Supporting Information

NMR Data

Table S 1. ^{1}H NMR shift assignments[a] for the $[(\eta^5\text{-}C_6H_7)Fe(\eta^6\text{-}Me_nC_6H_{6-n}]PF_6$ (**1**$^+$) salts

n	H(3)	arene H	H(2,4)	H(1,5)	arene Me	H(6)[b]
0	7.11	6.41(6)	4.95(2)	3.55(2)	-	2.83[c]
bz						1.07[d]
1	7.06	6.39(2)	4.93(2)	3.45(2)	2.48(3)	2.83[c]
tol		6.35(3)				1.09[d]
2	6.96	6.34	4.88(2)	3.31(2)	2.45(6)	2.81[c]
m-xyl		6.28				1.08[d]
		6.24(2)				
3	6.85	6.17(3)	4.83(2)	3.15(2)	2.44(9)	2.80[c]
mes						1.08[d]
4	6.78	6.14(2)	4.72(2)	3.04(2)	2.43(12)	2.77[c]
dur						1.05[d]
5	6.67	6.14	4.61(2)	2.87(2)	2.44(9)	2.71[c]
pmb					2.42(6)	1.01[d]
6	6.56	-	4.50(2)	2.72(2)	2.46(18)	2.65[c]
hmb						0.96[d]

[a] Measured in acetone-d_6, relative intensities higher than 1 in parentheses.
[b] Signals of the *exo*- and *endo*-component of the C(6)H_2 group, respectively.
[c] Multiplet. [d] Doublet $^1J_{H\text{-}H}$ ~ 12-15 Hz

Table S2. ^{1}H NMR shift assignments[a] for the $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}Me_nC_6H_{6-n}]PF_6$ (**2**$^+$) salts

***n* arene**	**arene H**	**Cp**	**arene Me**
0 bz	6.50(6)	5.25(5)	-
1 tol	6.41(5)	5.18(5)	2.57(3)
2 m-xyl	6.35	5.11(5)	2.53(6)
	6.31(3)		
3 mes	6.26(3)	5.04(5)	2.51(9)
4 dur	6.31(2)	4.97(5)	2.51(12)
5 pmb	6.25	4.86(5)	2.58(3)
			2.42(12)
6 hmb	-	4.78(5)	2.59(18)

[a] Measured in acetone-d_6, relative intensities higher than 1 in parentheses.
[b] Signals of the *exo*- and *endo*-component of the C(6)H_2 group, respectively.
[c] Multiplet. [d] Doublet $^1J_{H\text{-}H}$ ~ 12-15 Hz

Table S3. ^{13}C NMR shift assignments[a] for the $[(\eta^5\text{-}C_6H_7)Fe(\eta^6\text{-}Me_nC_6H_{6-n}]PF_6$ (**1**$^+$) salts

n	arene C	C(2,4)	C(3)	C(1,5)	C(6)	arene Me
0	91.6	86.4	85.9	40.3	24.6	-
bz						
1	106.7	86.9	85.9	40.5	24.6	20.0
tol	92.2 (2)					
	91.2 (2)					
	89.7 (1)					
2	106.3 (2)	87.2	86.0	40.8	24.5	19.8
***m*-xyl**	93.1					
	90.7					
	90.2 (2)					
3	105.8 (3)	87.7	86.1	41.1	24.5	19.7
mes	91.2 (3)					
4	103.7 (4)	88.3	86.0	40.9	24.2	17.7
dur	93.6 (2)					
5	103.7	88.7	86.0	40.9	23.9	19.1(2)
pmb	103.0(2)					16.1(2)
	102.9(2)					15.6
	92.7					
6	102.3 (6)	89.3	86.1	41.0	23.7	16.7
hmb						

[a] Measured in acetone-d_6, relative intensities higher than 1 in parentheses

Table S4. ^{13}C NMR shift assignments[a] for the $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}Me_nC_6H_{6-n}]PF_6$ (**2**$^+$) salts

n	**arene C**	**Cp C**	**arene Me**
0 bz	89.4(6)	77.6(5)	-
1 tol	104.8	77.9(5)	20.9
	89.8(2)		
	88.7(2)		
	87.5		
2 *m*-xyl	104.2 (2)	78.2(5)	20.7(2)
	90.6		
	88.0		
	87.8(2)		
3 mes	103.4(3)	78.5(5)	20.5(3)
	88.6(3)		
4 dur	101.3(4)	78.8(5)	18.7(4)
	90.9 (2)		
5 pmb	101.2	79.0(5)	20.0(2)
	100.5(2)		17.0
	100.3(2)		16.5(2)
	89.7		
6 hmb	99.7 (6)	79.3(5)	17.6(6)

[a] Measured in acetone-d_6, relative intensities higher than 1 in parentheses