The Reaction of Diazocyclopentadienyl Compounds with Cyclomanganated Arenes as a Route to Ligand-Appended Cymantrenes

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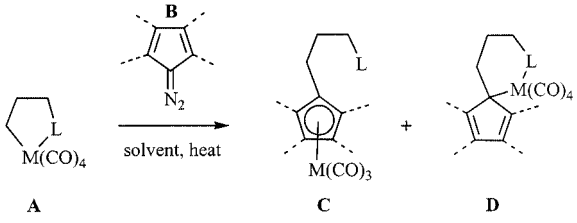
The thermolysis of various cyclomanganated arenes in the presence of 5-diazocyclopentadiene, 7-diazoindene or 9-diazofluorene afforded the corresponding arenes tethered with cymantrenyl, benzocymantrenyl or dibenzocymantrenyl groups in fair to good yields. This reaction implies a multifacetted mechanism that consists of three steps: the insertion of an alkylidene moiety into a C–Mn bond, a C_{Ar}–C bond formation and several haptotropic ring-slippages. The coupling reaction has proven to be particularly efficient with $Mn(CO)_4$ chelates derived from acetylarenes and nitrogen-containing heterocycles. In one case of a 2-phenyl-2-oxazoline complex, the coupling with 9-diazofluorene yields a new η^1-dibenzocymantrene complex in which the $Mn(CO)_4$ moiety is chelated and is part of a six-membered metallacycle. The results of this study are mainly supported by the molecular structures of nine new complexes obtained by X-ray diffraction analyses.

Introduction

We recently reported the thermolytic coupling of cyclomanganated compounds with non-cyclic diazoalkanes, which may efficiently yield new spiralenes.[1] We also showed that the same experiments carried out with 9-diazofluorene could lead to the corresponding tethered η^5-fluorenyl complex resulting from the insertion of a fluorenylidene into the $C_{Ar}-Mn$ bond of the substrate [Equation (1)].[1a] Such an insertion reaction of an alkylidene ligand into a $C_{Ar}-Mn$ bond of a cyclomanganated compound, which leads to an appended dibenzocymantrene derivative, was unprecedented, although similar insertions of alkylidenes were already known but never thoroughly applied to a wide range of substrates. The first reactions of that kind were between diazocyclopentadiene and $(CO)_5MnX$ (X = Cl, Br, I), and yielded halocymantrenes, as reported by Shaver and later by Herrmann.[2] More recently, a series of reactions involving carbonylrhenium complexes were disclosed by Katzenellenbogen and co-workers[3] who were focusing on the synthesis of cyrhetrenes (Re analogues of cymantrenes) for various applications as contrast agents in imaging.[4] Both cymantrenes and their Re analogues can be used as labels for biomolecules[5,6] and in radiopharmaceuticals.[7]



A C D (1)

Our previous results indicated that cymantrenes or -rhetrenes with either an η^5- or an η^1-bonding mode [**C** and **D**, Equation (1)] and appended with various internal ligands can be easily synthesised from readily available cyclomanganated complexes [**A**, Equation (1)] and 9-diazofluorene [**B**, Equation (1)]. One potential application of such complexes could be as chelating ligands for homogeneous catalysis.[8] Indeed, appended cyclopentadienyl-type ligands have received a great deal of attention and are widely investigated for the design of organometallic complexes of both early and late transition metals, which are expected to be active catalysts in various transformations such as the

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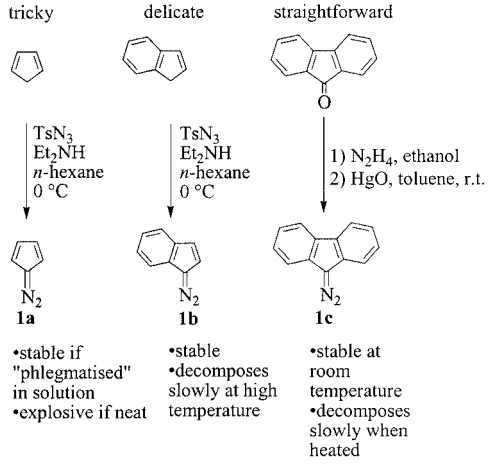
Ziegler−Natta polymerisation.[9] These valuable appended Cp-like ligands can be synthesized by several different methods. In this article we disclose our recent findings on the investigation of the reactivity of a series of cyclomanganated compounds towards 1-diazocyclopentadiene, 7-diazoindene and 9-diazofluorene. With the support of various examples, we show that arenes tethered by cymantrenes can be efficiently synthesised by a multi-facetted reaction consisting of three steps: the insertion of an alkylidene moiety into a C−Mn bond, C_{Ar}−C bond formation and a series of haptotropic ring-slippages. We further show that the supposedly temperature-sensitive diazocyclopentadiene and diazoindene react efficiently as alkylidene sources even at temperatures as high as 100 °C.

Results and Discussion

The Preparation of 5-Diazocyclopentadiene (1a), 7-Diazoindene (1b), and 9-Diazofluorene (1c)

The poor reputation of diazomethane has thrown a shadow of suspicion on all the members of this class of reagents, although recent research has contributed to give a better and friendlier image, at least, to diazocyclopentadienes. For instance, natural diazofluorenes, such as some kinamycins, are active antitumor and antibiotic agents as they display some capabilities to cleave DNA,[10,11] and diazocyclopentadiene (**1a**) has been found to regulate ethylene production in tomatoes.[12]

When we decided to synthesise **1a**−**c**, most of the problems we encountered were not related to the putative explosive and unstable nature of diazoalkanes, which is not marked for most aryl-substituted diazoalkanes, but rather to their purification. The chemical stability and the feasibility of the targeted reagents conditioned our choice of synthetic pathway among all the known methods (Scheme 1). There are several different ways to introduce the diazo function that were compiled and detailed in pertinent reviews or books several years ago; these procedures will therefore not be detailed here.[13]



Scheme 1

An efficient synthesis of 9-diazofluorene (**1c**) was achieved by oxidation of the commercially available fluorenone hydrazone by yellow mercury(II) oxide (or activated manganese dioxide).[14] This reaction afforded a stable, deep-purple crystalline compound that can be stored at −10 °C for months. The thermal decomposition of this reagent in solution in toluene mostly produces the corresponding azines and alkenes.[15]

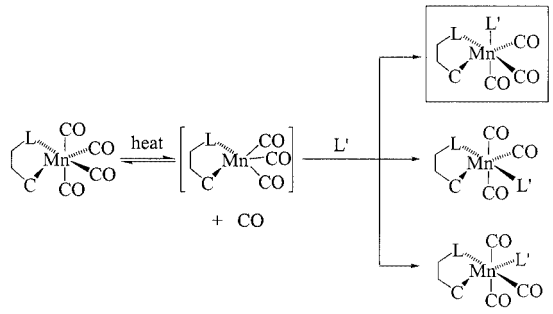
The synthesis of diazoindene **1b** was performed by applying the method described by Weil and Cais,[16] and improved by Rewicki and Tuchscherer by the diazo-transfer reaction of tosyl azide with a large excess of freshly distilled indene in the presence of diethylamine at 0 °C.[17] This reagent can also be obtained from a Bamford−Stevens-type transformation[18] of the indenone tosylhydrazone[19] prepared in several steps[20] from indanone. This diazoalkane is quite unstable and decomposes slowly in a non-explosive manner above 0 °C. When synthesised it can be stored for weeks if cooled to a temperature lower than −20 °C. In our hands, **1b** was formed in high yields and had to be extracted from a crude mixture that mostly contained limited amounts of insoluble tosylamide and large amounts of unchanged indene. The extraction and isolation of a highly enriched sample of diazoindene implied two critical and crucial steps, as already discussed by Herrmann and coworkers: (1) the removal of the large amounts of unchanged indene by distillation under reduced pressure, which had to be carried out carefully with mild and slow heating of the crude mixture in an oil-bath, and (2) a low-temperature (−10 °C) chromatographic separation on silica gel of the red-orange diazoindene **1b** from the brownish tar formed during step (1).

The synthesis of diazocyclopentadiene (**1a**) first reported by Doering and DePuy in 1953[21] and later improved by Weil and Cais and by Regitz and Liedhegener,[22] was even more tricky, although still possible. It was based on the above-mentioned diazo-transfer reaction between tosyl azide and freshly cracked cyclopentadiene in the presence of diethylamine in hexane at 0 °C. Because of its sensitive nature we did not attempt to isolate diazocyclopentadiene (**1a**) neat; it was handled instead in solution in an aliphatic solvent. It could be readily extracted from the crude reaction medium and purified by a low-temperature chromatographic separation on silica gel to remove tosylamide that was formed during the diazo-transfer reaction. The concentration of **1a** was readily assessed, as advocated by Weil and Cais, by a gravimetric titration of the phosphazine obtained from reaction of an aliquot of the mother solution with triphenylphosphane.

The Reaction of Monomanganated Complexes with 1a−c

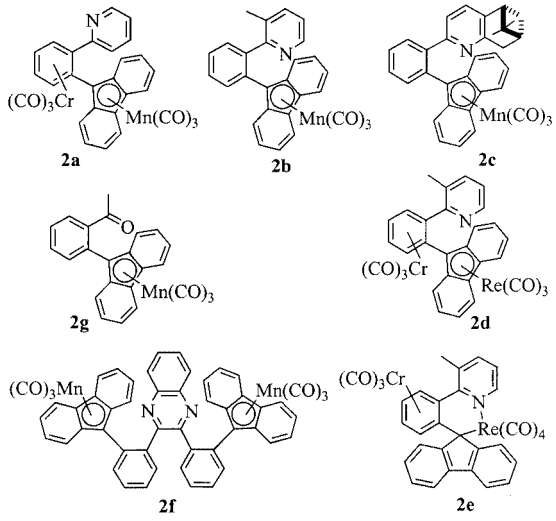
It has long been known that cyclomanganated complexes of formula *cis*-[(LC)Mn(CO)$_4$] (LC: carbanionic chelating ligand) can undergo the replacement of one carbonyl ligand by a σ-donor ligand upon heating (Scheme 2).[23] In every reported case the incoming ligand occupies the axial position formerly occupied by the displaced carbonyl ligand, although this does not mean that the thermolysis of tetra-

carbonylmanganese chelates proceeds by the selective expulsion of one of the axial ligands. Although the mechanism of this thermolytic decarbonylation is still not known, a thermodynamic control is probably responsible for the formation of a *fac*-tricarbonylmanganese chelate.

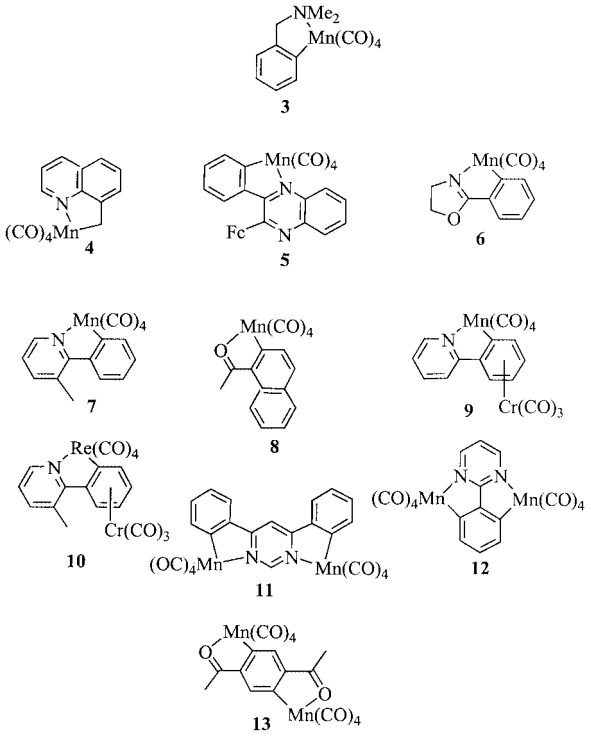


Scheme 2

Among all the possible adducts that may arise from the coordination of a donor ligand to the electron-deficient Mn^I centre, only the facial stereoisomer presents three *trans* influences that may significantly contribute to the stabilisation of the complex. When the exogenous ligand is a diazoalkane, we previously proposed that its coordination to Mn leads to a zwitterionic transient species — a manganese ylide — that evolves by elimination of N_2 to give a metallaalkylidene intermediate. A *cis* migration of the aromatic carbon atom bonded to the manganese atom creates a C−C bond between the exogenous alkylidene fragment and the chelate. At this point, we previously showed that the fluorenylidene species not only inserts into the carbon−metal bond, but the chelate itself is dismantled by the cleavage of the Mn−L bond, which is followed by a series of haptotropic shifts. In most cases, the final compounds are the corresponding [(η^5-fluorenyl)$Mn(CO)_3$] complexes **2a**−**d** and **2g**.



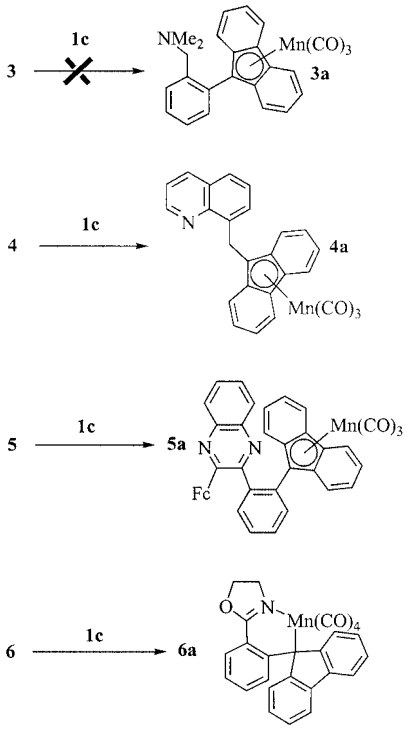
In the case of the rhenium(I) complex **2d**, we showed that it could undergo a haptotropic shift upon reaction with dissolved CO to give the [(η^1-fluorenyl)$Re(CO)_4$] complex **2e**. To check the validity of this coupling reaction with substrates containing various sorts of internal ligands, we decided to address the reactivity of diazocyclopentadienyl compounds such as **1a**−**c** with complexes **3**−**10**. Each thermolytic coupling reaction was carried out with an excess of the diazoalkane in order to compensate for the loss of reagent caused by a concomitant thermo-promoted conversion into azines and olefins. The course of the reaction could also be monitored by IR spectroscopy. The reaction was generally stopped when the characteristic four carbonyl-ligand stretching vibration bands generated by the $M(CO)_4$ group of the substrate completely faded out and were replaced by the characteristic two CO A_1 and E stretching vibration bands of the final product arising from the *fac*-$Mn(CO)_3$ fragment.



We first focussed our attention on the reactivity of **3** with **1c** [Equation (2) and Table 1, Entry 1]. Unfortunately, every attempted reaction between these two reagents led to the decomposition of **3** into dark-brown intractable compounds. More promising results were obtained with **4** [Equation (3)] and **5** [Equation (4)], which reacted readily and cleanly with **1c** to yield the corresponding substituted (η^5-fluorenylidene)$Mn(CO)_3$ complexes **4a** and **5a** (Table 1, Entries 2 and 3). The treatment of complex **6** with an excess of **1c** yielded a new brownish tetracarbonylmanganese chelate that was later identified by crystallographic means as complex **6a**, an analogue of **2e** [Equation (5) and Table 1, Entry 4]. The former plausibly arises from the carbonylation of the corresponding (η^5-fluorenyl)$Mn(CO)_3$ precursor, which was not isolated or detected in the crude mixture.

Table 1. Experimental conditions used for the thermolytic coupling of diazocyclopentadienes **1a–c** with cyclomanganated aromatic compounds **3–13**

Entry	Substrate	R_2CN_2	*T* [°C]	Solvent(s)	Product(s)	Isolated yields (%)
1	**3**	**1c**	50	pentane/toluene	**3a**	–
2	**4**	**1c**	100	heptane/toluene	**4a**	70
3	**5**	**1c**	70	hexane/toluene	**5a**	63
4	**6**	**1c**	80	cyclohexane/toluene	**6a**	74
5	**7**	**1a**	100	heptane/hexane	**7a**	67
6	**7**	**1b**	70	hexane/cyclohexane	**7b**	87
7	**8**	**1b**	100	heptane/toluene	**8a**	76
8	**9**	**1a**	100	heptane/cyclohexane	**9a**	66
9	**9**	**1b**	80	cyclohexane/toluene	*u*-**9b**/*l*-**9b** (4:1)	55
10	**10**	**1a**	100	heptane/hexane	**10a**	71
11	**11**	**1c**	100	heptane/toluene	**11a**	84
12	**12**	**1c**	110	toluene	**12a**	61
13	**13**	**1c**	70	hexane/toluene	**13a**	> 90



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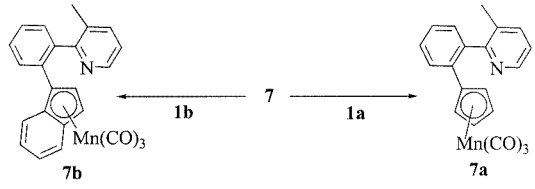
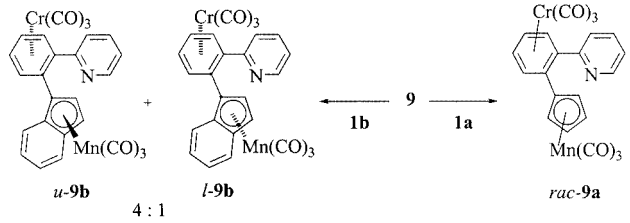
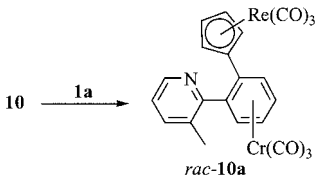


Scheme 3



Scheme 4

treated with **1b**; complex **7** yielded **7b** (Scheme 3 and Table 1, Entry 6). The latter displayed a surprising dynamic behaviour when analysed by NMR spectroscopy in $CDCl_3$. A sample of **7b** dissolved in $CDCl_3$ was analysed at various sub-ambient temperatures until the resolution of the spectrum was sufficient to assume that a slow exchange had been reached. At 243 K we observed two sets of signals belonging to two isomers of this tris(aromatic) organometallic compound in a 1:3 ratio (Figure 1). Figure 1 displays the two signals of the olefinic protons of the indenyl fragment and their dependence on temperature. At first we thought that one of the two species might result from a combination of reversible coordination of the internal pyridyl group to the Mn^I centre and a haptotropic shift — or ring slippage[24] — from an η^5 to an η^3 mode, which indeed should cancel out the isochronicity of the three carbonyl ligands of the $Mn(CO)_3$ moiety.



(6)

Complexes **7** (Scheme 3), **9** (Scheme 4) and **10** [Equation (6)] reacted readily with **1a** to give the corresponding substituted (η^5-cyclopentadienyl)$Mn(CO)_3$ complexes **7a**, **9a** and **10a**, respectively (Table 1, Entries 5, 8 and 10). Similar results were obtained when the same substrates were

A ^{13}C NMR spectrum recorded at −30 °C displayed only one intense signal at δ = 225 ppm, which is rather consistent with a rapidly rotating $M(CO)_3$ group (Figure 2). We therefore deduced that the observed dynamic effect was probably the consequence of a conformational equilibrium

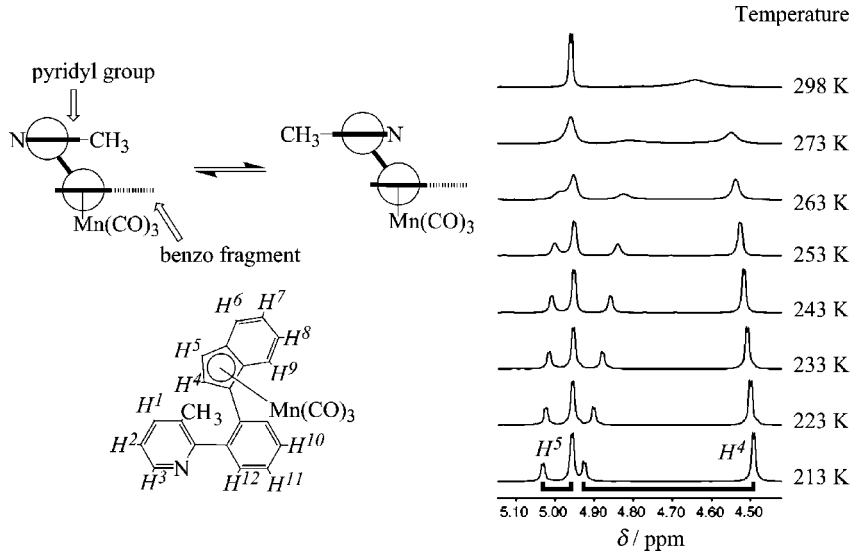


Figure 1. Temperature dependence of the ^{1}H NMR spectrum of **7b** in $CDCl_3$; enlargement of the olefinic indenyl protons region; the temperature dependency plausibly stems from a conformational equilibrium between two unequally populated conformers, whose Newman-type projections are depicted

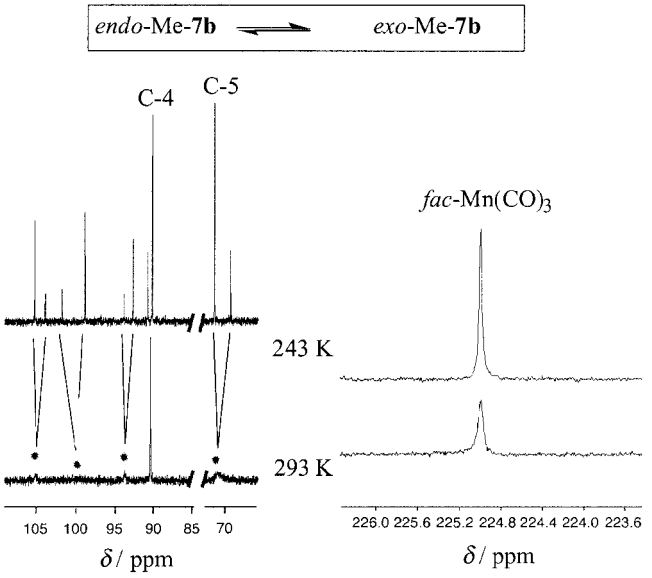
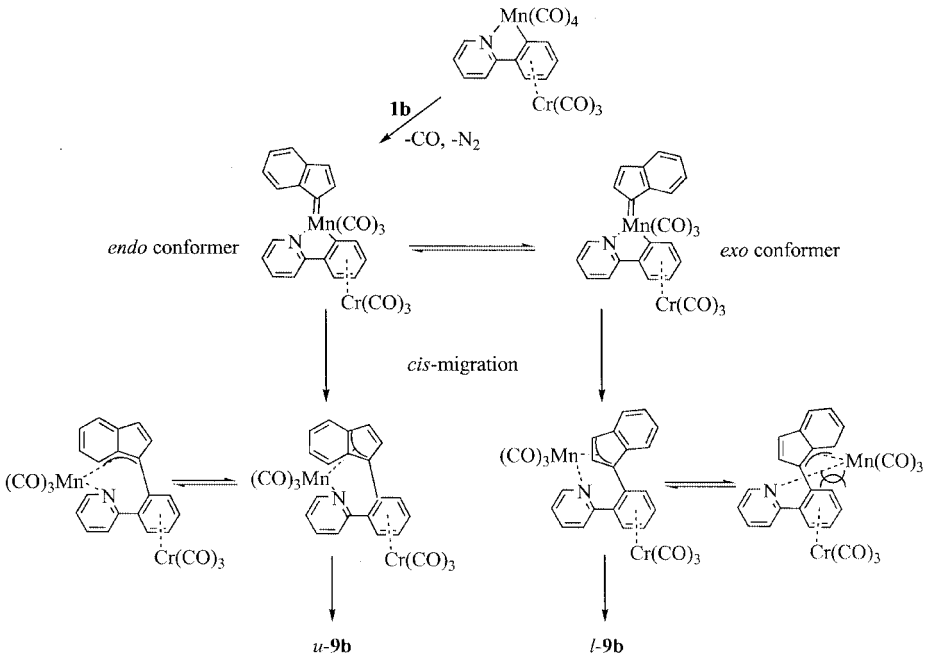


Figure 2. Temperature dependence of the ^{13}C NMR spectrum of **7b** in $CDCl_3$; enlargements of the areas of resonance of the η^5-bonded indenyl ^{13}C atoms (left) and of the $Mn(CO)_3$ fragment (right)

involving the rotation of the disubstituted pyridyl group. Such a conformational equilibrium should likely involve two conformers differing only in the orientation of the pyridyl group, which should place the methyl group either *endo* or *exo* with respect to the rest of the molecule (Figure 1). Strikingly, the ^{13}C NMR signals belonging to the indenyl group are distinguishable as sharp singlets only when the temperature drops down to 243 K. They appear as two sets of five signals between δ = 65 and 110 ppm (Figure 2). At room temperature, only the signal of the olefinic carbon atom C-4 (connected to 4-H) is well resolved since the difference in chemical shift between the two corresponding signals amounts to only 0.6 ppm at the slow exchange rate (Figure 2). From the analysis of the cross-peak correlation between the two sets of signals, a two-dimensional ^{1}H-^{1}H ROESY experiment carried out at 243 K allowed us to confirm that within the timescale of ^{1}H NMR a slow exchange exists between two unequally populated species (see Supporting Information). Unfortunately, we could not deduce any clue as to the structure of the major conformer because of the intricate mixing of the cross-peak correlations generated by pure nuclear Overhauser effects with those arising from the chemical exchange.

The reaction of complex **9** with **1b** yielded the two diastereomers *u*-**9b** and *l*-**9b** in a 4:1 ratio (Scheme 4 and Table 1, Entry 9). The predominance of *u*-**9b**, whose structure was firmly ascertained by X-ray diffraction analyses (vide infra), can be explained by the intervention of a late transition state in which the Mn-to-indenyl electronic interaction would define the activation barrier of the alkylidene insertion step. This is a proposal somewhat similar to that made for the mechanism of formation of "spiralenes".[1b] Indeed, prior to insertion, the indenylidene ligand may adopt several conformations, among which only two are rel-

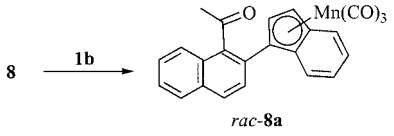


Scheme 5

evant for the *cis*-migration step: on the one hand, the benzo fragment of the indenylidene is placed at an *endo* position, and on the other the same fragment is found at an *exo* position with respect to the chelate (Scheme 5).

Upon insertion of the indenylidene, the formation of the carbon−carbon bond is accompanied by the creation of a vacant coordination site at the manganese centre that can be filled by an interaction with the π-system of the indenyl species. The ratio between the two products illustrates the intracyclic strains, which are putatively lower in the *endo* stereoisomer than in the *exo* isomer.

Complex **8** successfully reacted with an excess of **1b** to yield the aromatic ketone **8a** in good yield [Equation (7) and Table 1, Entry 7].



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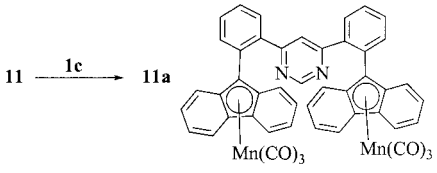

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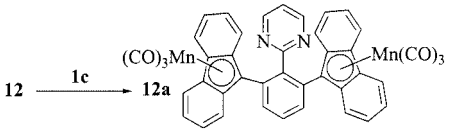

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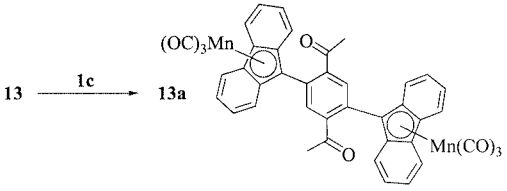


(10)

The Reaction of Dimanganated Complexes with 1c

Complexes **11** and **12**, derived from pyrimidine, were treated with an excess of **1c** and gave the corresponding dinuclear complexes **11a** and **12a** in good yields [Equations (8) and (9), Table 1, Entries 11 and 12]. Both complexes could be purified by column flash chromatography in spite of their polarity. The reaction of **13** with **1c** under the same conditions also afforded the corresponding dimetallic product **13a**, which precipitated immediately [Equation (10), Table 1, Entry 13].

This complex displays a pronounced insolubility even in polar solvents such as tetrahydrofuran, which prevented its purification by chromatography and its full characterisation by NMR spectroscopy. Its IR spectrum measured with a KBr pellet displays the expected stretching bands related to the $Mn(CO)_3$ group at $\tilde{\nu}$ = 2013 and 1926 cm^{-1} and that related to the ketone functions at $\tilde{\nu}$= 1694 cm^{-1}.

Structural and Spectroscopic Properties of Complexes 4−8a, 9b and 10−12a

Most of the new complexes reported here crystallised readily. In this article, we present the structures obtained by

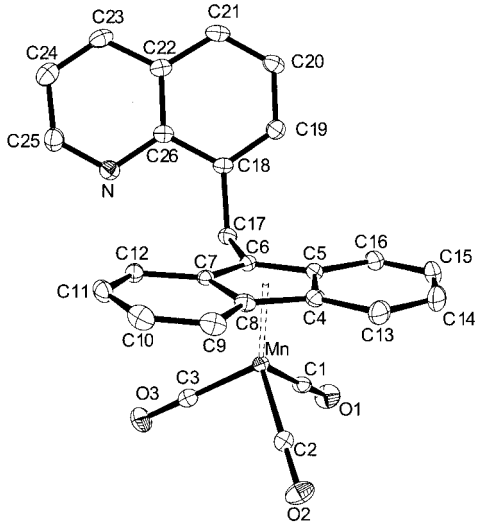


Figure 3. ORTEP diagram of compound **4a**, with the atom numbering scheme; hydrogen atoms have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å]: Mn−C6 2.126(2), Mn−C5 2.189(2), Mn−C8 2.202(2), Mn−C2 1.803(3), Mn−C1 1.783(3), Mn−C3 1.780(3), C6−C17 1.507(3), C6−C7 1.439(3), C8−C4 1.449(3)

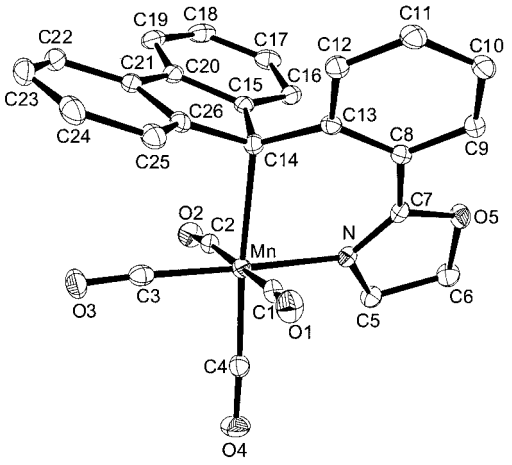


Figure 5. ORTEP diagram of compound **6a**, with the atom numbering scheme; the molecule of solvent and hydrogen atoms have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å] and angles [°]: Mn−C14 2.251(2), Mn−C1 1.869(2), Mn−C2 1.868(3), Mn−C3 1.821(3), Mn−N, 2.042(2), N−C7 1.285(3), O5−C7 1.348(3); N−Mn−C14 84.36(2), C8−C13−C12 116.6(2), C15−C14−C26 102.4(2)

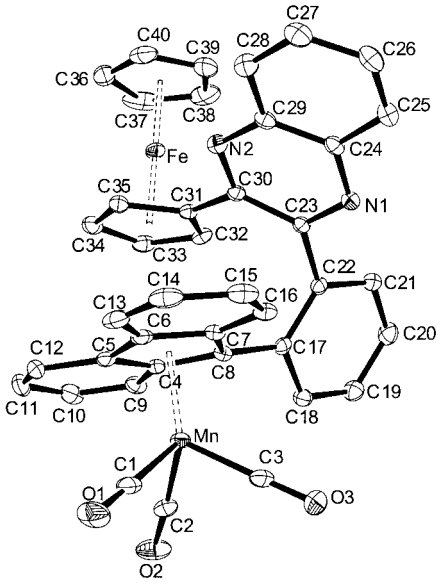


Figure 4. ORTEP diagram of compound **5a**, with the atom numbering scheme; the molecule of solvent and hydrogen atoms have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å] and angles [°]: Mn−C1 1.789(4), Mn−C2 1.786(3), Mn−C3 1.792(4), Mn−C4 2.181(3), Mn−C5 2.198(3), Mn−C6 2.203(3), Mn−C7 2.191(3), Mn−C8 2.157(3), Fe−C31 2.060(3), C8−C17 1.480(4), $centroid_{Fc}$−$centroid_{fluorene}$ 3.792(4); C1−Mn−C2 90.9(1), C1−Mn−C3 93.2(2), C2−Mn−C3 91.8(1)

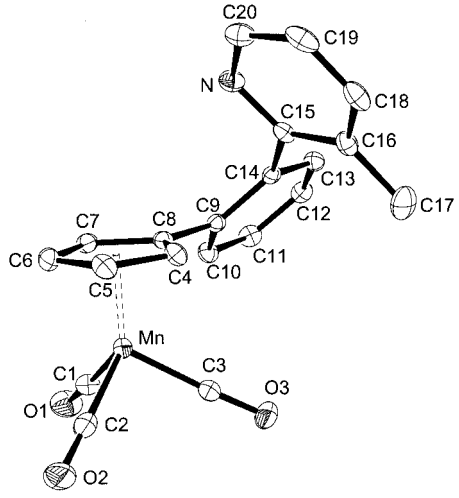


Figure 6. ORTEP diagram of compound **7a**, with the atom numbering scheme; atoms of hydrogen have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å] and angles [°]: Mn−C1 1.787(2), Mn−C2 1.804(3), Mn−C3 1.779(2), Mn−C8 2.154(2), Mn−C4 2.145 (2), Mn−C5 2.137(2), C8−C9 1.488(3); C4−C8−C7 106.4(2)

X-ray diffraction analyses for **4a** (Figure 3), **5a** (Figure 4), **6a** (Figure 5), **7a** (Figure 6), **8a** (Figure 7), **9a** (Figure 8), *u*-**9b** (Figure 9), **11a** (Figure 10) and **12a** (Figure 11). Main acquisition and refinement data are collected at the end of the Exp. Sect.; ORTEP diagrams of the relevant structures are given in the relevant figure, along with the atom numbering scheme and selected geometrical information.

In most structures where the Mn centre is bonded to the cyclopentadienyl moiety, there are disparities among the Mn−C_{Ar} bond lengths that reveal a sensitivity of the $Mn(CO)_3$ moiety to steric hindrance (Table 2). In η^5-fluorenyl complexes (Figures 3, 4, 10 and 11) the C_{ipso}−Mn distance can vary from 2.126(2) to 2.157(3) Å while the other C_{Ar}−Mn bonds remain unaffected, with an interatomic distance of about 2.195 Å. In a similar way, with η^5-indenyl complexes, the largest variation of the carbon−manganese distances is noticed for the C_{ipso}−Mn and $<C_{olefinic}-Mn>$ distances from 2.139(2) to 2.155(4) Å and from 2.126(2) to 2.141(2) Å in **8a** (Figure 7) and **9b** (Figure 9), respectively.

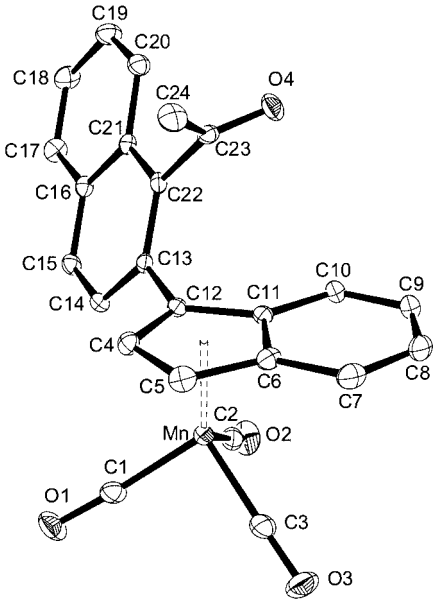


Figure 7. ORTEP diagram of compound **8a**, with the atom numbering scheme; atoms of hydrogen have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å] and angles [°]:Mn−C12 2.139(2), C12−C13 1.484(3), C22−C23 1.516(3), C23−O4 1.211(2); C4−C12−C11 106.4(2)

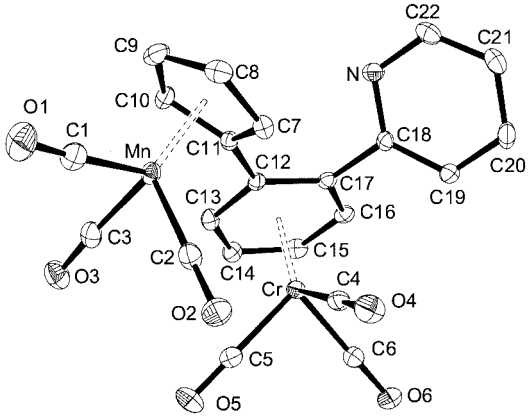


Figure 8. ORTEP diagram of compound *rac*-**9a**, with the atom numbering scheme; the molecule of solvent and hydrogen atoms have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å]: Cr−C12 2.240(4), Cr−C17 2.215(3), Cr−C15 2.217(4), Mn−C11 2.167(4), Mn−C9 2.137(4), Mn−C7 2.144(4), C17−C18 1.506(5), C11−C12 1.484(5)

Again the C_{Ar}−Mn bond lengths remain almost unaffected and remain at an average value of 2.202 Å.

Likewise, within the η^5-cyclopentadienyl complexes the disparity existing between C_{Cp}−Mn bond lengths is larger and directly related to the presence of bulky groups such as $Cr(CO)_3$ in the close vicinity of the $Mn(CO)_3$ group. For instance, in **7a** the C_{ipso}−Mn and the C4−Mn interatomic distances are the longest, with values of 2.154(2) and 2.145(2) Å, respectively, whereas the C(5−7)−Mn bond lengths are all equal to 2.137(2) Å (Figure 6). More dramatic distortions are observed in the dinuclear complex **9a**, in which C_{ipso}−Mn is the largest C_{Cp}−Mn distance with a value of 2.167(4) Å and C9−Mn is the smallest distance with a value of 2.137(4) Å (Figure 8). In the (η^6-aryl)tricarbonylchromium fragment the largest C−Cr distance is Cr−C12, with a value of 2.240(4) Å, whereas the remaining C(13−17)−Cr distances amount to about 2.216 Å.

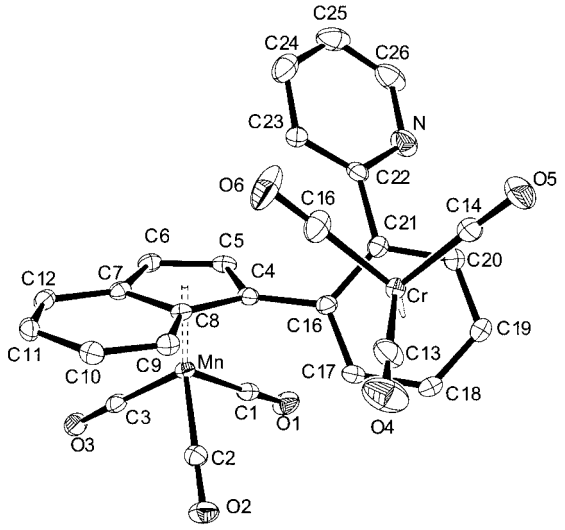


Figure 9. ORTEP diagram of compound *u*-**9b**, with the atom numbering scheme; atoms of hydrogen have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å]: Mn−C4 2.155(2), Mn−C5 2.138(2), Mn−C6 2.144(2), Cr−C16 2.259(2)

If we look closely at the reported structures of cymantrenes and benzo- and dibenzocymantrenes stored in the Cambridge Structural Database (CSD), we notice that the centroid−Mn distance clearly increases from cyclopentadienyl- to fluorenyl-type ligands. As already mentioned, and revealed previously by Calhorda and Veiros, this relative increase of the metal−cyclopentadienyl ligand distances stems from intrinsically different metal-to-π-system bonding modes, which is truly η^5 in Cp derivatives and seemingly more η^3-η^2 in indenyl derivatives.[24,25] The C_{ipso}−Mn distances seem much more sensitive to a factor such as steric hindrance than to changes in the electronic properties of neighbouring substituents. This can be readily assessed by the relative dispersion of the C_{ipso}−Mn distances collected from the CSD for monosubstituted cymantrenes.[26] Table 3 lists the statistical data related to centroid−Mn and C_{ipso}−Mn distances of 20 structures of monosubstituted cymantrenes deposited with the CSD.[27] For the benzo and dibenzo analogues, only two and three examples, respectively, have been selected based on their substitution pattern and their structural analogy with the complexes reported herein (Table 4).

In complex **6a**, the Mn atom sits in an octahedral environment (Figure 5). The manganese atom is chelated by the pentacyclic ligand and is included in a slightly twisted six-membered metallacycle consisting of atoms N, C7, C8, C13, C14 and Mn. The ^{13}C NMR analysis of a solution of this compound at room temperature reveals a dynamic

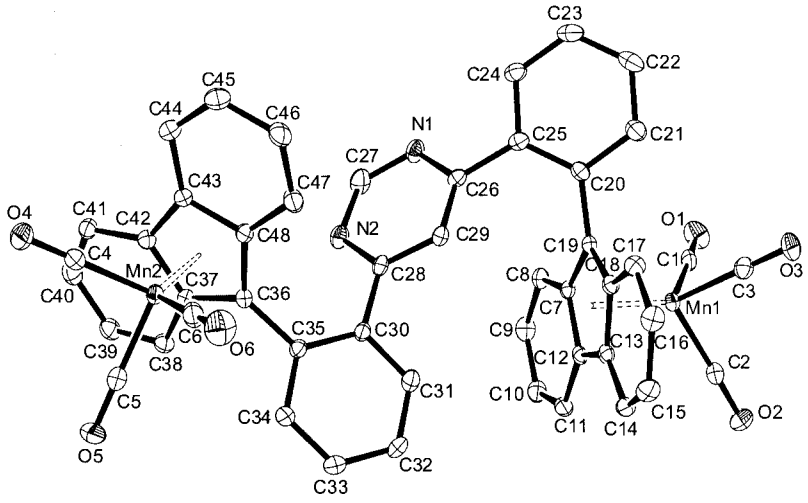


Figure 10. ORTEP diagram of compound **11a**, with the atom numbering scheme; the molecule of solvent and hydrogen atoms have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å] and angles [°]: Mn1−C1 1.798(4), Mn1−C2 1.793(4), Mn1−C3 1.793(4), Mn1−C7 2.194(3), Mn1−C12 2.187(3), Mn1−C13 2.197(4), Mn1−C18 2.191(4), Mn1−C19 2.155(4); C1−Mn1−C2 94.1(2), C1−Mn1−C3, 91.3(2); C1−Mn1−C7, 90.8(2)

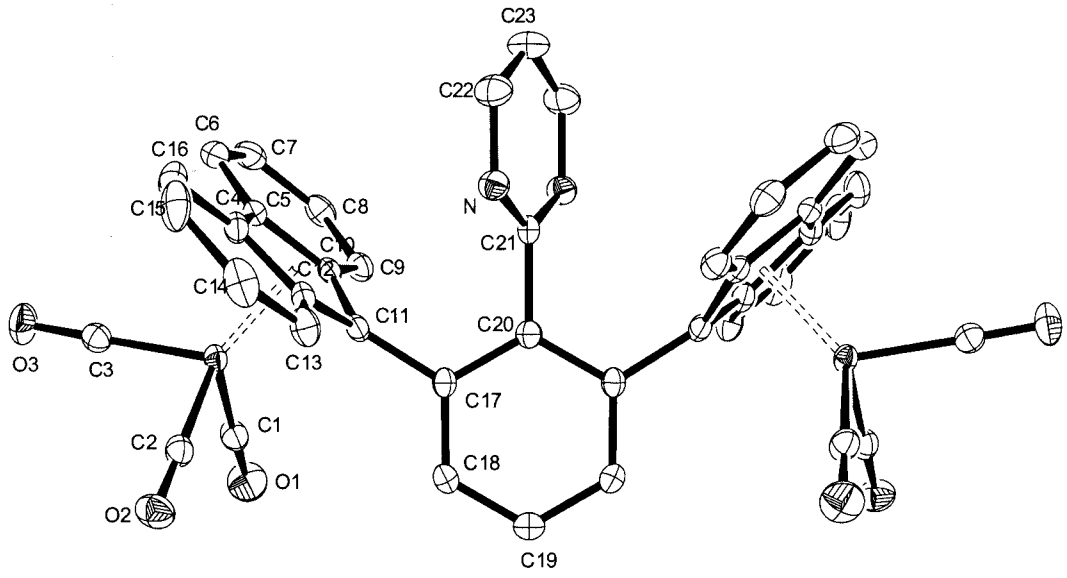


Figure 11. ORTEP diagram of compound **12a**, with the atom numbering scheme; atoms of hydrogen have been omitted for clarity; the ellipsoids are drawn at the 30% probability level; selected interatomic distances [Å] and angles [°]: Mn−C1 1.790(3), Mn−C2 1.787(3), Mn−C3 1.811(3), Mn−C4 2.205(3), Mn−C5 2.210(2), Mn−C10 2.198(2), Mn−C11 2.135(2), Mn−C12 2.191(2); C1−Mn−C2 92.2(1), C1−Mn−C3 93.0(1), C2−Mn−C3 91.4(1)

Table 2. Structural parameters for the cyclopentadienyl-to-manganese bonding interaction in compounds **4a**, **5a**, **7a**−**9a**, **9b**, **11a**−**12a**

Coordination mode[a]	η^5-Fl				η^5-In		η^5-Cp	
Compound	**4a**	**5a**	**11a**	**12a**	**8a**	*u*-**9b**	**7a**	*rac*-**9a**
C_{ipso}−Mn [Å]	2.126(2)	2.157(3)	2.155(4)	2.135(2)	2.139(2)	2.155(4)	2.154(2)	2.167(4)
$<C_{Ar}-Mn>$ [Å]	2.195(2)	2.193(2)	2.192(4)	2.201(3)	2.198(2)	2.207(2)		
<C−Mn> [Å]					2.126(2)	2.141(2)	2.139(3)	2.144(4)
<centroid−Mn> [Å]	1.805(2)	1.811(3)	1.807(4)	1.814(3)	1.782(2)	1.797(2)	1.771(3)	1.778(4)

[a] Abbreviations: Fl = fluorenyl; In = indenyl; Cp = cyclopentadienyl.

Table 3. Mn−centroid and Mn−C_{ipso} statistical distances obtained from 20 structures of monosubstituted cymantrenes deposited with the Cambridge Structural Database[27]

	<Centroid−Mn> [Å]	C_{ipso}−Mn [Å]
Minimum	1.752	2.120
Maximum	1.784	2.185
Points	20	20
Mean	1.767	2.144
Median	1.766	2.147
Std. deviation	0.007	0.017
Variance	0.00005	0.00031
Std. error	0.001	0.004
Skewness	0.04	0.34

Table 4. Mn−centroid and Mn−C_{ipso} distances in structures of benzo- and dibenzocymantrenes deposited with the Cambridge Structural Database[27b,27c]

CSD refcodes	Centroid−Mn [Å]	C_{ipso}−Mn [Å]	R
Benzocymantrene:			
BINCMN	1.791	2.127	Br
TURNID	1.799	2.155	[(η^6-C_6H_5)Cr-$(CO)_3$]
Dibenzocymantrene:			
BAHFEW	1.823	2.147	C_6H_4
MIYXAT	1.801	2.122	H
ZUKLOG	1.813	2.154	Ph

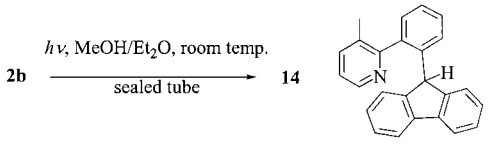
behaviour. The four carbonyl ligands give rise to three very broad and poorly resolved ^{13}C signals at δ = 213.6, 213.0 and 211.8 ppm. Decreasing the temperature to −50 °C allowed the detection of sharper signals at δ = 213.9, 212.7 and 211.51 ppm, but did not allow us to distinguish separate signals for the two non-isochronous axial carbonyl ligands. This dynamic behaviour possibly stems from the conformational changes of the six-membered metallacycle that imply a partial rotation of the organic ligand around the C14−Mn axis via a transition state wherein the Mn−N bond is eclipsed by the C14−C13 bond. A similar broadening was observed in the ^1H NMR spectra, although we could not assign this exactly. To the best of our knowledge **6a** is only the second example of a carbonyl(η^1-fluorenyl)-manganese complex that has been characterised by X-ray diffraction analyses.[28] The Mn−C distance of 2.254(2) Å is in the range reported for similar compounds.[29]

In the crystalline state the homodimetallic complex **11a** (Figure 10) consists of a pentaaromatic distorted helix of 1,2- and 1,3-disubstituted arenes. The distance between the two Mn atoms is ca. 1 nm (10.7 Å). In this compound the helical arrangement optimises the electrostatic repulsion and minimises the steric interactions. The C_2-symmetric compound **12a** (Figure 11) is a rare case of a 1,2,3-heterotrisubstituted arene with an encapsulated heterocyclic aromatic ligand. In this compound the pyrimidyl ring stands almost perpendicular to the trisubstituted benzene. The two metal centres are about 0.9 nm apart.

Conclusion

Cyclomanganated aromatic compounds are generally readily accessible by the thermolysis of (alkyl)pentacarbonylmanganese compounds in the presence of an aromatic ligand. Such complexes have been studied for their reactivity towards various inorganic and organic reagents. Most interesting are those reactions that yield new organomanganese compounds and allow further chemical or physical investigations. We have shown here a valuable synthetic method for appended cymantrenes that could be of interest in various domains such as the design of polytopic ligands for homogeneous catalysts or in the preparation of coordination polymers from bidentate ligands containing two dibenzocymantrenyl substituents.[1a] Most coupling reactions with diazocyclopentadienyl compounds gave excellent yields of cymantrenes when the manganated substrate contained a pyridyl ring, a parent heterocycle or a ketone as internal donor ligand. In all other cases, the course of the reaction was not clear and definitely deserves more attention. We have shown that dinuclear substrates could also react even when the steric congestion is important, as in the case of one di-*ortho*-manganated 2-phenylpyrimidine.

The release of the cyclopentadienyl ligand, or in other words the removal of the $Mn(CO)_3$ fragment, is seemingly readily achievable by applying the method recently suggested by Jaouen and co-workers.[30] In a preliminary experiment, the photolysis of complex **2b** in MeOH efficiently afforded compound **14** [Equation (11)] as a white solid in 71% yield.



(11)

In summary, two synthetic steps are necessary to convert an aromatic compound into a polycyclic tethered cymantrene. Both the cyclomanganation and the coupling steps involve neutral reagents and are overall relatively efficient.

Experimental Section

General Remarks: All experiments were carried out under dry argon with dry and degassed solvents. The (η^6-arene)tricarbonylchromium complexes were synthesised according to published procedures.[1b] Ligands such as 2-phenylpyrimidine,[31] 4,6-diphenylpyrimidine[32] and 2-ferrocenyl-3-phenylquinoxaline[33] as well as tetracarbonyl[8-(methyl-κ$C^{l'}$)quinoline-κN]manganese(I) (**4**)[34] were synthesised according to published procedures. Other ligands were purchased from commercial sources and used without further purification. NMR spectra were acquired with Bruker DRX 500 (^1H and ^{13}C nuclei) and AC 300 (^1H nucleus) spectrometers at room temperature unless otherwise stated. Chemical shifts are reported in ppm downfield of $SiMe_4$. IR spectra were measured with a Perkin−Elmer FT spectrometer. Mass spectra were recorded at

the Service of Mass Spectrometry of University Louis Pasteur (FAB+PEG matrix) or at the Analytical Centre of the Chemical Institute of the University of Bonn (EI). Elemental analyses were performed at the Service d'Analyses of the "Institut de Chimie de Strasbourg" and at the analytical centre of the "Institut Charles Sadron" in Strasbourg.

***p*-Tosyl Azide:** *p*-Toluenesulfonyl chloride (85 g, 0.45 mol) was added to a stirred solution of sodium azide (35 g, 0.54 mol) in a mixture of 35 mL of water and 500 mL of absolute ethanol. The resulting mixture was stirred overnight. After this time, 500 mL of water was added and the resulting slurry was extracted with diethyl ether. The organic phases were combined and dried with magnesium sulfate and then stripped of solvent under reduced pressure to afford a pale yellow oil.

5-Diazocyclopentadiene (1a): Freshly cracked cyclopentadiene (6.6 g, 0.1 mol), *p*-tosyl azide (19.7 g, 0.1 mol) and diethylamine (7.3 g, 10.4 mL, 0.1 mol) were dissolved in 50 mL of distilled acetonitrile and stirred under argon at 3 °C for 96 h. The resulting brownish reaction mixture was extracted with 300 mL of *n*-hexane and the organic phase was washed with 200 mL of water. The organic phase was washed twice with an aqueous solution of KOH (6% mass) and with water. The combined organic phases were dried with $MgSO_4$ and concentrated by the removal of half of the solvents under reduced pressure. The resulting solution was then loaded on the top of a column of SiO_2 packed in *n*-hexane and cooled to −10 °C. A large orange band containing the product was eluted with *n*-hexane and the corresponding solution was concentrated to 30 mL and titrated with triphenylphosphane. Thus, a 2-mL aliquot of mother solution was added to a solution of triphenylphosphane (1.8 g, 6 mmol) in diethyl ether and stirred under argon for 15 min. To the resulting mixture, 30 mL of *n*-hexane was added and the mixture stirred for an additional 15 min. The resulting orange precipitate was filtered off, washed with 40 mL of hexane and 30 mL of pentane, and dried under vacuum. The amount of cyclopentadienonetriphenylphosphazine (0.37 g, 1.04 mmol) recovered from this gravimetric titration gave an approximate concentration of 0.52 M of 5-diazocyclopentadiene. Yield: 1.44 g, 16%.

Diazoindene (1b): Freshly distilled indene (27.4 g, 0.236 mol) and *p*-tosyl azide (44.3 g, 0.224 mol) were dissolved in diethylamine (50 mL) and stirred at 0 °C under argon for 72 h. The resulting mixture was extracted with *n*-hexane and the organic phases washed with water and brine. The organic phases were combined, dried with Na_2SO_4 and concentrated under a reduced pressure of ca. 20 Torr at 30 °C. The resulting solution was distilled under a reduced pressure of 9 Torr, using a Vigreux column to improve the separation of the components of the raw mixture. A large fraction of indene was distilled at a temperature of 58 ± 4 °C. To avoid any explosive behaviour, the boiler was heated with an oil bath that was warmed slowly and whose temperature was homogenised by gentle stirring. The distillation of indene was stopped as soon as the temperature at the head of the Vigreux column started to fall. The boiler was then swiftly cooled to room temperature and the remaining residue separated by chromatography on an SiO_2 column refrigerated at 4 °C and packed in *n*-hexane. A red band containing the product was eluted with dry and distilled *n*-hexane. Removal of the solvent under reduced pressure afforded a red oil consisting of 92% of diazoindene and 8% of unchanged indene. This oil could be kept over long periods of time provided it was kept at a temperature lower than −20 °C. Yield: 15%.

9-Diazofluorene (1c): 9-Fluorenone hydrazone (1.0 g, 5.3 mmol) was dissolved in 75 mL of toluene and yellow mercuric oxide (3.41 g, 15.8 mmol) was added. The resulting suspension was stirred for 1 d, filtered and the filtrate dried with $MgSO_4$. The removal of solvents under reduced pressure afforded **1c** as a purple-red stable solid. Yield: 0.948 g, 94%.

General Procedure for the Reaction of 1a−c with Cyclometalated Arenes: The cyclometalated substrate was dissolved in a mixture of *n*-heptane and toluene and the resulting solution was brought to reflux. A solution of diazoalkane in toluene was added dropwise from a syringe and the resulting solution was stirred for an additional period of time. The solvents were then evaporated to dryness. The residue was dissolved in dichloromethane and SiO_2 was added. The suspension was stripped of solvent under reduced pressure and the coated silica gel was loaded on the top of a refrigerated SiO_2 column packed in *n*-hexane.

8-[1′-(Dibenzocymantren-1-yl)methyl]quinoline (4a): From **4** (0.32 g, 1 mmol), a 1:1 mixture of *n*-heptane (7 mL) and toluene (7 mL), and a solution of **1c** (0.4 g, 2.1 mmol) in toluene (4 mL). Addition 25 min, stirring for an additional 35 min. An initial SiO_2 column chromatography (60 μm, 5 °C) gave a raw sample of **4a** contaminated with various organic pollutants upon elution with pure dichloromethane. A second chromatographic separation (0 °C) with a different grade of SiO_2 (15−25 μm) gave **4a** after elution with dichloromethane/*n*-hexane (1:1). Yield: 0.35 g (70%). $C_{26}H_{16}MnNO_3$ (445.3): calcd. C 70.12, H 3.62, N 3.15; found C 69.79; H 3.54, N 3.01. IR (CH_2Cl_2): ṽ: 2015 vs, 1931 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.09 (d, ^3J = 2.9 Hz, 1 H), 8.17 (d, ^3J = 7.8 Hz, 1 H), 8.11 (m, 2 H), 7.66 (d, ^3J = 8.1 Hz, 4 H), 7.49 (m, 1 H), 7.20 (m, 4 H), 7.12 (d, ^3J = 7.0 Hz, 1 H), 5.31 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 225.5 (3 CO), 149.7, 146.4, 138.3, 136.7, 128.3, 127.8, 127.7, 126.6, 126.4, 125.3, 124.6, 123.6, 121.5, 107.2, 93.6, 77.7, 26.4 ppm.

Tetracarbonyl[2-ferrocenyl-3-(phenyl-κ$C^{2'}$)-quinoxaline-(κN^1)]-manganese(I) (5): 2-Ferrocenyl-3-phenylquinoxaline (0.37 g, 0.95 mmol) and $(PhCH_2)Mn(CO)_5$ (0.3 g, 1.1 mmol) were dissolved in a mixture of cyclohexane (10 mL) and toluene (5 mL). The resulting mixture was brought to reflux for 9 h, the solvents removed under reduced pressure and the resulting residue redissolved in dichloromethane. Silica gel was added to this solution and the suspension was stripped of solvent to afford a coated silica gel residue that was loaded on the top of a refrigerated (6 °C) SiO_2 column packed in *n*-hexane. A red band containing the product was eluted with a 1:1 mixture of *n*-hexane and dichloromethane. Compound **5** could be recovered as a red powder upon removal of the solvents under reduced pressure. Yield: 0.34 g, 65%. $C_{28}H_{17}FeMnN_2O_4$ (556.2): calcd. C 60.47, H 3.08, N 5.03; found C 60.18, H 3.14, N 4.90. IR (CH_2Cl_2): ṽ: 2075 w, 1993 vs, 1978 s, 1936 m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, ^3J = 7.9 Hz, 1 H), 8.11 (d, ^3J = 7.1 Hz, 1 H), 8.05 (d, ^3J = 7.3 Hz, 1 H), 7.72 (m, 2 H), 7.55 (d, ^3J = 8.2 Hz, 1 H), 7.20 (t, ^3J = 7.3 Hz, 1 H), 6.90 (t, ^3J = 7.6 Hz, 1 H), 4.98 (t, ^3J = 2.0 Hz, 2 H), 4.47 (t, ^3J = 1.9 Hz, 2 H), 4.05 (s, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 221.1 (CO), 214.3 (CO), 213.9 (2 CO), 178.9, 162.2, 153.4, 148.6, 141.9, 141.2, 140.7, 131.3, 130.0, 129.9, 129.7, 129.4, 126.7, 122.7, 85.3, 71.6 (2 C), 70.4 (5 C), 69.9 (2 C) ppm.

3-[2′-(Dibenzocymantren-1-yl)phenyl]-2-ferrocenylquinoxaline (5a): From **5** (0.124 g, 0.22 mmol), 10 mL of cyclohexane, 1 mL of toluene and a solution of **1c** (0.09 g, 0.47 mmol) in 2 mL of toluene. Addition for 20 min, additional stirring for 40 min. Chromatography on an SiO_2 column (6 °C) gave **5a** after elution with a 70:30 mixture of *n*-hexane/acetone. Deep red powder. Yield: 0.11 g (74%). $C_{40}H_{25}FeMnN_2O_3 \cdot 1/2CH_2Cl_2$ (734.8): calcd. C 60.80, H 3.44, N

3.42; found C 60.81, H 3.40, N 3.53. IR (CH_2Cl_2): ṽ: 2016 s, 1934 s cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, 263 K): δ = 8.18 (d, ^3J = 4.5 Hz, 1 H), 8.01 (d, ^3J = 8.4 Hz, 1 H), 7.96 (t, ^3J = 4.6 Hz, 1 H), 7.86 (d, ^3J = 8.6 Hz, 1 H), 7.78 (m, 3 H), 7.64 (t, ^3J = 8.4 Hz, 2 H), 7.58 (t, ^3J = 7.6 Hz, 1 H), 7.01 (m, 2 H), 6.95 (m, 1 H), 6.79 (t, ^3J = 7.6 Hz, 1 H), 6.66 (d, ^3J = 8.8 Hz, 1 H), 6.24 (t, ^3J = 7.6 Hz, 1 H), 4.24 (s, 1 H), 3.91 (s, 1 H), 3.83 (s, 1 H), 3.74 (s, 5 H), 3.44 (s,1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 225.3 (3 CO), 154.1, 152.1, 141.3, 141.1, 139.7, 135.0, 131.9, 130.1, 129.8, 129.7, 129.1, 128.7, 128.6, 127.9, 127.1, 125.2, 125.1, 124.8, 124.6, 124.3, 124.1, 123.2, 107.4, 103.2, 95.5, 90.9, 82.1, 81.5, 71.2, 70.1, 69.7, 69.6 (5 C), 68.2 ppm.

Tetracarbonyl[2-(phenyl-κ*C*^{2})-2-oxazoline-κ*N*]manganese(I) (6): 2-Phenyl-2-oxazoline and $(PhCH_2)Mn(CO)_5$ were dissolved in *n*-heptane and the resulting mixture was boiled for 9 h. The resulting suspension was stripped of solvent and the residue loaded on the top of an SiO_2 column packed in *n*-hexane. A pale yellow band was eluted with a 1:1 mixture of *n*-hexane/CH_2Cl_2, and the resulting solution stripped of solvents to afford a yellow powder. Yield: 1.61 g, 71%. M.p.: 106 °C. $C_{13}H_8MnNO_5$ (313.1): calcd. C 49.86, H 2.58, N 4.47; found C 49.70, H 2.61, N 4.45. HRMS: calcd. for $C_{13}H_8MnNO_5$ 312.9782; found 312.9782. IR (*n*-hexane): ṽ = 2077 w, 1991 vs, 1982 m, 1943 s cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.96 (ddd, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.0, $^5J_{H,H}$ = 0.6 Hz, 1 H), 7.52 (ddd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.5, $^5J_{H,H}$ = 0.6 Hz, 1 H), 7.35 (td, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.14 (ddd, $^3J_{H,H}$ = 7.6, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.0 Hz, 1 H), 4.75 (t, $^2J_{H,H}$ = 9.4 Hz, 2 H, N-CH_2), 3.82 (dd, $^2J_{H,H}$ = 9.6, $^2J_{H,H}$ = 9.3 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 219.6 (MnCO), 215.3 (MnCO), 213.3 (2 MnCO), 179.0, 175.3, 141.8, 133.6, 131.8, 126.7, 123.7, 71.3 (NCH_2), 54.1 (OCH_2) ppm. EI-MS: *m*/*z* = 313 [M^+], 285 [M^+ − CO], 257 [M^+ − 2 CO], 229 [M^+ − 3 CO], 157 [M^+ − 4 CO − C_3H_4NO − H], 147 [M^+ − $Mn(CO)_4$ + H].

Tetracarbonyl{9-[2′-(2′′-oxazolin-2′′-yl-κ*N*$^{3''}$)phenyl]-fluorenyl-κ*C*^{9}}manganese(I) (6a): From **6** (782 mg, 2.5 mmol), *n*-hexane (10 mL) and a solution of **1c** (5 mmol) in toluene (17.5 mL). Addition 60 min, stirring for an additional 60 min. Chromatography on SiO_2 (5 °C) gave a brownish mixture containing mainly **6a** after elution with *n*-hexane/dichloromethane (1:1). A second chromatographic separation gave a brown-yellow solution of **6a**. Yield: 0.76 mg (63%). The air sensitivity of **6a** prevented its complete characterisation by elemental analysis. HRMS: calcd. for $C_{25}H_{16}MnNO_4$ [M − CO] 449.0459; found 449.0453. IR (*n*-hexane): ṽ = 2071 w, 1993 vs, 1986 s, 1940 s cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.96 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, $H_{fluorene}$), 7.89 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.2 Hz, 1 H, H_{Ph}), 7.45 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, $H_{fluorene}$), 7.25 (m, 7 H), 4.75 (dd, $^2J_{H,H}$ = 9.8, $^3J_{H,H}$ = 9.5 Hz, 2 H, NCH_2), 4.01 (dd, $^2J_{H,H}$ = 9.8, $^3J_{H,H}$ = 9.5 Hz, 2 H, O-CH_2) ppm. ^1H NMR (500 MHz, $CDCl_3$, −50 °C): δ = 8.04 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H), 7.86 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H), 7.50 (br. s, 2 H), 7.36 (m, 3 H), 7.30 (m, 3 H), 7.21 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H), 4.83 (t, $J_{H,H}$ = 9.6 Hz, 2 H, NCH_2), 4.01 (t, $J_{H,H}$ = 9.6 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 213.7 (MnCO), 213.1 (MnCO), 211.7 (2 MnCO), 169.4 (OC=N), 157.6, 157.6 (2 C), 150.4, 133.5, 133.5 (2 C), 133.2, 130.2, 126.8, 126.1, 126.1, 125.0, 122.9, 122.8, 122.8, 120.8, 120.8, 120.1, 120.1, 67.5 (NCH_2), 61.1 (OCH_2), 52.2 ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 213.9 (MnCO), 212.7 (MnCO), 211.5 (2 MnCO), 168.8 (O-C=N), 157.3, 157.3 (2C), 149.4, 133.0, 133.0 (2 C), 132.9, 130.1, 126.5, 126.0, 126.0, 125.1, 122.4, 122.3, 122.3, 120.7, 120.7, 119.9, 119.9 (2 C), 67.4 (NCH_2), 61.0 (OCH_2), 51.5 (C-9) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 223 K): δ = 213.7 (MnCO), 212.9 (MnCO), 211.6 (2 MnCO), 169.1 (OC=N), 157.4, 157.4 (2 C), 150.0, 133.3, 133.3 (2 C), 133.2, 130.2, 126.6, 126.1, 126.1, 125.1, 122.7, 122.6, 122.6, 120.8, 120.8, 120.0, 120.0 (2 C), 67.4 (NCH_2), 61.0 (OCH_2), 51.9 (C-9) ppm. EI-MS: *m*/*z* = 449 [M^+ − CO], 421 [M^+ − 2 CO], 393 [M^+ − 3 CO], 369 [M^+ − 4 CO].

2-[2′-(Cymantren-1′′-yl)phenyl]-3-methylpyridine (7a): From **7** (0.205 g, 0.61 mmol), *n*-heptane (10 mL) and a solution of **1a** in *n*-hexane (2 mL, 1.04 mmol, 0.52 M). Addition 5 min and stirring for an additional 25 min. Chromatography on hydrated SiO_2 (5 °C) gave **7a** upon elution with a mixture of *n*-hexane and acetone (4:1). Canary-yellow powder. Yield: 0.149 g (66%). $C_{20}H_{14}MnNO_3$ (275.2): calcd. C 64.70, H 3.80, N 3.77; found C 64.51, H 3.68, N, 3.70. IR (CH_2Cl_2): ṽ = 2020 s, 1934 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, ^3J = 4.8 Hz, 1 H), 7.54 (d, ^3J = 7.7 Hz, 1 H), 7.50 (d, ^3J = 7.5 Hz, 1 H), 7.41 (t, ^3J = 7.1 Hz, 1 H), 7.35 (t, ^3J = 7.0 Hz, 1 H), 7.23 (m, 2 H), 4.53 (m, 4 H), 2.02 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 224.9 (3 CO), 158.8, 146.9, 139.2, 138.1, 132.0, 131.2, 129.9, 129.5, 128.4, 128.0, 122.9, 103.1, 84.6, 84.3, 82.0, 80.7, 19.2 ppm.

[1-(Acetyl-κ*O*)naphthyl-κ*C*^{2}]tetracarbonylmanganese(I) (8): $(PhCH_2)Mn(CO)_5$ (1.43 g, 5 mmol) and 1-acetylnaphthalene (1.02 g, 6 mmol) were dissolved in *n*-heptane (20 mL) and refluxed for 15 h. The resulting mixture was stripped of solvents and the residue subjected to flash chromatography on SiO_2. Compound **8** was eluted with a 1:1 mixture of dichloromethane/*n*-hexane. Yellow solid. Yield: 0.93 g (56%). $C_{16}H_9MnO_5 \cdot 1/2CH_2Cl_2$ (378.7): calcd. C 54.62, H 2.66; found C 54.65, H 2.71. HR-MS: calcd. for $C_{16}H_9MnO_5$ 335.9830; found 335.9831. IR (*n*-hexane): ṽ = 2082 m, 1997 vs, 1946 s, 1562 w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (d, ^3J = 8.8 Hz, 1 H), 8.27 (d, ^3J = 8.3 Hz, 1 H), 7.93 (d, ^3J = 8.1 Hz, 1 H), 7.81 (d, ^3J = 8.0 Hz, 1 H), 7.60 (t, ^3J = 7.7 Hz, 1 H), 7.47 (t, ^3J = 7.5 Hz, 1 H), 3.03 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.6 (CO), 215.1 (CO), 213.2 (CO), 210.9 (CO), 210.2 (CO), 140.7, 138.3, 134.2, 133.4, 132.4, 130.5, 128.1, 124.7, 121.7, 32.2 ppm. EI-MS: *m*/*z* = 336 [M], 280 [M − 2 CO], 252 [M − 3 CO], 224 [M − 4 CO], 196 [M − 5 CO], 170 [M − Mn − 4 CO].

1-Acetyl-2-(benzocymantren-1′-yl)naphthalene (8a): From **8** (0.2 g, 0.6 mmol), *n*-heptane (5 mL), toluene (5 mL) and **1b** (0.2 g, 1.4 mmol) in toluene (3 mL). Addition 30 min and stirring for an additional 30 min. Chromatography on a hydrated SiO_2 column (5 °C), elution with pure dichloromethane. Canary-yellow powder. Yield: 0.19 g (76%). $C_{24}H_{15}MnO_4$ (422.3): calcd. C 68.26, H 3.58: found C 68.12, H 3.40. IR (KBr): ṽ = 2017 vs, 1942 s, 1925 s, 1694 m cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, ^3J = 8.5 Hz, 2 H), 7.96 (m, 1 H), 7.76 (m, 1 H), 7.57 (m, 3 H), 7.49 (d, ^3J = 8.7 Hz, 1 H), 7.23 (t, ^3J = 7.4 Hz, 1 H), 7.16 (t, ^3J = 7.4 Hz, 1 H), 5.36 (d, ^3J = 2.7 Hz, 1 H), 5.25 (d, ^3J = 2.8 Hz, 1 H), 2.08 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 224.6 (3 CO), 206.9 (CO), 141.0, 133.1, 130.4, 129.8, 128.7, 128.6, 128.0, 127.9, 127.0, 126.6, 126.2, 124.6, 122.9, 105.9, 100.4, 92.8, 90.7, 77.4, 72.1, 32.8 ppm.

2-[2′-(Benzocymantren-1′′-yl)phenyl]-3-methylpyridine (7b): From **7** (0.22 g, 0.79 mmol) cyclohexane (15 mL), **1b** (0.24 g, 1.7 mmol) and *n*-hexane (3 mL). Addition 10 min, stirring for an additional 50 min. Chromatography on SiO_2 (5 °C), elution with *n*-hexane/acetone (70:30). Red waxy solid. Yield: 0.24 g (87%). $C_{24}H_{16}MnNO_3 \cdot 1/2CH_2Cl_2$ (463.7): calcd. C 63.45, H 3.69, N 3.02; found C 63.92, H 3.86, N 3.05. HRMS (FAB$^+$): calcd. for $C_{24}H_{17}NMnO_3$ [M^+] 422.058888; found 422.058890. IR (CH_2Cl_2): ṽ = 2018 vs, 1934 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 298 K):

δ = 8.38 (m, 1 H), 8.02 (d, ^3J = 7.5 Hz, 1 H), 7.57 (t, ^3J = 7.6 Hz, 1 H), 7.48 (t, ^3J = 7.5 Hz, 1 H), 7.41 (d, ^3J = 8.5 Hz, 1 H), 7.36 (m, 2 H), 7.29 (d, ^3J = 7.7 Hz, 1 H), 7.03 (m, 3 H), 4.96 (d, ^3J = 2.9 Hz, 1 H), 4.65 (m, 1 H), 1.74 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 225.0, 158.8, 146.7 (C-3), 141.2, 137.7 (C-1), 132.8, 131.8 (2 C), 129.8, 128.6, 128.3, 126.9 (broad), 125.9 (2 C), 123.0 (broad), 122.4, 105.0 (broad), 100.0 (broad), 93.7 (broad), 90.4 (C_5), 71.0 (broad), 19.1 (CH_3, broad) ppm. Major conformer: ^{1}H NMR (500 MHz, $CDCl_3$, 243 K): δ = 8.45 (d, ^3J = 4.0 Hz, $H_{pyridyl}$), 8.04 (d, ^3J = 7.5 Hz, H_{phenyl}), 7.58 (t, ^3J = 7.3 Hz, H_{phenyl}), 7.52 (d, ^3J = 8.8 Hz, H6), 7.49 (t, ^3J = 7.5 Hz, H_{phenyl}), 7.41 (d, ^3J = 8.6 Hz, 9-H), 7.37 (d, ^3J = 7.2 Hz, H_{phenyl}), 7.32 (d, ^3J = 10.8 Hz, $H_{pyridyl}$), 7.16 (t, ^3J = 7.5 Hz, H_7), 7.12 (t, ^3J = 7.1 Hz, $H_{pyridyl}$), 7.06 (t, ^3J = 7.7 Hz, 8-H), 4.95 (d, ^3J = 2.5 Hz, 5-H), 4.51 (d, ^3J = 2.6 Hz, 4-H), 1.55 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 243 K): δ = 224.9 (3 CO), 158.5, 146.6 (C-3), 140.8, 137.8 (C-1), 132.3, 131.8, 131.5, 129.5, 128.5, 128.2, 127.5, 126.2, 125.8, 122.5, 122.2, 105.2, 98.8, 92.6, 90.1 (C-5), 71.4 (C-4), 18.9 ppm. FAB-MS$^+$: *m*/*z* = 422 [M$^+$], 337 [M − 3 CO], 282 [M − Mn − 3 CO]. Minor conformer: ^{13}C NMR (125 MHz, $CDCl_3$, 243 K): δ = 224.9 (3 CO), 158.2, 146.7, 140.5, 137.8, 132.9, 131.7, 131.6, 129.9, 128.6, 128.2, 125.8, 125.7, 124.8, 124.2, 122.4, 103.8, 101.7, 93.8, 90.8, 69.3, 19.5 ppm.

Complex 9a: From **9** (0.2 g, 0.44 mmol), heptane (10 mL) and **1a** (2.1 mL, 1.1 mmol, 0.52 M). Addition 7 min, additional stirring for 30 min. Chromatography on hydrated SiO_2 (5 °C), elution with *n*-hexane/acetone (4:1). Canary yellow solid. Yield: 0.145 g (67%). $C_{22}H_{12}CrMnNO_6$ (493.3): calcd. C 53.57, H 2.45, N 2.84; found C 53.84, H 2.78, N 2.69. IR (CH_2Cl_2): ṽ = 2025 s, 1971 vs, 1939 s, 1899 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (d, ^3J = 4.2 Hz, 1 H), 7.68 (t, ^3J = 7.8 Hz, 1 H), 7.35 (d, ^3J = 7.9 Hz, 1 H), 7.30 (m, 1 H), 5.75 (d, ^3J = 6.1 Hz, 1 H), 5.52 (m, 2 H), 5.45 (t, ^3J = 5.7 Hz, 1 H), 5.29(m, 1 H), 4.64 (m, 1 H), 4.52 (m, 1 H), 4.26 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 232.4 [3CO (Cr)], 224.0 [3 CO (Mn)], 154.5, 149.3, 136.4, 126.7, 123.6, 110.4, 104.0, 99.2, 94.8, 94.3, 92.2, 91.6, 88.0, 86.4, 82.4, 79.8 ppm.

Complexes *u*-9b and (*rel*)-*l*-9b: From **9** (0.2 g, 0.4 mmol), cyclohexane (10 mL), toluene (1 mL) and a solution of **1b** (0.12 g, 0.9 mmol) in toluene (3 mL). Addition 20 min, stirring for an additional 25 min. Chromatography on SiO_2 (−5 °C), *u*- and (*rel*)-*l*-**9b** were eluted with *n*-hexane/acetone (70:30). ^{1}H NMR spectroscopy indicated that the two diastereomers are in a 78:22 ratio. Conversion: 0.13 g (55%). $C_{26}H_{14}CrMnNO_6$ (543.3): calcd. C 57.48, H 2.60, N 2.58; found C 57.67, H 2.42, N 2.65. IR (CH_2Cl_2): ṽ = 2023 s, 1970 vs, 1937m, 1899 m cm^{-1}. *u*-**9b**: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.42 (d, ^3J = 4.8 Hz, 1 H), 7.36 (d, ^3J = 8.7 Hz, 1 H), 7.25 (m,1 H), 7.19 (t, ^3J = 6.5 Hz, 1 H), 7.00 (m, 3 H), 6.85 (t, ^3J = 7.6 Hz, 1 H), 6.02 (d, ^3J = 6.4 Hz, 1 H), 5.90 (d, ^3J = 6.4 Hz, 1 H), 5.65 (t, ^3J = 6.3 Hz, 1 H), 5.59 (t, ^3J = 6.4 Hz, 1 H), 5.54 (d, ^3J = 3.0 Hz, 1 H), 5.14 (d, ^3J = 3.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 232.5 [$Cr(CO)_3$], 224.0 [$Mn(CO)_3$], 154.2, 149.1, 135.7, 126.8, 126.7, 125.6, 125.1, 123.2, 122.7, 112.5, 105.0, 103.2, 101.9, 99.0, 93.6, 93.5, 92.8, 91.1, 90.5, 69.5 ppm. (*rel*)-*l*-**9**: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.55 (d, ^3J = 5.4 Hz, 1 H), 7.97 (d, ^3J = 8.9 Hz, 1 H), 7.49 (m, 2 H), 7.30 (t, ^3J = 7.8 Hz, 1 H), 7.13 (m, 1 H), 6.91 (m, 2 H), 6.10 (d, ^3J = 6.4 Hz, 1 H), 5.96 (d, ^3J = 6.2 Hz, 1 H), 5.65 (t, ^3J = 6.3 Hz, 1 H), 5.59 (t, ^3J = 6.4 Hz, 1 H), 5.04 (d, ^3J = 3.4 Hz, 1 H), 4.49 (d, ^3J = 3.1 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 232.6 [$Cr(CO)_3$], 224.1 [$Mn(CO)_3$], 154.5, 149.4, 136.0, 128.0 (2 C), 126.4, 126.3, 123.5, 123.4, 109.7, 105.5, 105.4, 99.0, 93.6, 93.5, 92.8, 91.1, 90.5, 69.5 ppm.

Complex 10a: From **10** (0.2 g, 0.44 mmol), heptane (10 mL) and a solution of **1a** (1.9 mL, 1.0 mmol, 0.52 M) in *n*-hexane, added in 3 fractions: 1 mL was added over 7 min, followed by an additional 0.45 mL after 1 h of reaction, and finally 0.45 mL after 2 h of reaction. The reaction mixture was then stirred for an additional hour. Chromatography on SiO_2 (5 °C), elution of **10a** with *n*-hexane/acetone (9:1). Yellow powder. Yield: 0.112 g, 71%. $C_{23}H_{14}CrNO_6Re$ (638.6): calcd. C 43.26, H 2.21, N 2.19; found C 43.05, H 2.45, N 2.02. IR (CH_2Cl_2): ṽ = 2026 s, 1972 vs, 1928 s, 1901 m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, ^3J = 4.2 Hz, 1 H), 7.55 (t, ^3J = 7.6 Hz, 1 H), 7.28 (m, 1 H), 5.65 (m, 1 H), 5.49 (t, ^3J = 5.6 Hz, 1 H), 5.41 (d, ^3J = 6.6 Hz, 1 H), 5.38 (d, ^3J = 6.2 Hz, 1 H), 5.32 (t, ^3J = 5.8 Hz, 1 H), 5.20 (m, 1 H), 4.98 (m, 1 H), 4.84 (m, 1 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 232.4 [$Cr(CO)_3$], 193.5 [$Re(CO)_3$], 152.9, 147.3, 138.4, 132.6, 124.0, 102.0, 93.9, 92.1 (2 C), 91.9, 89.8 (2 C), 88.1, 87.8, 83.9, 82.6, 19.8 ppm.

[4,6-(Diphenyl-κ*C*$^{2'}$,κ*C*$^{2''}$)pyrimidine-(κ*N*^{1},κ*N*^{2})]bis(tetracarbonylmanganese(I)] (11): 4,6-Diphenylpyrimidine (0.4 g, 1.7 mmol) and $(PhCH_2)Mn(CO)_5$ (1.48 g, 5.2 mmol) were dissolved in a mixture of *n*-heptane (10 mL) and toluene (10 mL) and the resulting mixture heated to reflux for 11 h. The mixture was then stripped of its solvents, the residue was dissolved in dichloromethane and SiO_2 was added to this solution. After removal of the solvent under reduced pressure, the coated silica gel was loaded on the top of an SiO_2 column packed in *n*-hexane and refrigerated at 6 °C. A large band containing pure compound **11** was eluted with dichloromethane/*n*-hexane (3:2). Yellow powder. Yield: 0.71 g, 73%. $C_{24}H_{10}Mn_2N_2O_8$ (564.2): calcd. C 51.09, H 1.79, N 4.96; found C 50.97, H 1.46, N 5.03. IR (CH_2Cl_2): ṽ = 2082 w, 2000 vs, 1985 s, 1937 m cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 9.70 (s, 1 H), 8.79 (s, 1 H), 8.44 (d, ^3J = 7.3 Hz, 2 H), 8.01 (d, ^3J = 7.4 Hz, 2 H), 7.42 (t, ^3J = 7.3 Hz, 2 H), 7.29 (t, ^3J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 221.1 (CO), 214.7 (CO), 214.0 (2 CO), 180.2, 173.0, 166.4, 145.4, 142.2, 133.2, 128.3, 125.4, 109.2 ppm.

4,6-Bis[2′-(dibenzocymantren-1′′-yl)phenyl]pyrimidine (11a): From **11** (0.2 g, 0.35 mmol), *n*-heptane (5 mL), toluene (5 mL) and a solution of **1c** (0.27 g, 1.42 mmol) in toluene (3 mL). Addition 25 min, stirring for an additional 35 min. Chromatography on SiO_2 (6 °C), **11a** was eluted with pure acetone. Yellow powder. Yield: 0.25 g, 84%. $C_{42}H_{22}N_2Mn_2O_6 \cdot 1/3CH_2Cl_2$ (788.8): calcd. C 64.48, H 2.90, N 3.55; found C 64.38, H 2.97, N 3.61. IR (CH_2Cl_2): ṽ = 2016 s, 1935 s cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, ^3J = 7.7 Hz, 2 H), 8.08 (s, 1 H), 8.06 (d, ^3J = 8.2 Hz, 4 H), 7.67 (t, ^3J = 7.6 Hz, 2 H), 7.43 (t, ^3J = 7.6 Hz, 2 H), 7.17 (t, ^3J = 7.3 Hz, 4 H), 7.04 (m, 8 H), 6.71 (d, ^3J = 7.8 Hz, 2 H), 6.29 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 224.9 (3 CO), 165.2, 157.3, 139.4, 136.3, 130.6, 130.5, 129.5, 128.8, 128.2, 125.1, 124.8, 123.0, 120.6, 107.2, 92.9, 83.3 ppm.

[2-(Phenyl-κ*C*$^{2'}$,κ*C*$^{2''}$)pyrimidine-(κ*N*^{1},κ*N*^{2})]bis(tetracarbonylmanganese(I)] (12): 2-Phenylpyrimidine (0.79 g, 5.06 mmol) and $(PhCH_2)Mn(CO)_5$ (3.46 g, 1.21 mmol) were dissolved in a mixture of *n*-heptane (5 mL) and toluene (10 mL). The mixture was refluxed for 10 h and the solution was cooled to −20 °C overnight. Then the supernatant was removed and the solid residue was washed three times with 20 mL of diethyl ether and twice with 20 mL of pentane and dried under vacuum. Yield: 2.0 g (81%). $C_{18}H_6Mn_2N_2O_8$ (488.1): calcd. C 44.29, H 1.24, N 5.74; found C 44.49, H 1.15, N 5.60. IR (CH_2Cl_2): ṽ = 2072 w, 1997 vs, 1981 s, 1938 m cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.98 (d, ^3J =

5.4 Hz, 2 H), 7.53 (d, ^3J = 4.9 Hz, 2 H), 7.34 (t, ^3J = 5.5 Hz, 1 H), 7.21 (t, ^3J = 7.3 Hz, 1 H) ppm.

2-[2′,6′-Bis(dibenzocymantren-1′′-yl)phenyl]pyrimidine (12a): From **12** (0.3 g, 0.62 mmol), toluene (10 mL) and a solution of **1c** (0.47 g, 2.46 mmol) in toluene (3 mL). Addition 25 min, stirring for an additional 35 min. Chromatography on SiO_2 (5 °C), **12a** was eluted with dichloromethane/*n*-hexane (80:20). Yellow powder. Yield: 0.28 g (61%). $C_{42}H_{22}Mn_2N_2O_6{\cdot}1/3CH_2Cl_2$ (516.4): calcd. C 64.48, H 2.90, N 3.55; found C 64.38, H 2.97, N 3.61. IR (CH_2Cl_2): $\tilde{\nu}$ = 2018 s, 1934 s cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 263 K): δ = 8.52 (d, ^3J = 7.8 Hz, 2 H), 8.03 (t, ^3J = 7.7 Hz, 1 H), 7.98 (d, ^3J = 8.6 Hz, 4 H), 7.56 (d, ^3J = 4.9 Hz, 2 H), 7.29 (d, ^3J = 8.7 Hz, 4 H), 7.10 (t, ^3J = 7.6 Hz, 4 H), 7.05 (t, ^3J = 7.6 Hz, 4 H), 6.15 (t, ^3J = 4.9 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 263 K): δ = 225.3 (3 CO), 166.0, 155.3, 142.4, 136.2, 132.2, 130.1, 127.6, 124.6, 124.5, 123.9, 117.5, 107.3, 92.6, 84.6 ppm.

1,4-Diacetyl-2,5-bis(dibenzocymantren-1′-yl)benzene (13a): From **13** (0.22 mmol), *n*-hexane (7 mL) and a solution of **1c** (0.88 mmol) in toluene (5 mL). Addition 30 min, stirring for an additional 60 min. Compound **13a** precipitated as a yellow solid. Due to its insolubility in most polar solvents (THF, DMSO) it could not be further purified. This precipitate was washed several times with *n*-hexane and acetone and dried under reduced pressure. M.p. 233−240 °C. IR (KBr): $\tilde{\nu}$ = 2013 vs, 1926 s, 1694 w cm^{-1}. FAB-MS+: *m*/*z* = 767 [M + H]$^+$, 682 [M − 3 CO + H]$^+$, 613 [4 matrix + H]$^+$, 599 [M − $Mn(CO)_3$ − 3 CO + H]$^+$, 488 [M − 2 $Mn(CO)_3$]$^+$, 460 [3 matrix + H]$^+$.

2-{2′-(9-Fluorenyl)phenyl}-3-methylpyridine (14): Compound **2b** (0.2 g, 0.5 mmol) was dissolved in a mixture of diethyl ether (5 mL) and methanol (10 mL). The sealed Schlenk tube containing the solution was then irradiated with the aid of a medium-pressure Hg lamp. A slight precipitation of brownish air-sensitive solid was noticed shortly after the beginning of the UV irradiation. The organic product **14** was purified by chromatography on SiO_2 and recovered as an off-white solid. Yield: 0.1 g (71%). HRMS (FAB+): calcd. for $C_{25}H_{20}N$ [MH$^+$] 334.159565; found 334.159575. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (m, 1 H), 7.85 (d, ^3J = 7.5 Hz, 2 H), 7.77 (d, ^3J = 7.5 Hz, 1 H), 7.45 (m, 1 H), 7.34 (m, 6 H), 7.24 (t, ^3J = 7.4 Hz, 2 H), 7.14 (t, ^3J = 7.4 Hz, 1 H), 6.42 (d, ^3J = 6.7 Hz, 1 H), 4.88 (s, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D_6]acetone): δ = 160.1, 149.7, 147.7, 142.4, 141.1, 138.9, 132.6, 129.9, 129.1, 128.7, 128.2, 128.1, 127.2, 126.5 (2 C), 123.5, 120.6, 51.2, 19.8 ppm.

Experimental Procedure for the X-ray Diffraction Analysis of Compounds 4a, 5a, 6a, 7a, 8a, 9a, 9b, 11a and 12a: Acquisition and processing parameters are displayed in Tables 5 and 6. Reflections were collected with a Nonius KappaCCD diffractometer using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å). The structures were solved by direct methods and were refined against |*F*| with the Nonius OpenMoleN package.[35] Hydrogen atoms were introduced as fixed contributors. Flack's *x* parameter for **9a** was determined to be *x* = 0.36(2). CCDC-220450 to -220458 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: One- and two-dimensional (^{1}H-^{1}H COSY, ROESY and ^{1}H-^{13}C HETCORR) NMR spectra for compound **7b**

Table 5. Acquisition and refinement parameters for the X-ray diffraction analyses of complexes **4a−7a**

	4a	**5a**	**6a**	**7a**
Empirical formula	$C_{26}H_{16}MnNO_3$	$C_{40}H_{25}FeMnN_2O_3{\cdot}CH_2Cl_2$	$C_{26}H_{16}MnNO_5{\cdot}CH_2Cl_2$	$C_{20}H_{14}MnNO_3$
M	445.36	777.38	562.29	371.28
Crystal system	triclinic	monoclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pbca*
a [Å]	8.3364(2)	16.3945(3)	10.1810(3)	12.4955(2)
b [Å]	11.6063(4)	13.8198(3)	11.1509(4)	13.1900(2)
c [Å]	12.1151(4)	14.9630(4)	11.5676(4)	20.4495(4)
α [°]	101.778(5)	90	75.737(5)	90
β [°]	106.174(5)	94.573(5)	84.768(5)	90
γ [°]	108.494(5)	90	70.853(5)	90
V [Å^3]	1011.11(5)	3379.4(1)	1202.27(7)	3370.4(1)
Z	2	4	2	8
Crystal dim. [mm]	0.10 × 0.06 × 0.06	0.14 × 0.14 × 0.10	0.20 × 0.16 × 0.16	0.16 × 0.14 × 0.08
D_c [g·cm^{-3}]	1.46	1.53	1.55	1.46
*F*000	456	1584	572	1520
μ [mm^{-1}]	0.682	1.005	0.812	0.801
Trans. min./max.	0.9107/1.0000	0.865/0.904	0.9479/1.0000	0.9596/1.1284
hkl limits	−11, 11/−16, 14/−17, 15	−21, 21/−19, 17/−23, 23	−13, 13/−10, 15/−13, 15	−17, 17/−18, 18/−28, 28
θ limits [°]	2.5/30.11	2.5/30.02	2.5/29.13	2.5/30.03
Data measd.	6862	16735	8501	9815
Data with $I > 3\sigma(I)$	3392	4404	3850	2613
Number of var.	280	451	325	226
R	0.040	0.037	0.037	0.030
Rw	0.049	0.044	0.047	0.039
GOF	1.008	1.039	1.048	1.049
Largest peak in final diff. [e·Å^{-3}]	0.351	0.787	0.410	0.266

Table 6. Acquisition and refinement parameters for the X-ray diffraction analyses of complexes **8a**, **9a**, **9b**, **11a** and **12a**

	8a	*rac*-**9a**	(*rel*)-*u*-**9b**	**11a**	**12a**
Empirical formula	$C_{24}H_{15}MnO_4$	$C_{22}H_{12}CrMnNO_6{\cdot}CH_2Cl_2$	$C_{26}H_{14}CrMnNO_6$	$C_{48}H_{26}Mn_2N_2O_6{\cdot}2CH_2Cl_2$	$C_{42}H_{22}Mn_2N_2O_6$
M	422.32	578.21	543.34	1006.49	760.53
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	*Pbcn*	$P2_1/n$	*Pbcn*
a [Å]	8.5271(2)	9.1959(2)	38.2715(1)	8.0794(1)	8.2243(2)
b [Å]	10.4016(2)	13.6927(3)	7.6620(2)	18.4324(2)	15.4115(4)
c [Å]	11.2111(3)	18.1864(5)	15.1092(5)	30.1912(4)	26.9270(7)
α [°]	103.243(5)	90	90	90	90
β [°]	99.995(5)	90	90	93.110(5)	90
γ [°]	93.117(5)	90	90	90	90
V [Å^3]	948.63(4)	2289.97(9)	4430.6(2)	4489.53(9)	3413.0(2)
Z	2	4	8	4	4
Crystal dim. [mm]	0.10 × 0.08 × 0.06	0.20 × 0.10 × 0.08	0.16 × 0.12 × 0.08	0.12 × 0.12 × 0.10	0.12 × 0.10 × 0.08
D_c [g·cm^{-3}]	1.48	1.68	1.63	1.49	1.48
*F*000	432	1160	2192	2040	1544
μ [mm^{-1}]	0.724	1.300	1.105	0.854	0.794
Trans. min./max.	0.9678/1.0000	0.768/0.901	0.835/0.925	0.9482/1.0000	0.907/0.938
hkl limits	−12, 12/−14, 14/−15, 15	−12, 12/−19, 19/−25, 25	−10, 10/−20, 20/−52, 52	−10, 10/−24, 22/−39, 39	0, 10/0, 20/0, 34
θ limits [°]	2.5/30.06	2.5/30.01	2.5/29.11	2.5/27.85	2.5/27.48
Data measd.	8741	6365	11275	19403	4424
Data with $I > 3\sigma(I)$	3557	2661	3535	6102	2360
Number of var.	262	307	316	577	237
R	0.034	0.035	0.032	0.049	0.035
Rw	0.042	0.043	0.044	0.072	0.049
GOF	1.075	1.041	1.058	1.277	1.052
Largest peak in final diff. [e·Å^{-3}]	0.312	0.470	0.366	1.301	0.580

in $CDCl_3$ at 243 K (see also footnote on the first page of this article).

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