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# Selective Synthesis and Reactivity of $\eta^5$-Arylcyclohexadienyliron Complexes

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**Abstract:** A series of aryl-substituted cyclohexadienyliron complexes have been prepared by a general procedure that determines regioselectivity by correctly positioning leaving groups in the precursor complexes. The aryl groups at 1-C or 2-C have been shown to be ω directing by the study of reactions with a representative range of nucleophiles, and these regioselectivity properties have been related to the spectroscopic properties of the cationic cyclohexadienyliron complexes. A high level of electron-donating substituents on the arene, or switching between the $[Fe(CO)_3]$ and $[Fe(CO)_2PPh_3]$ series, reduces the minor *ipso* pathway, improving regiocontrol. Placing opposed directing groups in the arylcyclohexadienyliron complexes reverts reactivity to the *ipso* pathway with stabilised enolate nucleophiles, and when the additional directing group reinforces the effect of the aryl group, the *ipso* pathway is stopped.

**Keywords:** cations · iron · nucleophilic addition · regioselectivity · synthetic methods

## Introduction

The use of carbonyliron complexes in asymmetric synthesis continues to attract sustained attention[1] and forms the central strategy[2] in several recent target molecule syntheses[3,4] that build on the principles successfully established in examples employing cyclohexadienyliron complexes as controlled electrophiles to address stereochemical issues in routes to terpene[5] and alkaloid[6–10] natural products. These syntheses contain key steps that exploit the 100% stereoselectivity[11] of reactions of the organometallic electrophiles. Our own work has concentrated on alkenyl-,[12] alkynyl-[13] and aryl-[8–10] substituted structures in which the activation provided by the metal is employed both in the construction and utilization of the electrophilic carbonyliron complexes. In the aryl series, we have developed a versatile approach that employs the twelve-carbon arylcyclohexadienyl component as a "$C_{12}$ building block",[14] which can correspond to the central portion of many alkaloid targets.

The basis for our approach is to position leaving groups in simple organoiron starting materials. Access in this way to the symmetrical 3-C (**5**, Nu = Ph)[14] and 6-C (**7**, Nu = Ph)[11b,15] regioisomers has already been reported. We describe here the use of leaving groups at 1-C and 2-C of cyclohexadienyliron complexes to give efficient and selective access[16,17] to the unsymmetrical 1-C (**1**, Nu = Ph) and 2-C (**3**, Nu = Ph) substituted structures, and a study of the regiocontrol of their reactions with nucleophiles. The examples described here are all in the racemic series. Parts of this work have been the subject of preliminary communication[18] and the principles reported then have now been shown to be generally applicable and synthetically efficient. Scheme 1 shows the relationship between the positions of leaving groups and the structures of the resulting arylcyclohexadienyliron complexes. The key to gaining control in this chemistry is to understand the regiodirecting properties of substituents on the dienyl complex.[19] In structure **2** (X = OEt),[20] the 1-OEt group directs nucleophile addition to the *ipso* position, bringing nucleophiles in to the site of substitution. In the case of **4** (e.g. X = OMe[21]), the donor substituent is at an internal position, and the directing effect is ω.[19] In these reaction sequences, the OEt and OMe groups serve next as leaving groups in the steps that re-form the cyclohexadienyl complexes. Treatment with acid removes[14,20] the leaving group, either directly or following an acid-catalysed rearrangement of the position of the haptyl section of the

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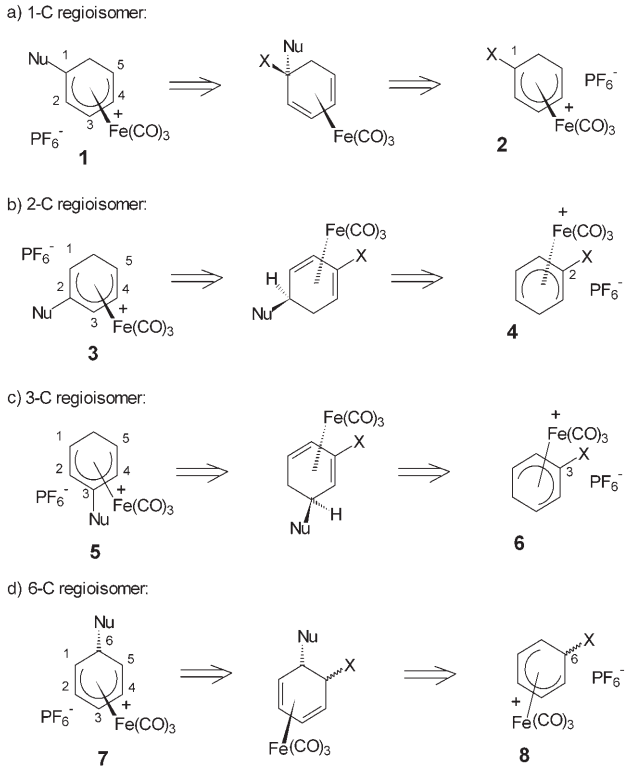


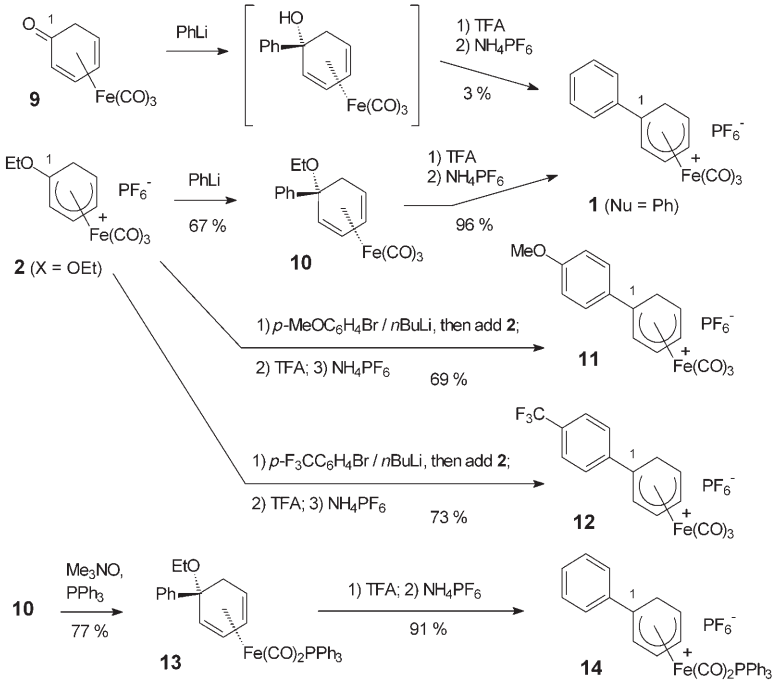

Scheme 1. Preparation of 1-arylcyclohexadienyliron complexes. Correctly positioned leaving groups (X) control the regioselective preparation of substituted cyclohexadienyliron complexes to introduce by nucleophile addition a substituent (Nu) at either 1-C, 2-C, 3-C or 6-C: examples of retrosynthesis to illustrate the design process.

ligand, placing a terminus of the dienyl moiety at the position in the ligand where the leaving group had been. Similarly with **6** and **8**, nucleophile addition followed by removal of the leaving group, produces the correctly substituted cyclohexadienyliron complex, but in these cases, there is no regioselectivity issue in the initial nucleophile addition step.

## Results and Discussion

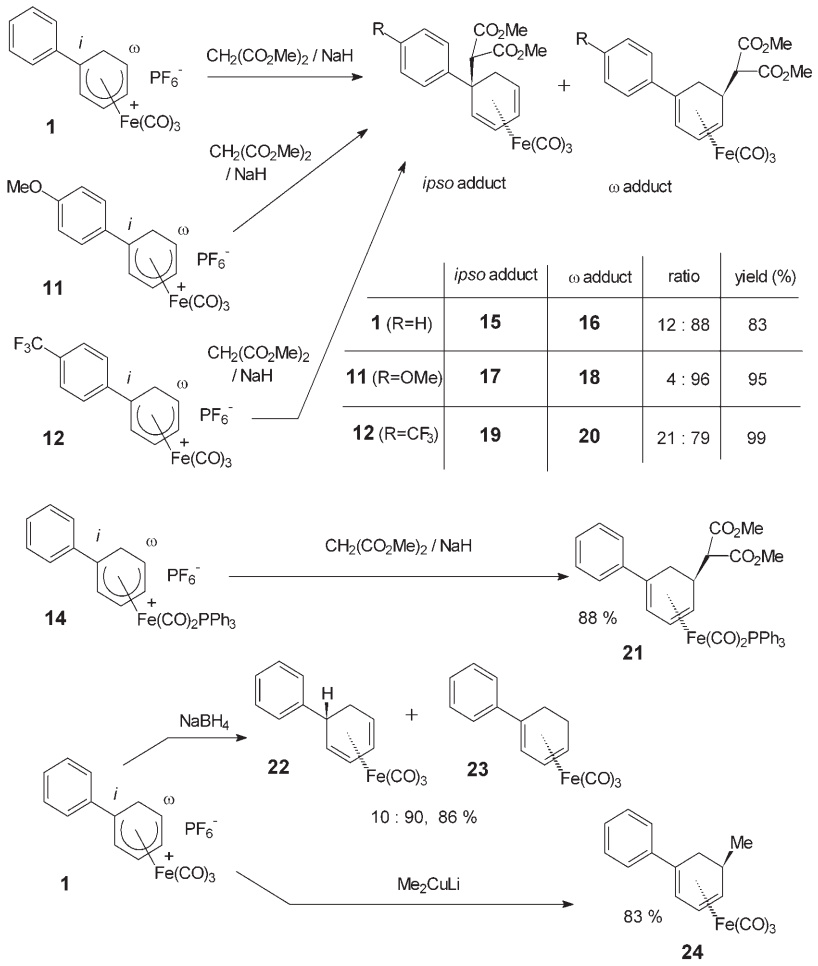
**1-Aryl regioisomer series**: Both the cyclohexadienone complex **9**,[21] and ether **2** (X = OEt),[20] have electrophilic centres in the correct position for the purpose shown in Scheme 1a. Reaction of **9** with phenyllithium (Scheme 2) gave a sensitive intermediate which was treated with trifluoroacetic acid (TFA). The expected product **1** was precipitated by addition of ammonium hexafluorophosphate, but was isolated in only 3% yield. In contrast, reaction of **2** with PhLi gave the intermediate **10** in 67% yield. This product was converted into **1** using TFA and $NH_4PF_6$ in 96% yield. Diphenylzinc and lithium diphenylcuprate reagents were tested with **2**, but gave none of the desired product. The aryllithium method, however, was successfully employed to give the 4′-OMe- and 4′-$CF_3$-substituted analogues **11** and **12** in 69 and 73% yield, respectively, starting from 4-bromoanisole and 4-bromotrifluoromethylbenzene. The products **1**, **11**, and **12** were required for a study of the influence of electronic effects on the regiodirecting properties of the aryl group. Changing auxiliary ligands on the metal can also be a useful way to explore the influence of electronic effects. Reaction of **10** with trimethylamine *N*-oxide and $PPh_3$ (a convenient method[20,23] to replace a CO ligand by the phosphine) gave the dicarbonylphosphine complex **13** in 77% yield. This was converted into the cyclohexadienyliron complex **14** in 91% yield by the same procedure that was employed in the tricarbonyliron series to form **1** (Nu = Ph). These reactions demonstrate that the addition of aryllithium reagents to **2**, followed by leaving group abstraction, provides a general method for regioselective access to the 1-arylcyclohexadienyliron complexes.

The salts **1**, **11**, and **12** were examined (Scheme 3) in reactions with $NaCH(CO_2Me)_2$ to explore the directing effect of the 1-aryl group. In all cases, addition occurred predominantly at the unsubstituted end of the dienyl complex indicating an ω-directing effect from the aryl group [omega/*ipso* (ω/*i*) ratios[19] for 1-$C_6H_4R$ substitution: R = OMe (**11**): 96:4 (95% yield); R = H (**1**, Nu = Ph): 88:12 (83% yield); R = $CF_3$ (**12**): 79:21 (99% yield)]. This contrasts with the report-




Scheme 2. Preparation of 1-arylcyclohexadienyliron complexes.




| | *ipso* adduct | ω adduct | ratio | yield (%) |
|---|---|---|---|---|
| **1** (R=H) | **15** | **16** | 12 : 88 | 83 |
| **11** (R=OMe) | **17** | **18** | 4 : 96 | 95 |
| **12** (R=$CF_3$) | **19** | **20** | 21 : 79 | 99 |

Scheme 3. Examples of nucleophile addition in the 1-aryl series.

ed[24] addition of $LiCH(CO_2Me)_2$ to a 1-phenyl substituted acyclic pentadienyliron complex, where the aryl group directed *ipso*.[25] In general, reactions of electrophilic π complexes with aryl substituents at an end of the π system give mixed results in both stoichiometric[26] and catalytic[27] systems. In the tricarbonyliron case, groups which stabilise positive charge (such as alkoxy and phenyl substituents) might be expected to behave similarly, and since a preference for *ipso* addition in the case of OEt substituents is clearly not a steric effect, it is ascribed to charge/orbital control. In contrast, nucleophile addition to the salts **1**, **11**, and **12** presumably corresponds to a steric effect, perhaps due to the effect of the presence of the $CH_2$ bridge in the cyclohexadienyl examples influencing the conformational preferences of the aryl group, compared to the acyclic case where the *ipso* pathway is open. However, although the effect is small, changing from electron-poor to electron-rich arenes is seen to increase the ω-directing power of the substituent. The ω-directing effect is thus not exclusively steric in origin. It appears that the electronic component operates by influencing the level of reactivity of the dienyliron cation, as the least electrophilic structure gives rise to the greatest degree of control, in line with the "reactivity–selectivity principle".[28]

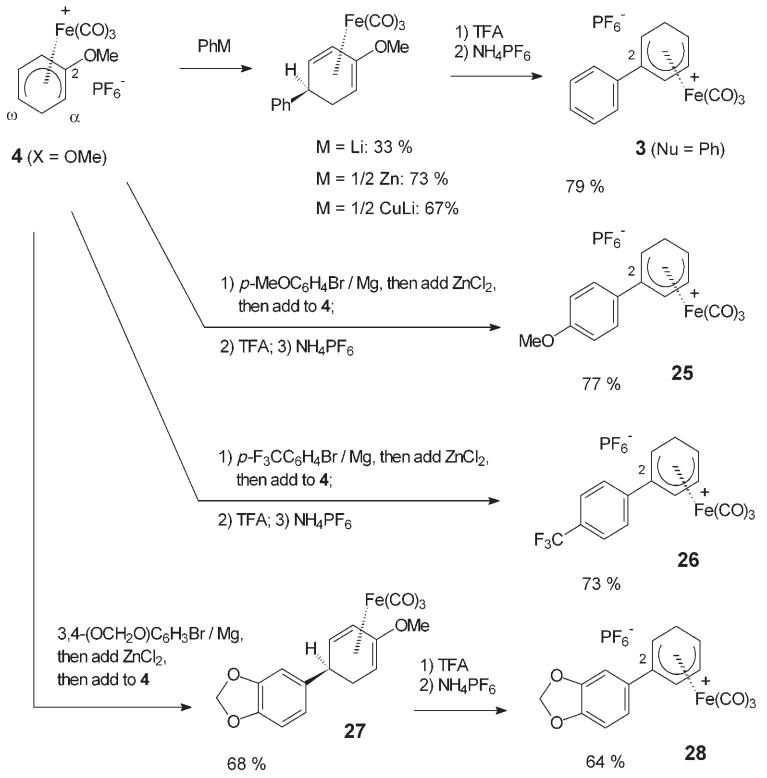
Addition of $NaCH(CO_2Me)_2$ to the $[Fe(CO)_2PPh_3]$ complex **14** (in which the phosphine ligand in place of CO substantially reduces[29] electrophilicity) gave results in accord with this interpretation,[30] as only the ω-adduct **21** was isolated in 88% yield. Care must be taken in interpreting this observation, however, as examples have been reported[31] where the conformational preferences of the $Fe(CO)_2$(phosphine) group appear to influence the regioselectivity of nucleophile addition (preferential addition opposite to the phosphine ligand has been described). For this to be the explanation in our case, however, the $PPh_3$ group would need to be beside the phenyl substituent on the cyclohexadienyl ligand.

The reactivity properties of the "parent" 1-phenyl-substituted complex were examined further with a selection of nucleophiles. Reduction with $NaBH_4$ gave a similar outcome [ω/*ipso* ratio: 90:10 (86% yield)] to that described above for $NaCH(CO_2Me)_2$. $Me_2CuLi$, however, proved more fully regiocontrolled, giving only the ω-adduct **24** in 83% yield.[32] In summary, these results indicate that terminally-positioned aryl directing groups give an ω selectivity, but with the more powerfully electrophilic examples (4′-$CF_3$ or H as substituents), and a suitable nucleophile (e.g. stabilized enolates), the *ipso* pathway is accessible (but only as a minor contribution to the reaction).

**2-Aryl regioisomer series**: As indicated in Scheme 1, access to structures with internally positioned aryl directing groups can be addressed (Scheme 4) by starting with the 2-methoxycyclohexadienyliron complex **4** (X = OMe).[21] Unlike the 1-alkoxy case, the addition of phenyllithium to **4** gave poor results (33% yield). The "softer" nucleophiles $Ph_2Zn$ and $Ph_2CuLi$ proved far superior, giving 73 and 67% yields, respectively. The product was reacted with TFA, followed by addition of ammonium hexafluorophosphate to produce the 2-phenyl salt **3** (Nu = Ph) in 79% yield as the only regioisomer.

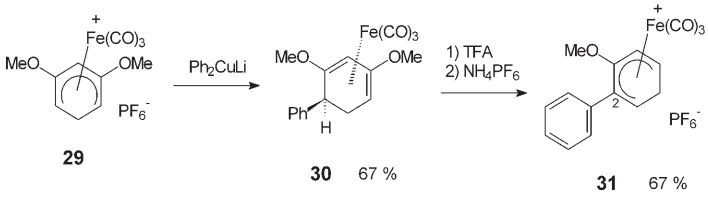
By omitting the purification of the intermediate adduct, the efficiency of production of the 2-phenyl salt can be improved to 79% for the two steps from **4**, generating the Grignard reagent from bromobenzene before adding zinc di-




Scheme 4. Preparation of 2-arylcyclohexadienyliron complexes.

chloride to form $Ph_2Zn$. This organozinc procedure was then applied with 4-bromoanisole and 4-bromotrifluoromethylbenzene to give the corresponding 2-arylcyclohexadienyliron complexes **25** and **26** in 77 and 73% yield, respectively. In a similar way, the 3′,4′-methylenedioxyaryl adduct **27** was obtained in 68% yield and converted into the 2-aryl salt **28** (64% yield). A more highly substituted example was also prepared (Scheme 5), starting from tricarbonyl[(1,2,3,4,5-η)-2,4-dimethoxycyclohexadienyl]iron(1+) hexafluorophosphate(1−) (**29**)[33] and exploiting our established[14] control of the acid-catalysed isomerisation of cyclohexadieneiron complexes, which retain the greatest number of charge-stabilising substituents on the cationic intermediates in the rearrangement reaction. Reaction of **29** with lithium diphenylcuprate afforded **30** in 67% yield, and this was converted into the single regioisomer **31**, again in 67% yield.




Scheme 5. Examples of nucleophile addition in the 2-aryl series.

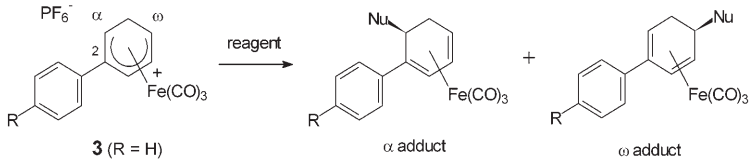
A selection of nucleophiles were used in reactions with the 2-aryl salts (Table 1) to make a comparison with the 1-aryl series. The reduction with sodium borohydride provided an easy test reaction [ω:α ratios[19] for 2-$C_6H_4R$ substitution: R = OMe (**25**): 86:14 (99% yield); R = H (**3**, Nu = Ph): 85:15 (92% yield); R = $CF_3$ (**26**): 80:20 (97% yield)]. Again, the least powerfully electrophilic example (**3**, R = OMe) gave the greatest access to the major pathway, and the results show that like the 1-aryl case, 2-aryl substituents on cyclohexadienyliron complexes direct strongly ω. The anisyl and phenyl examples were also examined using the stabilised enolate nucleophile NaCH-$(CO_2Et)_2$. With the more electron-rich arene, only ω addition producing **39** was observed, but with the phenyl directing group a small amount of the α-adduct **37** was also formed [ω/α ratios for 2-$C_6H_4R$ substitution: R = OMe (**25**): >99:<1 (80% yield); R = H (**3**, Nu = Ph): 85:15 (78% yield)]. Similarly with $Ph_2CuLi$, the anisyl case gave the greatest regioselectivity [ω/α ratios for 2-$C_6H_4R$ substitution: R = OMe (**25**): 95:5 (80% yield); R = H (**3**, Nu = Ph): 90:10 (83% yield); R = $CF_3$ (**26**): 89:11 (78% yield)]. The use of KCN as the nucleophile showed relatively poor control [ω/α ratio in the anisyl case: 88:12 (80% yield)] with similar results with a simple phenyl directing group [85:15 (92% yield)].

**Opposed directing groups in the 1-aryl regioisomer series**: Our first application[8] of aryl-substituted cyclohexadienyliron complexes in synthesis had addressed the small alkaloid *O*-methyljoubertiamine, with the intention of demonstrating that the quaternary centre in this structure could be made by a sequence of two nucleophile addition steps, culminating in addition of a stabilised enolate *ipso* to the aryl group. Since the aryl group needed for *O*-methyljoubertiamine carries a 4′-methoxy substituent, this can be viewed as a difficult test of the methodology, as this electron-rich arene would be strongly ω directing allowing the least access to the *ipso* electrophilic centre.

The approach (Scheme 6) was to use a second (internally positioned) OMe directing group to oppose the natural directing effect of the aryl group, as pioneered by Pearson[4–6] with alkyl groups on the far side of the dienyl complexes. This proved successful, and the method was extended to a formal total synthesis of lycoramine.[9] Based on the procedures outlined in Scheme 1, the correct starting material for these arylcyclohexadienyliron complexes is the 1,4-dime-

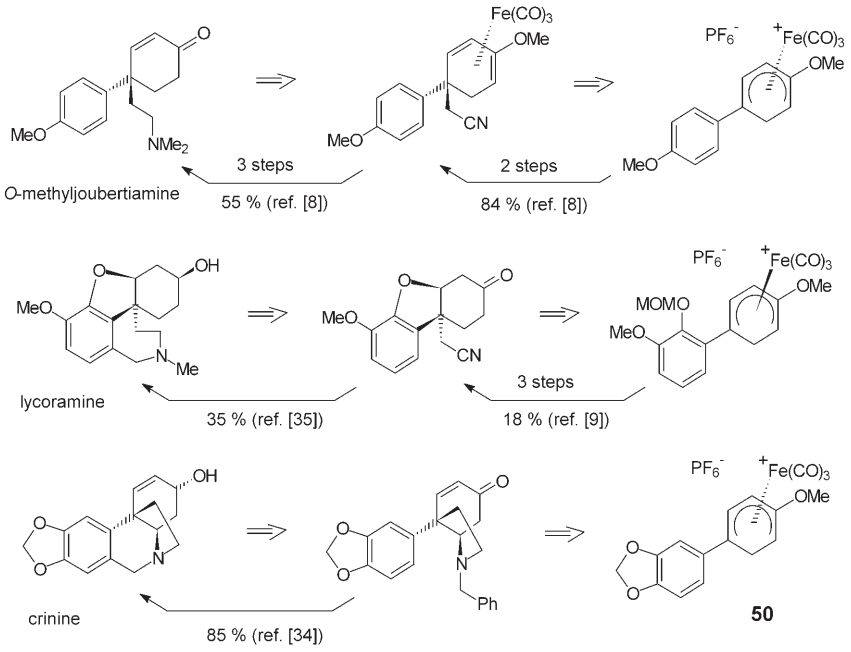
  

Table 1. Examples of nucleophile addition in the 2-aryl series.




**3** (R = H) α adduct ω adduct

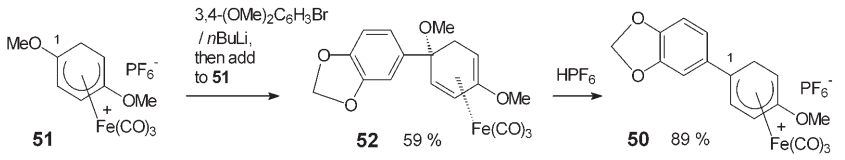
| | Reagent | Nu | α Adduct | ω Adduct | Ratio | Yield [%] |
|---|---|---|---|---|---|---|
| **3** (R = H) | $NaBH_4$ | H | **23** | **32** | 15:85 | 92 |
| **25** (R = OMe) | $NaBH_4$ | H | **33** | **34** | 14:86 | 99 |
| **26** ($R = CF_3$) | $NaBH_4$ | H | **35** | **36** | 20:80 | 97 |
| **3** (R = H) | $CH_2(CO_2Me)_2$/NaH | $CH(CO_2Me)_2$ | **37** | **38** | 15:85 | 78 |
| **25** (R = OMe) | $CH_2(CO_2Me)_2$/NaH | $CH(CO_2Me)_2$ | – | **39** | – | 80 |
| **3** (R = H) | $Ph_2CuLi$ | Ph | **40** | **41** | 10:90 | 83 |
| **25** (R = OMe) | $Ph_2CuLi$ | Ph | **42** | **43** | 5:95 | 80 |
| **26** ($R = CF_3$) | $Ph_2CuLi$ | Ph | **44** | **45** | 11:89 | 78 |
| **3** (R = H) | KCN | CN | **46** | **47** | 15:85 | 92 |
| **25** (R = OMe) | KCN | CN | **48** | **49** | 12:88 | 80 |




Scheme 6. Examples of applications of the opposed regiodirecting effects of aryl (this work) and methoxy (see syntheses by Pearson[5a–d,6] and by Knölker[3,7]) groups in retrosynthetic analysis for organoiron approaches to *O*-methyljoubertiamine,[8] lycoramine[9] and crinine.[34]

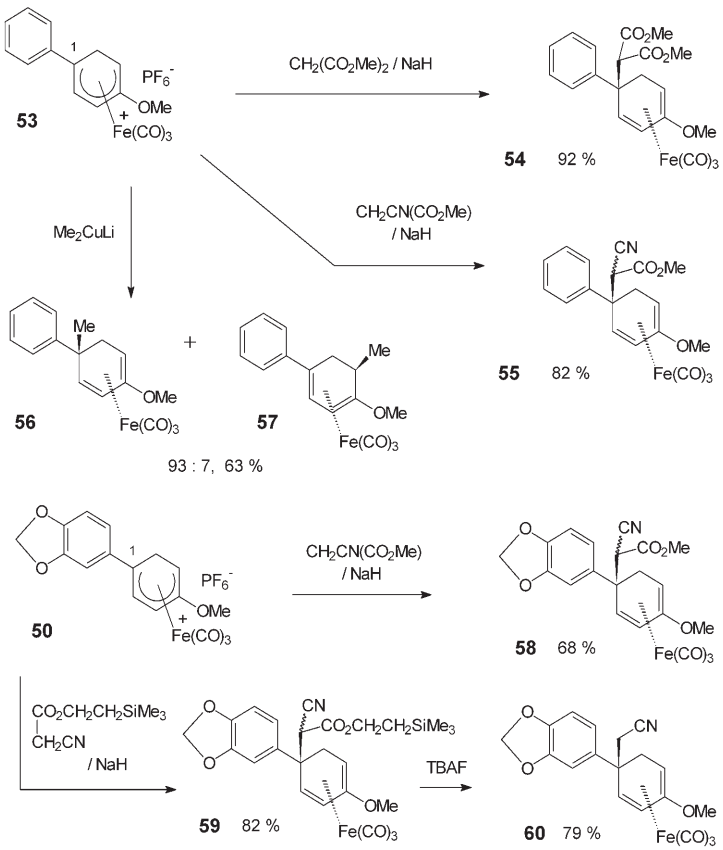
thoxy-substituted salt **51**[8] (Scheme 7) in which both OMe groups direct nucleophiles to the same position in the cyclohexadienyl ligand (they are "mutually reinforcing"[19]). This provides general access to the 1-aryl-4-methoxy series. Our method[10] to prepare the parent phenyl-substituted example **53** with phenyllithium (70% yield) was superior to the use of lithium diphenylcuprate (23%) or diphenylzinc (11%) and the step to remove the methoxy group was highly efficient (reaction with TFA/$NH_4PF_6$: 98%). This successful approach[8,10] has now been extended to the 3′,4′-methylenedioxy example **50** which has the correct aromatic substitution pattern (Scheme 6) for the alkaloid crinine.[34] The required cyclohexadienyliron complex **50** was prepared by generation of the aryllithium reagent[36] from 3,4-methylenedioxybromobenzene, addition to the 1,4-dimethoxy salt **51** (59%), and reaction with hexafluorophosphoric acid (89%).

The nucleophiles $NaCH(CO_2Me)_2$, $NaCH(CN)CO_2Me$, and $Me_2CuLi$ were tested first (Scheme 8) with the parent 1-phenyl-4-methoxy salt **53**. The stabilized enolates $NaCH(CO_2Me)_2$, $NaCH(CN)CO_2Me$ gave the expected adducts **54** and **55** with the required quaternary centres (nucleophile addition *ipso* to the Ph group: 92, 82% yields, respectively). The malonate adduct **54** was examined in a $^1$H NMR NOE experiment, irradiating the CH of the malonate $CH(CO_2Me)_2$ group at $\delta$ 3.83 ppm, to confirm the relative stereochemistry of nucleophile addition. The 6α-H was enhanced by 5% (an 11% enhancement of the Ph signal was also observed). With the dimethylcuprate reagent, regiocontrol was similar but less complete, and a 93:7 mixture of adducts **56** and **57** was isolated in 63% yield. Surprisingly, when methyllithium was used instead of the dimethylcuprate reagent, selectivity was reversed, but as the yield for this reaction was low (19%) this may not be a true switch in regioselectivity. In general, while organolithium reagents are the best choice with cyclohexadienyliron complexes bearing 1-C alkoxy substituents, they often perform badly with other cyclohexadienyliron com-



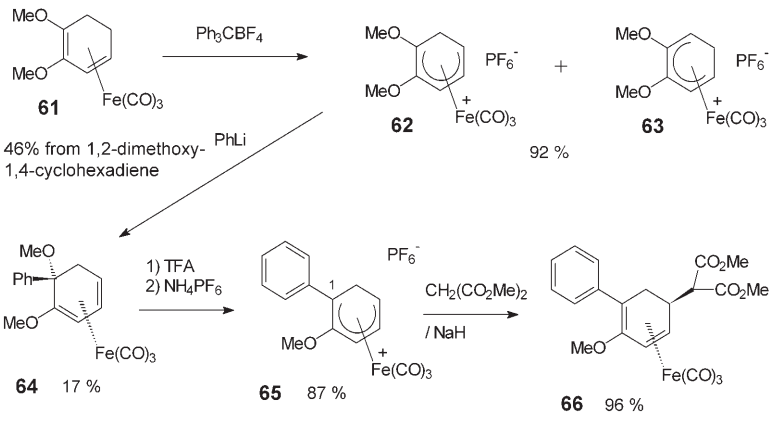

Scheme 7.




Scheme 8.

plexes. For this reason, this apparent switch in regioselectivity has not yet been further examined as it is unlikely to provide a synthetically efficient procedure. The reaction, however, did serve to provide a pure sample of **57**. The enolate $NaCH(CN)CO_2Me$ was reacted with **50** to produce **58** in 68% yield. In a trial series of experiments towards crinine, this successful formation of the required quaternary centre was also examined with the enolate $NaCH(CN)CO_2CH_2CH_2SiMe_3$[37] which we used in our work on the *O*-methyljoubertiamine[8] and lycoramine[10] targets. Addition to **50** proved similarly well regiocontrolled and gave **59** in 82% yield. The mixture of diastereoisomers obtained in this step was simplified to give the single stereoisomer **60** (79% yield) to demonstrate that the addition of the enolate to **50** was completely selective for reaction at the face of the cyclohexadienyliron complex opposite to the metal.




Scheme 9.

**Mutually reinforcing directing groups in the 1-aryl regioisomer series**: Starting from tricarbonyl[(1,2,3,4-η)-1,2-dimethoxycyclohexadiene)iron (**61**),[38] hydride abstraction (Scheme 9) afforded a mixture of regioisomers **62** and **63**. As expected[38] (opposed directing groups are present), the cyclohexadienyliron cation **62** gave a mixture of regioisomers when reacted with phenyllithium, but sufficient of the required *ipso* adduct **64** could be obtained pure by chromatography to allow tricarbonyl[(1,2,3,4,5-η)-1-phenyl-2-methoxycyclohexadienyl)iron(1+) hexafluorophosphate(1−) (**65**) to be prepared.

In this 1-phenyl-2-methoxy-substitued electrophile **65**, both directing groups promote nucleophile addition to the unsubstituted terminus of the dienyl ligand. This was confirmed by reaction with $NaCH(CO_2Me)_2$ which gave a single product **66** corresponding to ω selectivity in 96% yield.

**Structural and spectroscopic properties of the arylcyclohexadienyliron complexes**: Although both the 1- and 2-aryl substituents direct ω, the results obtained raise the possibility that the efficiency of the regiocontrol process depends on the level of reactivity of the dienyliron complex as an electrophile, with the most reactive examples giving highest contribution from the less-favoured addition pathway. A high level of electron density on the aromatic ring, on the other hand, tends to correspond to lower reactivity and better selectivity. The relative positions of the vibrational stretching bands of the carbonyl ligands give a good indication of the extent of intramolecular transfer of electron density between the aromatic ring and the dienyliron complex. Lower energy vibrational stretching bands indicate reduced positive charge on the metal complex, and so should correspond to reduced electrophilicity. The IR data presented in Table 2, correspond well to the directing ability of the substituents. The effect of electron-donating and electron-withdrawing substituents on the IR spectrum is greater (range: 9 $cm^{-1}$) in the 1-aryl series than in the 2-aryl series (range: 3 $cm^{-1}$). Similarly, the variation in selectivity for the ω pathway is greater in the 1-aryl series.

Table 2. Spectroscopic data for arylcyclohexadienyliron hexafluorophosphate complexes (NMR data in [$D_6$]acetone).

| | 1-Ph **1** | 2-Ph **3** | 1-(4′-OMe-Ar) **11** | 2-(4′-OMe-Ar) **25** | 1-(4′-$CF_3$-Ar) **12** | 2-(4′-$CF_3$-Ar) **26** | 2-(3′,4′-$OCH_2O$Ar) **28** |
|---|---|---|---|---|---|---|---|
| NMR $\delta_H$ [ppm] | | | | | | | |
| 1-H | – | 5.06 d[a] | – | 4.64 d[a] | – | 5.12 d[a] | 4.97 d[b] |
| 2-H | 6.65 d[c] | – | 6.43 d[d] | – | 6.81 d[d] | – | – |
| 3-H | 7.70 m | 7.70–7.53 | 7.51 t[d,e] | 7.56 d[e] | 7.70 t[d,e] | 8.11 d[f] | 7.92 d[g] |
| 4-H | 6.44 t[e,h] | 6.40 t[i,j] | 6.40 t [e,h] | 5.96 t[k,l] | 6.47 t[e,h] | 6.44 dd[f,m] | 6.36 t[g,n] |
| 5-H | 4.77 t[j,k] | 4.78 t[j,k] | 4.70 t[h,o] | 4.48 t[l,p] | 4.89 t[h,o] | 4.84 dd[m,o] | 4.73 t[j,q] |
| 6β-H | 3.95 dd[r,s] | 3.39 dt[b,r,s] | 4.00 dd[o,s] | 3.12 dt [a,o,t] | 4.01 dd[o] | 3.44 dt[a,u] | 3.32 dt[b,r,t] |
| 6α-H | 2.68 d[s] | 2.31 d[s] | 2.66 d[s] | 2.04 d[t] | 2.72 d[s] | 2.31 d[u] | 2.25 d[t] |
| 2′-H | 7.7–7.5 | 8.1–8.0 | 7.73 dm[v] | 7.82 dm[v] | 7.8–8.2 | 8.30 d[w] | 7.60 s |
| 3′-H | 7.7–7.5 | 7.7–7.5 | 7.14 dm[v] | 7.02 dm[v] | 7.8–8.2 | 7.93 d[w] | – |
| 4′-H | 7.7–7.5 | 8.1–8.0 | – | – | – | – | – |
| 5′-H | 7.7–7.5 | 7.7–7.5 | 7.14 dm[x] | 7.02 dm[x] | 7.8–8.2 | 7.93 d[y] | 7.01 d[y] |
| 6′-H | 7.7–7.5 | 8.1–8.0 | 7.73 dm[x] | 7.82 dm[x] | 7.8–8.2 | 8.30 d[y] | 7.59 d[y] |
| Ar-OMe | – | – | 3.93 s | 3.84 s | – | – | – |
| O-$CH_2$-O | – | – | – | – | – | – | 6.07 s |
| NMR $\delta_C$ [ppm] | | | | | | | |
| 1-C | 88.8 | 57.3 | 92.4 | 55.5 | 82.7 | 58.4 | 55.7 |
| 2-C | 96.2 | 121.8 | 95.9 | 123.2 | 98.5 | 119.6 | 123.1 |
| 3-C | 87.5 | 87.5 | 86.7 | 86.3 | 88.0 | 88.1 | 86.7 |
| 4-C | 101.8 | 100.3 | 100.8 | 100.8 | 102.4 | 100.6 | 100.7 |
| 5-C | 63.3 | 67.5 | 61.8 | 67.0 | 64.7 | 68.2 | 67.5 |
| 6-C | 27.4 | 25.8 | 27.2 | 25.8 | 27.3 | 25.7 | 25.9 |
| 1′-C | 135.1 | 133.4 | 126.1 | 123.5 | 139.9 | 136.7 | 125.7 |
| 2′-C | 127.4 | 129.0 | 129.7 | 130.8 | 128.2 | 130.0 | 124.6 |
| 3′-C | 130.6 | 130.3 | 116.2 | 115.6 | 127.4 q[A] | 127.8 q[A] | 149.9 |
| 4′-C | 132.2 | 131.8 | 163.7 | 164.3 | 132.5 q[B] | 133.8 q[C] | 152.6 |
| 5′-C | 130.6 | 130.3 | 116.2 | 115.6 | 127.4 q[A] | 127.8 q[A] | 109.6 |
| 6′-C | 127.4 | 129.0 | 129.7 | 130.8 | 128.2 | 130.0 | 108.6 |
| Ar-OMe | – | – | 56.1 | 56.0 | – | – | – |
| O-$CH_2$-O | – | – | – | – | – | – | 103.5 |
| Ar-$CF_3$ | – | – | – | – | 124.8 q[D] | 124.8 q[E] | – |
| Fe-CO | 203.8 | 202.7 | 203.6 | 203.6 | 202.7 | 202.8 | 203.6 |
| IR $\nu_{CO}$ [$cm^{-1}$] | | | | | | | |
| sym | 2109 | 2112 | 2105 | 2111 | 2112 | 2113 | 2113 |
| asym | 2061 | 2065 | 2056 | 2063 | 2066 | 2067 | 2063 |
| weighted mean[F] | 2077 | 2081 | 2072 | 2079 | 2081 | 2082 | 2080 |

[a] $^3J_{1\text{-H},6\beta\text{-H}}=6$ Hz. [b] $^3J_{1\text{-H},6\beta\text{-H}}=6.5$ Hz. [c] $^3J_{2\text{-H},3\text{-H}}=5.5$ Hz. [d] $^3J_{2\text{-H},3\text{-H}}=6$ Hz. [e] $^3J_{3\text{-H},4\text{-H}}=6$ Hz. [f] $^3J_{3\text{-H},4\text{-H}}=5.5$ Hz. [g] $^3J_{3\text{-H},4\text{-H}}=6.5$ Hz. [h] $^3J_{4\text{-H},5\text{-H}}=6$ Hz. [i] Apparent triplet because $^3J_{3\text{-H},4\text{-H}}=6$ Hz $\approx{}^3J_{4\text{-H},5\text{-H}}$. [j] $^3J_{4\text{-H},5\text{-H}}=6.5$ Hz. [k] Apparent triplet because $^3J_{3\text{-H},4\text{-H}}=6$ Hz $\approx J_{4\text{-H},5\text{-H}}$. [l] $^3J_{4\text{-H},5\text{-H}}=7$ Hz. [m] $^3J_{4\text{-H},5\text{-H}}=7.5$ Hz. [n] Apparent triplet because $^3J_{4\text{-H},5\text{-H}}=6.5$ Hz $\approx{}^3J_{3\text{-H},4\text{-H}}$. [o] $^3J_{5\text{-H},6\beta\text{-H}}=6$ Hz. [p] $^3J_{5\text{-H},6\beta\text{-H}}=7$ Hz. [q] Apparent triplet because $^3J_{5\text{-H},6\beta\text{-H}}=5.5$ Hz $\approx{}^3J_{4\text{-H},5\text{-H}}$. [r] $^3J_{5\text{-H},6\beta\text{-H}}=6.5$ Hz. [s] $^3J_{6\alpha\text{-H},6\beta\text{-H}}=16$ Hz. [t] $^3J_{6\alpha\text{-H},6\beta\text{-H}}=15.5$ Hz. [u] $^3J_{6\alpha\text{-H},6\beta\text{-H}}=15$ Hz. [v] $^3J_{2'\text{-H},3'\text{-H}}=9$ Hz. [w] $^3J_{2'\text{-H},3'\text{-H}}=8$ Hz. [x] $^3J_{3'\text{-H},6'\text{-H}}=9$ Hz. [y] $^3J_{3'\text{-H},6'\text{-H}}=8$ Hz. [A] $^3J_{F,3'\text{-C}}$ and $^3J_{F,5'\text{-C}}=3.8$ Hz. [B] $^2J_{F,4'\text{-C}}=32.5$ Hz. [C] $^2J_{F,4'\text{-C}}=35.3$ Hz. [D] $^1J_{F,C}=272$ Hz. [E] $^1J_{F,C}=273$ Hz. [F] In the IR spectra of tricarbonyliron complexes, there is one symmetric ($\nu_{sym}$) and two antisymmetric ($\nu_{asym}$) Fe-CO vibrational modes. When the antisymmetric bands are not resolved, the weighted mean is calculated as $(\nu_{sym}+2\nu_{asym})/3$.

The positions of carbon resonances for the dienyliron moiety in $^{13}C$ NMR spectra provide another widely accepted measure of positive charge within the ligand,[39] and this has been employed[39a] with success to interpret regiocontrol in the reactions of cyclohexadienyliron complexes with nucleophiles. In order to gain reliable $^{13}C$ NMR data to compare with the inferences drawn from IR spectroscopy, unambiguous assignments of the spectra were needed, and representative examples were chosen for $^{13}C$,$^1H$ correlation spectroscopy. In the 1-phenylcyclohexadienyliron case, the $^1H$ NMR resonances of the dienyl portion are relatively easy to assign, as 2-H appears as a doublet, while the rest of the hydrogens have triplet resonances. Because of its position at the centre of the dienyl structure, 3-H is typically at the highest chemical shift, and in the spectrum of **1** (Nu = Ph), appears at about $\delta$ 7.7 ppm, just visible down-field from the resonances of the phenyl group. The resonances for 2-H and 4-H are found at similar chemical shifts at about $\delta$ 6.5 ppm, leaving the triplet at 4.77 ppm to be assigned as 5-H. In common with other cyclohexadienyl complexes, the $CH_2$ bridge at 6-C is bent away from the iron, and 6α-H appears only as a doublet (the geminal coupling $^3J_{6\alpha\text{-H},6\beta\text{-H}}=15$–16 Hz). 6β-H, on the other hand, also couples to 5-H (coupling $^3J_{6\text{-H},6\beta\text{-H}}=6.0$–6.5 Hz), and appears as a doublet of doublets. This accounts for the apparent triplet observed for 5-H, since the coupling constants to 6β-H and 4-H are similar. With the $^1H$ NMR assignments on a firm footing, $^{13}C$,$^1H$ correlation completed the assignment of most of the signals in the $^{13}C$ NMR spectrum. Two quaternary carbons are present in this structure, and these resonances could be identified by their low relative intensities, and their absence from a DEPT spectrum. The signal at $\delta$ 88.8 ppm was assigned to

1-C, as the other signal (135.1 ppm) was in a typical position for a substituted carbon on an aromatic ring. All the other $^{13}C$ resonances clearly arose from C-H positions except for one signal at high field (27.4 ppm) which showed as a $CH_2$ in the DEPT experiment, and correlated with both 6α-H and 6β-H in the 2D spectrum. Comparison of the positions of resonances for 1-C–5-C (Table 2) reveals a clear pattern providing secure assignments for the other 1-arylcyclohexadienyliron complexes. As might be expected, the positions of the resonances for 5-C (the carbon ω to the aromatic ring) show a clear influence (range: 2.9 ppm) from the substituent on the arene, with the electron-donating OMe group giving the lowest chemical shift (61.8 ppm) and the electron-withdrawing $CF_3$ group giving the highest chemical shift (64.7 ppm). This provides evidence that electron transfer from the arene to the dienyl complex is significant. The signals for 1-C (the carbon bearing the aromatic ring), however, show the opposite trend with a greater range of values (9.7 ppm). The electron-donating OMe group produces the highest chemical shift at 1-C (92.4 ppm) and the electron-withdrawing $CF_3$ group gives the lowest chemical shift (82.7 ppm). This can be explained if there is increased double bond character at the central C–C bond joining the aromatic ring to the dienyliron complex in the case of the electron-rich methoxyarene, as would be expected as a consequence of greater intramolecular electron transfer which increases the π overlap at this central bond.

The $^1H$ NMR spectra in the 2-aryl series are more difficult to assign. While 3-H is easily identified as a doublet, and 4-H can be assigned on the basis of its chemical shift at around $\delta$ 6 ppm, the crucial 1-H and 5-H hydrogens (which are located at the electrophilic centres for α and ω addition) are more difficult to distinguish. Without this information, however, correlation spectroscopy cannot be used to assign the 1-C (α) and 5-C (ω) positions. This problem was solved with a NOESY spectrum of tricarbonyl[(1,2,3,4,5-η)-2-(4′-trifluoromethylphenyl)cyclohexadienyl]iron hexafluorophosphate (**26**) which showed a cross-peak between signals at $\delta$ 5.12 and 8.11 ppm. This allows 1-H to be assigned as 5.12 ppm (and also distinguishes the similar pairs of hydrogens on the *para*-substituted aromatic ring). Cross-peaks were also observed between the hydrogen at $\delta$ 6.46 ppm (4-H) and those at 8.11 ppm (3-H) and 4.84 ppm (5-H). A gCOSY spectrum was obtained to confirm the assignments of 4-H and 5-H. This experiment also demonstrated that the hydrogen assigned as 1-H couples only with 6β-H, while 5-H couples with both 6β-H and 4-H. A gHSQC spectrum was then used to assign the $^{13}C$ resonances and in this way 1-C was found to correspond to the signal at 58.4 ppm and 5-C was assigned as 68.2 ppm. Similar procedures allowed the unambiguous assignment of the $^{13}C$ resonances of tricarbonyl[(1,2,3,4,5-η)-1-phenyl-4-methoxycyclohexadienyl]iron hexafluorophosphate (**53**). Since differences in the substitution on the arene have only a small effect on the positions of the dienyl resonances, the remaining data presented in Table 2 could be assigned on the basis of these results.

In the 1-aryl series, the effect of changing R in 1-$C_6H_4R$ is clear in the position of resonances with signals for C-2-C-5, which move progressively to higher field when progressing from R = $CF_3$ to R = OMe. This is consistent with the presence of less positive charge at these carbons with the donor group on the arene. The IR vibrational bands of the tricarbonyliron group show the same trend, and this can be most clearly visualised by calculating the weighted means [($\nu_s$ + 2$\nu_{as}$)/3] of the $\nu_s$ and $\nu_{as}$ band positions (Table 2). As discussed above, the trend in the positions of the $^{13}C$ resonances of 1-C, however, ran in the opposite direction, an effect ascribed to a consequence of increasing π-overlap character in the centre of the complex. In the 2-aryl series, the 2-C chemical shifts move to lower field when progressing from R = $CF_3$ to R = OMe, but 5-C shows the same trend that was seen with C-1 substitution.

Since both 1-Ar and 2-Ar substituents have been found to be ω directing (nucleophiles add at 5-C), the positions of $^{13}C$ NMR resonances for the 5-C carbons were examined in more detail (Figure 1). The chemical shift values for 5-C and

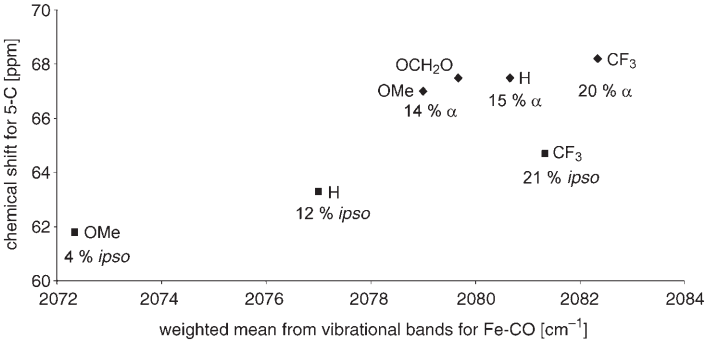



Figure 1. Tools to assess the degree of positive charge in the dienyliron complexes: relationship between the effects of positive charge on the Fe–CO vibrational bands ($\nu_{CO}$) in the IR spectrum and chemical shifts ($\delta_C$) of 5-C in the $^{13}C$ NMR spectrum (proportions of nucleophile addition by the minor α/*ipso* pathways are shown below each data point). ■ donates the 1-aryl series and ◆ donates the 2-aryl series. The labels indicate substituents at 4′-C (see Scheme 3 and Table 1) and 3′-C,4′-C in the case of $OCH_2O$ (Scheme 7).

the IR vibrational frequencies (the weighted means of the symmetric and antisymmetric vibrational bands) rise together as the positive charge on the complex increases as a consequence of the nature of the substitution on the arene, establishing that both are valid tools to measure positive charge in these complexes. The effect is most marked in the 1-aryl series, but the clear correspondence between $^{13}C$ NMR and IR properties is also apparent in the data for 2-arylcyclohexadienyliron complexes. The vibrational frequency of $\nu_{CO}$, however, is a measure of positive charge on the complex as a whole, while $\delta_C$ for 5-C is a measure of positive charge at the ω-electrophilic centre itself. If the ω-directing effect of the aromatic ring was a consequence of charge control, high ω/*ipso* and ω/α ratios would be expected to correspond to high values for $\delta_C$. In fact, the opposite is true; it is the level of positive charge on the complex as a

whole that facilitates the minority *ipso* and α pathways. The highest weighted means for the symmetric and antisymmetric vibrational bands correspond to the greatest percentages for nucleophile addition at the *ipso* and α electrophilic centres.

The effect of an internally-positioned OMe group on the position of the $^{13}C$ resonances of cyclohexadienyliron complexes has been established.[39a] The carbon at the end of the dienyl system adjacent to the OMe group becomes much less positively charged because of donation from the lone pairs of electrons on the oxygen. The resonance shifts from 63.7 ppm[40a] in the unsubstituted cyclohexadienyliron(1+) case[40] to 43.8 ppm[39a] when beside the methoxy group. The far end of the dienyl complex is barely effected (in fact there is a slight rise in $\delta_C$ to 65.8 ppm). This same effect can be seen in the 1-phenyl-4-methoxycyclohexadienyl complex **53**.[10] The resonance for 5-C (next to the OMe group) is shifted to a very similar value (43.4 ppm) and is no longer the preferred site for nucleophile addition. This trend was confirmed in the series of compounds prepared for our approach to the alkaloid crinine, with 5-C of the 1-(3′,4′-methylendioxyphenyl)-4-methoxy salt **50** appearing at 43.3 ppm. When the OMe group is beside the Ph substituent (in **65**), however, $\delta_C$ for 1-C is lowered from 88.8 to 65.0 ppm (a drop of about 20 ppm, similar to that seen in the case which lacks the aryl group[39a]). The resonance for C-5 is also shifted, but by nowhere near the same amount, and in fact is similar to that of the unsubstituted complex, and this position is effective as an electrophilic centre in reactions with nucleophiles.

## Conclusion

Both 1-Ar and 2-Ar substituents on cyclohexadienyliron complexes direct ω, but the minority *ipso*/α pathways are accessible. The selectivity for the ω pathway is not a consequence of charge control at 5-C, and so must arise from orbital control or steric effects. In contrast, it is the access to the minority *ipso*/α pathways that grows easier as the level of positive charge on the complex as a whole becomes greater. High levels of electrophilicity promote the *ipso* and α pathways. A donor substituent positioned to oppose the ω-directing effect of an aryl group can dominate the regiocontrol. This effect is ascribed to deactivation of the terminus of the dienyl complex next to the OMe group (evidence for this comes from $^{13}C$ NMR data), and is strong enough to allow the required *ipso* regiocontrol in the case where the aromatic ring bears the correct substitution pattern to address the alkaloid crinine, despite the fact that the presence of the powerful electron-donating methylenedioxy substituent on the arene should strongly favour the ω-addition pathway. When the OMe group and the aryl group both direct to the same position (mutually reinforcing), complete ω selectivity is observed.

## 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 an environment of dry, oxygen-free nitrogen. Diethyl ether and THF were dried by distillation from sodium/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. 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 on Avatar 360, Perkin–Elmer BX or Perkin–Elmer 1720X FTIR spectrometers. NMR spectra were recorded on Varian Unity Plus, Varian Gemini 2000, Jeol GX400, Jeol EX270, Bruker AC250 or Jeol EX90 spectrometers, and were referenced to $Me_4Si$ (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.

**General procedures**

***Preparation of arylcyclohexadienyliron complexes***

**De-alkoxylation of neutral diene complexes with TFA (general method A)**: By a modification[8] of the method of Birch and Kelly,[22a,b] TFA (1 mL per 1 g of complex) was added to the appropriate diene complex at 0 °C, and the mixture was stirred at that temperature until IR analysis showed that no starting material remained. The mixture was then cooled to −78 °C and a solution of ammonium hexafluorophosphate (ca. 1 g per 1 g of complex) in the minimum amount of water was added. The low temperature bath was removed and the mixture was stirred and warmed to 0 °C. Water, and if necessary, $Et_2O$, was added to precipitate the product, and stirring was continued at 0 °C until the formation of the yellow precipitate was complete. The product was collected by filtration and rinsed sparingly with cold water, then $Et_2O$, then dried under reduced pressure to give the cyclohexadienyliron hexafluorophosphate salt as a yellow powder.

**Hydride abstraction from neutral diene complexes with triphenylmethylium hexafluorophosphate (general method B)**: By a modification of the method of Fischer,[41] a solution of triphenylmethylium hexafluorophosphate (1.1 equiv) in dry dichloromethane was stirred briefly over potassium carbonate (ca. 1.5 g) and filtered through cotton wool into a solution of the cyclohexadieneiron complex (1 equiv) in dichloromethane. The reaction mixture was stirred for 7 h, then poured into $Et_2O$. The yellow precipitate which formed was collected by filtration, rinsed thoroughly with $Et_2O$, and dried under reduced pressure to give the cyclohexadienyliron hexafluorophosphate salt as a yellow powder.

***Reactions of cyclohexadienyliron complexes with nucleophiles***

**Reduction of arylcyclohexadienyliron salts with sodium borohydride (general method C)**: Based on the procedure of Birch and Stephenson,[42] sodium borohydride (4 equiv) was added in one portion to a solution of the arylcyclohexadienyliron salt (1 equiv) in dry acetonitrile at 0 °C. The mixture was stirred for 45 min. The solvent was removed under reduced pressure, and the residue was extracted with light petroleum. The combined extracts were filtered through Celite and the solvent was then removed under reduced pressure to give the crude product. This material was filtered through a short column of silica gel with 15% dichloromethane in hexane as the eluant to give the product as a yellow oil.

**Reaction of arylcyclohexadienyliron salts with sodium enolates generated from malonate diesters (general method D)**: Based on the method[21] of Birch and Lewis, sodium hydride (as a 60 or 80% dispersion in mineral oil, nominally 1.1 equiv) was washed with hexane, then stirred as a suspension in dry THF at 0 °C. A solution of the malonate diester

(1.1 equiv) in dry THF was added, and the mixture was stirred for 3 min at 0 °C to give a colourless solution. The appropriate salt (0.1–1.0 mmol, 1 equiv) was then added to the mixture against nitrogen back-pressure, and the reaction mixture was stirred for 15 min at 0 °C, then poured into a separating funnel charged with sat. aq. ammonium chloride, water, and $Et_2O$. The layers were separated, and the organic layer was washed thoroughly with water (to remove excess malonate diester) and sat. aq. NaCl, and then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave the crude product, which was purified by filtration through a short column of silica gel eluted with 30% ethyl acetate in light petroleum.

**Arylation of cyclohexadienyliron salts with organolithium reagents (general method E)**: Based on the method of Bandara, Birch and Khor,[43] the appropriate salt was dissolved in dry dichloromethane at RT to give a homogeneous solution, which was then cooled to −78 °C (internal temperature ≈ −70 °C). A solution of the organolithium reagent was then added, with care being taken to maintain the internal temperature of the reaction below −60 °C, and the reaction mixture was stirred for 15–30 min. Sat. aq. ammonium chloride, water, and $Et_2O$ were added, and the mixture was warmed to RT and transferred to a separating funnel. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined organic fractions were washed with water and sat. aq. NaCl, dried ($MgSO_4$), and filtered. The solvent was then removed under reduced pressure to give the crude product, which was purified by flash chromatography.

**Arylation of cyclohexadienyliron salts with organocuprate reagents (general method F)**: Based on the method of Pearson,[44] the organolithium reagent (in $Et_2O$, 4 equiv) was added slowly to a suspension of copper(I) iodide (2 equiv) in dry THF at 0 °C, and the mixture was stirred 5 min at that temperature to give a colourless solution. The cyclohexadienyliron salt (1 equiv) was then added against nitrogen back-pressure, and stirring was continued for 1 h at 0 °C. The mixture was then poured into a separating funnel charged with sat. aq. ammonium chloride and $Et_2O$, and the layers were separated. The aqueous layer was extracted with $Et_2O$, and the combined organic fractions were dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure afforded a dark yellow oil which was purified by chromatography on a silica gel eluting with light petroleum until the fast-running biaryl impurity was removed, then with 10% $Et_2O$ in light petroleum to remove all yellow material, which was concentrated under reduced pressure. This yellow fraction was recolumned, eluting with 10% $Et_2O$ in light petroleum to obtain, after evaporation under reduced pressure, the mixture of isomeric products as a yellow oil or crystals.

**Arylation of cyclohexadienyliron salts with organozinc reagents (general method G)**: Freshly distilled bromoarene (30.0 mmol) was added slowly to a stirred mixture of magnesium turnings (30.0 mmol) and 1,2-dibromoethane (2 drops), and the mixture was warmed to 30 °C. Upon initiation of the reaction, dry $Et_2O$ was added, and the mixture was heated at reflux for 30 min. Zinc(II) chloride etherate (1.0 M, 9 mmol) was added, and the mixture was heated at reflux for a further 2 h, then cooled to RT. The diarylzinc separated from the cooled mixture as a dark lower viscous oil. A portion of this oil was transferred using a wide-bore cannula into a suspension of the cyclohexadienyliron salt in THF at 0 °C, until dissolution of the salt was complete. The mixture was stirred for 10–20 min then poured into a separating funnel charged with sat. aq. ammonium chloride, water and $Et_2O$. The organic layer was collected and the aqueous phase was extracted with $Et_2O$. The combined organic layers were washed with water and sat. aq. NaCl, dried over $MgSO_4$. After concentration under reduced pressure, filtration through a pad of silica gel eluted with 10% $Et_2O$ in light petroleum gave a crude sample of the 2-methoxy-5α-aryl $\eta^4$-cyclohexadiene complex contaminated with a small amount of a biaryl impurity.

**Arylation of cyclohexadienyliron salts with KCN (general method H)**: Based on the method of Birch,[21,45] an excess of KCN (100–130 mg, 1.5–2.0 mmol) in a minimum volume of water was added to a solution of the appropriate salt (0.5–0.7 mmol) in acetonitrile and the reaction mixture stirred for 15 min at RT. The solvent was removed under reduced pressure and the residue extracted with light petroleum. The extracts were combined, and evaporation under reduced pressure afforded a mixture of isomeric products as a yellow oil or crystals.

## Experimental details

### *Preparation of arylcyclohexadienyliron complexes*

**Tricarbonyl[(1,2,3,4,5-η)-1-phenyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (1, Nu = Ph)**: Following general method E, phenyllithium (0.70 M solution in $Et_2O$, 9.14 mL, 6.40 mmol) was added to a solution of 1-ethoxy salt (**2**, X = OEt) (1.74 g, 4.27 mmol) in dry dichloromethane (50 mL). After the work-up, flash chromatography with 5% ethyl acetate in hexane as the eluant afforded tricarbonyl[(1,2,3,4-η)-5β-ethoxy-5α-phenyl-1,3-cyclohexadiene]iron(0) (**10**) (970 mg, 67%) as a yellow oil, which solidified upon refrigeration. M.p. 90.5–92.5 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.34–7.15 (m, 5H, Ph), 5.44 (m, 1H, 3-H), 5.37 (ddd, $^3J_{H,H}$ = 16, 4, 2 Hz, 1H, 2-H), 3.43 (dq, $^3J_{H,H}$ = 9, 7 Hz, 1H, $CH_2CH_3$), 3.22 (d, $^3J_{H,H}$ = 7 Hz, 1H, 4-H), 3.16 (m, 1H, 1-H), 3.10 (dq, $^3J_{H,H}$ = 9, 7 Hz, 1H, $CH_2CH_3$), 2.29 (dd, $^3J_{H,H}$ = 15.5, 4 Hz, 1H, 6β-H), 2.06 (dd, $^3J_{H,H}$ = 15.5, 2 Hz, 1H, 6α-H), 1.22 ppm (t, $^3J_{H,H}$ = 7 Hz, 3H, $CH_3$); MS (EI): *m/z* (%): 312 (1) $[M-CO]^+$, 284 (3), 256 (11), 210 (38), 154 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ = 2054 ($\nu_{sym}$ CO), 1991 ($\nu_{asym}$ CO), 1975 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{17}H_{16}FeO_4$ (340.15): C 60.0, H 4.7; found: C 60.4, H 4.9. Following general method A, a portion of this product (560 mg, 1.65 mmol) was treated with TFA (1.12 mL, 14.5 mmol) and addition of ammonium hexafluorophosphate (560 mg, 3.44 mmol) in water (2 mL) gave **1** (698 mg, 96%) as a yellow powder. For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2109 ($\nu_{sym}$ CO), 2061 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{15}H_{11}F_6FeO_3P$ (440.06): C 40.9, H 2.5; found: C 40.7, H 2.5.

**Complex 1 (Nu = Ph) from dienone complex 9**: Phenyllithium (1.27 M solution in $Et_2O$, 1.60 mL, 2.02 mmol) was added slowly to a solution of cyclohexadienone complex **9** (430 mg, 1.84 mmol) in dichloromethane (22 mL) at −78 °C, and the mixture was stirred at that temperature for 45 min. Sat. aq. ammonium chloride (5 mL) and 5% aq. HCl (2 mL) were added, and the mixture was warmed to RT. The layers were separated and the aqueous layer was extracted with light petroleum. The combined organic extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was filtered through a short column of basic alumina with 50% $Et_2O$ in light petroleum to give a yellow solid (120 mg). TFA (0.5 mL, 6.49 mmol) was added to this crude material at −78 °C, and the reaction mixture was stirred at RT until IR analysis showed that no neutral diene complex (signals at $\tilde{\nu}$ 2050, 1980, 1970 cm$^{-1}$) remained (2 h). The mixture was chilled to −78 °C, and a solution of ammonium hexafluorophosphate (300 mg, 1.84 mmol) in water (1 mL) was added. The mixture was warmed to RT, and $Et_2O$ was added. The yellow precipitate which formed was collected by filtration, rinsed sparingly with cold water and $Et_2O$, then dried under reduced pressure to give **1** (25 mg, 3%). The $^1$H NMR spectrum of this material corresponded to that obtained earlier.

**Complex 1 (Nu = Ph) by hydride abstraction from tricarbonyl[(1,2,3,4-η)-1-phenyl-1,3-cyclohexadiene]iron (23)**:

**a) *With triphenylmethylium tetrafluoroborate***: $[Fe_2(CO)_9]$ (4.69 g, 12.9 mmol was added to a solution of 1-phenylcyclohexadiene (prepared by the method of Reich and Wollowitz;[46] 1.00 g, 6.44 mmol) in $Et_2O$ (50 mL) and heated under reflux for 20 h. After cooling, the mixture was filtered through Celite and evaporated. Flash chromatography on silica gel eluted with petroleum ether gave **23**[16a] (1.30 g, 68%) as a yellow solid. By the method of Whitesides and Neilan,[16a] this product (1.13 g, 3.83 mmol) was dissolved in dry dichloromethane (10 mL). A solution of triphenylmethylium tetrafluoroborate (1.75 g, 5.30 mmol) in the minimum amount of dry dichloromethane (ca. 25 mL) was added, and the mixture was stirred at RT until IR analysis showed that no starting material remained (24 h), and was then poured into $Et_2O$ (100 mL). The yellow precipitate which formed was collected by filtration, rinsed thoroughly with $Et_2O$, and dried under reduced pressure to give a mixture of tricarbonyl[(1,2,3,4,5-η)-1-phenyl-2,4-cyclohexadien-1-yl]iron(1+) tetrafluoroborate(1−)[16a,b] and tricarbonyl[(1,2,3,4,5-η)-2-phenyl-2,4-cyclohexadien-1-yl]iron(1+) tetrafluoroborate(1−)[16a] (1.41 g), as a yellow powder. The ratio of the products was shown to be 8:1, by comparison of the NMR spectrum for the mixture with the data reported.[16a,b] This mix-

ture of salts was recrystallised from water to give the pure 1-phenyl substituted salt (340 mg). This tetrafluoroborate salt was re-dissolved in the minimum amount of water and a solution of ammonium hexafluorophosphate (220 mg, 1.35 mmol) in water (2 mL) was added. After 10 min, the yellow precipitate which had formed was collected by filtration, rinsed with water and $Et_2O$, and dried under reduced pressure to give the hexafluorophosphate salt (**1**, Nu = Ph) (320 mg, 19%) as a yellow powder. The $^1$H NMR spectrum of this material corresponded to that obtained earlier.

**b)** ***With triphenylmethylium hexafluorophosphate***: Following general method B, triphenylcarbenium hexafluorophosphate (705 mg, 1.82 mmol) in dry dichloromethane (10 mL) and **23**[16a] (489 mg, 1.65 mmol) in dry dichloromethane (20 mL) gave the product as a yellow powder after addition of $Et_2O$ (50 mL). The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography with light petroleum as the eluant to give recovered starting complex **23** (120 mg). Analysis of the yellow powder identified it as a 5:1 mixture of **1** and tricarbonyl[(1,2,3,4,5-η)-2-phenyl-2,4-cyclohexadien-1-yl]iron hexafluorophosphate (**3**, Nu = Ph) (505 mg, 92% yield based on consumed starting material) by comparison of $^1$H NMR data for the mixture with spectra of the pure salts. A portion (170 mg) of this product was dissolved in the hot acetonitrile, filtered, and cooled to −30 °C. $Et_2O$ was added and the sample was stored for 1 h in a freezer to produce a pure sample of the 1-phenyl regioisomer (**1**, Nu = Ph) (100 mg, 59%), which was collected by filtration.

**Tricarbonyl[(1,2,3,4,5-η)-2-phenyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (3, Nu = Ph)**: Using a combination of general methods A and G, bromobenzene (15.8 mL, 150 mmol), magnesium turnings (3.645 g, 150 mmol), one small crystal of iodine, dry $Et_2O$ (100 mL), and zinc chloride (45 mL of 1.0 M solution in dry $Et_2O$, 45 mmol) were used to prepare diphenylzinc, which, after a further addition of dry $Et_2O$ (50 mL) separated as a lower, dark oil (nominally 45 mmol). A portion of this oil (21 mL) was treated with the 2-methoxy salt (**4**, X = OMe) (5.32 g, 13.5 mmol) in THF (100 mL) [work-up: sat. aq. ammonium chloride (50 mL); water (200 mL); $Et_2O$ (25 mL); water (2 × 50 mL portions); sat. aq. NaCl (50 mL)] to produce yellow oil (4.1 g). This crude complex was stirred with TFA (8.05 mL, 105 mmol) at 0 °C for 2 h. Addition of ammonium hexafluorophosphate (3.0 g, 18.4 mmol) and $Et_2O$ (20 mL) precipitated **3** isolated as a yellow powder [4.66 g, 79% from the 2-methoxy salt (**4**, X = OMe)]. For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2112 ($\nu_{sym}$ CO), 2065 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{15}H_{11}F_6FeO_3P$ (440.06): C 40.9, H 2.5; found: C 40.8, H 2.4.

**Complex 3 (Nu = Ph) by thallium(III) oxidation of 23**: Based on the procedure of Stephenson,[17b] **23**[16a] (238 mg, 0.80 mmol) was ground slowly with thallium(III) trifluoroacetate (376 mg, 0.69 mmol) in a glass mortar, in a glove bag, for 20 min. Ammonium tetrafluoroborate (200 mg, 1.90 mmol) was then added and the mixture was ground for a further 10 min. Conc. sulfuric acid (10 drops) was then added, followed by water (50 mL), and the mixture was filtered through cotton wool. A solution of ammonium hexafluorophosphate (300 mg, 1.84 mmol) in water (2 mL) was added to the filtrate, and the yellow precipitate which formed was collected by filtration, washed with water (100 mL) and $Et_2O$ (50 mL), and dried under reduced pressure to give **3** (115 mg, 32%) as a yellow powder. The $^1$H NMR spectrum of this material corresponded to that obtained earlier.

**Dicarbonyl[(1,2,3,4,5-η)-1-phenyl-2,4-cyclohexadien-1-yl](triphenylphosphine)iron(1+) hexafluorophosphate(1−) (14)**: Following a method based on the method of Howell,[23a,b] but with modified stoichiometry, triphenylphosphine (630 mg, 2.4 mmol) and **10** (200 mg, 0.59 mmol) were added to a solution of trimethylamine *N*-oxide dihydrate (262 mg, 2.4 mmol) in a small amount of acetone (5 mL), and the mixture was heated at reflux until TLC analysis showed that the reaction was substantially complete (2 h). The cooled reaction mixture was then diluted with $Et_2O$ (10 mL) and filtered. The solvent was removed from the filtrate under reduced pressure, and a mixture of 10% ethyl acetate in light petroleum (25 mL) was added. Filtration and removal of the solvent then gave the crude product as a yellow oil. Flash chromatography eluting with a gradient (light petroleum to 10% ethyl acetate in light petroleum) gave dicarbonyl[(1,2,3,4,5-η)-5β-ethoxy-5α-phenyl-1,3-cyclohexadiene]-(triphenylphosphine)iron(0) (**13**) (259 mg, 77%) as a yellow solid. M.p. 58–59.5 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.55–7.08 (m, 20H, 5α-Ph, Fe-$PPh_3$), 4.94 (m, 2H, 2-H, 3-H), 3.33 (dq, $^3J_{H,H}$ = 9, 7 Hz, 1H, C*H*HCH$_3$), 3.03 (dq, $^3J_{H,H}$ = 9, 7 Hz, 1H, CH*H*CH$_3$), 2.68 (d, $^3J_{H,H}$ = 6 Hz, 1H, 4-H), 2.25 (m, 2H, 1-H, 6β-H), 1.82 (br d, $^3J_{H,H}$ = 14 Hz, 1H, 6α-H), 1.23 ppm (t, $^3J_{H,H}$ = 7 Hz, 3H, $CH_3$); MS (FAB): *m*/*z* (%): 574 (2) $[M]^+$, 472 (100); HRMS: *m*/*z*: calcd for $C_{34}H_{31}FeO_3P$: 574.1360 $[M]^+$; found 574.1381; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ = 1987 ($\nu_{sym}$ CO), 1931 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{34}H_{31}F_6FeO_2P_2$ (574.43): C 71.1, H 5.4; found: C 71.5, H 5.8. Following general method A, a portion (198 mg, 0.34 mmol) of this product was treated with TFA (0.40 mL, 5.19 mmol) and addition of ammonium hexafluorophosphate (201 mg, 1.23 mmol) in water (1 mL) gave **14** (212 mg, 91%) as a yellow powder. $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta$ = 7.69 (d, $J$ = 6.0 Hz, 1H, 3-H), 7.68–7.35 (m, 20H, 1-Ph, Fe-$PPh_3$), 6.23 (d, $^3J_{H,H}$ = 5.5 Hz, 1H, 2-H), 5.34 (m, 1H, 4-H), 3.71 (dd, $^3J_{H,H}$ = 15.5, 6 Hz, 1H, 6β-H), 3.53 (t, $^3J_{H,H}$ = 5.5 Hz, 1H, 5-H), 2.42 ppm (dd, $^3J_{H,H}$ = 15.5, 4 Hz, 1H, 6α-H); IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2041 ($\nu_{sym}$ CO), 1998 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{32}H_{26}F_6FeO_2P_2$ (674.34): C 57.0, H 3.9; found: C 57.0, H 3.8.

**Tricarbonyl[(1,2,3,4,5-η)-1-(4′-methoxyphenyl)-2,4-cyclohexadien-1-yl]-iron(1+) hexafluorophosphate(1−) (11)**: Following the general method E, a solution of 4-methoxyphenyllithium[47] in $Et_2O$/THF [prepared from 4-iodoanisole (5.75 mmol) and *n*-butyllithium (5.00 mmol) in hexane (14 mL) and redissolved in $Et_2O$/THF (30:1, 10 mL)] and 1-ethoxy salt (**2**, X = OEt) (816 mg, 2.00 mmol) in dry dichloromethane (25 mL) (flash chromatography with 5% ethyl acetate in light petroleum) gave tricarbonyl[(1,2,3,4-η)-5β-ethoxy-5α-(4-methoxyphenyl)-1,3-cyclohexadieneiron(0) (533 mg, 72%) as a yellow oil which solidified upon refrigeration. M.p. 96.0–98.5 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.21 (dm, $^3J_{H,H}$ = 9 Hz, 2H, 2′-H, 6′-H), 6.81 (dm, $^3J_{H,H}$ = 9 Hz, 2H, 3′-H, 5′-H), 5.42 (m, 1H, 3-H), 5.36 (m, 1H, 2-H), 3.79 (s, 3H, OMe), 3.32 (dq, $^3J_{H,H}$ = 9, 7 Hz, 1H, C$H_2$CH$_3$), 3.15 (m, 1H, 1-H), 3.08 (dq, $^3J_{H,H}$ = 9, 7 Hz, 1H, C$H_2$CH$_3$), 2.27 (dd, $^3J_{H,H}$ = 16, 4 Hz, 1H, 6β-H), 2.04 (dd, $^3J_{H,H}$ = 16, 2.5 Hz, 1H, 6α-H), 1.21 ppm (t, $^3J_{H,H}$ = 7 Hz, 3H, CH$_2$C$H_3$); MS (EI): *m*/*z* (%): 342 (0.5) $[M-CO]^+$, 314 (3), 286 (6), 240 (24), 184 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ = 2054 ($\nu_{sym}$ CO), 1991, 1975 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{18}H_{18}FeO_5$ (370.18): C 58.4, H 4.9; found: C 58.6, H 4.9. Following general method A, a portion (525 mg, 1.42 mmol) of the product was treated with TFA (1.05 mL, 13.6 mmol) and addition of ammonium hexafluorophosphate (530 mg, 3.25 mmol) in water (2 mL) gave **11** (639 mg, 96%; 69% over two steps) as an orange/yellow powder. For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2105 ($\nu_{sym}$ CO), 2056 cm$^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{16}H_{13}F_6FeO_4P$ (470.08): C 40.9, H 2.8; found: C 40.6, H 2.6.

**Tricarbonyl[(1,2,3,4,5-η)-2-(4′-methoxyphenyl)-2,4-cyclohexadien-1-yl]-iron(1+) hexafluorophosphate(1−) (25)**: Following a modification of general method G, 4-bromoanisole (16.45 g, 879 mmol), magnesium turnings (2.14 g, 87.9 mmol), copper(I) iodide (trace), one small crystal of iodine, dry $Et_2O$ (100 mL) and zinc chloride (26.3 mL of 1.0 M solution in dry $Et_2O$, 26.3 mmol) were used to prepare bis(4-methoxyphenyl)zinc[48] which separated as a lower, brown oil (nominally 26.3 mmol). A portion of this oil (14 mL) was reacted with the 2-methoxy salt (**4**, X = OMe) (4.10 g, 10.41 mmol) in THF (70 mL) to produce, after work-up [sat. aq. ammonium chloride (40 mL); water (150 mL); $Et_2O$ (15 mL); water (2 × 40 mL portions); sat. aq. NaCl (40 mL)], crude tricarbonyl[(1,2,3,4-η)-2-methoxy-5α-(4′-methoxyphenyl)-1,3-cyclohexadiene]iron(0)[49] as a yellow oil (4.3 g). Following general method A, this crude complex was stirred with TFA (9.0 mL) at RT for 2.25 h. Addition of ammonium hexafluorophosphate (2.0 g, 12.3 mmol) and $Et_2O$ (20 mL) precipitated product **25** as a yellow powder [3.74 g, 77% from the 2-methoxy salt (**4**, X = OMe)]. For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2111 ($\nu_{sym}$ CO), 2063 ($\nu_{asym}$ CO), 1608, 1470 cm$^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{16}H_{13}F_6FeO_4P$ (470.08): C 40.9, H 2.8; found: C 40.9, H 2.6.

**Tricarbonyl[(1,2,3,4,5-η)-1-(4′-trifluoromethylphenyl)-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (12)**: *n*-Butyllithium (1.30 M solution in hexanes, 1.63 mL, 2.12 mmol) was added to a solution of 4-bromotrifluoromethylbenzene (619 mg, 2.75 mmol) in dry $Et_2O$ (4 mL) at 0 °C,

and the mixture was stirred for 10 min at that temperature. Following the general method E, the resulting red solution of 4-trifluoromethylphenyllithium[50] was added to a solution of 1-ethoxy salt (**2**, X = OEt) (510 mg, 1.25 mmol) in dichloromethane (15 mL) to give, after flash chromatography with 1% ethyl acetate in light petroleum as the eluant, tricarbonyl[(1,2,3,4-η)-5β-ethoxy-5α-(4′-trifluoromethylphenyl)-1,3-cyclohexadiene]iron(0) (402 mg, 79%) as a yellow oil which solidified upon refrigeration. M.p. 61.5–63.5 °C; elemental analysis calcd (%) for $C_{18}H_{15}F_3FeO_4$ (408.15): C 53.0, H 3.6; found: C 53.4, H 3.7. Following general method A, a portion (315 mg, 0.77 mmol) of this product was reacted with TFA (0.63 mL, 8.18 mmol) and addition of ammonium hexafluorophosphate (315 mg, 1.93 mmol) in water (1 mL) gave **12** (365 mg, 93%; 73% over two steps) as a yellow powder. For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2112 ($\nu_{sym}$ CO), 2066 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{16}H_{10}F_9FeO_3P$ (508.05): C 37.8, H 2.0; found: C 37.9, H 1.8.

**Tricarbonyl[(1,2,3,4,5-η)-2-(4′-trifluoromethylphenyl)-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate (1−) (26)**: Following the general method G, 4-bromotrifluoromethylbenzene (5.60 mL, 40 mmol), magnesium turnings (960 mg, 40 mmol), dry $Et_2O$ (60 mL) and zinc chloride (12 mL of 1.0 M solution in dry $Et_2O$, 12 mmol) were used to prepare bis(4-trifluoromethylphenyl)zinc[51] as a pale brown solution (nominally 12 mmol). The whole of this solution was treated with the 2-methoxy salt (**4**, X = OMe) (3.95 g, 10 mmol) in THF (70 mL) to produce after work-up [sat. aq. ammonium chloride (40 mL); water (150 mL); $Et_2O$ (15 mL); water (2 × 40 mL portions); sat. aq. NaCl (40 mL)], crude tricarbonyl[(1,2,3,4-η)-2-methoxy-5α-(4′-trifluoromethylphenyl)-1,3-cyclohexadiene]iron(0) as a yellow oil. Following the general method A, this crude complex was stirred with TFA (7.5 mL, 98 mmol) at 0 °C for 3 h. Addition of ammonium hexafluorophosphate (2.5 g, 15.3 mmol) and $Et_2O$ (30 mL) precipitated **26** as a yellow powder [3.71 g, 73% from the 2-methoxy salt (**4**, X = OMe)]. For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2113 ($\nu_{sym}$ CO), 2067 ($\nu_{asym}$ CO), 1620 $cm^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{16}H_{10}F_9FeO_3P$ (508.05): C 37.8, H 2.0; found: C 37.8, H 1.9.

**Tricarbonyl[(1,2,3,4-η)-2-methoxy-5α-(3′4′-methylenedioxyphenyl)-1,3-cyclohexadiene]iron(0) (27)**: Following a modification of the general method G, 4-bromo-1,2-methylenedioxybenzene (4.28 g, 21.3 mmol), magnesium turnings (628 mg, 25.9 mmol), 1,2-dibromoethane (0.15 mL, 1.6 mmol), one small crystal of iodine, THF (60 mL) and zinc chloride (7.7 mL of 1.0 M solution in dry $Et_2O$, 7.7 mmol) were used to prepare bis(3,4-methylenedioxyphenyl)zinc.[52] This was added dropwise over 5 min to a suspension of the 2-methoxy salt (**4**, X = OMe) (778 mg, 2.0 mmol) in THF (20 mL) to give, after chromatography eluting with 5% $Et_2O$ in light petroleum, **27** as a yellow oil [221 mg, 73% from 2-methoxy salt (**4**, X = OMe)]. A portion of this product was recrystallised from light petroleum as yellow needles. M.p. 101.5–102.5 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.58 (m, 3H, 2′-H, 5′-H, 6′-H), 5.88 (s, 2H, $OCH_2O$), 5.14 (dd, $^3J_{H,H}$ = 6.5, 2.5 Hz, 1H, 3-H), 3.68 (s, 3H, OMe), 3.42 (dt, $^3J_{H,H}$ = 4, 2.5 Hz, 1H, 1-H), 3.12 (dt, $^3J_{H,H}$ = 11, 3.5 Hz, 1H, 5-H), 2.70 (dd, $^3J_{H,H}$ = 6.5, 3.5 Hz, 1H, 4-H), 2.34 (ddd, $^3J_{H,H}$ = 15, 11, 4 Hz, 1H, 6β-H), 1.65 ppm (ddd, $^3J_{H,H}$ = 15, 11, 4 Hz, 1H, 6α-H); $^{13}$C NMR (25 MHz, $CDCl_3$): $\delta$ = 211.5 (CO), 147.9, 146.0, 141.0, 140.5, 120.2, 108.2, 107.2, 101.0 ($OCH_2O$), 66.4 (3-C), 56.2, 54.5 (OMe), 53.4, 44.1 (5-C), 34.5 ppm (6-C); MS (CI): *m*/*z* (%): 371 (100) $[M+H]^+$, 341 (14) $[M+H-CO-2H]^+$, 231 (33) $[M+H-3CO-Fe]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ = 2046 ($\nu_{sym}$ CO), 1976 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{17}H_{14}FeO_6$ (370.14): C 55.2, H 3.8; found: C 55.4, H 3.8.

**Tricarbonyl[(1,2,3,4,5-η)-2-(3′,4′-methylenedioxyphenyl)cyclohexadienyl]iron(1+) hexafluorophosphate(1−) (28)**: Following the general method G, 4-bromo-1,2-methylenedioxybenzene (0.96 mL, 8.0 mmol), magnesium turnings (194 mg, 8.0 mmol), 1,2-dibromoethane (0.1 mL, 1.1 mmol), one small crystal of iodine, dry $Et_2O$ (30 mL) and zinc chloride (2.40 mL of 1.0 M solution in dry $Et_2O$, 2.40 mmol) were used to prepare bis(3,4-methylenedioxyphenyl)zinc[52] which separated as a very viscous brown oil (nominally 2.40 mmol). The whole of this oil was reacted with the 2-methoxy salt (**4**, X = OMe) (778 mg, 2.0 mmol) in THF (40 mL) [work-up: sat. aq. ammonium chloride (25 mL); water (50 mL); $Et_2O$ (10 mL); water (2 × 30 mL portions); sat. aq. NaCl (30 mL)] to give, after chromatography eluting with 10% $Et_2O$ in light petroleum, tricarbonyl[(1,2,3,4-η)-2-methoxy-5α-(3′4′-methylenedioxyphenyl)-1,3-cyclohexadiene]iron(0) (**27**) as a yellow oil [497 mg, 68% from 2-methoxy salt (**4**, X = OMe)]. Following the general method A, a portion (480 mg, 1.30 mmol) of this product was treated with TFA (1.0 mL, 13 mmol) and addition of ammonium hexafluorophosphate (500 mg, 3.07 mmol) in water (2 mL) gave **28** as a yellow powder (410 mg, 64%). For NMR data, refer to Table 2. IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2113 ($\nu_{sym}$ CO), 2063 ($\nu_{asym}$ CO), 1625 $cm^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{16}H_{11}F_6FeO_5P$ (484.07): C 39.7, H 2.3; found: C 39.8, H 2.3.

**Tricarbonyl[(1,2,3,4,5-η)-3-methoxy-2-phenyl-2,4-cyclohexadien-1-yl]-iron(1+) hexafluorophosphate(1−) (31)**: Following the general method F, phenyllithium (3.85 mL of a 1.30 M solution in $Et_2O$, 5.00 mmol), copper(I) iodide (475 mg, 2.49 mmol) in THF (20 mL), and addition of 2,4-dimethoxy salt **29**[33] (480 mg, 1.33 mmol) gave tricarbonyl[(1,2,3,4-η)-1,3-dimethoxy-6α-phenyl-1,3-cyclohexadiene]iron(0) (**30**), which was purified by column chromatography eluting with 10% $Et_2O$ in light petroleum to give a yellow oil (270 mg, 67%) which solidified upon refrigeration. M.p. 86–88 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.73–7.10 (m, 5H, Ph), 5.39 (d, $^3J_{H,H}$ = 2 Hz, 1H, 2-H), 3.72 (s, 3H, 3-OMe), 3.65 (dd, $^3J_{H,H}$ = 11.5, 3 Hz, 1H, 6-H), 3.39 (s, 3H, 1-OMe), 3.23 (m, 1H, 4-H), 2.39 (ddd, $^3J_{H,H}$ = 15, 11.5, 3.5 Hz, 1H, 5β-H), 1.73 ppm (dt, $^3J_{H,H}$ = 15, 3 Hz, 1H, 5α-H); MS (EI): *m*/*z* (%): 356 (2) $[M]^+$, 328 (22) $[M-CO]^+$, 300 (25) $[M-2CO]^+$, 272 (59), 194 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ = 2043 ($\nu_{sym}$ CO), 1976, 1969 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{17}H_{16}FeO_5$ (356.15): C 57.3, H 4.5; found: C 57.3, H 4.5. Following the general method A, a portion (144 mg, 0.40 mmol) of this product was reacted with TFA and ammonium hexafluorophosphate (140 mg, 0.86 mmol) in water (2 mL) to give [after addition of water (2 mL) and $Et_2O$ (5 mL)] **31** (152 mg, 80%) as a yellow powder. $^1$H NMR (300 MHz, [$D_6$]acetone): $\delta$ = 8.02 (d, $^3J_{H,H}$ = 7.2 Hz, 2H, 2′-H, 6′-H), 7.6–7.5 (m, 3H, 3′-H, 4′-H, 5′-H), 6.61 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, 4-H), 4.54 (d, $^3J_{H,H}$ = 4.8 Hz, 1H, 1-H), 4.5–4.4 (obsc., 1H, 5-H), 4.43 (s, 3H, OMe), 3.21 (ddd, $^3J_{H,H}$ = 15.0, 7.1, 4.8 Hz, 1H, 6β-H), 2.12 ppm (d, $^3J_{H,H}$ = 15.0 Hz, 1H, 6α-H); $^{13}$C NMR (75 MHz, $CD_3CN$): $\delta$ = 139.3 (3-C), 132.7 (4′-C), 132.5 (2C, 3′-C, 5′-C), 130.8 (1′-C), 129.2 (2C, 2′-C, 6′-C), 111.6 (4-C), 84.3 (2-C), 59.6 (1-C), 57.2 (OMe), 52.4 (5-C), 26.2 ppm (6-C); IR ($CH_3CN$): $\tilde{\nu}_{max}$ = 2102 ($\nu_{sym}$ CO), 2053 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{16}H_{13}F_6FeO_4P$ (470.08): C 40.9, H 2.8; found: C 40.8, H 2.6.

**Tricarbonyl[(1,2,3,4,5-η)-1,2-dimethoxy-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (62) and tricarbonyl[(1,2,3,4,5-η)-2,3-dimethoxy-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (63)**: Using a combination of the typical methods[8,21,53] for the complexation of 1,4-dienes, $[Fe(CO)_5]$ (81 mL, 0.61 mol) was added to 1,2-dimethoxycyclohexa-1,4-diene[54] (67 g, 0.48 mol) in di-*n*-butyl ether (540 mL), and the mixture was heated at reflux for 16 h, using an oil bath temperature of 152–157 °C. After cooling and filtration through Celite (pyrophoric residue) the solvent and excess $[Fe(CO)_5]$ were removed under reduced pressure using a dry ice condenser to ensure efficient trapping of $[Fe(CO)_5]$ and residual di-*n*-butyl ether, 1,2-dimethoxycyclohexa-1,4-diene and 1,2-dimethoxybenzene were then removed by distillation (90 °C, 0.005 mm Hg) using a kugelrohr. Recrystallisation from light petroleum at 0 °C gave the crude diene complex (20.6 g). The residue was combined with the distillates and returned to the reaction vessel and heated again with $[Fe(CO)_5]$. By recycling in this fashion additional portions of the crude diene complex (31 g and 10 g) were obtained. The combined crude products were purified by chromatography on silica eluting first with light petroleum and then with 10% $Et_2O$ in light petroleum to give (in order of elution), tricarbonyl[(1,2,3,4-η)-1-methoxycyclohexa-1,3-diene]iron(0)[21] and tricarbonyl[(1,2,3,4-η)-1,2-dimethoxycyclohexa-1,3-diene]iron(0) (**61**) (61.2 g, 46%)[38] as yellow crystals. M.p. 42–43 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.94 (d, $^3J_{H,H}$ = 6.7 Hz, 1H, 3-H), 3.75 (s, 3H, 2-OMe), 3.60 (s, 3H, 1-OMe), 2.50 (m, 1H, 4-H), 2.31 (ddd, $^3J_{H,H}$ = 15, 10, 5 Hz, 1H, 6β-H), 1.64 ppm (m, 3H, 5α-H, 5β-H, 6α-H); $^{13}$C NMR (25 MHz, $CDCl_3$): $\delta$ = 211.5 (3C, Fe-CO), 131.7 (2-C), 108.9 (1-C), 62.2 (3-C), 57.2, 55.0 (1-OMe, 2-OMe), 47.1 (4-C), 26.0, 23.4 ppm (5-C, 6-C); MS (EI): *m*/*z* (%): 280 (7) $[M]^+$, 252 (22) $[M-CO]^+$, 224 (32) $[M-2CO]^+$, 194 (79) $[M-3CO-2H]^+$, 164 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ = 2041

($\nu_{sym}$ CO), 1972, 1965 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{11}H_{12}FeO_5$ (280.06): C 47.2, H 4.3; found: C 47.2, H 4.2. Using the general method B, a portion (2.00 g, 7.14 mmol) of product **61** was dissolved in dry dichloromethane (5 mL) and treated with triphenylcarbenium hexafluorophosphate (3.50 g, 9.01 mmol) and poured into $Et_2O$ (50 mL) to give **62** and **63** (2.80 g, 92%) as a 7:1 mixture of isomers.[38] $^1H$ NMR (400 MHz, $CD_3CN$): for the major isomer **62**: $\delta = 6.96$ (d, $^3J_{H,H} = 6$ Hz, 1H, 3-H), 5.75 (t, $^3J_{H,H} = 6$ Hz, 1H, 4-H), 4.13 (t, $^3J_{H,H} = 6$ Hz, 1H, 5-H), 3.99 (s, 3H, 2-OMe), 3.86 (s, 3H, 1-OMe), 2.79 (dd, $^3J_{H,H} = 16$, 6 Hz, 1H, 6β-H), 2.51 ppm (d, $^3J_{H,H} = 16$ Hz, 1H, 6α-H); for the minor isomer **63**: $\delta = 6.25$ (d, $^3J_{H,H} = 7.4$ Hz, 1H, 4-H), 4.18 (s, 3H, 3-OMe), 3.70 (s, 3H, 2-OMe), 3.62 (t, $^3J_{H,H} = 7.4$ Hz, 1H, 5-H), 2.83 (dt, $^3J_{H,H} = 14.8$, 7.4 Hz, 6β-H), 1.83 ppm (d, $^3J_{H,H} = 14.8$ Hz, 1H, 6α-H); the signal for 1-H was obscured by signals from the major isomer. $^{13}C$ NMR (100 MHz, $CD_3CN$): for the major isomer **62**: $\delta = 204.4$ (3C, Fe-CO), 130.2 (2-C), 113.4 (1-C), 94.1 (4-C), 72.9 (3-C), 60.8 (5-C), 59.2, 58.1 (2-OMe, 3-OMe), 31.7 ppm (6-C); for the minor isomer **63**: $\delta = 203.6$ (3C, Fe-CO), 130.6 (2C, 2-C, 3-C), 85.4 (4-C), 59.5, 58.3 (2-OMe, 3-OMe), 50.5 (5-C), 41.9 (1-C), 27.7 ppm (6-C); IR ($CH_3CN$): $\tilde{\nu}_{max} = 2101$ ($\nu_{sym}$ CO), 2052 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{11}H_{11}F_6FeO_5P$ (424.01): C 31.2, H 2.6; found: C 30.7, H 2.5.

**Tricarbonyl[(1,2,3,4,5-η)-2-methoxy-1-phenyl-2,4-cyclohexadien-1-yl]iron-(1+) hexafluorophosphate(1−) (65)**: Following the general method E, phenyllithium (10.8 mL of a 0.63 M solution in $Et_2O$, 6.30 mmol) and the mixture of dimethoxy salts **62** and **63** [2.20 g; containing 1.92 g, 4.54 mmol of **64**] in dry dichloromethane (80 mL) at −78 °C gave, after flash chromatography eluting with 40% dichloromethane in light petroleum, tricarbonyl[(1,2,3,4-η)-1,6β-dimethoxy-6α-phenyl-1,3-cyclohexadiene]iron(0) (**64**) (272 mg, 17%) as a pale yellow solid. M.p. 84–85 °C; HRMS (EI): *m/z*: calcd for $C_{16}H_{16}FeO_4$: 328.0398; found 328.0398 $[M-CO]^+$. Following the general method A, a portion of this product (232 mg, 0.65 mmol) was treated with TFA (0.46 mL, 5.97 mmol) and addition of ammonium hexafluorophosphate (230 mg, 1.41 mmol) in water (1 mL) gave **65** (267 mg, 87%) as a yellow powder. $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta = 7.55$ (d, $J = 6.0$ Hz, 1H, 3-H), 7.50–7.40 (m, 5H, Ph), 6.43 (dd, $^3J_{H,H} = 6.4$, 6.0 Hz, 1H, 4-H), 4.70 (t, $^3J_{H,H} = 6.4$ Hz, 1H, 5-H), 4.28 (s, 3H, OMe), 3.57 (dd, $^3J_{H,H} = 14.8$, 6.4 Hz, 1H, 6β-H), 2.93 ppm (d, $^3J_{H,H} = 14.8$ Hz, 1H, 6α-H); $^{13}C$ NMR (75 MHz, [$D_6$]acetone): $\delta = 146.7$ (2-C), 135.1 (1′-C), 130.4 (4′-C), 129.7 (2C, 3′-C, 5′-C), 129.2 (2C, 2′-C, 6′-C), 101.1 (1-C), 99.1 (4-C), 73.6 (3-C), 64.4 (5-C), 58.3 (OMe), 33.3 ppm (6-C); IR ($CH_3CN$): $\tilde{\nu}_{max} = 2107$ ($\nu_{sym}$ CO), 2059 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{16}H_{13}F_6FeO_4P$ (470.08): C 40.9, H 2.8; found: C 40.8, H 2.6.

**Tricarbonyl[(1,2,3,4,5-η)-4-methoxy-1-(3′,4′-methylenedioxyphenyl)-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (50)**: 3,4-Methylenedioxybromobenzene[55] (0.804 g, 4 mmol) was dissolved in dry $Et_2O$ (5 mL) and cooled to −20 °C under nitrogen and *n*-butyllithium (1.6 M in hexanes) (4 mmol, *2.5* mL) was added to form 1-lithio-3,4-methylenedioxybenzene[36] as a white suspension by stirring for 2 h at −20 °C. Following a modification of the general method E, tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron(1+) hexafluorophosphate(1−) (**51**)[8] (1.098 g, 2.59 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 via a cannula at −100 °C and the mixture was stirred for 1 h. The reaction was quenched with water (25 mL) and $Et_2O$ (25 mL) at −100 °C and warmed to RT. Solvent extraction as described in general method E [sat. aq. ammonium chloride (10 mL); water (50 mL); $Et_2O$ (10 mL); water (2×20 mL portions); sat. aq. NaCl (20 mL)] and chromatography ($Et_2O$/petroleum ether gradient 0:100→20:80) gave tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(3,4-methylenedioxyphenyl)-1,3-cyclohexadiene]iron(0) (**52**) (0.615 g, 1.54 mmol, 59%) as a yellow oil. $^1H$ NMR (270 MHz, $CDCl_3$): $\delta = 6.79$–6.70 (m, 3H, Ar), 5.93 (s, 2H, $OCH_2O$), 5.04 (dd, $^3J_{H,H} = 6.9$, 2.6 Hz, 1H, 3-H), 3.64 (s, 3H, 2-OMe), 3.02 (s, 3H, 5-OMe), 3.37 (m, 1H, 1-H), 2.74 (d, $^3J_{H,H} = 6.9$ Hz, 1H, 4-H), 2.19 (dd, $^3J_{H,H} = 15.2$, 3.6 Hz, 1H, 6β-H), 2.10 ppm (dd, $^3J_{H,H} = 15.2$, 2.6 Hz, 6α-H); MS (EI): *m/z* (%): 327 (1) $[M-CO]^+$, 344 (6) $[M-2CO]^+$, 316 (17) $[M-3CO]^+$, 284 (57), 228 (100); IR (film): $\tilde{\nu}_{max} = 2046$ ($\nu_{sym}$ CO), 1976 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{18}H_{16}FeO_7$ (400.16): C 54.0, H 4.0; found: C 53.7, H 4.3. Further elution with $Et_2O$ gave tricarbonyl[(2,3,4,5-η)-4-methoxy-2,4-cyclohexadien-1-one]iron(0)[21] (0.110 g, 42 mmol, 14%). This procedure was repeated with similar results. Product **52** (850 mg, 2.13 mmol) was dissolved in acetic anhydride (5 mL) at 0 °C and hexafluorophosphoric acid (75% in water) (1 mL) was added. The reaction was stirred at 0 °C for 30 min and added dropwise into dry $Et_2O$ (200 mL) at 0 °C to give a brown gum. Ammonium hexafluorophosphate (200 mg, 1.23 mmol) in water (2 mL) was added and the mixture was stirred at RT for 30 min to afford an orange solid which was filtered and washed with dry $Et_2O$ (15 mL). Reprecipitation (acetone/$Et_2O$) gave **50** as an orange powder (973 mg, 89%). $^1H$ NMR (270 MHz, [$D_6$]acetone): $\delta = 7.31$ (dd, $^3J_{H,H} = 6.0$, 2.5 Hz, 1H, 3-H), 7.29 (dd, $^3J_{H,H} = 8.0$, 2.0 Hz, 1H, 6′-H), 7.14 (d, $^3J_{H,H} = 2.0$ Hz, 1H, 2′-H), 6.99 (d, $^3J_{H,H} = 8.0$ Hz, 1H, 5′-H), 6.58 (d, $^3J_{H,H} = 6.0$ Hz, 1H, 2-H), 6.16 (s, 2H, $OCH_2O$), 4.47 (m, 1H, 5-H), 4.05 (s, 3H, OMe), 3.97 (dd, $^3J_{H,H} = 15.5$, 6.6 Hz, 1H, 6β-H), 2.80 ppm (d, $^3J_{H,H} = 15.5$ Hz, 1H, 6α-H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 151.74$ (4-C), 150.94, 150.50 (3′-C, 4′-C), 128.61 (1′-C), 123.68 (2′-C), 109.99 (5′-C), 106.78 (6′-C), 103.58 ($OCH_2O$), 91.69 (1-C), 90.60 (2-C), 72.70 (3-C), 57.98 (OMe), 43.31 (5-C), 29.75 ppm (6-C obscured by [$D_6$]acetone but estimated from the position of its cross-peak with 6α-H in the gHSQC spectrum); HRMS (FAB): *m/z*: calcd for $C_{17}H_{13}FeO_6$: 369.0062; found 369.0062 $[M-PF_6]^+$; IR (acetone): $\tilde{\nu}_{max} =$ 2103 ($\nu_{sym}$ CO), 2053 ($\nu_{asym}$ CO), 1422, 1363 $cm^{-1}$; elemental analysis calcd (%) for $C_{17}H_{13}FeO_6PF_6$ (514.09): C 39.7, H 2.5; found: C 39.5, H 2.4.

***Reactions of arylcyclohexadienyliron complexes with nucleophiles***

**Reaction of 1 (Nu = Ph) with sodium borohydride**: Following general method C, sodium borohydride (19 mg, 0.50 mmol) and the 1-phenyl salt (**1**, Nu = Ph) (50 mg, 0.11 mmol) in acetonitrile (2 mL) gave a 9:1 mixture of 1-phenyl[16a] and 5β-phenyl[16b] regioisomers (29 mg, 86%) as a yellow oil. The major product was identified as **23**[16a] by comparison with the $^1H$ NMR spectrum recorded from an authentic sample prepared by the complexation of 1-phenylcyclohexadiene by reaction with $[Fe_2(CO)_9]$. The minor product [$^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 5.49$ (dd, $^3J_{H,H} = 6.0$, 4.0 Hz, 1H, 3-H), 5.30 (dd, $^3J_{H,H} = 6.0$, 5.0 Hz, 1H, 2-H), 3.30 (m, 1H, 4-H), 2.93 ppm (t, $^3J_{H,H} = 7.0$ Hz, 1H, 1-H); other signals obscured by peaks of the major product] was assigned as tricarbonyl[(1,2,3,4-η)-5β-phenyl-1,3-cyclohexadiene]iron(0) (**22**) on the basis of NMR data reported[16b] for the 5α-phenyl-1,3-cyclohexadiene and 5β-phenyl-1,3-cyclohexadiene stereoisomers.

**Reaction of 3 (Nu = Ph) with sodium borohydride**: Following general method C, sodium borohydride (150 mg, 3.9 mmol) and the 2-phenyl salt (**3**, Nu = Ph) (418 mg, 0.95 mmol) in acetonitrile (15 mL) gave an 85:15 mixture of the 2-phenyl and 1-phenyl regioisomers **32** and **23** as a yellow oil (259 mg, 92%). MS (EI): *m/z* (%): 296 (4) $[M]^+$, 268 (17) $[M-CO]^+$, 240 (15) $[M-2CO]^+$, 210 (100) $[M-3CO-2H]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max} = 2056$ ($\nu_{sym}$ CO), 1980, 1974 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{15}H_{12}FeO_3$ (296.10): C 60.8, H 4.1; found: C 60.8, H 4.2. The major isomer [$^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.52$ (dm, $^3J_{H,H} = 6.5$ Hz, 2H, 2′-H, 6′-H), 7.36–7.29 (m, 3H, 3′-H, 4′-H, 5′-H), 5.78 (dd, $^3J_{H,H} = 6.5$, 1.5 Hz, 1H, 3-H), 3.75 (dd, $^3J_{H,H} = 6.4$, 3.7 Hz, 1H, 1-H), 3.23 (ddm, $^3J_{H,H} = 6.4$, 3.7 Hz, 1H, 4-H), 2.4–1.6 ppm (m, 4H, 5β-H, 5α-H, 6β-H, 6α-H)] was identified as tricarbonyl(1,2,3,4-η)-2-phenyl-1,3-cyclohexadiene)iron(0) (**32**).[16a,b] The minor isomer **23** [16a] was identified by comparison with the $^1H$ NMR spectrum recorded from an authentic sample prepared by the complexation of 1-phenylcyclohexadiene by reaction with $[Fe_2(CO)_9]$.

**Reaction of 25 with sodium borohydride**: Following general method C, sodium borohydride (100 mg, 2.6 mmol) was added to a solution of the 2-(4′-methoxyphenyl) salt **25** (236 mg, 0.50 mmol) in acetonitrile (15 mL) and the reaction mixture stirred for 45 min. After the work-up, this afforded an 86:14 mixture of the 2-(4′-methoxyphenyl) and 1-(4′-methoxyphenyl) regioisomers **34** and **33** as a yellow oil (163 mg, 99%). $^1H$ NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[$\eta^4$-2-(4′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (**34**): $\delta = 7.45$ (d, $^3J_{H,H} = 9.0$ Hz, 2H, 2′-H, 6′H), 6.86 (d, $^3J_{H,H} = 9.0$ Hz, 2H, 3′-H, 5′-H), 5.71 (dd, $^3J_{H,H} = 6$, 1.8 Hz, 1H, 3-H), 3.82 (s, 3H, OMe), 3.72 (dt, $^3J_{H,H} = 3.6$, 1.8 Hz, 1H, 1-H), 3.18 (ddm, $^3J_{H,H} = 6.3$, 3.6 Hz, 1H, 4-H), 2.4–1.6 ppm (m, 4H, 5β-H, 5α-H, 6β-H, 6α-H); for minor isomer tricarbonyl[$\eta^4$-1-(4′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (**33**): $\delta = 7.36$ (d, $^3J_{H,H} = 9.0$ Hz, 2H, 2′-H, 6′-H), 6.82

(d, $^3J_{H,H}$=9.0 Hz, 2H, 3′-H, 5′-H), 5.84 (d, $^3J_{H,H}$=5 Hz, 1H, 2-H), 5.43 (t, $^3J_{H,H}$=5 Hz, 1H, 3-H), 3.78 (s, 3H, OMe), 3.22 ppm (m, 1H, 4-H), other signals obscured by major isomer; MS (EI): *m*/*z* (%): 326 (4) $[M]^+$, 298 (18) $[M-CO]^+$, 270 (12) $[M-2CO]^+$, 268 (11) $[M-2CO-2H]^+$, 240 (100) $[M-3CO-2H]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2045 ($\nu_{sym}$ CO), 1979, 1973 ($\nu_{asym}$ CO), 1610, 1575, 1520 $cm^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{16}H_{14}FeO_4$ (326.13): C 58.9, H 4.3; found: C 58.6, H 4.5.

**Reaction of 26 with sodium borohydride**: Following general method C, sodium borohydride (150 mg, 3.9 mmol) was added to a solution of 2-(4′-trifluoromethylphenyl) salt **26** (380 mg, 0.75 mmol) in acetonitrile (15 mL) and the mixture stirred for 30 min. After the work-up, this afforded an 80:20 mixture of the 2-(4′-trifluoromethylphenyl) and 1-(4′-trifluoromethylphenyl) regioisomers **36** and **35** as a yellow oil (264 mg, 97%) which solidified upon standing. $^1$H NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[$\eta^4$-2-(4′-trifluoromethylphenyl)-1,3-cyclohexadiene]iron(0) (**36**): $\delta$=7.60 and 7.59 (d, $^3J_{H,H}$=8.6 Hz, 2H, and d, $^3J_{H,H}$=8.6 Hz, 2H, 2′-H, 3′-H, 5′-H, 6′-H), 5.80 (dd, $^3J_{H,H}$=6.5, 1.8, 1H, 3-H), 3.70 (dt, $^3J_{H,H}$=5.5, 1.8 Hz, 1H, 1-H), 3.29 (dt, $^3J_{H,H}$=5.5, 2.8 Hz, 1H, 4-H), 1.94 (ddt, $^3J_{H,H}$=14.0, 11.0, 3.5 Hz, 1H, 6β-H), 1.88–1.68 ppm (m, 3H, 5β-H, 5α-H, 6α-H); for minor isomer tricarbonyl[$\eta^4$-1-(4′-trifluoromethylphenyl-1,3-cyclohexadiene]iron(0) (**35**): $\delta$=7.52 and 7.51 (d, $^3J_{H,H}$=8.9 Hz, 2H, and d, $^3J_{H,H}$=8.9 Hz, 2H, 2′-H, 3′-H, 5′-H, 6′-H), 5.86 (d, $^3J_{H,H}$=4.0 Hz, 1H, 2-H), 5.37 (dd, $^3J_{H,H}$=7.0, 4.0 Hz, 1H, 1-H), 3.31 (m, 1H, 4-H), 2.35 (ddd, $^3J_{H,H}$=14.0, 11.0, 3.5 Hz, 1H, 6β-H), 2.04 ppm (ddt, $^3J_{H,H}$=14.0, 11.0, 3.5 Hz, 1H, 5β-H), other signals obscured by major isomer; MS (EI): *m*/*z* (%): 364 (9) $[M]^+$, 336 (48) $[M-CO]^+$, 308 (30) $[M-2CO]^+$, 306 (36) $[M-2CO-2H]^+$, 278 (96) $[M-3CO-2H]^+$, 224 (36) $[M-2CO-2H-Fe]^+$, 222 (53), 205 (36), 222 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2048 ($\nu_{sym}$ CO), 1985, 1979 ($\nu_{asym}$ CO), 1620 $cm^{-1}$ (Ar, C=C): elemental analysis calcd (%) for $C_{16}H_{11}F_3FeO_3$ (364.10): C 52.8, H 3.0; found: C 53.2, H 3.25.

**Reaction of 1 (Nu=Ph) with the sodium enolate of dimethyl malonate**: Following general method D, the 1-phenyl salt (**1**, Nu=Ph) (50 mg, 0.11 mmol) in dry THF (3 mL) [work-up: sat. aq. ammonium chloride (10 mL); water (10 mL); $Et_2O$ (20 mL); water (3×20 mL portions); sat. aq. NaCl (10 mL)] gave the product (40 mg, 83%) as a yellow oil. $^1$H NMR analysis identified this material as an 88:12 mixture of the 5-phenyl and 1β-phenyl regioisomers **16** and **15**. Flash chromatography with 50% dichloromethane in hexane as the eluant gave the pure isomer **16** as a yellow oil. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.47–7.14 (m, 5H, Ph), 5.94 (d, $^3J_{H,H}$=4.5 Hz, 1H, 4-H), 5.36 (dd, $^3J_{H,H}$=7, 4.5 Hz, 1H, 3-H), 3.77 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.17–3.03 (m, 3H, $O_2CCHCO_2$, 1-H, 2-H), 2.77 (dd, $^3J_{H,H}$=15.5, 10 Hz, 1H, 6β-H), 1.55 ppm (dd, $^3J_{H,H}$=15.5, 2.5 Hz, 1H, 6α-H); MS (EI): *m*/*z* (%): 426 (0.2) $[M]^+$, 370 (6), 342 (18), 310 (4), 282 (5), 214 (5), 210 (16), 154 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2049 ($\nu_{sym}$ CO), 1984, 1980 ($\nu_{asym}$ CO), 1763, 1744 $cm^{-1}$ (ester carbonyl); HRMS (CI): *m*/*z*: calcd for $C_{20}H_{19}FeO_7$: 427.0480; found 427.0480 $[M+H]^+$. Data for the minor isomer tricarbonyl{dimethyl [(2,3,4,5-η)-1β-phenyl-2,4-cyclohexadien-1α-yl]propandioate}iron(0) (**15**) (from mixture): $\delta$=5.44 (m, 1H, 3-H or 4-H), 3.67 (s, 3H, OMe), 3.45 (s, 3H, OMe), 2.93 (dd, $^3J_{H,H}$=16, 2 Hz, 1H, 6β-H), 1.41 ppm (dd, $^3J_{H,H}$=16, 3.5 Hz, 1H, 6α-H), other peaks obscured by signals from the major isomer.

**Reaction of 11 with the sodium enolate of dimethyl malonate**: Following the general method D, 1-(4′-methoxyphenyl) salt **11** (200 mg, 0.43 mmol) in dry THF (6 mL) [work-up: sat. aq. ammonium chloride (15 mL); water (10 mL); $Et_2O$ (30 mL); water (3×30 mL portions); sat. aq. NaCl (15 mL)] gave a 96:4 mixture of 5-(4′-methoxyphenyl) and 1β-(4′-methoxyphenyl) regioisomers **18** and **17** was a yellow oil (186 mg, 95%) which solidified upon refrigeration. $^1$H NMR (250 MHz, $CDCl_3$): for the major isomer tricarbonyl{dimethyl [(2,3,4,5-η)-5-(4′-methoxyphenyl)-2,4-cyclohexadien-1α-yl]propandioate}iron(0) (**18**): $\delta$=7.33 (dm, $^3J_{H,H}$=9 Hz, 2H, 2′-H, 6′-H), 6.81 (dm, $^3J_{H,H}$=9 Hz, 2H, 3′-H, 5′-H), 5.89 (d, $^3J_{H,H}$=5 Hz, 1H, 4-H), 5.34 (t, $^3J_{H,H}$=5 Hz, 1H, 3-H), 3.79 (s, 3H, OMe), 3.76 (s, 3H, $CO_2$Me), 3.68 (s, 3H, $CO_2$Me), 3.16–2.99 (m, 3H, $O_2CCHCO_2$, 1-H, 2-H), 2.76 (dd, $^3J_{H,H}$=16, 10 Hz, 1H, 6β-H), 1.54 ppm (dd, $^3J_{H,H}$=16, 2 Hz, 1H, 6α-H); for the minor isomer tricarbonyl(dimethyl [(2,3,4,5-η)-1β-(4′-methoxyphenyl)-2,4-cyclohexadien-1α-yl]propandioate}iron(0) (**17**): $\delta$=3.66 (s, 3H, $CO_2$Me), 3.48 ppm (s, 3H, $CO_2$Me), other peaks obscured by signals from the major isomer. Recrystallisation of this mixture from $Et_2O$/light petroleum gave pure **18** as yellow platelets: M.p. 100.5–101.5 °C; MS (EI): *m*/*z* (%): 400 (2) $[M-2CO]^+$, 372 (5), 340 (1), 271 (1), 240 (4), 184 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2047 ($\nu_{sym}$ CO), 1980 ($\nu_{asym}$ CO), 1762, 1744 $cm^{-1}$ (ester carbonyl); elemental analysis calcd (%) for $C_{21}H_{20}FeO_8$ (456.23): C 55.3, H 4.4; found: C 55.25, H 4.2.

**Reaction of 12 with the sodium enolate of dimethyl malonate**: Following the general method D, 1-(4′-trifluoromethylphenyl) salt **12** (150 mg, 0.30 mmol) in dry THF (3 mL) [work-up: sat. aq. ammonium chloride (15 mL); water (10 mL); $Et_2O$ (30 mL); water (3×30 mL portions); sat. aq. NaCl (15 mL)] gave the product (144 mg, 99%) as a yellow oil which solidified upon refrigeration. $^1$H NMR analysis identified this material as a 79:21 mixture of the 5-(4′-trifluoromethylphenyl)-2,4-cyclohexadien-1α-yl and 1β-(4′-trifluoromethylphenyl)-2,4-cyclohexadien-1α-yl regioisomers. $^1$H NMR (250 MHz, $CDCl_3$): for the major isomer tricarbonyl{dimethyl [(2,3,4,5-η)-5-(4′-trifluoromethylphenyl)-2,4-cyclohexadien-1α-yl]-propandioate}iron(0) (**20**): $\delta$=7.53 and 7.50 (dm, $^3J_{H,H}$=8 Hz, 2H, and dm, $^3J_{H,H}$=8 Hz, 2H, 2′-H, 3′-H, 5′-H, 6′-H), 5.95 (d, 1H, *J* = 4.5 Hz, 4-H), 5.39 (dd, $^3J_{H,H}$=6, 4.5 Hz, 1H, 3-H), 3.77 (s, 3H, $CO_2$Me), 3.70 (s, 3H, $CO_2$Me), 3.18–3.04 (m, 3H, $O_2CCHCO_2$, 1-H, 2-H), 2.73 (dd, $^3J_{H,H}$=16, 9 Hz, 1H, 6β-H), 1.55 ppm (dd, $^3J_{H,H}$=16, 4 Hz, 1H, 6α-H); for the minor isomer tricarbonyl{dimethyl (2,3,4,5-η)-1β-(4′-trifluoromethylphenyl)-2,4-cyclohexadien-1α-yl]propandioate}iron(0) (**19**): $\delta$=7.59 and 7.46 (dm, $^3J_{H,H}$=8 Hz, 2H, and dm, $^3J_{H,H}$=8 Hz, 2H, 2′-H, 3′-H, 5′-H, 6′-H), 5.44 (m, 2H, 3-H, 4-H), 2.94 (dd, $^3J_{H,H}$=16, 3 Hz, 1H, 6β-H), 2.37 ppm (dd, $^3J_{H,H}$=16, 4 Hz, 1H, 6α-H), other peaks obscured by signals from the major isomer. Recrystallisation of this mixture from $Et_2O$/light petroleum gave pure **20** as yellow needles: M.p. 126.5–127.5 °C; MS (EI): *m*/*z* (%): 438 (2) $[M-2CO]^+$, 410 (4), 222 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2052 ($\nu_{sym}$ CO), 1985 ($\nu_{asym}$ CO), 1762, 1744 $cm^{-1}$ (ester carbonyl); elemental analysis calcd (%) for $C_{21}H_{17}F_3FeO_7$ (494.20): C 51.0, H 3.5; found: C 51.0, H 3.4.

**Reaction of 14 with the sodium enolate of dimethyl malonate**: Following the general method D, the 1-phenyl dicarbonyliron salt (**14**) (100 mg, 0.15 mmol) in dry THF (3 mL) [work-up: sat. aq. ammonium chloride (10 mL); water (10 mL); $Et_2O$ (20 mL); water (3×20 mL portions); sat. aq. NaCl (10 mL)] gave dicarbonyl{dimethyl [(2,3,4,5-η)-5-phenyl-2,4-cyclohexadien-1α-yl]propandioate}triphenylphosphineiron(0) (**21**) as a yellow foam (86 mg, 88%). M.p. 184.5–185.5 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.57–7.10 (m, 20H, 1-Ph, Fe-$PPh_3$), 5.83 (d, $^3J_{H,H}$=4 Hz, 1H, 4-H), 4.57 (m, 1H, 3-H), 3.60 (s, 3H, $CO_2$Me), 3.49 (s, 3H, $CO_2$Me), 2.90 (dm, $^3J_{H,H}$=10 Hz, 1H, 1-H), 2.85 (d, $^3J_{H,H}$=10 Hz, 1H, $O_2CCHCO_2$), 2.84 (ddd, $^3J_{H,H}$=15, 10, 4 Hz, 1H, 6β-H), 1.77 (m, 1H, 2-H), 1.40 (ddd, $^3J_{H,H}$=15, 5, 3 Hz, 1H, 6α-H); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=1971 ($\nu_{sym}$ CO), 1914 ($\nu_{asym}$ CO), 1753, 1734 $cm^{-1}$ (ester carbonyl); elemental analysis calcd (%) for $C_{37}H_{33}FeO_6P$ (660.48): C 67.3, H 5.0; found: C 67.2, H 5.2.

**Reaction of 65 with the sodium enolate of dimethyl malonate**: Following the general method D, 2-methoxy-1-phenyl **65** (100 mg, 0.21 mmol) in dry THF (3 mL) [work-up: sat. aq. ammonium chloride (10 mL); water (10 mL); $Et_2O$ (20 mL); water (3×20 mL portions); sat. aq. NaCl (10 mL)] gave tricarbonyl{dimethyl [(2,3,4,5-η)-4-methoxy-5-phenyl-2,4-cyclohexadien-1α-yl]propandioate}iron(0) (**66**) (93 mg, 96%) as a pale yellow oil which solidified. M.p. 152.5–153.5 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.54–7.49 (m, 2H, 2′-H, 6′-H), 7.34–7.17 (m, 3H, 3′-H, 4′-H, 5′-H), 5.04 (d, $^3J_{H,H}$=7 Hz, 1H, 3-H), 3.76 (s, 3H, $CO_2$Me), 3.69, 3.67 (2s, 2×3H, OMe, $CO_2$Me), 3.14 (d, $^3J_{H,H}$=9 Hz, 1H, $O_2CCHCO_2$), 2.83 (ddt, $^3J_{H,H}$=11, 9, 3.5 Hz, 1H, 1-H), 2.65 (dd, $^3J_{H,H}$=7, 3.5 Hz, 1H, 2-H), 2.38 (dd, $^3J_{H,H}$=15.5, 11 Hz, 1H, 6β-H), 1.64 (dd, $^3J_{H,H}$=15.5, 3.5 Hz, 1H, 6α-H); MS (EI): *m*/*z* (%): 456 (0.4) $[M]^+$, 400 (10), 372 (21), 271 (12), 240 (50), 225 (36), 184 (100); IR ($CH_3CN$): $\tilde{\nu}_{max}$=2045 ($\nu_{sym}$ CO), 1971 ($\nu_{asym}$ CO), 1753, 1735 $cm^{-1}$ (ester carbonyl); elemental analysis calcd (%) for $C_{21}H_{20}FeO_8$ (456.23): C 55.3, H 4.4; found: C 55.5, H 4.4.

**Reaction of tricarbonyl[(1,2,3,4,5-η)-4-methoxy-1-phenyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate(1−) (53) with the sodium enolate of dimethyl malonate**: Following the general method D, sodium hydride in mineral oil (10 mg, 0.25 mmol), dimethyl malonate (33 mg, 0.25 mmol), the 4-methoxy-1-phenyl salt (**53**) (107 mg, 0.23 mmol) in dry

THF (3 mL) [work-up: sat. aq. ammonium chloride (10 mL); water (10 mL); $Et_2O$ (20 mL); water (3×20 mL portions); sat. aq. NaCl (10 mL)] gave tricarbonyl{dimethyl [(2,3,4,5-η)-1β-phenyl-4-methoxy-2,4-cyclohexadien-1α-yl]propandioate}iron(0) (**54**) (95 mg, 92%) as pale yellow crystals. M.p. 110–113°C (decomp) (from hexane); $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.35–7.15 (m, 5H, Ph), 5.18 (dd, $^3J_{H,H}$=7, 2.5 Hz, 1H, 3-H), 3.83 (s, 1H, $O_2CCHCO_2$), 3.67 (s, 6H, OMe, $CO_2$Me), 3.45 (d, $^3J_{H,H}$=7 Hz, 1H, 2-H), 3.43 (s, 3H, $CO_2$Me), 3.32 (m, 1H, 5-H), 2.97 (dd, $^3J_{H,H}$=15.5, 3 Hz, 1H, 6β-H), 2.36 ppm (dd, $^3J_{H,H}$=15.5, 4 Hz, 1H, 6α-H); MS (FAB): *m/z* (%): 456 (30) $[M]^+$, 428 (31), 400 (28), 372 (100); IR ($CH_3CN$): $\tilde{\nu}_{max}$=2047 ($\nu_{sym}$ CO), 1974 ($\nu_{asym}$ CO), 1758, 1728 cm$^{-1}$ (ester carbonyl); HRMS (FAB): *m/z*: calcd for $C_{21}H_{20}FeO_8$: 456.0508; found 456.0505 $[M]^+$. A $^1$H NMR NOE experiment was performed: Irradiation of the propandioate CH at $\delta_H$ 3.83 ppm led to the following enhancements: 6α-H, +5.1%; and Ph, +11.2%.

**Reaction of 3 (Nu=Ph) with the sodium enolate of diethyl malonate**: Following a modification the general method D (excess diethyl malonate was removed at 100–120°C, $10^{-3}$ mm Hg), sodium hydride in mineral oil (350 mg, 8.7 mmol), diethyl malonate (1.19 gm, 7.4 mmol) and 2-phenyl salt **3** (229 mg, 0.52 mmol) gave an 85:15 mixture of the 4-phenyl and 2-phenyl regioisomers (**38**) and (**37**) as a dark yellow oil (184 mg, 78%). $^1$H NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl{diethyl [(2,3,4,5-η)-4-phenyl-2,4-cyclohexadien-1α-yl]propanedioate}iron(0) (**38**): $\delta$=7.51 (dm, $^3J_{H,H}$=8.2 Hz, 2H, 2′-H, 6′-H), 7.4–7.2 (M, 3H, 3′-H, 4′-H, 5′-H), 5.76 (dd, $^3J_{H,H}$=6.4, 1.9 Hz, 1H, 3-H), 5.59 (dt, $^3J_{H,H}$=3.9, 1.9 Hz, 1H, 5-H), 4.18 (q, $^3J_{H,H}$=7.0 Hz, 2H, O-C$H_2$-$CH_3$), 4.10 (q, $^3J_{H,H}$=7.0 Hz, 2H, O-C$H_2$-$CH_3$), 3.07 (dd, $^3J_{H,H}$=6.4, 3.3 Hz, 1H, 2-H), 3.06 (d, $^3J_{H,H}$=8.9 Hz, 1H, $O_2CCHCO_2$), 2.87 (ddt, $^3J_{H,H}$=10.5, 8.9, 3.2 Hz, 1H, 1β-H), 2.32 (ddd, $^3J_{H,H}$=15.0, 10.5, 3.9 Hz, 1H, 6β-H), 1.61 (ddd, $^3J_{H,H}$=15.0, 3.5, 2.3 Hz, 1H, 6α-H), 1.26 (t, $^3J_{H,H}$=7.0 Hz, 3H, $OCH_2CH_3$), 1.21 ppm (t, $^3J_{H,H}$=7.0 Hz, 3H, $OCH_2CH_3$); for minor isomer tricarbonyl{diethyl [(2,3,4,5-η)-2-phenyl-2,4-cyclohexadien-1α-yl]propanedioate}iron(0) (**37**): $\delta$=5.93 (d, $^3J_{H,H}$=4.4 Hz, 1H, 3-H), 5.36 (dd, $^3J_{H,H}$=6.4, 4.4 Hz, 1H, 4-H), 1.59 (dm, $^3J_{H,H}$=15.6 Hz, 1H, 6α-H), 1.29 (t, $^3J_{H,H}$=7.0 Hz, 3H, $OCH_2CH_3$), 1.23 ppm (t, $^3J_{H,H}$=7.0 Hz, 3H, $OCH_2CH_3$), other signals obscured by major isomer; MS (EI): *m/z* (%): 454 (1.6) $[M]^+$, 398 (16) $[M-2CO]^+$, 370 (60) $[M-2CO]^+$, 324 (18), 295 (13), 254 (12), 210 (45), 154 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2050 ($\nu_{sym}$ CO), 1985, 1979 ($\nu_{asym}$ CO), 1757, 1738 (ester carbonyl), 1610, 1468 cm$^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{22}H_{22}FeO_7$ (454.25): C 58.2, H 4.9; found: C 58.5, H 4.9.

**Reaction of 25 with the sodium enolate of diethyl malonate**: Following a modification the general method D (excess diethyl malonate was removed at 100–120°C, $10^{-3}$ mm Hg), sodium hydride in mineral oil (80 mg, 2 mmol), diethyl malonate (0.27 mg, 1.7 mmol) and the 2-(4′-methoxyphenyl) salt (**25**) (124 mg, 0.26 mmol) gave tricarbonyl{diethyl [(2,3,4,5-η)-4-(4′-methoxyphenyl)-2,4-cyclohexadiene-1α-yl]propanedioate}iron(0) (**39**) as a pale greenish yellow oil (102 mg, 80%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$=7.44 (dm, $^3J_{H,H}$=8.9 Hz, 2H, 2′-H, 6′-H), 6.87 (dm, $^3J_{H,H}$=8.9 Hz, 2H, 3′-H, 5′-H), 5.69 (dd, $^3J_{H,H}$=6.4, 1.9 Hz, 1H, 3-H), 4.19 (q, $^3J_{H,H}$=7.1 Hz, 2H, O-C$H_2$-$CH_3$), 4.11 (q, $^3J_{H,H}$=7.1 Hz, 2H, O-C$H_2$-$CH_3$), 3.82 (s, 3H, OMe), 3.58 (dt, $^3J_{H,H}$=4.6, 1.9 Hz, 1H, 5-H), 3.05 (d, $^3J_{H,H}$=8.9 Hz, 1H, $O_2CCHCO_2$), 3.02 (dd, $^3J_{H,H}$=6.4, 3.9 Hz, 1H, 2-H), 2.85 (m, 1H, 1β-H), 2.30 (ddd, $^3J_{H,H}$=15.2, 10.9, 4.6, 1H, 6β-H), 1.58 (dm, $^3J_{H,H}$=15.2 Hz, 1H, 6α-H), 1.25 (t, $^3J_{H,H}$=7.1 Hz, 3H, $OCH_2CH_3$), 1.20 ppm (t, $^3J_{H,H}$=7.1 Hz, 3H, $OCH_2CH_3$); MS (EI): *m/z* (%): 484 (1) $[M]^+$, 328 (6) $[M-2CO]^+$, 400 (24) $[M-3CO]^+$, 214 (17), 184 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2049 ($\nu_{sym}$ CO), 1983, 1978 ($\nu_{asym}$ CO), 1756, 1739 (ester carbonyl), 1618, 1585, 1520 cm$^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{23}H_{24}FeO_8$ (484.28): C 57.0, H 5.0; found: C 57.2, H 5.0.

**Reaction of 53 with the sodium enolate of methyl cyanoacetate**: The general method D for malonate diesters was modified for use with the cyanoacetate ester by generating the enolate over a period of 1 h and using a 1.5 h reaction time after addition of the arylcyclohexadienyliron complex. The product was purified by column chromatography (hexane/ethyl acetate 5:1 → 4:1). In this way, NaH (60% suspension in mineral oil, 120 mg, 3 mmol), methyl cyanoethanoate (300 mg, 3 mmol) and 4-methoxy-1-phenyl salt **53** (135 mg, 0.29 mmol) gave tricarbonyl{methyl [(2,3,4,5-η)-4-methoxy-1β-phenyl-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron(0) (**55**) as two inseparable diastereoisomers as a pale yellow gum (100 mg, 82%). $^1$H NMR (270 MHz, $CDCl_3$): $\delta$=7.36–7.26 (m, 3H, 3′-H, 4′-H, 5′-H), 7.24 (d, $^3J_{H,H}$=7.2 Hz, 2H, 2′-H, 6′-H), 5.30 (dd, $^3J_{H,H}$=6.7, 2.3 Hz, 0.6H, 3-H), 5.22 (dd, $^3J_{H,H}$=6.6, 2.6 Hz, 0.4H, 3-H), 3.70 (s, 1.8H, OMe), 3.66 (s, 1.2H, OMe), 3.64 (s, 0.4H, $O_2CCHCN$), 3.62 (s, 0.6H, $O_2CCHCN$), 3.59 (s, 1.2H, $CO_2$Me), 3.41 (s, 1.8H, $CO_2$Me), 3.33 (dd, $^3J_{H,H}$=5.6, 2.6 Hz, 1H, 5-H), 3.13 (d, $^3J_{H,H}$=6.6 Hz, 0.6H, 2-H), 3.09 (d, $^3J_{H,H}$=6.6 Hz, 0.4H, 2-H), 2.79 and 2.67 (dd, $^3J_{H,H}$=15.5, 2.6 Hz and dd, $^3J_{H,H}$=15.5, 2.6 Hz, 1H, 6β-H), 2.44 (dd, $^3J_{H,H}$=15.5, 3.3 Hz, 0.6H, 6α-H), 2.39 ppm (dd, $^3J_{H,H}$=15.5, 3.3 Hz, 0.4H, 6α-H); MS (CI): *m/z* (%): 441 (3) $[M+NH_4]^+$, 3258 (43), 184 (100); (EI): *m/z* (%): 367 (1) $[M-2CO]^+$, 339 (14) $[M-3CO]^+$, 240 (15), 184 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2247 (CN), 2048 ($\nu_{sym}$ CO), 1975 ($\nu_{asym}$ CO), 1745 (ester carbonyl), 1492 cm$^{-1}$ (Ar, C=C); HRMS (CI): *m/z*: calcd for $C_{20}H_{21}FeN_2O_6$: 441.0749; found: 441.0749 $[M+NH_4]^+$.

**Reaction of 50 with the sodium enolate of methyl cyanoacetate**: The general method D for malonate diesters was modified for use with the cyanoacetate ester by generating the enolate over a period of 1 h and using a 1.5 h reaction time after addition of the arylcyclohexadienyliron complex. The product was purified by column chromatography (50% $Et_2O$/50% cyclohexane). In this way, NaH (60% suspension in mineral oil, 62 mg, 1.56 mmol), methyl cyanoacetate (154 mg, 1.56 mmol) and 4-methoxy-1-(3′,4′-methylendioxyphenyl) salt **50** (400 mg, 0.78 mmol) gave tricarbonyl{methyl [(2,3,4,5-η)-4-methoxy-1β-(3′,4′-methylenedioxyphenyl)-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron(0) (**58**) as two inseparable diastereoisomers as a pale yellow gum (246 mg, 68%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=6.79–6.74 (m, 3H, Ar), 5.98 (s, 2H, O$CH_2$O), 5.31 (dd, $^3J_{H,H}$=6.8, 2.5 Hz, 0.5H, 3-H), 5.23 (dd, $^3J_{H,H}$=6.8, 2.5 Hz, 0.5H, 3-H), 3.80 (s, 1.5H, OMe), 3.70 (s, 1.5H, OMe), 3.67 (s, 1.5H, $CO_2$Me), 3.63 (s, 0.5H, $O_2CCHCN$), 3.59 (s, 0.5H, $O_2CCHCN$), 3.53 (s, 1.5H, $CO_2$Me), 3.36 (m, 1H, 5-H), 3.06 (d, 0.5H, *J* = 6.8, 2-H), 3.01 (d, *J* = 6.8, 0.5H, 2-H), 2.78 (dd, $^3J_{H,H}$=15.4, 2.5 Hz, 0.5H, 6β-H), 2.67 (dd, $^3J_{H,H}$=15.4, 2.5 Hz, 0.5H, 6β-H), 2.41 (dd, $^3J_{H,H}$=15.4, 3.5 Hz, 0.5H, 6α-H), 2.35 ppm (dd, $^3J_{H,H}$=15.4, 3.5 Hz, 0.5H, 6α-H); MS (EI): *m/z* (%): 383 (1) $[M-3CO]^+$, 284 (1) $[M-3CO-NCCH_2CO_2Me]^+$, 228 (100); HRMS: *m/z*: calcd for $C_{18}H_{17}FeNO_5$: 383.0456; found 383.0456 $[M-3CO]^+$; IR ($CH_2Cl_2$): $\tilde{\nu}_{max}$=2228 (CN), 2050 ($\nu_{sym}$ CO), 1975 ($\nu_{asym}$ CO), 1742 (ester carbonyl), 1490, 1237, 1040, 623 cm$^{-1}$; elemental analysis calcd (%) for $C_{21}H_{17}FeNO_8$ (467.21): C 54.0, H 3.7; N 3.0; found: C 54.2, H 3.9, N 3.4.

**Tricarbonyl[(1,2,3,4-η)-5α-cyanomethyl-2-methoxy-5β-(3′,4′-methylenedioxyphenyl)-1,3-cyclohexadiene]iron(0) (60)**: The general method D for malonate diesters was modified for use with the cyanoacetate ester by generating the enolate over a period of 1 h and using a 1 h reaction time after addition of the arylcyclohexadienyliron complex. The product was purified by column chromatography (30% $Et_2O$/70% cyclohexane). In this way, NaH (60% suspension in mineral oil, 34 mg, 0.86 mmol), trimethylsilylethyl cyanoethanoate[37] 158 mg, 0.86 mmol) and 4-methoxy-1-(3′,4′-methylendioxyphenyl) salt **50** (400 mg, 0.78 mmol) gave tricarbonyl{2-trimethylsilylethyl [(2,3,4,5-η)-4-methoxy-1β-(3′,4′-methylenedioxyphenyl)-2,4-cyclohexadien-1α-yl]cyanoethanoate}iron(0) (**59**) as two inseparable diastereoisomers as a pale yellow gum (351 mg, 0.63 mmol, 82%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=6.81–6.77 (m, 3H, Ar), 5.99 (s, 1H, O$CH_2$O), 5.98 (s, 1H, O$CH_2$O), 5.33 (dd, $^3J_{H,H}$=6.8, 2.3 Hz, 0.5H, 3-H), 5.24 (dd, $^3J_{H,H}$=6.8, 2.3 Hz, 0.5H, 3-H), 4.13 (m, 1H, O$CH_2CH_2$Si), 3.99 (m, 1H, O$CH_2CH_2$Si), 3.75 (s, 1.5H, 4-OMe), 3.70 (s, 1.5H, 4-OMe), 3.60 (s, 0.5H, $O_2CCHCN$), 3.57 (s, 0.5H, $O_2CCHCN$), 3.35 (m, 1H, H-5), 3.09 (d, $^3J_{H,H}$=6.8 Hz, 0.5H, H-2), 3.03 (d, $^3J_{H,H}$=6.8 Hz, 0.5H, 2-H), 2.81 (dd, $^3J_{H,H}$=15.3, 2.5 Hz, 0.5H, 6β-H), 2.67 (dd, $^3J_{H,H}$=15.3, 2.5 Hz, 0.5H, 6β-H), 2.42 (dd, $^3J_{H,H}$=15.3, 3.0 Hz, 0.5H, 6α-H), 2.36 (dd, $^3J_{H,H}$=15.3, 3.0 Hz, 0.5H, 6α-H), 0.93 (m, 1H, $CH_2$Si), 0.74 (m, 1H, $CH_2$Si), 0.06 ppm (s, 18H, $SiMe_3$); HRMS (CI): *m/z*: calcd for $C_{25}H_{27}FeNO_8SiNH_4$: 571.1199; found: 571.1200 $[M+NH_4]^+$; IR ($CH_2Cl_2$): $\tilde{\nu}_{max}$=2238 (CN), 2049 ($\nu_{sym}$ CO), 1974 ($\nu_{asym}$ CO), 1733 (ester carbonyl), 1490, 1236, 1042, 624 cm$^{-1}$. A portion of this product (294 mg, 0.53 mmol) was dissolved in dry THF (10 mL). Tetrabutylammonium fluoride (1M solution in THF, 0.63 mL, 0.63 mmol) was added. The mixture was heated at reflux for 1.5 h. The cooled solution was quenched with water (5 mL) and $Et_2O$ (5 mL) and extracted into $Et_2O$ (3×25 mL portions). The combined or-

ganic extracts were washed with water (3×25 mL portions), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a yellow gum. Column chromatography (30% $Et_2O$/70% cyclohexane) afforded **60** as a pale yellow solid (172 mg, 0.42 mmol, 79%). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=6.79–6.76 (m, 3H, Ar), 5.97 (s, 2H, $OCH_2O$), 5.28 (dd, $^3J_{H,H}$=6.8, 2.5 H, 1H, 3-H), 3.73 (s, 3H, OMe), 3.35 (m, 1H, 1-H), 2.95 (d, 1H, $^3J_{H,H}$=6.8 Hz, 1H, 4-H), 2.62 (d, $^3J_{H,H}$= 16.5 Hz, 1H, $CH_2CN$), 2.58 (dd, $^3J_{H,H}$=14.5, 3.5 Hz, 1H, 6β-H), 2.45 (d, $^3J_{H,H}$=16.5 Hz, 1H, $CH_2CN$), 2.19 ppm (dd, $^3J_{H,H}$=14.5, 3.0 Hz, 1H, 6α-H); MS (EI): *m/z* (%): 381 (6) $[M-CO]^+$, 353 (13) $[M-2CO]^+$, 325 (21) $[M-3CO]^+$, 284 (29) $[M-3CO-NCCH_3]^+$, 228 (20), 199 (6), 149 (11), 121 (23), 84 (100); IR ($CH_2Cl_2$): $\tilde{\nu}_{max}$=2253 (CN), 2048 ($\nu_{sym}$ CO), 1968 ($\nu_{asym}$ CO), 1968 (ester carbonyl), 1489, 1232, 912, 740 cm$^{-1}$; elemental analysis calcd (%) for $C_{19}H_{15}FeNO_6$ (409.17): C 55.8, H 3.7, N 3.4; found: C 55.8, H 3.5, N 3.3.

**Reaction of 1 (Nu=Ph) with lithium dimethylcuprate**: Following the general method E, methyllithium (1.40 M solution in $Et_2O$, 0.61 mL, 0.85 mmol), copper(I) iodide (81 mg, 0.43 mmol) in dry THF (5 mL) and 1-phenyl salt **1** (85 mg, 0.19 mmol) [work-up: sat. aq. ammonium chloride (10 mL); water (50 mL); $Et_2O$ (10 mL); water (2×20 mL portions); sat. aq. NaCl (20 mL)] gave tricarbonyl[(1,2,3,4-η)-5α-methyl-1-phenyl-1,3-cyclohexadiene]iron(0) (**24**) (50 mg, 83%) as a yellow oil, which solidified upon refrigeration. M.p. 81–83 °C; $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.50–7.12 (m, 5H, Ph), 5.96 (d, $^3J_{H,H}$=4.5 Hz, 1H, 2-H), 5.32 (dd, $^3J_{H,H}$=7, 4.5 Hz, 1H, 3-H), 3.18 (dd, $^3J_{H,H}$=7, 4 Hz, 1H, 4-H), 2.70 (dd, $^3J_{H,H}$= 15.5, 11 Hz, 1H, 6β-H), 2.48 (m, 1H, 5-H), 1.32 (dd, $^3J_{H,H}$=15.5, 3 Hz, 1H, 6α-H), 1.00 ppm (d, $J$ = 7 Hz, 3H, Me); MS (EI): *m/z* (%): 310 (2) $[M]^+$, 282 (19), 254 (12), 254 (13), 224 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2045 ($\nu_{sym}$ CO), 1979, 1974 cm$^{-1}$ ($\nu_{asym}$ CO); HRMS (EI): *m/z*: calcd for $C_{16}H_{14}FeO_3$: 310.0292; found 310.0292 $[M]^+$.

**Reaction of 3 (Nu=Ph) with lithium diphenylcuprate**: Following the general method F, phenyllithium (1.58 mL of 2.0 M solution in $Et_2O$, 3.16 mmol), copper(I) iodide (300 mg, 1.58 mmol), and 2-phenyl salt **3** (348 mg, 0.79 mmol) in dry THF (10 mL) [work-up: sat. aq. ammonium chloride (20 mL); $Et_2O$ (20 mL); extraction with $Et_2O$ (3×20 mL portions)] gave a 90:10 mixture of 2,5α-diphenyl and 1,6α-diphenyl regioisomers **41** and **40** as a yellow oil (244 mg, 83%). $^1$H NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[(1,2,3,4-η)-2,5α-diphenyl-1,3-cyclohexadiene]iron(0) (**41**): $\delta$=7.57 (d, $^3J_{H,H}$=8.4 Hz, 2H, 2′-H, 6′-H), 7.36–7.29 (m, 3H, 3′-H, 4′-H, 5′-H), 7.18 and 7.07 (m, 2H, and m, 3H, 5α-Ph), 5.80 (dd, $^3J_{H,H}$=6.5, 2.0 Hz, 1H, 3-H), 3.69 (dt, $^3J_{H,H}$=3.8, 2.0 Hz, 1H, 1-H), 3.36 (dt, $^3J_{H,H}$=3.8, 2 Hz, 1H, 5β-H), 3.12 (dd, $^3J_{H,H}$=6.5, 3.6 Hz, 1H, 4-H), 2.53 (ddd, $^3J_{H,H}$=15.1, 11.1, 4.0 Hz, 1H, 6β-H), 1.75 ppm (ddd, $^3J_{H,H}$=15.2, 3.8, 2.3 Hz, 1H, 6α-H); for minor isomer tricarbonyl[(1,2,3,4-η)-1,6α-diphenyl-1,3-cyclohexadiene]iron(0) (**40**): $\delta$=5.91 (d, $^3J_{H,H}$= 4.4 Hz, 1H, 2-H), 5.49 (dd, $^3J_{H,H}$=6.6, 4.4 Hz, 1H, 3-H), 3.86 (dd, $^3J_{H,H}$= 11.1, 3.0 Hz, 1H, 6β-H), 3.19 (dm, $^3J_{H,H}$=6.6 Hz, 1H, 4-H), 2.65 (ddd, $^3J_{H,H}$=15.0, 11.1, 3.4 Hz, 1H, 5β-H), 1.87 ppm (dm, $^3J_{H,H}$=15.0 Hz, 5α-H), other signals obscured by major isomer; MS (EI): *m/z* (%): 372 (4) $[M]^+$, 344 (18) $[M-CO]^+$, 316 (20) $[M-2CO]^+$, 288 (67) $[M-3CO]^+$, 286 (26) $[M-3CO-2H]^+$, 230 (79) $[M-3CO-2H-Fe]^+$, 210 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2047 ($\nu_{sym}$ CO), 1982, 1977 ($\nu_{asym}$ CO), 1600, 1495 cm$^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{21}H_{16}FeO_3$ (372.20): C 67.8, H 4.3; found: C 67.9, H 4.6.

**Reaction of 25 with lithium diphenylcuprate**: Following the general method F, phenyllithium (1.40 mL of 2.0 M solution in $Et_2O$, 2.80 mmol), copper(I) iodide (266 mg, 1.40 mmol), 2-(4′-methoxyphenyl) salt **25** (328 mg, 0.70 mmol) in dry THF (10 mL) [work-up: sat. aq. ammonium chloride (20 mL); $Et_2O$ (20 mL); extraction with $Et_2O$ (3×20 mL portions)] gave a 95:5 mixture of 2-(4′-methoxyphenyl)-5α-phenyl and 1-(4′-methoxyphenyl)-6α-phenyl regioisomers (**43**) and (**42**) as a yellow gum (248 mg, 80%). $^1$H NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[(1,2,3,4-η)-2-(4′-methoxyphenyl)-5α-phenyl-1,3-cyclohexadieneliron(0) (**43**): $\delta$=7.53 (dm, $^3J_{H,H}$=9.0 Hz, 2H, 2′-H, 6′-H), 7.20 and 7.11 (m, 2H and m, 3H, 5α-Ph), 6.90 (dm, $^3J_{H,H}$=9.0 Hz, 2H, 3′-H, 5′-H), 5.77 (dd, $^3J_{H,H}$=6.4, 1.9 Hz, 1H, 3-H), 3.80 (s, 3H, OMe), 3.71 (dt, $^3J_{H,H}$=3.9, 1.9 Hz, 1H, 1-H), 3.36 (dt, $^3J_{H,H}$=11.1, 3.4 Hz, 1H, 5β-H), 3.11 (dd, $^3J_{H,H}$=6.4, 3.4 Hz, 1H, 4-H), 2.54 (ddd, $^3J_{H,H}$=15.1, 11.1, 4.0 Hz, 1H, 6β-H), 1.76 ppm (ddd, $^3J_{H,H}$=15.1, 3.8, 2.3 Hz, 1H, 6α-H); for minor isomer tricarbonyl[(1,2,3,4-η)-1-(4′-methoxyphenyl)-6α-phenyl-1,3-cyclohexadiene]iron(0) (**42**): $\delta$=5.93 (d, $^3J_{H,H}$=4.4 Hz, 1H, 2-H), 5.52 (dd, $^3J_{H,H}$=5.9, 4.4 Hz, 1H, 3-H), 3.68 (s, 3H, OMe), 3.18 (m, 1H, 4-H), 2.65 (ddd, $^3J_{H,H}$=15.2, 10.4, 2.8 Hz, 1H, 5β-H), 1.87 ppm (dm, $^3J_{H,H}$=15.2 Hz, 5α-H), other signals obscured by major isomer; MS (EI): *m/z* (%): 374 (0.8) $[M-CO]^+$, 346 (0.8) $[M-2CO]^+$, 318 (2.4) $[M-3CO]^+$, 316 (0.9) $[M-3CO-2H]^+$, 260 (1.8) $[M-3CO-2H-Fe]^+$, 240 (4), 184 (28), 182 (35), 169 (12), 141 (16), 115 (15), 105 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2046 ($\nu_{sym}$ CO), 1981, 1976 ($\nu_{asym}$ CO), 1612, 1520 cm$^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{22}H_{18}FeO_4$ (402.22): C 65.7, H 4.5; found: C 66.0, H 4.55.

**Reaction of 26 with lithium diphenylcuprate**: Following the general method F, phenyllithium (1.40 mL of 2.0 M solution in $Et_2O$, 28 mmol), copper(I) iodide (266 mg, 1.40 mmol), and 2-(4′-trifluoromethylphenyl) salt **26** (356 mg, 0.70 mmol) in dry THF (10 mL) [work-up: sat. aq. ammonium chloride (20 mL); $Et_2O$ (20 mL); extraction with $Et_2O$ (3× 20 mL portions)] gave an 89:11 mixture of the 5α-phenyl-2-(4′-trifluoromethylphenyl) and 6α-phenyl-1-(4′-trifluoromethylphenyl) regioisomers (**45**) and (**44**) as yellow crystals (240 mg, 78%). $^1$H NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[(1,2,3,4-η)-5α-phenyl-2-(4′-trifluoromethylphenyl)-1,3-cyclohexadiene]iron(0) (**45**): $\delta$=7.71 and 7.65 (d, $^3J_{H,H}$=8.3 Hz, 2H, and d, $^3J_{H,H}$=8.3 Hz, 2H, 2′-H, 3′-H, 5′-H, 6′-H), 7.23 (m, 2H, 3″-H, 5″-H), 7.15 (t, $^3J_{H,H}$=7.3 Hz, 1H, 4″-H), 7.10 (d, $^3J_{H,H}$= 7.0 Hz, 2H, 2″-H, 6″-H), 5.91 (dd, $^3J_{H,H}$=6.5, 1.8 Hz, 1H, 3-H), 3.71 (dt, $^3J_{H,H}$=3.7, 1.8 Hz, 1H, 1-H), 3.42 (dd, $^3J_{H,H}$=11.1, 3.7 Hz, 1H, 5β-H), 3.24 (dd, $^3J_{H,H}$=6.5, 3.7 Hz, 1H, 4-H), 2.59 (ddd, $^3J_{H,H}$=15.1, 11.1, 3.9 Hz, 1H, 6β-H), 1.80 (ddd, $^3J_{H,H}$=15.1, 3.7, 2.3 Hz, 1H, 6α-H); for minor isomer tricarbonyl[(1,2,3,4-η)-6α-phenyl-1-(4′-trifluoromethylphenyl)-1,3-cyclohexadiene]iron(0) (**44**): $\delta$=7.37 and 7.29 (d, $^3J_{H,H}$=8.4 Hz, 2H, and d, $^3J_{H,H}$=8.4 Hz, 2H, 2′-H, 3′-H, 5′-H, 6′-H), 7.05 (t, $^3J_{H,H}$=7.2 Hz, 1H, H″-4), 6.90 (d, $^3J_{H,H}$=6.9 Hz, 4″-H), 6.00 (d, $^3J_{H,H}$=4.4 Hz, 1H, 2-H), 5.62 (dd, $^3J_{H,H}$=4.9, 4.4 Hz, 1H, 3-H), 3.32 (m, 1H, 4-H), 3.87 (dd, $^3J_{H,H}$=11.5, 3.1 Hz, 1H, 6β-H), 2.73 (ddd, $^3J_{H,H}$=15.1, 11.5, 3.7 Hz, 1H, 5β-H), 1.92 (dm, $^3J_{H,H}$=15.1 Hz, 1H, 5α-H), other signals obscured by major isomer; MS (EI): *m/z* (%):440 (6) $[M]^+$, 412 (14) $[M-CO]^+$, 384 (22) $[M-2CO]^+$, 356 (75) $[M-3CO]^+$, 354 (21) $[M-3CO-2H]^+$, 300 (19) $[M-3CO-Fe]^+$, 298 (37) $[M-3CO-2H-Fe]^+$, 298 (37), 279 (57), 278 (32), 203 (60), 184 (100); IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2060 ($\nu_{sym}$ CO), 1986, 1981 ($\nu_{asym}$ CO), 1618, 1490 cm$^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{22}H_{15}F_3FeO_3$ (441.34): C 59.9, H 3.4; found: C 60.1, H 3.5.

**Reaction of 53 with lithium dimethylcuprate and with methyllithium**: Following the general method F, methyllithium (1.40 M solution in $Et_2O$, 0.43 mL, 0.60 mmol), copper(I) iodide (57 mg, 0.30 mmol) and 4-methoxy-1-phenyl salt **53** (70 mg, 0.15 mmol) in dry THF (5 mL) [work-up: sat. aq. ammonium chloride (10 mL); $Et_2O$ (10 mL); extraction with $Et_2O$ (3×10 mL portions)] gave (after chromatography eluting with 20% dichloromethane in light petroleum) the product (32 mg, 63%) as a yellow oil. $^1$H NMR analysis of this product identified it as a 93:7 mixture of the 4-methoxy-5α-methyl-1-phenyl and 2-methoxy-5α-methyl-5β-phenyl regioisomers **56** and **57**. Careful flash chromatography with light petroleum as the eluant afforded a pure sample of **56** as a yellow solid, m.p. 124.5–125.5 °C. Similarly, following a modification of general method E, methyllithium (1.00 M solution in $Et_2O$, 2.04 mL, 2.04 mmol) was added slowly to the 4-methoxy-1-phenyl salt (**53**) (300 mg, 0.64 mmol) in dry dichloromethane (10 mL) at 0 °C, and the resulting clear yellow solution was stirred at that temperature for 45 min. Solvent extraction and flash chromatography with 20% dichloromethane in hexane as the eluant gave, in order of elution: 4-phenylanisole (32 mg, 27%) as colourless needles, m.p. 88–89 °C (from light petroleum) (lit.[56] 90 °C) and the product (41 mg, 19%) as a yellow oil. $^1$H NMR analysis of this product showed this to be a 91:9 mixture of the 2-methoxy-5α-methyl-5β-phenyl and 4-methoxy-5α-methyl-1-phenyl regioisomers (**57**) and (**56**). Careful flash chromatography of the mixture with light petroleum as the eluant afforded a pure sample of the major product **57** as yellow rhomboids. M.p. 111–112 °C (from light petroleum). Tricarbonyl[(1,2,3,4-η)-4-methoxy-5α-methyl-1-phenyl-1,3-cyclohexadiene]iron(0) (**56**): $^1$H NMR (250 MHz, $CDCl_3$): $\delta$=7.40–7.15 (m, 5H, Ph), 5.64 (d, $^3J_{H,H}$=5 Hz, 1H, 2-H), 5.35 (d, $^3J_{H,H}$=5 Hz, 1H, 3-H), 3.49 (s, 3H, OMe),

2.83 (m, 1H, 5-H), 2.76 (dd, $^3J_{H,H}$=14, 10 Hz, 1H, 6β-H), 1.49 (dd, $^3J_{H,H}$=14, 2 Hz, 1H, 6α-H), 1.06 ppm (d, $^3J_{H,H}$=6 Hz, 3H, Me); MS (EI): *m/z* (%): 340 (0.6) $[M]^+$, 312 (21), 284 (21), 254 (100); HRMS (EI): *m/z*: calcd for $C_{17}H_{16}FeO_4$: 340.0398; found 340.0398 $[M]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ 2041 ($\nu_{sym}$ CO), 1978, 1965 $cm^{-1}$ ($\nu_{asym}$ CO); tricarbonyl[(1,2,3,4-η)-2-methoxy-5α-methyl-5β-phenyl-1,3-cyclohexadiene]iron(0) (**57**): $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$=7.35–7.25 (m, 5H, Ph), 5.22 (dd, $^3J_{H,H}$=7, 2.5 Hz, 1H, 3-H), 3.71 (s, 3H, OMe), 3.37 (m, 1H, 1-H), 2.97 (d, $^3J_{H,H}$=7 Hz, 1H, 4-H), 2.22 (dd, $^3J_{H,H}$=15, 3 Hz, 1H, 6β-H), 2.16 (dd, $^3J_{H,H}$=15, 2.5 Hz, 1H, 6α-H), 1.32 ppm (s, 3H, Me); MS (EI): *m/z* (%): 312 (4) $[M-CO]^+$. 284(23), 256 (21), 200 (13), 184 (36), 178 (100); HRMS: *m/z*: calcd for $C_{16}H_{16}FeO_3$: 312.0449; found 312.0449 $[M-CO]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$ 2050 ($\nu_{sym}$ CO), 1984, 1973 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{17}H_{16}FeO_4$ (340.15): C 60.0, H 4.7; found: C 60.4, H 4.9.

**Reaction of 3 (Nu=Ph) with KCN**: Following the general method H, KCN (123 mg, 1.9 mmol), and 2-phenyl salt **3** (222 mg, 0.47 mmol) in acetonitrile (6 mL) [work-up: light petroleum 4×10 mL portions] gave an 85:15 mixture of the 5α-cyano-2-phenyl and 6α-cyano-1-phenyl regioisomers (**47**) and (**46**) as a yellow-orange oil (149 mg, 92%). $^1H$ NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[(1,2,3,4-η)-5α-cyano-2-phenyl-1,3-cyclohexadiene]iron(0) (**47**): $\delta$=7.65–7.2 (m, 5H, Ph), 5.89 (dd, $^3J_{H,H}$=6.4, 1.6 Hz, 1H, 3-H), 3.72 (dt, $^3J_{H,H}$=6.4, 3.4 Hz, 1H, 1-H), 3.10 (dd, $^3J_{H,H}$=6.4, 3.4 Hz, 1H, 4-H), 2.98 (dt, $^3J_{H,H}$=11.4, 3.4 Hz, 1H, 5β-H), 2.41 (ddd, $^3J_{H,H}$=15.1, 11.4, 3.5 Hz, 1H, 6β-H), 2.07 ppm (dm, $^3J_{H,H}$=15.1 Hz, 1H, 6α-H); for minor isomer tricarbonyl[(1,2,3,4-η)-6α-cyano-1-phenyl-1,3-cyclohexadiene]iron(0) (**46**): $\delta$=6.00 (d, $^3J_{H,H}$=4.4 Hz, 1H, 2-H), 5.51 (dd, $^3J_{H,H}$=6.5, 4.4 Hz, 1H, 3-H), 3.42 (dd, $^3J_{H,H}$=11.3, 2.9 Hz, 1H, 6β-H), 3.24 (m, 1H, 4-H), 2.52 (ddd, $^3J_{H,H}$=15.1, 11.3, 3.8 Hz, 1H, 5β-H), 2.17 ppm (dm, $^3J_{H,H}$=15.1 Hz, 1H, 5α-H), other signals obscured by major isomer; MS (EI): *m/z* (%): 321 (4) $[M]^+$, 293 (8) $[M-CO]^+$, 265 (23) $[M-2CO]^+$, 237 (36) $[M-3CO]^+$, 210 (100) $[M-3CO-HCN]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2225 (CN), 2057 ($\nu_{sym}$ CO), 1993, 1988 $cm^{-1}$ ($\nu_{asym}$ CO); elemental analysis calcd (%) for $C_{16}H_{11}FeNO_3$ (321.11): C 59.8, H 3.5; found: C 60.1, H 3.8.

**Reaction of 25 with KCN**: Following the general method H, KCN (126 mg, 1.94 mmol), in a volume minimum of water, was added to 2-(4′-methoxyphenyl) salt **25** (325 mg, 0.69 mmol) in acetonitrile (6 mL) and the reaction mixture stirred for 15 min. After the work-up [light petroleum 4×10 mL portions], this afforded an 88:12 mixture of the 5α-cyano-1-(4′-methoxyphenyl) and 6α-cyano-1-(4′-methoxyphenyl) regioisomers **49** and **48** as yellow crystals (193 mg, 80%). $^1H$ NMR (400 MHz, $CDCl_3$): for major isomer tricarbonyl[(1,2,3,4-η)-5α-cyano-1-(4′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (**49**): $\delta$=7.46 (d, $^3J_{H,H}$=8.8, 2H, 2′-H, 6′-H), 6.89 (d, $^3J_{H,H}$=8.8, 2H, 3′-H, 5′-H), 5.81 (dd, $^3J_{H,H}$=6.3, 1.8 Hz, 1H, 3-H), 3.71 (dt, $^3J_{H,H}$=3.5, 1.9 Hz, 1H, 1-H), 3.81 (s, 3H, OMe), 3.05 (dd, $^3J_{H,H}$=6.3, 3.4 Hz, 1H, 4-H), 2.95 (dt, $^3J_{H,H}$=11.3, 3.4 Hz, 1H, 5β-H), 2.39 (ddd, $^3J_{H,H}$=15.1, 11.3, 3.7 Hz, 1H, 6β-H), 2.05 ppm (ddd, $^3J_{H,H}$=15.1, 3.4, 2.4 Hz, 1H, 6α-H); for minor isomer tricarbonyl[(1,2,3,4-η)-6α-cyano-1-(4′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (**48**): $\delta$=7.33 (d, $^3J_{H,H}$=8.8, 2H, 2′-H, 6′-H), 6.86 (d, $^3J_{H,H}$=8.8 Hz, 2H, 3′-H, 5′-H), 5.95 (d, $^3J_{H,H}$=4,8 Hz, 1H, 2-H), 5.48 (dd, $^3J_{H,H}$=6.1, 4.8 Hz, 1H, 3-H), 3.77 (s, 3H, OMe), 3.39 (dd, $^3J_{H,H}$=11.7, 3.0 Hz, 1H, 6β-H), 3.19 (m, 1H, 4-H), 2.48 (ddd, $^3J_{H,H}$=15.4, 11.7, 3.6 Hz, 1H, 5β-H), 2.13 ppm (dt, $^3J_{H,H}$=15.4, 4.9, 1H, 5α-H), other signals obscured by major isomer; MS (EI): *m/z* (%): 351 (4) $[M]^+$, 323 (7) $[M-CO]^+$, 295 (20) $[M-2CO]^+$, 267 (38) $[M-3CO]^+$, 240 (100) $[M-3CO-HCN]^+$; IR ($C_6H_{12}$): $\tilde{\nu}_{max}$=2245 (CN), 2054 ($\nu_{sym}$ CO), 1981 ($\nu_{asym}$ CO), 1608, 1580, 1520 $cm^{-1}$ (Ar, C=C); elemental analysis calcd (%) for $C_{17}H_{13}FeNO_4$ (351.14): C 58.1, H 3.7, N 4.0; found: C 57.8, H 3.7, N 3.6.

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