

Preliminary communication

Transition metal mediated asymmetric synthesis

**VIII *. Preparation of tricarbonyl(cyclohexadienyl)iron(1 +)
cations with oxygenated side-chains**

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Abstract

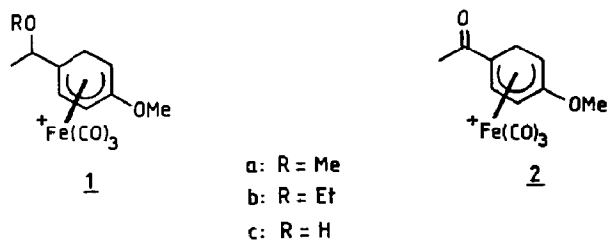
Tricarbonyl(cyclohexadiene)iron complexes bearing side-chain oxygen functionality and have been prepared and their reactions with triphenylcarbenium ion reagents examined. In the case of ethers, no hydride abstraction was observed and deoxygenation was completely dominant. An acyl-substituted complex also proved unsatisfactory as a substrate for hydride abstraction. Thallium oxidation was found to provide a successful alternative, affording the expected alkoxyethyl-substituted dienyl cations. The reaction of the acyl-substituted complex with thallium tri-trifluoroacetate was less efficient, but also produced the acyl cation in a better, though still low, yield.

Reliable methods for the conversion of η^4 -diene complexes into cationic η^5 -dienyl complexes hold the key to the general applicability of tricarbonyliron complexes in asymmetric synthesis. For the synthetically important cyclohexadiene/cyclohexadienyl ligand system, two situations currently limit the applicability of hydride abstraction with triphenylcarbenium reagents, the original [1] and still the most general reagents available for this purpose. These situations involve (i) the presence on the cyclohexadiene ring of blocking groups [1–3] which impede the approach of the bulky reagent, and (ii) the presence of labile substituents on the ligand, both of which can prevent normal hydride abstraction. We recently reported

* For part VII, see P.W. Howard, G.R. Stephenson, and S.C. Taylor, *J. Organomet. Chem.*, 339 (1988) C5.

[2] studies relating to methods applicable in the presence of blocking groups. We now describe preliminary results which demonstrate that our thallium oxidation [2,4] method can also be used to overcome the intervention by side-chain functionality which diverted the normal course of the hydride abstraction from complexes of type 6.

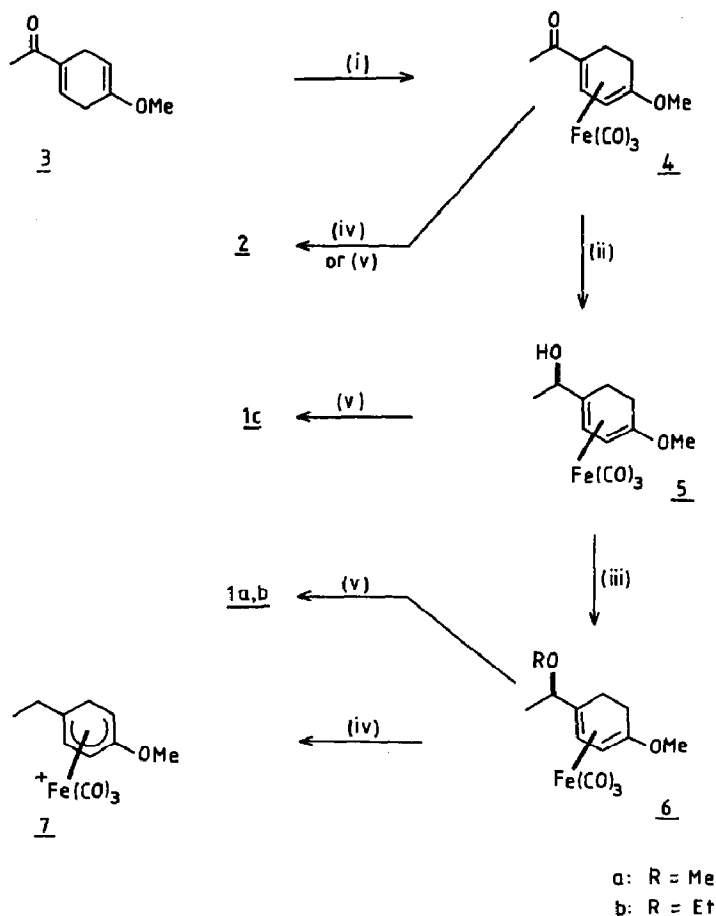
In experiments designed to probe the control of regioselectivity of reactions of tricarbonyliron complexes bearing synthetically important substituents, we have been trying to prepare cationic dienyl complexes of the types 1 and 2. Complexation



of the 1,4-diene **3** produced the 1,3-diene complex **4** in 52% yield. This complex was converted into the alcohol **5** in a stereocontrolled reduction by sodium borohydride. On the basis of previous examples [5,6] of the reduction of carbonyl groups adjacent to transition metal π -complexes, the relative stereochemistry of **5** shown in Scheme 1 was tentatively assigned. The product, obtained in 94% yield, was shown to be a single isomer by ^{13}C NMR spectroscopy. Replacement of the OH group by OMe or OEt was effected by reaction [7] of **5** with the appropriate *ortho*-ester in the presence of a catalytic amount of concentrated sulphuric acid; this reaction proceeded with almost complete retention of configuration and in near quantitative yield. In this way, the ethers **6a,b** were obtained on a multi-gram scale. It was expected that hydride abstraction from **6** would produce the required cations **1**. Reaction of **6** with triphenylcarbenium tetrafluoroborate in refluxing dichloromethane proceeded slowly, and 48 h was required for disappearance of all the neutral starting material. Although an η^5 -dienyl complex was obtained from this experiment, examination of its NMR spectrum indicated that the ether group had been lost in the course of the reaction. The product, **7** [8], was obtained in 16% yield by precipitation as the PF_6^- salt from water by addition of ammonium hexafluorophosphate. The preparation of **1** by the normal method had been frustrated by the intervention of the labile alkoxy substituent at the α -position in the side-chain. This limitation has been encountered by other researchers [9] working with complexes bearing similar functionality. Hydride abstraction, however, is successful [10] when the ether substituent is at the β carbon atom.

The formation of **7** can be accounted for by removal of the OMe substituent by electrophilic addition of the triphenylcarbenium ion at the oxygen atom. This would produce [11] a carbenium ion centre adjacent to the diene complex. Rearrangement of carbenium ions of this type are known [6] to produce cationic dienyl complexes. The identification of the methyl ether of triphenylmethanol as a side product of the reaction supports this explanation.

The use of thallium oxidation, followed immediately by acidification with concentrated sulphuric acid to form the dienyl complex, overcame the difficulty experienced in the preparation of **1**. Electrophilic attack by the thallium(III) was expected to take place at the metal centre rather than at the ether substituent.



Scheme 1. (i) $\text{Fe}(\text{CO})_5$, ${}^n\text{Bu}_2\text{O}$; (ii) NaBH_4 , MeOH ; (iii) $(\text{RO})_3\text{CH}$, ROH , H_2SO_4 ($\text{R} = \text{Me}, \text{Et}$); (iv) $\text{Ph}_3\text{C}^+\text{BF}_4^-$, CH_2Cl_2 ; NH_4PF_6 , H_2O ; (v) $\text{Tl}(\text{CF}_3\text{CO}_2)_3$; NH_4BF_4 ; H_2SO_4 ; NH_4PF_6 , H_2O .

Reaction of **6a** with thallium tris(trifluoroacetate) under the normal conditions [2] produced the required diene complex **1a** in moderate yield. The ethyl ether **1b** was obtained similarly. The alcohol **5** was also examined as a substrate for this reaction. The hydroxyethyl-substituted cation **1c**, isolated in the same way by precipitation with ammonium hexafluorophosphate in 25% yield was identified by comparison of its IR, ${}^1\text{H}$, and ${}^{13}\text{C}$ NMR spectra with data obtained for the ethers **1a,b**. This alcohol analogue was less stable than the corresponding ethers, and was not further characterised.

The preparation of acyl-substituted diene complexes of the type **2** was also examined. Hydride abstraction from **4** proceeded in only 6% yield [12 *]. The yield of **2** was improved to 15% by the use of the thallium oxidation.

In these thallium-mediated reactions, the products **1a,b,c** and **2** were precipitated as single regioisomers, and no further purification was necessary. In common with other examples of this reaction, 1-methoxydiene complexes were converted exclusively into 2-methoxy-substituted diene complexes. We plan to study modification

* Reference number with asterisk indicates a note in the list of references.

of the thallium oxidation procedure specifically to suit these more complicated substrates, and to examine the regiocontrol of nucleophile addition to cations of types 1 and 2. At present we have demonstrated that the thallium oxidation method is capable of producing cationic dienyl complexes with functionality which rules out the normal triphenylcarbenium reagent method. The dienyl complexes prepared in this investigation bear functionality which should make them of interest as intermediates in asymmetric organic synthesis. This is particularly the case for complexes of type 1, where good control of relative stereochemistry between the side-chain ether substituent and the planar chirality [13] of the transition metal π -complex has been obtained. In stereocontrolled alkylation reactions [14], the metal is expected to relay this chirality effectively to the second chiral centre formed at that stage.

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