Organometallics 1994, 13, 2890–2894

Electronic Effects of Arene Substituents in (η^6-Arene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphates[1]

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Received February 4, 1994[●]

$Fe(2p_{3/2})$ core electron binding energies were determined using X-ray photoelectron spectroscopy for a series of 20 $[(\eta^6\text{-arene})Fe(\eta^5\text{-}C_5H_5)]^+PF_6^-$ complexes, including two previously unreported examples. An orderly change in $Fe(2p_{3/2})$ binding energy was observed with increased substitution by chloro, methoxy, dimethylamino, and methyl substituents. Trends in $Fe(2p_{3/2})$ data demonstrate that the average electron-withdrawing ability of arene substituents decreases according to the series $NO_2 > COOCH_3 \approx CN > Cl$; average electron-releasing ability decreases according to the series $N(CH_3)_2 > OCH_3 \approx C_6H_5 > CH_3$. $Fe(2p_{3/2})$ values showed that the η^6-naphthalene ligand is approximately as electron-donating as tetramethylbenzene. A correlation of $Fe(2p_{3/2})$ values with $\delta(C_5H_5)$ determined by ^1H NMR is also presented.

Introduction

Because core orbitals are entirely atom-centered, metal core electron binding energies (CBEs), determined by X-ray photoelectron spectroscopy (XPS or ESCA), provide a direct experimental probe of substituent influences on coordinated metal atoms. A quantitative basis for understanding the relative electronic effects of substituents such as methyl, chloro, trifluoromethyl, trimethylsilyl, and benzo ring fusion in transition metal η^5-cyclopentadienyl complexes has already been established through the evaluation of CBEs.[3,4] Prompted by the isoelectronic relationship between η^5-C_5H_5 (Cp) and η^6-C_6H_6, we report herein efforts to expand our investigation to include η^6-arene complexes. The (η^6-arene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphates were a natural choice for CBE determination by XPS for three reasons. First, several (η^6-arene)$FeCp^+PF_6^-$ complexes with a wide range of electron-withdrawing and electron-releasing substituents are already available *via* published synthetic procedures. Second, the hexafluorophosphate salts are nonvolatile and largely stable to air and moisture, which makes ultrahigh-vacuum surface spectroscopic analysis of thin films of these substances more convenient and reliable. Third, $Fe(2p_{3/2})$ XPS signals are generally strong and sharp; the smaller $Fe(2p_{1/2})$ signals are well separated, which simplifies the mathematical regression of XPS spectra.

Throughout our XPS studies, we have provided supporting evidence for our conclusions in the form of electrochemical,[4a,f] structural,[4f,g] and spectroscopic[4b,h] data. In the present work, the $Fe(2p_{3/2})$ binding energies of (η^6-arene)$FeCp^+PF_6^-$ complexes are correlated with the ^1H NMR chemical shift of the η^5-C_5H_5 ligand, denoted $\delta(^1H)_{Cp}$.[5] Early fragmentary correlations of $\delta(^1H)_{Cp}$ with η^6-arene substituent effects[6] prompted us to consider this technique as a way to compare direct measurement of electron-richness at the metal center with electronic effects transmitted through coordinated metal fragments to ancillary ligands.[4g,h,6,7]

Experimental Section

General Considerations. Solvents and starting materials were purified by accepted procedures.[8] Infrared spectra were recorded on a Mattson Polaris FT-IR. Proton NMR spectra were recorded using an instrument operating at 200 MHz or higher; all ^{13}C NMR spectra are ^1H decoupled. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory (Herlev, Denmark).

XPS Experiments. X-ray photoelectron (XPS) spectra were recorded on a Physical Electronics Industries Model 548 spec-

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[†] Deceased April 21, 1993.

[●] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

(1) Part of this work has been presented orally: Deck, P. A.; Gassman, P. G. 201st National Meeting of the American Chemical Society, Atlanta, GA, Spring 1991; see Abstract INOR 398.

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0276-7333/94/2313-2890$04.50/0

trometer using Mg Kα X-radiation. Spectra were acquired at room temperature at a pressure of approximately 5 × 10^{-9} Torr. Under a nitrogen atmosphere, samples were mounted on polyethylene-coated aluminum wafers by evaporation of acetone solutions.[9] High-resolution (pass energy = 25 eV) data in the Fe($2p_{3/2}$) region were treated with a sigmoidal baseline correction[10] and fitted to a least-squares optimized[11] model function.[11a] The Fe($2p_{3/2}$) binding energies were corrected for static charging by using the C(1s) signal, arising primarily from the polyethylene substratum, as an internal standard, defined at 284.60 eV. The overall binding energy scale was externally calibrated against the Au($4f_{7/2}$) and the Cu($2p_{3/2}$) signals obtained using Ar$^+$-sputtered pure metal foils.[12]

Procedures and Analytical Data. Except where indicated otherwise, the previously reported (η^6-arene)FeCp$^+$PF$_6^-$ complexes were prepared by a general procedure.[13] Spectral data for analytical samples are provided because these data are often absent from earlier published work.

(η^6-Benzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (1).[14] Yellow-green flakes from dichloromethane: mp 250–270 °C dec; IR (KBr) 3126, 3106, 1449, 1421, 1012, 926, 831 s, 779, 557, 484, 468 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.49 (s, 6 H), 5.24 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 89.0, 77.3.

(η^6-Methylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (2). Yellow-green flakes from 1,2-dichloroethane: mp (sealed capillary) 240–250 °C dec (lit.[14] mp 265 °C dec); IR (KBr) 3130, 1466, 1421, 1391, 1044, 1012, 830, 557, 449, 471 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.37 (br s, 5 H), 5.15 (s, 5 H), 2.54 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 104.7, 89.5, 88.5, 87.3, 77.7, 20.7.

(η^6-1,2-Dimethylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (3).[14] Golden yellow flakes from aqueous acetone: mp (sealed capillary) 218–222 °C dec (lit.[14] mp 225 °C dec); IR (KBr) 3115, 2925, 1491, 1471, 1458, 1421, 1395, 1386, 1115, 1035, 1012, 834, 558, 500, 464, 450 cm^{-1}; ^{1}H NMR δ 6.35 (m, 2 H), 5.27 (m, 2 H), 5.08 (s, 5 H), 2.55 (s, 6 H); ^{13}C NMR δ 103.5, 89.8, 87.1, 77.9.

(η^6-1,4-Dimethylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (4).[14] Yellow flakes from aqueous acetone: mp (sealed capillary) 190–200 °C dec (lit.[14] mp 240 °C dec); IR (KBr) 3120, 2927, 1486, 1459, 1421, 1391, 1115, 1044, 833, 557, 473 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.32 (s, 4 H), 5.11 (s, 5 H), 2.51 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 102.9, 88.9, 78.1, 20.3.

(η^6-1,3,5-Trimethylbenzene)(η^5-cyclopentadineyl)iron(II) Hexafluorophosphate (5).[14] Green crystals from dichloromethane/acetone: mp 205–215 °C dec (lit.[14] mp 260 °C dec); IR (KBr) 3120, 2938, 1540, 1461, 1421, 1386, 1310, 1044, 1012, 837, 557, 511, 493, 463 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.23 (s, 3 H), 5.02 (s, 5 H), 2.49 (s, 9 H); ^{13}C NMR (acetone-d_6) δ 103.3, 88.4, 78.3, 20.3.

(η^6-1,2,3,4-Tetramethylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (6). According to a general procedure,[13] ferrocene (1.0 g), 1,2,3,4-tetramethylbenzene (30 mL), aluminum chloride (3.0 g), and aluminum powder (500 mg) were heated under nitrogen with mechanical stirring for 100 min; workup[13] gave 1.04 g (50%) of a yellow solid. Recrystallization from aqueous acetone afford bronze flakes: mp (sealed capillary) 240 °C dec; IR (KBr) 3116, 2930, 1462, 1420, 1392, 1112, 1078, 1029, 1012, 870, 839, 558, 500, 487, 477, 456 cm^{-1}; ^{1}H NMR (aceton-d_6) δ 6.20 (s, 2 H), 4.94 (s, 5 H), 2.55 (s, 3 H), 2.54 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 102.3, 101.8, 87.6, 78.5, 20.1, 16.3. Anal. Calcd for $C_{15}H_{19}F_6FeP$: C, 45.03; H, 4.79. Found, C, 45.14; H, 4.77.

(η^6-1,2,4,5-Tetramethylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (7).[15] Deep golden flakes from aqueous acetone: mp (sealed capillary) 260–265 °C dec; (lit.[15] mp 182–183 °C dec); IR (KBr) 3120, 2928, 1483, 1456, 1420, 1397, 1035, 836, 558, 497, 467 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.30 (s, 2 H), 4.96 (s, 5 H), 2.50 (s, 12 H); ^{13}C NMR (acetone-d_6) δ 101.2, 90.7, 78.6, 18.4.

(η^6-Pentamethylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (8).[15] Deep yellow flakes from acetone: mp (sealed capillary) 223–226 °C dec (lit.[15] mp 179–181 °C); IR (KBr) 3115, 2927, 2917, 1463, 1454, 1420, 1392, 1112, 1080, 1027, 1011, 868, 840, 558, 500, 487, 467 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.24 (s, 1 H), 4.84 (s, 5 H), 2.56 (s, 3 H), 2.51 (br s, 12 H); ^{13}C NMR (acetone-d_6) δ 101.0, 100.3, 100.1, 89.5, 78.8, 19.8, 16.8, 16.2.

(η^6-Hexamethylbenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (9).[13] Deep yellow feathery crystals from actone: mp (sealed capillary) 230–240 °C dec; IR (KBr) 3110, 2930, 1453, 1419, 1393, 1074, 1022, 1008, 840, 558, 503, 468 cm^{-1}; ^{1}H NMR (50 % dimethyl-d_6 sulfoxide in acetone-d_6) δ 4.75 (s, 5 H), 2.52 (s, 18 H); ^{13}C NMR (50 % dimethyl-d_6 sulfoxide in acetone-d_6) δ 99.1, 79.0, 17.4.

(η^6-Biphenyl)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (10).[16] Gold feathers from acetone/ether: mp 180–210 °C dec; ^{1}H NMR (acetone-d_6) δ 8.02 (m, 1 H), 7.62 (m, 4 H), 6.95 (m, 3 H), 6.68 (m, 2 H), 5.16 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 136.1, 131.0, 130.4, 128.7, 104.7, 89.2, 88.2, 87.3, 78.3.

(η^6-Naphthalene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (11). Deep red needles from acetone: mp 170–175 °C dec (lit.[17] mp 166–168 °C dec); ^{1}H NMR (acetone-d_6) δ 8.14 (m, 2 H), 7.89 (m, 2 H), 7.44 (m, 2 H), 6.58 (m, 2 H), 4.75 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 132.8, 87.6, 86.2, 85.9, 77.3, 77.2.

(η^6-Chlorobenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (12).[18] Yellow-green crystals from acetone: mp 190–210 °C dec; IR (KBr) δ 3125, 3120, 3104, 1504, 1450, 1441, 1422, 1413, 1096, 828, 707, 557, 510, 469 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.63 (d, ^3J = 6.4 Hz, 2 H), 6.60 (t, ^3J = 6.4 Hz, 2 H), 6.48 (t, ^3J = 6.2 Hz, 1 H), 5.32 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 108.2, 89.8, 89.2, 88.2, 79.9.

(η^6-1,4-Dichlorobenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (13).[18] Yellow-green flakes from acetone: mp (sealed capillary) 215–220 °C; IR (KBr) 3122, 3097, 2923, 1629, 1447, 1384, 1344, 1096, 1012, 911, 879, 839, 752, 697, 559, 473 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.97 (s, 4 H), 5.45 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 107.2, 89.3, 82.2.

(η^6-*N,N*-Dimethylaniline)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (14).[19] The published procedure[19] afforded an 85:15 mixture of 1 and 14, from which pure 14 was isolated by fractional crystallization from dichloromethane to afford golden needles: mp (sealed capillary) 150–165 °C (lit.[19] mp 153–156 °C); IR (KBr) 3122, 2924, 1567 s, 1493, 1445, 1420, 1367, 1231, 1189, 1133, 1072, 1002, 941, 843 s, 655, 558, 474, 467, 448 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.17 (t, 2 H), 6.09 (t, 1 H), 5.84 (d, 2 H), 5.15 (s, 5 H), 3.17 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 122.5, 85.2, 77.9, 66.8, 74.1, 28.2.

(η^6-1,4-Bis-(*N,N*-dimethylamino)benzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (15). A 25-mL Erlen-

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meyer flask was charged with 200 mg (0.484 mmol) of **13**. Dimethylamine solution (10 mL, 40% in water) was added, and the mixture was heated on a steam bath. Initially, the starting material dissolved, but as the dimethylamine boiled away, fine orange needles appeared. The mixture was cooled in an ice bath, and the supernatant liquid was decanted and discarded. This procedure was repeated with four additional 10-mL portions of dimethylamine solution. The resulting red-orange needles were collected on a sintered-glass filter funnel, washed with ice water (3 × 1 mL), and recrystallized from ethanol to obtain 110 mg (0.256 mmol, 53%) of fine red-orange needles: mp (sealed capillary) 210–220 °C dec; IR (KBr) 2981, 2904, 2820, 1587, 1536, 1445, 1349, 1233, 1187, 1134, 1112, 1067, 953, 839, 651, 598, 558 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.08 (s, 12 H), 4.99 (s, 5 H), 5.61 (s, 4 H); ^{13}C NMR (acetone-d_6) δ 123.1 74.3, 65.1, 40.2. HRMS (FAB) *m/e* calcd for $C_{15}H_{21}FeN_2$ $(M - PF_6)^+$ 285.1054, found 285.1069. Anal. Calcd for $C_{15}H_{21}F_6FeN_2P$: C, 41.88; H, 4.92; N, 6.51. Found: C, 41.98; H, 5.09; N, 6.54.

(η^6-Methoxybenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (16).[20] According to a published procedure,[20] 151 mg (0.4 mmol) of **12** was treated with sodium methoxide (216 mg, 4.0 mmol) in absolute methanol (5 mL) at 60 °C for 1 h to afford, after purification by column chromatography on alumina/dichloromethane, 85 mg (57%) of yellow crystals: mp (sealed capillary) 125–135 °C dec (lit.[18] mp 137 °C); ^{1}H NMR (acetone-d_6) δ 6.40 (m, 5 H), 6.23 (m, 1 H), 5.18 (s, 5 H), 4.08 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 123.5, 85.0, 77.3, 75.2, 57.3.

(η^6-1,4-Dimethoxybenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (17).[20] According to a published procedure,[20] 413 mg (1.00 mmol) of **13** was treated with sodium methoxide (1.04 g, 20 mmol) in absolute methanol at 60 °C for 1 h to afford, after purification by column chromatography on alumina, eluting with dichloromethane, 170 mg (0.42 mmol, 42%) of yellow crystals: mp (sealed capillary) 150–180 °C; IR (KBr) 3124, 1536, 1528, 1492, 1464, 1446, 1420, 1279, 1230, 1183, 1110, 1011, 843, 754, 590, 558, 541, 467, 449 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.32 (s, 4 H), 5.12 (s, 5 H), 4.12 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 125.8, 81.6, 77.7, 57.6.

(η^6-Benzonitrile)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (18).[21] A published procedure was followed[21] starting from **12** and sodium cyanide, and the crude product was crystallized from aqueous ethanol to afford tiny orange prisms: mp 150–160 °C dec (lit.[21] mp 210 °C dec); IR (KBr) 3123, 2254, 1459, 1423, 842, 557, 482, 462 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.03 (m, 2 H), 6.85 (m, 3 H), 5.50 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 116.7, 91.6, 91.1, 90.0, 89.2, 80.6.

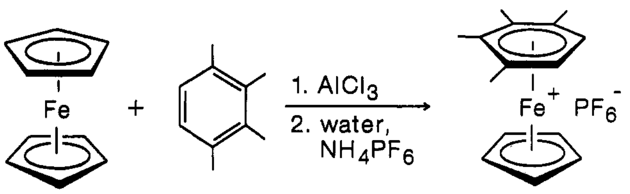
(η^6-Carbomethoxybenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (19).[22] According to a modified literature procedure,[23a,b] **2** was oxidized with boiling aqueous potassium permanganate; after cooling, reduction of the unreacted permanganate with ethanol and treatment with aqueous HPF_6 solution afforded the carboxylic acid $(\eta^6\text{-}C_6H_5COOH)FeCp^+PF_6^-$ (**21**): mp 195–210 °C dec (lit.[23a] mp 200–205 °C); IR (KBr) 3450 br, 3125, 1720 s, 1420, 1306, 1283, 836 s, 558, 499, 473, 419 cm^{-1}; ^{1}H NMR (acetone-d_6/D_2O) δ 6.97 (m, 2 H), 6.68 (m, 3 H), 5.25 (s, 5 H). Reaction of **21** (300 mg, 0.773 mmol) with oxalyl chloride (2 mL) in 1,2-dichloromethane (25 mL) under reflux for 3 h with stirring afforded, after cooling to room temperature and removal of the volatiles under reduced pressure, the intermediate acid chloride $(\eta^6\text{-}C_6H_5COCl)FeCp^+PF_6^-$ (**22**), which was not isolated. Methanol (20 mL) was then added to form the corresponding ester. After 5 min of stirring, the volatile components were removed *in vacuo*, and the black residue was subjected to column chromatography on neutral alumina. A yellow band was eluted with dichloromethane and evaporated to afford 195 mg (0.485 mmol, 63% based on **21**) of tiny yellow needles: mp 260–265 °C; IR (KBr) 3118, 3107, 3101, 1733 s, 1529, 1458, 1438, 1421, 1304, 1291, 1196, 1150, 1121, 1056, 1015, 955, 921, 832, 782, 679, 558, 518, 496, 474, 453 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 7.04 (m, 2 H), 6.74 (m, 3 H), 5.29 (s, 5 H), 4.07 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 166.6, 91.0, 89.9, 89.4, 89.2, 79.3, 54.3.

(η^6-Nitrobenzene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (20). *Caution! Complex **20** may explode upon heating above 200 °C.* The complex $(\eta^6\text{-}C_6H_5NH_2)FeCp^+PF_6^-$ (**23**) was prepared by following a published procedure;[24] however, the crude product was shown by ^{1}H NMR to consist mainly of **23** with 20% **1**. Purification of 2.4 g by fractional crystallization from dichloromethane afforded 1.1 g of orange crystals: mp 180–220 °C dec (lit.[24] mp 242 °C dec); ^{1}H NMR (acetone-d_6) δ 6.24 (t, 1 H), 6.18 (d, 2 H), 5.87 (t, 2 H), 5.2 (br s, 2 H), 4.95 (s, 5 H). According to a published procedure,[25] 300 mg of aniline complex **23** (0.836 mmol) was treated with 4 mL of 30% aqueous hydrogen peroxide solution and 4 mL of trifluoroacetic acid at 75 °C for 45 min. The workup procedure[25] afforded, after recrystallization from 1,2-dichloroethane/acetone (3:1), 122 mg (38%) of tiny orange prisms: mp 215 °C dec (*exploded*); IR (KBr) 3116, 2293, 1561, 1508, 1421, 1347, 915, 839, 697, 684, 558, 495, 471 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.59 (dd, ^3J = 6.8 Hz, ^4J = 0.6 Hz, 2 H), 6.96 (t, ^3J = 6.2 Hz, 2 H), 6.88 (t, ^3J = 6.2 Hz, 1 H), 5.48 (s, 5 H); ^{13}C NMR (acetone-d_6) δ 112.6, 92.1, 89.7, 85.5, 81.2.

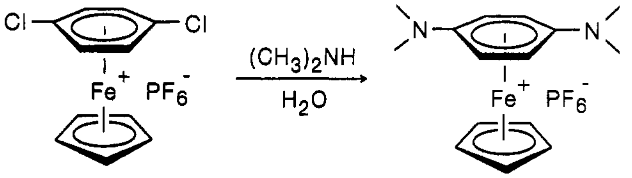
Results and Discussion

Synthesis. The $(\eta^6\text{-arene})FeCp^+PF_6^-$ skeleton is generally obtained by aluminum chloride promoted ligand exchange between ferrocene and the free arene (usually as the solvent) at temperatures exceeding 100 °C.[13] Several previously reported $(\eta^6\text{-arene})FeCp^+PF_6^-$ species, as well as the new complex **6** (Scheme 1), were readily prepared for the present study by this method. Other complexes were prepared by modifying the substituents on η^6-arene ligands.[26] Nucleophilic aromatic substitution of chloride was used to prepare the previously reported species **16**–**18**; the facility of this method is illustrated by the straightforward preparation of the new 1,4-bis(dimethylamino)benzene complex **15** (Scheme 2) by reaction of the 1,4-dichlorobenzene complex **13** with dimethylamine in warm aqueous solution. Oxidation of aliphatic side chains

Scheme 1



Scheme 2



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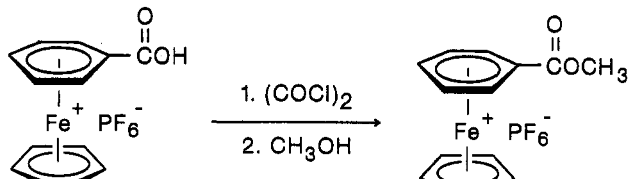
Scheme 3



Scheme 4

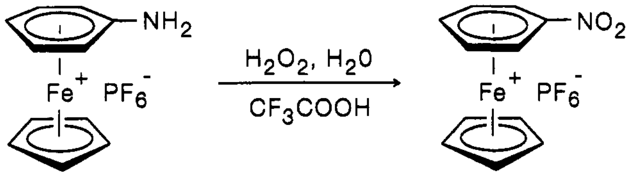


Table 1. Core Electron Binding Energies and ^{1}H NMR Chemical Shifts for (η^6-Arene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphates[a]

	η^6-arene substituents	BE(Fe(2p$_{3/2}$)), eV	δ(^{1}H)$_{Cp}$ ± 0.02, ppm
1	H	708.99 ± 0.05	5.23
2	CH$_3$	708.94 ± 0.05	5.17
3	1,2-(CH$_3$)$_2$	708.84 ± 0.05	5.12
4	1,4-(CH$_3$)$_2$	708.86 ± 0.05	5.11
5	1,3,5-(CH$_3$)$_3$	708.82 ± 0.05	5.04
6	1,2,3,4-(CH$_3$)$_4$	708.75 ± 0.05	4.93
7	1,2,4,5-(CH$_3$)$_4$	708.73 ± 0.05	4.95
8	(CH$_3$)$_5$	708.66 ± 0.05	4.86
9	(CH$_3$)$_6$	708.60 ± 0.07	4.76
10	Ph	708.86 ± 0.05	5.16
11	arene = naphthalene	708.75 ± 0.08	4.74
12	Cl	709.08 ± 0.05	5.33
13	1,4-Cl$_2$	709.19 ± 0.05	5.46
14	N(CH$_3$)$_2$	708.56 ± 0.09	5.13
15	1,4-[N(CH$_3$)$_2$]$_2$	708.30 ± 0.12	4.99
16	OCH$_3$	708.85 ± 0.07	5.20
17	1,4-(OCH$_3$)$_2$	708.65 ± 0.05	5.17
18	CN	709.12 ± 0.16	5.50
19	COOCH$_3$	709.15 ± 0.08	5.30
20	NO$_2$	709.25 ± 0.14	5.60

[a] Estimation of experimental errors is described in the text.

to the corresponding carboxylic acid was used in a modified preparation of the methyl benzoate complex **19** (Scheme 3): Reaction of the benzoic acid complex **21** with methanol and sulfuric acid[23a,b] failed to effect the desired esterification, but methanolysis of the corresponding acid chloride **22** afforded the ester **19**. The complex (η^6-aniline)FeCp$^+$PF$_6^-$ (**23**) was also readily oxidized to the corresponding η^6-nitrobenzene complex with hydrogen peroxide in aqueous trifluoroacetic acid (Scheme 4).[25]

Physical Measurements and Errors. Table 1 shows the Fe(2p$_{3/2}$) and δ(^{1}H)$_{Cp}$ values for (η^6-arene)FeCp$^+$PF$_6^-$ complexes. The error in δ(^{1}H)$_{Cp}$ is conservatively estimated to be ±0.02 ppm, although in practice the shifts relative to the parent η^6-benzene complex were reproducibly determined within ±0.01 ppm by using the latter complex as an *internal* chemical shift standard (δ(^{1}H)$_{Cp}$ ≡ 5.23 ± 0.00 ppm). Errors in Fe(2p$_{3/2}$) represent the greater of 0.05 eV and the average deviation from the mean value for at least three separate samples.[27] For about one-third of the complexes (those bearing alkyl, phenyl, or chloro substituents), the data were highly reproducible. The remaining binding energies were determined with somewhat less precision (±0.10 eV), perhaps due to slow decomposition of these samples under the experimental conditions. Whenever decomposition was suspected, the samples were loaded more heavily on the polyethylene surface to improve photoelectron yield in order to reduce the X-ray exposure times. The resulting increased interference in the C(1s) reference signal from carbon within the sample suggests greater uncertainty in the static charging correction.[28]

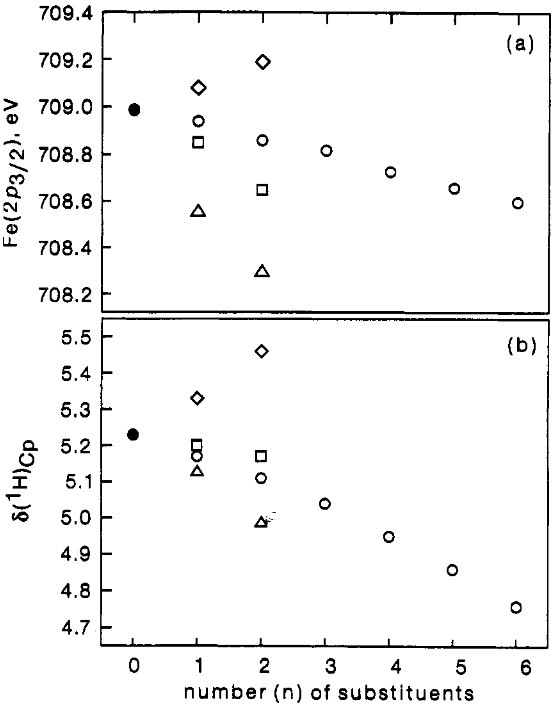


Figure 1. Fe(2p$_{3/2}$) binding energies (a) and δ(^{1}H)$_{Cp}$ chemical shifts (b) for (η^6-arene)FeCp$^+$PF$_6^-$ complexes as a function of increased arene substitution by methyl (○), chloro (◇), methoxy (□), and dimethylamino (△). The unsubstituted parent complex **1** is provided as a reference and denoted by a filled circle.

Electronic Substituent Effects. Table 1 reveals expected trends in Fe(2p$_{3/2}$) and δ(^{1}H)$_{Cp}$: Electron-withdrawing substituents (Cl, CN, CO$_2$CH$_3$, NO$_2$) increase Fe(2p$_{3/2}$) and δ(^{1}H)$_{Cp}$ values relative to that of hydrogen and electron-releasing substituents (CH$_3$, Ph, N(CH$_3$)$_2$, OCH$_3$, benzo ring fusion) have the opposite effect. Monotonic changes were observed in Fe(2p$_{3/2}$) and δ data (Figure 1) when increasing numbers of the same substituent were attached to the η^6-arene moiety. Comparison of **3** and **4** and of **6** and **7** by Fe(2p$_{3/2}$) and δ(^{1}H)$_{Cp}$ analysis showed that regioisomerism did not have a significant effect.

Noteworthy in Table 1 is the approximately 1.0-eV range spanned by the Fe(2p$_{3/2}$) binding energies. Furthermore, the Fe(2p$_{3/2}$) binding energies previously measured for ferrocene (708.0 eV) and decamethylferrocene (707.1 eV) increase the total range observed in the broader class of iron(II) sandwich complexes to more than 2.0 eV. A 1.0-eV increase in CBE has been associated with unit increase in the oxidation state of a given atom.[29] Thus, the range

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[27] The error in BE(Fe(2p$_{3/2}$)) should conservatively be taken as no less than 0.1 eV in the comparsion of data obtained on other instruments or by means of internal calibration.

[28] Damage to the samples was likely the result of X-ray exposure. Samples did not degrade simply by exposure to ultrahigh-vacuum conditions, and cooling the sample stage with liquid nitrogen during the experiments did not retard decomposition. A color change from yellow-orange to deep red was observed in longer experiments.

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Table 2. Average Effects of Substituents on Fe($2p_{3/2}$) and $\delta(^1H)_{Cp}$ in (η^6-Arene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphates

substituent	BE(Fe($2p_{3/2}$)), eV[a]	$\delta(^1H)_{Cp} \pm 0.02$, ppm
NO_2	0.26 ± 0.15	0.37
$COOCH_3$	0.16 ± 0.09	0.07
CN	0.13 ± 0.17	0.27
Cl	0.098 ± 0.05	0.11
H	(0.00)	(0.00)
CH_3	–0.065 ± 0.05	–0.08
Ph	–0.13 ± 0.06	–0.07
OCH_3	–0.17 ± 0.05	–0.03
benzo	–0.24 ± 0.09	–0.49
NMe_2	–0.35 ± 0.05	–0.12

[a] Errors in the average effect on Fe($2p_{3/2}$) were the greater of 0.05 eV and the error in the slope obtained from plots of binding energy against the number of substituents by using an adapted method[33] for estimating the effects of individual errors on the uncertainty in regression parameters.

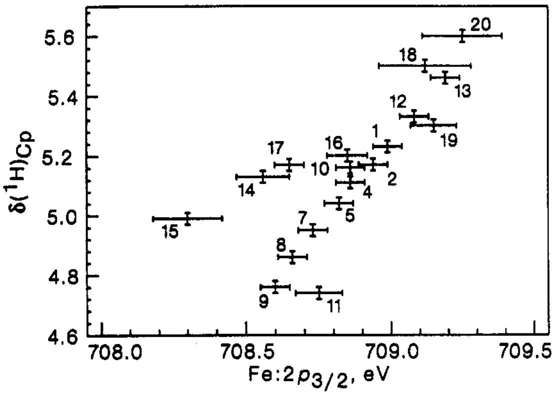

Figure 2. Plot of Fe($2p_{3/2}$) binding energies against $\delta(^1H)_{Cp}$ in (η^6-arene)$FeCp^+PF_6^-$. Complexes 3 and 6 (regioisomers of 4 and 7, respectively) were omitted for clarity.

observed for these formally isoelectronic iron complexes suggests that changes in the ligand (from Cp to η^6-arene) and the effects of ligand substituents can effect changes in the native electron-richness of the metal center analagous to a change of 2 in formal oxidation state.

The average effect of substituents, relative to hydrogen, on Fe($2p_{3/2}$) and $\delta(^1H)_{Cp}$ is summarized in Table 2. The Fe($2p_{3/2}$) data in Table 2 quantify electronic ring substituent effects on the native electron-richness of the iron center in η^6-arene complexes, while the $\delta(^1H)_{Cp}$ data reflect the tendency for electronic effects to be transmitted through the metal center to the opposing Cp ligand. The nitro substituent is therefore as electron-withrawing as about three chloro substituents, while one phenyl substituent has approximately the same electronic effect as two methyl groups. Furthermore, the Fe($2p_{3/2}$) value for (η^6-naphthalene)$FeCp^+PF_6^-$ (11, Table 1) suggests that *benzo* ring fusion has approximately the same electronic effect, versus H, on the iron center as 4 ± 1 methyl substituents. This enhancement of metal-centered electron-richness in η^6-arene complexes *via* benzo ring fusion was previously observed with η^5-indenyl and η^5-fluorenyl as compared to Cp.[4f] In spite of the increased electron-donating effect of benzo ring fusion, naphthalene complexes are generally much more kinetically labile than the corresponding benzene complexes.[30] The magnitudes of η^6-arene methyl and chloro substituent effects in Table 2 are the same, within experimental errors, as those previously observed for η^5-cyclopentadienide substitution in ruthenocenes[4f] and hafnocene dihalides.[4g]

Figure 2 presents a correlation of Fe($2p_{3/2}$) and $\delta(^1H)_{Cp}$ data. With cautious observance of experimental errors in Fe($2p_{3/2}$), we wish to offer a speculative interpretation of Figure 2. First, if complexes 11 and 14–17 are ignored in Figure 2, an overall linear correlation ($r^2 = 0.95$) is observed between Fe($2p_{3/2}$) and $\delta(^1H)_{Cp}$ data. The effect of methoxy and dimethyl amino substituents on Fe($2p_{3/2}$) values is quite large, however, in comparison to the effect on $\delta(^1H)_{Cp}$. For example, each methoxy substituent lowers $\delta(^1H)_{Cp}$ by 0.03 ± 0.02 ppm, only about *half* the average effect of a methyl substituent (0.07 ± 0.02 ppm), while, according to Fe($2p_{3/2}$), each methoxy group has approximately *twice* the electron-releasing effect as a methyl group. Similary, each dimethylamino substituent lowers $\delta(^1H)_{Cp}$ by 0.12 ± 0.02 ppm, which is less than the effect of two methyl substituents, while the same substituent exerts the strongest observed electron-releasing effect (–0.3 ± 0.1 eV), about the same as 3 ± 1 methyl substituents, on Fe($2p_{3/2}$). Although methoxy and dimethylamino substituents are known to exhibit strong resonance electron-releasing behavior,[31] it is not clear why Fe($2p_{3/2}$) values should reflect this influence differently from $\delta(^1H)_{Cp}$.[32]

Conclusions

Iron core electron binding energies of (η^6-arene)$FeCp^+$-PF_6^- complexes reveal a pronounced influence of arene substituents on the native electron-richness of the coordinated metal atom. A comparison of the trends in Fe($2p_{3/2}$) and $\delta(^1H)_{Cp}$ data provides insight into the distribution of these effects between the metal and the ancillary Cp ligand. Overall, shifts in Fe($2p_{3/2}$) agree well with analagous shifts in metal cyclopentadienyl complexes.

Acknowledgment. We are grateful to Professor John F. Evans and his group (University of Minnesota) for discussions and assistance with the XPS studies. This work was funded by the National Science Foundation under Grant CHE-8921744-06.

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