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Chiral Auxiliary-Promoted Asymmetric Nucleophile Additions To Arene-Manganese Tricarbonyl Complexes†

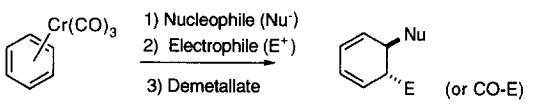
Anthony J. Pearson,* Alexander V. Gontcharov, and Ping Y. Zhu.

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

Abstract: Addition of a range of nucleophiles to arene-manganese tricarbonyl complexes, carrying a chiral non-racemic 2,5-dimethylpyrrolidine substituent, results in diastereomeric excesses of up to 94%. Dependence of the level of asymmetric induction on reactivity and steric bulk of the nucleophile is observed, revealing a rather complex set of controlling factors for the reaction.

Introduction

The addition of carbon nucleophiles to aromatic molecules that are activated by the attachment of a π-bound transition metal provides efficient methodology for the conversion of readily available aromatic compounds to cyclohexenones and cyclohexadienes that can be useful for organic synthesis.[1] Extensive studies of this kind of transformation for arene-chromium complexes have been made, notably by Semmelhack[2] and by Kündig.[3] Arene-manganese systems offer the capability of giving access to cyclohexenones that are complementary to those obtainable from the chromium complexes, in terms of relative stereochemistry of the substituents that can be attached. Thus, for example, while nucleophile addition to a benzene-$Cr(CO)_3$ complex produces an intermediate dienyl anion that can react with electrophiles to give, ultimately, a *trans*-disubstituted cyclohexadiene (Eq. 1), the benzene-$Mn(CO)_3$ system leads to an uncharged dienyl intermediate. The poor nucleophilicity of this latter intermediate dictates a different pathway for its further conversion to non-aromatic molecules. Sweigart and co-workers devised a route that involves replacing a CO ligand with NO^+, which converts the dienyl-manganese complex to an electrophile, which in turn reacts with nucleophiles *anti* to the metal, ultimately leading to *cis*-disubstituted cyclohexadienes (Eq. 2).[4]



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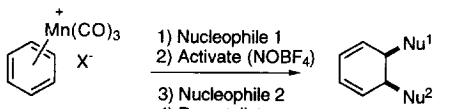
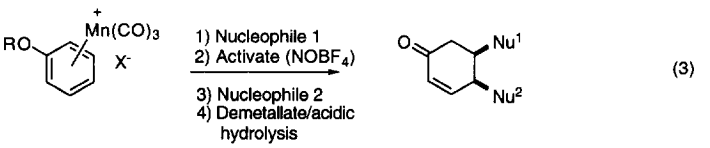


(2)

When the aromatic ligand carries an alkoxy substituent, nucleophiles are directed to the *meta* position. Further transformations of the dienyl products allows the construction of mono- or disubstituted cyclohexenones having defined regio- and relative stereochemistry. In this paper we shall restrict our attention to the arene-

† Dedicated to the memory of Arthur J. Birch

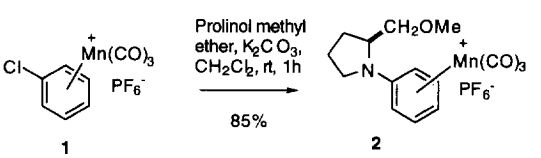
manganese systems, which offer powerful methodology for the construction of *cis*-4,5-disubstituted cyclohexenones (Eq. 3), of potential value as intermediates for organic synthesis efforts. As such efforts are usually directed toward the construction of natural products, the fact that these nucleophile additions produce racemic products, by reaction at the two equivalent *meta* positions, is a disadvantage. Consequently, we set out to develop methodology for the asymmetric addition of nucleophiles to arene-manganese complexes in which the substituent is a *meta*-directing chiral auxiliary. As far as we are aware, the only other report of asymmetric nucleophile additions to alkoxy-substituted arene-$Mn(CO)_3$ complexes is from Miles,[5] who examined the reactions of enolates bearing chiral auxiliaries with phenoxyarene-$Mn(CO)_3$ systems,[6] but it may be noted that Kündig has examined carbanion additions to arene-$Cr(CO)_3$ complexes that have *ortho*-directing chiral auxiliaries.[7]



(3)

Results and Discussion

In considering the type of *meta* directing chiral auxiliary that might show success, we decided that ether substituents would have too much conformational freedom to force a nucleophile to follow a particular trajectory during its approach to the *meta* carbons of the arene ring. We therefore turned our attention to the use of secondary amines, and in particular those amines that might have a clearly defined and rigid conformation when attached to the aromatic ligand. Pyrrolidine derivatives appeared to be well-suited for this purpose. We first examined the readily prepared prolinol methyl ether, which could be introduced by nucleophilic substitution on chlorobenzene-$Mn(CO)_3$ (**1**) to give complex **2** (Eq. 4). The main, fairly obvious, weakness of this system is the potential for the auxiliary to adopt two extreme rotational arrangements, each of which retains conjugation with the aromatic ligand, by 180° rotation about the C-N bond (Fig. 1). Conformation **A** might be expected to lead to a preference for nucleophile addition at the *meta* carbon that is more remote from the methoxymethyl group, assuming this is pseudo-axial (see later), while no such stereodirecting effect would be expected for conformation **B**. Indeed, the ^1H NMR spectrum of complex **2** in CD_3NO_2 at ambient temperature showed two sharp singlets for the methoxy group, at δ 3.43 and 3.30 ppm, with approximately equal integrated intensities. Coalescence was observed at 98 °C, to give one broad singlet (δ 3.35 ppm), and on re-cooling to ambient temperature the doubled peak reappeared, consistent with the conformational equilibrium shown in Eq. 1. Dynamic NMR measurements indicated that the barrier to interconversion of the two rotamers is 18.6 kcal/mol. Nucleophile additions to **2** resulted in rather poor diastereoselectivity (e.g., PhMgBr gave a 2.6:1 mixture of stereoisomers), consistent with these observations (compare this result with the analogous reactions of **3** and **4** described later).



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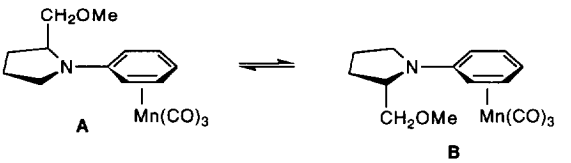

Figure 1 Extreme conformations of complex **2**.

A solution to the above problem of rotameric equilibrium is to use a C_2 symmetric substituted pyrrolidine, wherein a 180° rotation about the C-N bond would produce an identical spatial arrangement of substituents. In the present case (2*R*,5*R*)-dimethylpyrrolidine appeared to be an ideal candidate, since it is available in optically pure form by published procedures.[8] We studied the reactions of two complexes, **3** and **4**, which were readily prepared by reaction of the appropriate chloroarene-$Mn(CO)_3$ complex with the amine. Preliminary studies on complex **3** have already appeared in communication form,[9] and this article reports a more complete study of these reactions for two arene systems. Complexes **3** and **4** were chosen to determine whether the incorporation of a substituent at the *para* position (Me in **4**) would have a significant effect on the regio- and/or stereochemistry of nucleophile additions. At this point it was decided to establish whether the pyrrolidine substituent has the methyl groups in axial or equatorial orientation, this being a feature that could surely influence the stereoselectivity of nucleophile additions. Single crystal X-ray crystallography[9] on complex **3** confirmed that the methyls adopt axial orientation, which relieves non-bonded interactions with the *ortho* hydrogens. Interestingly, the crystal structure is exactly reproduced by the molecular mechanics minimized structure, with no applied constraints (PCModel®). Thus, we were confident that steric approach control would favor addition of a nucleophile at the *meta* position that is further away from the methyl that projects toward its approach trajectory, as indicated schematically in Figure 2. Such effects would favor product **5** over **6**. However, this would correspond to a 1,5-asymmetric induction, a rather large distance for transmission of steric effects, so experimental testing of the proposition would be interesting.

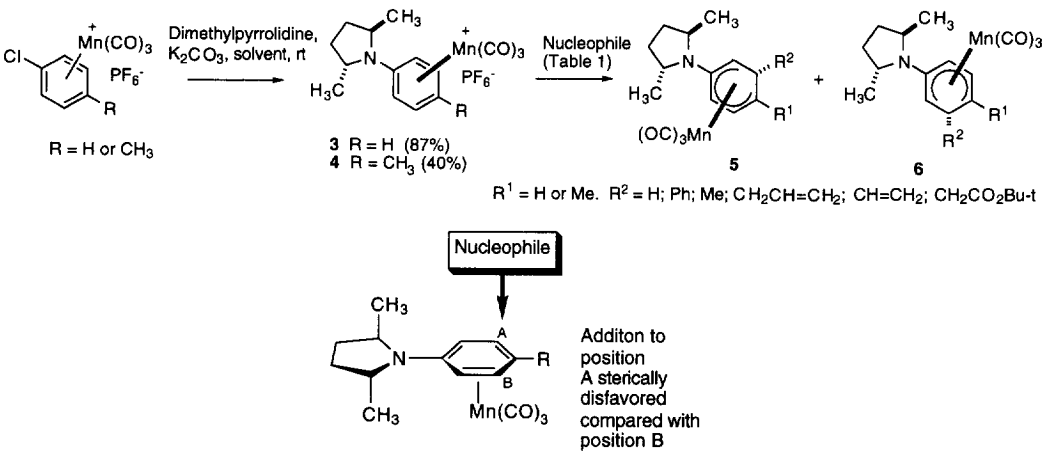

Figure 2 Approach of nucleophile to complexes **3** and **4**

Reactions of complexes **3** and **4** with a series of hydride and carbanion nucleophiles, in tetrahydrofuran as solvent, are collected in Table 1. Diastereoselectivities were determined by integration of ^1H NMR spectra of

the products, extensive purification being avoided to suppress any fortuitous fractionation, and potentially erroneous ratios. In fact the crude products from the vast majority of these nucleophile additions are free from side products, so NMR integration is quite reliable. However, it should be noted that broadening of all the pyrrolidine resonances occurs at lower temperatures, due to slow rotation about the dienyl-N bond; a sharp spectrum in this region is produced at either low (<-10 °C), or elevated (>60 °C) temperature. H(1) (*ca.* δ 3.0-2.5) and H(3) (*ca.* δ 5.0), which are closest to the chiral auxiliary, show chemical shifts that are well-separated for the two diastereomers, and clear of other protons; integration of these resonances was found to be the most reliable method for determining stereoselectivity. Analogous trends are noted for complexes having R^1=Me. The major diastereomer from reaction of phenylmagnesium bromide with complex **3** has been fully characterized by X-ray crystallography,[9] and the stereochemistries of all other dienyl complexes were assigned by comparison of NMR characteristics with the phenyl-substituted compounds. The H(3) resonance was found to be particularly diagnostic for this purpose; the major stereoisomer from PhMgBr addition shows a lower field signal (δ 5.21, ddd, J = 6.8, 2.3, 1.1 Hz) for this proton compared with the minor isomer (δ 5.14), and a consistent trend was noted for all other adducts from both complexes **3** and **4**. In this way, we were able also to recognize any reversal of diastereoselectivity that occurs with certain nucleophiles (see later).

Table 1. Reactions of Complexes **3** and **4** with Nucleophiles. All reactions were run in THF at -78 °C unless otherwise noted.

Entry	Complex	Nucleophile	Ratio **5:6**	Combined Yield (%)
1	**3**	PhLi	2.0:1	52
2	**4**	PhLi	6.6:1	78
3	**3**	PhMgBr	19:1	60
4	**4**	PhMgCl	48:1	93
5	**3**	VinylMgBr	1.6:1	50
6	**4**	VinylMgBr	3.6:1	36[a]
7	**4**	AllylMgBr	4.1:1	65
8	**3**	LS-Selectride®	11.5:1	84
9	**4**	LS-Selectride®	n.d.	no reaction[b]
10	**3**	L-Selectride®	5.3:1	77
11	**4**	L-Selectride®	5.7:1	30[b]
12	**3**	Superhydride®	2.8:1	75
13	**4**	Superhydride®	1.7:1	37[b]
14	**3**	$LiAlH_4$	2.1:1	81
15	**4**	$LiAlH_4$	1.0:1.4	83
16	**3**	$LiAl(t\text{-}OBu)_3H$	1.4:1	70
17	**4**	$LiAl(t\text{-}OBu)_3H$	*ca* 1:1	Trace[a]
18	**3**	$NaBH_4$	1:4.3	80
19	**4**	$NaBH_4$	1:3	93
20	**3**	$LiBH_4$	1:3.8	85
21	**4**	$LiBH_4$	1:8.2	73
22	**3**	MeLi[c]	1:3	60
23	**4**	MeLi	1:3.5	67
24	**4**	Vinyl-Li	1:2.5	62
25	**4**	$LiCH_2CO_2Bu^t$	1:2.8	65

[a]Unreacted starting material recovered. [b]Substantial decomplexation of arene complex observed. [c]Reaction conducted in CH_2Cl_2 at -95 to -85 °C, owing to very low yield in THF.

For a number of reactions the presence of the methyl group in complex **4** leads to a significant amplification of stereoselectivity. This may be due to the methyl causing the nucleophile approach trajectory to shift more towards the pyrrolidine auxiliary, but we do not have sufficient data to confirm such an hypothesis. The excellent diastereoselectivity of 48:1 that is observed during the addition of PhMgCl to **4** is particularly noteworthy, in view of the 1,5- relationship of the auxiliary stereogenic center to the site of nucleophile attack. However, for nucleophiles that are sterically very demanding, such as L- and LS-Selectrides, yields are compromised (30% from L-Selectride reaction with **4** vs. 77% from **3**; only traces of product from reaction of **4** with LS-Selectride vs. 84% from **3**). This suppression of the reaction is steric in origin.

Inspection of Table 1 reveals that an unexpected reversal of diastereoselectivity occurs when certain nucleophiles are used (see entries 18 - 25), and to some extent this also depends on the arene complex that is used (compare entries 14 and 15). Thus, our earlier proposition that asymmetric induction during these reactions could be anticipated based on consideration of the steric characteristics and conformation of the chiral auxiliary is an oversimplification. We shall further discuss these results later in this article.

Table 2 Effect of Solvent on Diastereoselectivity for Reactions of Complex **3**

Entry	Nucleophile	Solvent (temp. °C)	Ratio **5:6**	Yield(%)
1.	LS-Selectride®	THF (-100)	13:1	84
2.	LS-Selectride®	CH_2Cl_2 (-95)	24:1	73
3	L-Selectride®	THF (-78)	5.3:1	77
4	L-Selectride®	CH_2Cl_2 (-78)	7.0:1	67
5	PhLi	THF (-78)	2.0:1	52
6	PhLi	CH_2Cl_2 (-78)	8.0:1	57
7	PhMgBr	THF (0)	11:1	72[a]
8	PhMgBr	CH_2Cl_2 (0)	14:1	<10[a]

[a]Run at 0 °C because reaction in dichloromethane does not work at -78 °C

Table 3 Effect of Temperature on Diastereoselectivity for Reactions of Complex **3**

Entry	Nucleophile	Solvent	Temp. (°C)	Ratio **5:6**	Yield (%)
1	L-Selectride®	THF	+23	3.4:1	75
2	L-Selectride®	THF	0	3.9:1	64
3	L-Selectride®	THF	-78	5.0:1	77
4	L-Selectride®	THF	-95	6.0:1	61
5	LS-Selectride®	THF	-78	11:1	82
6	LS-Selectride®	THF	-100	13:1	84
7	PhLi	CH_2Cl_2	-45	6.4:1	33
8	PhLi	CH_2Cl_2	-78	7.7:1	57
9	PhLi	CH_2Cl_2	-90	9.5:1	47
10	PhMgBr	THF	0	11:1	72
11	PhMgBr	THF	-78	19:1	60

In several cases, we have observed that the reaction solvent affects the yield and stereoselectivity of nucleophile addition. The results that we have are collected in Table 2, although an exhaustive study has not been made. Generally, it appears that stereoselectivity is better when reactions are run in dichloromethane than in THF, but in some cases this improvement is offset by lower yields, particularly for the reaction of PhMgBr. We do not have a full rationalization for this effect, but it may be a result of changes in reactivity of the nucleophile with solvent, since, as we describe later, a more reactive nucleophile appears to produce better diastereoselectivity. However, the interplay of steric and electronic effects during these reactions is so poorly understood at present that we would not venture to interpret these results. We also observe a noticeable dependence of stereoselectivity on reaction temperature, which is to be expected when reaction pathways leading to diastereomeric products have different activation energies. Thus, as evident from the results collected in Table 3, there is an improvement in selectivity at lower temperatures.

As noted earlier, a reversal of diastereoselectivity is observed for some nucleophiles. We first observed this reversal when comparing the results of the reaction of complex **3** with lithium aluminum hydride and sodium borohydride, since the product is the same from both reactions, and NMR spectroscopy shows an obvious change.[10] It then became apparent that methyllithium, vinyllithium and some enolates also give reverse selectivity. This phenomenon appears to be general, occurring for both **3** and **4**, but is somewhat dependent on the complex used; the changeover appears to occur earlier for **4** vs **3** (see Table 1, entries 14 - 21). We have considered a number of explanations for this phenomenon:

(1) Change in mechanism: The majority of nucleophile additions to these kinds of complexes proceed *anti* to the metal, but there are a few documented cases where *syn* addition occurs.[11] It is possible that a change from *anti* to *syn* addition could lead to a reversal of diastereoselectivity because different controlling effects would prevail. It is unlikely, however, that complexes **3** and **4** would react with the same nucleophile ($LiAlH_4$ entries 14 and 15) by a different mechanism. We confirmed that no change from *anti* to *syn* addition occurs during the reaction of **3** with $LiAlH_4$ vs $NaBH_4$ by running reactions with the perdeuterated reagents. Since the *exo* and *endo* protons at C(6) show very different chemical shifts (δ 2.26 and 2.72 ppm, respectively), it is easy to determine whether such a change in stereochemistry occurs. In the present case, both nucleophiles showed only *anti* addition (resonance at 2.26 is lost), thereby ruling out a change in mechanism.

(2) Charge *vs* orbital control: The change in diastereoselectivity appears to correlate loosely with the reactivity of the nucleophile for a particular complex. Thus, more reactive nucleophiles give the 'expected' diastereomer while less reactive ones give more of the reverse product. This situation often corresponds to a change from frontier orbital control to charge control.[12] We have reported *ab initio* MO calculations that appear to rule out this possibility. Especially noteworthy is the observation that the *meta* carbons of these complexes are very close in the ^{13}C NMR spectrum (e.g., **3**: 105.8 and 106.4 ppm), indicative of an almost identical charge density at each position.[13] Moreover, since our MO calculations[10] indicate that any orbital control would lead to the same expected product as a steric approach controlled reaction (attack at the less sterically shielded *meta* position), we conclude that interplay of electronic and steric effects do not lead to selectivity reversal. Rather, both effects combine to produce high levels of stereoselectivity for reactive, sterically demanding nucleophiles, such as L-Selectride® or LS-Selectride®.

(3) Change in Transition State geometry: The last possibility that we considered is a change from an early to a late transition state as we progress from a very reactive nucleophile to a less reactive one. Should this occur, then different structural parameters might favor one diastereomer or the other. Thus, an early transition state would favor the addition trajectory analogous to a steric approach control, wherein little or no reorganization of bond angles and bond lengths has occurred within the arene ligand (reactant-like TS), and the nucleophile favors attack at the sterically more open position. Such an approach would undoubtedly favor the major products observed from, e.g., PhMgX reaction, where addition occurs at the *meta* carbon that is more remote from the methyl attached to the auxiliary. On the other hand, a late transition state (product-like) might show inverted relative energies corresponding to two diastereomeric products, since the degree of bond reorganization will correspond more closely to the product structures. Molecular mechanics calculations on the diastereomeric products is in accord with this hypothesis. For example MMX-minimized structures **5** and **6** for R^1 = Me (and other alkyls) show **6** to be lower in energy by *ca.* 0.2 kcal/mol. While this suggests that diastereoselectivity reversal might well correlate with such a change from early to late transition states, the small value of this energy difference, coupled with its questionable reliability, does not offer unambiguous support to the proposition.

Conclusions

In summary, good to excellent diastereoselectivity can be obtained during nucleophile additions to arene-manganese complexes that carry chiral pyrrolidine-based *meta* directing auxiliaries. There is a dependence of stereoselectivity on nucleophile reactivity and steric bulk that suggests a complicated set of control parameters. A combination of sterically demanding, very reactive nucleophile gives best results that can be understood based on an intuitive steric approach control model, while nucleophiles of lower reactivity give poorer or even reversed selectivity that appears to be consistent with a late transition state model. Clearly, more work is needed to fully understand these transformations. However, the realization that unusual effects play an important role in such reactions has prompted us to study candidates for chiral auxiliaries, such as ethers, that one would not intuitively expect to be useful. In this context, we have recently communicated preliminary results on the use of ether auxiliaries attached to arene-chromium tricarbonyl systems.[14] On a more negative note, we have made a large number of attempts to convert amine-substituted dienyl-$Mn(CO)_3$ complexes, of general structure **5**, through to substituted cyclohexenones, using known protocols, but so far without success. Despite this problem, we believe the results obtained from the present study are interesting and instructive, and provide some valuable insights into the chemistry of arene-metal complexes that should prove useful in the long term.

Experimental Section

General. All reactions were conducted under inert atmosphere of dry, oxygen-free nitrogen unless otherwise noted. Organic solvents were purified prior to use as follows: THF and ether were freshly distilled from Na/benzophenone; CH_3CN and CH_2Cl_2 were distilled from CaH_2, acetone was distilled from $CaSO_4$. For chromatography, distilled hexanes and ethyl acetate were used and ether was distilled over $LiAlH_4$. Column chromatography was performed on flash grade silica gel and the eluting solvents are reported as V/V percent mixtures. Thin layer chromatography was performed on E. Merck silica gel 60 F_{254} 0.25 mm plates and visualized with UV light, phosphomolybdic acid, or exposure to iodine. Concentrations of hydrides were

determined by titration using a gas buret. NMR (proton or ^{13}C) spectra were recorded on a Varian XL200 (200 MHz) or Varian Gemini-300 (300 MHz) spectrometer using $CDCl_3$, acetone-d_6 or CD_3CN as solvent with internal TMS standard. Infrared spectra were recorded for solutions in methylene chloride, acetonitrile, chloroform, or carbon tetrachloride using NaCl cell, or as a KBr pellet on a Perkin-Elmer 1600 series FTIR or a Nicolet Impact 400 FTIR spectrophotometer. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. Mass spectral analyses were performed by the Chemistry Department of Case Western Reserve University using a Kratos MS25A instrument. The purity of new compounds was assessed from their proton or carbon NMR spectra. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected.

η^6-[*N*-(2*R*,5*R*)-Dimethylpyrrolidinylbenzene]manganese Tricarbonyl Hexafluorophosphate (3). (2*R*,5*R*)-Dimethylpyrrolidine (335 mg, 3.38 mmol, 1.1 equiv.) in 15 mL methylene chloride was added dropwise to a stirred suspension of (chlorobenzene)manganese tricarbonyl hexafluorophosphate (1.22 g, 3.07 mmol) and K_2CO_3 (1.06 g, 7.69 mmol, 2.5 equiv.) in 20 mL of methylene chloride at room temperature. The reaction flask was wrapped in aluminum foil to prevent possible light induced decomplexation. After stirring at room temperature for 1.5 h, the reaction mixture was filtered through a Celite pad, and the filtrate was concentrated and added to 200 mL of pentane. A yellow precipitate formed immediately. The suspension was left in a refrigerator for about 2 h. Filtration followed by drying *in vacuo* afforded 1.227 g of complex **3** as fine yellow powder (yield: 87%). An analytical sample was prepared by recrystallization from methanol and methylene chloride. The crude complex was first dissolved in minimum amount of methylene chloride and then several drops of methanol were added. Then the vial was capped with a rubber septum pierced by a needle so that solvents could slowly evaporate in a freezer (*ca.* -12 °C) until crystals appeared. Mp 167 °C (d); $[\alpha]^{22}_D$ = -180.4° (c = 1.03, CH_2Cl_2); IR (CH_3CN) 2061, 1995, 1572, 848 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.91 (1H, ddd, *J* = 7.7, 6.1, 1.6 Hz, $H^{Ar\ meta}$), 6.84 (1H, ddd, *J* = 7.7, 6.1, 1.6 Hz, $H^{Ar\ meta}$), 6.04 (1H, t, *J* = 6.1 Hz, $H^{Ar\ para}$), 5.80 (1H, dd, *J* = 7.7, 2.8 Hz, $H^{Ar\ ortho}$), 5.69 (1H, dd, *J* = 7.7, 2.8 Hz, $H^{Ar\ ortho}$), 4.44, 4.35 (2H, quint's, *J* = 6.7 Hz, $C\underline{H}N^{pyr}$), 2.39, 1.84 (4H, m's, $C\underline{H}_2{}^{pyr}$), 1.42 (3H, d, *J* = 6.6 Hz, Me^{pyr}), 1.25 (3H, d, *J* = 6.4 Hz, Me^{pyr}); ^{13}C NMR (CD_3CN) δ 218.4, 144.4, 106.4, 105.8, 82.9, 77.5, 74.2, 57.5, 56.7, 30.5, 17.9, 16.7.

η^6-{*N*-[2*S*-(Methoxymethyl)pyrrolidino]benzene}manganese Tricarbonyl Hexafluorophosphate (2) was synthesized according to the above procedure: reaction of (2*S*)-methoxymethylpyrrolidine (136 μL, 1.1 mmol) with (chlorobenzene)manganese tricarbonyl hexafluorophosphate (396.5 mg, 1 mmol) in the presence of K_2CO_3 (346 mg, 2.5 mmol) gave 404 mg (85%) of complex **2** as yellow powder. Crystallization from MeOH and methylene chloride gave orange needles. Mp 141-142 °C, $[\alpha]^{22}_D$ = -131.7° (c = 1.16, CH_2Cl_2); IR (CH_2Cl_2) 3112, 3072, 2943, 2884, 2063, 1997, 1573, 1506, 1403, 1127, 1110, 848 cm^{-1}; ^1H NMR (CD_3CN) two conformations with a ratio of about 1.1:1 at room temperature. **Major conformer**: δ 6.51 (2H, m, $H^{Ar\ meta}$), 5.72 (1H, t, *J* = 5.7, $H^{Ar\ para}$), 5.57 (1H, dd, *J* = 7.7, 2.7 Hz, $H^{Ar\ ortho}$), 5.26 (1H, dd, *J* = 7.7, 2.7 Hz, $H^{Ar\ ortho}$), 4.21 (1H, m, $C\underline{H}N^{pyr}$), 3.52 (2H, m, $C\underline{H}_2OMe$), 3.35 (2H, m, $C\underline{H}_2N^{pyr}$), 3.25 (3H, s, $O\underline{Me}$), 1.96 (4H, m, $C\underline{H}_2{}^{pyr}$); **Minor conformer**: δ 6.51 (2H, m, $^{Ar\ meta}$), 5.64 (1H, t, *J* = 6.2, $H^{Ar\ para}$), 5.71 (1H, dd, *J* = 7.7, 2.7 Hz, $H^{Ar\ ortho}$), 5.31 (1H, dd, *J* = 7.7, 2.7 Hz, $H^{Ar\ ortho}$), 4.21 (1H, m,

CHNpyr), 3.52 (2H, m, CH_2OMe), 3.35 (2H, m, NCH_2^{pyr}), 3.36 (3H, s, OMe,), 1.96 (4H, m, CH_2^{pyr}); ^{13}C NMR (CD_3CN) **Major conformer**: δ 218.3-218.2 (broad), 142.9, 106.0, 105.5, 83.8, 73.9, 76.4, 75.2, 60.3, 59.4, 50.7, 29.0, 23.7; **Minor conformer**: 218.3-218.2 (broad), 146.2, 106.2, 105.5, 83.6, 79.2, 76.5, 75.0, 61.5, 59.2, 49.7, 28.7, 23.4. Variable temperature experiments, as described in the above Discussion, confirmed the assignment of the double set of peaks to two different conformations.

η^6-[4-*N*-(2*R*,5*R*)-Dimethylpyrrolidinotoluene]manganese Tricarbonyl Hexafluorophosphate (4). Solution of 0.30 mmol of dimethylpyrrolidine in 0.5 mL of acetone was added dropwise to the stirred mixture, containing 0.27 mmol of (*p*-chlorotoluene)manganese tricarbonyl hexafluorophosphate, 200 mg of K_2CO_3, and 2.5 mL of acetone. After 20 min stirring in the dark at room temperature the mixture was filtered through a short Celite column, then acetone was evaporated to 0.3-0.5 mL and 2-3 drops of ethanol were added to cause crystallization. The mixture was added to 2 mL of ether, crystals were filtered, washed with water, 1:1 mixture of ethanol and ether, pure ether and dried in vacuum. Yield 40%. $[\alpha]^{22}_D$ = -161° (c = 1.14, CH_2Cl_2); ^1H NMR (300 MHz, CD_2Cl_2) δ 6.41, 5.29, 5.15 (m's, 4H, H^{Ar}), 4.12, (m's, 2H, CHNpyr), 2.34 (s, 3H, Me^{Ar}), 2.29, 1.80 (m's, 4H, CH_2^{pyr}), 1.34, 1.16 (d's, *J* = 6.6, 6.3 Hz, 6H, Me^{pyr}); ^{13}C NMR (75 MHz, acetone-D_6) δ 218.6, 142.9, 115.1, 106.2, 106.0, 77.6. 73.2, 57.2, 56.3, 30.46, 30.48, 18.5, 18.1, 16.5; FTIR (KBr) 3133, 2972, 2059, 1958, 1581, 1534, 1395 cm^{-1}.

Procedure for Nucleophilic additions to 3 and 4. The procedures are described for nucleophile additions to complex **3**, those for complex **4** being essentially identical.

η^5-{2-*N*-[(2*R*,5*R*)-Dimethylpyrrolidino]-6-*exo*-phenyl-cyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = H, R^2 = Ph). PhMgBr (1.0 mL, 3.0 M in diethyl ether, 3.0 mmol) was added *via* syringe in one portion to a stirred suspension of [η^6-*N*-(2*R*,5*R*)-dimethylpyrrolidinylbenzene)manganese tricarbonyl hexafluorophosphate (**3**) (688.8 mg, 1.5 mmol) in 175 mL THF at -78 °C. After stirring overnight at -78 °C, excess of PhMgBr was destroyed by addition of 2 mL of saturated aqueous NH_4Cl solution. The resulting mixture was allowed to warm to room temperature and then rotary evaporated. The resulting residue was extracted with diethyl ether (3x60 mL), and the combined organic layer was dried over sodium sulfate. Removal of solvent *in vacuo* afforded the crude reaction product from which ^1H NMR spectrum was taken and diastereomer ratio was determined (90% *d.e.*). Purification by flash chromatography (silica gel, 2.5% ethyl acetate/hexanes) gave a mixture of **5** and **6** (307 mg, 53%). The same reaction on a smaller scale gave a higher yield (0.2 mmol scale, yield, 60%). Pure diastereomer **5** was obtained by repeated recrystallization from EtOAc-hexanes, and then pentane, the *minor* diastereomer **6** has a lower solubility than **5** and precipitates out first. **Major isomer (5)**: $[\alpha]^{25}_D$ = -187° (c = 0.88, CH_2Cl_2); R_f = 0.62 (30% ethyl acetate/hexanes); IR (CH_2Cl_2) 2975, 2001, 1919, 1514, 1494, 1349, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (3H, m, Ph), 6.93 (2H, m , Ph); 5.21 (1H, ddd, *J* = 6.8, 2.3, 1.1 Hz, H-3), 4.95 (1H, apparent t, *J* = 6.8 Hz, H-4), 3.97 (1H, broad s, NCHpyr), 3.86 (1H, t, *J* = 5.7 Hz, H-6), 3.66 (1H, broad s, NCHpyr), 3.38 (1H, ddt, *J* = 6.8, 5.7, 1.1 Hz, H-5), 2.95 (1H, dt, *J* = 5.7, 2.3 Hz, H-1), 2.15, 1.54 (4H, broad s's, CH_2^{pyr}), 1.32 (3H, broad s, Me^{pyr}), 0.99 (3H, broad s, Me^{pyr}); ^{13}C NMR and APT ($CDCl_3$) δ 223.8 (+), 149.1 (+), 134.5 (+), 128.2 (-), 126.14 (-), 125.4 (-), 94.2 (-), 64.9 (-), 56.4 (-), 54.6 (-), 52.8 (-), 42.8 (-), 37.4 (-), 30.5 (+), 30.2 (+), 19.7 (-),

18.2 (-); EI HRMS *m/z* 391.0988 [M+], calcd for $C_{21}H_{22}NO_3Mn$ 391.0980. **Minor isomer (6)**: ^1H NMR ($CDCl_3$) δ 7.18 (3H, m, Ph), 6.93 (2H, m , Ph); 5.14 (1H, dd, *J* = 6.8, 2.3 Hz, H-3), 5.09 (1H, t, *J* = 6.8 Hz, H-4), 4.00 (1H, t, *J* = 5.7 Hz, H-6), 3.97 (1H, broad s, NC$\underline{H}^{pyr}$), 3.66 (1H, broad s, NC$\underline{H}^{pyr}$), 3.38 (1H, ddt, *J* = 6.8, 5.7, 1.4 Hz, H-5), 2.69 (1H, dt, *J* = 5.7, 2.0 Hz, H-1), 2.15, 1.54 (4H, broad s's, C$\underline{H}_2^{pyr}$), 1.32 (3H, broad s, Me^{pyr}), 0.99 (3H, broad s, Me^{pyr}); ^{13}C NMR and APT ($CDCl_3$) δ 223.8 (+), 147.8 (+), 135.5 (+), 128.2 (-), 126.3 (-), 125.8 (-), 95.1 (-), 63.7 (-), 57.4 (-), 54.7 (-), 52.8 (-), 43.7 (-), 39.4 (-), 30.0 (+, overlap with **5**), 18.7 (-, overlap with **5**).

η^5-[2-*N*-(2*R*,5*R*)-Dimethylpyrrolidinocyclohexadienyl]manganese Tricarbonyl (5 and 6, R^1 = R^2 = H). *Procedure A:* $NaBH_4$ (4.0 mg, 0.106 mmol, 2.1 equiv.) was added in one portion to a stirred suspension of [η^6-*N*-(2*R*,5*R*)-dimethylpyrrolidinylbenzene)manganese tricarbonyl hexafluorophosphate (**3**) (23 mg, 0.05 mmol) in 3 mL THF at -78 °C. After stirring for 70 min at -78 °C, the reaction mixture was filtered through neutral Al_2O_3 and Celite and rotary evaporated. ^1H NMR spectrum was taken on the crude product mixture (almost pure addition product, only traces of decomplexation product were detected in NMR), and showed 62% *d.e.* favoring **6**. Purification by preparative TLC (silica gel, hexanes) gave a mixture of **5** and **6** (12.6 mg, 80%). Pure **6** was obtained by repeated precipitation from ethanol/pentane solution, and **6** has a lower solubility in these solvents than **5**. An analytical sample of **6** was obtained by recrystallization from methylene chloride/pentane/ethanol. **6** was first dissolved in minimum amount of methylene chloride and then several drops of pentane and ethanol were added. Then the vial was capped with a rubber septum pierced by a needle so that solvents could slowly evaporate in a freezer (*ca.* -12 °C) until crystals appeared. R_f = 0.59 (10% ethyl acetate/hexanes). **6:** (R^1 = R^2 = H): IR (CH_2Cl_2) 1999, 1914, 1512, 1501, 1265 cm^{-1}; ^1H NMR (C_6D_6) δ 4.69 (1H, dd, *J* = 6.0, 2.4 Hz, H-3), 4.41 (1H, t, *J* = 6.0 Hz, H-4), 3.40-3.08 (2H, broad m, NC$\underline{H}^{pyr}$), 2.63 (2H, m, H-5 and H-6^{endo}), 2.11 (1H, d, *J* = 11.2 Hz, H-6^{exo}), 1.71 (1H, dt, *J* = 5.4, 2.4 Hz, H-1), 1.54 (2H, broad m, C$\underline{H}_2^{pyr}$), 0.94-0.71 [8H, broad m, C$\underline{H}_2^{pyr}$ and 2Me^{pyr}); ^{13}C NMR (C_6D_6) δ 136.7, 96.3, 64.5, 53.5-53.4 (broad), 51.8, 30.3, 29.8, 27.6, 18.2; EI HRMS *m/z* [M+] 315.0662, calcd for $C_{15}H_{18}NO_3Mn$ 315.0667. *Procedure B:* LS-Selectride® (60 μL, 1.0 M in THF, 0.06 mmol, 1.2 equiv.) was added *via* syringe in one portion to a stirred suspension of [η^6-*N*-(2*R*,5*R*)-dimethylpyrrolidinylbenzene)manganese tricarbonyl hexafluorophosphate (**3**) (23 mg, 0.05 mmol) in 3 mL methylene chloride at -95 °C. After stirring for 40 min at -95 to -85 °C, the reaction mixture was filtered through neutral Al_2O_3 and Celite and rotary evaporated. ^1H NMR spectrum was taken on the crude product mixture, and diastereomeric ratio was determined to be 92% favoring **5**. Purification by microscale flash chromatography (silica gel, hexanes) gave a mixture of **5** and **6** (11.5 mg, 73%). **5**: ^1H NMR (C_6D_6) δ 4.79 (1H, dd, *J* = 5.9, 2.3 Hz, H-3), 4.46 (1H, t, *J* = 5.9 Hz, H-4), 3.36-3.05 (2H, broad m, NC$\underline{H}^{pyr}$), 2.55 (1H, m, H-6^{endo}) 2.49 (1H, apparent dt, *J* = 5.9, 1.2 Hz, H-5), 2.15 (1H, dt, *J* = 5.6, 2.3 Hz, H-1), 2.01 (1H, d, *J* = 11.4 Hz, H-6^{exo}) 1.56 (2H, broad m, C$\underline{H}_2^{pyr}$), 1.09-0.43 (8H, broad m, C$\underline{H}_2^{pyr}$ and 2Me^{pyr}); ^{13}C NMR (C_6D_6) δ 134.8, 96.2, 65.5, 54.5-52.5 (broad), 49.8, 31.2, 30.2, 27.4, 19.8-18.5 (broad).

η^5-[2-*N*-(2*R*,5*R*)-Dimethylpyrrolidino-6-*exo*-methylcyclohexadienyl]manganese Tricarbonyl (5 and 6, R^1 = H, R^2 = Me). MeLi (105 μL, 1.4 M in diethyl ether, 0.147 mmol) was added *via* syringe in one portion to a stirred suspension of [η^6-*N*-(2*R*,5*R*)-dimethylpyrrolidinylbenzene)manganese tricarbonyl

hexafluorophosphate (**3**) (23 mg, 0.05 mmol) in 3 mL methylene chloride at -90 °C. After stirring for 30 min at -95 to -85 °C, the reaction was quenched with several drops of saturated aqueous NH_4Cl solution. The resulting mixture was allowed to warm to room temperature and then rotary evaporated. The residue was extracted with diethyl ether, and the combined organic layer was filtered through a short pipette of Celite and sodium sulfate (2 cm length each). Removal of solvent *in vacuo* afforded the crude reaction product from which ^1H NMR spectrum was taken (50% *d.e.* favoring **6**). Purification by flash chromatography (silica gel, 4% ethyl acetate/hexanes) gave a mixture of **5** and **6** (9.9 mg, 60%) as a pale yellow oil: R_f = 0.53 (10% ethyl acetate/hexanes); IR (CH_2Cl_2) 3066, 2971, 2916, 1998, 1910, 1508. 1380, 1338, 1157, 1110, 1044 cm^{-1}; **5**: ^1H NMR ($CDCl_3$) δ 5.22 (1H, dd, *J* = 6.0, 1.8 Hz, H-3), 4.82 (1H, apparent t, *J* = 6.6 Hz, H-4), 3.91-3.65 (2H, broad m, NC<u>H</u>^{pyr}), 3.11 (1H, ddt, *J* = 7.2, 5.8, 1.8 Hz, H-5), 2.63 (1H, m, H-6), 2.75 (1H, dt, *J* = 6.0, 1.8 Hz, H-1), 2.09, 1.54 (4H, m's, C<u>H</u>$_2^{pyr}$), 1.21-1.02 (6H, broad s, Me^{pyr}), 0.52 (3H, d, *J* = 6.4 Hz, Me-6); ^{13}C NMR ($CDCl_3$) δ 224.1, 133.5, 93.6, 65.0, 57.5, 53.7, 53.4, 53.3, 53.2, 39.6, 33.2, 30.3 (broad), 29.6, 18.8 (broad); **6**: ^1H NMR ($CDCl_3$) δ 5.13 (1H, dd, *J* = 6.0, 1.8 Hz, H-3), 4.82 (1H, apparent t, *J* = 6.6 Hz, H-4), 3.91-3.65 (2H, broad m, NC<u>H</u>^{pyr}), 3.19 (1H, ddt, *J* = 7.2, 5.8, 1.8 Hz, H-5), 2.79 (1H, m, H-6), 2.42 (1H, dt, *J* = 5.8, 1.8 Hz, H-1), 2.09, 1.54 (4H, m's, C<u>H</u>$_2^{pyr}$), 1.21-1.02 (6H, broad s, Me^{pyr}), 0.52 (3H, d, *J* = 6.5 Hz, Me-6); ^{13}C NMR ($CDCl_3$) δ 224.1, 135.0, 93.9, 63.7, 59.1, 53.7, 53.4, 53.3, 53.2, 39.1, 33.6, 30.1(broad), 28.8, 18.8 (broad) ; EI HRMS *m/z* 329.0822 [M$^+$], calcd for $C_{16}H_{20}NO_3Mn$ 329.0824.

η^5-{2-*N*-[(2*R*,5*R*)-Dimethylpyrrolidino]-6-*exo*-vinylcyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = H, R^2 = CH=CH_2). Vinylmagnesium bromide (0.5 mL, 0.25 M in THF, 0.125 mmol) was added dropwise *via* syringe to a stirred suspension of η^6-[*N*-(2*R*,5*R*)-dimethylpyrrolidinobenzene]-manganese tricarbonyl hexafluorophosphate (**3**) (46 mg, 0.1 mmol) in 4 mL THF at -78 °C. After stirring for 50 min at -78 °C, the reaction was quenched with several drops of saturated aqueous NH_4Cl solution. The resulting mixture was allowed to warm to room temperature and then rotary evaporated. The resulting residue was extracted with diethyl ether, and the combined organic layer was filtered through a short pipette of Celite and sodium sulfate (2 cm length each). Removal of solvent *in vacuo* afforded the yellow crude product from which ^1H NMR spectrum was taken (23% *d.e.* favoring **5**). Purification by microscale flash chromatography (silica gel, 1% ethyl acetate/hexanes) gave a mixture of **5** and **6** (10 mg, 50%, 19.1 mg of unreacted **3** was recovered): R_f= 0.65 (10% ethyl acetate/hexanes); EI HRMS *m/z* 341.0830 [M$^+$], calcd for $C_{17}H_{20}NO_3Mn$ 341.0824; IR (CCl_4) 3077, 3056, 3972, 2880, 2006, 1929, 1915, 1509, 1497, 1381, 1347, 1337, 638, 618 cm^{-1}. **Isomer 5**: ^1H NMR ($CDCl_3$) δ 5.17 (1H, ddd, *J* = 17.1, 10.2, 5.9 Hz, C<u>H</u>^{vin}), 5.16 (1H, ddd, *J* = 6.0, 2.7, 1.2 Hz, H-3), 4.87 (1H, ddd, *J* = 7.1, 6.0, 1.1 Hz, H-4), 4.61 (1H, dt, *J* = 10.2, 1.4 Hz, CH<u>H</u>$^{vin\ cis}$), 4.53 (1H, dt, *J* = 17.1, 1.5 Hz, CH<u>H</u>$^{vin\ trans}$), 3.93, 3.67 (2H, broad m's, NC<u>H</u>^{pyr}), 3.16 (1H, m, H-5), 3.07 (1H, m, H-6), 2.69 (1H, dt, *J* = 5.9, 2.1 Hz, H-1), 2.09, 1.54 (4H, m's, C<u>H</u>$_2^{pyr}$), 1.47-0.86 (6H, broad m, Me^{pyr}); ^{13}C NMR ($CDCl_3$): δ 145.0, 134.5, 111.0, 94.2, 65.1, 53.9, 54.8-52.6 (broad), 41.1, 35.9, 30.3 (broad), 19.0-18.2 (broad). **Isomer 6**: ^1H NMR ($CDCl_3$) δ 5.14 (1H, ddd, *J* = 17.1, 10.2, 6.7 Hz, C<u>H</u>^{vin}), 5.10 (1H, dd, *J* = 6.0, 2.7, 1.2 Hz, H-3), 4.91 (1H, ddd, *J* = 7.1, 6.0, 1.1 Hz, H-4), 4.65 (1H, ddd, *J* = 17.1, 1.8, 1.2 Hz, CH<u>H</u>$^{vin\ trans}$), 4.59 (1H, ddd, *J* = 10.2, 1.8, 0.9 Hz, CH<u>H</u>$^{vin\ cis}$), 3.93, 3.67 (2H, broad m's, NC<u>H</u>^{pyr}), 3.30 (1H, m, H-6), 3.16 (1H, m, H-5), 2.39 (1H, dt, *J* = 5.9, 2.1 Hz, H-1), 2.09, 1.54 (4H,

m, C$\underline{H}_2^{pyr}$), 1.47-0.86 (6H, broad m, Me^{pyr}); ^{13}C NMR ($CDCl_3$): δ 144.5, 135.5, 111.2, 94.7, 64.0, 55.3, 54.8-52.6 (broad), 42.0, 36.9, 30.0, 19.8-19.6 (broad).

η^5-{4-[*N*-(2*R*,5*R*)-Dimethylpyrrolidino]-1-methyl-6-*exo*-phenylcyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = Me, R^2 = Ph): EI HRMS *m/z* 405 1147 [M$^+$], calcd for $C_{22}H_{24}NO_3Mn$ 405.1137; ^{1}H NMR (300 MHz, $CDCl_3$) δ **isomer 5:** 7.25 - 7.10, 6.95 - 6.90 (5H, m's, Ph), 5.09 (1H, dd, *J* = 2.6, 6.0 Hz, H-3), 4.69 (1H, d, *J* = 6.0 Hz, H-2), 3.93, 3.59 (2H, m's, broad, C$\underline{H}$N^{pyr}), 3.85 (1H, d, *J* = 5.9 Hz, H-6), 2.90 (1H, dd, *J* = 2.6, 5.9 Hz, H-5), 2.12, 1.50 (4H, m's, C$\underline{H}_2^{pyr}$), 1.63 (s, 3H, Me-1), 1.32, 0.95 (6H, broad, Me^{pyr}); **isomer 6:** 7.25 - 7.10, 6.95 - 6.90 (5H, m's, Ph), 5.01 (1H, dd, *J* = 2.6, 5.9 Hz, H-3), 4.78 (1H, d, *J* = 5.9 Hz, H-2), 3.93, 3.59 (2H, m's, broad, C$\underline{H}$N^{pyr}), 3.95 (d, *J* = 5.9 Hz, 1H, H-6*endo*), 2.63 (dd, *J* = 2.6, 5.9 Hz, 1H, H-5), 2.12, 1.50 (4H, m's, C$\underline{H}_2^{pyr}$), 1.60 (s, 3H, Me-1), 1.32, 0.95 (6H, broad, Me^{pyr})

η^5-{4-[*N*-(2*R*,5*R*)-Dimethylpyrrolidino]-1-methylcyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = Me, R^2 = H): EI HRMS *m/z* 301.0876 [M$^+$–(CO)], calcd for $C_{15}H_{20}NO_2Mn$ 301.0874l; 245.0983 [M$^+$–3(CO)], calcd for $C_{13}H_{20}NMn$ 245.0976; ^{1}H NMR (300 MHz, $CDCl_3$) δ **isomer 6:** 5.03 (1H, dd, *J* = 2.6, 5.8 Hz, H-3), 4.58 (1H, d, *J* = 5.8 Hz, H-2), 3.77 (2H, broad m, C$\underline{H}$N^{pyr}), 2.74 (dd, *J* = 5.9, 12.8 Hz, 1H, H-6*endo*), 2.50 (1H, d, *J* = 12.8 Hz, H-6*exo*), 2.12 (1H, dd, *J* = 2.6, 5.9 Hz, H-5), 2.09 (m, 2H, C$\underline{H}_2^{pyr}$), 1.55 (3H, s, Me-6), 1.52 (2H, "pseudo-d", C$\underline{H}_2^{pyr}$), 1.18 (6H, broad, Me^{pyr}); **isomer 5:** 5.14 (1H, dd, *J* = 2.6, 6.0 Hz, H-3), 4.61 (1H, d, *J* = 6.0 Hz, H-2), 3.77 (2H, broad m, C$\underline{H}$N^{pyr}), 2.64 (1H, dd, *J* = 6.0, 12.6 Hz, H-6*endo*), 2.38 (1H, d, *J* = 12.6 Hz, H-6*exo*), 2.09 (2H, m, C$\underline{H}_2^{pyr}$), 1.55 (3H, s, Me-6), 1.52 (2H, "pseudo-d", C$\underline{H}_2^{pyr}$), 1.18 (6H, broad, Me^{pyr})

η^5-{4-[*N*-(2*R*,5*R*)-Dimethylpyrrolidino]-1,6-*exo*-dimethylcyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = R^2 = Me). EI HRMS *m/z* 343.0987 [M$^+$], calcd for $C_{17}H_{22}NO_3Mn$ 343.0980; ^{1}H NMR (300 MHz, $CDCl_3$) δ **isomer 6:** 4.98 (1H, dd, *J* = 2.5, 5.8 Hz, H-3), 4.51 (1H, d, *J* = 5.8 Hz, H-2), 3.76 (2H, broad m, C$\underline{H}$N^{pyr}), 2.78 (1H, dq, *J* = 5.7, 6.6 Hz, H-6*endo*), 2.08 (2H, m, C$\underline{H}_2^{pyr}$), 1.58 (3H, s, Me-1), 1.51 (2H, m, C$\underline{H}_2^{pyr}$), 1.21 (6H, broad, Me^{pyr}), 0.56 (3H, d, *J* = 6.6 Hz, Me-6*exo*); **isomer 5:** 5.06 (1H, dd, *J* = 2.3, 4.4 Hz, H-3), 4.53 (1H, d, *J* = 4.4 Hz, H-2), 3.76 (2H, broad m, C$\underline{H}$N^{pyr}), 2.65 (1H, quint., *J* = 6.3 Hz, H-6*endo*), 2.38 (1H, m, H-5), 2.08 (2H, m, C$\underline{H}_2^{pyr}$), 1.58 (3H, s, Me-1), 1.51 (2H, m, C$\underline{H}_2^{pyr}$), 1.21 (6H, broad, Me^{pyr}), 0.49 (3H, d, *J* = 6.3 Hz, Me-6*exo*)

η^5-{6-*exo*-Allyl-4-[*N*-(2*R*,5*R*)-dimethylpyrrolidino]-1-methylcyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = Me, R^2 = CH$_2$CH=CH$_2$): EI HRMS *m/z* 328.0749 [M–(allyl)]$^+$, calcd for $C_{16}H_{19}NO_3Mn$ 328.0745; 285.1295 [M–3(CO)]$^+$, calcd for $C_{16}H_{24}NMn$ 285.1289; ^{1}H NMR (300 MHz, COSY, $CDCl_3$) **isomer 5:** δ 5.53 (1H, dddd, *J* = 16.9, 10.1, 8.1, 6.8 Hz, C$\underline{H}^{allyl}$), 5.03 (1H, dd, *J* = 2.4, 5.8 Hz, H-3), 4.94 (1H, dd, *J* = 2.1, 10.1 Hz, =CH$\underline{H}^{allyl}$ *cis*), 4.80 (1H, dd, *J* = 9.9, 2.1 Hz, =CH$\underline{H}^{allyl}$ *trans*), 4.59 (1H, d, *J* = 5.8 Hz, H-2), 3.65 - 4.00 (2H, 2 broad m's, C$\underline{H}$N^{pyr}), 2.67 (1H, dddd, *J* = 8.1, 6.5, 4.7, 1.3 Hz, H-6*endo*), 2.67 (1H, dd, *J* = 6.5, 2.4 Hz, H-5), 2.08, 1.50 (4H, m's, C$\underline{H}_2^{pyr}$), 1.84 (1H, ddd, *J* = 13.2, 6.87, 6.5 Hz, CH$\underline{H}^{allyl}$), 1.64 (s, 3H, Me-1), 1.29 (dt, 13.2, 8.1 Hz, 1H, C$\underline{H}$H^{allyl}), 1.25 - 0.83

(6H, 2 broad m's, Me^{pyr}); **isomer 6:** (partial data) 5.62 (1H, m, $C\underline{H}^{allyl}$), 4.99 (1H, dd, J = 2.5, 5.9 Hz, H-3), 4.89 (1H, dd, J = 1.9, 8.5 Hz, $CH\underline{H}^{allyl\ cis}$), 3.65 - 4.00 (2H, 2 m's, very broad, $C\underline{H}N^{pyr}$), 2.85 (1H, m, H-6*endo*), 2.40 (dd, J =5.7, 2.6 Hz, 1H, H-5), 2.08, 1.50 (4H, m's, $C\underline{H}_2^{pyr}$), 1.62 (s, 3H, Me-1), 1.25 - 0.83 (6H, 2 broad m's, Me^{pyr}).

η^5-{4-[*N*-(2*R*,5*R*)-Dimethylpyrrolidino]-1-methyl-6-*exo*-vinylcyclohexadienyl}-manganese Tricarbonyl. (5 and 6, R^1 = Me, R^2 = CH=CH_2) EI HRMS *m/z* 355.0996 [M^+], calcd for $C_{18}H_{22}NO_3Mn$ 355.0980; ^{1}H NMR (300 MHz, C_6D_6) δ **isomer 6:** 4.94 (1H, ddd, J = 17.1, 10.0, 7.6 Hz, $C\underline{H}^{vin}$), 4.56 (1H, dd, J = 17.1, 2.0 Hz, $CH\underline{H}^{vin\ trans}$), 4.55 (1H, dd, J = 2.5, 6.0 Hz, H-3), 4.53 (1H, dd, J = 10.0, 2.0 Hz, $CH\underline{H}^{vin\ cis}$), 4.31 (1H, d, J = 6.0 Hz, H-2), 3.25 (2H, broad m, $C\underline{H}N^{pyr}$), 3.19 (1H, dd, J = 5.9, 7.6 Hz, H-6*endo*), 2.55 (1H, dd, J = 2.5, 5.9 Hz, H-5), 1.59, 0.96 (4H, m's, $C\underline{H}_2^{pyr}$), 1.48 (3H, s, Me-1), 0.90 (6H, broad, Me^{pyr}); **isomer 5** (partial data): 5.05 (1H, ddd, J = 17.1, 10.2, 6.9 Hz, $C\underline{H}^{vin}$), 4.29 (1H, d, J = 6.0 Hz, H-2), 3.25 (2H, broad m, $C\underline{H}N^{pyr}$), 3.11 (1H, dd, J = 6.9, 6.0 Hz, H-6*endo*), 2.47 (1H, dd, J = 6.0, 2.7 Hz, H-5), 1.59, 0.96 (4H, m's, $C\underline{H}_2^{pyr}$), 1.50 (3H, s, Me-1), 0.90 (6H, broad, Me^{pyr}).

η^5-{6-*exo*-*tert*-Butylcarboxymethyl-4-[N-(2R,5R)-dimethylpyrrolidino]-1-methylcyclohexadienyl}manganese Tricarbonyl (5 and 6, R^1 = Me, R^2 = CH_2CO_2Bu-*t*): EI HRMS *m/z* 328.0751 [M–(CH_2CO_2Bu-*t*)]$^+$, calcd for $C_{16}H_{19}NO_3Mn$ 328.0745; 359.1669 [M–3(CO)]$^+$, calcd for $C_{19}H_{30}NO_2Mn$ 359.1657; ^{1}H NMR (300 MHz, $CDCl_3$) δ **isomer 6:** 4.99 (1H, dd, J = 2.6, 5.7 Hz, H-3), 4.59 (1H, d, J = 5.7 Hz, H-2), 3.78 (2H, broad m, $C\underline{H}N^{pyr}$), 3.20 (1H, ddd, J = 4.8, 5.8, 8.2 Hz, H-6*endo*), 2.48 (1H, dd, J = 2.6, 5.5 Hz, H-5), 2.07, 1.51 (4H, m's, $C\underline{H}_2^{pyr}$), 1.87, 1.65 (1H, dd, J = 15.6, 4.8 Hz, and 1H, dd, J = 15.6, 8.5 Hz, $C\underline{H}_2CO_2$-Bu-*t*), 1.60 (3H, s, Me-1), 1.40 (9H, s, Bu-*t*), 1.19 (6H, broad, Me^{pyr}); **isomer 5:** 5.05 (1H, dd, J = 2.6, 5.8 Hz, H-3), 4.61 (1H, d, J = 5.8 Hz, H-2), 3.78 (2H, broad m, $C\underline{H}N^{pyr}$), 3.03 (1H, m, H-6*endo*), 2.74 (1H, dd, J = 2.6, 5.9 Hz, H-5), 2.07, 1.51 (4H, m's, $C\underline{H}_2^{pyr}$), 1.94, 1.45 (1H, dd, J = 13.8, 5.0 Hz, and 1H, dd, J = 13.8, 8.7 Hz, $C\underline{H}_2CO_2$-Bu-*t*), 1.62 (3H, s, Me-1), 1.43 (s, 9H, Bu-*t*), 1.19 (6H, broad, Me^{pyr}).

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