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Stereospecific syntheses of functionalised iron alkyl complexes with a stereogenic metal center from an iron formyl precursor

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Abstract

Treatment of the stable formyl complex $Fe(C_5Ph_5)(CO)(PMe_3)CHO$ (**1**) with an excess of methyl triflate and subsequent addition of NH_4PF_6 produces the secondary carbene complex $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (**2**, 93%). Methyl lithium acts as a dealkylating reagent with **2** to regenerate **1** (81%). Treatment of methoxycarbene complex **2** with $LiAlH_4$ gives the methoxymethyl complex $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CH_2OMe)$ (**3**) in 95% yield. Similarly, reaction of **2** with $LiAlD_4$ gives a 90:10 mixture of $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CHDOMe)$ (**3 d$_1$**, 80%) diastereoisomers. The carbene complex **2** reacts with MeONa to give the iron dimethylacetal complex $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)\{CH(OMe)_2\}$ (**4**, 55%). The cyano(methoxy)methyl complex $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)\{CH(CN)(OMe)\}$ (**5**, 85%) is obtained from the reaction of **2** with 1 equivalent of KCN. NMR analyses of the crude product revealed that complex **5** was formed as a 85:15 mixture of diastereoisomers. The carbene complex **2** reacts with $TMSC{\equiv}CLi$ to afford a 90:10 mixture of diastereoisomers of the stable methoxy(trimethylsilylethynyl)methyl iron complexes $Fe(C_5Ph_5)(CO)(PMe_3)\{CH(OMe)(C{\equiv}CTMS)\}$ (**6**). After extraction and filtration **6** is isolated as a pure diastereoisomer in 63% yield.

Keywords: Fe; Formyl complex; Alkyls; Stereospecific syntheses; Pentaphenylcyclopentadienyl; Carbene complex

1. Introduction

Alkylation of transition metal formyl complexes constitutes a valuable route to secondary alkoxycarbene compounds. This has been shown in the preparation of molybdenum [1], manganese [2] and iron [3] carbene complexes. However, we have shown that the thermal instability of the formyl complex $Fe(\eta^5\text{-}C_5Me_5)(CO)(PMePh_2)CHO$ associated with its hydridic character produces a carbene complex in only low yield upon alkylation [3]. In contrast, the pentaphenylcyclopentadienyl formyl complex $Fe(C_5Ph_5)(CO)(PMe_3)(CHO)$ (**1**) is thermally stable and readily prepared in high yield [4]. An X-ray crystal structure analysis of **1** has shown that the phenyl rings are tilted relative to the plane of the five-membered ring through angles ranging from 42.9 to 53.5°. These peripheral substituents adopt a compromise between the sterically favored orthogonal orientation and the completely coplanar rotamer, which would maximize conjugation but yield acceptably short H...H distances [5]. As a result, the bulky and electron-withdrawing phenyl groups provide both kinetic and thermodynamic stabilization of the labile formyl fragment.

We report here an exploration of the electrophilic properties of the new secondary methoxycarbene complex $[Fe(C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (**2**), readily accessible from **1**, and its stereoselective reactions with nucleophiles to give alkyl complexes with a stereogenic iron center. Two principal findings emerge from this chemistry: (1) the organometallic moiety $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)$ is able to exert a stereocontrol as powerful as the well known chiral auxiliaries $[Re(C_5H_5)(NO)(PPh_3)]$ [6] and $[Fe(C_5H_5)(CO)(PPh_3)]$ [7–9]; (2) the secondary carbene complex **2**, stereogenic at the metal, appears to be a much better precursor to new and functionalised iron alkyl complexes than its $(\eta^5\text{-}C_5Me_5)$ analog [3].

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2. Results and discussion

2.1. Synthesis of the secondary carbene complex $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CHOMe)][PF_6]$ (2)

Treatment of a CH_2Cl_2 solution of the stable formyl complex $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)CHO$ (1) at −50°C with an excess of methyl triflate and subsequent addition of NH_4PF_6 produced after 4 h the secondary carbene complex $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (2). Complex 2 was isolated as an analytically pure and thermally stable yellow powder in 93% yield after crystallization from CH_2Cl_2/pentane:

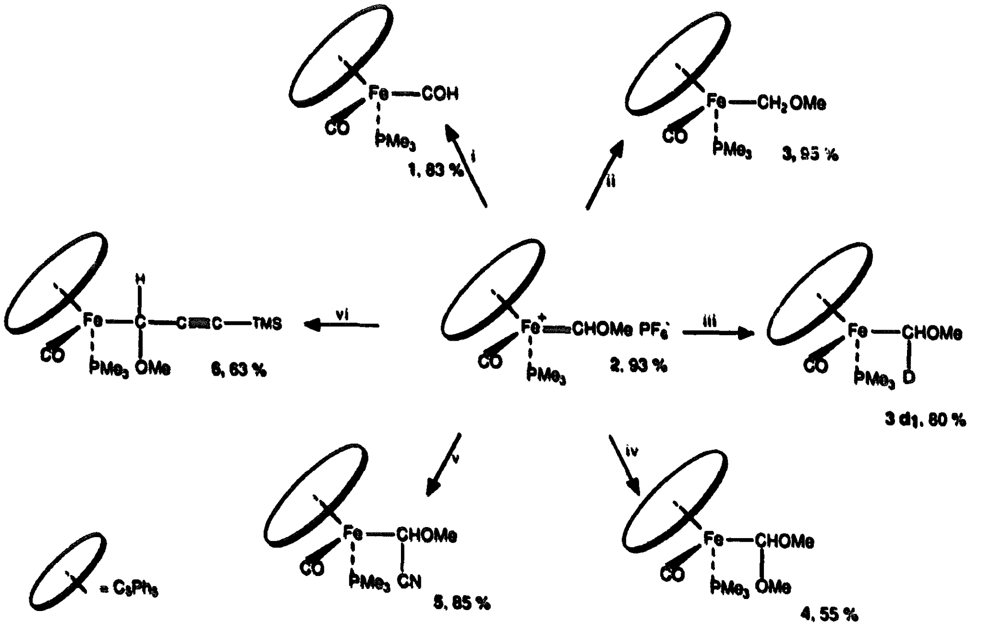
$$\underset{\mathbf{1}}{Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)CHO} + MeOTf + NH_4PF_6 \longrightarrow \underset{\mathbf{2}}{\left[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)\right][PF_6]} + NH_4OTf \qquad (1)$$

The carbene complex 2 was characterized by IR and ^1H, ^{31}P and ^{13}C NMR spectroscopies. The ^1H NMR (CD_2Cl_2, 25°C) spectrum of 2 exhibits a low-field doublet ($^3J_{PH}$ = 1.8 Hz) at δ 13.23 due to the carbene proton. The other signals corresponding to the PMe_3, methoxy and phenyl groups appear at δ 1.50, 4.51 and in the range 7–7.5 respectively. These ^1H chemical shifts compare well with those reported for the related (η^5-C_5Me_5) complex, namely $[Fe(\eta^5\text{-}C_5Me_5)(CO)(PMePh_2)(CHOMe)][SO_3CF_3]$ [3]. The ^{13}C resonance of the carbene atom appears as a doublet at δ 326.1 (δ, $^2J_{CP}$ = 21.8 Hz). This low field value agrees well with those usually observed for methoxycarbene derivatives [1–3,10,12a,13]. The IR spectrum (CH_2Cl_2) of 2 is similar to that of its counterpart from the C_5Me_5 series in displaying one carbonyl stretching band at 1969 (*cf.* 1967) cm^{-1}. This suggests that the electrophilic properties of these two secondary carbene complexes should be very close. The electron-withdrawing effect due to the substitution of the methyl by phenyl groups at the C_5 ring is balanced by a more electron-donating phosphine ligand.

Most often the formation of secondary carbene complexes by alkylation of a metal formyl precursor is precluded by a simultaneous intermolecular hydride transfer from the formyl to the intermediately formed carbene, giving rise to side products [3,10,11]. However, the steric protection provided by the C_5Ph_5 ligand is sufficient to inhibit the intermolecular hydride transfer reaction, allowing the isolation of the carbene complex in high yield. Therefore, the *O*-alkylation of the readily available formyl complex 1 provides simple synthetic access to a secondary carbene complex with a stereogenic metal center. As a consequence of the presence of a stereogenic iron center, it can be expected that nucleophilic attack should be faster at one face of the electrophilic carbon atom of the carbene 2. This has already been established for other transition metal carbene complexes [5–7].

2.2. Reduction of the carbene complex 2 and stereoselectivity of the hydride attack

Treatment of a −80°C THF solution of the carbene complex 2 with an excess of methyl lithium afforded,



Scheme 1. Reagents: i, MeLi, ii, $LiAlH_4$; iii, $LiAlD_4$; iv, CH_3ONa; v, KCN; vi, $Me_3SiC{\equiv}CLi$.

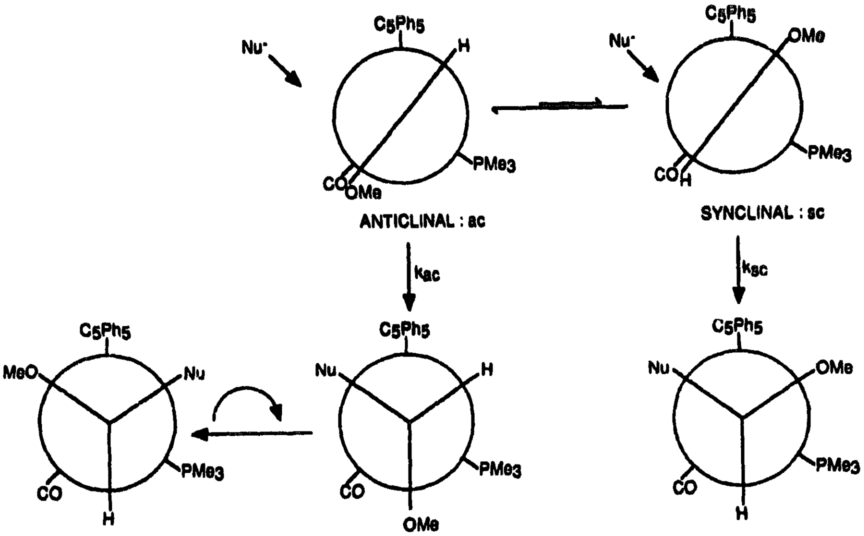
after stirring overnight, the iron formyl complex **1**, isolated in 83% yield (Scheme 1). The methyl lithium therefore reacts like a dealkylating reagent towards the carbene complex, which appears to act as a methylating agent (Eq. (2)). The reactivity of **2** towards methyl lithium strongly contrasts with that observed in the C_5H_5 series. Indeed, addition of alkyl- and aryl-lithium reagents to $[Fe(Cp)(CO)_2(=CHOMe)][PF_6]$ has been reported to give the corresponding methoxy(alkyl)methyl iron complexes in good yield [14].

$$\underset{\mathbf{2}}{\left[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)\right][PF_6]} + LiMe \longrightarrow \underset{\mathbf{1}}{Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CHO)} \quad (2)$$

The difference in the reactivity of these two iron carbene complexes towards methyl lithium can be explained in terms of nucleophilic attack vs. an electron transfer process. In the C_5H_5 series, the nucleophilic addition of the methyl anion yields the methyl(methoxy)methyl complex. In contrast, in the C_5Ph_5 series, the formyl derivative **1** is obtained through a one-electron reduction route. In a previous report on the one-electron reduction of pentamethylcyclopentadienyl iron carbene complexes we had postulated the formation of formyl intermediates, but their characterization was precluded by a low stability [15]. Now, the electron transfer product was unequivocally obtained in the C_5Ph_5 series by using a one-electron reduction reagent. Treatment of the carbene **2** with 1 equivalent of Cp_2Co gave the stable formyl complex **1** as the main product of the reaction, spectroscopically identified.

The alkoxycarbene complex **2** was treated with $LiAlH_4$ (1 equiv. THF, −80°C) to give the methoxymethyl complex $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CH_2OMe)$ (**3**) in 95% yield (Scheme 1). The new complex **3** was isolated as an analytically pure light brown powder and identified by IR and ^1H, ^{31}P and ^{13}C NMR. The characteristic diastereotopic methylene proton appeared in the ^1H NMR spectrum as a double AB system at δ 4.46 ($^2J_{HH}$ = 4.2 Hz, $^3J_{PH}$ = 4.1 Hz) and 4.75 ($^2J_{HH}$ = 4.2 Hz, $^3J_{PH}$ = 6.7 Hz). The methoxycarbene complex **2** was also reacted with $LiAlD_4$ to give **3** $\mathbf{d}_1$ (80% yield), a compound with two chiral centers. The ^1H NMR spectrum of **3** $\mathbf{d}_1$ in C_6D_6 indicated that one of the two diastereotopic hydrogen atoms observed in **3** was almost completely absent, while a doublet is observed at δ 4.44 ($^3J_{PH}$ = 3.6 Hz). Hence, the addition of D^- to **2** occurs stereospecifically on one face of the carbene. Only as little as 10% of the other possible diastereoisomer was observed.

The stereoselectivity of nucleophilic attack on metal carbene complexes has been reported and ascribed primarily to steric effect. The existence of two geometric isomers arising from the metal–carbon multiple bond was experimentally established for the first time with the rhenium benzylidene complex $[ReCp(NO)(PPh_3)(=CHPh)][PF_6]$ [6d]. However, owing to the low Fe=C rotation barrier [12], the synclinal (sc) and anticlinal (ac) geometric isomers of the alkoxycarbene complex **2** were not observed; the sc conformer should be higher in energy than the ac, which minimizes the steric repulsion between the bulky ligands. As shown in Scheme 2, the PMe_3 side of the carbene ligand is overcrowded by the phenyl rings of the bulky C_5Ph_5 ligand and the methyl groups of the phosphine. Thus, nucleophilic attack should occur preferentially on the opposite face. However, since it was established by Brookhart et al. [7a] that the synclinal isomers of the closely related alkylidene complexes $[CpFe(CO)(PR_3)(=CHR')]^+$ were more reactive than the anticlinal isomers, therefore the stereochemistry of the major isomer cannot be assigned on the



Scheme 2. Stereochemistry of nucleophilic attack at the carbene carbon atom.

basis of a conformational analysis of the starting material.

Most nucleophilic additions to carbenes involve triphenylphosphine containing compounds, with the exception of [CpRe(NO)(PMe_3)(=CHPh)][PF_6] and [CpFe(CO)(PMe_3)(=CHR)][PF_6]. From those results it seems that the presence of a bulky phosphine was usually required to observe high selectivity in rhenium compounds [6]. In our case, it appears that PMe_3 can effectively sterically shield one face of the carbene iron moiety [7]. The C_5Ph_5/PMe_3 couple coordinated to iron also provides good selectivity, as illustrated below.

2.3. Synthesis of functionalised alkoxy(alkyl)methyl complexes Fe(η^5-C_5Ph_5)(CO)(PMe_3)(CHROMe) (R = OMe, 4; CN, 5; C≡CTMS, 6)

The carbene complex **2** reacts with 1 equivalent of MeONa (THF, 20°C) to give an orange powder after toluene extraction and precipitation with cold pentane (−40°C), identified as the iron complex Fe(η^5-C_5Ph_5)(CO)(PMe_3){CH(OME)$_2$} (**4**). The dimethylacetal complex **4** is stable at room temperature and was isolated as an analytically pure solid in 55% yield. Complex **4** was identified by IR and ^{1}H, ^{31}P and ^{13}C NMR. The characteristic diastereotopic methoxymethyl protons appeared in the ^{1}H NMR spectrum as two singlets at δ 3.11 and 3.54.

The cyano(methoxy)methyl complex Fe(η^5-C_5Ph_5)(CO)(PMe_3)(CH(CN)(OMe)) (**5**) was obtained from the reaction of **2** with 1 equivalent of KCN, as a room temperature stable red–orange powder in 85% yield. The IR spectrum (Nujol, 2181 cm^{-1}) revealed the presence of the cyano group. The ^{1}H, ^{13}C and ^{31}P NMR spectra of the crude product indicated that the complex **5** was formed as a mixture of two diastereoisomers in an 85 : 15 ratio. The ^{31}P NMR spectrum exhibited two distinct resonances at δ 24.13 and 25.36 corresponding to the major and minor isomers respectively. The ^{1}H NMR spectrum of these two isomers showed the three sets of distinct resonances that were expected for the isomers: the resonances of methyl substituents of the PMe_3, the methoxy group, and the proton bound to the α carbon atom. Those for the major isomer are located at δ 1.44 (d, $^2J_{PH} = 9.3$ Hz), 3.37 and 5.51 (s, $^3J_{PH} = 3.2$ Hz) respectively, whereas they are observed at δ 1.30 (d, $^2J_{PH} = 9.4$ Hz), 3.00 and 5.40 (d, $^3J_{PH} = 1$ Hz) for the minor isomer. Two successive recrystallizations from a toluene/pentane mixture gave **5** with major/minor diastereoisomer ratios of 93 : 7 and 97 : 3 respectively (see Experimental section).

Treatment of a −80°C THF solution of the carbene complex **2** with 1 equivalent of TMSC≡CLi afforded the methoxy(trimethylsilylethynyl)methyl iron complex Fe(η^5-C_5Ph_5)(CO)(PMe_3){CH(OMe)(C≡CTMS)} (**6**) after stirring overnight. Complex **6** was isolated as a thermally stable orange powder (Scheme 1). ^{31}P NMR analysis of the crude product revealed the presence of two isomers in a 90 : 10 ratio. After washing with pentane the remaining solid was extracted with a diethyl ether/pentane 1/1 mixture and the extract filtered through a Celite column. After evaporation of the solvent, complex **6** was obtained in 63% yield as an analytically pure sample containing a single diastereoisomer spectroscopically identified. The IR spectrum (Nujol) provided evidence for the presence of the ethynyl fragment with $\nu_{(C\equiv C)}$ at 2130 cm^{-1}. The ^{1}H NMR spectrum of **5** showed two singlets at 0.39 and 5.74 for the trimethylsillyl group and the hydrogen atom bound to the α carbon atom respectively. The β and γ sp carbon atoms were identified in the ^{13}C NMR spectrum as an unresolved doublet at δ 116.8 a multiplet at δ 94.5 respectively. Both signals were observed as sharp singlets in the {^{1}H} ^{13}C NMR spectrum.

The Fe(η^5-C_5Ph_5)(CO)(PMe_3) moiety provides both convenient electrophilic properties of the secondary carbene fragment and good diastereoselectivity in nucleophilic attack. The compounds **4–6** are representative of a series of readily accessible iron functionalised alkyl complexes with a stereogenic metal center. The substituted methoxyalkyl complexes and especially the methoxy(trimethylsilylethynyl)methyl derivative can constitute valuable organometallic building blocks suitable for acceding to new bimetallic compounds with unsaturated carbon bridges.

3. Experimental section

3.1. General data

Reagent grade tetrahydrofuran (THF), diethyl ether and pentane were dried and distilled from sodium benzophenone ketyl prior to use. All chemicals were used as received. All the manipulations were carried out under an argon atmosphere using Schlenk techniques or in a Jacomex 532 dry box filled with nitrogen. NMR experiments were performed on a multinuclear Bruker 300 MHz instrument (AM300WB). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR spectra, and H_3PO_4 for ^{31}P NMR spectra. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Solaise, France.

3.1.1. Synthesis of [Fe(η^5-C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]

To Fe(η^5-C_5Ph_5)(CO)(PMe_3)(CHO) (1.04 g, 1.64 mmol) in CH_2Cl_2 at −50°C was added $CH_3SO_3CF_3$ (223 μl, 1.96 mmol). The solution was stirred for 1 h at −50°C before adding NH_4PF_6 (0.4 g, 2.46 mmol). The solution was then stirred at −50°C for 3 h and the solvent removed under vacuum. The residue was washed pentane (10 ml), dried, extracted with CH_2Cl_2 and concentrated in vacuo. Addition of pentane gave a precipitate which was washed with pentane (2 × 10 ml) and dried in vacuo to give 1.21 g (93%). Anal. Found: C, 61.47; H, 4.23. $C_{41}H_{38}FeF_6O_2P_2$ Calc.: C, 61.98; H, 4.83%. FT-IR (Nujol, cm^{-1}): 1969 (s, CO), 1051 (s, OMe), 838 (w, PF_6), ^{1}H NMR (CD_2Cl_2): δ_H 1.50 (d, 9H, $^2J_{PH} = 10$ Hz, $\mathrm{P(C}H_3)_3$); 4.51 (s, 3H, $\mathrm{OC}H_3$); 7–7.5 (m, 25H, $\mathrm{C_6}H_5$); 13.23 (d, 1H, $^3J_{PH} = 1.8$ Hz, $\mathrm{C}H\mathrm{OMe}$). ^{13}C NMR (CD_2Cl_2): δ_C 19.0 (d, $^1J_{CP} = 33.1$ Hz, $\mathrm{P(}C\mathrm{H_3)_3}$); 76.5 (s, $\mathrm{O}C\mathrm{H_3}$); 105.7 (s, C_5); 128.8 (C_{ipso}Ph); 129.3 (C_{para}Ph); 130.1 (C_{ortho}Ph); 132.5 (C_{meta}Ph); 216.3 (d, $^2J_{CP} = 32$ Hz, CO); 326.1 (d, $^2J_{CP} = 21.8$ Hz, CHOMe). ^{31}P NMR (CD_2Cl_2): δ_P 24.7 (s, PMe$_3$).

3.1.2. Reduction of $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$

(A) To $[(\eta^5\text{-}C_5Ph_5)Fe(CO)(PMe_3)(=CHOMe)][PF_6]$ (0.7 g, 0.88 mmol) in THF was added MeLi (83 μl, 2.64 mmol) and the mixture was stirred for 16 h at 80°C. The solvent then was removed under vacuum. The residue was extracted with toluene and hydrolysed with H_2O at −80°C. The solution was filtered and the solvent was removed under vacuum. The compound **1** (0.44 g, 83%) was identified by comparison of its IR and ^{1}H NMR spectroscopic data with those of an authentic sample. (B) To $[(\eta^5\text{-}C_5Ph_5)Fe(CO)(PMe_3)(=CHOMe)][PF_6]$ (0.14 g, 0.18 mmol) in toluene at −60°C was added cobaltocene (0.04 g, 0.2 mmol) and the mixture was stirred for 16 h while the cooling bath slowly warmed up to 20°C. The solution was then filtered, concentrated, and the complex **1** was precipitated by addition of pentane. The compound **1** (0.06 g, 0.10 mmol) was identified by comparison of its IR data with those of an authentic sample.

3.1.3. Synthesis of $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CH_2(OMe))$

To $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (0.92 g, 1.16 mmol) in THF at −80°C was added $LiAlH_4$ (0.04 g, 1.16 mmol). The mixture was stirred for 2 h at −80°C and gave a precipitate after addition of pentane which was dried under vacuum. The residue was extracted with toluene and the solvent was then removed under vacuum to give 0.71 g of complex (95%). Anal. Found: C, 75.52; H, 5.17. $C_{41}H_{39}FeO_2P$ Calc.: C, 79.69; H, 6.04%. FT-IR (Nujol, cm^{-1}): 1897 (s, CO). ^{1}H NMR (C_6D_6): δ_H 1.20 (d, 9H, $^2J_{PH} = 8.9$ Hz, $\mathrm{P(C}H_3)_3$); 3.21 (s, 3H, $\mathrm{OC}H_3$); 4.46 (dd, 1H, $^2J_{HH} = 4.2$ Hz, $^3J_{PH} = 4.1$ Hz, $\mathrm{C}H_2\mathrm{OMe}$); 4.75 (dd, 1H, $^2J_{HH} = 4.2$ Hz, $^3J_{PH} = 6.7$ Hz, $\mathrm{C}H_2\mathrm{OMe}$); 6.8–7.4 (m, 25H, $\mathrm{C_6}H_5$). ^{13}C NMR{^{1}H} (C_6D_6): δ_C 18.3 (qd, $J_{CP} = 27.2$ Hz, $^1J_{CH} = 128.5$ Hz, $\mathrm{P(}C\mathrm{H_3)_3}$); 63.0 (q, $^1J_{CH} = 139.2$ Hz, $\mathrm{O}C\mathrm{H_3}$); 71.5 (dt, $^2J_{CP} = 27$ Hz, $^1J_{CH} = 133.2$ Hz, $C\mathrm{H_2(OMe)}$); 100.5 (s, C_5); 125–135 (m, C_6H$_5$); 222.9 (d, $^2J_{CP} = 37$ Hz, CO). ^{31}P NMR (C_6D_6): δ_P 30.71 (s, PMe$_3$).

3.1.4. Synthesis of $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CHD(OMe))$

To $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (0.82 g, 1.03 mmol) in THF at −80°C was added $LiAlD_4$ (0.043 g, 1.03 mmol). After stirring for 2 h at −80°C addition of pentane gave a precipitate which was dried under vacuum. The residue was extracted with toluene and the solvent was then removed under vacuum to give 0.54 g (80%) of the desired complex. FT-IR (Nujol, cm^{-1}): 1890, 1904 (s, CO). ^{1}H NMR (C_6D_6): δ_H 1.20 (d, 9H, $^2J_{PH} = 8.9$ Hz, $\mathrm{P(C}H_3)_3$); 3.21 (s, 3H, $\mathrm{OC}H_3$); 4.44 (d, 1H, $^3J_{PH} = 3.6$ Hz, $\mathrm{C}H\mathrm{DOMe}$); 6.5–7.5 (m, 25H, $\mathrm{C_6}H_5$). ^{13}C NMR{^{1}H} (C_6D_6): δ_C 18.3 (d, $^1J_{CP} = 27.2$ Hz, $^1J_{CH} = 128.8$ Hz, $\mathrm{P(}C\mathrm{H_3)_3}$); 63.0 (q, $^1J_{CH} = 139.2$ Hz, $\mathrm{O}C\mathrm{H_3}$); 71.0 (dt, $^2J_{CP} = 22$ Hz, $^1J_{CD} = 21$ Hz, $C\mathrm{HD(OMe)}$); 100.5 (s, C_5); 125–135 (m, C_6H$_5$); 222.9 (d, $^2J_{CP} = 37$ Hz, CO). ^{31}P NMR (C_6D_6): δ_P 30.79 (s, PMe$_3$).

3.1.5. Synthesis of $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(CH(OMe)_2)$

$[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (0.06 g, 0.97 mmol) and CH_3ONa (0.77 mg, 0.97 mmol) in THF (10 ml) were stirred for 3.5 h at 20°C and the solvent was then removed under vacuum. The residue was extracted with toluene and the solution concentrated to low volume in vacuo. Addition of pentane at −40°C gave a precipitate which was washed with pentane (2 × 10 ml) and dried in vacuo to give 0.24 g (55%). Anal. Found: C, 73.62; H, 6.36. $C_{42}H_{41}FeO_3P$ Calc.: C, 74.12; H, 6.07%. FT-IR (Nujol, cm^{-1}); 1911 (s, CO). ^{1}H NMR (C_6D_6): δ_H 1.42 (d, 9H, $^2J_{PH} = 9.4$ Hz, $\mathrm{P(C}H_3)_3$); 3.11 (s, 3H, $\mathrm{OC}H_3$); 3.54 (s, 3H, $\mathrm{OC}H_3$); 6.23 (d, 1H, $^3J_{PH} = 5.2$ Hz, $\mathrm{C}H\mathrm{(OMe)}$); 6.5–7.5 (m, 25H, $\mathrm{C_6}H_5$). ^{13}C NMR{^{1}H} (C_6D_6): δ_C 19.7 (d, $^1J_{CP} = 26.4$ Hz, $^1J_{CH} = 128.9$ Hz, $\mathrm{P(}C\mathrm{H_3)_3}$); 56.7 (q, $^1J_{CH} = 139.8$ Hz, $\mathrm{O}C\mathrm{H_3}$); 57.8 (q, $^1J_{CH} = 140.2$ Hz, $\mathrm{O}C\mathrm{H_3}$); 63.5 (d, $^1J_{CH} = 127$ Hz, Fe–C); 100.8 (s, C_5); 125–135 (m, C_6H$_5$); 222.5 (d, $^2J_{CP} = 40.6$ Hz, CO). ^{31}P NMR (C_6D_6): δ_P 30.46 (s, PMe$_3$).

3.1.6. Synthesis of $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(C(H)(OMe)(CN))$

$[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(=CHOMe)][PF_6]$ (0.93 g, 1.17 mmol) and KCN (0.76 g, 1.17 mmol) in THF (10 ml) were stirred for 3 h at 20°C and the solvent was then removed under vacuum. The residue was extracted with toluene and reduced to low volume in vacuo. Addition of pentane gave a precipitate which was washed with pentane (2 × 10 ml) and dried in vacuo to give 0.67 g (85%). The complex $Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)(C(H)(OMe)(CN))$ exists as the mixture of two diastereoisomers (RR/SS, RS/SR). The diastereotopic ratio, determined by the ^{31}P NMR spectrum of the crude product, is 85 : 15. After successive crystallizations in toluene/pentane, the ratio changed from 93 : 7 to 97 : 3. Anal. Found C, 75.02; H, 5.82; N, 1.94. $C_{42}H_{38}FeNO_2P$ Calc.: C, 74.67; H, 5.67; N, 2.07%. FT-IR (Nujol, cm^{-1}): 1925 (s, CO); 2181 (w, CN). *Major product* ^{1}H NMR (300 MHz, C_6D_6): δ_H 1.44 (d, 9H, $^2J_{PH} = 9.3$ Hz, P(CH_3)$_3$); 3.37 (s, 3H, OCH_3); 5.51 (d, 1H, $^3J_{PH} = 3.2$ Hz, CH(OMe)(CN)); 6.5–7.5 (m, 25H, C_5H_6). ^{13}C NMR{^{1}H} (C_6D_6): δ_C 18.4 (d, $^1J_{CP} = 27.2$ Hz, $^1J_{CH} = 129.8$ Hz, P(CH$_3$)$_3$); 57.1 (dd, $^1J_{CH} = 154$ Hz, $^3J_{CP} = 5.2$ Hz, Fe–C); 61.2 (q, $^1J_{CH} = 141$ Hz, $^1J_{CP} = 2.3$ Hz, OCH$_3$); 99.9 (s, C_5); 120–135 (m, C_6H$_5$); 222.4 (d, $^3J_{CP} = 37.7$ Hz, CO). ^{31}P NMR (C_6D_6): δ_P 24.13 (s, PMe$_3$). *Minor product* ^{1}H NMR (C_6D_6): δ_H 1.3 (d, 9H, $^2J_{PH} = 9.4$ Hz, P(CH_3)$_3$); 3.0 (s, 3H, OCH_3); 5.41 (d, 1H, $^3J_{PH} = 1$ Hz, CH(OMe)(CN)); 6.5–7.5 (m, 25H, C_5H_6). ^{13}C NMR{^{1}H} (C_6D_6): δ_C 19.1 (d, $^1J_{CP} = 27.2$ Hz, $^1J_{CH} = 129.6$ Hz, P(CH$_3$)$_3$); 60.6 (q, $^1J_{CH} = 142$ Hz, $^3J_{CH} = 2.2$ Hz, OCH$_3$); 100.5 (s, C_5); 120–135 (m, C_6H$_5$). ^{31}P NMR (C_6D_6): δ_P 25.36 (s, PMe$_3$).

3.1.7. Synthesis of Fe(η^5-C_5Ph_5)(CO)(PMe_3)(C(H)-(OMe)(C=CTMS))

To [Fe($\eta^5C_5Ph_5$)(CO)(PMe_3)(=CHOMe)][PF_6] (0.5 g, 0.63 mmol) in THF at −80°C was added $Me_3SiC\equiv CLi$ [from $Me_3SiC\equiv CH$ (115 μl, 0.82 mmol) and MeLi/LiBr (0.511 μl, 0.82 mmol)]. Stirring was continued for 16 h, while the cooling bath was allowed to reach 20°C. The solvent was removed under vacuum and the residue washed with pentane, extracted with an ether/pentane mixture and filtered through a Celite column. The filtrate was evaporated, then the solid was washed with 10 ml of pentane and dried in vacuo to give 0.30 g (63%) of complex. Anal. Found: C, 73.95; H, 6.29. $C_{46}H_{46}FeO_2PSi$ Calc.: C, 74.08; H, 6.22%. FT-IR (Nujol, cm^{-1}): 2130 (w, C≡C); 1920 (s, CO). ^{1}H NMR (C_6D_6): δ_H 0.39 (s, 9H, Si(CH_3)$_3$); 1.39 (d, 9H, $^2J_{PH} = 9.3$ Hz, P(CH_3)$_3$); 3.19 (s, 3H, OCH_3); 5.74 (s, 1H, CH(OMe)); 7–7.5 (m, 2H, C_6H_5). ^{13}C NMR{^{1}H} (C_6D_6): δ_C 0.7 (q, $^1J_{CH} = 119.0$ Hz, Si(CH$_3$)$_3$); 19.4 (dq, $^1J_{CH} = 129.1$ Hz, $^1J_{CP} = 27.8$ Hz, P(CH$_3$)$_3$); 58.9 (q, $^1J_{CH} = 140.3$ Hz, OCH$_3$); 61.7 (ddq, $^1J_{CH} = 151.9$ Hz, $^2J_{CP} = 24.9$ Hz, $^3J_{CH} = 4.6$ Hz, C–H); 94.5 (m, C≡C–SiMe$_3$); 100.6 (s, C_5); 116.8 (m, C≡C–SiMe$_3$); 125–135 (m, C_6H$_5$); 222.2 (d, $^2J_{CP} = 41.8$ Hz, CO). ^{31}P NMR (C_6D_6): δ_P 26.50 (s, PMe$_3$).

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