

ZWITTERIONIC SPECIES FROM DEPROTONATION OF η^6 -TOLUIDINE- η^5 -CYCLOPENTADIENYLIRON CATIONS AND THEIR REACTIONS AS NUCLEOPHILES

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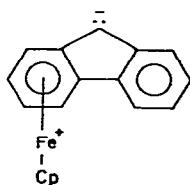
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Summary

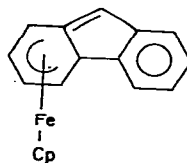
The three isomeric η^6 -toluidine- η^5 -cyclopentadienyliron cations have been prepared from ligand exchange reactions between ferrocene and *o*-, *m*- and *p*-toluidine. Treatment of these cations with *t*-BuOK in THF gave the neutral zwitterionic species with loss of proton from the amino group, and with no deprotonation from the methyl substituent. The use of these zwitterions *in situ* as nucleophiles in reactions with CH_3I , CS_2 , CH_3COCl , $\text{C}_2\text{H}_5\text{COCl}$ and $\text{C}_6\text{H}_5\text{COCl}$ were studied, and the products obtained were similar to those from analogous reactions with the zwitterion from deprotonation of the η^6 -aniline- η^5 -cyclopentadienyliron cation.

Introduction

Deprotonation from an α -carbon of the arene ligand in a complex such as the η^6 -fluorene- η^5 -cyclopentadienyliron cations has been studied by Johnson and Treichel [1] and by Helling and Hendrickson [2]. The neutral species obtained was formulated as the zwitterion Ia [1] or as the π -cyclohexadienyl complex Ib [2]. We have recently extended such studies to show that a variety of η^6 -arene- η^5 -cyclopentadienyliron cations, in which the arene ligand has an α -carbon

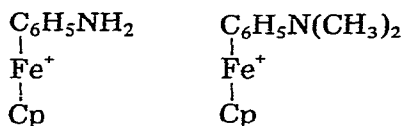


Ia



Ib

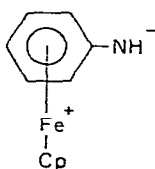
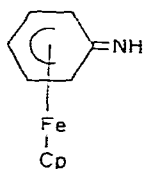
substituent containing one or more hydrogens, could be deprotonated to give the corresponding zwitterionic species, and these zwitterions could then react *in situ* as nucleophiles with various substrates to give a wide range of synthetic applications [3]. Helling and Hendrickson [4] have also demonstrated that deprotonation could occur at the amino, hydroxy or mercapto substituent on the arene ligand. For example, deprotonation of the η^6 -aniline- η^5 -cyclopentadienyliron cation (II) with NaNH_2 in CH_2Cl_2 , followed by treatment with an excess of CH_3I , resulted in the formation of the η^6 -*N,N*-dimethylaniline- η^5 -cyclopentadienyliron cation (III). The neutral species from deprotonation of



II

III

the aniline complex was written as the π -cyclohexadienyl complex IVa [4], although an alternative formulation as the zwitterion IVb is also possible.



IVa

IVb

Since deprotonation could occur from an α -carbon or from an amino substituent, it is of interest to investigate such reactions with complexes in which the arene ligand has both of these substituent groups. We have, therefore, carried out deprotonation studies on complexes from *o*-, *m*- and *p*-toluidines and investigated some further reactions with the resulting zwitterionic species as nucleophiles.

Results and discussion

Although Nesmeyanov et al. [5] were the first workers to carry out the AlCl_3 catalyzed ligand exchange between arenes and ferrocene. They were unable to effect such an exchange with aniline and ferrocene [6]. However, with the use of an excess of AlCl_3 , Helling and Hendrickson [4] were successful in preparing cation II from aniline. Using Helling's modification [4], with a molar ratio of 1 : 1 : 4 : 1 for toluidine : ferrocene : AlCl_3 : Al powder, and a procedure similar to that employed in our other ligand exchanges studies [7,8], the η^6 -*o*-, *m*- and *p*-toluidine- η^5 -cyclopentadienyliron cations (V, VI and VII, respectively) were prepared and isolated as the hexafluorophosphates. The pertinent data from these preparations are summarized in Table 1.

The deprotonation of cation V, VI or VII with *t*-BuOK in tetrahydrofuran (THF) [3], followed by treatment of the resulting neutral zwitterionic species

TABLE 1

DATA FROM THE PREPARATION OF η^6 -*o*-, *m*-, AND *p*-TOLUIDINE- η^5 -CYCLOPENTADIENYLIRON CATIONS

Product	Yield (%)	Analysis found (calcd.) (%)				$^1\text{H NMR}(\delta(\text{acetone-}d_6))$ ppm from TMS				
		C	H	N	Cp	Aromatic	NH ₂	CH ₃		
<i>o</i> -CH ₃ (NH ₂)C ₆ H ₄ FeCp ⁺ PF ₆ ⁻ (VPPF ₆)	63	38.25(38.63)	3.62(3.78)	3.60(3.75)	4.8(s)(5 H)	5.8-6.2(m)(4 H)	5.6(broad s)(2 H)	2.4(s)(3 H)		
<i>m</i> -CH ₃ (NH ₂)C ₆ H ₄ FeCp ⁺ PF ₆ ⁻ (VIPF ₆)	55	38.62(38.63)	3.86(3.78)	3.60(3.75)	4.9(s)(5 H)	5.8-6.2(m)(4 H)	5.8(broad s)(2 H)	2.5(s)(3 H)		
<i>p</i> -CH ₃ (NH ₂)C ₆ H ₄ FeCp ⁺ PF ₆ ⁻ (VIIPF ₆)	58	38.90(38.63)	3.70(3.78)	3.60(3.75)	4.9(s)(5 H)	5.8-6.2(m)(4 H)	5.5(broad s)(2 H)	2.4(s)(3 H)		

TABLE 2

DATA ON THE PRODUCTS FROM REACTIONS OF THE ZWITTERIONIC SPECIES FROM DEPROTONATION OF η^6 -ANILINE- η^5 -CYCLOPENTADIENYL-IRON CATION(II) WITH VARIOUS REACTANTS

Reactant	Product	Yield (%)	Analysis found(calcd.) (%)				$^1\text{H NMR}(\delta(\text{acetone-}d_6))$ ppm from TMS			
			C	H	N	Cp	Aromatic	Others		
CH ₃ I	C ₆ H ₅ N(CH ₃) ₂ FeCp ⁺ PF ₆ ⁻	83	40.81(40.33)	4.25(4.17)	3.50(3.62)	5.1(s)(5 H)	5.8-6.3(m)(5 H)	3.2(s)(6 H)CH ₃		
CS ₂	C ₆ H ₅ N=C(SCH ₃) ₂ FeCp ⁺ PF ₆ ⁻	44	36.55(36.30)	3.39(3.48)	3.10(3.02)	5.2(s)(5 H)	6.2-6.5(m)(5 H)	2.5(s)(6 H)CH ₃ ^a		
CH ₃ COCl	C ₆ H ₅ NHCOCH ₃ FeCp ⁺ PF ₆ ⁻	82	38.66(38.93)	3.42(3.52)	3.55(3.49)	5.1(s)(5 H)	6.3-6.9(m)(5 H)	2.2(s)(3 H)CH ₃ ^b		
C ₂ H ₅ COCl	C ₆ H ₅ NHCOC ₂ H ₅ FeCp ⁺ PF ₆ ⁻	63	40.15(40.50)	3.92(3.89)	3.40(3.37)	5.1(s)(5 H)	6.3-7.0(m)(5 H)	2.5(s)(2 H)CH ₂ ^b		
C ₆ H ₅ COCl	C ₆ H ₅ NHCOCC ₆ H ₅ FeCp ⁺ PF ₆ ⁻	79	46.82(46.68)	3.45(3.48)	3.10(3.02)	5.1(s)(5 H)	7.5-8.1(m)(5 H)	1.2(c)(3 H)CH ₃ ^b		

^a Additional confirmation from $^{13}\text{C NMR}$ showing C=N absorption at 171.4 ppm and SCH₃ absorption at 13.5 ppm. ^b The $^1\text{H NMR}$ absorption for the amide proton would appear farther downfield than was recorded. Confirmation of the amide structure in this type of complexes in Tables 2-5 was obtained from their IR spectra, which showed NH and C=O absorptions at 3300-3400 and 1650-1700 cm⁻¹, respectively.

TABLE 3

DATA ON THE PRODUCTS FROM REACTIONS OF THE ZWITTERIONIC SPECIES FROM DEPROTONATION OF η^6 -o-TOLUIDINE- η^5 -CYCLOPENTADIENYLIRON CATION (V) WITH VARIOUS REACTANTS

Reactant	Product	Yield (%)	Analysis found(calcd.) (%)				^1H NMR (δ (acetone- d_6) ppm from TMS)			
			C	H	N	Cp	Aromatic	Others		
CH_3I	$\text{o-CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{FeCp}^+\text{PF}_6^-$	73	42.08(41.92)	4.54(4.52)	3.61(3.49)	5.0(s)(5 H)	5.7-6.2(m)(4 H)	3.0(s)(3 H)NCH ₃		
CS_2	$\text{o-CH}_3\text{C}_6\text{H}_4\text{N}=\text{C}(\text{SCH}_3)_2\text{FeCp}^+\text{PF}_6^-$	49	38.11(37.75)	3.97(3.80)	2.91(2.94)	5.0(s)(5 H)	6.1-6.4(m)(4 H)	2.6(s)(3 H)ArCH ₃		
CH_3COCl	$\text{o-CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_3\text{FeCp}^+\text{PF}_6^-$	54	40.45(40.50)	3.98(3.89)	3.41(3.38)	5.1(s)(5 H)	6.2-7.1(m)(4 H)	2.4(s)(3 H)ArCH ₃ ^a		
$\text{C}_2\text{H}_5\text{COCl}$	$\text{o-CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_2\text{H}_5\text{FeCp}^+\text{PF}_6^-$	68	42.15(41.98)	4.20(4.23)	3.30(3.26)	5.0(s)(5 H)	5.7-6.2(m)(4 H)	2.2(s)(3 H)COCH ₃ ^b		
								2.5(s)(3 H)ArCH ₃ ^b		
								2.1(q)(2 H)CH ₂ , 1.2(t)(3 H)CH ₃		
$\text{C}_6\text{H}_5\text{COCl}$	$\text{o-CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_2\text{H}_5\text{FeCp}^+\text{PF}_6^-$	48	47.76(47.82)	2.78(3.80)	2.95(2.94)	5.1(s)(5 H)	6.0-6.4(m)(4 H)	2.5(s)(3 H)ArCH ₃ ^b		
							7.0-8.0(m)(5 H)	2.5(s)(3 H)ArCH ₃ ^b		

^a Additional confirmation from ^{13}C NMR showing C=N, ArCH₃, and SCH₃ absorptions at 171.0, 15.7 and 13.5 ppm, respectively. ^b See footnote b of Table 2.

TABLE 4

DATA ON THE PRODUCTS FROM REACTIONS OF THE ZWITTERIONIC SPECIES FROM DEPROTONATION OF η^6 -m-TOLUIDINE- η^5 -CYCLOPENTADIENYLIRON CATION (VI) WITH VARIOUS REACTANTS

Reactant	Product	Yield (%)	Analysis found(calcd.) (%)				^1H NMR (δ (acetone- d_6) ppm from TMS)			
			C	H	N	Cp	Aromatic	Others		
CH_3I	$\text{m-CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{FeCp}^+\text{PF}_6^-$	69	41.85(41.92)	4.50(4.52)	3.55(3.49)	4.8(s)(5 H)	5.5-5.9(m)(4 H)	3.1(s)(6 H)NCH ₃		
CS_2	$\text{m-CH}_3\text{C}_6\text{H}_4\text{N}=\text{C}(\text{SCH}_3)_2\text{FeCp}^+\text{PF}_6^-$	51	38.04(37.75)	3.79(3.80)	2.88(2.94)	5.1(s)(5 H)	6.1-6.5(m)(4 H)	2.4(s)(3 H)ArCH ₃		
CH_3COCl	$\text{m-CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_3\text{FeCp}^+\text{PF}_6^-$	66	40.52(40.50)	3.97(3.89)	3.40(3.38)	5.2(s)(5 H)	6.2-7.0(m)(4 H)	2.6(s)(9 H)SCH ₃ , ArCH ₃ ^a		
$\text{C}_2\text{H}_5\text{COCl}$	$\text{m-CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_2\text{H}_5\text{FeCp}^+\text{PF}_6^-$	62	42.10(41.98)	4.20(4.23)	3.30(3.26)	5.2(s)(5 H)	6.2-7.0(m)(4 H)	2.5(s)(3 H)ArCH ₃ ^b		
								2.2(s)(3 H)COCH ₃ ^b		
								2.5(s)(3 H)ArCH ₃ ^b		
$\text{C}_6\text{H}_5\text{COCl}$	$\text{m-CH}_3\text{C}_6\text{H}_4\text{CHCOCH}_2\text{H}_5\text{FeCp}^+\text{PF}_6^-$	58	47.90(47.82)	3.69(3.80)	2.99(2.94)	5.2(s)(5 H)	6.3-7.1(m)(4 H)	1.2(t)(2 H)CH ₂		
							7.5-8.2(m)(5 H)	2.7(s)(3 H)ArCH ₃ ^b		

^a Additional confirmation from ^{13}C NMR showing C=N, ArCH₃ and SCH₃ absorptions at 171.2, 18.6 and 13.6 ppm, respectively. ^b See footnote b of Table 2.

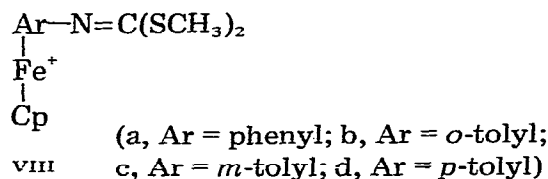
TABLE 5
DATA ON THE PRODUCTS FROM REACTIONS OF THE ZWITTERIONIC SPECIES FROM DEPROTONATION OF η^6 -*p*-TOLUIDINE- η^5 -CYCLOPENTA-DIENYLIRON CATION (VII) WITH VARIOUS REACTANTS

Reactant	Product	Yield (%)	Analysis found (calcd.) (%)			^1H NMR (δ (acetone- d_6) ppm from TMS)			
			C	H	N	Cp	Aromatic	Others	
CH_3I	$p\text{-CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{FeCp}^+\text{PF}_6^-$	79	40.08(41.92)	4.43(4.52)	3.37(3.49)	5.0(s)(5 H)	5.8(d)(2 H), 6.1(d)(2 H)	3.1(s)(6 H)NCH ₃ 2.4(s)(3 H)ArCH ₃	
CS_2	$p\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{C}(\text{SCH}_3)_2\text{FeCp}^+\text{PF}_6^-$	40	38.10(37.75)	3.95(3.80)	2.90(2.94)	5.2(s)(5 H)	6.3–6.6(m)(4 H)	2.6(s)(6 H)SCH ₃ 2.5(s)(3 H)ArCH ₃ ^a	
CH_3COCl	$p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCOCCH}_3\text{FeCp}^+\text{PF}_6^-$	48	40.65(40.50)	4.01(3.89)	3.35(3.38)	5.1(s)(5 H)	6.4(d)(2 H), 6.8(d)(2 H)	2.5(s)(3 H)ArCH ₃ 2.2(s)(3 H)COCH ₃ ^b	
$\text{C}_2\text{H}_5\text{COCl}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCOC}_2\text{H}_5\text{FeCp}^+\text{PF}_6^-$	61	42.00(41.98)	4.13(4.23)	3.38(3.26)	5.1(s)(5 H)	6.4(d)(2 H), 6.9(d)(2 H)	2.5(s)(3 H)ArCH ₃ 2.5(n)(2 H)CH ₂ , 2.2(t)(3 H)CH ₃ ^b	
$\text{C}_6\text{H}_5\text{COCl}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCOC}_6\text{H}_5\text{FeCp}^+\text{PF}_6^-$	85	47.27(47.82)	4.14(3.80)	2.90(2.94)	5.1(s)(5 H)	6.4(d)(2 H), 7.0(d)(2 H) 7.4–8.2(m)(5 H)	2.5(s)(3 H)ArCH ₃ ^b	

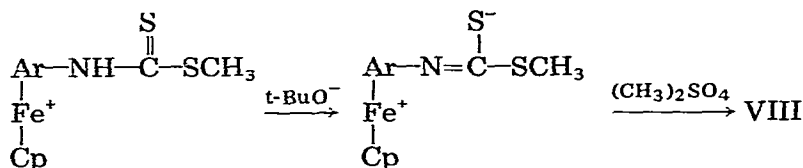
^a Additional confirmation from ^{13}C NMR showing C=N, ArCH₃ and SCH₃ absorptions at 172.1, 19.2 and 14.5 ppm, respectively. ^b See footnote b of Table 2.

with an excess of CH_3I , gave the corresponding *N,N*-dimethylated complex, indicating that the deprotonation took place solely from the amino group. Two molar equivalents of *t*-BuOK were used in each reaction to ensure dimethylation. If only one equivalent of base was used, an impure product would result, presumably because of the occurrence of both mono- and dimethylation. With the aniline complex II, a similar dimethylation was also effected by reaction with CH_3I after deprotonation with 2 equivalents of *t*-BuOK in THF, instead of using an excess of NaNH_2 in CH_2Cl_2 [4]. The results from these reactions are given in Tables 2–5.

In the earlier study on deprotonation from the α -carbon of η^6 -arene- η^5 -cyclopentadienyliron cations, one of the reactions investigated was that between the zwitterionic species and CS_2 , which, after treatment with $(\text{CH}_3)_2\text{SO}_4$, gave the η^6 -2-aryl-1,1-bis(methylthio)ethene- η^5 -cyclopentadienyliron cation as the final product [3]. An analogous reaction after deprotonation from the amino group would give the η^6 -*N*-aryl-bis(methylthio)methanimine- η^5 -cyclopentadienyliron cation (VIII). Since the uncomplexed bis(alkylthio)methanimino(bis(alkylthio)methyleneamino) group, $(\text{RS})_2\text{C}=\text{N}$, has been shown to be useful in further reactions with synthetic applications [9], we have included the reaction with CS_2 in the present study. Deprotonation of cations II, V, VI and VII with excess *t*-BuOK in THF followed by treatment with CS_2 and then with $(\text{CH}_3)_2\text{SO}_4$ indeed gave the expected bis(methylthio)methanimine complexes VIIIa–d, respectively. The formation of VIII apparently resulted from a base-

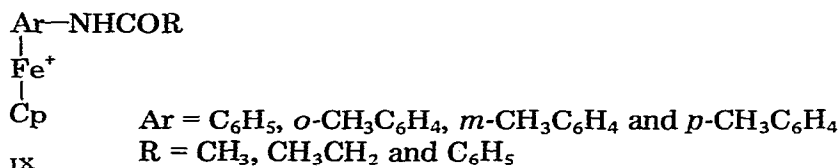


catalyzed enolization type of reaction in the initially formed dithiocarbamate complex, followed by a second methylation with $(\text{CH}_3)_2\text{SO}_4$:



The relevant data from the preparation of cations VIIIa–d are also given in Tables 2–5.

Besides the nucleophilic reactions with CH_3I and with CS_2 as described above, we have also shown that the zwitterions from deprotonation of cations II, V, VI and VII can be acylated to give various amide type of complexes. In the present work, acylation reactions were carried out using acetyl, propionyl and benzoyl chlorides, giving rise to a total of 12 amide type of complexes represented by structure IX. Except for the one case of the η^6 -acetanilide- η^5 -cyclopentadienyliron cation, which has been prepared by Nesmeyanov et al. [6], these amide complexes have not been reported previously. Again the pertinent data from these preparations are included in Tables 2–5.



The results from the present work definitely show that if an amino group and a methyl substituent are both present in the arene ligand of an η^6 -arene- η^5 -cyclopentadienyliron cation, deprotonation with base takes place exclusively at the amino group. Since N is more electronegative than C, the acidity of an amino H is greater than that of an alkyl H [10], and the preferential deprotonation observed is in agreement with what might be expected. It is, however, of interest to have shown that in the various reactions using the zwitterionic species as nucleophiles, pure products were obtained rather than mixtures that might have been formed if deprotonation were to occur at both C and N. The present work and our earlier studies [3] together with the work of Helling and Hendrickson on the alkylation of the amino, hydroxy and mercapto substituents [4] thus provide a general and useful procedure for effecting modifications on the structure of the arene ligand in η^6 -arene- η^5 -cyclopentadienyliron cationic type of complexes.

Experimental

η^6 -*o*-, *m*- or *p*-Toluidine- η^5 -cyclopentadienyliron hexafluorophosphate (V-PF₆, VI-PF₆ or VII-PF₆)

A mixture of 4.3 g (40 mmol) of *o*-, *m*- or *p*-toluidine, 7.4 g (40 mmol) of ferrocene, 21.4 g (160 mmol) of AlCl₃ and 1.1 g (40 mmol) of Al powder in 60 ml of decalin was heated with stirring and under N₂ for 5 h at 160 ± 5°C. The resulting material was cooled and then poured into 300 ml of ice-H₂O. After stirring for about 20 min to disperse any pasty material, any solid remaining was removed by vacuum filtration. The filtrate was washed three times with ether and then a concentrated aqueous solution of NH₄PF₆ was added. The precipitated crude product was collected by filtration, washed with H₂O and redissolved in CH₂Cl₂. After drying over MgSO₄, the CH₂Cl₂ was evaporated off, and the residual product was recrystallized from acetone-ether. The yields and other analytical data for the three products are given in Table 1.

Zwitterionic species from deprotonation and their reactions as nucleophiles

The η^6 -aniline- η^5 -cyclopentadienyliron cation (II) and the three toluidine complexes, V, VI and VII, as their hexafluorophosphate salts, were deprotonated by treatment with *t*-BuOK in THF. The resulting zwitterionic products were used *in situ* as nucleophiles in reactions with CH₃I, CS₂, CH₃COCl, C₂H₅CoCl and C₆H₅COCl. The results are summarized in Table 2–5. Some typical experimental procedures are given below.

η^6 -*N,N*-Dimethylaniline- η^5 -cyclopentadienyliron hexafluorophosphate (III-PF₆)

To a suspension of 0.72 g (2.0 mmol) of η^6 -aniline- η^5 -cyclopentadienyliron hexafluorophosphate (II-PF₆) in 30 ml of dry THF, under N₂ and at room tem-

perature, 0.45 g (4.0 mmol) of *t*-BuOK was added. A deep red color developed immediately. The mixture was stirred for 5 min and then an excess of CH₃I (2.0 ml, 32 mmol) was introduced. Stirring was continued for 2 h and the color changed gradually to orange. A concentrated solution of NH₄PF₆ was added and the resulting material was extracted with CH₂Cl₂. The extract was dried over MgSO₄, concentrated, and upon addition of ether, 0.64 g (83%) of product was precipitated.

η⁶-N-o-tolyl-bis(methylthio)methanimine-η⁵-cyclopentadienyliron hexafluorophosphate (VIIa-PF₆)

To a suspension of 0.75 g (2.0 mmol) of *η⁶-o-toluidine-η⁵-cyclopentadienyliron hexafluorophosphate* (VPF₆) in 35 ml of dry THF, under N₂ and at room temperature, 0.60 g (5.4 mmol) of *t*-BuOK was added. A deep red color developed immediately, and after 5 min of stirring, the mixture was treated with 2.0 ml (33 mmol) of CS₂. Stirring was continued for 2 h, and the resulting orange suspension, 4.0 ml (21 mmol) of (CH₃)₂SO₄ was introduced. The mixture was stirred at room temperature for an additional 2 h and then a concentrated solution of NH₄PF₆ was added. The mixture was extracted with CH₂Cl₂ and the extract was dried over MgSO₄, concentrated and purified by passage through an alumina column (activated alumina F-20, Sargent-Welch Scientific Co.) with elution by acetone. The eluate was concentrated and upon addition of ether, 0.47 g (49%) of product was obtained.

η⁶-acetanilide-η⁵-cyclopentadienyliron hexafluorophosphate

To a suspension of 0.72 g (2.0 mmol) of *η⁶-aniline-η⁵-cyclopentadienyliron hexafluorophosphate* (II-PF₆) in 30 ml of dry THF, under N₂ and at room temperature, 0.24 g (2.1 mmol) of *t*-BuOK was added. A deep red color developed immediately, and after the mixture was stirred for 5 min, 2.0 ml (28 mmol) of acetyl chloride was introduced. Stirring was continued for 2 h and the color changed gradually to yellow. (When the acylation was carried out with propionyl or benzoyl chloride, 5 h of stirring was needed.) A concentrated solution of NH₄PF₆ was added and the mixture was extracted with CH₂Cl₂. The extract was dried over MgSO₄, concentrated and the product precipitated by the addition of ether. The yield was 0.66 g (82%).

Acknowledgement

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