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Reactivity patterns in cationic tricarbonyliron complexes: crystallographic proof of stereoselectivity in long range asymmetric induction in the 1,3/1′,2′ series†

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The analysis of patterns of regioselectivity in cyclohexadienyl complexes illustrates the versatility and power of the iron-based methodology in reaction sequences that make multiple use of the metal to establish a series of chiral centres. The conversion of tricarbonyl(η^4-cyclohexadienone)iron(0) into the dimethyl malonate adduct 4, which contains two chiral centres at carbon besides the controlling chirality of the tricarbonyliron complex itself, provides an example of long-range asymmetric induction. The relative stereochemistry of the 1,3/1′,2′ product has been defined as *S,S,R*,R.**

Keywords: tricarbonyliron; η-5 trienyl; working ligand; asymmetric induction; diastereoselectivity; X-ray structure

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INTRODUCTION

The application of organometallic complexes as intermediates in organic synthesis has been a focus of research effort since the early days of organometallic chemistry, and a wide selection of metals and ligand types have been evaluated.[1] The electrophilic tricarbonyliron complexes of the cyclohexadienyl ligand originate from Fischer's classic preparation[2] of $(\eta^5\text{-}C_6H_7)Fe(CO)_3BF_4$ by hydride abstraction from the η^4-diene complex, and, soon afterwards, work on substituted examples initiated by Birch and Lewis[3] brought these complexes to the attention of organic chemists. Unlike the Whelland intermediate (e.g. $C_6H_7^+$) in electrophilic aromatic substitution, the iron complexed dienyl structures $(C_6H_7^+)Fe(CO)_2L$ do not readily deprotonate[4] from the C6 CH_2 group, but instead serve as powerful electrophiles that are capable of a wide range of carbon–carbon bond-forming reactions. An exception has been identified in the case of 1-arylcyclohexadienyliron complexes, which can be deprotonated to afford biaryls. This reactivity, combined with complete and reliable stereoselectivity, has proved valuable in organic synthesis, where the utility of tricarbonyliron complexes has been demonstrated by a number of research groups around the world, perhaps most notably at first by Birch and coworkers in Canberra who synthesized the amino acid gabaculine[5] and shikimic acid,[6] and subsequently through the terpene and alkaloid syntheses of Pearson and coworkers[7] at Case Western Reserve and Knölker and coworkers[8] at Karlsruhe. In Norwich, too, target molecule synthesis has been a major objective in our work exploring the reactivity patterns of cyclohexadienyliron complexes. The analogous acyclic diene and dienyl complexes have been similarly developed by Frank-Neumann and co-workers,[9] Grée and coworkers,[10] and Donaldson and co-workers.[11]

In applications such as these, one of the ligands becomes incorporated into the final target structure. This ligand is termed the 'working ligand'[12] (see Fig. 1a) and, in an efficient synthetic route, its substituents should match the desired substitution

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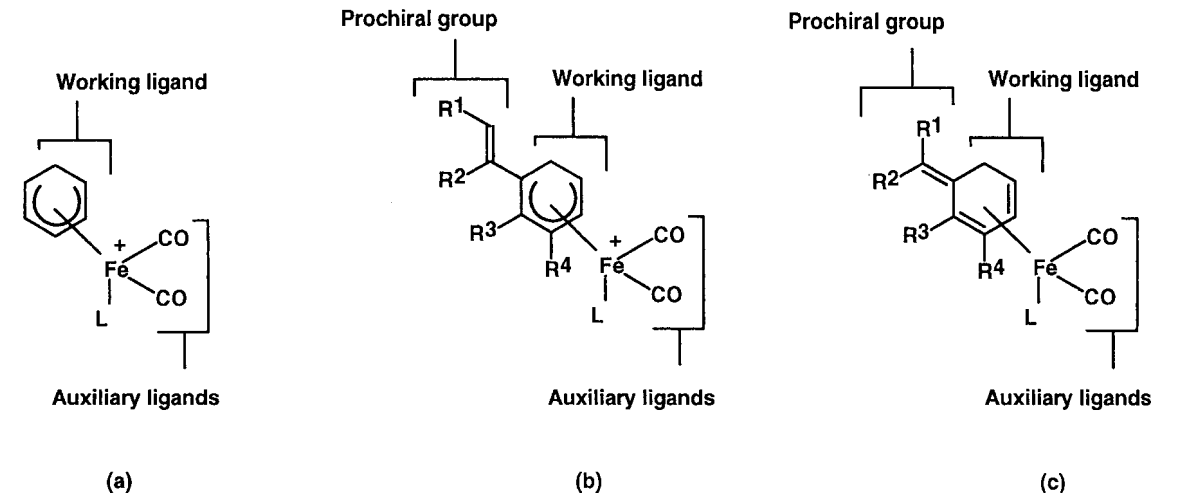


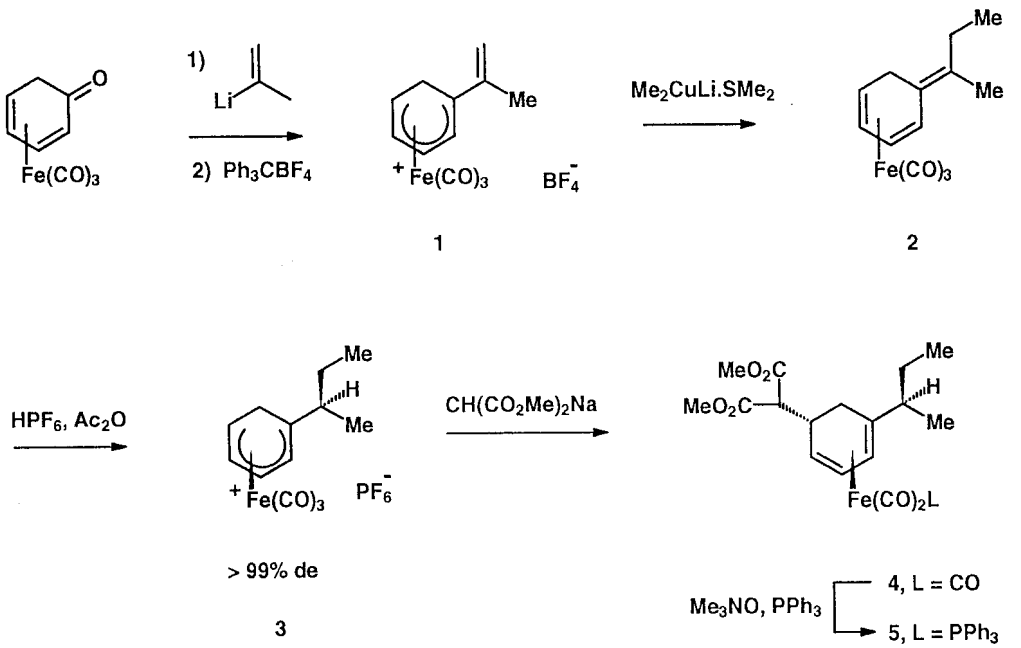
Figure 1 (a) Illustration of the concepts of 'working' and auxiliary ligands in synthesis design; an unsymmetrical working ligand forms a chiral complex that can influence sterochemistry at nearby prochiral organic functional groups in (b) cyclohexadienyl and (c) cyclohexadiene organoiron complexes.

pattern of the corresponding section of the target structure. The analysis of the reactivity properties (particularly regio- and stereoselectivity) of the working ligand is thus an important stage in the design process during the planning of a synthetic route. In recent work, this concept has been extended by the inclusion of prochiral substituents on the working ligand in both η^5 dienyl[13] and η^4 diene[14] forms (see Fig. 1b and 1c). Reactions at the working ligand itself typically proceed under complete stereocontrol, with nucleophiles adding to the face of the ligand opposite to that which bears the metal and auxiliary ligands. In the extended structures, the use of bulky auxiliary ligands has been shown to give good (up to 8:1) stereocontrol even two atoms out from the working ligand,[13] and adjacent to the working ligand the stereoselectivity can be complete[14] (see also Ref. 20).

RESULTS AND DISCUSSION

In this paper, the methods of analysis of these reactivity and stereocontrol patterns are presented, and the proof of relative stereochemistry is reported in a case of long-range asymmetric induction mediated by the tricarbonyliron control group. Even a simple sequence of two metal-mediated steps directly at the working ligand can offer versatile patterns for controlled sequential bond-formation.[15–19] The challenge in recent years has been to develop processes that allow selective access to each regioisomeric form, and now, in many cases, the required pattern of reactivity has been demonstrated in actual target-oriented routes (*O*-methyl joubertiamine,[15] lycoramine,[16] hippeastrine,[17] and the main structural features of the lycorine skeleton[18]).

The extension of this concept is illustrated in this paper with an example in which a sequence of three organoiron-mediated reactions are combined to implement long-range stereocontrol. Starting from the simple cyclohexadienone complex[3] (Scheme 1), nucleophile addition followed by elimination of the OH group allows the elongation of the π-system, introducing the C1′–C2′ alkene component, which is converted into the cyclohexadienyl form **1** by the usual procedure. The product **1** is elaborated by organocuprate addition at C2′ to afford **2**, which is prochiral at C1′. Protonation proceeds with complete control of stereochemistry, again producing a substituted cyclohexadienyl cation **3**. This sequence comprising two C—C bond-forming reactions can be classified as having a 1′,2′ regiocontrol pattern. The organometallic product at this stage is again an electrophilic cyclohexadienyl complex, so reaction with nucleophiles at the metal-bound portion of the working ligand will benefit from the normal complete diastereoselectivity that has made these complexes a focus of attention for development in asymmetric



Scheme 1

synthesis. To elucidate this point, reaction of **3** with the sodium enolate of dimethyl malonate was examined. A single product **4** (1,3 regioselectivity) was obtained, as expected. The reaction sequence, from **1** to **2** to **3** to **4**, makes use of three organoiron-promoted nucleophile addition steps, which, including the protonation step, creates two chiral centres four atoms apart. Because the planar chirality of the metal complex controls the formation of both centres, we have demonstrated in this reaction sequence a long-range relay of chirality via the metal.

The relative stereochemistry of the malonate anion addition could reasonably be assigned by reference to the many examples known of *trans* addition relative to the metal in this type of process, but the stereochemistry at C1′ is a more difficult issue. Protonation via the metal would afford the opposite product to that anticipated from direct addition of the proton to the exocyclic alkene. Attempts to obtain X-ray-quality crystals of the product **4** to resolve the issue were unsuccessful. This difficulty was eventually overcome by the conversion of **4** into the dicarbonyltriphenylphosphine analogue **5** by replacing CO by PPh_3 by reaction with trimethylamine *N*-oxide. This replacement of an auxiliary ligand does not interfere with the stereocentres in the working ligand. The product **5** was recrystallized to afford single crystals that proved suitable for X-ray analysis, and in this way the relative stereochemistry of the product was established. The direct nucleophile addition to the working ligand had, as expected, proceeded on the face of the ligand opposite to the metal. From the structure (Fig. 2, Table 1) it can be seen that the proton had also approached the exocyclic alkene from the face of the ligand opposite to the metal, since the *S*,*R**,*E* stereoisomer of the trisubstituted alkene had been converted into the *S*,*S*,*R**,*R** diastereoisomer of **4**. All the products reported in this paper have been prepared in racemic form, and stereoisomers drawn in the Scheme 1 depict only relative stereochemistry. The relative stereochemistry between C5 and C1′, formed by the long-range chirality relay, can thus be assigned as 5*S*,1′*S*,5*R**,1′*R**.[20]

EXPERIMENTAL

Tricarbonyl[(1,2,3,4,5-η)-1-(1′-methylethenyl)cyclohexadienylliron (1+) tetrafluoroborate(−1) 1

tert-Butyllithium (1.7 M in hexanes, 2.5 ml,

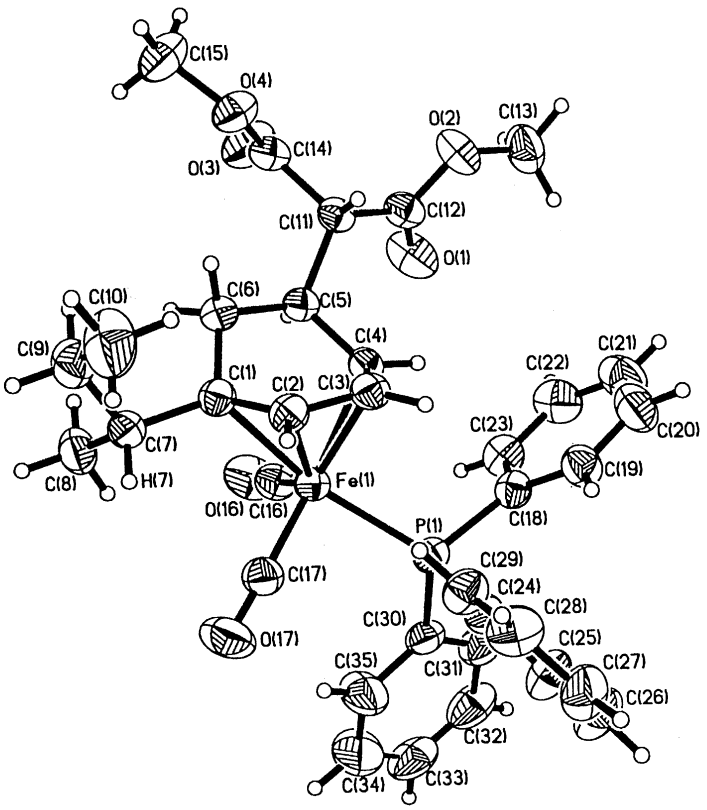


Figure 2 Crystal structure of dicarbonyl[dimethyl (2′,2′,4′,5′η)-2-(5′-(1′′-methylpropyl)-2′,4′-cyclohexadien-1′-yl)propanedioate]-triphenylphosphineiron(0), **5**.

4.26 mmol) was added to a solution of 2-bromopropene (0.257 g, 2.13 mmol) in THF (15 ml) at −70 °C and held at this temperature for 30 min. The solution was transferred by cannula to a solution of tricarbonyl(cyclohexa-2,4-dien-1-one)iron(0)[3] (0.5 g, 2.13 mmol) in dichloromethane (10 ml) at −100 °C. After 1 h at −100 °C, the solution was allowed to warm to room temperature and stirred for a further 1 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride (20 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic layers were then dried with anhydrous magnesium sulfate and filtered through celite. The solvent was removed *in vacuo* to yield *tricarbonyl[(1,2,3,4-η)-5β-hydroxy-5α-(1′-methylethenyl)-1,3-cyclohexadiene]iron(0)* as an unstable brown oil. The oil was dissolved in dichloromethane (5 ml), cooled to 0 °C and triphenylcarbenium tetrafluoroborate (0.7 g, 2.13 mmol) was added to the solution and stirred for 30 min. The reaction mixture was then added to diethyl ether (50 ml) to effect precipitation. The salt was collected by filtration and re-precipitated from acetone (1 ml) into dry diethyl ether (50 ml) to yield *tricarbonyl[(1,2,3,4,5-η)-1-(1′-methylethenyl) cyclohexadienyl]iron(1+) tetrafluoroborate(−1)* as a dark yellow powder (0.443 g, 60%). ν_{max} (CH_3CN)/cm^{-1} 2108 and 2058; δ_H (270 MHz, d_6-acetone) 7.47 (1H, br, 3-H), 6.49 (1H, t, *J* 6, 4-H), 6.1 (1H, d, *J* 6, 2-H), 5.82 (1H, s, C=C*H*), 5.49 (1H, s, C=C*H*), 4.68 (1H, t, *J* 6, 5-H), 3.61 (1H, dd, *J* 14, 6 6β-H), 2.38 (1H, d, *J* 14, 6-α) and 1.91 (1H, s, CH_3); *m/z* (FAB) 259 (M^+, 100), 243 (28), 231 (26), 203 (9), 175 (11), 165 (10%); found: 259.0078. Calc. for $C_{12}H_{11}O_3Fe^+$ 259.0079.

(1*E*)-tricarbonyl[(2,3,4,5-η)-1-(1′-methylpropylidene)-2,4-cyclohexadiene]iron(0) 2

Methyllithium (1.25 M, 1.15 ml, 1.44 mmol) was

Table 1 Selected bond lengths (Å) and angles (°) for **5**

Fe(1)—C(16)	1.760(3)	C(16)—O(16)	1.149(4)
Fe(1)—C(17)	1.768(3)	C(17)—O(17)	1.149(4)
Fe(1)—P(1)	2.238(1)	Fe(1)—C(1)	2.167(3)
Fe(1)—C(2)	2.044(3)	Fe(1)—C(3)	2.047(3)
Fe(1)—C(4)	2.101(3)	C(1)—C(2)	1.437(4)
C(2)—C(3)	1.405(4)	C(3)—C(4)	1.420(4)
C(4)—C(5)	1.504(4)	C(5)—C(6)	1.529(4)
C(6)—C(1)	1.512(4)	C(1)—C(7)	1.521(4)
C(5)—C(11)	1.550(4)	C(7)—C(8)	1.534(5)
C(7)—C(9)	1.534(5)	C(9)—C(10)	1.500(6)
C(16)—Fe(1)—C(17)	101.9(2)	C(16)—Fe(1)—P(1)	99.6(1)
C(17)—Fe(1)—P(1)	90.5(1)	O(16)—C(16)—Fe(1)	177.6(3)
O(17)—C(17)—Fe(1)	177.8(3)	C(6)—C(1)—C(2)	114.7(3)
C(1)—C(2)—C(3)	114.5(3)	C(2)—C(3)—C(4)	115.6(3)
C(3)—C(4)—C(5)	121.9(3)	C(4)—C(5)—C(6)	108.4(2)
C(5)—C(6)—C(1)	112.3(2)	C(2)—C(1)—C(7)	119.7(3)
C(6)—C(1)—C(7)	115.8(2)	C(1)—C(7)—C(8)	111.7(3)
C(1)—C(7)—C(9)	112.3(3)	C(8)—C(7)—C(9)	109.3(3)
C(7)—C(9)—C(10)	114.1(3)		

added to a solution of copper(I) bromide–dimethyl sulfide complex (0.148 g, 0.72 mmol) in THF (10 ml) at 0 °C. After 30 min, the yellow solution was cooled to −100 °C and tricarbonyl[(1,2,3,4,5-η)-1-(1′-methylethenyl)cyclohexadienyl]iron(1+) tetrafluoroborate(1−) (0.5 g, 1.44 mmol) was added, producing a dark solution which was stirred for 1 h at −100 °C. On warming to room temperature, the reaction was quenched by the addition of saturated aqueous ammonium chloride (30 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo* to yield a dark red oil. Purification on silica gel eluted with diethyl ether:hexane (1:99) afforded (1*E*)-tricarbonyl[(2,3,4,5-η)-1-(1′-methylpropylidene)-2,4-cyclohexadiene]iron(0) (0.28 g, 70%) as a light yellow oil. ν_{max} (thin film)/cm^{-1} 2041, 1970 and 1637; δ_H (270 MHz, $CDCl_3$) 5.42 (1H, t, *J* 5, 3-H), 5.29 (1H, m, 4-H), 3.93 (1H, d, *J* 6, 2-H), 3.30 (1H, m, 5-H), 2.42 (1H, dd, *J* 15, 3, 6β-H), 2.17 (1H, d, *J* 15, 6α-H), 1.91 (1H, dq, *J* 14, 7, C=C—C*H*), 1.74 (1H, dq, *J* 14, 7, C=C—C*H*), 1.65 (3H, s, C=CCH_3), 0.9 (3H, t, *J* 7, CH_2CH_3) δ_C (67.8 MHz; $CDCl_3$) 212 (Fe—CO), 127.6. 127.2 (C=C) 83.8, 82.8 (3-C and 4-C), 64.6, 59.4 (2-C and 5-C), 28.0, 27.6 (1-C and C=C*C*H_2), 16.6 (C=C—*C*H_3) and 11.7 (CH_2*C*H_3); *m*/*z* (CI) 275 (M^++H, 50), 155 (8) 150 (29), 138 (25), 133 (100), 132 (41), 130 (14%); found: 275.0371. Calc. for $C_{13}H_{15}O_3Fe^+$: 275.0371.

Tricarbonyl[(1,2,3,4,5-η)-1-(1′-methylpropyl)-1,3-cyclohexadiene]iron(1+) hexafluorophosphate(1−) 3

A pre-mixed solution of hexafluorophosphoric acid (1 ml) in acetic anydride (2 ml) at −10 °C was added to a flask containing (1*E*)-tricarbonyl-[(2,3,4,5-η)-1-(1′-methylpropylidene)-2,4-cyclohexadiene]iron(0) (0.2 g, 0.73 mmol). The resulting solution was held at −10 °C. After 1 h, the reaction mixture was added to saturated aqueous ammonium hexafluorophosphate (10 ml). The salt was collected by filtration, and was reprecipitated from acetone (1 ml) by addition to dry diethyl ether (30 ml). Filtration afforded *tricarbonyl[(1,2,3,4,5-η)-1-(1′-methylpropyl)-1,3-cyclohexadiene]iron(1+) hexafluorophosphate(1−)* as a yellow powder (0.252 g, 82%). δ_H (270 MHz, $CDCl_3$) 7.01 (1H, t, *J* 5, 3-H), 6.0 (1H, t, *J* 5, 4-H), 5.56 (1H, d, *J* 5, 2-H), 4.23 (1H, t, *J* 5, 5-H), 3.0 (1H, dd, *J* 15, 5, 6-βH), 2.25 (1H, d, *J* 15, 6α-H), 1.60 (1H, q, *J* 7, $CHCH_3$) 1.20 (1H, m, $CHCH_2$), 1.18 (3H, d, *J* 6, $CHCH_3$) 0.9 (3H, t, *J* 7, CH_2CH_3); *m*/*z* (FAB) 257 (M^+, 100), 247 (36), 191 (19), 161 (6%); found: 275.0394. Calc. for $C_{13}H_{15}O_3Fe^+$: 275.0371.

Tricarbonyl[dimethyl (2′,3′,4′,5′η)-2-(5′-(1″-methylpropyl)-2′,4′-cyclohexadien-1′α-yl) propanedioate]iron(0) 4

Sodium hydride (0.046 g, 1.9 mmol) was added to a

stirred solution of dimethyl malonate (0.25 g, 1.9 mmol) in THF (5 ml) at 0 °C. After 1 h, the solution was cooled to −70 °C and tricarbonyl [(1,2,3,4,5-η)-1-(1′-methylpropyl)-1,3-cyclohexadiene]iron hexafluorophosphate(1−) (0.8 g, 1.9 mmol) was added. The solution was stirred for 1 h at −70 °C, allowed to warm to room temperature, and stirred for a further 1 h. Saturated aqueous. ammonium chloride (10 ml) was added, and after extraction with dichloromethane (3 × 15 ml) the combined organic layers were dried over magnesium sulfate, filtered and evaporated *in vacuo* to leave a yellow oil. Purification by column chromatography on silica gel eluted with diethyl ether: hexane (1:4) yielded *tricarbonyl[dimethyl (2′,3′,4′,5′-η)-2-(5′-(1″-methylpropyl)-2′,4′-cyclohexadien-1′α-yl)propanedioate]iron(0)* as a pale yellow crystalline solid (0.592 g, 77%), m.p. 95 °C. ν_{max} (CH_2Cl_2)/cm^{-1} 2042, 1969, 1738 and 1732; δ_H (270 MHz, $CDCl_3$) 5.26 (1H, d, *J* 4, 2′-H), 5.15 (1H, dd, *J* 4, 6, 3′-H), 3.73 (3H, s, 1-H), 3.70 (3H, s, 3-H), 3.12 (1H, d, *J* 8, 2-H), 2.85 (2H, m, 4′-H and 5′β-H), 2.14 (1H, dd, *J* 5, 11, 6′β-H), 1.4 (3H, m, C*H*CH_3 and C*H*$_2$$CH_3$), 1.2 (1H, m, 6′α-H), 1.15 (3H, d, *J* 6, CHC*H*$_3$), 0.92 (3H, t, *J* 7, CH_2C*H*$_3$); δ_C (67.8 MHz; $CDCl_3$) 211 (Fe—CO), 168.5, 168.4 (*C*O_2CH_3 and *C*O_2CH_3), 89.5 (2′-C), 86.7 (1′-C), 80.5 (3′-C), 59.7 (4′-C), 59.4 (2-C), 52.5, 52.7 (OCH_3 and OCH_3), 45.2 (*C*HCH$_3$), 37.6 (5′-C), 29.7 (*C*H_2CH_3), 26.1 (6′-C), 20.3 (CH*C*H$_3$), 12.6 (CH_2*C*H$_3$); *m/z* (FAB) 424 (M^++NH_4, 4) 275 (15), 150 (100), 137 (13), 133 (16%); found: 424.1059. Calc. for $C_{18}H_{26}NO_7Fe^+$: 424.1059.

Dicarbonyl[dimethyl (2′,3′,4′,5′-η)-2-(5′-(1″-methylpropyl)-2′,4′-cyclohexadien-1′α-yl)propanedioate] triphenylphosphineiron(0) 5

Trimethylamine-*N*-oxide dihydrate (0.53 g, 4.73 mmol) was added to a solution of tricarbonyl[dimethyl (2′,3′,4′,5′-η)-2-(5′-(1″-methylpropyl)-2′,4′-cyclohexadien-1′α-yl)propanedioate]iron-(0) (0.277 g, 0.68 mmol) and triphenylphosphine (1.43 g, 5.45 mmol) in acetone (10 ml) and then heated at reflux for 1 h. The reaction was cooled to room temperature, and the solvent was removed *in vacuo* to leave a solid. Purification on silica gel eluted with diethyl ether:hexane (1:5) yielded dicarbonyl[dimethyl (2′,3′,4′,5′-η)-2-(5′-(1″-methylpropyl)-2′,4′-cyclohexadien-1′α′-yl)propanedioate]-triphenylphosphineiron(0) as pale yellow crystals (0.384 g, 88%), m.p. 121 °C. ν_{max} (CH_2Cl_2)/cm^{-1} 1967, 1907, 1738 and 1733; δ_H (270 MHz, $CDCl_3$) 7.4 (15H, br m, aromatic), 5.18 (1H, d, *J* 6, 2′-H), 4.39 (1H, m, 3-H), 3.6, 3.4 (OCH3 and OCH_3), 2.8 (2H, m, 2-H and 5′-H), 2.22 (1H, m, 6′β-H), 1.58 (1H, m, C*H*CH_3, 4′-H), 1.4 (2H, t, *J* 7, CH_2CH_3), 1.28 (3H, d, *J* 7, CHC*H*$_3$), 1.0 (1H, m, 6′α-H), 0.9 (3H, t, *J* 7, CH_2C*H*$_3$); δ_C (67.8 MHz; $CDCl_3$) 216.5, 216.1 (Fe—CO), 168.6, 168.6 (*C*O_2CH_3 and *C*O_2CH_3), 136.0, 135.5, 133.1, 132.9, 129.5, 128.1, 128.0, (aromatics), 86.6 (2′-C), 81.5 (3′-C), 78.5 (1′-C), 62.8 (4″H), 60.4 (2-C), 52.1, 52.0 (OCH_3 and OCH_3), 44.8 (*C*HCH$_3$), 37.4 (5′-C), 29.6 (*C*H_2CH_3), 27.8 (6′-C), 20.3 (CH*C*H$_3$), 12.7 (CH_2*C*H$_3$); *m/z* (FAB) 584 (M^+−2CO, 12), 551 (5), 509 (95), 450 (100), 380 (33), 349 (42), 318 (40), 263 (21), 239 (19), 183 (24%); found: 584.1760. Calc. for $C_{33}H_{37}O_4PFe^+$: 584.1779. Crystal data and structure refinement for **5** are as follows. Empirical formula: $C_{35}H_{37}FeO_6P$; formula weight: 640.47; temperature: 293(2) K; wavelength: 0.710 73 Å; triclinic; *P*1; *a* = 11.736(2), *b* = 12.181(3), *c* = 12.840(2) Å; α = 86.29(2), β = 86.49(1), γ = 62.33(2)°; *U* = 1621.3(6) Å^3; *Z* = 2; ρ_{calc} = 1.312 Mg m^{-3}; μ(MoKα) = 0.558 mm^{-1}; *F*(000) = 672; crystal off-white block: 0.35 × 0.25 × 0.20 mm^3; 4.0 < 2θ < 50.0° reflections collected: 6522; 5611 unique (R_{int} = 0.0241); absorption correction: none; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 5606/0/409; ωR_2 = 0.1492, *s* = 0.974 (all data); R^1 = 0.0426 [$I > 2\sigma(I)$]; largest diff. peak and hole: 0.291 and −0.274 e Å^{-3}.

CONCLUSIONS

The analysis of patterns of reactivity in cyclohexadienyl complexes illustrates the versatility and power of the iron-based methodology in reaction sequences that make multiple use of the metal to establish a series of chiral centres. This, combined with procedures that use the concept of the 'working ligand' to define the point of attachment of the metal within the structure of the target molecule, constitutes a valuable conceptual approach to synthesis design that exploits the full potential of the metal control group. By the repeated use of the metal, long-range asymmetric induction can be achieved, and the relative stereochemistry in the case described here has been defined as *S*,*S*,*R**,*R**.

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