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Synthesis and Properties of (η^2-C,X) Chelate Arylcarbene Complexes [Fe(C_5Me_5)(L){η^2-C(OMe)C_6H_4-*o*-X}][OTf] (L = CO, PMe_3; X = OMe, Cl)

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The methoxycarbene complexes [Fe(C_5Me_5)$(CO)_2${=C(OMe)C_6H_4-*o*-X}][OTf] (**2a**, X = OMe; **2b**, X = Cl) are good precursors of the corresponding (η^2-C,X) chelate carbene complexes [Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-X}][OTf] (OTf = CF_3SO_3) (**5a,b**). The η^2-chloro derivative **5b** has been characterized by X-ray diffraction, confirming the formation of a five-membered ring metallacycle. All the new carbene complexes, including the nonheteroatom-stabilized carbene complex [Fe(C_5Me_5)$(CO)_2${=C(H)C_6H_4-*o*-OMe}][OTf] (**4a**), have been fully characterized by ^{1}H and ^{13}C NMR spectrocopy. The lability of the chelating *o*-substituent is chemically demonstrated by the formation of the corresponding neutral iodo carbene complexes [Fe(C_5Me_5)(CO)(I){η^1-C(OMe)C_6H_4-*o*-X}] (**6a,b**), the competitive O-demethylation process being thus inhibited. Selective ligand exchange reactions of **5a,b** afford various substituted complexes such as [Fe(C_5Me_5)$(CO)_n$(PMe_3){η^x-C(OMe)C_6H_4-*o*-OMe}][OTf] (**11**, $n = 1$, $x = 1$; **12**, $n = 0$, $x = 2$); the mono- and bis(acetonitrile) complexes [Fe(C_5Me_5)(L)(CH_3CN){η^1-C(OMe)C_6H_4-*o*-Cl}][OTf] (**14**, L = CH_3CN; **15**, L = CO) have been also synthesized. The reactivity of **5a** toward $NaBH_4$ is highly dependent on the solvent. Specific hydride addition occurs in 9:1 THF−MeOH to give the expected complex [Fe(C_5Me_5)(CO){η^2-CH(OMe)C_6H_4-*o*-OMe}] (**9**) as a single diastereoisomer, while reduction in pure THF affords the organoborohydride complex [Fe(C_5Me_5)(CO){η^2-$H_2BHCH_2C_6H_4$-*o*-OMe}] (**10**). The latter reaction involves a formal insertion of BH_3 into a Fe−C bond, promoted by the potential vacant coordination site. The carbene ligand is easily displaced and recovered as free carbonyl-containing organic substrates (aldehyde or ester) from both types of carbene complexes upon bubbling of O_2.

Introduction

Arylcarbene complexes represent good models for the investigation of the structural, spectral, and chemical reactivity patterns of iron−carbene complexes:[1] the absence of β-hydrogen atoms inhibits any side rearrangement reactions, and the thermal stability of these electrophilic species is enhanced by the electronic delocalization of the positive charge into the aryl group.[1,2] Our investigations deal with arylcarbene complexes [Fe(C_5Me_5)$(CO)_2${η^1-C(R)C_6H_4-*o*-X}]$^+$, which possess a coordinating *ortho*-substituent X (X = OMe, Cl) on the C_6 ring; the presence of this dissymmetrically substituted ring allows (i) additional conformational information to be obtained and (ii) access to (η^2-C,X) chelate carbene complexes. The chelating group X is expected to dissociate easily in order to favor reaction within the coordination sphere of the metal. Moreover, these complexes constitute useful precursors for the complexation of new ligands, especially when direct routes cannot be applied due to side reactions with the carbene ligand.

In a preliminary communication,[3] we reported the original reactivity of the (η^2-C,O) chelated carbene complex [Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-OMe}][OTf] (**2a**), precursor of the organoborato complex [Fe(C_5Me_5)(CO){η^2-$H_2BHCH_2C_6H_4$-*o*-OMe}] (**10**). This led us to extend our investigations to the related (η^2-C,Cl)

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complex [Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-Cl}][OTf] (**2b**), since substitution-labile halocarbon complexes are currently of structural and synthetic interest, especially for the activation of small molecules.[4]

We report here a full account of the synthesis, structure, and reactivity of the (pentamethylcyclopentadienyl)iron−carbene complexes [Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-X}][OTf] (X = OMe, Cl).

Results and Discussion

Synthesis of the Dicarbonyl Carbene Complexes. Reactions of the metal anion [Fe(C_5Me_5)$(CO)_2$][K] with acylating or alkylating agents provide a convenient route to metal−acyl[5] or -alkyl complexes, whereas the use of aryl halides is generally inefficient.[6] The *o*-anisoyl complex [Fe(C_5Me_5)$(CO)_2${C(O)C_6H_4-*o*-OMe}] (**1a**) is thus prepared in 80% yield after extraction and crystallization in ether. The *ortho*-iodo-substituted analogue is not accessible in this way, an electron transfer leading to the starting material [Fe(C_5Me_5)$(CO)_2]_2$. In contrast, nucleophilic attack occurs specifically when [Fe(C_5Me_5)$(CO)_2$][K] is treated with the *ortho*- or *para*-chlorobenzoyl chloride *o*-,*p*-ClC_6H_4C(O)Cl, affording the desired chlorobenzoyl complexes [Fe(C_5Me_5)$(CO)_2${C(O)C_6H_4Cl}] (**1b**, *o*-Cl (62% yield); **1c**, *p*-Cl (79% yield)). The corresponding methoxycarbene complexes [Fe(C_5Me_5)$(CO)_2${η^1-C(OMe)-C_6H_4X}][OTf] (**2a**−**c**) (OTf = OSO_2CF_3) are then obtained from **1a**−**c** by O-methylation (MeOTf, CH_2Cl_2, 16 h) according to classical procedures.[7] Complex [Fe(C_5Me_5)$(CO)_2${η^1-CH(OMe)C_6H_4-*o*-OMe}] (**3a**) is then prepared by reduction of the methoxycarbene **2a** with $NaBH_4$ in 9:1 THF−MeOH, the presence of methanol being essential to obtain specifically **3a** in good yield. Further reduction occurs by using pure THF as solvent, leading to a mixture of **3a** and [Fe(C_5Me_5)$(CO)_2${η^1-$CH_2C_6H_4$-*o*-OMe}], a feature widely observed.[7,8] The nonheteroatom-substituted anisylcarbene complex [Fe(C_5Me_5)$(CO)_2${η^1-C(**H**)C_6H_4-*o*-OMe}][OTf] (**4a**) is thus generated from **3a** by α-methylate abstraction using Me_3SiOTf[1,2] (Scheme 1).

NMR Studies and Conformational Analysis. All the new complexes **2a**−**c** exhibit ^{1}H and ^{13}C resonance patterns characteristic of the methoxycarbene ligand (Table 1).[1,2,7] The nonheteroatom-stabilized carbene complex [Fe(C_5Me_5)$(CO)_2${η^1-C(H)C_6H_4-*o*-OMe}][OTf] (**4a**) was directly generated in an NMR tube. The ^{1}H NMR spectrum (CD_2Cl_2) shows at −80 °C two low-field singlets at δ 15.61 and 15.28 (=CH) in intensity ratio 20:80, respectively; these signals coalesce at T_C (300 MHz) = −62 °C giving rise to a unique singlet at δ 15.16. Since the rotation around the Fe−C_α bond cannot be frozen out in such complexes, as already mentioned for related carbene−iron derivatives,[7,9] this feature arises from restricted rotation about the C_α−C_{ipso} bond. Therefore, complex **4a** can exist as two geometric isomers which differ from each other in the orientation of the anisyl group; the observed ratio probably results from steric requirements of the *ortho*-substituent (barrier to aryl rotation $\Delta G^\ddagger$ = 9.7 kcal mol^{-1}). These results are in agreement with those described by Brookhart for the parent Cp complex [Fe(C_5H_5)$(CO)_2${η^1-C(H)C_6H_4-*p*-OMe}][OTf], when a unique isomer is observed as indicated by a single signal for the carbene hydrogen in the ^{1}H NMR spectrum at low temperature; the aromatic protons appear as a set of four distinct signals assigned to the nonequivalent *o*,*o*′- and *m*,*m*′-hydrogens.[7a] It has been proposed that the aryl group is aligned with the Fe−C_α−C_{ipso} plane (see the Newman projection in Scheme 2), a conformation providing better electronic delocalization of the positive charge.[7a,10] Moreover, the ^{13}C resonance at −40 °C (a temperature at which the interconversion is rapid) for the carbene carbon atom of **4a** appears as a typical low-field singlet at δ 322.6. It is noteworthy that one CO resonance at δ 210.6 is observed, whereas for the methoxycarbene complexes **2a**,**b** the ^{13}C NMR ($CDCl_3$, 25 °C) spectra show that the two carbonyl ligands are magnetically nonequivalent. In contrast, the CO ligands of the parent *para*-substituted complex [Fe(C_5Me_5)$(CO)_2$-{η^1-C(OMe)C_6H_4-*p*-Cl}][OTf] (**2c**) also give rise to a unique singlet (^{13}C ($CDCl_3$): δ_{CO} 210.9). These data suggest that the conformation is different for each type of carbene complex, but we cannot definitely assign the carbene orientation.[7a,11] In the case of the methoxycarbene complexes **2**, the resonance stabilization provided by the better π-bonding methoxy carbene substituent would be substantial, compared with that of the aromatic ring, and moreover, steric interactions can also govern the carbene conformation, especially in the

Scheme 1

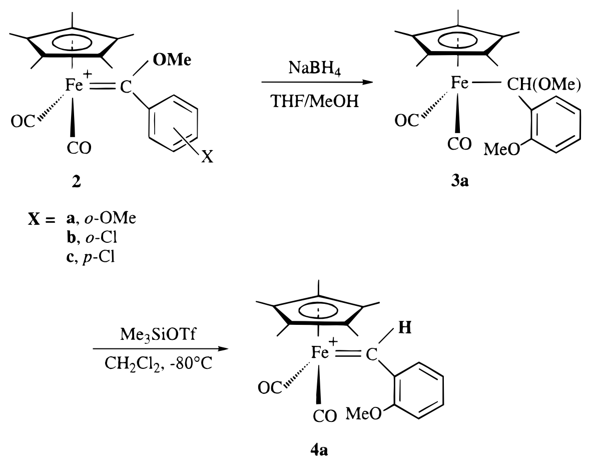

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Table 1. Selected ^{13}C NMR ($CDCl_3$, δ in ppm versus TMS, 25 °C) Data

cationic carbene complexes $[Fe(C_5Me_5)(CO)_n\{\eta^x\text{-}C(OMe)C_6H_4X\}]^+$ ($x = 1$, $n = 2$; $x = 2$, $n = 1$) (**a**, X = *o*-OMe; **b**, X = *o*-Cl; **c**, X = *p*-Cl)

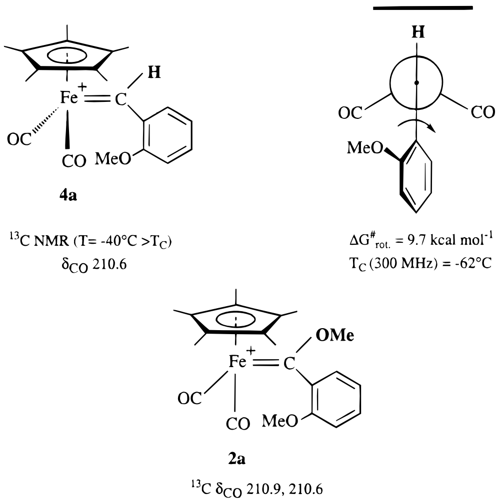
complex	=C	CO	Ar_X	Ar_{ipso}
4a[a]	322.6	210.6	159.5 (br s)	144.0
2a	328.2	210.9, 210.6	148.9	138.8
2b	323.5	210.7, 210.2	122.8	147.4
2c	326.0	210.9	147.3	138.1
5a	325.8	213.1	167.7	134.8
5b	329.1	211.5	144.9	145.5

neutral carbene complexes $[Fe(C_5Me_5)(CO)(X')\{\eta^1\text{-}C(OMe)C_6H_4\text{-}o\text{-}X)]$

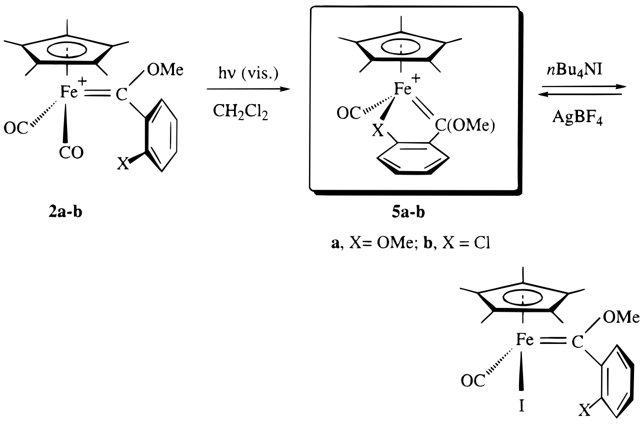
complex	X′	=C	CO	Ar_X	Ar_{ipso}
6a[b]	I	334.9	221.6	149.9	141.8
6b	I	328.1	220.2	124.6	149.4
7a	Cl	335.1	218.7	149.5	141.9
8	X = X′ = O	311.1	214.6	187.0	139.4

[a] $[Fe(C_5Me_5)(CO)_2\{=C(H)C_6H_4\text{-}o\text{-}OMe\}][OTf]$ (−40 °C). [b] C_6D_6.

Scheme 2



Scheme 3



C_5Me_5 series. We have previously shown that the secondary methoxycarbene complex $[Fe(C_5Me_5)(CO)_2\text{-}\{=CH(OMe)\}][PF_6]$ is generated at −80 °C as a C$\cdots$O *cis* isomer (in which the methoxy substituent is directed toward the $[Fe(C_5Me_5)(CO)_2]$ fragment); subsequent irreversible isomerization gives the thermodynamic *trans* form,[9] a feature not observed for the related Cp complex.[7d]

Neutral and Cationic Chelate Carbene Complexes. The cationic (η^2-C,X) chelate–carbene complexes $[Fe(C_5Me_5)(CO)\{\eta^2\text{-}C(OMe)C_6H_4\text{-}o\text{-}X\}][OTf]$ (**5a,b**) are formed from **2a,b** by irradiation in CH_2Cl_2 (visible light, overnight) (Scheme 3). Both compounds **5a,b** are isolated as black crystals in good yields by crystallization from a CH_2Cl_2/Et_2O mixture; they can be stored indefinitely under argon in the solid state without decomposition. The monodecarbonylation/chelation reaction is easily monitored by IR spectroscopy, the two initial $\nu(C\equiv O)$ absorptions being replaced by a new absorption at 1977 (**5a**) or 1990 (**5b**) cm^{-1}. The difference in the spectra of the unchelated complex **2b** and the chelated one **5b** comes, in particular, from the ^{13}C NMR signal of the Ar_{Cl} carbon; the resonance is shifted downfield from δ 122.8 to 144.9, respectively. The chlorine atom, like the oxygen atom in **5a**, acts as a neutral $2e^-$ donor ligand (Lewis acid–base interaction) allowing the formation of a five-membered metallacycle.[12]

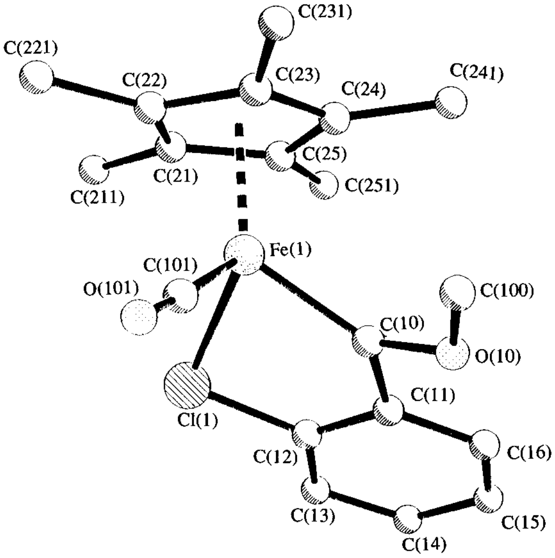


Figure 1. Molecular structure of $[Fe(C_5Me_5)(CO)\{\eta^2\text{-}C(OMe)C_6H_4\text{-}o\text{-}Cl\}][OTf]$ (**5b**) showing the atom-labeling scheme.

The structure of the complex **5b** was unequivocally established by an X-ray crystal structure analysis. Figure 1 shows the molecular structure of complex **5b**; selected bond distances and angles are given in Table 2, and positional parameters, in the Supporting Information. The environment about the iron atom corresponds to that of a slightly distorted three-legged piano stool: in the metallacycle, the ring angle at the iron center is reduced to 84.7(2)° (C(10)−Fe−Cl); the other angles C(101)−Fe−C(10) and C(101)−Fe−Cl are 95.8(3) and 100.0(2)°, respectively. The Fe−C_α distance of 1.857(6) Å is similar to the Fe−carbene distance found for the related (dppe)-substituted methoxycarbene com-

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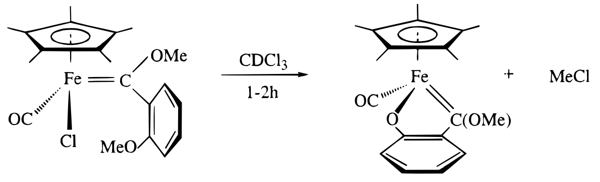
Table 2. Selected Bond Lengths and Angles for 5b

Bond Lengths (Å)			
Fe(1)−Cl(1)	2.310(2)	C(10)−C(11)	1.493(9)
Fe(1)−C(10)	1.857(6)	Cl(1)−C(12)	1.753(7)
Fe(1)−C(101)	1.766(8)	C(10)−O(10)	1.304(7)

Bond Angles (deg)			
C(101)−Fe(1)−C(10)	95.8(3)	C(12)−Cl(1)−Fe(1)	96.9(2)
C(10)−Fe(1)−Cl(1)	84.7(2)	O(101)−C(101)−Fe(1)	174.0(7)
C(101)−Fe(1)−Cl(1)	100.0(2)	O(10)−C(10)−C(11)	108.3(6)

Scheme 4



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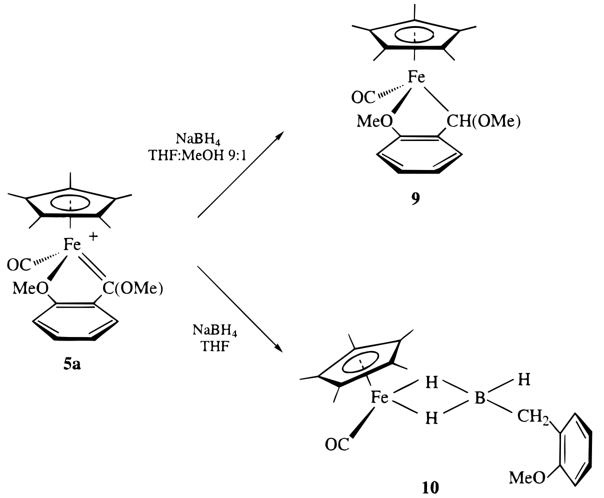
8

plex [Fe(C$_5$Me$_5$)(η^2-PPh$_2$CH$_2$CH$_2$PPh$_2$){=C(OMe)H}][PF$_6$] (1.82(2) Å).[13−15] The Fe−Cl bond (2.310(2) Å) is comparable to that of the terminal chloride complex [Fe(C$_5$Me$_4$Et)(CO)$_2$(Cl)] (2.304(2) Å).[16] The Cl−C$_{Ar}$ bond distance (1.753(7) Å) is slightly shorter than that of the chelate chloroarene complex [MePt{η^2-Ph$_2$P(C$_6$H$_4$-*o*-Cl}{η^1-Ph$_2$P(C$_6$H$_4$-*o*-Cl}][BF$_4$][17] (chelated Cl−C$_{Ar}$: 1.788(5) Å).

The chelate−carbene complexes **5a,b** react with 1 equiv of [*n*Bu$_4$N][I] to give the neutral carbene complexes [Fe(C$_5$Me$_5$)(CO)(I){η^1-C(OMe)C$_6$H$_4$-*o*-X}] (**6a,b**), the chelated group X being displaced by the halide (Scheme 3). This reaction is chemospecific, only one product being formed in good yield. Two pathways could be *a priori* considered: the well-established O-demethylation process of the methoxycarbene substituent,[8] which is observed for the dicarbonyl complexes **2a,b** (the reverse reaction of **1** → **2**), or the substitution reaction allowing access to neutral halogeno carbene complexes. The chelation process is reversible; complex **6b** reacts with 1 equiv of AgBF$_4$ to regenerate **5b**−BF$_4^-$. Analogously, **5a** is converted, in the presence of [(PPh$_3$)$_2$N][Cl], to the parent chloro derivative [Fe(C$_5$Me$_5$)(CO)(Cl){η^1-C(OMe)C$_6$H$_4$-*o*-OMe}] (**7**), but spontaneous elimination of MeCl occurs in CDCl$_3$ solution within several hours to yield the new neutral chelate carbene complex [Fe(C$_5$Me$_5$)(CO){η^2-C(OMe)C$_6$H$_4$-*o*-O}] (**8**) (Scheme 4). This reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy; the OMe$_{Ar}$ signal decreases, and simultaneously, resonances at δ (^{1}H) 3.02 and δ (^{13}C) 25.9 attributed to MeCl appear. The mechanism of the formation of **8**, which results formally from a demethylation of the *o*-methoxy group, is still not clear.

Scheme 5



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5a

10

Related neutral carbene complexes have been previously prepared by different procedures. Winter reported that the complexes [M(C$_5$H$_5$)(CO)(I){=C(OEt)Ph}] (M = Fe, Ru) are accessible from the tin derivatives [M(C$_5$H$_5$)(CO)(SnPh$_3$)(=C(OEt)Ph)] by treatment with iodine.[15] An original route, recently described by Werner, consists of reacting the acetato−ruthenium complex [Ru(C$_5$H$_5$)(PPh$_3$)(η^2-O$_2$CMe)] with diaryldiazomethanes; subsequent addition of Et$_3$NHCl leads to the formation of [Ru(C$_5$H$_5$)(PPh$_3$)(Cl)(=CArAr′)].[18]

The reactivity of the methoxy-chelate carbene complex **5a** toward hydride reagents is highly dependent on the reaction conditions. The neutral chelate complex [Fe(C$_5$Me$_5$)(CO){η^2-CH(OMe)C$_6$H$_4$-*o*-OMe}] (**9**) is formed upon reduction at −80 °C of **5a** by using either NaBH$_4$ in a mixture of 9:1 THF−MeOH or LiBEt$_3$H in pure THF (Scheme 5). Extraction with pentane gives an orange-brown powder in 93% yield, the NMR (^{1}H and ^{13}C) spectra of which display one set of signals, assigned to the presence of one diastereoisomer.[19] Formally, the formation of this latter species arises from an hydride attack at the electrophilic carbene carbon atom. However, since in the present case the methoxy group is labile, it is plausible to suggest that the addition should initially occur at the iron center. This proposal is supported by the above results concerning nucleophilic substitution at the metal center by halides, but we have not been able to observe any intermediate. Such migration processes (hydride, alkyl, vinyl, or aryl) have been extensively proposed for group 8 metal−carbene complexes, but the transient species are quite often not spectroscopically detected.[18,20,21] An alternative route to **9** is *via* irradiation (visible light) of the dicarbonyl complex **3a**; however, the reaction is slow and involves some decomposition. As we have already noticed in this

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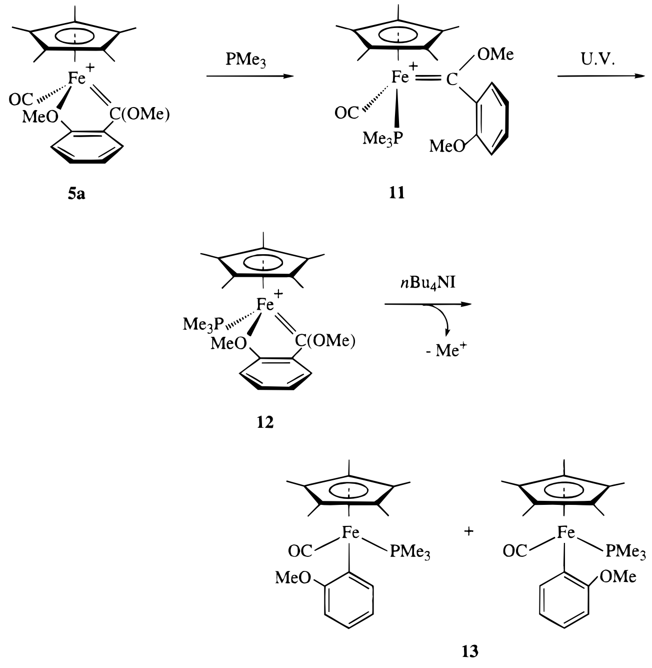
series, cationic species are more robust toward irradiation than the neutral derivatives.[22]

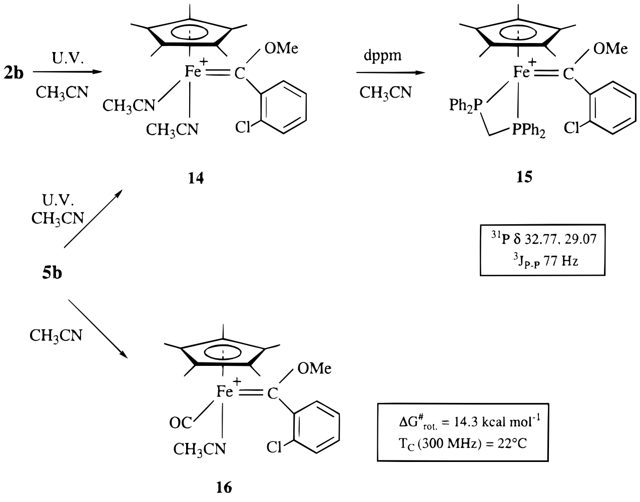
In contrast, reaction of **5a** with $NaBH_4$ in pure THF does not give the simple hydride addition product **9** but leads to the formation of the organoborohydride complex $[Fe(C_5Me_5)(CO)\{\eta^2\text{-}H_2BHCH_2C_6H_4\text{-}o\text{-}OMe\}]$ (**10**) (Scheme 5). Complex **10** has been fully characterized by IR, mass and NMR (^1H, ^{13}C, ^{11}B) spectra, elemental analysis, and an X-ray diffraction study.[3] A well-resolved spectrum shows a low-field pseudoquartet at δ 6.35 with a $^1J_{B-H}$ value of *ca.* 108 Hz characteristic of a B−H terminal coupling constant. The two bridging hydrogens appear at δ −17.87 (pseudoquartet, $^1J_{B-H}$ 43 Hz). Upon boron decoupling, both pseudoquartets give rise to singlets. These chemical shifts, as well as that of the boron ($\delta(^{11}B)$ 55.33), compare well with those of the dihapto complexes $[(C_5H_5)_2Ta\{\eta^2\text{-}H_2BHSi(t\text{-}Bu)_2H\}]$ and $[(C_5H_5)_2Ta\{\eta^2\text{-}BH_4\}]$.[23,24] Moreover, this assignment is corroborated by the methylene resonance located at δ 2.60 (dt, $^3J_{H-BH}$ 5 Hz, $^3J_{H-BH_2}$ 2.5 Hz). Besides the reduction of the =CHOMe fragment into a methylene group (*vide supra*), the reaction involves a formal insertion of BH_3 into a Fe−C bond. As suggested for the former reaction, the hemilabile ligand could promote the formation of a monodentate borohydride BH_4^- intermediate; the insertion of BH_3 would then occur within the coordination sphere of the metal. Such a monodentate borohydride iron complex $[FeH(dmpe)_2(\eta^1\text{-}BH_4)]$ has been reported.[25]

The hemilabile ligand OMe_{Ar} in **5a** is easily substituted by neutral nucleophiles such as PMe_3 (room temperature, CH_2Cl_2) to give the cationic complex $[Fe(C_5Me_5)(CO)(PMe_3)\{\eta^1\text{-}C(OMe)C_6H_4\text{-}o\text{-}OMe\}][OTf]$ (**11**). Substitution by PMe_3 cannot be directly accomplished for **2a**, due to the competitive electrophilic attack at the carbene carbon atom. Complex **11** is then converted *via* photo-induced decarbonylation into the phosphine-substituted chelate complex $[Fe(C_5Me_5)(PMe_3)\{\eta^2\text{-}C(OMe)C_6H_4\text{-}o\text{-}OMe\}][OTf]$ (**12**) (Scheme 6). In the permethylated-Cp series, complete decarbonylation always requires UV irradiation.[26] Addition of $[nBu_4N][I]$ to **12** quantitatively affords the *o*-anisyl complex $[Fe(C_5Me_5)(PMe_3)(CO)\{\eta^1\text{-}C_6H_4\text{-}o\text{-}OMe\}]$ (**13**) as a mixture of two diastereoisomers in 65:35 ratio (Scheme 6). They are clearly distinguished in the ^1H, ^{13}C, and ^{31}P NMR spectra of **13**. This can be explained by the presence of both the stereogenic iron center and a hindered Fe−C_{ipso} rotation (assimilated to an atropisomerism). The chemoselectivity of the reaction of iodide toward chelate complexes changes upon substitution of a carbonyl ligand by PMe_3: the electrophilic character of the metal center is weakened by the electron-donating phosphine. The competitive demethylation occurs, and decoordination of the OMe_{Ar} group then promotes the deinsertion/migration of the C=O group.[22]

Scheme 6



Scheme 7



Irradiation of **2b** or **5b** in CH_3CN (UV light, 5 h) gives the bis(acetonitrile) complex $[Fe(C_5Me_5)(CH_3CN)_2\{\eta^1\text{-}C(OMe)C_6H_4\text{-}o\text{-}Cl\}][OTf]$ (**14**) (Scheme 7). Due to the high lability of the CH_3CN ligands, compound **14** decomposes in other organic solvents, even in diethyl ether. Therefore, compound **14** is precipitated in nearly quantitative yield as a brown powder by addition of pentane. NMR studies in CD_3CN confirm the proposed structure; the presence of a single C_5Me_5 signal at δ 1.42 in the ^1H NMR spectrum of the crude product indicates the formation a single product, and the Ar_{Cl} resonance located at δ 125.2 compares well with that of the unchelated dicarbonyl complex **2b**. Complex **14** reacts (CH_3CN, room temperature) with (diphenylphophino)methane (dppm) to give the diphosphine−carbene complex $[Fe(C_5Me_5)(dppm)\{\eta^1\text{-}C(OMe)C_6H_4\text{-}o\text{-}Cl\}][OTf]$ (**15**) as an orange powder (Scheme 7). The ^{31}P NMR ($CDCl_3$) spectrum of **15** exhibits an AB system at δ 32.77 and 29.07 ($^2J_{P-P}$ 77 Hz); as for the parent dicarbonyl complex **2b**, the ancillary ligands are magnetically nonequivalent. For spectroscopic comparison, the mono(acetonitrile) derivative $[Fe(C_5Me_5)(CO)(CH_3CN)\{\eta^1\text{-}C(OMe)\text{-}$

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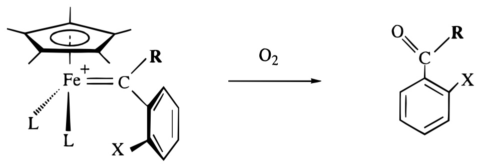
Scheme 8



4a (L= CO, R= H) or **14** (L= CH_3CN, R= OMe)
2b (L= CO, R= OMe) no reaction

R = H, OMe

C_6H_4-*o*-Cl}][OTf] (**16**) was prepared; it is readily formed upon dissolving complex **5b** in CH_3CN and isolated as red microcrystals. Proton NMR studies reveal that complex **16** exists as two $C_\alpha-C_{ipso}$ geometric isomers in a 75:25 ratio at low temperature (T_C (300 MHz) = 22 °C; barrier to aryl rotation $\Delta G^\ddagger = 14.3$ kcal mol^{-1}); they are particularly well-differentiated in the ^{13}C NMR spectrum (see Experimental Section). Thus, it is possible to access to a series of methoxycarbene complexes, the conformation of which depends on the nature of the ancillary ligands.

Complex **14** was expected to be a useful precursor to electron-rich N-heterocyclic-containing iron complexes, but attempts to substitute the CH_3CN ligands by the chelating 4,4′-*tert*-butyl-2,2′-bipyridine (bipy*) ligand[27] (CH_3CN, O °C) results in a mixture of $[Fe(bipy^*)_3]^{2+}$ and the unreacted starting complex **14**. This result shows that substitution of labile ligands in cationic iron complexes, although very efficient in the cases of diphosphines, cannot be applied to strong σ-donor N,N-ligands.[28,29]

Displacement of the Carbene Ligand. Carbene transfer from iron complexes to olefins has been extensively developed,[1] and high enantioselective cyclopropanation has been achieved by using the (*R*) and (*S*) chiral-at-iron complexes $[Fe(C_5H_5)(CO)(PPh_2R^*)\{{=}CH(CH_3\}]^+$.[30] To the best of our knowledge the displacement of the carbene ligand as a carbonyl organic substrate, such as aldehyde or ester, has not been investigated. The electrophilic anisylcarbene complex **4a**, generated *in situ* at −80 °C in CH_2Cl_2, reacts with molecular dioxygen (bubbling for 30 s) to give the *o*-anisaldehyde *o*-$MeOC_6H_4CHO$ and the triflate derivative $[Fe(C_5Me_5)(CO)_2(OTf)]$[31] (Scheme 8). These two compounds are readily separated in quantitative yield by extraction with pentane and ether, respectively. In contrast, the related dicarbonyl methoxycarbene complex **2b** is inert toward O_2; the starting complex is recovered even after 2 days of reaction. The nature of the ancillary ligands dramatically influences the release of carbene. Thus, the bis(acetonitrile) complex **14** reacts with O_2 to give *o*-$ClC_6H_4C(O)OMe$ (Scheme 8) whereas the neutral iodo carbene complex **6b** remains intact in solution in DMSO over several days.

There is no precedent for such a reaction for carbene complexes of a group 8 transition metal, whereas the metal−carbene bond of complexes of group 6 is easily cleaved by oxidizing reagents.[32] It should be pointed out that the above reactions differ from that involved in the formation of the formaldehyde complex $[Re(C_5H_5)(NO)(PPh_3)(\eta^2\text{-}CH_2{=}O)][PF_6]$ reported by Gladysz, obtained by reacting the methylene complex $[Re(C_5H_5)(NO)(PPh_3)({=}CH_2)][PF_6]$ with the nucleophilic iodosylbenzene.[33] On the other hand, the formation of benzophenone has been observed upon photolysis of diphenyldiazomethane in the presence of oxygen.[34]

In summary, despite the entropic effect of the chelation, the *ortho*-chlorine or methoxy ligand is labile and the O-demethylation pathway can thus be inhibited. Convenient routes to various substituted neutral and cationic iron−carbene complexes have been developed; consequently, the synthetic utility of which will be further investigated.

Experimental Section

General Data. All manipulations were carried out under an argon atmosphere with Schlenk or glovebox techniques. Solvents were dried and distilled under nitrogen before use by standard methods. Photolysis experiments were carried out by using an Original Hanau 150 W (Hg, high pressure) lamp; visible irradiation reactions were performed using a glass vessel whereas a quartz tube was used for near-UV irradiation. NMR spectra (^1H, 300 MHz; ^{13}C, 75.47 MHz; ^{31}P, 121.5 MHz; ^{11}B, 96.295 MHz) were recorded on Bruker WP-80 or AC 3000 spectrometers by S. Sinbandhit (CRMPO, Université de Rennes 1). Infrared spectra were obtained with a Nicolet 205 FT-IR spectrometer. Mass spectra were recorded on a Varian MAT 311 (70 eV) instrument at the CRMPO. Microanalyses were performed by the “Centre de Microanalyse du CNRS” at Vernaison, France.

Preparation of $[Fe(C_5Me_5)(CO)_2\{C(O)C_6H_4\text{-}X\}]$ (1: a, X = *o*-OMe; b, X = *o*-Cl; c, X = *p*-Cl). General Procedure. A suspension of 6 mmol (3 g) of $[Fe(C_5Me_5)(CO)_2]_2$ and 12 mmol (468 mg) of potassium in 20 mL of THF was refluxed for 2 h. To the resulting orange mixture was added at room temperature 12 mmol of the appropriate acid chloride $XC_6H_4C(O)Cl$. The solution was stirred for 30 min, and the solvent was removed in vacuo. Compound **1** was extracted with ether (3 × 20 mL); chromatography on alumina (eluant pentane/ether: 80/20) afforded a yellow crystalline solid.

1a (80% yield): ^1H NMR ($CDCl_3$) δ 7.13 (dt, $^3J_{H-H}$ 8 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 6.86 (dt, $^3J_{H-H}$ 7 Hz, $^4J_{H-H}$ 0.9 Hz, 1H, Ar), 6.81 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 6.65 (dd, $^3J_{H-H}$ 7 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 3.78 (s, 3H, OMe), 1.83 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 263.9 (C=O), 215.9 (CO), 151.2 (Ar_{ipso}), 147.8 (Ar_{OMe}), 127.7 (Ar), 120.9 (Ar), 120.3 (Ar), 110.9 (Ar), 97.7 (C_5Me$_5$), 55.1 (OMe), 9.6 (C_5*Me*$_5$); IR (CH_2Cl_2) 1613 (s, $\nu_{C=O}$), 1943 (s, ν_{CO}), 2000 (s, ν_{CO}). Anal. Calcd for $C_{20}H_{22}O_4Fe$: C, 62.85; H, 5.80. Found: C, 62.56; H, 5.73.

1b (62% yield): ^1H NMR ($CDCl_3$) δ 7.23 (dd, $^3J_{H-H}$ 7.2 Hz, $^4J_{H-H}$ 1.2 Hz, 1H, Ar), 7.19 (td, $^3J_{H-H}$ 7.4 Hz, $^4J_{H-H}$ 1.3 Hz, 1H, Ar), 7.08 (td, $^3J_{H-H}$ 7.6 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 6.78 (dd, $^3J_{H-H}$ 7.5 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 1.85 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 262.4 (C=O), 215.6 (CO), 155.4 (Ar_{ipso}), 129.5 (Ar), 127.5 (Ar), 126.8 (Ar), 124.1 (Ar_{Cl}), 122.2 (Ar), 98.2 (C_5Me$_5$), 9.5 (C_5*Me*$_5$); IR (CH_2Cl_2) 1610 (s, $\nu_{C=O}$), 1947 (s, ν_{CO}),

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2003 (s, ν_{CO}). Anal. Calcd for $C_{19}H_{19}O_3ClFe$: C, 59.02; H, 4.95. Found: C, 59.03; H, 5.03.

1c (79% yield): ^1H NMR ($CDCl_3$) δ 7.36 (m, AA′BB′, 4H, Ar), 1.79 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 262.0 (C=O), 216.0 (CO), 147.7 (Ar_{ipso}), 136.0 (Ar_{Cl}), 128.1 (Ar), 127.5 (Ar), 97.4 (C_5Me_5), 9.7 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) 1601 (s, $\nu_{C=O}$), 1943 (s, ν_{CO}), 2003 (s, ν_{CO}). Anal. Calcd for $C_{19}H_{19}O_3ClFe$: C, 59.02; H, 4.95. Found: C, 58.96; H, 5.06.

Preparation of [Fe(C_5Me_5)(CO)$_2${η^1-C(OMe)C_6H_4X}][CF_3SO_3] (2: a, X = *o*-OMe; b, X = *o*-Cl; c, X = *p*-Cl). A CH_2Cl_2 solution (20 mL) of 2.5 mmol of **1** was treated with 2.5 mmol (282 μL) of $CH_3OSO_2CF_3$. The mixture was stirred overnight, and the solution was then reduced in volume under vacuum to *ca.* 3–5 mL. Compound **2** was precipitated by addition of diethyl ether giving yellow microcrystals.

2a (98% yield): ^1H NMR ($CDCl_3$) δ 7.42, 7.12, 7.00, 6.82 (4 × m, 4H, Ar), 4.41 (s, 3H, OMe), 3.88 (s, 3H, OMe_{Ar}), 1.92 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 328.2 (=C), 210.9 (CO), 210.6 (CO), 148.9 (Ar_{OMe}), 138.8 (Ar_{ipso}), 132.6 (Ar), 121.7 (Ar), 121.5 (Ar), 111.7 (Ar), 102.2 (C_5Me_5), 70.2 (OMe), 55.9 (OMe_{Ar}), 9.7 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) 2004 (s, ν_{CO}), 2047 (s, ν_{CO}). Anal. Calcd for $C_{22}H_{25}O_7FeSF_3$: C, 48.37; H, 4.61. Found: C, 48.44; H, 4.70.

2b (88% yield): ^1H NMR ($CDCl_3$) δ 7.50, 7.42 (2 × m, 3H, Ar), 7.19 (dd, $^3J_{H-H}$ 7.3 Hz, $^4J_{H-H}$ 1 Hz, 1H, Ar), 4.44 (s, 3H, OMe), 1.95 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 323.5 (=C), 210.7 (CO), 210.2 (CO), 147.4 (Ar_{ipso}), 131.6 (Ar), 129.9 (Ar), 128.6 (Ar), 122.8 (Ar_{Cl}), 122.7 (Ar), 102.8 (C_5Me_5), 70.7 (OMe), 9.6 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) 2009 (s, ν_{CO}), 2051 (s, ν_{CO}). Anal. Calcd for $C_{21}H_{22}O_6ClFeSF_3$: C, 45.80; H, 4.03. Found: C, 45.90; H, 4.08.

2c (55% yield): ^1H NMR ($CDCl_3$) δ 7.50 (d, $^3J_{H-H}$ 8.5 Hz, 2H, Ar), 7.19 (d, $^3J_{H-H}$ 8.5 Hz, 2H, Ar), 4.52 (s, 3H, OMe), 1.90 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 326.0 (=C), 210.9 (CO), 147.3 (Ar_{ipso}), 138.1 (Ar_{Cl}), 129.6 (Ar), 123.5 (Ar), 102.4 (C_5Me_5), 71.1 (OMe), 9.7 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) 2004 (s, ν_{CO}), 2048 (s, ν_{CO}). Anal. Calcd for $C_{21}H_{22}O_6ClFeSF_3$: C, 45.80; H, 4.03. Found: C, 45.59; H, 4.01.

Preparation of [Fe(C_5Me_5)(CO)$_2${η^1-CH(OMe)C_6H_4-*o*-OMe}] (3a). To 0.8 mmol (454 mg) of **2a** and 1.2 mmol (46 mg) of $NaBH_4$ was added 20 mL of THF/MeOH (9:1) at −80 °C. The reaction mixture was stirred at −80 °C for 30 min and then allowed to warm to room temperature. The solvent was removed in vacuo, and the residue was extracted with pentane (2 × 15 mL). Concentration of the solution afforded 245 mg (74%) of orange microcrystals: ^1H NMR (C_6D_6) δ 7.84 (dd, $^3J_{H-H}$ 7 Hz, $^4J_{H-H}$ 2 Hz, 1H, Ar), 7.02 (m, 2H, Ar), 6.64 (dd, $^3J_{H-H}$ 7 Hz, $^4J_{H-H}$ 2 Hz, 1H, Ar), 5.45 (s, 1H, CH), 3.52 (s, 3H, OMe), 3.25 (s, 3H, OMe_{Ar}), 1.60 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 219.3 (CO), 218.1 (CO), 152.8 (Ar_{OMe}), 142.6 (Ar_{ipso}), 124.7 (Ar), 124.5 (Ar), 121.4 (Ar), 109.8 (Ar), 95.8 (C_5Me_5), 79.8 (CH), 60.5 (OMe), 54.4 (OMe_{Ar}), 9.3 ($C_5\mathit{Me}_5$); IR (pentane) 1996 (s, ν_{CO}), 1945 (s, ν_{CO}). Anal. Calcd for $C_{21}H_{26}O_4Fe$: C, 63.33; H, 6.58. Found: C, 63.05; H, 6.65.

Reaction of [Fe(C_5Me_5)(CO)$_2${η^1-C(OMe)C_6H_4-*o*-OMe}][CF_3SO_3] (2a) with $NaBH_4$ in THF. To 0.8 mmol (454 mg) of **2a** and 1.2 mmol (46 mg) of $NaBH_4$ was added 20 mL of THF at −80 °C. The reaction was stirred at −80 °C for 30 min and then allowed to warm to room temperature. The solvent was removed in vacuo, and the residue was extracted with pentane (2 × 15 mL). Concentration of the solution afforded a mixture of **3a** and [Fe(C_5Me_5)(CO)$_2${η^1-$CH_2C_6H_4$-*o*-OMe}], the ratio of which depends on the experiment. Data for [Fe(C_5Me_5)(CO)$_2${η^1-$CH_2C_6H_4$-*o*-OMe}]: ^1H NMR (C_6D_6) δ 7.47 (d, $^3J_{H-H}$ 7 Hz, 1H, Ar), 6.96 (m, 2H, Ar), 6.64 (dd, $^3J_{H-H}$ 7 Hz, 1H, Ar), 3.58 (s, 3H, OMe_{Ar}), 2.41 (s, 2H, CH_2), 1.46 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 219.1 (CO), 155.8 (Ar_{OMe}), 143.1 (Ar_{ipso}), 128.6 (Ar), 124.1 (Ar), 120.8 (Ar), 109.9 (Ar), 94.7 (C_5Me_5), 54.5 (OMe_{Ar}), 10.0 (CH_2), 9.2 ($C_5\mathit{Me}_5$).

Generation of [Fe(C_5Me_5)(CO)$_2${η^1-CH(C_6H_4-*o*-OMe)}][CF_3SO_3] (4a). An NMR tube was charged with a $CDCl_3$ solution of 0.38 mmol (150 mg) of **3a** and cooled to −80 °C. Then 0.56 mmol (110 μL) of $Me_3SiOSO_2CF_3$ was added: ^1H NMR ($CDCl_3$, 20 °C) δ 15.42 (s, 1H, =CH), 7.96 (m, 1H, Ar), 7.77 (m, 1H, Ar), 7.16 (m, 2H, Ar), 4.15 (s, 3H, OMe_{Ar}), 2.00 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$, −40 °C) δ 322.6 (=CH), 210.6 (CO), 159.5 (br s, Ar_{OMe}), 145.7 (Ar), 144.0 (Ar_{ipso}), 137.6 (Ar), 122.0 (Ar), 113.4 (Ar), 105.7 (C_5Me_5), 56.7 (OMe_{Ar}), 10.1 ($C_5\mathit{Me}_5$); ^1H NMR (CD_2Cl_2, −80 °C) δ 15.61 (br s, 0.2H, =CH_b), 15.07 (br s, 0.8H, =CH_a), 7.99 (m, 1H, Ar), 7.59 (m, 1H, Ar), 7.22 (m, 2H, Ar), 4.21 (s, 3H, OMe_{Ar}), 1.98 (s, 15H, C_5Me_5); T_C (300 MHz) = −62 °C; δ (−50 °C) 15.16 (br s, 1H, =CH); IR (CH_2Cl_2) 2045 (s, ν_{CO}), 1995 (s, ν_{CO}).

Preparation of [Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-X}][CF_3SO_3] (5: a, X = OMe; b, X = Cl). In a Schlenk tube, a CH_2Cl_2 solution (10 mL) of 1 mmol (547 mg) of **2a** or **2b** was irradiated overnight. After removal of the solvent under vacuum, the solid was washed with ether, and crystallization from CH_2Cl_2/Et_2O gave brown crystals.

5a (96% yield): ^1H NMR ($CDCl_3$) δ 7.65 (m, Ar), 7.43 (d, Ar), 7.21 (m, Ar), 4.78 (s, 3H, OMe), 3.95 (s, 3H, OMe_{Ar}), 1.61 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 325.8 (=C), 213.1 (CO), 167.7 (Ar_{OMe}), 137.2 (Ar), 134.8 (Ar_{ipso}), 125.0 (Ar), 118.9 (Ar), 115.9 (Ar), 95.0 (C_5Me_5), 71.4 (OMe), 69.9 (OMe_{Ar}), 9.5 ($C_5\mathit{Me}_5$); IR (Nujol) 1977 (s, ν_{CO}). Anal. Calcd for $C_{21}H_{25}O_6FeSF_3$: C, 48.66; H, 4.86. Found: C, 48.70; H, 4.80.

5b (70% yield): ^1H NMR ($CDCl_3$) δ 7.95 (dd, $^3J_{H-H}$ 7.8 Hz, $^4J_{H-H}$ 1.5 Hz, 1H, Ar), 7.86 (dd, $^3J_{H-H}$ 8.2 Hz, $^4J_{H-H}$ 0.8 Hz, 1H, Ar), 7.75 (td, $^3J_{H-H}$ 7.8 Hz, $^4J_{H-H}$ 1.6 Hz, 1H, Ar), 7.57 (td, $^3J_{H-H}$ 7.6 Hz, $^4J_{H-H}$ 1 Hz, 1H, Ar), 4.96 (s, 3H, OMe), 1.67 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 329.1 (=C), 211.5 (CO), 145.5 (Ar_{ipso}), 144.9 (Ar_{Cl}), 136.3 (Ar), 129.4 (Ar), 127.2 (Ar), 122.9 (Ar), 95.7 (C_5Me_5), 70.7 (OMe), 9.6 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) 1990 (s, ν_{CO}). Anal. Calcd for $C_{20}H_{22}O_5ClFeSF_3$: C, 45.95; H, 4.24. Found: C, 45.74; H, 4.35.

Preparation of [Fe(C_5Me_5)(CO)(I){η^1-C(OMe)C_6H_4-*o*-X}][CF_3SO_3] (6: a, X = OMe; b, X = Cl). A CH_2Cl_2 solution (10 mL) of 1 mmol of **5a** or **5b** was treated with 1.2 mmol (443 mg) of [$n$$Bu_4$N][I]. After removal of the solvent under vacuum, the solid was extracted with ether. Crystallization from Et_2O gave black crystals.

6a (85% yield): ^1H NMR (C_6D_6) δ 7.89 (d, $^3J_{H-H}$ 7 Hz, 1H, *o*-Ar), 6.93 (t, $^3J_{H-H}$ 7 Hz, 1H, *p*-Ar), 6.72 (t, $^3J_{H-H}$ 7 Hz, 1H, *m*-Ar), 6.36 (d, $^3J_{H-H}$ 8 Hz, 1H, *m*-Ar), 3.48 (s, 3H, OMe), 3.17 (s, 3H, OMe_{Ar}), 1.72 (s, 15H, C_5Me_5); ^1H NMR (DMSO) δ 7.89 (t, $^3J_{H-H}$ 7.7 Hz, 1H, Ar), 7.20 (d, $^3J_{H-H}$ 7.2 Hz, 1H, Ar), 7.06 (d, $^3J_{H-H}$ 8.4 Hz, 1H, Ar), 6.91 (t, $^3J_{H-H}$ 7.7 Hz, 1H, Ar), 3.97 (s, 3H, OMe), 3.80 (s, 3H, OMe_{Ar}), 1.73 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 334.9 (=C), 221.6 (CO), 149.9 (Ar_{OMe}), 141.8 (Ar_{ipso}), 129.4 (Ar) (one Ar signal is obscured by C_6D_6), 121.4 (Ar), 110.3 (Ar), 97.3 (C_5Me_5), 63.5 (OMe), 54.6 (OMe_{Ar}), 10.5 ($C_5\mathit{Me}_5$); IR (Nujol) 1930 (s, ν_{CO}). Anal. Calcd for $C_{20}H_{25}O_3FeI$: C, 48.42; H, 5.08. Found: C, 48.80; H, 5.04.

6b (68% yield): ^1H NMR ($CDCl_3$) δ 7.66 (m, 1H, Ar), 7.33 (m, 1H, Ar), 7.20 (m, 2H, Ar), 4.02 (s, 3H, OMe), 1.84 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 328.1 (=C), 220.2 (CO), 149.4 (Ar_{ipso}), 129.3 (Ar), 129.1 (Ar), 128.2 (Ar), 126.8 (Ar), 124.6 (Ar_{Cl}), 98.2 (C_5Me_5), 64.4 (OMe), 10.4 ($C_5\mathit{Me}_5$); IR (CH_2Cl_2) 1952 (s, ν_{CO}). Anal. Calcd for $C_{19}H_{22}O_2ClFeI$: C, 45.59; H, 4.43. Found: C, 45.95; H, 4.67.

Preparation of [Fe(C_5Me_5)(CO)(Cl){η^1-C(OMe)C_6H_4-*o*-OMe}] (7) and [Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-O}] (8). To a methylene chloride solution of 1 mmol (518 mg) of **5a** was added 1.2 mmol (688 mg) of [$(PPh_3)_2$N][Cl] at −80 °C. The reaction mixture was allowed to warm to room temperature while stirring, and the solvent was then removed in vacuo. The resulting solid was extracted with ether, and red microcrystals (344 mg, 85%) crystallized at −20 °C. Complex **7** in $CDCl_3$ solution turned into **8** and MeCl.

[Fe(C_5Me_5)(CO)(Cl){η^1-C(OMe)C_6H_4-*o*-OMe}] (7). Data are as follows: ^1H NMR ($CDCl_3$) δ 7.25 (m, Ar), 6.97 (m, Ar), 6.88 (m, Ar), 4.13 (s, 3H, OMe), 3.81 (s, 3H, OMe_{Ar}), 1.60 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 335.1 (=C), 218.7 (CO), 149.5 (Ar_{OMe}), 141.9 (Ar_{ipso}), 129.4 (Ar), 123.7 (Ar), 121.1 (Ar), 110.1 (Ar), 98.1 (C_5Me_5), 64.5 (OMe), 55.3 (OMe_{Ar}), 9.6 (C_5Me_5); IR (Nujol) 1930 (s, ν_{CO}).

[Fe(C_5Me_5)(CO){η^2-C(OMe)C_6H_4-*o*-O}] (8). Data are as follows: ^{1}H NMR ($CDCl_3$) δ 7.26 (d, $^3J_{H-H}$ 7 Hz, 1H, *o*-Ar), 7.10 (t, $^3J_{H-H}$ 7 Hz, 1H, *p*-Ar), 6.75 (d, $^3J_{H-H}$ 8 Hz, 1H, *m*-Ar), 6.37 (t, $^3J_{H-H}$ 8 Hz, 1H, *m*-Ar), 4.44 (s, 3H, OMe), 3.02 (s, 3H, MeCl), 1.62 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 311.1 (=C), 214.6 (CO), 187.0 (Ar_O), 139.4 (Ar_{ipso}), 134.7 (Ar), 119.4 (Ar), 118.7 (Ar), 113.2 (Ar), 93.8 (C_5Me_5), 65.7 (OMe), 25.9 (MeCl), 9.4 (C_5Me_5); IR (Nujol) 1931 (s, ν_{CO}). Anal. Calcd for $C_{19}H_{22}O_3Fe$: C, 64.42; H, 6.26. Found: C, 64.39; H, 6.16.

Preparation of [Fe(C_5Me_5)(CO){η^2-CH(OMe)C_6H_4-*o*-OMe}] (9). To a suspension of 1 mmol (518 mg) of **5a** in 15 mL of a mixture of 9:1 THF−MeOH, previously cooled to −80 °C, was added 1 mmol (38 mg) of $NaBH_4$ or 1 mmol (1 mL, 1 M solution in THF) of $LiBEt_3H$ by using pure THF as solvent. The solution was then allowed to warm to room temperature. The initial brown color turned into yellow-orange at −30 °C. The solvent was evaporated to dryness, and the residue was extracted with pentane (2 × 10 mL). Cooling the resulting solution at −20 °C gave 344 mg (93%) of **9** as orange-brown microcrystals: ^{1}H NMR (C_6D_6) δ 6.85 (m, 1H, Ar), 6.43 (m, 2H, Ar), 5.99 (d, $^3J_{H-H}$ 6 Hz, 1H, Ar), 4.35 (s, 1H, CH), 3.25 (br s, 6H, OMe and OMe_{Ar}), 1.37 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 224.3 (CO), 158.5 (Ar), one Ar signal is obscured by C_6D_6, 125.6 (Ar), 123.2 (Ar), 102.4 (Ar), 93.6 (Ar), 87.7 (C_5Me_5), 69.6 (CH), 58.1 (OMe), 54.2 (OMe_{Ar}), 8.8 (C_5Me_5); IR (pentane) 1929 (s, ν_{CO}). Anal. Calcd for $C_{20}H_{26}O_3Fe$: C, 64.88; H, 7.08. Found: C, 64.33; H, 7.05.

Preparation of [Fe(C_5Me_5)(CO){η^2-$H_2BH(CH_2C_6H_4$-*o*-OMe)}] (10). In a Schlenk tube were added 1 mmol (518 mg) of **5a** and 2 mmol (76 mg) of $NaBH_4$ and then 15 mL of THF cooled to −80 °C. The solution was then allowed to warm to room temperature. The initial brown color turned yellow-orange at −30 °C. The THF was evaporated to dryness, and the residue was extracted with pentane (2 × 10 mL). Cooling the resulting solution at −20 °C gave 0.301 mg (85%) of **10** as brown microcrystals: ^{1}H NMR (C_6D_6) δ 7.29 (dd, $^3J_{H-H}$ 7 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 7.06 (td, $^3J_{H-H}$ 8 Hz, $^4J_{H-H}$ 1.8 Hz, 1H, Ar), 6.93 (td, $^3J_{H-H}$ 7 Hz, $^4J_{H-H}$ 1 Hz, 1H, Ar), 6.65 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 6.35 (br pseudo-q, $^1J_{B-H}$ 108 Hz, 1H, $BH_{terminal}$), 3.46 (s, 3H, OMe_{Ar}), 2.60 (br s, 2H, CH_2), 1.39 (s, 15H, C_5Me_5), −17.87 (br pseudo-q, $^1J_{B-H}$ 43 Hz, 2H, Fe−$H_{bridging}$): (the low-field resonance at δ 6.35 is too broad to be observed in the normal spectrum, but its presence is revealed upon B (55 ppm) or/and bridging H (−17.87 ppm) decoupling); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 218.8 (CO), 157.4 (Ar_{OMe}), 134.8 (Ar_{ipso}), 130.3 (Ar), 125.3 (Ar) , 120.9 (Ar) , 110.8 (Ar), 90.8 (C_5Me_5), 55.0 (OMe_{Ar}), 33.3 (br m, BCH_2), 10.1 (C_5Me_5); $^{11}B\{H\}$ NMR (C_6D_6/C_6H_6, $Et_2O\cdot BF_3$ as external reference) δ 55.33 (br s); IR (Nujol) 1962 (s, ν_{CO}); zero field Mössbauer data (298 K) IS = 0.104 $mm\cdot s^{-1}$ vs Fe, QS = 1.898 $mm\cdot s^{-1}$; high resolution MS (70 eV) (*m*/*z*) calcd for $[M - 2H]^+$ $C_{19}H_{25}O_2BFe$ 352.12968, found 352.1301. Anal. Calcd for $C_{19}H_{27}O_2BFe$: C, 64.45; H, 7.69. Found: C, 64.55; H, 7.62.

Preparation of [Fe(C_5Me_5)(CO)(PMe_3){η^1-C(OMe)C_6H_4-*o*-OMe}][CF_3SO_3] (11). An excess of PMe_3 was added to 518 mg (1 mmol) of **2a** dissolved in 10 mL of CH_2Cl_2. The solution was stirred for 30 min, and the maroon color became orange. After removal of the solvent, the residue was washed with ether (3 × 20 mL) and then crystallized from a CH_2Cl_2/ether mixture. Orange crystals were collected (505 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 7.47 (m, $^3J_{H-H}$ 8 Hz, 1H, Ar), 7.12 (m, 2H, Ar), 6.93 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 4.20 (s, 3H, OMe), 3.85 (s, 3H, OMe_{Ar}), 1.82 (s, 15H, C_5Me_5), 1.37 (d, $^2J_{P-H}$ 13 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 328.9 (d, $^2J_{P-C}$ 27 Hz, =C), 216.7 (d, $^2J_{P-C}$ 30 Hz, CO), 148.4 (Ar_{OMe}), 137.8 (Ar_{ipso}), 133.6 (Ar), 131.7 (Ar), 121.5 (Ar), 111.3 (Ar), 98.7 (C_5Me_5), 67.9 (OMe), 55.4 (OMe_{Ar}), 17.6 (d, $^1J_{P-C}$ 32 Hz, PMe_3), 10.1 (C_5Me_5); $^{31}P\{^1H\}$ NMR ($CDCl_3/H_3PO_4$ external) δ 31.0 (s, PMe_3); IR (Nujol) 1955 (s, ν_{CO}). Anal. Calcd for $C_{24}H_{34}O_6FePSF_3$: C, 48.50; H, 5.77. Found: C, 48.22; H, 5.77.

Preparation of [Fe(C_5Me_5)(PMe_3){η^2-C(OMe)C_6H_4-*o*-OMe}][CF_3SO_3] (12). UV irradiation of 1 mmol (595 mg) of **11** in 210 mL of CH_2Cl_2 was performed for 90 min. The initial orange color turned yellow-green. The solvent was removed, and the resulting solid was crystallized from a CH_2Cl_2/ether mixture affording 538 mg (95%) of yellow microcrystals. ^{1}H NMR (CD_2Cl_2) δ 7.98 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 7.48 (t, $^3J_{H-H}$ 8 Hz, 1H, Ar), 7.08 (t, $^3J_{H-H}$ 8 Hz, 1H, Ar), 6.85 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 4.65 (s, 3H, OMe), 3.70 (s, 3H, OMe_{Ar}), 1.41 (s, 15H, C_5Me_5), 1.35 (d, $^2J_{H-H}$ 8 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 315.1 (d, $^2J_{P-C}$ 25 Hz, =C), 164.6 (Ar_{OMe}), 135.3 (Ar_{ipso}), 132.6 (Ar), 123.9 (Ar), 117.3 (Ar), 111.8 (Ar), 87.9 (C_5Me_5), 69.3 (OMe), 63.9 (OMe_{Ar}), 18.6 (d, $^1J_{P-C}$ 26 Hz, PMe_3), 10.4 (C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2/H_3PO_4 external) δ 24.8 (s, PMe_3). Anal. Calcd for $C_{23}H_{34}O_5FePSF_3$: C, 48.77; H, 6.05. Found: C, 48.38; H, 5.93.

Reaction of 12 with [*n*Bu_4N][I]. Preparation of [Fe(C_5Me_5)(PMe_3)(CO){η^1-C_6H_4-*o*-OMe}] (13). According to the procedure described for the preparation of **6a,b**, workup gave 362 mg (90% yield) of **13** as a yellow powder. NMR data showed the presence of two isomers in a 65:35 ratio. Anal. Calcd for $C_{21}H_{31}O_2FeP$: C, 62.70; H, 7.77. Found: C, 62.51; H, 7.68.

Major isomer: ^{1}H NMR (C_6D_6) δ 8.00 (m, $^3J_{H-H}$ 7 Hz, 1H, Ar), 6.93 (m, 2H, Ar), 6.50 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 3.34 (s, 3H, OMe_{Ar}), 1.49 (s, 15H, C_5Me_5), 0.95 (d, $^2J_{H-H}$ 8 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 223.5 (d, $^2J_{P-C}$ 33 Hz, CO), 167.0 (Ar_{OMe}), 154.7 (d, $^2J_{P-C}$ 25 Hz, Ar_{ipso}), 146.1 (Ar), 122.8 (Ar), 119.8 (Ar), 107.8 (Ar), 92.1 (C_5Me_5), 53.6 (OMe_{Ar}), 19.2 (d, $^1J_{P-C}$ 25 Hz, PMe_3), 10.2 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6/H_3PO_4 external) δ 32.0 (s, PMe_3); IR (pentane) 1907 (s, ν_{CO}).

Minor isomer: ^{1}H NMR (C_6D_6) δ 7.47 (m, $^3J_{H-H}$ 7 Hz, 1H, Ar), 7.09 (m, 2H, Ar), 6.63 (d, $^3J_{H-H}$ 8 Hz, 1H, Ar), 3.66 (s, 3H, OMe_{Ar}), 1.54 (s, 15H, C_5Me_5), 0.88 (d, $^2J_{H-H}$ 8 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 223.6 (d, $^2J_{P-C}$ 34 Hz, CO), 166.7 (Ar_{OMe}), 156.2 (d, $^2J_{P-C}$ 26 Hz, Ar_{ipso}), 128.6 (Ar), 122.6 (Ar), 120.4 (Ar), 109.1 (Ar), 91.4 (C_5Me_5), 55.4 (OMe_{Ar}), 17.9 (d, $^1J_{P-C}$ 25 Hz, PMe_3), 10.1 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6/H_3PO_4 external) δ 36.3 (s, PMe_3); IR (pentane) 1911 (s, ν_{CO}).

Preparation of [Fe(C_5Me_5)(CH_3CN)$_2${η^1-C(OMe)C_6H_4-*o*-Cl}][CF_3SO_3] (14). A CH_3CN (200 mL) solution of 1.5 mmol (833 mg) of **2b** was irradiated (UV) for 5 h. The initial yellow color turned yellow-brown. The CH_3CN was evaporated to dryness by using a trap to trap procedure. The oily residue was washed with pentane (2 × 10 mL) to give a brown powder. Compound **14**, only stable in CH_3CN, was not crystallized: ^{1}H NMR (CD_3CN) δ 7.39 (d, $^3J_{H-H}$ 7.6 Hz, 1H, Ar), 7.36 (t, $^3J_{H-H}$ 7.5 Hz, 1H, Ar), 7.27 (t, $^3J_{H-H}$ 7.3 Hz, 1H, Ar), 6.90 (d, $^3J_{H-H}$ 7.3 Hz, 1H, Ar), 4.30 (s, 3H, OMe), 1.96 (s, CH_3CN/CD_3CN), 1.42 (s, 15H, C_5Me_5); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 321.0 (=C), 149.1 (Ar_{ipso}), 134.0 (CN), 130.1 (Ar), 129.8 (Ar), 127.9 (Ar), 125.2 (Ar_{Cl}), 124.0 (Ar), 94.6 (C_5Me_5), 65.3 (OMe), 9.5 (C_5Me_5), 2.0 (CH_3CN/CD_3CN).

Preparation of [Fe(C_5Me_5)(η^2-dppm){η^1-C(OMe)C_6H_4-*o*-Cl}][CF_3SO_3] (15). To a CH_3CN solution of 1.2 mmol (692 mg) of **14** was added 1.2 mmol (398 mg) of dppm. The reaction mixture was stirred for 16 h. The residue was washed with ether (3 × 20 mL) to give an orange powder (85%): ^{1}H NMR (CD_3CN) δ 7.60−7.25 (m, 23H, PPh_2 + Ar), 6.45 (d, $^3J_{H-H}$ 6.9 Hz, 1H, Ar), 5.13 (dt, $^2J_{H-H}$ 15 Hz, $^3J_{P-H}$ 12 Hz, 1H, CH_2), 4.62 (dt, $^2J_{H-H}$ 15 Hz, $^3J_{P-H}$ 10 Hz, 1H, CH_2), 2.69 (s, 3H, OMe), 1.25 (s, 15H, C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_3CN/H_3PO_4 external) δ 32.77 (d, $^2J_{P-P}$ 77 Hz, PPh_2), 29.07 (d, $^2J_{P-P}$ 77 Hz, PPh_2); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 307.7 (t, $^2J_{P-C}$ 28 Hz, =C), 147.7 (Ar_{ipso}), 136.9 (dd, $C_{ipso}PPh_2$), 135.7 (dd, $C_{ipso}PPh_2$), 133.9 (dd, 2 × $C_{ipso}PPh_2$), 132.3−127.5 (PPh_2 + Ar), 127.1 (Ar_{Cl}), 98.1 (C_5Me_5), 61.9 (OMe), 43.2 (t, $^1J_{P-C}$ 23 Hz, CH_2), 10.9 (C_5Me_5). Anal.

Calcd for $C_{44}H_{44}O_4P_2FeClSF_3$: C, 60.11; H, 5.04. Found: C, 59.56; H, 5.02.

Preparation of [Fe(C_5Me_5)(CO)(CH_3CN){η^1-C(OMe)-C_6H_4-*o*-Cl}][CF_3SO_3] (16). Complex **5b** (0.5 mmol, 261 mg) was dissolved in 5 mL of CH_3CN, and the brown solution immediately became deep-red. Crystallization from CH_3CN/Et_2O gave red crystals (225 mg): ^{1}H NMR (CD_3CN, −40 °C) δ 7.41 (m, 3H, Ar), 7.03 (d, $^3J_{H-H}$ 7 Hz, 0.75H, Ar_{maj}, 75%), 6.83 (d, $^3J_{H-H}$ 7 Hz, 0.25H, Ar_{min}, 25%), 4.24 (s, 3H, OMe), 2.08 (s, 0.75H, CH_3CN_{min}), 1.84 (s, 2.25H, CH_3CN_{maj}), 1.66 (s, 15H, C_5Me_5); ^{1}H NMR (CD_3CN, +50 °C) δ 7.43 (m, 3H, Ar), 6.99 (d, 1H, $^3J_{H-H}$ 7 Hz, Ar), 4.31 (s, 3H, OMe), 1.96 (s, 3H, CH_3CN), 1.70 (s, 15H, C_5Me_5).

Major isomer: ^{13}C{^{1}H} NMR (CD_3CN, −40 °C) δ 325.7 (=C), 219.8 (CO), 146.2 (Ar_{ipso}), 132.5 (CN), 131.4 (Ar), 130.4 (Ar), 128.9 (Ar), 124.7 (Ar_{Cl}), 123.6 (Ar), 119.8 (q, CF_3SO_3), 99.6 (C_5Me$_5$), 68.90 (OMe), 9.6 (C_5Me_5), 4.2 (CH_3CN).

Minor isomer: ^{13}C{^{1}H} NMR (CD_3CN, −40 °C) δ 332.0 (=C), 218.5 (CO), 147.9 (Ar_{ipso}), 133.0 (CN), 131.5 (Ar), 130.8 (Ar), 128.7 (Ar), 124.1 (Ar_{Cl}), 123.1 (Ar), 99.7 (C_5Me$_5$), 68.94 (OMe), 9.7 (C_5Me_5), 5.0 (CH_3CN); IR (CH_2Cl_2) 1989 (s, ν_{CO}). Anal. Calcd for $C_{22}H_{25}O_5NFeClSF_3$: C, 46.87; H, 4.47. Found: C, 46.62; H, 4.51.

Reaction of [Fe(C_5Me_5)($CO)_2${η^1-CH(C_6H_4-*o*-OMe)}] (4a) with O_2. A Schlenk tube was charged with 0.38 mmol (150 mg) of **3a** and cooled to −80 °C. Then 0.56 mmol (110 μL) of $Me_3SiOSO_2CF_3$ was added generating **4a** *in situ*. Dioxygen was bubbled through the resulting reaction mixture for 30 s, and the solution was allowed to warm to room temperature. The *o*-anisaldehyde *o*-$MeOC_6H_4CHO$ was extracted with pentane, and the triflate derivative [Fe(C_5Me_5)($CO)_2$(OSO_2CF_3)], soluble in ether, was identified by comparison with an authentic sample.[31] Data for *o*-$MeOC_6H_4CHO$: ^{1}H NMR ($CDCl_3$) δ 10.48 (s, 1H, CHO), 7.84 (d, $^3J_{H-H}$ 7.6 Hz, 1H, Ar_{H6}), 7.56 (t, $^3J_{H-H}$ 7.7 Hz, 1H, Ar_{H4}), 7.03 (t, $^3J_{H-H}$ 7.4 Hz, 1H, Ar_{H5}), 7.00 (d, $^3J_{H-H}$ 8.2 Hz, 1H, Ar_{H3}), 3.93 (s, 3H, OMe); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 189.9 (CHO), 161.9 (Ar_{OMe}), 136.0 (Ar), 128.6 (Ar), 124.9 (Ar_{CHO}), 120.7 (Ar), 111.7 (Ar), 55.7 (OMe); IR (CH_2Cl_2) 1601.9 (m, $\nu_{C=O}$).

Reaction of [Fe(C_5Me_5)($CH_3CN)_2${η^1-C(OMe)C_6H_4-*o*-Cl}]-[CF_3SO_3] (14) with O_2. Complex **14** (0.3 mmol, 173 mg) was dissolved in 10 mL of CH_3CN, and O_2 was bubbled through the solution for 30 s. The reaction mixture was stirred overnight and the solvent removed under vacuum. The residue was extracted with $CDCl_3$ and the solution filtered through a short alumina pad. The ^{1}H NMR spectrum showed the presence of the spectroscopically pure ester derivative *o*-$ClC_6H_4C(O)OMe$: ^{1}H NMR ($CDCl_3$) δ 7.83 (dd, $^3J_{H-H}$ 7.8 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 7.47 (dd, $^3J_{H-H}$ 8 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 7.42 (td, $^3J_{H-H}$ 8 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 7.32 (td, $^3J_{H-H}$ 7.3 Hz, $^4J_{H-H}$ 1.7 Hz, 1H, Ar), 3.94 (s, 3H, OMe); ^{3}C{^{1}H} NMR ($CDCl_3$) δ 166.2 (C=O), 133.7 (Ar), 132.6 (Ar), 131.4 (Ar), 131.1 (Ar), 130.2 (Ar), 126.6 (Ar), 52.3 (OMe).

Structure Determination of [Fe(C_5Me_5)(CO){η^2-C(OMe)-C_6H_4-*o*-Cl}][CF_3SO_3] (5b). Crystals of **5b** suitable for X-ray diffraction analysis were grown from a solution of a solvent mixture of CH_2Cl_2/Et_2O by slow evaporation of the solvent. A crystal was mounted on the end of a glass fiber and transferred to a Stoe four-circle diffractometer equipped with Mo $K\alpha$ radiation. The unit cell was determined from 25 randomly selected reflections. Crystal data, data collection parameters, and results of the refinement are listed in Table 3. All data processing was performed on a Viglen 486PC computer using SHELXTL-PLUS[35] and SHELXL 93.[36] Lorentz−polarization (*Lp*) corrections were applied as was a semi-empirical absorption correction based on five azimuthal Ψ-scans. The structure was solved by a combination of direct methods (TREF) and Fourier difference techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atom. In the final cycles of refinements the weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 14.03P]$, where $P = 2F_c^2/3$, was applied, as this gave a fairly flat analysis of variance.

Table 3. Crystallographic Data for [Fe(C_5Me_5)($CO)_2${η^2-C(OMe)C_6H_4-*o*-Cl}][CF_3SO_3] (5b)

formula	$C_{20}H_{22}ClF_3FeO_5S$
fw	522.74
temp	293(2) K
wavelength (Mo $K\alpha$)	0.710 73 Å
cryst system	orthorhombic
space group	*Pbca*
unit cell dimens	$a = 12.700(3)$ Å
	$b = 14.305(3)$ Å
	$c = 24.390(5)$ Å
V	4431(2) Å^3
Z	8
D(calcd)	1.567 Mg/m^3
abs coeff	0.950 mm^{-1}
F(000)	2144
cryst size	0.49 × 0.43 × 0.38 mm
θ range for data collcn	2.72−22.55°
index ranges	$-2 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 26$
reflcns collcd	3007
indepdt reflcns	2902 ($R_{int} = 0.0125$)
struct solution	direct methods
Ψ scans (T_{max} , T_{min})	0.490, 0.463
refinement method	full-matrix least squares on F^2
data/restaints/params	2856/0/286
goodness-of-fit on F^2	1.056
final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0495$, w$R_2{}^b = 0.0963$
R indices (all data)	$R_1 = 0.1107$, w$R_2 = 0.2327$
largest diff peak and hole	0.416 and −0.316 e Å^{-3}

[a] Definition of R indices: $R_1 = \{\Sigma(F_o - F_c)\}/\Sigma(F_o)$; w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]^{1/2}\}/\{\Sigma[w(F_o^2)^2\}$.

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Supporting Information Available: Tables of complete atom coordinates and U values, anisotropic displacement parameters, and complete bond distances and angles and ORTEP diagrams for **5b** (5 pages). Ordering information is given on any current masthead page.

OM960711Z

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[35] SHELXTL-PLUS Rev. 4.0, Siemens Analytical X-ray Instruments, Madison, WI, 1990.

[36] SHELXL 93: Sheldrick, G. M. University of Göttingen, Germany, 1993.