2h.
Scheme 4.

The presence of only one signal at 32.1 ppm in the ^{13}C-NMR spectrum assigned for the *ortho*-*ortho'* methylene linkage confirms the proposed structure. In random novolaks, methylene linkages appear at 31.7 (*ortho*-*ortho'*), 35.7 (*ortho*-*para'*) and 40.6 ppm (*para*-*para'*) [11].

All-*ortho* novolak was dissolved in dichloromethane and reacted with (α-methylbenzyl ether)$Cr(CO)_3$ in the presence of boron trifluoride diethyl etherate. The presence of tricarbonylchromium units in the structure of polymer **3** was confirmed by IR spectroscopy (ν_{CO}, 1857 and 1954 cm^{-1}).

We have also investigated, with positive results, the posibility of obtaining organometallic polymers having the tricarbonylchromium unit in the main-chain using the reaction between bifunctional arene complex **17** and *m*-dimethoxybenzene (Scheme 5). The product was insoluble in most solvents, rendering further characterization difficult. However its IR spectrum showed the characteristic bands for the tricarbonylchromium as well as the complete dissapearance of the $\nu_{C=O}$ band of the acetate groups. Experimental details will be published in a subsequent paper.

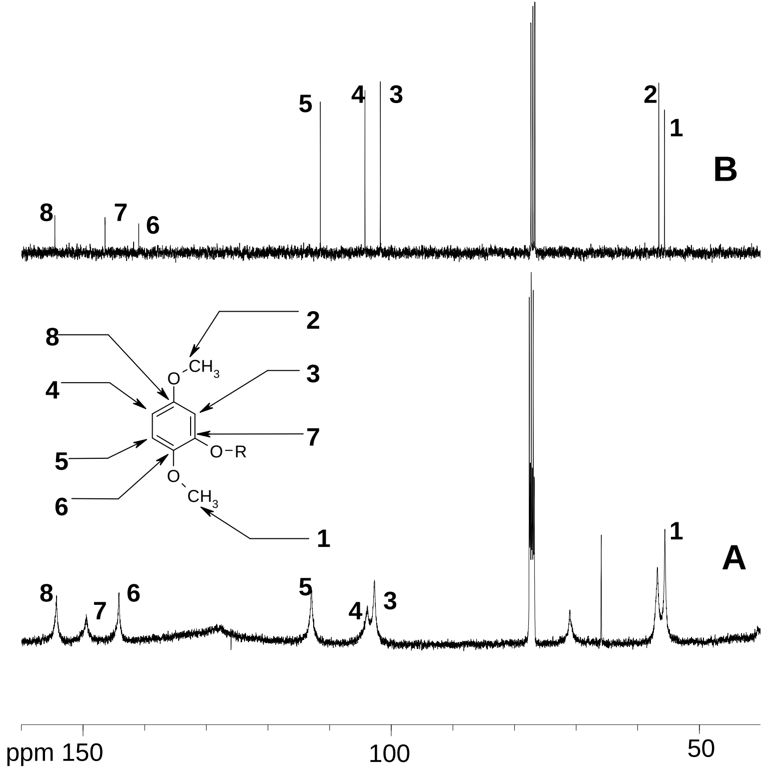
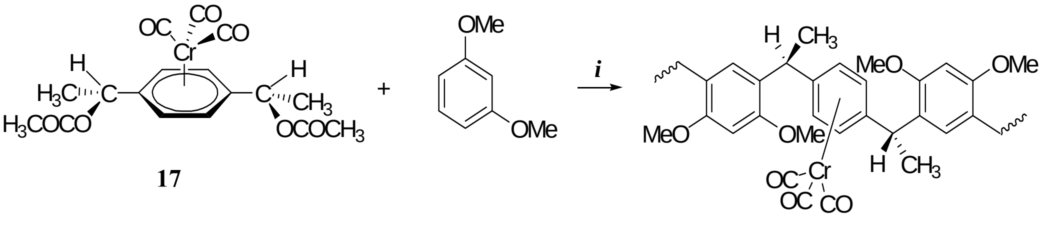


Fig. 4. Gel-phase ^{13}C-NMR spectrum of product **15** swollen in $CDCl_3$ (A) and solution-phase ^{13}C-NMR spectrum of 2,5-Dimethoxyphenol in $CDCl_3$ (B).



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i: $CHCl_3$, $BF_3{\cdot}Et_2O$, rt, 2 h
Scheme 5.

4. Conclusions

The paper describes the synthesis and characterization of several organometallic polymers containing π-arene tricarbonylchromium complexes. These polymers can be used as chiral solid-phase supported catalysts.

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