Transition-metal Mediated Asymmetric Synthesis. Part 6.† Organometallic Approaches to the Enantiomer Synthesis of Tridachione: A Role for Planar Chirality in Synthesis Design

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Two series of complexes which contain planar chirality have been examined as intermediates for the synthesis of tridachione. Alkylation of tricarbonyl(η^5-2-methoxy-3,5-dimethylcyclohexadienyl)-iron(1+) hexafluorophosphate(1−) with trimethylsilyl cyanide and reaction of the nitrile product with ethyl-lithium afforded an acyl-substituted intermediate for the synthesis of tridachione. Complexation of 1-methoxy-2,4-dimethylbenzene by $Mn(CO)_3^+$ gave a complex that was alkylated by vinyl Grignard reagents at the correct position to introduce the 1-methylpropenyl group in tridachione. Methylmagnesium bromide gave predominantly an unexpected regioisomer. These products were converted into $Mn(CO)_2NO^+$ dienyl complexes. The influence of the use of planar chirality on the design of synthetic strategies is discussed.

Transition metal π-complexes of unsymmetrically substituted ligands contain planar chirality in which the metal has distinguished the two enantiofaces of the ligand. This distinction renders the complexes chiral and provides an efficient chemical differentiation between the faces of the ligand, through alkylation reactions that are subject to complete stereocontrol by the metal. Since the metal totally dominates stereocontrol, a series of alkylation reactions would offer reliable *cis*-relative stereochemistry of substituents introduced by nucleophile addition despite the effect of chiral centres formed during the reaction sequence, that might otherwise be expected to exert an influence of their own on subsequent alkylations. We have now completed a series of preliminary studies that prepare the way to illustrate this concept in target-oriented synthetic work. In parallel with these studies with a view to the eventual use of our methods in enantioselective synthesis, we have examined[1] the use of optically active complexes which contain planar chirality which is immune to racemisation if correctly substituted. We recently described[1] a simple example of this concept in which the resolution and alkylation of tricarbonyliron complexes was examined.

By the development and application of the chemistry of π-complexes of iron and manganese, we now seek to determine the factors that are required to allow such reactions to be employed efficiently in the enantioselective organic synthesis of a number of biologically important substances, and to define the benefits arising from such an approach. In the case of tridachione (**1**),[2] an antibiotic natural product isolated[3] from the mollusc *Tridachiella diomedea*,‡ a synthesis in which the formation of two key C–C bonds with *cis*-relative stereochemistry is controlled by the transition metal complex can be based (Scheme 1) on the prospective cyclohexenone intermediate (**2**). Organometallic intermediates (**4**) and (**5**) for the construction of (**2**) were chosen on the basis of the synthetic equivalence[4] of resolved[1,5] methoxy-substituted dienyl complexes such as (**5c**) to chiral enone cation synthons.

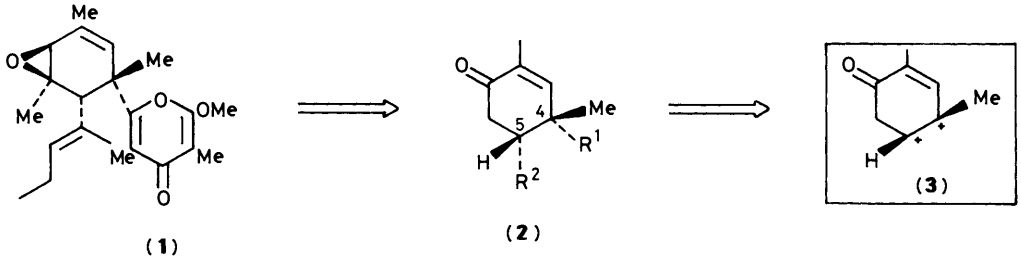
In this paper we describe the first stage of this endeavour, in which the preparation and alkylation of two separate series of model complexes has confirmed the feasibility of the introduction of both the vinyl or acyl groups at the required positions relative to the methoxy substituent in the ligand, at the sites destined to become C-4 and C-5, respectively, of the enone intermediate (**2**). In the course of this work we have discovered[6] an unusual reversal of the expected pattern of regiocontrol of nucleophile additions, and have developed an alkylation procedure[7] that is suitable for use at sterically hindered positions in highly substituted complexes. The results of these preliminary studies serve to emphasize the importance of regiocontrol in the design of synthetic routes based on organometallic π-complexes, and the high degree of flexibility inherent in such an approach, once steric factors have been overcome.

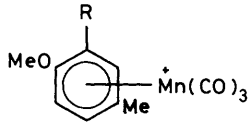
Results

Introduction of the C-4 *Substituent: the Organoiron Series.*— Tricarbonyl(η^5-2-methoxycyclohexadienyl)iron(1+) complexes are well suited for use as synthetic equivalents of C-4 cations of cyclohexenones, since the 2-methoxy substituent directs nucleophile addition to C-5.[8] The starting material for these studies, the dimethyl substituted complex (**5a**), was readily available[9] on a convenient scale by Birch reduction of 2,4-dimethylanisole, complexation by $Fe(CO)_5$, and reaction of the resulting mixture with triphenylcarbenium tetrafluoroborate by the usual procedure. The salt (**5a**) is formed as the single product without the need for further purification or for chromatographic separation of the intermediates, since only one of the isomers present undergoes hydride abstraction.

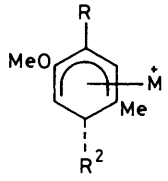
Reaction of (**5a**) with cyanide was at first attempted following the procedure successfully employed by Pearson[10] for the 2-methoxy-5-methyl complex (**5c**). Reaction of (**5a**) with sodium cyanide, however, resulted only in the formation of an unstable oil that appeared to arise from deprotonation of the C-5 methyl substituent to form a triene complex. Similar deprotonation side reactions have been encountered[11] in other systems where severe steric hindrance interferes with the approach of the reagent to the cyclohexadienyl ring, but it was unexpected that the introduction of a single methyl substituent so distant from the site of reaction should induce a change of mechanism from alkylation to deprotonation. For our purpose, a far less basic source of the nitrile nucleophile was required. The problem was overcome (Scheme 2) by use of the reagent trimethylsilyl cyanide which is present in solution as an equilibrium mixture with the isocyanide isomer (**6**).[12] In contrast to reactions of the free cyanide anion, trimethylsilyl cyanide reacted slowly requiring an excess of the reagent, but effected alkylation rather than deprotonation. In this way the adduct (**7**) was obtained in 60—

† For Part 5, see ref. 14.
‡ Structures drawn in this paper indicate only relative sterochemistries as depicted in ref. 3.



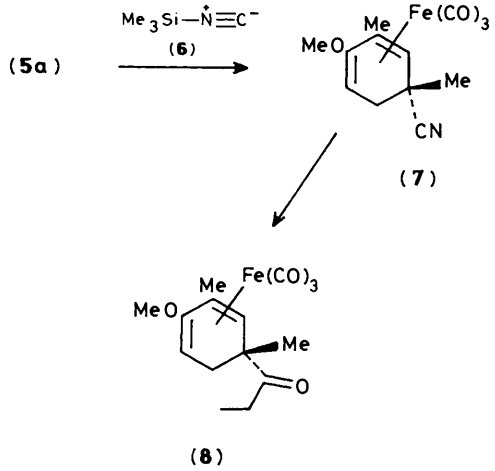


(4) **a**; R = Me
b; R = H



(5) **a**; M = $Fe(CO)_3$, R = Me, R^2 = H
b; M = $Mn(CO)_2NO$
c; M = $Fe(CO)_3$, R = R^2 = H
d; M = $Mn(CO)_2NO$, R = H, R^2 = CH = CH_2
e; M = $Mn(CO)_2NO$, R = H, R^2 = Me

Scheme 1.



Scheme 2.

95% yield. We have since shown [12] that trimethylsilyl cyanide is in general a far superior reagent to those previously used with tricarbonyliron complexes, and is particularly suited for reaction at substituted positions.

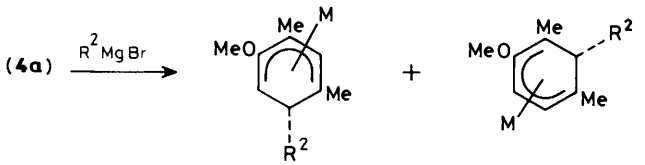
A number of reaction conditions for hydride abstraction from (7) were examined. Because of the presence of a blocking substituent *trans* to the metal, direct hydride abstraction was not expected to proceed at room temperature, and under forcing conditions decomposition occurred. The prospect [13] that other reagents might react by the recently proposed electron-transfer mechanism, prompted us to examine some alternatives. Dichlorodicyanoquinone–HBF_4, a new reagent system that is successful [14] with simple tricarbonyliron complexes, was unsatisfactory when used with (7). Reaction of trimethyloxonium tetrafluoroborate with a model nitrile adduct, tricarbonyl(η^4-5α-cyano-2-methoxy-5β-methylcyclohexa-1,3-diene)iron(0), did form a cationic product but this proved to be (**5c**), produced by removal of the nitrile group. An example of a blocked complex lacking the nitrile leaving group was also examined. Reaction of tricarbonyl(η^5-2-methoxy-3,5α-dimethylcyclohexadiene)iron(0) with trimethyloxonium tetrafluoroborate resulted in loss of the methoxy group to form a tricarbonyl(η^5-2,4-dimethylcyclohexadienyl)iron(1+) salt in low yield.

In order to circumvent the lability of the nitrile substituent in (7), we have examined its conversion into the acyl substituent (required for the eventual introduction of the pyrone ring), prior to further attempts to reform the η^5 salt. Grignard reagents have been used successfully in the presence of the tricarbonyliron group in reactions with a nitrile substituent in a simple complex, but in the case of (7), the reaction was unsatisfactory. Reaction of trimethylaluminium was also unsuccessful, but the use of ethyl-lithium in light petroleum afforded the required ethyl ketone (**8**) in 52% yield. The ability to perform functional group interconversions at substituents within a complex, while retaining the tricarbonyliron group for subsequent use, is an important aspect of this chemistry. The successful masking of the cyclohexenone ketone by the metal complex indicates useful possibilities for the further elaboration of substituent R^1 (Scheme 1) towards the required pyrone ring at a subsequent stage in the synthesis prior to decomplexation.

Introduction of the C-5 *Substituent: the Organomanganese Series.*—Both organoiron [16] and organomanganese [17] complexes have been used to produce C-5 substituted cyclohexenones and enol ethers suitable for hydrolysis to cyclohexenones. The procedures developed by the Pauson [18] and Sweigart [19] groups for the alkylation of anisole complexes at the *meta* position seemed particularly suited to the task in hand, since neutral tricarbonylmanganese dienyl complexes, such as those obtained by alkylation of (**4b**), can be converted [20] into cationic nitrosyl complexes [*e.g.* (**5e**)] which would provide a useful

parallel[21] with the tricarbonyliron cations discussed above, and would offer the prospect of a simple, sequential introduction of R^2 and R^1.

The arene complex (**4a**) was conveniently prepared in 57% yield by reaction of 2,4-dimethylanisole with $Mn(CO)_5Br$ in the presence of aluminium trichloride, following the usual procedure.[18] Our principal objective at this initial stage was to examine the effect of the C-2 methyl substituent as a directing group in alkylation reactions, and so confirm the suitability of (**4a**), or analogues in which triphenylphosphine replaces carbon monoxide,[20] as potential starting materials for a synthesis of tridachione. While the *meta*-directing influence of methoxy groups in arene π-complexes has been studied in some detail, no information was available concerning the effect of additional substituents in the $Mn(CO)_3$ series of complexes. Large groups, however, have been employed[22] as blocking groups to control the alkylation of neutral $Cr(CO)_3$ complexes. On the basis that steric effects might be important, we anticipated that alkylation should occur at C-5, the less hindered of the two *meta* positions. In the event, however, somewhat surprising results were obtained (Scheme 3).



R^2	(9a) : (10a)
Me	1 : 4
CH = CH_2	4 : 1
CH = CHMe	9 : 1

Scheme 3.

Alkylation of (**4a**) with methylmagnesium bromide gave a 1:4 mixture of (**9a**; R^2 = Me) and (**10a**; R^2 = Me). The neutral tricarbonylmanganese dienyl complexes proved unstable and were converted directly to the corresponding cationic $Mn(CO)_2NO$ complexes (**9b**; R^2 = Me) and (**10b**; R^2 = Me) which were obtained in 39% overall yield. In this case alkylation had proceeded predominantly at C-3, the more hindered of the two positions.

Fortunately, the effect of factors influencing regiocontrol of the alkylation was reversed in the case of vinyl Grignard reagents, perhaps due to π interactions between the Grignard reagent and the top face of the arene ligand. Reaction with vinylmagnesium bromide afforded a 4:1 mixture of (**9a**; R^2 = CH=CH_2) and (**10a**; R^2 = CH=CH_2). These products were also unstable but could be separated by chromatography. The major product (**9a**; R^2 = CH=CH_2) was converted immediately into the nitrosyl cation (**9b**; R^2 = CH=CH_2) which was produced in 50% overall yield. The use of the Grignard reagent obtained from (*E,Z*)-1-bromopropene was also examined. A 9:1 mixture of regioisomers was obtained in this case. The greater selectivity observed in this reaction augers well for the successful introduction of the more elaborate vinyl group required in (**1**). The products were again separated by chromatography to afford (**10a**; R = CH=CHMe) which was produced in 75% yield as a mixture of double bond stereoisomers, reflecting the stereochemical inhomogeneity of the bromoalkene starting material.

Discussion

In this work we have described the development of methods that allow successful alkylations of the types needed to construct the chiral enone (**2**), despite complications arising from the high level of substitution around the complex. At an empirical level, this work defines the regioselectivity and chemical selectivity aspects of these reactions and demonstrates the prospects for the development of metal complexes as synthetic equivalents of the chiral dication synthon (**3**). An important feature in this work is the correct choice of nucleophile for the alkylation reaction. A balance must be struck between nucleophilicity and basicity, and reactivity and susceptibility to steric effects. The successful use of trimethylsilyl cyanide and vinyl Grignard reagents in this investigation emphasizes the importance that, in order that they may be of general applicability as intermediates in synthesis, organometallic electrophiles should be compatible with a wide variety of nucleophilic reagents. Dienyl complexes in the organoiron series admirably meet this criterion,[8] but further work is required to determine whether the organomanganese complexes share this virtue.

The complexes described in this paper form part of a much larger class of metal π-complexes[1] which, once resolved, are immune to racemisation if substituents are placed to ensure that symmetrical intermediates cannot be encountered, regardless of the degree of rearrangement of the π-system, or changes to the extent of π-bonding to the metal, to which the complexes are subjected. This makes compounds of this type particularly well suited for use in enantiomer synthesis.

Conclusions

Transition metal π-complexes offer synthetic chemists a simple method to elaborate resolved ring systems in a manner that can preclude racemisation, that offers, in principle, the ability to control a series of alkylations, and permits the unmasking of key functionality at a later stage. In our model studies for the synthesis of tridachione described here, we have demonstrated the essential alkylation reactions required for the purpose. Although a direct approach to the reformation of cationic intermediates from (**7**) or (**8**), in the case of the iron complexes, appears unattractive, further development of new reactivation procedures[13,14] offers a useful alternative for future investigation. In the manganese series, reactivation can be achieved by standard methods[20] but more work is required to define alkylation procedures for the nitrosyl products.

Our investigation of the organometallic route for the synthesis of tridachione has reached the stage where it is possible to draw attention to the principle requirements for the design of efficient syntheses based on this general approach. When stoicheiometric metal complexes are employed, the transition metal centre should be used as a control centre more than once in the synthesis. Substituent positions should be selected to preclude the formation of symmetrical intermediates, and the regiochemical directing influence of substituents must be carefully assessed. This last criterion points to an important area for further work; despite a considerable body of experimental results it is difficult to go beyond empirical predictions of regiocontrol. The results described in this paper emphasize the great influence small changes in substrate and reagent can have on the overall outcome of reactions of this type and hence the importance of a clearer understanding of these effects to place synthetic work of this nature on a firmer footing.

Experimental

All reactions were performed under a nitrogen atmosphere, unless otherwise stated. I.r. spectra were recorded using a Perkin-Elmer 257 spectrometer; metal carbonyl i.r. bands were measured on expanded scale and calibrated against a carbon monoxide gas cell. Routine n.m.r. spectra were measured with JEOL PMX 60 (^{1}H n.m.r.) and JEOL FX 100 (^{13}C n.m.r.) spectrometers at 60 and 25.2 MHz, respectively. Mass spectra were recorded with a Kratos MS 25 spectrometer. Light petroleum refers to the fraction b.p. 40—60 °C. Ether refers to diethyl ether. Acetonitrile, dichloromethane, and 1-methoxy-2,4-dimethylbenzene were distilled from calcium hydride. Ether, THF, and light petroleum were dried using sodium–benzophenone. Radial chromatography refers to the use of a 'Chromatatron' fitted with 1- or 2-mm preparative silica plates.

Large Scale Preparation of Tricarbonyl(η^5-2-*methoxy*-3,5-*dimethylcyclohexa*-1,3-*dienyl*)*iron*(1+) *Hexafluorophosphate*-(1−).—This was performed by a modification of our established[9] procedure without purification of intermediate complexes. Reduction of 1-methoxy-2,4-dimethylbenzene (68 g, 0.5 mol) with lithium (15 g, 2.1 mol) using 2-methylpropan-2-ol (270 ml, 2.9 mol) in THF (150 ml) and liquid ammonia[21] afforded the dihydroarene (53.8 g, 78%) which was converted directly to the reported mixture of tricarbonyliron complexes (30 g, 28%) by reaction with $Fe(CO)_5$. Reaction with triphenylcarbenium tetrafluoroborate (24 g, 73 mmol) in dichloromethane (250 ml) afforded the *product* (15.9 g, 35%) after precipitation with ether (the filtrate was retained for use in the reaction described below), hydrolytic destruction of any 1-methoxy isomer present by heating in water (100 ml) on a steam bath for 15 min, precipitation by addition of ammonium hexafluorophosphate (11.25 g, 69 mmol), and reprecipitation from acetonitrile with ether.

Tricarbonyl(η^5-2,4-*dimethylcyclohexa*-1,3-*dienyl*)*iron*(1+) *Hexafluorophosphate*(1−).—This was obtained from the filtrate described above by reaction with TFA and precipitation from water (100 ml) with ammonium hexafluorophosphate (22.5 g, 138 mmol) (16.5 g, 39%). The n.m.r. and i.r. properties of the products were consistent with those reported earlier.[9]

Tricarbonyl(η^4-5α-*cyano*-2-*methoxy*-3,5β-*dimethylcyclohexa*-1,3-*dienyl*)*iron*(0) (**7**).—Trimethylsilyl cyanide (2.48 g, 25 mmol) was added to a stirred suspension of tricarbonyl(η^5-2-methoxy-3,5-dimethylcyclohexa-1,3-dienyl)iron(1+) hexafluorophosphate(1−) (2.11 g, 5 mmol) in dry acetonitrile (25 ml) under an argon atmosphere at room temperature. The reaction mixture was heated to reflux. The course of the reaction was followed by i.r. spectroscopy, completion being indicated by the absence of cationic carbonyl absorbances. The reaction mixture was allowed to cool to room temperature and poured into water (50 ml). The product was extracted twice with ether (2 × 50 ml) and the combined ethereal washings were dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. Purification by radial chromatography (10% ether–light petroleum elution) gave the pure *product* (1.44 g, 95%) (Found: C, 51.5; H, 4.2; N, 4.55. $C_{13}H_{13}FeNO_4$ requires C, 51.52; H, 4.32; N, 4.62%); $\nu_{max.}$(CH_2Cl_2) 2 240 (CN), 2 040 (CO), and 1 980 cm^{-1}; δ_H($CDCl_3$) 3.60 (3 H, s, OMe), 3.38 (1 H, t, *J* 3 Hz, 1-H), 2.72 (1 H, s, 4-H), 2.26 (1 H, m, 6-H), 2.20 (3 H, s, 3-Me), 1.72 (1 H, d, *J* 3 Hz, 6-H), and 1.32 (3 H, s, 5-Me); δ_C($CDCl_3$) 193.4, 123.1, 108.7, 68.4, 59.2, 44.4, 38.9, 28.6, 25.4, 15.4, and 9.9; *m/z* 303 (M^+). The reaction was repeated on a larger scale, using trimethylsilyl cyanide (4.96 g, 50 mmol), tricarbonyl(η^5-2-methoxy-3,5-dimethylcyclohexa-1,3-dienyl)iron(1+) hexafluorophosphate-(1−) (4.22 g, 10 mmol) and acetonitrile (50 ml). The *product* (1.83 g, 60%) was isolated by column chromatography on silica eluting with 10% ether in light petroleum.

Tricarbonyl(η^4-2-*methoxy*-3,5β-*dimethyl*-5α-(1-*oxopropyl*-*cyclohexadienyl*)*iron*(0) (**8**).—A stock solution of ethyl-lithium (1.8M) was prepared by reaction of ethyl bromide with thin sheets of lithium (2% sodium) in dry ether under an argon atmosphere. A portion of this solution (0.56 ml, 1 mmol EtLi) was transferred to a flask sealed with a rubber septum. The ether was removed by evaporation using a vacuum line, and replaced by light petroleum (5 ml) to form a white suspension which was cooled to −78 °C. A solution of the nitrile (**7**) (0.152 g, 0.5 mmol) in light petroleum (2 ml) was added and the reaction mixture was allowed to warm to room temperature and was stirred for 30 min. Water was added and the mixture was extracted with ether. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by radial chromatography (10% ether–light petroleum) to afford the *product* (87 mg, 52%) as a yellow gum (Found: C, 54.1; H, 5.35. $C_{15}H_{18}FeO_5$ requires C, 53.92; H, 5.43%); $\nu_{max.}$(MeCN) 2 039 and 1 963 cm^{-1} (CO); δ_H($CDCl_3$; 400 MHz) 3.56 (3 H, s, OMe), 3.36 (1 H, t, *J* 3 Hz, 1-H), 2.51 (1 H, s, 4-H), 2.47 (2 H, q, *J* 7 Hz, $COCH_2$), 2.06 (3 H, s, 3-Me), 1.34 (2 H, dd, *J* 12.3 Hz, 6-H), 1.15 (3 H, s, 5-Me), and 1.01 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 334 (M^+).

Reaction of Tricarbonyl(η^4-5α-*cyano*-2-*methoxy*-5β-*methylcyclohexa*-1,3-*diene*)*iron*(0) *with* $Me_3O^+BF_4$.—Tricarbonyl (0.096, 0.33 mmol) and $Me_3O^+BF_4^-$ (0.98 g, 0.66 mmol) were heated under reflux in dichloromethane (4 ml) until the i.r. spectrum of the reaction mixture showed that the neutral tricarbonyliron complex had been consumed. Addition of ether to the reaction mixture resulted in the formation of precipitate which was collected by filtration and washed with 'wet' ether (reagent grade ether that had not been specially dried). The product (0.011 g, 80%) was identified as tricarbonyl(η^5-2-methoxy-5-methylcyclohexa-1,3-dienyl)iron(1+) BF_4^- by comparison of its n.m.r. spectrum with that of an authentic sample.

Reaction of Tricarbonyl(η^4-2-*methoxy*-3,5α-*dimethylcyclohexa*-1,3-*diene*)*iron*(0) *with* Me_3O^+ BF_4^-.—The reaction was performed by the method described above. The precipitate was identified[1] as tricarbonyl(η^5-2,4-dimethylcyclohexa-1,3-dienyl)iron(1+) BF_4^- by comparison of its n.m.r. spectrum with that of an authentic sample of the PF_6^- salt. The filtrate contained a trace of a rearranged complex tricarbonyl(η^4-1,-4,6α-trimethoxycyclohexa-1,3-diene)iron(0) which was identified by comparison of its n.m.r. spectrum with that of an authentic sample.[9]

Tricarbonyl(η^6-1-*methoxy*-2,4-*dimethylbenzene*)*manganese*-(1+) *Hexafluorophosphate*(1−) (**4a**).—Pentacarbonylmanganese bromide (2.75 g, 10 mmol) was added to 1-methoxy-2,4-dimethylbenzene (30 ml, 0.21 mmol) in a dried 50 ml-three-necked flask, filled with nitrogen and equipped with a reflux condenser and a magnetic stirring bar. Aluminium trichloride (19.5 mmol, 5.2 g) was added. The reaction mixture was then heated at 100 °C for 4 h with occasional swirling to ensure that the $Mn(CO)_5Br$ did not sublime. After having been cooled, the reaction mixture was poured into toluene (20 ml) and extracted twice with water (50 ml). The combined aqueous layers were washed with light petroleum (50 ml). Ammonium hexafluorophosphate was added to precipitate the *product* (2.39 g, 57%) which was collected by filtration and dried under reduced pressure (Found: C, 34.25; H, 2.7. $C_{12}H_{12}F_6MnO_4P$ requires C, 34.31; H, 2.88%); $\nu_{max.}$(MeCN) 2 079 and 2 009 cm^{-1} (CO); δ_H(CD_3CN), 6.46 (1 H, s, 3-H), 6.36—5.84 (2 H, m, 5-H, 6-H),

3.90 (3 H, s, OMe), and 2.22 (6 H, s, 2-Me, 4-Me); $\delta_C(CD_3CN)$ 145.4, 108.5, 105.7, 105.3, 100.9, 80.4, 59.2, 19.1, and 15.7.

Reaction of Tricarbonyl(η^6-1-*methoxy*-2,4-*dimethylbenzene*)-*manganese*(1+) *Hexafluorophosphate*(1−) (**4a**) *with Grignard Reagents.*—A solution of the Grignard reagent (1.5 mmol) was added to a stirred suspension of the arene complex (0.420 g, 1 mmol) in THF at −78 °C. The mixture was allowed to warm slowly to room temperature, the reaction appearing to begin at approximately −60 °C. The reaction mixture was poured into a solution (20 ml) of ammonium chloride, which was then extracted twice with ether (20 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to afford the crude alkylation products. These compounds proved relatively unstable and were converted into nitrosyl cations for full characterisation (see below). In some cases the tricarbonylmanganese complexes were separated by chromatography on silica (ether–light petroleum). The following compounds were obtained in this way.

Tricarbonyl(η^5-2-*methoxy*-1,5,6α-*trimethylcyclohexadienyl*)-*manganese*(0) (**10a**; R = Me): $\delta_H(CDCl_3)$ 5.42 (1 H, d, *J* 5 Hz, 3-H), 4.37 (1 H, d, *J* 5 Hz, 4-H), 3.68 (3 H, s, OMe), 2.68 (1 H, q, *J* 7 Hz, 6β-H), 1.6 (6 H, s, 1-Me, 5-Me), and 0.50 (3 H, d, 7 Hz, 6α-Me).

Tricarbonyl(η^5-2-*methoxy*-3,5,6α-*trimethylcyclohexadienyl*)-*manganese*(0) (**9a**; R = Me): $\delta_H(CDCl_3)$ *inter alia* 4.64 (1 H, s, 4-H), 3.38 (3 H, s, OMe), 3.08 (1 H, d, *J* 6 Hz, 1-H), 2.46 (3 H, s, 3-Me), 1.60 (3 H, s, 5-Me), and 0.48 (3 H, d, 7 Hz, 6-Me). Other signals were obscured by the major isomer. The above two compounds were obtained as a 4:1 mixture of isomers (Found: C, 54.1; H, 5.1. $C_{13}H_{15}MnO_4$ requires C, 53.81; H, 5.21%) which was converted directly into the nitrosyl complexes.

Tricarbonyl(η^5-6α-*ethenyl*-2-*methoxy*-3,5-*dimethylcyclohexadienyl*)*manganese*(0) (**9a**; R = $CH{=}CH_2$): $\delta_H(CDCl_3)$ 5.40—4.40 (4 H, $HC{=}CH_2$, 4-H), 3.40 (3 H, s, OMe), 3.00—3.26 (1 H, m, 1-H), 2.46 (3 H, s, 3-Me), 3.40—2.10 (1 H, m, 6β-H), and 1.60 (3 H, s, 5-Me).

Tricarbonyl(η^5-6α-*ethenyl*-2-*methoxy*-1,5-*dimethylcyclohexadienyl*)*manganese*(0) (**10a**; R = $CH{=}CH_2$): $\delta_H(CDCl_3)$ *inter alia* 3.69 (3 H, s, OMe). Other signals were obscured by signals due to the major product. The above two isomers were obtained as an unstable oil comprising a 4:1 mixture of isomers (Found: C, 56.25; H, 5.05. $C_{14}H_{15}MnO_4$ requires C, 55.64; H, 5.00%) from which the major product was separated by chromatography and converted directly to the corresponding nitrosyl complex.

Tricarbonyl(η^5-2-*methoxy*-3,5-*dimethyl*-6α-*prop*-1-*enylcyclohexadienyl*)*manganese*(0) (**9a**; R = CH=CHMe. This was isolated in 75% yield by chromatography (Chromatotron, 2-mm plate, 10% dichloromethane–light petroleum) (Found: C, 57.15; H, 5.35. $C_{15}H_{17}MnO_4$ requires C, 56.97; H, 5.42%); $\nu_{max.}$(MeCN) 2 004 and 1 914 cm^{-1} (CO); $\delta_H(CD_2Cl_2$; 400 MHz) 5.09 [1 H, complex multiplet (*E*, *Z* isomers), *J* 9.5, 7 Hz, 2′-H], 4.71 (1 H, s, 4-H), 4.49 (1 H, tm, *J* 9.5 Hz, 1′-H), 3.50 (1 H, dd, *J* 9.5, 6 Hz, 6β-H), 3.39 (3 H, s, OMe), 3.09 (1 H, d, *J* 6 Hz, 1-H), 2.48 (3 H, s, 3-Me), 1.61 (3 H, d, *J* 9.5 Hz, 3′-H_3), 1.60 (3 H, d, *J* 9.5 Hz, 3′-H_3), and 1.56 (3 H, s, 5-Me); *m/z* 316 (M^+, 8%), 288 (9), 232 (100), 177 (28), 176 (13), and 175 (10). A minor product (7% yield) was discarded. On the basis of n.m.r. spectra of the mixture of regioisomers, measured before separation, which included a small signal at 6.82 p.p.m. (br s, 3-H) the minor product was identified as (**10a**; R = CH=CHMe).

Formation of (*Dicarbonyl*)(*nitrosyl*)*manganese*(1+) *Salts.*—Nitrosonium hexafluorophosphate (0.175 g, 1 mmol) was added in one portion to a stirred solution of the tricarbonylmanganese(0) complex (1 mmol) in dichloromethane (5 ml at 0 °C). Carbon monoxide was evolved. The reaction mixture was stirred for 30 min, filtered, and poured into ether to precipitate the product, which was collected by filtration and dried under reduced pressure. The following complexes were obtained in this way.

Dicarbonyl(2-*methoxy*-1,5,6α-*trimethylcyclohexadienyl*)-(*nitrosyl*)*manganese*(1+) *hexafluorophosphate*(1−) (**10b**; R = Me): $\nu_{max.}$(MeCN) 2 097 and 2 068 (CO) and 1 823 cm^{-1} (NO); $\delta_H(CD_2Cl_2)$ 6.64 (1 H, d, *J* 6 Hz, 3-H), 5.46 (1 H, d, *J* 6 Hz, 4-H), 4.02 (3 H, s, OMe), 2.98 (1 H, q, *J* 7 Hz, 6β-H), 1.94 (3 H, s, Me), 1.80 (3 H, s, Me), and 0.98 (3 H, d, *J* 7 Hz, 6α-Me).

Dicarbonyl(2-*methoxy*-3,5,6α-*trimethyl-cyclohexadienyl*)-(*nitrosyl*)*manganese*(1+) *hexafluorophosphate*(1−) (**9b**; R = Me): $\delta_H(CD_2Cl_2)$ *inter alia* 5.63 (1 H, s, 4-H), 4.31 (1 H, d, 6 Hz, 1-H), 3.78 (3 H, s, OMe), 2.63 (3 H, s, 3-Me), 2.17 (3 H, s, 5-Me), and 0.95 (3 H, d, *J* 7 Hz, 6α-Me). Other signals were obscured by the major isomer. Yield 39% from (**4a**) as a 4:1 mixture of isomers (Found: C, 33.1; H, 3.35; N, 3.05. $C_{12}H_{15}F_6MnNO_4P$ requires C, 32.97; H, 3.46; N, 3.20%).

Dicarbonyl(6α-*ethenyl*-2-*methoxy*-3,5-*dimethylcyclohexadienyl*)(*nitrosyl*)*manganese*(1+) *hexafluorophosphate*(1−) (**9b**; R = $CH{=}CH_2$) (Found: C, 34.85; H, 3.1; N, 2.97. $C_{13}H_{15}F_6MnNO_4P$ requires C, 34.84; H, 3.15; N, 3.13%): $\nu_{max.}$(MeCN) 2 099 and 2 054 (CO) and 1 823 cm^{-1} (NO); $\delta_H(CD_3CN)$ 5.76 (1 H, s, 4-H), 4.08—5.32 (3 H, m, $CH{=}CH_2$), 4.30 (1 H, d, *J* 6 Hz, 1-H), 3.78 (3 H, s, OMe), 3.61 (1 H, m, 6β-H), 2.60 (3 H, s, 3-Me), and 1.90 (3 H, s, 5-Me).

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