Unprecedented (η^5-Formylcyclohexadienyl)$Mn(CO)_3$ Complexes: Synthesis, Structural and Theoretical Characterizations, and Resolution of the Planar Chirality

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The synthesis of the (η^5-formylcyclohexadienyl)$Mn(CO)_3$ complexes **5**−**8** was successfully achieved after lithiation and then electrophilic quench by DMF of variously substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes. Their full experimental characterization is reported, together with a theoretical study that allowed the consequences of the regiochemistry on the electronic properties of the complexes to be understood. Rearomatization of complex **6** led to the formation of the cationic [(η^6-2-methoxybenzaldehyde)$Mn(CO)_3$]$^+$ complex **11**, first example of a benzaldehyde derivative coordinated to the $Mn(CO)_3^+$ entity. The electrophilic reactivity of the formyl group of complex **5** was tested with hydrides and a Grignard reagent as the nucleophiles. The corresponding alcohols were isolated in high yields and the excellent diastereoselectivity could be explained by steric factors clearly identified thanks to the crystal structure determination of the starting aldehyde **7b**. By using the enantiopure (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine, the corresponding aminals were obtained and their resolution afforded, after acidic treatment, the enantioenriched (η^5-formylcyclohexadienyl)$Mn(CO)_3$ with very high enantiomeric excess. The X-ray analysis of two of these aminals **14** and **15** allowed the assignment of the absolute configurations of the planar chiral η^5 moieties.

Introduction

Aromatic activation by a tricarbonylmetal fragment $M(CO)_3$ (M = Cr, Mn) provides organometallic half-sandwich complexes possessing interesting chemical properties.[1] The reactivity of the aromatic ring is greatly modified by the high electrophilicity of the organometallic tripod, allowing a variety of transformations.[2] For instance, nucleophilic aromatic substitutions[3] or additions[4] become feasible, and functionalizations based on a lithiation step are made easier by the increase in the acidity of the aromatic hydrogens.[5] Moreover, the planar chirality of complexes bearing an unsymmetrically di- or polysubstituted aromatic ring makes them even more attractive in modern organometallic chemistry. Among them, the planar chiral formyl-substituted derivatives have received much more attention. Thanks to the versatile reactivity of the formyl group, they have proven to be attractive building blocks, leading to widespread applications in asymmetric synthesis[6] or in ligand design for enantioselective catalysis.[7] The (η^6-arylaldehyde)-

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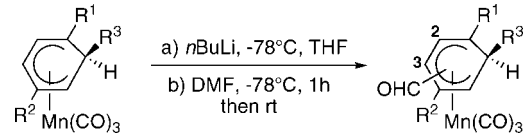
$Cr(CO)_3$ complexes are undoubtedly the best-known examples of such chiral precursors.[6–10] These developments are also found in a weaker extent with formyl-cymantrene ($CpMn(CO)_3$) derivatives,[7c,11] but to the best of our knowledge, they are inexistent for their isoelectronic $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes. Whereas the enhanced electrophilic character of these cationic complexes compared to neutral ones is of great potential, a major drawback in their chemistry has been for many years the restricted number of arenes able to coordinate the $[Mn(CO)_3]^+$ fragment.[12] $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes substituted by electron-withdrawing groups such as the benzaldehyde derivatives were unknown, the aromatic ring being too electron-deficient for complexation. Unlike their corresponding isoelectronic chromium complexes, no coordination of the arene occurs even if the resonance electron withdrawal is disrupted by the formation of a ketal, for instance.[12] Moreover, the Swern oxidation efficiently applied to the synthesis of (η^6-arylaldehyde)$Cr(CO)_3$ complexes[13] cannot be viewed with the corresponding manganese substrates, because primary benzylic alcohols do not coordinate the $Mn(CO)_3^+$ fragment whatever the complexation procedure used.[12] This drawback has considerably slowed down the development of applications based not only on the cationic η^6-arene complexes but also on their isoelectronic neutral analogues: the (η^5-cyclohexadienyl)$Mn(CO)_3$ derivatives, efficiently obtained by addition of a broad range of nucleophiles to the arene ring.[4] The first breakthrough was realized in our group in 2001 with the development of an efficient functionalization pathway based on palladium-catalyzed carbonylation reactions.[14] Various nucleophiles were employed giving for the first time access to ketone, ester, or amide derivatives. Despite that, the synthesis of a formyl derivative by combining the carbonylative conditions with the use of a hydride source was still unsuccessfull.[14] Recently, a new route for efficient and versatile functionalization of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes based on a lithiation/electrophilic quench sequence was developed.[15] The synthesis of the first formyl-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ complex could then be achieved by using DMF as the electrophile.[15a] We describe here an extension of this approach to other substrates and the structural characterization of the new (η^5-formylcyclohexadienyl)$Mn(CO)_3$ complexes. Their reactivity toward hydride abstraction and nucleophilic addition is also studied. Finally a strategy for the resolution of their planar chirality is presented.

Table 1. Formylation Conditions for Complexes 1–4



Entry	Substrate	R^1	R^2	R^3	Product	Yield [%]	C^2:C^3
1[a]	**1**[b]	H	OMe	Ph	**5**	68	C^3
2	**2**[b]	H	OMe	H	**6**	67	C^3
3	**3**[c]	Cl	OMe	Ph	**7a** + **7b**	90	60:40
4	**4**[d]	H	H	Ph	**8a** + **8b**	66	80:20

[a] Reference 15a. [b] 1.6 equiv of *n*BuLi, 1.6 equiv of TMEDA, 2 equiv of DMF, reaction time = 1 h. [c] 1.4 equiv of *n*BuLi, 1.8 equiv of DMF, reaction time = 15 min. [d] 2 equiv of *n*BuLi, 2 equiv of TMEDA, 2.5 equiv of DMF, reaction time = 2 h.

Results and Discussion

Synthesis and Characterization. Complexes **1–4** used as starting material in this study were synthesized by complexation of anisole, *para*-chloroanisole, or benzene to give the corresponding $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes,[12] followed by nucleophilic addition of either PhMgCl (R^3 = Ph; complexes **1**, **3**, **4**)[16] or $LiAlH_4$ (R^3 = H; complex **2**).[17] The best experimental conditions for the lithiation/electrophilic quench sequence of each susbtrate were determined in a previous study,[15b] which revealed that the lithiation step is highly substrate dependent. For instance, complete conversion of **3**, the most reactive substrate of the series, is achieved by reaction with 1.4 equiv of *n*BuLi for only 15 min at −78 °C, whereas 2 equiv of *n*BuLi and tetramethylethylenediamine (TMEDA) for 2 h are required to optimize the lithiation of complex **4**. In the present study, these conditions were associated with the use of DMF as the electrophile (Table 1), in order to synthesize the first (η^5-formylcyclohexadienyl)$Mn(CO)_3$ derivatives.[15a]

The expected (η^5-formylcyclohexadienyl)$Mn(CO)_3$ derivatives **5–8** were isolated with yields ranging from 66% to 90%. For the anisole derivatives **1–2**, the lithiation proceeded with complete regiocontrol thanks to the presence of the methoxy *ortho*-directing group. Starting with the *para*-chloroanisole derivative **3**, two regioisomers were obtained in a C^2:C^3 ratio of 60:40, and were separated by chromatography on silica gel to give the pure aldehydes **7a** and **7b**. The formylation of complex **4**, with an unsubstituted cyclohexadienyl moiety, gave two regioisomers functionalized at C^2 and C^3 in a 80:20 ratio. This is in agreement with the regioselectivity of the silylation of complex **4** by the lithiation/electrophilic quench sequence.[15b] According to a theoretical investigation, this regioselectivity relies mainly on the intrinsic stabilities of the deprotonated intermediates, the species lithiated at C^2, eclipsed by a Mn−CO bond, being the most stable one.[15b]

NMR characterization of products **5–8** confirmed unambiguously the functionalization of the cyclohexadienyl skeleton by

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Table 2. Selected ^{1}H NMR Data ($CDCl_3$, δ in ppm) for Complexes 1–8

Entry	Complex	H^2	H^3	H^4	CHO
5	**1**		5.73	5.00	
6	**2**		5.83	4.86	
7	**3**	5.23	5.57		
8	**4**	4.97	5.78	4.97	
9	**5**			5.75	10.62 (C^3)
10	**6**			5.58	10.66 (C^3)
11	**7a**		6.07		10.04 (C^2)
12	**7b**	5.97			10.54 (C^3)
13	**8a**		6.30	5.13	9.31 (C^2)
14	**8b**	5.58		5.58	9.92 (C^3)

Table 3. Selected IR Spectral Data (cm^{-1}) for Complexes 1–8

Entry	Substrate	Structure[a]		$\tilde{\nu}_{CO}$(A1)	$\tilde{\nu}_{CO}$(E)	
15	**1**			2007	1907	
16	**2**			2004	1903	
17	**3**			2009	1921	
18	**4**			2002	1895	
	Aldehyde	Structure[a]		$\tilde{\nu}_{CO}$(A1)	$\tilde{\nu}_{CO}$(E)	$\tilde{\nu}_{CHO}$
19	**5**		C^3	2018	1924	1673
20	**6**		C^3	2014	1914	1668
21	**7a**		C^2	2020	1933	1704
22	**7b**		C^3	2025	1937	1676
23	**8a**		C^2	2013	1919	1710
24	**8b**		C^3	2020	1928	1683

[a] The $Mn(CO)_3$ tripod is omitted for clarity.

a formyl group; the aldehydic proton signature is indeed observed between 9.3 and 10.7 ppm (Table 2), depending on the cyclohexadienyl substitution, together with a downfield shift ($\Delta\delta = +0.5$ to $+0.75$ ppm) for the cyclohexadienyl protons *ortho* to CHO. We have also recorded IR spectra for complexes **5**–**8** and the data are presented in Table 3. The main feature of these spectra is the presence of two vibrational bands associated with the carbonyl ligands of the $Mn(CO)_3$ tripod and one with the aldehydic function. It is well-known that the carbonyl $\tilde{\nu}_{CO}$ vibrations reflect π-back-bonding into the CO π^* orbitals and are therefore very sensitive to changes in electron density at the metal.[18] The observed IR frequencies are higher for complexes **5**–**8** than for substrates **1**–**4** ($\Delta\tilde{\nu} = +10$ to $+20$ cm^{-1}), in agreement with the strong electron-withdrawing character of the formyl group (Table 3). More interesting is the comparison of the formyl $\tilde{\nu}_{CHO}$ vibrations with the substitution pattern of the cyclohexadienyl moiety. Indeed, our synthetic methodology allows the substitution either at the C^2 carbon or at the C^3 one, the regioselectivity being controlled by the presence of *ortho*-directing groups (entries 15–17) or by the intrinsic reactivity of the cyclohexadienyl ligand in the complex (entry 18).[15b]

The observed $\tilde{\nu}_{CHO}(C^2)$ and $\tilde{\nu}_{CHO}(C^3)$ frequencies were compared for the *para*-chloroanisole derivatives **7a**,**b** (entries 21 and 22) and the benzene derivatives **8a**,**b** (entries 23 and 24). They are found to be higher for the C^2-formylated complexes than for the C^3-formylated ones ($\tilde{\nu}_{CHO}(C^2) - \tilde{\nu}_{CHO}(C^3) = 28$ cm^{-1} for **7a**,**b** and $\tilde{\nu}_{CHO}(C^2) - \tilde{\nu}_{CHO}(C^3) = 27$ cm^{-1} for **8a**,**b**). This difference suggests that the electronic delocalization between the carbonyl and the π-system is better when $-$CHO is linked to the C^3 carbon rather than to the C^2 carbon of the cyclohexadienyl.

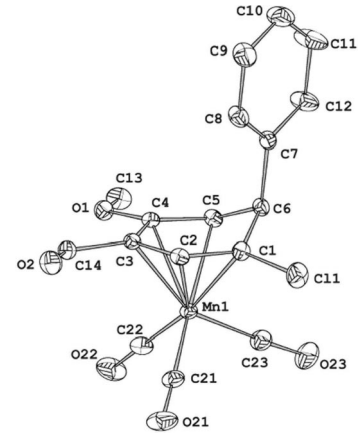

Figure 1. Molecular structure of complex **7b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Pleasingly, monocrystals of complex **7b** were readily obtained by slow evaporation of a diethyl ether/pentane solution of the complex, providing the first crystal structure of a formyl-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ complex. The ORTEP view shown in Figure 1 indicates that the formyl group is indeed located adjacent to the methoxy group, and does not modify the η^5-cyclohexadienyl structure, with five coplanar sp^2 carbons and the remaining sp^3 carbon located 38.10° above this plane. The conformation of the $Mn(CO)_3$ tripod is in agreement with what is usually observed, the sp^3 carbon being eclipsed by one Mn$-$CO bond. Due to steric hindrance, the aldehyde conformation is *anti* with respect to the methoxy group. The presence of the aldehyde function does not modify the Mn$-$C bond lengths in the range 2.2469(13) to 2.1334(12), with the Mn$-C^3$ bond being the shortest one (Table 7).

Finally, the formyl group is nearly coplanar with the cyclohexadienyl moiety, the angle between the two planes being 8.3°. This might again indicate a good conjugation between the aldehyde and the π electrons of the η^5 complex. It is interesting to compare this structure to those of benzaldehyde derivatives coordinated to the $Cr(CO)_3$ entity in a η^6 manner. To our knowledge, only three structures of *ortho*-substituted benzaldehyde $Cr(CO)_3$ have been reported in the literature[19] and all of them are in line with the one of complex **7b**. Indeed, the aldehyde functions are *anti* to the *ortho* substituents (an aminal group[19a] or an ether group[19b,c]), and in each case, the C=O bond is almost in the same plane as the arene ring. Furthermore, $C^{14}-O^2$ (1.214(2)) and $C^{14}-C^3$ (1.4804(18)) bond lengths of complex **7b** have values very close to the analogous bonds in the chromium complexes of the literature: 1.101(9) and 1.56(1),[19a] 1.196(7) and 1.483(8),[19b] 1.193(10) and 1.596(11),[19c] respectively.

Computational Approach. Computational studies were undertaken to get a better understanding of the electronic properties of these (η^5-formylcyclohexadienyl)$Mn(CO)_3$ derivatives and especially within the differences observed between the regioisomers. Complexes **8a** and **8b** were therefore chosen

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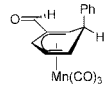
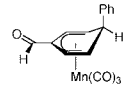
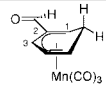
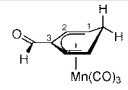
Table 4. Selected Computed $\tilde{\nu}_{CHO}$ IR Frequencies (in cm^{-1}) for Structures 8–10 and Relative Energies for Structures b with Respect to a (in kcal·mol^{-1})[a]

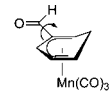
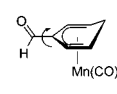
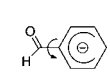
Entry			
		8a	**8b**
25	E	+ 4.6	0
26	$\tilde{\nu}_{CHO}$	1792	1759
27	δ(CHO) - δ(H^4)	4.18	4.34
			
		9a	**9b**
28	E	+ 4.5	0
29	$\tilde{\nu}_{CHO}$	1792	1760
			
		10a	**10b**
30	E	20.6	0
31	$\tilde{\nu}_{CHO}$	1708	1633

[a] The computed NMR aldehydic proton signature (reported as δ(CHO) − δ(H^4), in ppm) is given for structures **8**.

as model compounds. The closely related structures **9a** and **9b** bearing an H instead of a Ph in the *exo* position were also used to limit the computational cost.

(a) Structural Description. Geometry optimizations were first undertaken on the model compounds **9** to determine the lowest energy conformation of each regioisomer. In all the cases, the C═O bond is found to lie within the plane of the ring with a maximal deviation of 16.6°. In particular, a 9.3° value is obtained for the O═C—C^3—C^2 dihedral angle in structure **9b**, a value in perfect agreement with the one obtained by X-ray analysis of the related C^3-formylated complex **7b** (8.3°). The C═O (1.220 Å) and (O)C^3—C^2 (1.472 Å) bond distances are found to be within 0.01 Å of the X-ray values. For **9a**, substituted at C^2, two minima are obtained depending on the orientation of the carbonyl group. The conformer with the C═O bond pointing toward the H^3 proton (as presented in Table 4) is the lowest energy conformer by only 0.5 kcal·mol^{-1} with respect to that with the C═O bond pointing at H^1. The orientation of the tripod was then examined for species **9a** and **9b**. A conformation eclipsing the C^2, C^4, and C^6 carbons is obtained for the minima similar to the one of all the η^5 complexes described up to now. No effect of the substitution by an electron-withdrawing group such as CHO is thus observed, in strong contrast with the well-known relationship between tripod conformation and electronic properties of the substituents in the (η^6-arene)-$M(CO)_3$ complexes (M = Cr,[20] Mn^+ [14]). The structures in which C^6 is *anti*-eclipsed with respect to the CO ligands are found to be transition states (TS) between two eclipsed

Table 5. Selected Parameters Illustrating the Conjugation of the CHO moiety[a]

Entry					
		9a	**9b**	**10a**	**10b**
32	ΔE_{rot}	6.5	10.6	9.7	31.3
33	$\Delta\nu_{rot}$	8	34	9	97

[a] ΔE_{rot} is the lowest rotation barrier (in kcal·mol^{-1}) of the CHO moiety; $\Delta\nu_{rot}$ is the corresponding increase of the ν_{CHO} vibrational frequency (in cm^{-1}).

structures, associated to rotation barriers of 7.8 (**9a**) and 12.6 kcal·mol^{-1} (**9b**). These values are perfectly in line with the one we previously reported for the unsubstituted η^5 structure (9.9 kcal·mol^{-1}).[15b] The lower energy conformations of the tripod and of the CHO group were assumed to be the same ones for complexes **8**, differing only by the C^6 substituent.

(b) CHO Vibrational Frequency and ^{1}H NMR Shielding Constants. The lowest energy conformers were then used to study the spectroscopic properties of each regioisomer, either the C^2-substituted **a** or the C^3-substituted **b** (Table 4). The computed IR vibrational frequencies of the conformers proved to be significantly larger than the experimental ones (Table 3, entries 23 and 24), as expected from computations carried out within the framework of the harmonic approximation. However, correcting the computed values by applying a scaling factor according to the standard procedure (a factor of 0.97 is used here)[21] yields $\tilde{\nu}_{CHO}$ of 1738 cm^{-1} for **8a** and 1706 cm^{-1} for **8b**, in good agreement with the experimental ones (1710 and 1683 cm^{-1}, respectively). In particular, the frequency shift between **8a** and **8b** amounts to 33 cm^{-1}, very close to the 27 cm^{-1} experimentally observed.

The excellent correlation between theory and experiment is also highlighted by the computational evaluation of the NMR shielding constants for complexes **8a** and **8b** (Table 4, entry 27). The aldehydic proton signature was examined by computing the difference δ(CHO) − δ(H^4) (referred as Δδ below). For complex **8a**, a Δδ of 4.26 ppm is obtained, very close to the experimentally observed 4.18 ppm (Table 2). In the case of complex **8b**, due to the existence of two minimas depending on the orientation of the CHO group, the computed H^2 and H^4 protons are not equivalent, in contrast with the experimental results (Table 2). This can be correlated with the transition state of 10.6 kcal·mol^{-1} reported below for the parent structure **9b** (Table 5, entry 32), associated with the rotation of the CHO group, and corresponding to a fast interconversion at room temperature with respect to the NMR time scale. The reported Δδ value for **8b** (Table 4, entry 27) is thus the average of the calculated H^4 and H^2 shielding constants and is also in good agreement with the experimental value ($\Delta\delta_{exp}$ = 4.34 ppm). In addition, a downfield shift for the *ortho* proton in the case of **8a** (evaluated from δ(H^3) − δ(H^4)) was found within 0.18 ppm from the experimental value.

(c) CHO Conjugation Properties. The relative energies of the two regioisomers were then examined. The energy difference of **9a** with respect to **9b** was evaluated to be 4.5 kcal·mol^{-1} (Table 4, entry 28). The C^2-formylated structure **8a** was also found to be 4.6 kcal·mol^{-1} less stable than its corresponding regioisomer **8b** (Table 4, entry 25). This preference for the CHO-substitution at the C^3 position of the cyclohexadienyl is inverted

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Table 6. Crystallographic Data for 7b, 11a, (*R*,*R*,6*R*,1*pS*)-12, and (*R*,*R*,6*S*,2*pR*)-13[15a]

	7b	**11a**	(*R*,*R*,6*R*,1*pS*)-**12**	(*R*,*R*,6*S*,2*pR*)-**13**
empirical formula	$C_{17}H_{12}Cl_1Mn_1O_5$	$C_{23}H_{19}Mn_1O_5$	$C_{25}H_{28}Cl_1Mn_1N_2O_4$	$C_{25}H_{29}Mn_1N_2O_4$
mol wt (g cdt.mol^{-1})	388.66	430.33	510.89	476.44
crystal dimensions (mm^3)	0.10 × 0.12 × 0.15	0.10 × 0.12 × 0.22	0.06 × 0.10 × 0.14	0.10 × 0.13 × 0.18
a (Å)	12.2077(13)	8.9297(8)	9.4528(12)	10.5344(14)
b (Å)	12.2447(11)	10.7940(10)	12.0818(9)	13.9240(8)
c (Å)	12.4319(14)	11.1264(13)	21.7123(17)	16.439(2)
α (deg)	90	72.273(8)	90	90
β (deg)	114.101(8)	80.503(11)	90	90
γ (deg.)	90	88.397(8)	90	90
V (Å^3)	1693.9(3)	1007.23(18)	2479.7(3)	2411.3(3)
Z	4	2	4	4
cryst system	monoclinic	triclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	P	$P2_12_12_1$	$P2_12_12_1$
μ (cm^{-1})	9.60	6.87	6.73	5.80
T (K)	250	200	295	250
ρ_{calcd} (g·cm^{-3})	1.52	1.42	1.37	1.31
θ limits (deg)	3–30	3–23	2–30	3–30
k, *k*, *l* limits	−17/13, –17/15, –17/17	−12/12, –15/15, –15/15	−13/13, –16/16, –30/30	−14/14, –19/19, –22/23
no. of reflns collected	17431	19938	35415	21873
no. of unique data	4921	5835	7237	6866
no. of reflns used	3499 ($I > 3\sigma(I)$)	4782 ($I > 2\sigma(I)$)	5642 ($I > 3\sigma(I)$)	4532 ($I > 3\sigma(I)$)
R^a	0.0274	0.043	0.0232	0.0303
$R_w{}^b$	0.0336	0.051	0.0259	0.0321
GoF	1.113	1.366	1.052	1.100
no. of variables	219	263	301	292
$\Delta\rho_{min}$ (e·Å^{-3})	−0.37	−0.40	−0.272	−0.25
$\Delta\rho_{max}$ (e·Å^{-3})	0.26	0.46	0.254	0.30
Flack's *x* parameter			0.044(9)	0.106(14)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

to what is reported in the litterature for the methoxy-substituted [(η^5-cyclohexadienyl)Cr(CO)$_3$]$^-$ species,[22] as could be expected from the opposite electronic demand of the OMe group with respect to CHO. The comparison between the two energy differences for **8** and **9** species (only 0.1 kcal·mol^{-1}) shows unambiguously that the impact of the sp^3 carbon substituent is negligible. The same trend is also observed for the computed ν_{CHO} vibrational frequencies (Table 4, entry 26 compared to 29), validating therefore the use of the model structures **9a** and **9b**.

The vibrational frequencies of the aldehydic function as well as the energy difference between structures **9a** and **9b** can be put into perspective with the data obtained for the two "virtual" cyclohexadienyl ligands **10a**,**b** (Table 4, entries 30 and 31). Such a comparison with an uncoordinated ligand has also proven its usefulness in the computational studies of aryl[23] or benzyl[24] anions, radicals, and cations of (η^6-arene)Cr(CO)$_3$ complexes and also in the theoretical investigation of the lithiated (η^5-cyclohexadienyl)Mn(CO)$_3$ species.[15b] In the present study, it appears that ligand **10a** substituted at C^2 is less stable than its regioisomer **10b** (Table 4, entry 30). The energy difference amounts to more than 20 kcal·mol^{-1}, which is much larger than in the case of the corresponding complexes **9**. The energy difference between the two formylated regioisomers is thus drastically decreased by coordination of the cyclohexadienyl ring at the metal fragment. Moreover, when comparing the interaction of the unsubstituted cyclohexadienyl ligand with the metal center (242 kcal·mol^{-1}) with that of the formyl-substituted ones (224 kcal·mol^{-1} for **9a** and 208 kcal·mol^{-1} for **9b**), it appears that the functionnalization by the CHO group diminishes significantly the binding energy to the metal center.

All the same, if considering the CHO vibrational frequencies, the ν_{CHO} difference between **10a** and **10b** amounts to 75 cm^{-1} (Table 4, entry 31) and is also strongly reduced upon coordination to the metal center (only a 32 cm^{-1} difference between **9a** and **9b**).

The previous results shed light on the essential role played by the position of the CHO moiety on the electronic properties of the complexes. This was further investigated with the following experiment: the conjugation of the formyl group with the cyclohexadienyl π-system was broken by rotation of the aldehyde group about the C$^{2/3}$−CHO bond. Such a rotation of the CHO moiety can occur either clockwise or counterclockwise, yielding transition states (TS) with the C═O bond pointing either toward the tripod side or in the opposite direction. The two corresponding TS structures are found to be quasi-isoenergetic, the latter one being more stable by less than 1 kcal·mol^{-1}. The lowest TS localized for **9a**,**b** and **10a**,**b** are referred below (Figure 2) as **TS(9a)**, **TS(9b)**, **TS(10a)**, and **TS(10b)**, respectively. They correspond to structures where the C═O bond is quasiperpendicular to the ring (O═C−C−C dihedral angle between 87.8° and 104.6°). The associated rotation barrier ΔE_{rot} (in kcal·mol^{-1}) was calculated for each structure (Table 5) together with the corresponding variation of the IR vibrational frequencies ΔE_{rot} (in cm^{-1}) between the transition states and the lowest energy conformers.

A 10.6 kcal·mol^{-1} rotation barrier is obtained for the CHO group in the case of structure **9b**, whereas it is 4.1 kcal·mol^{-1} smaller in **9a** (Table 5, entry 32). Considering that structure **9b** is also 4.5 kcal·mol^{-1} more stable than **9a** (Table 4, entry 28), **TS(9a)** and **TS(9b)** are thus quasi-isoenergetic (**9b** stabilized by only 0.5 kcal·mol^{-1} as shown in Figure 2, left). All the same, the energy difference between **10a** and **10b** is almost perfectly canceled upon rotation of the CHO moiety (1.0 kcal·mol^{-1} in favor of **10a**). The same trend is observed for the $\tilde{\nu}_{CHO}$ vibrational frequencies (Figure 2, right). Breaking the

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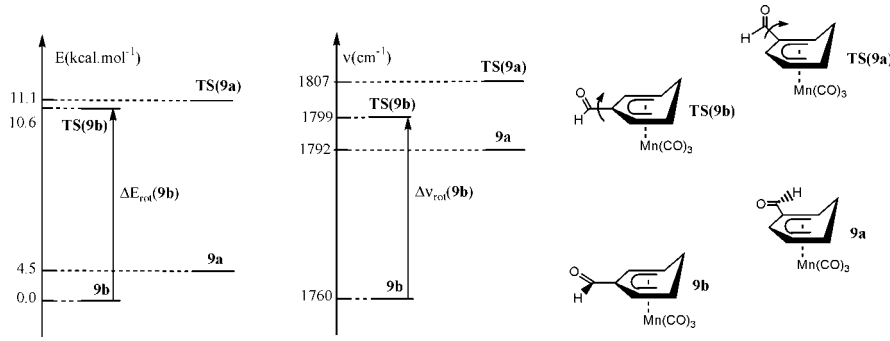


Figure 2. Computed ν_{CHO} vibrational frequencies and energies (relative to the most stable structure) for the lowest energy conformers and for the lowest transition states of structures **9a** and **9b**.

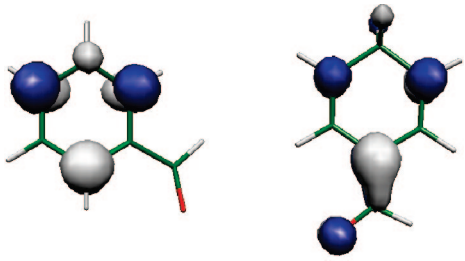


Figure 3. Highest occupied molecular orbitals for **10a** (left) and **10b** (right). Isodensity equal to 0.7.

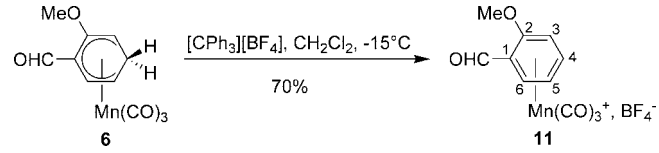
conjugation by rotation brings $\tilde{\nu}_{CHO}$ for species **TS(9a)** and **TS(9b)** only 8 cm^{-1} apart.

The computational results can be rationalized as follows: conjugation of the CHO system with the cyclohexadienyl moiety is larger in position 3 than in position 2, due to the presence of a node in the C^2 position of the cyclohexadienyl highest occupied orbital (HOMO).[25] Nevertheless, this conjugation, by decreasing the energy and the coefficient of the ring carbons of the HOMO, results in a weaker interaction of the cycle with the Mn(CO)$_3^+$ metal fragment.[26] The resulting differences between species **9a** and **9b** (either in energy or in $\tilde{\nu}_{CHO}$) are thus much smaller than those in the corresponding fully organic system **10a** and **10b** (Figure 3).

In conclusion, the present computational study demonstrates that the energy and $\tilde{\nu}_{CHO}$ differences observed between regioisomers **8a** and **8b** are fully associated with the conjugation between the CHO moiety and the cyclohexadienyl π-system, and that no other phenomenon (steric effects, inductive effects, . . .) needs to be proposed.

Reactivity Study of the (η^5-Formylcyclohexadienyl)Mn(CO)$_3$ Complexes. As the functionalization by the lithiation/electrophilic quench sequence does not affect the complexed η^5-cyclohexadienyl fragment, we decided to take advantage of the property of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes to undergo *exo* hydride abstraction at the sp^3 carbon[27] to achieve the synthesis of the first (η^6-arylaldehyde)Mn(CO)$_3^+$. Indeed, the electron density of the benzaldehyde ring or of other arenes substituted by conjugated electron-withdrawing groups is too low to allow a direct coordination to the Mn(CO)$_3^+$ moiety.[12] In an earlier study, we have been able to circumvent this restriction and we have prepared the first (η^6-arene)Mn(CO)$_3^+$ complexes with resonance electron-withdrawing substituents

Scheme 1. Rearomatization of Complex (η^5-3-Formyl-2-methoxycyclohexadienyl)Mn(CO)$_3$ (6)



(ketones, esters, and amides) by rearomatization of the corresponding (η^5-cyclohexadienyl)Mn(CO)$_3$ synthesized by carbonylative palladium-catalyzed cross-couplings.[14] This has demonstrated that the limitation was not an intrinsic instability of the (η^6-arene)Mn(CO)$_3^+$ complexes substituted by conjugated electron-withdrawing groups but the lack of an adequate method for their preparation.

The first synthetic attempts were realized following the experimental procedure for the rearomatization of variously functionalized η^5-cyclohexadienyl complexes,[14,15b] using an excess of [CPh$_3$][BF$_4$] in dichloromethane at room temperature. Under these conditions, complex **11** could be isolated as an impure sticky solid and in a relatively poor yield (20%). It was therefore necessary to adjust the quantity of trityl salt to 1 equiv together with a decrease of the temperature to optimize the yield and the quality of the cationic aldehyde **11**. Thus, at −15 °C, the aromatization of the (η^5-formylcyclohexadienyl)Mn(CO)$_3$ complex **6** by hydride abstraction proceeded smoothly to give the [(η^6-2-methoxybenzaldehyde)Mn(CO)$_3$][BF$_4$] complex **11** in 70% yield as a yellow powder (Scheme 1).

The presence of the aldehyde on the aromatic ring is characterized by its signature at 10.40 ppm on the ^{1}H NMR spectrum and at 187.2 ppm in the ^{13}C NMR spectrum of complex **11** in acetone-d_6. Its ^{1}H NMR spectrum is otherwise characteristic of a cationic (η^6-arene) manganese complex with the most deshielded protons, H^4 and H^6, appearing at 7.51 and 7.56 ppm, respectively, and the less deshielded ones, H^3 and H^5, at 6.82 and 6.49 ppm, respectively. Such a difference in the chemical shifts of the aromatic protons is attributable to the electronic distribution created by the resonance-withdrawing group CHO located *ortho* to the electron-donating group OMe. This observation is in good agreement with an *anti*-eclipsed conformation in solution of the Mn(CO)$_3$ tripod with respect to the electron-withdrawing group. Unfortunately, an X-ray diffraction analysis could not be realized to study complex **11** conformation in the solid state; several attempts were made to grow suitable crystals, all unsuccessful because of the relative instability of **11**.

This unprecedented (η^6-arylaldehyde)Mn(CO)$_3^+$ complex indeed proved to be much more reactive than the cationic complexes substituted by keto-, ester-, or amido-groups. First,

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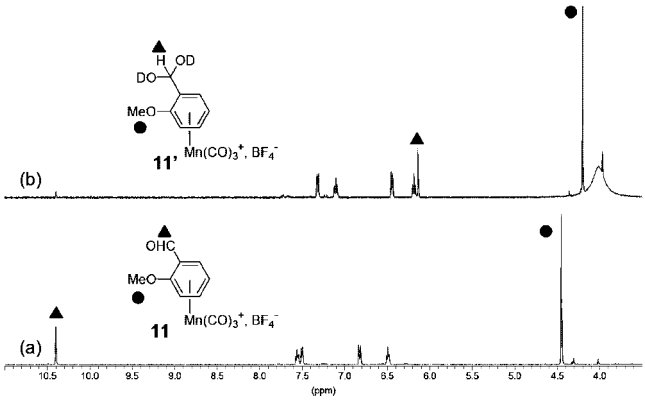

Figure 4. ^{1}H NMR spectra (400 MHz, acetone-d_6): (a) complex [(η^6-1-formyl-2-methoxybenzene)$Mn(CO)_3$][BF_4] **11** and (b) the corresponding *gem*-diol **11′** after addition of D_2O.

the conjugation of the formyl group with the metal-complexed aromatic ring seems to strongly increase its electrophilicity. Indeed, the addition of D_2O to an NMR sample of complex **11** in acetone-d_6 resulted in the almost quantitative formation of the corresponding *gem*-diol complex **11′** as indicated by the disappearance of the aldehydic ^{1}H NMR signal at 10.40 ppm and the appearance of a singulet at 6.14 ppm for the resonance of the benzylic proton of the *gem*-diol group (Figure 4).

The metal center itself in the (η^6-arylaldehyde)$Mn(CO)_3^+$ complex appears also very electrophilic compared to the various cationic complexes that we previously synthesized.[14,15b] This was revealed by the fast appearance of ^{1}H NMR signals corresponding to the free aromatic ligand as a consequence of the decoordination of the $Mn(CO)_3$ entity by a nucleophilic attack of acetone-d_6. These observations seem to be in line with the computational evaluation of the coordination of the anisole ring to the $Mn(CO)_3^+$ moiety; it is indeed found to be decreased by 8.1 kcal·mol^{-1} upon *ortho* functionalization by a formyl group.

We then turned our attention toward the reactivity of the (η^5-formylcyclohexadienyl)$Mn(CO)_3$ complexes toward nucleophiles. The synthesis and reactivity of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes functionalized by an alcohol function α to the π system are currently under investigation in our group. Such η^5 derivatives cannot be obtained from the corresponding η^6 cationic complexes, the benzylic alcohol function being incompatible with the complexation procedures.[12] Two pathways have already been described to prepare such functionalized complexes. The first one relies on the reduction of a ketone function stemming from a palladium-catalyzed carbonylative coupling.[28] The second one is based on the lithiation/electrophilic quench procedure with use of a carbonyl electrophile, either aldehyde or ketone.[15b] The easy access to the formylcyclohexadienyl complexes **5**–**8** opens a third pathway to this class of complexes, as illustrated below by the study of their reactivity toward a hydride source ($NaBH_4$) and a Grignard reagent (PhMgCl), under experimental procedures generally used for reductions.

The first observation that can be made is the high chemoselectivity of these two reactions. Indeed, the starting (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes possess three electrophilic sites, namely the cyclohexadienyl system, the $Mn(CO)_3$ fragment, and the formyl group. Nonetheless, the alcohol derivatives

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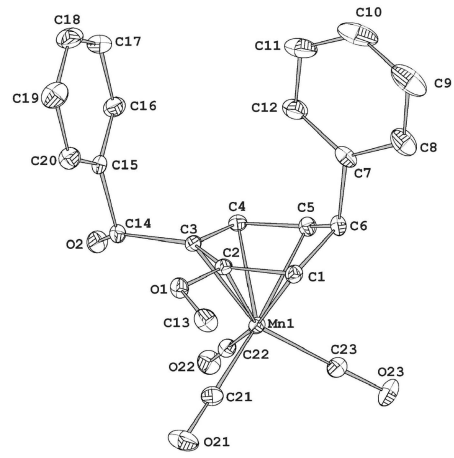
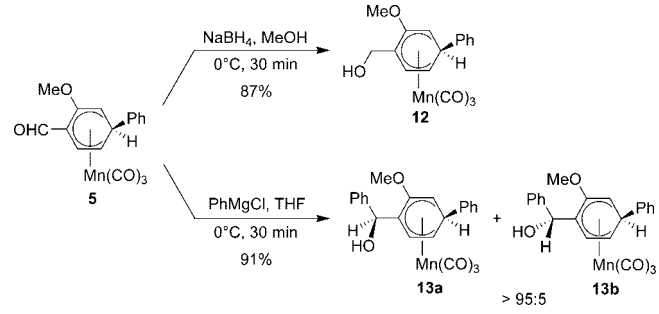


Figure 5. Molecular structure of complex **13a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Scheme 2



resulting from a nucleophilic addition on the aldehyde function were isolated in high yields (87% for the unprecedented hydroxymethyl derivative **12** and 91% for **13**) and no side products were identified in the ^{1}H NMR of the crude mixture. Specially, no addition of hydride to the π system was observed in contrast with our previous study[28] dealing with the reactivity of keto-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes toward hydrides.

Second, a new stereogenic center is created during the addition of PhMgCl on the racemic planar chiral complex **5**. Of the two possible (racemic) diastereoisomers, only one was identified by ^{1}H NMR analysis of the crude mixture. A monocrystal suitable for X-ray diffraction analysis was readily obtained by slow evaporation of a dichloromethane/pentane solution of the purified diastereoisomer. The molecular structure was established (ORTEP view presented in Figure 5) and allowed the assessment of the relative configuration (*R*) for the newly created sp^3 carbon C^{14} associated with the (2*pS*) configuration for the metal-coordinated cyclohexadienyl moiety, thus corresponding to diastereoisomer **15a** (Scheme 2). The selectivity for this relative stereochemistry can be understood according to the following two factors. For steric reasons, the formyl group in complex **5** adopts an *anti* conformation with respect to the methoxy group. This is, for instance, observed in the crystal structure of the aldehyde **7b** (Figure 1). Additionally, the $Mn(CO)_3$ tripod blocks one face of the cyclohexadienyl, so that the addition of PhMgCl preferentially occurs *exo* with respect to the metal. Although such a high diastereoselectivity could be predicted,[9] it represents the first example of a diastereoselective nucleophilic addition to a formyl group attached to a planar chiral (η^5-cyclohexadienyl)$Mn(CO)_3$ backbone. Diastereoisomeric complexes **13** have been previously

obtained by the lithiation/electrophilic quench of complex **1**, using benzaldehyde as the electrophile.[15b] But in this synthetic approach, a mixture of the two diastereoisomers **13a** and **13b** was obtained in a 44:56 ratio. This lack of diastereoselectivity was attributed to a very low facial stereodiscrimination of the benzaldehyde C═O bond by the planar chiral η^5-cyclohexadienyl anion.

Resolution of Planar Chiral (η^5-Formylcyclohexadienyl)-Mn(CO)$_3$ Complexes. The electrophilic reactivity of the formyl group was also exploited to introduce a chiral auxiliary on the η^5 complex. Indeed, among the newly synthesized (η^5-formylcyclohexadienyl)Mn(CO)$_3$ complexes, compounds such as **5**, **6**, and **7a** possess a planar chirality. Up to now, to the best of our knowledge, no general method for preparing enantiopure (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes has been developed. However, several attempts employing different approaches demonstrate an enduring and undoubted interest in these planar chiral entities, especially for the enantioselective synthesis of natural products containing polysubstituted cyclohexadienes or cyclohexenes.[2b] Miles et al. reported the addition of chiral nonracemic enolates to prochiral cationic [(η^6-arene)Mn(CO)$_3$]$^+$ complexes to generate η^5-cyclohexadienyl complexes.[29] In spite of the low stereoselectivity in the formation of the η^5-cyclohexadienyl system, subsequent separation of the diastereoisomeric mixture by recrystallization enabled the establishment of a formal synthesis of (+)-juvabione.[30] Using a different approach, Pearson et al. studied the addition of various achiral nucleophiles to η^6-arene manganese complexes bearing a chiral amino auxiliary.[31] Despite good diastereoselectivities, this class of compound has only limited applications because it is not straightforward to remove the chiral auxiliary from the final product. More recently, Chung and co-workers developed an enantioselective addition of nucleophiles to prochiral (η^5-oxocyclohexadienyl)Mn(CO)$_3$ complexes in the presence of chiral ligands.[32] This approach remains nevertheless specifically devoted to the formation of acetoxy-subtituted enantioenriched η^5-cyclohexadienyl complexes. The development of new synthetic approaches is therefore still highly demanded in view of the chemical richness of these complexes. We have previously described the resolution of racemic planar chiral *ortho*-substituted (η^6-benzaldehyde)tricarbonylchromium complexes using an enantiopure diamine with a C_2 symmetry axis.[8b] We therefore decided to apply the same methodology for the resolution of racemic (η^5-formylcyclohexadienyl)Mn(CO)$_3$ mixtures.

The description of the chirality of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes is not as straightforward as that for the closely related planar chiral [(η^6-arene)Mn(CO)$_3$]$^+$ precursors and deserves some comments. All the (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes unsymmetrically substituted on the cyclohexadienyl system are chiral as, for example, the C^1- or C^2-substituted complexes presented in Figure 6. But, considering for instance a regioselective nucleophilic *meta*-addition to complex **I** (Figure 6), two different situations arise. When Nu = H, the resulting complexes **III** and *ent*-**III** contain a single stereogenic element, the chiral plane. However if Nu ≠ H, the nucleophilic addition

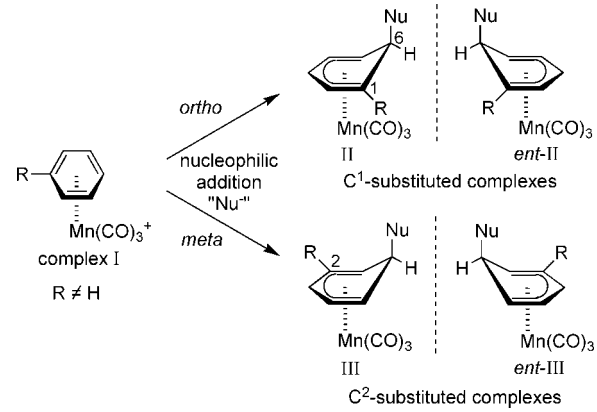
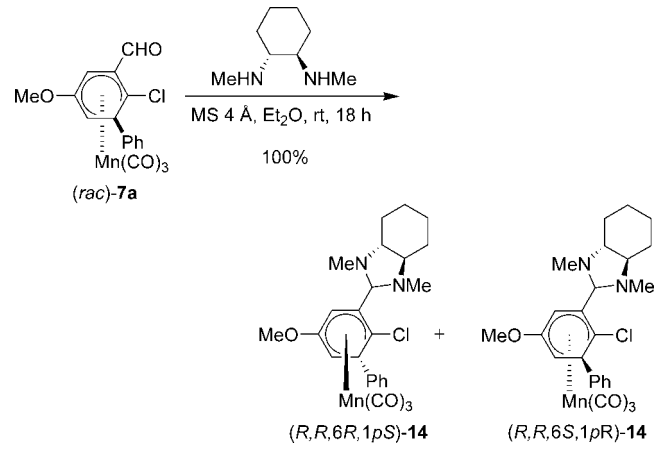


Figure 6. Chirality of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes.

Scheme 3



to the prochiral [(η^6-arene)Mn(CO)$_3$]$^+$ complex **I** (Figure 6) creates two stereogenic elements, a plane and a center (C^6). Thus, four stereoisomers (two pairs of enantiomers) should theoretically be formed, but the nucleophilic addition always being *exo* stereospecific,[4] only a single pair of enantiomers **III** and *ent*-**III** (alternatively **II** and *ent*-**II** for a nucleophilic *ortho*-addition) is in fact obtained.

In the following study, the chirality of the various complexes will be conventionally described by the configuration at the chiral plane,[33] together with the corresponding configuration at the C^6 center if chiral, and by the configuration of the chiral auxiliary when present on the molecule.

Recently, we reported the first resolution of a racemic mixture of formyl-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes, namely compound (*rac*)-**5**.[15a] The extension of this methodology to complexes **6** and **7a** has been studied and is presented below. After reaction of the racemic aldehydes **5**, **6**, or **7a** with enantiopure (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine,[34] two diastereomeric aminals were obtained. Careful chromatographic separation of the mixtures was then performed on neutralized silica gel or on basic alumina to prevent the hydrolysis of the chiral auxiliary.

The complete conversion of compound (*rac*)-**7a** to the corresponding aminals was reached after 18 h of reaction at room temperature (Scheme 3). The best separation conditions were obtained with basic alumina and afforded diastereoisomer (*R*,*R*,6*R*,1*pS*)-**14** with ≥95% diastereoisomeric excess (de) and 18% yield. The diastereoisomeric purity was ascertained by NMR analysis, the signals of the H^3 protons of the diastereoisomers being clearly separated by 0.43 ppm (Figure 7). Moreover, the determination of the molecular structure of

(29) Miles, W. H.; Smiley, P. M.; Brinkman, H. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1897.
(30) Miles, W. H.; Brinkman, H. R. *Tetrahedron Lett.* **1992**, *33*, 589.
(31) (a) Pearson, A. J.; Zhu, P. Y.; Youngs, W. J.; Bradshaw, J. D.; McConville, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 10376. (b) Pearson, A. J.; Milletti, M. C.; Zhu, P. Y. *J. Chem. Soc., Chem. Commun.* **1995**, 853. (c) Pearson, A. J.; Gontcharov, A. V.; Zhu, P. Y. *Tetrahedron* **1997**, *53*, 3849.
(32) Son, S. U.; Park, K. H.; Lee, S. J.; Seo, H.; Chung, Y. K. *Chem. Commun.* **2002**, 1230.

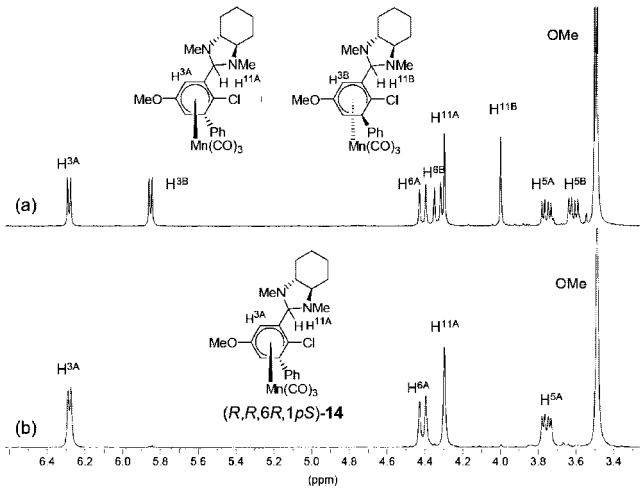


Figure 7. Selected sections of ^{1}H NMR spectra (200 MHz, $CDCl_3$): (a) crude mixture of diastereoisomers (*R*,*R*,6*R*,1*pS*)-**14** and (*R*,*R*,6*S*,1*pR*)-**14**; (b) after chromatographic separation: (*R*,*R*,6*R*,1*pS*)-**14** with ≥95% de.

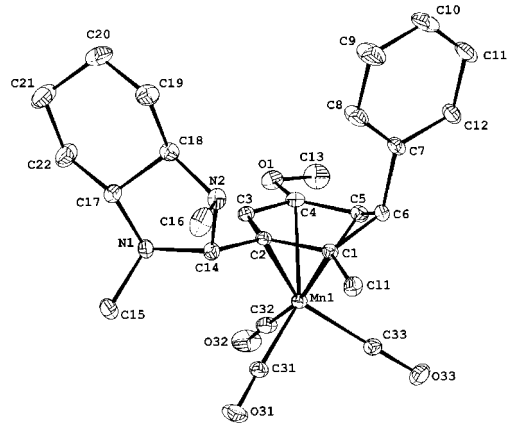
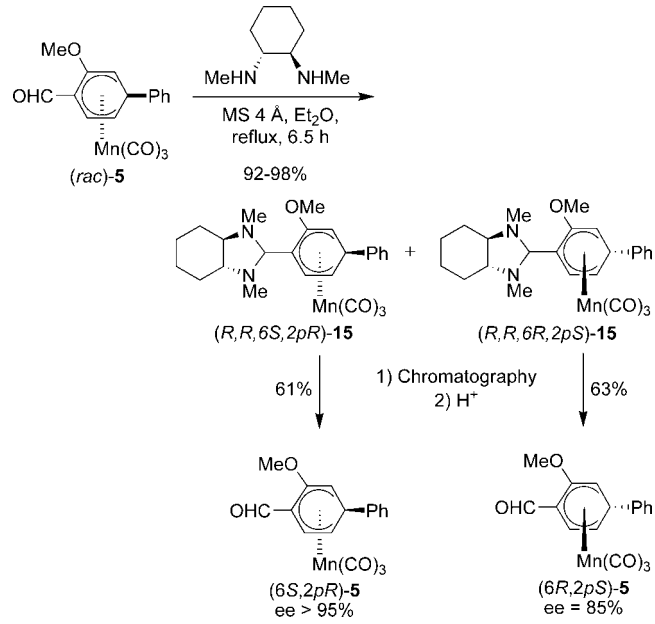


Figure 8. Molecular structure of complex (*R*,*R*,6*R*,1*pS*)-**14** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

(*R*,*R*,6*R*,1*pS*)-**14** allowed us to assign the absolute configuration of the stereogenic center and of the planar chiral η^5-cyclohexadienyl moiety. Indeed, complex (*R*,*R*,6*R*,1*pS*)-**14** was readily recrystallized by slow evaporation of a diethylether/pentane solution giving monocrystals suitable for X-ray diffraction analysis. An ORTEP view is presented in Figure 8 and reveals the (6*R*) and (1*pS*) configurations associated with the (*R*,*R*) configuration of the enantiopure diamine.[35]

This methodology was more successful with the anisole series. Refluxing (*rac*)-**5** and the enantiopure diamine with molecular sieves in diethyl ether gave diastereoisomeric aminals **15** with conversions up to 98% (Scheme 4). The separation of these compounds was achieved by chromatography on neutralized silica gel affording the two diastereoisomers in 33% and 32% yield with ≥95% and 85% de, respectively. The separation could be optimized (de ≥95% for both complexes; spectra presented in Figure 9) although with lower yields (25% and 27%, respectively). The diastereomeric composition was readily determined by ^{1}H NMR spectroscopic analysis: the aminalic protons H^{11A} and H^{11B} of these compounds resonate at δ 4.19 and 5.17 ppm respectively, a difference of almost 1 ppm (Figure 9). The aminals were then easily converted by acid-catalyzed hydrolysis into the pure enantioenriched aldehydes (*pR*)-**5** and

Scheme 4



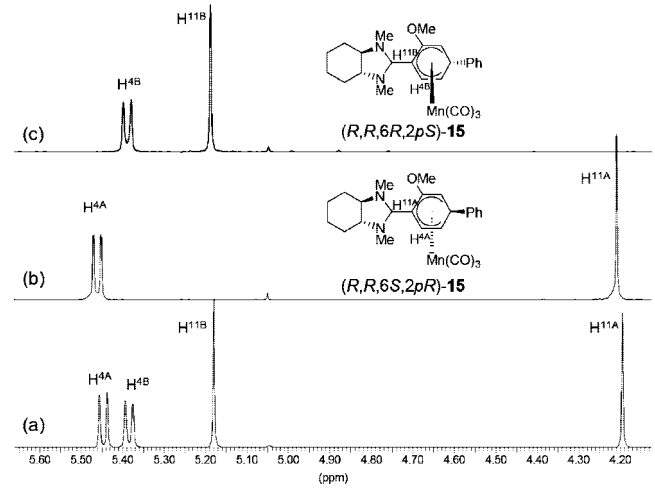


Figure 9. Selected sections of ^{1}H NMR spectra (400 MHz, $CDCl_3$): (a) crude mixture of diastereoisomers (*R*,*R*,6*S*,2*pR*)-**15** and (*R*,*R*,6*R*,2*pS*)-**15**; after chromatographic separation, (b) (*R*,*R*,6*S*,2*pR*)-**15** with ≥95% de and (c) (*R*,*R*,6*R*,2*pS*)-**15** with ≥95% de.

(*pS*)-**5** in 93% and 99% yield after chromatography and with ≥95% and 85% ee, respectively.

The assignment of the configurations of the chiral center and of the planar chiral η^5-cyclohexadienyl moiety was possible through X-ray analysis of suitable crystals of one of the diastereomeric aminals **15** (>95% de, $\delta(H^{11A}) = 4.19$ ppm).[15a] (6*S*) and (2*pR*) configurations connected with the (*R*,*R*) configuration of the enantiopure diamine were observed for this diastereoisomer (Figure 10).[35] On this basis, the absolute configurations of the formyl derivatives (*pR*)-**5** and (*pS*)-**5** could also be unambiguously assigned.

We also considered the resolution of (*rac*)-**6**. The corresponding diastereoisomeric aminals were prepared with conversions ranging from 95% to 100% after 7 to 8 h of reaction in diethyl ether at 30 °C (Scheme 5). Separation by chromatography on neutralized silica gel provided the two diastereoisomers in 33% and 25% yield with ≥95% and 92% de, respectively. As above, ^{1}H NMR spectroscopic analysis is a suitable method for the determination of diastereoisomeric excesses: the signals

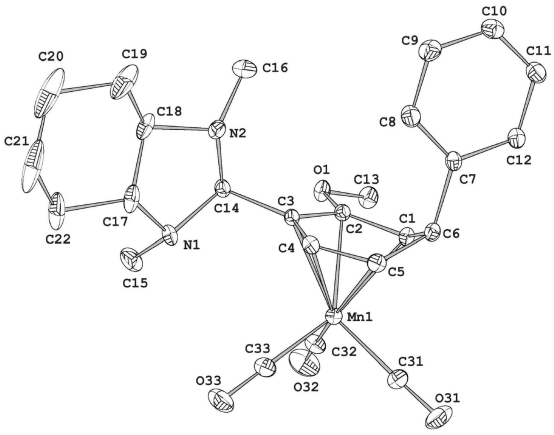
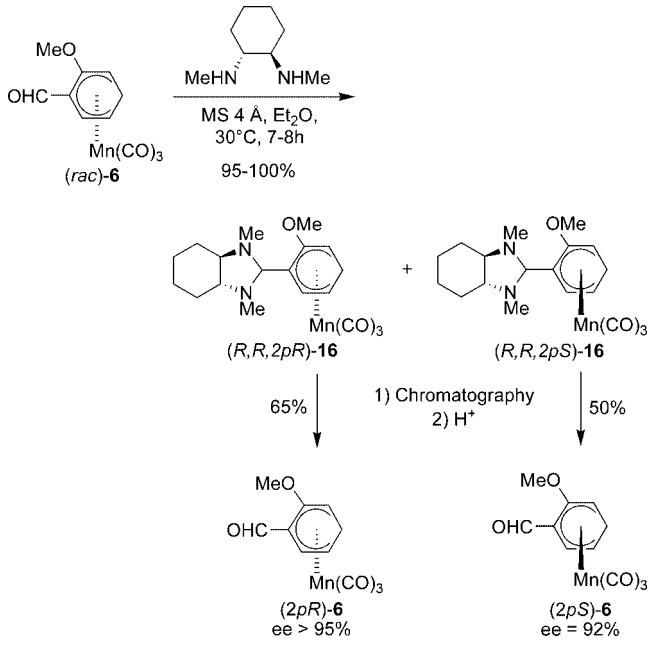


Figure 10. Molecular structure of complex (*R*,*R*,6*S*,2*pR*)-**15**[15a] with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Scheme 5



of the aminalic protons H^{7A} (δ 4.32 ppm) and H^{7B} (δ 5.23 ppm) of the two diastereoisomers are clearly separated (Figure 11). Between 4 and 6 ppm, the region corresponding to H^4 and aminalic protons, the ^{1}H NMR spectra of diastereoisomers **16** are very similar to those of compounds **15** (see Figure 9, parts b and c) with a strong separation of almost 1 ppm for the signals corresponding to the aminalic protons of each diastereoisomeric complex. Furthermore, signals at 4.32 and 5.23 ppm for the aminalic protons of diastereoisomers **16** correlate with signals at 4.19 and 5.17 ppm for the corresponding protons of (*R*,*R*,2*pR*)-**15** and (*R*,*R*,2*pS*)-**15**, respectively. The only difference between these two complexes is the nature of the *exo*-substituent at C^6. Therefore, one could assume that the absolute configuration of the planar chiral cyclohexadienyl moiety plays a major role in the strong difference between the chemical shifts of the aminalic protons of diastereoisomeric complexes. Thus, the absolute configuration (*R*,*R*,2*pR*) could be assigned to one of the diastereoisomer (≥95% de, $\delta(H^7A) = 4.32$ ppm) and the configuration (*R*,*R*,2*pS*) to the other one (92% de, $\delta(H^7B) =$ 5.23 ppm).

Once separated, the diastereoisomers (*R*,*R*,2*pR*)-**16** and (*R*,*R*,2*pS*)-**16** were hydrolyzed under acidic conditions to give

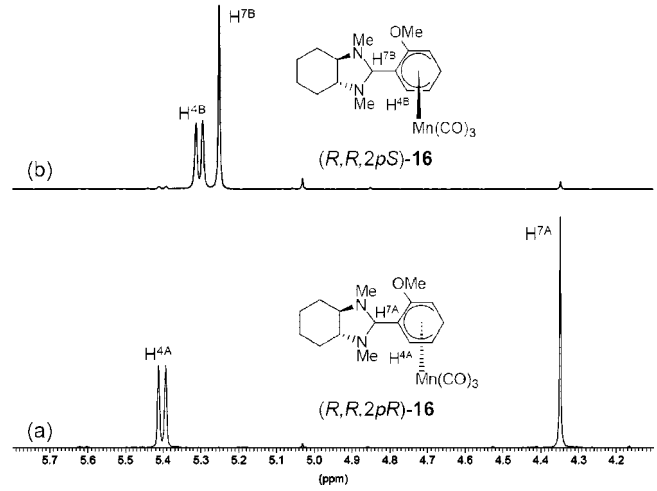


Figure 11. Selected sections of ^{1}H NMR spectra (400 MHz, $CDCl_3$): after chromatographic separation of the diastereoisomeric mixture (a) (*R*,*R*,2*pR*)-**16** (≥95% de) and (b) (*R*,*R*,2*pS*)-**16** (de = 92%).

Table 7. Selected Interatomic Distances for 7b, 11a, (*R*,*R*,6*R*,1*pS*)-12, and (*R*,*R*,6*S*,2*pR*)-13

	7b	11a	(*R*,*R*,6*R*,1*pS*)-**12**	(*R*,*R*,6*S*,2*pR*)-**13**
$Mn-C^1$	2.2347 (14)	2.2277 (14)	2.1589 (12)	2.206 (2)
$Mn-C^2$	2.1423 (12)	2.2154 (14)	2.1614 (12)	2.2055 (19)
$Mn-C^3$	2.1334 (12)	2.1483 (13)	2.1399 (12)	2.1659 (18)
$Mn-C^4$	2.2129 (13)	2.1482 (14)	2.2018 (13)	2.139 (2)
$Mn-C^5$	2.2469 (13)	2.2546 (15)	2.2262 (13)	2.252 (2)
C^2-C^{14}			1.5329 (18)	
C^3-C^{14}	1.4804 (18)	1.5304 (19)		1.515 (3)
$C^{14}-O^2$	1.214 (2)	1.4455 (17)		
$C^{14}-N^1$			1.4800 (19)	1.481 (3)
$C^{14}-N^2$			1.4774 (19)	1.485 (3)

after chromatography the enantioenriched formyl-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ (2*pR*)-**6** and (2*pS*)-**6** in 98% and quantitative yield and with ≥95% and 92% ee, respectively (Tables 6 and 7).

Conclusion

Using DMF as the electrophile, we successfully applied the lithiation/electrophilic quench sequence developed for the functionalization of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes to the synthesis of the first formyl derivatives in this family of organometallic compounds. These new (η^5-formylcyclohexadienyl)$Mn(CO)_3$ complexes were obtained in good yields and were structurally characterized in solution by NMR and in the solid state by IR spectroscopy and X-ray diffraction analysis. Moreover, a computational study highlighted the influence of the CHO position and of the coordination to the $Mn(CO)_3$ tripod on the strength of conjugation between the aldehyde and the cyclohexadienyl ring. The method of functionalization, preserving the methylene *exo* fragment, allows the rearomatization of η^5 complexes by hydride abstraction and led to the first cationic (η^6-arylaldehyde)$Mn(CO)_3^+$ complex. The reactivity of (η^5-

(33) The planar chirality was assigned according to the extended Cahn–Ingold–Prelog (CIP) rules described in ref 7a.

(34) For the preparation of the enantiopure diamine see:(a) Alexakis, A.; Mutti, S.; Mangeney, P. *J. Org. Chem.* **1992**, *57*, 1224. (b) Alexakis, A.; Chauvin, A.-S.; Stouvenel, R.; Vrancken, E.; Mutti, S.; Mangeney, P. *Tetrahedron: Asymmetry* **2001**, *12*, 1171.

(35) The assignment of absolute configurations from the structures of **14** and **15** is validated by pertinent values of the Flack's parameter (Table 6) : Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908.

formylcyclohexadienyl)Mn(CO)$_3$ complexes toward nucleophilic addition was also investigated. Particularly interesting in this matter is the reaction of planar chiral formyl derivatives with an enantiopure diamine to give the corresponding aminals and their subsequent resolution. This procedure led to the preparation of novel enantiopure (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes, opening up new perspectives for the applications of η^5-manganese complexes in organometallic and organic asymmetric syntheses.

Computational Details

Full geometry optimizations were systematically conducted with no symmetry restraints by using the Gaussian 03 program[36] within the framework of the Density Functional Theory (DFT), using the hybrid B3LYP exchange-correlation functional[37] and the 6-31+G** basis set for all atoms. This level of theory has been widely used in modeling arene−Cr(CO)$_3$ complexes and has proved to give good results from both geometrical[38] and energetical basis.[39] Frequencies were evaluated within the harmonic approximation and are reported, unless otherwise mentioned, unscaled. NMR shielding constants are evaluated by using the standard procedure implemented within the GAUSSIAN software. The nature of the transition states was ensured by confirming the presence of a single imaginary frequency. The connection between transition states and minima was ensured by carrying out small displacements of all atoms in the two directions along the imaginary frequency mode and carrying out geometry optimization with these geometries as starting points.

Experimental Section

General Methods. All reactions were routinely performed under a dry nitrogen atmosphere with standard Schlenk techniques. THF and Et_2O were dried over sodium benzophenone ketyl and distilled. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was distilled over KOH and stored under nitrogen over 4 Å molecular sieves. CH_2Cl_2 and DMF were distilled over CaH_2. NMR spectra were recorded on a Bruker ARX 200 MHz or Avance 400 MHz spectrometer. ^{1}H and ^{13}C signals of NMR solvents were used as internal standards respectively at δ 7.26 and 77.36 ppm in $CDCl_3$ and at δ 2.09 and 30.60 ppm in acetone-d_6. The Mn(CO)$_3$ carbonyl signal is known to be difficult to observe, specially when only low quantities of complex are available. Infrared spectra were measured on a Bruker Tensor 27 spectrometer. Elemental analyses were performed by the Service Central d'Analyze du CNRS. Mass spectra were performed for MALDI-TOF by the Plate-Forme Spectrométrie de Masse et Protéomique (IFR83, UPMC), for ES-MS by the Groupe de Spectrométrie de Masse (UMR 7613, UPMC), and for the EI-MS by the Service de Spectrométrie de Masse de l'ENS (Chemistry Dpt, Paris). Optical rotations were measured on a Perkin-Elmer 343 polarimeter at 589 nm.

Complexes **1**,[16] **2**,[17b] **3**,[14b] and **4**[16] were synthesized according to procedures previously described in the literature.

Preparation of Complex (η^5-3-Formyl-2-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ (5). A solution of complex **1** (0.404 g, 1.25 mmol, 1 equiv) and freshly distilled TMEDA (0.30 mL, 2.00 mmol, 1.6 equiv) in 12 mL of THF was cooled to −78 °C. A solution of *n*BuLi (1.6 M in hexanes, 1.25 mL, 2.00 mmol, 1.6 equiv) was slowly added. The mixture was stirred for 1 h at −78 °C before the addition of DMF (0.195 mL, 2.50 mmol, 2 equiv). It was stirred for another hour at −78 °C before being warmed to room temperature and quenched by addition of H_2O. After extraction of the reaction mixture with Et_2O, the combined organic layers were washed with a saturated aqueous NaCl solution and dried over $MgSO_4$. After concentration in vacuo, the crude mixture was purified by flash chromatography on silica gel to afford **5** as a yellow oil (0.298 g, 0.85 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.50 (s, 3H, OCH_3), 3.59 (dd, ^3J = 6.2 Hz, ^4J = 1.5 Hz, 1H, H^1), 3.82 (m, 1H, H^5), 4.08 (t$_{app}$, ^3J = 6.2 Hz, 1H, H^6), 5.75 (d, ^3J = 7.6 Hz, 1H, H^4), 6.93 (d, ^3J = 7.4 Hz, 2H, H^{Ph}), 7.19 (t, ^3J = 7.4 Hz, 1H, H^{Ph}), 7.26 (t$_{app}$, ^3J = 7.4 Hz, 2H, H^{Ph}), 10.62 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.2 (C^6), 45.7 (C^1), 55.1 (OCH_3), 65.2 (C^5), 79.4 (C^3), 92.0 (C^4), 125.7 (CH^{Ph}), 127.5 (CH^{Ph}), 129.0 (CH^{Ph}), 145.5 (C^2 or C^{Ph}), 146.8 (C^2 or C^{Ph}), 189.8 (CHO), 217.3 (CO (Mn)). IR (neat): $\bar{\nu}$ (cm^{-1}) 1673 (CHO), 1924 (Mn(CO)$_3$), 2018 (Mn(CO)$_3$). MS (ESI, positive mode): *m*/*z* 352.8 (M$^+$). HRMS (EI, positive mode): *m*/*z* 352.0152 (M$^+$, calcd for $C_{17}H_{13}MnO_5$: 352.0143).

Preparation of Complex (η^5-3-Formyl-2-methoxycyclohexadienyl)Mn(CO)$_3$ (6). A solution of complex **2** (0.295 g, 1.19 mmol, 1 equiv) and freshly distilled TMEDA (0.27 mL, 2.00 mmol, 1.6 equiv) in 10 mL of THF was cooled to −78 °C. A solution of *n*BuLi (1.6 M in hexanes, 1.20 mL, 1.78 mmol, 1.6 equiv) was slowly added. The mixture was stirred for 1 h at −78 °C before the addition of DMF (0.165 mL, 2.14 mmol, 2 equiv). It was stirred for another hour at −78 °C before being warmed to room temperature and quenched by addition of H_2O. After extraction of the reaction mixture with Et_2O, the combined organic layers were washed with a saturated aqueous NaCl solution and dried over $MgSO_4$. After concentration in vacuo, the crude mixture was purified by flash chromatography on silica gel to afford **6** as a yellow powder (0.208 g, 0.75 mmol, 63%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.40 (d, ^2J = 13.2 Hz, 1H, H^{6exo}), 2.85–3.06 (m, 2H, H^1 and H^{6endo}), 3.37 (t$_{app}$, ^3J = 6.8 Hz, 1H, H^5), 3.44 (s, 3H, OCH_3), 5.58 (d, ^3J = 7.7 Hz, 1H, H^4), 10.66 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5 (C^6), 37.9 (C^1), 55.0 (OCH_3), 59.1 (C^5), 80.1 (C^3), 93.6 (C^4), 146.2 (C^2), 190.3 (CHO), 217.3 (CO (Mn)). IR (neat): $\bar{\nu}$ (cm^{-1}) 1668 (CHO), 1914 (Mn(CO)$_3$), 2014 (Mn(CO)$_3$). HRMS (MALDI-TOF, positive mode): *m*/*z* 274.9619 (M − H$^-$, calcd for $C_{11}H_8MnO_5$: 274.9752). Anal. Calcd for $C_{11}H_9MnO_5$: C, 47.85; H, 3.29. Found: C, 47.69; H, 3.36.

Preparation of Complexes (η^5-1-Chloro-2-formyl-4-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ (7a) and (η^5-1-Chloro-3-formyl-4-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ (7b). At −78 °C, a solution of *n*BuLi (1.6 M in hexanes, 0.44 mL, 0.70 mmol, 1.4 equiv) was slowly added to a solution of complex **3** (0.178 g, 0.50 mmol, 1 equiv) in 5 mL of THF. The mixture was stirred for 15 min at −78 °C before the addition of DMF (0.062 mL, 0.80 mmol, 1.8 equiv). It was then stirred for another hour at −78 °C before being warmed to room temperature and quenched by addition of H_2O. After extraction of the reaction mixture with Et_2O, the combined organic layers were washed

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with a saturated aqueous NaCl solution, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography on silica gel then enabled the separation of **7a** (yellow oil, 0.115 g, 0.30 mmol, 60%) and **7b** (yellow solid, 0.058 g, 0.15 mmol, 30%). **7a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H, OCH_3), 3.66 (dd, ^3J = 6.5 Hz, ^4J = 2.8 Hz, 1H, H^5), 4.47 (d, ^3J = 6.5 Hz, 1H, H^6), 6.07 (d, ^4J = 2.8 Hz, H^3), 7.01–7.03 (m, 2H, H^{Ph}), 7.25–7.32 (m, 3H, H^{Ph}), 10.04 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.1 (C^5), 53.7 (C^6), 55.5 (OCH_3), 61.1 (C^3), 83.1 (C^1), 93.1 (C^2), 126.3 (CH^{Ph}), 128.3 (CH^{Ph}), 129.0 (CH^{Ph}), 141.9 (C^4 or C^{Ph}), 143.3 (C^4 or C^{Ph}), 192.5 (CHO), 220.4 (CO (Mn)). IR (neat): $\bar{\nu}$ (cm^{-1}) 1704 (CHO), 1933 ($Mn(CO)_3$), 2020 ($Mn(CO)_3$). MS (EI, positive mode): *m*/*z* 302 (M^+ − 3CO). HRMS (EI, positive mode): *m*/*z* 385.9751 (M^+, calcd for $C_{17}H_{12}ClMnO_5$: 385.9754). **7b**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.51 (s, 3H, OCH_3), 3.72 (d, ^3J = 6.4 Hz, 1H, H^5), 4.42 (dd, ^3J = 6.4 Hz, ^4J = 1.5 Hz, 1H, H^6), 5.97 (d, ^4J = 1.5 Hz, 1H, H^2), 6.97–7.01 (m, 2H, H^{Ph}), 7.26–7.34 (m, 3H, H^{Ph}), 10.54 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.5 (C^5), 52.1 (C^6), 55.7 (OCH_3), 76.0 (C^3), 86.7 (C^1), 90.7 (C^2), 126.3 (CH^{Ph}), 128.5 (CH^{Ph}), 129.1 (CH^{Ph}), 143.4 (C^4 or C^{Ph}), 144.0 (C^4 or C^{Ph}), 189.0 (CHO), 216.6 (CO (Mn)). IR (neat): $\bar{\nu}$ (cm^{-1}) 1676 (CHO), 1937 ($Mn(CO)_3$), 2025 ($Mn(CO)_3$). HRMS (EI, positive mode): *m*/*z* 385.9750 (M^+, calcd for $C_{17}H_{12}ClMnO_5$: 385.9754).

Preparation of Complexes (η^5-2-Formyl-6-phenylcyclohexadienyl)Mn(CO)$_3$ (8a) and (η^5-3-Formyl-6-phenylcyclohexadienyl)Mn(CO)$_3$ (8b). A solution of complex **4** (0.147 g, 0.50 mmol, 1 equiv) and freshly distilled TMEDA (0.15 mL, 1.00 mmol, 2 equiv) in 5 mL of THF was cooled to −78 °C. A solution of *n*BuLi (1.6 M in hexanes, 0.625 mL, 1.00 mmol, 2 equiv) was slowly added. The mixture was stirred for 2 h at −78 °C before the addition DMF (0.100 mL, 1.25 mmol, 2.5 equiv). It was stirred for another hour at −78 °C before being warmed to room temperature and quenched by addition of H_2O. After extraction of the reaction mixture with Et_2O, the combined organic layers were washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography on silica gel then enabled the separation of **8a** (yellow solid, 0.093 g, 0.28 mmol, 58%) and **8b** (yellow solid, 0.013 g, 0.040 mmol, 8%). **8a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (m, 1H, H^5), 3.94 (ddd, ^3J = 6.0 Hz, ^4J = 1.8 Hz, ^4J = 1.8 Hz, 1H, H^1), 4.06 (t_{app}, ^3J = 6.0 Hz, 1H, H^6), 5.13 (dd, ^3J = 5.4 Hz, ^3J = 7.3 Hz, 1H, H^4), 6.30 (ddd, ^3J = 5.4 Hz, ^4J = 1.8 Hz, ^4J = 1.8 Hz, 1H, H^3), 6.91 (d, ^3J = 7.3 Hz, 2H, H^{Ph}), 7.17 (t, ^3J = 7.3 Hz, 1H, H^{Ph}), 7.23 (t_{app}, ^3J = 7.3 Hz, 2H, H^{Ph}), 9.31 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.5 (C^6), 58.7 (C^1), 60.1 (C^5), 78.6 (C^3), 96.4 (C^4), 102.5 (C^2), 125.8 (CH^{Ph}), 127.5 (CH^{Ph}), 128.9 (CH^{Ph}), 146.4 (C^{Ph}), 192.4 (CHO), 221.4 (CO (Mn)). IR (neat): $\bar{\nu}$ (cm^{-1}) 1710 (CHO), 1919 ($Mn(CO)_3$), 2013 ($Mn(CO)_3$). HRMS (ESI, positive mode): *m*/*z* 344.9935 (M + Na^+, calcd for $C_{16}H_{11}MnNaO_4$: 344.9930). **8b**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.88 (t, ^3J = 7.4 Hz, 2H, $H^{1,5}$), 4.01 (t, ^3J = 7.4 Hz, 1H, H^6), 5.58 (d, ^3J = 5.4 Hz, 2H, $H^{2,4}$), 6.89–6.95 (m, 2H, H^{Ph}), 7.18–7.30 (m, 3H, H^{Ph}), 9.92 (s, 1H, CHO). ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.6 (C^6), 65.0 ($C^{1,5}$), 88.4 (C^3), 98.1 ($C^{2,4}$), 125.9 (CH^{Ph}), 127.7 (CH^{Ph}), 129.0 (CH^{Ph}), 146.5 (C^{Ph}), 190.8 (CHO). IR (neat): $\bar{\nu}$ (cm^{-1}) 1683 (CHO), 1928 ($Mn(CO)_3$), 2020 ($Mn(CO)_3$). HRMS (ESI, positive mode): *m*/*z* 344.9934 (M + Na^+, calcd for $C_{16}H_{11}MnNaO_4$: 344.9930).

Preparation of Complex [(η^6-2-methoxybenzaldehyde)Mn(CO)$_3$][BF$_4$] (11) by Rearomatisation of 6. At −15 °C, a solution of triphenylcarbenium tetrafluoroborate (0.165 g, 0.50 mmol, 1 equiv) in CH_2Cl_2 (10 mL) was added to a solution of complex **6** (0.138 g, 0.50 mmol, 1 equiv) in CH_2Cl_2 (5 mL). After being stirred at room temperature for 1.5 h, 50 mL of freshly distilled Et_2O was added to induce the precipitation of **11**. The resulting yellow powder (0.126 g, 0.35 mmol, 70%) was isolated by filtration and washed with Et_2O. ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ 4.45 (s, 3H, OCH_3), 6.48 (t_{app}, ^3J = 6.4 Hz, 1H, H^5), 6.82 (d, ^3J = 7.4 Hz, 1H, H^3), 7.53 (m, 2H, H^4 and H^6), 10.40 (s, 1H, CHO). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 60.6 (OCH_3), 82.3 (C^3), 90.6 (C^5), 104.2 (C^4 or C^6), 109.5 (C^4 or C^6), 187.2 (CHO). IR (neat): $\bar{\nu}$ (cm^{-1}) 1698 (CHO), 1999 ($Mn(CO)_3$), 2027 ($Mn(CO)_3$), 2071 ($Mn(CO)_3$). HRMS (MALDI-TOF, positive mode): *m*/*z* 274.9709 (M − BF_4^-, calcd for $C_{11}H_8MnO_5$ 274.9752).

Preparation of Complex 12. At 0 °C, $NaBH_4$ (0.026 g, 070 mmol, 1.1 equiv) was slowly added to a solution of complex **5** (0.224 g, 0.64 mmol, 1 equiv) in MeOH (10 mL). After being stirred for 0.5 h, the reaction was quenched by addition of 1 mL of a concentrated HCl solution then diluted with H_2O. After extraction of the reaction mixture with Et_2O, the combined organic layers were washed with H_2O, then with a saturated aqueous NaCl solution, dried over $MgSO_4$, and concentrated in vacuo to give **12** (0.198 g, 0.55 mmol, 87%) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.18 (t, ^3J = 6.4 Hz, 1H, OH), 3.32 (m, 2H, H^1 and H^5), 3.43 (s, 3H, OCH_3), 3.92 (t, ^3J = 5.9 Hz, 1H, H^6), 4.74 (dd, ^{2}J = 12.5 Hz, ^3J = 6.3 Hz, 1H, CH_2), 5.00 (dd, ^2J = 12.5 Hz,^3J = 5.3 Hz, 1H, CH_2), 5.16 (d, ^3J = 7.2 Hz, 1H, H^4), 6.92–6.96 (m, 2H, H^{Ph}), 7.15–7.26 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.3 (C^1), 42.8 (C^6), 54.8, (OCH_3), 56.7 (C^5), 61.0 (CH_2), 88.5 (C^3), 95.2 (C^4), 125.7 (CH^{Ph}), 127.2 (CH^{Ph}), 128.8 (CH^{Ph}), 142.5 (C^2 or C^{Ph}), 147.5 (C^2 or C^{Ph}). IR (neat): $\bar{\nu}$ (cm^{-1}) 1907 ($Mn(CO)_3$), 2009 ($Mn(CO)_3$). HRMS (ESI, positive mode): *m*/*z* 377.0187 (M + Na^+, calcd for $C_{16}H_{11}MnNaO_4$ 377.0192).

Preparation of Complex 13a.[15b] At –15 °C, PhMgCl (2 M in THF, 0.47 mL, 1.94 mmol, 2 equiv) was slowly added to a solution of complex **5** (0.165 g, 0.47 mmol, 1 equiv) in THF (10 mL). After being stirred for 0.5 h, the reaction was quenched by addition of 15 mL of an aqueous HCl solution (2 M) and diluted with 30 mL of H_2O. After extraction of the reaction mixture with Et_2O, the combined organic layers were washed with H_2O, then with a saturated aqueous NaCl solution, and dried over $MgSO_4$. After concentration in vacuo, the crude mixture was purified by flash chromatography on silica gel to afford **13a** as a yellow powder (183 mg, 0.43 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (d, ^3J = 2.6 Hz, 1H, OH), 3.29–3.36 (m, 2H, H^1 and H^5), 3.39 (s, 3H, OCH_3), 3,85 (t_{app}, ^3J = 5.8 Hz, 1H, H^6), 5.36 (d, ^3J = 7.4 Hz, 1H, H^4), 6.34 (d, ^3J = 2.6 Hz, 1H, C*H*(OH)Ph), 6.64 (d, ^3J = 7.1 Hz, 2H, H^{Ph}), 7.03–7.08 (m, 3H, H^{Ph}), 7.35–7.43 (m, 3H, H^{Ph}), 7.61 (d, ^3J = 7.3 Hz, 2H, H^{Ph}).

Preparation of Complex (*R*,*R*,6*R*,1*pS*)-14. Complex **7a** (0.310 g, 0.80 mmol, 1 equiv) and (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine (0.114 g, 0.80 mmol, 1 equiv) were stirred in distilled Et_2O (10 mL) in the presence of 4 Å molecular sieves for 18 h. After filtration through Celite, the solution was concentrated in vacuo and the mixture of the two diastereoisomers was isolated in quantitative yield. Separation of the diastereoisomeric mixture by chromatography on basic alumina (eluent: EP/Et_2O 99/1) gave (*R*,*R*,6*R*,1*pS*)-**14** (0.075 g, 0.147 mmol) as a yellow powder in 18% yield and with ≥95% de. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27–1.42 (m, 4H, H^{Cy}), 1.87 (m, 3H, H^{Cy}), 2.18 (m, 1H, H^{Cy}), 2.33 (s, 3H, NCH_3), 2.47–2.54 (m, 2H, H^{Cy}), 2.73 (s, 3H, NCH_3'), 3.44 (s, 3H, OCH_3), 3.71 (dd, ^3J = 6.6 Hz, ^4J = 3.0 Hz, 1H, H^5), 4.25 (s, 1H, H^{11}), 4.37 (d, ^3J = 6.6 Hz, 1H, H^6), 6.24 (d, ^4J = 3.0 Hz, 1H, H^3), 7.10–7.20 (m, 5H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9 (CH_2^{Cy}), 25.4 (CH_2^{Cy}), 27.6 (CH_2^{Cy}), 31.0 (CH_2^{Cy}), 38.0 (NCH_3), 42.7 (NCH_3'), 47.3 (C^5), 53.9 (C^6 or OCH_3), 54.9 (C^6 or OCH_3), 65.0 (CH^{Cy}), 68.0 (CH^{Cy}), 68.3 (C^3), 74.0 (C^1), 88.0 (C^{11}), 112.0 (C^2), 126.2 (CH^{Ph}), 127.2 (CH^{Ph}), 128.5 (CH^{Ph}), 140.2 (C^4 or C^{Ph}), 144.6 (C^4 or C^{Ph}), 222.2 (CO (Mn)). IR (neat): $\bar{\nu}$ (cm^{-1}) 1916 ($Mn(CO)_3$), 2013 ($Mn(CO)_3$). HRMS (ESI, positive mode): *m*/*z* 511.1187 (M + H^+, calcd for $C_{25}H_{29}MnClN_2O_4$ 511.1191). $[\alpha]_D$ −112 (*c* 0.220, $CHCl_3$).

Preparation of Complexes (*R*,*R*,6*S*,2*pR*)-15 and (*R*,*R*,6*R*,2*pS*)-15. Complex **5** (0.291 g, 0.83 mmol, 1 equiv) and (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine (0.141 g, 0.99 mmol, 1.2 equiv) were refluxed in distilled Et_2O (6 mL) in the presence of 4 Å molecular sieves for 6.5 h. After filtration through Celite, the solution was concentrated in vacuo and the mixture of the two diastereoisomers was isolated in quantitative yield. Separation of the diastereoisomeric mixture by preparative TLC on neutralized silica (eluent: EP/Et_2O/Et_3N 9/1/1) gave (*R*,*R*,6*S*,2*pR*)-**15** (0.129 g, 0.27 mmol, 33%) with ≥95% de and (*R*,*R*,6*R*,2*pS*)-**15** (0.126 g, 0.26 mmol, 32%) with 85% de. (*R*,*R*,6*S*,2*pR*)-**15**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21–1.30 (m, 3H, H^{Cy}), 1.48–1.54 (m, 1H, H^{Cy}), 1.81–1.87 (m, 2H, H^{Cy}), 1.97–2.00 (m, 2H, H^{Cy}), 2.08–2.13 (m, 1H, H^{Cy}), 2.42 (s, 3H, NCH_3), 2.47 (s, 3H, NCH_3), 2.88–2.95 (m, 1H, H^{Cy}), 3.31 (dd, ^3J = 6.0 Hz, ^4J = 1.8 Hz, 1H, H^1), 3.37 (s, 3H, OCH_3), 3.39 (m, 1H, H^5), 3.92 (t_{app}, ^3J = 6.0 Hz, 1H, H^6), 4.19 (s, 1H, H^{11}), 5.44 (d, ^3J = 7.3 Hz, 1H, H^4), 6.98 (d, ^3J = 7.2 Hz, 2H, H^{Ph}), 7.14 (t, ^3J = 7.2 Hz, 1H, H^{Ph}), 7.22 (t_{app}, ^3J = 7.2 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5 (CH_2^{Cy}), 25.5 (CH_2^{Cy}), 26.9 (CH_2^{Cy}), 29.1 (CH_2^{Cy}), 37.4 (NCH_3), 37.5 (NCH_3), 40.4 (C^1), 43.2 (C^6), 54.5 (OCH_3), 58.0 (C^5), 66.9 (CH^{Cy}), 69.1 (CH^{Cy}), 86.7 (C^{11}), 90.7 (C^3), 93.9 (C^4), 126.0 (CH^{Ph}), 126.9 (CH^{Ph}), 128.7 (CH^{Ph}), 142.9 (C^2 or C^{Ph}), 147.7 (C^2 or C^{Ph}). IR (neat): $\bar{\nu}$ (cm^{-1}) 1912 ($Mn(CO)_3$), 2007 ($Mn(CO)_3$). HRMS (ESI, positive mode): *m*/*z* 477.1576 ($M + H^+$, calcd for $C_{25}H_{30}MnN_2O_4$ 477.1581). $[\alpha]_D$ −99 (*c* 0.218, $CHCl_3$). (*R*,*R*,6*R*,2*pS*)-**15**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15–1.33 (m, 4H, H^{Cy}), 1.79–1.82 (m, 2H, H^{Cy}), 1.86–1.90 (m, 1H, H^{Cy}), 1.98–2.01 (m, 1H, H^{Cy}), 2.10 (s, 3H, NCH_3), 2.16–2.29 (m, 2H, H^{Cy}), 2.56 (s, 3H, NCH_3′), 3.39 (m, 2H, H^1 and H^5), 3.44 (s, 3H, OCH_3), 3.98 (t_{app}, ^3J = 6.1 Hz, 1H, H^6), 5.17 (s, 1H, H^{11}), 5.37 (d, ^3J = 7.6 Hz, 1H, H^4), 6.94 (d, ^3J = 7.3 Hz, 2H, H^{Ph}), 7.11 (t, ^3J = 7.3 Hz, 1H, H^{Ph}), 7.21 (t_{app}, ^3J = 7.3 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6 (CH_2^{Cy}), 24.6 (CH_2^{Cy}), 28.9 (CH_2^{Cy}), 29.9 (CH_2^{Cy}), 34.1 (NCH_3), 40.0 (C^1), 41.2 (NCH_3′), 41.6 (C^6), 54.6 (C^5 or OCH_3), 55.0 (C^5 or OCH_3), 66.4 (CH^{Cy}), 71.2 (CH^{Cy}), 80.7 (C^{11}), 87.9 (C^3), 93.3 (C^4), 125.2 (CH^{Ph}), 126.6 (CH^{Ph}), 128.5 (CH^{Ph}), 143.4 (C^2 or C^{Ph}), 147.8 (C^2 or C^{Ph}). IR (neat): $\bar{\nu}$ (cm^{-1}) 1911 ($Mn(CO)_3$), 2006 ($Mn(CO)_3$). HRMS (MALDI-TOF, positive mode): *m*/*z* 477.1489 ($M + H^+$, calcd for $C_{25}H_{30}MnN_2O_4$ 477.1586). $[\alpha]_D$ +60 (*c* 0.217, $CHCl_3$).

Preparation of Complexes (*R*,*R*,2*pR*)-16 and (*R*,*R*,2*pS*)-16. Complex **6** (0.110 g, 0.40 mmol, 1 equiv) and (*R*,*R*)-*N*,*N*′-dimethylcyclohexane-1,2-diamine (0.068 g, 0.48 mmol, 1.2 equiv) were stirred in distilled Et_2O (3 mL) at 30 °C in the presence of 4 Å molecular sieves for 7 h. After filtration through Celite, the solution was concentrated in vacuo and the mixture of the two diastereoisomers was isolated in quantitative yield. Separation of the diastereoisomeric mixture by preparative TLC on neutralized silica (eluent: EP/Et_2O/Et_3N 7/3/1) gave (*R*,*R*,2*pR*)-**16** (0.053 g, 0.133 mmol, 33%) with ≥95% de and (*R*,*R*,2*pS*)-**16** (0.040 g, 0.100 mmol, 25%) with 92% de. (*R*,*R*,2*pR*)-**16**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22–1.35 (m, 3H, H^{Cy}), 1.53 (m, 1H, H^{Cy}), 1.81–1.88 (m, 2H, H^{Cy}), 1.97–2.06 (m, 2H, H^{Cy}), 2.18 (m, 1H, H^{Cy}), 2.19 (d, ^2J = 12.6 Hz, 1H, H^{6exo}), 2.48 (s, 3H, NCH_3), 2.58 (s, 3H, NCH_3′), 2.72 (m, 1H, H^{6endo}), 2.79 (dd, ^3J = 6.0 Hz, ^4J = 1.2 Hz, 1H, H^1), 2.87 (t_{app}, ^3J = 6.7 Hz, 1H, H^5), 2.93 (m, 1H, H^{Cy}), 3.31 (s, 3H, OCH_3), 4.32 (s, 1H, H^7), 5.38 (d, ^3J = 7.3 Hz, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6 (CH_2^{Cy}), 25.5 (CH_2^{Cy}), 27.0 (CH_2^{Cy}), 27.6 (C^6), 29.5 (CH_2^{Cy}), 33.3 (C^1), 37.9 (NCH_3), 38.4 (NCH_3′), 51.3 (C^5), 54.3 (OCH_3), 67.0 (CH^{Cy}), 69.2 (CH^{Cy}), 87.3 (C^7), 91.0 (C^3), 94.8 (C^4), 143.6 (C^2). IR (neat): $\bar{\nu}$ (cm^{-1}) 1907 ($Mn(CO)_3$), 2004 ($Mn(CO)_3$). $[\alpha]_D$ −166 (*c* 0.214, $CHCl_3$). (*R*,*R*,2*pS*)-**16**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19–1.35 (m, 4H, H^{Cy}), 1.82–1.87 (m, 2H, H^{Cy}), 1.97–2.04 (m, 2H, H^{Cy}), 2.13 (d, ^2J = 12.6 Hz, 1H, H^{6exo}), 2.33 (m, 1H, H^{Cy}), 2.41 (m, 1H, H^{Cy}), 2.52 (s, 3H, NCH_3), 2.58 (s, 3H, NCH_3′), 2.74 (m, 1H, H^{6endo}), 2.80–2.84 (m, 2H, H^1 and H^5), 3.31 (s, 3H, OCH_3), 5.23 (s, 1H, H^7), 5.28 (d, ^3J = 7.3 Hz, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7 (CH_2^{Cy}), 24.8 (CH_2^{Cy}), 27.5 (C^6), 28.9 (CH_2^{Cy}), 30.1 (CH_2^{Cy}), 33.9 (C^1), 34.7 (NCH_3), 41.1 (NCH_3′), 49.1 (C^5), 54.3 (OCH_3), 66.4 (CH^{Cy}), 70.5 (CH^{Cy}), 81.5 (C^7), 87.7 (C^3), 94.1 (C^4), 143.2 (C^2). IR (neat): $\bar{\nu}$ (cm^{-1}) 1909 ($Mn(CO)_3$), 2005 ($Mn(CO)_3$). $[\alpha]_D$ +141 (*c* 0.210, $CHCl_3$).

Typical Procedure for the Hydrolysis of the Chiral Auxiliary. A solution of the aminalic complex in Et_2O (20 mL) and a 0.1 M HCl solution (10 mL) was vigorously shaken. After decantation and phase separation, the aqueous phase was extracted with Et_2O (10 mL). The combined organic phases were washed with water (10 mL), a saturated $NaHCO_3$ solution (10 mL), water (10 mL), and finally a saturated NaCl solution (10 mL). They were dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography on silica gel then gave the pure enantioenriched formyl-substituted complex.

(6*S*,2*pR*)-(η^5-3-Formyl-2-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ ((6*S*,2*pR*)-5). Following the above procedure, the hydrolysis of (*R*,*R*,6*S*,2*pR*)-**15** (0.129, 0.27 mmol, ≥95% de) gave (6*S*,2*pR*)-**5** (0.089 g, 0.25 mmol, ≥95% ee) in 93% yield. $[\alpha]_D$ +171 (*c* 0.210, $CHCl_3$).

(6*R*,2*pS*)-(η^5-3-Formyl-2-methoxy-6-phenylcyclohexadienyl)Mn(CO)$_3$ ((6*R*,2*pS*)-5). Following the same procedure, the hydrolysis of (*R*,*R*,6*R*,2*pS*)-**15** (0.126 g, 0.26 mmol, 85% de) gave (6*R*,2*pS*)-**5** (0.092 g, 0.26 mmol, 85% ee) in 99% yield. $[\alpha]_D$ −145 (*c* 0.230, $CHCl_3$).

(2*pR*)-(η^5-3-Formyl-2-methoxycyclohexadienyl)Mn(CO)$_3$ ((2*pR*)-6). Following the same procedure, the hydrolysis of (*R*,*R*,2*pR*)-**16** (0.041 g, 0.103mmol, ≥95% de) gave (2*pR*)-**6** (0.028 g, 0.101 mmol, ≥95% ee) in 98% yield. $[\alpha]_D$ +132 (*c* 0.216, $CHCl_3$).

(2*pS*)-(η^5-3-Formyl-2-methoxycyclohexadienyl)Mn(CO)((2*pS*)-6). Following the same procedure, the hydrolysis of (*R*,*R*,2*pS*)-**16** (0.035 g, 0.087 mmol, 92% de) gave (2*pS*)-**6** (0.024 g, 0.087 mmol, 92% ee). $[\alpha]_D$ −124 (*c* 0.206, $CHCl_3$).

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Supporting Information Available: ^{13}C NMR spectra of compounds **5**–**8**, **11**, **12**, and **14**–**16** and CIF files giving crystallographic data for complexes **7b**, **13a**, (*R*,*R*,6*R*,1*pS*)-**14**, and (*R*,*R*,6*S*,2*pR*)-**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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