Chiral “Metallo-Spiralenes”: Helical Molecules Conformationally Stabilised by an Organometallic Scaffold**

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Abstract: The synthesis of a series of chiral cyclomanganated 2-[(η^6-phenyl)-$Cr(CO)_3$]pyridine complexes derived from (−)-β-pinene enables, by a “spirogenic transformation”, the preparation of four different chiral helical heterobimetallic *syn*-facial complexes or Cr^0/Mn^I–spiralenes, among which two possess a right-handed *P* molecular helicity and two other a left-handed *M* one. These organometallic helical molecules are synthesised by applying two different methods to the chiral cyclomanganated (η^6-arene)tricarbonylchromium substrates. The first method is the so-called “Fischer route” which involves a sequential addition of PhLi and MeOTf. The second method based on reaction of the cyclomanganated complex with diphenyldiazomethane which has been tested on achiral bimetallic substrates is a reasonable neutral alternative to the “Fischer methodology” for the synthesis of Cr^0/Mn^I–spiralenes. The crystal structure of one of these heterobimetallic chiral helical compounds serves as a starting point in the configurational and structural assessment of the synthesised chiral (η^6-arene)tricarbonylchromium complexes. Application of the “Fischer route” to a cyclomanganated chiral 2-phenylpyridine generates a single chiral η^3-benzylic complex—or Mn^I–spiralene—bearing a left-handed *M* helicity which has been characterized by X-ray diffraction analysis. Circular dichroic spectroscopic measurements underline the predominant contribution of the chiral and chirally induced aromatic chromophores to the sign of the Cotton effects and confirm the helical configurations of the considered heterobimetallic species.

Keywords: arene complexes · chromium · helical structures · manganese · spirogenic reaction

Introduction

Organometallic chemistry increasingly contributes to material sciences by providing physico-chemists with a wide variety of new substrates.[1] Among the wide panel of materials that are of interest is the class of molecules/molecular assemblies that possess helical shapes. Chiral molecular helicity results on the one hand from an ordered arrangement and combination in the space of molecular units that bear either “point” and/or “planar” chirality[2] and on the other hand from a conformational stabilization through low-energy interactions such as H-bonding,[3] CH−π[4] and π−π[5] interactions, and high barriers to changes of conformation. The most popular examples are proteins, and DNA and RNA molecules. From a synthetic point of view, helical molecular assemblies can be formed by several strategies among which two have been extensively applied. The first one entails a careful tailoring of fused aromatic rings to generate pure organic helical architectures of which aromatic derivatives such as helicenes,[6] “geländer” molecules,[7] and cyclophanes[8] provide the most representative examples. The second synthetic approach takes advantage of the numerous modes of coordination of transition metals and applies them to the elaboration of polymetallic helicates in which helicity stems from an ordered arrangement of polydentate chelating ligands.[9] This latter approach ensures a higher conformational stability to the helical structures than in organic helicenes which may undergo thermally promoted isomerization and, in the case of chiral examples, racemization.[10]

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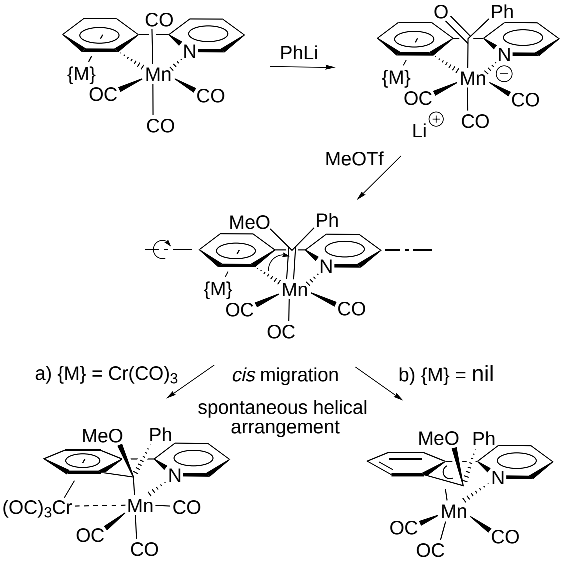
[**] List of abbreviations used throughout this paper: phenyllithium, PhLi; methyl trifluoromethylsulfonate, MeOTf; 1.2-dimethoxyethane, DME; Cotton effect, CE; circular dichroism, CD.

Our interest in helical molecules arose from some of our recent results.[11] In our continuing efforts to uncover new chemical properties of organometallic compounds, we recently discovered the unprecedented generation of heterobimetallic helical structures by a selective C–C bond-forming "spirogenic" [12] reaction. The synthesis of these helical *syn*-facial heterobimetallic (η^6-aryl)benzyl[11a] ($M = Cr(CO)_3$, path (a), Scheme 1) and mononuclear η^3-benzylic complexes[11b] (M = nil, path (b), Scheme 1) was performed by applying the "E. O. Fischer methodology"[13] to cyclomanganated (η^6-arene)tricarbonylchromium complexes[14] and aromatic compounds,[15] respectively (Scheme 1). The latter consists of two elementary steps:



Scheme 1. Synthesis of helical *syn*-facial heterobimetallic (η^6-aryl)benzyl and mononuclear η^3-benzylic complexes.

1) nucleophilic addition at a CO ligand of the $Mn(CO)_4$ moiety;[16]
2) O-alkylation of the acylmanganate species with a hard electrophilic reagent. In the second step, the anionic intermediate is converted upon O-alkylation into a transient electrophilic carbene species that evolves by *cis*-migration toward the final *syn*-facial heterobimetallic (η^6-aryl)benzyl species ($M = Cr(CO)_3$, path (a), Scheme 1) or η^3-benzylic complex (M = nil, path (b), Scheme 1). In all the cases that we addressed so far, the aryl group originating from the aryllithium reagent spontaneously placed itself in the product above the heterocyclic ring, hence providing a helical shape to the molecule.[11]

Although many questions still remain to be answered with regard to the origin of the stereoselectivity of this "spirogenic" reaction, our recent results introduced a new organometallic methodology for the elaboration of conformationally stable helical three-dimensional structures in which the $Mn(CO)_3$ entity constitutes a necessary molecular scaffold. A pertinent metaphore applied to our system would be to identify the bimetallic Cr^0,Mn^I-centred unit and the mononuclear $Mn(CO)_3$ moiety with the supporting core of an "organic molecular spiral staircase" (Figure 1). Such a familly of complexes being consequently named under the generic terms of binucleo- and mononucleo-"spiralenes"[17] (Figure 1). Furthermore, we propose to name the compounds that we are interested in as "Cr^0/Mn^I–spiralenes" as the organic spiroidal skeleton is maintained due to the presence of a composite chromium–manganese "pillar".[11a] This trivial terminology may likely be applied to the related mononuclear helical η^3-benzylic manganese(I) complexes[11b] that could be refered to as "Mn^I–spiralenes"(Figure 1).

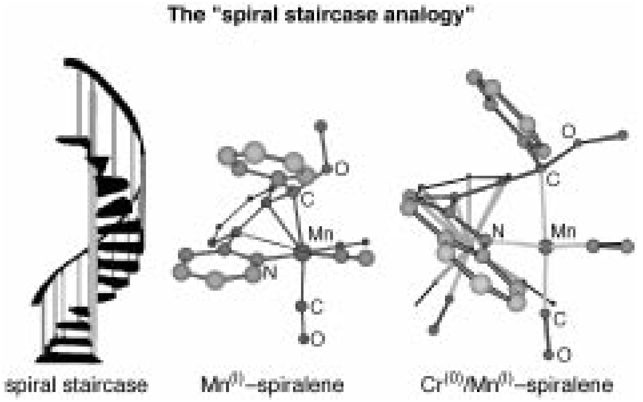
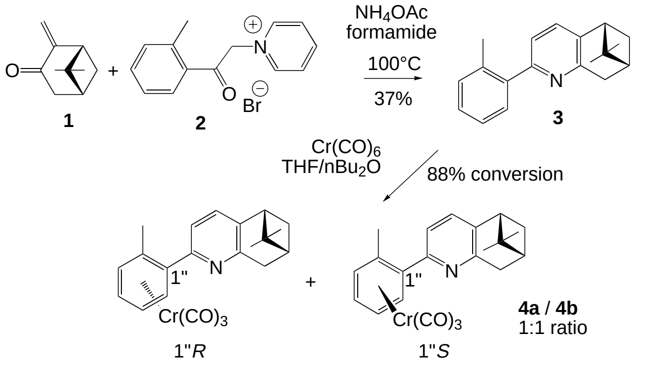


Figure 1. The geometrical analogy between two "spiralenes" (right) and a "spiral staircase"(left). The manganese(I) centre sustains the helical molecular arrangement in a fashion similar to that of a pillar (in light grey) in a spiral staircase. In the figure representing an example of a Cr^0/Mn^I–spiralene, the shadowed $Cr(CO)_3$ tripod is located in the background, occulted by the quinolinyl fragment of the molecule.

We were very much interested in investigating the synthesis of a chiral series of helical systems—or spiralenes—by exploiting the potential offered by a familly of recently developed and synthetically accessible chiral 2-arylpyridines. Herein, we describe the synthesis of a series of chiral cyclomanganated 2-[(η^6-phenyl)$Cr(CO)_3$]pyridine complexes derived from (−)-β-pinene which allowed us to prepare, by two distinct methods, four different chiral Cr^0/Mn^I–spiralenes among which two examples possess right-handed *P* helicity and two others left-handed *M* helicity, respectively. We show that the thermally promoted reaction of 1,1-diphenyldiazomethane with cyclomanganated compounds is a reasonable neutral alternative to the "Fischer methodology" for the synthesis of Cr^0/Mn^I–spiralenes. The crystal structure of one of these chiral helical compounds serves as a starting point in the configurational and structural assessment of the compounds described herein. We also demonstrate that the steric bulk generated by the pinene fragment in a cyclomanganated chiral 2-phenylpyridine provides stereocontrol over the nucleophilic attack of PhLi that permits the diastereoselective synthesis of a single chiral η^3-benzylic complex (or Mn^I–spiralene) bearing left-handed molecular *M* helicity.

Results and Discussion

Synthesis of the chiral 2-phenylpyridine 3 by application of the Kröhnke condensation reaction: In recent reports, several authors have described the preparations of chiral bipyridine as well as 2-arylpyridine derivatives that are based on the use of chiral cyclic terpenes.[18] These heterocyclic chiral compounds have been mainly applied to investigations dealing with the photophysical and structural properties of the corresponding transition metal complexes and helicates,[19] and used as chiral auxiliaries in metal-mediated catalysis.[20] Our attention was mostly attracted by the elegant application of the Kröhnke condensation of chiral β-unsaturated ketones to the synthesis of optically active arylpyridines.[21] Our quest for an adequate candidate for the conception of chiral Cr^0/Mn^I – spiralenes led us to choose the chiral arylpyridine **3** as a first synthetic target, for it could be readily synthesised from (+)-pinocarvone (**1**) (obtained from commercial chiral (−)-β-pinene by SeO_2 oxidation[22]) and the pyridinium salt **2** (obtained from 2-methylacetophenone by α-bromination and subsequent pyridination[23]) in the presence of $NH_4^+OAc^-$ (Scheme 2). The reaction between **1** and **2** was carried out in formamide at 100 °C under conditions that were optimized by adjusting the concentration of the reagents and the reaction time. Our adapted procedure allowed us to recover ligand **3** in 37 % yield after purification (Scheme 2).



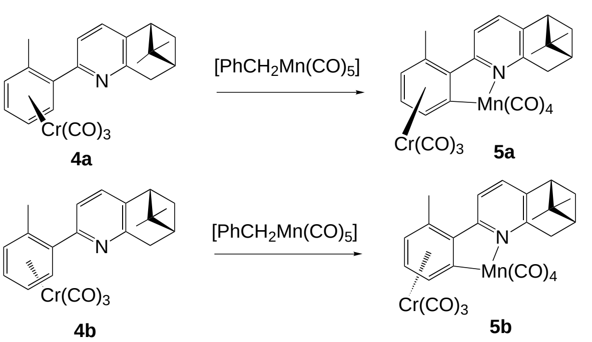
Scheme 2. Synthesis of **4a, b**.

Synthesis of chiral 2-{(η^6-phenyl)tricarbonylchromium(0)}pyridine derivatives 4a,b: Compound **3** was then submitted to the thermally promoted reaction with $Cr(CO)_6$ to generate the two diastereoisomeric (η^6-arene)tricarbonylchromium complexes **4a** and **4b**. Notably, the presence of a methyl group at the *ortho* position with respect to the pyridyl substituent confers metallocenic planar asymmetry to the chromium-coordinated arene ligand thus offering solely two diastereomeric products.[24a] The reaction between **3** and $Cr(CO)_6$ afforded a 1:1 oily mixture of **4a** and **4b** with 88 % overall conversion (Scheme 2).

The separation of the latter two diastereomers could not be carried out by conventional chromatography over SiO_2 gel, for the two components of the mixture having very close rate factors. Better results were obtained by repeated successive recrystallizations of the mixture that allowed us to recover 81 % of the original content in **4a**, while only 27 % of compound **4b** were isolated in pure form. Compounds **4a, b** were characterized by polarimetry and displayed rotatory $[\alpha]_D$ values at 25 °C opposite in sign. Complexes **4a, b** were determined to be dextrorotatory and levorotatory, respectively, at 589 nm (cf. Experimental Section). This change of chiroptical behaviour as compared to **3** suggests, in good accord with Drude's formalism,[24c] that the chiral [(η^6-aryl)$Cr(CO)_3$] chromophores in **4a**, **b** provide a predominant contribution to the optical rotatory power. This significant contribution combined to that of the chiral pinene fragment presumably determines the sign of the resulting rotatory optical power at the sodium D-line[24b] owing to the proximity in wavelength of related metal-to-ligand charge transfer absorption bands.

The proton NMR spectra of **4a, b** showed no major differences that could have allowed an unambiguous structural identification. In addition, neither diastereoisomers gave suitable mono-crystals that would have allowed an early determination by X-ray diffraction analysis of the absolute configurations at aromatic carbons of the planar chiral arene ring.

Cyclomanganation of chiral 2-{(η^6-phenyl)tricarbonylchromium(0)}pyridine derivatives 4a, b: With these two compounds in our hands we proceeded to the next step, that was the selective cyclomanganation of **4a** and **4b**, separately, by a thermally promoted reaction with $[Mn(CH_2Ph)(CO)_5]$. The experiments were carried out on both compounds in refluxing heptane and afforded complexes **5a** and **5b** with yields of 81 % and 62 %, respectively (Scheme 3). Analytical data gave satisfactory results in both cases. However, attempts to generate single crystals that would have allowed an unequivocal identification of the structures of the two bimetallic products failed again. The values of $[\alpha]_D$ for the two compounds **5a** and **5b** were determined as being close in absolute value and again opposite in sign. Compounds **5a** and **5b** displayed dextrorotatory and levorotatory characters, respectively, at 589 nm.

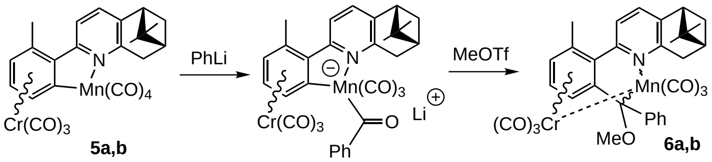


Scheme 3. Synthesis of **5a, b**.

Application of the "Fischer methodology" to the binuclear complexes 5a and 5b; X-ray crystal structural determination of the product 6a: Complex **5a** was treated with a stoichiometric amount of PhLi at −50 °C. The resulting mixture was kept at that temperature to avoid possible deprotonations of the cyclic aliphatic part of the molecule (vide infra) and was subsequently treated with the alkylating agent MeOTf (Scheme 4). Chromatographic separation afforded **6a** in satisfactory yields. A sample of the latter was successfully crystallized from a mixture of CH_2Cl_2 and hexane.

Table 1. Acquisition and processing data for compounds **6a**, **8** and **15**.

	6a	**8**	**15**
formula	$C_{33}H_{28}NO_7CrMn$	$2(C_{35}H_{23}NO_6PCrMn)\cdot CH_2Cl_2$	$C_{29}H_{26}NO_4Mn$
M_r	657.53	1467.90	507.47
crystal system	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P12_1/c1$	$P2_12_12_1$
a [Å]	8.8350(3)	11.991(2)	8.7457(2)
b [Å]	17.8980(3)	13.232(1)	15.259(1)
c [Å]	18.6730(6)	19.955(2)	18.6796(7)
β [°]		95.89(1)	
V [Å^3]	2952.7(2)	3149(1)	2492.9(3)
Z	4	2	4
colour	red	orange	orange
crystal size [mm]	0.16 × 0.14 × 0.08	0.35 × 0.35 × 0.30	0.20 × 0.12 × 0.10
ρ_{calcd} [g cm^{-3}]	1.48	1.67	1.35
F_{000}	1352	1640	1056
μ [mm^{-1}]	0.846	0.910	0.564
T [K]	173	173	173
λ [Å]	0.71073	0.71073	0.71073
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
diffractometer	KappaCCD	MACH3 Nonius	KappaCCD
scan mode	ϕ scans	$\theta/2\theta$	ϕ scans
$h/k/l$ limits	$-12,12/-19,19/-26,26$	$-14,14/0,16/0,24$	$-9,11/-21,15/-19,26$
θ limits [°]	2.5/32.45	2.5/26.29	2.5/32.54
data measured	20414	6852	19396
data with $I > 3\sigma(I)$	3429	4787	12613
weighting scheme	$4F_o^2/(\sigma^2(F_o^2)+0.0064F_o^4)$	$F_o^2/(\sigma^2(F_o^2)+0.0049F_o^4)$	$4F_o^2/(\sigma^2(F_o^2)+0.0016F_o^4)$
number of variables	388	430	316
R	0.038	0.029	0.037
R_w	0.053	0.043	0.045
GOF	1.036	1.006	1.043
largest peak in final difference [e Å^{-3}]	0.357	0.321	0.840



Scheme 4. Synthesis of **6a, b**.

An orthorhombic single crystal of this bright red chiral compound was analyzed by X-ray diffraction to crystallize in the noncentrosymmetric space group $P2_12_12_1$ without any solvation molecule. Acquisition and calculation data are reported in Table 1. Selected interatomic bond lengths and angles are reported in Table 2.

An ORTEP drawing of the molecular structure of **6a** is given in Figure 2. The helical system formed by C12-C11-C4-C5-C19-N1-Mn affords a left-handed Λ-type of helix that extends at the molecular level to a M-type helical arrangement.[25] The molecular structure of **6a** possesses strong similarities with that of racemic compounds that we previously reported. The intermetallic Cr–Mn distance of 3.010(4) Å remains in the range of values reported previously.[11a] The coordinated aromatic ring undergoes a slight distortion at C4 and C5 with a torsional angle C11-C4-C5-C19 amounting to 15° and a slight folding of the arene ligand represented by an interplanar angle of 10° between planes C5-

Table 2. Selected interatomic distances [Å] and angles [°] for compound **6a**.

Mn–Cr	3.010(4)	C11–O4	1.432(4)
Cr–C5	2.235(4)	Cr–C6	2.229(4)
Cr–C7	2.186(4)	Cr–C8	2.228(4)
Cr–C9	2.274(4)	Mn–C11	2.146(4)
Mn–N	2.111(3)	C4–C11	1.455(5)
C6–C10	1.508(5)	C11–C12	1.519(5)
C1-Cr-C2	81.6(2)	C1-Cr-C3	83.6(2)
C11-Mn-N	83.3(1)	C11-Mn-C32	176.5(2)
C2-Cr-C3	94.0(2)	C5-C4-C9	116.8(3)
C4-C5-C6	121.4(3)	C5-C6-C7	117.9(3)
C6-C7-C8	121.5(3)	C4-C9-C8	120.7(3)

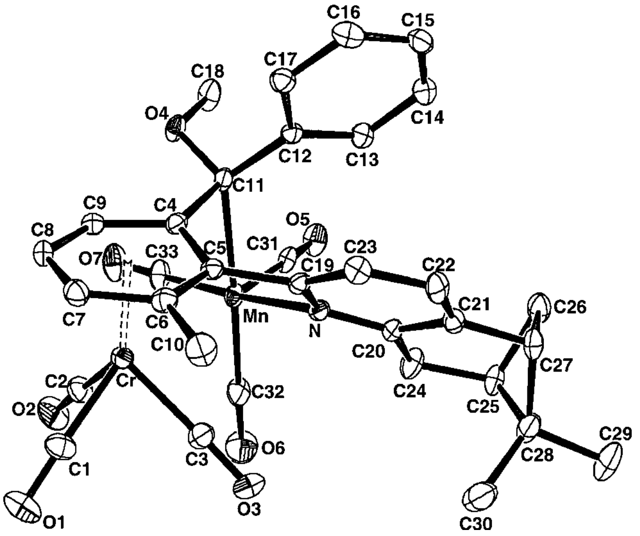


Figure 2. ORTEP diagram with atom-numbering scheme of the molecular structure of **6a**. Hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at the 30% probability level.

C6-C7-C8-C9 and C5-C4-C9. A significant π-stacking interaction between the pyridyl and the phenyl groups is confirmed by particularly short π–π distances and a corresponding interplanar angle of 25°. These structural features are summarized in Figure 3.

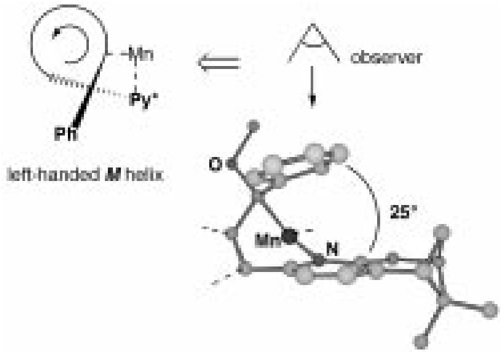


Figure 3. The helical/spiroidal intramolecular arrangement in **6a**. A part of the [(η^6-arene)Cr(CO)$_3$] fragment has been omitted for clarity. The scheme on the left side represents a schematic view from the top of the helical geometrical arrangement of the relevant aromatic rings.

The spacial arrangement of the chiral fragment originating from (−)-β-pinene allowed us to firmly identify the structures of the pairs of diastereomers **4a** and **4b**, and **5a** and **5b**. The dimethylmethylene bridge of the aliphatic part of **6a** is located on the same side as the Cr(CO)$_3$ group. In the reaction that leads to **6a** starting from **5a**, the attack of the nucleophile PhLi takes place at the axial CO group located *trans* with respect to the chromium tripod.[26] Hence, we may deduce that in **5a** the Me$_2$C bridge and the Cr(CO)$_3$ group are cofacial. Consequently, position 1 at the (η^6-aryl) group in **4a** bears an *S* absolute configuration (Scheme 2). Reciprocally, in **4b** the configuration of the same aromatic carbon is determined to be *R* (Scheme 2).

A reaction that was performed under the same conditions and with the same stoichiometry between **5b** and PhLi afforded **6b** with 66 % yield after chromatographic purification. Spectroscopic investigations confirmed the existence of an overall helical shape of the plausible right-handed *P*-type. The ^{1}H NMR spectrum of **6b** revealed the signals generated by the benzylic carbon-attached phenyl group as a series of two and three well-resolved doublets and triplets, respectively. This indicated clearly a slowed rotational motion of the considered phenyl group and consequently its very probable location above the pyridyl fragment.[11]

The main structural differences between **6a** and **6b** could be confirmed by analyzing and comparing their ^{1}H NMR spectra. The ^{1}H NMR signal corresponding to the *endo* methyl group of the Me$_2$C bridge in **6a** is shielded by a value of $\delta_{6b} - \delta_{6a} = 0.4$ with respect to that in **6b**. By observing the orientation of the pinene fragment in the structure of **6a** one may notice that the *endo* Me group points toward the Cr(CO)$_3$ moiety, whereas in **6b** it must be located in the vicinity of the phenyl group that eclipses the pyridyl fragment. Therefore, the relative shift in frequency observed here might be the consequence of a major shielding effect of the magnetically anisotropic Cr(CO)$_3$ entity. In addition, the *endo* proton of the CH$_2$ bridge which is in the close vicinity with the phenyl group in **6a** resonates at $\delta = 1.14$, while in **6b** it is detected at $\delta = 0.75$. The protons of the coordinated arene ligand appear at roughly the same chemical shift values in both **6a** and **6b** at $\delta = 4.4$ (d), 5.1(t) and 6.2 (d). Significant is also the upfield shift of the pyridyl group proton resonances of a value of about $\delta = 1$ with respect to values obtained for the uncoordinated ligand **3**.

A ^{13}C NMR spectrum measured at 253 K with a sample of **6a** exhibited four signals in the metal–CO resonance region, among which three could be easily identified as those generated by the static CO ligands of the Mn(CO)$_3$ fragment, while the remaining broad one was assigned undoubtedly to the slowed Cr(CO)$_3$ rotor. A different pattern could be measured for a sample of **6b** which was analyzed at 273 K. At this temperature we detected two sets of resonances that differed by their line shape: a first set of three sharp singlets at $\delta = 219.9$, 230.4, 231.8 was identified as being produced by the static *fac*-Mn(CO)$_3$ moiety and a second set of broad signals at $\delta = 231.1$, 235.5, 237.0 was identified as being produced by the slackened Cr(CO)$_3$ rotor.[27] We have recently determined the barrier to rotation of a ^{13}C-enriched Cr(CO)$_3$ moiety of a similar binuclear complex to be in the range of 15 kcal mol^{-1} at 253 K.[27b] Both complexes **6a** and **6b** displayed a strong optical rotatory strength with values of $[\alpha]_D$ amouting to +728 and −906, respectively.

For the class of chiral cyclomanganated complexes that we dealt with during this study, we were interested in developing an alternative "neutral" route for the generation of the necessary metal carbene transient species. The main motivation for this was to avoid any interaction of the reactants with adjacent chiral aliphatic parts of the *C*,*N* chelating ligand. Indeed, the main problem that might have arisen in the application of the "Fischer methodology" to the cyclomanganated chiral aromatic compounds we describe here, would have been the undesired deprotonation of the chiral aliphatic part by a fraction of unreacted organolithium reagent, as it has been reported for analogous ligands.[28] To circumvent this problem we chose a reasonable solution from the numerous established methodologies leading to the synthesis of metal carbene complexes L$_n$M=C(R)(R′).

Thermally promoted reactions of cyclomanganated and -rhenated [(η^6-arene)Cr(CO)$_3$] complexes with N$_2$=CPh$_2$; insertion of a carbene species in the C$_{Ar}$–M (M = Re, Mn) bond: It is well established that labile and electron-deficient transition metal complexes may react with diazoalkane reagents N$_2$=C(R)(R′) to form new metal carbene complexes with concomitant release of dinitrogen.[29] This is a common route used for the synthesis of metal carbene complexes and in systems devised for the metal-mediated cyclopropanation of olefins.[30] From our standpoint, the introduction of a carbene species starting from a diazoalkane would offer the advantage of requiring absolutely neutral conditions. The creation of the necessary vacant coordination site on Mn(CO)$_4$ or Re(CO)$_4$ moieties chelated by C,N ligands could be secured mainly by three methods: photolytic decarbonylation,[31] oxidative decarbonylation by reaction with tertiary amine oxides,[32] and thermally promoted decarbonylation.[33]

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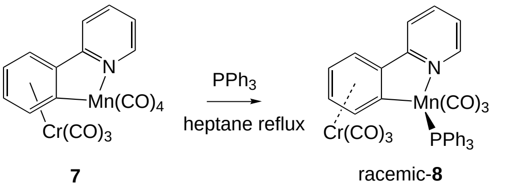
However, the first two aforementioned methods were not suitable for the class of bimetallic substrates that we studied, since they are not selective and may have initiated an unpredictable amount of decomposition as a result of undiscriminated decarbonylations at Cr or Mn centres. The last of these three methods, namely thermal decarbonylation, happened in fact to be promising.

In an experiment intended to test the feasibility of the thermally promoted mono-decarbonylation of cyclomanganated compounds, PPh_3 and complex **7** were treated in refluxing heptane [Eq. (1)]. The reaction was undertaken under a continuous flow of argon and it cleanly afforded the new compound **8**. IR spectroscopic measurements of a solution of the latter in CH_2Cl_2 suggested a net change of coordination environment around the Mn centre and the presence of two different facial metal-tricarbonyl moieties. Indeed, two different sets of typical $A_1 + E$ absorption bands at 2014 and 1898 cm^{-1} and at 1948 and 1873 cm^{-1} could be assigned to the $Mn(CO)_3$ moiety and to the $Cr(CO)_3$ moiety, respectively. Compound **8** was isolated, crystallized and structurally characterized by a single-crystal X-ray diffraction analysis. The acquisition data are compiled in Table 1. Selected interatomic distances and angles are given in Table 3.



(1)

Table 3. Selected interatomic distances [Å] and angles [°] for compound **8**.

Cr–C4	2.220(2)	Cr–C5	2.316(2)
Cr–C6	2.224(2)	Cr–C7	2.223(2)
Cr–C8	2.226(2)	Cr–C9	2.225(2)
Mn–C5	2.037(2)	Mn–N	2.075(2)
Mn–C15	1.818(2)	Mn–C16	1.833(2)
Mn–C17	1.792(2)	Mn–P	2.3442(6)
C1-Cr-C2	86.6(1)	C1-Cr-C3	90.4(1)
C2-Cr-C3	87.4(1)	C5-Mn-P	88.39(6)
N-Mn-C15	89.32(9)	N-Mn-P	94.43(5)
C5-C4-C9	122.6(2)	C4-C5-C6	115.2(2)
C5-C6-C7	122.6(2)	C6-C7-C8	120.1(2)
C7-C8-C9	120.1(2)	C4-C9-C8	119.0(2)

Figure 4 displays an ORTEP drawing of the molecular structure of compound **8**. From this structure it can be concluded that the relatively bulky PPh_3 ligand has displaced selectively the less sterically hindered axial CO ligand, for example, the one located *trans* with respect to $Cr(CO)_3$. The structural trends of compound **8** are similar to those of analogous examples[34] (Figure 4).

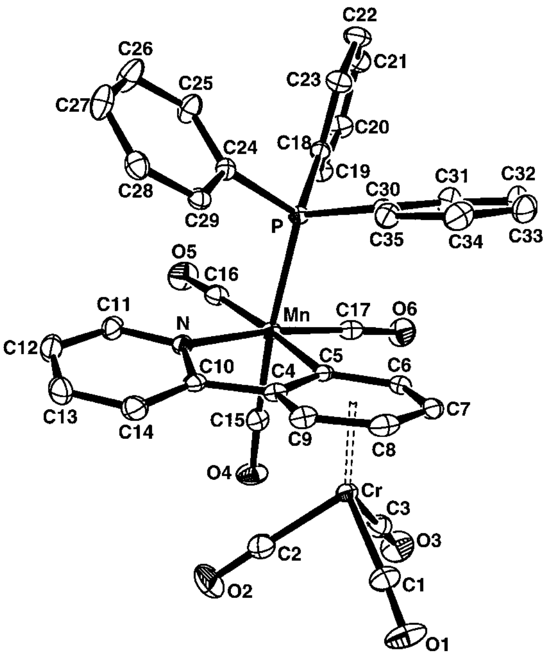
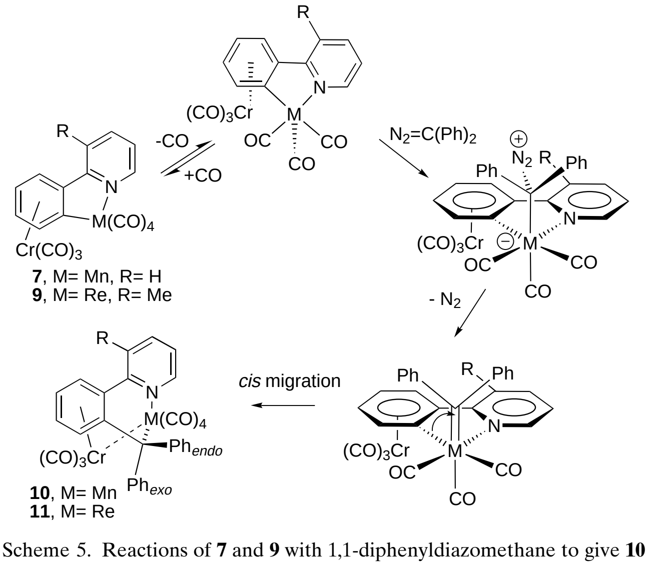


Figure 4. ORTEP diagram with atom-numbering scheme of the molecular structure of **8**. Hydrogen atoms and a molecule of CH_2Cl_2 have been omitted for clarity. The ellipsoids are drawn at the 40% probability level.

The ready access to **8** upon thermal treatment of **7** in presence of a two-electron σ-donor ligand such as PPh_3 prompted us to attempt a similar experiment with a diazoalkane reagent in order to generate in situ a transient metal carbene species that would eventually evolve by *cis* migration of the coordinated arene ring towards the formation of a new “binucleospiralene”.

This idea was tested on cyclomanganated and cyclorhenated $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes **7** and **9**, which were both treated with 1,1-diphenyldiazomethane (Scheme 5). Separate treatment of **7** and **9** with a large excess of $N_2{=}CPh_2$ yielded two products **10** and **11**, respectively, that could be unambiguously identified from their spectroscopic properties as belonging to the class of *syn*-facial heterobimetallic Cr^0/Mn^I-spiralenes that we reported previously [11a] (Scheme 5). The proton NMR spectra of **10** and **11** suggested that among the two phenyl groups attached to the benzylic carbon atom and within the time scale of the NMR spectroscopy, the one

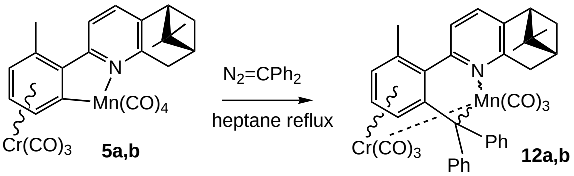


Scheme 5. Reactions of **7** and **9** with 1,1-diphenyldiazomethane to give **10** and **11**, respectively.

located above the pyridyl group (Ph_{endo}) rotates much slower than its neighbour (Ph_{exo}). A two-dimensional $^1H-^1H$ COSY experiment carried out with **10** in C_6D_6 allowed the detailed assignment of the ^1H NMR spectrum. Indeed, five signals located at $\delta = 6.49$ (t), 6.57 (t), 6.69 (t), 7.08 (d) and 8.39 (d) could be attributed to the protons of the *endo* phenyl group. The three other signals at $\delta = 6.88$ (t), 7.10 (t) and 8.01 (d) could be attributed to the protons of the freely rotating *exo* phenyl group. A similar assignment was accomplished for **11**. Interestingly, three out of the four proton resonances of the $[(\eta^6\text{-aryl})Cr(CO)_3]$ moiety resonated, in both **10** and **11**, at significantly high field at $\delta = 3.05$, 3.18 and 3.65, whereas similar protons are usually expected to resonate at around $\delta = 4$.[35] Such a shielding might be explained by the magnetic anisotropy of the *exo*-phenyl group of the Ph_2C fragment. The IR spectra of complexes **10** and **11** presented similar trends. They both displayed in CH_2Cl_2 two distinct sets of intense absorption bands related to the A_1 and E vibration modes of the $M(CO)_3$ units.

These successful attempts to introduce a carbene species on cyclomanganated complexes by using diazoalkanes strengthen the mechanistic hypothesis of the intervention of a metal carbene transient species in the process leading to *syn*-facial heterobimetallic helical complexes (Scheme 5). They also offer a new synthetic route towards a rhenium(I) series of "binucleospiralenes" that might be of interest in the scope of photophysical investigations.[36]

Synthesis of Cr^0/Mn^I-spiralenes 12a, b by reaction of the binuclear complexes 5a, b with $N_2{=}CPh_2$: Application of the thermally promoted insertion of a "Ph_2C:" carbene fragment in the C_{Ar}–Mn bond of compounds **5a** and **5b** was carried out under conditions similar to those described previously for the synthesis of **10** and **11**. The two products, that is complexes **12a** and **12b**, were isolated in satisfactory yields after workup and subsequent chromatographic purification [Eq. (2)].

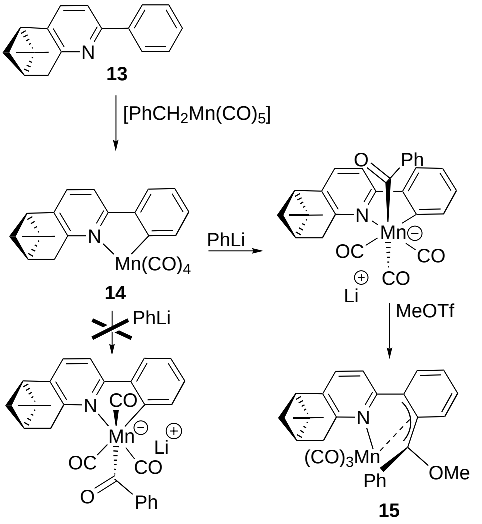


(2)

The proton NMR spectra of compounds **12a** and **12b** presented in the resonance region of the pinene fragment very similar trends to those noticed previously for **6a** and **6b**. The ^{13}C NMR spectrum of **12b** indicated that the steric interaction between the two metals are much stronger than in **6b**. At room temperature, the $Cr(CO)_3$ tripod of **12b** generated three distinct broad signals at $\delta = 232.0$, 235.2 and 238.2 suggesting that the barrier to rotation of the Cr-centred rotor is higher in **12b** than in **6b**. It must be remembered that the Me_2C bridging fragment of the aliphatic part in both **6b** and **12b** is likely to point toward the C_{benzyl}-attached phenyl group. The thus induced steric hindrance possibly causes a twisting of the pyridyl group that tilts the manganese centre toward the $Cr(CO)_3$ unit. This distortion consequently might alter the rotational motion of $Cr(CO)_3$ by further slackening it.

The "Fischer methodology" applied to a substrate exempt of planar metallocenic chirality; the case of the mononuclear complex 14: We have shown that the nucleophilic attack of organolithium reagents takes place with total selectivity on the axial, Mn-bonded CO ligand located *trans* to the $Cr(CO)_3$ moiety of a cyclomanganated $[(\eta^6\text{-arene})Cr(CO)_3]$ complex. This selectivity indicates that a discrimination between two apparently chemically equivalent axial CO ligands is particularly efficient when the stereocontrol has a pure steric origin. We decided to check this concept with the chiral mononuclear cyclomanganated complex **14**, in which we expected that the presence of the bulky dimethylmethylene bridge could induce sufficient stereocontrol over the nucleophilic attack of PhLi to yield a chiral helical η^3-benzylic manganese(I) complex or Mn^I-spiralene.

Complex **14** was synthesised by cyclomanganation of ligand **13** in 70% yield. Compound **14** was then treated with PhLi and MeOTf by following the procedure that we established previously for the synthesis of η^3-benzylic manganese(I)[11b] (Scheme 6). Our experiment afforded a crude mixture of which only one stable orange-yellow product, **15**, was isolated with 68% yield (calculated with respect to **14**) (Scheme 6). Compound **15** was crystallized and structurally characterized by an X-ray diffraction analysis (Figure 5). Acquisition and calculation data are presented in Table 1. Selected interatomic distances and angles are gathered in Table 4. This complex crystallizes, like **6a**, in the noncentrosymmetric space group $P2_12_12_1$ without molecules of solvation. The molecular structure of compound **15** shows a typical helical arrangement of the *M*-type, and the structural features resemble those encountered in the first case of chelated racemic η^3-benzylic complex we reported.[11b] The Mn atom resides in a quasi-octahedral coordination configuration, wherein atoms N, C1, C2, C3, C22 occupy ideally the vertices; atom C16 is located at an anomalous sixth coordination site. A dissymmetric η^3-bonding mode[11b] between the metal centre and the organic ligand can be deduced from the analysis of the distances between Mn and C16, C17 and C22 (Table 4). The phenyl



Scheme 6. Synthesis of **15**.

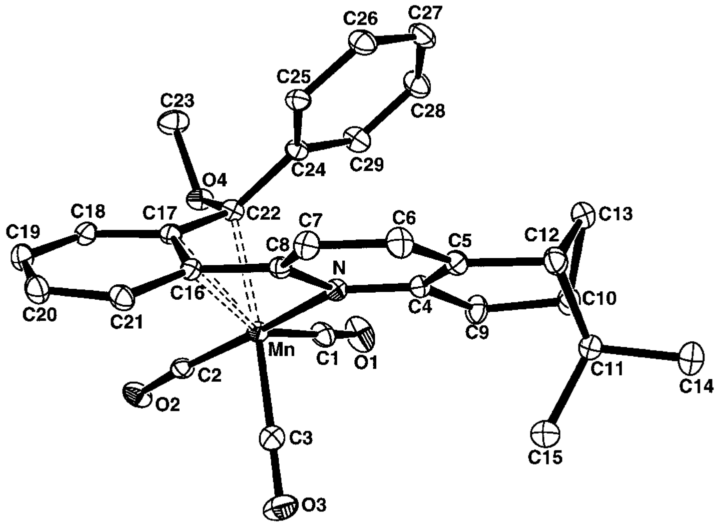


Figure 5. ORTEP diagram with atom-numbering scheme of the molecular structure of **15**. Hydrogen atoms have been omitted for clarity. The ellipsoids are drawn at the 30% probability level.

Table 4. Selected interatomic distances [Å] and angles [°] for compound **15**.

Mn–N	2.042(1)	Mn–C17	2.238(1)
Mn–C22	2.101(2)	C16–C17	1.440(2)
C16–C21	1.430(2)	C17–C18	1.436(2)
C17–C22	1.471(2)	C18–C19	1.359(2)
C19–C20	1.405(3)	C20–C21	1.360(2)
C22–O4	1.423(2)	C22–C24	1.504(2)
O4–C23	1.445(2)		
C1-Mn-C2	88.26(7)	C1-Mn-C3	98.26(8)
C1-Mn-N	100.89(6)	N-Mn-C22	85.06(6)
C17-Mn-C22	39.47(6)	Mn-C22-C17	75.29(9)
C17-C22-O4	113.2(1)	C17-C22-C24	121.1(1)
O4-C22-C24	112.1(1)		

group attached to the benzylic carbon forms with the pyridyl moiety an interplanar angle of about 37°. Interatomic distances between planes C25-C24-C29 and C4-N-C8-C7 are equal or less than 3.5 ± 0.1 Å. The aryl–pyridine system is twisted by $-46°$ (the torsional angle C17-C16-C8-N), presumably to minimize steric interactions between C13 and the phenyl group. As in the first example of Mn^I–spiralene,[11b] the aromatic ring coordinated to the Mn atom undergoes a slight distortion around the junctions at C16 with the pyridyl group and at C17 with the benzylic carbon atom, as illustrated by a value of about 13° for the torsional angle C22-C17-C16-C8. The aromatic ring coordinated to the manganese atom by atoms C17 and C16 possesses metallocenic-like planar chirality.[24a] The chirality of this system may be defined following the rules established for other cyclopentadienyl– and arene–metal complexes.[37] Therefore, application of the Cahn–Ingold–Prelog priority rule to the manganese-bonded atom C17 (Figure 5) results in an *S* configuration.

The stereocontrol provided by the R_2C ($R = H$ or Me) bridge of the chiral pyridine in the mononuclear complex **14** is, however, far less important than that of the $Cr(CO)_3$ group in complexes **5a** and **5b**. In the case of the latter bimetallic substrate, its conversion into complexes **6b** or **12b** takes place with satisfactory yields even though the Me_2C bridge presumably occupies the side at which the reactions take place. Owing to a larger molecular flexibility of the Cr^0/Mn^I–spiralenes the steric interactions between bulky fragments are more easily counteracted by intramolecular conformational rearrangements than in Mn^I–spiralenes. This distinctive behaviour is presumably related to the different coordination modes of the Mn^I centre in these two classes of compounds. In Mn^I–spiralenes, the Mn^I centre is coordinated to the organic part in a rigid η^3-like mode, while in Cr^0/Mn^I–spiralenes it is probably coordinated in a loose η^1 manner (Figure 2). Several pieces of spectroscopic information reported previously by us, suggest indeed that the Mn^I centre is probably not engaged in a strong bonding interaction with the chromium atom of the $Cr(CO)_3$ unit.[27b]

Circular dichroic absorption spectroscopy is often used as a qualitative tool for structural assessment and conformational studies of organic, inorganic and organometallic compounds.[38] A few theoretical models and "sector rules"[24d, 37a] can actually model CD spectra from structural information and predict, with variable precisions, the sign of Cotton effects related to given classes of electronic transitions and chromophores.[39] Some empirical and semi-empirical methods may be applied with relative success to simple combinations of chromophores with straightforward conformational behaviours.[28a, 40]

Chiroptical properties of helical molecules 6a, b, 12a, b and 15: For molecules with multiple and different chromophores, such as those found for instance in **6a**, no computational method is yet able to afford reliable modelling and predictions of CD spectra. The corresponding experimental CD spectra most often result from inextricable combinations of contributions from different active electronic transitions and from probable multiple exciton couplets,[28a] respectively.

In general, there are two prerequisites for CD to occur.[41] Firstly, the substance must possess optical rotatory activity, which produces birefringence, that is characterized by $[\alpha]_\lambda^T$. Secondly, the substance must possess one or more chiral and chirally induced chromophores that produce dichroism.

In *syn*-facial binuclear molecules such as **6a,b** and **12a,b**, one may define at least four aromatic and metal-centred chromophores that each shall produce clusters of "chiral" electronic transitions ($\pi-\pi^*$, n-π^*, metal-to-ligand, metal-centred low-lying ligand field d–d, metal-to-metal transitions) and consequently generate complex series of Cotton effects in the UV-visible region that was investigated here (175–600 nm): that is the phenyl group, the pyridyl group, the $Mn(CO)_3$ moiety and the disubstituted (η^6-aryl)tricarbonylchromium fragment. Among these four chromophores only the latter one is strictly chiral since it possesses metallocenic planar chirality.[37] Due to the overall molecular asymmetry and helicity, and to the conformational strains within the molecule, the former three chromophores undergo chiral-induced dissymmetries or "chiral perturbations" that produce complex circular dichrograms (Figure 6). In other terms, these apparently achiral fragments are typically chirotopic.[24d] The *endo* phenyl group that eclipses the N-heterocycle in **6a,b** and **12a,b** is expected to undergo an induction of chirality that influences the sign of the Cotton effect of its ^1L_b transition at

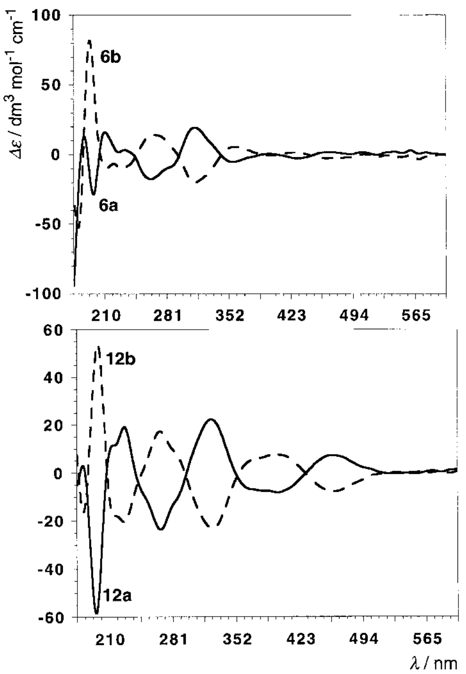


Figure 6. CD spectra of pairs of related complexes **6a**,**b** and **12a**,**b** recorded in a mixture of CH_2Cl_2 and hexane at room temperature.

around 240–270 nm.[39c] The pinene aliphatic fragment is also expected to generate detectable Cotton effects from the related σ–σ* transitions but essentially around 180 nm. Notably, UV/Vis spectra of complexes **6a**,**b** and **12a**,**b** in solutions of hexane and CH_2Cl_2 (0.6% in volume) display in all cases a continuum of absorption from about 600 nm up to 200 nm with increasing values of absorption coefficients ε varying from around 10^3 up to 10^4 dm^{3}mol^{-1}cm^{-1}.

The CD spectra shown in Figure 6 were measured with the two pairs of diastereomeric compounds **6a**,**b** and **12a**,**b**. From 180 nm up to 370 nm **6a** and **12a**, which are both formed starting from diastereomer **5a**, display Cotton effects with high absolute values of $\Delta\varepsilon$ at similar λ_{CE}. The common structural characteristics that are responsible for the similar shape of their CD spectra pertain plausibly to a similar arrangement of the dissymmetric chromophores. A "quasi mirror-image" relationship exists between the CD spectra of **6a** and **6b** with more than seven alternating Cotton effects occurring in the wavelength range 180–535 nm (Figure 6). Similarly, compound **12b** generates an almost perfect mirror image of the spectrum of **12a** with six alternating Cotton effects from 180 nm to 535 nm (Figure 6) although the two considered compounds are diastereomers. Apparently the contribution of the aliphatic chiral part in **6a**,**b** and **12a**,**b** in the region from 180 to 200 nm seems not important enough to have a predominant effect over the sign of the resulting Cotton effects. One could therefore consider the strongest Cotton effects observed for **6a**,**b** and **12a**,**b** at about 193–198 nm as a convenient probe of the molecular helicity, a positive and a negative value of $\Delta\varepsilon$ being connected to a *M* and a *P* helicity, respectively. For compounds **6a** and **6b** the value of $\Delta\varepsilon$ is -28.6 ($\lambda_{CE} = 197$ nm) and $+81.7$ ($\lambda_{CE} = 193$ nm), respectively. For compounds **12a** and **12b** the value of $\Delta\varepsilon$ is -58.6 ($\lambda_{CE} = 195$ nm) and $+53.3$ ($\lambda_{CE} = 198$ nm), respectively.

The mononuclear compound **15** displays also a strong CD activity (Figure 7). Several intense Cotton effects are detected from $\lambda = 180$ to 535 nm with a particularly intense band at $\lambda = 216.5$ nm ($\Delta\varepsilon = +21.4$) (Figure 7).

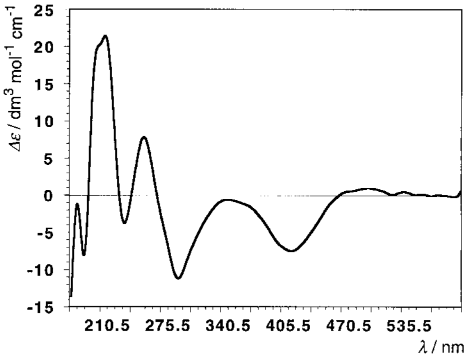


Figure 7. CD spectrum of compound **15** recorded in a mixture of CH_2Cl_2 in hexane at room temperature.

Any further interpretation of the CD behaviour of **6a**,**b**, **12a**,**b** and **15** is unfortunately hampered by a lack of comprehensive knowledge about the electronic transitions that are involved in such systems and which are relevant in such a spectroscopy. We shall address, in a future report, the issues pertaining to the spectrophysical properties of mono- and bi-nucleospiralenes.

Conclusion

We have demonstrated that the construction of chiral helical organometallic species was conceivable thanks to the "spirogenic" nature of the reaction leading to mononuclear or heterobinuclear spiralenes. The preparation of right- and left-handed helical systems from a (−)-β-pinene-derived 2-phenylpyridine was made possible by introducing planar metallocenic chirality by coordination of $Cr(CO)_3$ to an *ortho*-disubstituted aryl fragment. The syntheses of these chiral helical Cr^0/Mn^I-spiralenes were achieved by either the classical two-step "E. O. Fischer methodology" or the "insertion" of a carbene species originating from a diazoalkane in the $Mn-C_{Ar}$ bond. The latter result supports the hypothesis of the intervention of a manganese–carbene species in the mechanistic scheme that rationalizes the formation of "spiralenes". It also constitutes a mild method that does not require the use of basic organolithium reagents and opens wide perspectives for the elaboration of rhenium(I)-containing complexes which are of interest in the fields of photophysics and photochemistry. We have also shown that the "Fischer methodology" applied to a mononuclear chiral cyclomanganated 2-phenylpyridine, which does not have planar metallocenic asymmetry, leads to a single left-handed helical compound. As a consequence of the stereocontrol provided by the pinene-derived fragment further syntheses of right-handed helical mononuclear molecules could be achieved only by using the corresponding enantiomeric cyclomanganated substrate.

Experimental Section

General: All reactions were carried out under a dry argon atmosphere. (η^6-Arene)tricarbonylchromium complexes were prepared by using the procedure of Pauson and co-workers.[42] Benzylpentacarbonylmanganese[43] and complexes **7**[14d] and **9**[26] were prepared by following literature procedures. (−)-(1*S*,5*S*)-2,3-(2′-Phenyl-1′-aza-benzo)-6,6-dimethylbicyclo[3.1.1]heptane, compound **13**, was synthesised according to published procedures.[18a] (+)-pinocarvone was obtained by SeO_2 oxidation of commercially available (−)-(1*S*,5*S*)-β-pinene ($[\alpha]_D = -21°$ (neat)).[22] Mild α-bromination and subsequent pyridination of 2-methylacetophenone was done following established procedures.[23] 1,1-Diphenyldiazomethane has been prepared by oxidation of $Ph_2C{=}N{-}NH_2$ by yellow HgO.[44] The reaction products were separated by flash chromatography on silica gel (Merck, 60 μm) under a dry argon atmosphere. High-resolution mass spectra were recorded at the Mass Spectrometry Service of the University Louis Pasteur. Elemental analyses were done in the presence of a combustion aid (V_2O_5) at the “Service de Microanalyse de l’Institut de Chimie”, Strasbourg, France and at the “Service Central d’Analyse du CNRS” at Vernaison, France. Infrared spectra were recorded with a Perkin-Elmer FT spectrometer. NMR spectra were acquired on Bruker AC 300 and DRX 500 instruments (300 MHz and 500 MHz for ^1H, 75 MHz and 125 MHz for ^{13}C). ^{13}C NMR spectra reported herein were all carried out with proton decoupling. Optical absorption circular dichroism has been measured with a circular 0.100 cm quartz cell on a JASCO J-720 spectropolarimeter at the Kekulé Institut für Organische Chemie und Biochemie in Bonn, Germany. UV/Vis spectroscopic measurements were done on a Perkin Elmer Lambda 8 spectrometer with 1.00 cm quartz cells. All the solutions of compounds subjected to optical absorption studies were prepared by dissolving a given complex in dry and degassed CH_2Cl_2 (0.6 mL) and by completing to 100 mL with dry and degassed hexane. All CD spectra were systematically corrected by blank substraction. The atom numbering used in the systematic nomenclature of the compounds described in this Experimental Section does not follow necessarily the one used for convenience in the molecular structures of complexes **6a**, **8** and **15**.

Kröhnke condensation of the pyridinium salt 2 with (+)-pinocarvone 1: synthesis of (−) (1*S*,5*S*)-2,3-[2′-(2″-methylphenyl)-1′-azabenzo]-6,6-dimethylbicyclo[3.1.1]heptane, compound 3: To a solution of **1** (33.5 g, 0.22 mol) in formamide (100 mL) were added the pyridinium salt **2** (32.5 g, 0.11 mol) and NH_4OAc (17.2 g, 0.22 mol). This mixture was stirred for 72 h at 100 °C. The reaction medium was then cooled to room temperature and poured into an aqueous solution of HCl (200 mL at 10 % mass). The acidic solution was washed with hexane (3 × 300 mL) and basified by reaction with an ice-cooled concentrated aqueous solution of KOH. An oily layer appeared on the surface of the solution that was extracted with hexane (300 mL). The organic phase was then washed with brine, dried over $MgSO_4$, filtered over a short column of activated alumina and the solvent was evaporated under reduced pressure. The slightly reddish oily residue (11 g, 0.042 mol, 37 % yield calculated with respect to **2**) was analysed as being reasonably pure for use in further synthetic steps. Two consecutive kugelrohr distillations at reduced pressure provided colourless samples for complete analytical characterizations. Compound **3** :$[\alpha]_D = -73.9 \pm 0.2°\,dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 9.9$ mM); $C_{19}H_{21}N$ (%): calcd: C 86.65, H 8.04, N 5.32; found: C 86.18, H 8.18, N 5.38; HR MS (FAB^+) calcd for $C_{19}H_{22}N$ (MH^+): m/z: 264.1752; found m/z (%): 264.1741 (100); ^1H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 0.70$ (s, 3 H; Me), 1.34 (d, 1 H, $^2J(H,H) = 9.5$ Hz), 1.42 (s, 3 H; Me), 2.38 (s, 3 H; Me), 2.40 (m, 1 H), 2.72 (m, 1 H), 2.79 (dd, 1 H, $^3J(H,H) = 5.6$ and 5.9 Hz), 3.16 (m, 2 H), 7.05 (d, 1 H, $^3J(H,H) = 7.5$ Hz), 7.25 (m, 4 H), 7.40 (m, 1 H); $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 20.5$, 21.4, 26.2, 32.1, 36.8, 39.6, 40.4, 46.4, 120.5, 125.9, 127.9, 129.7, 130.7, 133.1, 135.9, 139.7, 141.0, 156.3, 157.1.

Synthesis and isolation of the two diastereoisomers of (1*S*, 5*S*)-2,3-[2′-(tricarbonyl{η^6-2″-methylphenyl}chromium(0))-1′-azabenzo]-6,6-dimethylbicyclo[3.1.1]heptane, compounds (1″*R*)-4a and (1″*S*)-4b: Compound **3** (3 g, 0.011 mol) and $[Cr(CO)_6]$ (3.7 g, 0.017 mol) were dissolved in a mixture of THF (15 mL) and di-*n*-butyl ether (150 mL). The mixture was refluxed for three days and the resulting bright orange solution was cooled to room temperature and filtered over Celite. The solvents were evaporated under reduced pressure. The resulting orange oil was redissolved in CH_2Cl_2, and dry SiO_2 was added and the solvent removed in vacuo. The coated silica gel was loaded on the top of a SiO_2 column packed in dry hexane. The mixture of complexes **4a** and **4b** was eluted with a 10:1 mixture of CH_2Cl_2 and acetone. After evaporation of the solvents the orange oil (3.7 g, 0.01 mol, 81 % conversion) was analysed by ^1H NMR spectroscopy and fouund to contain a 1:1 mixture of **4a** and **4b**. The latter two complexes were separated by repeated successive recrystallizations from Et_2O/hexane mixtures. Compound **4a** often precipitated in a pure form and in high amounts (1.5 g, 3.7 mmol, 22 % yield with respect to **3**). In contrast, **4b** often failed to give pure yellow solids after recrystallizations of residual mixtures on the first attempt. However a reasonable amount of **4b** could be obtained in analytically pure form after several recrystallizations (500 mg, 1.2 mmol, 11 % yield with respect to **3**). Complex **4a**: $[\alpha]_D = +77 \pm 1°\,dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 8$ mM); $C_{22}H_{21}NO_3Cr$: calcd (%): C 66.16, H 5.30, N 3.50; found: C 66.20, H 5.44, N 3.52; IR (CH_2Cl_2): $\tilde{\nu} = 1964$, 1886 cm^{-1} (CO); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 0.50$ (s, 3 H; Me), 1.06 (d, 1 H, $^2J(H,H) = 9$ Hz), 1.16 (s, 3 H; Me), 2.03 (m, 4 H), 2.38 (m, 1 H), 2.42 (t, 1 H), 3.04 (m, 2 H), 4.40 (t, 1 H), 4.44 (d, 1 H, $^3J(H,H) = 6.1$ Hz), 4.66 (t, 1 H), 5.28 (d, 1 H, $^3J(H,H) = 6.4$ Hz), 6.81 (d, 1 H, H_{py}, $^3J(H,H) = 7.6$ Hz), 7.16 (d, 1 H, H_{py}); ^{13}C NMR (75 MHz, C_6D_6, 20 °C): $\delta = 20.2$, 21.1, 25.9, 32.0, 36.8, 39.3, 40.4, 46.4, 88.8, 92.9, 94.5, 97.6, 109.8, 111.0, 121.8, 133.4, 141.1, 153.0, 156.3, 233.8 (CO). Complex **4b**:$[\alpha]_D = -146 \pm 1°\,dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 8$ mM); $C_{22}H_{21}NO_3Cr$ (%): calcd: C 66.16, H 5.30, N 3.50; found: C 66.37, H 5.28 N 3.65; IR (CH_2Cl_2): $\tilde{\nu} = 1964$, 1886 cm^{-1} (CO); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 0.53$ (s, 3 H; Me), 1.04 (d, 1 H, $^2J(H,H) = 9.0$ Hz), 1.15 (s, 3 H, Me), 2.04 (m, 4 H), 2.35 (m, 1 H), 2.42 (t, 1 H), 3.07 (m, 2 H), 4.37 (m, 2 H), 4.62 (t, 1 H), 5.34 (d, 1 H, $^3J(H,H) = 6.5$ Hz), 6.79 (d, 1 H, $^3J(H,H) = 8.0$ Hz; H_{py}), 7.16 (d, 1 H; H_{py}); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C): $\delta = 20.0$, 21.1, 25.8, 31.9, 36.8, 39.4, 40.3, 46.4, 88.8, 92.8, 94.4, 97.8, 109.5, 111.1, 121.7, 133.3, 141.1, 152.8, 156.4, 233.8 (CO).

General procedure for the cyclomanganation of compounds 4a, 4b and 13: In a Schlenk tube $[Mn(CH_2Ph)(CO)_5]$ and the corresponding substrate were mixed and dry degassed heptane was added to the resulting solid mixture. The resulting mixture was stirred for 5–6 h at 110 °C. An abundant red precipitate formed in the course of the reaction. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The solid residue was then dissolved in a minimum volume of CH_2Cl_2 and SiO_2 was added. The solvent was removed in vacuo and the resulting coated silica gel loaded on the top of a SiO_2 column packed with dry and degassed hexane. The cyclomanganated product was eluted with a 6:4 mixture of CH_2Cl_2 and hexane and the compound was isolated pure after removal of the solvents under reduced pressure.

(+)-Tetracarbonyl[(1*S*, 5*S*, 6″*R*)-2,3-[2′-(tricarbonyl{η^6-2″-methylphenyl-$\kappa C^{6''}$}chromium(0))-1′-azabenzo-κN]-6,6-dimethylbicyclo[3.1.1]heptane] manganese(I), complex 5a: Compound **4a** (1.21 g, 3.4 mmol), $[Mn(CH_2Ph)(CO)_5]$ (1.30 g, 5.1 mmol) and heptane (10 mL) were allowed to react to give **5a** in 81 % yield after chromatographic purification (1.40 g, 2.5 mmol). Compound **5a**: $[\alpha]_D = +338 \pm 2°\,dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 8$ mM); $C_{26}H_{20}NO_7CrMn$ (%): calcd: C 55.23, H 3.56, N 2.48; found: C 55.51, H 3.61 N 2.45; IR (CH_2Cl_2): $\tilde{\nu} = 2084$, 2003, 1982, 1947, 1872 cm^{-1} (CO); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 0.35$ (s, 3 H; Me), 0.67 (d, 1 H, $^2J(H,H) = 9.8$ Hz), 1.04 (s, 3 H; Me), 1.89 (m, 1 H), 2.00(s, 3 H; Me), 2.14 (m, 1 H), 2.21 (t, 1 H), 3.05 (d, 1 H, $^2J(H,H) = 17.2$ Hz), 3.19 (d, 1 H, $^2J(H,H) = 17.2$ Hz), 4.66 (d, 1 H, $^3J(H,H) = 6.3$ Hz), 4.81 (t, 1 H), 5.85 (d, 1 H, $^3J(H,H) = 5.8$ Hz), 6.56 (d, 1 H, $^3J(H,H) = 8.3$ Hz), 7.27 (d, 1 H, $^3J(H,H) = 8.0$ Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 21.3$, 23.6, 25.5, 31.3, 38.7, 40.9, 43.1, 46.6, 93.2, 97.1, 103.6, 106.5, 113.2, 121.3, 135.2, 141.0, 143.0, 161.4, 163.4, 210.8 (Mn-CO), 211.7 (Mn-CO), 212.7 (Mn-CO), 220.0 (Mn-CO), 235.3(Cr-CO).

(−)-Tetracarbonyl[(1*S*, 5*S*, 6″*S*)-2,3-[2′-(tricarbonyl{η^6-2″-methylphenyl-$\kappa C^{6''}$}chromium(0))-1′-azabenzo-κN]-6,6-dimethylbicyclo[3.1.1]heptane] manganese(I), complex 5b: Compound **4b** (250 mg, 0.62 mmol), $[Mn(CH_2Ph)(CO)_5]$ (268 mg, 0.93 mmol) and heptane (10 mL) were allowed to react to give **5b** in 62 % yield after chromatographic purification (219 mg, 0.39 mmol). Compound **5b**: $[\alpha]_D = -353 \pm 2°\,dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 8$ mM); $C_{26}H_{20}NO_7CrMn$ (%): calcd: C 55.23, H 3.56, N 2.48; found: C 55.39, H 3.85 N 2.50; IR (CH_2Cl_2): $\tilde{\nu} = 2084$, 2004, 1982, 1947, 1872 cm^{-1} (CO); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 0.25$ (s, 3 H; Me), 0.70 (d, 1 H, $^2J(H,H) = 9.8$ Hz), 1.01 (s, 3 H; Me), 1.88 (m, 1 H), 1.96 (s, 3 H; Me), 2.13 (m, 1 H), 2.20 (t, 1 H), 3.09 (d, 1 H, $^2J(H,H) = 17.2$ Hz), 3.19 (d, 1 H, $^2J(H,H) = 17.2$ Hz), 4.64 (d, 1 H, $^3J(H,H) = 5.6$ Hz), 4.80 (dd, 1 H,

^{3}J(H,H) = 6.1 and 6.4 Hz), 5.87 (d, 1 H, ^{3}J(H,H) = 6.2 Hz), 6.53 (d, 1 H, ^{3}J(H,H) = 8.3 Hz), 7.27 (d, 1 H, ^{3}J(H,H) = 8.3 Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 21.0$, 23.2, 25.4, 30.8, 39.0, 40.9, 42.9, 46.6, 93.3, 96.9, 103.4, 106.9, 112.8, 121.5, 135.2, 141.4, 143.1, 161.3, 163.3, 211.0 (Mn-CO), 211.5 (Mn-CO), 212.7 (Mn-CO), 220.1 (Mn-CO), 235.3 (Cr-CO).

General procedure for the synthesis of chiral complexes 6a, b: Bimetallic complexes **5a**, **b** were separately dissolved in DME and the solution was cooled to −50 °C. A solution of phenyllithium (1.8 M in cyclohexane/diethyl ether, Aldrich Chemicals) was then added and the temperature of the reaction mixture was allowed to reach −20 °C. After 10 min at −20 °C, the reaction mixture was cooled to −40 °C. MeOTf was added and the reaction mixture slowly warmed to room temperature. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 and mixed with silica gel, the solvent was then removed under reduced pressure. The resulting coated silica gel was loaded on the top of a silica gel column that was packed in dry and degassed hexane and eluted with 70:30 mixtures of CH_2Cl_2 and hexane.

Preparation of (+)-(1*S*, 5*S*, 6″*S*, *αR*)-tricarbonyl[2,3-{2′-{tricarbonyl-[1″,2″,3″,4″,5″-*η*^{5}-3″-methyl, 6″-(*α*-methoxybenzylidene)cyclohexadienyl-*κC*^{α}]chromium(0)}-1′-azabenzo-*κN*}-6,6-dimethylbicyclo[3.1.1]heptane]-manganese(I), 6a, by the "Fischer method" starting from compound 5a: Complex **5a** (170 mg, 0.30 mmol), PhLi (0.17 mL, 0.30 mmol, in hexane), DME (10 mL) and MeOTf (0.15 g, 0.90 mmol) were allowed to react to give **6a** (180 mg, 0.27 mmol, 91 % yield): $[\alpha]_D = +728 \pm 6°$ dm^{-1} g^{-1} mL (CH_2Cl_2, 20 °C, $c = 1.67$ mM); $C_{33}H_{28}NO_7CrMn$ (%): calcd: C 60.28, H 4.29, N 2.13; found: C 59.96, H 4.29, N 2.20; HR MS (FAB^{+}) for $C_{33}H_{28}NO_7CrMn$: calcd: 657.06513; found (%): 657.06482 (4.4); CD (hexane/CH_2Cl_2, 25 °C, $c = 0.031$ mM): λ ($\Delta\varepsilon$) = 469.5 (1.61), 431.0 (−2.97), 356.0 (−5.59), 313.0 (19.2), 263.0 (−17.7), 232.5 (3.21), 210.0 (15.9), 197.0 (−28.6), 186.5 nm (12.7 dm^{3} mol^{-1} cm^{-1}); UV/Vis (hexane/CH_2Cl_2): λ_{max} (ε) = 459 (2.09×10^{3}), 285 (1.68×10^{4}), 243 (2.60×10^{4}), 221 nm (3.63×10^{4} mol^{-1} dm^{3} cm^{-1}); IR (CH_2Cl_2): $\tilde{\nu} = 2012$, 1958, 1926, 1885 cm^{-1} (CO); ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 0.29$ (s, 3 H; Me), 1.14 (d, 1 H, ^{2}J(H,H) = 5.8 Hz), 1.29 (s, 3 H; Me), 1.61 (s, 3 H; Me), 2.42 (t, 1 H), 2.45 (m, 1 H), 2.63 (m, 1 H), 3.20 (d, 1 H, ^{2}J(H,H) = 18.1 Hz), 3.39 (s, 3 H; −OMe), 3.65 (d, 1 H, ^{2}J(H,H) = 17.0 Hz), 4.48 (d, 1 H, ^{3}J(H,H) = 7.6 Hz; H_{ArCr}), 5.18 (t, 1 H; H_{ArCr}), 5.66 (d, 1 H, ^{3}J(H,H) = 6.3 Hz; H_{py}), 6.23 (d, 1 H, ^{3}J(H,H) = 6.0 Hz; H_{ArCr}), 6.36 (d, 1 H, ^{3}J(H,H) = 7.7 Hz; H_{py}), 6.90 (t, 1 H; $H_{meta,\ \mathrm{Ph}\text{-}endo}$), 6.99 (t, 1 H; $H_{para,\ \mathrm{Ph}\text{-}endo}$), 7.12 (t, 1 H; $H_{meta,\ \mathrm{Ph}\text{-}endo}$), 7.37 (d, 1 H, ^{3}J(H,H) = 7.8 Hz; $H_{ortho,\ \mathrm{Ph}\text{-}endo}$), 7.55 (d, 1 H, ^{3}J(H,H) = 7.0 Hz; $H_{ortho,\ \mathrm{Ph}\text{-}endo}$); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, −20 °C): $\delta = 20.3$, 20.5, 25.4, 31.5, 38.3, 38.9, 40.4, 46.2, 54.7, 81.0, 89.2, 90.5, 92.3, 98.5, 98.7, 120.6, 126.7, 127.2, 128.4, 132.5, 133.2, 133.9, 141.9, 142.6, 152.2, 160.7, 219.9 (Mn-CO), 230.3 (Mn-CO), 232.0 (Mn-CO), 236.2 (br.; $Cr(CO)_3$).

Preparation of (−)-(1*S*, 5*S*, 6″*R*, *αS*)-tricarbonyl[2,3-{2′-{tricarbonyl-[1″,2″,3″,4″,5″-*η*^{5}-3″-methyl, 6″-(*α*-methoxybenzylidene)cyclohexadienyl-*κC*^{α}]chromium(0)}-1′-azabenzo-*κN*}-6,6-dimethylbicyclo[3.1.1]heptane]-manganese(I), 6b, by the "Fischer method" starting from compound 5b: Complex **5b** (364 mg, 0.64 mmol), PhLi (0.35 mL, 0.64 mmol, in hexane), DME (10 mL) and MeOTf (0.316 g, 1.8 mmol) were allowed to react to give **6b** (280 mg, 0.42 mmol, 66 % yield): $[\alpha]_D = -906 \pm 12°$ dm^{-1} g^{-1} mL (CH_2Cl_2, 20 °C, $c = 1.67$ mM); $C_{33}H_{28}NO_7CrMn$ (%): calcd: C 60.28, H 4.29, N 2.13; found: C 59.97, H 4.33, N 2.12; HR MS (FAB^{+}) for $C_{33}H_{28}NO_7CrMn$: calcd: 657.06513; found (%): 657.06485 (4.0); CD (hexane/CH_2Cl_2, 25 °C, $c = 0.036$ mM): λ ($\Delta\varepsilon$) = 464.0 (−2.91), 427.0 (1.16), 359.0 (5.37), 313.0 (−20.0), 267.0 (13.8), 229.5 (−10.2), 212.5 (−9.44), 193.0 nm (81.7 dm^{3} mol^{-1} cm^{-1}); UV/Vis (hexane/CH_2Cl_2): λ_{max} (ε) = 460 (2.56×10^{3}), 283 (1.96×10^{4}), 244 (2.81×10^{4}), 221 nm (4.11×10^{4} mol^{-1} dm^{3} cm^{-1}); IR (CH_2Cl_2): $\tilde{\nu} = 2004$, 1955, 1920, 1877 cm^{-1} (CO); ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 0.73$ (s, 3 H; Me), 0.75 (d, 1 H, ^{2}J(H,H) = 9.5 Hz), 1.32 (s, 3 H; Me), 1.61 (s, 3 H; Me), 2.42 (m, 2 H), 2.46 (m, 1 H), 3.25 (d, 1 H, ^{2}J(H,H) = 18.0 Hz), 3.35 (s, 3 H; OMe), 3.49 (d, 1 H, ^{2}J(H,H) = 18.0 Hz), 4.43 (d, 1 H; H_{ArCr}), 5.17 (t, 1 H; H_{ArCr}), 5.74 (d, 1 H; H_{ArCr}), 6.23 (d, 1 H, ^{3}J(H,H) = 5.8 Hz), 6.42 (d, 1 H, ^{3}J(H,H) = 7.9 Hz), 6.93 (t, 1 H), 6.98 (t, 1 H), 7.10 (t, 1 H), 7.34 (d, 1 H, ^{3}J(H,H) = 7.7 Hz), 7.79 (d, 1 H, ^{3}J(H,H) = 7.6 Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 0 °C): $\delta = 20.4$, 21.1, 25.5, 30.7, 38.2, 38.5, 39.9, 46.2, 54.7, 80.7, 81.4, 88.4, 90.6, 92.4, 98.9, 99.2, 120.7, 126.7, 127.7, 128.1, 132.6, 132.9, 134.3, 141.6, 142.5, 152.1, 160.4, 219.9 (Mn-CO), 230.4 (Mn-CO), 231.1 (br.; Cr-CO), 231.8 (Mn-CO), 235.5 (br.; Cr-CO), 237.0 (br.; Cr-CO).

Determination of the molecular structure of 6a by X-ray diffraction analysis: Acquisition and processing parameters are displayed in Table 1. A total of 3429 reflections having $I > 3\sigma(I)$ were collected on a KappaCCD diffractometer using $Mo_{K\alpha}$ graphite-monochromated radiation. The structure was determined using direct methods and refined against |F|. Hydrogen atoms were introduced as fixed contributors. The absolute structure was determined by refining Flack's *x* parameter. For all computations the Nonius OpenMoleN package was used.[45]

Thermally promoted CO displacement reaction of compound 6 with PPh_3, synthesis of *fac*-(tricarbonyl)(triphenylphosphane)[2-{(*η*^{6}-phenyl)tricarbonylchromium(0)-*κC*$^{2'}$}pyridine-*κN*]manganese(I), compound 8: Complex **6** (329 mg, 0.72 mmol) and excess triphenylphosphane (567 mg, 2.16 mmol) were dissolved in dry degassed heptane (15 mL) and the resulting suspension was refluxed for about 4 h. The solvent was removed in vacuo from the resulting red solution, and the resulting residue was dissolved in CH_2Cl_2 and silica gel added. The solvent was evaporated under reduced pressure and the coated silica gel loaded on the top of a SiO_2 column packed in hexane. The orange-red compound **8** was eluted with a 1:1 mixture of CH_2Cl_2 and hexane. After evaporation of the solvents and recrystallisation, compound **8** (472 mg, 0.68 mmol, 94 % yield) was obtained in a monocrystralline form suitable for X-ray diffraction analysis. Compound **8** : $C_{35}H_{23}NO_6CrMn$ (%): calcd: C 60.80, H 3.35, N 2.03; found: C 60.56, H 3.20 N 1.94; IR (CH_2Cl_2): $\tilde{\nu} = 2014$, 1948, 1898, 1873 cm^{-1} (CO); ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 4.94$ (t, 1 H, ^{3}J (H,H) = 6.1 Hz), 5.34 (t, 1 H, ^{3}J(H,H) = 6.7 Hz), 5.40 (d, 1 H, ^{3}J(H,H) = 5.8 Hz), 6.17 (d, 1 H, ^{3}J(H,H) = 6.1 Hz), 6.80 (t, 1 H, ^{3}J(H,H) = 6.6 Hz), 7.13–7.25 (m, 16 H), 7.60 (t, 1 H, ^{3}J(H,H) = 7.6 Hz), 8.32 (d, 1 H, ^{3}J(H,H) = 5.4 Hz); ^{13}C {^{1}H}NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 86.4$, 90.6, 93.9, 107.5, 113.1, 119.2, 123.1, 128.2 (d, 6C, J(P,C) = 8.8 Hz), 129.6 (d, 3C, J(P,C) = 1.7 Hz), 132.4 (d, 3C, J(P,C) = 34.9 Hz), 133.1 (d, 6C, J(P,C) = 9.6 Hz), 136.8, 152.2 (d, 1C, J(P,C) = 18.9 Hz; C_{ArCr}-Mn), 153.5, 164.4, 216.9 (Mn-CO), 217.3 (Mn-CO), 225.6 (s, 1C, J(P,C) = 21.9 Hz, Mn-CO), 235.8 ($Cr(CO)_3$); ^{31}P NMR ($CDCl_3$, 20 °C): $\delta = 54.9$ (s).

Determination of the molecular structure of 8 by X-ray diffraction analysis: Acquisition and processing parameters are displayed in Table 1. Reflections were collected on a MACH3 Nonius diffractometer using $Mo_{K\alpha}$ graphite-monochromated radiation. Empirical absorption corrections from the ψ scans of seven reflections, absorption factors: 0.94/1.00. The structure was solved by using direct methods and refined against |F|. Hydrogen atoms were introduced as fixed contributors. The solvent molecule is disordered over two positions related by an inversion centre. The absolute structure was determined by refining Flack's *x* parameter. For all computations the Nonius OpenMoleN package was used[45].

General procedure for the thermally promoted reaction of compounds 7, 9, 5a and 5b with 1,1-diphenyldiazomethane: Compound **7** (**9**, **5a**, **5b**) and $N_2{=}CPh_2$ were dissolved in dry, degassed heptane. The mixture was then refluxed for 1 h. A reddish precipitate appeared. An additionnal amount of $N_2{=}CPh_2$ was added to the medium and the suspension was refluxed for an additional 30 min period. The reaction mixture was then cooled to room temperature and the solvent evaporated under reduced pressure to afford a cotton-like solid. The latter was dissolved in CH_2Cl_2 and SiO_2 was added. The solvent was evaporated in vacuo and the coated silica gel loaded on the top of a SiO_2 column packed in hexane. The deep orange band containing complex **10** (**11**, **12a**, **12b**) was eluted with a 4:1 mixture of CH_2Cl_2 and hexane.

2-{1′,2′,3′,4′,5′-*η*^{5}-[6′(*α*-phenylbenzylidene)cyclohexadienyl-*κC*$^{α'}$]tricarbonylchromium(0)}(pyridine-*κN*)tricarbonylmanganese(I), complex 10: Complex **7** (110 mg, 0.22 mmol) and $N_2{=}CPh_2$ (250 mg, 1.3 mmol) in heptane (10 mL) were allowed to react to give complex **10** (120 mg, 0.20 mmol, 91 % yield): $C_{30}H_{18}NO_6CrMn$ (%): calcd: C 60.52, H 3.05, N 2.35; found: C 60.29, H 3.53 N 2.34; IR (CH_2Cl_2): $\tilde{\nu} = 2010$, 1960, 1929, 1891 cm^{-1} (CO); ^{1}H NMR (500 MHz, C_6D_6, 20 °C): $\delta = 3.05$ (d, 1 H; H_{ArCr}), 3.18 (d, 1 H; H_{ArCr}), 3.65 (t, 1 H; H_{ArCr}), 5.29 (t, 1 H; H_{ArCr}), 5.32 (d, 1 H; H_{py}), 5.38 (t, 1 H; H_{py}), 5.91 (t, 1 H; H_{py}), 6.49 (t, 1 H; $H_{\mathrm{paraPh\text{-}endo}}$), 6.57 (t, 1 H; $H_{\mathrm{metaPh\text{-}endo}}$), 6.69 (t, 1 H; $H_{\mathrm{meta,\ Ph\text{-}endo}}$), 6.88 (t, 1 H; $H_{para,\ \mathrm{Ph}\text{-}exo}$), 7.08 (d, 1 H; $H_{\mathrm{ortho,\ Ph\text{-}endo}}$), 7.10 (t, 1 H; $H_{\mathrm{meta,\ Ph\text{-}exo}}$), 7.30 (d, 1 H; H_{py}), 8.01 (d, 2 H; $H_{\mathrm{ortho,\ Ph\text{-}exo}}$), 8.39 (d, 1 H; $H_{\mathrm{ortho,\ Ph\text{-}endo}}$); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 54.4$, 81.1, 83.5, 86.3, 87.6, 89.8, 94.3, 117.6, 122.3, 124.9, 125.7, 127.4, 128.7, 128.8, 129.4, 133.3, 134.3, 137.1, 147.4, 149.3, 152.3, 160.4, 219.6, (Mn-CO), 230.1 (Mn-CO), 232.1 (Mn-CO), 235.0 (w br.; $Cr(CO)_3$).

[2-{1′,2′,3′,4′,5′-*η*^{5}-[6′-(*α*-phenylbenzylidene)cyclohexadienyl-*κC*$^{α'}$]tricarbonylchromium(0)},3-methyl(pyridine-*κN*)]tricarbonylrhenium(I), com-

plex 11: Complex **9** (150 mg, 0.25 mmol) and $N_2{=}CPh_2$ (580 mg, 3 mmol) in heptane (15 mL) were allowed to react to give complex **11** (124 mg, 0.17 mmol, 67 % yield): $C_{31}H_{20}NO_6CrRe$: calcd: C 50.27, H 2.72, N 1.89; found: C 50.59, H 3.06 N 2.15; IR (CH_2Cl_2): $\tilde{\nu} = 2016, 1968, 1927, 1885\ cm^{-1}$ (CO); ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 2.00$ (s, 3H; Me), 3.91 (d, 1H; H_{ArCr}), 4.48 (d, 1H; H_{ArCr}), 4.87 (d, 1H; H_{ArCr}), 6.18 (t, 1H; H_{ArCr}), 6.53 (dd, 1H), 6.68 (t, 1H), 6.78 (t, 1H), 6.88 (m, 2H), 7.01 (t, 1H), 7.19–7.32 (m, 3H), 7.68 (d, 1H), 7.77 (d, 2H), 8.13 (d, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 20.6$, 51.2, 78.5, 87.6, 88.4, 89.0, 93.4, 95.4, 122.9, 124.8, 125.6, 127.8, 128.7, 129.2, 129.9, 131.3, 133.6, 140.2, 147.9, 150.2, 151.2, 158.0, 194.4 (Re-CO), 197.4 (Re-CO), 203.3 (Re-CO), 233.0 (w br.; $Cr(CO)_3$).

Reaction of complex 5a with $N_2{=}CPh_2$, synthesis of (+)-(1*S*, 5*S*, 6″*S*)-tricarbonyl[2,3-{2′-{tricarbonyl[1″,2″,3″,4″,5″-η^5-3″-methyl, 6″-(α,α-diphenylmethylene)cyclohexadienyl-κC^{α}]chromium(0)}-1′-aza-benzo-κN}-6,6-dimethylbicyclo[3.1.1]heptane]manganese(I), 12a: Complex **5a** (113 mg, 0.2 mmol) and $N_2{=}CPh_2$ (316 mg, 0.8 mmol) in heptane (10 mL) were allowed to react to give complex **12a** (90 mg, 0.13 mmol, 64 %): $[\alpha]_D = +242 \pm 1°\ dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 1.56$ mM); $C_{38}H_{30}NO_6CrMn$ (%): calcd: C 64.87, H 4.30, N 1.99; found: C 64.78, H 4.37 N 1.92; HR MS (FAB^+) for $C_{38}H_{30}NO_6CrMn$: calcd: 703.08587; found (%): 703.08662 (2.2); CD (hexane/CH_2Cl_2, 25 °C, $c = 0.102$ mM): λ ($\Delta\varepsilon$) = 460.5 (7.39), 399.5 (−8.16), 324.5 (22.3), 268.0 (−23.6), 227.5 (19.1), 215.0 (11.5), 195.3 nm (−58.6 $dm^3 mol^{-1} cm^{-1}$); UV/Vis (hexane/CH_2Cl_2): λ_{max} (ε) = 459 (2.28×10^3), 325 nm ($1.17 \times 10^4\ mol^{-1} dm^3 cm^{-1}$); IR ($CH_2Cl_2$): $\tilde{\nu} = 2004, 1953, 1921, 1880\ cm^{-1}$ (CO); ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 0.32$ (s, 3H; Me), 1.04 (d, 1H, $^2J(H,H) = 9.5$ Hz), 1.28 (s, 3H; Me), 1.76 (s, 3H; Me), 2.36 (t, 1H), 2.44 (m, 1H), 2.56 (m, 1H), 3.27 (d, 1H, $^2J(H,H) = 17.9$ Hz), 3.55 (d, 1H, $^3J(H,H) = 7.8$ Hz; H_{ArCr}), 3.63 (d, 1H, $^2J(H,H) = 17.8$ Hz), 4.70 (m, 1H; H_{ArCr}), 5.80 (d, 1H, $^3J(H,H) = 7.7$ Hz; H_{py}), 6.32 (m, 2H; $H_{py} + H_{ArCr}$), 6.70 (t, 1H; $H_{meta,\ Ph-endo}$), 6.82 (m; 2$H_{meta,para,\ Ph-endo}$), 7.01 (t, 1H; $H_{para,\ Ph-exo}$), 7.22 (t, 2H; $H_{meta,\ Ph-exo}$), 7.42 (d, 1H; $^3J(H,H) = 7.8$ Hz; $H_{ortho,\ Ph-endo}$), 7.88 (d, 1H, $^3J(H,H) = 8.0$ Hz; $H_{ortho,\ Ph-endo}$), 7.95 (d, 2H, $^3J(H,H) = 8.4$ Hz; $H_{ortho,\ Ph-exo}$); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 20.6$, 21.1, 25.5, 31.2, 38.3, 38.9, 40.6, 46.4, 56.3, 83.6, 85.8, 87.2, 92.1, 97.5, 98.1, 121.5, 125.0, 125.8, 127.7, 128.5, 128.9, 131.8, 132.2, 133.0, 133.9, 141.9, 148.1, 149.3, 153.8, 160.5, 220.0 (Mn-CO), 231.8 (Mn-CO), 233.5 (Mn-CO), 235.0 (w br.; $Cr(CO)_3$).

Reaction of complex 5b with $N_2{=}CPh_2$, synthesis of (−)-(1*S*, 5*S*, 6″*R*)-tricarbonyl[2,3-{2′-{tricarbonyl[1″,2″,3″,4″,5″-η^5-3″-methyl, 6″-(α,α-diphenylmethylene)cyclohexadienyl-κC^{α}]chromium(0)}-1′-aza-benzo-κN}-6,6-dimethylbicyclo[3.1.1]heptane]manganese(I), 12b: Complex **5b** (100 mg, 0.18 mmol) and $N_2{=}CPh_2$ (223 mg, mmol) in heptane (10 mL) were allowed to react to give complex **12b** (90 mg, 0.13 mmol, 72 %): $[\alpha]_D = -402 \pm 1°\ dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 1.56$ mM); $C_{38}H_{30}NO_6CrMn \cdot CH_2Cl_2$ (%): calcd: C 59.40, H 4.09, N 1.77; found: C 59.61, H 3.86 N 1.88; HR MS (FAB^+) for $C_{38}H_{30}NO_6CrMn$: calcd: 703.08587; found (%): 703.08431 (12.0); CD (hexane/CH_2Cl_2, 25 °C, $c = 0.110$ mM): λ ($\Delta\varepsilon$) = 463.0 (−7.67), 395.5 (7.64), 326.0 (−23.2), 267.5 (17.3), 227.0 (−20.4), 215.0 (−17.5), 198.0 nm (53.3 $dm^3 mol^{-1} cm^{-1}$); UV/Vis (hexane/CH_2Cl_2): λ_{max} (ε) = 459 (2.16 10^3), 326 nm ($1.20 \times 10^4\ mol^{-1} dm^3 cm^{-1}$); IR ($CH_2Cl_2$): $\tilde{\nu} = 2004, 1954, 1920, 1881\ cm^{-1}$ (CO); ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 0.41$ (s, 3H; Me), 0.50 (d, 1H, $^2J(H,H) = 9.7$ Hz), 0.96 (s, 3H; Me), 1.15 (s, 3H; Ar-*Me*), 1.86 (d, 2H, $^3J(H,H) = 5.6$ Hz), 1.97 (m, 1H), 3.38 (d, 1H; H_{ArCr}), 3.47 (d, 1H, $^2J(H,H) = 18.7$ Hz), 3.59 (d, 1H, $^2J(H,H) = 18.8$ Hz), 3.73 (t, 1H; H_{ArCr}), 5.37 (d, 1H, $^3J(H,H) = 7.8$ Hz; H_{py}), 5.44 (d, 1H, $^3J(H,H) = 5.4$ Hz; H_{ArCr}), 5.67 (d, 1H, $^3J(H,H) = 7.5$ Hz; H_{py}), 6.58 (t, 1H; $H_{para,\ Ph-endo}$), 6.68 (m, 2H; $H_{meta,\ Ph-endo}$), 6.88 (t, 1H; $H_{para,\ Ph-exo}$), 7.13 (m, 2H; $H_{meta,\ Ph-exo}$), 7.28 (d, 1H, $^3J(H,H) = 7.5$ Hz; $H_{ortho,\ Ph-endo}$), 8.13 (d, 2H; $H_{ortho,\ Ph-exo}$), 8.30 (d, 1H, $^3J = 8.5$ Hz; $H_{ortho,\ Ph-endo}$); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 21.0$, 21.6, 25.7, 30.9, 38.3, 38.9, 40.4, 46.6, 53.5, 55.8, 83.0, 85.4, 87.4, 92.1, 98.4, 121.4, 124.9, 125.7, 127.5, 128.8, 129.1, 131.4, 132.3, 133.1, 134.0, 142.1, 148.3, 149.2, 154.0, 160.1, 220.1 (Mn-CO), 231.7 (Mn-CO), 232.0 (br.; Cr-CO), 233.7 (Mn-CO), 235.2 (br.; Cr-CO), 238.2 (br.; Cr-CO).

(−)-(1*S*, 5*S*)-2,3-(2′-phenyl,1′-azabenzo)-6,6-dimethylbicyclo[3.1.1]heptane, compound 13: $[\alpha]_D = -122 \pm 1°\ dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 1.99$ mM); $C_{18}H_{19}N$ (%): calcd: C 86.70, H 7.68, N 5.61; found: C 86.89, H 7.60, N 5.53; ^1H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 0.68$ (s, 3H), 1.31 (d, 1H, $^2J(H,H) = 9.3$ Hz), 1.41 (s, 3H), 2.39 (m, 1H), 2.71 (m, 1H), 2.79 (m, 1H), 3.18 (d, 2H, ^2J (H,H) = 3.0 Hz), 7.23 (m, 1H), 7.38 (m, 4H), 7.94 (m, 2H); ^{13}C {^1H} NMR (125 MHz, C_6D_6, 20 °C): $\delta = 21.3$, 26.0, 32.2, 37.1, 39.5, 40.5, 46.4, 116.7, 127.0, 128.3, 128.5, 128.8, 133.4, 140.2, 154.7, 156.9.

Preparation of (−) tetracarbonyl{(1*S*, 5*S*)-2,3-[(2′-phenyl-$\kappa C^{2''}$),1′-azabenzo-κN]-6,6-dimethylbicyclo[3.1.1]heptane}manganese(I), compound 14: Compound **13** (1 g, 4 mmol) and $[Mn(PhCH_2)(CO)_5]$ (1.72 g, 6 mmol) in heptane (15 mL) were refluxed for 7 h. Elution of **14** with CH_2Cl_2/hexane (4:1). Compound **14** (1.165 g, 2.82 mmol, 70 % yield): $[\alpha]_D = -64.7 \pm 0.1°\ dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 3.32$ mM); $C_{22}H_{16}NO_4Mn$ (%): calcd: C 63.93, H 3.90, N 3.38; found: C 63.50, H 4.28, N 3.44; IR (CH_2Cl_2): $\tilde{\nu} = 2074, 1993, 1976, 1935\ cm^{-1}$ (CO); ^1H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 0.66$ (s, 3H), 1.29 (d, 1H, $^2J(H,H) = 9.22$ Hz), 1.44 (s, 3H), 2.54 (m, 1H), 2.70 (m, 1H), 2.81 (t, 1H), 3.39 (dd, 1H, $^2J(H,H) = 17.0$ Hz, $^2J(H,H) = 3.0$ Hz), 3.45 (dd, 1H, $^2J(H,H) = 17.0$ Hz $^2J(H,H) = 3.0$ Hz), 7.19 (m, 1H), 7.28 (t, 1H), 7.33 (d, 1H, $^3J(H,H) = 8.0$ Hz), 7.66 (d, 1H, $^3J(H,H) = 8.0$ Hz), 7.72 (d, 1H), 8.03 (d, 1H, $^3J(H,H) = 7.3$ Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 21.0$, 25.4, 31.0, 38.6, 40.7, 42.6, 46.6, 116.0, 123.6, 123.9, 129.5, 135.4, 141.2, 141.7, 147.3, 160.7, 164.3, 171.4, 214.4 (Mn-CO), 214.5 (Mn-CO), 214.7 (Mn-CO), 221.4 (Mn-CO).

Synthesis of (−) tricarbonyl{(1*S*, 5*S*, 1″*S*, αR)-2,3-[[1″,2″-η^2-2″-(α-methoxybenzylidene)phenyl-κC^{α}],1′-azabenzo-κN]-6,6-dimethylbicyclo[3.1.1]heptane}manganese(I), 15: To a solution of complex **14** (140 mg, 0.33 mmol) in DME (10 mL) was added a stoichiometric amount of a solution of PhLi in hexane (0.187 mL, 0.33 mmol) at −50 °C and the mixture was stirred at that temperature for 30 min. The resulting dark brown solution was then warmed to −30 °C and an excess of MeOTf (0.10 mL, 0.92 mmol) was added. The mixture was allowed to warm slowly to room temperature and the solvents were evaporated under reduced pressure. The resulting residue was redissolved in dry Et_2O and deactivated silica gel was added. The mixture was stirred and solvents were then removed under reduced pressure. The coated silical gel was loaded on the top of a deactivated SiO_2 column packed in dry hexane. Compound **15** was the only coloured product to be eluted with a mixture of Et_2O/hexane (3:2). After evaporation of the solvents under vacuum, compound **15** was recovered as a solid and then washed three times with cold pentane. The product **15** was recrystallized from pentane to afford orange-yellow crystals (116 mg, 0.23 mmol, 68 % yield). Complex **15:** $[\alpha]_D = -299.3 \pm 0.6°\ dm^{-1}g^{-1}mL$ (CH_2Cl_2, 20 °C, $c = 1.73$ mM); $C_{29}H_{26}NO_4Mn$ (%): calcd: C 68.64, H 5.16, N 2.76; found: C 67.93, H 5.13, N 2.73; MS (FAB^+) *m/z*: 507.2 $[M]^+$, 476.2 $[M - MeO]^+$, 451.1 $[M - 2\,CO]^+$, 423.1 $[M - 3\,CO]^+$, 368.2 $[M - Mn(CO)_3]^+$; HR MS (FAB^+) for $C_{29}H_{26}NO_4Mn$: calcd: 507.124230; found (%): 507.126135 (15); CD (hexane/CH_2Cl_2, 25 °C, $c = 0.151$ mM): λ ($\Delta\varepsilon$) = 500.0 (0.911), 417.5 (−7.53), 295.0 (−11.2), 258.0 (7.81), 237.0 (−3.76), 216.5 (21.4), 210.5 (20.1), 193.5 nm (−8.03 $dm^3 mol^{-1} cm^{-1}$); UV/Vis (hexane/CH_2Cl_2): λ_{max} (ε) = 426 (2.71×10^3), 351 (6.52×10^3), 289 nm ($1.69 \times 10^4\ mol^{-1} dm^3 cm^{-1}$); IR ($CH_2Cl_2$): $\tilde{\nu} = 1998, 1913, 1897\ cm^{-1}$ (CO); ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 0.50$ (s, 3H), 0.60 (d, 1H, $^2J(H,H) = 9.5$ Hz), 1.30 (s, 3H), 2.23 (m, 1H), 2.38 (m, 1H), 2.42 (t, 1H), 2.63 (dd, 1H, $^2J(H,H) = 17.9$ Hz $^3J = 3.0$ Hz), 2.80 (dd, 1H, $^2J(H,H) = 17.9$ Hz $^3J(H,H) = 2.5$ Hz), 3.53 (s, 3H), 6.50 (d, 1H, $^3J(H,H) = 7.5$ Hz), 6.85 (t, 1H), 6.89 (d, 1H, $^3J(H,H) = 7.7$ Hz), 7.39 (m, 1H), 7.61 (d, 1H, $^3J(H,H) = 8.1$ Hz), 7.65 (t, 1H), 7.98 (d, 1H, $^3J(H,H) = 8.6$ Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$, 20 °C): $\delta = 20.9$, 25.5, 30.3, 34.9, 38.6, 39.4, 45.8, 57.8, 96.2, 108.4, 109.5, 118.1, 125.5, 126.7 (br.), 131.1, 131.4 (br.), 132.8, 133.6, 140.4, 141.6, 155.0, 158.2, 220.1 (Mn-CO), 220.9 (Mn-CO), 231.0 (Mn-CO).

Determination of the molecular structure of 15 by X-ray diffraction analysis: Acquisition and processing parameters are displayed in Table 1. Reflections were collected on a KappaCCD diffractometer using $Mo_{K\alpha}$ graphite-monochromated radiation. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. The absolute structure was determined by refining Flack's *x* parameter. For all computations the Nonius OpenMoleN package was used.[45]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-128866 (**6a**), CCDC-128867 (**8**) and CCDC-128868 (**15**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge C2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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