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CONDENSATION REACTIONS OF PLANAR CHIRAL TRICARBONYL-CHROMIUM-COMPLEXED BENZYLIC ALCOHOLS AND ACETATES WITH REACTIVE ARENES

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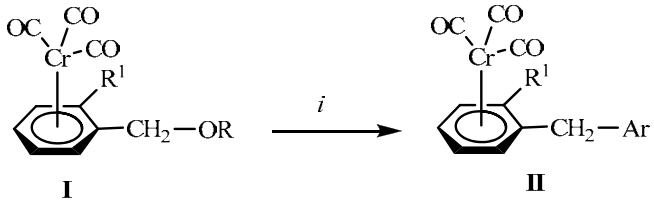
The condensation reaction of planar chiral 2- and 2,5-substituted tricarbonyl-chromium complexed benzylic alcohols and acetates with reactive arenes (durene, anisole, 1,3-dimethoxybenzene, diphenyl ether) is reported. The reactions were performed in both racemic and enantiomeric versions, optically pure *R*-(+)- and *S*-(-)-[2-methoxybenzyl alcohol]-tricarbonyl-chromium being prepared by $LiAlH_4$ reduction of diastereomeric, t.l.c. separated, (-)-menthyl esters of [2-methoxybenzoic acis]-tricarbonyl-chromium. The condensation of the difunctional complex [1,4-diacetoxymethylene-2,5-dimethoxybenzene]-tricarbonyl-chromium with an excess of anisole proved the same reactivity at both reactive benzylic sites thus serving as a model for possible polycondensation process. Corresponding optically pure difunctional starting complexes were obtained by t.l.c. separation of diasteromeric diesters with *R*-(-)-lactic or *S*-(-)-mandelic acids.

INTRODUCTION

We have previously reported the acid catalyzed condensation of tricarbonyl-chromium complexed benzylic alcohols and acetates[1] with reactive arenes, as an efficient route of access to unsymmetrical diarylmethanes (Scheme 1, $R^1 = H$).



i: Ar-H, BF_3OEt_2, r.t., 2-4 hrs, 85-95% yield
R : H, CH_3CO, CH_3
R^1: H, OCH_3, CH_3

Scheme 1 – Unsymmetrical complexed diarylmethanes obtained *via* tricarbonyl-chromium complexed benzylic alcohols, acetats and ethers.

The aim of the present work is to extend the above reaction for the synthesis of planar chiral diarylmethanes-tricarbonyl-chromium complexes (Scheme 1, $R^1 = CH_3$, OCH_3) suitable for enantioselective catalysis. Arene-tricarbonyl-chromium complexes have been known to serve as catalyst for a variety of organic transformations (see an excellent review[2] and examples of hydrogenation,[3,4] isomerization,[3] addition of halocarbons to alkenes,[5] hydroxylation,[6] cycloaddition[7] etc).

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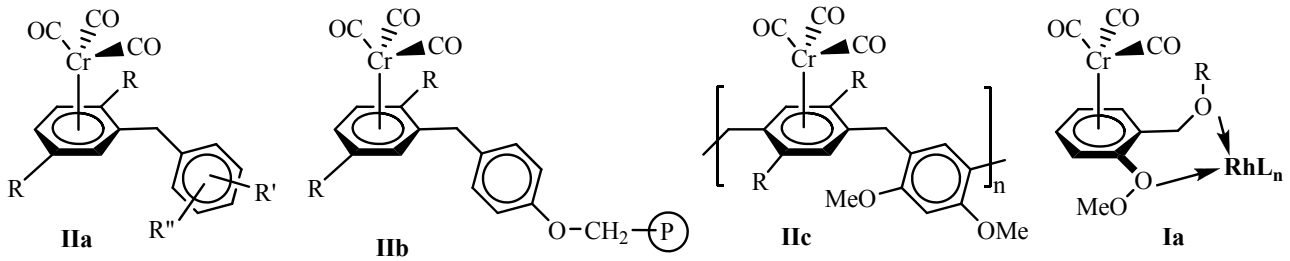
In the planar chiral complexes (displaying an unsymmetrical 1,2- or 1,3-disubstitution pattern) the transition metal atom is placed in a chiral environment and therefore is suitable for enantioselective catalysis.

In this respect the condensation reaction described in the present paper is aiming to provide: (a) the access to versatile structures of type **IIa** using a variety of reactive arenes (*e.g.* polyalkyl- mono- and polymethoxy-, phenoxy-benzenes) thus achieving the possibility to modulate important physical (*e.g.* solubility) or stereochemical properties; (b) a convenient reaction model (condensation with anisole) applicable for embedding potentially catalytic moiety onto a Merrifield resin, thus combining the advantages of homogenous catalysis and solid phase technique (structure **IIb**); (c) the condensation of the chiral complexes bearing two reactive benzylic sites, as useful model for the polycondensation reactions involving arenes exhibiting at least two reactive positions (*e.g.* 1,3-dimethoxybenzene, structure **IIc**).

It is worthy to notice also, that the starting planar chiral complexes containing two donor atoms are potentially useful as chiral ligands for various transition metals (structure **Ia**). Similar planar chiral complexes containing O, N, S or P donor atoms have been successfully used in enantioselective catalysis (see recent reviews[8,9] and application in catalytic hydrogenation,[10,11] hydroboration,[12] hydrosilylation[13] or Heck[14,15] or Diels-Alder[16] reactions.



RESULTS AND DISCUSSION

The selection of the complexes and reactive arenes for condensation reactions is presented in Scheme 2 and was established according to the following structural requirements: for complexes, a structure of benzylic acetates (*R,S*-**1**, *R,S*-**2**) or alcohols (*R*-**3**, *S*-**4**) as reactive site and an *ortho*-substituted (essential to acquire planar chirality) were devised. As *ortho*-substituent, methoxy group appeared to be a convenient candidate due to its favorable electronic effect and relatively low steric hindrance; moreover it provides a donor oxygen atom for potential use as chiral chelating auxiliary. *ortho*- Methyl substituent was designed to test the influence on the reactivity of larger sterical demands and 2,5-dimethyl substitution pattern resulted from the facilities in the synthesis (to avoid regioisomers in the ring substitution steps).

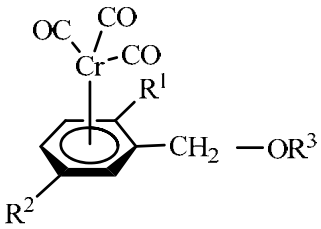
As difunctional benzylic complex, a diester (acetate, **9**, lactate, **10** and mandelate, **11**, respectively) of tricarbonyl-chromium complexed 2,5-dimethoxy-1,4-dimethylol and anisole as reactive arene were used.

Racemic version of the synthesis of the starting complexes and the condensation reactions with arenes is outlined in Scheme 3 and Scheme 4.

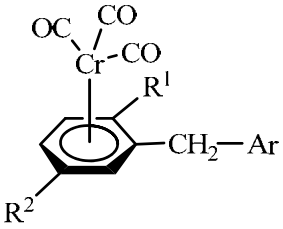
Salicylaldehyde was transformed into 2-methoxybenzylacetate, **1**, by three consecutive steps (Scheme 3). Synthesis of 2,5-dimethylbenzylacetate, **2**, was performed as depicted in Scheme 4 by chloromethylation of *para*-xylene followed by nucleophilic substitution according to literature data.[17-19]

The corresponding racemic complexes *R,S*-(2-methoxybenzyl)-tricarbonyl-chromium, *R,S*-**1** and *R,S*-(2,5-dimethylbenzyl-acetate)-tricarbonyl-chromium**,** *R,S*-**2** were prepared by direct complexation in a thermal reaction with chromium hexacarbonyl following the general procedure previously described.[1,20]

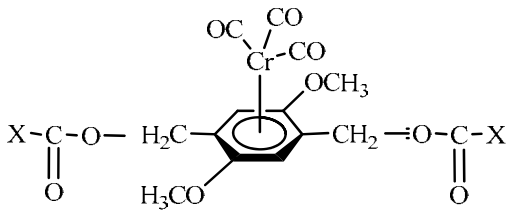
The condensation reactions were performed in chloroform as solvent and in the presence of BF_3 OEt_2 as catalyst, at 20°C, for a reaction time of 2 hours.



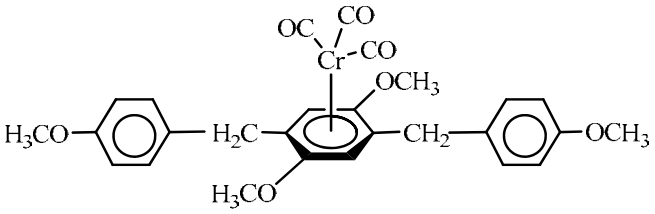
	R^1	R^2	R^3
R,S-**1**	OCH_3	H	Ac
R,S-**2**	CH_3	CH_3	Ac
R-**3**	OCH_3	H	H
S-**3**	OCH_3	H	H



	R^1	R^2	Ar
4	OCH_3	H	4-methoxyphenyl
5	OCH_3	H	2,3,5,6-tetramehylphenyl
6	OCH_3	H	2,4-dimethoxyphenyl
7	OCH_3	H	4-phenoxyphenyl
8	CH_3	CH_3	2,3,5,6-tetramehylphenyl



	X
9	CH_3
R,R - **10**	*R*-(-)-1-hydroxyethyl
R,S - **10**	*R*-(-)-1-hydroxyethyl
S,R - **11**	*S*-(-)-1-hydroxybenzyl
*S,*S - **11**	*S*-(-)-1-hydroxybenzyl



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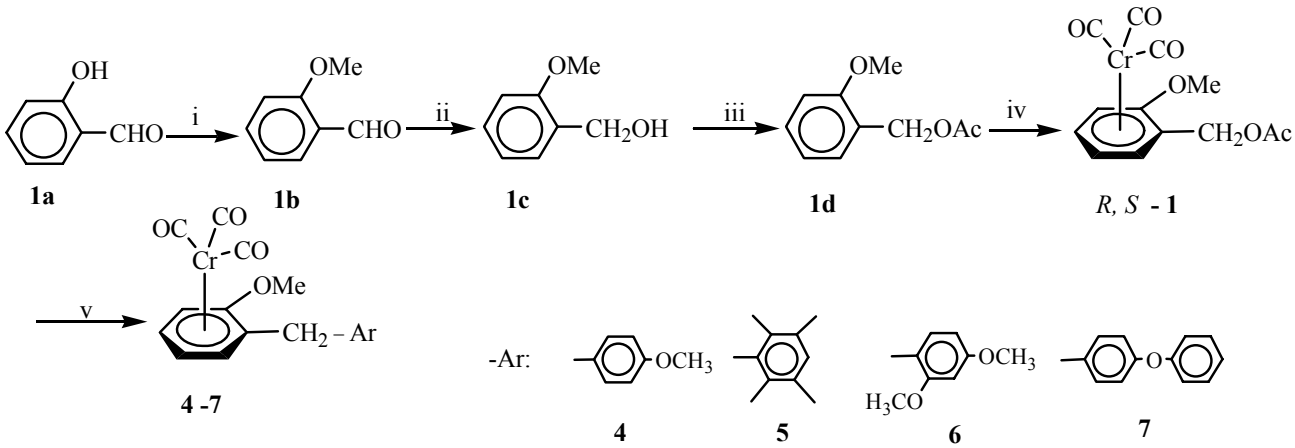
Scheme 2 – Selection of tricarbonyl-chromium complexes and reactive arenes for condensation reactions.



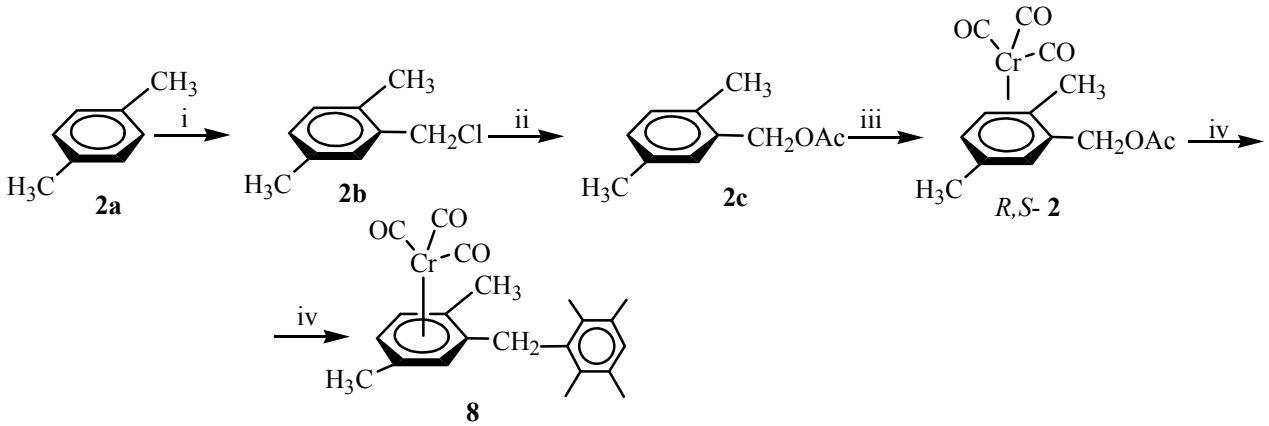
1a **1b** **1c** **1d** *R, S* - **1**

4 -7

-Ar: **4** **5** **6** **7**

i: **1a** (0.12 moles), KOH (0.17 moles), CH_3I (0.18 moles) in 40 mL CH_3OH; reflux 9 hrs; liquid, b.p. = 100°C / 10 mmHg; yield 72%.
ii: **1b** (0.047 moles), $LiAlH_4$ (0.04 moles) in 10mL Et_2O anh; reflux 4 hrs; **1c**, liquid, b.p. = 115°C / 7 mmHg; yield 55%.
iii: **1c** (0.22 moles), Ac_2O (0.044 moles), Py (0.066 moles); 24 hrs, r.t.; 1d, liquid, b.p. = 130-131°C / 7 mmHg; yield 65%.
iv: **1d** (6 mmoles), $Cr(CO)_6$ (8 mmoles) in 12 mL diglyme : n-heptan 1:5, reflux, argon (160°C) 4 hrs.; separation by column chromatography (Al_2O_3, ether); (*R*, *S*) – **1** yellow crystals, m.p. = 71°C (n-heptane); yield 45%.
v: (*R*, *S*) – **1** (0.38 mmoles), anisole (0.9 mmoles), BF_3Et_2O (0.1 mL) in 5 mL $CHCl_3$, 2 hrs. at 20°C; **4**, yellow crystals, m.p. = 105°C (n-heptane); yield 92%. The same procedure for: **5**, m.p. = 180°C; yield 88%; **6** m.p. = 117°C; yield 86%; **7**, m.p. = 161°C; yield 24%;

Scheme 3 – Synthesis of tricarbonyl-chromium complexes *R,S*-**1** and **4-7.**



i: *p*-xylene, **2a** (1 mole), formol 35%(265 mL, 1.3 moles), HCl_g 8 hrs; liquid, b.p. = 103°C / 12 mmHg (lit.[1] 81°C / 7mmHg); yield 62%.
ii: Conf. lit.[19]: (0.071 moles) **2b**, CH_3COOK anh. (0.107 moles), Me_4NBr (0.002 moles) in 300 mL MeCN; reflux 18 hrs., **2c**, liquid, b.p. = 97-98°C / 8 mmHg (lit.[3] 112-114°C / 10 mmHg); yield 93%.
iii: **2c** (5 mmoles), $Cr(CO)_6$ (5 mmoles), in 10 mL diglyme, reflux (160°C), 4 hrs.; **2**, yellow solid, m.p.=. 71°C; yield 47%.
iv: *R,S*-**2**,(0.5 mmoles), duren (1 mmole), BF_3 Et_2O (0.1 mL) in 5 mL $CHCl_3$, 24 hrs., 20°C; yield 10%.

Scheme 4 – Synthesis of tricarbonyl-chromium complexes *R,S*-**2**, and **8**.

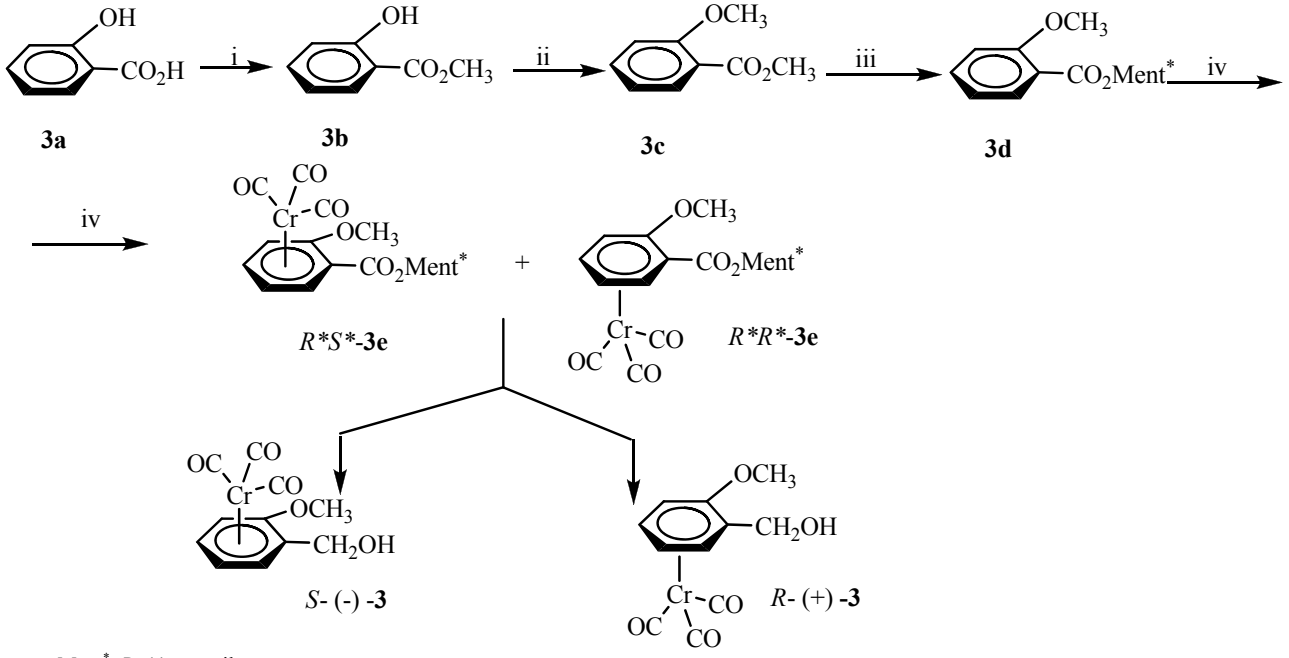
The results of the condensation reaction outlined in Schemes 3 and 4 show that the reactivity (as expressed by condensation yields) depends mainly on the nucleophilicity of the arene and the steric hindrance exerted by *ortho*-substituents from the benzylic complex: while strongly activated arenes containing methoxy, **4**, tetramethyl, **5** and 1,3-dimethoxy, **6** groups gave high condensation rates (~ 90%), diphenylether, **7**, showed only a modest reactivity (24 % yield); on the other hand, the comparison of *ortho*-methoxy (88% yield) and *ortho*-methyl (10% yield) substituents stands for the importance of steric influence (larger steric repulsion exerted by methyl group especially in interaction with 2,6-dimethyl hindered reaction site of the arene).

The access to optically active complexes is outlined in Scheme 5 (for the monofunctional complex) and Scheme 6 (for the difunctional complex). For the synthesis of enantiomeric (2-methoxybenzylalcohol)-tricarbonyl-chromium, *S*-(-)-**3** and *R*-(+)-**3**, the procedure consisted in the preparation of the (-)-menthyl esters of 2-methoxybenzoic acid (transesterification with *R*-(-)-menthol of 98% *e.e.*). The configuration of the transesterified product was carefully checked by ^{1}H- and ^{13}C-NMR spectra (see Scheme 7) as well as by chromatographic methods providing the lack of any contamination with other stereoisomers.

After direct $Cr(CO)_6$ complexation the crude mixture of *R*R** and *R*S** diastereomers (approximately 1:1) was separated by t.l.c. (silicagel, petroleum ether: diethylether = 7:3 as eluting solvent) to afford pure diastereomers (*d.e.*>94%) slightly differentiated by ^{1}H-NMR spectra (δ = 3.83 ppm and 3.81 ppm for OCH_3) $LiAlH_4$ reduction of the separated diastereomers gave the corresponding alcohols, *S*-(-)-**3** and *R*-(+)-**3**.

The absolute configuration was deduced by comparison of the measured optical rotation with values reported in the literature $[\alpha]_D^{20}$ = + 225° (lit.[22] +243° for enantiomer *R*) and $[\alpha]_D^{20}$ = - 228° (lit.[21] -243° for enantiomer *S*).

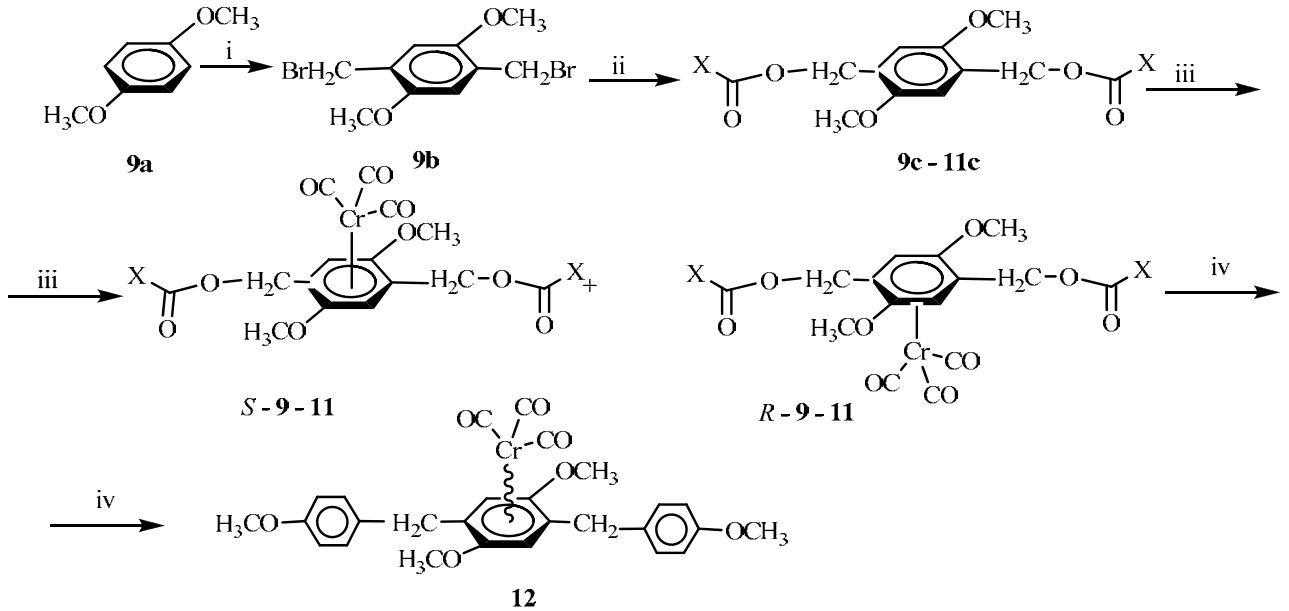
In the Scheme 6 is outlined the access to optically active difunctional complexes consisting in the sequence of *bis*-bromomethylation of 1,4-dimethoxybenzene and then nucleophilic substitution of benzylic bromine atoms by potassium salt of *R*-(-)-lactic acid. Complexation of the resulted enantiomeric dilactates **10b** gave a mixture of diastereomeric complexes *RR*-**10** and *RS*-**10**, (first stereochemical descriptor refers to the configuration of the lactate moiety and the second describes planar configurations). The low yield of complexation (17 - 42% for difunctional complexes) allowed simply t.l.c. separation of diastereomeric complexes but not a univocal attribution of the absolute configuration. Other procedures of complexation, hopefully more efficient, are now under current investigation in our laboratory.



Ment*: *R*- (-) -mentil

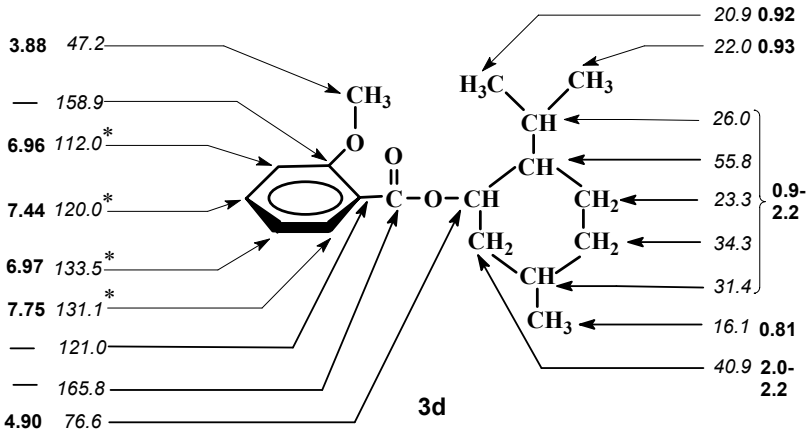
i: CH_3OH / H_2SO_4; ii: **3b** (0.2 moles), KOH (0.2 moles), CH_3I (0.56 moles) in 70 mL MeOH; reflux, 3 hrs.; **3c**, liquid, b.p. = 129ºC / 15 mmHg; yield 53%; iii: **3c** (0.03 moles), *R*–(-)–menthol (0.06 moles), H_2SO_4 conc. (1.5 mL), 2 hrs. at 120ºC, Ar; **3d**, liquid, b.p.= 190ºC / 1 mmHg (lit.[4] 226ºC / 15 mmHg; yield 80%; iv: **3d** (5 mmoles), $Cr(CO)_6$ (5 mmoles) in 10 mL diglim, 5 hrs at 160ºC; raw mixture of diastereomers **3e** and **3f**, yield 73%; v: Mixture of **3e** and **3f** (0.155 g), t.l.c separation, (silica, petroleum ether:Et_2O =7 : 3), *R*, ***R*-3e,** Rf = 0.15, m.p.= 97ºC, yield 27%.; $LiAlH_4$ reduction (8 mmoles / 0.7 mmoles **3e**, and **3f** respectively) resulted: *S*-(-)–**3**, yellow solid, m.p. = 98ºC, $[\alpha]_D^{20}$ = - 228º (c = 1.2, $CHCl_3$) e.e. = 94% and *R*- (+) – **3,** yellow solid, m.p.= 99ºC, $[\alpha]_D^{20}$ = + 225º (c = 1.1 $CHCl_3$) e.e. = 92%.

Scheme 5 – Synthesis of enantiomeric (2-methoxybenzylalcohol)-tricarbonyl-chromium, *S*-(-)-**3** and *R*-(+)-**3**complexes.



i: **9a** (0.1 moles), CH_2O (0.2 moles), HBr (0.3 moles) 45% in NaOH; **9b**, white solid.m.p.= 204ºC;yield 88%; ii: **9b** (0.0126 moles), CH_3COOK (0.1 moles) in 55 mL $CHCl_3$, 18 mL MeCN and NEt_4Br (0.5 g), 24 hrs. at 90ºC; yield 93%; the same procedure applied for dilactate **10c** using $CH_3CH(OH)CO_2K$, yield 78% and dimandelate **11c** using *S*-(-)–mandelic acid, potassium salt, yield 73%, m.p.= 116-117ºC; iii: Complexation with $Cr(CO)_6$ according to the general procedure yielded *R,S*-**9** (42%) and **10** (17%) respectively (as a mixture of diastereomers see Experimental part.). Due to poor reaction yields complex **11** was not obtained in a pure form; iv: *R,S* - **9** (0.24 mmoles), anisole (14 mmoles), BF_3Et_2O (0.05 mL) in 4 mL chloroform, 24 hrs. at 20ºC, **12**, yield 24% (see Experimental part).

Scheme 6 – Synthesis of optically active difunctional complexes **9-12**.



Scheme 7 – Chemical shifts **^{1}H-NMR** and *^{13}C-NMR* assigned for *R*-(-)-menthyl esters of 2-methoxybenzoic acid, **3d**.

EXPERIMENTAL PART

^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer. Approximately 0.2 M (for ^{1}H-NMR spectra) solution in $CDCl_3$ and TMS as internal standard were used. Reported data refer to chemical shifts (ppm, TMS), multiplicity, intensity of the signal and attribution. IR spectra were recorded on FTIR Bruker Equinox 55 equipment in KBr. GC-MS analyses were performed using a Varian 3400 gas-chromatograph coupled with Saturn II mass spectrometer provided with ion trap. Optical rotation was measured with Jasco P-2000 polarimeter.

Melting points were determined using a Boetius type microscope with electric plate and are uncorrected. Solvents were purified according to procedures described in literature and kept on 4Å molecular sieves.

The intermediates **1a-d**, **2a-c**, **3a-d**, **9a-c**, **10c** and **11c,** respectively, were readily prepared according to usual literature procedures and were completely characterized by spectral methods.

R,S-(2-Methoxybenzylacetate)-tricarbonyl-chromium, *R,S* **- 1**, was prepared by direct complexation of acetate **1d** with $Cr(CO)_6$. From **1d** (6 mmoles) and $Cr(CO)_6$ (8 mmoles) in 12 mL diglyme:n-heptan 1:5, 4 hrs. at reflux (160^{O}C) under argon, after solvent removal and separation by column chromatography (Al_2O_3, ether) racemic *R*, *S*–**1** was obtained as yellow crystals, m.p. = 71^{o}C (n-heptane); yield 47%.

^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 5.04 (d, 6.6, 1H, H^3); 5.55 (td, 6.6, 1.4, 1H, H^4); 4.87 (td, 6.2, 0.9, 1H, H^5); 5.76 (dd, 6.2, 1.4, 1H, H_6); 4.98, d and 4.85, d (AB, 13, 2H, CH_2–OAc), 2.12 (s, 3H ,CH_3CO); 3.77 (s, 3H OCH_3).

^{13}C-RMN ($CDCl_3$, δ, ppm,)*:* 93.13 (C^1); 142.24 (C^2); 73.17 (C^3); 94.25 (C^4); 84.4 (C^5); 97.09 (C^6); 60.09 (CH_2–OAc); 20.74 (CH_3CO-); 55.9 (CH_3O-); 232.36 (CO).

R,S-(2,5-Dimethylbenzyl-acetate)-tricarbonyl-chromium, *R,S*-**2** was prepared from 2,5-dimethylbenzyl–acetate, **2c** (5 mmoles) and $Cr(CO)_6$ (5 mmoles) in 10 mL diglyme, 4 hrs. at reflux (160^{o}C), under argon. Solvent removal and separation by column chromatography (Al_2O_3, ether) affords *R*, *S* – **2** as yellow crystals, m.p. = 71^{o}C (n-heptane); yield 45%.

^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 5.40 (s, 1H, H^6); 5.25 (d, 7.2, 1H, H^3); 5.16, (d, 7.2, 1H, H^4); 4.92, d and 4.84, d (AB, 12.4, 2H, CH_2); 2.20 (s, 6H, CH_3 psn 2 and 5); 2.11 (s, 3H, $COCH_3$).

[S–(-)–2-metoxibenzyl-alcohol]-tricarbonyl-chromium, *S-3* and ***[R–(-)–2-methoxibenzyl-alcohol]-tricarbonyl-chromium,*** *R*–**3**, were obtained by $LiAlH_4$ reduction of the corresponding diastereomeric complexed menthyl esters **3e**, and **3f**, respectively. Thus from $LiAlH_4$ (8 mmoles) and **3e** (0.7 mmoles) and $LiAlH_4$ (8 mmoles) and **3f** (0.7 mmoles), respectively, in 20 mL anhydrous ether, *S*-(-)–**3** as yellow solid, m.p. = 98^{o}C, $[\alpha]_D^{20}$ =-228^o (c= 1.2, $CHCl_3$) e.e.= 94% and *R*-(+)–**3** as yellow solid, m.p.= 99^{o}C, $[\alpha]_D^{20}$ = + 225^o (c=1.1, $CHCl_3$) e.e. = 92% were obtained in quantitatively yield.

^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 5.76 (dd, 6.2, 1.4, 1H, H^6); 5.52 (td, 6.6, 1.4, 1H, H^4); 5.07 (dd, 6.7, 0.9, 1H, H^3); 4.95 (td, 6.2, 0.9, 1H, H^5); 4.49, d and 4.52, d (AB, 13, 2H, CH_2); 3.77 (s, 3H, OCH_3).

R,S-4'-Methoxybenzyl-[2-methoxyphenyl-tricarbonyl-chromium], *R,S*-**4** was prepared by the condensation reaction previously described.[1] Thus from *R*, *S*–**1** (0.38 mmoles), anisole (0.9 mmoles), BF_3Et_2O (0.1 mL) in 5 mL $CHCl_3$, 2 hrs. at 20^{o}C, after catalyst removal and purification by column chromatography (Al_2O_3, ether) *R,S*-**4**, as yellow crystals, m.p. = 105^{0}C (n-heptane) was obtained in 92 % yield.

^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 7.19 (d, 8.5, 2H, $H^{2'}$ and $H^{6'}$); 6.87 (d, 8.5, 2H, $H^{3'}$ and $H^{5'}$); 5.27, dd, 1H (H^6); 5.40, td, 1H (H^4); 5.07, dd, 1H (H^3); 4.85, td, 1H (H^5); 3.88 and 3.76 (AB) 2H (CH_2); 3.80, s, 3H (OCH_3).

^{13}C-NMR ($CDCl_3$, δ, ppm):159.5 (C^4); 141.0 (C^2); 131.4 ($C^{1'}$); 130.6 ($C^{2'}$, $C^{6'}$); 114.4 ($C^{3'}$, $C^{5'}$); 101.5 (C^1); 96.7, 93.7 and 86.4 (C^4, C^5, C^6); 74.7 (C^3); 55.9 and 56.2 (OCH_3^2, OCH_3^6); 28.9 (CH_3).

R,S-2',3',5',6'–Tetramethylbenzyl-[2-methoxiphenyl-tricarbonyl-chromium], *R,S*-**5** was prepared following the procedure described for *R,S*-**4** as a yellow solid, m.p.=180^{o}C in 88% yield.

^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 6.95 (s, 1H, $H^{4'}$); 5.44 (td, 6.3, 0.9, 1H, H^5); 5.09 (dd, 6.3, 1.3, 1H, H^6); 4.98 (dd, 6.6, 0.9 1H, H^3); 4.71 (td, 6.6, 1.3, 1H, H^4); 4.01, d and 3.91, d (AB, 13, 2H, CH_2); 3.84 (s, 3H, OCH_3^2); 2.26, s, 6H, CH_3- durene) and 2.19 (s, 6H, CH_3 - durene).

^{13}C-NMR ($CDCl_3$, δ, ppm):141.5 (C^2); 133.1, 133.4, 134.8 (C^1, C^2, C^3); 130.6 (C^4); 110.3 (C^1); 84.7, 93.9, 96.3 (C^4, C^5, C^6); 73.5 (C^3); 55.8 (OCH_3^2); 28.9 (CH_2); 20.6 and 15.9 (CH_3 - durene).

R,S-2,4–Dimethoxybenzyl-[2-methoxyphenyl-tricarbonyl-chromium], *R,S*-**6** was prepared following the procedure described for *R,S*-**4** as a yellow solid, m.p. = 117^{o}C in 86% yield.

^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 5.05 (d, 6.9, 1H, H^3); 5.39 (t, 6.9, 1H, H^4); 4.82 (t, 6.9, 1H, H^5); 5.38 (d, 6.9, 1H, H^6); 3.77 (s, 3H, $OCH_3{}^2$); 6.47 (s, 1H, $H^{3'}$); 6.46 (d, 8, 1H, $H^{5'}$); 7.13 (d, 8, 1H, $H^{6'}$); 3.81, s and 3.82, s (3H, 3H, $OCH_3{}^{4'}$,$OCH_3{}^{2'}$).
^{13}C-NMR ($CDCl_3$, δ, ppm): 93.29 (C^1); 74.22 (C^3); 85,68 (C^5); 98.46 (C^6); 55.95 (CH_2); 145.49 ($C^{1'}$); 158.45, 160.02 ($C^{2'}$,$C^{3'}$); 188.90 ($C^{4'}$); 55.26 ($OCH_3{}^2$), 55.37, 55.82 ($OCH_3{}^{2'}$,$OCH_3{}^{4'}$).
IR: 1954 cm^{-1}, 1891.9 cm^{-1} (ν_{CO}); 2837.8 cm^{-1}, (ν_{CH3});

R,S-4'–Phenoxybenzyl-[2-methoxyphenyl-tricarbonyl-chromium), *R,S*-**7,** was prepared following the procedure described for *R,S*-**4** as a yellow solid, m.p.= 161°C in 24% yield.
^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 5.05 (d, 7, 1H, H^3); 5.49 (t, 7, 1H, H^4); 4.93 (t, 7, 1H, H^5); 5.76 (d, 7, 1H, H^6); 3.75 (s, 3H, OCH_3); 4.09, d and 4.55, d (AB, 12.4, 2H, CH_2); 7.01 (d, 8.2, 2H, $H^{2'}$, $H^{6'}$); 6.89 (d, 8.2, 2H, $H^{3'}$, $H^{5'}$); 6.96 – 7.21 (m, 5H, C_6H_5).

R,S-(Bis-2,5-Dimethoxy-1,4-xylyl-O-acetyl-lactate)-tricarbonyl-chromium, *R,S*-**10**, was prepared by direct complexation of the corresponding dilactate **10c** with $Cr(CO)_6$ according to the general procedure. Thus *R,S*-**10** was obtained in 17% yield as a mixture of diastereomers.
^{1}H-NMR ($CDCl_3$, δ, ppm):
Diastereoizomer 1: 5.40 (s, 2H, H^3, H^6); 3.76 (s, 6H, O-$CH_3{}^2$, O-$CH_3{}^5$); 2.20 (s, 6H, CH_3-COO).
Diastereoizomer 2: 5.46 (s, 2H, H^3, H^6); 3.74 (s, 6H, O-$CH_3{}^2$, O-$CH_3{}^5$); 2.16 (s, 6H, CH_3-COO).

[2,5-Dimethoxy-1,4-bis-4'-metoxibenzyl-phenyl]-tricarbonyl-chromium, **12**, was prepared following the procedure described for *R,S*-**4.** Thus from *R,S*- **9** (0.24 mmoli), anisole (14 mmoli) and BF_3Et_2O (0.05 mL) condensation product **12** was obtained as a yellow solid, m.p.= 161°C in 24% yield.
^{1}H-NMR ($CDCl_3$, δ, ppm, J Hz): 5.53 (s, 2H, H^3, H^5); 7.12 (d, 8.2, 2H, $H^{2'}$, $H^{6'}$); 6.81 (d, 8.2, 2H, $H^{3'}$, $H^{5'}$); 3.77 (s, 6H, O-$CH_3{}^2$, O-$CH_3{}^5$); 3.87 (s, 6H, $OCH_3{}^{4'}$).
^{13}C-NMR ($CDCl_3$, δ, ppm): 78.17 (C^3, C^6); 130.74 ($C^{1'}$); 129.76 ($C^{2'}$, $C^{6'}$); 114.26 (C^3, $C^{5'}$); 55.24 (CH_2); 55.76 and 56.25 (O-CH_3 moiety); 218.68 (CO).

CONCLUSIONS

1. Condensation reactions of planar chiral tricarbonyl-chromium complexes containing one or two reactive benzylic sites (alcohol or ester) with various reactive arenes takes place in the presence of BF_3 OEt_2 as catalyst in good yields (~90%) under mild conditions (r.t. 2 hrs.)

2. The yields depend on the reactivity of arene and the nature of *ortho*-substituent from planal chiral staring complex.

Arenes of high nucleophilicity (anisole, 1,3-dimethoxybenzene, durene) give best results (yields of 86-92%) while less activated arenes afford lower yields (*e.g.* 24% for diphenylether).

ortho-Methoxy substituent in the planar chiral starting complex favors condensations (88% yield) but an *ortho*-methyl group drastically diminishes the reaction yield (10%) presumable by exerting a steric hindrance in the transition state of the condensation reaction.

3. Efficient routes of access to enantiomerically pure planar chiral complexes with one or two benzylic reactive sites, based on t.l.c. separations of diasteromeric mixtures of complexes (esters prepared with optically pure auxiliaries) are devised.

4. The above reported condensation reaction may serve for modulating properties of enantioselective catalysts, their embedding in a solid-phase system or for the synthesis of materials with controlled configuration (configurationally pure metallated oligo- or polymers).

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REFERENCES

1. S. Roşca, R. Stan and S. I. Roşca, *Rev.Roum.Chim.,* **2002**, *47*, 409.
2. J. H. Rigby and M. Kondratenko, *Topics Organomet. Chem.,* **2004**, *7*, 181.
3. M. Sudeoka and M. Shibasaki, *Synthesis,* **1993**, 643.
4. E. P. Kündig, M. A. Kondratenko and P. Romamems, *Angew.Chem.Int.Ed.,* **1998**, *37*, 3146.
5. W. J. Bland, R. Davies and J. L. M. Durrant, *J. Organomet. Chem.,* **1985**, *280*, 95.
6. J. F. Harrod, A. Shaver and A. Tucka, *Organometallics*, **1985**, *4*, 2166.
7. E. P. Kündig, F. Robvieux and M. A. Kondratenko, *Synthesis*, **2002**, 2053.
8. K. Muniz, *Topics Organomet.Chem.,* **2004**, *7*, 205.
9. (a) S. E. Gibson and H. Ibrahim, *Chem.Commun.,* **2002**, 2465; (b) S. E. Gibson and H. Ibrahim, *Chem.Commun.,* **2001**, 1070; (c) S. E. Gibson, H. Ibrahim, C.Pasquier and J. W. Steed, *Tetrahedron*, **2002**, *58*, 4617.
10. U. Englert, C. Hu, A. Salzer and E. Alberico, *Organometallics*, **2004**, *23*, 5419.
11. W. Braun, B. Calmuschi-Cula and A. Salzer, *J.Organomet.Chem.,* **2006**, *691*, 2263.
12. I. Weber and G. B. Jones, *Tetrahedron Lett.*, **2001**, *42*, 6983.
13. U. Son, H. –Y. Jang, J. W. Han, I. Slee and Y. K. Chung, *Tetrahedron Asymmetry*, **1999**, *10*, 347.
14. S. E. Gibson, H. Ibrahim, C. Pasquier and V. M. Swamy, *Tetrahedron Asymmetry*, **2004**, *15*, 465.
15. S. E. Gibson, J. T. Rendell and M. Rudd, *Synthesis*, **2006**, 3631.
16. J. B. Jones, M. Guzel and S. B. Heaton, *Tetrahedron Asymmetry*, **2000**, *11*, 4303.
17. C. D. Shackett and H. A. Smith, *J.Am.Chem.Soc.,* **1951**, *73*, 766.
18. B. Wang and M. Wasielewski, *J.Am.Chem.Soc.,* **1997**, *119*, 12.
19. J. Bergman and L. Engman, *J.Org.Chem.,* **1982**, *47*, 5191.
20. S. Roşca, C. Orfanu, R. Stan and S. I. Roşca, *Rev.Roum.Chim.,* **1992**, *37*, 1225.
21. A. Meyer, *Ann.Chim.,* **1973**, *8*, 397.