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A sonochemically promoted route to new iron pentaphenylcyclopentadienyl cationic complexes

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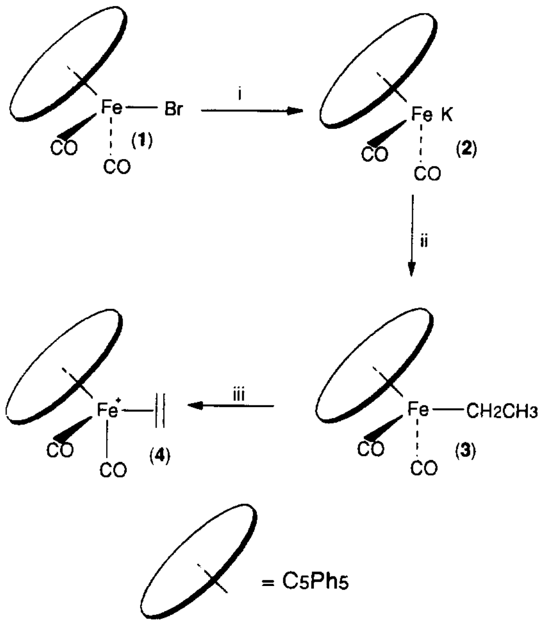
Abstract

A sonochemical procedure has enabled the synthesis of the new species $[Fe(C_5Ph_5)(CO)_2(C_2H_4)]PF_6$ via $[Fe(C_5Ph_5)(CO)_2Et]$. The reactivity of the new species towards two-electron ligand exchange provides a route to a series of new cationic species $[Fe(C_5Ph_5)(CO)_2L]PF_6$.

Numerous η^5-cyclopentadienyl derivatives of most of the transition metals are known [1]. In the past decades attention has been focused on transition metal complexes containing peralkylated η^5-cyclopentadienyl groups, particularly those containing the pentamethylcyclopentadienyl ligand [2]. When compared with their relevant cyclopentadienyl analogues such complexes usually possess properties reflecting their increased bulk, steric character, and higher electron density in the ring. It might be predicted therefore that perphenylation of the C_5 ring would give C_5Ph_5 complexes with new electronic properties complementary to those containing C_5Me_5, as previously shown in palladium chemistry [3]. Despite some interesting findings [3–5], little attention has been given to use of the C_5Ph_5 ligand even though it is easier to prepare than the C_5Me_5 ligand. Thus, iron complexes in this series are still scarce, although $Fe(C_5Ph_5)(CO)_2Br$ [6] has been known since 1965 and its crystal structure was recently reported [7]. The major barrier to extension of pentaphenylcyclopentadienyl derivatives chemistry is the poor solubility of both the neutral and cationic complexes in common organic solvents.

We now report that the use of high intensity ultrasound [8] dramatically enhances the reactivity of insoluble transition metal complexes towards potassium metal dispersion, thus enabling preparation of the novel cationic Fe(II) complex $[Fe(C_5Ph_5)(CO)_2(C_2H_4)]PF_6$ (**4**), which provides a convenient entry to the $[Fe(C_5Ph_5)(CO)_2L]PF_6$ series.

Typically potassium metal was subjected (10 min; toluene/THF: 80/20, 20 °C) to a 20 kHz ultrasonic irradiation before a stoichiometric amount of the poorly soluble $Fe(C_5Ph_5)(CO)_2Br$ (**1**) was added *. The grey-blue colloidal solution



Scheme 1. Reagents and conditions: (i) equivalent K, toluene:THF (80:20), 20 kHz, 10 min 20 ° C; (ii) 1 equivalent CH_3CH_2I, toluene:THF (80:20), 20 kHz, 15 min, 20 ° C; (iii) 1 equivalent Ph_3CPF_6, CH_2Cl_2, 1 h, −50 ° C, 80%.

changed immediately to the dark-orange of $[Fe(C_5Ph_5)(CO)_2]K$ (**2**) (ν(CO): 1800, 1770 cm^{-1}, THF). This previously unknown air-sensitive organometallic salt was not isolated, but treatment in situ with CH_3CH_2I for 5 min (20 ° C) under the same sonochemical conditions gave, after work-up and recrystallization (CH_2Cl_2/Et_2O), yellow microcrystals of $Fe(C_5Ph_5)(CO)_2CH_2CH_3$ (**3**) in 80% yield based on **1** (Scheme 1). Treatment of **3** with Ph_3CPF_6, at −50 ° C in CH_2Cl_2 (1 h) gave the expected cationic ethylene complex $[Fe(C_5Ph_5)(CO)_2C_2H_4]PF_6$ (**4**) in 80% yield. Reversal of this reaction by treatment of **4** with $NaBH_4$ regenerated **3**, which was isolated in 70% yield.

The ^1H 300 MHz NMR (CD_2Cl_2) spectrum of **4** exhibits three multiplets at δ 7.21, 7.70 and 8.29 for the phenyl protons of the C_5Ph_5 ligand, together with a sharp singlet at δ 4.04 corresponding to the coordinated C_2H_4. The ^{13}C chemical shift of the coordinated C_2H_4 is much more sensitive to the phenyl substitution than to the methyl substitution in the C_5R_5 ligand ($R = CH_3$, δ 59.5 [9]; $R = H$, δ 57.2 [10]; $R = Ph$, δ 66.3). The magnetic equivalence of the four hydrogen atoms and that of the two carbon atoms respectively indicates that the ethylene rapidly rotates about the iron–alkene axis.

The complex **4** reacts cleanly with CO (3 atm) and with CH_3CN to give respectively the air and moisture sensitive complex $[Fe(C_5Ph_5)(CO)_3]PF_6$ (**5**) (70%)

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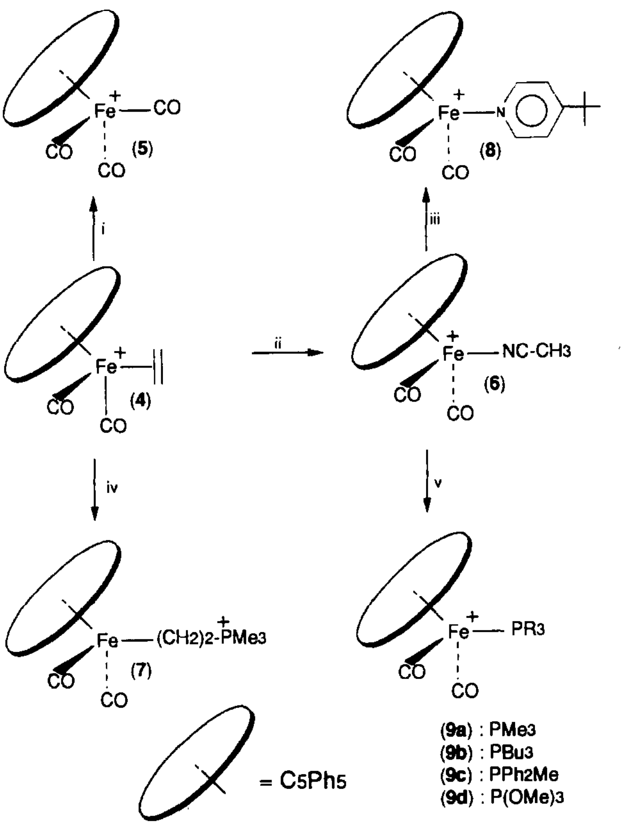
* The reactions were performed under argon in 100 mL Schlenk tube equipped with a side-arm for introduction of the electrophilic reagent. Ultrasonic irradiations involved a collimated 20 kHz beam from a 600 W generator and a titanium amplifying horn (Vibra-Cell Model VC 600) introduced into the solution through a stainless steel collar with O-rings.



Scheme 2. Reagents and conditions: (i) CO (3 atm), CH_2Cl_2, 12 h, 40 °C, 65%; (ii) 3 equivalents CH_3CN, CH_2Cl_2, 7 h, 40 °C, 90%; (iii) 1 equivalent PMe_3, CH_2Cl_2, 5 min, 0 °C, 60%; (iv) 2 equivalents 4-Bu^t-C_5H_4N, CH_2Cl_2, 2 h, 20 °C, 70%; (v) a: 1 equivalent PMe_3, CH_2Cl_2, 3 h, 20 °C, 80%; b: 1 equivalent P $(Bu^n)_3$, CH_2Cl_2, 3 h, 20 °C, 83%; c: 1 equivalent PPh_2Me, CH_2Cl_2, 24 h, 40 °C, 75%; d: 1 equivalent $P(OMe)_3$, CH_2Cl_2, 6 h, 40 °C, 70%.

and the acetonitrile compound $[Fe(C_5Ph_5)(CO)_2CH_3CN]PF_6$ (**6**) (90%) (Scheme 2). This route to **5** is of interest because the Fischer-type ligand exchange reaction [11] cannot be used to prepare **5** from **1**. When **4** is treated with 1 equivalent of PMe_3 nucleophilic attack on the ethylene carbon atom leads to the phosphonium salt $[Fe(C_5Ph_5)(CO)_2(CH_2CH_2PMe_3)]PF_6$ (**7**). The acetonitrile complex **6** undergoes clean ligand exchange reactions with 4-tert-butylpyridine, phosphine and phosphite ligands to give the corresponding complexes $[Fe(C_5Ph_5)(CO)_3(4\text{-}Bu^t\text{-}C_5H_4N)]PF_6$ (**8**) and $[Fe(C_5Ph_5)(CO)_2PR_3]PF_6$ (**9a–d**) in good yields (Scheme 2).

We are currently investigating the electrochemistry and electrophilic properties of such new compounds. Use of ultrasound greatly facilitates the reduction of transition metal complexes, especially when they are sparingly soluble allowing the reaction to be performed in a short time at room temperature. Moreover the use of a stoichiometric amount of the reducing reagent simplifies studies of the chemistry of the formed highly reactive species, emphasizing the range of advantages of sonochemistry.

The new complexes reported gave satisfactory elemental analyses, and ^1H, ^{13}C and ^{31}P NMR spectra were as expected.

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