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Transition metal mediated asymmetric synthesis

XIV*. A new strategy for the reactivation of tricarbonyliron complexes

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Abstract

Protonation of an *exo*-substituted η^4-triene complex results in a hydrogen shift that removes the effect of a blocking group and so provides a means of regenerating the η^5-cation in situations in which hydride abstraction would be prevented by the *exo*-substituent.

1. Introduction

Reactivation following nucleophile addition is the key to the multiple use of stoichiometric organometallic control groups in asymmetric synthesis. Efficient use of the control centre requires that it can be employed repeatedly to effect asymmetric induction in a series of separate steps within a reaction sequence. The more powerful the control group, the more general will be its application. The tricarbonyliron control group is capable of exceptionally high levels of stereocontrol [2], but its use in multistep reaction sequences is impeded by a need for new methods to facilitate multiple utilisation. The cationic η^5-tricarbonyliron complexes are particularly attractive as intermediates because of their compatibility with a wide variety of nucleophiles [3], but since they are consumed in the nucleophile addition step by conversion into neutral η^4 products, reactivation is needed to regenerate the cationic η^5-bonding mode after an initial alkylation reaction [4,5].

Reactivation by hydride abstraction using triphenylcarbenium reagents is hindered by the *exo*-disposition of the substituent introduced by nucleophile addition, and usually fails for η^4-cyclohexadiene complexes; the procedure is normally viable only for seven-membered (or larger) rings [5,6]. A number of studies have already addressed the problem of reactivation in six-membered rings, since these are of particular importance in synthetic chemistry. Alternative procedures for the formation of cationic η^5-complexes in hindered situations have been examined. Acid-catalysed demethoxylation of enolether complexes have been widely used [7], but involves a rearrangement in which the site of attachment of the π-complexes is changed. This process removes the chiral centre formed in the preceeding nucleophile addition step, since the substituent that is introduced in this way becomes located at an sp^2 centre in the final product. Cyclisation by intramolecular addition of a pendant nucleophile using $FeCl_3$, MnO_2 or Tl^{III} reagents, followed by ring-opening reactions, provides an effective reactivation strategy [8], but is most suitable in synthetic applications in which heteroatom functionality is ultimately required in the side-chain substituents.

We have been seeking alternatives to hydride abstraction, particularly methods that function by shifting the reaction centre away from the blocking substituent on the ring, to less hindered locations in the η^4 substrate. We have reported [9] a regioselective oxymetallation procedure in which the initial approach of the reagent occurs at the metal centre. Protonation at C-6 OMe substituents, followed by elimination of methanol, has also proved useful as a reactivation method [10].

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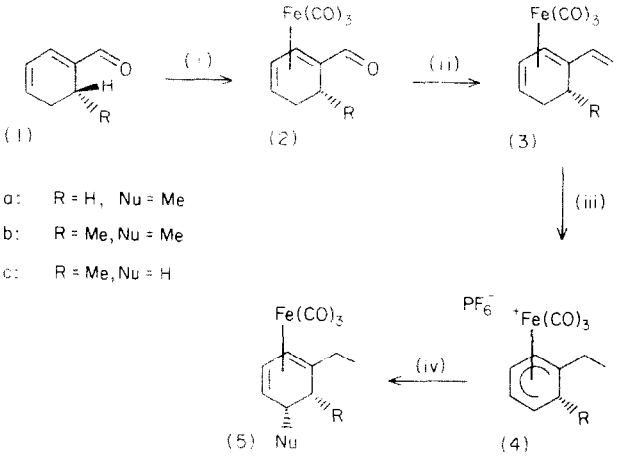
We now describe a complementary study in which the site of initial reaction is displaced to a β-position in an alkenyl side-chain, where steric effects would not be expected to interfere, even when large substituents are present on the cyclic ligand. Since hydrogen migration in the metal-bound ring normally proceeds on the face of the ring bearing the metal, we expected that *exo*-substituents would also not interfere with this process when employed to transfer a hydrogen from the ring to a side-chain position. This type of hydrogen shift is known [11,12] to give access to η^5-complexes, and so seemed an excellent prospect for use with blocked substrates.

2. Results and discussion

Our initial objective was to identify suitable reaction conditions by a re-investigation of the protonation–rearrangement step. The η^5-triene complex **3a** was chosen for this purpose. This complex was conveniently prepared by complexation of **1a** [11] ($Fe_2(CO)_9$, ether, 55% yield) followed by Wittig olefination (Ph_3PCH_2, 77% yield). The results of the protonation experiments are shown in Table 1.

Monitoring of the reaction by IR spectroscopy showed that the rate of conversion of the neutral starting material (ν(co) 2045, 1980, 1973 cm^{-1}) into cationic products (ν(co) *ca.* 2110 and 2060 cm^{-1}) was surprisingly slow and in many cases (entries 1–4) mixtures of neutral and cationic products were present, even after extended time. With trifluoroacetic acid several days were needed to bring the reaction to completion (entry 5). Use of trifluoromethanesulfonic acid was required to achieve effective conversion within a reasonable time [13]. In this case (entry 6), the product **4a** [11], precipitated by addition of aqueous ammonium hexafluorophosphate, was isolated as a yellow powder in 71% yield. Reaction of the product with dimethylcuprate proceeded in the expected manner, affording the 1-ethyl-5-*exo*-methyl substituted complex **5a** in 70% yield.



Scheme 1. (i) $Fe_2(CO)_9$, Et_2O, reflux: (a) 55%; (b) 50%; (ii) $Ph_3P{=}CH_2$, THF, 0°C: (a) 74%; (b) 66%; (iii) F_3CSO_3H, 0°C, then NH_4PF_6 aq.: (a) 71%; (b) 64%; (iv) Me_2CuLi, THF, 0°C: (a) 70%; (b) 48%; $NaBH_4$, CH_3CN, r.t.: (c) 81%.

We chose complex **3b** for the examination of the reactivation method in a situation in which the blocking effect of an *exo*-substituent is present. The complex **3b** should be accessible by complexation of the aldehyde **1b**, [14] followed by methylenation. Reaction of **1b** with $Fe_2(CO)_9$ gave complex **2b** in 50% yield. It was important to determine the stereochemical relationship between the methyl group and the metal. Hydride abstraction should not take place if an *exo*-substituent is present [15]. Even under forcing conditions at reflux, complex **2b** was recovered unchanged (91% recovery) after treatment with triphenylcarbenium tetrafluoroborate. This result was ascribed to blocking of the *exo*-face by the C-6 methyl substituent. Wittig olefination of **2b** in 66% yield completed the preparation of **3b**, in which the required *exo*-blocking substituent was located at C-6. Protonation of **3b**, under the best conditions found for **3a** and a reaction time of 2 h, successfully converted the blocked substrate **3b** into the 6-*exo*-substituted salt **4b**) (ν(co) 2110, 2063 cm^{-1} in CH_3CN), which was isolated in 64% yield by precipitation with aqueous ammonium hexafluorophosphate.

Alkylation with lithium dimethylcuprate gave the

TABLE 1. Conditions for the protonation of **3a**

Entry	Acid used [a]	Reaction temp.	Time (h)	IR data [b] (cm^{-1})
1	TFA (6 eq.)	room temp.	1	2045, 1981, 1973.
2			24	2110, 2061, 2040, 1967.
3	TFA (12 eq.)	room temp.	48	2110, 2060, 2040, 1967.
4	$HBF_4.Et_2O$ (3 eq.)	room temp.	29	2110, 2060, 2040, 2066.
5	TFA added (3 eq.)	room temp.	115	2110, 2060.
6	CF_3SO_3H (6 eq.) [c]	0°C, then warming to room temp.	2	2110, 2060.

[a] Added neat, with stirring to the complex under a nitrogen atmosphere.
[b] Measured in CaF_2 IR solution cells by withdrawing a small portion of the reaction mixture.
[c] The salt (**4a**) was precipitated in 71% yield by addition of aqueous ammonium hexafluorophosphate at low temperature.

5,6-disubstituted product **5b** in 48% yield. As is normally the case with hindered tricarbonyliron dienyl complexes, this reaction proved less efficient than the corresponding alkylation in the absence of the *exo*-substituent [16]. Indeed a more bulky nucleophile, sodium dimethylmalonate, failed to give any of the expected nucleophilic addition product. Reduction of **4b** with sodium borohydride, however, proceeded normally and the η^4 product **5c** was isolated in 81% yield after chromatography.

Our results indicate that protonation of a tricarbonyl(η^4-alkenylcyclohexadiene)iron(0) complex, followed by a hydrogen shift, leads to reactivation of the complex as an η^5-species. This procedure is most efficient when the strong acid CF_3SO_3H is employed. Application of the procedure to the complex **3b** demonstrates that the method offers an attractive option for the reactivation of η^4-tricarbonyliron complexes in cases where a blocking substituent makes the normal hydride abstraction method unsuitable. An advantage of this approach is the inherent regioselectivity of the protonation-hydrogen shift reaction which results in the formation of a C-1 alkyl substitution pattern in the η^5 product.

3. Experimental details

Reactions were performed under a nitrogen atmosphere. IR spectra were recorded using Perkin Elmer 257 or 297 spectrometers. PMR spectra were recorded at 60 MHz using a Jeol PMX 60i instrument; CMR spectra were recorded at 25.05 MHz using a Jeol FX 100 instrument, or at 100 MHz using a Jeol GX 400 instrument. High field PMR spectra were measured using the GX 400 operating at 400 MHz. All NMR spectra were measured in deuterochloroform, unless a particular alternative solvent is indicated. Tetramethylsilane was used as an internal standard. Mass spectra were recorded on a Kratos MS25 spectrometer, and elemental analysis was performed at the University of East Anglia by Mr A. Saunders. The tricarbonyliron complexes were prepared thermally by reaction of the free ligands with diiron nonacarbonyl, using standard conditions [17].

3.1. Tricarbonyl[η^4-1-(1'-ethylene)cyclohexa-1,3-diene]iron (3a)

n-Butyllithium (2.5 ml of a 1.6 M solution in hexanes, 4.0 mmol) was added to a solution of methylenetriphenyl-phosphonium bromide (1.44 g, 4.0 mmol) in THF (30 ml). The resulting clear orange solution was cooled to 0°C and a solution of the aldehyde complex **2a** (1.0 g, 4.0 mmol) was added in THF (5 ml). The reaction mixture was stirred for 2 h, allowing the solution to gradually warm to room temperature over this time. Water (50 ml) was added to the resulting solution, which was then extracted with ether (3 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$) and concentrated to give the crude product, containing triphenylphosphine oxide. Purification was performed by trituration with light petroleum, followed by filtration through celite, in order to remove the excess triphenylphosphonine oxide, and concentration of the organic solvent. Column chromatography (light petroleum) afforded the triene complex **3a** (0.73 g, 73%) as a light yellow oil. Anal. Found: C, 53.92; H, 4.01. $C_{11}H_{10}O_3Fe$ calc.: C, 53.70; H, 4.10%. IR: ν(max) ($Fe(CO)_3$) 2045, 1980, 1973 cm^{-1}. ^1H NMR: 1.16–2.44 (m, 4H, 2 × CH_2); 3.22 (m, 1H, C(4)H); 4.82–5.42 (m, 4H, $=CH_2$, 2 × CH); 5.80–6.22 (dd, 1H, J = 9.6 Hz, J = 16.8 Hz, =CH) ppm. m/z 246 (M^+, 4); 218 (M–CO, 22); 190 (M–2CO, 8); 162 (M–3CO, 9); 160 (100%).

3.2. Attempted protonation of tricarbonyl[η^4-1-(1'-ethylene)cyclohexa-1,3-diene]iron (3a) using trifluoroacetic acid

Anhydrous trifluoroacetic acid (0.30 g, 0.20 ml, 2.60 mmol) was added to the triene complex **3a** (0.10 g, 0.41 mmol) and the resultant dark-red solution was stirred at room temperature for 24 h. Periodically small samples were removed from the reaction mixture, diluted with acetonitrile and the IR spectrum recorded in order to determine whether the cyclohexadienyl complex had been formed. After the initial 24 h period, starting material was still present, therefore additional trifluoroacetic acid (0.30 g, 0.2 ml, 2.60 mmol) was added. Stirring was continued for a further 24 h, after which time starting material was still evident. The reaction mixture was cooled to −78°C, and a solution of ammonium hexafluorophosphate (0.2 g) in water (0.4 ml) was added. The mixture was then allowed to reach room temperature, when ether (5 ml) was added. However, a salt was not precipitated from the solution, even on cooling to 0°C.

3.3. General procedure for the protonation of tricarbonyl[η^4-1-(1'-ethylene)cyclohexa-1,3-diene]iron (3a) using anhydrous strong acid (see Table 1)

The acid under investigation was added to a sample of the triene complex **3a** (0.10 g, 0.41 mmol) and the reaction mixture stirred for the required period of time. The course of the reaction was followed by IR spectroscopy, and in each protonation reaction carried out, no attempt was made to precipitate the cationic material that had formed after the specified time period. For details of the quantity and type of acid used, the reaction temperature and the time period for which the reaction mixture was stirred, see Table 1.

*3.4. Tricarbonyl(η^5-1-ethylcyclohexadienyl)iron(1 +) hexafluorophosphate(1 −) (**4a**)[11]*

Anhydrous trifluoromethane sulphonic acid (0.68 g, 0.4 ml, 4.52 mmol) was added to the triene complex (**3a**) (0.15 g, 0.61 mmol) at 0°C, and the reaction mixture was stirred until IR spectroscopy suggested that the reaction had gone to completion, (Usually 2 h). The cationic complex was cooled to −78°C, and a solution of ammonium hexafluorophosphate (0.20 g) in water (0.40 ml) was added. The mixture was allowed to reach room temperature, when ether (5 ml) was added. The precipitate that formed was filtered off, and washed thoroughly with water (10 ml), then ether (30 ml), to give ethyl salt (**4a**) [11] (0.17 g, 71%). Anal. Found: C, 33.47; H, 2.62. $C_{11}H_{11}O_3FePF_6$ calc.: C, 33.70; H, 2.83%. IR: ν(max) $(Fe(CO)_3)$ (MeCN) 2110 and 2060 cm^{-1}.

*3.5. Tricarbonyl(η^4-1-ethyl-5-exo-methylcyclohexa-1,3-diene)iron (**5a**)*

Methyllithium (1.20 ml of a 1.4 M solution in hexanes, 1.68 mmol) was added to a stirring suspension of copper(I) iodide (0.16 g, 0.84 mmol) in THF (5 ml), and stirred until the solution turned colourless. The ethyl salt **4a** (0.15 g, 0.38 mmol) was then added, and the reaction mixture was stirred for 2 min. After this time, the reaction was quenched by the addition of saturated ammonium chloride solution, and extracted with ether (2×50 ml). The combined ethereal extracts were washed with water (50 ml), dried ($MgSO_4$), and concentrated to give a brown oil. Purification by column chromatography (light petroleum) gave tricarbonyl(η^4-1-ethyl-5-exo-methylcyclohexa-1,3-diene)iron (**5a**) (0.07 g, 69%). Anal. Found: C, 55.28; H, 5.24. $C_{12}H_{14}O_3Fe$ calc.: C, 54.99; H, 5.39%. IR: ν(max) $(Fe(CO)_3)$ 2041, 1974, 1968 cm^{-1}. ^1H NMR: 0.96 (d, 3H, $J = 6.0$ Hz, CH_3); 1.02 (t, 3H, $J = 4.8$ Hz, CH_3); 1.20–2.40 (m, 5H, $2 \times CH_2$, C(5 endo)H); 3.02 (m, 1H, CH); 5.02–5.44 (m, 2H, C(2)H, C(3)H ppm. m/z 262 (M^+, 2); 234 (M−CO, 20); 206 (M−2CO, 4); 177 (M−3CO and H, 14); 176 (100%).

*3.6. Tricarbonyl[η^4-1-(1'-ethylene)-6-exo-methyl-cyclohexa-1,3-diene]iron (**3b**)*

To a stirring suspension of methylenetriphenylphosphonium bromide (0.82 g, 2.29 mmol) in THF (20 ml), was added n-butyllithium (1.44 ml of a 1.4 M solution in hexanes). The resulting orange solution was cooled to 0°C, and stirred at this temperature for 30 min before the aldehyde complex **2b** (0.60 g, 2.29 mmol) in THF (2 ml) was added. The reaction mixture was stirred for a total period of 24 h, allowing the solution to reach room temperature over this period. The remaining dark-brown solution was slowly poured into water (50 ml), and extracted with ether (3×30 ml). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to give a dark oil. The removal of the triphenylphosphine oxide was performed by trituration with light petroleum, filtration through celite and concentration of the remaining solvent, followed by column chromatography (light petroleum) giving the triene complex **3b** (0.32 g, 65%), based on recovered starting material (0.11 g). Anal. Found: C, 55.69; H, 4.66. $C_{12}H_{12}O_3Fe$ calc.: C, 55.42; H, 4.65%. IR: ν(max) $(Fe(CO)_3)$ 2040, 1978, 1971 cm^{-1}. ^1H NMR (250 MHz): 0.91 (d, 3H, $J = 7.2$ Hz, CH_3); 1.47 (dm, 1H, $J = 14.5$ Hz, C(5 *exo*)H); 2.27–2.42 (ddd, 1H, $J_{5,4} = 4.2$ Hz, $J_{5,6} = 10.4$ Hz, $J_{5,5} = 16.7$ Hz, C(5 endo)H); 2.57 (m, 1H, C(6)H); 3.03 (m, 1H, C(4)H); 5.00 (d, 1H, $J = 10.4$ Hz, =CH); 5.17 (d, 1H, $J = 16.6$ Hz, =CH); 5.20–5.28 (dd, 1H, $J = 4.2$ Hz and 6.2 Hz, C(3)H); 5.42 (d, 1H, $J = 4.2$ Hz, C(2)H); 5.82–5.93 (dd, 1H, $J = 10.4$ Hz, $J = 16.6$ Hz, =CH) ppm. m/z 260 (M^+, 1); 232 (M−CO, 16); 204 (M−2CO, 9); 176 (M−3CO, 11); 174 (100%).

*3.7. Tricarbonyl(η^5-1-ethyl-6-exo-methyl-cyclohexadienyl)iron-(1 +)hexafluorophosphate(1 −) (**4b**)*

Anhydrous trifluoromethane sulphonic acid (5.9 g, 3.5 ml, 39.55 mmol) was added to the complex **3b** (1.69 g, 6.50 mmol) at 0°C. The dark-red solution was stirred at room temperature for 2 h, when the IR spectrum of the mixture showed the reaction had gone to completion. The solution was then cooled to −78°C and a solution of ammonium hexafluorophosphate (1.75 g) in water (3.5 ml) was added. After the addition was complete, the solution was brought to room temperature, when ether (10 ml) was added. The precipitated hexafluorophosphate salt was collected by filtration, and washed with water and ether, to give the dienyl salt **4b** (1.70 g, 64%). Anal. Found: C, 35.5; H, 3.1. $C_{12}H_{13}O_3FePF_6$ calc: C, 35.4; H, 3.2%. IR: ν(max) $(Fe(CO)_3)$ (MeCN) 2110 and 2063 cm^{-1}. ^1H NMR (200 MHz, CD_3CN): 0.72 (d, 3H, $J = 6.7$ Hz, CH_3); 1.05 (t, 3H, $J = 7.3$ Hz, CH_3); 2.00–2.42 (m, 2H, CH_3-CH_2); 3.03 (q, 1H, $J = 6.7$ Hz, C(6 *endo*)H); 4.38 (t, 1H, $J = 6.7$ Hz, C(5)H); 5.50 (d, 1H, $J = 5.8$ Hz, C(2)H); 5.80 (t, 1H, $J = 6.7$ Hz, C(4)H); 6.92 (t, 1H, $J = 5.8$ Hz, C(3)H) ppm.

*3.8. Tricarbonyl(η^4-1-ethyl-5-exo-methyl-6-exo-methyl-cyclohexa-1,3-diene)iron (**5b**)*

Methyllithium (1.56 ml of a 1.4 M solution in hexanes, 2.18 mmol) was added to a stirring suspension of copper(I) iodide (0.21 g, 1.10 mmol) in THF (5 ml), and stirred until the solution turned colourless. The 1-ethyl salt **4b** (0.20 g, 0.49 mmol) was then added, and the reaction mixture was stirred for 2 min only. After this

time, the reaction was quenched by the addition of saturated ammonium chloride solution, and extracted with ether (2 × 50 ml). The combined organic extracts were washed with water (50 ml), dried ($MgSO_4$), and concentrated to give a brown oil. Purification by column chromatography (light petroleum) gave the di-*exo*-methyl derivative **5b** (0.065 g, 47%). Anal. Found: C, 56.74; H, 5.83. $C_{13}H_{16}O_3Fe$ calc.: C, 56.55; H, 5.84%. IR: ν(max) ($Fe(CO)_3$) 2041, 1972, 1967 cm^{-1}. ^1H NMR: 0.76–1.24 (m, 9H, 3 × CH_3); 1.36–2.52 (m, 4H, CH_2, 2 × CH); 2.95 (m, 1H, C(4)H); 5.03–5.20 (m, 1H, C(3)H); 5.28 (d, 1H, J = 3.3 Hz, C(2)H ppm.

3.9. Tricarbonyl(η^4-1-ethyl-6-exo-methylcyclohexa-1,3-diene)iron (5c)

Sodium borohydride (0.04 g, 1.06 mmol) was added to a solution of the 1-ethyl salt (**4b**) (0.40 g, 0.98 mmol) in acetonitrile (5 ml). After stirring at room temperature for 30 min the reaction mixture was poured into water (20 ml) and extracted with ether (2 × 50 ml). The combined ether layers were washed with brine, dried ($MgSO_4$) and concentrated to give a yellow oil. Purification by column chromatography (light petroleum) gave tricarbonyl(η^4-1-ethyl-6-*exo*-methylcyclohexa-1,3-diene)iron (**5c**) (0.21 g, 81%). Anal. Found: C, 55.28; H, 5.41. $C_{12}H_{14}O_3Fe$ calc.: C, 54.99; H, 5.39%. IR: ν(max) ($Fe(CO)_3$) 2041, 1974, 1968 cm^{-1}. ^1H NMR: 0.86 (d, 3H, J = 4.8 Hz, CH_3); 0.96 (t, 3H, J = 7.2 Hz, CH_3–CH_2); 1.16–2.56 (m, 5H, 2 × CH_2, C(6 *endo*)H); 2.92 (m, 1H, C(4)H); 5.00–5.40 (m, 2H, C(2)H and C(3)H) ppm. m/z 262 (M^+, 2); 234 (M–CO, 22); 206 (M–2CO, 5); 178 (M–3CO, 2); 176 (100%).

3.10. Attempted preparation of tricarbonyl(η^4-1-ethyl-5-exo-dimethylpropanedioate-6-exo-methylcyclohexa-1,3-diene)iron

Dimethyl malonate (0.65 g, 4.92 mmol) was added to a stirring suspension of sodium hydride (0.20 g, 5.00 mmol) in THF (10 ml) at 0°C. The solution was stirred for 15 min, after which time a portion of the resulting dimethyl sodiomalonate (1.0 ml, 0.49 mmol) was added to the 1-ethyl salt **4b** (0.20 g, 0.49 mmol) in THF (5 ml). The reaction mixture was stirred for 30 min at room temperature, poured into water (50 ml) and extracted with ether (2 × 50 ml). The combined ethereal extracts were washed with brine, dried ($MgSO_4$) and concentrated to give a brown oil (0.03 g, 17%). TLC analysis of the crude product showed there to be a complex mixture of products, while the ^1H NMR spectrum showed an absence of the characteristic C(4)H signal for the title complex, in addition to the presence of aromatic material; (δ_H 7.12–7.20).

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