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Stereomanipulation of (η^5-1-Arylcyclohexadienyl)iron Complexes

Christopher E. Anson,[a][‡] Andrei V. Malkov,[a][‡‡] Caroline Roe,[a] Elizabeth J. Sandoe,[a] and G. Richard Stephenson*[a]

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A crystallographic investigation comparing five 1-aryl-substituted tricarbonyl[(1–5-η)-cyclohexadienyl]iron(1+) salts demonstrates that introducing additional electron density on the aromatic ring increases π overlap between the arene and the cyclohexadienyl ligand, thus flattening the structures sufficiently to make available a conformation in which nucleophiles can approach the site of substitution, despite the steric blockade of *o*-benzyl substituents.

Introduction

The 100% stereoselectivity available in the reactions of chiral (cyclohexadienyl)iron complexes[1] offers a powerful strategy for asymmetric synthesis,[2] especially in reaction sequences that make multiple use of the organoiron group. Consequently, the use of organoiron complexes in synthesis[3] has become established as a valuable and effective approach to promote bond formation and stereocontrol. We have recently described[4] a generally applicable methodology to gain efficient access to both (1- and 2-arylcyclohexadienyl)iron electrophilic carbonylmetal complexes, which offer a convenient "C_{12} building block strategy"[5] for use in alkaloid synthesis. This is illustrated in Figure 1 with examples which make iterative use of the metal in two different ways. When the two C–C bond-formation steps take place at the same position in the multihapto ligand, this is referred to as a "*1,1* strategy"[6] (the product of the *1,1* sequence has a single stereogenic quaternary centre, as for example in target molecules **1**[7] and **4**[8]). When the reactions take place at adjacent positions (a "*1,2* strategy"[6]) two adjacent stereogenic centres are formed (this is illustrated in our work towards target molecules **2**[10] and **5**[11]). In these synthetic routes, the 1-arylcyclohexadienyl ligand in **3**[4] corresponds to a central portion of the target structure.

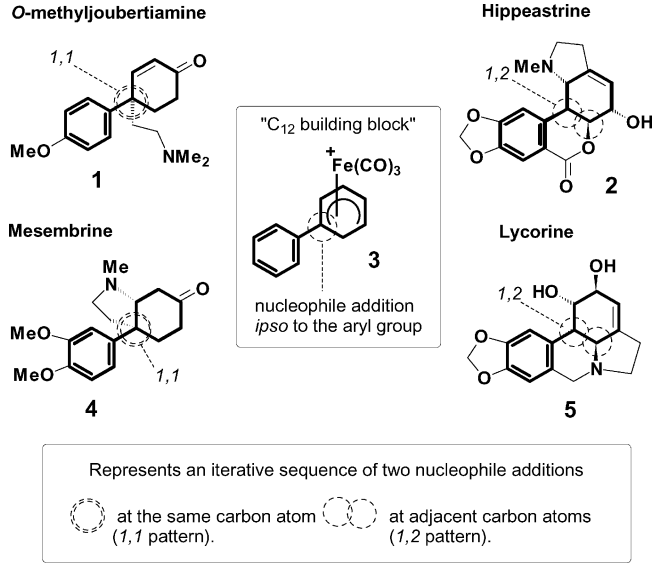


Figure 1. Examples of alkaloid target molecules to illustrate a general organoiron-mediated approach that makes multiple use of the metal: a "C_{12} building block" based on an arylcyclohexadienyl complex corresponds to the central pair of six-membered rings in structures of this type (the requirements for iterative[9] metal-mediated bond formation are indicated as *1,1* or *1,2*[6,7] by the dashed circles).

Figure 2 gives an example of a more advanced target structure that combines iterative *1,1* and *1,2* bond-formation strategies, and like many alkaloid targets (e.g. lycoramine,[12] or hippeastrine[10] and lycorine[11] shown in Figure 1) the structure also contains an additional challenge. The aryl substituents in these cases bear a benzylic carbon atom adjacent to their attachment to the (cyclohexadienyl)iron complex. Often in alkaloid synthesis, this type of feature is introduced quite late in the synthetic route (e.g. by a Pictet–Spengler reaction[13]), but to ensure a high degree of conver-

[a] Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia
Norwich, NR4 7TJ, UK
Fax: +44-1603-592003
E-Mail: g.r.stephenson@uea.ac.uk
[‡] Present address: Institut für Anorganische Chemie der Universität Karlsruhe,
Engesserstrasse Geb. 30.45, 76128 Karlsruhe, Germany
[‡‡] Present address: WestChem, Department of Chemistry, Joseph Black Building, University of Glasgow,
Glasgow, G12 8QQ, UK

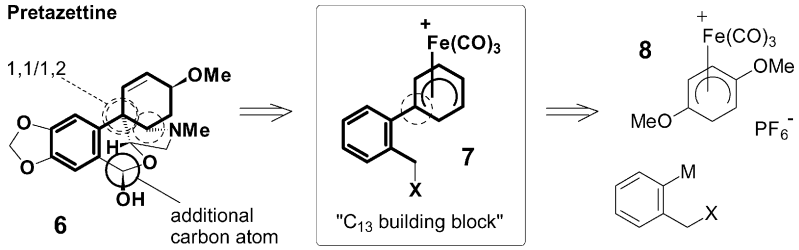


Figure 2. Example of a retrosynthetic analysis for pretazettine combining an iterative sequence of three metal-mediated bond-formation steps (and using both *1,1* and *1,2* patterns[6,7]). For a convergent approach that includes the additional benzylic carbon atom [see also hippeastrine and lycorine (Figure 1)] there is a need for *ipso* addition adjacent to the aryl group in a "C_{13} building block".

gence in our synthetic strategy (Figure 2) we have set ourselves the more difficult task of bringing this *ortho* substituent in at an early stage of the route. Thus ideally, the "C_{12}" building blocks (Figure 1) that suit *O*-methyljoubertiamine[7] and the Ackland–Pinhey–Martin intermediate for lycoramine,[14] develop into a "C_{13}" central building block strategy (Figure 2) corresponding to a [(1–5-η)-1-(*o*-substituted-aryl)cyclohexadienyl]iron complex, for the more highly substituted target structures. To establish this chemistry we have now carried out a detailed study of the regiocontrol properties of this class of structures, on the basis of an extensive X-ray crystallographic investigation of the effects of substituents on the orientation of the aryl group relative to the plane of the haptyl section of the (cyclohexadienyl)iron complex. These results are reported in this paper.[15] The requirement for success is the presence of suitable electron-donating substituents on the aromatic ring, which is the case for most of the typical biologically active[16] natural target structures of this type.

Results and Discussion

General Access to 4-Methoxy-Substituted (1-Arylcyclohexadienyl)iron(1+) Complexes

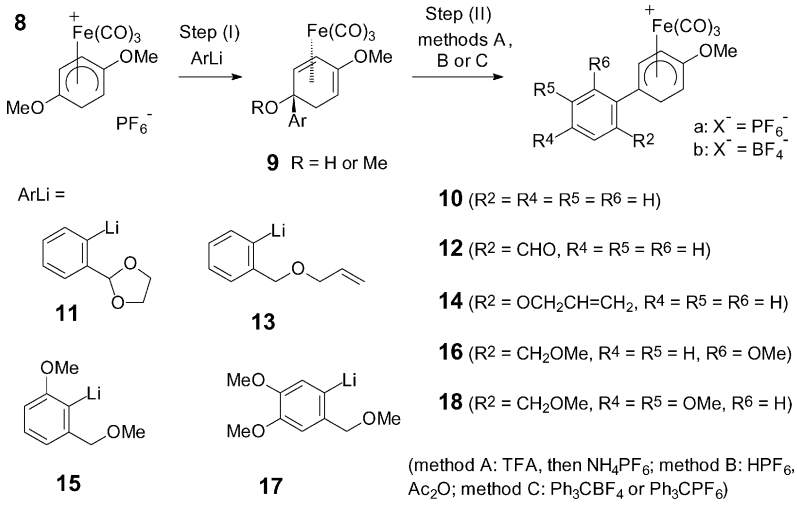
The extension of our general method[4,8] for the preparation of (1-arylcyclohexadienyl)iron complexes to examples with a methoxy directing group on the dienyl complex has already been described.[4,5,7,12] The parent example,[5] tricarbonyl[(1–5-η)-1-phenyl-4-(methoxycyclohexadienyl)]-iron(1+) hexafluorophosphate(1–) salt (**10**) has been obtained from tricarbonyl[(1–5-η)-1,4-(dimethoxycyclohexadienyl)]iron(1+) hexafluorophosphate(1–) (**8**) by reaction with phenyllithium and demethoxylation, and the method has been successfully employed in our synthesis of *O*-methyljoubertiamine (**1**)[7] and to prepare a more highly substituted example with a methylenedioxy group correctly placed[4] on the aromatic ring for the target molecule crinine. The success of this approach (Figure 2) stems from the initial combination of the *ipso*-directing C(1)–OMe group and the ω-directing C(4)–OMe group in a mutually reinforcing fashion[17] to ensure nucleophile addition at C(1) of **8**. We now report the successful use of this strategy with a wide range of aryllithium reagents, including examples with significant steric hindrance around the site of C–C bond formation. When all the substituents on the dienyl complex are mutually reinforcing, the use of the organoiron electrophiles is now well understood. The introduction of the aromatic group leaves the C(1)–OMe substituent correctly placed as a leaving group to facilitate the return to the η^5-cyclohexadienyl form of the complex. Acids,[18] triphenylcarbenium ion reagents,[19] and trialkyloxonium ion reagents[20] are all suitable to promote this reaction, and our alkoxide abstraction approach overcomes the problem that conventional hydride abstraction is usually[21] blocked after the first nucleophile addition step. A considerable effort[5,22] has been made to understand the step that introduces the aryl group, and the reaction has been shown to be compatible with flanking substituents such as OMe and CH_2OMe.

For the "C_{13} building block" strategy summarised in Figure 2, it would be useful to have a formyl group as the flanking substituent, to allow later elaboration at this position by reductive amination. This has now been addressed by addition of *o*-$LiC_6H_4CH(-OCH_2CH_2O-)$ (**11**)[23] to **8**, followed by reaction with triphenylcarbenium tetrafluoroborate which afforded the *o*-benzaldehyde derivative **12** as the BF_4^- salt **12b**. Use of TFA and ammonium hexafluorophosphate gave the corresponding PF_6^- salt **12a**. The BF_4^- salt **12b** was crystallized from acetonitrile/diethyl ether to obtain crystals suitable for X-ray analysis. To provide a comparison, an example was chosen with a protected donor substituent in the place of the formyl group in **12**. The required aryl nucleophile was prepared from 2-bromophenol by allylation and conversion into the organolithium reagent **13**. Reaction of **13** with **8**, and demethoxylation with HPF_6 in acetic anhydride gave the expected product **14** which was crystallized from acetone/diethyl ether for X-ray analysis. A more hindered doubly flanked example with an *o*-CH_2OMe group was also prepared. Initially, directed metallation[24] of 3-methoxybenzyl methyl ether was examined as a means to produce the required organolithium reagent, but this procedure proved difficult (even trapping with $BrCF_2$–CF_2Br gave none of the expected 2-bromo product) and would also produce an organolithium reagent of a different type to that made by the lithium/bromine exchange reaction, so an alternative was developed. Metallation of 3-methoxybenzyl alcohol with 2 equiv. of *n*-butyllithium was followed by quenching with $BrCF_2$–CF_2Br to give the 2-bromo derivative, which was then converted into the methyl

Table 1. Preparation of (1-arylcyclohexadienyl)iron complexes and the regioselectivity of their reactions with nucleophiles.

Entry	Substitution pattern Ar	Preparation of the η^5 electrophile Step (I)	Yield (%)	Step (II)	Yield (%)	Reaction with nucleophiles Step (III)	Yield *ipso*[a] (%)	Yield ω[a] (%)
1	C_6H_5	(i)[b]	70[b]	(ii) X– = PF_6^-	98[b]	(iii)	82	0
2	2-($MeOCH_2$)C_6H_4	(i)[b]	58[b]	(ii) X^- = PF_6^-	98[b]	(iii)	0	71
3	2-$MeOC_6H_4$	(i)[b]	67[b]	(ii) X^- = PF_6^-	80[b]	(iii)	80	0
4	2-(H_2C=$CHCH_2O$)C_6H_4	(iv)	53	(v) X^- = PF_6^-	82	(iii)	79	0
5	2-(OHC)C_6H_4	(i)	87[c]	(ii)/(v) X^- = PF_6^- (vi) X^- = BF_4^-	69/70 73	(iii)[d]	0	72[e]
6	2-($MeOCH_2$)-6-$MeOC_6H_3$	(iv)	66[f]	(vii) X^- = PF_6^-	64	(iii)	0	84[g]
7	2-($MeOCH_2$)-4,5-$(MeO)_2C_6H_2$	(iv)	46	(vii) X^- = PF_6^-/K_2CO_3	65	(iii)	61	16[h]

[a] *ipso*/ω (see ref.[4]) with the aryl group as the reference substituent. [b] See ref.[5] [c] 2:1 mixture of OMe and OH. [d] X^- = PF_6^-. [e] A second molecule of methyl 2-cyanoacetate added to the aldehyde. [f] Tricarbonyl[(2–5-η)-4-methoxycyclohexadien-1-one]iron also formed (37% yield). [g] 4,6′-Dimethoxy-2′-(methoxymethyl)biphenyl also formed (4% yield). [h] 4,4′,5′-Trimethoxy-2′-(methoxymethyl)biphenyl also formed (9% yield). Reaction conditions: (i): CH_2Cl_2, –78 °C; (ii): TFA, then NH_4PF_6, 0 °C; (iii): $NaCH(CO_2Me)CN$, THF, 0 °C; (iv): CH_2Cl_2, –100 °C; (v): HPF_6, Ac_2O, 0 °C; (vii) $Ph_3C^+X^-$, CH_2Cl_2, 0 °C.



Scheme 1. Prepartion of (1-arylcyclohexadienyl)iron complexes.

ether. Formation of the organolithium reagent **15** from this ether by our usual procedure, reaction with **8** and demethoxylation using Ph_3CPF_6, afforded the η^5 salt **16**. The corresponding benzyl methyl ether **18** with OMe groups at the *meta* and *para* positions was also prepared. This lacks the flanking substituent present in **16**, and so provides a more direct comparison with the simple *o*-benzyl methyl ether case described in our earlier work.[5] The required aryllithium reagent **17** is available by standard methods[25] (reduction, ether formation, and lithium/bromine exchange) from 2-bromo-4,5-dimethoxybenzaldehyde, and reacted with **8** to afford the expected adduct which was converted into the salt **18** by the Ph_3CPF_6 method. Details of these synthetic routes are presented in Table 1 (columns 2–6) and Scheme 1.

X-ray Crystallographic Investigation of (1-Arylcyclohexadienyl)iron(1+) Complexes

Selected bond lengths from the structures of **10**, **12b**, **14**, **16** and **18** are compared in Table 2. To quantify the degree of rotation of the aryl ligand about the C(1)–C(8) bond relative to the plane of the dienyl unit, we determined the

Table 2. Selected bond lengths [Å] for the dienyliron portion of the electrophiles.

	Fe–C(1)	Fe–C(2)	Fe–C(3)	Fe–C(4)	Fe–C(5)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(4)–O
10[a]	2.233(2)	2.123(3)	2.094(2)	2.204(2)	2.168(2)	1.411(3)	1.413(3)	1.422(3)	1.405(3)	1.336(3)
10[b]	2.249 2)	2.125(3)	2.095(3)	2.207(2)	2.171(3)	1.405(4)	1.412(4)	1.418(4)	1.397(4)	1.337(3)
12[a]	2.225(3)	2.152(4)	2.080(3)	2.190(3)	2.149(3)	1.389(5)	1.407(5)	1.408(5)	1.390(5)	1.339(4)
12[b]	2.234(3)	2.126(3)	2.083(3)	2.188(3)	2.148(3)	1.385(5)	1.410(5)	1.411(5)	1.397(5)	1.331(4)
14	2.304(2)	2.118(2)	2.100(2)	2.185(2)	2.134(2)	1.397(3)	1.422(3)	1.412(3)	1.403(3)	1.340(3)
16	2.303(4)	2.326(5)	2.093(4)	2.171(3)	2.128(4)	1.417(5)	1.426(6)	1.417(5)	1.404(5)	1.346(4)
18	2.313(3)	2.136(3)	2.093(3)	2.181(3)	2.139(3)	1.403(4)	1.422(4)	1.412(4)	1.409(4)	1.341(4)
Mean	2.266	2.158	2.091	2.189	2.148	1.401	1.416	1.414	1.401	1.339

[a] Molecule 1. [b] Molecule 2 in asymmetric unit.

dihedral angle between the two planes. A *positive* dihedral angle indicates that, for the enantiomer shown (which is consistent for all structures) the aryl moiety is rotated *anticlockwise* about the C(1)–C(8) bond. This corresponds to the side of the aryl ring that is *cis* to the methylene carbon atom C(6) on the cyclohexadienyl ring being rotated up and away from the iron centre. Because the cyclohexadienyl ring itself is not flat, the flattest overall structure for the arylcyclohexadienyl moiety is obtained with a dihedral angle of ca. +20°.

The X-ray crystallographic study of this series of aryl-substituted electrophiles began with an examination of the simplest of the (1-arylcyclohexadienyl)iron complexes (**10**), which was available from our earlier work.[5] This has only a phenyl substituent opposite to the 4-methoxy-directing group on the dienyl ligand. Compound **10** crystallises with two independent molecules in the asymmetric unit, which have rather similar structures. The cyclohexadienyl ring was found to have the expected form (Figure 3), with the saturated CH_2 position bent away from the iron atom. One of the three carbonyl ligands lies directly below the CH_2 group, placing the other two CO groups in positions that eclipse the C(2) and C(4) inner sp^2 carbon atoms on the dienyl section. The five carbon atoms of each η^5-dienyliron moiety are coplanar to within 0.055 Å, and the aromatic rings are rotated out of this plane, with dihedral angles of +26.99(7)° and +14.01(10)° for molecules 1 and 2, respectively. From Figure 3 it is clear that positive angles of this magnitude give an overall conformation that is the most open in terms of access to C(1) of the dienyl group.

With the allyloxy donor substituent installed at the *ortho* position of the aromatic ring in **14**, the general form of the structure remains the same (Figure 4), but the aromatic ring is now twisted further away from the plane of the dienyl carbon atoms at +36.15(7)°. In the solid state, the arene takes up a conformation in which the *ortho* substituent lies below the plane, and the unsubstituted CH–CH edge is roughly aligned with the CH_2 group of the cyclohexadienyl ligand, now lying slightly above it as a consequence of the bulk of the $OCH_2CH{=}CH_2$ group below the ring. The allyloxy oxygen atom is perhaps interacting with the carbon atom of one of the carbonyl ligands, because O(2)···C(22) at 2.914 Å is less than the sum of the van der Waals radii. Although any such interaction would be very weak, it might be sufficient to stabilize the observed conformation compared to the alternative with the allyloxy group above the dienyl plane.

Switching from an electron-donating substituent to an electron-withdrawing formyl group at the *ortho* position in **12b** proved to have a large effect on the solid-state structure (Figure 5). There are again two independent molecules in the asymmetric unit, but in both cases the substituted side of the aromatic ring now lies above the plane, with dihedral angles of +78.38° and 85.18° for molecules 1 and 2, respectively. The two planes have now become much closer to perpendicular. In molecule 1, the oxygen atom [O(2)] of the formyl group lies directly above the terminus of the dienyl system; the C(1)···O(2) separation of 2.768 Å is well within the sum of the van der Waals radii for carbon and oxygen atoms (3.25 Å) suggesting a significant interaction between the two atoms. The formyl group is disordered in the second

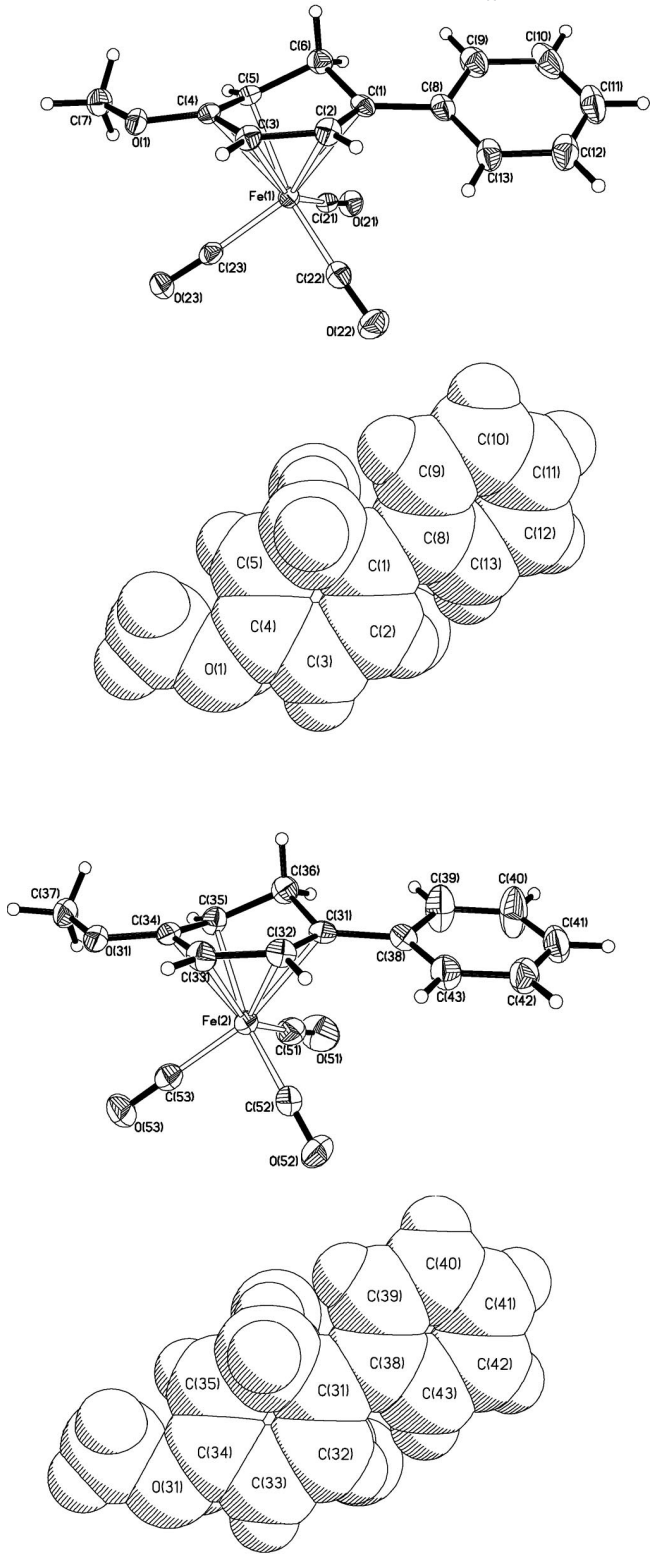


Figure 3. ORTEP and space-filling representations of molecules 1 (top) and 2 (bottom) in the X-ray structure of tricarbonyl[(1–5-η)-4-methoxy-1-phenylcyclohexadienyl]iron hexafluorophosphate (**10**).

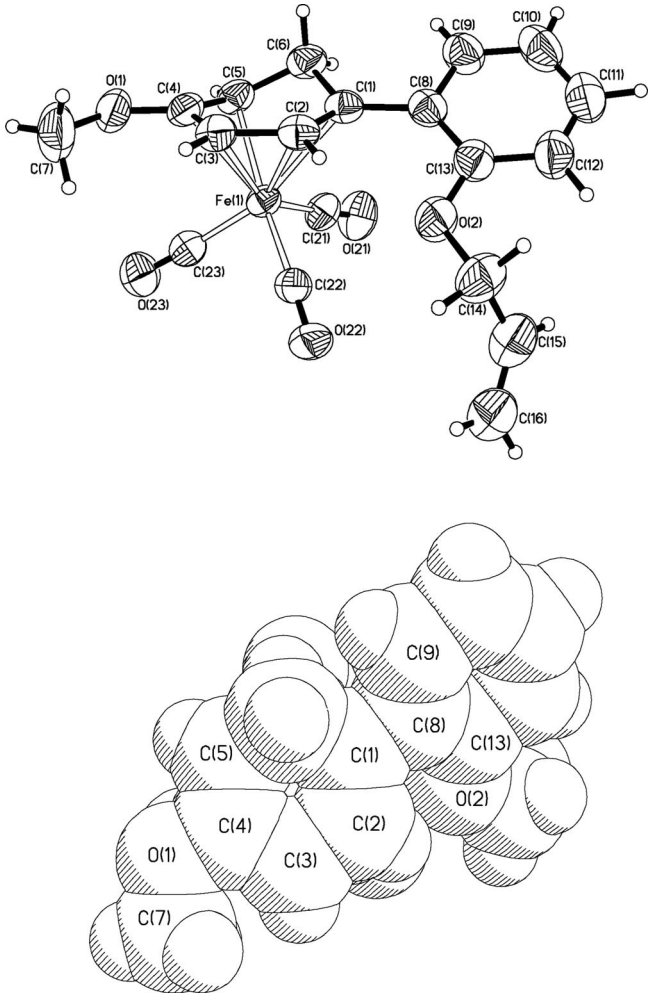


Figure 4. ORTEP and space-filling representations of the X-ray structure of tricarbonyl[(1–5-η)-1-(2′-allyloxyphenyl)-4-methoxycyclohexadienyl]iron hexafluorophosphate (**14**).

molecule, between the equivalent conformation to that in molecule 1 and the conformation resulting from a 180° rotation about the aryl–formyl C–C bond [so that the formyl oxygen atom is now directed away from the dienyl group, and the formyl hydrogen atom now above C(1) of the dienyl group]. These two conformers are present in a ratio of 0.45:0.55, so the conformation with the formyl oxygen atom above C(1) predominates in the solid state in a ratio of 2.6:1.

In the crystal structure of **16** (Figure 6), the aryl ring is again almost perpendicular to the dienyl plane, with the dihedral angle now +95.23°, as expected because of the steric effects of the pair of flanking *ortho* substituents. The methoxy group is again located below the cyclohexadienyl ring on the side bearing the $Fe(CO)_3$ group. However, compared to **14**, where the methoxy oxygen atom occupied the space between a carbonyl ligand and the dienyl carbon atom C(2), in **16** it is forced down into the region of the tripod of the CO ligands. There must be a weak but significant interaction between the lone pairs on the methoxy oxygen atom and the rather electron-deficient carbon atoms

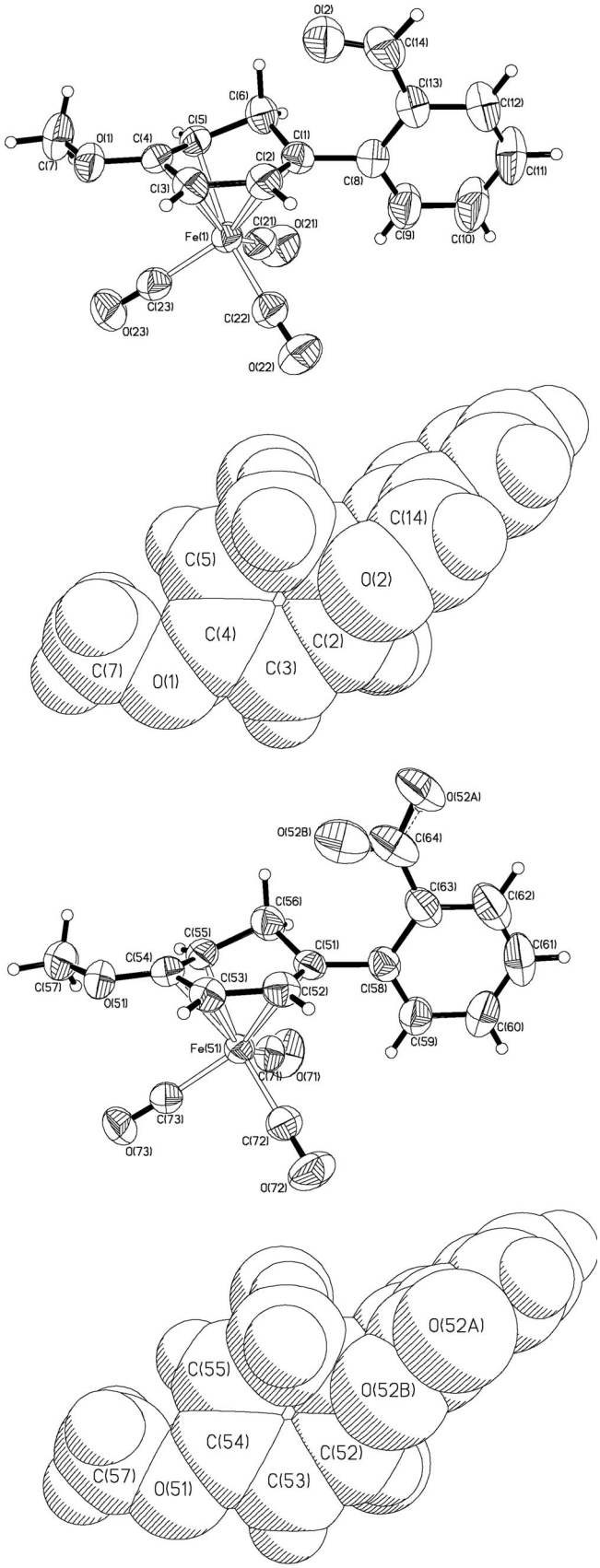


Figure 5. ORTEP and space-filling representations of molecules 1 (top) and 2 (bottom) of tricarbonyl[(1–5-η)-1-(2′-formylphenyl)-4-methoxycyclohexadienyl]iron tetrafluoroborate (**12b**).

of the carbonyl ligands, because the distances O(2)···C(21) (2.766 Å) and O(2)···C(22) (2.888 Å) are well within the sum of the van der Waals radii. It should be noted that the opposite conformation of the aryl ring, with the methoxymethyl group now below the dienyl plane, is sterically impossible, as the two methylene hydrogen atoms would make totally unrealistic close approaches to the carbonyl ligands.

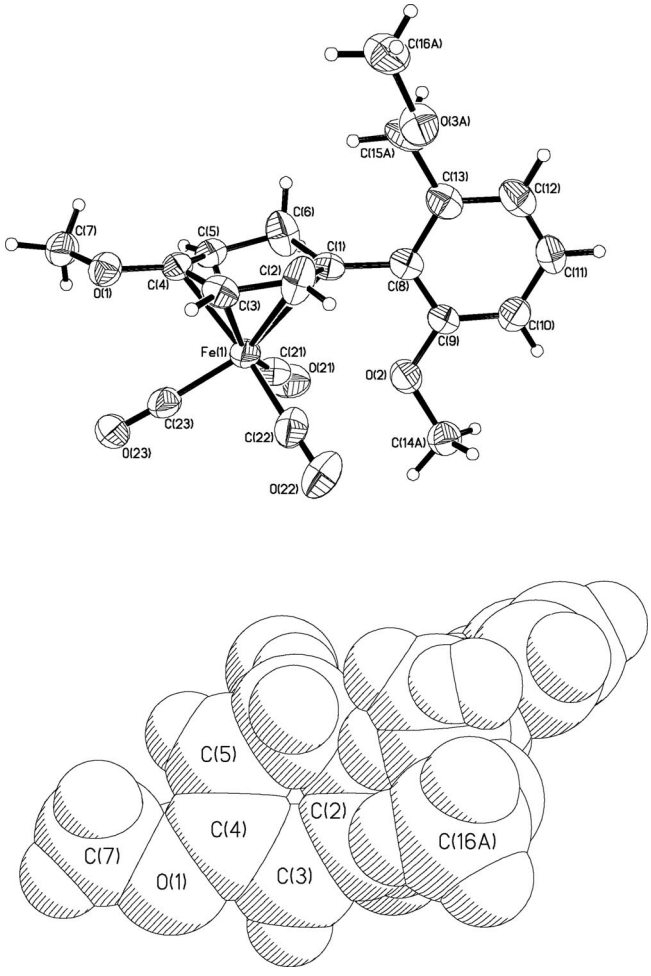


Figure 6. ORTEP and space-filling representations of the X-ray structure of tricarbonyl[(1–5-η)-1-(2′-methoxymethy-6′-methoxylphenyl)-4-methoxycyclohexadienyl]iron hexafluorophosphate (**16**). For clarity, only the major conformers of disordered methoxy groups are shown.

The bonding within the dienyliron sections shows a high degree of consistency across this set of five structures (Table 2), with bond lengths between the iron atom and the five carbon atoms varying only slightly. C(1), which carries the aryl substituent, has the longest Fe–C bond length in each case (mean Fe–C distance 2.27 Å). The distance to the other end of the dienyl ligand is significantly shorter in each case (mean Fe–C distance 2.15 Å), showing that the Fe-$(CO)_3$ group is displaced slightly towards the unsubstituted end of the ligand. The distance between the iron atom and the carbon atom bearing the OMe group [C(4)] also shows relatively little variation (0.04 Å between the extremes), indicating a consistent degree of electron donation from the OMe group to the cationic metal complex.

The data for the C(4)–O(1) bond length, which also shows virtually no variation in length, supports this conclusion, and at a mean length of 1.34 Å is short enough to suggest that donation of electron density to the metal complex is significant. This is commonly accepted as the explanation[25,26] for the ω-directing properties of the OMe group. As is to be expected in cases where the lone pairs interact with the π system, and CH_3–O bond is aligned close to the plane of the dienyl carbon atoms, and the CH_3–O–C(4) bond angle is fairly constant at about 118°, consistent with sp^2 hybridization at the oxygen atom. The variation of the orientation of the MeO group relative to C(3) is ascribed to random variation in crystal packing effects. However, the consistency of the C(4)–C(5) and C(4)–O(1) bond lengths and the CH_3–O–C(4) bond angle all support the view that there is a similar degree of donation of electron density from the oxygen atom across the series, regardless of the orientation and substitution pattern of the aromatic ring.

It follows from this, that differences in the additions of nucleophiles to these structures (see below) must arise from the effect of the aromatic ligand itself on the dienyl system. Despite the long Fe–C(1) separation, the C(1)–C(2) bond lengths remain quite short at about 1.4 Å. This shows that the relative weakening of the bonding to the iron atom at C(1) is not pre-distorting the starting material to react with nucleophiles at this position, as to approach the neutral η^4 structure, the C(1)–C(2) bond in the starting material will lengthen to a C–C single bond as the Fe–C(1) bond breaks and the bond forms between C(1) and the nucleophile. This type of pre-distortion towards the transition state has been proposed[27] in some cases to account for the regioselectivity of nucleophile addition to electrophilic π complexes. Despite these pronounced similarities, besides the clear changes in the dihedral angle (Figures 3 to 7), there are also significant variations in the bond lengths between C(1) and the aryl substituent in these structures. This is discussed below, and holds the key to understanding and manipulating the observed patterns of regioselectivity in the reactions with nucleophiles. A further systematic discrepancy can be seen in the bond-length data for complex **16** which has unusually long C(1)–C(2) and C(2)–C(3) bonds. The Fe–C(2) bond is also much longer (2.32 Å) than all the others (mean 2.18 Å). These effects are ascribed to distortion of the ligand by steric effects caused by the presence of the flanking OMe group beside the iron atom in **16**. Indeed, the mean Fe–C distance calculated from bond lengths of the dienyliron system in **16** is 2.20 Å, significantly longer than the corresponding values (2.16–2.18 Å) in the other four structures. The consistency of these dimensions in **10**, **12**, **14** and **18** shows that the transfer of electron density from the arene to the dienyliron complex (see Discussion section) has little influence on the position of the iron atom relative to the plane of the dienyl ligand. In contrast, steric effects from aryl substituents on the same side of the ligand as the Fe-$(CO)_3$ group have a large effect. Conversely, because

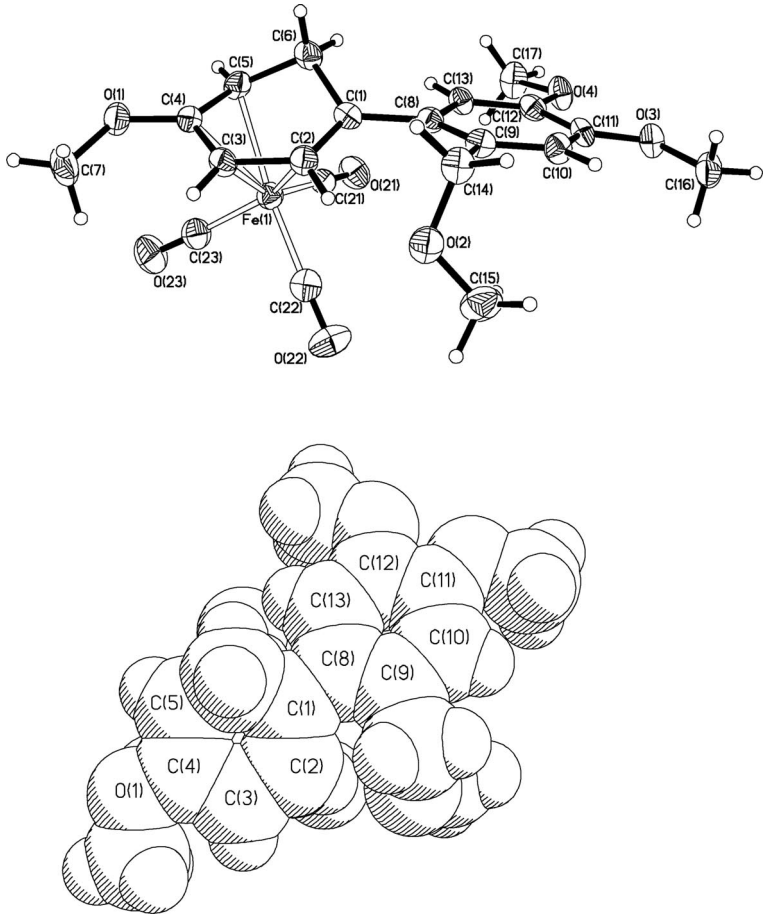


Figure 7. ORTEP and space-filling representations of the X-ray structure of tricarbonyl{(1–5-η)-1-[4′,5′-dimethoxy-2′-(methoxymethyl)-phenyl]-4-methoxycyclohexadienyl}iron hexafluorophosphate (**18**).

structure **14** fits the normal pattern, it can be concluded that, despite its proximity, the allyloxy substituent has no substantial steric interaction with the $Fe(CO)_3$ group in the conformation adopted in the solid state.

Table 3 presents a comparison of trends in dihedral angles and the lengths of the central carbon–carbon bond that joins the arene and the dienyliron moiety [C(1)–C(8)]. Large dihedral angles tend to correspond to structures with long central bonds. The shorter C(1)–C(8) distances in the flatter structures are consistent with greater double-bond character. Despite the benzylic *ortho* substituent present in **18**, a small dihedral angle and relatively short central bond have been observed in the solid state. This is consistent with substantial π overlap in the centre of the structure. This π overlap would be promoted by transfer of electron density from the electron-rich π system of the arene to the cationic dienyliron compex. On this basis, it can be expected that increasing the electron density on the arene will increase the extent of π overlap, and so flatten the structure, reducing the dihedral angle. If this factor is also significant in solu-

Table 3. Central C–C bond lengths and dihedral angles for structures **10**, **12**, **14**, **16**, and **18**.

	Substitution pattern on aromatic ring				C(1)–C(8)	Dihedral angle[a]	Directing effect
	R^2	R^4	R^5	R^6	[Å]	[°]	
16	CH_2OMe	H	H	OMe	1.500(5)	95.93(13)[b]	ω
12[c]	CHO	H	H	H	1.500(5)	85.18(13)[b]	ω
12[c]	CHO	H	H	H	1.493(4)	78.38(15)[b]	
18	CH_2OMe	OMe	OMe	H	1.490(4)	20.88(16)[d]	*ipso* > ω[e]
10[c]	H	H	H	H	1.489(3)	26.99(7)[b]	*ipso*
10[c]	H	H	H	H	1.488(4)	14.01(10)[b]	*ipso*
14	H	H	H	$OCH_2CH{=}CH_2$	1.484(3)	36.15(7)[b]	*ipso*

[a] Positive values correspond to *anticlockwise* rotation of the aryl ring out of the dienyl plane, so that the side of the aryl ring *cis* to the methylene atom C(6) is rotated away from the iron atom. [b] Positive dihedral angle. [c] Data from two independent molecules in the unit cell. [d] Negative dihedral angle. [e] *ipso*/ω = 4:1.

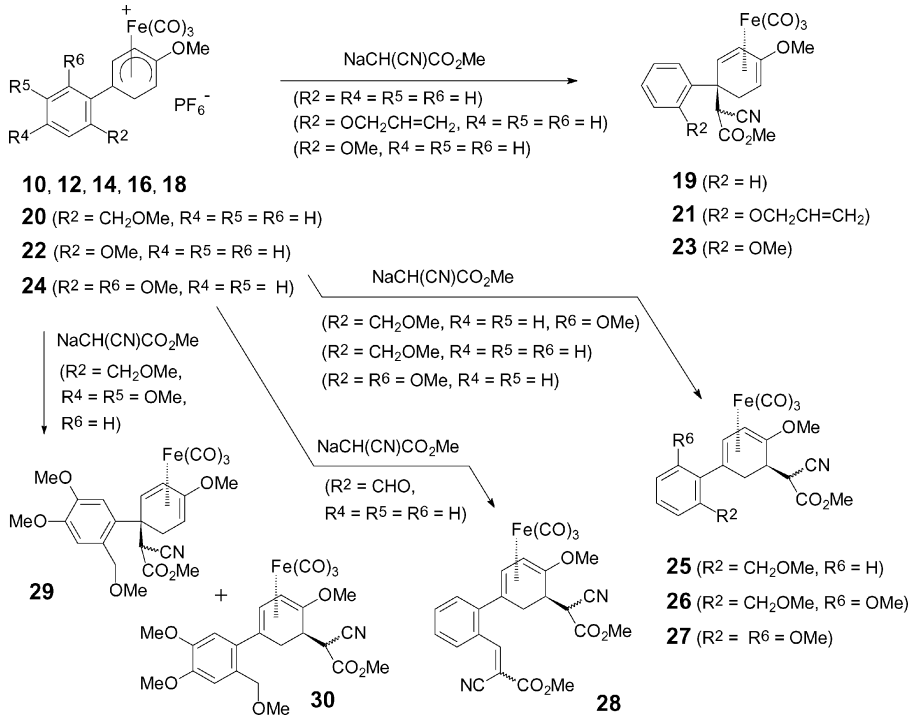
tion, the change in conformation could account for the improved access to *ipso* addition products from reactions with nucleophiles (see below).

Regiocontrol in the Reactions of 1-Aryl(cyclohexadienyl)-iron(1+) Complexes with Nucleophiles

The natural directing effect of aryl substituents on metal-bound π systems has been a subject of considerable investigation, because fundamental properties of this type must be properly understood to support efforts to apply these complexes in organic synthesis. A phenyl substituent at the terminus of the haptyl section of the ligand has been studied in η^2-alkene,[28] η^3-allyl,[29] η^4-diene[30] and η^5-dienyl[4,9,31] complexes, and regiocontrol is typically consistent with an ω-directing effect. There are exceptions, however, as in the η^3 case, steric blocking by methyl groups at the ω position allows the *ipso* pathway to proceed.[32] Palladium-catalyzed allylic substitution is the most widely studied case of nucleophile addition to η^3 complexes, which are electrophilic intermediates in the catalytic cycle, and with a phenyl group at C(1) of the allyl ligand, substituted styrenes are produced.[33] These result from ω addition relative to the Ph group. This outcome has been shown[34] to hold true irrespective of the position of the leaving group in the allyl substrate. In catalytic systems employing other metals, however, the control effect is less clear, and examples of either *ipso* or ω addition can be found.[35] Similarly in the η^4 case, although BuLi, PhLi, $LiCMe_2CO_2Et$, $LiCMe_2CN$, gave only ω products, reaction with benzyllithium followed the *ipso* and ω pathways with almost equal ease.[30] Results obtained with η^5-pentadienyliron complexes are further complicated by the possibility of formation of (*Z*)- or (*E*)-alkenes in the products, indicating two different mechanisms for nucleophile addition. The clearest results have been obtained with PPh_3 as the nucleophile,[36,37] giving rise to the ω-addition product with the (*Z*) relative stereochemistry expected for reaction with the *cisoid* form of the dienyl complex. This reaction, however, has been shown[31] to be reversible, and so may operate under thermodynamic control. Fortunately, kinetic control can be assessed from the results reported for hydride delivery from $NaBH_3CN$. Both pathways were observed, with *ipso* and ω products isolated in a ratio of 2:5; thus, in this case the ω pathway predominates.[38] In contrast, the use of allylsilane or furan as the nucleophile has been found to give (*E*) products according to the *ipso*-addition pathway to the *transoid* pentadienyliron complex.[36] An *ipso* product has also been obtained with $LiCH(CO_2Me)_2$ as the nucleophile,[37,39] and with the more bulky reagent $LiCMe(CO_2Me)_2$, a mixture of *ipso*-, ω- and internal addition products is formed.[37] Thus, in general it is clear that although the ω pathway is usually preferred, both *ipso*- and ω-addition pathways are possible with a phenyl group at the terminus of the haptyl section of the ligand, and that the nature of the metal atom, the nucleophile, and the geometry of the ligand can influence the outcome. Our initial study[4,8] of the (1-phenylcyclohexadienyl)iron system, fits this conclusion, as the aryl group directed most nucleophiles to the ω position. Stabilized enolate nucleophiles such as malonate enolates, however, were found also to give small amounts of *ipso* products, indicating that the *ipso* pathway was accessible to nucleophiles. This effect has been shown to vary with the nature of *para* substituents on the aryl group (*ipso* pathway: $CF_3 > H > OMe$[4]).

The key to the application of (1-arylcyclohexadienyl)iron complexes in the synthesis of structures with the quaternary centres that are produced by a *1,1* addition sequence, is the inclusion[7,12,26,40] of an OMe group at the internal position on the cyclohexadienyl ligand opposite to the aryl group, thus reducing the electrophilicity of the complex.[41] This deactivation is most profound adjacent to the OMe group (α to the OMe group;[26] ω to the aryl group) switching off nucleophile addition ω to the aryl group and promoting the sterically accessible but normally disfavoured pathway for *ipso*-nucleophile addition next to the aryl group, which now dominates the nucleophile-addition process. This has been used successfully, even with the more difficult[4] *p*-methoxyaryl system,[7] and the methylenedioxy-substituted case[4] needed to access crinine, to effect malonate and malononitrile addition at the site bearing the aryl group. The crystallographic study of **10** (see above) has shown that an accessible conformation for the molecule has the aryl group slanted to one side, leaving clear the access for the nucleophile at C(1).

To explore the regiocontrol of nucleophile addition (Table 1; columns 7–9), we have chosen as a test nucleophile a cyanoacetate-derived reagent of the type used in our synthetic applications (Figure 1; see also refs.[4,5,7,8]) to gain access to the CH_2CH_2NMe and $CH_2CH_2NMe_2$ side-chains that are present in the natural product targets *O*-methyljoubertiamine and lycoramine. Reaction of **10** with $NaCH(CO_2Me)CN$ in THF at 0 °C (Scheme 2) afforded the expected[42] product **19** in 82% yield (Table 1, Entry 1). The good yield indicates that there is efficient access for nucleophiles at the atom that bears the aryl group, and this reaction is interpreted as proceeding by a reactive conformation of the electrophile that resembles the conformation defined in the structural study (Figure 3). The simple methyl benzyl ether system **20** (Table 1, Entry 2) was available from our earlier work,[5] and offered a case where the entire "C_{13} building block" for the more advanced targets was present. Reaction with $NaCH(CO_2Me)CN$ was examined, but gave the opposite regiochemical outcome, with the only product **25** (71% yield) corresponding to addition of the nucleophile at the end of the dienyl ligand furthest from the benzyl ether substituent. Compared to the unsubstituted phenyl group, the 2′-(methoxymethyl)aryl group proved to be too strongly ω-directing and easily overcame the opposed regiodirecting effect of the OMe group on the dienyl ligand. The same experiment was performed with the 2-(formyl)-aryl example (Table 1, Entry 5; electrophile **12**) which reacted with 2 equiv. of the nucleophile to afford **28** in 72% yield. The formation of **28** is best accounted for by initial addition of the nucleophile at the highly electrophilic (cy-



Scheme 2. Nucleophile addition to (1-arylcyclohexadienyl)iron complexes.

clohexadienyl)iron complex, to produce an intermediate diene complex, that reacts with a second equivalent of the nuclophile at the aldehyde. The structure of the product **28** indicates that, like the 2-CH_2OMe substituent, the presence of the 2-CHO group renders the aryl group strongly ω-directing. Because the CH_2OMe and CHO substituents behave similarly, this result is ascribed to a steric effect, and the nearly perpendicular conformation seen in the structure of **12** in Figure 5 is proposed to give a good guide to the nature of the complex in solution. It is clear that this conformation predominates sufficiently to strongly influence the approach of the nucleophile, and that flatter conformations or those where the substituent lies below the plane of the dienyl ligand, are not sufficiently available to allow the *ipso* pathway relative to the aryl group to proceed. A further flanked example (**24**), with OMe groups at both *ortho* positions, was also available from earlier work,[5] and behaved similarly in reaction with $NaCH(CO_2Me)CN$, affording only the ω adduct **27**.

With the 2-$OCH_2CH{=}CH_2$ ether substituent, the crystallographic study (Figure 4) had demonstrated that a conformation was possible with the *ortho* substituent on the side of the ligand bearing the metal atom. The reaction of **14** with $NaCH(CO_2Me)CN$ (Table 1, Entry 4) afforded only the *ipso* product **21** in 79% yield, showing that in this case the opposed OMe group on the dienyl ligand could overcome the ω-directing effect of the aryl group. From this it is clear that the conformation identified in the solid state is also available in solution, and to a sufficient degree that it can determine the properties of the electrophile in reactions with nucleophiles. Addition of $NaCH(CO_2Me)CN$ to the *o*-anisyl structure **22**[5] (Table 1, Entry 3) showed the same regiocontrol (**23**: 80% yield) suggesting that this conformation is generally accessible in the *o*-aryl ether case. The electrophile **16** has both CH_2OMe and OMe groups, and in the structural study (Figure 6) had the OMe group below the plane of the dienyl ligand. The CH_2OMe group is on the side from which the nucleophile must approach (as with **20**). As expected, the reaction with $NaCH(CO_2Me)CN$ (Table 1, Entry 6) afforded only the ω product **26** (84% yield).

Whereas the *o*-CH_2OMe substituents in electrophiles **16** and **20** are clearly sufficiently bulky to completely block nucleophile addition at the nearby end of the dienyl complex, and the conformation in which this effect operates can be seen to be sufficiently preferred in solution to dominate the regiocontrol of the reactions, the introduction of additional OMe groups on the aromatic ring in **18** has been found to have a significant and useful effect. The crystallographic study (Figure 7) identified a new conformation in the solid state, with the CH_2OMe rotated away from C(1), potentially leaving open the path for nucleophiles to approach at the atom bearing the aryl group. If this conformation was also significant in solution, the *ipso*-addition pathway required for access to the natural product targets (Figures 1 and 2) might be opened up, despite the strong ω-directing effect identified in **16** and **20** with the *o*-CH_2OMe group installed on the aryl substituent. Reaction of **18** with $NaCH(CO_2Me)CN$ (Table 1, Entry 7) confirmed this was the case, producing the adducts **29** and **30** in 77% yield (*ipso*/ω = 4:1). This is the first example of the required *ipso* addition to the "C_{13} building block" (see Figure 2) to produce a quaternary centre. The success of this reaction is attributed to the effect of the additional OMe groups on

the aromatic ring and so is applicable in the proposed applications of the "C_{13} electrophiles" because the target structures typically have highly oxygenated aromatic rings.

Conclusions

The structures of (1-arylcyclohexadienyl)iron complexes vary considerably, depending on the nature and position of substituents on the arene portion of the ligand. This variation corresponds to differences in regioselectivity of nucleophile addition reactions, which can proceed *ipso* to the arene when conformations are easily accessible in which the plane of the arene lies close to the plane of the dienyl carbon atoms. Flanking substitution, or electron-withdrawing substituents, twist the two planes towards a perpendicular alignment, and in these cases the aryl group directs strongly ω. The crystallographically defined conformations provide models for the reactive conformations in solution. The two examples with crystallographically distinct molecules in the asymmetric unit give support to the argument that the defined conformations are not solely artefacts of intermolecular solid-state interactions, because in both cases the two molecules show similar dihedral angles, even though the packing environments are inequivalent. Results from this analysis fit well with observed regiocontrol effects in completed synthetic work in the *O*-methyljoubertiamine[7] and lycoramine series.[12] In this conformation, increased π overlap in the centre of the structure and increased transfer of electron density from the arene to the dienyl ligand is evidenced by shortening of the central C–C bond. Low dihedral angles and good *ipso* selectivity go together in this set of structures. In general, the variability of directing effects of aryl subsituents in the entire series (η^2–η^5) is ascribed to variation in conformational preferences defining the orientation of the arene relative to the haptyl section of the ligand.

This approach has led for the first time to the successful construction of a quaternary centre at C(1) in *o*-substituted (arylcyclohexadienyl)iron complexes of type **7**, showing the practicality of the proposed (Figure 2) "C_{13} building block" approach. This is the first case in which deliberate manipulation of the conformational effects in chiral electrophilic transition metal π complexes has been used as a strategy to gain access to the construction of hindered quaternary centres, and sets our on-going target synthesis work on a firm footing.

Experimental Section

General Conditions: Chemicals were reagent grade and used as supplied unless otherwise stated. All chiral compounds were prepared as racemic mixtures. All reactions were carried out in oven- or flame-dried glassware, under dry, oxygen-free nitrogen. Diethyl ether and THF were dried by distillation from sodium and benzophenone; dichloromethane was dried by distillation from calcium hydride. Reaction temperatures: –78 °C refers to acetone/dry ice; 0 °C refers to ice/water; –100 °C refers to diethyl ether/liquid nitrogen cooling. Light petroleum refers to the fraction with b.p. 40–60 °C. Brine refers to a saturated aqueous solution of sodium chloride. Filtration refers to filtration under water-pump suction. Column chromatography was performed using Merck 7734 silica gel and BDH alumina (Brockmann 1). TLC was performed using Camlab Polygram® SIL G/UV_{254} plates, visualized by UV irradiation (254 nm) or exposure to alkaline potassium permanganate solution followed by heating. IR spectra were recorded as a thin film or as a solution in the specified solvent with Avatar 360, Perkin–Elmer BX or Perkin–Elmer 1720X FTIR spectrometers. NMR spectra were recorded with Varian Unity Plus, Varian Gemini 2000, Jeol GX400, Jeol EX270, Bruker AC250 or Jeol EX90 spectrometers, and were referenced to Me_4Si (δ = 0 ppm). Microanalysis (Carlo Erba EA1108) and low-resolution EI mass spectrometry (Kratos MS25) were performed by A. W. R. Saunders at the University of East Anglia. CI, FAB and high-resolution mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Wales, Swansea.

X-ray Crystallography: Data were collected with Siemens P4 (**12b**) and Rigaku AFC7R (**14** and **18**) 4-circle diffractometers and a Bruker SMART Apex CCD diffractometer (**10** and **16**). Details of the data collection and structure refinement are summarized in Table 4. Structures were solved by direct methods and refined by full-matrix least-squares refinement against F^2 (all data) using the SHELXTL software package.[43] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-657027, -657028, -657029, -657030 and -657031contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Tricarbonyl{(2′′–5′′-η)-2-[2′-(1β′′,4′′-dimethoxycyclohexadien-1′′-yl)phenyl]-1,3-dioxolane}iron(0) [9, R = Me, Ar = 2-(OCH_2CH_2O)-CHC_6H_4] and Tricarbonyl{(2′′–5′′-η)-2-[2′-(1β′′-hydroxy-4′′-methoxycyclohexadien-1′′-yl)phenyl]-1,3-dioxolane}iron(0) [9, R = H, Ar = 2-(OCH_2CH_2O)CHC_6H_4]: A solution of *n*-butyllithium in hexane (1.2 M, 2.2 mL, 2.6 mmol) was added to a stirred solution of 2-(2′-bromophenyl)-1,3-dioxolane (360 mg, 1 mmol) in diethyl ether (2 mL) at –78 °C. Diethyl ether (4 mL) was added to the resulting suspension, and the mixture was stirred at –78 °C for 1 h. A solution of tricarbonyl[(1–5-η)-1,4-dimethoxycyclohexadienyl]iron(1+) tetrafluoroborate(1–) (620 mg, 2.7 mmol) in dichloromethane (30 mL) at –78 °C was added, and stirring was continued at this temperature for 2 h. After warming to room temp., water (5 mL) was added, and the mixture was extracted with dichloromethane (20 mL). The extracts were washed with water, dried ($MgSO_4$), and purified by chromatography on silica eluting with hexane/ethyl acetate (10:1) to give tricarbonyl{(2′′–5′′-η)-2-[2′-(1β′′,4′′-dimethoxycyclohexadien-1′′-yl)phenyl]-1,3-dioxolane}iron(0) [**9**, R = Me, Ar = 2-(OCH_2CH_2O)CHC_6H_4] (250 mg, 58%) and tricarbonyl-{(2′′–5′′-η)-2-[2′-(1β′′-hydroxy-4′′-methoxycyclohexadien-1′′-yl)-phenyl]-1,3-dioxolane}iron(0) [**9**, R = H, Ar = 2-(OCH_2CH_2O)-CHC_6H_4] (100 mg, 29%). Tricarbonyl[(2–5-η)-4-methoxycyclohexadien-1-one]iron(0)[44] (40 mg, 15%) was eluted with hexane/ethyl acetate (2:1). Tricarbonyl{(2′′–5′′-η)-2-[2′-(1β′′,4′′-dimethoxycyclohexadien-1′′-yl)-phenyl]-1,3-dioxolane}iron(0): ^{1}H NMR (89.5 MHz, $CDCl_3$): δ = 7.65 (m, 1 H, 3′-H or 6′-H), 7.41 (m, 1 H, 3′-H or 6′-H), 7.30–7.20 (m, 2 H, 4′-H, 5′-H), 6.33 (s, 1 H, 2-H), 5.26 (dd, $^3J_{H,H}$ = 6.7, 2.3 Hz, 1 H, 3′′-H), 4.2–3.9 (m, 4 H, $–CH_2–CH_2–$), 3.58 (s, 3 H, 4′′-OMe), 3.28 (m, 1 H, 5′′-H), 3.00 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 2′′-H), 2.91 (s, 3 H, 1′′-OMe), 2.26 (d, $^3J_{H,H}$ = 3 Hz, 2 H, 6′′α,β-H) ppm. MS (EI): *m*/*z* (%) = 372 (3) [M – 2 CO]$^+$, 344 (9) [M – 3 CO]$^+$, 312 (100) [M – 3 CO – CH_3OH]$^+$, 284

Table 4. Crystal data.

	10	12b	14	16	18
Empirical formula	$C_{16}H_{13}F_6FeO_4P$	$C_{17}H_{13}BF_4FeO_5$	$C_{19}H_{17}F_6FeO_5P$	$C_{19}H_{19}F_6FeO_6P$	$C_{20}H_{21}F_6FeO_7P$
Formula mass	470.08	439.93	526.15	544.16	574.19
Crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	10.3950(11)	10.008(4)	10.7012(8)	12.1223(16)	8.578(3)
b [Å]	10.9668(12)	12.421(5)	10.8260(10)	16.684(2)	10.878(5)
c [Å]	16.6880(18)	15.841(5)	19.2856(15)	11.4022(16)	13.032(5)
α [°]	74.377(2)	95.67(3)	90	90	97.58(4)
β [°]	73.342(2)	95.10(3)	103.755(6)	105.447(2)	100.52(3)
γ [°]	83.411(2)	111.36(3)	90	90	104.39(4)
V [Å^3]	1753.8(3)	1808.3(12)	2170.2(3)	2222.8(5)	1137.8(9)
Z	4	4	4	4	2
T [K]	100	295	291	100	193
F(000)	944	888	1064	1104	584
$D_{calcd.}$ [Mg m^{-3}]	1.780	1.616	1.610	1.626	1.676
μ(Mo-K_α) [mm^{-1}]	1.033	0.900	0.848	0.834	0.823
Data measured	8933	6784	6626	9194	4232
Unique data	7505	6389	6310	3898	4001
R_{int}	0.0173	0.0279	0.0186	0.0354	0.0533
Data with $I \geq 2\sigma(I)$	6186	5232	4158	2963	3069
Parameters	525	607	394	331	325
wR_2 (all data)	0.1096	0.1161	0.1104	0.1298	0.1022
R_1 [$I \geq 2\sigma(I)$]	0.0410	0.0466	0.0367	0.0528	0.0385
S (all data)	1.017	1.080	1.011	1.022	1.032
Largest difference peak/hole	+1.79/–1.22	+0.48/–0.45	+0.37/–0.38	+0.51/–0.42	+0.74/–0.76

(45), 266 (90), 255 (47). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2047 (ν_{sym} CO), 1980, 1969 (ν_{asym} CO), 1667, 1603, 1495, 1230, 1105, 1075, 1025 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{20}FeO_5$ 372.0660; found 372.0660 [M – 2 CO]$^+$. Tricarbonyl{(2′′–5′′-η)-2-[2′-(1β′′-hydroxy-4′′-methoxycyclohexadien-1′′-yl)phenyl]-1,3-dioxolane}iron(0): ^{1}H NMR (89.5 MHz, $CDCl_3$): δ = 7.61 (m, 1 H, Ar-H), 7.41–7.16 (m, 3 H, Ar-H), 6.36 (s, 1 H, 2-H), 5.14 (dd, $^3J_{H,H}$ = 6.5, 2.4 Hz, 1 H, 3′′-H), 4.15–3.95 (m, 4 H, CH_2–CH_2), 4.0–3.6 (br. s, 1 H, OH), 3.61 (s, 3 H, 4′′-OMe), 3.33 (m, 1 H, 5′′-H), 2.79 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, 2′′-H), 2.32 (m, 2 H, 6′′α,β-H) ppm. MS (EI): *m*/*z* (%) = 358 (3) [M – 2 CO]$^+$, 330 (8) [M – 3 CO]$^+$, 312 (100) [M – 3 CO – H_2O]$^+$, 284 (47), 268 (82), 266 (96), 255 (83). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3450 (OH), 2046 (ν_{sym} CO), 1974, 1965 (ν_{asym} CO), 1602, 1490, 1225, 1105, 1075, 1025 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{18}FeO_5$ 358.0504; found 358.0504 [M – 2 CO]$^+$.

Tricarbonyl](1–5-η)-1-(2′-formylphenyl)-4-methoxy-2,4-cyclohexadienyl]iron(1+) Hexafluorophosphate(1–) (12a) and Tetrafluoroborate(1–) (12b): A 2:1 mixture of tricarbonyl{(2′′–5′′-η)-2-[2′-(1β′′,4′′-dimethoxycyclohexadien-1′′-yl)phenyl]-1,3-dioxolane}-iron(0) [**9**, R = Me, Ar = 2-(OCH_2CH_2O)CHC_6H_4] and tricarbonyl{(2′′–5′′-η)-2-[2′-(-(1β′′-hydroxy-4′′-methoxycyclohexadien-1′′-yl)phenyl]-1,3-dioxolane}iron(0) [**9**, R = H, Ar = 2-(OCH_2CH_2O)CHC_6H_4] (250 mg, 0.595 mmol) was dissolved in dichloromethane and added to a solution of triphenylcarbenium tetrafluoroborate (220 mg, 0.667 mmol) in dichloromethane (5 mL) at 0 °C. The mixture darkened and was stirred at 0 °C for 2 h. The reaction mixture was added dropwise to diethyl ether (50 mL), and the precipitate was collected by filtration and dried to give the product **12b** as a yellow powder (190 mg, 73%). ^{1}H NMR (89.5 MHz, CD_3CN): δ = 9.88 (s, 1 H, CHO), 7.91 (m, 1 H, Ar-H), 7.76–7.65 (m, 2 H, Ar-H), 7.43, (m, 1 H, Ar-H), 6.95 (dd, $^3J_{H,H}$ = 6.15, 2.64 Hz, 1 H, 3-H), 5.89 (d, $^3J_{H,H}$ = 6.15 Hz, 1 H, 2-H), 4.11 (ddd, $^3J_{H,H}$ = 6.4, 2.6, 1.3 Hz, 1 H, 5-H), 3.80 (s, 3 H, 4-OMe), 3.13 (dd, $^3J_{H,H}$ = 15.8, 6.4 Hz, 1 H, 6α-H), 2.73 (d, $^3J_{H,H}$ = 15.8 Hz, 1 H, 6α-H) ppm. ^{13}C NMR (22.4 MHz, CD_3CN): δ = 192.93 (CHO), 135.13, 134.82, 133.22, 131.72, 130.65 (DEPT: 4× CH), 99.72 (2-C), 71.59 (3-C), 57.87 (OMe), 44.03 (5-C), 34.70 (DEPT: CH_2; 6-C) ppm. IR (acetone): $\tilde{\nu}_{max}$ = 2110 (ν_{sym} CO), 2066 (ν_{asym} CO), 2053 (ν_{sym} CO[45]), 1975 (ν_{asym} CO[45]), 1703 (C=O), 1480, 1270 cm^{-1}. A portion of the product was crystallised from acetonitrile/diethyl ether for X-ray crystallography. $C_{17}H_{13}BF_4FeO_5$ (439.93): calcd. C 46.41, H 2.98; found C 46.43, H 2.84. The corresponding hexafluorophosphate salt was prepared by dissolving the same mixture of the ether and alcohol in trifluoroacetic acid (2 mL) at 0 °C. The mixture was stirred at this temperature for 30 min. Satd. aq. ammonium hexafluorophosphate was added until no further precipitate formed. The product was collected by filtration and purified by precipitation from acetonitrile by addition of diethyl ether to afford tricarbonyl[(1–5-η)-1-(2′-formylphenyl)-4-methoxy-2,4-cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (**12a**) as a yellow powder (160 mg, 69%). ^{1}H NMR (89.5 MHz, CD_3CN): δ = 9.87 (s, 1 H, CHO), 7.88 (m, 1 H, Ar-H), 7.76–7.63 (m, 2 H, Ar-H), 7.45, (m, 1 H, Ar-H), 6.89 (dd, $^3J_{H,H}$ = 6, 2.5 Hz, 1 H, 3-H), 5.85 (d, $^3J_{H,H}$ = 6 Hz, 1 H, 2-H), 4.05 (m, 1 H, 5-H), 3.80 (s, 3 H, 4-OMe), 3.13 (dd, $^3J_{H,H}$ = 16, 6.1 Hz, 1 H, 6β-H), 2.70 (d, $^3J_{H,H}$ = 16 Hz, 1 H, 6α-H) ppm. ^{13}C NMR (67.5 MHz, CD_3CN): δ = 193.4 (CHO[46]), 150.9 (4′-C), 137.5 (3′-C or 6′-2), 135.6, 135.4, 133.8 (3′-C or 6′-C), 131.2, 100.1 (2-C[46]), 92.0 (1-C), 72.1 (3-C[46]), 44.6 (5-C[46]), 35.1 (6-C[46]) ppm.

Preparation of 1-Allyloxy-2-bromobenzene:[47] A solution of 2-bromophenol (1 equiv., 10.0 g, 58 mmol) in dry THF (20 mL) was added to NaH (60% suspension in mineral oil) (2.3 g, 58 mmol) in dry THF (20 mL) at 0 °C over 1 h. The reaction mixture was stirred at 0 °C for 30 min to give a pale brown solution. Allyl bromide (10.5 g, 87 mmol) was added at 0 °C. The reaction mixture was heated at reflux for 16 h. The reaction was quenched with water (50 mL) and diethyl ether (50 mL) and the mixture extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford 1-alloxy-2-bromobenzene as a clear liquid (10.7 g, 87%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.52 (dd, $^3J_{H,H}$ = 7.9, 1.6 Hz, 1 H, Ar), 7.21 (ddd,

$^3J_{H,H}$ = 8.3, 7.3, 1.6 Hz, 1 H, Ar), 6.86 (m, 2 H, Ar), 6.03 (ddt, $^3J_{H,H}$ = 17.2, 10.6, 5.0 Hz, 1 H, CH_2CH =CH_2), 5.46 (dq, $^3J_{H,H}$ = 17.2, 1.6 Hz, 1 H, CH_2CH=CH_2), 5.28 (dq, $^3J_{H,H}$ = 10.6, 1.6 Hz, 1 H, CH_2CH=CH_2), 4.58 (dt, $^3J_{H,H}$ = 5.0, 3.5 Hz, 1 H, OCH_2) ppm. MS (EI): *m*/*z* (%) = 214 (38) $[M]^+$, 212 (39) $[M]^+$, 174 (19) $[M - CH_2CH=CH_2]^+$, 172 (21) $[M - CH_2CH=CH_2]^+$, 133 (37) $[M - Br]^+$, 41 (100). IR (film): $\tilde{\nu}_{max}$ = 2921, 1587, 1479, 1278, 1032, 747 cm^{-1}. HRMS (EI): calcd. for C_9H_9OBr 211.9837; found 211.9837 $[M]^+$.

[(1–4-η)-5α-(2′-Allyloxyphenyl)-2,5β-dimethoxy-1,3-cyclohexadiene]tricarbonyliron(0) [9, R = Me, Ar = 2′-(H_2C=$CHCH_2O$)-C_6H_4]: 1-Allyloxy-2-bromobenzene (2 equiv., 1.3 g, 6.1 mmol) was dissolved in dry diethyl ether (5 mL) and cooled to –78 °C under nitrogen. *n*BuLi (1.6 M in hexanes, 6 mmol, 3.8 mL) was added and 1-(allyloxy)-2-lithiobenzene[47,48] was formed by stirring at –78 °C for 30 min. Salt **8** (1.1 g, 3.0 mmol) was dissolved in dry dichloromethane (5 mL) and cooled to –100 °C. The solution of the nucleophile was added through a cannula at –100 °C, and the mixture was stirred for 10 min. The reaction was quenched at –100 °C with water (25 mL) and diethyl ether (25 mL) and the mixture warmed to room temp. The mixture was extracted with diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a pale brown gum. Column chromatography (20% diethyl ether/80% petroleum ether) afforded [(1–4-η)-5α-(2′-allyloxyphenyl)-2,5β-dimethoxy-1,3-cyclohexadiene]tricarbonyliron(0) [**9**, R = Me, Ar = (2-H_2C=$CHCH_2O$)-C_6H_4] as a pale yellow gum (649 mg, 53%). ^1H NMR (270 MHz, $CDCl_3$): δ = 7.47 (dd, $^3J_{H,H}$ = 7.9, 2.2 Hz, 1 H, Ar), 7.22 (m, 1 H, Ar), 6.85 (m, 2 H, Ar), 6.02 (ddt, $^3J_{H,H}$ = 17.8, 9.6, 4.6 Hz, 1 H, CH_2CH=CH_2), 5.28 (m, 2 H, CH_2CH=CH_2), 5.01 (dd, $^3J_{H,H}$ = 6.9, 2.3 Hz, 1 H, 3-H), 4.51 (dt, $^3J_{H,H}$ = 4.0, 10.8 Hz, 1 H, OCH_2), 3.59 (s, 3 H, 2-OMe), 3.01 (m, 1 H, 1-H), 2.99 (s, 3 H, 5-OMe), 2.89 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 4-H), 2.47 (dd, $^3J_{H,H}$ = 15.2, 2.3 Hz, 1 H, 6β-H), 2.19 (dd, $^3J_{H,H}$ = 15.2, 3.6 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 356 (4) $[M - 2\ CO]^+$, 328 (9) $[M - 3\ CO]^+$, 286 (27), 255 (100). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2048 (ν_{sym} CO), 1977 (ν_{asym} CO) cm^{-1}. $C_{20}H_{20}FeO_6$ (412.22): calcd. C 58.3, H 4.9; found C 58.5, H 4.9.

[(1–5-η)-1-(2′-Allyloxyphenyl)-4-methoxy-2,4-cyclohexadienyl]-tricarbonyliron(1+) Hexafluorophosphate(1–) (14): Hexafluorophosphoric acid (75% in water, 1 mL) was added to a solution of tricarbonyl[(1–4-η)-5α-(2′-allyloxyphenyl)-2,5β-dimethoxy-1,3-cyclohexadiene]iron(0) [**9**, R = Me, Ar = 2′-(H_2C=$CHCH_2O$)C_6H_4] (567 mg, 1.38 mmol) in acetic anhydride (10 mL) at 0 °C. The reaction mixture darkened and was stirred for 10 min. The reaction mixture was added dropwise to dry diethyl ether (200 mL) cooled to 0 °C, and a yellow precipitate formed. Recrystallisation (acetone/diethyl ether) afforded [(1–5-η)-1-(2-allyloxyphenyl)-4-methoxy-2,4-cyclohexadienyl]tricarbonyliron(1+) hexafluorophosphate(1–) (**14**) as orange crystals (598 mg, 82%). ^1H NMR (270 MHz, CD_3COCD_3): δ = 7.52 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar), 7.44 (dd, $^3J_{H,H}$ = 7.9, 1.7 Hz, 1 H, Ar), 7.30 (dd, $^3J_{H,H}$ = 6.3, 2.6 Hz, 1 H, 3-H), 7.15 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar), 7.09 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar), 6.51 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, 2-H), 6.07 (ddt, $^3J_{H,H}$ = 17.5, 10.6, 5.3 Hz, 1 H, CH_2CH=CH_2) 5.33 (m, 2 H, CH_2CH=CH_2), 4.86 (m, 1 H, 5-H), 4.05 (s, 3 H, OMe), 3.75 (dd., $^3J_{H,H}$ = 15.5, 5.6 Hz, 1 H, 6β-H), 2.95 (d, $^3J_{H,H}$ = 15.5 Hz, 1 H, 6α-H) ppm. ^{13}C NMR (67.5 MHz, CD_3COCD_3): δ = 158.4 (2′-C), 151.5 (4-C), 134.2 (4′-C), 132.1 (=CH), 131.5 (6′-C), 123.0 (5′-C), 122.6 (1′-C), 119.4 (=CH_2), 115.4 (3′-C), 95.5 (2-C), 93.5 (1-C), 73.3 (CH_2-O), 70.1 (3-C), 43.5 (5-C), 33.9 (6-C) ppm. MS (EI): *m*/*z* (%) = 381 (100) $[M - PF_6]^+$, 353 (9) $[M - PF_6 - CO]^+$, 297 (5) $[M - PF_6 - 3\ CO]^+$. IR (CD_3COCD_3): $\tilde{\nu}_{max}$ = 2098 (ν_{sym} CO), 2049 (ν_{asym} CO) cm^{-1}. $C_{19}H_{17}F_6FeO_5P$ (526.15): calcd. C 43.4, H 3.3; found C 43.4, H 3.2.

Preparation of 2-Bromo-3-methoxybenzyl Alcohol:[49] According to the method of Trost,[23] 3-methoxybenzyl alcohol (1 equiv., 2 g, 14.5 mmol) was dissolved in dry hexane (50 mL). *n*BuLi (31.9 mmol, 19.9 mL) was added at 0 °C with stirring. The mixture was warmed to room temp., and a pink solution was formed. After 2 h, the solution had turned orange. The mixture was cooled to –78 °C, and $BrCF_2CF_2Br$ (31.9 mmol, 8.28 g, 3.8 mL) was added. The mixture was stirred for 30 min and then warmed to 0 °C. The mixture turned yellow after 1 h. The reaction was quenched with water (50 mL) and diethyl ether (50 mL) and the mixture extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to afford a yellow solid. Recrystallisation (60% diethyl ether/40% cyclohexane) afforded 1-bromo-3-methoxybenzyl alcohol as white crystals (1.262 g, 40%). ^1H NMR (270 MHz, $CDCl_3$): δ = 7.30 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, 5-H), 7.10 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4-H), 6.86 (d., $^3J_{H,H}$ = 8.0 Hz, 1 H, 6-H), 4.77 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 3.91 (s, 3 H, OMe), 2.06 (t, $^3J_{H,H}$ = 6.8 Hz, 1 H, OH) ppm. MS (EI): *m*/*z* (%) = 218 (96) $[M]^+$, 216 (100) $[M]^+$, 201 (7) $[M - OH]^+$, 199 (5) $[M - OH]^+$. IR (mull): $\tilde{\nu}_{max}$ = 3285 (OH), 2843, 1594, 1474, 1293, 1047, 765 cm^{-1}. $C_8H_9O_2Br$ (217.06): C 44.3, H 4.2, Br 36.8; found, C 44.4, H 4.1, Br 36.5.

Preparation of 1-Bromo-2-Methoxy-6-(methoxymethyl)benzene:[50] NaH (60% suspension in mineral oil) (0.208 g, 5.23 mmol) was suspended in dry THF (20 mL) at 0 °C. A solution of 2-bromo-3-methoxybenzyl alcohol (1.13 g, 5.23 mmol) in dry THF (5 mL) was added at 0 °C and the mixture was stirred at 0 °C for 30 min to give a clear brown solution. Methyl iodide (0.5 mL, 7.81 mmol) was added at 0 °C and the mixture stirred at room temp. for 18 h. The reaction was quenched with water (50 mL) and diethyl ether (50 mL) and the mixture extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to afford a yellow solid. Column chromatography (30% diethyl ether/70% cyclohexane) afforded 1-bromo-2-methoxy-6-(methoxymethyl)benzene as a white crystalline solid (1.038 g, 86%). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.29 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4-H), 7.09 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 3-H), 6.85 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 5-H), 4.55 (s, 2 H, CH_2), 3.90 (s, 3 H, Ar-OMe), 3.47 (s, 3 H, OMe) ppm. MS (EI): *m*/*z* (%) = (EI) 232 (96) $[M]^+$, 230 (100) $[M]^+$, 201 (55) $[M - OMe]^+$, 199 (54) $[M - OMe]^+$, 151 (75) $[M - Br]^+$, 121 (60) $[M^+ - Br - OMe + H]^+$. IR (mull): $\tilde{\nu}_{max}$ = 2932, 2820, 1593, 1469, 1294, 1126, 1029, 776 cm^{-1}. $C_9H_{11}BrO_2$ (231.08): calcd. C 46.8, H 4.8, Br 34.6; found C 46.9, H 4.7, Br 34.5.

Attempted Preparation of Tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[2′-methoxy-6′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) (9, R = Me, Ar = 2′-MeO-6′-$HOCH_2C_6H_3$); Formation of Tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[6′-(hydroxymethyl)-2′-methoxyphenyl]-1,3-cyclohexadiene}iron(0) (9, R = Me, Ar = 2′-MeO-6′-$HOCH_2C_6H_3$) and Tricarbonyl[(2–5-η)-4-methoxy-2,4-cyclohexadienone]iron(0): According to the method of Trost,[23] 3-methoxybenzyl alcohol (276 mg, 2 mmol) was dissolved in dry hexane (5 mL). *n*BuLi (2.6 mL, 4.1 mmol) was added at 0 °C with stirring. The mixture was warmed to room temp., and a pink solution formed. After 2 h, an orange solution had formed, and the mixture was cooled to –100 °C. Tricarbonyl[(1–5-η)-1,4-dimethoxy-2,4-cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (**8**) (1 equiv.,

366 mg, 1.0 mmol) was dissolved in dry dichloromethane (10 mL) and cooled to –100 °C. The solution of the nucleophile at –100 °C was added to the salt through a cannula at –100 °C, and the mixture turned black and was stirred at –100 °C for 2 h. The reaction was quenched with water (25 mL) and diethyl ether (25 mL) at –100 °C and the mixture warmed to room temp. The mixture was extracted with diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to afford a brown oil. Column chromatography (60% diethyl ether/40% cyclohexane) gave a trace of a yellow gum which was provisionally identified as tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[6′-(hydroxymethyl)-2′-methoxyphenyl]-1,3-cyclohexadiene}iron(0) (**9**, R = Me, Ar = 2′-MeO-6′-$HOCH_2C_6H_3$) (14 mg, 3%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.20 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 4′-H), 7.09 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, 3′-H), 6.82 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, 5′-H), 5.05 (d, $^3J_{H,H}$ = 13.5 Hz, 1 H, CH_2), 4.91 (dd, $^3J_{H,H}$ = 7.0, 2.5 Hz, 1 H, 3-H), 4.59 (dd, $^3J_{H,H}$ = 13.5, 7.5 Hz, 1 H, CH_2), 3.79 (s, 3 H, Ar-OMe), 3.64 (s, 3 H, 2-OMe), 3.33 (m, 1 H, 1-H), 3.28 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, 4-H), 3.06 (s, 3 H, 5-OMe), 2.96 (br. s, 1 H, OH), 2.61 (dd, $^3J_{H,H}$ = 14.8, 2.5 Hz, 1 H, 6β-H), 2.25 (dd, $^3J_{H,H}$ = 14.8, 3.0 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 356 (2) [M – MeOH – CO]$^+$, 328 (6) [M – MeOH – 2 CO]$^+$, 300 (10) [M – MeOH – 3 CO]$^+$, 244 (15) [M – MeOH – 3 CO – Fe]$^+$, 138 (100), 109 (45). IR (acetone): $\tilde{\nu}_{max}$ = 3370 (OH), 2042 (ν_{sym} CO), 1966 (ν_{asym} CO), 1490, 1260, 1074, 1031, 624 cm^{-1}. The main product from this reaction was tricarbonyl[(2–5-η)-4-methoxy-2,4-cyclohexadienone]-iron(0)[48] (97 mg, 37%).

Tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[2′-methoxy-6′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) (9, R = Me, Ar = 2′-MeO-6′-MeOCH$_2$C$_6$H$_3$): 1-Bromo-2-methoxy-6-(methoxymethyl)-benzene (2 equiv., 462 mg, 2 mmol) was dissolved in dry diethyl ether (25 mL) and cooled to –78 °C under nitrogen. *n*BuLi (1.6 M in hexanes, 1.25 mL, 2.0 mmol) was added and 1-lithio-2′-methoxy-6′-(methoxymethyl)benzene[51] was formed as a white suspension by stirring at –78 °C for 2 h. Tricarbonyl[(1–5-η)-1,4-dimethoxy-2,4-cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (**8**) (366 mg, 1.0 mmol) was dissolved in dry dichloromethane (10 mL) and cooled to –100 °C. The solution of the nucleophile at –100 °C was added to the salt at –100 °C through a cannula, and the mixture was stirred for 2 h. The reaction was quenched with water (25 mL) and diethyl ether (25 mL) at –100 °C and the mixture warmed to room temp. The mixture was extracted with diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a brown oil. Column chromatography (40% diethyl ether/60% cyclohexane) afforded tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[2′-methoxy-6′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) (**9**, R = Me, Ar = 2′-MeO-6′-$MeOCH_2C_6H_3$) (285 mg, 66%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.3–6.7 (m, 3 H, Ar), 4.88 (dd, $^3J_{H,H}$ = 6.8, 2.5 Hz, 1 H, 3-H) ppm. 4.82 (d, $^3J_{H,H}$ = 13.0 Hz, 1 H, CH_2), 4.61 (d, $^3J_{H,H}$ = 13.0 Hz, 1 H, CH_2), 4.44 (s, 3 H, Ar-OMe), 3.77 (s, 3 H, CH_2OMe), 3.62 (s, 3 H, 2-OMe), 3.34 (m, 1 H, 1-H), 3.24 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.97 (s, 3 H, 5-OMe), 2.66 (dd, $^3J_{H,H}$ = 14.7, 3.3 Hz, 1 H, 6β-H), 2.14 (dd, $^3J_{H,H}$ = 14.7, 3.0 Hz, 1 H, 6α-H) ppm. IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2044 (ν_{sym} CO), 1976, 1966 (ν_{asym} CO), 1489, 1262, 1104, 913, 742 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{22}FeO_5$ 374.0817; found 374.0817 [M – 2 CO]$^+$. Also isolated, was tricarbonyl[(2–5-η)-4-methoxy-2,4-cyclohexadienone]iron(0)[47] (47 mg, 18%).

Tricarbonyl{(1–5-η)-4-methoxy-1-[2′-methoxy-6′-(methoxymethyl)-phenyl]-2,4-cyclohexadienyl}iron(1+) Hexafluorophosphate(1–) (16): Triphenylcarbenium hexafluorophosphate (37 mg, 0.353 mmol) was dissolved in freshly distilled dichloromethane (10 mL) at 0 °C. Tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[2′-methoxy-6′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) (**9**, R = Me, Ar = 2′-MeO-6′-$MeOCH_2C_6H_3$) (152 mg, 0.353 mmol) was dissolved in dichloromethane (10 mL) and was added to the solution. The reaction mixture darkened slowly while being stirred at 0 °C for 3 h. The reaction mixture was added dropwise into dry diethyl ether (200 mL) at 0 °C and a yellow precipitate formed. Reprecipitation (acetone/diethyl ether) afforded tricarbonyl{(1–5-η)-4-methoxy-1-[2′-methoxy-6′-(methoxymethyl)phenyl]-2,4-cyclohexadienyl}-iron(1+) hexafluorophosphate(1–) (**16**) as a yellow solid (123 mg, 64%). ^{1}H NMR (270 MHz, CD_3COCD_3): δ = 7.42 (t, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4′-H), 7.12 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 3′-H), 7.06 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, 3-H), 7.02 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 5′-H), 5.85 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, 2-H), 4.38 (d, $^3J_{H,H}$ = 12.3 Hz, 1 H, CH_2), 4.25 (d, $^3J_{H,H}$ = 12.3 Hz, 1 H, CH_2), 4.12 (m, 1 H, 5-H), 4.08 (s, 3 H, 4-OMe), 3.80 (s, 3 H, Ar-OMe), 3.35 (dd, $^3J_{H,H}$ = 16.5, 6.3 Hz, 1 H, 6β-H), 3.31 (s, 3 H, CH_2OMe), 2.52 (d, $^3J_{H,H}$ = 16.5 Hz, 1 H, 6α-H) ppm. ^{13}C NMR (75 MHz, CD_3COCD_3): δ = 156.1 (2′-C), 150.3 (4-C), 139.3 (6′-C), 131.8 (4′-C), 124.5 (1′-C), 124.2 (3′-C), 122.6 (5′-C), 100.5 (2-C[46]), 89.8 (1-C), 73.6 (CH_2–O), 71.9 (3-C[46]), 58.3 (Ar-OMe), 57.9 (2′-OMe), 55.6 (4-OMe), 46.9 (5-C[46]), 34.8 (6-C) ppm (the signals at δ = 58.3 and 57.9 ppm were distinguished by HSQC in which the ^{13}C NMR signal at δ = 58.3 ppm correlated with the CH_2–OMe methoxy resonance at δ = 3.33 ppm). IR (acetone): $\tilde{\nu}_{max}$ = 2106 (ν_{sym} CO), 2058 (ν_{asym} CO), 1500, 1252, 838, 558 cm^{-1}. HRMS (FAB): calcd. for $C_{19}H_{19}FeO_6$ 399.0531; found 399.0531 [M – PF_6]$^+$. $C_{19}H_{19}F_6FeO_6P$ (544.16): calcd. C 41.9, H 3.5; found C 42.1, H 3.4.

Preparation of 2-Bromo-4,5-dimethoxybenzyl Alcohol:[25,52] $NaBH_4$ (0.539 g, 13.5 mmol) was added to a solution of l-bromo-4,5-dimethoxybenzaldehyde (3.0 g, 12.2 mmol) in dry THF (80 mL) and methanol (20 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min. The reaction was quenched with water (50 mL) and diethyl ether (50 mL) and the mixture extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a white solid (2.957 g, 98%). Recrystallisation (ethanol/water) afforded l-bromo-4,5-dimethoxybenzyl alcohol as fluffy fine white crystals (2.097 g, 69%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.02 (s, 1 H, Ar), 7.01 (s, 1 H, Ar), 4.70 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH_2), 3.90 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 1.93 (t, $^3J_{H,H}$ = 6.0 Hz, 1 H, OH) ppm. MS (EI): *m*/*z* (%) = 248 (98) [M]$^+$, 246 (100) [M]$^+$, 231 (19) [M – OH]$^+$, 229 (14) [M – OH]$^+$, 185 (5), 167 (9), 139 (53), 123 (11). IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 3501 (OH), 2967, 2855, 1607, 1504, 1257, 1207, 1062, 799, 581, 511 cm^{-1}. $C_9H_{11}BrO_3$ (247.08): calcd. C 43.7, H 4.5, Br 32.3; found C 43.6, H 4.3, Br 32.0.

Preparation of l-Bromo-3,4-dimethoxy-6-(methoxymethyl)benzene:[25] NaH (60% suspension in mineral oil) (0.162 g, 4.045 mmol) was suspended in dry THF (20 mL) at 0 °C. A solution of 2-bromo-4,5-dimethoxybenzyl alcohol (1.0 g, 4.045 mmol) in dry THF (5 mL) was added at 0 °C, and the mixture was stirred at 0 °C for 30 min to give a clear solution of sodium (2-bromo-4,5-dimethoxyphenyl)methoxide. Methyl iodide (0.3 mL, 4.453 mmol) was added at 0 °C and the mixture stirred at room temp. for 4 h. The reaction was quenched with water (50 mL) and diethyl ether (50 mL) and the mixture extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to afford a yellow oil. Column chromatography (30% diethyl ether/70% cyclohexane) afforded 1-bromo-3,4-

dimethoxy-6-(methoxymethyl)benzene as a white solid (0.961 g, 91%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.01 (s, 1 H, Ar), 6.98 (s, 1 H, Ar), 4.46 (s, 2 H, CH_2), 3.88 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 3.45 (s, 3 H, CH_2OMe) ppm. MS (EI): *m*/*z* (%) = 262 (84) $[M]^+$, 260 (85) $[M]^+$, 231 (99) $[M - OMe]^+$, 229 (100) $[M^+ - OMe]^+$, 181 (74), 151(14), 107 (12). IR ($CDCl_3$): $\tilde{\nu}_{max}$ = 2933, 2836, 1609, 1504, 1384, 1160, 1103, 966, 804, 596 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_{13}BrO_3$ 260.0048; found 260.0048 $[M]^+$. $C_{10}H_{13}BrO_3$ (261.11): calcd. C 46.0, H 5.0; found C 45.9, H 4.8.

Tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) [9, R = Me, Ar = 4′,5′-(MeO)$_2$-2′-MeOCH$_2$C$_6$H$_3$]: 1-Bromo-3,4-dimethoxy-6-(methoxymethyl)benzene (3.132 g, 12 mmol) was dissolved in dry diethyl ether (50 mL) and cooled to –78 °C under nitrogen. *n*BuLi (1.6 M in hexanes, 7.5 mL, 12 mmol) was added, and 1-lithio-3,4-dimethoxy-6-(methoxymethyl)benzene was formed as a white suspension by stirring at –78 °C for 1 h. Tricarbonyl[(1–5-η)-1,4-dimethoxy-2,4-cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (**8**) (2.2 g, 6.0 mmol) was dissolved in dry dichloromethane (20 mL) and cooled to –100 °C. The solution of the nucleophile at –100 °C was added to the salt through a cannula at –100 °C, and the mixture was stirred for 2 h. The reaction was quenched with water (50 mL) and diethyl ether (50 mL) at –100 °C and the mixture warmed to room temp. The mixture was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to afford a brown oil. Column chromatography (40% diethyl ether/60% cyclohexane) afforded tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) [**9**, R = Me, Ar = 4,5-(MeO)$_2$-2-MeOCH$_2$C$_6$H$_3$] as a nearly colourless oil (0.865 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (s, 1 H, 3′-H), 7.04 (s, 1 H, 6′-H), 5.28 (dd, $^3J_{H,H}$ = 6.8, 2.4 Hz, 1 H, 3-H), 4.53 (s, 2 H, CH_2), 3.92 (s, 3 H, Ar-OMe), 3.88 (s, 3 H, Ar-OMe), 3.64 (s, 3 H, 2-OMe), 3.40 (s, 3 H, CH_2OMe), 3.31 (ddd, $^3J_{H,H}$ = 3.9, 2.4, 2.4 Hz, 1 H, 1-H), 2.99 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 2.93 (s, 3 H, 5-OMe), 2.31 (dd, $^3J_{H,H}$ = 14.7, 3.9 Hz, 1 H, 6β-H), 2.17 (dd, $^3J_{H,H}$ = 14.7, 2.3 Hz, 1 H, 6α-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.8 (4′-C or 5′-C), 146.2 (4′-C or 5′-C), 140 (2-C), 134.2 (1′-C or 2′-C), 130.8 (1′-C or 2′-C), 111.9 (2 C, 3′-C and 6′-C), 82.4 (6-C), 71.6 (CH_2), 65.0 (3-C), 58.3 (CH_2OMe), 56.1 (5′-OMe), 55.8 (4′-OMe), 54.8 (4-C), 54.6 (2-OMe), 51.5 (1-C), 49.4 (5-OMe), 42.9 (6-C) ppm. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2048 (ν_{sym} CO), 1979, 1968 (ν_{asym} CO), 1266, 1106, 747 cm^{-1}. HRMS (EI): calcd. for $C_{19}H_{24}FeO_6$ 404.0922; found 404.0922 $[M - 2\ CO]^+$. Also isolated, was tricarbonyl[(2–5-η)-4-methoxy-2,4-cyclohexadienone]iron(0)[47] (0.279 g, 18%).

Tricarbonyl{(1–5-η)-1-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-4-methoxy-2,4-cyclohexadienyl}iron(1+) Hexafluorophosphate(1–) (18): Triphenylcarbenium hexafluorophosphate (388 mg, 1 mmol) was dissolved in freshly distilled dichloromethane (10 mL) and the mixture stirred with potassium carbonate (100 mg, 1 mmol) at 0 °C for 5 min. Tricarbonyl{(1–4-η)-2,5β-dimethoxy-5α-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-1,3-cyclohexadiene}iron(0) [**9**, R = Me, Ar = 4′,5′-(OMe)$_2$-2′-MeOCH$_2$C$_6$H$_3$] (462 mg, 1 mmol) was dissolved in freshly distilled dichloromethane (2 mL) and added to the solution at 0 °C. The reaction mixture darkened and was stirred at 0 °C for 1 h. The reaction mixture was added dropwise to dry diethyl ether (200 mL) at 0 °C, and an orange precipitate formed. Reprecipitation (acetone/diethyl ether) afforded tricarbonyl{(1–5-η)-1-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-4-methoxy-2,4-cyclohexadienyl}iron(1+) hexafluorophosphate(1–) (**18**) as an orange solid (363 mg, 65%): ^{1}H NMR (270 MHz, CD_3COCD_3): δ = 7.38 (m, 1 H, 3-H), 7.13 (s, 1 H, Ar), 7.06 (s, 1 H, Ar), 6.32 (m, 1 H, 2-H), 4.44 (m, 1 H, 5-H), 4.38 (d, $^3J_{H,H}$ = 9.6 Hz, 2 H, CH_2OMe), 4.05 (s, 3 H, 4-OMe), 3.93 (s, 3 H, Ar-OMe), 3.88 (s, 3 H, Ar-OMe), 3.88 (m, 2 H, 6-H), 3.31 (s, 3 H, CH_2OMe) ppm. ^{13}C NMR (101 MHz, CD_3COCD_3): δ = 151.1 (4-C or 4′-C or 5′-C), 150.8 (4-C or 4′-C or 5′-C), 149.6 (4-C or 4′-C or 5′-C), 130.7 (1′-C or 2′-C), 128.1 (1′-C or 2′-C), 115.7 (3′-C), 114.8 (6′-C), 98.3 (1-C), 96.4 (2-C), 73.0 (CH_2-O), 72.1 (3-C), 57.9 (2 C, 4-OMe and benzylic OMe), 56.2 (4′-OMe or 5′-OMe), 56.1 (4′-OMe or 5′-OMe), 43.4 (5-C), 34.6 (6-C) ppm. IR (acetone): $\tilde{\nu}_{max}$ = 2105 (ν_{sym} CO), 2049 (ν_{asym} CO), 1171, 963, 846 cm^{-1}. HRMS (FAB): calcd. for $C_{20}H_{21}FeO_7$ 429.0637; found 429.0637 $[M - PF_6]^+$.

General Procedure for the Addition of Methyl 2-Cyano-2-sodioacetate to (1-Arylcyclohexadienyl)iron(1+) Salts: Methyl 2-cyanoacetate was dissolved in dry THF (5 mL) and cooled to 0 °C under nitrogen. NaH (60% suspension in mineral oil) was added, and methyl 2-cyano-2-sodioacetate was formed as a milky suspension by stirring at 0 °C for 15 min. This was added to a suspension of the (1-arylcyclohexadienyl)iron(1+) salt in THF (5 mL) at 0 °C, and the mixture was stirred for 1 h. The reaction was quenched with water (25 mL) and diethyl ether (25 mL) and the mixture extracted with diethyl ether (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to afford a yellow oil which was purified by chromatography.

Tricarbonyl{methyl 2-cyano-2-[(2–5-η)-4-methoxy-1β-phenyl-2,4-cyclohexadien-1α-yl]acetato}iron(0) (19): According to the general procedure, methyl 2-cyanoacetate (300 mg, 3 mmol), NaH (60% suspension in mineral oil) (120 mg, 3 mmol) in THF (20 mL) and the salt **10** (135 mg, 0.29 mmol) afforded a yellow oil. Column chromatography (hexane/ethyl acetate gradient; 5:1 to 4:1) afforded **19** as two inseparable diastereoisomers as a golden oil (100 mg, 82%).^{1}H NMR (270 MHz, $CDCl_3$) (major diastereoisomer): δ = 7.4–7.2 (m, 5 H, Ar-H), 5.30 (dd, $^3J_{H,H}$ = 6.7, 2.3 Hz, 1 H, 3-H), 3.70 (s, 3 H, Ar-OMe), 3.59 (s, 1 H, CO_2Me) 3.62 (s, 1 H, CHCN), 3.33 (m, 1 H, 5-H), 3.13 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, 3-H), 2.67 (dd, $^3J_{H,H}$ = 15.5, 2.6 Hz, 1 H, 6β-H); 2.44 (dd, $^3J_{H,H}$ = 15.5, 3.3 Hz, 1 H, 6α-H); (minor diastereoisomer): δ = 7.4–7.2 (m, 5 H, Ar-H), 5.22 (dd, $^3J_{H,H}$ = 6.6, 2.6 Hz, 1 H, 3-H), 3.66 (s, 3 H, Ar-OMe), 3.64 (s, 1 H, CHCN), 3.41 (s, 1 H, CO_2Me), 3.33 (m, 1 H, 5-H), 3.09 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, 3-H), 2.79 (dd, $^3J_{H,H}$ = 15.5, 2.6 Hz, 1 H, 6β-H); 2.39 (dd, $^3J_{H,H}$ = 15.5, 3.3 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 376 (1) $[M - 2\ CO]^+$, 339 (12) $[M - 3\ CO]^+$, 240 (14), 184 (100), 169 (56), 141 (50) 115 (44). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2247 (CN), 2048 (ν_{sym} CO), 1975, 1745 (ν_{asym} CO), 1600, 1492 cm^{-1}. HRMS (CI): calcd. for $C_{20}H_{21}FeN_2O_6$ 441.0749; found 441.0749 $[M + NH_4]^+$.

Tricarbonyl{methyl 2-[(2–5-η)-1β-(2′-allyloxyphenyl)-4-methoxy-2,4-cyclohexadien-1α-yl]-2-cyanoacetato}iron(0) (21): According to the general procedure, methyl 2-cyanoacetate (297 mg, 3 mmol), NaH (60% suspension in mineral oil) (120 mg, 3 mmol) and the salt **14** (300 mg, 0.57 mmol) afforded a yellow oil. Column chromatography (70% diethyl ether/30% petroleum ether) afforded **21** as two inseparable diastereoisomers as a pale yellow gum (214 mg, 79%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.48–6.84 (m, 8 H, Ar), 6.02 (tdd, $^3J_{H,H}$ = 17.2, 10.2, 5.0 Hz, 2 H, $CH_2CH{=}CH_2$) 5.39 (m, 4 H, $CH_2CH{=}CH_2$), 5.32 (m, 1 H, 3-H), 5.19 (dd, *J* = 6.6, 2.3 Hz, 1 H, 3-H), 4.88 (s, 1 H, 2′-H), 4.84 (s, 1 H, 2′-H), 4.56 (d, $^3J_{H,H}$ = 5.3 Hz, 4 H, OCH_2), 3.84 (s, 3 H, 4-OMe), 3.77 (s, 3 H, 4-OMe), 3.66 (s, 3 H, CH_2OMe), 3.39 (s, 3 H, CH_2OMe), 3.28 (m, 2 H, 5-H), 3.03 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, 2-H), 2.98 (dd, $^3J_{H,H}$ = 16.2, 2.6 Hz, 1 H, 6β-H), 2.84 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, 2-H), 2.54 (dd,

$^3J_{H,H}$ = 16.2, 2.3 Hz, 1 H, 6β-H), 2.20 (dd, $^3J_{H,H}$ = 16.2, 3.3 Hz, 1 H, 6α-H), 2.07 (dd, $^3J_{H,H}$ = 16.2, 3.3 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 451 (1) $[M - CO]^+$, 423 (1) $[M - 2\ CO]^+$, 395 (18) $[M - 3\ CO]^+$, 354 (27), 322 (23), 255 (76), 199 (100). IR (film): $\tilde{\nu}_{max}$ = 2246 (CN), 2048 (ν_{sym} CO), 1971 (ν_{asym} CO), 1743 (C=O), 1599, 1489, 1042, 752 cm^{-1}. $C_{23}H_{21}FeNO_7$ (479.26): calcd. C 57.6, H 4.4, N 2.9; found C 57.8, H 4.5, N 3.2.

Tricarbonyl{methyl 2-[(2–5-η)-1β-(2′-anisyl)-4-methoxy-2,4-cyclohexadien-1α-yl]-2-cyanoacetato}iron(0) (23): According to the general procedure, methyl cyanoacetate (495 mg, 5 mmol), NaH (60% suspension in mineral oil) (200 mg, 5 mmol) and the salt **22**[4] (500 mg, 1.0 mmol) afforded a yellow oil. Column chromatography (50% diethyl ether/50% petroleum ether) afforded **23** as pale yellow solids. Diastereoisomer 1 (168 mg, 37%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.29–7.24 (m, 2 H, Ar), 7.00–6.86 (m, 2 H, Ar), 5.39 (dd, $^3J_{H,H}$ = 7.0, 3.0 Hz, 1 H, 3-H), 4.80 (s, 1 H, 2′-H), 3.85 (s, 3 H, 4-OMe), 3.77 (s, 3 H, Ar-OMe), 3.39 (s, 3 H, CO_2Me), 3.28 (m, 1 H, 5-H), 2.84 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 2-H), 2.50 (dd, $^3J_{H,H}$ = 16.2, 2.6 Hz, 1 H, 6β-H), 2.15 (dd, $^3J_{H,H}$ = 16.2, 3.3 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 369 (2) $[M - 3\ CO]^+$, 319 (2), 255 (2) 214 (40), 184 (7), 121 (19), 43 (100). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2048 (ν_{sym} CO), 1972 (ν_{asym} CO) cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{19}FeNO_4$ 369.0663; found 369.0663 $[M - 3\ CO]^+$. Diastereoisomer 2 (195 mg, 43%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.46–6.88 (m, 4 H, Ar), 5.18 (dd, $^3J_{H,H}$ = 6.9, 2.6 Hz, 1 H, 3-H), 4.75 (s, 1 H, 2′-H), 3.84 (s, 3 H, C4-OMe), 3.82 (s, 3 H, Ar-OMe), 3.81 (s, 3 H, CO_2Me), 3.28 (m, 1 H, 5-H), 3.03 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, 2-H), 2.94 (dd, $^3J_{H,H}$ = 16.2, 2.6 Hz, 1 H, 6β-H), 2.03 (dd, $^3J_{H,H}$ = 16.2, 3.3 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 425 (1) $[M - CO]^+$, 397 (1) $[M - 2\ CO]^+$, 369 (8) $[M^+ - 3\ CO]^+$, 313 (12) $[M^+ - 3\ CO - Fe]^+$, 214 (100). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2051 (ν_{sym} CO), 1978 (ν_{asym} CO) cm^{-1}. $C_{21}H_{19}FeNO_7$ (453.23): calcd. C 55.7, H 4.2, N 3.1; found C 55.8, H 4.1, N 3.1.

Tricarbonyl(methyl 2-cyano-2-{(2–5-η)-5-[2′-methoxy-6′-(methoxymethyl)phenyl]-2,4-cyclohexadien-1α-yl}acetato)iron(0) (25): According to the general procedure, methyl 2-cyanoacetate (46 mg, 0.46 mmol), NaH (60% suspension in mineral oil) (18 mg, 0.46 mmol) and the salt **16** (125 mg, 0.23 mmol) afforded a yellow oil. Column chromatography (10% diethyl ether/90% petroleum ether) afforded **25** as two inseparable diastereoisomers as a pale yellow gum (96 mg, 88%). ^{1}H NMR (270 MHz, $CDCl_3$) (major diastereoisomer): δ = 7.25 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar), 7.07 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, Ar), 6.85 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, Ar), 5.63 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 3-H), 5.59 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 4-H), 4.68 (d, $^3J_{H,H}$ = 10.6 Hz, 1 H, C*H*$_2$OMe), 4.46 (d, $^3J_{H,H}$ = 10.6 Hz, 1 H, C*H*$_2$OMe), 3.96 (s, 3 H, Ar-OMe), 3.89 (d, $^3J_{H,H}$ = 3.3 Hz, 1 H, 1′-H), 3.74 (s, 3 H, 2-OMe), 3.52 (s, 3 H, CO_2Me), 3.51 (s, 3 H, CH$_2$O*Me*), 3.30 (m, 1 H, 1-H), 2.42 (dd, $^3J_{H,H}$ = 15.2, 10.9 Hz, 1 H, 6β-H), 1.56 (dd, $^3J_{H,H}$ = 15.2, 3.3 Hz, 1 H, 6α-H) ppm. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2245 (CN), 2045 (ν_{sym} CO), 1975 (ν_{asym} CO), 1752 (C=O), 1630, 1384, 1266, 1079, 738 cm^{-1}. HRMS (EI): calcd. for $C_{20}H_{23}FeNO_5$ 413.0926; found 413.0926 $[M - 3\ CO]^+$. Also isolated, was 2,4′-dimethoxy-6-(methoxymethyl)biphenyl (3 mg, 0.012 mmol, 4%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.33 (t, *J* = 7.9 Hz, 1 H, Ar), 7.19–7.13 (m, 3 H, Ar), 6.98–6.89 (m, 3 H, Ar), 4.16 (s, 2 H, CH_2), 3.86 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 3.27 (s, 3 H, CH$_2$O*Me*) ppm. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1598, 1468, 1384, 1260, 1079, 740 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{18}O_3$ 258.1256; found 258.1256 $[M]^+$.

Tricarbonyl{methyl 2-cyano-2-[(2–5-η)-5-(2′,6′-dimethoxyphenyl)-2-methoxy-2,4-cyclohexadien-1α-yl]acetato}iron(0) (27): According to the general procedure, methyl 2-cyanoacetate (112 mg, 1.13 mmol), NaH (60% suspension in mineral oil) (45 mg, 1.13 mmol) and the salt **24** (400 mg, 0.75 mmol) afforded a yellow oil. Column chromatography (50% diethyl ether/50% petroleum ether) afforded **27** as two inseparable diastereoisomers as a pale yellow gum (40 mg, 11%). ^{1}H NMR (270 MHz, $CDCl_3$) (major diastereoisomer): δ = 7.18 (t, $^3J_{H,H}$ = 8.3 Hz, 1 H, Ar), 6.55 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, Ar), 5.64 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 3-H), 5.51 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, 4-H), 3.93 (s, 3 H, Ar-OMe), 3.86 (s, 3 H, Ar-OMe), 3.83 (d, $^3J_{H,H}$ = 3.3 Hz, 1 H, 1′-H), 3.73 (s, 3 H, 2-OMe), 3.49 (s, 3 H, CO_2Me), 3.26 (m, 1 H, 1-H), 2.29 (dd, $^3J_{H,H}$ = 15.2, 11.1 Hz, 1 H, 6β-H), 1.62 (dd, $^3J_{H,H}$ = 15.2, 3.3 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 244 (100) $[M]^+$. IR (film): $\tilde{\nu}_{max}$ = 2250 (CN), 2038 (ν_{sym} CO), 1968 (ν_{asym} CO), 1750 (C=O), 1593, 1473, 1257, 1111, 728 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3071, 1487, 1135 cm^{-1}. HRMS (EI): calcd. for $C_{20}H_{21}FeNO_6$ 427.0718; found 427.0718 $[M - 2\ CO]^+$. Also isolated, was 2,2′,4-trimethoxybiphenyl[53] (42 mg, 0.172 mmol, 23%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.27 (m, 3 H, Ar), 6.95 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, Ar), 6.65 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, Ar), 3.84 (s, 3 H, OMe), 3.74 (s, 6 H, OMe, OMe) ppm. $C_{15}H_{16}O_3$ (244.29): calcd. C 73.8, H 6.6; found C 73.6, H 6.7.

Tricarbonyl{methyl 2-cyano-2-[(2–5-η)-5-{[2′′-cyano-2′′-(methoxycarbonyl)ethenyl]phenyl}-2-methoxy-2,4-cyclohexadien-1α-yl]-acetato]iron(0) (28): According to the general procedure, methyl 2-cyanoacetate (300 mg, 3 mmol), NaH (60% suspension in mineral oil) (120 mg, 3 mmol) and the salt **12b** (150 mg, 0.3 mmol) afforded a yellow oil. Column chromatography (hexane/ethyl acetate gradient; 5:1 to 2:1) afforded **28** as a mixture of inseparable diastereoisomers as a yellow gum (116 mg, 72%). ^{1}H NMR (270 MHz, $CDCl_3$) (major diastereoisomer): δ = 8.69 (s, 1 H, 1′-H), 8.01 (d, $^3J_{H,H}$ = 8 Hz, 1 H, Ar-H), 7.6–7.2 (m, 3 H, Ar-H), 5.58 (dm, $^3J_{H,H}$ = 5.1 Hz, 1 H, 3-H or 4-H), 5.31 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H, 3-H or 4-H), 3.91 (s, 3 H, Ar-OMe), 3.9–3.7 (m, 1 H, CHCN), 3.72 (s, 3 H, CO_2Me), 3.44 (s, 3 H, CO_2Me), 2.70 (dd, $^3J_{H,H}$ = 15.8, 4 Hz, 1 H, 1-H), 2.33 (dd, $^3J_{H,H}$ = 15.8, 11 Hz, 1 H, 6β-H), 1.75 (dd, d, $^3J_{H,H}$ = 15.8, 3 Hz, 1 H, 6α-H); (minor diastereoisomer): δ = 8.67 (s, 1 H, 1′-H), 7.99 (d, $^3J_{H,H}$ = 8 Hz, 1 H, Ar-H), 7.6–7.2 (m, 3 H, Ar-H), 5.60 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H, 3-H or 4-H), 5.28 (d, $^3J_{H,H}$ = 5.1 Hz, 1 H, 3-H or 4-H), 3.92 (s, 3 H, Ar-OMe), 3.9–3.8 (m, 1 H, CHCN), 3.81 (s, 3 H, Ar-CO_2Me), 3.42 (s, 3 H, Ar-CO_2Me), 2.65 (dd, $^3J_{H,H}$ = 15.8, 4 Hz, 1 H, 1-H), 2.47 (dd, $^3J_{H,H}$ = 15.8, 11 Hz, 1 H, 6β-H), 1.80 (dd, $^3J_{H,H}$ = 15.8, 3 Hz, 1 H, 6α-H) ppm. MS (EI): *m*/*z* (%) = 448 (14) $[M - 3\ CO]^+$, 349 (27), 295 (32), 234 (55), 195 (83), 165 (100) $[M]^+$, 152 (55). IR (film): $\tilde{\nu}_{max}$ = 2956, 2925, 2849 (CN), 2048 (ν_{sym} CO), 1968 (ν_{asym} CO), 1735 (C=O) cm^{-1}. HRMS (CI): calcd. for $C_{25}H_{24}FeN_3O_8$ 550.0913; found 550.0910 $[M + NH_4]^+$.

Tricarbonyl(methyl 2-cyano-2-{(2–5-η)-1β-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-2,4-cyclohexadien-1α-yl}acetato)iron(0) (29): According to the general procedure, methyl 2-cyanoacetate (86 mg, 0.871 mmol), NaH (60% suspension in mineral oil) (35 mg, 0.871 mmol) and **18** (250 mg, 0.436 mmol) afforded a yellow oil. Column chromatography (40% diethyl ether/60% petroleum ether) afforded **29** as two inseparable diastereoisomers as a pale yellow gum (139 mg, 0.264 mmol, 61%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.19 (s, 1 H, Ar), 7.03 (s, 1 H, Ar), 6.87 (s, 1 H, Ar), 6.85 (s, 1 H, Ar), 5.35 (dd, $^3J_{H,H}$ = 6.6, 2.3 Hz, 1 H, 3-H), 5.20 (dd, *J* = 6.6, 2.3 Hz, 1 H, 3-H), 4.83 (s, 1 H, 1′-H), 4.75 (s, 1 H, 1′-H), 4.52 (dd, $^3J_{H,H}$ = 17.2, 11.2 Hz, 2 H, C*H*$_2$OMe), 4.18 (dd, $^3J_{H,H}$ = 11.2, 4.3 Hz, 2 H, C*H*$_2$OMe), 3.97 (s, 3 H, Ar-OMe), 3.92 (s, 3 H, Ar-OMe), 3.89 (s, 6 H, Ar-OMe, ArOMe), 3.87 (s, 3 H, 4-OMe), 3.79 (s, 3 H, 4-OMe), 3.68 (s, 3 H, CO_2Me), 3.48 (s, 3 H, CO_2Me), 3.38 (s, 3 H, CH$_2$O*Me*), 3.36 (s, 3 H, CH$_2$O*Me*), 3.32 (m, 2 H, 5-H), 3.07 (m, 2 H, 6β-H, 2-H), 2.82 (d, $^3J_{H,H}$ = 6.6 Hz, 1 H, 2-H), 2.68

(dd, $^3J_{H,H}$ = 14.8, 2.3 Hz, 1 H, 6β-H), 3.30 (dd, $^3J_{H,H}$ = 14.8, 3.3 Hz, 1 H, 6α-H), 2.18 (dd, $^3J_{H,H}$ = 14.8, 3.3 Hz, 1 H, 6α-H) ppm. IR (film): $\tilde{\nu}_{max}$ = 2254 (CN), 2048 (ν_{sym} CO), 1972 (ν_{asym} CO), 1743 (C=O), 1496, 1228, 1123, 914, 734 cm^{-1}. HRMS (EI): calcd. for $C_2H_{25}FeNO_6$ 443.1031; found 443.1031 $[M - 3\ CO]^+$. Also isolated, was tricarbonyl{(2–5-η)-methyl 2-cyano-5-[4′,5′-dimethoxy-2′-(methoxymethyl)phenyl]-2-methoxy-2,4-cyclohexadien-1α-yl]acetato}iron(0) (**30**) (36 mg, 16%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.93 (s, 1 H, Ar), 6.87 (s, 1 H, Ar), 5.68 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, 4-H), 5.58 (dd, $^3J_{H,H}$ = 4.6, 1.0 Hz, 1 H, 3-H), 4.56 (d, $^3J_{H,H}$ = 10.6 Hz, 1 H, CH_2OMe), 4.44 (dd, $^3J_{H,H}$ = 10.6 Hz, 1 H, CH_2OMe), 3.93 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, 1′-H), 3.88 (s, 6 H, Ar-OMe), 3.76 (s, 3 H, 2-OMe), 3.52 (s, 3 H, CO_2Me), 3.51 (s, 3 H, CH_2OMe), 3.34 (m, 1 H, 1-H), 2.37 (dd, $^3J_{H,H}$ = 16.2, 11.2 Hz, 1 H, 6β-H), 1.82 (dd, $^3J_{H,H}$ = 16.2, 2.3 Hz, 1 H, 6α-H) ppm. IR (film): $\tilde{\nu}_{max}$ = 2249 (CN), 2044 (ν_{sym} CO), 1967 (ν_{asym} CO), 1748 (C=O), 1607, 1507, 1343, 1088, 1028, 737 cm^{-1}. HRMS (EI): calcd. for $C_{21}H_{25}FeNO_6$ 443.1031; found 443.1042 $[M - 3\ CO]^+$. Also isolated, was 2-(methoxymethyl)-4,4′,5-trimethoxybiphenyl (11 mg, 9%). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.6 Hz, 2 H, Ar), 7.03 (s, 1 H, Ar), 6.96 (d, J = 8.6 Hz, 2 H, Ar), 6.78 (s, 1 H, Ar), 4.27 (s, 2 H, CH_2OMe), 3.94 (s, 3 H, C4′-OMe), 3.88 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 3.34 (s, 3 H, CH_2O*Me*) ppm. HRMS (EI): calcd. for $C_{17}H_{20}O_4$ 288.1362; found 288.1362 $[M]^+$.

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