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Imidazolidinium ferrate complexes: Synthesis and catalytic properties

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ABSTRACT

The new well-defined and air stable anionic iron complexes bearing an imidazolidinium ligand (**2a–d**) have been synthesized and characterized by elemental analysis and single-crystal X-ray diffraction studies. Starting from FeBr₂, [imidazolidinium][FeBr₄] complexes **2a** and **2b** were prepared. The reaction of imidazolidinium chlorides with Fe(OAc)₂, followed by a recrystallization in the air led to bis(imidazolidinium) μ-oxido-bis[trichloroferrate(III)] complexes **2c** and **2d**. The catalytic activity of these novel complexes has been evaluated in the cross-coupling reactions of alkyl halides with Grignard reagents.

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1. Introduction

Transition-metal-catalyzed cross-coupling reaction is one of the most powerful tools in molecular synthesis [1], and plays an important role in the synthesis of many drugs, natural products, optical devices, and industrially important starting materials [2]. In this area, nowadays, palladium-catalyzed cross-coupling reactions represent over 60% of the carbon-carbon bond formation reactions used in medicinal chemistry [3]. However, the use of transition metals such as palladium raises the issue of the presence of residual contamination in the synthetic drugs or intermediates that may affect either subsequent chemical transformations or that meet government requirements about maximum ppm level of residual metal in medicinal compounds [4]. In this context, the investigation of new cross-coupling reactions catalyzed by more benign metals is highly required. In this perspective, iron is

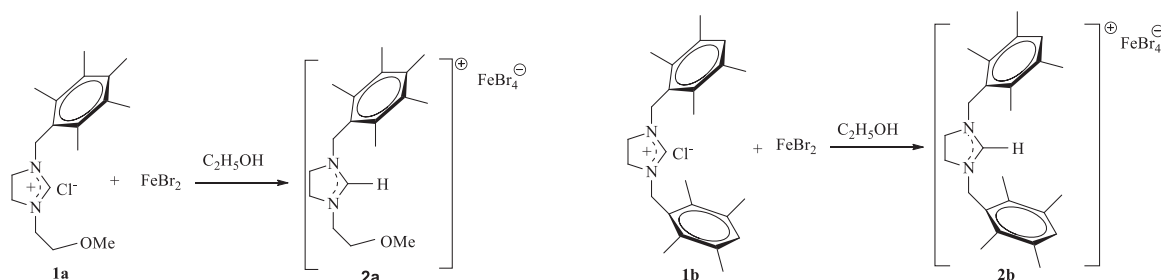
a valuable alternative as it is a cheap, abundant and ecofriendly metal. Furthermore, during the last decade, iron was intensively studied in catalytic transformations [5]. In particular, iron complexes were used as catalysts in synthetic chemistry for carbon-carbon bond formation reactions [6], oxidation [7], and reduction reactions [8–10], which offer attractive industrial possibilities in terms of sustainable chemistry.

In the field of the extensively investigated transition-metal-catalyzed cross-coupling carbon-carbon bond formation [11], the Kumada–Corriu cross-coupling reaction of aryl Grignard reagents with primary or secondary alkyl halides was mainly dominated by palladium or nickel-based catalysts [12]. In 1971, Kochi et al. first reported Fe-catalyzed cross-coupling reactions of vinyl bromides with alkyl Grignard reagents [13]. Since this pioneering contribution, numerous reports on iron-catalyzed cross-coupling have appeared in the literature [14], and it became an obvious alternative to palladium-catalyzed processes, even in total synthesis.

On another hand, *N*-heterocyclic carbenes (NHCs) are certainly the class of ligands that has attracted the most

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Scheme 1. Preparation of ferrate imidazolium complexes.

attention since Arduengo isolation of the first stable NHC species in 1991 [15], following the pioneering report of Wanzlick in 1968 [16]. They have become a unique class of ligands due to their electronic and steric features: NHC ligands are generally known as strong σ -donors and weak π -acceptors and have tunable steric properties. They are widely used in many areas from organocatalysis [17], biochemistry and medicine [18] to transition-metal coordination and catalysis [19]. Despite the first iron–NHC complexes reported in the 1970s [20], the organometallic chemistry of such complexes was less extensively studied than that of the other noble transition metals, but has been a growing field over the past decade [21,22]. Thus, some NHC–iron catalytic systems have shown high activities in homogeneous catalysis [23], and in particular in cross-coupling reactions [24]. In the area of NHC–ferrate complexes, imidazolium and benzimidazolium complexes have been already described and were successfully used in cross-coupling reactions [25].

In a continuation of our research on the organometallic chemistry of iron with *N*-heterocyclic carbenes, we report herein the synthesis and molecular structures of imidazolium ferrate complexes and the preliminary results on catalytic cross-coupling Kochi reactions of alkyl halides in the presence of Grignard reagents.

2. Results and discussion

2.1. Synthesis and characterization of ferrate NHC complexes

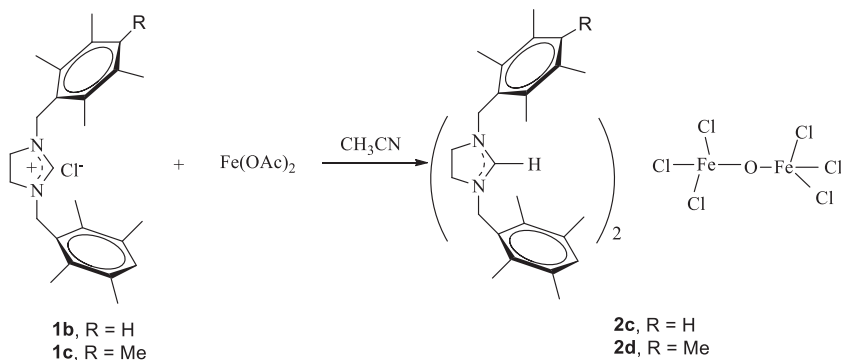
First, 1,3-disubstituted imidazolium salts **1a–c** were prepared according to the reported procedure by reaction of the *N*-substituted imidazoline with an alkyl

halide for 10–12 h at 80 °C in DMF [26]. Then, the reaction of FeBr_2 with one equivalent of imidazolium salts **1a** and **1b** in ethanol was performed at 70 °C for 72 h. After removal of the solvent under vacuum, recrystallization from a $\text{CHCl}_3/\text{Et}_2\text{O}$ mixture led to the ferrate complexes **2a** and **2b**, which were isolated in 39 and 42% yields, respectively, as red–orange crystals, which were air stable both in the solid state and in solution (Scheme 1). Notably, they can be dissolved in CH_2Cl_2 , CHCl_3 , and DMSO, leading to a red orange solution, but they are insoluble in diethyl ether and *n*-hexane.

When the reaction was performed starting from $\text{Fe}(\text{OAc})_2$ (2 equiv) as the iron precursor, with 1 equiv of imidazolium salts **1b** and **1c** in acetonitrile at 60 °C for 48 h, the corresponding complexes (imidazolium)₂(- Fe_2OCl_6) **2c** and **2d** were isolated in 36 and 40% yield, respectively, as white solids that are air stable both in the solid state and in solution (Scheme 2).

All obtained complexes are paramagnetic and were then characterized by elemental analysis and by crystallographic analysis. The crystals of **2a**, **2c** and **2d**, obtained from a chloroform solution layered with diethyl ether under air atmosphere, were suitable for X-ray single-crystal diffraction analysis. The crystallography and measurement data are shown in Figs. 1 and 2. The molecular structures of the complexes, with the atom numbering scheme, are shown in Figs. 1 and 2 (Tables 1 and 2).

As shown in Fig. 1, the iron center is coordinated by four bromide atoms in a distorted tetrahedral geometry with angles at iron in the range 107.53(7)–112.84(7)°, with a mean value of 109.48° close to the ideal angle in tetrahedral structure. The Fe–Br distances are between

Scheme 2. Preparation of (imidazolium)₂(Fe_2OCl_6) complexes.

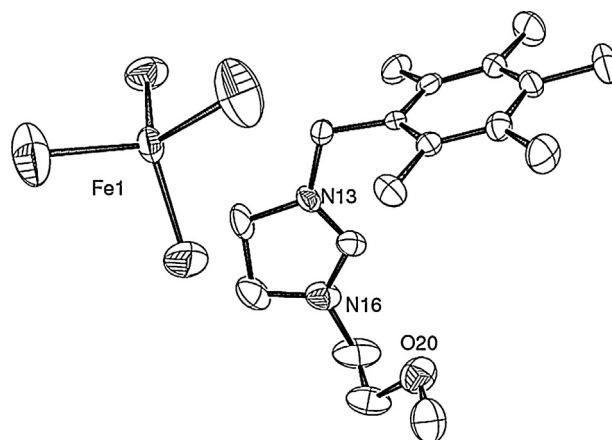


Fig. 1. Molecular structure of **2a**. Selected bond lengths (Å) and angles (deg): Fe(1)–Br(1) = 2.3192(18), Fe(1)–Br(2) = 2.2960(18), Br(4)–Fe(1) = 2.3079(16), Br(3)–Fe(1) = 2.2760(19); Br(3)–Fe(1)–Br(2) = 109.14(8), Br(3)–Fe(1)–Br(4) = 107.90(7), Br(2)–Fe(1)–Br(4) = 112.84(7), Br(3)–Fe(1)–Br(1) = 111.39(8), Br(2)–Fe(1)–Br(1) = 108.08(7), Br(4)–Fe(1)–Br(1) = 107.53(7).

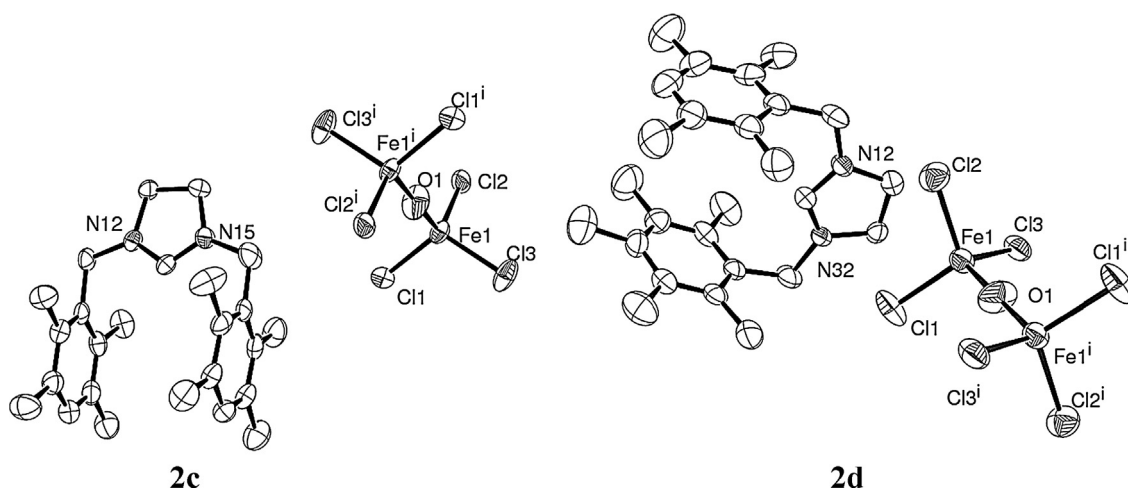


Fig. 2. Molecular structures of **2c** and **2d**.

2.2760(19) and 2.3192(18) Å, with a mean value of 2.300 Å, in accordance with those already reported [25d–f,27]. As already described, for example, with palladium [28], or nickel [29], complex **2a** results in the combination of two ion pairs, the imidazolidinium one and FeBr_4^- .

When using $\text{Fe}(\text{OAc})_2$ as the iron salt source, the reaction led also to the complexes resulting in the combination of ion pairs, two imidazolidinium moieties, and one $(\text{FeCl}_3)_2\text{O}$ ion.

In both structures **2c** and **2d**, the iron center of the $(\text{OFe}_2\text{Cl}_6)^{2-}$ counter-ion is in a distorted tetrahedral geometry with angles at iron with mean values of 109.473° and 109.475°, respectively, close to the ideal angle in tetrahedral structure. Furthermore, bridging oxide O atom displays a linear Fe–O–Fe with an angle of 180° [30]. The Fe–Cl bond lengths range from 2.2211(14) Å to 2.2326(14) Å (mean value of 2.225 Å) for **2c** and from 2.2133(11) Å to 2.2279(11) Å (mean value of 2.219 Å) for **2d**. The Fe–O distances are 1.7444(6) Å and 1.7411(5) Å for **2c** and **2d**, respectively. Such values are in accordance with the described $(\text{OFe}_2\text{Cl}_6)^{2-}$ -type complexes. Notably, for these

two complex structures, the two aromatic rings for the benzyl arm of the imidazolidinium moiety are parallel, which differs from the corresponding [bis(1,3-benzylimidazolidinium)][$(\text{FeCl}_3)_2\text{O}$] [31].

2.2. Imidazolidinium ferrate-catalyzed cross-coupling reaction with Grignard reagents

The catalytic activity of anionic iron complexes **2a–2d** was then examined for the coupling reaction of a simple aryl/alkyl chloride and bromide with Grignard reagents (Table 3).

The cross-coupling reaction of phenyl magnesium bromide with bromocyclohexane was chosen as a test reaction because it is a common benchmark example of an aryl Grignard with a secondary alkyl halide bearing a hydrogen atom in β -position.

In THF, the reaction proceeded in 10 minutes using 2.5 mol% of complex **2a** at room temperature and provided the cross-coupling product **3a** in 66% yield, with 34% of biphenyl **4a** resulting from the homocoupling of the

Table 1
X-ray crystallographic data for complexes **2a**, **2c**, and **2d**.

	2a	2c	2d
Empirical formula	C ₁₈ H ₂₉ Br ₄ FeN ₂ O	C ₅₀ H ₆₆ Cl ₆ Fe ₂ N ₄ O	C ₅₂ H ₇₄ Cl ₆ Fe ₂ N ₄ O
fw	664.92	1063.47	1095.55
Temperature (K)	150(2)	150(2)	150(2)
λ(Mo Ka) (Å)	0.71073	0.71073	0.71073
Cryst syst	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pcab</i>	<i>P2₁/a</i>	<i>P2₁/a</i>
Unit cell dimension			
<i>a</i> (Å)	9.7617(3)	13.9025(13)	13.9317(8)
<i>b</i> (Å)	21.8705(7)	11.0340(12)	10.8833(6)
<i>c</i> (Å)	22.5179(8)	19.1209(19)	18.6985(12)
β (deg)	90	110.711	92.533(2)
<i>V</i> (Å ³)	4807.4(3)	2743.6(5)	2832.4(3)
<i>Z</i>	8	2	2
<i>D</i> _{calc} (g·cm ⁻³)	1.837	1.287	1.285
μ (mm ⁻¹)	7.287	0.858	0.833
<i>F</i> (000)	2600	1112	1152
Crystal size (mm)	0.3 × 0.25 × 0.03	0.16 × 0.14 × 0.07	0.25 × 0.24 × 0.02
θ range (deg)	3.55–27.48	2.92–27.48	2.93–27.48
Number of reflns collected	32,053	18,783	23,902
Number of reflns unique, <i>R</i> _{int}	5297, 0.0651	6076, 0.0768	6475, 0.0783
Goodness-of-fit on <i>F</i> ²	1.04	1.018	0.986
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0819, 0.2418	0.064, 0.1531	0.0553, 0.1244
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1499, 0.2926	0.1293, 0.1924	0.126, 0.1554

fw: formula weight; cryst syst: crystal system; reflns: reflections.

Grignard reagent (entry 1). When the reaction was performed in diethyl ether under similar conditions, the cross-coupling product **3a** was obtained in 69% in association with 31% of biphenyl **4a** (entry 2). When decreasing the catalytic loading to 1 mol%, 82% of cyclohexylbenzene **3a** can be obtained within 10 min at r.t. and 85% within 10 min at 0 °C (entries 3 and 5). The decrease in the loading to 0.5 mol had a deleterious effect as only 42% of **3a** is obtained with 58% of **4a**. Under the optimized conditions (1 mol% of complex, in diethyl ether at room temperature for 10 min), complex **2b** led to 73% of **3a** and 27% of **4a**, whereas complexes **2c** and **2d** gave no

reaction (entries 6–8). With *p*-tolylmagnesium bromide, to reach full conversions, the reactions were performed at room temperature for 3 h; with complexes **2a** and **2b**, the cross-coupling compound **3b** was obtained in 65 and 62% yields, respectively, in mixture with the homocoupling bis-*p*-tolyl derivative **4b** (entries 9 and 10). By contrast, complexes **2c** and **2d** led exclusively to the homocoupling product **4b** in 80 and 70% yields, respectively, which shows that μ-oxido-bis[trichloroferrate(III)] complexes have a different chemoselectivity (entries 11 and 12). Cahiez has shown that alkyl Grignard reagents react with alkenyl halides in the presence of [Fe(acac)₃] to give excellent yields of the cross-coupling product when NMP is used as a co-solvent [32]. Also, Fürstner has described and demonstrated the generality of the iron-catalyzed coupling reactions with alkyl Grignard reagents with the use of NMP as a co-solvent [33]. In this work, we described the cross-coupling reaction between halides (alkyl or aryl) and aryl Grignard reagents. We also tried the use of NMP as a co-solvent and observed 41% cross-coupling product and 59% homocoupling product yields with *p*-tolylmagnesium bromide and cyclohexylbromide with **2a** catalyst. We obtained better results without NMP as a co-solvent under the same reaction conditions (entry 9).

The reaction was then done with different alkyl and aryl halides and phenylmagnesium bromide. With 2-cyclohexylmethyl bromide, the cross-coupling compound 2-phe-

Table 2
Selected bond lengths (Å) and angles (°) for **2c** and **2d**.

	2c	2d
Fe(1)–O(1)	1.7444(6)	1.7411(5)
Fe(1)–Cl(1)	2.2217(13)	2.2133(11)
Fe(1)–Cl(2)	2.2326(14)	2.2165(11)
Fe(1)–Cl(3)	2.2211(14)	2.2279(11)
O(1)–Fe(1a)	1.7444(6)	1.7411(5)
O(1)–Fe(1)–Cl(1)	107.08(5)	111.01(4)
O(1)–Fe(1)–Cl(2)	111.15(5)	107.35(4)
Cl(1)–Fe(1)–Cl(2)	108.91(5)	111.08(5)
O(1)–Fe(1)–Cl(3)	110.90(5)	110.81(4)
Cl(1)–Fe(1)–Cl(3)	111.04(6)	107.49(4)
Cl(2)–Fe(1)–Cl(3)	107.76(5)	109.11(4)
Fe(1a)–O(1)–Fe(1)	180	180.00(3)

Table 3
Iron-catalyzed cross-coupling of aryl or alkyl halides and arylmagnesium bromide^a.

Entry	R-X	[Fe] (mol%)	Conditions	Yields (%) ^b	
				3	4
1		2a (2.5)	THF, RT, 10 min	66	34
2		2a (2.5)	Et ₂ O	69	31
3		2a (1.0)	Et ₂ O	82	18
4		2a (0.5)	Et ₂ O	42	58
5		2a (1.0)	Et ₂ O	85	15
6		2b (1.0)	Et ₂ O	73	27
7		2c (1.0)	Et ₂ O	–	–
8		2d (1.0)	Et ₂ O	–	–
9		2a ^c (1.0)	Et ₂ O	65	35
10		2b ^c (1.0)	Et ₂ O	62	38
11		2c ^c (1.0)	Et ₂ O	–	80
12		2d ^c (1.0)	Et ₂ O	–	71
13		2a (1.0)	Et ₂ O, RT, 15 h	67	33
14		2b (1.0)	Et ₂ O	63	37
15		2c (1.0)	Et ₂ O	–	94
16		2a (1.0)	Et ₂ O, RT, 15 h	5	95
17		2c (1.0)	Et ₂ O, RT, 15 h	–	13
18		2a (1.0)	Et ₂ O, RT, 3 h	41	59
19		2b (1.0)	Et ₂ O	37	63
20		2c (1.0)	Et ₂ O	–	9
21		2a (1.0)	Et ₂ O, RT, 15 h	32	68
22		2b (1.0)	Et ₂ O, RT, 15 h	26	74

^a Reaction conditions: all reactions were carried out in THF or Et₂O at room temperature with 1 mmol of aryl or alkyl halides, 1.5 mmol of PhMgBr (3 M in Et₂O) and iron catalyst (0.5–2.5 mol %).

^b Yields were determined by GC–MS.

^c Reaction with 1.5 mmol (1.5 equivalent) of *p*-tolylmagnesium bromide.

nyl-1-cyclohexylmethane **3b** was obtained in 67 and 63% yields using complexes **2a** and **2b**, respectively, but in mixture with the biphenyl **4a**, whereas complex **2c** led specifically to the homocoupling derivative **3a** (entries 13–15). By contrast, using aromatic halides such as *p*-anisyl bromide, *p*-anisyl iodide and *p*-tolyl bromide led to the homocoupling compound **4a** as the major product (entries 16–22). The most efficient catalyst for the cross-coupling reaction is complex **2a**, whereas complex **2c** pertains to the formation of the homocoupling product **4**.

3. Conclusions

In summary, two tetrabromoferrate and two μ -oxido-bis[trichloroferrate] imidazolidinium complexes have been synthesized, starting from the corresponding imidazolium bromides and iron salts. Notably, they have been structurally characterized by X-ray analysis. The two tetrabromoferrate imidazolidinium complexes **2a** and **2b**

were pre-catalysts for the cross-coupling reaction of alkyl halides with aromatic Grignard reagents under mild conditions at room temperature, whereas complexes **2c** and **2d** led to homocoupling compounds.

Further investigations of these ferrate complexes containing *N*-heterocyclic carbene ligands are currently evaluated in our laboratories.

4. Experimental

All reactions were performed under an argon atmosphere using standard Schlenk tubes and vacuum line techniques. Solvents were distilled under argon over sodium/benzophenone (THF and Et₂O) and degassed prior to use. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK). Imidazolidinium salts were synthesized in our laboratory according to the literature [26]. Elemental analyses were performed using a LECO CHNS-932 elemental analyzer. Melting points were

measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. All catalytic reactions were monitored on a Agilent 6890 N GC system by GC-FID with a HP-5 column of length 30 m, diameter 0.32 mm, and film thickness 0.25 μm . Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

4.1. General experimental procedure for the preparation of the anionic iron complexes

4.1.1. Synthesis of 2a and 2b complexes

A mixture of imidazolidinium salts (1 mmol) and FeBr_2 (1 mmol) in ethanol (25 mL) was stirred at 70 °C for three days. The solvent was removed under vacuum and the crude product was crystallized from $\text{CHCl}_3/\text{Et}_2\text{O}$ and yielded reddish–purple crystals suitable for elemental analyses and X-ray diffraction determination. NMR spectra could not be recorded as it is a paramagnetic compound.

4.1.1.1. Complex 2a. Yield after recrystallization: 259 mg (39%), m.p.: 123–124 °C, m/z 289.18 [M^+] calculated for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{O}$. Anal. calcd for $\text{C}_{18}\text{H}_{29}\text{N}_2\text{OBr}_4\text{Fe}$: C, 32.52; H, 4.40; N, 4.21, found: C, 32.60; H, 4.51; N, 4.25%.

4.1.1.2. Complex 2b. Yield after recrystallization: 310 mg (42%), m.p.: 171–172 °C, m/z 363.4 [M^+] calculated for $\text{C}_{25}\text{H}_{35}\text{N}_2$. Anal. calcd for $\text{C}_{25}\text{H}_{35}\text{N}_2\text{Br}_4\text{Fe}$: C, 40.63; H, 4.77; N, 3.79, found: C, 40.72; H, 4.71; N, 3.84%.

4.1.2. Synthesis of 2c and 2d complexes

A mixture of imidazolidinium salts (2 mmol) and $\text{Fe}(\text{OAc})_2$ (1 mmol) in dry acetonitrile (25 mL) was stirred at 60 °C for 2 days. The solvent was removed under vacuum and the crude product was crystallized in the air from $\text{CHCl}_3/\text{Et}_2\text{O}$ and yielded yellow crystals suitable for elemental analyses and X-ray diffraction determination. NMR spectra could not be recorded as it is a paramagnetic compound.

4.1.2.1. Complex 2c. Yield after recrystallization: 384 mg (36%), m.p.: 298–299 °C, m/z 363.3 [M^+] calculated for $\text{C}_{25}\text{H}_{35}\text{N}_2$. Anal. calcd for $\text{C}_{50}\text{H}_{70}\text{N}_4\text{Cl}_6\text{Fe}_2\text{O}$: C, 56.25; H, 6.61; N, 5.25, found: C, 56.31; H, 6.67; N, 5.18%.

4.1.2.2. Complex 2d. Yield after recrystallization: 438 mg (40%), m.p.: 285–286 °C, m/z 377.5 [M^+] calculated for $\text{C}_{26}\text{H}_{37}\text{N}_2$. Anal. calcd for $\text{C}_{52}\text{H}_{74}\text{N}_4\text{Cl}_6\text{Fe}_2\text{O}$: C, 57.01; H, 6.81; N, 5.11, found: C, 57.13; H, 6.77; N, 5.20%.

4.2. General method for Grignard reagents cross-coupling with aryl/alkyl halides

Under a nitrogen atmosphere and at room temperature, 1.0 mmol of aryl/alkyl halides, iron catalyst (0.5–2.5 mol %) and a solution of 1.5 mmol of phenylmagnesium bromide (3 M solution in Et_2O) or *p*-tolylmagnesium bromide (1 M in THF) were added in THF or Et_2O (3 mL) as the solvent. The mixture was stirred at room temperature or 60 °C for 10 min–48 h. The reaction mixture was

quenched with H_2O (5 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over anhydrous MgSO_4 and evaporated under reduced pressure. The crude material was purified by column chromatography to afford the desired coupling product in high purity. ^1H NMR and GC–MS were consistent with the known material.

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References

- [1] (a) A. de Meijere, F. Diederich (Eds.), *Metal-Catalyzed Cross-Coupling Reactions*, second ed., Wiley-VCH, New York, 2004; (b) N. Miyaura, in: N. Miyaura (Ed.), *Cross-Coupling Reactions: A Practical Guide in Topics in Current Chemistry*, Vol. 219, Springer, Berlin, 2002, p. 1159.
- [2] J.-P. Corbet, G.R. Mignani, *Chem. Rev.* 106 (2006) 2651.
- [3] S.D. Roughley, A.M. Jordan, *J. Med. Chem.* 54 (2011) 3451.
- [4] C.E. Garrett, K. Prasad, *Adv. Synth. Catal.* 346 (2004) 889.
- [5] (a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* 104 (2004) 6217; (b) B. Plietker, in: B. Plietker (Ed.), “Iron Catalysis in Organic Chemistry”, Wiley-VCH Verlag, Weinheim, 2008; (c) W.M. Czaplik, M. Mayer, J. Cvangros, A. Jacobi von Wangelin, *ChemSusChem* 2 (2009) 396; (d) C.L. Sun, B.J. Li, Z.J. Shi, *Chem. Rev.* 111 (2011) 1293; (e) K. Gopalaiah, *Chem. Rev.* 113 (2013) 3248.

Selected examples

- [6] (a) W.M. Czaplik, M. Mayer, S. Grupe, A. Jacobi von Wangelin, *Pure Appl. Chem.* 82 (2010) 1545; (b) A. Fürstner, *Angew. Chem. Int. Ed.* 48 (2009) 1364; (c) A. Leitner, in: B. Plietker (Ed.), *Iron Catalysis in Organic Chemistry*, Wiley-VCH, Weinheim, Germany, 2008, p. 147; (d) B.D. Sherry, A. Fürstner, *Acc. Chem. Res.* 41 (2008) 1500; (e) A. Fürstner, R. Martin, *Chem. Lett.* 34 (2005) 624; (f) A. Fürstner, A. Leitner, M. Méndez, H. Krause, *J. Am. Chem. Soc.* 124 (2002) 13856.

Selected examples

- [7] (a) D.H.R. Barton, M.J. Gastiger, W.B. Motherwell, *J. Chem. Soc., Chem. Commun.* 1 (1983) 41; (b) M.S. Chen, M.C. White, *Science* 318 (2007) 783; (c) L. Que, W.B. Tolman, *Nature* 455 (2008) 333.

Selected reviews

- [8] (a) K. Junge, K. Schröder, M. Beller, *Chem. Commun.* 47 (2011) 4849; (b) M. Zhang, A. Zhang, *Appl. Organometal. Chem.* 24 (2010) 751; (c) B.A.F. Le Bailly, S.P. Thomas, *RSC Adv.* 1 (2011) 1435; (d) R.H. Morris, *Chem. Soc. Rev.* 38 (2009) 2282.

Selected recent examples

- [9] (a) S. Fleischer, S. Zhou, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* 52 (2013) 5120; (b) S. Das, B. Wendt, K. Möller, K. Junge, M. Beller, *Angew. Chem., Int. Ed.* 51 (2012) 1662; (c) S. Das, Y. Li, K. Junge, M. Beller, *Chem. Commun.* 48 (2012) 10742; (d) A.M. Tondreau, C.C. Holilla Atienza, K.J. Weller, S.A. Nye, K.M. Lewis, J.G.P. Delis, P.J. Chirik, *Angew. Chem. Int. Ed.* 335 (2012) 567;

- (e) J. Yang, T.D. Tilley, *Science* 49 (2010) 10186;
 (f) T. Inagaki, A. Ito, J.-I. Ito, H. Nishiyama, *Angew. Chem. Int. Ed.* 49 (2010) 9384;
 (g) G. Wienhöfer, F.A. Westerhaus, R.V. Jagadeesh, K. Junge, H. Junge, M. Beller, *Chem. Commun.* 48 (2012) 4827;
 (h) R.P. Yu, J.M. Darmon, J.M. Hoyt, G.W. Margulieux, Z.R. Turner, P.J. Chirik, *ACS Catal.* 2 (2012) 1760;
 (i) R. Langer, Y. Diskin-Posner, G. Leitus, L.J.W. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* 50 (2011) 9948;
 (j) C.P. Casey, H. Guan, *J. Am. Chem. Soc.* 131 (2009) 2499;
 (k) C. Sui-Seng, F. Freutel, A.J. Lough, R.H. Morris, *Angew. Chem. Int. Ed.* 49 (2008) 940.
- [10] (a) D. Bézier, G.T. Venkanna, L.C. Misal Castro, J. Zheng, T. Roisnel, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* 354 (2012) 1879;
 (b) D. Bézier, F. Jiang, T. Roisnel, J.-B. Sortais, C. Darcel, *Eur. J. Inorg. Chem.* 9 (2012) 1333;
 (c) J. Zheng, L.C. Misal Castro, T. Roisnel, C. Darcel, J.-B. Sortais, *Inorg. Chim. Acta* 380 (2012) 301;
 (d) L.C. Misal Castro, J.-B. Sortais, C. Darcel, *Chem. Commun.* 48 (2012) 151;
 (e) D. Bézier, G.T. Venkanna, J.-B. Sortais, C. Darcel, *ChemCatChem* 3 (2011) 1747;
 (f) L.C. Misal Castro, D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* 353 (2011) 1279.

Representative reviews

- [11] (a) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* 102 (2002) 1359;
 (b) E.A.B. Kantchev, C.J. O'Brien, M.G. Organ, *Angew. Chem. Int. Ed.* 46 (2007) 2768;
 (c) A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C.L. Yang, S.P. Nolan, *J. Organomet. Chem.* 653 (2002) 69;
 (d) C.C.C. Johansson Seechurn, M.O. Kitching, T.J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* 51 (2012) 5062.

Selected examples

- [12] (a) J. Huang, S.P. Nolan, *J. Am. Chem. Soc.* 121 (1999) 9889;
 (b) J. Terao, H. Watanabe, A. Ikumi, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* 124 (2002) 4222;
 (c) L. Ackermann, A.R. Kapdi, C. Schulzke, *Org. Lett.* 12 (2010) 2298;
 (d) R. Ghosh, A. Sarkar, *J. Org. Chem.* 75 (2010) 8283;
 (e) P. Knochel, T. Thaler, C. Diene, *Isr. J. Chem.* 50 (2010) 547;
 (f) N. Liu, Z.-X. Wang, *J. Org. Chem.* 76 (2011) 10031.
- [13] (a) M. Tamura, J.K. Kochi, *J. Am. Chem. Soc.* 93 (1971) 1487;
 (b) M. Tamura, J.K. Kochi, *Synthesis* (1971) 303;
 (c) M. Tamura, J.K. Kochi, *J. Organomet. Chem.* 31 (1971) 289;
 (d) M. Tamura, J.K. Kochi, *Bull. Chem. Soc. Jpn.* 44 (1971) 3063;
 (e) J.K. Kochi, *Acc. Chem. Res.* 7 (1974) 351;
 (f) S.M. Neumann, J.K. Kochi, *J. Org. Chem.* 40 (1975) 599;
 (g) R.S. Smith, J.K. Kochi, *J. Org. Chem.* 41 (1976) 502;
 (h) J.K. Kochi, *J. Organomet. Chem.* 653 (2002) 11.

For recent reviews of iron-catalyzed cross-coupling using Grignard reagents, see

- [14] (a) A. Fürstner, A. Leitner, M. Méndez, H. Krause, *J. Am. Chem. Soc.* 124 (2002) 13856;
 (b) A. Fürstner, R. Martin, *Chem. Lett.* 34 (2005) 624;
 (c) B.D. Sherry, A. Fürstner, *Acc. Chem. Res.* 41 (2008) 1500;
 (d) W.M. Czaplik, M. Mayer, S. Grube, A. Jacobi von Wangelin, *Pure Appl. Chem.* 82 (2010) 1545.
- [15] A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* 113 (1991) 361.
- [16] H.W. Wanzlick, H.J. Schönherr, *Angew. Chem. Int. Ed. Eng.* 7 (1968) 141.
- [17] (a) N. Marion, S. Diez-Gonzalez, S.P. Nolan, *Angew. Chem. Int. Ed.* 46 (2007) 2988;
 (b) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* 107 (2007) 5606;
 (c) V. Nair, S. Vellelath, B.P. Babu, *Chem. Soc. Rev.* 37 (2008) 2691;
 (d) A.T. Biju, N. Kuhl, F. Glorius, *Acc. Chem. Res.* 44 (2011) 1182.
- [18] (a) G. Gasser, I. Ott, N. Metzler-Nolte, *J. Med. Chem.* 54 (2011) 3;
 (b) A. Kascatan-Nebioglu, M.J. Panzner, C.A. Tessier, C.L. Cannon, W.J. Youngs, *Coord. Chem. Rev.* 251 (2007) 884;
 (c) M.-L. Teyssot, A.-S. Jarrousse, M. Manin, A. Chevy, S. Roche, F. Norre, C. Beaudoin, L. Morel, D. Boyer, R. Mahiou, A. Gautier, *Dalton Trans.* 35 (2009) 6894.
- [19] (a) F.E. Hahn, L. Wittenbecher, D. Le Van, R. Frohlich, *Angew. Chem. Int. Ed.* 39 (2000) 541;

- (b) E. Peris, R.H. Crabtree, *Coord. Chem. Rev.* 248 (2004) 2239;
 (c) C.M. Crudden, D.P. Allen, *Coord. Chem. Rev.* 248 (2004) 2247;
 (d) D. Pugh, A.A. Danopoulos, *Coord. Chem. Rev.* 251 (2007) 610;
 (e) J.A. Mata, M. Poyatos, E. Peris, *Coord. Chem. Rev.* 251 (2007) 841;
 (f) S. Diez-Gonzalez, N. Marion, S.P. Nolan, *Chem. Rev.* 109 (2009) 3612;
 (g) F.E. Hahn, M.C. Jahnke, *Angew. Chem. Int. Ed.* 47 (2008) 3122;
 (h) H.D. Velazquez, F. Verpoort, *Chem. Soc. Rev.* 41 (2012) 7032;
 (i) L.-A. Schaper, S.J. Hock, W.A. Herrmann, F.E. Kuhn, *Angew. Chem. Int. Ed.* 52 (2013) 270.
- [20] (a) K. Öfele, C.G. Kreiter, *Chem. Ber.* 105 (1972) 529;
 (b) G. Huttner, W. Gartzke, *Chem. Ber.* 105 (1972) 2714;
 (c) M.F. Lappert, J.J. MacQuitty, P.L. Pye, *J. Chem. Soc., Chem. Commun.* 12 (1977) 411.

For a recent review, see

- [21] M.J. Ingleson, R.A. Layfield, *Chem. Commun.* 48 (2012) 3579.
- [22] (a) P. Buchgraber, L. Toupet, V. Guerschais, *Organometallics* 22 (2003) 5144;
 (b) A.A. Danopoulos, N. Tsoureas, J.A. Wright, M.E. Light, *Organometallics* 23 (2004) 166;
 (c) I. Nieto, F. Cervantes-Lee, J.M. Smith, *Chem. Commun.* 30 (2005) 3811;
 (d) A.A. Danopoulos, J.A. Wright, W.B. Motherwell, *Chem. Commun.* 6 (2005) 784;
 (e) L. Merces, G. Labat, A. Neels, A. Ehlers, M. Albrecht, *Organometallics* 25 (2006) 5648;
 (f) S.A. Llewellyn, M.L.H. Green, J.C. Green, A.R. Cowley, *Dalton Trans.* 21 (2006) 2535;
 (g) Y.S. Wang, H.M. Sun, X.P. Tao, Q. Shen, Y. Zhang, *Chin. Sci. Bull.* 52 (2007) 3193;
 (h) L. Merces, A. Neels, M. Albrecht, *Dalton Trans.* 41 (2008) 5570;
 (i) V. César, N. Luga, G. Lavigne, *J. Am. Chem. Soc.* 130 (2008) 11286;
 (j) Y. Ohkiv, T. Hatanaka, K. Tatsumi, *J. Am. Chem. Soc.* 130 (2008) 17174;
 (k) O. Kaufhold, F.E. Hahn, T. Pape, A. Hepp, *J. Organomet. Chem.* 693 (2008) 3435;
 (l) J.J. Scepianiak, M.D. Fulton, R.P. Bontchev, E.N. Duesler, M.L. Kirk, J.M. Smith, *J. Am. Chem. Soc.* 130 (2008) 10515;
 (m) A.A. Danopoulos, D. Pugh, H. Smith, J. Saßmannshausen, *Chem. Eur. J.* 15 (2009) 5491;
 (n) D. Pugh, N.J. Wells, D.J. Evans, A.A. Danopoulos, *Dalton Trans.* 35 (2009) 7189;
 (o) L. Merces, H. Stoeckli-Evans, M. Albrecht, *Dalton Trans.* 35 (2009) 7168;
 (p) C.-H. Hsieh, M.Y. Darensbourg, *J. Am. Chem. Soc.* 132 (2010) 14118;
 (q) A. Flores-Figueroa, T. Pape, J.J. Weigand, F.E. Hahn, *Eur. J. Inorg. Chem.* 19 (2010) 2907;
 (r) S. Zlatogorsky, C.A. Muryn, F. Tuna, D.J. Evans, M.J. Ingleson, *Organometallics* 30 (2011) 4974;
 (s) J.M. Smith, J.R. Long, *Inorg. Chem.* 49 (2010) 11223;
 (t) V.V.K.M. Kandepi, J.M.S. Cardoso, E. Peris, B. Royo, *Organometallics* 29 (2010) 2777;
 (u) R.A. Layfield, J.J.W. McDouall, M. Scheer, C. Schwarzmaier, F. Tuna, *Chem. Commun.* 47 (2011) 10623;
 (v) L. Xiang, J. Xiao, L. Deng, *Organometallics* 10 (2011) 2018;
 (w) J.A. Przyojski, H.D. Arman, Z.J. Tonzetich, *Organometallics* 31 (2012) 3264;
 (x) S. Zlatogorsky, M.J. Ingleson, *Dalton Trans.* 41 (2012) 2685;
 (y) A.A. Danopoulos, P. Braunstein, M. Wesolek, K.Y. Monakhov, P. Rabu, V. Robert, *Organometallics* 31 (2012) 4102;
 (z) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi, F. Glorius, *Organometallics* 31 (2012) 4474.

For a review

- [23] D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* 355 (2013) 19.
- [24] (a) R.B. Bedford, M. Betham, D.W. Bruce, A.A. Danopoulos, R.M. Frost, M. Hird, *J. Org. Chem.* 71 (2006) 1104;
 (b) S.K. Ghorai, M. Jin, T. Hatakeyama, M. Nakamura, *Org. Lett.* 14 (2012) 1066;
 (c) T. Hatakeyama, M. Nakamura, *J. Am. Chem. Soc.* 129 (2007) 9844;
 (d) T. Hatakeyama, S. Hashimoto, K. Ishizuka, M. Nakamura, *J. Am. Chem. Soc.* 131 (2009) 11949;
 (e) L. Xiang, J. Xiao, L. Deng, *Organometallics* 30 (2011) 2018;
 (f) A.L. Silberstein, S.D. Ramgren, N.K. Garg, *Org. Lett.* 14 (2012) 3796.

For Imidazolium ferrate complexes, see

- [25] (a) K. Bica, P. Gaertner, *Org. Lett.* 8 (2006) 733;
(b) H.H. Gao, C.H. Yan, X.P. Tao, Y. Xia, H.M. Sun, Q. Shen, Y. Zhang, *Organometallics* 29 (2010) 4189;
(c) C.H. Yan, L.L. Wang, H.H. Gao, H.M. Sun, Q. Shen, *Chin. Sci. Bull.* 57 (2012) 1953;
(d) H.N. Deng, Y.L. Xing, C.L. Xia, H.M. Sun, Q. Shen, Y. Zhang, *Dalton Trans.* 41 (2012) 11597;
(e) Y. Xia, C.H. Yan, Z. Li, H.H. Gao, H.M. Sun, Q. Shen, Y. Zhang, *Chin. Sci. Bull.* 58 (2013) 493;
(f) For benzimidazolium ferrate complexes, see C.-L. Xi, C.-F. Xie, Y.-F. Wu, H.-M. Sun, Q. Shen, Y. Zhang, *Org. Biomol. Chem.* 11 (2013) 8135.
- [26] S. Demir, İ. Özdemir, B. Çetinkaya, *J. Organomet. Chem.* 694 (2009) 4025.
- [27] (a) C. Jia, S.-X. Liu, C. Ambrus, G. Labat, A. Neels, S. Decurtins, *Polyhedron* 25 (2006) 1613;
(b) A. Abedi, N. Safari, V. Amani, H.R. Khavasi, *Dalton Trans.* 40 (2011) 6877;
(c) T. Bäcker, O. Breunig, M. Valldor, K. Merz, V. Vasylyeva, A.-V. Mudring, *Cryst. Growth Des.* 11 (2011) 2564.

As an example with palladium

- [28] X. Yang, Z. Fei, T.J. Geldbach, A.D. Phillips, C.G. Hartinger, Y. Li, P.J. Dyson, *Organometallics* 27 (2008) 3971.

As an example with nickel, see

- [29] P.B. Hitchcock, K.R. Seddon, T. Welton, *J. Chem. Soc., Dalton Trans.* 2 (1993) 2639.
- [30] (a) J.-C. Chang, W.-Y. Ho, I.-W. Sun, Y.-K. Chou, H.-H. Hsieh, T.-Y. Wu, S.-S. Liang, *Polyhedron* 29 (2010) 2976;
(b) G. Haselhorst, K. Wieghardt, S. Keller, B. Schrader, *Inorg. Chem.* 32 (1993) 520.
- [31] E.M. Mutambi, C.J. Adams, A.G. Orpen, *Acta Cryst. E66* (2010) m846.
- [32] (a) G. Cahiez, H. Avedissian, *Synthesis* 8 (1998) 1199;
(b) G. Cahiez, O. Gager, J. Buendia, C. Patinote, *Chem. Eur. J.* 18 (2012) 5860.
- [33] (a) A. Fürstner, A. Leitner, M. Méndez, H. Krause, *J. Am. Chem. Soc.* 124 (2002) 13856;
(b) A. Fürstner, A. Leitner, *Angew. Chem. Int. Ed.* 41 (2002) 609.