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Synthesis and characterization of the chiral iron secondary methoxycarbene $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHOMe})][\text{SO}_3\text{CF}_3]$

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Abstract

The chiral iron secondary methoxycarbene $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHOMe})][\text{SO}_3\text{CF}_3]$ (**10**) can be conveniently made by direct *O*-alkylation of the isolated neutral iron formyl $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHO})$ (**9**). This procedure appears efficient to prepare **10**, since the trityl salt $[\text{Ph}_3\text{C}][\text{PF}_6]$ reacts with the methoxymethyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2\text{OMe})$ (**2**) to give the thermally unstable methylene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2)][\text{PF}_6]$ (**4**).

Introduction

Whereas the secondary heterocarbene complexes $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{L}^1)(\text{L}^2)(\text{CHOMe})][\text{X}]$ are readily accessible for $\text{L}^1 = \text{L}^2 = \text{CO}$ (**3**) [1] and $\text{L}^1 = \text{L}^2 = \text{dppe}$ [2], the chiral carbene compounds ($\text{L}^1 = \text{CO}$; $\text{L}^2 = \text{PR}_3$) were previously unknown. We thus decided to undertake the synthesis and the characterization of the new compound $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PR}_3)(\text{CHOMe})][\text{PF}_6]$. The procedure previously used to make to the C_3H_5 analog being unsatisfactory [3], we devised two routes to such compounds namely (i) hydride abstraction from the iron alkoxymethyl derivative $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2\text{OMe})$ (**2**) by a methylene complex, and (ii) alkylation of the iron formyl precursor $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHO})$ (**9**). The isolation and the characterization of this scarce neutral iron species are also described.

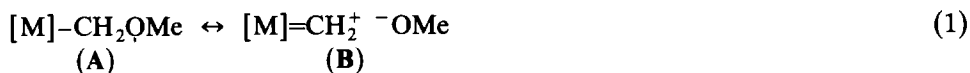
Results and discussion

1. Reaction of the trityl salt $[\text{Ph}_3\text{C}][\text{PF}_6]$ with $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2\text{OMe})$ (**2**)

The chiral iron secondary methoxycarbene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CHOMe})][\text{PF}_6]$ (**5**) cannot be prepared by the procedure used for the C_3H_5 relatives [3] or the C_5Me_5 dicarbonyl analog (**3**) [1], i.e. hydride abstraction by the trityl cation from the corresponding methoxymethyl precursor. Methoxide abstraction

occurs upon treatment of the methoxymethyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2\text{OMe})$ (**2**) with the trityl salt, affording the known [4] methylene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2)][\text{PF}_6]$ (**4**) in quantitative yield as indicated by the low temperature NMR spectrum. The formation of methoxytriphenylmethane was confirmed by GC analysis (Scheme 1).

The reaction of the trityl reagent with metal α -alkoxyalkyl compounds proceeds either by alkoxide [5] or α -hydride abstraction. In all cases, the reaction is chemospecific, a single product being formed. Alkoxide abstraction has usually been observed [5], there are only a few cases of hydride abstraction [1,3a]. This dual of reaction mode can be attributed to the electronic structure of the starting alkyl compound: the more electron rich the metal, the more important is the contribution of the mesomeric form **B** (eq. 1) and the easier is the methoxide abstraction. We assume that the hydride abstraction occurs only if the ancillary ligands coordinated to the metal are not sufficiently electron releasing to give significant weight to the canonical form **B**.



2. Hydride abstraction by the iron methylene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CH}_2)][\text{PF}_6]$ (**4**)

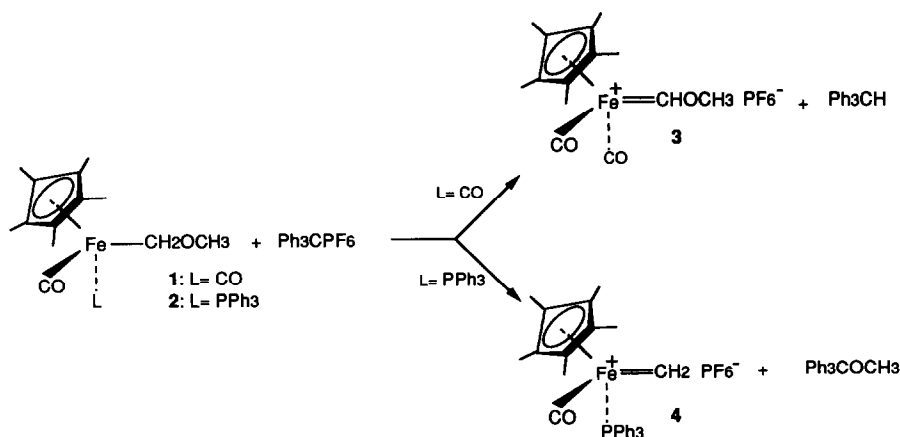
As shown by low-temperature ^1H NMR experiments, the methoxycarbene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CHOMe})][\text{PF}_6]$ (**5**) is produced by intermolecular hydride transfer reaction. Treatment of the methoxymethyl complex **2** with half an equivalent of $[\text{Ph}_3\text{C}][\text{PF}_6]$ *in situ* generates the transient methylene complex **4**, which can abstract a hydride from the unchanged starting material to give both the methyl derivative **6** and the desired secondary methoxycarbene $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(\text{CHOMe})][\text{PF}_6]$ (**5**) (Scheme 2) [6*].

The ability of methylene complexes to abstract hydride has been previously observed in several cases [7]. The formation of **5** and **6** is instantaneous at -80°C and the methoxycarbene is formed in a 25% (by spectroscopy) yield. Along with these two compounds there is another unidentified by-product. From a reaction performed on one mmole scale we could not isolate **5** as a pure compound. The synthetic interest of this reaction is limited by its non-specific character and the formation of the desired compound in only low yield.

3. Synthesis, isolation and characterization of the iron formyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHO})$ (**9**)

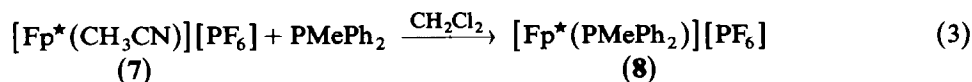
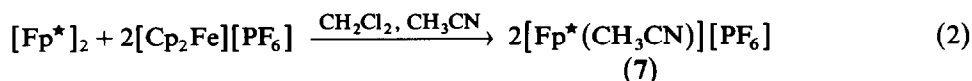
Alkylation of a formyl precursor provides an alternative route to chiral secondary alkoxycarbene compounds [8]. We have previously shown, in the case of molybdenum complexes, that this route can be of synthetic interest, and this was nicely confirmed by Gibson's group in the preparation of manganese carbene complexes [9]. As we observed previously, this reaction requires a stabilized metal formyl complex with a low hydridic character as starting material [8], and so the phosphine PMePh_2 , which has a moderate electron releasing ability, was chosen. The cationic complex

* Reference number with asterisk indicates a note in the list of references.



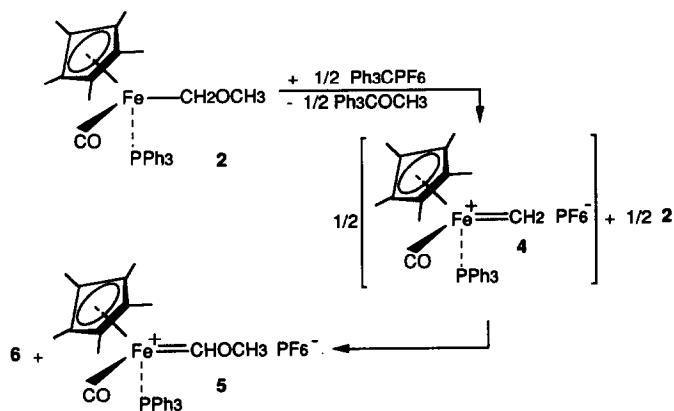
Scheme 1.

$[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2(\text{PMePh}_2)][\text{PF}_6]$ (**8**) was prepared by previously described procedure [10] that we improved by using acetonitrile in place of THF (eqs. 2 and 3).



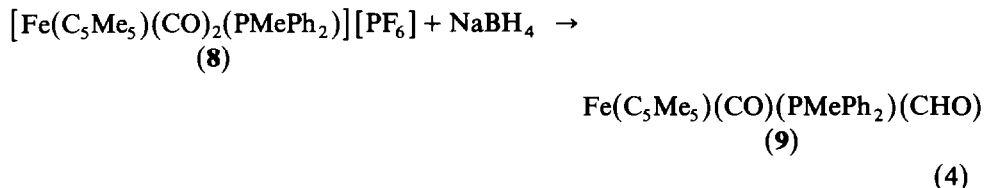
($\text{Fp}^* = \text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2$)

The iron formyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHO})$ (**9**) was prepared by carefully mixing, the solid organometallic salt **8** with 4 equivalents of solid sodium borohydride before adding a CH_2Cl_2 - CH_3OH (85/15) mixture at -80°C . As the temperature rose slowly overnight to -15°C reduction takes place. The neutral iron formyl complex was isolated as a yellow powder after removal of the solvent under vacuum at -20°C , washing twice with cold pentane, and extracting with



Scheme 2.

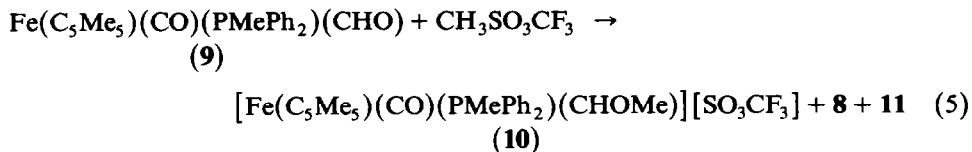
diethyl ether at -50°C . Solid **9** can be stored at -20°C , but decomposes into the iron hydride $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\text{H}$ [11] at 0°C . The single resonance observed in the ^1H NMR spectrum (-30°C) of **9** at δ 1.47 (C_5Me_5) indicated that the formyl complex was isolated pure (eq. 4).



The resonance of the formyl proton appears as a broad signal at δ 14.20, and the formyl carbon atom resonates at 290.5, as expected [11]. The solid state infrared spectrum (Nujol mull) exhibits a CO bond stretching at 1590 cm^{-1} for the $\nu(\text{CO})$ absorption of the CHO ligand. It is noteworthy that most of iron formyl complexes were previously characterized in solution [11], and the iron formyl **9** is only the second example of an isolated neutral iron formyl complex [12].

4. Synthesis of the secondary carbene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHOMe})][\text{SO}_3\text{CF}_3]$ (**10**)

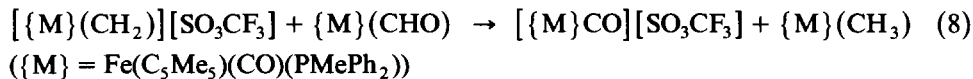
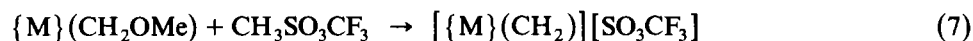
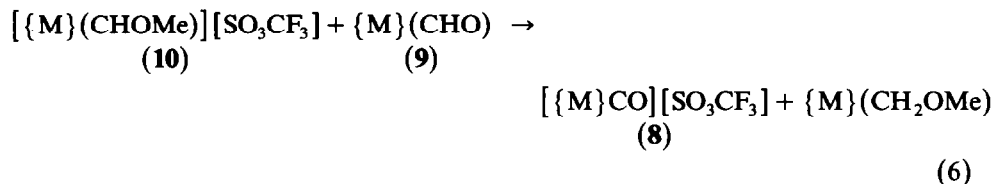
When one equivalent of methyl triflate was added to a -50°C diethyl ether solution of the formyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHO})$ (**9**), a yellow precipitate slowly appeared. After 3 h, the reaction was complete, and the solid was filtered off at -50°C and shown to be $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2(\text{PMePh}_2)][\text{SO}_3\text{CF}_3]$ (**8**, 25%). The carbene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CHOMe})][\text{SO}_3\text{CF}_3]$ (**10**), precipitated from the filtrate overnight, as a greenish solid as the temperature rose to -15°C [15*]. It was isolated pure (39%), and found to be thermally stable. The filtrate yielded the pure methyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CH}_3)$ (**11**) (13%) when the solvent was removed under vacuum (eq. 5).



The carbene complex **10** was characterized by IR and ^1H , ^{31}P and ^{13}C NMR spectroscopy. The ^1H NMR spectrum (CD_2Cl_2 , 25°C) of **10** exhibits a low-field broad signal at δ 12.40 due to the carbene proton. The other signals corresponding to the C_5Me_5 , and methoxy groups appear at δ 1.64 and 4.17 respectively; these substituents give proton resonances at δ 1.94 and 4.67 in the case of the previously reported dicarbonyl analog $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2(\text{CHOMe})][\text{PF}_6]$ (**3**) [1], indicating an increase in the electronic density at the metal center. The ^{13}C resonance of the carbene carbon atom appears as a doublet at δ 324.8 ($^2J(\text{CP}) = 21.4\text{ Hz}$); such a low field value is usually observed for methoxycarbene compounds, and confirms the structure [1,14].

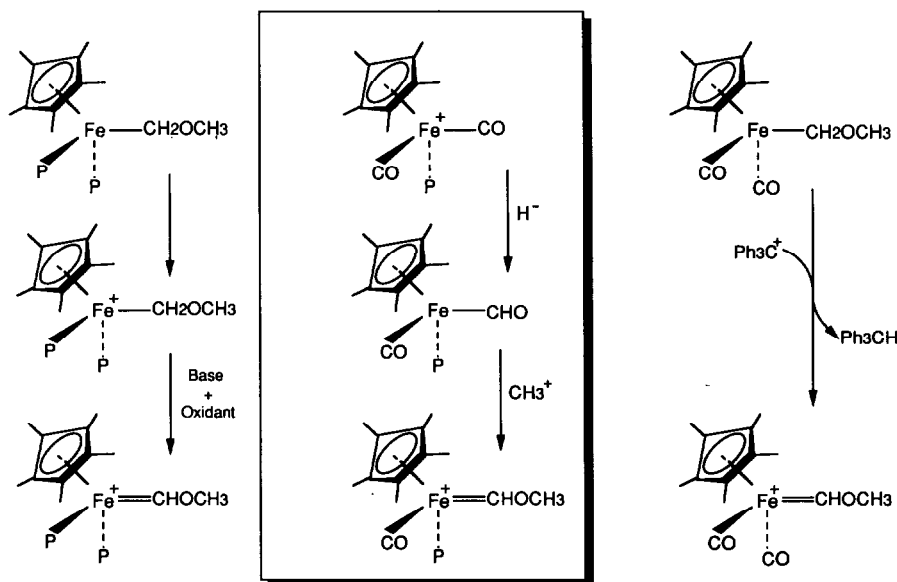
As we have shown, successful synthesis of a secondary heterocarbene complex by direct *O*-alkylation of a metal formyl precursor requires that the hydridic formyl compound is sufficiently kinetically stable to avoid *in situ* hydride transfer to the

electrophilic carbene derivative formed [7b,8b]. We have obtained both the carbene derivative and the methyl complex, associated with the cationic compound; the *O*-alkylation reaction competes with the subsequent hydride transfer reactions by the mechanism established by Gladysz [7b]. The formation of the methyl compound **11** and the cationic carbonyl complex **8** results from a hydride transfer between the carbene **10** and the unchanged formyl **9** to give the salt **8** and the methoxymethyl complex $\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMePh}_2)(\text{CH}_2\text{OCH}_3)$, which reacts *in situ*, with the methyl triflate. Subsequent elimination of dimethyl ether generates the unstable methylene complex, which is reduced to the methyl complex **11** by the formyl **9** to give a second equivalent of compound **8** (eqs. 6–8).



Concluding remarks

Although the reaction is not chemospecific, the three products can be successively isolated pure without need for any further purification. This procedure provides a convenient route to compound **10**, the first secondary heterocarbene of the C_5Me_5 series chiral at the metal. The *O*-alkylation of metal formyl complexes



Scheme 3.

does not provide a simple route to metal carbene compounds but its synthetic potential is becoming increasingly evident: this procedure has been now extended to molybdenum [8,9a], manganese [9b], and iron complexes. Moreover, electrophilic additions to cationic metal formyl complexes have been shown to give the expected dicationic carbene compounds [15].

The secondary heterocarbene $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{L}^1)(\text{L}^2)(\text{CHOMe})][\text{X}]$ can now be made with L^1 and L^2 either a carbonyl or a phosphine ligand and the best route to these compounds depends on the nature of the ancillary ligands coordinated to the iron center. The synthesis of the electrophilic dicarbonyl complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\text{-CHOMe}][\text{X}]$ is conveniently achieved by a classical hydride abstraction by the trityl salt from the corresponding methoxymethyl complex [1]. The electron-rich methoxycarbene compound $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{dppe})(\text{CHOMe})][\text{X}]$ was previously prepared by an original three step-one pot procedure: one electron oxidation, proton abstraction and one electron oxidation (ECE mechanism) [2] (Scheme 3). Now, we can make methoxycarbene compounds of the $\text{Fe}(\text{C}_5\text{Me}_5)$ series with a wide range of electronic properties, and this should be valuable for our research program on carbene reactivity, including electron transfer activation process [16] and stereochemistry.

Experimental

General data

Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were dried and distilled over sodium benzophenone ketyl prior to use. Acetonitrile was refluxed over P_2O_5 and distilled over Na_2CO_3 . All the manipulations were carried out under argon by Schlenk techniques or in a Jacomex 532 dry box filled with nitrogen. Routine NMR spectra were recorded with a Bruker AW 80 MHz spectrometer. High field NMR spectra were recorded on a multinuclear Bruker instrument. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and to 85% aqueous H_3PO_4 for ^{31}P NMR spectra. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Villeurbanne.

1. Reaction of $\text{Fe}(\text{C}_5\text{Me}_5)(\text{PPh}_3)(\text{CO})(\text{CH}_2\text{OMe})$ (**2**) with $[\text{Ph}_3\text{C}][\text{PF}_6]$

A solution of 0.02 mmol (10 mg) of **2** in CD_2Cl_2 was filtered through a canula into a 5 mm-NMR tube. To the solution cooled to -80°C was added a CD_2Cl_2 solution of 0.02 mmol (8 mg) of $[\text{Ph}_3\text{C}][\text{PF}_6]$. The low-temperature ^1H NMR spectrum revealed the quantitative formation of the corresponding methylene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{PPh}_3)(\text{CO})(\text{CH}_2)][\text{PF}_6]$. The structure of the later was assigned on the basis of the similarity of its spectrum to that of the corresponding triflate generated by treatment of **2** with Me_3SiOTf [4].

2. Generation and spectral characterization of $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{PPh}_3)(\text{CO})(\text{CHOMe})][\text{PF}_6]$ (**5**)

In the procedure described above, 0.02 mmol (10 mg) of (**2**) was treated at -80°C with 0.5 equivalents (0.01 mmol, 4 mg) of $[\text{Ph}_3\text{C}][\text{PF}_6]$. The spectrum showed the presence of the corresponding methoxycarbene **5** and the methyl derivative [11]. ^1H NMR (CD_2Cl_2): 12.65 (br s, 1H, =CH); 7.32 (m, Ph); 3.92 (s, 3H, OMe); 1.55 (s, 15H, C_5Me_5).

3. Synthesis of $[Fe(C_5Me_5)(CO)_2(PMePh_2)][PF_6]$ (**8**)

To a solution of 4 mmol (1.73 g) of $[Fe(C_5Me_5)(CO)_2(CH_3CN)][PF_6]$ (**10**) in 20 mL of CH_2Cl_2 was added a slight excess of $PMePh_2$ (800 μ L). The mixture was refluxed for 1 h and the solvent removed under vacuum. Recrystallization from acetone–ethanol gave a pure yellow solid (1.85 g; 80%). IR (cm^{-1} , CH_2Cl_2): 2050, 2000 ($\nu(CO)$). 1H NMR ($CDCl_3$): 1.60 (s, 15H, C_5Me_5); 2.11 (d, 3H, $^2J(PH) = 9.6$ Hz, PMe); 7.50 (m, 10H, Ph). $\{^1H\}^{13}C$ NMR ($CDCl_3$): 212.5 (d, $^2J(PC) = 16.5$ Hz, CO); 131.9 (d, $^4J(PC) = 8.2$ Hz, C_{para}); 131.3 (d, $^3J(PC) = 10$ Hz, C_{meta}); 129.6 (d, $^2J(PC) = 10.3$ Hz, C_{ortho}); 100.4 (s, C_5Me_5); 16.9 (d, $^2J(CP) = 32.0$ Hz, Me); 9.6 (s, C_5Me_5). $\{^1H\}^{31}P$ NMR ($CDCl_3$): 48.2 (s, $PMePh_2$). Anal. Found: C, 50.51; H, 4.72. $C_{25}H_{28}FeF_6O_2P_2$ calcd.: C, 50.70; H, 4.76%.

4. Synthesis of $Fe(C_5Me_5)(CO)(PMePh_2)(CHO)$ (**9**)

A mixture of 1 mmol (0.580 g) of $[Fe(C_5Me_5)(PMePh_2)(CO)_2][PF_6]$ (**8**) and 4 mmol (0.148 g) of $NaBH_4$ was carefully ground in a mortar before being placed in a Schlenk tube. The mixture was deaerated *in vacuo* for 10 min, then cooled to $-80^\circ C$, and 5 mL of a cold CH_2Cl_2 – CH_3OH (85/15) mixture was added. The suspension was stirred and allowed to warm slowly to $-15^\circ C$ overnight. The solvents were removed under vacuum at $-20^\circ C$ and the solid residue washed twice with 2×20 mL of cold pentane ($-80^\circ C$). The formyl complex was extracted with ether (3×20 mL) at $-50^\circ C$. After removal of the solvent under vacuum, the formyl compound (**9**) was obtained as a yellow powder (0.40 g, 0.90%), found to decompose at room temperature into the known metal hydride $Fe(C_5Me_5)(CO)_2(H)$. IR (cm^{-1} , Nujol), 1913, 1596 ($\nu(CO)$). 1H NMR (CD_2Cl_2 , $-30^\circ C$): 14.20 (d, 1H, $^3J(PH) = 2.2$ Hz, CHO); 7–7.5 (m, 10H, Ph); 2.24 (m, 3H, PMe) 1.47 (s, 15H, C_5Me_5). $\{^1H\}^{13}C$ NMR (CD_2Cl_2 , $-30^\circ C$) 290.5 (d, $^2J(PC) = 25.1$ Hz, CHO); 219.9 (d, $^2J(PC) = 27.1$ Hz, CO); 136.1 (d, $^1J(PC) = 41.2$ Hz, C_{ipso}); 134.9 (d, $^1J(PC) = 38.4$ Hz, C_{ipso}); 132.2 (d, $^2J(PC) = 10.3$ Hz, C_{ortho}); 132.1 (d, $^2J(PC) = 11.5$ Hz, C_{ortho}); 130.2 (d, $^4J(PC) = 7.5$ Hz, C_{para}); 128.6 (d, $^3J(PC) = 9.1$ Hz, C_{meta}); 128.5 (d, $^3J(PC) = 9.2$ Hz, C_{meta}); 94.9 (s, C_5Me_5); 17.2 (d, $^2J(PC) = 34.9$ Hz, PMe); 9.0 (s, C_5Me_5). $\{^1H\}^{31}P$ NMR (CD_2Cl_2 , $-30^\circ C$): 61.6 (s, $PMePh_2$).

5. Synthesis of $[Fe(C_5Me_5)(PMePh_2)(CHOCH_3)][SO_3CF_3]$ (**10**)

To a cold ($-50^\circ C$) solution of $Fe(C_5Me_5)(PMePh_2)(CHO)$ (**9**) (0.9 mmol, 0.40 g) in diethyl ether, contained in a Schlenk tube, was added 1 mmol (150 μ L) of $CH_3SO_3CF_3$. The solution was stirred at $-50^\circ C$ for 3 h, during which a yellow precipitate slowly appeared. The solid residue was filtered off, washed twice with ether, and dried (0.140 g, 27%). It was identified as $[Fe(C_5Me_5)(CO)_2(PMePh_2)][SO_3CF_3]$. The filtrate was stirred at $-20^\circ C$ overnight during which a second precipitate separated. This was filtered off and washed twice with ether; the light green $[Fe(C_5Me_5)(CO)(PMePh_2)(CHOMe)][SO_3CF_3]$ (**10**) was obtained pure in 39% yield (0.230 g). Removal of the solvent from the filtrate left a yellow solid (0.057 g, 13%), which was identified as $Fe(C_5Me_5)(CO)(PMePh_2)(CH_3)$ (**11**). IR (cm^{-1} , CH_2Cl_2): 1967 ($\nu(CO)$). 1H NMR ($(CD_3)_2CO$, $25^\circ C$): 12.40 (br s, 1H, CH); 7–7.5 (m, 10H, Ph); 4.17 (s, 3H, OMe); 2.14 (d, 3H, $^2J(PH) = 9.6$ Hz, PMe); 1.64 (s, 15H, C_5Me_5). $\{^1H\}^{13}C$ NMR ($(CD_3)_2CO$, $25^\circ C$): 324.8 (d, $^2J(PC) = 21.4$ Hz, =CH); 217.5 (d, $^2J(PC) = 25.5$ Hz, CO); 134.3 (d, $^1J(PC) = 47.7$ Hz, C_{ipso}); 133.9 (d, $^1J(PC) = 45.7$ Hz, C_{ipso}); 132.7 (d, $^2J(PC) = 10.3$ Hz, C_{ortho}); 132.4 (d, $^2J(PC) = 9.5$

Hz, C_{ortho}); 132.3 (d, $^4J(PC) = 9.5$ Hz, C_{para}); 129.8 (d, $^3J(PC) = 11.1$ Hz, C_{meta}); 129.7 (d, $^3J(PC) = 11.1$ Hz, C_{meta}); 100.5 (s, C_5Me_5); 75.0 (s, OMe); 16.3 (d, $^2J(PC) = 33$ Hz, PMe); 9.4 (s, C_5Me_5). $\{^1H\}^{31}P$ NMR ($(CD_3)_2CO$, $25^\circ C$): 54.8 (s, $PMePh_2$). Anal. Found: C, 52.84; H, 5.52. $C_{27}H_{32}FeF_3O_5PS$ calcd.: C, 52.95; H, 5.27%.

6. Characterization of $Fe(C_5Me_5)(CO)(PMePh_2)(CH_3)$ (II)

1H NMR (C_6D_6 , $25^\circ C$): 7–7.5 (m, 10H, Ph); 1.62 (d, 3H, $^2J(PH) = 7.6$ Hz, PMe); 1.43 (s, 15H, C_5Me_5); -0.13 (d, 3H, $^3J(PH) = 6.8$ Hz, CH_3). ^{13}C NMR (C_6D_6 , $25^\circ C$): 225.0 (d, $^2J(PC) = 30$ Hz, CO); 139.5 (d, $^1J(CP) = 38.2$ Hz, C_{ipso}); 137.4 (d, $^1J(CP) = 31.7$ Hz, C_{ipso}); 132.8 (d, $^2J(PC) = 10.2$ Hz, C_{ortho}); 132.3 ($^3J(PC) = 9.3$ Hz, C_{ortho}); 130.9 (d, $^4J(PC) = 9.4$ Hz, C_{para}); 91.1 (s, C_5Me_5); 17.0 (d, $^1J(PC) = 22$ Hz, PMe); 9.7 (s, C_5Me_5); -12.2 (d, $^2J(PC) = 22$ Hz, CH_3). (C_{meta} are obscured by C_6D_6 resonances.) ^{31}P NMR (C_6D_6 , $25^\circ C$): 64.5 (s, $PMePh_2$).

Acknowledgments

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