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Addition of aryl substituents to cyclohexadienyliron electrophiles in the development of routes to C_{12} central building blocks for alkaloid synthesis

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Abstract

Novel iron–aroyl complexes or synthetically prized arylcyclohexadienyl complexes can be formed from tricarbonyl(η^5-1,4-dimethoxycyclohexadienyl)iron(1 +) hexafluorophosphate(1 −) by correct control of reaction sequences that exploit the addition of aryllithium reagents to introduce the aromatic group. Bimetallic products are obtained when a tricarbonylchromium-bound aryllithium reagent or the corresponding cuprate are employed.

Keywords: Acyliron complexes; Aryllithium nucleophiles; (Aryllithium)chromium complexes; Cyclohexadienyliron electrophiles; Alkaloid synthesis

1. Introduction

Versatile building blocks for use in organic synthesis are especially valuable when they correspond to the central portion of a common feature of a class of important target structures. When organometallic complexes are used for this purpose, additional advantages such as potent stereocontrol effects are available, and since the metal can be brought into use repeatedly during a synthesis, the organometallic reactions can play a central role in the development of the synthetic strategy [1]. For example, many alkaloid structures contain in the central part of the molecule, aromatic and partially saturated six-membered rings joined at a stereogenic centre [2]. Because of their wide ranging biological activity, these compounds are extensively addressed as target structures, and recent work has identified the possibility that aryl-substituted cyclohexadienyliron complexes can provide a central C_{12} electrophilic component around which syntheses can be based. Examples of this approach (Fig. 1) can be seen in a demonstration synthesis [3] of *O*-methyljoubertiamine (**1**), a formal total synthesis [4] of lycoramine (**2**), and the synthesis [5] of the ABC ring section of the hippeastrine (**3**) carbon skeleton. An important challenge in the optimisation of procedures of this type concerns the proper definition and control of regioselectivity properties in reactions of organometallic electrophiles with nucleophiles, and over recent years, work in Norwich [6] and in Paris [7] with η^5 and η^6 electrophiles has explored these reactions. The choice of types of nucleophiles, solvents, and reaction conditions can all play an important role, and on occasions, small changes in structure can result in wide differences in reactivity properties. The development of C_{12} electrophilic intermediates provides an important illustration that has in part been the subject of a preliminary communication [8], and is now reported in full.

The lycoramine class of targets [9] contain an *ortho* carbon substituent ($R^1 = CH_2$–X in **4**) on the aromatic ring and although often this is introduced late in a

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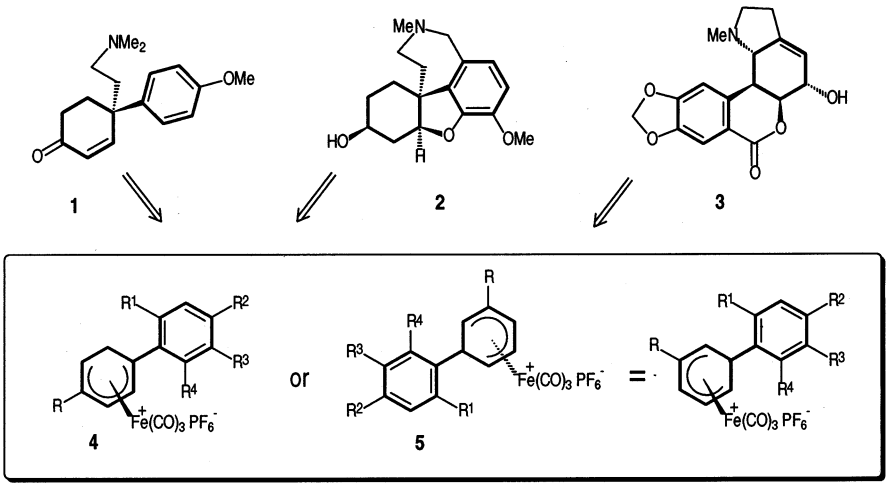


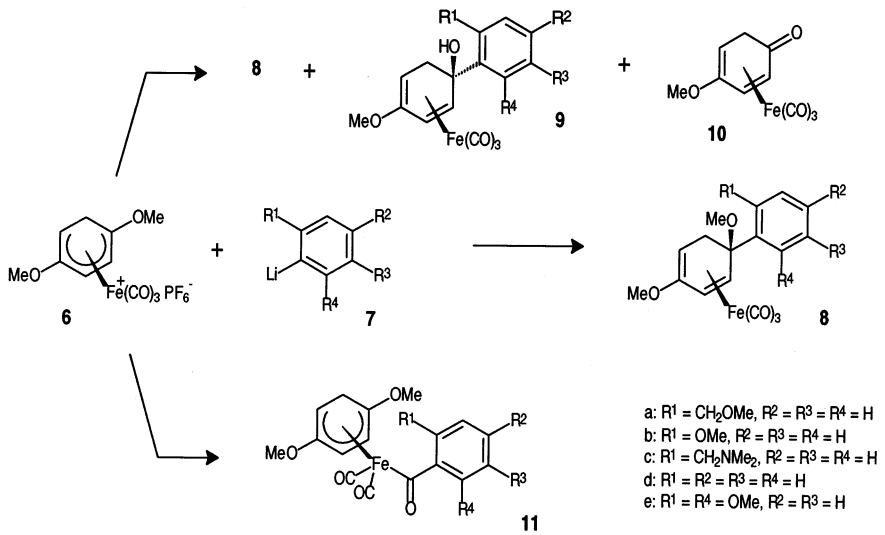
Fig. 1. Examples of C_{12} organoiron building block (indicated by bold lines) for alkaloid synthesis (for **1**: **4**, R = OMe, $R^1 = R^3 = R^4 = H$, $R^2 = OMe$; for **2**: **4**, R = OMe, $R^1 = CH_2X$, $R^2 = H$, $R^3 = OMe$, $R^4 = O$(prot.); for **3**: **5**, $R = CH_2CH_2X$, $R^1 = CO_2H$, $R^2–R^3 = O–CH_2–O$, $R^4 = H$).

synthesis [10], more efficient routes would put this substituent in place at the beginning. Because of the easy access [11] to (arylcyclohexadienyl)iron complexes by elaboration of more simple cyclohexadienyl complexes equipped with suitably placed leaving groups, in the case of organometallic building blocks based on these structures it is possible to address the inclusion of this additional carbon atom on the initial C_{12} component (i.e. a '$C_{12}–CH_2–X$' organometallic electrophile). Early attempts to prepare such components, however, quickly established that these reactions were intrinsically more complicated and less efficient than those which introduce aromatic groups without *ortho* substituents. Besides products from aryl addition to the dienyl intermediate, attack at carbonyl ligands was also observed, and in some cases, the resulting acyl products could be isolated and fully characterised for first time. Such complexes have often been proposed to explain inefficient examples of the normally reliable nucleophile addition procedure, but until these investigations, the identity of the acyl products had not been established in the case of η^5 organoiron electrophiles (corresponding structures from η^6 organomanganese complexes are known [12]).

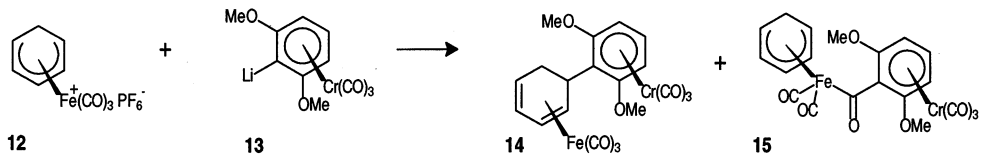
2. Results and discussion

We have found that the choice of solvent has a large effect on the product distribution in the organoiron series, with the original Birch dichloromethane (DCM) procedure [13] providing efficient access to the ('$C_{12}–CH_2–X$')$Fe(CO)_3^+$ building blocks needed to address the routes to lycoramine, while ether solvents such as THF and DME allow substantial quantities of the unstable acyl (aroyl) products to be isolated. Under these conditions, the acyl structure is sometimes the only nucleophile addition product observed although yields are then generally very low. Furthermore, if the property of the nucleophile is sufficiently modified, the access to acyl structures is no longer restricted [8] to aryl nucleophile addition to 1-alkoxy-substituted cyclohexadienyl complexes (e.g. **6**), and the simple parent $(C_6H_7)Fe(CO)_3^+$ cyclohexadienyl electrophile **12** has now also been converted into an (acyl)(cyclohexadienyl)$Fe(CO)_2$ product. In this work, a selection of novel acyliron complexes (**11**) (Scheme 1), including a bimetallic example (**12**) (Scheme 2), have been prepared, and reliable methods have been defined to switch between this reaction pathway and the access route to C_{12} building blocks which are now generally accessible for evaluation in alkaloid synthesis.

Working at 0° in THF, the aryllithium reagent prepared from *o*-$MeOCH_2C_6H_4Br$ and n-butyllithium was added to the 1,4-dimethoxy-substituted cyclohexadienyl complex **6** [3] to afford (Table 1, entry 1) the organoiron acyl **11** ($R^1 = CH_2OMe$, $R^2 = R^3 = R^4 = H$) as the sole product of nucleophile addition, together with traces (TLC) of the cyclohexadienone complex **10** [14] arising from demethoxylation of the C1 OMe group. Under these conditions, the acyl product was formed in only 10% yield, but it was found to be possible to improve the yield by switching (entry 2) to the more strongly coordinating diether solvent DME. At 0°C, the yield of the acyl product was improved to 30% and sufficient cyclohexadienone was now formed (5%) for this by-product to be isolated. The reaction is sensitive to temperature effects. In THF at −78°C (entry 3), no nucleophile addition products were formed at all, while in DME at −78°C (entry 4), the demethoxylation to the cyclohexadienone was suffi-



Scheme 1.



Scheme 2.

ciently favoured to allow the production both of larger amounts of this complex (10%) and the product of its reaction with the aryllithium reagent. This aryl-substituted hydroxydiene complex **9** was now the main product (35%) of the reaction. Other *ortho*-substituted aryllithium nucleophiles also afforded the acyl products, though in much lower yields (Table 1, entries 5–7), reflecting the much reduced stability of these products. In contrast to these results, phenyllithium itself afforded none of the acyl product when used in DME (entry 8), and substantial amounts of the aryl-substituted hydroxydiene complexes were formed instead. The reaction of the unsubstituted cyclohexadienyliron complex has been examined with an aryllithium reagent **13** generated from a tricarbonylchromium complex of 1,3-dimethoxybenzene. Even in THF (Table 1, entry 18), a metal acyl complex **15** could be isolated (13%), and with the complications arising from demethoxylation now unable to intervene, the diene complex **14** formed by nucleophile addition at the cyclohexadienyl ring was also obtained (34%). With 1-alkoxy-substituted cyclohexadienyl complexes, organocuprate reagents have been shown to be less effective than their lithium counterparts, but when this C1 substituent is absent, improved results are often obtained with organocopper reagents. Thus in the case of the electrophile **12**, it was decided to compare results from the lithium reagent (entry 18) with those obtained (entry 19) with the diarylcuprate formed from 2 equiv. of the metallated chromium complex and copper(I) iodide. As anticipated, the overall efficiency of the reaction improved from 48 to 75%. Selectivity for the acyl structure was also increased, and this procedure gave the most efficient (48%) access to this new structural class. Because of their considerable instability, the acyl structures were characterised mainly by IR and NMR spectroscopy. In addition to metal carbonyl vibrational stretching bands at frequencies typical for neutral products, a characteristic acyl CO band was observed between 1611 and 1597 cm^{-1} (Fig. 2[1]). The NMR spectra corresponded to the normal patterns and multiplicities of peaks expected for dienyl complexes, but shifted to higher field as should be the case for a neutral product. In some cases, characteristic molecular ions could be seen in the mass spectra of the acyl products, together with fragmentations involving losses of $Fe(CO)_2$ and H_2, presumably leaving a diarylketone-based fragment ion. Attempts to emulate this fragmentation by deliberate decomplexation, however, were unsuccessful, nor could acyl migration be achieved chemically by heating the acyl complex with a phos-

[1] When reported in the preliminary communication (Ref. [8]) the wavenumber scale in this figure was miss-numbered in the region 2000–1600 cm^{-1}; the illustration is reproduced here with the corrected scale, placing the characteristic acyl vibrational band at 1607 cm^{-1} for **11a**.

Table 1

Entry	Electrophile	Nucleophile [a]			Solvent [b]	Proc. [c]	Products	Yields (%)	Solvent [d]	Temperature (°C)
		Subst	R^1	R^4						
1	**6**	**7**	CH_2OMe	H	THF/hex	**A**	**11a**	10	THF	0
							10	trace		
2	**6**	**7**	CH_2OMe	H	DME/hex	**A**	**11a**	30	DME	0
							10	5		
3	**6**	**7**	CH_2OMe	H	THF/hex	**A**	– [e]	– [e]	THF	−78
4	**6**	**7**	CH_2OMe	H	DME/hex	**A**	**9a**	35	DME	−78
							11a	10		
							10	10		
5	**6**	**7**	OMe	H	DME/hex	**A**	**10**	6	DME	−60
							11b	1		
6	**6**	**7**	OMe	H	DME/hex	**A**	**11b**	1	DME	0
7	**6**	**7**	CH_2NMe_2	H	DME/hex	**A**	**10**	10	DME	0
							11c	5		
8	**6**	**7**	H	H	DME/hex	**A**	**9d**	37	DME	−78
							10	10		
9	**6**	**7**	H	H	DME/hex	**A**	– [e]	– [e]	DME	0
10	**6**	**7**	H	H	DME/hex/TMEDA	**B**	**9d**	60	DME	−78
							10	10		
11	**6**	**7**	H	H	Et_2O/cy	**C**	**8d**	72	DCM	−78
							9d	13		
							10	9		
12	**6**	**7**	H	H	THF/hex	**A**	**8d**	3	THF	−78
13	**6**	**7**	H	H	Et_2O/hex	**C**	**8d**	21	Et_2O	−78
14	**6**	**7**	H	H	Et_2O/hex	**C**	**8d**	58	DCM	−78
15	**6**	**7**	H	H	Et_2O	**B**	**8d**	70	DCM	−78
16	**6**	**7**	H	H	THF/hex/1/2CuI	**D**	**8d**	72	THF	−78
17	**6**	**7**	H	H	THF/hex/1/2CuI	**D**	– [e]	– [e]	DCM	−78
18	**12**	**13**	OMe	OMe	THF/hex	**E**	**14**	34	THF	−78
							15	14		
19	**12**	**13**	OMe	OMe	THF/hex/1/2CuI	**F**	**15**	48	THF	−78
							14	27		
20	**12**	**13**	OMe	OMe	THF/hex	**E**	– [e]	– [e]	DCM	−78
21	**6**	**7**	OMe	OMe	Et_2O/hex	**G**	**8e**	73	DCM	−100
							10	5		
22	**6**	**7**	OMe	H	Et_2O/hex	**G**	**8b**	50	DCM	−100
23	**6**	**7**	OTBDMS	H	Et_2O/hex	**H**	**10**	68	DCM	−100
24	**6**	**7**	OMe	H	Et_2O/hex	**A**	**8b**	43	DCM	−78
							9b	24		
							10	17		
25	**6**	**7**	CH_2O	MeH	Et_2O/hex	**A**	**8a**	58	DCM	−78
							9a	15		
							10	10		
26	**6**	**7**	CH_2O	MeH	DME/hex	**A**	**10**	50	DCM	−78
27	**6**	**7**	CH_2NMe_2	H	Et_2O/hex	**A**	**10**	42	DCM	−78
28	**6**	**7**	CH_2NMe_2	H	Et_2O/hex	**A**	**8c**	14	DCM	−110
							9c	4		
							10	5		

[a] Nucleophile (substituents R^2 and R^3 in Scheme 1 = H).
[b] Solvents/reagents used in the generation of the organolithium or cuprate reagents.
[c] See Section 3.
[d] Solvent for the electrophile, to which the solution of the nucleophilic reagent was added.
[e] No products isolated.

phine ligand. In the mass spectrum, however, formation of $M^+-Fe(CO)_2-H_2$ was seen to be facile. The most stable acyl product (arising from reaction of *o*-$(MeOCH_2)C_6H_4Li$ with the 1,4-dimethoxycyclohexadienyliron complex **6**) was selected for full characterisation. Even in this case, the product is heat sensi-

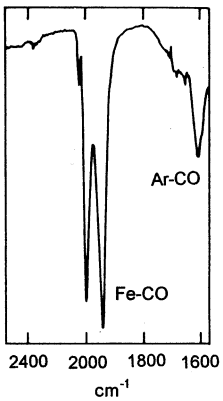


Fig. 2. Typical IR spectrum for novel metal acyl complexes of dicarbonyl(η^5-cyclohexadienyl)iron(II).

tive and unstable even under vacuum, so characterisation was performed immediately after the final chromatographic purification of the product. IR and NMR data match the general pattern of the whole series, and the mass spectrometric properties were fully defined. By FAB ionisation, $M^+ + Na$ was confirmed by high resolution mass measurements, and by CI, accurate mass measurements confirmed the identity of an $MH^+ - Fe(CO)_2 - H_2$ ion at 287, corresponding to the $M^+ - Fe(CO)_2 - H_2$ fragment at 286 in the EI mass spectrum. Under EI, $M^+ - 2CO$ was observed at 344, but no parent molecular ion could be observed.

As with Birch's original investigations of the use [13] of organolithium reagents with cyclohexadienyliron electrophiles, the use of DCM as solvent proved to favour direct addition at the dienyl ligand, at least with simple aryllithium nucleophiles (Table 1, entries 11, 14, 15). The tricarbonylchromium-complexed lithium reagent, on the other hand, gave neither acyl nor diene complexes when used in DCM (entry 20), and in this case the best access to the diene complexes was in THF/hexane (entry 18). Typically, though, in DCM using a procedure comparable to that which affords acyl structures in DME, considerable quantities of the required aryl-substituted methoxy- and hydroxycyclohexadiene complexes (**8** and **9**, respectively) can be obtained (65–87%) together with the cyclohexadienone product **10** (17–9%). In these reactions, the aryllithium was used as purchased in the case of phenyllithium (in cyclohexane/ether), or generated from the aryl bromide in hexane/ether by addition of n-butyllithium in hexanes, except in one case where the lithium/halogen exchange was performed in DME, allowing sufficient of the coordinating solvent to be present to modify the properties of the nucleophile. This experiment was performed to establish whether the formation of the acyl products was possible as a competing reaction in DCM through the influence of lithium-bound DME. The small amount of DME present was sufficient to completely disfavour the addition of the aryl group to the cyclohexadienyl ligand (Table 1, entry 26), but under these conditions and at -78°C no acyl products were observed, and the cyclohexadienone complex from demethoxylation was isolated in 50% yield.

We have observed before that including nitrogen-containing substituents in aryl nucleophiles can lead to inefficient nucleophile addition reactions [15]. With simple cyclohexadienyliron complexes, organocuprate reagents can be used to overcome this limitation [15,16], but since these are not normally suitable for use with 1-alkoxy-substituted cyclohexadienyl complexes, the use of $Me_2NCH_2C_6H_4Li$ at very low temperature was examined instead, to obtain diene complexes comparable to the $FeCOC_6H_4CH_2NMe_2$ acyl product **11** that was obtained in low yield in the earlier stages of these investigations. Performing the reaction in DCM at -110°C, 18% yield of a 3:1 mixture of methoxy- and hydroxydiene complexes was possible (Table 1, entry 28) while the yield of the cyclohexadienone complex dropped (from 42% at -78°C) to just 5%.

The formation of mixtures of methoxy- and hydroxy-substituted cyclohexadieneiron complexes complicates product purification at the intermediate stage, but does not make inefficient the route to the '$C_{12}-CH_2-X$' organometallic electrophiles because both products can be converted into the same aryl-substituted cyclohexadienyl complex by reaction in the normal way with acid. Either $HBF_4 \cdot Et_2O$ or trifluoroacetic acid followed by addition of ammonium hexafluorophosphate can be used for this purpose, with comparable results, and yields are good (Scheme 3). Thus if the intermediate diene complexes prepared in DCM are taken on by this method without separation, high overall yields of cyclohexadienyliron complexes with *ortho*-substituted aryl substituents at C1 are possible. From the point of view of access to alkaloid structures, the benzyl ether case is the best prospect, and this can be made in over 55% yield 'salt-to-salt' from the simple 1,4-dimethoxycyclohexadienyl complex **6**, which is itself available on a large scale by Birch reduction of 1,4-dimethoxybenzene, followed by complexation and hydride abstraction [3]. The addition of the aryllithium reagents in this procedure, however, is very sensitive to the precise fashion the reaction is performed. For example, to gain large-scale access to the '$C_{12}-CH_2-X$' electrophiles it has been possible to establish protocols (Table 1, entries 21, 22) that avoid demethoxylation and the formation of alcohols, allowing the preparation of a single arylcyclohexadiene complex as the intermediate. In this version of the reaction, the metallation to form the organolithium reagent is performed in ether in the usual way, but the solution is then cooled to -100°C and added to a suspension of the salt in DCM at -100°C. This

usually has little effect on overall yields 'salt-to-salt' but is experimentally more convenient.

3. Experimental

All reactions were performed under an atmosphere of dry, oxygen-free nitrogen and in the cases that yield acyl products, glassware was oven-dried and twice evacuated and filled with the nitrogen. Ether refers to diethyl ether; water refers to distilled water. All solvents were of reagent grade and used as supplied commercially unless specified as dry, in which case they were dried and distilled immediately before use as follows: ether and tetrahydrofuran (THF) from sodium/benzophenone; dimethoxyethane (DME) from sodium hydride; dichloromethane (DCM) from calcium hydride. Reaction temperatures of −110, −78 and 0°C refer to absolute ethanol/liquid-nitrogen, acetone/dry-ice and water/ice bath cooling, respectively. Filtration refers to filtration under water-pump suction. Analytical TLC was performed on silica or alumina plates, and visualised by ultraviolet irradiation (254 nm). Column chromatography was performed using Merck silica gel or BDH neutral alumina. Low resolution EI mass spectrometry (Kratos MS25 mass spectrometer) and elemental analyses were performed at the University of East Anglia by Mr A.W.R. Saunders; other mass spectra were measured at the EPSRC National Mass Spectrometry Service Centre at University of Wales, Swansea. IR spectra were recorded as a thin film using a Perkin–Elmer 1420 or 1720X FT-IR spectrometer. NMR spectra were recorded on Jeol EX90 (^{1}H, 90 MHz), Jeol EX270, Bruker AC250 or Bruker ARX (^{1}H, 400 MHz) spectrometers. Chiral metal complexes were prepared in racemic form and illustrations in Schemes 1–3 indicate relative stereochemistry only.

3.1. *A: General procedure for the reaction of the 1,4-dimethoxy-substituted salt with aryllithium reagents*

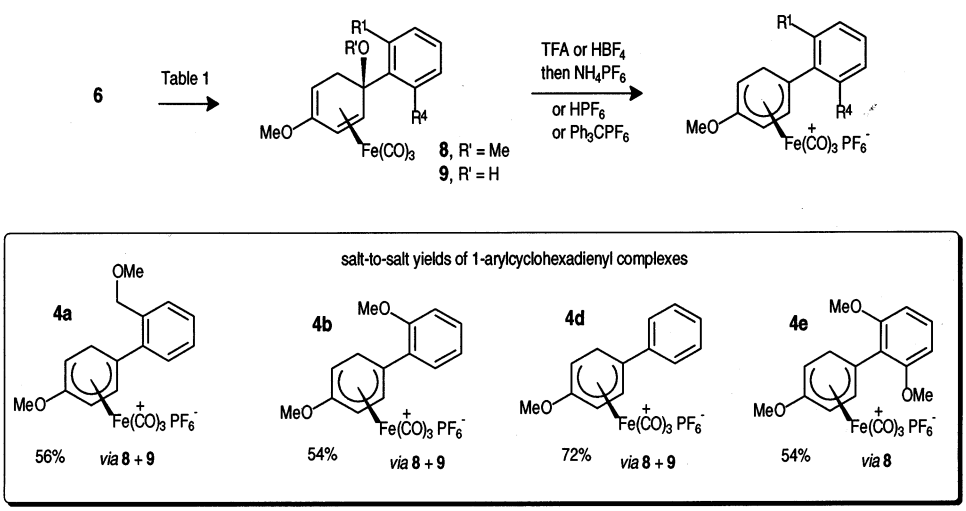
n-Butyllithium (2 ml of a 1.27 M solution in hexanes, 2.54 mmol) was added to a solution of the aryl bromide (2.6 mmol) in dry ether, THF or DME (3–5 ml) at −78°C, and the mixture was stirred at that temperature for 30 min and then transferred into a solution of the cyclohexadienyl salt **6** (360 mg, 1 mmol) in dry THF, DME or DCM (25-30 ml) at 0, −78 or −110°C. After addition of water and extraction with ether, chromatography on silica gel or alumina (in the case of products from the nitrogen-containing nucleophile) with 5% ethyl acetate in hexane as eluant gave in order of elution methoxy- and hydroxy-substituted cyclohexadiene complexes **8** and **9**. Using mixture of hexane/ethyl acetate (2:1) the cyclohexadienone complex **10** [14] was eluted.

3.2. *B: Modified procedures for the reaction of the 1,4-dimethoxy-substituted salt with phenyllithium — TMEDA*

The procedure was the same as described in **A**, using DME and hexanes, except that TMEDA (1 equiv.) was added to the solution of the organolithium reagent before reaction with the organoiron salt (Table 1, entry 10).

3.3. *C: Modified procedures for the reaction of the 1,4-dimethoxy-substituted salt with phenyllithium*

Phenyllithium (1.5 ml of a 1.70 M solution in cyclohexane/ether (7:3), 2.55 mmol) was added to a solution of the salt **6** (360 mg, 1 mmol) in dry THF, DME or DCM (25–30 ml). Work-up and chromatography was performed as described in **A**. Similarly, phenyllithium



Scheme 3.

(7.80 ml of a 0.78 M solution in ether, 6.08 mmol) was added to a solution of the salt **6** (2.00 g, 4.72 mmol) in dry DCM (30 ml) at −78°C. After the work-up, flash chromatography (30% DCM in light petroleum) afforded complex **8d** (1.18 g, 70%). In other cases (Table 1, entries 13, 14), phenyllithium was prepared by stirring n-butyllithium (0.63 ml of a 1.45 M solution in hexanes, 0.91 mmol) with bromobenzene (14.4 mg, 0.92 mmol) in dry ether (2 ml) at room temperature (r.t.) for 20 min. This reagent solution was reacted, as described above, with a solution of the salt **6** (300 mg, 0.71 mmol) in dry DCM (10 ml) at −78°C. The work-up and flash column chromatography gave the product **8d** (146 mg, 58%). The same procedure was used with suspensions of the salt in ether or THF.

3.4. *D: Modified procedure for the reaction of the 1,4-dimethoxy-substituted salt with lithium diphenylcuprate*

n-Butyllithium (4.20 ml of a 1.52 M solution in hexanes, 6.37 mmol) was added to a solution of bromobenzene (1.00 g, 6.37 mmol) in dry THF or DCM at −78°C. The mixture was warmed to r.t. and added by syringe to a stirred suspension of copper(I) iodide (591 mg, 3.10 mmol) in dry THF (5 ml) at 0°C. After 5 min, the organoiron salt (600 mg, 1.42 mmol) was added against nitrogen back-pressure, and stirring was continued 5 min at 0°C. The mixture was then poured into a separating funnel charged with saturated aqueous ammonium chloride (50 ml) and extracted with ether (3 × 30 ml). The combined extracts were washed with water (30 ml), dried ($MgSO_4$), and filtered, and the solvent was removed under reduced pressure. Flash chromatography with 30% DCM in light petroleum as the eluant afforded the product **8d** (72%).

3.5. *E: Modified procedure for the reaction of the unsubstituted salt with a chromium-complexed aryllithium reagent*

n-Butyllithium (1.27 M solution in hexanes, 1.1 mmol) was added to a solution of tricarbonyl(η^6-1,3-dimethoxybenzene)chromium(0) (0.274 g, 1 mmol) in THF (15 ml) at −78°C. After stirring at this temperature for 1 h, the resulting solution of the aryllithium reagent was transferred by syringe to a solution of tricarbonyl(η^5-cyclohexadienyl)iron(1+) hexafluorophosphate(1−) (0.44 g, 1.2 mmol) in THF (10 ml) at −78°C. The mixture was allowed to warm and was stirred at r.t. for 5 min. Water (20 ml) was added and the mixture was extracted with ether (2 × 30 ml). The extracts were washed with brine and dried ($MgSO_4$), filtered through Celite, and evaporated without heating with a stream of nitrogen gas. The residue was purified by chromatography (silica/30% ether in petroleum ether) to separate recovered tricarbonyl(η^6-1,3-dimethoxybenzene)chromium(0) (0.11 g, 0.4 mmol, 40%), and then 45% ether in petroleum ether to elute the bimetallic η^6,η^4 product **14** (0.167 g, 34%) and with 60% ether in petroleum ether to afford the bimetallic η^6,η^5 acyl complex **15** (0.064 g, 13%).

3.6. *F: Modified procedure for the reaction of the unsubstituted salt with a chromium-complexed diarylcuprate reagent*

Procedure **E** was employed except that the flask was fitted with a solids addition side-arm charged with copper(I) iodide (0.5 mmol) and after generation of the chromium-complexed aryllithium reagent, the copper salt was added under nitrogen at −78°C and the mixture was stirred for a further 20 min before the reagent was transferred to the flask containing the cyclohexadienyliron complex.

3.7. *G: Modified procedure to prepare **8e** avoiding the formation of alcohol and dienone byproducts (**9** and **10**)*

Following the method of Snieckus [17], 1,3-dimethoxybenzene (2 equiv., 1.66 g, 12 mmol) was dissolved in dry ether (10 ml) under nitrogen. n-Butyllithium (1.6 M in hexanes, 12.0 mmol, 7.5 ml) was added and the mixture was heated at reflux for 2 h after which time 1-lithio-2,6-dimethoxybenzene was formed as a yellow suspension. The cyclohexadienyliron salt (2.196 g, 6.0 mmol) was dissolved in dry DCM (20 ml) and cooled to −100°C. The solution of the nucleophile at −100°C was added through a cannula at −100°C. The mixture turned black and was stirred for 2 h. The reaction was quenched with water (25 ml) and ether (25 ml) at −100°C and warmed to r.t. The mixture was extracted into ether (3 × 25 ml) and water (3 × 25 ml). The combined organic extracts were washed with water (3 × 25 ml), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a brown oil which was purified by column chromatography on silica eluted with ether/cyclohexane (1:1).

3.8. *H: Procedure for the attempted reaction of the 1,4-dimethoxy-substituted salt with 1-lithio-2-t-butyldimethylsilyloxybenzene*

A solution of 2-bromophenol (5 g, 29 mmol) in dry THF (20 ml) was added over 1 h to NaH (60% suspension in mineral oil) (1.2 g, 29 mmol) in dry THF (20 ml) at 0°C. The reaction mixture was stirred at 0°C for 1 h to give a pale brown solution. t-Butyldimethylsilyl chloride (4.36 g, 29 mmol) was added at 0°C. The reaction mixture was stirred at r.t. for 18 h during which time a white precipitate formed. The mixture was quenched with water (50 ml) and ether (50 ml) and extracted with

ether (3 × 50 ml). The combined organic extracts were washed with water (3 × 25 ml), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure. Column chromatography (10% ether/89% petroleum ether/1% Et_3N) afforded 1-bromo-2-t-butyldimethylsilyloxybenzene [18] as a clear liquid (6.96 g, 24 mmol, 85%). HRMS (EI) (Found: 286.0389. $C_{12}H_{19}OBrSi$ (M^+) requires 286.0389). δ_H ($CDCl_3$) 0.24 (6H, s, $SiMe_2$), 1.04 (9H, s, Me_3CSi), 6.79 (1H, ddd, $J = 8.9$, 7.3, 1.7, Ar), 6.86 (1H, d, $J = 8.3$, 1.7, Ar), 7.14 (1H, ddd, $J = 8.9$, 7.3, 1.7, Ar), 7.50 (1H, dd, $J = 8.3$, 1.7, Ar). This product (0.89 g, 3.1 mmol) was dissolved in dry ether (5 ml) and cooled to −30°C under nitrogen. n-Butyllithium (1.6 M in hexanes, 2.0 ml, 3.1 mmol) was added after stirring for 1 h at −30°C, 1-lithio-2-t-butyldimethylsilyloxybenzene was formed as a white suspension and was cooled to −100°C. The organoiron salt (1.1 g, 3 mmol) was dissolved in dry DCM (10 ml) and cooled to −100°C. The solution of the nucleophile was added through a cannula and the mixture was stirred for 30 min. The mixture was quenched with water (25 ml) and ether (25 ml), and extracted with ether (3 × 25 ml). The combined extracts were washed with water (3 × 25 ml), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to afford a brown oil. Column chromatography on silica (ether/petroleum ether gradient) afforded the cyclohexadienone complex **10** [14] (0.54 g, 68%).

Using these procedures, the following compounds were prepared (for yields, see Table 1):

*3.8.1. Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-methoxymethylphenyl)-1,3-cyclohexadiene]iron(0) (**8a**) by procedure **A***

Viscous pale yellow oil. IR: ν_{max} (cm^{-1}) 2051, 1982, 1964 (CO). δ_H ($CDCl_3$) 2.12 (1H, dd, $J = 14.7$, 2.6 Hz, 6_{exo}-H), 2.34 (1H, dd, $J = 14.7$, 3.5 Hz, 6_{endo}-H), 2.91 (3H, s, 5-OMe), 3.01 (1H, d, $J = 6.8$ Hz, 4-H), 3.28 (1H, m, 1-H), 3.40 (3H, s, 2′-OMe), 3.63 (3H, s, 2-OMe), 4.60 (2H, s, 2′-CH_2), 5.32 (1H, dd, $J = 6.8$, 2.4 Hz, 3-H), 7.10–7.59 (4H, m, 3′-6′-H). m/z (EI) 372 (M^+–CO, 0.1%), 346 (M^+–2CO, 0.2%). Found m/z (CI) MH^+–MeOH, 369.0425. $C_{19}H_{20}O_6Fe$ requires MH^+–MeOH, 369.0425.

*3.8.2. Tricarbonyl[(1,2,3,4-η)-5β-hydroxy-2-methoxy-5α-(2′-methoxymethylphenyl)-1,3-cyclohexadiene]iron(0) (**9a**) by procedure **A***

Viscous pale yellow oil. IR: ν_{max} (cm^{-1}) 3402 (OH), 2048, 1978 (CO). δ_H ($CDCl_3$) 2.34 (2H, m, 6-CH_2), 2.84 (1H, d, $J = 6.6$ Hz, 4-H), 3.33 (1H, m, 1-H), 3.38 (3H, s, 2′-OMe), 3.66 (3H, s, 2-OMe), 4.42 (1H, d, $J = 11.6$ Hz, 2′α-H), 4.82 (d, 1H, $J = 11.6$ Hz, 2′β-H), 5.20 (1H, dd, $J = 6.7$, 2.5 Hz, 3-H), 7.21–7.52 (4H, m, 3′-6′-H). m/z (EI) 330 (M^+–2CO, 2%).

*3.8.3. Dicarbonyl[1′-carboxy(2′-methoxymethylphenyl)]-[(1,2,3,4,5-η)-2,5-dimethoxy-2,4-cyclohexadienyl]-iron(II) (**11a**) by procedure **A***

Yellow solid, heat sensitive, unstable in vacuum. IR: ν_{max} (cm^{-1}) 1999, 1942 (CO); 1607 (ArCOFe). δ_H ($CDCl_3$) 2.59 (1H, d, $J = 14.5$ Hz, 6_{exo}-H), 3.05 (1H, ddd, $J = 14.9$, 5.7, 1.5 Hz, 6_{endo}-H), 3.33 (3H, s, 2′-OMe), 3.37 (3H, s, 1-OMe), 3.60 (3H, s, 4-OMe), 3.63 (2H, m, 2,5-H), 4.32 (2H, m, 2′-CH_2), 5.64 (1H, dd, $J = 5.7$, 2.6 Hz, 3-H), 7.14–7.34 (4H, m, 3′-6′-H). δ_H (benzene-d_6) 2.06 (1H, d, $J = 15.4$ Hz, 6_{exo}-H), 2.59 (3H, s, OMe), 2.72 (1H, dd, $J = 15.4$, 5.1 Hz, 6_{endo}H), 2.90 (2H, m, 2-H and 5-H), 3.18 (3H, s, 1-OMe), 3.22 (3H, s, 4-OMe), 4.47 (1H, d, $J = 10.0$ Hz, 2′α-H), 4.66 (1H, d, $J = 10.0$ Hz, 2′β-H), 5.13 (1H, m, 3-H), 7.00–7.48 (4H, m, 3′-6′-H). m/z (EI) 344 (M^+–2CO, 1.05%), 286 (M^+–$Fe(CO)_2$–H_2, 2%). Found m/z (FAB) $M^+ + Na$, 423.0514. $C_{19}H_{20}O_6Fe$ requires $M^+ + Na$, 423.0507. Found m/z (CI) MH^+–$Fe(CO)_2$–H_2, 287.1283. $C_{19}H_{20}O_6Fe$ requires MH^+–$Fe(CO)_2$–H_2, 287.1283.

*3.8.4. Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (**8b**) by procedures **A** and **G***

Grey–white solid. IR: ν_{max} (cm^{-1}) 2050, 1985, 1964 (CO). δ_H ($CDCl_3$) 2.14 (1H, dd, $J = 15.1$, 3.5 Hz, 6_{endo}-H), 2.39 (1H, dd, $J = 15.0$, 2.6 Hz; 6_{exo}-H), 2.90 (1H, d, $J = 7.5$ Hz, 4-H), 2.95 (3H, s, 5-OMe), 3.27 (1H, m, 1-H), 3.58 (3H, s, 2-OMe), 3.74 (3H, s, 2′-OMe), 5.01 (1H, dd, $J = 6.8$, 2.4 Hz, 3-H), 6.76–7.48 (4H, m, 3′-6′-H). m/z (EI) 358 (M^+–CO, 1%), 330 (M^+–2CO, 2.5%). Found: C, 56.38; H, 4.65. $C_{18}H_{18}O_6Fe$ requires: C, 55.98; H, 4.70%. Found m/z (CI) MH^+–MeOH, 355.0269. $C_{18}H_{18}O_6Fe$ requires: MH^+–MeOH, 355.0269.

*3.8.5. Tricarbonyl[(1,2,3,4-η)-5β-hydroxy-2-methoxy-5α-(2′-methoxyphenyl)-1,3-cyclohexadiene]iron(0) (**9b**) by procedure **A***

Viscous pale yellow oil. IR: ν_{max} (cm^{-1}) 3534 (OH), 2046, 1975 (CO). δ_H ($CDCl_3$) 2.25 (2H, m, 6-CH_2), 2.86 (1H, d, $J = 7.0$ Hz, 4-H), 3.27 (1H, m, 1-H), 3.60 (3H, s, 2-OMe), 3.83 (3H, s, 2′-OMe), 5.17 (1H, dd, $J = 7.0$, 2.8 Hz, 3-H), 6.70–7.45 (4H, m, 3′-6′-H). m/z (EI) 344 (M^+–CO, 0.3%), 316 (M^+–2CO, 0.3%). Found m/z (CI) M^+–CO, 344.0347 and MH^+–H_2O, 355.0269. $C_{17}H_{16}O_6Fe$ requires M^+–CO, 344.0347 and MH^+–H_2O, 355.0269.

*3.8.6. Dicarbonyl[1′-carboxy(2′-methoxyphenyl)]-[(1,2,3,4,5-η)-2,5-dimethoxy-2,4-cyclohexadienyl]-iron(II) (**11b**) by procedure **A***

Yellow solid, heat sensitive, unstable in vacuum. IR: ν_{max} (cm^{-1}) 1996, 1937 (CO); 1597 (ArCOFe). δ_H

(benzene-d_6) 2.07 (1H, d, $J = 15.4$ Hz, 6_{exo}-H), 2.64 (1H, m, 6_{endo}-H), 2.96 (3H, s, 1-OMe), 3.14 (1H, m, 5-H), 3.34 (6H, s, 4- and 2′-OMe), 5.12 (1H, m, 3-H), 6.60–7.20 (4H, m, 3′-6′-H). *m/z* (EI) 272 ($M^+ - Fe(CO)_2$-H_2, 4%), 242 ($M^+ - Fe(CO)_2 - MeOH$, 1.5%).

*3.8.7. Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′-dimethylaminomethylphenyl)-1,3-cyclohexadiene]-iron(0) (**8c**) by procedure **A***

Viscous pale yellow oil. IR: ν_{max} (cm^{-1}) 2045, 1976, 1963 (CO). δ_H ($CDCl_3$) 2.15 (2H, m, 6-CH_2), 2.19 (6H, s, NMe_2), 2.85 (3H, s, 5-OMe), 3.03 (1H, d, $J = 7.2$ Hz, 4-H), 3.24 (1H, m, 1-H), 3.54 (2H, m, 2′-CH_2), 3.60 (3H, s, 2-OMe), 5.29 (1H, dd, $J = 6.8$, 2.5 Hz, 3-H), 7.10–7.72 (4H, m, 3′ and 6′-H). *m/z* (EI) 385 (M^+–CO, 0.6%), 329 (M^+–3CO, 2%). Found *m/z* (CI) MH^+, 414.1004. $C_{20}H_{23}NO_5Fe$ requires MH^+, 414.1004.

*3.8.8. Tricarbonyl[(1,2,3,4-η)-5β-hydroxy-2-methoxy-5α-(2′-dimethylaminomethylphenyl)-1,3-cyclohexadiene]-iron(0) (**9c**) by procedure **A***

Viscous pale yellow oil. IR: ν_{max} (cm^{-1}) 3430 (OH), 2048, 1980, 1969 (CO). δ_H ($CDCl_3$) 2.16 (6H, s, NMe_2), 2.28 (2H, m, 6-CH_2), 2.88 (1H, d, $J = 6.6$ Hz, 4-H), 3.02 (1H, d, $J = 12.3$ Hz, 2′α-H), 3.61 (3H, s, 2-OMe), 3.92 (1H, d, $J = 12.5$ Hz, 2′β-H), 5.22 (1H, dd, $J = 6.6$, 2.6 Hz, 3-H), 6.99–7.62 (4H, m, 3′-6′-H). *m/z* (EI) 343 (M^+–2CO, 2%). Found *m/z* (CI) MH^+, 400.0847. $C_{19}H_{21}NO_5Fe$ requires MH^+, 400.0847.

*3.8.9. Dicarbonyl[1′-carboxy(2′-dimethylamino-methylphenyl)][(1,2,3,4,5-η)-2,5-dimethoxy-2,4-cyclohexadienyl]iron(II) (**11c**) by procedure **A***

Yellow solid, heat sensitive, unstable in vacuum. IR: ν_{max} (cm^{-1}) 1998, 1940 (CO), 1611 (ArCOFe). δ_H ($CDCl_3$) 2.17 (6H, s, NMe_2), 2.59 (1H, d, $J = 15.0$ Hz, 6_{exo}-H), 3.05 (1H, ddd, $J = 15.0$, 5.7, 1.5 Hz; 6_{endo}-H), 3.35 (3H, s, 1-OMe), 3.36 (1H, d, J 5.7 Hz, 2-H), 3.60 (3H, s, 4-OMe), 3.60 (3H, m, 5-H, 2′-CH_2), 5.64 (1H, dd, $J = 5.7$, 2.4 Hz, 3-H), 7.00–7.26 (4H, m, 3′-6′-H). *m/z* (EI) 299 (M^+–$Fe(CO)_2$–H_2, 4%). Found *m/z* (CI) MH^+ $Fe(CO)_2$–H_2, 300.1600. $C_{20}H_{23}NO_5$ requires MH^+–$Fe(CO)_2$–H_2, 300.1600.

*3.8.10. Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-phenyl-1,3-cyclohexadiene]iron(0) (**8d**) by procedures **A**, **C**, **D** and **G***

Viscous pale yellow oil which solidified on refrigeration. M.p. 84–86°C. IR: ν_{max} (cm^{-1}) 2046 and 1966 (CO). δ_H ($CDCl_3$) 2.21 (2H, m, 6-CH_2), 2.80 (1H, d, $J = 7.0$ Hz, 4-H), 3.05 (3H, s, 5-OMe), 3.41 (1H, m, 1-H), 3.64 (3H, s, 2-OMe), 5.05 (1H, dd, $J = 7.0$, 2.8 Hz, 3-H), 7.20–7.60 (5H, m, Ph). Found *m/z* (CI) MH^+, 357.0391. $C_{17}H_{16}O_5Fe$ requires MH^+, 357.0425.

*3.8.11. Tricarbonyl[(1,2,3,4-η)-5β-hydroxy-2-methoxy-5α-phenyl-1,3-cyclohexadiene]iron(0) (**9d**) by procedures **B** and **C***

Viscous pale yellow oil. IR: ν_{max} (cm^{-1}) 3448 (OH), 2047 and 1975 (CO). δ_H ($CDCl_3$) 2.27 (2H, m, 6-CH_2), 2.70 (1H, d, $J = 7.0$ Hz, 4-H), 3.49 (1H, m, 1-H), 3.74 (3H, s, 2-OMe), 5.09 (1H, dd, $J = 7.0$ and 3.0 Hz, 3-H), 7.15–7.50 (5H, m, Ph). *m/z* (EI) 314 (M^+–CO, 0.4%), 258 ($M^+ - 3CO$, 2%).

*3.8.12. Tricarbonyl[(1,2,3,4-η)-2,5β-dimethoxy-5α-(2′,6′-dimethoxyphenyl)-1,3-cyclohexadiene]iron(0) (**8e**) by procedure **G***

IR: ν_{max} (cm^{-1}) 2040, 1966, (CO), 1589, 1488, 1251, 1110, 622, 583. δ_H ($CDCl_3$) 7.17 (1H, t, $J = 8.5$, ArH-4), 6.54 (2H, d, $J = 8.5$, ArH-2, ArH-5), 5.02 (1H, dd, $J = 6.9$, 3.0, H-3), 3.80 (6H, s, Ar–OMe), 3.66 (1H, d, $J = 6.9$, H-4), 3.56 (3H, s, C2-OMe), 3.27 (1H, m, H-1), 3.00 (3H, s, C5-OMe), 2.47 (1H, dd, $J = 15.5$, 2.5, H-6β), 2.36 (1H, dd, $J = 15.5$, 3.8, H-6α). *m/z* (EI) (M^+–$(CO)_2$ 388. Found *m/z* (EI) 388.0609 (M^+–CO). $C_{18}H_{20}FeO_6$ (M^+–CO) requires 388.0609.

*3.8.13. Nonacarbonyl{(1,2,3,4-η)-2,5β-dimethoxy-5α-[(1′,2′,3′,4′,5′,6′-η)-2′,6′-dimethoxyphenyl]chromium(0)]-1,3-cyclohexadiene}-iron(0) (**14**) by procedures **E** and **F***

Pale yellow solid. IR: ν_{max} (cm^{-1}) 2030, 1960, 1865 (CO). δ_H (400 MHz, $CDCl_3$) 1.74 (1H, dm, $J = 14.2$ Hz, 6α-H), 2.06 (1H, ddd, $J = 14.2$, 11.7, 4.1 Hz, 6β-H), 2.87 and 3.10 (2H, m, 1-H and 4-H), 3.69 (1H, m, 5β-H and 6H, s, 2MeO), 4.61 and 4.66 (2H, d, $J = 7$ Hz, 3′-H and 5′-H), 5.36 (2H, m, 2-H and 3-H), 5.47 (1H, t, $J = 7$ Hz, 4′-H). Found: C, 48.67; H, 3.26. $C_{20}H_{16}O_8Fe$ requires: C, 48.81; H, 3.28%.

*3.8.14. Octacarbonyl{1′-carboxy[(1′,2′,3′,4′,5′,6′-η)-2′,6′-dimethoxyphenyl]chromium(0)}[(1,2,3,4,5-η)-2,5-dimethoxy-2,4-cyclohexadienyl]iron(II) (**15**) by procedures **E** and **F***

Yellow solid. IR: ν_{max} (cm^{-1}) 2040, 2000, 1965, 1865 (CO), 1605 (ArCOFe). δ_H (400 MHz, $CDCl_3$) 1.83 (1H, d, $J = 14.2$ Hz, 6α-H), 2.62 (1H, m, 6β-H), 3.50 (2H, m, 1-H and 5-H), 3.73 (6H, s, 2MeO), 4.64 (2H, d, $J = 6.3$ Hz, 3′-H and 5′-H), 4.72 (2H, m, 2-H and 4-H), 5.43 (1H, t, $J = 6.3$ Hz, 4′-H), 6.49 (1H, t, $J = 5.3$ Hz, 3-H).

3.8.15. Preparation of cyclohexadienyliron complexes with TFA or $HBF_4 \cdot Et_2O$

The mixture of complexes **8** and **9** (1 mmol) was stirred with trifluoroacetic acid (TFA) (10 mmol) or $HBF_4 \cdot Et_2O$ (10 mmol) at 0°C for 30 min. Addition of a saturated solution of ammonium hexafluorophosphate afforded corresponding salt as a yellow powder which was reprecipitated from acetonitrile/ether.

3.8.16. Preparation of cyclohexadienyliron complexes with aqueous HPF_6

Hexafluorophosphoric acid (75% in water, 0.5 ml, 4.68 mmol) was added to a cooled solution (0°C) of the cyclohexadiene complex (0.145 g, 0.38 mmol) in acetic anhydride (20 ml), and was stirred for 30 min. The mixture was warmed to r.t. and cold (0°C) dry ether (25 ml) was added dropwise. A brown oil formed. Saturated aqueous ammonium hexafluorophosphate solution was added to produce an orange precipitate which was collected by filtration and washed with cold dry ether.

3.8.17. Preparation of cyclohexadienyliron complexes with Ph_3CPF_6

The cyclohexadiene complex **8e** (1.81 g, 4.36 mmol) was dissolved in DCM and added to a solution of triphenylcarbenium hexafluorophosphate (1.69 g, 4.36 mmol) in DCM (5 ml) at 0°C. The mixture darkened and was stirred at 0°C for 2 h. The reaction mixture was added dropwise into dry ether (200 ml) at 0°C to produce the product as a yellow precipitate.

Using these procedures, the following compounds were prepared.

*3.8.18. Tricarbonyl[(1,2,3,4,5-η)-1-(2′-methoxymethylphenyl)-4-methoxy-2,4-cyclohexadienyl]iron(1 +) hexafluorophosphate(1 −) (**4a**, R = OMe)*

56% overall yield via **8** and **9** by procedure **A** (72% yield) followed by the TFA/NH_4PF_6 method (98% yield), (see Scheme 3). IR: ν_{max} (cm^{-1}) 2108, 2053 (CO). δ_H (acetone-d_6) 2.92 (1H, d, $J = 15.2$ Hz, 6α-H), 3.22 (3H, s, 2′-OMe), 3.49 (1H, dd, $J = 15.9$, 5.9 Hz, 6β-H), 3.99 (3H, s, 4-OMe), 4.36 (1H, m, 5-H), 4.37 (2H, s, 2′-CH_2), 6.22 (1H, d, $J = 5.3$ Hz, 2-H), 7.28–7.42 (5H, m, 3-H, 3′-6′-H). Found: C, 42.25; H, 3.24. $C_{18}H_{17}O_5FePF_6$ requires: C, 42.05; H, 3.33%.

*3.8.19. Tricarbonyl[(1,2,3,4,5-η)-1-(2′-methoxyphenyl)-4-methoxy-2,4-cyclohexadienyl]iron(1 +) hexafluorophosphate(1 −) (**4b**, R = OMe)*

54% overall yield via **8** and **9** by procedure **A** (67% yield) followed by the TFA/NH_4PF_6 method (80% yield), (see Scheme 3), or 29% overall yield via purified **8** by procedure **G** (72% yield) followed by the HPF_6 method (58% yield). IR: ν_{max} (cm^{-1}) 2100, 2052, 2044 (CO). δ_H (acetone-d_6) 2.98 (1H, d, $J = 15.5$ Hz, 6α-H), 3.76 (1H, dd, $J = 15.5$, 6.3 Hz, 6β-H), 3.93 (3H, s, OMe), 4.05 (3H, s, OMe), 4.36 (1H, m, 5-H), 6.49 (1H, d, $J = 6$ Hz, 2-H), 7.11 (1H, t, $J = 7.6$ Hz, Ar) 7.20 (1H, d, J 8.3, Ar), 7.29 (1H, dd, $J = 6.3$, 2.6, 3-H), 7.42 (1H, t, $J = 7.6$, Ar), 7.53 (1H, t, $J = 8.3$, Ar). Found: C, 40.84; H, 2.97. $C_{17}H_{15}O_5FePF_6$ requires: C, 40.83; H, 3.02%.

*3.8.20. Tricarbonyl[(1,2,3,4,5-η)-1-phenyl-4-methoxy-2,4-cyclohexadienyl]iron(1 +) hexafluorophosphate(1 −) (**4d**, R = OMe)*

72% overall yield via **8** and **9** by procedure **A** (85% yield) followed by the TFA/NH_4PF_6 method (85% yield), (see Scheme 3), or 70% overall yield via purified **8** by procedure **C** (72% yield) followed by the TFA/NH_4PF_6 method (98% yield). IR: ν_{max} (cm^{-1}) 2100, 2045 (CO). δ_H (acetone-d_6) 2.75 (1H, d, $J = 14.9$ Hz, 6α-H), 3.97 (1H, dd, $J = 14.9$, 6.6 Hz, 6β-H), 3.99 (3H, s, OMe), 4.43 (1H, dd, $J = 6.6$, 2.7 Hz, 5-H), 6.63 (1H, d, $J = 6.2$ Hz, 2-H), 7.29 (1H, dd, $J = 6.2$, 2.7 Hz, 3-H), 7.5 (5H, m, Ph). δC (62.5 MHz, acetone-d_6) 30.4 (C-6), 43.4 (C-5), 58.0 (OMe), 73.5 (C-3), 86.5 (C-1), 93.4 (C-2), 127.3 (C-2′, C-6′), 130.5 (C-3′, C-5′), 131.6 (C4,), 135.1 (C-1′), 151.1 (C-4), and 206.3 (CO). Found: C, 40.8; H, 2.65. $C_{16}H_{13}F_6FeO_4P$ requires: C, 40.9; H, 2.8%.

*3.8.21. Tricarbonyl[(1,2,3,4,5-η)-1-(2′,6′-dimethoxyphenyl)-4-methoxy-2,4-cyclohexadienyl]-iron(1 +) hexafluorophosphate(1 −) (**4e**, R = OMe)*

54% overall yield via purified **8** by procedure **G** (73% yield) followed by the Ph_3CPF_6 method (74% yield), (see Scheme 3). IR: ν_{max} (cm^{-1}) 2103, 2052 (CO), 1595, 1499, 1250, 837, 558. δ_H (acetone-d_6, 250 MHz) 2.73 (1H, d, $J = 16.5$, 6α-H), 3.29 (1H, dd, $J = 16.5$, 6.0, 6β-H), 3.82 (3H, s, 4-OMe), 3.85 (6H, s, Ar–OMe), 3.96 (1H, m, 5-H), 5.70 (1H, d, $J = 6.3$, 2-H), 6.71 (2H, d, $J = 8.5$, Ar), 6.98 (1H, dd, $J = 6.3$, 2.5, 3-H), 7.42 (1H, t, $J = 8.5$, Ar). m/z (FAB) 385 ($M^+ - PF_6$). Found: 385.0375 $C_{18}H_{17}FeO_6$ ($M^+ - PF_6$) requires: 385.0375).

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