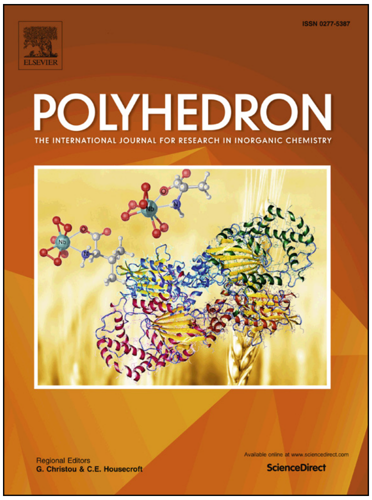

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Iron(II) bipyridine complexes for the cross-coupling reaction of bromocyclohexane with phenylmagnesium bromide

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Keywords

Iron complexes; Bipyridine ligand; Cross-coupling reaction; X-ray diffraction study

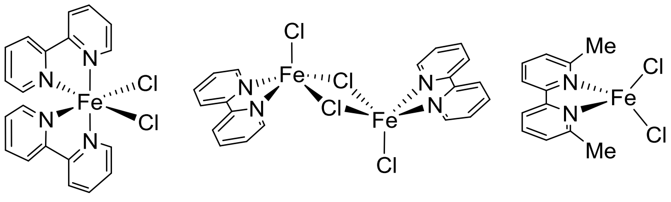
Abstract

Three known iron(II) complexes bearing a bipyridine ligand, [$FeCl_2(bpy)_2$] (**1**), [$FeCl_2(bpy)$]$_2$ (**2**) and [$FeCl_2$(dmbpy)] (**3**) (bpy = 2,2’-bipyridine and dmbpy = 6,6’-dimethyl-2,2’-bipyridine) were employed for the cross-coupling reaction of bromocyclohexane (**4**) with phenylmagnesium bromide (**5**). These complexes catalyzed the cross-coupling reaction. Among the three catalysts, complex **2** acted as an effective catalyst to afford the cross-coupled product phenylcyclohexane (**6**) in 92% yield. The X-ray crystal structure analyses of **2** and **3** were demonstrated.

1. Introduction

Bipyridines are one of the most ubiquitous classes of ligands in coordination chemistry. They are able to bind to a wide range of metal ions and to stabilize different oxidation states. Furthermore, the introduction of substituents on the bipyridine ring can be tunable for specific electronic and steric properties of the metal center [1]. Therefore, the rich chemistry of bipyridine complexes has been demonstrated in supramolecular [2], nanomaterial [3], macromolecular [4] and photophysical chemistry [5]. Here, we turned our attention to the combination of bipyridines with iron; these iron complexes have been subject to intense study on crystal polymorphs and their magnetic properties. For instance, [$FeCl_2$(bpy)] has been described as forming two polymorphs; one is an orange tetrahedral monomer and the other is a red-rose octahedral polymer [6]. Although an X-ray diffraction study was not performed due to the complex's low crystallinity, based on ^{57}Fe Mössbauer and magnetic studies, a pentacoordinate iron(II) complex bearing terminal and bridging chloride ligands was proposed [7]. On the other hand, iron bipyridine complexes have focused on as catalysts for carbon-carbon bond forming reactions, e.g. atom transfer radical addition (ATRA) [8] and Ziegler-type polymerization [9].

Transition metal catalyzed cross-coupling reactions of organic halides as electrophiles with organometallic reagents are one of the most promising procedures for synthetic organic chemistry. Various transition metals, such as Ni, Pd and Co, have been employed as effective catalysts for these reactions [10]. Recently iron complexes have been actively investigated as a catalysts, because iron is a practical, ideal transition metal due to its low cost, non-toxicity and availability [11]. Although various nitrogen, phosphorus and carbon donor ligands have been utilized in iron-catalyzed cross-coupling reactions [12,13], to the best of our knowledge, there has been no report on an iron bipyridine complex as a catalyst. Therefore, we were interested in the investigation of iron bipyridine complexes on cross-coupling reactions. In this paper we investigated the cross-coupling reaction of bromocyclohexane with phenylmagnesium bromide using the three iron(II) complexes depicted in Chart 1.



1 **2** **3**

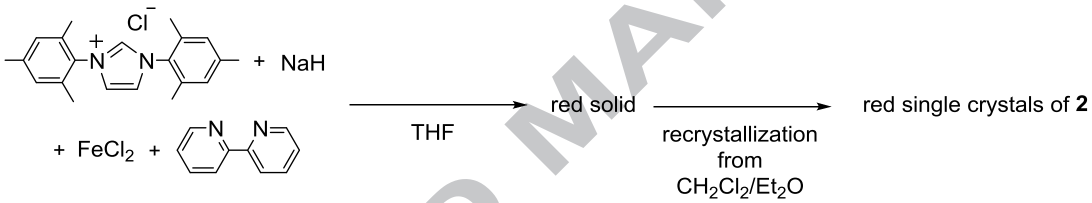
Chart 1. Iron(II) bipyridine complexes

2. Results and Discussion

*2.1. Synthesis of iron complexes **1-3***

Complex **1** was prepared according to the literature method [9b], namely the thermal decomposition of $[Fe(bpy)_3]Cl_2$ at 80 °C under reduced pressure afforded complex **1** as a deep blue solid. This complex obeys the 18-electron rule and shows a diamagnetic nature. Therefore, complex **1** is easily characterized by NMR spectroscopy by referring to the literature data. Complex **1** is composed of $FeCl_2$ and bipyridine in the ratio of 1:2 and the mutually *cis* positions would act as reactive sites in an octahedral geometry [9].

As described in the introductory part, in previous studies on $[FeCl_2(bpy)]$, two polymorphs (orange and red-rose polymorphs) were recognized. Recently, Stephens, Miller and co-workers reported that the orange polymorph is a pentacoordinate square pyramidal iron(II) dimer, **2** as shown in Chart 1, which was determined with synchrotron powder diffraction data [14]. We examined the direct preparation of complex **2** by the reaction of anhydrous $FeCl_2$ with one equivalent of bipyridine in CH_2Cl_2, from which a red powder was isolated. Our attempts to grow single crystals from the red powder were unsuccessful. In the course of our study on iron bipyridine complexes, we tried to prepare a mixed-ligand iron complex bearing both bipyridine and *N*-heterocyclic carbene ligands (Scheme 1). The reaction mixture afforded a red solid and red crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. The X-ray diffraction study revealed that the crystal was not the desired mixed-ligand complex, but the dinuclear iron bipyridine complex **2** (vide infra). Fortunately, we carried out an X-ray diffraction study of **2**. Although [$FeCl_2$(bpy)] has been recognized as two polymorphs, as mentioned above, our results showed that the red crystal has also a pentacoordinate square pyramidal iron(II) dimer structure, which has the same structural properties as determined by the synchrotron powder diffraction study [14]. At present, we have no additional evidence to explain this result. Further investigations on the polymorphs of [$FeCl_2$(bpy)] might be needed in the future. In the cross-coupling reaction, the red powder was used as catalyst **2**, prepared by the direct complexation of $FeCl_2$ and bipyridine in a molar ratio of 1:1.



Scheme 1. Synthetic procedure for obtaining single crystals of **2**

Complex **3** was prepared as in the literature via the reaction of anhydrous $FeCl_2$ with one equivalent of 6,6’-dimethyl-2,2’-bipyridine (dmbpy) [15]. This ligand would provide steric hindrance to prevent the coordination of a second ligand as well as the formation of chloride-bridged dimer structure. Thus complex **3** shows a monomeric tetrahedral structure and is a paramagnetic compound. Although the structure of complex **3** has been already determined by an X-ray diffraction study [15], in order to confirm the formation of complex **3**, we carried out an X-ray diffraction study of **3**. Yellow single crystals of **3** were easily obtained by recrystallization from CH_2Cl_2/hexane.

*2.2. X-ray crystal structures of the iron complexes **2** and **3***

The ORTEP drawings of **2** and **3** are shown in Figure 1. Selected bond lengths and angles for these complexes are listed in Tables 1 and 2.

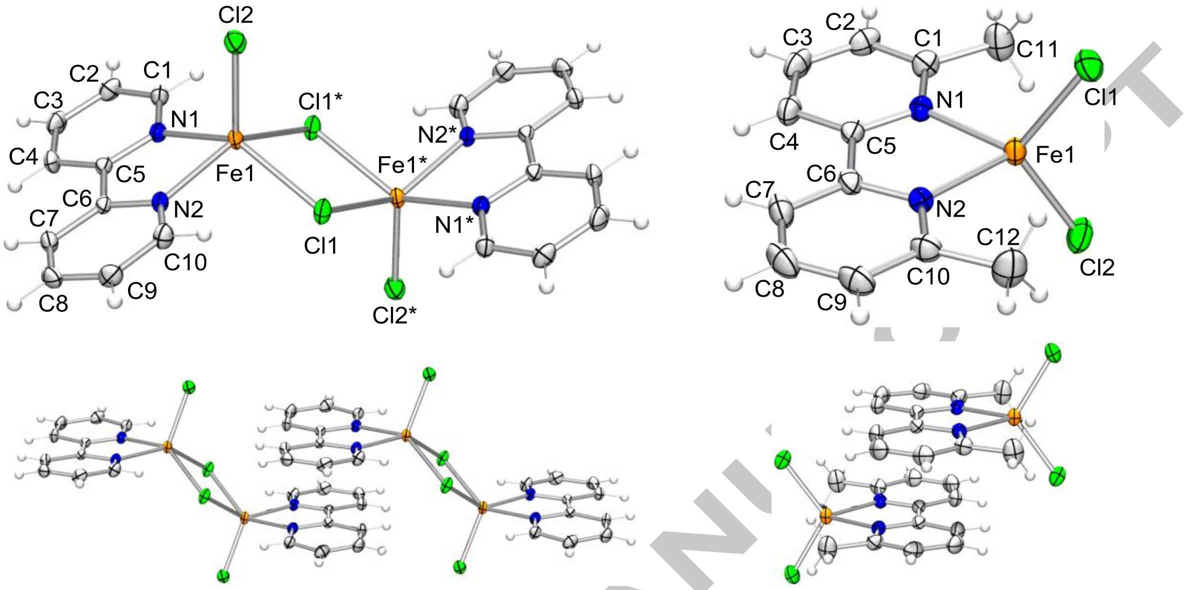


Figure 1. ORTEP drawings (upper) and π-stacking conformation diagrams (bottom) of complexes **2** (left) and **3** (right) with thermal ellipsoids of 30% probability.

Complex **2** shows a chloride-bridged dinuclear structure and each iron(II) ion is in a square pyramidal environment. The basal Fe1-Cl1 and Fe1-Cl1* bond lengths are almost equivalent, being 2.4603(8) and 2.4602(13) Å, respectively. The apical Fe1-Cl2 (2.2612(12) Å) bond length is shorter than the basal Fe1-Cl1 (Cl1*) bond lengths. These bond lengths show the characteristic feature observed in d^6 square pyramidal complexes [16]. The Cl1-Fe1-Cl1* bond angle is 82.55(3) °. The Fe-N bond lengths are 2.151(2) and 2.148(4) Å, which are identical within their uncertainties and the N1-Fe1-N2 bond angle is 79.49(12) °. The intramolecular Fe1···Fe1* distance is 3.6979(7) Å. These structural parameters are in reasonable agreement with those of a synchrotron powder diffraction study [14]. The bipyridine ligands show a π-stacking conformation between different dinuclear complexes. The distances between the nearest bipyridine ligands are in the range 3.417(4)-3.538(5) Å.

Baird has already reported the X-ray diffraction study of complex **3** [15]. In his report, two polymorphs of **3** were found. These crystals showed different cell parameters and space groups, whereas both structural parameters were very similar. In our experiment for **3**, one of the polymorphs was obtained. The Fe-Cl bond lengths are 2.2349(5) Å for Fe1-Cl1 and 2.2360(6) Å for Fe1-Cl2. The Cl1-Fe1-Cl2 bond angle is 114.94(2) °. The Fe-N1 and Fe1-N2 bond lengths are 2.1134(13) and 2.1096(13) Å, respectively, and the N1-Fe1-N2 bond angle is 77.65(5) °. The structural parameters are in good agreement with those of Baird's report [15]. In complex **3**, the bipyridine ligands prefer a π-stacking conformation between different complexes. The distances between the nearest bipyridine ligands are in the range 3.479(2)-3.579(2) Å. These distances are consistent with the values observed in complex **2**.

Table 1. Selected bond lengths (Å) and angles (°) for **2**.

Fe1-Cl1	2.4603(8)
Fe1-Cl1*	2.4602(13)
Fe1-Cl2	2.2612(12)
Fe1-N1	2.151(2)
Fe1-N2	2.148(4)
Fe1···Fe1*	3.6979(7)
Cl1-Fe1-Cl1*	82.55(3)
Cl1-Fe1-Cl2	108.93(4)
Cl1-Fe1-N1	145.10(8)
Cl1-Fe1-N2	90.52(7)
Cl1*-Fe1-Cl2	107.39(5)
Cl1*-Fe1-N1	90.11(10)
Cl1*-Fe1-N2	143.69(8)
Cl2-Fe1-N1	105.83(8)
Cl2-Fe1-N2	108.57(8)
N1-Fe1-N2	75.49(12)
Fe1-Cl1-Fe1*	97.45(4)

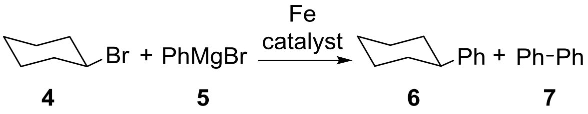
Table 2. Selected bond lengths (Å) and angles (°) for **3**.

Fe1-Cl1	2.2349(5)
Fe1-Cl2	2.2360(6)
Fe1-N1	2.1134(13)
Fe1-N2	2.1096(13)
Cl1-Fe1-Cl2	114.94(2)
Cl1-Fe1-N1	116.59(4)
Cl1-Fe1-N2	114.74(4)
Cl2-Fe1-N1	114.33(4)
Cl2-Fe1-N2	113.34(4)
N1-Fe1-N2	77.65(5)

*2.3. Cross-coupling reaction catalyzed by iron complexes **1-3***

We prepared three iron(II) complexes, **1-3**. Complex **1** has two bpy ligands in an octahedral geometry. In complex **2**, one bpy ligand coordinates to the iron center and a chloride-bridged dimeric structure forms. Complex **3** has one dmbpy ligand bonded to the iron centre as a mononuclear complex in a tetrahedral geometry. Next, we examined the cross-coupling reaction of bromocyclohexane (**4**) with phenylmagnesium bromide (**5**), using the three iron(II) complexes as catalysts. The results are summarized in Table 3.

Table 3. Cross-coupling reaction catalyzed by the iron complexes [a]



Entry	Fe catalyst	[Fe] /mol% [b]	Solvent	Time /h	Yield/% [c]	
					6	**7**
1	**1**	5	CPME	1	52	26
2	**2**	5	CPME	1	68	25
3	**3**	5	CPME	1	50	27
4	**2**	5	THF	1	49	36
5	**2**	5	Et_2O	1	49	24
6	**2**	5	DME	1	58	45
7	**2**	4	CPME	1	77	22
8	**2**	3	CPME	1	81	21
9	**2**	2.5	CPME	1	73	22
10	**2**	3	CPME	2	87	26
11	**2**	3	CPME	3	92	21
12	**1**	3	CPME	3	83	34
13	**3**	3	CPME	3	71	26

[a] The reaction was carried out with 0.5 mmol of **4** and 0.6 mmol of **5**.

[b] The amount of catalyst was based on the Fe atom.

[c] The yields of **6** and **7** were determined by GLC analysis using undecane as an internal standard. Yields of **6** and **7** were based on **4** and **5**, respectively.

First of all, to evaluate the catalytic activity of the three iron complexes **1**-**3** for the cross-coupling reaction of bromocyclohexane (**4**) with phenylmagnesium bromide (**5**), the reaction was conducted in CPME (cyclopentyl methyl ether) at room temperature for 1 h in the presence of 5 mol% of the iron catalyst (Entries 1-3). It was found that these complexes acted as a catalyst for the cross-coupling reaction and that complex **2** showed the best result. Complex **2** afforded the cross-coupled product, phenylcyclohexane (**6**), in 68% yield along with the formation of the homo-coupled product, biphenyl (**7**), in 25% yield (Entry 2). In order to investigate the influence of solvent on the cross-coupling reaction, the reaction was conducted in some ethereal solvents (Entries 4-6). In a THF solution, the yield of product **6** decreased (49%) and the formation of the homo-coupled product **7** increased (36%)

(Entry 4). Et_2O gave similar results as those in THF (Entry 5). In DME (1,2-dimethoxyethane), product **6** was formed in 58% yield, whereas the formation of **7** increased (45%) (Entry 6). From these results, CPME was a suitable solvent for this coupling reaction. Next, we investigated the effect of the amount of the iron complex **2** (Entries 7-9). On decreasing the amount of complex **2**, the yield of **6** increased. In the presence of 3 mol% of **2**, product **6** was formed in 81% yield (Entry 8). On the other hand, using 2.5 mol% of **2**, the yield of **6** decreased (73%) (Entry 9). The reaction time was also investigated (Entries 10 and 11). When the reaction was conducted for 2 h in the presence of 3 mol% of **2**, the yield of **6** increased (Entry 10). For 3 h, the cross-coupled product **6** was formed in 92% yield (Entry 11). An increase in the product yield of **6** was not observed on further elongation of the reaction time. From these results, the reaction conditions catalyzed by complex **2** were optimized as those in Entry 11. Finally, catalytic activities of complexes **1** and **3** were reinvestigated under the optimized reaction conditions. In the case of complex **1**, product **6** was formed in 83% yield. Complex **3** afforded product **6** in 71% yield. In comparison with the first investigations (Entries 1 and 3), the cross-coupled product **6** increased. However, among the three iron complexes, complex **2** showed the best result for the coupling reaction.

3. Conclusions

We investigated the cross-coupling reaction of bromocyclohexane (**4**) with phenylmagnesium bromide (**5**) using the three iron(II) bipyridine complexes **1-3**. Among these iron complexes, complex **2** was found to be an effective catalyst for the coupling reaction. In complex **2**, one bpy ligand coordinates to the iron center and a chloride-bridged dimeric structure forms. In the catalytic reaction, we assumed that the monomeric iron-bpy species acts as an effective catalyst. Complex **1** has two bpy ligands and in complex **3**, the dmbpy ligand coordinates to the iron center. These situations would provide steric hindrance to prevent the reaction of substrates on the iron center. Although electronic effects at the iron center might not be ruled out, we assumed that the steric hindrance around the iron center is the main reason for decreasing the catalytic activity. Further investigations on the catalytic mechanism and the coupling reactions of various organometallic reagents with organic electrophiles are now in progress.

4. Experimental

4.1. General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an atmosphere of dry nitrogen, which was purified by SICAPENT (Merck Co., Inc.), using a standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. Iron complexes **1** [9b] and **3** [15] were prepared according to literature methods. ^{1}H NMR spectra were recorded on a BRUKER DRX-300 spectrometer at ambient temperature. ^{1}H NMR chemical shifts were recorded in ppm relative to Me_4Si as an internal standard. GLC was recorded on a Shimadzu GC-17A gas chromatograph using a ULBON HR-1 capillary column (0.25 ID X 25 m, Shinwa Chemical Industries Ltd.).

*4.2. Preparation of **2** for use as a catalyst*

Anhydrous $FeCl_2$ (205.1 mg, 1.62 mmol), 2,2'-bipyridine (254.2 mg, 1.63 mmol) and CH_2Cl_2 (10 mL) were put in a Schlenk tube. The reaction mixture was stirred at room temperature for 18 h, and then a red powder precipitated. After removing the mother liquor, the residual red solid was washed with THF (10 mL, 2 times), Et_2O (15 mL) and hexane (10 mL), and dried in vacuo at 80 °C to yield **2** (429.8 mg, 0.76 mmol, 94%).

4.3. Experimental procedures for the X-ray cryatallography

Single crystals of **2** were obtained by the following procedures, as shown in Scheme 1. The reaction of $FeCl_2$, bipyridine, NaH and 1,3-bis(trimethylphenyl)imidazolium chloride in THF afforded a red solid. The red solid was recrystallized from CH_2Cl_2/Et_2O at room temperature to grow suitable single crystals of **2**. Suitable single crystals of **3** were obtained by recrystallization from CH_2Cl_2/hexane at room temperature. Single crystals were individually mounted on glass fibers. Diffraction measurements of these complexes were made on a Rigaku Mercury 70 diffractometer using graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum 2θ value of 60 °. A total of 744 oscillation images were collected. The crystal-to-detector distance was 45.00 mm. Readout was performed in the 0.068 mm pixel mode. Data were collected using CrystalClear (Rigaku) [17] and processed using CrysAlisPro (Rigaku Oxford Diffraction) [18]. In the reduction of the data, an empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects.

The crystallographic data and the results of the measurements are summarized in Table 4. The structures were solved by direct methods (SHELXT) [19] for these complexes, and expanded using Fourier techniques. Least-square refinements were carried out using SHELXL [20]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at ideal positions and refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package [21].

4.4 Typical procedure for the cross-coupling reaction (Table 3, Entry 11)

Iron complex **2** (4.1 mg, 0.0072 mmol), CPME (5 mL), undecane (51.8 mg, 0.070 mL, 0.33 mmol) and bromocyclohexane (82.0 mg, 0.062 mL, 0.5 mmol) were put in a Schlenk tube. Phenylmagnesium bromide (0.6 mL of its 1.0 M THF solution, 0.6 mmol) was added at once to the reaction mixture. After stirring for 3 h at room temperature, 1 M hydrochloric acid (5 mL) was added to quench the reaction. The products were extracted with Et_2O (10 mL, 5 times) and then the yields of products **6** and **7** were determined by GLC analysis using undecane as an internal standard.

Table 4. Summary of crystal data for **2** and **3**.

	2	**3**
Empirical formula	$C_{20}H_{16}Cl_4Fe_2N_4$	$C_{12}H_{12}Cl_2FeN_2$
Formula weight	565.88	310.99
Crystal color, habit	red, plate	yellow, prism
Crystal size (mm)	0.150 x 0.050 x 0.050	0.500 x 0.500 x 0.250
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Lattice parameters		
a (Å)	8.2171(5)	7.5596(3)
b (Å)	8.4313(5)	10.0260(3)
c (Å)	8.7480(7)	17.7908(7)
α (°)	110.398(6)	90.000
β (°)	105.462(6)	94.775(3)
γ (°)	94.045(5)	90.000
V (Å^3)	538.47(7)	1343.73(9)
Z	1	4
D_c (g cm^{-3})	1.745	1.537
F(000)	284.00	632.00
μ (Mo Kα) (cm^{-1})	18.570	14.959
Reflection measured	4246	9564
Independent reflections	2447	3020
R_{int}	0.0382	0.0152
No. variables	136	154
Reflection/parameter ratio	17.99	19.61
Residuals: R; R_w	0.0843; 0.0782	0.0306; 0.0737
Residuals: $R1$ [$I > 2\sigma(I)$]	0.0465	0.0277
Goodness-of-fit (GOF) on F^2	1.004	1.055
$\delta\rho_{max, min}$ (e Å^{-3})	0.38, -0.42	0.41, -0.35

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Appendix A. Supplementary material

CCDC 1502443 and 1502444 contain the supplementary crystallographic data for complexes **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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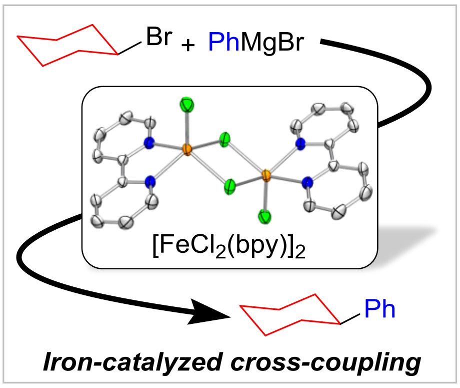
Graphical Abstract



Synopsis

A cross-coupling reaction of bromocyclohexane with phenylmagnesium bromide catalyzed by iron(II) bipyridine complexes was examined. The iron complex [FeCl$_2$(2,2’-bipyridine)]$_2$ was found to be an effective catalyst for the cross-coupling reaction.