# A Novel Iron Complex for Cross-Coupling Reactions of Multiple C–Cl Bonds in Polychlorinated Solvents with Grignard Reagents

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Abstract A novel iron(III) complex (2) of a pincer ligand [1, N2,N6-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide] was developed and used for remediation of polychlorinated solvents via sp<sup>3</sup>-sp<sup>3</sup> coupling of Grignard reagents with C-Cl bonds. The use of an iron catalyst for such coupling reactions is highly desirable due to its greener and more economical nature. Complex 2 was characterized using various spectroscopic techniques: electrospray ionization mass spectrometer (ESI-MS, m/z 575.1), cyclic voltammetry (E<sub>1/2</sub>, 0.03 V and  $\Delta E$ , 0.97 V), and ultraviolet visible (UV/Vis) spectroscopic techniques. The iron(III) complex showed efficient activation of multiple C-Cl bonds and catalyzing C-C coupling of polychlorinated alkyl halides, such as dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), chloroform (CHCl<sub>3</sub>), and carbon tetrachloride (CCl<sub>4</sub>), with various Grignard reagents under ambient reaction conditions. Complex 2 showed exceptional activity with reactions approaching near completion in about 5 min. With the required catalyst loading as low as 0.2 mol%, considerably high turnover numbers (TON = 483) and turnover

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Center for Integrative Nanotechnology Sciences, University of Arkansas at Little Rock, 2801 South University Avenue, Little Rock, AR 72204, USA frequency (TOF = 5,800 h<sup>-1</sup>) were obtained. None of the products detected during the reaction contained any chlorine, indicating an efficient dechlorination method while synthesizing products of synthetic and commercial interest. Interestingly, the catalyst was capable of replacing all chlorine atoms in each polychlorinated solvent under the investigations with high conversion.

**Keywords** Pincer complex · C–C coupling · Catalyst design · Cross-coupling · Iron

## 1 Introduction

Large quantities of chlorinated organic molecules, especially polychlorinated alkanes continue to be broadly used in various industrial and research applications. In the light of growing concerns about the disposal of the chlorinated organic molecules, their use as synthetic feedstock can provide a valuable alternative to the traditional disposal while enabling the synthesis of high value chemical products. One promising approach in using the chlorinated solvents as feedstock is to catalytically couple the solvents with Grignard reagents.

C–C coupling of organometallic reagents and organic electrophiles using transition metal catalysts has evolved into a significant area of research in synthetic chemistry [1, 2]. Within this area, a progression in the transition-metal-catalyzed cross coupling of activated aryl and alke-nyl halides with organometallic nucleophiles has been observed due to their general applicability, ready availability and high selectivity [3]. While various nickel [4–19] and palladium [20, 21] catalysts have been studied for Kumada-Corriu coupling of Grignard reagents with activated aryl and alkenyl halides, not many studies have been

reported concerning the cross-coupling of Grignard reagents with unactivated alkyl halides. One impediment in this pursuit may be the complexity of alkyl halides, especially those with  $\beta$ -hydrogen atoms. Moreover, their inability to undergo oxidative addition and participation in side reactions are other limitations for the selective cross-coupling of alkyl halides.

Even though there have been attempts to activate multiple C-Cl bonds in a carbon center of a polychloroalkane, only a few have proved promising. Activation of the C-Cl bonds has been reported in the presence of Ag-complex [22] and a P.N-ligand coordinated Rh<sup>I</sup> complex [23]. However, the products formed as a result of these C-Cl activations did not result in any multiple C-C bond formations. To the best of our knowledge, only two groups have reported the coupling of multiple C-Cl bonds of di or polychloroalkanes with Grignard reagents to form C-C bonds via sp<sup>3</sup>-sp<sup>3</sup> coupling [24, 25]. Ni-pincer catalyst was reported for an efficient and highly selective activation of multiple C-Cl bonds in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> [24] and other polychlorinated alkanes [26]. The use of these metals has its own limitations. A few disadvantages associated with previous studies include high costs, toxicity, harsh reaction conditions, and low conversions of the substrates. These issues require us to look for greener and more economic alternatives.

Recently, the development of new iron complexes for coupling reactions has gained much interest owing to the fact that they are environmentally benign and less costly. Having been first reported by Kochi [27, 28] in 1971, this research opportunity has not been exploited until recently. Among the reports on the use of iron catalyst for the cross coupling of Grignard reagent with activated alkyl halides and sp<sup>3</sup>-sp<sup>3</sup> coupling with unactivated alkyl halides [29-41], only a few studies on the activation of C–Cl bond have been reported [42, 43]. The activation of multiple C-Cl bonds in polychlorinated compounds has not been studied extensively using an iron catalyst. Thus far, only one study of the multiple C-Cl activation of CH<sub>2</sub>Cl<sub>2</sub> has been reported [25] using iron catalysts. The use of iron-based catalysts for multiple C-Cl bonds activation and their subsequent coupling with Grignard reagents is a field which has largely remained unexplored and thus provides the motivation for the present work.

Their unique electronic and structural properties, along with ease of synthesis and ready availability of starting materials, renders the use of pincer complexes for catalysis an effective and economic approach. Pd and Ni complexes of pincer ligands have been found to be efficient catalysts for Kumada coupling [24]. Further reports using metal complexes of amido-based pincer ligands for the C–C coupling have described the high activity of N,N,P- and N,N,N chelating ligands over P,N,P pincer ligands [44]. In



Fig. 1 N2,N6-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide (1) and its iron complex (2)

the present study, we likewise used a diamidopyridine based N,N,N pincer ligand. The synthesis and use of the ligand [1, N2,N6-bis(2,6-diisopropylphenyl)pyridine-2,6dicarboxamide] (Fig. 1) has been reported previously [45]. The authors reported synthesis and characterizations of Ru and Ni complexes using a deprotonated form of the ligand for ring closing metathesis. The nickel complexes of this ligand and analogous ligands have also been reported for reaction with carbon dioxide and other ligands [46, 47]. The iron(III) complex (2) (Fig. 1) of the ligand, however, was not reported. This is the first time the iron(III) complex of this ligand has been synthesized and put under investigation for its catalytic activity.

In this report, we discuss the iron (III) complex (2)catalyzed cross-coupling of polychlorinated solvents, such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>, with Grignard reagents (Scheme 1). Catalyst 2 was able to activate multiple C-Cl bonds leading to various cross-coupled products. In this manner, polychlorinated solvents can be turned into less toxic and high value-added molecules. No special conditions or special equipment were required and reactions could be performed at room temperature with an inert atmosphere provided by nitrogen. The catalyst (2) showed unprecedented activity with reactions completed in 5 min. A turnover number (TON) and turnover frequency (TOF) as high as 483 and 5,800  $h^{-1}$ , respectively, with a catalyst loading of only 0.2 mol% was obtained for the reaction. While reacting CH<sub>2</sub>Cl<sub>2</sub> with Grignard reagent, iron(III) catalyst (2) showed a TOF of  $3,780 \text{ h}^{-1}$  which is 40–80 times higher than the previous reports of CH<sub>2</sub>Cl<sub>2</sub> coupling with Grignard reagent using FeCl<sub>3</sub>, Fe(acac)<sub>3</sub>, and the Fe complex of an amine-bis(phenolate) ligand [25]. It is also 40 times more efficient than the most active catalyst, a Ni complex of a pincer NN<sub>2</sub> ligand, reported previously [24]. Furthermore, previous studies required special reaction conditions, such as high temperature (100 °C or so), microwave irradiation [25], or conducting reactions at temperatures below 0 °C [24]. This is the first such report of a novel iron complex synthesized and studied extensively for the activation of multiple C-Cl bonds in different polychlorinated solvents.



**Scheme 1** General scheme for products formed in the cross coupling reaction of CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> with Grignard reagents

### 2 Experimental

### 2.1 Materials and Methods

All of the chemicals and solvents were obtained either from Aldrich Chemical Co., USA, or Fisher Scientific Company, USA, and used as-obtained without further purification unless otherwise stated. Tetrahydrofuran (THF), acetonitrile, hexanes, toluene, chloroform, and carbon tetrachloride were purified according to procedures described in the literature [48]. Anhydrous dichloromethane was purchased from Aldrich Chemical Co., USA, and used without further purification. CCl<sub>4</sub> was used in very small quantity and very cautiously as per regulations.

<sup>1</sup>H-NMR spectra were obtained using a Brüker 600 MHz nuclear magnetic resonance (NMR) instrument. The spectra were collected at 25 °C, and chemical shifts are in ppm ( $\delta$ ) relative to tetramethylsilane (TMS) as an external standard unless otherwise stated. Infrared spectra were obtained on a Shimadzu FT-IR Affinity-1 spectrophotometer. Electrospray ionization mass spectra (ESI-MS) were obtained using an Agilent 100 series MSD VL spectrometer. gas chromatography-mass spectrometry (GC-MS) were obtained using an Agilent technologies 6890N network GC system and equipped with Agilent Technologies 5975 inert XL mass selective detector. Ultraviolet-visible spectra (UV-Vis) were recorded using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Elemental analysis was performed at the Midwest Microlab, LLC, Indianapolis, USA. Cyclic voltammetry was conducted using Pine Bipotentiostat and following a conventional three-electrode method. An Ag/AgCl reference electrode was used for the measurement.

#### 2.2 Synthesis of 1 and 2

**1** was synthesized according to the literature procedure with slight modifications [45]. **1** was deprotonated with *n*-butyllithium in THF and reacted with anhydrous ferric chloride (FeCl<sub>3</sub>) to obtain **2**. Detailed synthetic methods of **1** and **2** are described in the Supporting information.

# 2.3 Cross-Coupling of CH<sub>2</sub>Cl<sub>2</sub> with Butylmagnesium Chloride

Cross-coupling reactions were performed according to the following general method. Catalyst **2** (0.5 mg, 0.87  $\mu$ mol) in 0.5 mL THF was taken in a 5 mL round bottom flask (purged with N<sub>2</sub>), and to this solution 2 M *n*-butylmagnesium chloride solution in THF (0.42 mL, 0.84 mmol) was added. To the reaction mixture (27  $\mu$ L, 0.42 mmol) of CH<sub>2</sub>Cl<sub>2</sub> in 2 mL THF was added slowly using a syringe pump at the rate of 24 mL/h. After 5 min, the reaction was completely stopped by destroying the excess Grignard reagent using methanol, and the reaction products were analyzed using GC–MS technique. An internal standard decane was used to quantify the product formed.

# 2.4 Cross Coupling of CHCl<sub>3</sub> and CCl<sub>4</sub> with Grignard Reagent

Catalyst **2** (0.5 mg, 0.87  $\mu$ mol) in 0.5 mL THF was taken in a 5 mL round bottom flask (purged with N<sub>2</sub>), and to this solution 2 M *n*-butylmagnesium chloride in THF (0.63 mL, 1.26 mmol) was added. To the reaction mixture, CHCl<sub>3</sub> (34  $\mu$ L, 0.42 mmol) was added. In case of reaction with CCl<sub>4</sub> (40  $\mu$ L, 0.42 mmol), 1.68 mmol of Grignard reagent was added. After 5 min, the reaction was stopped by destroying the excess Grignard reagent using methanol, and the reaction products were analyzed using GC–MS technique. An internal standard decane was used to quantify the product formed. All reactions were performed in duplicate to check for the reproducibility of the reactions.

# **3** Results and Discussion

With slight modifications made to the previously reported method [45], the ligand was synthesized in two steps. An acid chloride of 2,6-pyridinedicarboxylic acid was obtained which was finally reacted with 2,6-diisopropyl aniline in the presence of triethylamine to obtain the desired ligand. Pure white crystalline ligand was obtained by crystallization from hot ethanol solution. Detailed synthesis of the ligand is described in the Supporting information (Fig. S1). The ligand was characterized using various spectroscopic techniques. <sup>1</sup>H-NMR of the ligand showed the characteristic peaks at 1.29 ppm (isopropyl CH<sub>3</sub>, d) and 3.25 ppm (isopropyl CH, m). The presence of the amide (9.11 ppm) and aromatic hydrogens was also observed at the expected positions confirming the formation of the ligand (Fig. S2, Supporting information). <sup>13</sup>C-NMR spectrum of the ligand also confirms the formation of the ligand (Fig. S2, inset). ESI-MS of the ligand (Fig. S3, Supporting information) in negative ion mode showed a peak at m/z 484.5 (M-H) which was in agreement with the formulation of the ligand. The Fourier transform infrared spectroscopic (FT-IR) analysis showed the characteristic carbonyl stretching corresponding to the amide bonds at  $1.660 \text{ cm}^{-1}$  and NH stretching at 3,363 and 3,287 cm<sup>-1</sup> further confirming the formation of the ligand.

The iron(III) complex (2) of the ligand was synthesized according to the scheme shown in Fig. S1 (Supporting information). Synthesis of 2 was performed in THF under nitrogen atmosphere. A strong base (n-butyllithium) was used to deprotonate the amide protons; reaction of the deprotonated ligand with anhydrous FeCl<sub>3</sub> yielded a dark red complex (2). We believe that the iron coordinates with the deprotonated amide of the ligand to form complex 2 (Fig. 1). However, a different kind of coordination between metal and ligand was reported in the crystal structures of the ruthenium complexes of 1 [45]. Hence, coordination of iron with the oxygen of the amide group is another possibility that cannot be refuted. The higher coordination number is also not unlikely in this case. The complex was further characterized using ESI-MS (m/z 575.1; Fig. 2). The inset of Fig. 2 shows the theoretical simulation of the mass spectrum following the formula of complex 2. The ESI-MS shows the incorporation of a Cl atom into the



Fig. 2 Electrospray ionization mass spectrum (ESI-MS) of the iron complex (negative ion mode, m/z) and its theoretical isotope distribution (*inset*)

complex: thus, we formulated the square-planar structure of the complex. The presence of Cl was further checked by dissolving the complex in acetonitrile and then adding silver nitrate which yielded stoichiometric precipitate of chloride. The complex is also miscible in low polarity solvents, such as benzene, toluene, and ether, indicating that it is a charge neutral species. The UV-Vis spectrum of the iron complex in THF shows a major peak at 364 nm which eventually tails to the visible region giving rise to the yellowish color in the solution (Fig. S10, Supporting information). The cyclic voltammetry (Fig. S4, Supporting information) of the iron complex shows a quasi-reversible peak with  $E_{1/2}$  of 0.03 V and  $\Delta E_p$  of 0.97 V with respect to an Ag/AgCl reference electrode. FT-IR shows a peak at around  $1,620 \text{ cm}^{-1}$ , corresponding to the amide peak of the complex. Repeated attempts were made to grow the crystals of the iron complex. However, we have been unsuccessful in growing diffraction quality crystals.

The cross-coupling reaction of  $CH_2Cl_2$  with butylmagnesium chloride was performed for preliminary screening of the catalyst activity. Catalyst **2** was taken in a 5 mL round bottom flask (purged with N<sub>2</sub>), and 2 M of butylmagnesium chloride solution in THF was added to it. To the solution,  $CH_2Cl_2$  dissolved in 2 mL THF was added slowly using a syringe pump at the rate of 24 mL/h (see "Experimental"). The samples were taken for analysis after 5 min at the end of the slow addition. Reaction products were analyzed using GC–MS technique. An internal standard (Decane) was used to quantify the product formed.

Three products were formed in the cross-coupling of  $CH_2Cl_2$  with butylmagnesium chloride using 2 (Scheme 1). A cross-coupling product of one butyl group by activation of one C-Cl bond, which eventually on elimination yielded pentene, was detected in significant amount during the reaction. However, it is also possible that the iron center in complex 2 was reduced by the Grignard reagents [14]. Thus, chloropentane, which is first produced by reaction of one Cl atom of CH<sub>2</sub>Cl<sub>2</sub> with butylmagnesium chloride, may oxidatively add to the reduced iron center and, on further  $\beta$ -H elimination, yield pentene. Nonane is also formed in a significant quantity by the cross-coupling of two butyl groups with the two C-Cl bonds of CH<sub>2</sub>Cl<sub>2</sub>. Another product detected during the reaction was hexane, which may be due to the coupling of chloro pentane with another CH<sub>2</sub>Cl<sub>2</sub> and then further dechlorination. It was observed that the products at the end of the reaction were dechlorinated alkanes or alkenes. The iron complex may form a hydride intermediate by virtue of  $\beta$ -H elimination of the Grignard reagent which could further assist in the dechlorination process. In addition to the Grignard reagent, the solvent THF may act as a source of hydrogen in a similar fashion facilitating the replacement of all of the Cl

Table 1 TON and TOF of different substrate to catalyst ratio reactions

Entry	Catalyst 2 (mol%)	Yield (%)	TON	TOF $(h^{-1})$
1	0.8	100	125	1,500
2	0.4	89.4	218	2,616
3	0.2	54.5	263	3,160
4	0.04	13	315	3,780

 $CH_2Cl_2$  (27  $\mu L,$  0.42 mmol), butylmagnesium chloride 2 M in THF (0.42 mL, 0.84 mmol) at room temperature and slow addition of  $CH_2Cl_2$  over 5 min. Yield (%) is the total % of  $CH_2Cl_2$  cross coupled

atoms with hydrogen in the products. Further investigation will be required to understand the mechanistic pathways in detail.

Various reactions were next carried out in order to understand the effect of various reaction parameters: catalyst to substrate ratio, the effect of temperature, and the equivalence of Grignard reagent to the substrate (CH<sub>2</sub>Cl<sub>2</sub>). Reactions were carried out using varying amounts of catalyst to CH<sub>2</sub>Cl<sub>2</sub> ratios. Almost all of the CH<sub>2</sub>Cl<sub>2</sub> crosscoupled when 0.4 mol% of the catalyst was used (Table 1). A further increase in the catalyst concentration to 0.8 mol% leads to the completion of the reaction and to a decrease in the overall TON to 125. The highest TON of 315 was observed using 0.04 mol% catalyst, though the percentage of CH<sub>2</sub>Cl<sub>2</sub> coupled was only 13 %. Use of 0.2 mol% catalyst increased the yield to 54.5 % with a relatively high TON of 263. Interestingly, a higher TON was observed when less of the catalyst was used. This may be due to the fact that, when a large amount of catalyst was employed, the homo-coupling reaction of the Grignard reagent increased, thus reducing the overall TON and TOF of the desired hetero-coupling reaction.



**Fig. 3** Effect of temperature (-15 to 70 °C) on the coupling of butylmagnesium chloride with CH<sub>2</sub>Cl<sub>2</sub>. CH<sub>2</sub>Cl<sub>2</sub> (27 µL, 0.42 mmol), *n*-butylmagnesium chloride 2 M in THF (0.42 mL, 0.84 mmol), reaction time 5 min. "Dichloromethane" is unreacted CH<sub>2</sub>Cl<sub>2</sub>



Fig. 4 Effect of ratio of  $CH_2Cl_2$  to butylmagnesium chloride on the cross coupling reactions.  $CH_2Cl_2$  (27 µL, 0.42 mmol), at room temperature and reaction time 5 min. "Dichloromethane" is unreacted  $CH_2Cl_2$ 

Reactions were also carried out at different temperatures in order to understand the effect of temperature on the cross-coupling. Reactions were performed following the procedure described above but at temperatures ranging from -15 to 70 °C. It was observed that, with increasing temperatures, more products formed. During the reaction, an increase in TON from 203 at -15 °C to 364 at 70 °C was obtained. As shown in Fig. 3, the percent of CH<sub>2</sub>Cl<sub>2</sub> coupled is highest at 70 °C with the formation of pentene, hexane, and nonane increasing with the increase in temperature. Further studies were conducted at room temperature. We found that the catalyst was highly active at room temperature, with a percentage yield and TON of 54.5 % and 263, respectively.

As shown in Fig. 4, an increase in the concentration of the Grignard reagent (butylmagnesium chloride) also leads to an increased reaction rate and increased yield of product. Experiments were performed using different CH<sub>2</sub>Cl<sub>2</sub> to Grignard reagent ratios ranging from 1:1 to 1:12. As revealed by Fig. 4, with the increase in the amount of Grignard reagent, the percentage of CH<sub>2</sub>Cl<sub>2</sub> coupled increased. Almost all of the CH2Cl2 was found to be consumed when 12 equivalents of the Grignard reagent was used indicating that use of excess Grignard reagent increased the cross-coupled products. The TON of the reaction increased from a mere 190 to 482 as the ratio of CH<sub>2</sub>Cl<sub>2</sub> to Grignard reagent was increased from 1:1 to 1:12. However, a larger amount of undesirable homocoupled product was also detected when excess Grignard reagent was used. On the other hand, using just two equivalents of Grignard reagent still resulted in a significant amount of conversion with minimal side products. As a result, we decided to carry out the remainder of the reactions keeping a CH<sub>2</sub>Cl<sub>2</sub> to Grignard reagent ratio of 1:2.

Cross-coupling of  $CH_2Cl_2$  with various Grignard reagents was also performed. Scheme 1 shows the major cross-coupling products formed on the reaction of  $CH_2Cl_2$ 

Grignard reagent		CH <sub>2</sub> Cl <sub>2</sub>			CHCl <sub>3</sub>			CCl <sub>4</sub>						
		a'	b	b′	%	a	b	с	%	a	b	с	d	%
1	MgCl	29.7	5.4	19.4	54.5	27.9	50.9	21.1	99.9	_	22	61	14	97
2	MgCl	84	_	_	99.5	1.6	72	12.6	86.2	16	30.7	38.2	-	85.9
3		48	10.9	17.2	81.5	37	35	26.7	98.7	22.5	60.6	14.1	-	97.2
4	≫∽^MgCl	49.6	5.6	-	55.3	54.6	19	5.5	99.1	29.1	45.3	7.6	-	82
5		41.4	3	16.7	69.2	23	75.6	1.2	99.8	14.1	56	22.9		94
6	MgCl	40.2	-	5.4	55.9	67	17.6	5.4	80	34.8	22.7	11.6	-	69.1
7	MgCl	9.4 <sup>a</sup>	29.5	-	39.7	Trace	3.5	96.4	99.9	Trace	24.1	72	-	86.1
8	MgCl	53.1	17.6	22.8	98	12.6	46	36.6	95.2	17.9	56	11	-	84.9
9	MgCl	22.4	8.9	6	71.4	6.3	55.6	30.4	92.3	30	18.1	29.5	-	77.6
10	MgCl	28.8	5	17	57.8	36.3	52	11.5	99.8	15.3	37.5	42		94.8

Table 2 Cross coupling of CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> with various Grignard reagents

Reactions in THF using 2 (0.5 mg,  $0.87 \mu$ mol), CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> (0.42 mmol) and Grignard reagent (1 equivalent to the number of C–Cl bonds) at room temperature. Samples were analyzed after 5 min of the reaction

a' = Single C–Cl bonds of  $CH_2Cl_2$  coupled with the Grignard reagent

b' = One C-Cl bond of  $CH_2Cl_2$  coupled with Grignard reagent and one C-Cl bond coupled with another  $CH_2Cl_2$  molecule

a, b, c and d = mono, di, tri and tetra substituted coupled products

% is the total percentage of the substrate coupled

<sup>a</sup> The product is toluene, which is 'a' type product instead of the 'a'' type product

with a Grignard reagent. Table 2 shows the percentage of different major cross-coupling products formed along with the total  $CH_2Cl_2$  coupled. For the cross-coupling reaction with phenylmagnesium chloride (entry 7; Table 2), 39.7 % of total  $CH_2Cl_2$  coupled; 29.5 % of the product was 'b' type product, a result of the activation of both C–Cl bonds. Use of phenethylmagnesium chloride resulted in 17.6 % phenethyl di-substituted products (entry 8; Table 2) with a 98 % conversion of  $CH_2Cl_2$ . When benzylmagnesium chloride (entry 9; Table 2) was used, additional coupling product—other than those shown in the Scheme 1—was observed. Apart from obtaining 1,3-diphenylpropane

(Ph–(CH<sub>2</sub>)<sub>3</sub>–Ph), 1,4-diphenylbutane (Ph–(CH<sub>2</sub>)<sub>4</sub>–Ph) was also observed in good amount during the reaction. Similar product was also observed in earlier reports by another research group when Fe(acac)<sub>3</sub> was used as the catalyst [25]. The use of ethylmagnesium chloride (entry 2; Table 2) showed predominantly 'a'' type, single C–Cl activated product. Double C–Cl substituted products like pentane, as described in the Scheme 1, were not observed. Similarly, primarily single C–Cl activated products were observed while using cyclopentylmagnesium chloride (entry 6; Table 2). As shown in Table 2, 40.2 % out of the total 55.9 % CH<sub>2</sub>Cl<sub>2</sub> (entry 6) coupled were singly coupled products. Coupling of both C–Cl bonds with the cyclopentylmagnesium chloride (entry 6; Table 2) was not observed at all. It was also observed that, similar to the cyclopentylmagnesium chloride, all of the alkyl and allyl Grignard reagents primarily gave monosubstituted products. As seen in Table 2, hexylmagnesium chloride (entry 3), octylmagnesium chloride (entry 5) and allylmagnesium chloride (entry 4) yielded 48, 41.4, and 49.6 percentages of monosubstituted products, respectively. When using ethylmagnesium chloride (entry 2; Table 2), 84 % of monosubstituted product was produced primarily due to activation of only one C–Cl bond in CH<sub>2</sub>Cl<sub>2</sub>.

Cross-coupling of some other chlorinated solvents was also carried out using various Grignard reagents at room temperature. Almost all of the CHCl<sub>3</sub> was coupled up with butylmagnesium chloride within 5 min of the reaction time. A high TON of 483 was obtained for the reaction involving CHCl<sub>3</sub>. Cross-coupling of phenylmagnesium chloride with CHCl<sub>3</sub> produced 96.4 % of triphenylmethane product as seen in entry 7 in Table 2. Upon using benzylmagnesium chloride, 30.4 % of 'c' type trisubstituted product, and 55 % 'b' type disubstituted products were formed (entry 9; Table 2). 36.6 % of trisubstituted product was also obtained (entry 8) when CHCl<sub>3</sub> was cross-coupled with phenethylmagnesium chloride. Reactions with ethylmagnesium chloride and octylmagnesium chloride, however, showed predominantly 2 C-Cl bond activated products. As shown in entry 2 (Table 1), 72 % of CHCl<sub>3</sub> coupled with ethylmagnesium chloride to form pentane. Similarly, the reaction with octyl magnesium chloride primarily gave heptadecane (75.6 %) as shown in entry 5 in Table 2. Using isopropylmagnesium chloride, 52 % of disubstituted and 36.3 % of monosubstituted product were formed. The reactions with cyclopentylmagnesium chloride (entry 6) and allylmagnesium chloride (entry 4) yielded 67 and 54.6 % of monosubstituted products, respectively, with only about 5 % of all 3 C-Cl activated products formed in both cases.

Cross-coupling of carbon tetrachloride (CCl<sub>4</sub>) was also performed with different Grignard reagents in a similar fashion (Scheme 1). Most of the reactions resulted in 3 C-Cl activated products. Reaction with phenylmagnesium chloride gave 72 % of triphenylmethane (entry 7). Ethylmagnesium chloride (entry 2) gave 38.2 % of 3 C-Cl bonds activated product and 30.7 % of 2 C-Cl activated product. Most of the alkyl Grignard reagents, such as hexylmagnesium chloride (entry 3) and octylmagnesium chloride (entry 5), primarily produced 2-Cl activated products. Further, cyclopentylmagnesium chloride (entry 6) produced 34.8 % of 1-Cl activated product as the major product. Interestingly, the reaction of CCl<sub>4</sub> with butylmagnesium chloride gave 14 % of 'd' type (Fig. S9)-the product derived from substitution of four chlorine atoms and 61 % of trisubstituted product. The creation of all-carbon quaternary centers, such as the 'd' type products (Scheme 1) mentioned above, is synthetically challenging due to the steric repulsion of the carbon substituents, as well as the number of degrees of freedom that are accessible from the acyclic precursors [49-52]. However, 2 is capable of forming quaternary substituted alkanes in the cross-coupling reaction indicating the high efficiency of the catalyst. Better substitution of multiple C-Cl bonds, especially in reactions with CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, were observed with the use of Grignard reagents with bulkier aromatic groups, such as phenyl, benzyl, and phenethyl groups. Entry 1 in Table 2 shows the cross-coupling reaction yields of CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> with butylmagnesium chloride at room temperature. The results indicate that using 0.2 mol% of 2, 54.5 % of CH<sub>2</sub>Cl<sub>2</sub>, 99.9 % CHCl<sub>3</sub>, and 97 % of CCl<sub>4</sub>, respectively, could be cross-coupled with butylmagnesium chloride within 5 min. The TONs for these reactions were found to be 263, 483, and 467 for CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>, respectively. The results are evidence of the high reactivity of the catalyst (2).

The mechanism of the cross-coupling reaction is currently under investigation. However, we have detected a key species which is most likely responsible for the catalytic reactions. Similar intermediates have been previously detected and postulated for such coupling reactions [24, 25]. The addition of butylmagnesium chloride to THF solution of 2 changes the color of the solution immediately from yellow to red-orange. The UV/Vis spectrum indicated the disappearance of a peak of the iron catalyst (2) at 364 nm, and a new peak at 465 nm appeared indicating generation of a possible reactive intermediate (Fig. S10, Supporting information). The intermediate was postulated to be the butyl substitution of Cl atom in 2. A similar change in color was also observed upon addition of different other Grignard reagents to the catalyst solution (Fig. S10, Supporting information). UV/Vis spectra were found to be similar with a maximum peak at around 465 nm (Fig. S10). The addition of cyclopentylmagnesium chloride, however, shifted the peak to 498 nm (Fig. S10, Supporting information). Formation of the intermediate was further confirmed by the ESI-MS. The iron catalyst (2) on interaction with butylmagnesium chloride forms an alkylated species, and the species was detected by ESI-MS (m/z, 597.4; Fig. S11). A decrease in the absorbance of a peak at 465 nm of the 2-butyl complex was observed upon addition of CH<sub>2</sub>Cl<sub>2</sub> indicating a decrease in the intermediate concentration as the reaction approached completion (Fig. S12, Supporting information).

### 4 Conclusions

By a simple method, we were able to synthesize a new and efficient iron(III) catalyst that is capable of activating

multiple C-Cl bonds in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> leading to their cross-coupled products with various Grignard reagents. By this method, we efficiently converted toxic polychlorinated solvents into benign and value-added products. These reactions were performed at ambient temperature and under an inert atmosphere. The reaction time was in minutes, with most of the chlorinated molecules coupled with the Grignard reagent in as few as 5 min. The catalyst was found to be highly active and showed a TON and TOF as high as 483 and 5,800  $h^{-1}$ , respectively, during the coupling reaction of CHCl<sub>3</sub> with Grignard reagent. The required catalyst loading for all of the reactions was low, only 0.2 mol%. An increase in temperature and the amount of the Grignard reagent led to an increase in the cross-coupling products. However, a change in these parameters for increasing the selectivity toward any particular product was not observed. Use of bulkier aromatic Grignard reagents was found to be more selective towards multiple C-Cl bonds activation. For example, phenylmagnesium chloride formed the most multiple C-Cl activated products. In the case of  $CH_2Cl_2$ , ~29.5 % of 2 C–Cl activated product was formed. On the other hand, in the case of CHCl<sub>3</sub> and CCl<sub>4</sub>, respectively, 96.4 and 72 % of 3 C-Cl activated products were observed. The mechanistic details, scope, and utility of the catalytic applications are currently under further investigation. Additional applications of the catalyst for different coupling reactions and chemical transformations are other also under investigation.

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