An efficient protocol for the synthesis of thioethers via iron-catalyzed cross-coupling reaction and its mechanistic investigation

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ABSTRACT

One of the most straightforward methods for the synthesis of diaryl sulfides is the transition metal catalyzed C—S coupling reaction. Herein we report a study on the iron-catalyzed protocol for cross-coupling reaction of aryl halides with thiols. Structurally diverse diaryl sulfides were prepared efficiently by using a catalyst system involving cheap and environment-friendly $FeCl_3$ and non-toxic universal ligand L-proline. The reaction mechanism for the iron-catalyzed C—S coupling reaction was investigated by means of density functional theory (DFT) methods on a model system. The calculations were performed using hybrid PBE1PBE functional in conjugation with the LANL-2DZ basis set. The key step involved in the mechanism is the formation of a reactant complex in which both reactants are electrostatically bound to Fe(III) proline complex catalyst. The elimination of HI occurs with a much lower TS energy (20.0 kcal/mol) than the uncatalyzed reaction (44.7 kcal/mol).

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1. Introduction

Transition metal catalyzed carbon-heteroatom cross-coupling reactions are very important in organic synthesis, as the products of these reactions serve as building blocks for various biologically active compounds [1–11]. Over the years, many protocols have been developed for the C—N and C—O linkages, but C—S bond formation leading to substituted thioethers is less studied, despite the fact that these bonds are prevalent in many naturally occurring molecules, drugs and polymeric materials [12–22]. This may be due to the undesired formation of disulfides and catalyst deactivation by binding with metals [23].

The classical methods for the synthesis of thioethers involve some non-metal mediated routes such as anti-Markovnikov addition of aryl thiols on alkenes, nucleophilic aromatic substitutions of activated aromatic halides, Leuckert thiophenol reaction of a potassium alkyl xanthate with aryl diazonium salt, Sandmeyer-type reaction of diazonium salts with thiols and the reduction of sulfones or sulfoxides by DIBAL-H or $LiAlH_4$ etc [24–26]. However, these methods suffer from some limitations such as the use of polar solvents like HMPA at high temperature (>200 °C) and the lack of obtaining high regioselectivity and functional group tolerance [27].

The use of transition metal complexes as catalysts has brought a dramatic revolution in this field and nowadays transition metal-catalyzed cross-coupling reactions between thiols or disulfides and aryl halides are widely used for the rapid and efficient synthesis of aryl sulfides. In 1978, Migita and co-workers reported the first Pd-catalyzed coupling reaction of aryl halides with thiols [28]. The high cost, low turnover numbers, and sensitivity to air are the limitations of Pd catalysts which restrict the application of these catalysts in large scale preparations. Thus considerable attention has been focused on exploring new catalytic systems in which several transition metal catalysts like palladium [29–37], nickel [38–42], cobalt [43,44], copper [45–50], rhodium [51], indium [52], iron [53–55] and zinc [56] serve as the metal sources along with appropriate ligands have emerged in recent years. In continuation of our efforts in iron catalyzed coupling reactions [57–59], we propose an efficient iron catalyzed C—S coupling reaction with L-proline ligand. Iron catalysts have certain advantages such as low toxicity, low cost, and are compatible with many readily available and cheap ligands. The ligand L-proline is very cheap, non-toxic and readily available and when used in combination with $FeCl_3$ provides an excellent catalytic system that can be used for the coupling of aryl halides including bromides and chlorides with aryl thiols with good yields.

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2. Results and discussion

In this study, we wish to report an efficient $FeCl_3$-catalyzed S-arylation of thiols with aryl halides using L-proline as the ligand. It is proven that in the absence of the ligand, the C—S coupling product was obtained in lesser amount, and diphenyl disulfide was the main product. When our proposed approach for the formation of C—S bond is compared with other existing methods, the following features are worth mentioning: (i) the approach makes use of an environment-benign and inexpensive catalytic system that is a combination of readily available iron salt and a universal ligand; (ii) in this approach, a broader scope of substrates, various substituted aryl halides including bromides and chlorides, can be applied.

Initially, we carried out a set of experiments using 4-iodoacetophenone (1 equiv.) and thiol (1.2 equiv.) as model substrates for optimizing the reaction conditions, and the results are summarized in Table 1.

The product was obtained in 34% yield when $FeCl_3$ and L-proline were used as the catalyst and ligand respectively with K_2CO_3 as base at 120°C in toluene (Table 1, Entry 1). The presence of molecular ion peak at m/z 228 ($[M]^+$, $C_{14}H_{12}OS$) in MS and carbonyl absorption band at 1675 cm^{-1} in IR spectrum suggest the formation of **3**. The ^1H and ^{13}C NMR of **3** also agreed with the structure. It was also observed that when the coupling reaction was carried out in presence of air or in oxygen atmosphere, low yield of **3** was obtained. The decrease in yield may be attributed to the oxidative homocoupling of thiophenols.

We then examined the influence of bases towards the coupling reactions by conducting a series of experiments using $FeCl_3$ as the catalyst in toluene at 120°C. When the reaction was carried out using Cs_2CO_3 as the base, less than 30% of the coupling product **3** was isolated. (Table 1, Entry 2) Other bases like NaO^{t}Bu improved the product yield to 40%. (Table 1, Entry 6)

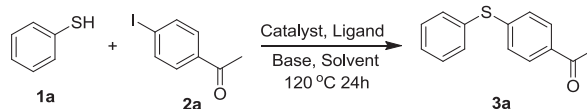We then examined the influence of solvents by conducting the reaction in different solvents. Among the solvents screened, DMF, acetonitrile and 1,2-dimethoxyethane (DME) were proved to be effective solvents. (Table 1, Entries 3, 7 and 9). The reaction showed high water tolerance and 3:2 water/ethanol biphasic system as solvent yielded 87% of the product (Table 1, Entry 9). But the reaction carried out in water resulted in low yield (Table 1, Entry 10). The reactions carried out at lower temperatures yielded lesser amount of the product (Table 1, Entries 5 and 8) showing the importance of high temperature in this reaction. Thus the optimized condition for C—S cross-coupling reaction involves the utilization of 10 mol% $FeCl_3$ and 20 mol% L-proline as the catalytic system and 2 equiv. of K_2CO_3 as the base in DME solvent at 120°C for 24 h. When we performed the reaction by taking a 1:1 ratio of iron catalyst:ligand, the yield of the product was reduced to 42% (Table 1, Entry 11).

As part of control experiments, we carried out the reaction in the absence of base, ligand and catalyst. In the absence of base, only trace amounts of product could be detected in GC–MS analysis (Table 1, Entry 12). In the absence of $FeCl_3$, lower amount of the product (26%) was obtained (Table 1, Entry 13). Conducting the reaction in the absence of L-proline afforded a small amount (18%) of the desired C—S coupling product along with the diphenyldisulfide side product (Table 1, Entry 14). The control experiments revealed that even in the absence of catalytic system, the reaction proceeds presumably through nucleophilic aromatic substitution reaction of thiols on aryl halides due to the high nucleophilic character of thiolate ions. [60] But the yield of the desired coupled product was notably low. The catalyst along with the ligand may facilitate the reaction by shifting the equilibrium more towards the desired product. [61]
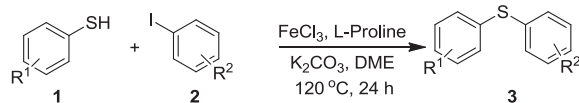
3. Substrate scope

With the optimized reaction conditions in hand, we then investigated the scope of this catalytic protocol for the cross-coupling of different halides with thiophenols. As shown in the Table 2, the coupling of thiophenol with aryl iodides was successful, leading to the desired products in good yields.

Table 1
C—S cross-coupling between thiophenol and 4-iodoacetophenone in different solvents.

Entry	Catalyst	Ligand	Base	Solvent	Yield[a] (%)
1	$FeCl_3$	L-Proline	K_2CO_3	Toluene	34
2	$FeCl_3$	L-Proline	Cs_2CO_3	Toluene	<30
3	$FeCl_3$	L-Proline	K_2CO_3	DMF	87
4	$FeCl_3$	L-Proline	K_2CO_3	DME	98
5[b]	$FeCl_3$	L-Proline	K_2CO_3	DME	43
6	$FeCl_3$	L-Proline	NaO^{t}Bu	Toluene	47
7	$FeCl_3$	L-Proline	NaO^{t}Bu	CH_3CN	96
8[b]	$FeCl_3$	L-Proline	NaO^{t}Bu	CH_3CN	44
9	$FeCl_3$	L-Proline	K_2CO_3	3:2Water/Ethanol	87
10	$FeCl_3$	L-Proline	K_2CO_3	Water	38
11[c]	$FeCl_3$	L-Proline	K_2CO_3	DME	42
12	$FeCl_3$	L-Proline	–	DME	trace
13	–	L-Proline	K_2CO_3	DME	26
14	$FeCl_3$	–	K_2CO_3	DME	18

Reaction conditions: **1** (1.2 equiv.), **2** (1.0 equiv.), $FeCl_3$ (0.1 equiv.), ligand (0.2 equiv.), base (2.0 equiv.), solvent (3 mL), 120°C, 24 h. a: isolated yield. b: Performed at 80°C for 40 h. c: ligand (0.1 equiv.) was used.

Table 2
FeCl$_3$ catalyzed C—S cross-coupling of thiophenol with aryl halides.

Entry	R-SH	Ar-X	Product	Yield[a] (%)
1	SH	I-C6H4-C(O)CH3	Ph-S-C6H4-C(O)CH3	98
2	SH	Br-C6H4-C(O)CH3	Ph-S-C6H4-C(O)CH3	60
3	SH	Cl-C6H4-C(O)CH3	Ph-S-C6H4-C(O)CH3	46
4	SH	I-C6H5	Ph-S-Ph (3b)	80
5	SH	I-C6H4-CN	Ph-S-C6H4-CN (3c)	71
6	SH	I-C6H4-NO2	Ph-S-C6H4-NO2 (3d)	71
7	SH	I-C6H4-OMe	Ph-S-C6H4-OMe (3e)	53
8	Me-C6H4-SH	I-C6H4-C(O)CH3	Me-C6H4-S-C6H4-C(O)CH3 (3f)	77
9	MeO-C6H4-SH	I-C6H4-C(O)CH3	MeO-C6H4-S-C6H4-C(O)CH3 (3g)	51
10	MeO-C6H4-SH	I-C6H4-NO2	MeO-C6H4-S-C6H4-NO2 (3h)	78

[a] Isolated yield.

Electron-deficient, electron-neutral and electron-rich aryl iodides efficiently coupled with thiols and the desired products are obtained in moderately good yields. Furthermore, aryl iodides reacted with substituted thiols and the products are obtained in moderate yields. Notably, most of the earlier reports did not afford any S-arylated product with aryl bromides and aryl chlorides. Contrary to this, our catalytic system shows good tolerance to both aryl bromides and aryl chlorides with 60% and 46% yield respectively.

4. Mechanistic studies using computational techniques

Metal-catalyzed cross-coupling reactions have been studied computationally by various groups to unravel their mechanistic pathways [62,63]. There are many probable pathways evaluated to describe the mechanism of this reaction but the study of all possible pathways is challenging as this need mapping of multidimensional potential energy surfaces. In addition to conventional methods of optimized point geometries, the state-of-the-art transition state theory is also used as a valuable tool to provide reliable results in studies of reaction mechanisms [64]. Here we report a theoretical study of the catalytic cycle of the iron-catalyzed C—S cross-coupling of aryl halides with thiols using density functional theory [65] (DFT). The reaction between 4-iodoacetophenone and thiophenol was taken as the representative reaction for the DFT study. A reaction pathway involving the elimination of HI in absence and presence of the tetra-coordinated iron (III) complex of proline formed *in situ* has been studied to suggest a probable mechanism. As evident from the control experiments, the reaction is facilitated by an *in situ* generated iron-proline complex. Moreover Dzierzak et al isolated a tetra-coordinated Fe-Proline complex encapsulated in Zeolites used as oxidizing agents in several organic reactions [66].
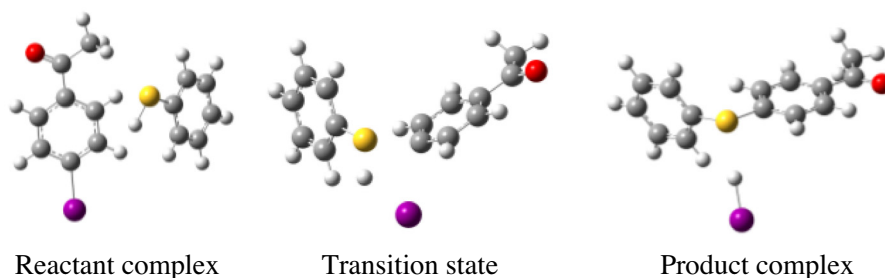
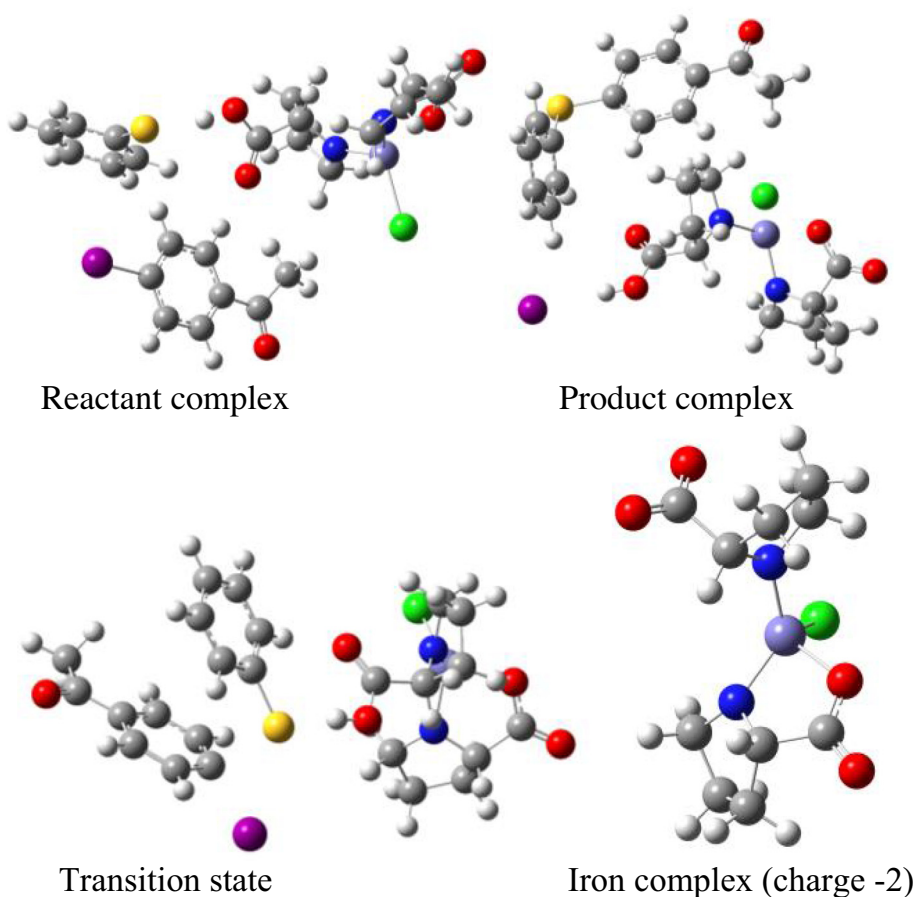**Fig. 1.** Optimized structures for the uncatalyzed reaction.

Fig. 2. Optimized structures.

5. Computational calculations and results

The mechanistic studies of this reaction were performed using DFT calculations incorporated with Gaussian 09 program [67]. PBE1PBE [68] hybrid functional with LANL2DZ [69] basis set was used for the calculations. All optimized structures were subjected to frequency calculations to ensure that there are no imaginary frequencies. The transition states were confirmed by the presence of one negative frequency and by performing intrinsic reaction coordinate (IRC path) calculations [70]. First, the uncatalyzed reaction between 4-iodoacetophenone and thiophenol was modeled by DFT calculations. The optimization of 4-iodoacetophenone in presence of thiophenol resulted in a reactant complex in which the SH hydrogen of thiophenol is 6.00 Å from the iodine atom, Fig. 1. The elimination of HI from the reactant complex occurs with the formation of C—S bond and involves only one transition state. The HI gets separated and remains attracted to the sulfide yielding a product complex. The energy of the transition state (TS) relative to the reactant complex is 44.7 kcal/mol which is high. The relative energy of the product complex is 4.5 kcal lower than the reactant complex. The experiments conducted without the catalyst show only traces of product is being formed.

6. Reaction in presence of catalyst

Several possible structures of the Fe(III) complexed with two molecules of proline and varying numbers of chloride ions, charge and multiplicity were investigated by DFT calculations at PBE1PBE/ LANL2DZ method. An optimized structure of the iron complex obtained was with two molecules of proline dianion formed by
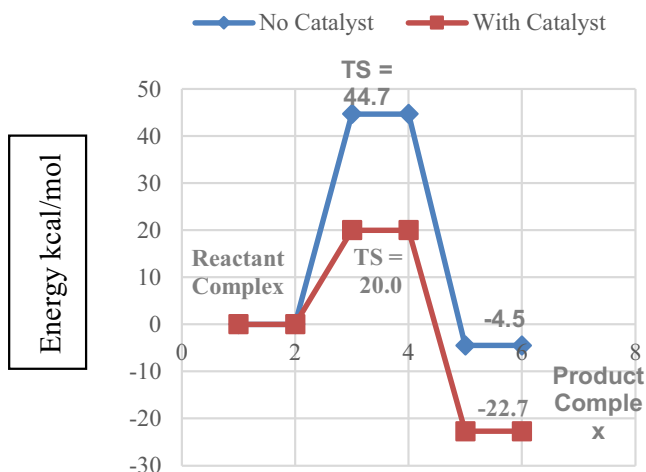
Fig. 3. Energy profile of the reaction. Relative energies in kcal/mol.

base, and one chloride ion so that the overall charge of the complex is −2 and multiplicity is sextet, a high spin complex. Note that Fe^{3+} ion contains five unpaired electrons. In the complex one of the prolines is binding through the N-atom and O-atom (bidentate) while the second proline binds through the N-atom only (monodentate). The complex has a tetra-coordinated structure with one of the COO^- part of the proline pointing out and is unbound to Fe, Fig. 2. The counter ion is likely to be potassium cation.

The formation of a reactant complex between 4-iodo-acetophenone and thiophenol was examined in the presence of the iron complex. A reactant complex (charge = −2) could be identified in which both 4-iodoacetophenone and thiophenol are attracted to the carboxylate anion, Fig. 2. SH hydrogen is electrostatically bound to the carboxylate anion and consequently the thiophenol is partially ionized. Optimization of a product complex formed after the expulsion of HI resulted in a structure in which the HI is hydrogen bonded to the carboxylate anion. A transition state for the elimination of HI was optimized. The relative energy of transition state with respect to the reactant complex is 20.0 kcal/mol which is much lower than that of the uncatalyzed reaction. In addition, the product complex has significantly lower energy compared to the reactant complex, −22.7 kcal/mol. The HI goes away during work up of the reaction.

In the TS structure the C–I distance is 2.266 Å, C—S distance is 2.393 Å. It showed one negative frequency corresponding to C—S bond formation. The TS structure was further confirmed by IRC path calculation. The energy profile diagram of the reaction is given in Fig. 3, gives a comparison of the TS energies of the uncatalyzed reaction and catalyzed reaction. The iron catalyst provides an alternate pathway with low TS energy and the reaction pathway was found to be in good agreement with the experimental observations. Since the complex is ionic, $K_2[Fe(proline)_2Cl]$, solubility is more in polar solvents and hence the yield of the reaction is more in ionic solvents such as DMF and DME.

7. Conclusion

Experimental and computational efforts are reported which illuminate the mechanism of a novel iron-catalyzed thioetherification reaction that offers a new protocol for the formation of C—S bond using a cheap and universal ligand L-proline.

This promising protocol for the S-arylation of aryl thiols are tested with differently substituted aryl halides including bromides and chlorides. The processes are efficiently promoted by a catalyst system that is a combination of a cheap and environment-friendly

$FeCl_3$. The versatility and low cost of this method, in addition to the high yields it provides, makes it viable for use in synthetic organic chemistry. Currently, we are exploring the substrate scope, greener protocols and applications of the proposed iron-catalyzed S-arylation with regard to the synthesis of biologically active molecules.

8. General procedure for preparation

Synthesis of 1-(4-phenylsulfanyl-phenyl)-ethanone (3a): A sealed tube was charged with 1 mmol of 4-iodoactophenone (0.246 mg), 20 mol% of L-proline (0.023 mg) and 2 equiv. of K_2CO_3 (0.276 mg) followed by the addition of 10 mol% $FeCl_3$ (0.016 mg) and 3 ml of DME under nitrogen. 1.2 mmol of thiophenol (0.12 ml) was added to it and the sealed tube was then heated in an oil bath which was preheated to 120°C and the reaction mixture was stirred under the same conditions for 24 hours. The cooled reaction mixture was partitioned between saturated NaCl (10 ml) and EtOAc (20 ml). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 10 ml). The combined organic layer was dried using Na_2SO_4 and the solvent was evaporated in a rotary evaporator to get a residue. Purification of the residue by column chromatography using hexane-EtOAc as the eluent gave the desired product as a colourless solid (0.223 g, 98%); Mp 65°C. IR: 2994, 1675, 1586, 1555, 1472, 1397 cm^{-1}. ^{1}HNMR (CDCl$_3$, 400 MHz) δ 7.81–7.83 (d, J = 8.0 Hz, 2H), 7.48–7.51 (m, 2H), 7.39–7.41 (m, 3H), 7.20–7.22 (d, J = 8.0 Hz, 2H), 2.55 (s, 3H); ^{13}CNMR (100 MHz, CDCl$_3$) δ: 197.09, 144.91, 134.54, 133.86, 132.16, 129.68, 128.90, 128.79, 127.52, 26.45; GCMS (EI) m/z 228 $(M)^+$.

Any additional relevant notes should be placed here.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2018.11.004.

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