Journal of Organometallic Chemistry 774 (2014) 35–42

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Microwave irradiation and flow chemistry for a straightforward synthesis of piano-stool iron complexes

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ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form
16 September 2014
Accepted 23 September 2014
Available online 12 October 2014

Keywords:
Iron
Microwave
Flow chemistry
Organometallic synthesis

ABSTRACT

Two series of piano-stool iron(II) complexes bearing bidentate phosphine or mixed phosphorus–nitrogen ligands have been prepared upon reaction with $CpFe(CO)_2I$ or $[CpFe(naphthalene)][PF_6]$ under microwave irradiation or using flow chemistry.

Introduction

Driven by economic and environmental considerations, the use of iron in catalysis has witnessed tremendous activity in recent years [1,2]. Cyclopentadienyl iron complexes play a pivotal role in organic [3] and organometallic chemistry [4] and materials science [5]. Due to the potential of these organo-iron derivatives, several methods have been reported for their preparation. One of the most used procedures is a two step reaction involving addition of a bidentate ligand onto iron(II) chloride followed by halide-cyclopentadienyl anion exchange, but suffers from formation of ferrocene as a by-product. An alternative is a ligand exchange on $[CpFe(CO)_2X]$ but this generally requires long heating times or UV irradiation.

Microwave irradiation in polar solvents allows rapid heating to high temperatures enabling short reaction times, and often improved yields. Since its introduction, there has been tremendous growth in applications to organic chemistry [6] but its use in organometallic synthesis (namely for the preparation of organometallic species) is still in its infancy [7]. Its use in the synthesis of piano-stool iron complexes is rare [8]. Flow chemistry provides convenient access to high temperatures and pressures together with very fast heat-up and cool-down, and hence precise control of heating times [9,10]. The first examples of application of flow chemistry to organometallic synthesis have recently appeared [11] though it has not yet been used for the synthesis of iron complexes. We report here a new and rapid methodology involving either microwave irradiation or flow chemistry for the preparation of piano-stool iron complexes bearing monodentate, bidentate diphosphine or bidentate mixed P–N ligands.

Results and discussion

Organometallic synthesis using microwaves technology

The iron precursors $[CpFeX(CO)_2]$ (X = I (**2**) and Br (**3**)) were prepared using classical method from iron dimer, $[CpFe(CO_2)]_2$ (**1**) [12]. Initially the replacement of the halogen ligand in complex **2** by triphenylphosphine was investigated using the procedure described by Wilson and co-workers [8a]. After optimization of the reaction conditions, the green iron complex **4** was obtained in 90% isolated yield (Scheme 1) [13]. Even if an excess of triphenylphosphine was used only one equivalent coordinated to the metal center to give **4** as the only product.

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http://dx.doi.org/10.1016/j.jorganchem.2014.09.031
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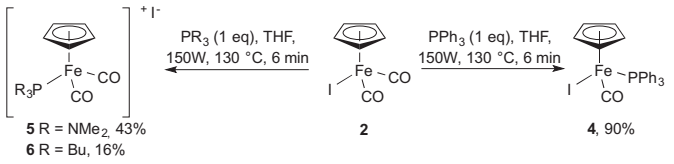


Scheme 1. Synthesis of $CpFePPh_3(CO)(I)$ **4** and $[CpFe(CO)_2PR^3][I]$.

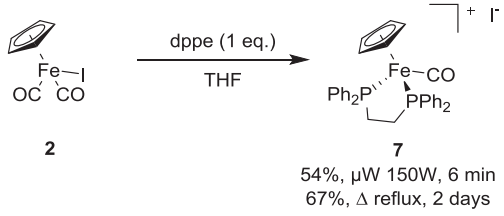
However, repeating the synthesis with PBu_3 and $P(NMe_2)_3$ gave the bis-carbonyl cationic species **5** and **6** (Scheme 1). The lower yields were due to difficulty in isolating the pure products. The formation of either neutral or cationic iron complexes by reaction of various neutral ligands with $CpFe(CO)_2X$ has been reported to give either the neutral or cationic products, or both [8a,12a,13]. Catalysis of conversion of cationic to neutral complexes by $[CpFe(CO)_2]_2$ has been demonstrated [13a,f]. In our case the retention of liberated CO in the microwave pressure tube seems to favor the cationic complexes when electron rich monodentate ligands are used.

We next investigated the coordination of bidentate ligands. Using the same reaction conditions, diphenylphosphinoethane (dppe) gave the cationic iron complex, [CpFe(dppe)(CO)][I] (**7**) in 54% isolated yield (Scheme 2, Table 1). To attempt improving the yield several solvents were tried. All gave diphosphine/CO ligand exchange as monitored by ^{31}P NMR spectroscopy but in DMSO and DMF, purification was problematic and pure complex **7** could not be isolated. In polar and protic solvents, such as methanol, ethanol, *iso*-propanol and butanol, the control of the reaction temperature turned out to be difficult. Nevertheless, in *iso*-propanol, we were able to isolate 21% of complex **7**. In non-polar solvents such as toluene, the reaction time had to be increased to 15 min to obtain **7** in 30% isolated yield. Based on these experiments we identified THF as the best solvent. To demonstrate the benefit of microwave irradiation, the same ligand exchange was also carried out under thermal conditions. Complex **7** was isolated in 67% yield but required a two-day reaction time (Scheme 2).

With optimized conditions in hand, the scope of the reaction was investigated using a variety of diphosphine ligands. Results are presented in Table 1.

In all cases the cationic complexes were formed. The length of the tether had an important effect on the isolated yield. Dppe, dppp, dppf, and to a lesser extent dppb, led to the corresponding iron complexes in better yields (54–66%, Table 1 entries 1, 4, 6, 7) than dppm, (10% yield, entry 3, Table 1). The nature of the halide in the iron precursor has also an impact on the reactivity, iodide **2** leading to 33–40% higher yields than the corresponding bromide **3** (Table 1, entries 1 *vs.* 2 and 4 *vs.* 5).

To unambiguously establish the atom connectivity in the complexes, single crystals for X-ray diffraction (XRD) were grown by slow evaporation of a solution of [CpFe(dppp)(CO)][Br] **11** in dichloromethane. An ellipsoid representation of complex **11** is presented in Fig. 1. The X-ray diffraction analysis confirmed the presence of one CO ligand in complex **11**, and its cationic nature as the bromine atom is an outer sphere counter-anion.



Scheme 2. Synthesis of [CpFe(dppe)(CO)][I] **7**.

Table 1
Synthesis of cationic iron complexes under microwave irradiation starting from precursors **2** or **3**.[a]

Entry	X	Ligand	Complex	Yield[b]
1	I	dppe	[CpFe(dppe)(CO)][I] (**7**)	54
2	Br	dppe	[CpFe(dppe)(CO)][Br] (**8**)	21
3	I	dppm	[CpFe(dppm)(CO)][I] (**9**)	10
4	I	dppp	[CpFe(dppp)(CO)][I] (**10**)	60
5	Br	dppp	[CpFe(dppp)(CO)][Br] (**11**)	20
6	I	dppb	[CpFe(dppb)(CO)][I] (**12**)	47
7	I	dppf	[CpFe(dppf)(CO)][I] (**13**)	66

[a] Reaction conditions: $[CpFe(CO)_2X]$ (0.16 mmol), ligand (0.16 mmol), degassed THF (1 mL) under an argon atmosphere, microwave irradiation (150 W) at 130 °C for 6 min.
[b] Isolated yield.

As the CO ligand is not labile and can be problematic for catalytic activity, we investigated the possibility to replace it with acetonitrile. To avoid the coordination of iodide to the metal centre during this ligand exchange, we replaced it with PF_6^-. For example reaction of **7** with KPF_6 gave **14** in 95% isolated yield. The oxidative carbonyl ligand removal from **14** was conducted in the presence of Me_3NO in acetonitrile within 3 h at room temperature [14]. With these reaction conditions, complex **15** was obtained in 90% yield (Scheme 3).

Although we have defined a straightforward procedure for the synthesis of several cyclopentadienyl iron complexes, we thought to extend this methodology to a more direct synthesis of cationic acetonitrile ligated complexes such as **15**. The cyclopentadienyl arene iron complex [CpFe(napth)][PF_6] **16**, described by Kündig *et al.* [15], is a pertinent piano-stool iron precursor, as the arene ligand is known to be labile at high temperature. Treatment of ferrocene with aluminum chloride, aluminum powder and $TiCl_4$ in heptane at 90 °C for 3 h and subsequent addition of KPF_6 afforded the expected sandwich complex **16** in 91% isolated yield (Scheme 4).

We next examined the reaction between complex **16** and dppe. The expected complex **15** was obtained in 92% isolated yield after microwave irradiation (40 W) for 3.5 min in a 2:1 mixture of THF/CH_3CN (Scheme 5). This two-step procedure from ferrocene is a much more convenient and efficient methodology for the synthesis of substituted piano-stool iron complex **15** (84% overall yield) than the four-step route from dimer $[CpFe(CO)_2]_2$ (47% overall yield).

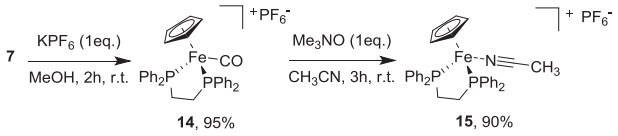
The scope and limitation of the arene displacement were studied with various diphosphine ligands, triphenylphosphine and the mixed P–N ligand, dimethylaminophosphine **19** (Fig. 2) [16] and the results are presented in Table 2.

Under the reaction conditions above, complexes **15**, **17** and **18** were obtained in high yields and purity (87–92%, entries 2–4, Table 2). For complexation of **19**, dppm or ddpf replacement of THF by toluene was needed to obtain pure products. Thus in a 2/1 mixture of toluene/acetonitrile, complexes **20**, **21** and **22**, bearing ligand **19**, dppm and dppf, respectively, were prepared in 70, 89 and 55% yield (Table 2, entries 5–7). Unfortunately, either in the presence of one or two equivalents of triphenylphosphine, no complex $[CpFe(PPh_3)(CH_3CN)_2][PF_6]$ nor $[CpFe(PPh_3)_2(CH_3CN)][PF_6]$ were obtained (Table 1, entry 1).

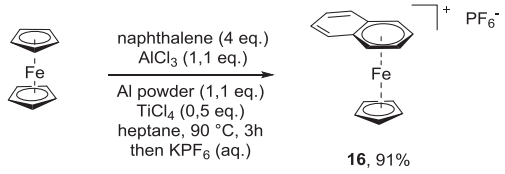
In order to unambiguously confirm the structure of these complexes, a single crystal of complex [CpFe(dppb)(CH_3CN)][PF_6] **18** was grown for XRD analysis. The crystal was obtained by slow evaporation of a solution of **18** in dichloromethane. An ellipsoid representation of complex **18** is presented in Fig. 3. The presence of only one molecule of acetonitrile coordinated to the metal center was confirmed, as well as the presence of the outer sphere counter-anion PF_6^-.

Formula	$C_{35}H_{33}BrCl_6FeOP_2$	[CpFe(dppp)CO]Br
M/g.mol^{-1}	880.01	
Crystal system	Monoclinic	
Space group	*Cc*	
a/Å	15.354(5)	
b/Å	14.056(9)	
c/Å	18.441(7)	
α/°	90.00	
β/°	108.977(17)	
γ/°	90.00	
V/Å^3	3763(3)	
Z	4	
T/K	150(2)	
ρ_{calcd}/ g.cm^{-3}	1.553	
μ (Mo K_α)/mm^{-1}	2.00	
N° of meas. rfls	31816	
R_{int}	0.022	
N° of unique reflections	9548	
***R*1, w*R*2**	0.0245, 0.0656	
***R*1, *wR*2 (all)**	0.0254, 0.0661	
GOF	1.06	

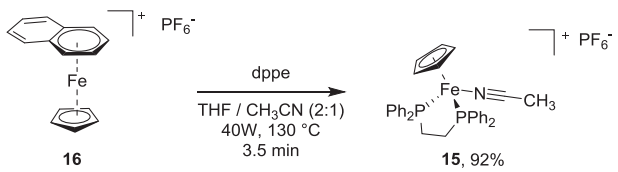
Fig. 1. Ellipsoid representation of complex [CpFe(dppp)(CO)][Br] **11**. Selected bonds (Å) and angles (°): Fe1–C33 1.757(2), Fe1–P2 2.2050(10), Fe1–P1 2.2143(8), P2–Fe1–P1 91.99(4).



Scheme 3. Synthesis of cationic iron complex **15**.



Scheme 4. Synthesis of complex [CpFe(napth)][PF_6] **16**.



Scheme 5. Synthesis of complex [CpFe(dppe)(CH_3CN)][PF_6] **15** from precursor **16**.

Organometallic synthesis using flow chemistry technology

Because microwave-assisted chemistry is mainly driven by temperature phenomenon [7f–h], we hypothesized that flow chemistry would be an interesting alternative. Indeed, such technology provides much faster heat-up and cool-down times than microwave heating, with precisely defined residence times at high temperature, and consequently may diminish thermal decomposition [9–11]. We could only find two examples of the use of flow chemistry for organotransition metal complex synthesis, and neither deals with iron chemistry [11]. Our initial explorations in this field concentrated on the reaction of [CpFe($CO)_2$I] and phosphines (Schemes 1 and 2 above), but they were hampered by the rapid release of gas and extrusion of

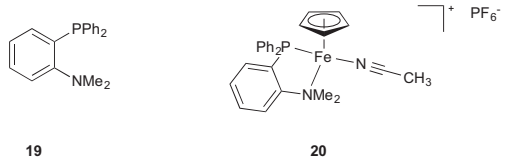


Fig. 2. Hemilabile bidentate monophosphine **19** and the corresponding iron complex **20**.

Table 2
Synthesis of cationic iron complexes under microwave irradiation.[a]

Entry	Ligand	Complex	Yield (%)[b]
1	PPh_3	–	–
2	dppe	[CpFe(dppe)(CH_3CN)][PF_6] (**15**)	92
3	dppp	[CpFe(dppp)(CH_3CN)][PF_6] (**17**)	87
4	dppb	[CpFe(dppb)(CH_3CN)][PF_6] (**18**)	90
5[c]	**19**	[CpFe(**17**)(CH_3CN)][PF_6] (**20**)	70
6[c]	dppm	[CpFe(dppm)(CH_3CN)][PF_6] (**21**)	89
7[c]	dppf	[CpFe(dppf)(CH_3CN)][PF_6] (**22**)	55

[a] Reaction conditions: [CpFe(napth)][PF_6] (0.16 mmol), ligand (0.16 mmol), degassed solution of THF/CH_3CN (2/1) under an argon atmosphere, microwave irradiation (40 W) at 130 °C for 3.5 min.
[b] Isolated yield.
[c] Reaction performed in a 2/1 mixture of toluene/CH_3CN.

reaction mixture during the thermal process, which occurred beyond 90 °C. With these experimental limitations, we decided to focus on the displacement of the labile aromatic ligand from **16** (Scheme 5).

The second route proved to be more robust and reliable. The microwave procedure (Scheme 5) was transferred into a flow process with minor adjustments. Introduction of in-line filtration through alumina was needed to avoid blocking of the backpressure regulator (Fig. 4).

When scaling the synthesis from 50 mg (2 mL) to 150 mg (6 mL), higher yields were obtained especially when a more concentrated solution was used (150 mg in 2 mL), although precipitation in the reactor became a problem. Under the lower concentration conditions this corresponds to conversion of 2.5 mmol/h and of 12.5 mmol/h under the higher temperature conditions (160 °C, 4 min). The reaction with dppf ligand required dichloromethane in the solvent to prevent precipitation in the flow apparatus, and a slightly higher temperature. The results are summarized in Table 3.

The flow chemistry method starting from cationic naphthalene cyclopentadienyl iron complex allowed the synthesis of several piano stool iron complexes with various bidentate phosphine ligands and provides a useful alternative to the microwave procedure with the potential for continuous production.

Formula	$C_{36}H_{38}Cl_2F_6FeNP_3$	**[CpFe(dppb)(CH_3CN)][PF_6]**
M/g.mol^{-1}	818.33	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
a/Å	13.6299(4)	
b/Å	14.1423(4)	
c/Å	19.6407(7)	
α/°	90.00	
β/°	96.463(2)	
γ/°	90.00	
V/Å^3	3761.8(2)	
Z	4	
T/K	296(2)	
ρ_{calcd}/ g.cm^{-3}	1.445	
μ (Mo K_α)/mm^{-1}	0.73	
N° of meas. rfls	66803	
R_{int}	0.034	
N° of unique reflections	10991	
***R*1, w*R*2**	0.0452, 0.1244	
***R*1, *wR*2 (all)**	0.0690, 0.1417	
GOF	1.03	

Fig. 3. Ellipsoid representation of complex [CpFe(dppb)(CH_3CN)][PF_6] **18**. Selected bonds (Å) and angles (°): Fe1–N1 1.9167(18), Fe1–P2 2.2284(5), Fe1–P3 2.2353(6), P2–Fe1–P3 98.11(2).

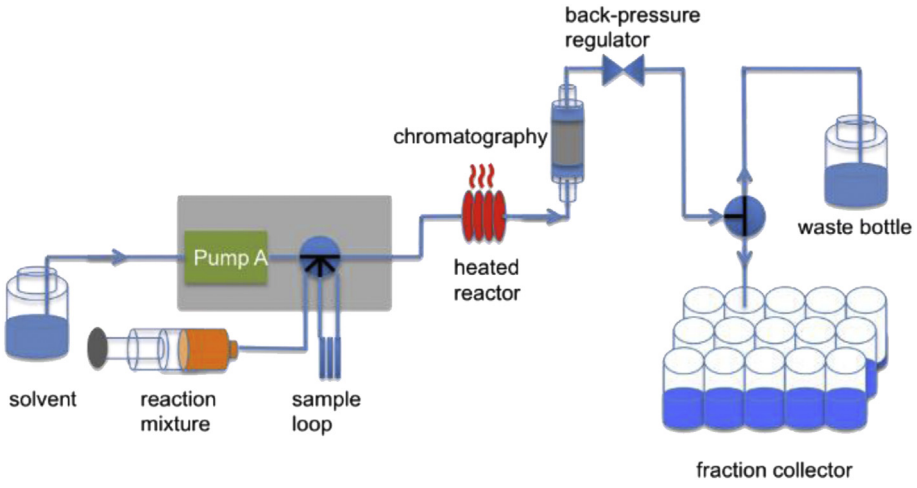


Fig. 4. Modified flow setup with in-series filtration.

Table 3
Synthesis of piano-stool iron complexes from **16** using flow-chemistry.

Ligand	Product	Scale/isolated yield	
		50 mg, 160 °C, 2 mL, 4 min	150 mg, 140 °C, in 6 mL, 20 min
dppe	**15**	80%	72% (83%)[a]
dppp	**18**	57%	77% (89%)[a]
dppm	**19**	63%	55%
dppf	**22**	17%[b]	53%[c]

[a] Values in brackets in 2 mL solvent.
[b] CH_2Cl_2:THF:CH_3CN = 8:1:1, 140 °C.
[c] THF:CH_3CN:CH_2Cl_2 = 2:1:0.1, 160 °C.

Conclusions

We reported a straightforward synthesis of various cyclopentadienyl iron complexes using either microwave or flow technologies. Since their introduction, there has been a tremendous growth in applications to organic chemistry but their use in organometallic synthesis (namely for the preparation of organometallic species) are still rare, and flow technology had no precedence in the literature for the synthesis of iron complexes.

Experimental

General considerations

Reactions were carried out in Schlenk tube freshly with distilled solvents under an atmosphere of dry Argon. All solvents were degassed prior to use by freeze–pump–thaw procedure (4 times). Microwave synthesis was carried out using microwave reactor (10 mL) with teflon lid under an atmosphere of dry Argon. The reactions were realized using single-mode automatic microwave synthesizers *Synthesis System Explorer* from CEM Corporation. Organometallic commercial compounds and phosphine ligands were used without purification. The starting materials [CpFe(CO)$_2$I] and [CpFe(CO)$_2$Br] were prepared according to published methods [12]. All other reagents were commercially available and were used without further purification. NMR spectra were recorded on an ARX Bruker 400 MHz spectrometer using solvent residual peak as reference. HRMS analyses were performed on Q-TOF Micro WATERS by electrospray ionization (ESI) by LCMT analytical services. Infrared (IR) spectra were recorded with a Perkin Elmer 16 PC FT-IR spectrometer. Crystallographic data sets were collected from single crystal samples using a Bruker Kappa APEXII CCD diffractometer. Mo *Kα* radiation at $\lambda = 0.71073$ Å with a graphite monochromator was used. Cell refinement and data reduction were performed with SAINT (Bruker AXS). The structure was solved by direct methods and refined using SHELXL-97 (Sheldrick). All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized positions.

*Synthesis of iron complexes **4**–**13***

In a 10 mL dry microwave reactor were introduced [CpFe(CO)$_2$I] (49 mg, 0.16 mmol) and the ligand (0.16 mmol, 1 eq.) in degassed THF (1 mL) under argon atmosphere. The homogeneous solution was placed in a microwave reactor with a power fixed at 150 W, for 6 min at 130 °C. The dark green solution was filtered through a pad of deactivated alumina (3% H_2O). Then, the cake was washed with EtOH. The complex was recovered in the EtOH and transferred in a Schlenk tube under argon atmosphere. The solvent was removed under vacuum and the crude product was washed with dry and degassed Et_2O (3 × 10 mL). The supernatant liquid was removed with Pasteur pipette and the resulting solid was dried under vacuum.

CpFe(PPh$_3$)(CO)(I) ***4***

Following the general procedure above using PPh_3 (42 mg, 0.16 mmol), complex **4** was obtained as green crystals (78 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.49 (m, 6H, H^{Ar}), 7.47–7.32 (m, 9H, H^{Ar}), 4.48 (s, 5H, H^{Cp}) ppm. ^{31}P{1H} NMR (162 MHz, $CDCl_3$): δ 67.4 (s) ppm. ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 220.8 (s, C, C^{CO}), 135.9 (d, 3C, Cq^{Ar}, $J^1_{(C-P)}$ = 43.4 Hz), 133.8 (d, 6H, CH^{Ar}, $J^2_{(C-P)}$ = 9.5 Hz), 130.3 (d, 3C, CH^{Ar}, $J^4_{(C-P)}$ = 2.4 Hz), 128.4 (d, 6H, CH^{Ar}, $J^3_{(C-P)}$ = 9.8 Hz), 83.0 (s, 5H, CH^{Cp}) ppm. IR (neat): ν 1940 (large CO stretch) cm^{-1}. HRMS (*m*/*z*) ESI+ $[M - I^-]^+$ calculated for $C_{24}H_{20}FeOP$ 411.0601; found: $[M]^+$ 411.0410 (7%). HRMS (*m*/*z*) ESI+ $[M - CO - I^-]^+$ calculated for $C_{23}H_{20}FeP$: 383.0652; found: $[M]^+$ 383.0460 (100%). Data consistent with that previously reported [13e].

[CpFe(P(NMe$_2$)$_3$) (CO)$_2$][I] ***5***

Following the general procedure for the synthesis of cationic iron complex using P(NMe$_2$)$_3$ (26 mg, 0.16 mmol), complex **5** was obtained as gray powder (78 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.61 (s, 5H, H^{Cp}), 2.75 (s, 9H, H^{Me}), 2.72 ppm (s, 9H, H^{Me}) ppm. ^{31}P{1H} NMR (162 MHz, $CDCl_3$): δ 140.6 (s) ppm. ^{13}C{1H} NMR

(126 MHz, $CDCl_3$) (decoupled from phosphorus): δ 211.0 (2C, C^{CO}), 87.4 (5C, CH^{Cp}), 38.8 (6C, CH_3) ppm. IR (neat): ν 2032, 1983 (CO stretch) cm^{-1}. HRMS (*m*/*z*) ESI+ $[M - I^-]^+$ calculated for $C_{13}H_{23}FeN_3O_2P$ 340.0877; found 340.0863.

[CpFe(P(n-Bu)$_3$)(CO)$_2$][I] **6**

Following the general procedure for the synthesis of cationic iron complex using P(*n*-Bu)$_3$ (32 mg, 0.16 mmol), complex **6** was obtained as green powder (11 mg, 13%). ^{1}H NMR (400 MHz, MeOD): δ 5.52 (d, 5H, H^{Cp}, J = 1.4 Hz), 2.04 (dd, 6H, CH_2, $J^2_{(H-P)}$ = 16.2 Hz, $J^3_{(H-H)}$ = 9.9 Hz), 1.64–1.43 (m, 12H, CH_2), 1.01 (t, 9H, CH_3, $J^3_{(H-H)}$ = 7.0 Hz) ppm. ^{31}P{1H} NMR (162 MHz, MeOD): δ 53.9 (s) ppm. ^{13}C{1H} NMR (126 MHz, $CDCl_3$) (decoupled from phosphorus): δ 210.4 (2C, C^{CO}), 87.6 (5C, CH^{Cp}), 29.2 (3C, CH_2), 26.2 (3C, CH_2), 24.0 (3C, CH_2), 13.9 (3C, CH_3) ppm. IR (neat): ν 2041, 1996 (CO stretch) cm^{-1}. HRMS (*m*/*z*) ESI+ $[M - I^-]^+$ calculated for $C_{19}H_{32}FeO_2P$: 379.1489; found: 379.1506.

[CpFe(dppe)(CO)][I] **7**

Following the general procedure for the synthesis of cationic iron complex using dppe (64 mg, 0.16 mmol), complex **7** was obtained as yellow powder (58 mg, 54%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85–7.77 (m, 4H, H^{Ar}), 7.64–7.49 (m, 12H, H^{Ar}), 7.36–7.27 (m, 4H, H^{Ar}), 5.06 (s, 5H, H^{Cp}), 2.99–2.86 (m, 2H, CH_2), 2.82–2.67 (m, 2H, CH_2) ppm. ^{31}P{1H} NMR (162 MHz, DMSO-d_6): δ 92.9 (s) ppm. ^{13}C{1H} NMR (126 MHz, DMSO-d_6) (5 Cq are not observed): 132.6 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.8 Hz), 131.5 (s, 2C, CH^{Ar}), 131.1 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.8 Hz), 131.0 (s, 2C, CH^{Ar}), 129.3 (t, 4C, CH_{Ar}, $J^3_{(C-P)}$ = 4.8 Hz), 129.1 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 5.1 Hz), 85.0 (s, 5C, CH_{Cp}), 28.5 (t, 2C, CH_2, $J^1_{(C-P)}$ = 21.7 Hz) ppm. ^{13}C{1H} NMR (126 MHz, DMSO-d_6) (decoupled from phosphorus): δ 214.2 (1C, C^{CO}) 135.3 (2C, Cq), 132.8 (2C, Cq), 132.6 (4C, CH^{Ar}), 131.5 (2C, CH^{Ar}), 131.1 (4C, CH^{Ar}), 131.0 (2C, CH^{Ar}), 129.3 (4C, CH^{Ar}), 129.1 (4C, CH^{Ar}), 85.0 (5C, CH^{Cp}), 28.5 (2C, CH_2) ppm. IR (neat): ν 1984 (CO stretch) cm^{-1}. Data consistent with those previously reported [13g].

[CpFe(dppm)(CO)][I] **8**

Following the general procedure for the synthesis of cationic iron complex using dppm (61 mg, 0.16 mmol), complex **8** was obtained as yellow powder (10 mg, 10%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.80–7.69 (m, 4H, H^{Ar}), 7.61–7.41 (m, 16H, H^{Ar}), 5.41–5.28 (m, 1H, CH_2), 5.21 (s, 5H, H^{Cp}), 4.56–4.45 (m, 1H, CH_2). ^{31}P{1H} NMR (162 MHz, DMSO-d_6): δ 27.2 (s). ^{13}C{1H} NMR (126 MHz, DMSO-d_6) (decoupled from phosphorus): δ 216.7 (1C, C^{CO}), 133.2 (2C, Cq), 132.6 (2C, Cq), 131.6 (4C, CH_{Ar}), 131.6 (2C, CH_{Ar}), 131.3 (2C, CH_{Ar}), 131.2 (4C, CH_{Ar}), 129.3 (4C, CH_{Ar}), 129.0 (4C, CH_{Ar}), 83.1 (5C, C_{Cp}), 41.89 (1C, CH_2) ppm. IR (neat): ν 1967 (CO stretch) cm^{-1}. HRMS (*m*/*z*) ESI+ $[M]^+$ calculated for $C_{31}H_{27}FeOP_2$: 533.0887; found: 533.0869. Data consistent with those previously reported [13g].

[CpFe(dppe)(CO)][Br] **9**

Following the general procedure for the synthesis of cationic iron complex using $[CpFe(CO)_2Br]$ (41 mg, 0.16 mmol) and dppe (64 mg, 0.16 mmol), complex **9** was obtained as a brown powder (21 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.66 (m, 4H, H^{Ar}), 7.59–7.54 (m, 4H, H^{Ar}), 7.54–7.50 (m, 4H, H^{Ar}), 7.36–7.29 (m, 8H, H^{Ar}), 4.86 (s, 5H, H^{Cp}), 3.15–3.08 (m, 2H, CH_2), 2.84–2.78 (m, 2H, CH_2) ppm. ^{31}P{1H} NMR (162 MHz, DMSO-d_6): δ 92.3 (s). Data consistent with those previously reported [13g].

[CpFe(dppp)(CO)][I] **10**

Following the general procedure for the synthesis of cationic iron complex using dppp (66 mg, 0.16 mmol), complex **10** was obtained as a green powder (67 mg, 60%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.61–7.46 (m, 12H, H^{Ar}), 7.38 (t, 4H, H^{Ar}, $J^3_{(H-H)}$ = 7.0 Hz), 7.35–7.26 (m, 4H, H^{Ar}), 4.97 (s, 5H, H^{Cp}), 2.43–2.29 (m, 1H, CH_2), 3.02–2.85 (m, 2H, CH_2), 2.11 (t, 2H, CH_2, $J^3_{(H-H)}$ = 13.8 Hz), 1.57–1.41 (m, 1H, CH_2) ppm. ^{31}P{1H} NMR (162 MHz, $CDCl_3$): δ 52.0 (s) ppm. ^{13}C{1H} NMR (126 MHz, DMSO-d_6): δ 215.8 (s, 1C, C^{CO}), 137.1 (t, 2C, Cq, $J^1_{(C-P)}$ = 26.1 Hz), 133.2 (t, 2C, Cq, $J^1_{(C-P)}$ = 21.0 Hz), 132.7 (t, 4C,CH_{Ar}, $J^2_{(C-P)}$ = 4.7 Hz), 131.4–131.1 (m, 4C, C^{Ar}), 131.2 (s, 2C, CH^{Ar}), 130.8 (s, 2C, CH^{Ar}), 129.1 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.9 Hz), 128.8 (t, 4C, CH_{Ar}, $J^3_{(C-P)}$ = 4.7 Hz), 86.0 (s, 5C, CH^{Cp}), 28.5 (t, 2C, CH_2, $J^1_{(C-P)}$ = 17.1 Hz), 19.9 (s, 1C, CH_2) ppm. ^{13}C{1H} NMR (126 MHz, DMSO-d_6) (decoupled from phosphorus): δ 215.8 (1C, C^{CO}), 137.1 (2C, Cq), 133.2 (2C, Cq), 132.7 (4C, CH^{Ar}), 131.2 (4C, C^{Ar}), 131.2 (2C, CH^{Ar}), 130.8 (2C, CH^{Ar}), 129.1 (4C, CH^{Ar}), 128.8 (4C, CH^{Ar}), 86.0 (5C, CH^{Cp}), 28.5 (2C, CH_2), 19.9 (1C, CH_2) ppm. IR (neat): ν 1959 (CO stretch) cm^{-1}. Data consistent with those previously reported [13g].

[CpFe(dppp)(CO)][Br] **11**

Following the general procedure for the synthesis of cationic iron complex using $[CpFe(CO)_2Br]$ (41 mg, 0.16 mmol) and dppp (66 mg, 0.16 mmol), complex **9** was obtained as a brown powder (21 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, 2H, H^{Ar}, $J^3_{(H-H)}$ = 7.5 Hz), 7.51–7.47 (m, 6H, H^{Ar}), 7.47–7.34 (m, 8H, H^{Ar}), 7.31–7.24 (m, 4H, H^{Ar}), 4.81 (t, 5H, $J^3_{(H-H)}$ = 1.3 Hz), 3.01–2.80 (m, 2H, CH_2), 2.69–2.53 (m, 1H, CH_2) 2.25–2.08 (m, 2H, CH_2), 1.81–1.64 (m, 1H). ^{31}P{1H} NMR (162 MHz, $CDCl_3$): δ 52.0 (s) ppm. Data consistent with those previously reported [13g].

[CpFe(dppb)(CO)][I] **12**

Following the general procedure for the synthesis of cationic iron complex using dppb (68 mg, 0.16 mmol), complex **12** was obtained as yellow powder (53 mg, 47%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.80–7.32 (m, 20H, H^{Ar}), 4.62 (s, 5H, H^{Cp}), 3.04–2.84 (m, 2H, CH_2), 2.51–2.31 (m, 2H, CH_2), 1.75–1.44 (m, 4H, CH_2). ^{31}P{1H} NMR (162 MHz, DMSO-d_6): δ 59.6 (s) ppm. ^{13}C{1H} NMR (126 MHz, $CDCl_3$) (decoupled from phosphorus): δ 217.9 (1C, C^{CO}), 136.1 (2C, Cq), 133.5 (2C, Cq), 132.3 (2C, CH^{Ar}), 132.2 (4C, CH^{Ar}), 131.6 (4C, CH^{Ar}), 131.4 (2C, CH^{Ar}), 130.0 (4C, CH^{Ar}), 129.7 (4C, CH^{Ar}), 86.9 (5C, CH^{Cp}), 32.3 (2C, CH_2), 23.9 (2C, CH_2) ppm. IR (neat): ν 1954 (CO stretch) cm^{-1}. Data consistent with those previously reported [13g].

[CpFe(dppf)(CO)][I] **13**

Following the general procedure for the synthesis of cationic iron complex using dppf (89 mg, 0.16 mmol), complex **13** was obtained as yellow powder (87 mg, 66%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.71 (t, 2H, H^{Ar}, $J^3_{(H-H)}$ = 7.4 Hz), 7.58–7.45 (m, 18H, H^{Ar}), 4.90 (s, 2H, H^{Cp}), 4.58 (s, 2H, H^{Cp}), 4.56–50 (m, 7H, H^{Cp}), 4.31 (s, 2H, H^{Cp}) ppm. ^{31}P{1H} NMR (162 MHz, CD_3CN): δ 68.9 (s) ppm. ^{13}C{1H} NMR (126 MHz, DMSO-d_6) (decoupled from phosphorus): δ 218.8 (1C, C^{CO}), 138.4 (2C, Cq), 133.9 (4C, CH^{Ar}), 132.7 (2C, Cq), 131.7 (4C, CH^{Ar}), 131.6 (2C, CH^{Ar}), 130.5 (2C, CH^{Ar}), 128.7 (4C, CH^{Ar}), 128.6 (4C, CH^{Ar}), 89.0 (2C, Cq^{Cp}), 86.6 (5C, CH^{Cp}), 84.5 (4C, CH^{Cp}), 74.4 (1C, CH^{Cp}), 73.4 (1C, CH^{Cp}), 73.3 (1C, CH^{Cp}), 70.4 (1C, CH^{Cp}) ppm. IR (neat): ν 1956 (CO stretch) cm^{-1}. HRMS (*m*/*z*) ESI+ calculated for $C_{40}H_{33}Fe_2OP_2$: 703.0705; found 703.0738.

Synthesis of cationic iron complexes ***15***, ***17–18*** *and* ***20–22***

(Method A) In a 10 mL dry microwave reactor, [CpFe(naphthalene)][PF_6] (63 mg, 0.16 mmol) and the ligand (0.16 mmol) were introduced in a 2:1 mixture of degassed THF/CH_3CN (1.5 mL) under an argon atmosphere. The homogeneous solution was placed in a microwave reactor (40 W) at 130 °C for 3.5 min. The crude red solution was filtered through a pad of deactivated alumina (3% H_2O) with dry and degassed CH_3CN. This solution was transferred in a Schlenk tube under argon atmosphere. The solvent was removed

under vacuum and the crude product was dissolved in 1 mL of dry and degassed CH_3CN. The naphthalene was eliminated by hot extraction with pentane (60 °C). The complex was precipitated with Et_2O (3 × 10 mL) and dried under vacuum.

(Method B) a 2:1 toluene/CH_3CN (1.5 mL) was used.

[CpFe(dppe)(CH_3CN)][PF_6] ***15***

Following the general procedure (method A) using dppe (64 mg, 0.16 mmol), complex **15** was obtained as a red powder (103 mg, 92%). ^{1}H NMR (CD_3CN, 400 MHz): δ 7.87–7.79 (m, 4H, H^{Ar}), 7.58–7.52 (m, 6H, H^{Ar}), 7.52–7.44 (m, 6H, H^{Ar}), 7.41–7.31 (m, 4H, H^{Ar}), 4.35 (t, 5H, H^{Cp}, J = 1.4 Hz), 2.59–2.49 (m, 2H, CH_2), 2.43–2.34 (m, 2H, CH_2), 1.96 (s, 3H, CH_3) ppm. ^{31}P{1H} NMR (CD_3CN, 162 MHz): δ 97.2 (s), −144.6 (sept, $J^1_{(P-F)}$ = 706.2 Hz) ppm. ^{13}C{1H} NMR (CD_3CN, 100 MHz) (2C of CH_3CN were not observed): δ 137.9 (t, 2C, Cq, $J^1_{(C-P)}$ = 20.5 Hz), 133.7 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.7 Hz), 133.1 (t, 2C, Cq, $J^1_{(C-P)}$ = 20.3), 132.5 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.8 Hz), 131.5 (s, 2C, CH_{Ar}) 131.3 (s, 2C,CH^{Ar}) 129.9 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.8 Hz), 129.8 (t, 4C, CH_{Ar}, $J^3_{(C-P)}$ = 4.8 Hz), 79.7 (s, 5C, CH_{Cp}) 28.4 (t, 2C, CH_2, $J^1_{(C-P)}$ = 21.3 Hz) ppm. IR (neat): ν 3059 (C–H Ar), 2268 (CN) cm^{-1}. HRMS (m/z) ESI+ [M− PF_6^-]$^+$ calculated for $C_{33}H_{32}FeNP_2$: 560.1359; found: 560.1346. HRMS (m/z) ES− [M]$^+$ calculated for PF_6, 144.9642; found 145.0724.

[CpFe(dppp)(CH_3CN)][PF_6] ***17***

Following the general procedure (method A) using dppp (66 mg, 0.16 mmol), complex **17** was obtained as a red powder (100 mg, 87%). ^{1}H NMR (CD_3CN, 400 MHz): δ 7.68–7.61 (m, 4H, H^{Ar}), 7.55–7.47 (m, 8H, H^{Ar}), 7.34–7.28 (m, 4H, H^{Ar}), 7.28–7.22 (m, 4H, H^{Ar}), 4.21 (s, 5H, H^{Cp}), 2.63–2.51 (m, 3H, CH_2), 2.09 (s, 3H, CH_3), 1.85–1.72 (m, 3H, CH_2) ppm. ^{31}P{1H} NMR (CD_3CN, 162 MHz): δ 55.9 (s), −144.6 (sept, $J^1_{(P-F)}$ = 706.2 Hz) ppm. ^{13}C{1H} NMR (CD_3CN, 100 MHz) (2C of CH_3CN were not observed): δ 139.6 (t, 2C, Cq, $J^1_{(C-P)}$ = 20.6 Hz), 136.8 (t, 2C, Cq, $J^1_{(C-P)}$ = 21.3 Hz), 133.9 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.8 Hz), 132.6 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.6 Hz), 131.4 (s, 2C, CH^{Ar}), 131.0 (s, 2C, CH^{Ar}), 129.7 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.6 Hz), 129.4 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.7 Hz), 80.7 (s, 5C, CH^{Cp}), 27.2 (t, 2C, CH_2, $J^1_{(C-P)}$ = 13.3 Hz), 20.9 (s, 1C, CH_2) ppm. IR (neat): ν 3058 (C–H Ar), 2258 (CN) cm^{-1}. HRMS (m/z) ESI+ [M]$^+$ calculated for $C_{34}H_{34}FeNP_2$: 574.1516; found: 574.1513.

[CpFe(dppb)(CH_3CN)][PF_6] ***18***

Following the general procedure (method A) using [CpFe(-napht.)][PF_6] (63 mg, 0.16 mmol) and dppb (68 mg, 0.16 mmol), complex **18** was obtained as a red powder (106 mg, 90%). ^{1}H NMR (CD_3CN, 400 MHz): 7.63–7.50 (m, 16H, H^{Ar}), 7.44–7.32 (m, 4H, H^{Ar}), 3.93 (t, 5H, H_{Cp}, J = 1.4 Hz), 2.68–2.60 (m, 2H, CH_2), 2.25–2.20 (m, 2H, CH_2), 1.96 (s, 3H, CH_3), 1.59–1.50 (m, 2H, CH_2), 1.41–1.31 (m, 2H, CH_2) ppm. ^{31}P{1H} NMR (CD_3CN, 162 MHz): δ 62.0 (s), −144.7 (sept, $J^1_{(P-F)}$ = 706.2 Hz) ppm. ^{13}C{1H} NMR (CD_3CN, 100 MHz) (2C of CH_3CN are not observed): δ 138.7 (t, 2C, Cq, $J^1_{(C-P)}$ = 20.2 Hz), 136.7 (t, 2C, Cq, $J^1_{(C-P)}$ = 19.9 Hz), 133.3 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.5 Hz), 132.8 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.3 Hz), 131.5 (s, 2C, CH^{Ar}), 130.8 (s, 2C, CH^{Ar}), 129.8 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.5 Hz), 129.6 (t, 4C, CH_{Ar}, $J^3_{(C-P)}$ = 4.5 Hz), 80.6 (s, 5C, CH_{Cp}), 30.1 (t, 2C, CH_2, $J^1_{(C-P)}$ = 11.0 Hz), 24.5 (s, 2C, CH_2) ppm. IR (neat): ν 3058 (C–H Ar), 2265 (CN) cm^{-1}. HRMS (m/z) ESI+ [M − CH_3CN]$^+$ calculated for $C_{33}H_{33}FeP_2$: 547.1407; found: 547.1385.

*[CpFe(**19**)(CH_3CN)][PF_6]* ***20***

Following the general procedure (Method B) using [CpFe(-napht.)][PF_6] (79 mg, 0.20 mmol) and ligand **19** (61 mg, 0.20 mmol), complex **20** was obtained as a violet powder (85 mg, 70%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.82–7.71 (m, 2H, H^{Ar}), 7.69–7.63 (m, 2H, H^{Ar}), 7.61–7.50 (m, 7H, H^{Ar}), 7.46–7.40 (m, 2H, H^{Ar}), 7.30–7.21 (m, 1H, H^{Ar}), 4.27 (s, 5H, H^{Cp}), 3.57 (s, 3H, CH_3), 2.90 (s, 3H, CH_3), 1.96 (s, 3H, CH_3^{AcN}) ppm. ^{31}P{1H} NMR (162 MHz, CD_3CN): δ 73.5 (s), −144.6 (sept. $J^1_{(P-F)}$ = 706.2) ppm. ^{13}C{1H} NMR (126 MHz, CD_3CN): (2C of CH_3CN, 4C of Cq and 4C of C^{Ar} are not observed): δ 135.0 (d, 2C, CH^{Ar}, $J^2_{(C-P)}$ = 9.9 Hz), 133.4 (d, 2C, CH^{Ar}, $J^2_{(C-P)}$ = 9.7 Hz), 132.0 (s, 1C, CH^{Ar}), 131.5 (s, 1C, CH^{Ar}), 130.2 (d, 2C, CH^{Ar}, $J^3_{(C-P)}$ = 8.6 Hz), 129.9 (d, 2C, CH^{Ar}, $J^3_{(C-P)}$ = 10.3 Hz), 75.2 (s, 5C, CH^{Cp}), 63.0 (s, 1C, CH_3), 55.8 (s, 1C, CH_3) ppm. The complex is air sensitive and need to be handled and stored under argon atmosphere.

[CpFe(dppm)(CH_3CN)][PF_6] ***21***

Following the general procedure (method B) using dppm (61 mg, 0.16 mmol), complex **21** was obtained as a pink powder (61 mg, 55%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.73–7.66 (m, 4H, H^{Ar}), 7.54–7.39 (m, 16H, H^{Ar}), 4.97–4.87 (m, 1H, CH_2), 4.49 (s, 5H, H^{Cp}), 3.93–3.83 (m, 1H, CH_2) ppm. ^{31}P{1H} NMR (162 MHz, CD_3CN): δ 36.0 (s), −144.6 (sept, $J^1_{(P-F)}$ = 706.2 Hz) ppm. ^{13}C{1H} NMR (101 MHz, CD_3CN) (2C of CH_3CN, 4Cq and 1C CH_2 are not observed): δ 133.1 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 5.7 Hz), 132.4 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 5.0 Hz), 131.7 (s, 2C, CH^{Ar}), 131.6 (s, 2C, CH^{Ar}),130.0 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 5.0 Hz), 129.8 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 5.0 Hz), 77.9 (s, 5C, CH^{Cp}) ppm. IR (neat): ν 3054 (C–H Ar), 2270 (CN) cm^{-1}. HRMS (m/z) ESI+ [M]$^+$ calculated for $C_{32}H_{30}FeNP_2$: 546.1203; found: 546.1167 (32%). HRMS (m/z) ESI+ [M − CH_3CN]$^+$ calculated for $C_{32}H_{30}FeNP_2$: 505.0937; found: 505.0846 (100%).

[CpFe(dppf)(CH_3CN)][PF_6] ***22***

Following the general procedure (Method B) using [CpFe(napht.)][PF_6] (63 mg, 0.16 mmol) and dppf (89 mg, 0.16 mmol), complex **22** was obtained as a red powder (123 mg, 89%). ^{1}H NMR (400 MHz, CD_3CN): δ 7.70–7.64 (m, 4H, H^{Ar}), 7.64–7.58 (m, 2H, H^{Ar}), 7.58–7.46 (m, 14H, H^{Ar}), 4.44 (s, 2H, H^{Cp}), 4.34 (s, 2H, H^{Cp}), 4.24–4.23 (m, 4H, H^{Cp}), 3.93 (t, 5H, H^{Cp}, J = 1.6 Hz), 1.96 (s, 3H, CH_3) ppm. ^{31}P{1H} NMR (CD_3CN, 162 MHz): δ 63.0 (s), −144.6 (sept, $J^1_{(P-F)}$ = 706.2 Hz) ppm. ^{13}C{1H} NMR (CD_3CN, 126 MHz) (2C of CH_3CN are not observed): 139.7 (t, 2C, Cq, $J^1_{(C-P)}$ = 19.7 Hz), 136.9 (t, 2C, Cq, $J^1_{(C-P)}$ = 21.7 Hz), 135.1 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 5.1 Hz), 133.9 (t, 4C, CH^{Ar}, $J^2_{(C-P)}$ = 4.8 Hz), 131.5 (s, 2C, CH^{Ar}), 130.8 (s, 2C, CH^{Ar}), 129.2 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.5 Hz), 129.1 (t, 4C, CH^{Ar}, $J^3_{(C-P)}$ = 4.7 Hz), 86.1 (t, 2C, Cq, $J^1_{(C-P)}$ = 20.5 Hz), 80.7 (s, 5C, CH^{Cp}), 74.9 (s, 2C, CH^{Cp}), 74.8 (s, 2C, CH^{Cp}), 73.3 (s, 2C, CH^{Ar}), 70.7 (s, 2C, CH^{Ar}) ppm. IR (neat): ν 3059 (C–H Ar), 2260 (CN) cm^{-1}. HRMS (m/z) ESI+ [M − CH_3CN]$^+$ calculated for $C_{39}H_{33}Fe_2P_2$: 675.0756; found: 675.2050.

Representative procedure for flow chemistry

A solution of [CpFe(naphthalene)][PF_6] (0.148 g, 0.375 mmol) and 1,2-bis(diphenylphosphino)ethane (0.164 g, 0.413 mmol) was prepared in THF/CH_3CN 2:1 (6 mL) and transferred to Vapourtec R2/R4 platform, which was set up for sample loop reactions (10 mL sample loop). The sample loop was directly connected to a heated stainless steel reactor (1 mm i.d., 10 mL capacity), followed by alumina column (omnifit, x = 6 mm, 5 cm, grade II, neutral alumina) and backpressure regulator. The reactor was set to the indicated temperature and flow rate. The collected sample was concentrated under reduced pressure, re-dissolved in CH_3CN (10 mL) and naphthalene was removed by hot hexane extraction (5 × 10 mL, 60 °C). The CH_3CN layer was then concentrated *in vacuo*, dry loaded on a column (neutral alumina, grade II, 80 g) and the column flushed with ether (3 column volumes). The title complex was then flushed off the column with CH_3CN and solvent removed *in vacuo*. The resulting red gum crystallized after prolonged exposure to high vacuum. Characterisations were carried out as described above.

Remark: The flow chemistry was carried out with a backpressure regulator (250 psi) to ensure that boiling did not occur. The system is capable of up to 500psi pressure - limited by the pumps.

Acknowledgements

This work has been performed within the «CRUNCH» interregional network. We gratefully acknowledge financial support from the "Ministère de la Recherche et des Nouvelles Technologies" (PhD grant for A.O.), CNRS (Centre National de la Recherche Scientifique), the "Région Basse-Normandie", the European Union (FEDER funding), INTERREG IVA program (ISCE:Chem) and the EPSRC (EP/G027986/1).

Appendix A. Supplementary material

CCDC 856653 and 855917 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.09.031.

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