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Preparation of alkyl-Fp [Fp = $(C_5H_5)Fe(CO)_2$] complexes via organometallic reagents: reactions of RMgX and RLi with Fp–I and Fp–$THF^+BF_4^-$

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Abstract

The preparation of alkyl substituted Fp complexes [Fp = $(C_5H_5)Fe(CO)_2$] by the reaction of Grignard or alkyl lithium reagents with Fp–I and Fp–$THF^+BF_4^-$ has been investigated. Small alkyl substituents (Me, Et, Bu) provided moderate yields of Fp–R in the reaction of the corresponding lithium or magnesium reagent with Fp–I. Cyclohexyl and phenyl Grignard reagents showed coupling of the organic fragments and concomitant production of Fp_2. Increased yields of Fp–R and decreased generation of Fp_2 were observed when Fp–THF^+ was used in place of Fp–I. Secondary nucleophiles gave substantially lower yields.

Fp–alkyls [Fp = $(C_5H_5)Fe(CO)_2$] have been prepared in a number of different ways. The most common routes involve nucleophilic addition to Fp–olefin complexes [1], the reaction of Fp anion with alkyl halides or alkyl tosylates [2], decarbonylation of Fp–acyl complexes [3] and reduction of Fp–carbene species [4]. We have been studying the chemical shift anisotropy of the Fp-group as a substituent on six-membered rings (cyclohexyl, tetrahydropyranyl, dioxanyl) and required a number of Fp–alkyl compounds [5]. In the course of preparing these compounds for analysis, we encountered difficulties in the reaction of Na^+Fp^- with sterically crowded alkyl substrates and in cases where elimination reactions were favored. Large amounts of Fp_2 were recovered, along with apparently dimerized alkyl products and none of the desired Fp-alkyls. Because the Fp–olefin or Fp–carbene complexes required for the alternate preparative routes were not readily available, we sought another technique for synthesizing Fp–alkyl complexes.

The most obvious alternative was a simple umpolung of the reagents; carbon nucleophiles reacting with Fp electrophiles. A search of the literature revealed few examples of such a reaction. Hallam and Pauson prepared cyclopentadienyl–Fp, [$(\eta^1$-$C_5H_5)Fe(CO)_2(\eta^5$-$C_5H_5)$] in 15% yield by the reaction of Fp–Br with NaC_5H_5, but reported the reduction of Fp–Br to Fp_2 upon treatment with PhLi or PhC≡CNa [6]. Rosenblum and co-workers [7] successfully prepared cyclopentadienyl–Fp by treatment of Fp–I with NaC_5H_5. However, the acetyl analogue, [$(\eta^1$-$C_5H_5)Fe$-

$$\begin{array}{lll} Fp\text{–}I & & \\ (\mathbf{1}) & R\text{–}MgX & \\ \text{or} & + \text{ or} & \xrightarrow[1\,h]{THF,\ -78\,^{\circ}C \text{ to r.t.}} Fp\text{–}R + Fp_2 + R\text{–}R \\ & & (\mathbf{3}) \\ Fp\text{–}THF^{+}BF_4^{-} & R\text{–}Li & \end{array}$$

Scheme 1.

$(CO)_2(\eta^5\text{-}C_5H_4C(O)CH_3)]$, was not preparable by the reaction of NaC_5H_5 with $(\eta^5\text{-}CH_3C(O)C_5H_4)(CO)_2FeI$. Pretreatment of the acetylated Fp–I with silver trifluoroacetate to form the free cation, followed by addition of NaC_5H_5, did yield the desired alkylated product. The preparation of a number of cyclopentadienylmetal alkyls and aryls was reported by Piper and Wilkinson [8]. They observed only traces (3–5%) of alkyl product from the reaction with PhMgBr with Fp–I along with substantial amounts of Ph–Ph and Fp_2, and no Fp–alkyl from EtMgBr, but obtained Me–Fp in good yield (50%) from Fp–I and MeMgBr. Encouraged by these results, we began our investigation of the reactions of organolithium and organomagnesium reagents with Fp–I, **1**, and $Fp\text{–}THF^{+}BF^{-}{}_4$, **2**.

Results and discussion

Reactions of Fp–I with alkyl lithium and magnesium reagents gave mixtures of the desired Fp–alkyl complexes along with Fp_2 and coupled alkyl products (Scheme 1). The results of reactions with five different nucleophiles are shown in Table 1. The yield of Fp–alkyl was reasonable for methyl nucleophile (as methyl lithium), but fell off rapidly as the size of the nucleophile increased. Butyl and propyl anions gave only fair yields, while phenyl and cyclohexyl nucleophiles produced little or none of the desired Fp–R product. Not surprisingly, the amount of Fp_2 recovered from these reactions increased as the production of Fp–alkyl dropped. Finally, for the phenyl and cyclohexyl cases, we isolated the dimerized hydrocarbons, biphenyl and bis-4-^{t}Bu-cyclohexyl in fair to excellent yields.

The isolation of biphenyl and the 4-^{t}butylcyclohexyl dimer suggested that the reaction was not following the desired course. We perceived two possible paths for the production of Fp_2 and R_2. The first, a polar mechanism, involved nucleophilic

Table 1

Reaction [a] of R–M with Fp–I

Nucleophile	Yield (%)		
	Fp–R	Fp–Fp	R–R
MeLi	60	10	
PrMgBr	46	36	
BuLi	26	53	[b]
PhMgBr	12	70	47
PhMgBr [c]	0	70	89
4-^{t}Bu-^{c}HexMgBr	0	55	38

[a] All reactions run at −78 °C for 1 h, except as noted. [b] Observed, but not isolated. [c] Reaction run at 0 °C.

Table 2

Reaction [a] of R–M with $Fp–THF^+ BF_4^-$

Nucleophile	Yield (%)	
	Fp–R	Fp–Fp
MeLi	70	trace
PrMgBr	80	trace [c]
BuLi	50	trace
4-^{t}Bu-^{c}HexMgBr	10	trace [c]
1-Me-^{c}HexMgBr	[b]	trace [c]

[a] All reactions run at −78°C for 1 h. [b] None detected. [c] Fp–Br observed as well.

attack by R^- at iodine, displacing Fp anion. Subsequent reaction of the resulting R–I with another equivalent of R^- would produce the organic dimer. Likewise, reaction of Fp^- with another equivalent of Fp–I would yield Fp_2 and I^-. The corresponding R_2 compounds were not observed for R = Me, Pr, or Bu, but, due to their low boiling points, any of these compounds formed during the reaction would have been lost during work-up.

The second alternative was a free-radical pathway. A single electron transfer from R^- to Fp–I could produce R, Fp and I^-, similar to the intermediates suggested by Krusic and co-workers [9] in the reaction of Fp^- with alkyl halides. Subsequent homo-coupling of the Fp and alkyl radicals would produce the observed products. If the production of R_2 occurred via the polar pathway, we felt that we could reduce or eliminate that side reaction by substituting $Fp–THF^+BF_4^-$ [10] for Fp–I. Nucleophilic attack at the coordinated THF moiety would be very unlikely. The results of these experiments are presented in Table 2.

Reaction of MeLi, PrMgBr and BuLi with $Fp–THF^+BF^-_4$ gave the corresponding Fp–alkyls in 70, 80, and 50% isolated yields respectively, all significantly improved compared to the yield from reaction with Fp–I. The yield of 4-^{t}butylcyclohexyl–Fp was still disappointing (10%), but none the less an improvement over the Fp–I reaction (no observed Fp–R).

An attempt to push the reaction sequence to its limits by using a tertiary Grignard (1-methylcyclohexyl–MgBr) showed no production of Fp–R. No cyclohexyl containing product was isolated, although major decomposition was observed during chromatography and small amounts of Fp_2 and Fp–Br were obtained. It is possible that the very crowded 1-methylcyclohexyl–Fp compounds did form, but decomposed via an elimination reaction on the alumina column. More likely, elimination occured to give Fp–H, which decomposed during the purification, and an olefin. Production of olefins and metal hydrides has been observed previously in the reaction of Cp(bisphosphine)FeBr with 2° and 3° Grignard reagents [11]. The resulting 1-methylcyclohexene would have been lost during removal of solvent from the collected fractions, accounting for the lack of an observed organic product.

In conclusion, we believe that the reaction of $Fp–THF^+BF^-_4$ with primary alkyl lithium and Grignard reagents provides a useful alternative for the synthesis of Fp–alkyls. Secondary alkyl reagents are significantly less effective, but do produce low yields of the corresponding species.

Experimental

Reactions were carried out under argon or nitrogen atmosphere using standard Schlenk technique. Solvents were distilled under nitrogen from sodium/benzophenone (ether and THF) or CaH_2 (CH_2Cl_2 and hexane). Alumina refers to Basic Alumina Activity IV. MeLi, PrMgBr, BuLi and PhMgBr were purchased as solutions from Aldrich Chemical Company and used without further purification. Fp–I was prepared by the reaction of Fp_2 with I_2 in THF solution. IR spectra were recorded on a PE-1330 spectrophotometer and were calibrated against a polystyrene standard. ^{1}H- and ^{13}C-NMR spectra were taken on a Bruker AC-200 Spectrometer (courtesy of the Worcester NMR Consortium) in $CDCl_3$ and referenced to TMS (^{1}H) or solvent (^{13}C). All products have been previously reported.

General procedure for the reaction of Fp–I with R–M

Fp–I (0.50 g, 1.6 mmol) is dissolved in 15 mL of THF and cooled to −78 °C. One equivalent of the appropriate Grignard or lithium reagent is added dropwise over the course of several minutes and the reaction mixture stirred for one hour at −78 °C. TLC [alumina, 10% ether/petroleum ether (b.p. 30–60 °C) (v/v)] is used to determine the extent of reaction and if unreacted Fp–I is present, small additional portions of nucleophile are added until no starting material is detected. The reaction mixture is then allowed to warm to room temperature, filtered through a short plug of alumina to remove salts and the solvent removed from the filtrate *in vacuo*. The residue is then chromatographed on alumina with 10% ether/petroleum ether (b.p. 30–60 °C) (v/v) and the solvent removed from the collected fractions *in vacuo*. Metal-containing fractions are easily identified by color: Fp–R, yellow; Fp–X, red-brown; Fp_2, reddish-purple. Intermediate fractions may be collected and examined for the presence of organic by-products. Yields reported below are of isolated material, pure according to IR and NMR.

General procedure for the reaction of Fp–THF$^+BF_4^-$ (2) [10] with R–M

A mixture of **1** (0.50 g, 1.6 mmol) and $AgBF_4$ (0.32 g, 1.6 mmol) is stirred in 15 mL of THF at room temperature for 3 h. The resulting solution of Fp–THF$^+BF^-_4$ is filtered via cannula into a second flask and cooled to −78 °C. The appropriate nucleophile is added dropwise via syringe and the reaction worked-up as for reactions of **1**, above.

*Methyl-η^5-cyclopentadienyldicarbonyliron(II), **3a** [8].* From CH_3Li (1.2 *M* in diethyl ether) and **1**, 0.18 g (60%); and **2**, 0.21 g (70%). IR (neat): 1990, 1930 (C≡O) cm^{-1}. ^{1}H-NMR δ: 0.15 (s, 3H, CH_3); 4.72 (s, 5H, Cp). ^{13}C-NMR δ: −23.4 (CH_3); 85.0 (Cp); 217.4 (C≡O).

*Propyl-η^5-cyclopentadienyl dicarbonyliron(II), **3b** [12].* From $CH_3CH_2CH_2MgBr$ (2.0 *M* in diethyl ether) and **1**, 0.15 g (46%); and **2**, 0.26 g (80%). IR (neat): 2000, 1950 (C≡O) cm^{-1}. ^{1}H-NMR δ: 0.97 (bm, 2H, $FeCH_2$); 1.5–1.1 (bm, 5H, CH_2CH_3); 4.71 (s, 5H, Cp). ^{13}C-NMR δ: 6.5 (FpCH_2); 19.3 (CH_3); 31.4 (CH_2CH_3); 85.3 (Cp); 217.7 (C≡O).

*Butyl-η^5-cyclopentadienyldicarbonyliron(II), **3c** [2].* From BuLi (2.5 *M* in hexane) and **1**, 0.08 g (26%); and **2**, 0.18 g (50%). IR (neat): 2000, 1965 (C≡O) cm^{-1}. ^{1}H-NMR δ: 0.8 (bm, 3H, CH_3); 1.3 (bm, 6H, CH_2's); 4.62 (s, 5H, Cp). ^{13}C-NMR δ: 3.4 (FpCH_2); 13.9 (CH_3); 27.8, 40.7 (CH_2's); 85.3 (Cp); 217.4 (C≡O).

Phenyl-η^5-cyclopentadienyldicarbonyliron(II), 3d [8]. From PhMgBr (3.0 *M* in diethyl ether) and **1** at −78°C, 0.05 g (12%). IR (neat): 2000, 1950 (C≡O) cm^{-1}. ^{1}H-NMR δ: 4.86 (s, 5H, Cp); 7.4–6.9 (bm, 5H, Ph). ^{13}C-NMR δ: 85.8 (Cp); 122.8 (*p*-Ph); 127.5 (*m*-Ph); 145.1 (*o*-Ph); 145.4 (*i*-Ph); 216.1 (C≡O).

trans-*4-'Butylcyclohexyl-η^5-cyclopentadienyldicarbonyliron(II), 3e [5].* 1-Bromo-4-'butylcyclohexane (mixed isomers) was prepared according to the method of Eliel [13]. The corresponding Grignard reagent (1.0 *M* in diethyl ether) was prepared by treatment of the alkyl halide with Mg in diethyl ether. Once the Grignard was prepared, the same general procedure was followed and gave 0.06 g (10%). IR (neat): 1990, 1935 (C≡O) cm^{-1}. ^{1}H NMR δ: 0.80 (s, 9H, CH_3's); 1.9–0.9 (m, 8H, CH_2's); 2.01 (m, 1H, 'Bu–C*H*); 2.50 (m, 1H, Fp–CH); 4.68 (s, 5H, Cp). ^{13}C NMR δ: 27.3 (CH_3); 28.0 (Fp–CH); 32.4 [$(CH_3)_3C$]; 32.4, 44.1 (CH_2's); 48.5 ('Bu–*C*H); 85.7 (Cp); 218.1 (C≡O).

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