The Reaction of $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]BF_4$ with Fluoride Revisited. Formation of $(\eta^4\text{-5-fluorocyclohexa-1,3-diene})Fe(CO)_3$ and the Mechanism of the Decomposition Pathway To Give the Carbon–Carbon Linked Dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$

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The complex $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ has been prepared *in situ* in CD_2Cl_2 from the reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ with either KF/18-crown-6 or $[(Me_2N)_3S][Me_3SiF_2]$. On standing, $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ decomposes to give the C–C linked dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ as the major product together with significant amounts of benzene and Fe(III) species. A mechanism is proposed to account for the formation of $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ from $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ and the mechanism extended to the reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ with hydroxide. Exposure of $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ to H_2O rapidly gives the diiron ether complex $\{(\eta^4\text{-}C_6H_7)_2O\}Fe_2(CO)_6$.

Introduction

While selective fluorination reactions are of considerable interest, very few carbon–fluorine bond forming reactions occurring via the addition of the fluoride ion to cationic organometallic complexes are known. Because of their rather limited number and potential importance, a more in depth study was clearly required into delineating the pathways accessible to the fluoride ion in its reactions with organometallic substrates. In this regard, we are currently investigating the reactions of the fluoride ion with a range of cationic organometallic complexes, primarily with a view to identifying C–F bond forming reactions.[1] Known examples are the addition of fluoride to cationic carbyne complexes leading to fluorocarbene complexes (eq 1)[2] and the formation of fluoroalkanes from

$$[(OC)_5Cr{\equiv}C{-}NEt_2]^+ + F^- \rightarrow (OC)_5Cr{=}CF(NEt_2) \qquad (1)$$

$$[CpRu(CO)(PPh_3)(RI)]^+ + F^- \rightarrow CpRuI(CO)(PPh_3) + RF \qquad (2)$$

the reaction of fluoride with the cationic iodoalkane complexes $[CpRu(CO)(PPh_3)(RI)]PF_6$ (eq 2).[1,3] An early report[4] that $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]BF_4$ (1) reacts with KF/18-crown-6 to give $(\eta^4\text{-5-exo-fluorocyclohexa-1,3-diene})Fe(CO)_3$ has since been shown to be incorrect.[5] Under the reaction conditions of the earlier report the *isolated* product was in fact the diiron ether complex $\{(\eta^4\text{-}C_6H_7)_2O\}Fe_2(CO)_6$ (2). Under rigorously anhydrous conditions the isolated products from the reaction of 1 with KF/18-crown-6 in acetonitrile solution were the starting material 1 (65%) and the carbon–carbon linked dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ (3) (5%). The second study concluded with the statement that the "...cation $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ does not capture fluoride ion".[5] We here present evidence to show that the cation $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ does capture fluoride to give $(\eta^4\text{-5-fluorocyclohexa-1,3-diene})Fe(CO)_3$ (4) but that this complex readily loses fluoride to give the carbon–carbon linked dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ (**3**). The formation of the dimer 3 in varying amounts has also been observed previously in the reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (1) with alkoxides or hydroxide in aprotic solvent.[6,7] A mechanism is proposed to account for the formation of 3 when 1 is reacted with strong nucleophiles.

Results and Discussion

The fluoro complex $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ (4) is readily obtained *in situ* in CD_2Cl_2 when $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ is reacted with either KF/18-crown-6 or $[(Me_2N)_3S][Me_3SiF_2]$ under anhydrous conditions (eq 3). The ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR data for $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ are given in Table I. The observed values of $^1J_{^{19}F-^{13}C}$ (177 Hz) and $^2J_{^{19}F-^1H}$ (57 Hz) are typical for fluorocarbon compounds.[8] It is assumed that the stereochemistry of 4 involves exo F^- addition, though an endo configuration

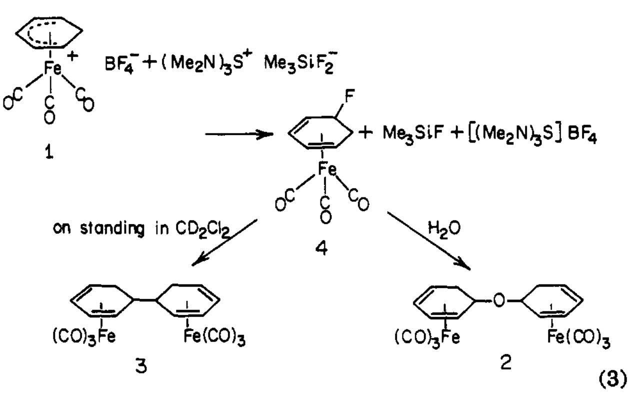

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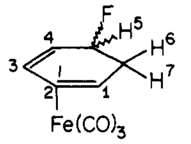
Table I. NMR Data (δ, ppm) for $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ in CD_2Cl_2[a]

	^{19}F NMR
	−137.58 (ddd), $J_{^{19}F-^{1}H}$ = 56.3, 23.7, 13.9 Hz
	$^{13}C\{^1H\}$ NMR[b]
C^1	54.6 (d), $J_{^{19}F-^{13}C}$ = 3.9 Hz
C^2	88.5 (s),
C^3	85.2 (d), $J_{^{19}F-^{13}C}$ = 3.3 Hz
C^4	57.6 (d), $J_{^{19}F-^{13}C}$ = 14.6 Hz
C^5	89.9 (d), $J_{^{19}F-^{13}C}$ = 176.9 Hz
C^6	31.2 (d), $J_{^{19}F-^{13}C}$ = 29.1 Hz
CO	211.4 (s)
	^1H NMR[b]
H^1, H^4	2.95, 2.90 (br singlets), $J_{H^1-H^2}$ = 4 Hz
H^2, H^3	5.55 and 5.65 (br singlets)
H^5	5.04 (br d of d), $J_{^{19}F-^{1}H}$ = 57 Hz, $J_{H^5-H^7}$ = 8 Hz
H^6_{exo}	1.66 (d of d), $J_{^{19}F-^{1}H}$ = 24 Hz, $J_{H^6-H^7}$ = 16 Hz
H^7_{endo}	2.37 (complex mult), $J_{^{19}F-^{1}H}$ = 14 Hz, $J_{H^6-H^7}$ = 16 Hz, $J_{H^5-H^7}$ = 8 Hz

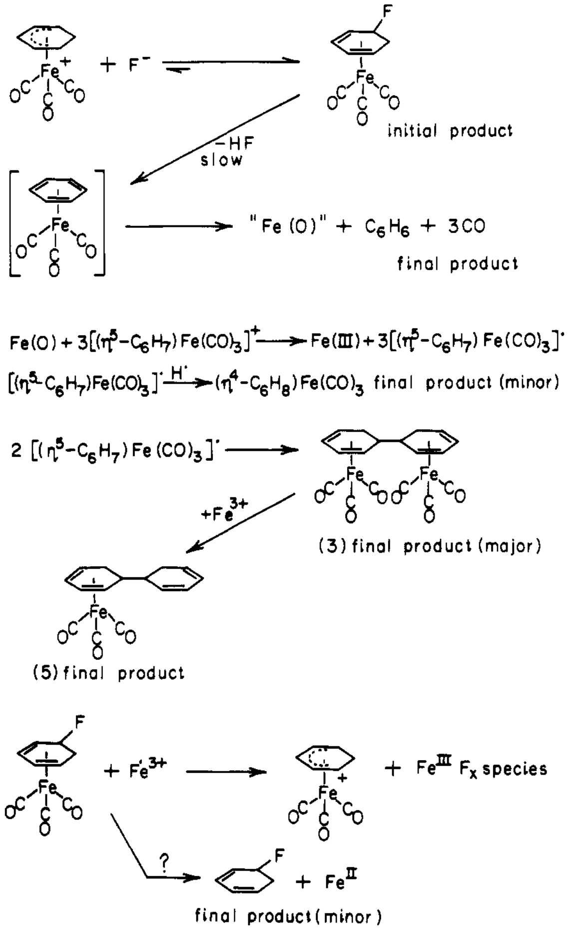
[a] Solution also contains $[(Me_2N)_3S][BF_4]$ and Me_3SiF or 18-crown-6. [b] For atom labeling scheme use the following structure



cannot be excluded. The complex $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ is hydrolytically unstable, rapidly reacting to give the diiron ether complex $\{(\eta^4\text{-}C_6H_7)_2O\}Fe_2(CO)_6$ (**2**) on exposure to water. The fluoro complex $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ is also not very stable even under anhydrous conditions and, on standing in CD_2Cl_2 (20 °C) for 22 h, decomposes to give the carbon–carbon linked dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ (**3**) as the major product (*ca.* 53% based on the amount of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ consumed) together with a small amount of the starting cation $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (5%) which crystallizes from solution (essentially insoluble in CD_2Cl_2). $^{13}C\{^1H\}$ NMR monitoring of the reaction indicates that the formation of the C–C dimer **3** is accompanied by the formation of significant amounts of free benzene and carbon monoxide. The $^{13}C\{^1H\}$ NMR spectrum becomes broader as the reaction proceeds, suggesting the formation of paramagnetic Fe(II) or Fe(III) species. After all the $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ had been consumed, an aqueous extraction and spectroscopic analysis confirmed the formation of Fe(III) and Fe(II) species in 27% yield (ratio Fe(III):Fe(II) = 9:1). The ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectral analyses indicate the presence of the C–C dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ (*ca.* 53%), $(\eta^4\text{-}C_6H_8)Fe(CO)_3$ (*ca.* 9%), benzene (*ca.* 15%), and two other products which are thought to be $(\eta^4\text{-}C_6H_7\text{-}C_6H_7)Fe(CO)_3$ (*ca.* 17%, complex **5**—the product from the partial oxidative loss of an $Fe(CO)_3$ unit from the C–C dimer **3**)[9] and 5-fluorocyclohexa-1,3-diene (*ca.* 6%).[10] Yields are based on the amount of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ that is consumed in the reaction.

The above observations can be reasonably rationalized by the mechanistic pathways outlined in Scheme I. The initial product is $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ which very probably has the exo structure. This reaction is reversible. A slower but irreversible process involves elimination of HF which presumably leads to the formation of the kinetically unstable species $(\eta^4\text{-}C_6H_6)Fe(CO)_3$. This can be viewed as functioning as a reducing agent either via direct electron transfer or via decomposition to liberate benzene, carbon monoxide, and Fe(0). Electron transfer from either $(\eta^4\text{-}C_6H_6)Fe(CO)_3$ or Fe(0) to the cation $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ produces the 19 electron organometallic radicals $(\eta^5\text{-}C_6H_7)Fe(CO)_3$ which can rapidly dimerize to the C–C dimer $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ or scavange H• to give $(\eta^4\text{-}C_6H_8)Fe(CO)_3$. {It is also conceivable that electron transfer occurs from Fe(0) to $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ followed by loss of fluoride to give the 19 electron radical species $(\eta^5\text{-}C_6H_7)Fe(CO)_3$.} The iron(III) is expected to strongly complex fluoride and thereby facilitates the re-formation of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ from the initially formed product $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$. This increases the concentration of the cation above its solubility limit, and consequently, $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ recrystallizes from solution. The products tentatively identified as $(\eta^4\text{-}C_6H_7\text{–}C_6H_7)Fe(CO)_3$

Scheme I. Reaction Pathways for the Decomposition of $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$[a]



[a] While the formation of a minor amount of a noncomplexed fluorocarbon is confirmed, its formulation as 5-fluoro-1,3-cyclohexadiene is tentative (see text).[10]

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(8) Pretsch, E.; Seibl, J.; Clerc, T.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: New York, 1983, pp C240, H355.

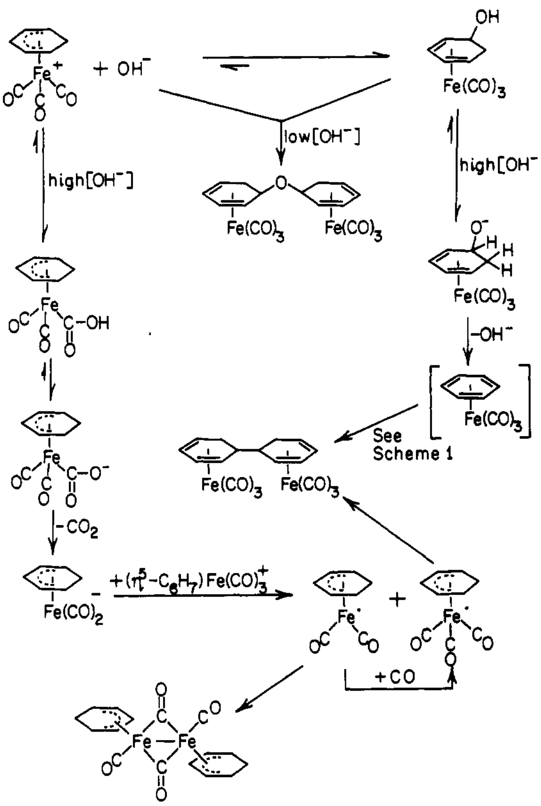
(9) (a) The complex $(\eta^4\text{-}C_6H_7\text{-}C_6H_7)Fe(CO)_3$ (**5**) is also observed as an intermediate in the oxidation of $(\eta^4\text{-}C_6H_7)_2Fe_2(CO)_6$ to a meso and racemic mixture of 5,5′-di-1,3-cyclohexadiene using excess Me_3NO.[9b] (b) Bandara, B. M. R.; Birch, A. J.; Kelly, L. F. *J. Org. Chem.* **1984**, *49*, 2496. $^{13}C\{^1H\}$ NMR data for complex **5** ($CDCl_3$): δ 212.2 (CO); 129.1, 125.8, 124.9, 124.4 (noncoordinated olefin carbons); 85.6–85.4, 64.6, 64.1, 60.2, 60.1 (coordinated olefin carbons); 42.3, 42.1, 39.9, 39.7 (methine ring junction carbons); 28.6, 28.2, 27.0 (–CH_2 carbons).

(10) The formation of a fluorocarbon compound tentatively identified as 5-fluorocyclohexa-1,3-diene is based on the following observations. (i) The ^1H NMR spectrum of the mixture of reaction products from the decomposition of $(\eta^4\text{-}C_6H_7F)Fe(CO)_3$ contains a weak doublet resonance at δ 4.55 ppm with a separation of 56 Hz, a typical value for $^2J_{^{19}F-^{1}H}$,[8] and (ii) the ^{19}F NMR contains a multiplet resonance at δ −146.7 ppm which exhibits a $^2J_{^{19}F-^{1}H}$ of ~59 Hz.

(**5**) and 5-fluorocyclohexa-1,3-diene can be envisioned as being the products of Fe(III) oxidation of (η^4-C_6H_7)$_2$-$Fe_2(CO)_6$ and (η^4-C_6H_7F)Fe(CO)$_3$, respectively (see Scheme I). The combined yields of benzene, C_6H_7F, and half the quoted yield of (**5**) (*ca.* 30%—products from the oxidative release of Fe(CO)$_3$ units) correlate reasonably well with the amount of Fe(II)/Fe(III) species formed (27%). An assumption that all the electrons released on oxidizing Fe(0) to Fe(II) and Fe(III) (1:9 ratio) are used in the production of the 19 electron radical species (η^5-C_6H_7)-Fe(CO)$_3$ gives a predicted maximum theoretical yield for C–C coupled products {(**3**) + (**5**)} and (η^4-C_6H_8)Fe(CO)$_3$ (**6**) of *ca.* 75% (*ca.* 79% observed *in situ* yield). Synthetically, we have obtained isolated yields of the C–C dimer **3** as high as 68% based on the starting cation from the reaction of [(η^5-C_6H_7)Fe(CO)$_3$]BF$_4$ with hydroxide (see below). Previously reported observations provide support for the proposed mechanism: (i) Wrighton *et al.*[11] have obtained quantitative yields of the C–C linked dimers (η^4-C_6H_7)$_2$Fe$_2$(CO)$_4$L$_2$ (L = CO, PPh$_3$) by either thermal or photochemical homolysis of the Fe–Fe dimer (η^5-C_6H_7)$_2$-Fe$_2$(CO)$_4$ (**7**) in the presence of the ligand L. Initial homolytic cleavage of **7** gives the 17 electron species (η^5-C_6H_7)Fe(CO)$_2$ which, in the presence of CO, reacts to give the 19 electron species (η^5-C_6H_7)Fe(CO)$_3$, the precursor to the C–C linked dimer. (ii) Davis *et al.*[12] have shown that the reducing agent Cr^{2+}(aq) reacts with [(η^5-C_6H_7)Fe-(CO)$_3$]BF$_4$ in aqueous solution to give the C–C dimer, although isolated yields were low. It should be noted that the cycloheptadienyl C–C dimer (η^4-C_7H_9)$_2$Fe$_2$(CO)$_6$ (the analogue of **3**) is obtained in reasonable yield from the reduction of [(η^5-C_7H_9)Fe(CO)$_3$]BF$_4$ with zinc dust.[14] (iii) McKennis *et al.*[6,7] found that the C–C dimer **3** (12% yield) together with (η^4-C_6H_8)Fe(CO)$_3$ (33% yield) could be produced simply by heating CH_3CN solutions of [(η^5-C_6H_7)Fe(CO)$_3$]BF$_4$ in the absence of oxygen. If however oxygen was bubbled through the solution, no C–C dimer was observed. Based on our mechanistic proposals (Scheme I) any decomposition process that produces Fe(0) will result in formation of the C–C dimer. However in the presence of oxygen it is probable that reduction of O_2 is kinetically competitive with electron transfer to the cation [(η^5-C_6H_7)Fe(CO)$_3$]$^+$, thereby suppressing C–C dimer formation.

Besides the high yield of **3** obtained from the decomposition of the fluoro complex **4** in CD_2Cl_2 (Scheme I) we have also found that significant amounts of **3** can be obtained from the reaction of **1** with excess hydroxide. Addition of a CH_3CN solution containing [(η^5-C_6H_7)Fe-(CO)$_3$]BF$_4$ to a heterogeneous mixture consisting of a 7-fold excess of [Me$_4$N]OH·5H$_2$O in CH_3CN gave the C–C linked dimer (**3**) and the Fe–Fe dimer (η^5-C_6H_7)$_2$Fe$_2$(CO)$_4$ (**7**) in yields of 34 and 26%, respectively, as determined by IR spectroscopy. The remaining 40% of the Fe was unaccounted for. Under similar conditions, accompanied by the addition of carbon monoxide to the reaction mixture, C–C linked dimer **3** (95%) and (η^4-C_6H_8)Fe(CO)$_3$ (5%) were obtained in a combined 68% overall yield. Significantly, with the addition of CO, no Fe–Fe dimer was observed, consistent with the photochemical studies of Wrighton *et al.*[11] Furthermore the formation of the C–C dimer occurs more rapidly with hydroxide than with fluoride. In contrast, using only a 30% excess of [Me$_4$N]OH·5H$_2$O together with CO resulted in the formation of both the C–C linked dimer **3** and the diiron ether complex **2** (70:30 ratio based on the $^{13}C\{^1H\}$ NMR spectrum) in an isolated combined yield of 70%. Formation of C–C dimer when **1** is reacted with hydroxide can be rationalized along similar lines to Scheme I but with fluoride replaced by hydroxide (see Scheme II). Deprotonation of the initially formed 5-hydroxycyclohexa-1,3-diene complex facilitates H^+ abstraction from carbon no. 6 to give the intermediate species (η^4-C_6H_6)Fe(CO)$_3$ which can then react further as outlined in Scheme I to give the C–C dimer. An alternative route that probably leads to both C–C and Fe–Fe dimers involves addition of hydroxide to a carbonyl ligand of [(η^5-C_6H_7)Fe(CO)$_3$]$^+$ with subsequent loss of CO_2 to give the anionic species [(η^5-C_6H_7)Fe(CO)$_2$]$^-$.[13] Electron transfer from this anion to the cation [(η^5-C_6H_7)Fe(CO)$_3$]$^+$ would give the 17 electron species (η^5-C_6H_7)Fe(CO)$_2$ (precursor to the Fe–Fe dimer) and the 19 electron species (η^5-C_6H_7)Fe(CO)$_3$ (precursor to the C–C dimer). The probability of the intially formed 5-hydroxycyclohexadiene complex reacting with the starting cation to give the diiron ether complex {(η^4-C_6H_7)$_2$O}Fe$_2$(CO)$_6$ (**2**) will be most favored by low hydroxide concentrations.

Scheme II



Experimental Section

General Data. All operations unless otherwise specified were carried out under an atmosphere of dry N_2 or argon, using dry

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[11] Chaofeng, Z.; Ahmed, K. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1133.

[12] Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213.

[13] (a) The proposed mechanism for the formation of the Fe–Fe bonded dimer (η^5-C_6H_7)$_2$Fe$_2$(CO)$_4$ via hydroxide attack on a coordinated CO is similar to the mechanism recently proposed to account for the formation of the Mn–Mn bonded dimer (η^6-C_6Me_6)$_2$Mn$_2$(CO)$_4$ from the reaction of [(η^6-C_6Me_6)Mn(CO)$_3$]$^+$ with hydroxide.[13b] (b) Morken, A. M.; Eyman, D. P.; Wolff, M. A.; Schauer, S. J. *Organometallics* **1993**, *12*, 725.

[14] Hashmi, M. A.; Munro, J. D.; Pauson, P. L.; Williamson, J. M. *J. Chem. Soc. A* **1967**, 240.

solvents that were degassed with N_2 or argon prior to use. Deuterated solvents were dried over 4-Å molecular sieves and freeze–thaw degassed. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to tetramethylsilane and recorded at either 200 or 400 MHz. ^{19}F NMR spectra were referenced to $CFCl_3$ and recorded at 300 MHz. UV/vis spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer.

Starting Materials. "Spray dried" KF, $[(Me_2N)_3S][Me_3SiF_2]$, 18-crown-6, and $[Ph_3C]BF_4$ were purchased from Aldrich Chemical Co. The complex (η^4-cyclohexa-1,3-diene)$Fe(CO)_3$ was purchased from Strem Chemical Inc. The complex [(η^5-cyclohexadienyl)$Fe(CO)_3]BF_4$ was prepared according to the literature method.[14]

***In Situ* Preparation of (η^4-C_6H_7F)$Fe(CO)_3$ (4) and Its Subsequent Decomposition.** In an argon drybox a dry CD_2Cl_2 solution containing 0.185 g (0.671 mmol) of $[(Me_2N)_3S][Me_3SiF_2]$ was added to 0.181 g (0.592 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$. The resultant pale yellow solution was filtered into an NMR tube which was then sealed and the ^{19}F, $^{13}C\{^1H\}$, and ^1H NMR spectra were recorded (Table I). The instability of the fluoro complex (η^4-C_6H_7F)$Fe(CO)_3$ has precluded further characterization by microanalyses or mass spectroscopy.

In a separate experiment, 4 mL of dry CD_2Cl_2 was added to a solid mixture consisting of 1.281 g (4.19 mmol) of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ and 1.25 g (4.54 mmol) of $[(Me_2N)_3S][Me_3SiF_2]$, and the resultant mixture was stirred rapidly for 5 min. The pale yellow solution was decanted away from unreacted, CD_2Cl_2 insoluble, $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.171 g) and filtered into a tared volumetric flask. The original reaction vessel was washed with fresh CD_2Cl_2 (1 mL), and the filtered washings were combined with the original filtrate to give 8.488 g of solution. An aliquot of reaction solution (3.212 g), the "benzene analysis" portion, was transferred to a 10-mm NMR tube for the purpose of monitering by $^{13}C\{^1H\}$ NMR spectroscopy the decomposition of the fluoro complex (η^4-C_6H_7F)$Fe(CO)_3$ and determining the yield of benzene produced using an internal standard of hexamethylbenzene (0.0936 g). The remainder of the reaction solution, the "Fe analysis" portion (5.113 g), was left to stand overnight in the sealed volumetric flask. After all the fluoro complex (η^4-C_6H_7F)$Fe(CO)_3$ had been consumed (22 h), the reaction solution in the volumetric flask was separated from a small amount (29.4 mg) of crystalline $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ and extracted with water (200 mL). The aqueous extracts were separated from the CH_2Cl_2 layer, combined, and made up to 1 L in a volumetric flask. The total amount of water soluble Fe (i.e. $Fe^{II} + Fe^{III}$) was determined spectrophotometrically as the complex $Fe(o\text{-phen})_3^{2+}$ [15] and found to be 27 mg. Similarly, the ratio of Fe^{III}/Fe^{II} was found to be 9:1.[15] The organic layer (diluted with fresh CH_2Cl_2) was dried over $MgSO_4$, filtered, and concentrated to dryness to afford a golden yellow oil. The oil was taken up in pentane, and the resultant solution was filtered and concentrated to dryness to afford a yellow oily solid (0.283 g). ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra recorded for this solid in $CDCl_3$ showed it to be comprised of C–C dimer **3** (0.16 g, 40%), (η^4-C_6H_8)$Fe(CO)_3$(**6**) (0.01 g, 3%),[16] diiron ether complex **2** (0.08 g),[17] and the products tentatively identified as (η^4-C_6H_7-C_6H_7)$Fe(CO)_3$ (**5**) (0.03 g, 13%)[9] and 5-fluorocyclohexa-1,3-diene (3 mg, 2%).[10] From the relative integration in the $^{13}C\{^1H\}$ NMR of the reaction solution prior to workup the *in situ* product distribution was found to be C–C dimer **3** (*ca.* 53%), (η^4-C_6H_7-C_6H_7)$Fe(CO)_3$ (**5**) (*ca.* 17%), (η^4-C_6H_8)$Fe(CO)_3$ (**6**) (*ca.* 9%), benzene (*ca.* 15%), and 5-fluorocyclohexa-1,3-diene (*ca* 6%). Yields are based on the amount of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ consumed.

Preparation of (η^4-C_6H_7)$_2Fe_2(CO)_6$ (3). To a mixture containing $[Me_4N]OH{\cdot}5H_2O$ (2.0 g, 11.04 mmol) in CH_3CN (15 mL) that had been purged with CO for 5 min was added over a period of 5 min a solution of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.449 g, 1.47 mmol) in CH_3CN (10 mL) while purging vigorously with CO. After the resultant deep orange mixture was purged with CO for another 20 min, the solvent was removed in vacuo (no heat). Diethyl ether (75 mL) and water (50 mL) were added to the residue, the two-phase system was transferred to a separating funnel, and the ether layer was separated. The aqueous solution was extracted with an additional 2 × 50 mL of diethyl ether. The combined ether layers were washed with 2 × 40 mL of aqueous NaCl solution, dried over $MgSO_4$, and concentrated to dryness to afford a pale yellow solid. The pale yellow solid was taken up in pentane, and the resultant solution was filtered and concentrated to dryness to afford a pale yellow solid (0.22 g, 68% yield). The ^1H and $^{13}C\{^1H\}$ NMR data showed this to be composed of the C–C dimer **3**[11] (~95%) and (η^4-C_6H_8)$Fe(CO)_3$ (~5%).[16]

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[15] (a) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*; Saunders College Publishing: New York, 1982; p 790. (b) Vogel, A. I. *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th ed.; Longman: New York, 1978; p 742.

[16] Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1679.

[17] A small quantity of the diiron ether complex **2** is formed via trace H_2O hydrolysis of the fluoro complex (η^4-C_6H_7F)$Fe(CO)_3$ (**4**). Yield calculations for the decomposition of **4** to the C–C dimer **3** exclude the diiron ether complex.