

Electronic control of the competitive π donation in heteroatom substituted $\text{CpFe}(\text{CO})_2(\text{olefin})\text{BF}_4$ complexes and the resulting influence on the symmetry of the metal to olefin bond

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Abstract

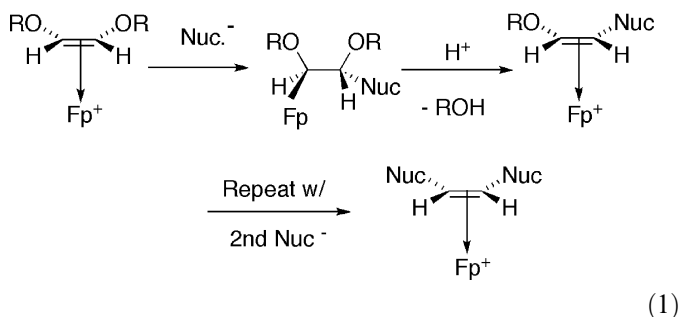
Nucleophilic, single substitution of $\text{CpFe}(\text{CO})_2(\text{cis-}\eta^2\text{-(EtO)CHCH(OEt)})^+\text{BF}_4^-$ with *para* substituted anilines was used to prepare a series of *cis* Fp olefin complexes **10–14** of the general formula, $\text{CpFe}(\text{CO})_2[\eta^2\text{-(EtO)CHCHNH}(p\text{-C}_6\text{H}_4\text{X})]^+\text{BF}_4^-$, where X = OMe (**10**), Me (**11**), Cl (**12**), COMe (**13**), and CN (**14**). These complexes contain both vinyl oxygen and vinyl nitrogen π donors capable of $p\text{--}\pi$ donation to the olefin. This series allows a comparison of competitive π donor strengths as X is varied across the series. Correlation of the Hammett σ_{para} parameters for X with the ^{13}C NMR shifts of the metal coordinated vinyl carbons demonstrated that as the electron withdrawing character of the *para* substituent was increased, the aniline (while still the dominant π donor) competed less effectively with the *cis* ethoxy group, moving the Fp^+ moiety toward a more central point along the olefin face. The implication of such control for the nucleophilic substitution chemistry of these complexes is discussed.

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1. Introduction

Cationic Fp complexes of *cis* dialkoxyolefins (where Fp = Cyclopentadienyl iron(II) dicarbonyl) undergo sequential disubstitution with a wide range of carbon and alkoxy nucleophiles (Eq. (1)) [1–3]



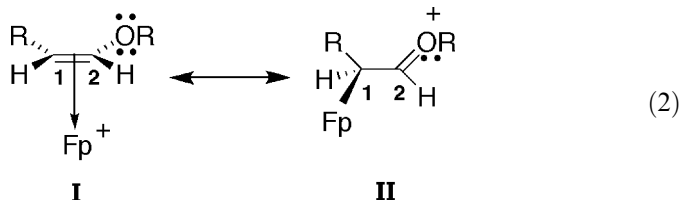
With carbon nucleophiles, initial substitution (with subsequent loss of alcohol), leaves one alkoxy group that has lone pairs still capable of π overlap with the adjacent vinyl carbon. This π overlap has been experimentally demonstrated [4,5] to displace the Fp moiety along the olefin face toward the remaining olefinic carbon (as in **II**, Eq. (2)), thereby activating [4] the second substitution. While such

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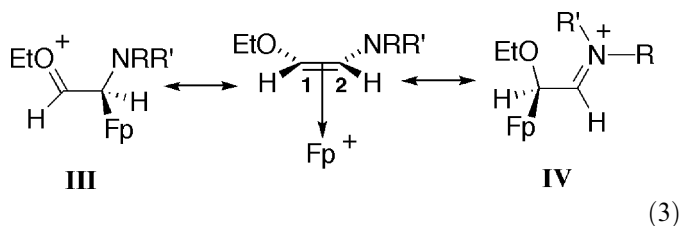
¹ Contributed as undergraduate researchers at Grand Valley State University.

displacement is not a prerequisite for nucleophilic substitution chemistry on the coordinated olefin [6], limited displacement has been observed (both experimentally and theoretically) to facilitate substitution at the site of heteroatom substitution [4,7–9]



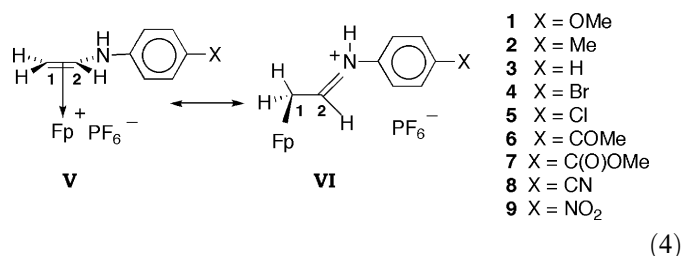
When the entering nucleophile is an alcohol (or alkoxide), the unsymmetric dialkoxy intermediate product results in a competition between similar π donors. In such cases, the Fp moiety favors one side by some small [10] amount, often displaced away from the larger alkoxy fragment [11]. The use of these alkoxy disubstitution reactions has been extended to the synthesis of multi-oxygen containing heterocyclic products [12]. It is interesting to note that while attack on Fp vinyl ethers by heteroatomic nucleophiles other than oxygen (including S, P, N) are also known [13], there exists no report of disubstitution by these nucleophiles. As a result, their use as synthetic backbones for potentially interesting multiple nitrogen or sulfur containing heterocycles remains unreported.

The lack of such disubstitutions with nitrogen nucleophiles is presumably due to a stronger π donation from nitrogen than from oxygen, as demonstrated by the relative extent of metal to olefin bond asymmetry in the crystal structures [4,14] of $\text{Fp}(\eta^2\text{-CH}_2\text{CH}(\text{OMe}))^+\text{BF}_4^-$ and $\text{Fp}(\eta^2\text{-CH}_2\text{CH}(\text{NMe}_2))^+\text{BF}_4^-$ [15]. The product of the first substitution of $\text{Fp}(\text{cis-1,2 diethoxyethylene})^+\text{BF}_4^-$ by a nitrogen nucleophile would be a mixed heteroatom disubstituted olefin complex, setting up a competition between the N and O lone pairs for overlap with their adjacent olefinic carbons (Eq. (3))



To facilitate the second substitution, the Fp moiety must be able to move back toward carbon 2 (favoring **III**). The enhanced overlap of the nitrogen lone pair with carbon 2, however, may greatly stabilize structure **IV**, preventing or impairing the second substitution. Control of the π donation from nitrogen might enable the design a system capable of overcoming this barrier to double nitrogen substitution in cationic Fp olefin complexes.

In previous work, we demonstrated [5,16,17] this control in singly substituted olefin complexes by synthesizing the series of *para* substituted, Fp vinyl aniline complexes, **1–9** (Eq. (4)). Correlation of the ^{13}C NMR shifts of the coordinated olefin carbons with the Hammett σ_{para} parameter for each derivative clearly demonstrated the ability to move the Fp cation along the olefin face, and hence along the continuum represented by structures **V** and **VI**



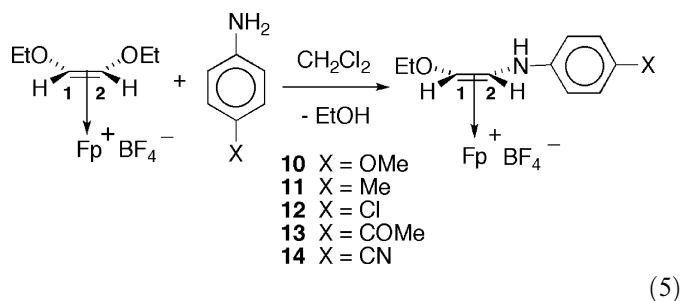
As the electron donating properties of the *p*-substituent increased, the contribution from resonance structure **VI** increased, reflected by an increasing separation in the ^{13}C peaks for the olefin carbons [18]. The increased separation of the ^{13}C peaks was structurally correlated to the increased displacement of the Fp fragment toward carbon 1 by comparing the X-ray structures of $\text{Fp}(\eta^2\text{-CH}_2\text{CH}(\text{OMe}))^+\text{BF}_4^-$ and $\text{Fp}(\eta^2\text{-CH}_2\text{CH}(\text{NMe}_2))^+\text{BF}_4^-$ [4], with those of derivatives **2** and **6** [5].

This paper addresses the competitive π donor abilities of oxygen and nitrogen substituents in mixed Fp(*cis*-1,2 ethoxy vinyl aniline) complexes and the ability to control this competition. We report the synthesis of a series of five new complexes **10–14** of the general formula, $\text{Fp}[\eta^2\text{-cis}(\text{EtO})\text{CHCHNH}(p\text{-C}_6\text{H}_4\text{X})]\text{BF}_4^-$, [19] where the electron donor/acceptor abilities of X are varied across the series. The ^{13}C NMR shifts of the coordinated olefin carbons are correlated to the Hammett σ_{para} constants for X as a probe of the relative asymmetry in the metal olefin bonding for each derivative.

2. Results and discussion

2.1. Synthesis of Fp^+ ethoxy vinyl aniline complexes, **10–14**

Exploiting the susceptibility of $\text{Fp}(\text{cis-1,2 diethoxyethylene})\text{BF}_4$ to nucleophilic substitution [1,20], we prepared a series of $\text{Fp}(\text{cis-1,2 ethoxyvinyl aniline})\text{BF}_4$ complexes, **10–14** (see Eq. (5)), which vary at the aniline *para* position. Treatment of a yellow CH_2Cl_2 solution of $\text{Fp}(\text{cis-1,2 diethoxyethylene})\text{BF}_4$ with a slight molar excess of the appropriate *p*-substituted aniline, at room temperature, precipitated the product over the course of several hours. The products are all powdered solids that vary from bright to dark orange



2.2. The influence of competitive π donation on metal olefin bond symmetry

Complexes **10–14** are examples of the mixed heteroatom intermediate products that would form during the currently unprecedented double nitrogen substitution of $\text{Fp}(1,2\text{-diethoxyethylene})\text{BF}_4$. As such, they reveal the competitive π donation between the oxygen at C_1 and the nitrogen at C_2 . We know from Taskinen's work with mixed *cis*-dialkoxyethylenes [11], as well as our previous work with various Fp olefin complexes [5], that when competition for p - π overlap exists, the ^{13}C shift of the carbon bonded to the dominant π donor will move downfield while the remaining olefin carbon moves upfield. The distance between these peaks (in an analogous series) is therefore a reasonable measure of each heteroatom's ability to compete for π overlap with the olefin. The ^{13}C shifts (CD_3NO_2) for carbons 1 and 2, along with the vinyl proton shifts in the ^1H NMR (CD_3NO_2) are given for complexes **10–14** in Table 1.

In the absence of the competing π donor (complexes **1–9**), the separation between the ^{13}C peaks [21] for carbons 1 and 2 ranged from 154.8 ppm in **1** to 128.4 ppm in **9**, and reflects the significance of resonance form **VI** (Eq. (4)) in the structure of those complexes. The introduction of the ethoxy functionality in **10–14** causes the ^{13}C shift of carbon 1 to increase and that of carbon 2 to decrease. This is illustrated in Fig. 1, which shows the range of ^{13}C shifts for C_1 and C_2 in both series of complexes. The separation between ^{13}C shifts for C_1 and C_2 is substantially decreased in complexes **10–14** (shaded in the figure), implying competing p - π donation from both heteroatoms but with a slight dominance from the aniline nitrogen on C_2 . Fig. 1 illustrates that both carbons have moved toward the reference

Table 1
 ^{13}C and ^1H NMR shifts (ppm in CD_3NO_2) for the coordinated olefin of complexes **10–14**

Complex	C_1 (ppm)	C_2 (ppm)	$\Delta^{13}\text{C}$ shift (ppm)	H_1 (ppm)	H_2 (ppm)
10 : X = OMe	77.9	137.2	59.3	6.06	8.11
11 : X = Me	79.0	132.2	53.2	6.11	8.06
12 : X = Cl	82.3	120.8	38.5	6.23	7.81
13 : X = C(O)Me	86.6	108.8	22.2	6.41	7.63
14 : X = CN	89.0	102.0	13.0	6.49	7.42

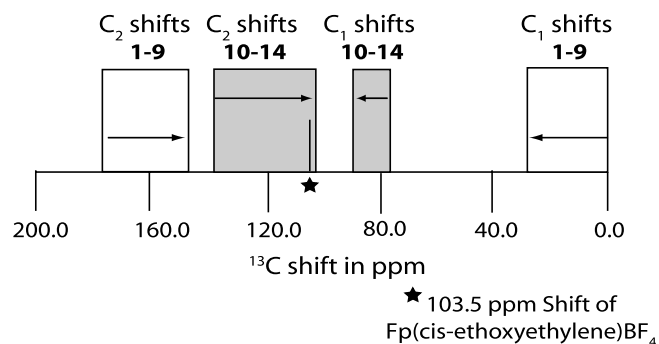


Fig. 1. Comparison of the olefin ^{13}C shifts for the Single (**1–9**) and disubstituted (**10–14**) $\text{Fp} + \text{olefin}$ complexes. The arrows show the shift of the ^{13}C peaks in response to increasing electron withdraw at the para position.

point defined by the highly reactive, symmetrically substituted $\text{Fp}(1,2\text{-diethoxyethylene})\text{BF}_4$ at 103.5 ppm [20], demonstrating a more symmetric structure [22] than in the absence of the ethoxy substituent.

It is obvious that simply substituting a vinyl H with an OEt group would cause the ^{13}C shift of carbon 1 to be significantly deshielded. This by itself does not, however, explain the observed shifts in **10–14**, which are upfield from either a typical vinyl ether or its Fp^+ complex. Table 2 compares the ^{13}C NMR shifts for the olefin carbons in the free ligand methyl vinyl ether [23], in the $\text{Fp}(\text{methoxyethylene})\text{PF}_6$ complex [20] and in the disubstituted $\text{Fp}(\text{cis-1,2-dimethoxyethylene})\text{BF}_4$ [20]. Upon complexation, the oxygen bearing carbon of the methyl vinyl ether is shielded slightly but most notably, the separation of the two olefin carbon peaks is greatly increased as the presence of the Fp cation increases the significance of the p - π donation from the oxygen. When the second methoxy ligand is added, the π donation is balanced, and the oxygen bearing carbons are further shielded.

When the alkoxy group competes as a π donor with the nitrogen of the vinylaniline in **10–14** (compare values in Table 1 with those in Table 2), the oxygen bearing carbon is pushed even farther upfield. These complexes show a ^{13}C shift of between 77.9 and 89.1 ppm for this carbon, placing them only 10–25 ppm downfield of an sp^3 carbon bound to oxygen. Thus, while the oxygen of the ethoxy group competes significantly with the nitrogen of the aniline for p - π

Table 2
Comparison of ^{13}C NMR shifts for olefin carbons in free and Fp^+ complexed methoxy vinyl ethers

Compound	O-Bonded carbon (ppm)	Vinyl CH_2 (ppm)	$\Delta^{13}\text{C}$ shift (ppm)
Methyl vinyl ether ^a	158.2	85.5	72.7
$\text{Fp}(\text{Methyl vinyl ether})\text{PF}_6^b$	146.2	27.3	118.9
$\text{Fp}(\text{cis-1,2-dimethoxyethylene})\text{BF}_4^b$	104.7		0.0

^a In CDCl_3 , see Ref. [23].

^b In CD_3NO_2 , see Ref. [20].

overlap with the olefin, it does not dominate. The resulting structures of **10–14** are more symmetric than seen for **1–9**, but the Fp group remains displaced toward carbon 1, favoring structure **IV** (Eq. (3), where R = *p*-aniline derivative and R' = H).

The chemical shift of carbon 2 is particularly significant, since comparison between equivalent members of both series (i.e. **1** vs. **10**) is a direct measure of the influence of competitive π donation from the OEt group. In each case, the presence of the ethoxy group acts to move the ^{13}C peak of carbon 2 about 30–40 ppm upfield. This is the result of an increased contribution from resonance structure **III** (Eq. (3)) to the overall description of the metal olefin bonding in response to competitive π donation from oxygen.

Further evidence of the increased symmetry in the metal to olefin bonding in **10–14** can be seen in two features of the ^1H NMR spectroscopy [24]: the chemical shift of the olefin protons and the lack of demonstrable rotation about the $\text{C}_1\text{--C}_2$ bond at room temperature. First, unlike complexes **1–9**, the ^1H NMR shift for H– C_1 in **10–14** is downfield in the region expected for vinyl protons (less of the sp^3 character associated with large Fp displacements). This shift is well in excess of the shift expected for alpha oxygen substitution alone.

Second, any increase in the double bond character resulting from increased bonding symmetry in **10–14** should be reflected in an increased barrier to rotation about the $\text{C}_1\text{--C}_2$ bond relative to the facile rotation seen with the strongly asymmetric complexes **1–9** [16,17]. While the ^{13}C NMR argues for some displacement of the Fp group toward carbon 1, the ^1H NMR shows no evidence for olefin rotation at room temperature. If this rotation were occurring, the coupling constant between the vinyl protons would be (in the limit of fast exchange) [25] an average of the *cis* and *trans* values [26]. To the contrary, this coupling constant in **10–14** is either small (<2 Hz) or unresolved in CD_3NO_2 . While this splitting is small for a typical free *cis* olefin, the reported coupling constant for Fp(1,2 methoxyethoxyethylene) BF_4 is also only 2 Hz [20].

The reason for the small coupling constants in **10–14** is not clear. While it is conceivable that the structure is partially rotated and sterically locked at a dihedral angle that reduces the coupling constant by the Karplus relationship [27], a purely steric argument collapses in light of the facile *trans* to *cis* isomerization of mixed alkyl, alkoxy complexes formed during dialkyl substitutions of Fp(1,2 diethoxyethylene) BF_4 at room temperature [1]. To date, we have been unable to grow crystals of **10–14** that are suitable for X-ray analysis.

2.3. Hammett correlation study demonstrating electronic control of competitive π donation

The ability to regulate electron donation to C_2 from the *p*-position of the vinyl aniline, previously demonstrated with **1–9** [5,16], affords the opportunity to control the com-

petition between these π donors and their influence on the metal olefin bond asymmetry. Control of this competition should determine a molecule's placement along the continuum between resonance structures **III** and **IV** (Eq. (3)) and provide insight into the design of the first successful double nitrogen substitution with known vinyl dication equivalents such as Fp(*cis*-1,2 diethoxyethylene) BF_4 .

Figs. 2 and 3 show the correlation [28] between the Hammett σ_{para} parameters for the aniline substituent and the ^{13}C shifts for C_1 and C_2 respectively. Both carbons are clearly affected by changes in the electron donating properties of the *p*-substituent on the vinyl aniline. While the ^{13}C shift of the olefin carbons would be

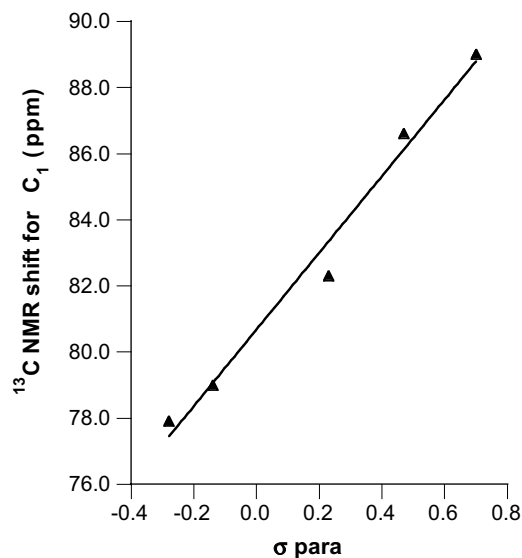


Fig. 2. Correlation plot for ^{13}C chemical shift (CD_3NO_2) of olefin C_1 carbon vs. Hammett σ_{para} parameters for complexes **10–14**.

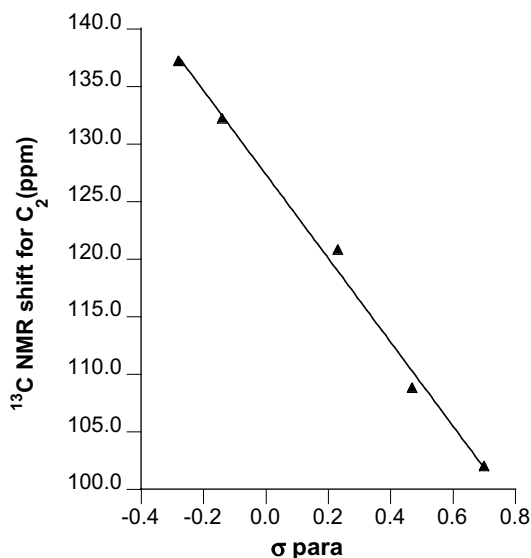


Fig. 3. Correlation plot for ^{13}C chemical shift (CD_3NO_2) of olefin C_2 carbon vs. Hammett σ_{para} parameters for complexes **10–14**.

expected to differ based on O vs. N substitution, the movement of both peaks in response to changes in the *p*-position of the aniline demonstrates that these shifts reflect changes in the competition between π donors. As the electron withdrawing ability of X increases (σ_{para} increases), the overlap between the nitrogen lone pair and C₂ decreases slightly [16], increasing the π donation from the oxygen at C₁. This causes the ¹³C shift of C₁ to increase and that of C₂ to decrease as the oxygen π donor competes more effectively. The result is increasing symmetry in the metal olefin bonding as one proceeds across the series from **10** to **14**. This is illustrated by the arrows in Fig. 1, which show how the ¹³C shift of each carbon changes as the value of σ_{para} (and hence the electron withdrawing power of X) increases.

3. Conclusions

In summary, a series of Fp(*cis*-1,2 ethoxyvinyl aniline)BF₄ complexes **10–14**, varying in the *p*-substituent on the aniline, have been synthesized to study the effect of competitive heteroatom π overlap on the symmetry of the metal to olefin bonding. The ¹³C spectra of **10–14** showed a decrease in the difference between the C₁ and C₂ shifts relative to their analogs in the series **1–9**. Attaching the ethoxy group in the present series created a competing π donation that shifted the Fp moiety back toward the nitrogen bearing carbon, thus increasing the symmetry of the metal to olefin bonding. Changing the electron donating properties of the *p*-substituent on aniline enabled us to alter the π overlap from the nitrogen lone pair, shifting the structure along the continuum between structures **III** and **IV**. As the electron withdrawing properties of this *para* group increased, π overlap from the nitrogen lone pair decreased, allowing for enhanced contributions from resonance structure **III** and further increasing the symmetry of the metal to olefin bonding. Even with the *p*-CN derivative, **14**, there is still asymmetry that favors displacement of the Fp toward carbon 1. Complex **14** is still too asymmetric to enable the first successful disubstitution of Fp(1,2 diethoxyethylene)BF₄ with nitrogen nucleophiles. Instead, substitution at the nitrogen bearing carbon appears to dominate. This continues to be an active area of work within our group.

4. Experimental

4.1. General procedures

All reactions were carried out under N₂ using standard Schlenk line techniques. Solvents were distilled under a N₂ atmosphere off of appropriate drying and/or deoxygenating reagents (CH₂Cl₂: CaH₂, Et₂O: Na/benzophenone). CD₃NO₂ was dried on P₂O₅ and distilled by vacuum transfer prior to use. CD₃NO₂ NMR tubes were prepared in an inert atmosphere glovebox. CD₃COCD₃ was dried on 3 Å

molecular sieves and vacuum transferred directly into the NMR tube. NMR spectra were recorded on a JEOL Eclipse 300 at 300.52 MHz for ¹H and 75.57 MHz for ¹³C. All chemical shifts were referenced to the residual protons in the deuterated solvents. Vinylic carbon ¹³C shift assignments used in the Hammett plots were confirmed using an HMQC NMR experiment. Values for the various σ parameters were obtained from the text “Advanced Organic Chemistry” by J. March [29]. Samples of the ethyl vinyl ether starting material, CpFe(CO)₂(EtOCHCHO-Et)⁺BF₄⁻, were prepared by reported literature methods [30]. All *p*-substituted anilines were sublimed prior to use. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. These Fp⁺ salts tend to retain solvent (particularly acetone and diethyl ether), making elemental analysis more difficult. We have included successful analyses of complexes **13** and **14** as representative of the series.

4.2. Typical procedure for the preparation of Fp(ethoxyvinylaniline)⁺BF₄⁻ complexes according to Eq. (5)

To a yellow solution of CpFe(CO)₂(EtOCHCHO-Et)⁺BF₄⁻ (0.150 g, 0.399 mmol) in CH₂Cl₂ (10 mL) was added a 5–10 mol % excess of the *p*-substituted aniline species as a solution in 4–5 mL of CH₂Cl₂. The resulting dark orange solution was stirred at room temperature for 2 h. The length of time was increased as the nucleophilicity of the aniline species decreased. As the reaction proceeded, the ionic product began to precipitate from solution as a dark red-orange powder. The solvent from the reaction mixture was then reduced under vacuum and diethyl ether was added to complete precipitation. The residue was then recrystallized from either dichloromethane/diethyl ether or acetone (better solubility)/diethyl ether. The resulting powder was isolated by filtration and dried under vacuum to give respectively **10** (83.5% isolated yield), **11** (76.7% isolated yield), **12** (69.0% isolated yield), **13** (70.0% isolated yield) and **14** (80.1% isolated yield).

4.3. Characterization of complexes **10–14**

4.3.1. Characterization data for *p*-OMe derivative, **10**

¹H NMR (nitromethane-*d*₃, 300.53 MHz) δ 1.30 (t, 3H, *J* = 6.5 Hz, OCH₂CH₃), 3.86 (s, 3H, ArOCH₃), 3.89 (mult., 1H, diastereotopic OCH₂CH₃), 4.09 (mult., 1H, diastereotopic OCH₂CH₃), 5.30 (s, 5H, Cp), 6.06 (d, 1H, *J*_{cis} = 1.65 Hz, vinylic proton, -C(OEt)H), 7.07 (d, 2H, *J* = 8.81 Hz, aromatic), 7.46 (d, 2H, *J* = 8.81 Hz, aromatic), 8.11 (d, 1H, *J*_{H-NH} = 11.3 Hz, vinylic proton, -CHNAr), 8.54 (br d, 1H, *J* = 12.4 Hz, NH). ¹³C {¹H} (nitromethane-*d*₃, 75.58 MHz) δ 15.0 (OCH₂CH₃), 56.4 (ArOCH₃), 69.7 (OCH₂CH₃), 77.7 (olefin CH(OEt)), 88.0 (Cp), 116.5, 121.0 (CH aromatic), 132.1, 160.0 (C aromatic), 137.2 (olefin CHN), 212.6, 214.1 (Fe-CO). IR (KBr) 2003, 2045 cm⁻¹.

4.3.2. Characterization data for *p*-Me derivative, **11**

^1H NMR (nitromethane- d_3 , 300.53 MHz) δ 1.32 (t, 3H, $J = 6.7$ Hz, OCH_2CH_3), 2.37 (s, 3H, ArCH_3), 3.92 (mult., 1H, diastereotopic OCH_2CH_3), 4.11 (mult., 1H, diastereotopic OCH_2CH_3), 5.33 (s, 5H, Cp), 6.11 (d, 1H, $J_{\text{cis}} = 1.10$ Hz, vinylic proton, $-\text{C}(\text{OEt})\text{H}$), 7.36 (mult., 4H, aromatic), 8.06 (d of d, 1H, $J_{\text{H-NH}} = 12.9$ Hz, $J_{\text{cis}} = 1.10$ Hz vinylic proton, $-\text{CHNAr}$), 8.34 (br d, 1H, $J_{\text{H-NH}} = 13.2$ Hz, NH). ^{13}C $\{^1\text{H}\}$ (nitromethane- d^3 , 75.58 MHz) δ 15.0 (OCH_2CH_3), 20.9 (ArCH_3), 69.8 (OCH_2CH_3), 79.0 (olefin $\text{CH}(\text{OEt})$), 88.1 (Cp), 119.1, 131.9 (CH aromatic), 132.2 (olefin CHN), 136.7, 138.2 (C aromatic), 212.4, 213.8 (Fe–CO). IR (KBr) 1985, 2030 cm^{-1} .

4.3.3. Characterization data for *p*-Cl derivative, **12**

^1H NMR (nitromethane- d_3 , 300.53 MHz) δ 1.33 (t, 3H, $J = 6.7$ Hz, OCH_2CH_3), 4.00 (mult., 1H, diastereotopic OCH_2CH_3), 4.22 (mult., 1H, diastereotopic OCH_2CH_3), 5.37 (s, 5H, Cp), 6.23 (br s, 1H, vinylic proton, $-\text{C}(\text{OEt})\text{H}$), 7.46 (mult., 4H, aromatic), 7.81 (d, 1H, $J_{\text{H-NH}} = 13.2$ Hz, vinylic proton, $-\text{CHNAr}$), 7.94 (br d, 1H, $J_{\text{H-NH}} = 13.2$ Hz, NH). ^{13}C $\{^1\text{H}\}$ (nitromethane- d_3 , 75.58 MHz) 14.9 (OCH_2CH_3), 70.2 (OCH_2CH_3), 82.4 (olefin $\text{CH}(\text{OEt})$), 88.3 (CH_{Cp}), 120.1, 131.3, (CH aromatic), 120.8 (olefin CHN), 131.6, 138.6 (C aromatic) 212.0, 213.3 (Fe–CO) ppm. IR (KBr) 1977, 2042 cm^{-1} .

4.3.4. Characterization data for *p*-COMe derivative, **13**

^1H NMR (nitromethane- d_3 , 300.53 MHz) δ 1.36 (t, 3H, $J = 6.9$ Hz, OCH_2CH_3), 2.58 (s, 3H, ArCOCH_3), 4.10 (mult., 1H, diastereotopic OCH_2CH_3), 4.33 (mult. under solvent peak, diastereotopic OCH_2CH_3), 5.44 (s, 5H, Cp), 6.41 (br s, 1H, vinylic proton, $-\text{C}(\text{OEt})\text{H}$), 7.48 (d, $J = 8.6$ Hz, 2H, aromatic), 7.63 (br s, 2H, NH overlapping with vinylic proton $\text{CHN}(\text{H})\text{Ar}$), 8.07 (d, $J = 8.6$ Hz, 2H, aromatic). ^{13}C $\{^1\text{H}\}$ (nitromethane- d^3 , 75.58 MHz) δ 15.0 (OCH_2CH_3), 26.7 (ArCOCH_3), 70.6 (OCH_2CH_3), 86.6 (olefin $\text{CH}(\text{OEt})$), 88.5 (Cp), 108.8 (olefin CHN), 117.6, 131.8 (CH aromatic), 134.6, 144.1 (C aromatic), 198.4 (COCH_3), 211.3, 212.5 (Fe–CO). IR (KBr) 2003, 2044 cm^{-1} . Anal. Calc. for $\text{C}_{19}\text{H}_{20}\text{NO}_4\text{BF}_4\text{Fe}$: C, 48.66; H, 4.30; N, 2.99. Found: C, 48.14; H, 4.21; N, 2.87%.

4.3.5. Characterization data for *p*-CN derivative, **14**

^1H NMR (nitromethane- d_3 , 300.53 MHz) δ 1.36 (t, 3H, $J = 5.8$ Hz, OCH_2CH_3), 4.16 (mult., 1H, diastereotopic OCH_2CH_3), 4.33 (mult. under solvent peak, diastereotopic OCH_2CH_3), 5.46 (s, 5H, Cp), 6.49 (br s, 1H, vinylic proton, $-\text{C}(\text{OEt})\text{H}$), 7.42 (br s, 2H, NH overlapping with vinylic proton $\text{CHN}(\text{H})\text{Ar}$), 7.49 (d, $J = 7.4$ Hz, 2H, aromatic), 7.79 (d, $J = 7.4$ Hz, 2H, aromatic). ^{13}C $\{^1\text{H}\}$ (nitromethane- d^3 , 75.58 MHz) δ 14.9 (OCH_2CH_3), 71.0 (OCH_2CH_3), 88.7 (Cp), 89.1 (olefin $\text{CH}(\text{OEt})$), 102.0 (olefin CHN), 107.8 (CN), 117.9, 135.5 (CH aromatic), 91.3, 144.41 (C aromatic), 211.0, 212.1 (Fe–CO). IR (KBr) 2012, 2056 cm^{-1} . Anal. Calc. for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3\text{BF}_4\text{Fe}$: C, 47.83; H, 3.79; N, 6.20. Found: C, 47.23; H, 3.79; N 6.20%.

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References

- [1] M. Marsi, M. Rosenblum, J. Am. Chem. Soc. 106 (1984) 7264–7266.
- [2] M. Rosenblum, M.M. Turnbull, B.M. Foxman, Organometallics 5 (1986) 1062–1063.
- [3] M.M. Turnbull, B.M. Foxman, M. Rosenblum, Organometallics 7 (1988) 200–210.
- [4] T.C.T. Chang, B.M. Foxman, M. Rosenblum, C. Stockman, J. Am. Chem. Soc. 103 (1981) 7361–7362.
- [5] S.A. Matchett, B.R. Schmiede-Boyle, J. Cooper, D. Frattarelli, J. Thommen, D. Tigelaar, F. Winkler, Organometallics 22 (2003) 5047–5053.
- [6] A.D. Cameron, V.H. Smith, M.C. Baird, J. Chem. Soc., Dalton Trans. (1988) 1037–1043.
- [7] O. Eisenstein, R. Hoffmann, J. Am. Chem. Soc. 103 (1981) 4308–4320.
- [8] O. Eisenstein, W.M. Butler, A.J. Pearson, Organometallics 3 (1984) 1150–1157.
- [9] S.M. Sakaki, Katsuhiko Maruta, Ohkubo Katsutoshi, Inorg. Chem. 26 (1987) 2499–2505.
- [10] The ^{13}C NMR (CD_3NO_2) of the *cis*-methoxy, ethoxy vinyl Fp^+ complex shows a difference of approximately 1 ppm between the olefin carbons. These are seen at 104.6 ppm for vinyl carbon bound to the methoxy group and 103.8 ppm for the vinyl carbon bound to the ethoxy group.
- [11] E. Taskinen, Magn. Reson. Chem. 36 (1998) 573–578.
- [12] M. Rosenblum, B.M. Foxman, M.M. Turnbull, Heterocycles 25 (1987) 419–431.
- [13] P. Lennon, M. Madhavarao, A.M. Rosan, M. Rosenblum, J. Organomet. Chem. 108 (1976) 93–109.
- [14] L.A. Watson, B. Franzman, J.C. Bollinger, K.G. Caulton, New J. Chem. 27 (2003) 1769.
- [15] The difference between Fe to vinyl carbon distances in the vinyl ether complex is reported to be 0.23 Å [4] or 0.3 Å [14], while the difference for the vinyl amine was 0.69 Å [4,14].
- [16] S.A. Matchett, G.-R. Zhang, D. Frattarelli, Organometallics 23 (2004) 5440–5449.
- [17] G.R. Zhang, S.A. Matchett, L.Y. Dai, J.X. Lu, J. East China Normal Univ. 2 (2003) 46–53.
- [18] The shift of the alpha carbon moves upfield as it develops increasing sp^3 character while the shift of the beta carbon moves downfield in response to the development of iminium character as it overlaps with the nitrogen lone pair.
- [19] The assignment of a *cis* olefin geometry is based on the small coupling constant of ~ 2 Hz.
- [20] E.J. Crawford, T.W. Bodnar, A.R. Cutler, J. Am. Chem. Soc. 108 (1986) 6202–6212.
- [21] The solvent used for all ^{13}C spectra in this work and those used for reference was CD_3NO_2 .
- [22] While the crystal structure of $\text{Fp}(\text{cis-1,2 diethoxyethylene})\text{BF}_4$ is not reported, it is reasonable to assume a symmetric structure from the single ^{13}C shift for both olefin carbons. The structure of the cyclic $\text{Fp}(\text{dioxene})\text{BF}_4$ complex is reported, where the Fe to alpha C and Fe to beta C distances differ by only 0.03 Å. See reference [3].
- [23] E. Taskinen, J. Org. Chem. 43 (1978) 2776–2780.
- [24] One would also anticipate a correlation with the IR spectra, showing increasing back bonding to CO (lower ν_{CO} values) as the olefin becomes a better σ donor. The trend in the data holds for complexes **10–12** but reverses for complexes **13** and **14**. Without a set of crystal

structures to show exact spacial relationships, the authors have withheld speculation on this observed behavior in the IR data.

- [25] Variable temperature ^1H NMR (acetone- d_6) down to -40°C showed no changes in the spectrum. This temperature was previously sufficient to freeze out rotation in complexes **1–9** (see Ref. [16]).
- [26] Trans coupling constants in mixed Fp(alkoxy, alkyl ethylene) complexes are reported to be 11 Hz, while *cis* coupling constants in

similar species were 6 Hz. A.R. Cutler, S. Raghu, M. Rosenblum, J. Organomet. Chem. 77 (1974) 381–391.

- [27] M. Karplus, J. Chem. Phys. 30 (1959) 11.
- [28] R^2 for Fig. 2 is 0.983 and R^2 for Fig. 3 is 0.994.
- [29] J. March, Advanced Organic Chemistry, Wiley and Sons, New York, 1985, p. 244.
- [30] E.L. Weinberg, J.T. Burton, M.C. Baird, M.Z. Herberhold, Naturforsch. B: Anorg. Chem. Org. Chem. 36B (1981) 485–487.