Preliminary communication

Alkynylcyclohexadienyl tricarbonyliron complexes: a new directing effect for organoiron-mediated synthesis

Ester van den Beuken, Sylvie Samson, Elizabeth J. Sandoe, G. Richard Stephenson *

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Abstract

The first example of an alkyne-substituted tricarbonyl(η^5-cyclohexadienyl)iron(1 +) complex has been prepared and the ω directing effect of the phenylethynyl substituent has been demonstrated in nucleophile addition reactions. Addition of NC^- also occurs at the α position to form an unusual η^1,η^3-structure.

Keywords: Iron; Carbonyl; Alkynylcyclohexadienyl; Directing effects

1. Introduction

Unsymmetrically placed substituents on chiral tricarbonyliron cyclohexadienyl complexes control the regiochemistry of the diastereoselective addition of nucleophiles to η^5 ligands [1]. For these organometallic electrophiles to be used in organic synthesis, the directing effects of substituents must be understood. Although the effect of alkoxy and ester groups is well known and demonstrated in synthetic applications [2–4], it is only recently that the directing effects of other simple substituent groups (e.g. phenyl [5], ethenyl [6], and trifluoromethyl [7]) have been defined. Alkynes are important organic functional groups because of their many applications in skeletal bond-forming reactions, but examples of alkyne-substituted cyclohexadienyl complexes have not been reported. In this communication, we describe the preparation of the first examples of complexes of this type (3), and define the directing effect of the phenylethenyl substituent in 3a.

2. Results

Our approach to the synthesis of 3a was based on general methods developed in Norwich for the

introduction of 1-aryl substituents from aryllithium reagents [8]. The acetylide $PhC{\equiv}CLi$ was chosen as a convenient nucleophile for our purposes. Reaction with the 1-ethoxycyclohexadienyl complex 1 proceeded in the normal [9] *ipso* fashion to afford 2, which was converted into 3a by reaction with HPF_6 in acetic anhydride. The product was precipitated in 70% yield as a stable yellow powder by addition of the reaction mixture to diethyl ether.

A representative selection of nucleophiles (Table 1) was used to examine the regiodirecting effect of the alkynyl substituent. The sodium enolate of dimethyl

Table 1
Addition of nucleophiles to the 1-alkynyl-substituted tricarbonyl(cyclohexadienyl)iron complex 3a

Nucleophile	Solvent [a]	Product	$\nu(CO)$ [b] (cm^{-1})	Yield (%)
$NaCH(CO_2Me)_2$	THF	4a	2053, 1990	79 [c]
$NaBH_4$	CH_3CN	4b	2047, 1976	81 [c]
Me_2CuLi	THF	4c	2047, 1977	48 [c]
$^nBu_2CuLi$	THF	4d	2048, 1979	62 [c]
KCN (aq.)	CH_3CN/ H_2O	4e	2056, 1986	69 [c]
		5	2066, 2001	15 [d]

[a] Reactions performed at 0 °C.
[b] Measured in solution in CH_2Cl_2.
[c] ω Addition relative to the alkyne.
[d] α Addition relative to the alkyne.

* Corresponding author.
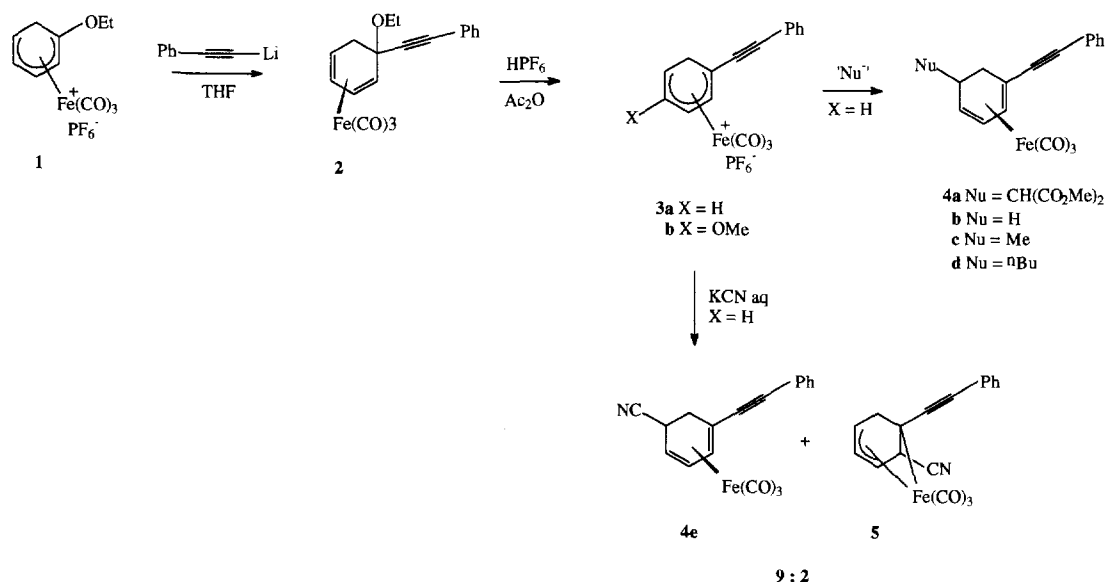
Scheme 1. The synthesis and reactivity of the phenylethynyl-substituted salt complexes.

propanedioate and sodium borohydride both reacted at the unsubstituted terminus of the η^5 portion of the ligand to afford the ω addition products **4a** and **4b** in 79–81% yield. Organocuprate nucleophiles add to ethenyl-substituted cyclohexadienyliron complexes by a conjugate addition pathway [6]. With an alkyne in the place of the alkene, this conjugate mode of addition would introduce allene functionality into the product. With this possibility in mind, two lithium dialkylcuprate reagents were employed in reactions with **3a** in THF. Both Me_2CuLi and Bu_2CuLi, however, reacted directly at the metal-bound portion of the alkynylcyclohexadienyl ligand, following the same ω-regiochemistry, forming **4c** and **4d** in 48 and 62% yield respectively. Either the transition state required for access to a cumulated series of double bonds is disfavoured, or the steric bulk of the Ph substituent blocks the transfer of the alkyl group to the alkyne.

With cyanide as the nucleophile, the major product was again that arising from ω-addition (complex **4e**, 69%). In this case a second product was also isolated (15% yield). The unusual position ($2001 \, cm^{-1}$) of the antisymmetric vibrational mode of the $Fe(CO)_3$ group in the solution (CH_2Cl_2) IR spectrum of this product led us to suspect that this was not an allene arising from conjugate addition, but that internal attack had taken

Fig. 1. Sites of nucleophilic addition to phenylethynyl-substituted complexes.

place at the α-position (Fig. 1) of the η^5-cyclohexadienyl ring. This was confirmed by measurement of the ^{13}C NMR spectrum which contained a high field (1.2 ppm) resonance indicating the presence of a σ-bound carbon atom. In this way, and by examination of the multiplicities of signals in the ^1H NMR spectrum, the second product from reaction of NC^- with **3a** was identified as **5** (Scheme 1).

The procedure described for the preparation of **3a** shows promise as a general route to alkynylcyclohexadienyl complexes, since 1-alkoxy starting materials of type **1** should be readily accessible [10] by reaction of tricarbonyl($2,3,4,5$-η-cyclohexadien-1-one)iron(0) complexes with Et_3OPF_6, or directly by hydride abstraction from $1,2,3,4$-η^1-alkoxycyclohexadiene complexes [11]. Furthermore, purification of the intermediates of type **2** is often not essential in nucleophile addition/alkoxy leaving group displacement routes to substituted η^5-cyclohexadienyl complexes, since the cationic end-products are easily separated from neutral by-products at the precipitation step after reaction with HPF_6. To illustrate these possibilities, tricarbonyl(η^5-$1,4$-dimethoxycyclohexadienyl)iron($1 +$) hexafluorophosphate($1 -$) was treated with $PhC \equiv CLi$ by the procedure described for the preparation of **2**. The reaction was worked up in the usual fashion by solvent extraction and rapid chromatography to afford a crude sample of a neutral intermediate which was taken on directly to the reaction with HPF_6, affording the expected 1-alkynyl-substituted complex **3b** in 72% overall yield.

3. Discussion

In these investigations we have demonstrated that alkyne-substituted tricarbonyliron complexes are easily
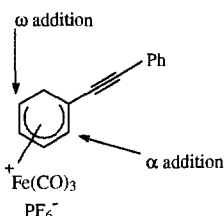
accessible stable compounds. Their reactions with nucleophiles are fully stereocontrolled (as is the case in general with nucleophile additions to tricarbonyl(η^5-cyclohexadienyl)iron complexes) and are also highly regioselective, giving reliable access to ω addition products. These results indicate that organoiron complexes of type **3** will be well suited to application as electrophiles in organic synthesis. Recently, the regiodirecting influence of a CN substituent in an acyclic η^5-pentadienyl tricarbonyliron complex has been reported [12]. Like the electron-withdrawing CO_2Me substituent used in the cyclohexadienyl series to give regiocontrol in syntheses of gabaculine [3] and shikimic acid [4], this terminal electron-withdrawing CN substituent directs ω. In view of this, it is notable that the ω directing effect of $PhC\equiv C$ defined in our study arises from a group that (in contrast to CN) strongly stabilises adjacent positive charge. This comparison suggests that the directing effect of $PhC\equiv C$ arises solely from steric blocking of the substituted terminus, while CN may control regiochemistry through a combination of steric and electronic effects. On this basis, $PhC\equiv C$ might be expected to be a weaker ω directing group than CN.

Acknowledgements

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