Pergamon

Tetrahedron, Vol. 53, No. 11, pp. 4095-4104, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00020-3

Ester Functionalised Alkene-Extended Cyclohexadienyliron Complexes†

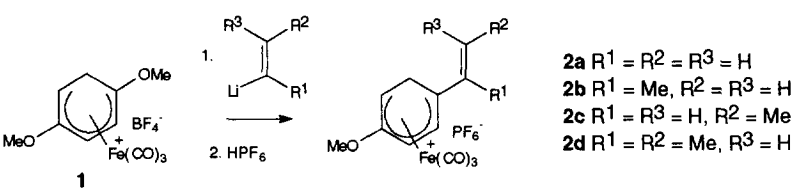
Richard D.A. Hudson[a], Simon A. Osborne[b] and G. Richard Stephenson[a]*

[a] School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, UK.

[b] Parke Davis Neuroscience Research Centre, Forvie site, Hills Road, Cambridge, CB2 2QB, UK.

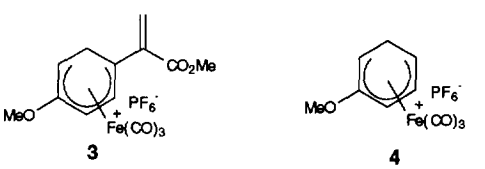
Abstract : A BF_3 adduct of a tricarbonyl(cyclohexadienone)iron complex **5** is converted into an ester-functionalised alkene-extended dienyl complex **13** by reaction with a nucleophile obtained by hydroalumination of methyl propiolate, ligand exchange with PPh_3, and removal of OH with acid. The product was characterised by X-ray crystallography and undergoes stereocontrolled conjugate addition reactions with R_2CuLi reagents.

The conjugate addition of nucleophiles to 1-alkene-substituted tricarbonyl(cyclo-hexadienyl)iron(1+) complexes demonstrates that the powerful activating effect of the cationic metal centre can impart reactivity at positions remote from the site of attachment of the metal. In our development of this chemistry, we have shown that products arise from a single conformation of the alkene relative to the dienyl system,[1] that this same conformation is also favoured in the solid state,[2] and that in the dicarbonyl(triphenylphosphine)iron series, substantial stereocontrol (up to 8:1) is possible in reactions of prochiral alkenes.[3] A selection of propenyl-substituted complexes have been prepared (Scheme 1) by an improved route in which alkenyllithium reagents are added to the 1-alkoxycyclohexadienyl complex **1**.[3] This same procedure gives access to the original η^5-1-ethenylcyclohexadienyliron complex **2a** in two steps and 69% overall yield which compares well with our initial procedure[1] that employed 5 steps and gave a yield of <20%.



Scheme 1

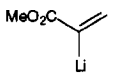
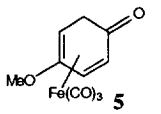
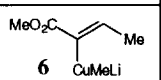
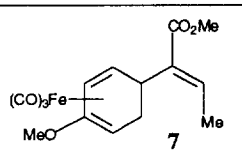
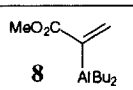
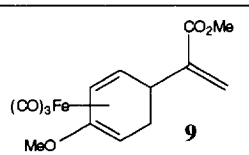
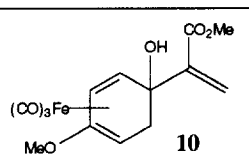
Introduction of functionalised alkenes, however, is less straight-forward. In this paper, we report an investigation of the ester derivative **3**.



†This paper is dedicated to Professor Arthur J. Birch.

In **3**, both the methoxycyclohexadienyl complex and the ester are promoting electrophilicity at the β position in the side-chain, so the regiochemistry of reactions with nucleophiles should be well controlled. Our efforts to prepare **3** are summarised in Table 1 below, and have led us to examine the first combination of hydroalumination-derived nucleophiles with cyclohexadienyl complexes during which we have discovered novel zwitterionic organoiron-based electrophiles.

Table 1. Results for the addition of alkenylmetal nucleophiles to various organoiron complexes.

Entry	Electrophile	Nucleophile	Product	Yield (recovery)
1	**1**		 **5**	80%
2	**1**	 **6**	**5**	84%
3	**4**	**6**	 **7**	33%
4	**1**	 **8**	**5**	63%
5	**4**	**8**	 **9**	50%
6	**5**	**6**	Starting material	(98%)
7	**5**	**8**	Starting material	(98%)
8	**5** : $BF_3.OEt_2$ 1 : 1	**8**	 **10**	31%
9	**5** : $BF_3.OEt_2$ 1 : 10	**8**	**10**	61%

The results of attempted reactions of alkenylmetal nucleophiles with **1** are presented in Table 1. Organolithium reagents are usually better than organocuprates for this purpose,[4] but CH_2=$CLiCO_2Me$ yielded

only the dienone complex **5**. Dealkoxylation side-reactions of this type have been reported in our work on aryl-substituted structures.[5] In this alkenyl case, this pathway entirely blocked the desired process. We turned next to a less reactive nucleophile. Carbocupration of propargylic esters gives convenient access[6] to suitable alkenylcuprates. The use of alkenylcuprates with tricarbonyliron complexes is precedented[7] and selective transfer of the alkenyl group from this reagent to an acid chloride has been described by Marino.[8] The carbometallation was performed by the Marino protocol, but addition of **1** again resulted only in the formation of the dienone complex **5**. Since the simple 2-methoxylcyclohexadienyl complex **4** is usually more suitable for use with organocuprate reagents,[9] we tested the success of the carbocupration stage by the use of this alternative electrophile. The expected η^4-cyclohexadiene complex **7** was obtained in 50% yield in this case (entry 3).

The use of DIBAL for hydroalumination of propargyl esters is known,[10] despite the possibility of competing reduction of the ester group. The di*iso*butylaluminium reagent obtained in this way provides the aluminium counterpart of the organolithium reagent employed in entry 1. With the 1,4-dimethoxy salt **1** (entry 4), dealkylation again prevented nucleophile addition but, as before, the 2-methoxy salt **4** (entry 5) was successfully converted into the alkenyl-substituted product **9**. The use of the nucleophiles **6** and **8** directly with the dienone **5** has also been examined (entries 6 and 7), but starting material **5** was recovered. In an extension[11] of his original work on hydroalumination, Tsuda employed Lewis acids to enhance electrophilicity, and in this way (entries 8 and 9) we have been able obtain the required carbon-carbon bond formation. The product **10** is equipped with a leaving group to facilitate return to the η^5 bonding mode. Comparison of entries 8 and 9 indicate that a considerable excess of Lewis acid is needed for this reaction to proceed efficiently. Boron trifluoride diethyl etherate is known to activate the unsubstituted tricarbonyl(cyclohexadienone)iron complex towards acetylide addition and in this case also, an excess of Lewis acid was employed.[12] Entries 5, 8 and 9 provide the first examples of the combination of alkenylaluminium reagents with tricarbonyliron-based electrophiles; until now only lithium,[3] cadmium,[13] and copper[7] reagents have been used as the source of an alkene group, although the use of aluminium acetylides to introduce alkynes is known.[14]

The role of the Lewis acid in the production of **10** has been examined in detail. Progressive addition of $BF_3.OEt_2$ to a solution of **5** in dichloromethane at room temperature was followed by IR spectroscopy which revealed that ν(CO) bands at 2057 and 1982 cm^{-1} (typical of neutral η^4 tricarbonyliron complexes) are gradually replaced by new stretching modes at 2090 and 2025 cm^{-1}. Although at lower wavenumbers than is typical for tricarbonyl(η^5-cyclohexadienyl)iron complexes, the result indicated the conversion of the dienone complex into a more positively charged (and hence more electrophilic) species. The spectra (Figure 1) show well defined isosbestic points at 2072 and 2006 cm^{-1}. By addition of diethyl ether to the reaction mixture, it is possible to isolate a product **11** as a yellow precipitate which exhibited the same cationic bands in the IR spectrum when redissolved in dichloromethane. The product, however, was too unstable for full characterisation, and gave broadened signals in its ^1H n.m.r. spectrum. The nature of this species was examined by ^{19}F n.m.r. spectroscopy which showed a single signal in acetone-d_6 at -148.5 ppm referenced to fluorotrichloromethane (at 0 ppm). For comparison, a spectrum of the BF_4^- salt **1** was measured under the same conditions. The signal for fluorine in BF_4^- was observed at -147.9 ppm. A solution of $BF_3.OEt_2$ in acetone-d_6 showed a ^{19}F resonance at -149.1 ppm[15] assigned to $BF_3.O{=}C(CD_3)_2$. The ^{19}F signal for the O-BF_3^- moiety in **11** appears between the positions of resonance for the $BF_3.O{=}C(CD_3)_2$ and BF_4^- reflecting the difference in anionic character on boron in **11** (compared to $BF_3.O{=}C(CD_3)_2$) due to the zwitterionic structure of the organometallic adduct **11**. This is consistent with the IR evidence for a positively charged iron centre, and on this basis the adduct **11** has been assigned the structure shown in Scheme 2. Because of its instability, the electrophile is generated and alkylated *in situ*. The stoichiometry employed in entry 9 (Table 1), however, is that based on the quantity of $BF_3.OEt_2$ needed to take the conversion into **11** to completion, and was chosen on the basis of the results shown in Figure 1.

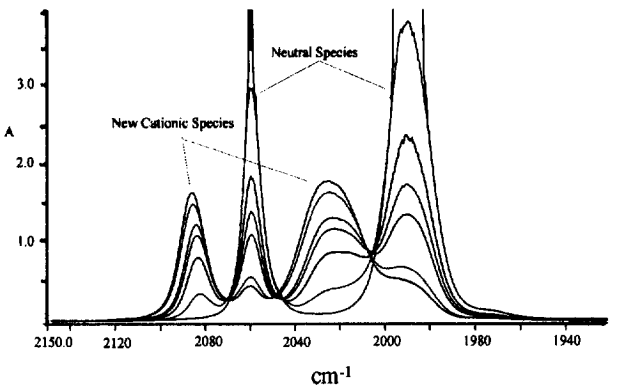
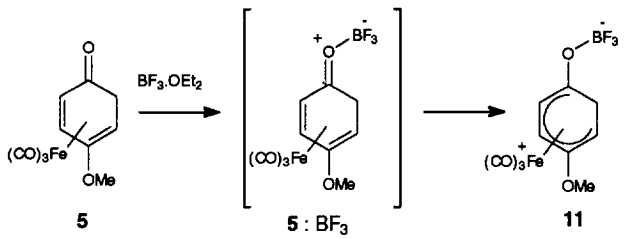


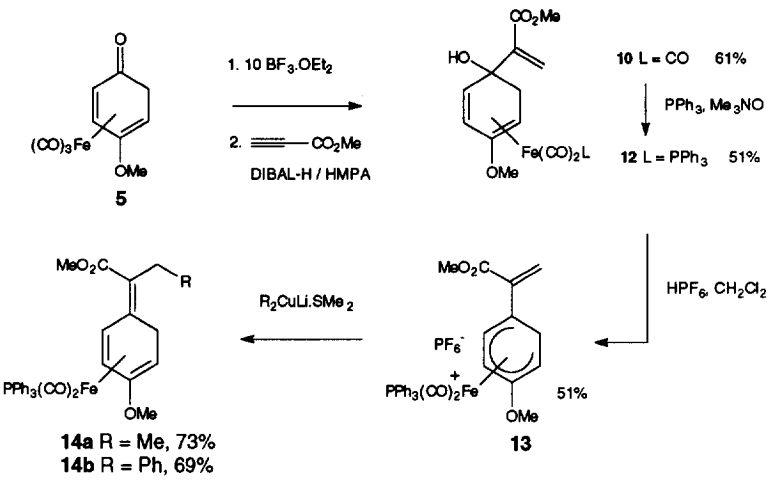
Figure 1. IR spectra showing conversion of **5** into **11** by the addition of 1, 2, 4, 6, 7, 9 and 10 equivalents of BF_3. OEt_2 to a solution of **5** in dichloromethane at room temperature.



Scheme 2.

The product of nucleophile addition **10** was converted into a cationic cyclohexadienyl complex by removal of the OH group with acid. Evidence for the cationic product was obtained by IR measurements of the reaction mixture [ν(CO) 2110 and 2058 cm^{-1}], but although addition diethyl ether addition forced out the product as a cloudy precipitate, this quickly collapsed to a sticky intractable gum. Similar results were obtained with HPF_6/Ac_2O, HPF_6/CH_2Cl_2, and TFA (aq.)/NH_4PF_6, and also when Ph_3CBF_4 was used in place of the acid. The problem was solved (Scheme 3) by conversion of **10** into the dicarbonyliron phosphine analogue **12**. Reaction with HPF_6/CH_2Cl_2 was repeated and the required product **13** was now easily isolated by precipitation with ether in the normal way. The product was recrystallised from acetone by allowing diethyl ether to diffuse slowly into the solution, and an X-ray structure determination[2] showed (Figure 2) that this ester-functionalised product adopted the same conformation as the other alkene-extended structures.

Similarly, conjugate nucleophile addition should give stereodefined products. This has been confirmed by reaction with Me_2CuLi and Ph_2CuLi, which each afforded single stereoisomers (73 and 69% yields, respectively). With the ester group in place, the relative positions of substituents around the exocyclic alkene in the products could not be proved by nOe experiments as we did[1,3] in our earlier examples with hydrogen at this position. The relative stereochemistry shown in Scheme 3 is inferred from the similarity of the n.m.r. spectra of these products to our other examples and the similarity of the X-ray structure of **13** (Figure 2) to that of the corresponding $Fe(CO)_2PPh_3$ complex[3] with CH=CHMe as the side-chain. Since nucleophile addition to **13** gives single stereoisomers (**14a,b**) there is no evidence in this (or any other of the many examples now examined[1,3]) for an alternative mode of addition *via* the opposite conformation of the alkene.



5 13

Scheme 3.

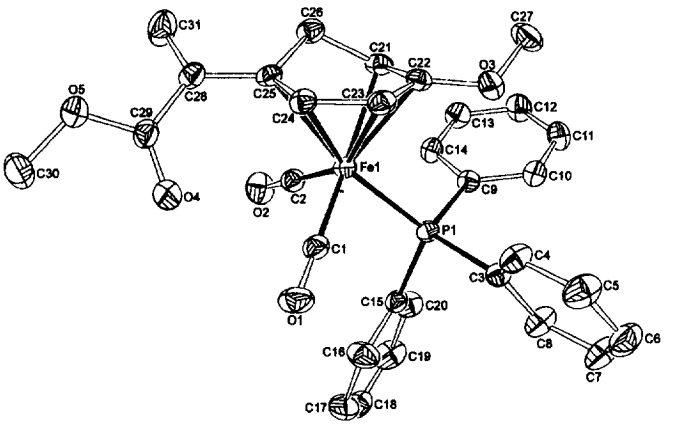


Figure 2. X-ray structure of **13**; triclinic, space group P-1, Z=2, D_c = 1.549 gcm^{-1}.

The combination of hydroalumination/BF_3 activation provides an attractive procedure for elaboration of η^4-tricarbonyliron complexes of cyclohexadienones, an intriguing class of structures in which phenols are locked in the keto form by complexation. Although known from the beginnings of tricarbonyliron chemistry,[16] these dienone structures, until recently,[3,17] have been relatively little used in synthetic applications. Our work has shown that by the hydroalumination route, they are excellent precursors for functionalised alkene-extended cyclohexadienyl complexes of $Fe(CO)_2PPh_3^+$, which should be valuable as functionalised electrophiles in synthetic applications.[18]

Acknowledgements. We thank the EPSRC and Parke Davis for financial support (to RDAH), the EPSRC Mass Spectrometry Centre (Swansea) for FAB and high resolution mass spectrometric measurements, Parke Davis and Dr M. F. Mahon (University of Bath) for the X-ray analysis of **13**, Mr. C. MacDonald (UEA) for help with the fluorine n.m.r. of **11**, and Dr C. E. Anson (UEA) for assistance with FTIR spectroscopy of **11** for the measurement of isosbestic points.

General: All reactions were performed under inert atmosphere (nitrogen or argon). Infrared spectra were recorded on a Perkin Elmer 1720X FTIR spectrometer; only selected resonances are reported. ^{1}H n.m.r. spectra were recorded at 60 MHz on a JEOL JNM-PMX60si spectrometer, at 270 MHz on a Jeol EX 270 spectrometer, and at 400 MHz on a Varian Unity 400 spectrometer. ^{13}C n.m.r. spectra were recorded at 67 MHz on a Jeol EX 270 spectrometer. ^{19}F n.m.r. spectra were measured at 84.1 MHz on a Jeol EX90Q spectrometer. Compounds **1** and **4** were prepared according to the procedures of Stephenson[17] and Birch[19] respectively.

Attempted addition of the alkenyllithium reagent prepared from methyl 2-bromopropenoate to tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron(1+) hexafluorophosphate(1-) 1. Following the method[3] used previously for the lithiation and addition of simple alkenyl bromides to organoiron salts, ^{t}BuLi (1.7 M in hexanes, 6.5 ml, 10.9 mmol) was stirred at -78 °C in dry diethyl ether (25 ml) and a solution of methyl 2-bromopropenoate (0.902 g, 5.5 mmol) in dry diethyl ether (4 ml) was added dropwise over 10 min. The mixture was stirred for a further 30 min after which the temperature was lowered to -100 °C (acetone / petroleum ether / liquid nitrogen slush bath) and a cooled (-100 °C) solution of **1** (1.00 g, 2.7 mmol) in dichloromethane (5 ml) was added *via* a cannula. The reaction mixture was stirred for 1 h after which it was allowed to warm to room temperature and was quenched by the addition of water (50 ml). The solution was extracted with diethyl ether (3 x 50 ml) and the organic portions were combined and washed with water (2 x 50 ml) and brine (1 x 50 ml) before being dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* leaving a brown oil. Purification by column chromatography on silica gel eluted with 50% diethyl ether / 50% petroleum ether afforded *tricarbonyl[(2,3,4,5-η)-4-methoxycyclohexadien-1-one]iron(0) 5* (0.570 g, 80%). δ_H(60MHz, $CDCl_3$) 5.6 (1H, dd, *J* 7.2, 2.4 Hz, C3-H), 3.80 (3H, s, OCH_3), 3.52 (1H, m, C5-H), 2.85 (1H, d, *J* 7.2 Hz, C2-H), 2.34 ppm (2H, m, C6-H). [Lit[20] δ_H (CCl_4) 5.6 (1H, dd, *J* 7.0, 3 Hz, C3-H), 3.75 (3H, s, OCH_3), 3.46 (1H, m, C5-H), 2.75 (1H, d, *J* 7.0 Hz, C2-H), 2.23 ppm (2H, m, C6-H).]

Attempted addition of 6 to tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron(1+) hexafluorophosphate(1-) 1. Following the procedure of House,[21] lithium dimethylcuprate was prepared by the addition of copper(I) bromide-dimethyl sulfide complex (0.52 g, 2.54 mmol) as a solid, to a solution of methyllithium (1.0 M in THF / cumene, 5.1 ml, 5.1 mmol) in dry THF (2 ml) at -30 °C. After stirring for 30 min, a yellow solution had formed. Methyl propiolate (0.22 g, 2.6 mmol) was added following the procedure described by Marino.[8] The mixture was stirred at -30 °C for a further 1 h giving a clear brown solution containing **6**. The temperature was lowered to -78 °C and **1** (0.40 g, 1.0 mmol) was added as a solution in dry dichloromethane (5 ml). The mixture was stirred for 30 min and allowed to warm to room temperature after which it was poured into a separating funnel charged with sat. aqueous ammonium chloride (30 ml) and extracted with diethyl ether (3 x 50 ml). The organic portions were combined and washed with brine (1 x 100 ml) and water (3 x 100 ml) before being dried over anhydrous magnesiuim sulfate. Purification by column chromatography on silica gel eluted with 50% diethyl ether / 50% petroleum ether afforded *tricarbonyl[(2,3,4,5-η)-4-methoxycyclohexadien-1-one]iron(0) 5* (0.222 g, 84%), having the same spectral characteristics as before.[20]

Tricarbonyl[methyl E-2-((2,3,4,5-η)-4-methoxycyclohexa-2,4-dien-1-yl)but-2-enoate]iron(0) 7. Following the same procedure as above, **6** was prepared on the same scale and **4** (0.50 g, 1.3 mmol) was added as a solution in dichloromethane (10 ml). The mixture was stirred for 30 min before being worked up as above. The solution was concentrated under vacuum and the residues were purified by column chromatography on silica gel, eluting with 5% diethyl ether / 95% petroleum ether to afford **7** (0.146 g, 33%) as a yellow solid. ν_{max}(solution in hexane) 2044 and 1975 (neutral MC≡O stretches), 1723, 1636, 1425, 1265, 1231, 1199, 1126 cm^{-1}; δ_H(270MHz, $CDCl_3$) 6.67 (1H, q, *J* 7.3 Hz, C=C*H*CH_3), 5.10 (1H, dd, *J* 6.6 and 2.3 Hz, C3-H), 3.68 (3H, s, OCH_3), 3.67 (3H, s, OCH_3), 3.38 (1H, m, C5-H), 3.15 (1H, m, C1-H), 2.45 (1H, dd, *J* 6.6 and 3.3 Hz, C2-H), 2.02 (1H, ddd, *J* 14.5, 10.9 and 3.6 Hz, C6β-H), 1.78 (3H, d, *J* 7.3 Hz C=CHCH_3), 1.74 ppm (1H, ddd, *J* 14.2, 4.0 and 2.3 Hz, C6α-H); δ_C(67MHz, $CDCl_3$) 211.5 (MC≡O), 167.4 (CH_3O_2CC=CH), 140.0 (CH_3O_2CC=CH), 137.5 (CH_3O_2CC=*C*H), 135.8 (C4), 67.0 (C3), 54.4 (C2), 52.9 (OCH_3), 52.8 (OCH_3), 51.3

(C5), 35.9 (C1), 29.7 (C6), 14.0 ppm (C=CH*C*H_3); *m/z* (EI) 348 (M^+, 4), 320 (M^+-CO, 9), 292 (M^+-2CO, 60), 264 (M^+-3CO, 100), 262 (57), 249 (27), 204 (46), 184 (16%). Found: C, 51.9, H, 4.5. $C_{15}H_{16}O_6Fe$ requires: C, 51.8, H, 4.6%.

Attempted addition of ***8*** *to tricarbonyl[(1,2,3,4,5-η)-1,4-dimethoxycyclohexadienyl]iron(1+) tetafluoroborate(1-)* ***1****.* Following the procedure of Tsuda,[11] DIBAL-H (1.0 M in pentane, 1.5 ml, 1.5 mmol) was added to a solution of HMPA (0.25 ml, 1.5 mmol) in THF (3 ml) at 0 °C. The mixture was stirred for 30 min and methyl propiolate (1.25 g, 15.0 mmol) was added dropwise. Stirring was continued for a further 30 min to give a solution containing **8**, and **1** (0.464 g, 1.3 mmol) was added as a solution in dichloromethane (10 ml). The reaction was allowed to warm to room temperature overnight after which the mixture was poured into a separating funnel charged with water (50 ml) and was extracted with diethyl ether (3 x 50 ml). The organic portions were combined and washed with water (2 x 50 ml) and brine (1 x 50 ml) before being dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and purification by column chromatography on silica gel eluted with 50% diethyl ether / 50% petroleum ether afforded *tricarbonyl[(2,3,4,5-η)-4-methoxycyclohexadien-1-one]iron(0)* ***5*** (0.211 g, 63%), having the same spectral characteristics as before.[20]

Tricarbonyl[methyl 2-((2,3,4,5-η)-4-methoxycyclohexa-2,4-dien-1-yl)prop-2-enoate]iron(0) ***9****.* Following the same procedure[11] as above, **8** was prepared in the same amount and **4** (0.50 g, 1.3 mmol) was added as a solution in dichloromethane (10 ml). The mixture was stirred for 30 min before being worked up as described above. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel eluted with 5% diethyl ether / 95% petroleum ether to afford **9** (0.21 g, 50%) as a yellow oil. ν_{max}(thin film) 2049 and 1984 (neutral MC≡O stretches), 1718, 1626, 1425, 1383, 1228, 1154, 1095 cm^{-1}; δ_H(270MHz, $CDCl_3$) 6.04 (1H, s, C=C*H*$_2$), 5.64 (1H, s, C=C*H*$_2$), 5.19 (1H, dd, *J* 6.6 and 2.3 Hz, C3-H), 3.71 (3H, s, OC*H*$_3$), 3.64 (3H, s, OC*H*$_3$), 3.33 (1H, m, C5-H), 3.04 (1H, ddd, *J* 11.2, 3.7 and 3.6 Hz, C1-H), 2.62 (1H, dd, *J* 6.6 and 3.6 Hz, C2-H), 2.25 (1H, ddd, *J* 14.8, 11.2 and 3.9 Hz, C6β-H), 1.50 ppm (1H, ddd, *J* 14.9, 3.7 and 2.7 Hz, C6α-H); *m/z* (EI) 334 (M^+, 2), 306 (M^+-CO, 6), 278 (M^+-2CO, 46), 250 (M^+-3CO, 84), 235 (19), 195 (18), 190 (35), 164 (100%). Found: C, 50.5, H, 4.0. $C_{14}H_{14}O_6Fe$ requires: C, 50.3, H, 4.2%.

Attempted addition of ***6*** *or* ***8*** *to tricarbonyl[(2,3,4,5-η)-4-methoxycyclohexadien-1-one]iron(0)* ***5****.* Following the same procedures[8,11] as before, **6** or **8** were prepared on the same scales and in each case **5** (0.3 g, 1.3 mmol) was added in dichloromethane (10 ml). The solutions were stirred overnight at room temperature. No reaction was observed by tlc and **5** was recovered in almost quantitative yield (0.335 g, 98% and 0.324 g, 95% respectively) from both experiments.

Reaction of $BF_3.OEt_2$ *with* ***5****, preparation of tricarbonyl[(1,2,3,4,5-η)-(4-methoxycyclohexadien-1-yl)-1-oxytrifluoroborate]iron(1+)* ***11****.* Boron trifluoride diethyl etherate (1.136 g, 1.0 ml, 8.0 mmol) was added in aliquots to a solution of ***5*** (0.219 g, 0.8 mmol), in dichloromethane (5 ml) and the IR spectrum of the solution was recorded after each addition (fig. 1). The reaction mixture was stirred for 2 h at room temperature after which time a precipitate had begun to appear. Dry diethyl ether (5 ml) was added and a dense yellow precipitate was formed. This was collected by filtration and washed with dry diethyl ether (10 ml) taking care not to expose the solid to air for longer than was necessary. The material was dried under vacuum at room temperature to afford *tricarbonyl[(1,2,3,4,5-η)-(4-methoxycyclohexadien-1-yl)-1-oxytrifluoroborate]iron(1+)* **11**, as a yellow solid (0.196 g, 71% crude). Purification from dichloromethane by reprecipitation on addition to dry diethyl ether was attempted but resulted in loss of material. ν_{max} (solution in CH_2Cl_2) 2090 and 2025 cm^{-1} (cationic MC≡O stretches); ^1H n.m.r. spectroscopy was attempted but very broad signals were observed. Approximately 20 to 30 mg of **11** were dissolved in 1.5 ml of acetone-d_6 at room temperature and filtered through a plug of cotton wool into a 507 n.m.r. tube which was capped in air; δ_F(84.1MHz, Acetone-d_6) -148.5 (OB*F*$_3$ in **11**) and -144.3 ppm (relative intensity *circa* 0.5%).[15]

Tricarbonyl[methyl 2-((2,3,4,5-η)-1-hydroxy-4-methoxycyclohexa-2,4-dien-1-yl)prop-2-enoate]iron(0) ***10****. Method A.* A solution of **5** (0.55 g, 2.35 mmol) in THF (20 ml) was stirred with boron trifluoride etherate

(2.3 ml, 2.35 mmol) for 30 min at room temperature to form the BF_3 adduct **11**. The same procedure[11] as before was followed to prepare **8** using HMPA (1.0 ml, 6.0 mmol), DIBAL-H (6.0 ml, 6.0 mmol) and methyl propiolate (0.5 ml, 5.0 mmol). The Lewis acid modified dienone **11** was added to the nucleophile and the reaction mixture was stirred overnight. The mixture was poured into a separating funnel charged with water (50 ml) and extracted with diethyl ether (3 x 50 ml). The organic portions were combined and washed with water (2 x 50 ml) and brine (1 x 50 ml). The solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel eluted with 5% diethyl ether / 95% petroleum ether to afford **10** (0.254g, 31%) as an unstable yellow oil. ν_{max}(thin film) 2048 and 1980 cm^{-1} (neutral MC≡O stretches); δ_H(270MHz, $CDCl_3$) 6.05 (1H, s, C=CH_2), 5.83 (1H, s, C=CH_2), 5.11 (1H, dd, *J* 6.6 and 2.3 Hz, C3-H), 3.93 (1H, s, O*H*), 3.76 (3H, s, OCH_3), 3.65 (3H, s, OCH_3), 3.26 (1H, m, C5-H), 2.67 (1H, d, *J* 6.6 Hz, C2-H), 2.17 ppm (2H, m, C6β-H, C6α-H). This compound was converted into the dicarbonyltriphenylphosphine derivative **12** which was fully characterised.

Method B. The same conditions as above were employed with the exception that the boron trifluoride diethyl etherate was added in tenfold excess as suggested by IR spectroscopy (Figure 1). The yield was 61% following this protocol.

Tricarbonyl[methyl 2-((1,2,3,4,5-η)-4-methoxycyclohexadien-1-yl)prop-2-enoate]iron(1+) hexafluorophosphate(1-) 3. Method A. A solution of **10** (0.25 g, 0.72 mmol) in acetic anhydride (4 ml) and cooled to 0 °C. Excess hexafluorophosphoric acid (70% in water, 5 drops) was added and the solution immediately darkened. Inspection of the IR spectrum revealed only cationic MC≡O stretches (ν_{max} 2110 and 2058 cm^{-1}) and the solution was poured into diethyl ether (50 ml). A yellow precipitate formed which quickly became a sticky oil. This was taken up into acetone and reprecipition was attempted, but this resulted in the loss of the compound.

Method B. A solution of **10** (0.5 g, 1.43 mmol) in acetic anhydride (10 ml) and cooled to 0 °C. Triphenylcarbenium tetrafluoroborate (0.566 g, 1.71 mmol) was added as a solution in dry dichloromethane (20 ml). The reaction was stirred for 10 min after which only cationic carbonyl stretches could be seen in the IR spectrum of the mixture. The reaction mixture was poured into dry diethyl ether under argon and a dense yellow precipitate formed. However on settling this became a sticky yellow oil. Further reprecipitations from acetone / diethyl ether gave **3** as a dirty yellow oil which could not be further purified. ν_{max}(thin film) 2110 and 2058 (cationic MC≡O ligands), 1733, 1516, 1253, 1045 cm^{-1}; δH (270MHz, d_6-acetone) 7.35 (1H, d, *J* 4.2 Hz, C3-H), 6.78 (1H, s, C=CH_2), 6.47 (1H, d, *J* 5.9 Hz, C2-H), 6.40 (1H, s, C=CH_2), 4.40 (1H, d, *J* 5.6 Hz, C5-H), 4.03 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.55 (1H, m, C6β-H), 2.59 ppm (1H, m, C6α-H).

Dicarbonyl[methyl 2-((2,3,4,5-η)-1-hydroxy-4-methoxycyclohexa-2,4-dien-1-yl)prop-2-enoate]-triphenylphosphineiron(0) 12. Following the procedure of Birch,[22] **10** (0.504 g, 1.44 mmol) was added to a solution of triphenylphosphine (2.264 g, 8.64 mmol) and trimethylamine *N*-oxide (0.820 g, 7.20 mmol) in acetone (50 ml). The mixture was heated at reflux under a nitrogen atmosphere for 5 h after which only the characteristic neutral dicarbonyl stretches could be seen in the IR spectrum. The mixture was allowed to cool to room temperature and water (50 ml) was added. The solution was extracted with diethyl ether (3 x 100 ml) and the combined extracts were reduced to half their volume using a rotary evaporator. Petroleum ether (50 ml) was added and a fine, off-white precipitate of triphenylphosphine was formed. This was removed by filtration through a glass sinter. The precipitation procedure was repeated 3 times until most of the triphenylphosphine had been removed. The solution was washed with water (2 x 100 ml) and brine (1 x 100 ml) and the solvent was removed *in vacuo* to give an oily yellow cake of crystals. The crude product was taken up in dichloromethane (5 ml) and purified by column chromatography on silica gel eluted with 20% diethyl ether/ 79% petroleum ether and 1% triethylamine to afford **12** (0.420 g, 51%) as a yellow solid. ν_{max}(thin film) 1976 and 1916 (neutral MC≡O stretches), 1713, 1410, 1325, 1210, 1105, 616 cm^{-1}; δ_H(270MHz, $CDCl_3$) 7.63 (15H, m, ArH), 5.88 (1H, s, C=CH_2), 5.62 (1H, s, C=CH_2), 3.98 (1H, s, O<u>H</u>), 3.77 (1H, m, C3-H), 3.70 (3H, s, OCH_3), 3.49 (1H, d, *J* 5.2 Hz, C2-H), 3.30 (3H, s, OCH_3), 3.03 (1H, m, C5-H) 2.17 ppm (2H, m, C6β–H,

C6α-H); *m/z* (FAB) 584 (M^+, 8), 567 (M^+-CO, 32), 528 (M^+-2CO, 24), 510 (72), 441 (15), 349 (80), 335 (66), 318 (100), 263 (66), 183 (85%); *m/z* (FAB) Found: 585.1142. $[C_{31}H_{30}O_6FeP]^+$ requires: 585.1129 (M^++1).

*Dicarbonyl[methyl 2-((1,2,3,4,5-η)-4-methoxycyclohexadien-1-yl)prop-2-enoate]triphenylphosphine-iron(1+) hexafluorophosphate(1-) **13**.* Hexafluorophosphoric acid (70% in water, 3 drops) was added to a solution of **12** (0.420 g, 0.72 mmol) in cooled (0 °C) acetic anhydride (3 ml). Salt formation occurred at once (IR) and the cationic complex was precipitated by dropwise addition of the reaction mixture to cooled (0 °C) diethyl ether (50 ml). A dense yellow precipitate was formed which was collected by filtration and further purified by reprecipitation from acetone (5 ml) and diethyl ether (50 ml) to afford **13** (0.262 g, 51%) as a yellow powder. A small portion of the salt (0.050 g) was placed in a sample vial and dissolved in acetone (1 ml). The tube was placed in a desiccator with enough diethyl ether in the base to provide an atmosphere saturated with solvent vapour. Crystallisation took place overnight and an analytically pure sample of **13** was obtained in the form of orange needles. ν_{max}(thin film) 2043 and 1998 (cationic MC≡O stretches), 1721, 1461, 1238, 1213, 1169, 988, 949 cm^{-1}; δ_H(400MHz, DMSO, 80 °C) 7.50 (16H, m, ArH, C=CH_2), 7.07 (1H, d, *J* 5.6 Hz, C3-H), 6.44 (1H, s, C2-H), 6.14 (1H, s, C=CH_2), 5.97 (1H, d, *J* 5.2 Hz, C5-H), 3.73 (3H, s, OCH_3), 3.31 (1H, dd, *J* 15.2 and 6.0 Hz, C6β-H), 3.15 (3H, s, OCH_3), 2.24 ppm (1H, d, *J* 15.2 Hz, C6α-H); *m/z*(FAB) 568 (M^+-PF_6, 36), 567 (M^+-PF_6-H, 100), 540 (M^+-PF_6-CO, 3), 539 (M^+-PF_6-CO-H, 6), 512 (M^+-PF_6-2CO, 11), 511 (M^+-PF_6-2CO-H, 22), 349 (97), 318 (17), 263 (20), 183 (22%). Found: C, 52.1, H, 3.8. $C_{31}H_{28}O_5P_2F_6Fe$ requires: C, 52.2, H, 3.9%. The structure of this product was also proved by X-ray analysis (Figure 2).[2]

*(2Z)-Dicarbonyl[methyl 2-((2,3,4,5-η)-4-methoxycyclohexa-2,4-dien-1-ylidiene)butanoate]triphenyl-phosphineiron(0) **14a**.* Dimethylcuprate was made by the addition of solid copper(I) bromide-dimethyl sulphide complex (0.028 g, 0.15 mmol) to a solution of a methyllithium (1.0 M in THF / cumene, 0.3 ml, 0.3 mmol) in THF (20 ml) at -30 °C followed by stirring for 30 min until the copper(I) bromide-dimethyl sulfide complex had dissolved. The solution was cooled to -78 °C and **13** (0.050 g, 0.07 mmol) was added as a solid. The solution was allowed to warm to room temperature after which the reaction was quenched by the addition of sat. aqueous ammonium chloride (50 ml). The mixture was extracted with diethyl ether (3 x 50 ml) and the organic portions were combined and washed with water (2 x 50 ml) and brine (50 ml). The solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel eluted with 20% diethyl ether / 79% petroleum ether and 1% triethylamine to afford **14a** (0.029g, 73%) as a yellow oil. ν_{max}(thin film) 1972 and 1914 (neutral MC≡O stretches), 1683, 1547, 1488, 1434, 1214, 1126, 1095 cm^{-1}; δ_H(400MHz, $CDCl_3$) 7.3-7.6 (15H, m, ArH), 4.00 (1H, bs, C3-H), 3.90 (1H, dd, *J* 6.8 and 6.9 Hz, C2-H), 3.49 (3H, s, OCH_3), 3.44 (3H, s, OCH_3), 3.21 (1H, bs, C5-H), 2.82 (1H, bd, *J* 19.2 Hz, C6β-H), 2.44 (1H, dd, *J* 19.2 and 5.6 Hz, C6α-H), 2.18 (1H, dq, *J* 16.0 and 7.6 Hz, CC$H_2$$CH_3$), 2.04 (1H, dq, *J* 16.0 and 7.6 Hz, CC$H_2$$CH_3$), 0.99 ppm (3H, t, *J* 7.6 Hz, CCH_2CH_3), *m/z* (FAB) 583 (M^++H, 9), 582 (M^+, 8), 526 (M^+-2CO, 100), 349 (26), 318 (27), 263 (PPh_3+H, 12), 183 (15%), *m/z* (FAB) Found: 583.1352. $[C_{32}H_{32}O_5FeP]^+$ requires: 583.1337 (M^++1).

*(2Z)-Dicarbonyl[methyl 2-((2,3,4,5-η)-4-methoxycyclohexa-2,4-dien-1-ylidiene)-3-phenylpropan-oate]triphenylphosphineiron(0) **14b**.* The same procedure as above was followed to make lithium diphenylcuprate using phenyllithium (0.8 ml, 1.4 mmol) and copper(I) bromide-dimethyl sulfide complex (0.145 g, 0.70 mmol). Stirring was continued for 30 min after which **13** (0.250 g, 0.35mmol) was added as a solid to the solution at -30 °C. Work up and purification as described before afforded **14b** (0.156 g, 69%) as a yellow oil. ν_{max}(thin film) 1977 and 1920 (neutral MC≡O stretches), 1693, 1568, 1489, 1434, 1219, 1124, 1087 cm^{-1}; δ_H(400MHz, $CDCl_3$) 7.1-7.6 (20H, m, ArH), 4.02 (2H, m, C3-H, C2-H), 3.64 (1H, d, *J* 16.0 Hz, CCH_2Ph), 3.46 (3H, s, OCH_3), 3.44 (3H, s, OCH_3), 3.41 (1H, d, *J* 16.0 Hz, CCH_2Ph), 3.18 (1H, bs, C5-H), 2.82 (1H, bd, *J* 19.2 Hz, C6β-H), 2.42 (1H, dd, *J* 19.2 and 5.6 Hz, C6α-H); *m/z* (FAB) 645 (M^++H, 17), 644 (M^+, 14), 588 (M^+-2CO, 52), 349 (31), 326 (M^+-2CO-PPh_3,100), 263 (PPh_3+H, 21), 183 (23%), *m/z* (FAB) Found: 645.1514. $[C_{37}H_{34}O_5FeP]^+$ requires: 645.1494 (M^++1).

References and notes.

1. Stephenson, G. R.; Voyle, M.; Williams, S. *Tetrahedron Lett.* **1990**, *31*, 3979.
2. Parke Davis and Mahon, D. M. F. University of Bath, unpublished results.
3. Hudson, R.D.A.; Osborne, S. A.; Roberts, E.; Stephenson, G. R. *Tetrahedron Lett.*, accepted.
4. Bandara, B. M. R.; Birch, A. J.; Khor, T.-C. *Tetrahedron Lett.* **1980**, *21*, 3625.
5. Malkov, A. V.; Stephenson, G. R. *J. Organomet. Chem.* **1995**, *489*, C44.
6. Normant, J. F.; Alexakis, A.; *Synthesis* **1981**, 841.
7. Potter, G. A.; McCague, R. *J. Chem. Soc., Chem. Commun.* **1992**, 635.
8. Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1981**, *46*, 3696.
9. Pearson, A. J.; *Aust. J. Chem.* **1976**, *28*, 1101.
10. Tsuda, T.; Yoshida, T.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1987**, *52*, 1624.
11. Tsuda, T.; Yoshida, T.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 1037.
12. Smyth, D. G. *Ph.D. Thesis*, **1994**, University of East Anglia
13. Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954.
14. Reddy, B. R. *J. Organomet. Chem.* **1989**, 375, C51.
15. A small signal at -144.3 ppm was also observed. At first it was thought that this corresponded to a small percentage of $BF_3.OEt_2$ at equilibrium with $BF_3.O{=}C(CD_3)_2$, so the ^{19}F n.m.r. spectrum of $BF_3.OEt_2$ was measured in a non-coordinating solvent ($CDCl_3$) for comparison. Under these conditions, a single signal at -153.3 ppm was observed. This is consistent with the position of the other signals observed, since the boron atom might be expected to be less anionic in $BF_3.OEt_2$ than in $BF_3.O{=}C(CD_3)_2$. It seems probable that the fluorine atoms in the ether adduct would resonate at a similar chemical shift in the solvent $O{=}C(CD_3)_2$, but no signal at this position was observed, indicating that the equilibrium completely favoured $BF_3.O{=}C(CD_3)_2$. The small signal at -144.3 ppm had an intensity of ca. 0.5% relative to the signal for $BF_3.O{=}C(CD_3)_2$, and has been tentatively assigned to the adduct of $O{=}C(CD_2H)(CD_3)$ since this would be present in about this proportion in the commercial $O{=}C(CD_3)_2$ used for the experiment.
16. Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A. *Chem. & Ind. (Lond.)*, **1964**, 838.
17. Stephenson, G. R.; Finch, H.; Owen, D. A.; Swanson, S. *Tetrahedron* **1993**, *49*, 5649.
18. To illustrate this possibility in a route to β-amino acids, we have examined, in a preliminary experiment, the introduction of a nitrogen-centred nucleophile by means of Yamamoto's amide-derived cuprate reagent $[Me_3Si(Bn)N]_2CuLi$ (Ref. 23). An unstable product was isolated in 61% yield. The n.m.r. spectrum of this complex indicated the introduction of an NHBn group in place of the methyl group in **14a**. Although this formulation is supported by the presence of a correct molecular ion in the FAB mass spectrum of the product, this ion was too weak for high resolution measurement, and the complex was too unstable for characterisation by microanalysis. The generalisation of the use of **13** as a general precursor for β, γ, and δ amino acids awaits further work with a range of nitrogen-containing nucleophiles.
19. Birch, A. J.; Chamberlain, M. A.; Haas, D. T.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1,* **1973**, 1882; Birch, A. J.; Williamson, D. H. *J. Chem. Soc., Perkin Trans. 1,* **1973**, 1892.
20. Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem, Soc., (A)* **1968**, 332.
21. House, H. O.; Chu, C. Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.
22. Birch, A. J.; Kelly, L. F. *J. Organomet. Chem.* **1985**, *286*, C5.
23. Yamamoto, Y.; Asao, N.; Uyehara, T. *J. Am. Chem. Soc.* **1992**, *114*, 5427.

(*Received in UK* 31 *October* 1996; *revised* 16 *December* 1996; *accepted* 8 *January* 1997)