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Synthesis and Characterization of η^6-Acetophenone-η^5-cyclopentadienyliron Hexafluorophosphate

UDAI S. GILL

Department of Chemistry, McGill University, Montreal, Que., H3A 2K6, Canada

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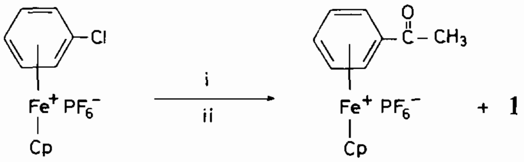
The aluminium chloride catalized ligand exchange reaction between ferrocene (FcH) and arenes, first described by Nesmeyanov [1] has been extensively used in the preparation of sandwich complexes of the type arene $FeCp^+PF_6^-$ [2]. Nonetheless, the need to use aluminium chloride severely limits the possible arene substituents. To the best of our knowledge, no synthesis of $CpFe^+$ complexed ketoarene via direct ligand exchange between ketoarene and FcH was reported. The present note describes an indirect way of preparing the title compound, $C_6H_5COCH_3$-$FeCp^+PF_6^-$ (2) in good yield (eqn. (1)):



1 2

(1)

(i) K_2CO_3 / $CH_3CH_2NO_2$; (ii) HCl / C_2H_5OH

Activation toward S_NAr substitution of normally unreactive arene halides by complexation to transition metal cations is well known [2, 3]. Recently, we have discovered that the organometallic complex, $C_6H_5ClFeCp^+PF_6^-$ (1) could readily undergo S_NAr substitution of the chloride atom with enolate anions to give corresponding substituted benzene complexes [4]. We have now applied this method for the synthesis of cation 2. The reaction of the cation 1 with an excess of nitroethane ($C_2H_5NO_2$) in the presence of 3.0 molar equivalent of K_2CO_3 for 30 h at RT under N_2, followed by HCl/Ethanol work up, gave 1/1 mixture of **1** and **2** [5]*. The η^6-acetophenone-η^5-cyclopentadienyliron cation (2) can be obtained in a pure form (35–40% yield) after chromatographic separation through alumina column with elution by acetone. *Anal.* Calc. for C_{13}-$H_{13}OFePF_6$: C, 40.44; H, 3.39. Found: C, 40.33; H, 3.40%. Melting point 171–173 °C. IR (KBr, cm^{-1}) 1740 (CO). ^1H NMR (acetone-d_6) 6.9–7.2 (m, 2H), 6.6–6.9 (m, 3H) aromatic; 5.3 (s, 5H, Cp) and 2.8 (s, 3H, CH_3).

In conclusion, the nucleophilic substitution of the chlorine atom in cation 1 with carbanion derived from nitroethane provided a convenient route to the synthesis of cation 2.

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*Nef reaction.

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