Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 4725

www.rsc.org/obc

**PERSPECTIVE**

# Planar chiral ($\eta^5$-cyclohexadienyl)- and ($\eta^6$-arene)-tricarbonylmanganese complexes: synthetic routes and application

**Francoise Rose-Munch and Eric Rose**

***Received 25th January 2011, Accepted 14th April 2011***
**DOI: 10.1039/c1ob05137g**

Planar chiral arenetricarbonylchromium complexes have been intensively investigated and they have been applied as valuable building blocks for asymmetric synthesis and as ligands for asymmetric catalysis. In contrast, in the field of the isoelectronic cationic $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes, until these last 10 years, very few studies were published involving nonracemic planar chiral cationic complexes and their potential applications, certainly because of the difficult access to enantiopure starting material. In 2009, however, the discovery of the first resolution of such compounds opened a new area for their application in the field of organic as well as of organometallic enantioselective syntheses. We felt it important to write a *review* on this subject to give an up-to-date summary of the methodologies used to prepare enantiomerically pure planar chiral neutral $[(\eta^5\text{-cyclohexadienyl})Mn(CO)_3]$ and cationic $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes as well as their potential in enantioselective synthesis.

## 1. Introduction

Coordination of a tricarbonyl metal entity to an *ortho*- or *meta*-substituted arene leads to a differentiation of the top and bottom half of the arene plane and results in a molecule without a symmetry element. This is realized by complexation, for example, to a $Cr(CO)_3$ or a $Mn(CO)_3^+$ fragment leading to usually yellow ($\eta^6$-arene)-$Cr(CO)_3$ or slightly orange -$Mn(CO)_3^+$ crystalline compounds, abbreviated $\eta^6$-Mn, which present a tetrahedral structure often compared to a "three leg piano stool". As a consequence two complexes are formed that are non-superimposable mirror images, which have been termed *planar chiral enantiomers* (Fig. 1).[1–3]

*UPMC Univ Paris 6, IPCM, CNRS: UMR 7201, Bât. F, porte 239, Case 181, Laboratoire de Chimie Organique et Organométallique, 4, Place Jussieu, 75005 Paris, France. E-mail: francoise.rose@upmc.fr, eric.rose@upmc.fr*

**Françoise Rose-Munch**

*Françoise Rose-Munch was born in Metz, France. She studied at the University P. et M. Curie, Paris and received her PhD in 1976 working on Pd complexes. After a postdoctoral period in 1976 and 1977 at the University of Stanford, California, USA with Prof. J. P. Collman in the field of dinuclear Fe complexes, she returned to Paris. She was appointed researcher at the CNRS «Centre National de la Recherche Scientifique» in 1975 at the University Paris 6 and became «Directrice de Recherche» in 1992. Her research interests concern the organometallic chemistry of Pd, Fe, Cr, Mn complexes, the nucleophilic substitutions in arene–metal complexes as well as their application in non-linear optics, enantioselective synthesis and catalysis.*

**Eric Rose**

*Eric Rose was born in Nancy, France. He studied at the University of Nancy and then in Paris and received his PhD in 1975 from the University P. et M. Curie, Paris, working on steroids and alkaloids synthesis. After a postdoctoral period in 1976 and 1977 with Prof. J. P. Collman, CA, USA, involving synthesis of heme protein models, he returned to Paris to become Director of Research at the CNRS in 1985. His research interests lie in the general area of organic and organometallic chemistry, in particular in the preparation of chiral porphyrins as catalysts for the enantioselective epoxidation and cyclopropanation of olefins and the preparation and the reactivity of arenetricarbonylchromium and manganese complexes.*

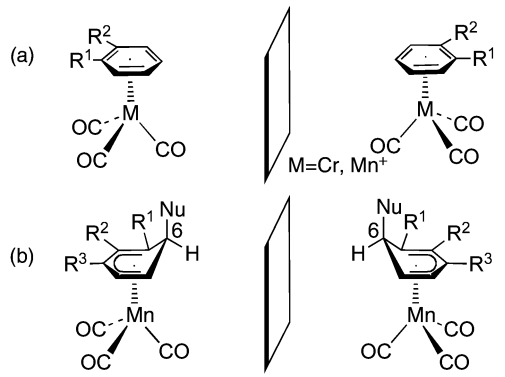


**Fig. 1** Chirality of $\eta^6$- and $\eta^5$-metal tricarbonyl complexes.

The stereochemical description of these systems has been considered (Fig. 2a). Thus, in the case of (*m*-methyl-anisole)$Mn(CO)_3^+$ complex for example, the $C^1$ carbon bearing the methoxy group of the two enantiomers **1** and *ent*-**1** are substituted by (a): the metal atom, (b): the methoxy group, (c): the $C^2$ carbon and (d): the $C^6$ carbon. They are considered to be pseudo-tetrahedral and the priorities are assigned according to the Cahn–Ingold–Prelog rules[4] $(Mn)^a > (OMe)^b > (C^2)^c > (C^6)^d$.

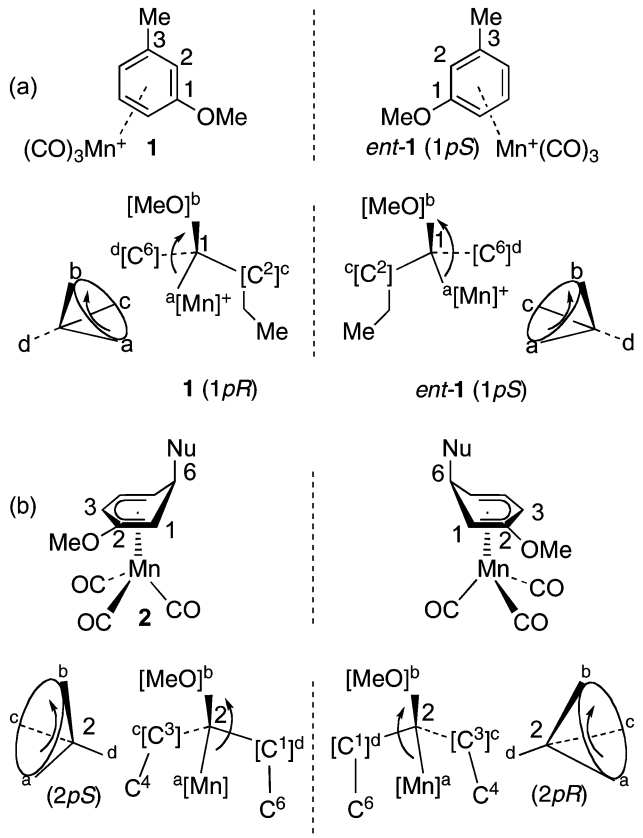
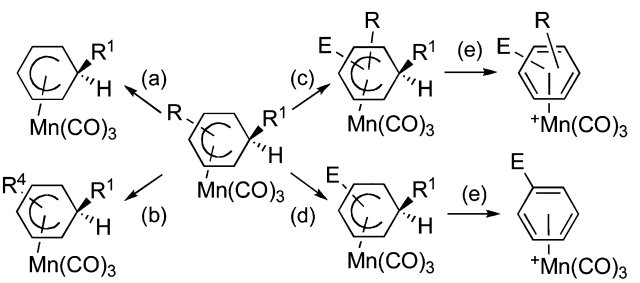


**Fig. 2** Stereochemical description of $\eta^6$ and $\eta^5$ -$Mn(CO)_3$ complexes.

The tetrahedron centered to the $C^1$ carbon is written so that the position of the lowest priority (d) is the furthest from the observer. In this case, a clockwise screw put the substituent a to the substituent b, thus the $C^1$ carbon is (*R*), Fig. 2a. Finally, to specify the element of chirality, the letter (*p*) for planar is put in front the assignment attributed to the planar chirality which describes complex **1** as **1** (1*pR*) and complex *ent*-**1** as (1*pS*). Similarly, complex **1** is (3*pS*) and complex *ent*-**1** is (3*pR*) Fig. 2a. Another rule which is less employed, has been firstly introduced by Schlögl and gives the opposite sign.[5]

The description of the chirality of ($\eta^5$-cyclohexadienyl)-$Mn(CO)_3$, abbreviated $\eta^5$-Mn, complexes obtained by addition of a nucleophile $Nu^-$ to the coordinated cationic arene is not as straightforward as for the $\eta^6$-Cr or -Mn complexes. This deserves short comments: all $\eta^5$-Mn complexes unsymmetrically substituted on the cyclohexadienyl unit are chiral. When Nu is an hydrogen, the $\eta^5$-Mn contains a single stereogenic element: the chiral plane (Fig. 1b, Nu = H). If Nu is different from an hydrogen atom, another stereogenic element at the $C^6$ $sp^3$ carbon is created. Thus, four stereoisomers are formally formed as two pairs of enantiomers. However, with the nucleophilic addition occurring usually *exo* to the Mn tripod, only a single pair of enantiomers is in fact formed, (Fig. 1b, Nu ≠ H). Thus, mono substituted $\eta^5$-Mn complexes are chiral if substituted at the $C^1$ or $C^2$ carbon. Moreover, $\eta^5$-Mn complexes substituted twice by the same group are chiral if they are not located at symmetrical positions with respect to the plane orthogonal to the π-system including the $sp^3$ carbon. In the example reported in Fig. 2b, the tetrahedron centered to the $C^2$ carbon is written so that the position of the lowest priority (d) is the furthest from the observer. In this case, an anti-clockwise screw put the substituent a to the substituent b, thus the $C^2$ carbon of complex **2** is (*S*): *2pS* Fig. 2b.

Preparation of enantiopure neutral ($\eta^6$-arene)$Cr(CO)_3$ complexes is well precedented in the literature. Indeed Cr complexes have been widely applied as stoichiometric intermediates for asymmetric synthesis of biologically active substrates as well as ligands for asymmetric catalysis.[6–8] They are obtained by resolution, by diastereoselective syntheses, or by enantioselective methods.[9] In contrast, little is known in the field of planar chirality for the isoelectronic cationic ($\eta^6$-arene)$Mn(CO)_3^+$ derivatives and the neutral ($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ complexes.[10–12] However, they are taking a growing place in organic and organometallic chemistry thanks firstly to the discovery of *cine* and *tele* nucleophilic substitutions for $\eta^5$-Mn complexes,[13] (we called *cine*,[14] *tele-meta*[15] and *tele-para*[16] nucleophilic substitutions the reactions discovered for ($\eta^6$-arene)$Cr(CO)_3$ complexes in contrast to *ipso*[17] $S_NAr$, (Scheme 1, path a). Recently, general functionalization of the neutral



(a) $H^-$ then $H^+$; $S_N$ *cine* and *tele* : R=OMe, Cl, $NR_2$, SR
(b) Pd cross-coupling, [Pd], $R^4M$ , R=Cl
(c) *n*BuLi then $E^+$, R=Cl
(d) *n*BuLi then $E^+$, R=Br
(e) Rearomatization, $CPh_3^+BF_4^-$, $R^1$=H

**Scheme 1** Reactivity of ($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ complexes.

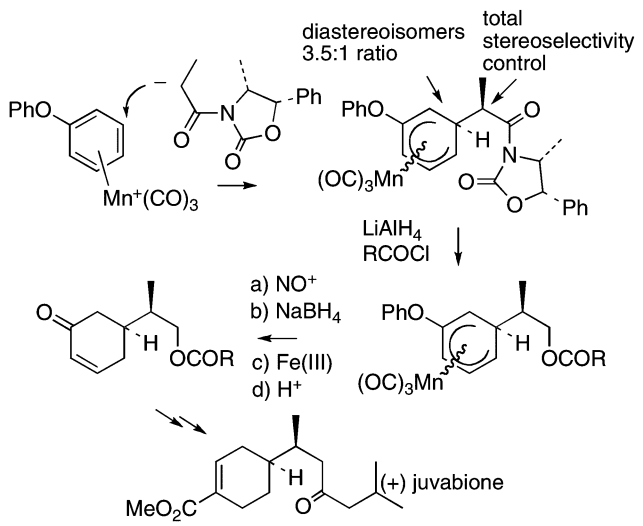
($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ complexes was developed *via* Pd-catalyzed cross coupling reactions,[18] (Scheme 1, path b), lithiation *ortho* to the chloride atom of chloro derivatives,[19] (Scheme 1, path c) and *ipso* lithiation by bromine/lithium exchange of bromo derivatives, (Scheme 1, path d).[20] These new functionalization pathways open novel perspectives for the development of $\eta^5$ complexes and at the same time, provide an easy access to a large range of diversely substituted $\eta^6$ arenes after rearomatization of the cyclohexadienyl ring, (Scheme 1, path e). Thus before explaining our own results concerning the resolution of $\eta^5$- and cationic $\eta^6$-Mn derivatives, we will describe briefly the state of the art of this research including the synthesis of enantiopure planar chiral and chiral-at-the metal $\eta^5$-Mn complexes.

## 2 Synthesis of enantiopure ($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ complexes

### 2.1 Diastereoselective addition to ($\eta^6$-arene)$Mn(CO)_3^+$ complexes

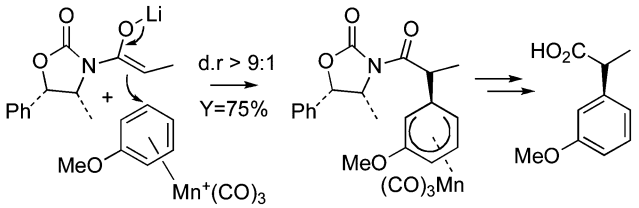
Three representative examples are based on the addition of chiral, non racemic enolates (Evans' enolate, Schöllkopf's and William's enolates) to substituted $\eta^6$ cationic complexes. Miles *et al.* reacted a chiral non-racemic enolate derived from *N*-acyloxazolidinones (Evan's enolate) with the prochiral ($\eta^6$-diphenylether)$Mn(CO)_3^+$ complex.[21]

The stereoselectivity is perfectly controlled at the carbon α to the *N*-acyloxazolidinone but not at the $sp^3$ carbon of the $\eta^5$-Mn complex. Two diastereoisomers were formed in the ratio of 3.5 : 1. These inseparable compounds were reduced to alcohol complexes which were trapped with 4-nitrobenzoylchloride to afford esters which were separated by recrystallization in 63% yield based on the alcohol complex. A CO ligand was exchanged with $NO^+$ and addition of $NaBH_4$ gave an $\eta^4$-cyclohexadiene Mn complex which liberated the free cyclohexadiene in the presence of $FeCl_3$. Finally, an aqueous acid hydrolysis yielded the homochiral 5-substituted cyclohexenone which was converted to (+)-juvabione by the usual workup (Scheme 2).




**Scheme 2** Synthesis of juvabione.

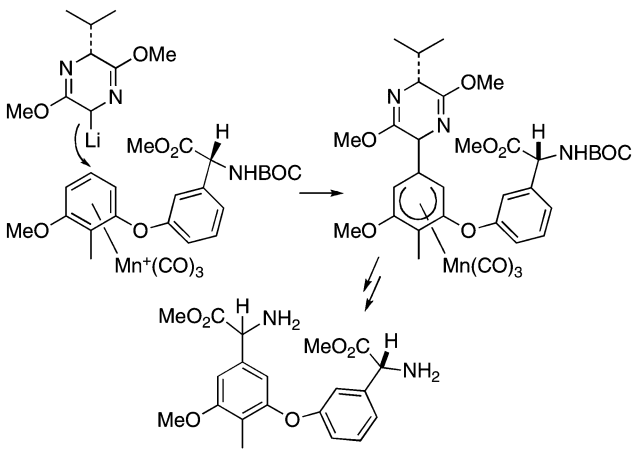
These authors reported also the addition of the same carbanion to ($\eta^6$-anisole)- and ($\eta^6$-*p*-dimethoxybenzene)$Mn(CO)_3^+$ which allowed diastereoselective phenylation (Scheme 3).[22]




**Scheme 3** Diastereoselective phenylation.

(*S*)-2-Phenylpropionic acid was obtained in greater than 95% ee. This reaction with diphenylether Mn complex gave (*S*)-2-(3-phenoxyphenyl)propionic acid, which is the most biologically active enantiomer of phenoprofen, an anti-inflammatory drug usually marketed as the calcium dihydrate salt.

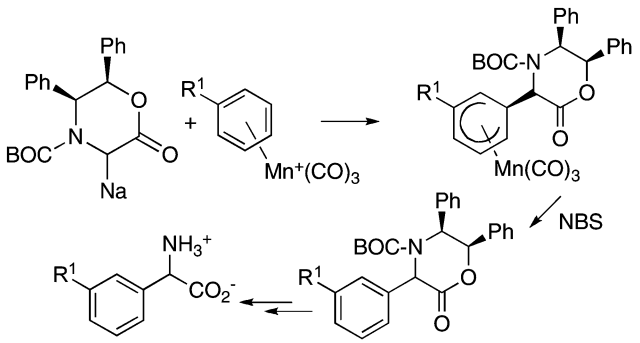
Pearson *et al.* reported the addition of Schöllkopf's chiral glycine enolate equivalent to an $\eta^6$-Mn complex with a good selectivity and a modest degree of asymmetric induction. The synthesis of deoxyristomycinic acid derivatives was realized in 35–44% yield and 60–95% de, (Scheme 4).[23,24]




**Scheme 4** Addition of Schöllkopf's chiral glycine enolate.

Treatment of ($\eta^6$-anisole)- and ($\eta^6$-veratrole)$Mn(CO)_3^+$ complexes with William's chiral glycine sodium enolate equivalent gave the corresponding substituted ($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ derivatives with high diastereoselectivity. But purification of the $\eta^5$-Mn complexes occurred with significant decomposition on the silica gel chromatography column. So direct treatment of the reaction mixture with NBS was preferred and afforded the aryloxazinones in 59% yield, de = 90%, $R^1$ = OMe, (Scheme 5).[25]

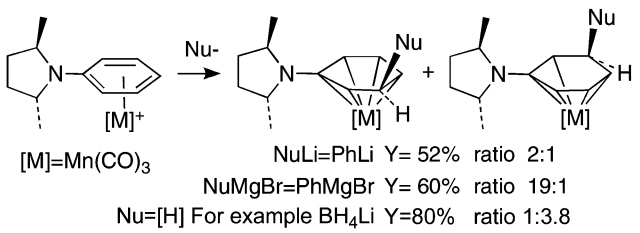
Pearson *et al.* studied the *meta* stereoselective addition of achiral nucleophiles ($[H]^-$, PhLi, PhMgBr, vinylBr, MeLi) to $\eta^6$-Mn complexes without planar chirality but bearing a chiral pyrrolidine auxiliary with a C2 symmetry. The stereodifferentiation between the two diastereotopic *meta* positions occurred efficiently thanks to the steric effects of the methyl groups which are oriented differently with respect to the arene ring. According to the nature of the nucleophile, unexpected diastereoselectivities were observed. For example, a 2 : 1 ratio between the two regioisomers with PhLi was obtained whereas this ratio was 19 : 1 with PhMgBr.



**Scheme 5** Addition of William's chiral glycine sodium enolate.

This was rationalized on the basis of steric approach control at the sterically more accessible *meta* position. However, hydride addition revealed a reversal of selectivity to the two *meta* carbons. For example, $LiBH_4$ afforded a 1 : 3.8 ratio of the two *meta* positions. A change in transition state location was proposed as the reactivity of the nucleophile was varied.[26] The authors concluded that sterically demanding very reactive nucleophiles gave best results that can be understood based on an intuitive steric approach control model, while nucleophiles of lower reactivity give poorer or even reversed selectivity that appears to be consistent with a late transition state model.

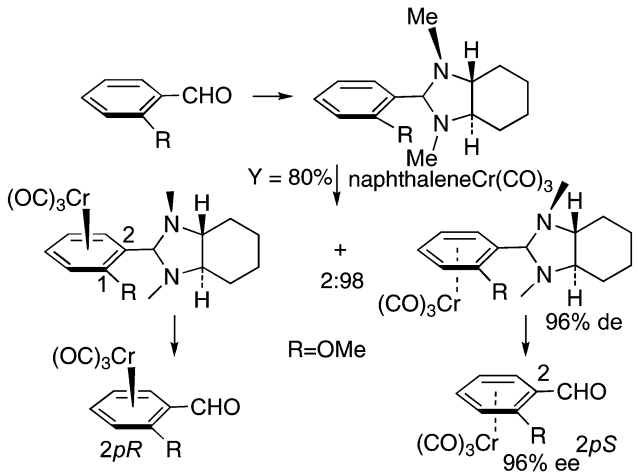
This represented a promising application to differentiate two diastereotopic *meta* positions even if the parameters governing this selectivity were not yet understood (Scheme 6).[27] We have used another representation of the $\eta^5$-cyclohexadienyl unit for clarity reasons with five Mn–C bonds.




**Scheme 6** Addition of a nucleophile to a $\eta^6$-Mn complex bearing a chiral pyrrolidine auxiliary.

The influence of the two methyl groups at the nitrogen at the C2 and C5 carbons of the pyrrolidine group can be compared with the steric role played by the two methyl groups of the diamine: (*R,R*)-1,2-bis(*N*-methylamino)cyclohexane possessing a C2 axis of symmetry during the complexation of the aminal of *ortho*-methoxybenzaldehyde by the $Cr(CO)_3$ unit (Scheme 7).

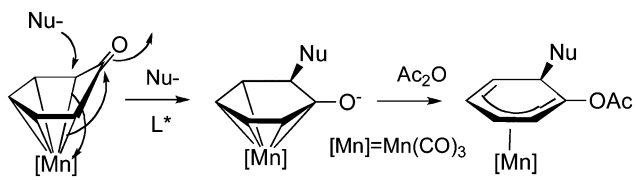
Indeed, chromium transfer from naphthalenetricarbonylchromium to this aminal easily occurred to deliver stereomeric aminals in a 2/98 ratio in 94 and 96% de. After purification and hydrolysis, each of them lead to the formation of the enantiopure benzaldehyde derivative complex (Scheme 7). The two differently oriented methyl groups of the aminal probably could permit the differentiation of the two faces of the π-system.[28] This study confirmed the crucial role of the conformation of the $Cr(CO)_3$ tripod with respect to the arene ring.[29]




**Scheme 7** Enantioselective coordination of benzaldehyde derivatives to the $Cr(CO)_3$ unit.

### 2.2 Enantioselective addition to $\eta^5$-Mn complexes

Such a reaction was described in one example involving very specific $\eta^5$ complexes derived from ($\eta^6$-phenol)$Mn(CO)_3^+$ complex. Thus, Chung *et al.* reported the deprotonation of ($\eta^6$-phenol)$Mn(CO)_3^+$ derivatives into ($\eta^5$-oxocyclohexadienyl)$Mn(CO)_3$ complexes, which are a mesomeric form of the zwitterionic ($\eta^6$-phenate)Mn complex.[30] It reacted with a nucleophile $Nu^-$ to give an alcoholate which could be trapped with an electrophile $E^+$. The corresponding neutral $\eta^5$-Mn complex bears a new $sp^3$ carbon substituted by $Nu^-$. This reaction is stereospecific *anti* to the $Mn(CO)_3$ tripod and occurs always at the end of the π-system. If the $\eta^5$-Mn complex was not substituted, the two ends of the π-system are identical and prochiral. Thus an asymmetric induction is possible. Indeed, in the presence of a chiral non racemic ligand such as (–)-sparteine or an aminoalcohol, the nucleophile could add preferentially to one of these two positions in 7 to 54% ee by addition of PhMgBr and trapping with $Ac_2O$, Nu = Ph. The best result was obtained with (*S*)-binaphthol which affords the acylated $\eta^5$-Mn complex in 95% ee and 78% yield. However, organolithium derivatives such as PhLi and organocuprates such as PhLi/CuI did not induce significant asymmetric induction (Scheme 8).

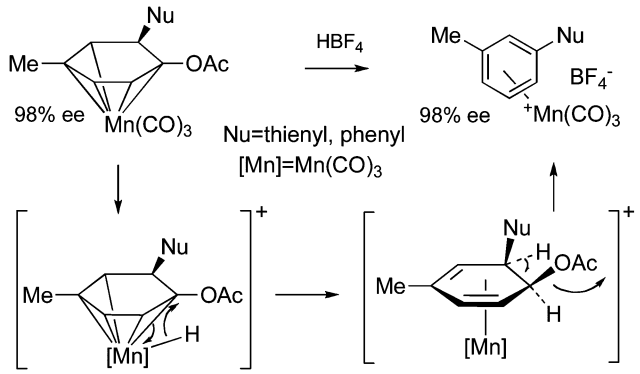



**Scheme 8** Addition of a nucleophile to an ($\eta^5$-oxocyclohexadienyl)-$Mn(CO)_3$ complex.

The reaoromatization of the enantioenriched $\eta^5$-Mn by $HBF_4$ afforded quantitatively tetrafluoroborate salts of the cationic $\eta^6$-Mn complexes after elimination of AcOH (Nu = Ph, ee = 95%). The driving force of this reaction corresponds to the elimination of the acetoxy group. As no mechanism is proposed by the authors, we suggest the protonation of the Mn atom followed by the migration of the hydride to the $\eta^5$-moiety to provide a cationic $\eta^4$-Mn intermediate which can eliminate AcOH. The absolute

configuration of the two *meta* substituted derivatives, 3-phenyl and 3-thienyl toluene-$Mn(CO)_3BF_4$ complexes, has been determined by X-ray crystallography (Scheme 9).




**Scheme 9** Acidic treatment of an ($\eta^5$-acetoxycyclohexadienyl)$Mn(CO)_3$ complex.

### 2.3 Resolution of racemic $\eta^5$-Mn complexes

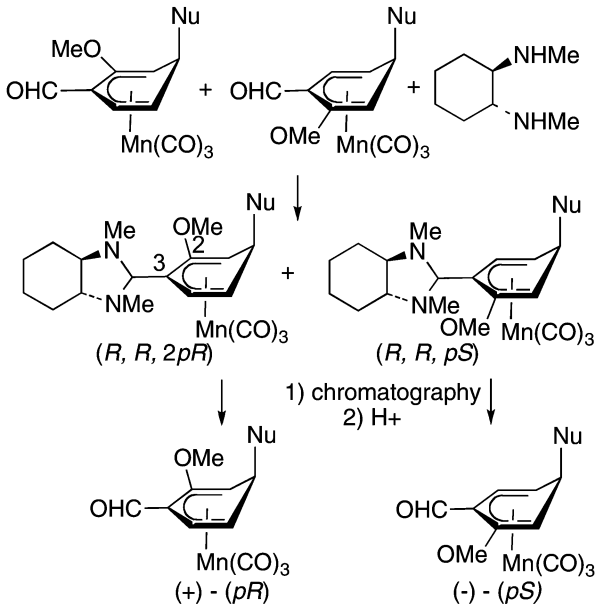
Resolution of ($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ complexes can be realized when the cyclohexadienyl unit is substituted by specific functions such as an aldehyde or a phosphine. Indeed, we previously mentioned the efficiency of the (*R*,*R*)-*N*,*N*′-1,2-dimethyldiaminocyclohexane to resolve racemic planar *ortho*-disubstituted ($\eta^6$-benzaldehyde)$Cr(CO)_3$ complexes (paragraph 2.1);[28] we used the same strategy for the resolution of racemic $\eta^5$-Mn-formyl derivatives.

Treatment of *rac*-($\eta^5$-1-chloro-2-formyl-4-methoxy-6-phenylcyclohexadienyl)$Mn(CO)_3$ complex with the chiral diamine afforded two diastereomeric aminals which could be separated with basic alumina, the first fractions eluted a single diastereoisomer with ee > 95% whose absolute configuration has been determined by X-ray crisytallography.[19] For the (*rac*)-(2-methoxy, 3-formyl, 6-phenylcyclohexadienyl)$Mn(CO)_3$ complex, the same reaction with the enantiopure diamine afforded two diastereomeric aminals *R*,*R*,*pR* and *R*,*R*,*pS* in 33 and 32% yield with >95 and >85% de, respectively (Scheme 10). These aminals were converted into the enantioenriched aldehydes (*pR*) and (*pS*) by acid-catalyzed hydrolysis in 93 and 99% yield and >95 and 85% ee, respectively. The X-ray analysis of the diastereomeric aminal (*R*,*R*,*pR*) permitted to unambiguously assign the absolute configuration of the formyl derivatives (*pR*) and (*pS*), Nu = Ph (Scheme 10).[19,31]

The extension of this methodology has been applied for *rac*-(2-methoxy-3-formylcyclohexadienyl)$Mn(CO)_3$ complex, with a $CH_2$ group at the $C^6$ carbon, Nu = H. This methodology based on the well precedented derivatization of formyl compounds into aminals constituted the first resolution of $\eta^5$-Mn complexes described in the literature.

A second resolution method has been developed for $\eta^5$-Mn complexes substituted by a phosphine, (Scheme 11).[32] In that case, a chiral non racemic transition metal complex can coordinate the phosphorous atom to deliver two diastereomers. After purification and decomplexation of the phosphorous group, the enantioenriched $\eta^5$-Mn complex can be isolated.

This strategy was applied to the resolution of phosphino-substituted $\eta^5$-Mn complexes using the enantiopure

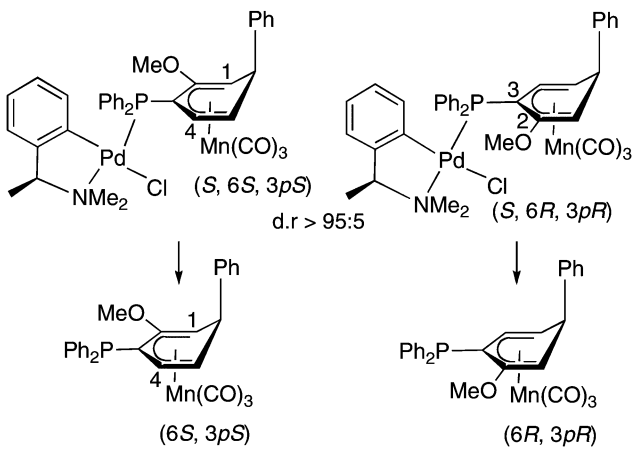



For the 1-Cl, 2-CHO, 4-OMe, 6-Ph-cylohexadienyl-$Mn(CO)_3$:
diastereomers difficult to separate

Nu=Ph 2 separable diastereomers de>95% and de>85%
2 aldehydes ee>95% and ee>85%

Nu=H 2 separable diastereomers de>92% and de>95%
2 aldehydes ee>92% and ee>95%

**Scheme 10** Resolution of formyl-substituted $\eta^5$-Mn.



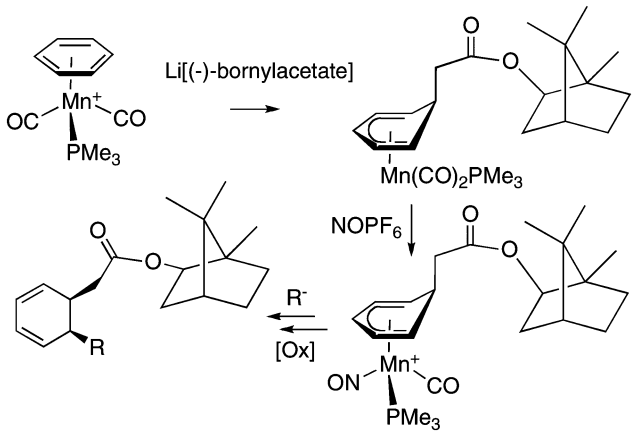

**Scheme 11** Resolution of phosphino-substituted $\eta^5$-Mn complexes.

dimeric palladium complex (*S*)-(+)-di-μ-chlorobis-[2-[dimethylamino)ethyl]phenyl-$C^2$,N]dipalladium, as the resolving agent (Scheme 11). The two Pd diastereoisomers (*S*,6*S*,3*pS*) and (*S*,6*R*,3*pR*) were obtained in 40 and 31% yields, respectively, with a d.r. > 95 : 5. The enantiopure complexes 6*S*,3*pS* and 6*R*,3*pR* were recovered in 77 and 84% yields, respectively, by treating each diastereoisomer with ethylenediamine.

## 3 Chiral-at-the-metal Mn complexes

Sweigart *et al.* observed high diastereoselectivity by adding the chiral enolate of (–)-bornylacetate to the cationic ($\eta^6$-benzene)$Mn(CO)_2(PMe_3)^+$ complex which gave the neutral Mn

complex in 72% yield. The key step was the excellent activation with $NOPF_6$ which displaced a CO ligand and which was found to be stereospecific in favor of a single diastereoisomer in 73% yield. This could suggest that this cationic $\eta^5$-Mn complex should react with nucleophiles $R^-$ and oxidant [Ox] to produce two enantiomerically pure *cis*-cyclohexadienes. (Scheme 12).[33]




**Scheme 12** Synthesis of chiral-at-the-metal Mn complexes.

## 4 Synthesis of enantiopure ($\eta^6$-arene)$Mn(CO)_3^+$ complexes

Besides the two specific examples of rearomatization of enantiopure $\eta^5$ complexes represented in Scheme 9, two other methods of preparation of enantioenriched $\eta^6$-Mn complexes are known and described below.

### 4.1 Diastereoselective complexations

Sweigart *et al.* reported the diastereoselective complexation of arenes in the case of steroids. It gave two diastereoisomers $\alpha$ and $\beta$ in a 2 : 3 ratio which can not be separated, using $BrMn(CO)_5/AgBF_4$ and 3-methoxyestrone. However, the diastereoselection is not general because the complexation of 3,17-dimethoxyestradiol afforded an equimolecular mixture of the two diastereoisomers, (Fig. 3.[34]

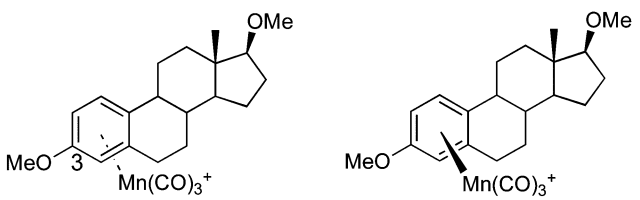



**Fig. 3** Diastereoselective complexation of steroids.

Another example concerns the dimethylated derivative of podocarpic acid which reacted with $Mn(CO)_5BF_4$ ($BrMn(CO)_5/AgBF_4$) in $CH_2Cl_2$ solution to afford a 1.1 : 1.0 isomeric distribution of the $\eta^6$ $BF_4$ salts, in which the metal is located on the $\alpha$ or $\beta$ face, respectively.

The authors describe that they did not succeed to separate the isomers. However, they separated the $\alpha$ and the $\beta$ isomers for the $\eta^6$ $PF_6$ salts by fractional crystallization from $CH_2Cl_2/Et_2O$ (Fig. 4).[35]

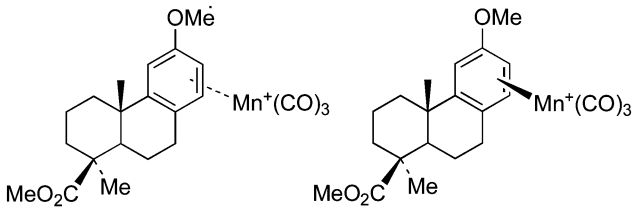
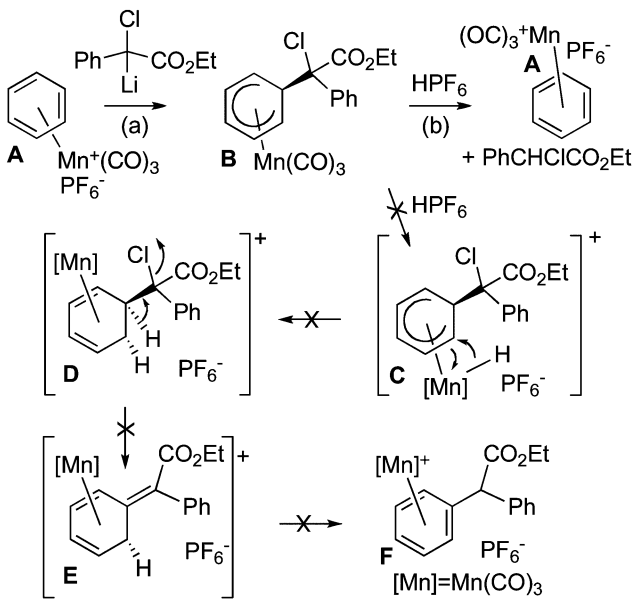



**Fig. 4** Diastereoselective complexation of podocarpic acid derivatives.

### 4.2 Resolution of $\eta^6$-Mn complexes

Very recently, the first method of resolution of polysubstituted $\eta^6$-Mn complexes was published by our group. It relies on an efficient round trip of a chiral enolate to an $\eta^6$-arene Mn complex. But before the description of this methodology, it is worthy to note how this idea emerged. It had been reported that $\alpha$ halogenoester carbanion $LiCHClCO_2Et$ reacted with $[\eta^6$-(benzene)$Mn(CO)_3]^+BF_4^-$ **A** to give the corresponding ($\eta^5$-cyclohexadienyl-$CHClCO_2Et$)$Mn(CO)_3$ **B**.[36]

F. Balssa,[37] one of our PhD students, in 1995 noticed that this neutral complex was not stable in the presence of acid and much more important that it gave back the $[(\eta^6$-benzene)$Mn(CO)_3]^+PF_6^-$ complex **A** in the presence of $HPF_6$ and $CF_3CO_2H$. Initially, the idea was to form a cationic $\eta^5$-manganese-hydride [Mn–H]$^+$ **C** with acid which could give a cationic $\eta^4$-cyclohexadiene-Mn intermediate **D**, which could eliminate HCl to afford a $\eta^4/\eta^2$ complex **E**. Finally the $\eta^6$-Mn substituted by –$CHPh(CO_2Et)$ could be formed *via* a mechanism similar to the one involved in the case of *cine* and *tele* nucleophilic substitutions [14] (Scheme 13). Unfortunately, this did not succeed. However, this experiment showed clearly the irreversible addition of a nucleophile such as $LiCHClCO_2Et$, path a, and that the reverse reaction was achieved with strong acid ($CF_3CO_2H/HPF_6$) with the recovery of the protonated nucleophile $PhCHClCO_2Et$ and $[(\eta^6$-benzene)$Mn(CO)_3]^+PF_6^-$, path b (Scheme 13). The use of $HPF_6$ permitted the introduction of the polarizable anion $PF_6^-$ which is poorly nucleophilic and




**Scheme 13** Recovery of ($\eta^6$-benzene)$Mn(CO)_3^+$ complex.

necessary for the stabilization of the cationic counterpart ($\eta^6$-benzene)$Mn(CO)_3^+$.

This reaction does not present noticeable interest as far as the nucleophile is an achiral carbanion. But if a chiral non-racemic carbanion was used with a substituted $\eta^6$-Mn complex, this reaction would form two diastereoisomeric $\eta^5$ complexes whose physicochemical properties could be different enough to allow their separation. The elimination of the chiral auxiliary would recover enantioenriched $\eta^6$-Mn. Thus, Antoine Eloi,[37] PhD student in our group in 2009, suggested to achieve such an addition elimination sequence $\eta^6/\eta^5$ and $\eta^5/\eta^6$ only based on the intrinsic electrophilic character of the Mn derivatives and which does not need a special arene functionalization by an aldehyde or a phosphine group for example.

If the principle of this methodology looked simple and attractive, the two necessary steps of the round trip of the nucleophile should be unlocked. Indeed, the choice of the chiral nucleophile should be judicious and general to permit the separation by chromatography of the stable diastereoisomers which should have very different dipolar moments. Furthermore, the reactants able to undertake the rearomatization should operate under milder experimental conditions than those previously reported with $CF_3CO_2H$ and $HPF_6$.[13]

**4.2.1 Choice of the arene and of the chiral auxiliary.** The first experiments have been tested with a *meta*-disubstituted complex which gives only one regioisomer by addition of a nucleophile. Thus the cationic ($\eta^6$-*m*-methylanisole)$Mn(CO)_3^+$ complex was selected because addition of the nucleophile occurs only *meta* to the methyl and methoxy groups.

The choice of the chiral auxiliary should respect at least three rules. It should contain an enolisable π-acceptor function to permit its addition and its elimination. It should be available as an inexpensive enantiopure compound. Finally it should avoid the creation of new stereogenic centers which increase the number of stereoisomers. Each new stereogenic center doubles the number of diastereoisomers.

The lithium enolates of acetates of (*R*)-phenylethanol, (–)-menthol and of *N*-acetyl of (*S*)-α-methylbenzylamine, have been tested (Fig. 5). The diastereomeric mixture of complexes corresponding to the *meta* addition of the chiral nucleophile was recovered but was not differentiated by tlc plates and by $^1$H NMR analysis of the crude mixture. Thus, another enolate, the binaphthyl derivative (R = $CH_2OCH_3$) was chosen[38] because the distance between the rigid binaphthyl residue and the cyclohexadienyl unit is shorter. Again, the diastereoisomers could not be separated by column chromatography and this procedure was abandoned even if the fingerprint of the crude $^1$H NMR was slightly better indicating the presence of the two diastereoisomers.

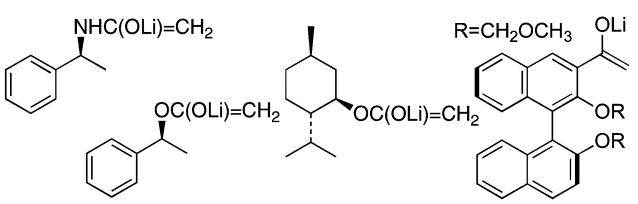



**Fig. 5** Enolates of chiral esters and amide.

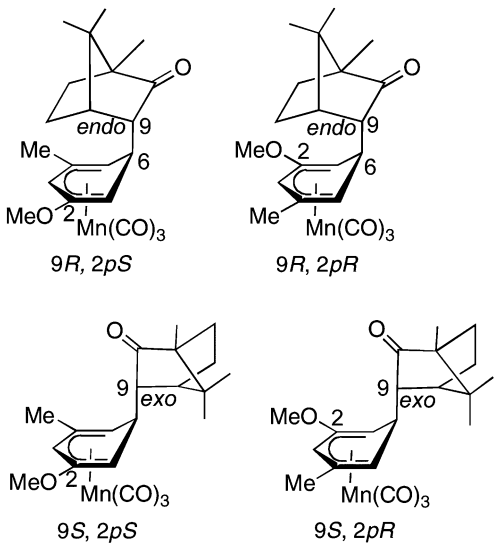



**Fig. 6** Diastereoisomers 9*R*,2*pS*; 9*R*,2*pR*; 9*S*,2*pS* and 9*S*,2*pR*.

Finally, camphor enolate revealed to be the best one for many reasons. Dextrogyre camphor is naturally enantiopure and cheap. Its rigid bicyclic structure could permit the differentiation of the diastereoisomers by column chromatography as well as by $^1$H NMR spectroscopy. Thus, the lithium enolate of (D)-(+)-camphor reacted with ($\eta^6$-*m*-methyl-anisole)$Mn(CO)_3^+$ to give the $\eta^5$-Mn complexes.[39] Analysis of the crude mixture indicates the formation of the four expected diastereoisomers in the ratio 45/45/5/5 due to the planar chirality of the cyclohexadienyl unit by the *exo* addition of the enolate at the C6 carbon and to the $C^9$ carbon, which is now a stereogenic center.[40,41]

**4.2.2 Epimerization.** To obtain only one planar chirality per fraction, one diastereoisomer had to be almost suppressed. Thus, the less polar fraction containing the complexes (9*R*, 2*pR*) and (9*S*,2*pS*) in the ratio 30/70 was epimerized with $K_2CO_3$ in MeOH for 12 h in order to transform the *exo* kinetic diastereoisomer into the *endo* thermodynamic one at the $C^9$ carbon. The four diastereoisomers (9*R*,2*pR*), (9*R*,2*pS*), (9*S*,2*pR*) and (9*S*,2*pS*) were recovered in the ratio 27/63/3/7.

A tlc plate indicated the presence of two spots which were separated by chromatography. The less polar fraction contained the two diastereoisomers (9*R*,2*pR*) and (9*S*,2*pS*) in the ratio 27/7 whereas the polar fraction contained the diastereoisomers (9*R*,2*pS*) and (9*S*,2*pR*) in the ratio 63/3 (Fig. 7). Epimerization did not occur quantitatively, thermodynamic equilibrium was reached for a 9/1 *endo*/*exo* ratio. Thus, after purification, (9*R*,2*pS*) was recovered with a 90% de. The same study can be done with the more polar fraction containing diastereoisomers (9*R*,2*pS*) and (9*S*,2*pR*) in the ratio 30/70.[42] $^1$H NMR analysis showed the four diastereoisomers (9*R*,2*pR*), (9*R*,2*pS*), (9*S*,2*pR*) and (9*S*,2*pS*) in the ratio 45/46/4/5. Epimerization of the crude material

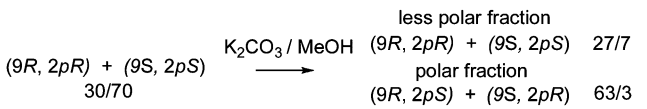



**Fig. 7** Epimerization of the less polar fraction.

afforded also a *endo*/*exo* ratio ranging between 30/70 and 90/10 (Fig. 8).[40,41]

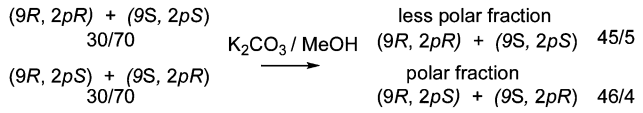
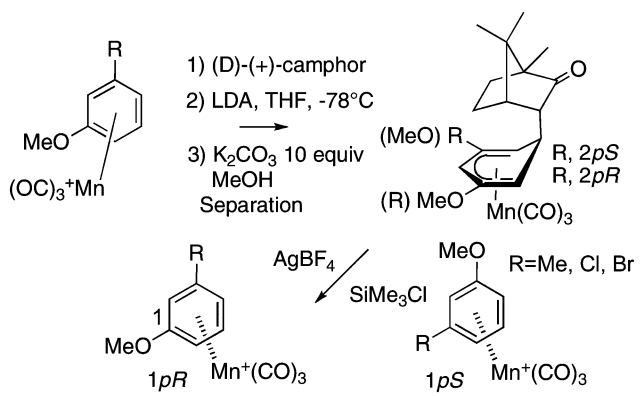



**Fig. 8** Epimerization of the crude mixture (two fractions).

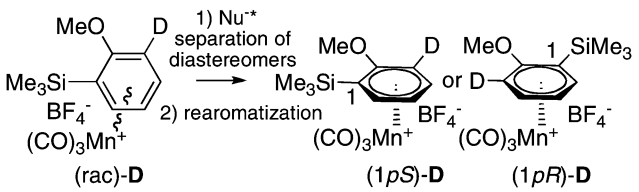
The two diastereoisomers (9*R*,2*pR*) and (9*R*,2*pS*) were separated by chromatography in 44 and 48% yield with >80 and 84% de, respectively, recrystallized with de > 98% and analyzed by X-ray structures to confirm the absolute configurations.[43] To follow the resolution, the next step consisted of the rearomatization with the elimination of the chiral entity to isolate two *meta*-disubstituted complexes having the $Mn(CO)_3$ tripod above or under the arene ring.

**4.2.3 Rearomatization.** In order to improve the elimination step, each diastereoisomer was refluxed in $CF_3CO_2H$ for 24 h and after addition of $HPF_6$, the cationic $\eta^6$-arene Mn complex was recovered in only 30% yield. So, A. Eloi treated the $\eta^5$-Mn complexes with $AgBF_4/SiMe_3Cl$ at rt to favor the enolate trapping by creating a strong Si–O bond of a silylated enolate ether, while $BF_4^-$ played the role of the counter anion. The equilibrium was completely displaced in favor of the rearomatization reaction. An alternative method has been recently discovered avoiding the expensive silver salt. Indeed, the rearomatization was also achieved with the same yield using $HBF_4$·OMe. Thus, the $\eta^6$-Mn complexes were isolated in 94 and 96% yield with >98% ee each, R = Me (Scheme 14).[44] The methodology has been successfully extended to the resolution of several *ortho* and *meta* disubstituted complexes. *meta*-Chloro and bromo-anisole complexes were similarly resolved with camphor enolate round trip. The $\eta^5$-Mn complexes obtained in 45 and 49% yield for the chloro derivative and 41 and 42% yield for the bromo derivative are quantitatively transformed into the corresponding enantioenriched $\eta^6$-Mn complexes, ee > 98%. We observed that the diastereoisomeric excess of the $\eta^5$-Mn complexes calculated by $^1H$ NMR was directly related to the enantiomeric excess of the $\eta^6$-Mn complexes. This was confirmed by X-ray analyses in the solid state and by NMR in a poly-γ-benzyl-L-glutamate solution.




**Scheme 14** Rearomatization of the $\eta^5$-Mn.

**4.2.4 Determination of ee of $\eta^6$-Mn complexes by NMR in polypeptide chiral liquid crystals.** A NMR technique was used in order to definitively prove that the de's determined easily for $\eta^5$-Mn complexes are identical to the ee's for $\eta^6$-Mn complexes obtained after the rearomatization reaction. Indeed, neither the europium chiral shift reagents nor chiral HPLC nor derivatization by anion exchange with TRISPHAT[45] was successful. Proton-decoupled deuterium 2D NMR in chiral liquid crystals (CLC) made of poly-γ-benzyl-L-glutamate (PBLG) developed by Lesot *et al.* proved to be an efficient tool for the determination of the enantiomeric purity of planar chiral [($\eta^6$-arene)$Cr(CO)_3$] complexes.[46] Thus, a labeled deuterated Mn complex was prepared and studied by $^2H[^1H]$ 2D NMR spectroscopy. Deuterated (*rac*)-$\eta^6$-**D** complex as well as (–)-$\eta^6$-**D** and (+)-$\eta^6$-**D** obtained *via* our methodology using the camphor enolate round trip were prepared in racemic and different enantioenriched series before and after recrystallisation of the $\eta^5$-Mn parent derivatives (Scheme 15). The ee observed after recrystallisation proved that no racemization occurred during the rearomatization step in good agreement with our initial assumption.[41] Thus, NMR in the chiral mesophase is a perfect tool for analyzing chiral charged metallic complexes.

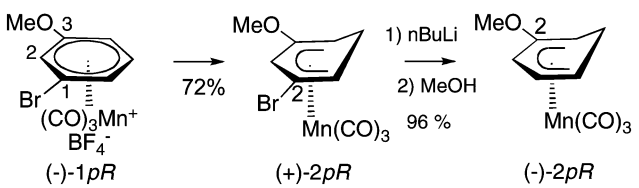



**Scheme 15** Synthesis of deuterated $\eta^6$-Mn complexes.

### 4.3 Application

The round trip methodology was then applied to enantioselective syntheses of phosphinoarene-Mn complexes and cyclohexenones.

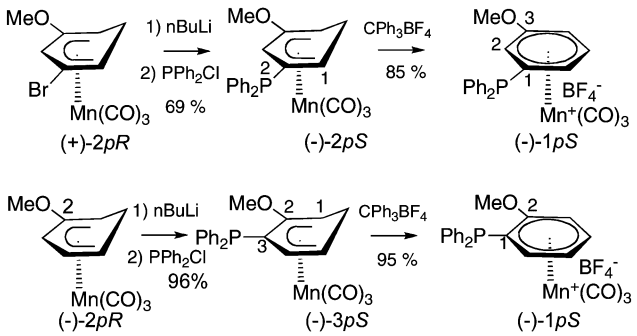
**4.3.1 Enantioselective synthesis of ($\eta^6$-phosphinoarene)-$Mn(CO)_3^+$ complexes.** The direct synthesis of enantiopure (2-methoxy-cyclohexadienyl)$Mn(CO)_3$ complex is not possible because the parent (anisole)$Mn(CO)_3^+$ complex is not chiral. However this $\eta^5$-Mn complex is an interesting chiral synthon which can be used for enantiopure organometallic complex preparation but also for enantiopure organic compounds synthesis, *vide infra.* Thus, it was synthesized starting from the enantiopure (–)-(1*pR*) ($\eta^6$-*meta*-bromoanisole)$Mn(CO)_3^+$ complex which reacted with $LiAlH_4$ to afford the corresponding (+)-(2*pR*) ($\eta^5$-bromocyclohexadienyl)$Mn(CO)_3$ in 72% yield. After bromine/lithium exchange and treatment with MeOH, the enantiopure (–)-2*pR* complex was isolated in 96% yield. Its absolute configuration was deduced from the configuration of the parent $\eta^6$-Mn complex (Scheme 16).




**Scheme 16** Preparation of enantiopure 2-methoxy $\eta^5$-Mn complex.

This chiral synthon is an important building block for enantioselective synthesis of potential ligands in asymmetric catalysis. For example a phosphino group could be introduced *via* lithiation and quenching with $PPh_2Cl$ (Scheme 17). Interestingly, starting from the bromo derivative (+)-(2*pR*), bromine/lithium exchange followed by $PPh_2Cl$ trapping delivered another regioisomer in 69% yield. The rearomatization of both of these enantiopure phosphino-substituted $\eta^5$-Mn complexes delivered the enantiopure cationic *meta* (–)-(1*pS*) and *ortho* (–)-(1*pS*) disubstituted arene complexes in 95 and 85% yield, respectively, whose absolute configurations derived from those of the starting material.[40,41] These cationic $\eta^6$-Mn complexes being soluble in water, enantioselective catalysis could be envisaged in aqueous medium using these new types of ligands.

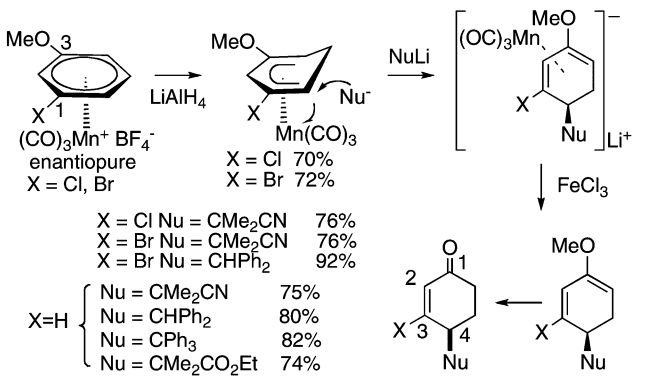



**Scheme 17** Preparation of enantiopure disubstituted $\eta^6$-Mn complexes.

**4.3.2 Enantioselective cyclohexenone synthesis.** Metal-mediated dearomatization has been widely used with arenetricarbonylchromium complexes. However, very few studies are known in the $\eta^6$-Mn series.[12] Treatment of cationic $\eta^6$-Mn complexes with two nucleophiles gives cyclohexadienes if the reaction medium is treated in the presence of $O_2$.[47,48] An indirect route has been described involving the reactivation of the neutral $\eta^5$-Mn complex into a cationic one by replacement of a CO ligand with $NO^+$.[49–51] As formation of cyclohexenones had been reported starting from ($\eta^6$-methoxyarene)$Cr(CO)_3$ derivatives,[52] it was interesting to determine whether double nucleophilic addition to enantiopure ($\eta^6$-anisole)$Mn(CO)_3^+$ complexes could be a good methodology to prepare enantiopure cyclohexenones.

Regioselective addition of hydride to enantiopure ($\eta^6$-*m*-chloro or -bromoanisole) Mn complexes afforded in 70 or 72% yield the corresponding neutral ($\eta^5$-chloro or -bromo) Mn complexes. *Exo* addition of a second nucleophile NuLi (Nu = $CMe_2CN$, $CHPh_2$) delivered the anionic $\eta^4$-cyclohexadiene Mn intermediates which generated the enantiopure 3-chloro- or 3-bromocyclohexenones in 76 to 92% yields using $FeCl_3$ as oxidant. Similarly, treatment of enantiopure $\eta^5$ without any halogen substituent, X = H with NuLi (Nu = $CMe_2CN$, $CHPh_2$, $CPh_3$, $CMe_2CO_2Et$) liberated the four corresponding cyclohexenones in 74 to 82% yields, (Scheme 18).

The X-ray studies of one of the cyclohexenones: the (–)-3-bromo-4-isobutyronitrile cyclohexenone and of the $\eta^6$ parent complex are in good agreement with an *exo* addition of both nucleophiles ($H^-$ and $Nu^-$) with respect to the $Mn(CO)_3$ tripod. This definitively rules out a possible *endo* migration from an alkylmanganese intermediate which could have been formed by




**Scheme 18** Enantioselective synthesis of cyclohexenones.

a direct addition of the nucleophile to the electrophilic carbon of the MnCO unit. Indeed, such a mechanism had been observed by adding phenyllithium with an ($\eta^5$-cyclohexadienyl)$Mn(CO)_3$ complex.[50]

## 5 Summary and prospects

A major limitation in the chemistry of cationic $\eta^6$ arene-Mn complexes was their polarity often associated with a poor solubility in classical organic solvents. This limitation caused unsolved challenges for their purification and their transformation into enantiopure form. A solution to this problem was found these last years. It takes advantage of the straightforward transformation of cationic $\eta^6$-Mn complexes into $\eta^5$ complexes by a nucleophile addition. These $\eta^5$ complexes are stable, neutral, soluble in most organic solvents and thus, readily purified by silica gel column chromatography. Furthermore, after rearomatization these $\eta^5$ complexes can transform back, by hydride or nucleophile abstraction, into the corresponding $\eta^6$ compounds: the chemistry of both $\eta^6$ and $\eta^5$ complexes is therefore intimately related. This review summarizes the studies that were consequently launched on these $\eta^5$ derivatives, especially investigating the preparation of their enantiopure forms. Undoubtedly, the breakthrough in this type of chemistry is the discovery of the first method of resolution of $\eta^6$ complexes *via* their $\eta^5$ derivatives and the very substance of the key steps of this method is reported in the present work. This opens up the way to new applications in the field of enantioselective syntheses in organic as well as in organometallic chemistry. It will not come as a surprise to see new contributions of chiral enantiopure $\eta^6$ arene-Mn complexes appear in the neary future.

## Acknowledgements

F.R.M and E.R. thank the CNRS for continuous financial support over the last 15 years. A total of 12 PhD students worked on Mn chemistry and contributed to the efficiency of our small group. The quality of their research and their enthusiastic involvement always made up for their restricted number: Frédéric Balssa (1995), Anne Perrotey (1996), Claudine Susanne (1996), Vanessa Gagliardini (1998), Christophe Renard (1998), Audrey Auffrant (2002), Stéphanie Schouteeten (2005), Béatrice Jacques (2006), Anne Lise Roy (2007), Romain Germaneau (2007), Antoine

Eloi (2010), Derya Cetiner (2010). We thank the "Ministère de l'Enseignement et de la Recherche" for 4 PhD grants: FB, VG, AA, DC; the ENS for a grant: BJ; the ENS for a financial support for AE as "Agrégé Préparateur"; the CNRS for 1 grant: ALR and pharmaceutical companies for PhD student grants.

## References


1 S. G. Davies, T. J. Donohoe and M. J. Williams, *Pure Appl. Chem.*, 1992, **64**, 379.
2 A. Pape, K. P. Kaliappan and E. P. Kündig, *Chem. Rev.*, 2000, **100**, 2917.
3 S. E. Gibson and H. Ibrahim, *Chem. Commun.*, 2002, 2465.
4 R. S. Cahn, C. Ingold and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 385.
5 K. Schögl, *Top. Stereochem.*, 1967, **1**, 30.
6 E. P. Kündig, *Top. Organomet. Chem.*, 2004, **7**, 1–232.
7 C. Bolm and K. Muniz, *Chem. Soc. Rev.*, 1999, **28**, 51.
8 (*a*) D. Astruc, *Organometallic Complexes and Catalysis*, Springer, Heidelberg, 2007, 243; (*b*) J. P. Djukic, F. Rose-Munch and E. Rose, *Eur. J. Inorg. Chem.*, 2000, 1295.
9 M. Rosillo, G. Dominguez and J. Pérez-Castells, *Chem. Soc. Rev.*, 2007, **36**, 1589.
10 (*a*) J. P. Djukic, F. Rose-Munch, E. Rose and Y. Dromzee, *J. Am. Chem. Soc.*, 1993, **115**, 6434; (*b*) F. Rose-Munch and E. Rose, *Eur. J. Inorg. Chem.*, 2002, 1269.
11 (*a*) D. Prim, B. Andrioletti, F. Rose-Munch, E. Rose and F. Couty, *Tetrahedron*, 2004, **60**, 3325; (*b*) F. Rose-Munch, E. Rose and A. Eloi, *Cationic ($\eta^6$-arene)- and neutral ($\eta^5$-cyclohexadienyl)tricarbonylmanganese complexes: Synthesis and Reactivity. Patai's Chemistry of Functional Groups*, 2010, 70 pages. Editors I. Marek and Z. Rappoport, The Chemistry of Organomanganese Compounds. DOI: 10.1002/9780470682531.pat0538.
12 D. A. Sweigart, J. A. Reingold and S. U. Son, in *Comprehensive Organometallic Chemistry*, 3rd ed.; R. H. Crabtree and D. M. P. Mingos, ed.; Elsevier: Oxford, 2006; Vol. **5**, Chapter 10, pp 761–814.
13 F. Balssa, V. Gagliardini, F. Rose-Munch and E. Rose, *Organometallics*, 1996, **15**, 4373.
14 *Cine*, *tele-meta* and *tele-para* substitutions correspond to the addition of a nucleophile *ortho*, *meta* and *para* to a good leaving group X of a complex when the reaction medium is treated with a nucleophile and then with an acid (*a*) F. Rose-Munch, E. Rose and A. Semra, *J. Chem. Soc., Chem. Commun.*, 1986, 1551; (*b*) F. Rose-Munch, E. Rose, A. Semra, Y. Jeannin and F. Robert, *J. Organomet. Chem.*, 1988, **353**, 53; (*c*) F. Rose-Munch, E. Rose, A. Semra and C. Bois, *J. Organomet. Chem.*, 1989, **363**, 103; (*d*) J. P. Djukic, F. Rose-Munch and E. Rose, *J. Chem. Soc., Chem. Commun.*, 1991, 1634; (*e*) F. Rose-Munch, O. Bellot, L. Mignon, A. Semra, F. Robert and Y. Jeannin, *J. Organomet. Chem.*, 1991, **402**, 1; (*f*) J. P. Djukic, F. Rose-Munch, E. Rose, F. Simon and Y. Dromzee, *Organometallics*, 1995, **14**, 2027.
15 J. C. Boutonnet, F. Rose-Munch and E. Rose, *Tetrahedron Lett.*, 1985, **26**, 3989.
16 F. Rose-Munch, E. Rose and A. Semra, *J. Chem. Soc., Chem. Commun.*, 1987, 942.
17 *Ipso* substitution is a nucleophilic substitution on the carbon bearing the leaving group without treatment of an acid. (*a*) F. Rose-Munch, E. Rose, A. Semra, J. Garcia-Oricain and C. Knobler, *J. Organomet. Chem.*, 1989, **363**, 297; (*b*) F. Rose-Munch, K. Aniss and E. Rose, *J. Organomet. Chem.*, 1990, **385**, C1; (*c*) F. Rose-Munch, K. Aniss, E. Rose and J. Vaisserman, *J. Organomet. Chem.*, 1991, **415**, 223.
18 (*a*) A. Auffrant, D. Prim, F. Rose-Munch, E. Rose and J. Vaissermann, J., *Organometallics*, 2001, **20**, 3214; (*b*) A. Auffrant, D. Prim, F. Rose-Munch, E. Rose, S. Schouteeten and J. Vaissermann, *Organometallics*, 2003, **22**, 1898.
19 B. Jacques, M. Chavarot, F. Rose-Munch and E. Rose, *Angew. Chem., Int. Ed.*, 2006, **45**, 3481.
20 A. Eloi, F. Rose-Munch, E. Rose and P. Lennartz, *Organometallics*, 2009, **28**, 5757.
21 W. H. Miles and H. R. Brinkman, *Tetrahedron Lett.*, 1992, **33**, 589.
22 W. H. Miles, P. M. Smiley and H. R. Brinkman, *J. Chem. Soc., Chem. Commun.*, 1989, 1897.
23 A. Pearson, S.-H. Lee and F. Gouzoules, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2251.
24 A. J. Pearson, P. R. Bruhn, F. Gouzoules and S.-H. Lee, *J. Chem. Soc., Chem. Commun.*, 1989, 659.
25 S.-H. Lee and S.-W. Nam, *Bull. Korean Chem. Soc.*, 1998, **19**, 613.
26 A. J. Pearson, M. C. Milletti and P. Y. Zhu, *J. Chem. Soc., Chem. Commun.*, 1995, 853.
27 A. J. Pearson, A. V. Gontcharov and P. Y. Zhu, *Tetrahedron*, 1997, **53**, 3849.
28 A. Alexakis, P. Mangeney, I. Marek, F. Rose-Munch, E. Rose and F. Robert, *J. Am. Chem. Soc.*, 1992, **114**, 8288.
29 (*a*) J. C. Boutonnet, J. Levisalles, E. Rose, G. Precigoux, C. Courseille and N. Platzer, *J. Organomet. Chem.*, 1983, **255**, 317; (*b*) J. C. Boutonnet, F. Rose-Munch, E. Rose, Y. Jeannin and F. Robert, *J. Organomet. Chem.*, 1985, **297**, 185.
30 S. U. Son, K. H. Park, S. J. Lee, H. Seo and Y. K. Chung, *Chem. Commun.*, 2002, 1230.
31 B. Jacques, A. Chanaewa, M. Chavarot-Kerlidou, F. Rose-Munch, E. Rose and H. Gérard, *Organometallics*, 2008, **27**, 626.
32 D. Cetiner, B. Jacques, E. Payet, M. Chavarot-Kerlidou, F. Rose-Munch, E. Rose, J. P. Tranchier and P. Herson, P., *J. Chem. Soc., Dalton Trans*, 2009, 27.
33 R. D. Pike and D. A. Sweigart, *Synlett*, 1990, 565.
34 K. Woo, G. B. Carpenter and D. A. Sweigart, *Inorg. Chim. Acta*, 1994, **220**, 297.
35 K. Woo, Y. Cao, H. Li, K. Yu, G. B. Carpenter, D. A. Sweigart and B. H. Robinson, *J. Organomet. Chem.*, 2001, **630**, 84.
36 F. Balssa, V. Gagliardini, C. Le Corre-Susanne, F. Rose-Munch, E. Rose and J. Vaisserman, J., *Bull. Soc. Chim. Fr.*, 1997, **134**, 537.
37 F. Balssa: PhD student, University Pierre et Marie Curie, Paris, January 23, 1995; A. Eloi: PhD student, University Pierre et Marie Curie, Paris, June 11, 2010.
38 These derivatives gave excellent results in enantioselective catalysis using chiral binaphthyl handle porphyrins (*a*) E. Rose, Q.-Z. Ren and B. Andrioletti, B, *Chem.–Eur. J.*, 2004, **10**, 224; (*b*) E. Rose, E. Gallo, N. Raoul, L. Bouché, A. Pille, A. Caselli and O. Lequin, *J. Porphyrins Phthalocyanines*, 2010, **14**, 646.
39 Two configurations *endo* and *exo* are possible at the $C^9$ carbon, corresponding respectively to small and important steric interactions and thus four diastereoisomers are formed, (9*R*,2*pR*), (9*R*,2*pS*), (9*S*,2*pR*) and (9*S*,2*pS*), (Fig. 6). Two spots are detected by tlc plates with $R_f$ of 0.40 and 0.60 using a 30 : 70 mixture of petroleum ether PE and $Et_2O$ indicating clearly different physicochemical properties of the diastereoisomers. After separation of these two spots by silica gel chromatography with a 99 : 1 mixture of PE : $Et_2O$, $^1$H NMR indicated that each fraction contains two diastereoisomers and the structures of them (9*R*,2*pR*) and (9*S*,2*pS*) have been determined by X-ray crystallography of the less polar fraction. A comparison of their $^1$H NMR spectra showed that the major isomer is the (9*S*,2*pS*). It can be deduced that the more polar fraction contains the two diastereoisomers (9*R*,2*pS*) and (9*S*,2*pR*). It is worthy to note that the two diastereoisomers of each fraction fortuitously present inverse chiralities. For each fraction, the major diastereoisomers have the 9*R* configuration which corresponds to an *exo* configuration.
40 A. Eloi, F. Rose-Munch and E. Rose, *J. Am. Chem. Soc.*, 2009, **131**, 14178.
41 A. Eloi, F. Rose-Munch, E. Rose, A. Pille, P. Lesot and P. Herson, *Organometallics*, 2010, **29**, 3876.
42 This process was undertaken only to understand the distribution of the diastereoisomers. Of course, during our study, the simplest following process was used: addition of the camphor enolate at −78 °C, warming the solution at rt and epimerization with $K_2CO_3$/MeOH for 12 h.
43 The two diastereoisomers (9*R*,2*pR*) and (9*R*,2*pS*) can also be recovered with de > 95% by a second epimerization reaction of the two fractions obtained after the first epimerization. Thus, the two diastereoisomers were prepared with an *endo* camphyl configuration and two different planar chiralities.
44 The assignment of the absolute configuration of the planar chiral $\eta^5$-Mn complex was realized by X-ray crystallography of the $\eta^5$-(*R*,2*pR*)-Mn and the $\eta^6$-(1*pR*)-Mn complexes. It confirmed that no planar chirality was lost during the rearomatization process.

45 J. Giner Planas, D. Prim, F. Rose-Munch, E. Rose, D. Monchaud and J. Lacour, J., *Organometallics*, 2001, **20**, 4107.
46 O. Lafon, P. Lesot, P. M. Rivard, M. Chavarot, F. Rose-Munch and E. Rose, *Organometallics*, 2005, **24**, 4021.
47 M. Brookhart and A. Lukacs, *J. Am. Chem. Soc.*, 1984, **106**, 4164.
48 B. C. Roell, K. F. McDaniel, W. S. Vaughan and T. S. Macy, *Organometallics*, 1993, **12**, 224.
49 T. Y. Lee, Y. K. Kang, Y. K. Chung, R. D. Pike and D. A. Sweigart, *Inorg. Chim. Acta*, 1993, **214**, 125.
50 J. D. Sheridan, R. S. Padda, K. Chaffee, C. Wang and Y. Huang, *J. Chem. Soc., Dalton Trans.*, 1992, 1539.
51 A. J. Pearson, A. V. Gontcharov and P. Y. Zhu, *Tetrahedron*, 1997, **53**, 3849.
52 M. F. Semmelhack and H.-G. Schmalz, *Tetrahedron Lett.*, 1996, **37**, 3089.