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

Anastassiya Pagnoux-Ozherelyeva [a], David Bolien [b], Sylvain Gaillard [a], Flavie Peudru [a], Jean-François Lohier [a], Richard J. Whitby [b, **], Jean-Luc Renaud [a, *]

[a] Normandie University, University of Caen Basse Normandie, Laboratoire de Chimie Moléculaire et Thioorganique, CNRS, UMR, 6507, 6 boulevard du Maréchal Juin, 14050 Caen, France
[b] Chemistry, University of Southampton, Southampton SO17 1BJ, UK

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

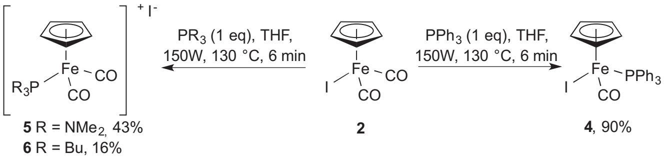
Organometallic synthesis using microwaves technology

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.

---

* Corresponding author. Tel.: +33 (0)231452842; fax: +33 (0)231452877.
** Corresponding author. Tel.: +44 (023)80592777; fax: +44 (023)80593781.
E-mail addresses: R.J.Whitby@soton.ac.uk (R.J. Whitby), jean-luc.renaud@ensicaen.fr, jean-luc.renaud@unicaen.fr (J.-L. Renaud).

http://dx.doi.org/10.1016/j.jorganchem.2014.09.031
0022-328X/



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

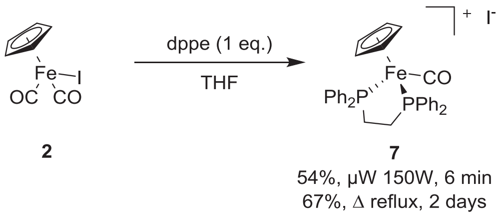
However, repeating the synthesis with PBu_3 and $P(NMe_2)_3$ gave the bis-carbonyl cationic species **5** and **6** (Scheme 1). The lower yields were due to difficulty in isolating the pure products. The formation of either neutral or cationic iron complexes by reaction of various neutral ligands with $CpFe(CO)_2X$ 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^-.