

SYNLETT Spotlight 52

Iron Pentacarbonyl – Fe(CO)₅

Compiled by Yoann Coquerel



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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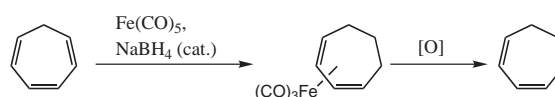
Introduction

The title compound¹ [and its higher order congeners Fe₂(CO)₉ and Fe₃(CO)₁₂] exhibits several features which have made it particularly attractive as a reagent in organic synthesis. These features include: (i) the nucleophilic attack at one of the CO ligands to generate iron carbonylates;² (ii) carbonyl insertion reactions; and (iii) its ability to undergo under thermal or photochemical conditions an in situ dissociative loss of one or more CO ligand and subsequent complexation of the coordinatively unsaturated iron to an organic substrate. Pattern (i) has proven useful mainly due to the reducing properties of iron carbonylates (Abstract A). Pattern (ii) now allows the efficient preparation of cyclohexenones (Abstract B), β-, γ- or δ-lactones and lactams (Abstract C) and also cyclopentadienones (Abstract D), compounds which have all proven useful in total synthesis. Finally and most importantly, reactions of

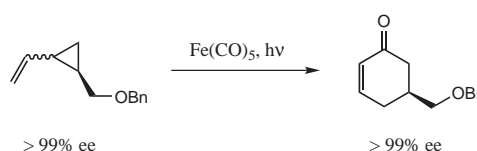
type (iii) include the isomerisation of olefins with either a stoichiometric or catalytic amount of Fe(CO)₅,³ the use of tricarbonyl iron group for the stabilization of highly labile molecules, the use of tricarbonyl(η⁴-1,3-diene)iron complexes⁴ to protect, under a number of reaction conditions, (e.g. hydrogenation, acylation, hydroboration, cycloaddition, epoxydation, osmylation and Michael addition) a 1,3-diene unit (Abstract E), the use of the tricarbonyl iron moiety to control the stereoselectivity of reactions on a neighboring functional group (Abstract E), and mainly, the well known reactivity of the corresponding η⁵-dienyl salt (Abstract F). It should be noted here that, though the tricarbonyliron complexes are easy to prepare on a large scale, are stable and easily handled in classical laboratory conditions, the title reagent Fe(CO)₅ is highly toxic and volatile, and therefore great care must be taken in its handling and storage conditions.

Abstracts

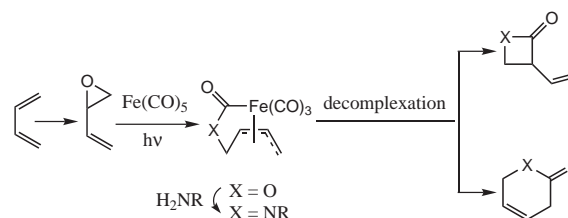
(A) Fe(CO)₅ and a catalytic amount of sodium borohydride react with cycloheptatrienes in protic solvents to yield the corresponding tricarbonyl(η⁴-1,3-diene)iron complexes in a one-pot procedure, which has been found to be particularly efficient for the synthesis of the useful tricarbonyl(cycloheptadiene)iron complex and, after oxydative removal of the iron moiety, of the cycloheptadiene itself.⁵



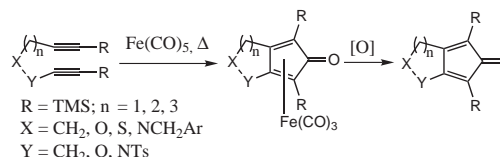
(B) 5-Alkyl cyclohexenones of high enantiomeric purity can be obtained in good yields by ultraviolet irradiation of enantiomerically pure alkenyl cyclopropanes in the presence of Fe(CO)₅. Given the many strategies for the preparation of enantiomerically pure alkenyl cyclopropanes that are available, this promises to be a versatile method for the construction of cyclohexane derivatives.⁶



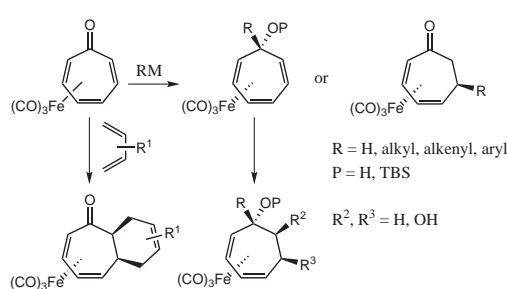
(C) On irradiation in the presence of $\text{Fe}(\text{CO})_5$, vinyl epoxydes are readily transformed into $(\pi\text{-allyl})\text{tricarboxyliron}$ lactone complexes, which can be further transformed into the corresponding lactam complexes. Oxidative decomplexation of these iron complexes subsequently affords β - or δ -lactones and lactams. This method is of considerable value for natural product synthesis due to the number of methods available for the preparation of optically active epoxides.⁷



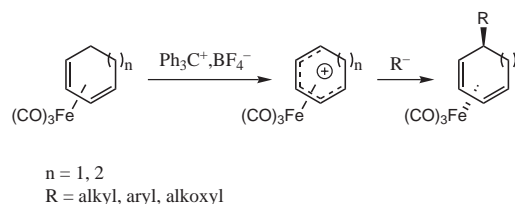
(D) The iron-mediated $[2+2+1]$ cycloaddition of diynes provides a broad scope of carbo- and heterobicyclic cyclopentadienones complexes which can be easily decomplexed and further manipulated for transformation in biologically active natural and non-natural products.⁸



(E) The reactivity of the tricarboxyl(troponone)iron complex is a good example of both the protecting and stereodirecting properties of the tricarboxyl(η^4 -1,3-diene)iron moiety. Indeed, this complex can undergo stereoselective Diels–Alder cycloadditions and 1,2 or 1,4 nucleophilic additions.⁹ Various other reactions can be achieved stereoselectively on the uncomplexed double bond.¹⁰ The same stereoselectivity is observed on nucleophilic addition to acyclic precursors bearing a $\text{C}=\text{X}$ ($\text{X} = \text{O}, \text{N}$) double bond adjacent to the tricarboxyl(η^4 -1,3-diene)iron unit.¹¹ The $(\pi\text{-allyl})\text{tricarboxyliron}$ lactone complexes presented in Abstract C are also excellent stereodirecting groups.¹²



(F) Upon treatment with the trityl cation, tricarboxyl(η^4 -diene)iron complexes undergo hydride abstraction to give the corresponding η^5 -dienyl complex, which react with nucleophiles to yield regio- and stereoselectively the 5-*anti*-substituted η^4 -diene complex. It is the cyclohexadiene derivatives which have led to the largest number of applications (recent work includes the synthesis of carbazole alkaloids¹³ and carbo- and heterospirocyclic frameworks),¹⁴ but the cycloheptadiene derivatives also have proven to be very useful.^{5,15}



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