

### Preliminary communication

## SYNTHESIS AND CHARACTERIZATION OF $C_5(CH_3)_5Fe(CO)_3^+PF_6^-$ AND $C_5(CH_3)_5Fe(CO)_2^-K^+$

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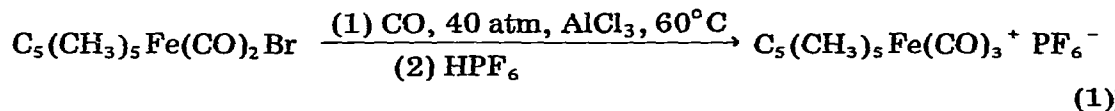
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### Summary

$C_5(CH_3)_5Fe(CO)_3^+PF_6^-$  is obtained in 67% yield by reaction of  $C_5(CH_3)_5Fe(CO)_2Br$  with  $AlCl_3$  at  $60^\circ C$  under a 40-atm CO pressure.  $\{C_5(CH_3)_5Fe(CO)_2\}_2$  does not react with  $Na/Hg$ , but a 2 h reduction on K mirror in THF at  $20^\circ C$  provides  $C_5(CH_3)_5Fe(CO)_2^-K^+$ , which can be alkylated by  $CH_3I$  to give  $C_5(CH_3)_5Fe(CO)_2CH_3$  in 80% overall yield.

Despite the utility of the  $C_5(CH_3)_5(Cp')$  ligand [1], its only iron complexes reported are  $Cp'_2Fe$ ,  $Cp'_2Fe_2(CO)_4(Fp'_2)^*$  [2] and some of the  $Cp'Fe$  arene series [3]. Much work has been carried out with the  $Fp$  series [4], starting from  $Fp^-$  [4] or  $Fp(CO)^+$  [5] and we now report the synthesis and characterization of  $Fp'^-K^+$  and  $Fp'(CO)^+PF_6^-$ .

The most convenient route to  $FpCO^+$  is probably the ligand exchange between ferrocene and CO in the presence of  $AlCl_3$  [6]. However, this method does not apply to  $Fp'CO^+$  because of the inertness of  $Cp'_2Fe$  toward cleavage [7].  $Fp'(CO)^+PF_6^-$  is easily obtained using the original Fischer-type synthesis from  $Fp'Br$ , under CO pressure, and  $AlCl_3$  [8] (eq. 1).



Typically 3.27 g of  $Fp'Br$  (10 mmol) and 4 g of  $AlCl_3$  (30 mmol) are suspended in 150 ml of heptane and a 40-atm CO pressure is admitted to the autoclave. The best yields are obtained at  $60-80^\circ C$ . After reaction overnight, the autoclave is cooled down and the mixture hydrolyzed with 150 ml of

\* $Fp = C_5H_5Fe(CO)_2 \cdot Fp = C_5(CH_3)_5Fe(CO)_2$ .

ice water. To the aqueous layer containing the soluble salt  $\text{Fp}'\text{CO}^+ \text{Cl}^-$  is added 2 ml of 5 N  $\text{HPF}_6$ , which causes  $\text{Fp}'\text{CO}^+ \text{PF}_6^-$  to precipitate. This salt is filtered off, dissolved in acetone, reprecipitated by ether and recrystallized from 1/2 acetone/ethanol, which gives light yellow needles (2.80 g, 67% yield). Yields are  $66 \pm 1\%$  for reaction temperatures of 60–80°C and 50% at 110°C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ).  $\delta$  2.25 ppm ( $\text{Me}_4\text{Si}$ ). Other spectroscopic data for  $\text{FpCO}^+ \text{PF}_6^-$  and  $\text{Fp}'\text{CO}^+ \text{PF}_6^-$  are given in Table 1. Analysis Found C, 37.35; H, 3.46; Fe, 13.24.  $\text{C}_{13}\text{H}_{15}\text{O}_3\text{FePF}_6$  calcd: C, 37.17; H, 3.60; Fe, 13.29%

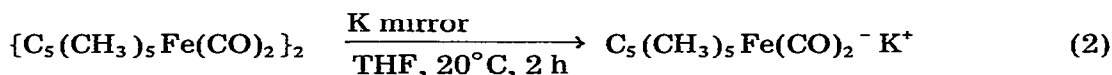
TABLE 1

SPECTROSCOPIC DATA FOR  $\text{FpCO}^+ \text{PF}_6^-$  AND  $\text{Fp}'\text{CO}^+ \text{PF}_6^-$ 

	IR $\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) Nujol	$^{13}\text{C}$ NMR $\delta$ (ppm)			Mössbauer ( $\text{mm s}^{-1}$ ) 77 K	
		$\text{CD}_3\text{CN}$	$\text{Me}_4\text{Si}$		IS (vs Fe)	QS
$\text{Fp}(\text{CO})^+ \text{PF}_6^-$	2072, 2135 <sup>a</sup>	203.2 <sup>c</sup>	91.1 <sup>c</sup>		0.08 <sup>b</sup>	1.88 <sup>b</sup>
$\text{Fp}'(\text{CO})^+ \text{PF}_6^-$	2078, 2130	206.3	105.21	9.86	0.08	1.85

<sup>a</sup> Ref. 6 and 8 <sup>b</sup> Ref. 9. <sup>c</sup> This work

Although  $\text{Fp}^-$  can be produced inter alia by Na/Hg reduction of  $\text{Fp}_2$  [10], this is not the case for  $\text{Fp}'_2$  because of its insolubility and its very negative reduction potential ( $E_{1/2} = -1.80$  V/SCE in DMF +  $\text{Bu}_4\text{N}^+\text{Br}^-$ , i.e. 0.36 V more negative than that for  $\text{Fp}_2$ ). Good results are obtained only by a 2 h reduction of  $\text{Fp}'_2$  in THF with a K mirror (eq. 2)



Since no significant color change (dark brown purple) can be observed, and in view of the extreme air sensitivity of  $\text{Fp}'^- \text{K}^+$ , the reduction kinetics are best followed by TLC analysis of samples of the reaction mixture quenched with  $\text{CH}_3\text{I}$  (which gives  $\text{Fp}'\text{CH}_3$ ). The THF solution of  $\text{Fp}'^- \text{K}^+$  is filtered through a filter stick and evaporated to dryness (85% crude yield).  $\text{Fp}'^- \text{K}^+$  is insoluble in  $\text{CH}_3\text{CN}$  and was not recrystallized. Its purity is shown by the presence of only two IR stretches in the CO region of the IR spectrum and a clean Mössbauer doublet (compare  $\text{Fp}^- \text{K}^+$  (or  $\text{Na}^+$ ) and  $\text{Fp}'^- \text{K}^+$  in Table 2).

On a 10 mmol scale, addition of  $\text{CH}_3\text{I}$  to a THF solution of  $\text{Fp}'^- \text{K}^+$  at 20°C affords, after removal of THF in vacuo and sublimation (70°C, 1 mmHg), 4.2 g

TABLE 2

IR AND MÖSSBAUER DATA FOR  $\text{Fp}'^- \text{K}^+$ 

	IR $\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	Mössbauer <sup>c</sup> ( $\text{mm s}^{-1}$ ), 77 K	
		IS (vs Fe)	QS
$\text{Fp}^- \text{M}^+$	1868, 1792, 1772, ( $\text{K}^+$ , THF) <sup>a</sup> 1880, 1735 ( $\text{K}^+$ , Nujol) <sup>b</sup>	$\text{Na}^+$ 0.11	2.06
$\text{Fp}'^- \text{K}^+$	1985, 1845 (THF)	0.11	2.00

<sup>a</sup> Splitting of asymmetric CO stretch of  $\text{Fp}^- \text{K}^+$  was observed in THF and attributed to ion pair formation, see ref. 11 <sup>b</sup> Ref. 12. <sup>c</sup> This work.

(16 mmol) of  $\text{Fp}'\text{CH}_3$  (80% yield from  $\text{Fp}'_2$ ) as yellow crystals. Analysis Found: C, 59.65; H, 7.02; Fe, 21.38.  $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Fe}$  calcd.. C, 59.57; H, 6.92; Fe, 21.30%. IR  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ): 1985 and 2040; NMR ( $\delta$  (ppm),  $\text{Me}_4\text{Si}$ )  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ ) 0.08 (s,  $\text{CH}_3\text{Fe}$ ); 1.45 (s,  $\text{CH}_3\text{Cp}$ ),  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $-13.1$  ( $\text{CH}_3\text{Fe}$ ); 9.2 ( $\text{CH}_3\text{Cp}$ ); 105.2 ( $\text{Cp}'$ ); 219.5 (CO). Mössbauer (77 K,  $\text{mm s}^{-1}$ ):  $IS = 0.12$ ;  $QS = 1.88$ .

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